DFA OF CALIFORNIA AN ASSOCIATION OF DRIED FRUIT AND TREE NUT PROCESSORS
303 Brokaw Road • P. O. Box 270A • Santa Clara, California 95052 • (408) 727-9302

Correct Project Number: 83-R10
Two Part Project
Part 1 Aflatoxin Monitoring Program (Mosebar/Steffan)
Part 2 Fumigation Studies (Mosebar/Stanley)

FRESNO DISTRICT OFFICE
1855 S. Van Ness - P. O. Box 86
Fresno, California 93707
233-7249

March 20, 1984

RECEIVED
MAR 22 1984
ALMOND BOARD

Project No. 83-09

Cooperator:

DFA of California
P. O. Box 270-A
303 Brokaw Road
Santa Clara, CA 95052

Research Administrator: Frank A. Mosebar

Project Leader: Edward D. Steffen, Ph.D.
DFA of California
P. O. Box 86
1855 So. Van Ness Ave.
Fresno, CA 93721
Phone: (209) 233-7249

Project: Aflatoxin Monitoring Program

Objective: (1) To continue the programs of monitoring aflatoxins in various almond projects which have been in effect since 1973. (2) To continue participation in an aflatoxin analytical check program carried out by the American Oil Chemist Society and the World Health Organization.

Part 1 - Aflatoxin Monitoring

Progress: The monitoring program, which has been continued since 1973, is intended to demonstrate the concern of the almond industry in policing itself and, more importantly, monitoring the yearly trend of removing aflatoxins from edible products intended for human consumption. This monitoring program, as always, remains extremely important to: (1) demonstrate the industry's concern for maintaining a high quality product free of aflatoxins and (2) provide regulatory officials with the opportunity to direct their resources to more likely areas of food contamination.

| Type Sample | Samples Collected | Number Contaminated | Level ppb |
|---|---|---|---|
| Select Nuts | 98 | 3 | 150, 5.5, 7 |
| Mfg. Stock | 40 | 1 | 10 |
| Hulls | 21 | 1 | 6.6 |
| Oil Stock * | 1 | 1 | 62.0 |

* Note: Survey Not Complete

The previous table gives the data collected during the 1983-84 year.

Part 2 - Check Sample Program

The Smalley Subcommittee aflatoxin check samples in corn meal, cottonseed meal, and peanut meal, along with the World Health Organization are in the process of being completed. So far the results obtained in the last report from the World Health Organization have been excellent.

| | SELECT NUTS | | MFG. STOCK | | OIL STOCK | | HULLS | |
|---|---|---|---|---|---|---|---|---|
| | # Contaminated / # Sampled | % | # Contaminated / # Sampled | % | # Contaminated / # Sampled | % | # Contaminated / # Sampled | % |
| 1973 | 0/11 | 0 | 10/39 | 27 | NS | NS | NS | NS |
| 1974 | 0/34 | 0 | 8/62 | 13 | 13/22 | 60* | NS | NS |
| 1975 | NS | NS | 13/100 | 13 | 11/11 | 100 | NS | NS |
| 1976 | NS | NS | 7/56 | 12 | 30/50 | 60* | NS | NS |
| 1977 | 1/89 | 1 | 1/30 | 1 | 10/10 | 100 | 0/20 | 0 |
| 1978 | 5/100 | 5 | 2/41 | 4 | 10/10 | 100 | 3/20 | 15 |
| 1979 | 1/100 | 1 | 2/40 | 5 | 10/10 | 100 | 0/20 | 0 |
| 1980 | 2/100 | 2 | 1/41 | 2.4 | 10/10 | 100 | 2/21 | 9.5 |
| 1981 | 3/114 | 3 | 2/41 | 5 | 10/10 | 100 | 1/14 | 7.1 |
| 1982 | 4/94 | 4 | 2/41 | 5 | 6/9 | 67 | 4/20 | 20 |
| 1983 | 3/98 | 3.1 | 1/40 | 2.5 | 1/1** | 100 | 1/21 | 4.8 |

NS = No Samples Taken
* = Reject Nuts, Not Press Cake Meal
** = Not Completed

Project 83-R10 - Tree and Crop Research
Part 2 - Fumigation Studies

Research Administrator: Frank A. Mosebar (408) 727-9302
DFA of California
Post Office Box 270-A
303 Brokaw Road
Santa Clara CA 95052

Project Director: Dr. William L. Stanley (415) 233-5796
8368 Kent Drive
El Cerrito CA 94530

Cooperators: Howard Nelson, Preston Hartsell, Ed Soderstrom, HCRL Fresno and Glenn Fuller, WRRC Berkeley

Objectives: (1) To complete the Methyl Bromide Manual. (2) To explore alternate methods for insect control. (3) To maintain contacts with U.S. Codex officials and foreign agencies involved in residue problems. (4) To make a study of phosphine as an insect control fumigant. (5) To aid in coordinating the $CO_2$ and controlled atmosphere experiments.

Interpretive Summary:

During the 1982-1983 season, new treatment parameters for fumigation of inshell almonds and kernels with methyl bromide were developed based on thorough studies carried out at the USDA Horticultural Crops Research Laboratory. This work was done by Mr. Preston L. Hartsell with the assistance of Mr. Darrel D. Schulte. Guidance in experimental design and supervision was provided by Mr. Howard D. Nelson and Dr. Pat V. Vail.

The following table gives the revised conditions for fumigation of almonds:

| Temperature, ° Fahrenheit | Time, Hours | Methyl Bromide Dosage, Pounds per 1000 cu. ft. | |
|---|---|---|---|
| | | Kernels | Inshell |
| 50 | 12 | 1 | 1.5 |
| 60 | 8 | 1 | 1.5 |
| 80 | 4 | 1 | 1.5 |

Compared to conventional label directions these new schedules offer the advantages of lower dosages and residues, shorter turn around time, and better worker safety.

Initially the new schedules were tested under pilot scale conditions. Work this fall tested the new schedules on inshell almonds in an industrial setting using a 19,400 and a 194,000 cubic foot chamber. The smaller chamber had been pressure tested and passed for certification. The larger chamber showed no visible leakage by the smoke bomb test. In both chambers (about 50% filled with inshell almonds) all navel orangeworm stages were killed with a dosage of 1.5 pounds of methyl bromide per 1000 cu. ft.; time was 4 hours and temperature was about 75° F.

The dosages recommended with these revised schedules are only about double the lethal dosage threshold. It is, therefore, essential that chambers be tightly sealed and be equipped with circulating fans. The California Department of Food and Agriculture has issued a special local needs registration for these schedules which currently stipulates that they can only be used in certified chambers. Label provisions are being developed for use of these schedules in chambers which are not certified. As a further precaution, it is recommended that the concentration of methyl bromide in the chamber air be monitored with a Fumiscope or other comparable device during fumigation once or twice during the operating season to assure that normal depletion curves are not exceeded.

Some assistance was provided in coordinating the $CO_2$ and controlled atmosphere testing and in taste tests. Other items listed under objectives have been given low priority, though not ignored, because of the need to concentrate efforts on completing the methyl bromide studies.

ALMOND BOARD
OF CALIFORNIA P.O. BOX 15920 • SACRAMENTO, CA 95852 • 1900 POINT WEST WAY • (916) 929-6506

February 1984

Handlers and Members of the Almond Industry

Enclosed you will find a copy of the booklet, "Methyl Bromide Fumigation of Almonds and Almond Products, 1983 Studies on New Schedules Included." This booklet has information on new treatment parameters for fumigation of inshell almonds and kernels with methyl bromide. These were developed through studies carried out by the USDA Horticultural Crops Research Laboratory during the 1982-1983 season. The following are the revised conditions for fumigation of almonds:

| Temperature, Fahrenheit | Time, Hours | Methyl Bromide Dosage Pounds per 1000 cu. ft. | |
|---|---|---|---|
| | | Kernels | Inshell |
| 50 | 12 | 1 | 1.5 |
| 60 | 8 | 1 | 1.5 |
| 80 | 4 | 1 | 1.5 |

Compared to conventional label directions these new schedules offer the advantages of lower dosages and residues, shorter turn around time, and better worker safety.

The dosages recommended with these revised schedules are only about double the lethal dosage threshold. It is, therefore, essential that chambers be tightly sealed and be equipped with circulating fans. As a further precaution, it is recommended that the concentration of methyl bromide in the chamber air be monitored with a Fumiscope or other comparable device during fumigation once or twice during the operating season to assure that normal depletion curves are not exceeded. Information on this equipment is included in the manual.

The California Department of Food and Agriculture has issued a special local need registration for these schedules (copy enclosed). The registration stipulates that these schedules can be used only in chambers which have been inspected and currently certified by the CDFA Division of Plant Industry. Until January 1, 1985, these schedules can be used in chambers which are inspected and are conditionally certified. Certification criteria are outlined in "Standards for Approved Fumigation Facilities" (Q. C. Circular No. 218), which is enclosed. You will also find a memorandum of understanding which states the criteria for conditional certification. For more information on inspection, certification and conditional certification, contact Bill Routhier, Clarence Mayott or Michael Hetrick; CDFA Commodity Treatment Project, 2889 North Larkin,#106, Fresno California 93727, (209) 445-5031.

Please note that the new schedules are in addition to the existing labels; they do not nullify or supersede existing labels.

Within the next few months, it is our intent to compile information on personnel safety, chamber design and testing, and chamber sealing. When completed this will be sent to you.

Sincerely,

Bob Curtis

Robert K. Curtis
Research Coordinator

RC:cr

Enclosure

STATE OF CALIFORNIA, DEPARTMENT OF
FOOD AND AGRICULTURE
PEST EXCLUSION

Q. C. Circular No. 218
6-3-82
Effective November 1, 1982

STANDARDS FOR APPROVED FUMIGATION FACILITIES

GENERAL PROVISIONS

In addition to the following all county, State and Federal Health and Safety Regulations shall be followed.

All fumigation for plant quarantine purposes shall be conducted in an approved treatment facility except when provisions are made for railway cars, highway vans or other treatment facilities to meet special circumstances. An approved fumigation chamber must meet the general and permanent facility requirements.

Employers must provide each employee with sufficient training including, but not limited to safety procedures, protective clothing, safety equipment, common symptoms of poisoning, where to go for emergency medical treatment, and applicable laws and regulations.

The appropriate Special Local Needs registration and product label shall be in the possession of the person doing the fumigation during the entire fumigation period. The requirements stated in the SLN or label shall be followed.

PERMANENT FUMIGATION FACILITIES

All fumigation chambers must be approved by an authorized USDA, CDFA or County inspector prior to use. Periodic checks will be made to determine that the chamber is being properly maintained.

All fumigation treatment facilities used in California to meet plant quarantine or phytosanitary requirements shall be approved based upon the criteria established by the California Department of Food and Agriculture, Division of Plant Industry.

Initial certification is made on inspection and air tightness test of the facility. Reinspection of the fumigation facility is made on an annual basis. Additional air tightness tests will be made by the County or State specialist as required. An opening, with a 2-inch threaded pipe, shall be provided for the introduction of air to create a positive pressure in the chamber. The internal pressure of the chamber is measured as the difference between the kerosene level in the two arms of an open-arm manometer. The time lapse for the chamber pressure to recede from 50 to 5 mm must be 30 seconds or longer. For E.D.B. the time lapse must be 60 seconds or longer. A 1/4- to 1-inch opening shall be provided for the manometer.

For fumigation chambers that have been certified, any alterations, changes, or modifications in the chamber or its construction, or in the fumigant delivery system shall void the certification. Such chambers must be inspected and recertified.

Material to be Used in the Interior of Fumigation Rooms: The inner lining of the chamber (floor; ceiling, and walls) may consist of either masonite (tempered), plywood, plaster, flat sheets of galvanized sheet iron, brick, cement, cement blocks or tongue-and-groove wood.

If masonite or plywood is used to seal the room, the sheets must be nailed securely to the supporting wall. The seams must be well caulked and the joints may be covered with lath strips. If masonite sheets are used, leave an opening of about one-eighth (1/8) inch between the joints for expansion.

If brick, cement, or cement blocks are used, the surface must be covered with plaster to fill all openings. Vinyl plastic may also be used to seal cracks and crevices in brick, cement, cement blocks, or tongue-and-groove walls. If vinyl plastic is used, it may be applied by suitable paint spray equipment in the hands of experienced personnel; however, it must be applied sufficiently thick to close all openings.

If sheet metal is used to line the inside of the chamber, the sheet metal may be joined by the lock seam method, crimped, or the sheets may be overlapped at least two inches. Caulking compound must be placed between the sheets where they overlap and they may be fastened to the wall or other supports by a double or parallel row of nails placed close together.

When sheet metal is used, the inner surface need not be painted. If the interior chamber walls are made of masonite, plywood, or coated with plaster or covered with vinyl plastic, the exposed surface shall be painted with at least two coats of epoxy paint.

The facility shall be equipped with a thermometer or temperature recording device readable from the outside. A small marine port is ideal for viewing the instruments from the outside.

False Floors: All fumigation enclosures must have slatted false floors. The floor joists should extend in the direction that will allow free movement of air to the blower intake. The distance between sub-floor and false floors will depend upon the size of the enclosure. Pallets may be used to meet this requirement in small rooms; the distance can be as little as four inches, but may vary up to ten inches in large rooms. (Consult a USDA or CDFA inspector before building). Slatted false floors and sub-floors must be painted with epoxy paint.

Gas Introduction System: The facility shall have a closed introduction system and shall be equipped with proper accessories for measuring the fumigant.

When applicable a volatilizer shall be installed to ensure fumigant introduction in a gaseous state. Separate volatilizers shall be used for each fumigant.

The fumigant shall be introduced within the chamber through the main air stream.

Circulation and Exhaust Equipment Required and Method of Installing: Fumigation facilities shall have circulation fans of the proper size and type to circulate the fumigant and to maintain uniform temperature within the chamber during fumigation. The circulation and exhaust fans must exchange at least 1/3 chamber volume per minute. Exhaust stack height and type varies with local safety ordinances, but may not be less than seven feet above the structure.

The facility shall have a circulation and exhaust system which will draw from the bottom of the load or beneath the false floor. The facility shall have a fresh air inlet or port hole opening for admitting fresh air during the evacuation process at the end of the fumigation. The fresh air inlet is located at the opposite end from the exhaust opening and shall be of sufficient size to allow adequate introduction of fresh air. The fresh air port should open inward so it can be opened with the exhaust fans on.

The facility shall be vented in such a manner as to keep work areas free of contamination from the fumigant.

Fumigated commodities release absorbed fumigant for a period of time after the actual fumigation, therefore, aeration in a well ventilated area must be provided for.

Every effort should be made to provide a safe work environment by having an exhaust system free from leaks.

Health and Safety: The facility shall have a proper NIOSH approved set of leak detectors available and used for each kind of fumigant employed.

Owners and operators shall have available at the site appropriate NIOSH approved safety equipment for respiratory protection and first aid.

The facility shall have a locked and posted storage area for the stored fumigant and equipment associated with fumigation.

A warning sign must be posted on the storage enclosure. Warning must read: "Danger, poison storage area, all unauthorized persons keep out, keep door locked when not in use." Warning must be readable from a distance of 25 feet.

The facility shall have proper bilingual warning signs posted on the chamber.

Employer shall provide an emergency washing facility.

The owner or operator shall post on the chamber the operating procedures and a check list for conducting a fumigation.

Listed below are major items to be checked when inspecting a fumigation chamber.

1. Doors: Warping which prevents door from closing tightly at all points. Damage to doors and gaskets, especially at 6-8 inches above the floor. Loose hinges or latches.

2. Door Gaskets: Gaskets cut or torn by fruit trucks entering or leaving the chamber. Gaskets cut or rolled out of position by opening and closing the door. Separation of gaskets at joints or splices.

3. Exhaust Door: Gaskets out of position. Exhaust door not shutting tight.

4. A smoke test under pressure is a satisfactory method of checking for leaks.

5. Blower: Poor air and gas distribution and circulation caused by cones or baffles becoming dislocated during loading or unloading of the chamber. Leaks through seams in metal duct work and seams on the fan housing.

6. Walls: Breaks in metal, masonite, plaster or plywood. Paint worn or chipped off walls. Cracks in caulking.

7. False Floor: Broken boards. Decrease of gas circulation due to openings between walls and false floor or between false floor and blower or intake duct.

8. Sub-Floor: Excessive amounts of leaves and trash, especially near the door, which will choke off the air and gas circulation.

9. Vaporizer or volatilizer: Make sure the unit is operating properly.

TEMPORARY FUMIGATION FACILITIES

All temporary facilities such as tarpaulins, railroad cars or truck vans shall be approved by the Department of Food and Agriculture or the County Agricultural Commissioner to meet special circumstances.

Railway Cars and Highway Vans

Gas tight and well constructed metal freight cars, reefers, van trucks, storage buildings, and comparable enclosures may be used as temporary fumigation chambers when provided with a suitable circulation system. The blower or fans must have a CFM capacity of 1/3 the cubic space of the enclosure, and be placed to move gas down the length of the car and operated for not less than thirty minutes at the start of the fumigation. The articles to be fumigated are to be placed on pallets or floor racks to permit space for unrestricted gas circulation beneath the load. Containers are loaded to provide space for unrestricted gas circulation at the top, ends, and sides of the container. Cars and vans or other structures must be carefully examined for gas tightness before use and all apparent sources of leakage caulked, covered with masking tape or otherwise eliminated. Drains in reefers may be sealed with putty. Floors should be covered with kraft paper, lightweight roofing papers, or other gas-impervious material (overlaps sealed together, outer edges sealed to floor) unless the need for such covering is obviously unnecessary. Particular attention should be given to sealing the doors after loading. The appropriate leak detector for the fumigant being used is required. Use the gas analyzer to determine that the fumigant is uniformly distributed through the load. Use the Halide leak detector around the external areas of the structure to determine that no gas leaks are occurring.

Tarpaulin Enclosures

When tarpaulins are used to construct a fumigation enclosure, they shall be carefully examined for holes, tears, and wear, particularly at the creases and folds. All tarpaulins must be at least 6-gauge in weight (.006 inches or 6 mil in thickness) and made of such gas-impervious materials as vinyl or neoprenecoated nylon, polyethylene, or an equivalent fabric. A 6 mil tarpaulin may not be used more than four times. The heavy oiled type canvas tarpaulins are not to be used. In cases where more than one tarpaulin is required, the tarps shall be lapped at least twelve inches at the unions, the laps tightly rolled together and fastened with spring clamps placed at intervals of not more than twelve inches along the entire length of the roll, or by placing wooden 2-inch laths along each of the rolled margins and clamping these together with C clamps placed at 12 to 14 inch intervals. The spring clamps are preferable as they provide greater flexibility and conform better to the shape of the load. When a frame is erected, tarps may be joined with plastic cement making a permanent union. In cases where several large quantitites of commodities are to be fumigated over an extended period of time, this construction may be more useful.

The fumigation shall be conducted on concrete, asphalt, well dampened firm soil, or a tarpaulin. The tarpaulin cover shall be of sufficient size to provide for a lip at the base of the enclosure of not less than 18 inches and shall be securely sealed against the floor by piling sand or soil on the exposed margin of the tarp or by laying sand or water snakes on it so that the ends overlap rather than butt against each other. Sand or water snakes shall not be less than three inches in diameter and made of canvas or polyethylene tubing. Polyethylene tubing can also be filled with water to make water snakes.

Articles to be fumigated under tarpaulins shall be stacked on pallets or frames to permit free air passage along the bottom of the load. A single tarpaulin enclosure shall not exceed 10 feet in height, 25 feet in width, or 50 feet in length. The commodity stack shall be arranged with the individual containers or with frames, so that the tarpaulin is held approximately two feet above the top of the load and one foot from the center of each end of the load to permit free air circulation (head space). Multiple stacks may be fumigated under a common tarpaulin cover arranged so that adequate air circulation can be accomplished. When finely milled products, such as cottonseed meal or flour, are to be fumigated, the stacks shall not be greater than five feet in cross or vertical dimensions, since fumigant penetration is very slow.

When the tarpaulin is used as an envelope, care must be taken to avoid pinholes in the bottom of the tarp. Care must be taken when heavy equipment is used in loading. Sharp corners of the load should be padded with burlap or a soft material to avoid tear or punctures.

The volume to be fumigated shall be carefully calculated to determine cubic capacity and dosage. Avoid rough estimates in favor of actual measurements. In large tarpaulin fumigations, fractional dosages may be rounded off to the next higher pound. Volatilizers are required for all methyl bromide fumigations. The appropriate gas analyzer shall be used to determine that the fumigant is uniformly distributed. The gas sampling tubes shall be placed throughout the load.

For loads up to 3,000 cubic feet, two 18-inch office type fans may be used in lieu of a blower. The fans should be placed at opposite ends of the load, one high and one low, both directed to the center. Blowers or fans must remain in operation during the period the gas is being introduced and for at least 30 minutes thereafter. Blowers may be discontinued when the gas analyzer shows the gas is evenly distributed.

For large loads or in space fumigation, the blower must be capable of circulating 1/3 of the area per minute and shall be placed to pick the air up from the floor and discharge it over the top of the commodity.

SPECIAL CONSIDERATIONS

The facility may be exteriorly insulated to avoid temperature fluctuation.

The facility may be equipped with controlled heating equipment to permit temperature regulation.

The facility may be equipped with a humidifier.

An approved humidity gauge readable from the outside is necessary when treating nursery stock and propagative plant materials.

No fans are needed for circulation during a phosphine fumigation but exhaust fans are required.

WARNING: Do not use phosphine under vacuum fumigation. Such a procedure will create a dangerous explosive situation.

The scales used to weigh methyl bromide cylinders must be industrial platform scales. The scales must be equipped with a means to secure the cylinder.

The facility should be constructed to protect plants or commodity from direct effects of heat, air blast, air movement or other adverse conditions.

Material such as natural rubber, sponge rubber, sulfonated rubber compounds, or plastics shall not be used. These substances form mercaptans when exposed to methyl bromide or E.D.B rendering the chamber unusable.

SPECIAL CONSIDERATIONS FOR ETHYLENE DIBROMIDE

Only permanent chambers may be used for ethylene dibromide fumigation.

A minimum 50 feet buffer zone around each chamber is required. Should conditions merit, wider buffer zones may be required. Prevailing winds should be parallel to any inhabited dwellings or work places.

Chambers shall have a 40 foot exhaust stack.

Chambers shall be equipped with an approved closed introduction system of E.D.B. resistant material capable of transporting E.D.B. from the storage container to the volatilizer in a safe and efficient manner. All air vents shall be vented into the exhaust stack.

Plastic or tygon tubing shall not be used for transporting liquid E.D.B.

Volatilization of the E.D.B. should be completed within 15-20 minutes, but not more than 30 minutes from the time E.D.B. begins to boil.

Circulation fans shall be of sufficient size to circulate 60 chamber volumes per hour.

Exhaust fans shall be of sufficient size to exhaust 100 chamber volumes per hour.

Only the product label Great Lakes Chemical Company Ethylene Dibromide EPA Reg. 5785-28-AA shall be used.

Warnings must be posted, in at least four directions, 50 feet from the chamber. Warnings must be in English and Spanish and must read: "Danger, premises fumigated with E.D.B., persons entering this area must wear a self contained breathing apparatus."

Prepared by California Department of Food and Agriculture Pest Detection/Emergency Projects.

# WORKER HEALTH AND SAFETY GUIDELINES

These guidelines pertain specifically to precautions that should be followed by persons inspecting trucks, rail cars, aircraft, ships, vans or containers containing shipments of fumigated plant materials or commodities. Since these containers contain unknown levels of hazardous fumigants, extreme caution must be exercised. Because we are unaware of all the fumigants that persons in the Exclusion and Detection program, as well as county personnel, may be exposed to, these guidelines are general and must not be considered specific and all inclusive for every situation. Additional information is contained in the Worker Health and Safety Unit's Pesticide Safety Information Series (HS 641(a), October 13, 1981) for seven of the most used fumigants. It must be emphasized that all state and county employees come under the jurisdiction of Cal/OSHA regulations pertaining to safety and health. Pesticide users, on the other hand, must comply with the provisions of the Food and Agriculture Code that pertain to pesticides.

The following equipment should be provided and used as recommended:

Respiratory Protection - When initially entering into or opening for inspection any container that holds fumigated materials, Cal/OSHA regulations require that Self Contained Breathing Apparatus (SCBA) be worn. Gas masks equipped with organic vapor or special canisters, i.e. Vicane (Sulfuryl fluride), do not afford adequate protection in unknown concentrations of fumigant gasses. Once the container has been tested for the specific fumigant and found to be lower than the concentrations listed below, respiratory protection is not required.

| | Pesticide | |
|---|---|---|
| Methyl bromide | 15 ppm | |
| ethylene dibromide | 130 ppb | |
| Phostoxin (phosgene gas) | 100 ppb | |
| sulfuryl floride | 5 ppb | |
| carbon disulfide | 20 ppm | Ceiling - 100 ppm |
| carbon tetrachloride | 10 ppm | Ceiling - 200 ppm |
| chloropicrin | 100 ppb | |
| ethylene dichloride | 50 ppm | Ceiling - 200 ppm |

Halide Detector - The halide detector flame can be used to detect levels of halogenated fumigants (those containing chlorine, bromine, fluorine) at or above 25-40 ppm. The halide detector is primarily a leak detector and should not be used to determine safe entry into a fumigated area. The halide detector must be kept clean. It is difficult to observe changes in the flame color in bright light conditions. The halide detector should be used in compliance with the guidelines presented in Section II, Part 2 of the USDA Plant Protection and Quarantine Treatment Manual.

Colorimetric Detector Tubes - These tubes can be used only with the matching brand name pump for reliable results, i.e., MSA tubes with MSA pump; Drager tubes with Drager pump. The glass tubes contain reagents which, when exposed to specific gasses, change color in a direct relationship to the gas concentration. Specific tubes should be provided for each fumigant likely to be encountered. These tubes are sufficiently sensitive to detect those gasses whose Permissable Exposure Limits (PEL) are in the ppm range. In general, more sophisticated equipment is required for those gasses whose PEL fall in the ppb ranges.

California law places the responsibility for providing a safe and healthful workplace on the employer. This does not relieve individual inspectors in the field of the responsibility to use and encourage safe work practices. If a van or rail car has been fumigated enroute, there may be hazardous levels of fumigant remaining inside. Even if it has been opened for a few hours, the fumigant may pool inside sealed cartons or in areas difficult to ventilate such as corners. Significant levels of gas may be released upon opening individual cartons or removing them from the interior of the container.

Proper and diligent use of required respiratory protection and gas detection devices in suspect situations will lead to minimizing the risk of overexposure.

Prepared by California Department of Food and Agriculture Worker Health and Safety.

# METHYL BROMIDE

## Fumigation of Almonds and Almond Products

### *1983 Studies on New Schedules Included*

ALMOND BOARD
OF CALIFORNIA
P.O. BOX 15920 • SACRAMENTO, CA 95852 • 1900 POINT WEST WAY • (916) 929-6506

# METHYL BROMIDE FUMIGATION OF ALMONDS AND ALMOND PRODUCTS, 1983 STUDIES ON NEW SCHEDULES INCLUDED

by

Preston L. Hartsell,
USDA Horticultural Crops Research Laboratory, Fresno

Howard D. Nelson,
USDA Horticultural Crops Research Laboratory, Fresno

William L. Stanley,
Research Consultant for the Almond Board and the DFA of California

February 1984

LIST OF TABLES

TABLE OF CONTENTS

Figure | Page

LIST OF FIGURES

## SUMMARY

Fumigation of almonds following original label directions, may result in levels of inorganic bromide residues in the product approaching or even exceeding some foreign residue tolerances. This has not been a problem in the domestic market where the allowed tolerance is 200 ppm, but has become an increasing concern in export markets where much lower tolerances are being imposed by some countries.

A thorough study was carried out during the 1982-83 season at the USDA Horticultural Crops Research Laboratory in Fresno to determine minimum dosage levels and fumigation conditions necessary for navel orangeworm (NOW) mortality. From this study conditions for scaled up treatments were selected to simulate processing plant operation at three temperatures - 50, 60, and 80° F. - and tested in triplicate for NOW mortality and inorganic bromide residues. The research results reported here were used in support of developing new fumigation schedules for inshell almonds and kernels.

The use of these new treatment parameters will result in inorganic bromide residues that are much lower than those associated with original label directions; and also will provide for better worker safety and shorter turn around times. Using the new schedule, almond kernels can be fumigated with a methyl bromide dosage of one pound per 1000 cu. ft. at temperatures from 50 to 80° F. with complete mortality of all NOW life stages. The time of exposure to fumigant is inversely proportional to temperature. When shells are present the dosage should be increased to 1.5 pounds per 1000 cu. ft., particularly if Mission almonds are fumigated. A single fumigation should result in residues of no more than 10 ppm inorganic bromide in the kernels when either inshell or shelled almonds are fumigated.

Table I

OPTIMUM CONDITIONS SELECTED FOR COMMERCIAL SCALE FUMIGATION

| Temperature, Fahrenheit | Time, Hours | Methyl Bromide Dosage Pounds per 1000 cu. ft. | |
|---|---|---|---|
| | | Kernels | Inshell |
| 50 | 12 | 1 | 1.5 |
| 60 | 8 | 1 | 1.5 |
| 80 | 4 | 1 | 1.5 |

It is imperative that the fumigation procedures used in these studies be followed strictly inorder to obtain desired control and residues. The dosages recommended with these revised schedules are only about double the lethal dosage threshold. It is, therefore, essential that chambers be tightly sealed and be equipped with circulating fans. As a further precaution, it is recommended that the concentration of methyl bromide in the chamber air be monitored with a Fumiscope or other comparable device during fumigation once or twice during the operating season to assure that normal depletion curves are not exceeded.

The California Department of Food and Agriculture has issued a special local need registration for these schedules. The registration stipulates that these schedules can be used only in chambers which have been inspected and currently certified by the CDFA Division of Plant Industry. Until January 1, 1985, these schedules can be used in chambers which are inspected and are conditionally certified. Certification criteria are outlined in "Standards for Approved Fumigation Facilities" (Q. C. Circular No. 218) published June 3, 1982 by CDFA. For more information on inspection, certification and conditional certification, contact the CDFA Commodity Treatment Project, 2889 North Larkin,#106, Fresno California 93727, (209) 445-5031.

Modified aeration procedures are outlined in this manual. Additional deposit of inorganic bromide does occur during aeration; therefore, proper aeration is important not only for worker safety, but also, to minimize residues of both unreacted methyl bromide (called "organic bromide") and residues of inorganic bromide in product going to consumers. Accepted practice has been to aerate for a period of time equal to the fumigation period. This is best done by keeping the chamber closed and exhausting fumigant with fans. However, product in cartons should be aerated longer because methyl bromide diffuses from the carton air space at a relatively slow rate. In these studies, the first stage of aeration (with chamber doors closed and the exhaust fans on) was completed in 8 hours as usual. When the chamber doors were open and the exhaust fans turned off, air was then blown over and through the load. Fans were directed at the bottom of the load because methyl bromide settles there. Eight hours additional aeration of cartons with fans was sufficient to bring methyl bromide concentration in the carton air space below 15 ppm and therefore total aeration time was 16 hours. Without fans, total aeration may take as long as 30 hours to reach this level. Fifteen ppm is the Cal OSHA average permissible exposure limit (PEL) that workers can be exposed to during an 8 hour work day. Aerating to this extent will afford a substantial margin of worker safety for two reasons. First, 15 ppm is the average exposure during the work day - the five minute excursion limit is 25 ppm with a ceiling limit of 50 ppm. Second, 15 ppm is the concentration of methyl bromide in the carton airspace, not the air inhaled by workers. More rapid turn around time is possible if loads are moved to a separate area for final aeration, but only after the first stage of aeration within the chamber is completed.

These studies also show that at operating temperatures of 60° F and above, if wooden bins are adequately ventilated with screening or slots, additional aeration is not needed. The bins can be moved immediately after the customary aeration period (i.e. elapsed aeration time in the chamber with exhaust fans running equals the elapsed time of fumigation).

PHYSICAL PROPERTIES AND CHEMICAL ACTIVITY OF METHYL BROMIDE

Methyl bromide ($CH_3Br$, molecular weight 95) changes from a liquid to a gas at about 40° Fahrenheit. It should be noted, as indicated later in the section headed "Fumigation Conditions", that this temperature is well below the effective temperatures for fumigation of nuts. In gaseous form methyl bromide is about three times as heavy as air. Because of this greater density, it is most effective to introduce methyl bromide into the air space above the load. The gas is poisonous to man and animals (there is no specific antedote for methyl bromide poisoning) and it is practically odorless, so great care must be exercised in its use.

Methyl bromide is not particularly soluble in water but dissolves readily in oily materials. Residues of methyl bromide (often referred to as organic bromide) in almonds may be found in the oil of the kernels. However, because of its great volatility, most of the organic bromide rapidly disppears when fumigation chambers are vented and the almonds are allowed to aerate.

Methyl bromide is absorbed by the shells and almond kernels in two ways, either by dissolving unchanged in the oil particles or by chemically reacting with organic matter. Because of its volatility, as mentioned above, most of this dissolved methyl bromide evaporates away when the almonds are aerated. However, since Codex Alimentarius, an agency of the United Nations World Health Organization, has proposed a tentative allowance of 0.5 ppm methyl bromide (referred to as organic bromide) in the product, aeration after fumigation is a very important step.

On the other hand, the products of the chemically reacted methyl bromide are not volatile and remain in the almonds after aeration. In this chemical reaction methyl bromide is broken down into two parts, the methyl part attaching (methylation) to certain amino acids in the protein and to phenolic materal (probably tannins and lignin). The bromide part is released as bromide ion (referred to as inorganic bromide). In most countries around the world, residue allowances imposed by regulatory agencies at the present time are based on the inorganic bromide content.

Because of this methylation reaction, methyl bromide is rapidly depleted from the void space between almonds, especially when shells are present. The hard shell varieties have a higher lignin content and have been observed to absorb methyl bromide more avidly than the softshell varieties. Methyl bromide, because of its high density, will tend to accumulate in the bottom of the chamber. For these reasons it is important to provide adequate circulation of the air in the chamber. It is vital to expose all almonds in the fumigation chamber to the lethal dosage as soon as possible because many insects when exposed to low levels of toxicant can undergo temporary metabolic arrest (sometimes referred to as protective stupefaction) and thereby survive fumigation.

The difference in reactivity of methyl bromide with the different parts of the almond fruit are shown in the bar graph (Figure 1) for inorganic bromide in fumigated inhull almonds. The reaction with shell components is clearly predominant. Having shells present results in a rapid reduction in the concentration of methyl bromide in the chamber air. This effect is particularly pronounced with Mission almonds Figure 2 (see also Figure 13 where four varieties are compared). The difference in rate of evaporation of methyl bromide from shells and kernels during aeration after fumigation is shown in Figures 3, 4, 5 and 6. The effect of depletion of methyl bromide by shells is not all unfavorable, however, because it also results in lower deposit of residue in the kernel.

## RESIDUES

Residues in the product resulting from fumigation with methyl bromide consist of unreacted, dissolved fumigant which is called "organic bromide" and bromide ion, which is called "inorganic bromide". Inorganic bromide is released when methyl bromide reacts with components in the commodity. Because organic bromide is quite volatile, it is evaporated rapidly out of the product during aeration and very little remains. As a consequence the tolerance generally recommended for organic bromide is quite low at 0.5 ppm. Inorganic bromide is not volatile and all inorganic bromide deposited during the fumigation and aeration steps remains with the product as a residue. In most countries around the world, residue allowances imposed by regulatory agencies at the present time are based on the inorganic bromide content.

If the supplier has to meet the lower tolerance levels (30 to 50 ppm), he should keep the number of fumigations with methyl bromide to the bare minimum. This will mean special handling from field to final shipment and will result in higher costs. Fortunately, residues can be lowered considerably by following the new fumigation and aeration conditions recommended in this manual. Fumigation in the field should only be with hydrogen phosphide and fumigation with methyl bromide reserved for permanent installations where operating conditions can be closely controlled.

## ANALYSIS FOR METHYL BROMIDE CONCENTRATION DURING FUMIGATION

In order to have assured insect control and also maintain the accurate dosage of methyl bromide required to get low residues, provision should be made for monitoring the concentration of methyl bromide in the chamber air during fumigation. By sampling air from several locations in the chamber, the operator can make sure that distribution of fumigant throughout the product is uniform. Properly managing the levels initially and during the fumigation period will minimize guesswork and economize on the amount of methyl bromide use. Effectiveness of insect kill is directly proportional to the concentration of toxicant in the air multiplied by the time of exposure to the toxicant. If the toxicant level falls, the exposure time must be increased proportionally to make up for it.

One way to determine the concentration of methyl bromide in the chamber air is with the "Fumiscope" (Figure 7). Samples of the air/fumigant mixture are drawn through 1/4 inch o.d. hard plastic tubing (rubber or latex tubing should not be used) from within the enclosure. Four sections of tubing are needed and should be situated so as to draw samples of air from the following locations in the chamber:

1. Center of head space above the load.
2. About 2 feet below the surface of the almonds in one of the top corners of the stack.
3. Near the center of the load.
4. One foot above the floor and one foot in from the walls in the bottom corner opposite position #2 above.

The outlet end of each section of tubing outside the chamber should be numbered for proper identification.

The apparatus for running the analyses, the Fumiscope, is not expensive (under $500) and is simple to operate. A picture of the instrument appears in Figure 7. The instrument will come from the manufacturer accurately calibrated. It should hold calibration for a long time. Should problems eventually arise, i.e., it does not function at all or suddenly gives erratic readings) the Fumiscope can be returned to the manufacturer for repair and recalibration. The instrument should be securely wrapped for shipping and marked for careful handling. The Fumiscope must be handled with care at all times and stored when not in use where it will be protected from dust, dirt and moisture. The instrument is small and easily portable for use in the field or for testing individual chambers too far from each other to be connected by a common manifold system. Chamber air can be cycled through the Fumiscope and back into the chamber for continuous monitoring. The instrument is not sensitive enough for measuring the low levels allowed around general work areas (15 to 50 ppm) and the Draeger tube should be used for this purpose. It is important to keep drying agent (Drierite), located in the intake tube of the Fumiscope, to provide efficient removal of moisture from the air/fumigant mixture being drawn into the instrument. The presence of moisture in the sensing unit of the Fumiscope will result in erratic readings.

## COMPARISON OF METHYL BROMIDE MONITORING METHODS AND EQUIPMENT

### Air space analysis for methyl bromide

1. Fumiscope - Robert K. Hassler & Co., P.O. Box C-14, Mammoth Lakes, CA 93546, Tel. (714) 934-6719
   Cost: approximately $500.
   Reliability: very reliable, rugged instrument, portable.
   Sensitivity: about 2 oz./1000 cu. ft. (500 ppm), depending on how well the instrument is calibrated and maintained.
   Comments: This instrument is excellent for monitoring methyl bromide during fumigation and can be hooked up to a recorder for an automatic and permanent record. It does not require highly trained people to operate.

2. Air monitoring tubes/kits - Draeger, Auer, SKC, Kitagawa. Draeger and Auer tubes and pumps are available from Bernardo Chemicals, 9550 Flair Drive, Suite 406, El Monte, CA 91731, Tel. (213) 442-9090. SKC can be contacted at P.O. Box 2805, Fullerton, CA 92633. Kitagawa equipment is sold by the Matheson Co., 6775 Central Avenue,Newark, CA 94560, Tel. (415) 793-2559.
   Reliability: good
   Sensitivity: 3-100 ppm
   Comments: does not require technical personnel to operate.

3. Gas chromatography - Equipment supplied by many scientific supply houses.
Reliability: excellent.
Sensitivity: flame ionization or thermal conductivity detectors adequate for chamber air analyses during fumigation; electron capture detector for worker safety range 5-50 ppm.
Comments: requires technical personnel to operate, expensive initial investment (10 to 20,000 dollars). An excellent means of determining low or high levels of methyl bromide. Can be hooked up either to a microprocessor for automation or to a recorder.

Residue analysis for inorganic and organic bromide

1. Wet method - gives both inorganic and organic bromide.
Reference: Sharader, S. A., Beshgetoor, W. W., and Stenger, V.A. (1942). Determination of total and inorganic bromide in foods fumigated with methyl bromide. Ind. and Eng. chem. Vol. 4: 1-4.
Reliability: good for almonds.
Sensitivity: 2 ppm.
Comments: requires chemist or experienced technician trained in analytical chemistry. A long procedure taking about 1.5 days to obtain results.

2. Gas chromatography - inorganic and organic bromide.
Reference: Heuser, S. G. and Scudamore, K. A. (1970). Selective determination of ionized bromide and organic bromide in food stuffs by gas-liquid chromatography with special reference to fumigant residues. Pestic. Sci., Vol. 1, Nov.-Dec. 244-8.
Reliability: good for almonds, some sample clean-up problems.
Sensitivity: inorganic bromide - 0.05 ppm or less.
Comments: Requires unit with electron capture detector and operation by highly trained and experienced technician.

3. Gas chromatography - organic bromide only.
References: King, J. R., Benschoter, C. A., and Burditt, A. K., Jr. 1981. Residues of methyl bromide in fumigated grapefruit determined by a rapid headspace assay. J. Agric. Food Chem., Vol. 29, No. 5, 1003-5
Reliability: very reliable.
Sensitivity: 0.002 ppm.
Comments: requires equipment with electron capture detector and highly trained and experienced personnel.

4. X-ray fluorescence - inorganic and organic bromide if samples prepared (extracted) specifically for one or the other. Calibration being prepared by Hartsell at USDA, ARS, Fresno.
Reliability: good, very rapid, about 10 minutes per sample.
Sensitivity: less than 2 ppm.
Comments: requires X-ray fluorescence unit (cost about $20,000) and experienced personnel.

5. Specific ion electrode - inorganic bromide only.
Procedures are being developed by Rodney Austin USDA, ARS Fresno and will be published soon.
Reliability: good for some commodities.
Sensitivity: about 0.5 ppm.
Comments: Requires relatively inexpensive equipment, can be used with a standard pH meter by calibration or a meter with ppm scale. Does not require highly trained personnel.

6. Ion Chromatography - inorganic bromide only.
An instrument that separates anions and cations based on ion exchange separation and quantitates by conductivity detector.
Reliability: good, very rapid.
Sensitivity: ppb to ppt.
Comments: requires ion chromatograph and experienced laboratory personnel.

7. Neutron activation analysis: The method involves activating the stable bromine (Br-81) with neutrons to the radioactive form (Br-82) and measuring the latter with suitable equipment. Measures total bromine.
Sensitivity: to 0.003 micrograms.
Comments: not practical for rountine plant analysis but in special cases could be used by contract with an agency having an installation.
Analytical service can be obtained at General Activation Analyses, Inc., 11575 Sorrento Valley Road, San Diego, CA 93546. Tel. (619) 755-5121

## FUMIGATION TESTS

Small Scale Mortality Tests - Small scale tests were initiated to determine the proper dosages and times for NOW mortality at various temperatures. With inshell almonds it took a slightly more severe treatment to get complete kill than with kernels alone. With inshell almonds at 60° F. and with an 8 hour exposure, all insect stages were killed at dosages of 3/4 pound of methyl bromide/1000 cu. ft. and above. With kernels under the same time and temperature conditions, all insect stages were killed at 1/2 pound/1000 cu. ft. and above (Figures 8 and 9).

The above information for inshell almonds was obtained by means of small scale fumigations (1 cu. ft. chamber) made using a series of dosages from 1 ounce to 1.5 pounds/1000 cu. ft. at temperatures of 50, 60, and 80° F. and at exposure times of 4, 8, and 12 hours. From experience gained in these tests it was decided to limit the tests on almond kernels to an exposure time of eight hours at 60° F. using dosages of 4 ounces to 1.5 pounds/1000 cu. ft. Mortalities for all fumigations were determined on eggs, larvae and pupae of the navel orangeworm (NOW) in cages imbedded in the loads.

Large scale fumigation tests - Based on the minimum conditions for NOW mortality determined in the small scale tests, the following conditions were selected as capable of providing adequate assurance of accomplishing total insect kill on a commercial scale:

Table II

RECOMMENDED CONDITIONS FOR COMMERCIAL SCALE FUMIGATION

| Temperature | Time Hours | Methyl Bromide Dosage Ounces/1000 cu. ft. | |
|---|---|---|---|
| | | Kernels | Inshell |
| 50° F | 12 | 16 oz. (1 lb.) | 24 oz. (1.5 lb.) |
| 60° F | 8 | 16 oz. (1 lb.) | 24 oz. (1.5 lb.) |
| 80° F | 4 | 16 oz. (1 lb.) | 24 oz. (1.5 lb.) |

These conditions were tested in triplicate in a larger 110 cubic foot chamber with: 1) inshell Nonpareil almonds (1000 pounds, loading factor 70-75%) in slotted bins (500 pounds per bin); 2) Nonpareil kernels (2400 pounds, loading factor 80%) in 50 pound cardboard cartons. Dosage was kept at 16 ounces for both kernels and inshell almonds. Eggs, larvae, and pupae of NOW were imbedded in selected spots in the loads. After the fumigations, the exhaust fans were run for 8 hours, the chamber was opened, and aeration continued an additional 64 hours (total aeration time 72 hours). Air samples taken at three points in the load were analyzed for methyl bromide during the fumigation and during aeration. Samples of almonds were removed for inorganic and organic bromide analysis.

Under the conditions given in Table II (but with a dosage of 16 ounces for both kernels and inshell almonds), complete mortality of all NOW life stages for the triplicated tests was achieved. The inorganic bromide residues found in the kernels are given in Table III, as averages of the three runs.

Table III

INORGANIC BROMIDE RESIDUES IN KERNELS FOR LARGE SCALE FUMIGATIONS OF INSHELL AND SHELLED NONPAREIL ALMONDS

| Temperature | Methyl Bromide Dosage Ounces/1000 cu. ft. | Time Hours | Kernel Inorganic Bromide ---ppm--- | |
|---|---|---|---|---|
| | | | Inshell (1) | Shelled (2) |
| 50° F | 16 | 12 | 7.8 | 8.5 |
| 60° F | 16 | 8 | 6.5 | 7.5 |
| 80° F | 16 | 4 | 5.7 | 7.6 |

1 In slotted bins, after 72 hours aeration

2 In cartons, after 72 hours aeration

If the fumigation chamber is tightly sealed, it should be possible to get complete insect kill with inorganic bromide residues of less than 10 ppm in one fumigation by adhering to the above given conditions. A second fumigation will approximately double the amount of residue, if operating conditions are kept the same. The effect of three successive fumigations on inorganic bromide residues in kernels fumigated in cartons at 60 ° F. for 8 hours using 16 ounces of methyl bromide/1000 cu. ft. is shown in Figure 10.

The effect of multiple fumigations on inorganic bromide residues in kernels and shells of inshell almonds is shown in Figures 11 and 12. For these fumigations inshell Nonpareil almonds were fumigated in slotted bins. These figures show that more methyl bromide is taken up and converted to inorganic bromide by shells than by kernels. There is also a difference between shells and kernels in retention of organic bromide during aeration as seen in Figures 3, 4, 5 and 6. These differences are more pronounced in Mission almonds than in the other varieties tested. Nonpareil shells take up the least, Mission take up more, presumably because the shells are higher in lignin and tannin. Shells, also, can have a marked effect on the rate of methyl bromide depletion from the fumigation chamber air. This is shown graphically in Figure 13 where Nonpareil, Merced, Carmel, and Mission varieties are compared. Because absorption of methyl bromide is so rapid, it is recommended to increase the methyl bromide dosage from 16 ounces (1 lb.) to 24 ounces (1-1/2 lbs.)/1000 cu. ft. when fumigating inshell almonds, particularly Mission. The inorganic bromide residues in kernels for the four varieties tested are given in Figure 14. The higher rate of methyl bromide absorption by the shell of the Mission almonds results in these kernels having the lowest inorganic bromide residues.

Chamber Fumigant Depletion - Curves for runs at 50° F. for 12 hours, 60° F. for 8 hours, and 80° F. for 4 hours for inshell almonds appear in Figure 15. Corresponding curves for kernels at 50° F. for 12 hours, 60° F. for 8 hours and 80° F. for 4 hours appear in Figure 16. These curves may be useful in operating commercial units, as comparison of similar curves from a commercial operation will reveal whether equipment is functioning properly and if leakage is excessive.

## EFFECT OF TEMPERATURE ON RESIDUES

The higher the temperature in the chamber during fumigation, the more rapidly insects are killed. Also, the higher the temperature, the greater will be the deposition of inorganic bromide. The effect of temperature on inorganic bromide residues for kernels is shown in Figure 17 and for inshell almonds in Figure 18 where the dosage of methyl bromide was 16 ounces/1000 cu. ft. for 8 hours. The increase in inorganic bromide residue for almond kernels is approximately 4 ppm for a 10° F. rise in temperature. For inshell almonds the increase in inorganic bromide is approximately 2 ppm for a 10° F. rise in temperature. The effect of temperature change on inorganic bromide content will be somewhat different at other dosage levels.

## AERATION TESTS

During aeration after fumigation, containers used to hold the product may affect the release of methyl bromide. The methylation reaction of methyl bromide continues during aeration resulting in a further deposit of inorganic bromide residue. Also, proper aeration will minimize the level of unreacted methyl bromide remaining in the product. Therefore, it is important to aerate as efficiently as possible to minimize residues of both inorganic and organic bromide. Lastly, there can be hazard to personnel handling the product in the chamber and in storage areas if aeration is not adequate.

Kernels in Cartons - Cardboard cartons were used in the tests with shelled almonds reported here because they were considered to represent the most rigorous test for both insect control and gas release during aeration. Wood bins with open and closed slots were tested with inshell almonds.

To discuss the aeration tests it is necessary to present the complete fumigation process. The fumigation of kernels in cartons was in a 110 cubic foot chamber containing 2400 pounds of kernels in 50 pound cartons (a load factor of 80%). Gas sampling tubes were inserted into cartons in three positions in the chamber (bottom front, center of stack, and top rear (see Figure 20 for placement) so that carton air samples could be taken periodically during fumigation and aeration and analyzed for methyl bromide. During the fumigation, gas equilibration (determined from these analyses) was reached in the first hour, at which time the circulating fan was turned off (Figure 19, the vertical bars at 1/2 and 1 hour represent the spread in concentration between the sampling positions). The fumigant depletion curve for methyl bromide in cartons was drawn through the average values.

When the fumigation was completed (8 hours), aeration was begun by starting the chamber exhaust fan. During this aeration time, gas samples for methyl bromide analysis were taken at intervals of 4 and 8 hours, then the fan was turned off, the door opened, and further sampling continued at 12, 24, 48, and 72 hours (Figure 20, top). Analyses also were made for methyl bromide residue in kernels from a randomly selected carton during the aeration period (Figure 21). Because a different carton was sampled in the second run, comparison of the two curves would not be valid. However, the curves both show how slowly the last traces of organic bromide are released from the kernels under these conditions. After the 72 hour aeration period inorganic bromide residues were determined in kernels taken from the cartons in the three spots for gas sampling (Figure 22). The analyses show that the methyl bromide concentration was much higher in the bottom carton because of poor air circulation.

In a second fumigation a fan was placed in front of the open chamber door and left running during the aeration period. This resulted in more rapid and even release of methyl bromide from the cartons in the three locations in the chamber. In this run methyl bromide in the airspace of the center carton actually was higher than in the other two (Figure 20, bottom). Having the fan operating also evened out the rate of loss of organic bromide residue from kernels in the random sample (Figure 21).

Figure 22 shows that inorganic bromide was higher in the bottom and middle cartons than in the top carton in the first fumigation and aeration, whereas in the second, the net increase in inorganic bromide was reversed.

An important consequence of the slow desorption of methyl bromide is its effect on inorganic bromide in the kernels. In Figure 10, kernel inorganic bromide residues before and after the 72 hour aeration are given for each of three successive fumigations. It is apparent that deposit of inorganic bromide is continuing during the aeration period even though the methyl bromide concentration in the cartons is only about 10 to 20 ppm during the first 8 to 40 hours of aeration (see Figure 20).

Additional aeration with fans (bottom Figure 20) kept the methyl bromide concentration in the air space of all cartons below 15 ppm. Fifteen ppm is the Cal OSHA average permissible exposure limit (PEL) that workers can be exposed to during an eight work day. Aerating to this extent affords a substantial margin of safety for two reasons. First, 15 ppm is the average exposure during the work day - the five minute excursion limit is 25 ppm with a ceiling limit of 50 ppm. Second, the 15 ppm is the concentration of methyl bromide in the carton air space, not the air inhaled by workers.

From a safety standpoint, accepted practice has been to aerate for a period of time equal to the fumigation period. This is best done by keeping the chamber door closed and exhausting with fans. An additional eight hours of aeration with fans should reduce and keep the concentration of methyl bromide in all cartons below 15 ppm. This additional step can be done before moving the load out of the fumigation chamber, as done in this test, or if more rapid turn around time is needed, the load can be moved to a separate area for final aeration.

Wooden Bins - When inshell almonds were fumigated in slotted wooden bins, the increase in inorganic bromide residue in both the kernels and shells was much less during aeration than for kernels in cartons under similar conditions. There was good circulation of air through the slots in the bins. The reactivity of the shells with methyl bromide also contributed to lowering the inorganic bromide in the kernels during aeration. When the shells have become saturated as appears to occur after three successive fumigations, this protective effect from shells is greatly diminished (Figure 23).

Furthermore, these studies show that at operating temperatures of 60° F. and above, if wooden bins are adequately ventilated with screening or slots, additional aeration is not needed. After the customary aeration period (i.e. elapsed aeration time in the chamber with exhaust fan running equals the elapsed fumigation time), the methyl bromide in the bin airspace was well below the 15 ppm worker PEL mentioned above.

When the slots in the wooden bins were closed in one run, it took ten hours total aeration for the methyl bromide concentration in the void space of the bin to drop to 15 ppm. When the slots were open the methyl bromide level was below 8 ppm in 4 hours of aeration (Figure 24).

Figure 25 compares the change in methyl bromide concentration in container air during aeration of cartons and slotted bins. Release of methyl bromide from shells and kernels during aeration is also shown in Figures 3, 4, 5 and 6.

## EFFECT OF INCREASED DOSAGE ON INORGANIC BROMIDE RESIDUES

As dosage is increased, with all other conditions held constant, the inorganic bromide concentration will increase. One direct comparison is presented here. Inshell Nonpareil almonds were fumigated at 60° F. for 8 hours with dosages of 16 and 24 ounces/1000 cubic feet. The resulting inorganic bromide in the kernels is given in Figure 26.

## ALMOND VARIETAL DIFFERENCES

The chief difference between the four major commercial almond varieties (Nonpareil, Merced, Carmel, and Mission) in respect to the action of methyl bromide appears to be related to differences in the shell. The physical strength of the shell is probably a function of its lignin content. The greater reactivity of methyl bromide with hard shell Missions is presumed to result from methylation of phenolic groups in the lignin and tannins. Nonpareils have the softest shell, Missions the hardest, with Merceds and Carmels somewhere in between. As mentioned earlier, inshell Missions deplete methyl bromide from the chamber air more rapidly and completely than inshell Nonpareils. The changes in gas content after 1 and 4 hours of fumigation (at 60° F. with 16 ounces of methyl bromide/1000 cubic feet for eight hours) for the four varieties is given in Table IV (see also Figure 13).

Table IV

VARIETAL EFFECT ON CHANGES IN METHYL BROMIDE CONCENTRATION OF CHAMBER AIR DURING FUMIGATION

Methyl Bromide at 16 Ounces/1000 cubic feet for 8 hours at 60° F.

| Variety | oz./1000 cu. ft. Methyl Bromide in Air | | |
|---|---|---|---|
| | Initial | 1 hour | 4 hours |
| Mission | 16.8 | 4.5 | 3.5 |
| Carmel | 18.0 | 7.7 | 5.5 |
| Merced | 19.0 | 9.0 | 7.0 |
| Nonpareil | 19.0 | 11.0 | 7.5 |

In this series of tests all life forms of NOW were killed. However, one pupa in the Mission test was still alive but moribund after 7 days post fumigation and was found dead after 14 days. Evidently, the uptake of methyl bromide by the Mission shells was so rapid that the fumigant level in the air had fallen very close to the minimum lethal dose level (Figure 8). In the study reported by Sinclair and Lindgren using a dosage of 2 pounds of methyl bromide/1000 cubic feet the methyl bromide level in the air had dropped to about 7 ounces/1000 cubic feet in the first hour (Figure 2). For comparison, adequate control was attained in this test with Carmel almonds (Table IV) where the methyl bromide level dropped to 7.7 ounces/1000 cubic feet in the first hour. Thus even for inshell Mission dosage of methyl bromide of 24 ounces (1 1/2 lbs.)/1000 cu. ft. will assure protection with an adequate safety factor.

The inorganic bromide residues found in the four varieties after fumigation is shown in Figure 14. The Mission kernels contained the least inorganic bromide residue, resulting in part from the rapid uptake of methyl bromide by the shell. In fact, the residues in the four varieties were inversely proportional to the rate of disappearance of methyl bromide from the chamber gas.

## FUMIGATION OF ALMOND PRODUCTS

No tests at the shorter time (8 hours) and lower dosages (1 to 1.5 pounds of methyl bromide/1000 cubic feet) have been made with almond products. However, it is assumed that adequate protection against NOW will be possible under these less rigorous conditions with correspondingly reduced inorganic bromide residues. The conditions given in Table II should be adequate for protection of roasted and manufactured products.

The available data are for fumigation with 3.5 pounds of methyl bromide/1000 cubic feet. All products show residues the same as or less than those found for natural and blanched Nonpareil kernels (Table V). Residue data for two single fumigations are given, one for 12 hours and one for 24 hours fumigation time. For the purpose of making comparisons at the same dosage Table VI and VII have been included. These present the inorganic residues for Nonpareil almonds fumigated inshell and as natural kernels at 3.5 pounds/1000 cubic feet for 24 hours.

As expected the inorganic bromide in whole natural kernels and blanched whole kernels (Tables V and VI) was much higher than in inshell almonds (Table VII). The effect in multiple fumigations was even more pronounced (Figure 27), the 24 hour 3-fold treatment of natural and blanched kernels going well over 200 ppm. The depletion of fumigant from the air space for all products was relatively slow (Figure 28) in comparison to inshell almonds (Figure 2). The similarity of the depletion curves for natural and blanched kernels suggests that the skins contribute only in a minor degree to the depletion of fumigant and formation of inorganic bromide residue.

Table V

INORGANIC BROMIDE RESIDUES AFTER SINGLE FUMIGATION OF ALMOND PRODUCTS

3.5 pounds methyl bromide/1000 cu. ft. at 80° F.

| | Inorganic Bromide, ppm 12 hr | Inorganic Bromide, ppm 24 hr |
|---|---|---|
| Nonpareil, natural kernels | 71 | 76 |
| Blanched kernels | 67 | 84 |
| Blanched diced | 43 | 62 |
| Roasted salted kernels | 30 | 31 |
| Natural meal | 26 | 37 |
| Sliced natural | 12 | 29 |

Table VI

MULTIPLE FUMIGATIONS OF NONPAREIL KERNELS

Methyl Bromide at 3.5 pounds/ 1000 cu. ft. at 80° F. for 24 hrs.

| Number of Fumigations | Inorganic Bromide, ppm | Increase ppm |
|---|---|---|
| 1 | 82.0 | - |
| 2 | 160.7 | 78.7 |
| 3 | 244.4 | 83.7 |
| 4 | 306.2 | 61.8 |

Table VII

MULTIPLE FUMIGATIONS OF INSHELL NONPAREIL ALMONDS

Methyl bromide 3.5 pounds/1000 cu. ft. at 80° F. for 24 hrs.

| | Number of Fumigations | Inorganic Bromide, ppm | Increase ppm |
|---|---|---|---|
| Kernels | 1 | 12.2* | - |
| | 2 | 40.7 | 28.5 |
| | 3 | 64.5 | 23.8 |
| | 4 | 80.9 | 16.4 |
| Shells | 1 | 31.3 | - |
| | 2 | 97.8 | 66.5 |
| | 3 | 131.5 | 33.7 |
| | 4 | 194.3 | 62.8 |

* Handlers report higher residues (as much as 30 ppm) under actual plant operating conditions.

Blanched diced and natural meal removed methyl bromide rapidly from the air space, but surprisingly contained less inorganic bromide than the natural and blanched whole kernels (Table V). Cutting and grinding, by exposing more surface, may have made it easier for methyl bromide to dissolve in the oil particles dispersed through the meat. As long as the methyl bromide is in the oil it is unable to react with protein and phenolic components to deposit inorganic bromide residue. When the chambers are vented this dissolved methyl bromide residue will evaporate off before having a chance to react and some may just stay in the oil without evaporating away. Analyses for methyl bromide residue should be made right after opening the chambers and after a reasonable aeration time to see if this is indeed the case. The blanched diced material is somewhat anomalous in that it contained more inorganic bromide than one would expect, to be consistent with the other broken up materials (Table V).

Another unanticipated result in this study was the behavior of roasted salted kernels. Depletion of fumigant from the air in the chamber (Figure 28) was slow, as was likewise observed for the other unbroken products (Nonpareil natural and blanched whole kernels). However, accumulation of inorganic bromide was, surprisingly, about as low as for the sliced natural and natural meal products (Table V). An explanation may be that oil used in roasting absorbed the methyl bromide, but the rate of absorption was slow.

A consequence of the above observations is the concern that some of these fumigated products (i.e., diced and meal) may release methyl bromide more slowly than inshell almonds and kernels. They could, conceivably, retain levels of unreacted methyl bromide residue well above those recommended by some countries and regulatory agencies(i.e., 0.5 ppm). Until data have been obtained to confirm or refute this, using methyl bromide for fumigating these products is not recommended.

ACKNOWLEDGEMENTS

The dedicated assistance of Darrel D. Schulte in executing test fumigations is deeply appreciated. The assistance of Rodney Fries who reared the insects used in this study is also appreciated.

FIGURE 1 - DISTRIBUTION OF INORGANIC BROMIDE RESIDUE IN HULLS, SHELLS, AND KERNELS WITH FUMIGATION OF INHULL ALMONDS. FUMIGATION UNDER TARPS WITH 2 LBS. METHYL BROMIDE/1000 CU.FT.

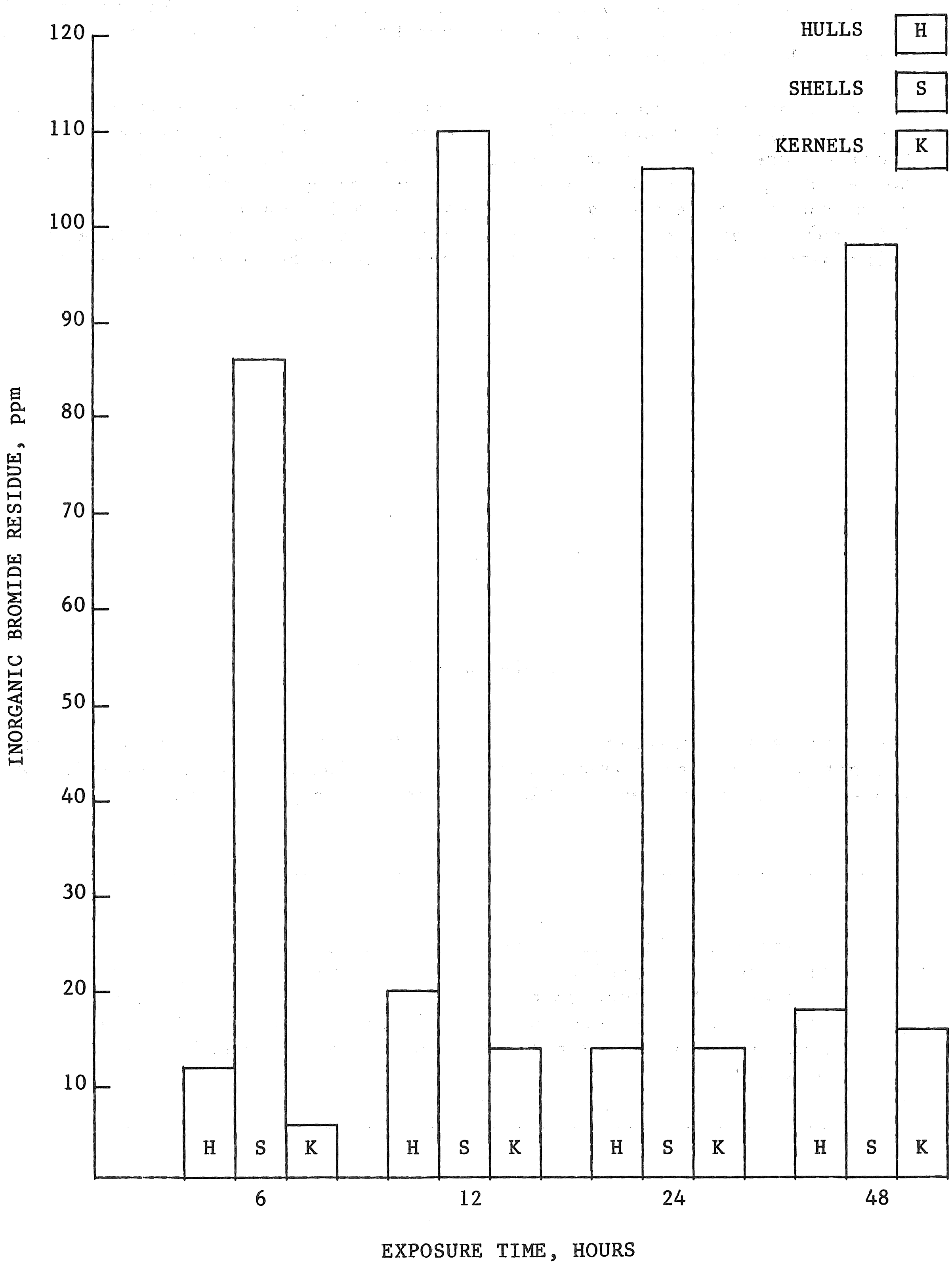


FIGURE 2 - CHANGE IN METHYL BROMIDE IN AIR SPACE DURING FUMIGATION OF INSHELL ALMONDS. FROM W. B. SINCLAIR AND D. L. LINDGREN JOURNAL OF ECONOMIC ENTOMOLOGY, 51, 891 - 900 (1958)

(INITIAL CONC. 2 LB./1000 cu.ft.)

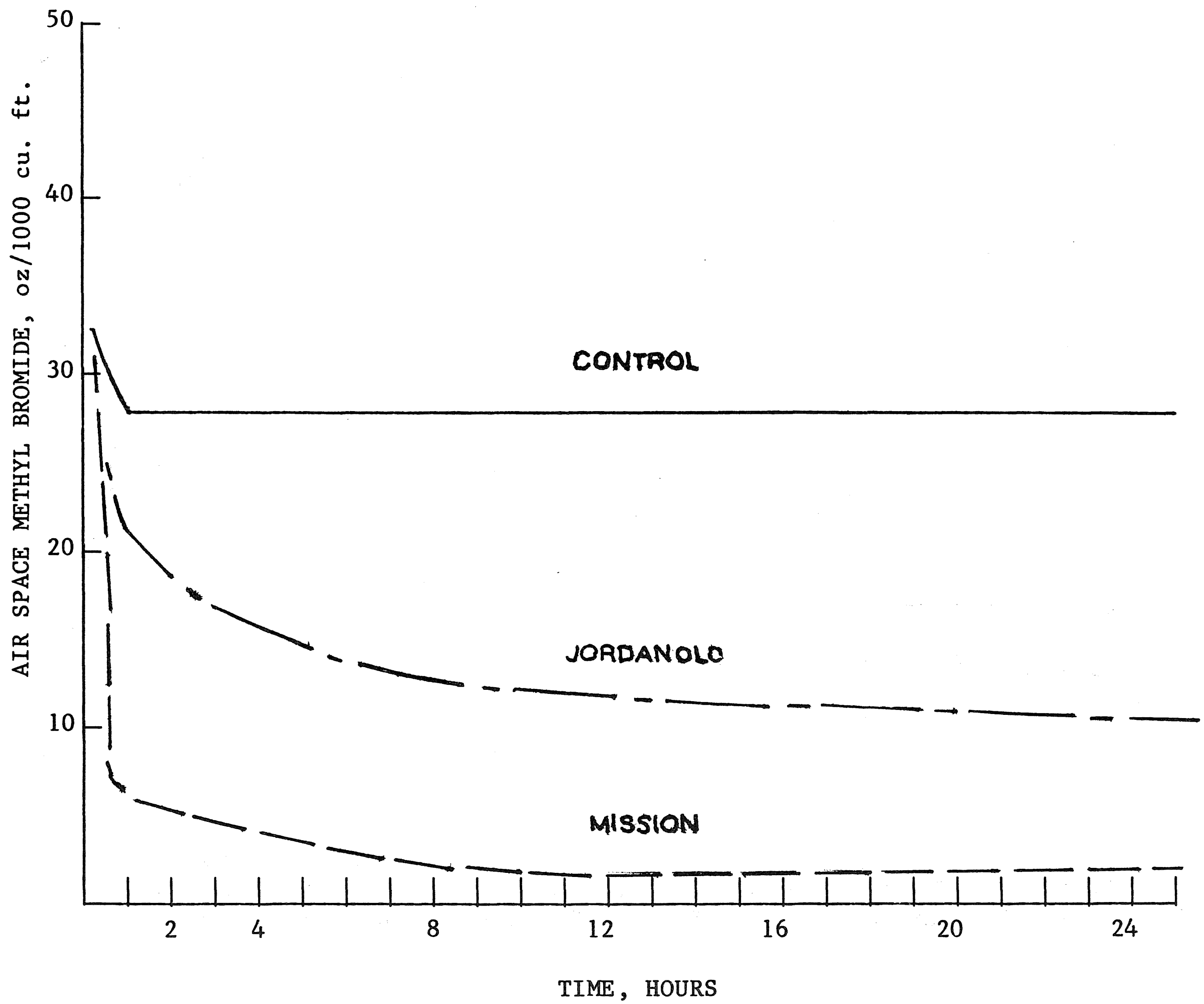


FIGURE 3 - EVAPORATION OF METHYL BROMIDE DURING AERATION. MEASURED BY ORGANIC BROMIDE RESIDUE IN ALMOND SHELLS AND KERNELS. FUMIGATION OF INSHELL NONPAREIL ALMONDS IN SLOTTED WOODEN BINS AT 1 LB./1000 CU. FT. FOR 12 HOURS AT 50° F.

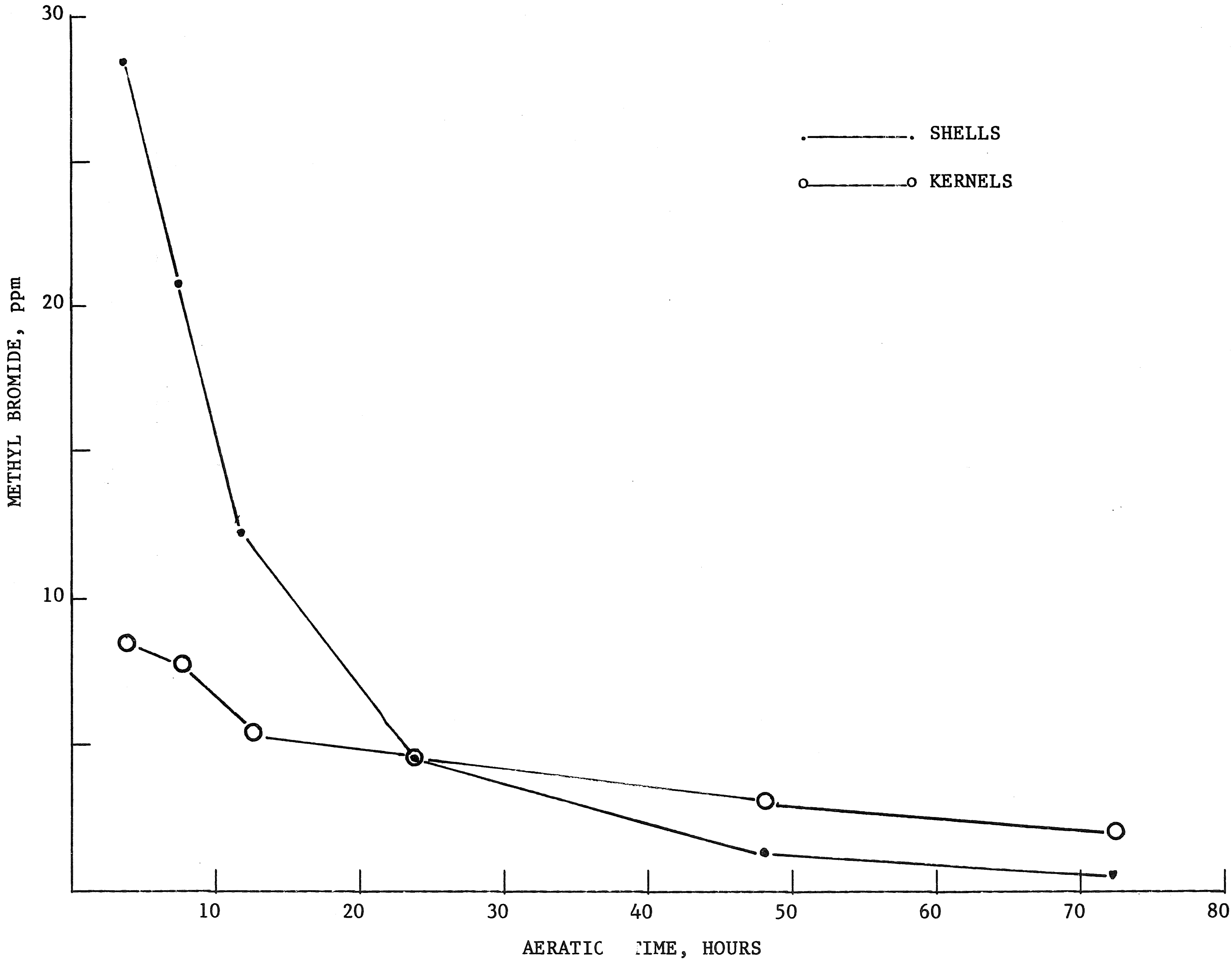


FIGURE 4 - EVAPORATION OF METHYL BROMIDE DURING AERATION. MEASURED BY ORGANIC BROMIDE RESIDUES IN ALMOND SHELLS AND KERNELS. FUMIGATION OF INSHELL NONPAREIL ALMONDS IN SLOTTED WOODEN BINS AT 1 LB./1000 CU. FT. FOR 8 HOURS AT 60° F.

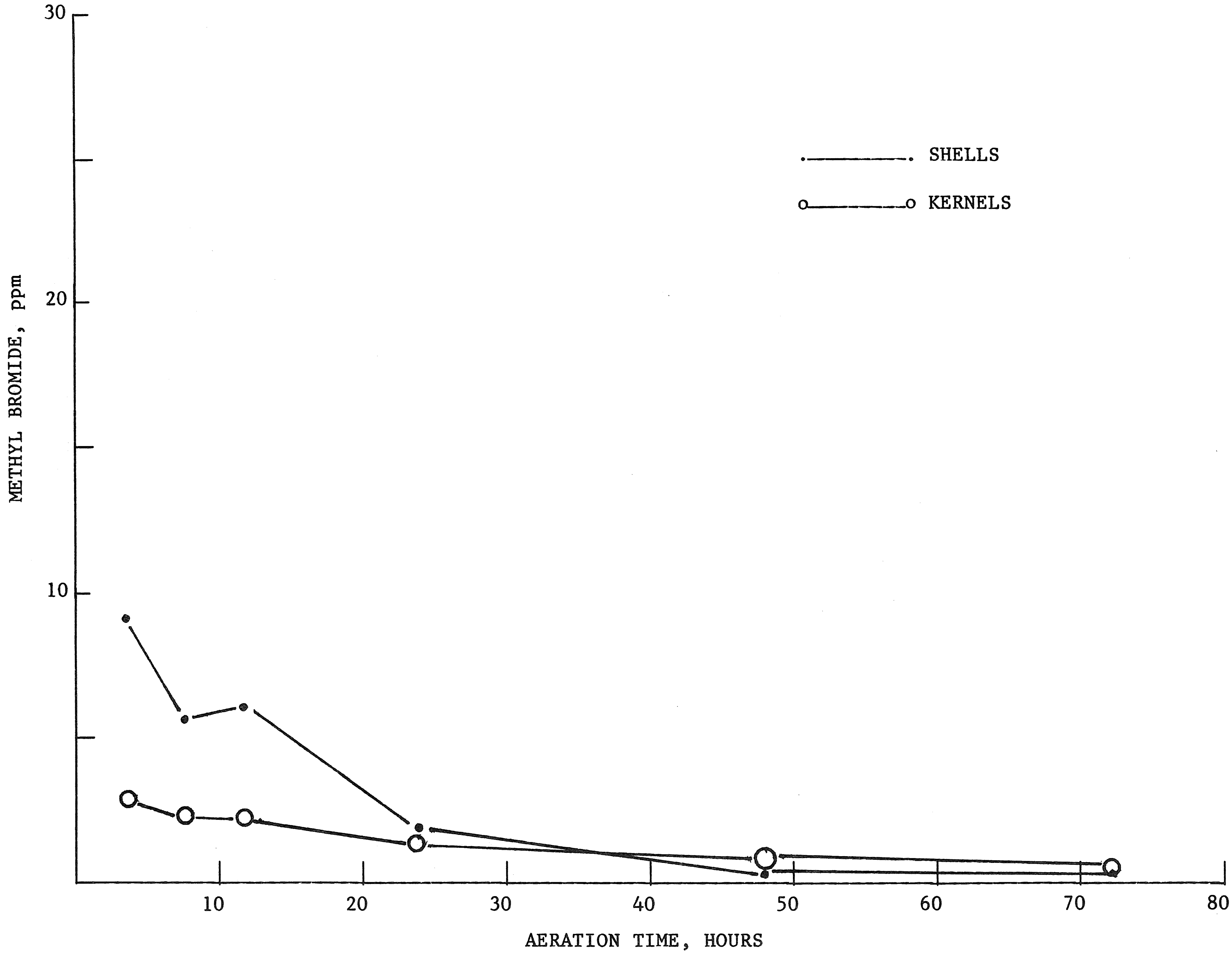


FIGURE 5 - EVAPORATION OF METHYL BROMIDE DURING AERATION. MEASURED BY ORGANIC BROMIDE RESIDUE IN ALMOND SHELLS AND KERNELS. FUMIGATION OF INSHELL NONPAREIL ALMONDS IN UNSLOTTED WOODEN BINS AT 1 LB./1000 CU. FT. FOR 8 HOURS AT 60° F.

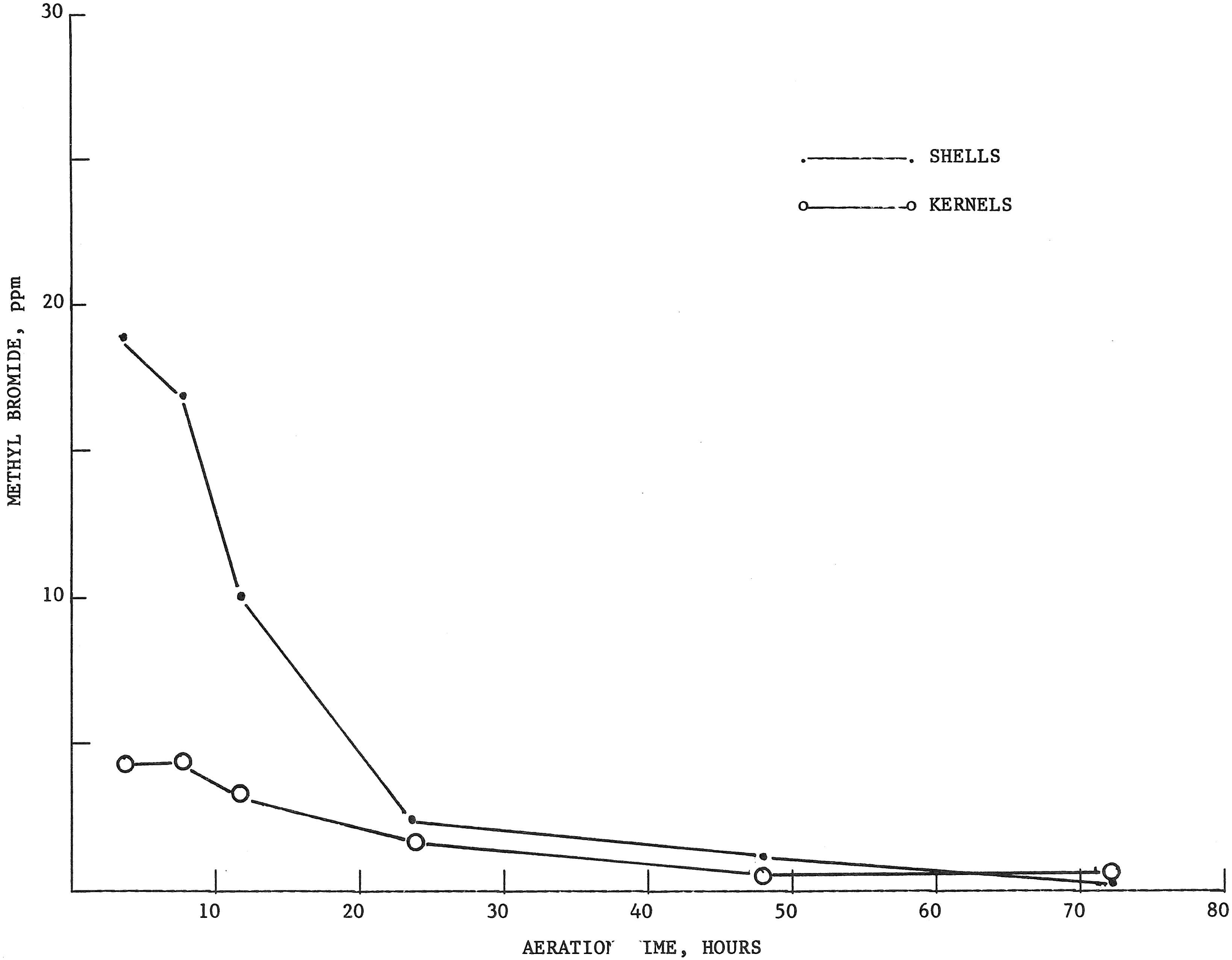


FIGURE 6 - EVAPORATION OF METHYL BROMIDE DURING AERATION. MEASURED BY ORGANIC BROMIDE RESIDUE IN ALMOND SHELLS AND KERNELS. FUMIGATION OF INSHELL NONPAREIL ALMONDS IN SLOTTED WOODEN BINS AT 1 LB./1000 CU. FT. FOR 4 HOURS AT 80° F.

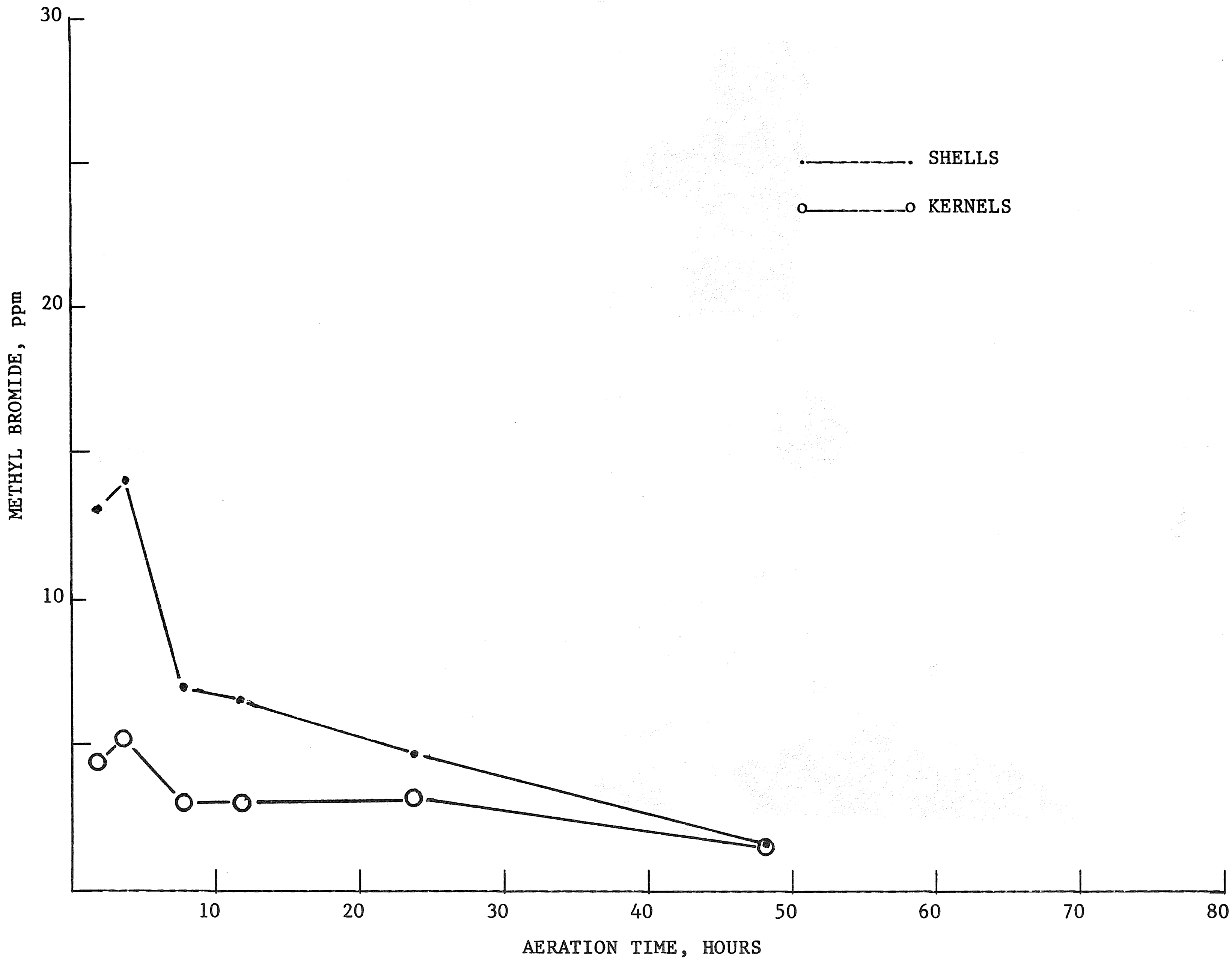
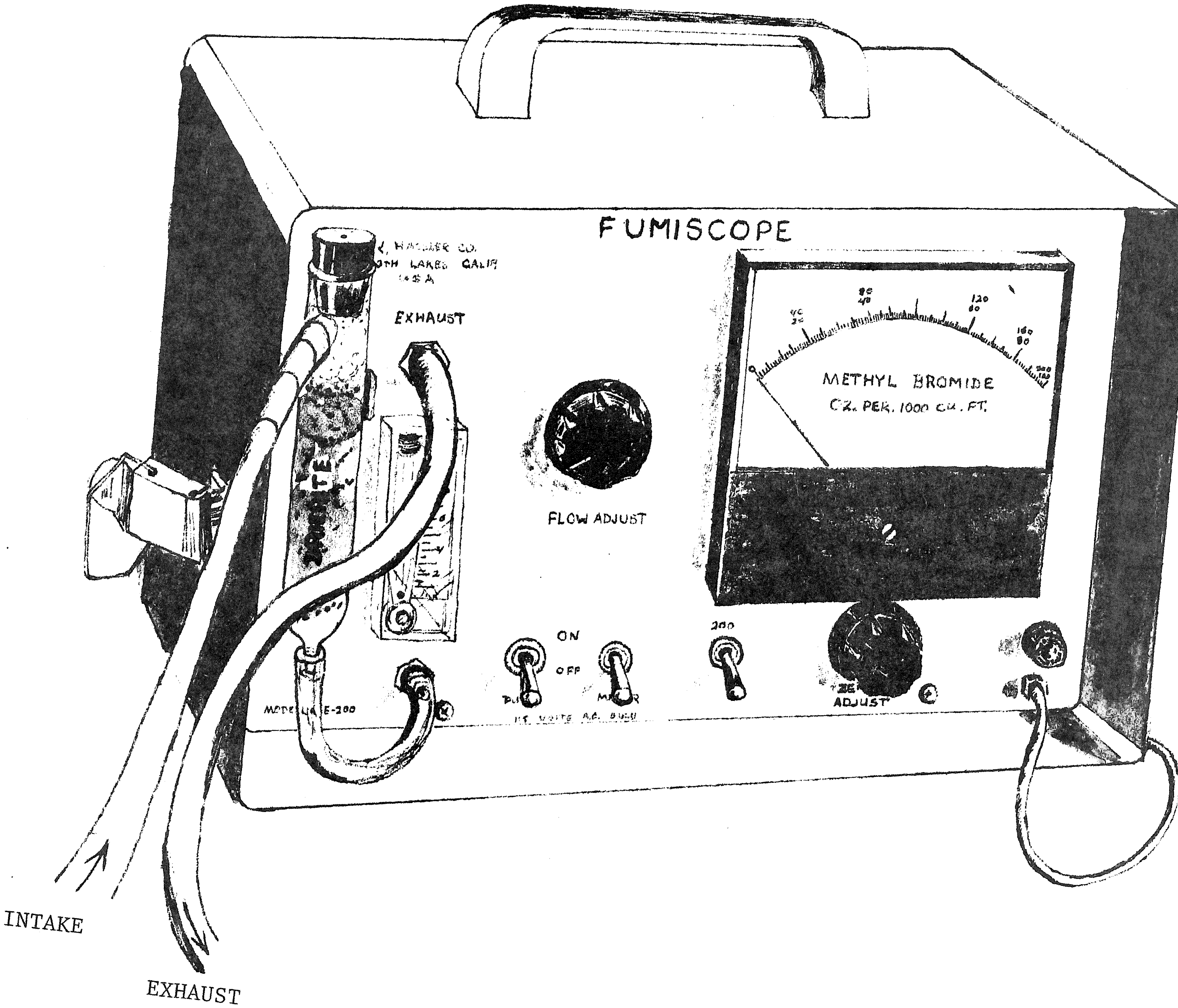


FIGURE 7




FUMISCOPE, MODEL E-200

R. K. HASSLER CO.
P. O. BOX C-14
MAMMOTH LAKES, CA 93546

FIGURE 8 - EFFECT OF METHYL BROMIDE DOSAGE ON NAVEL ORANGEWORM MORTALITY. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF INSHELL NONPAREIL ALMONDS FOR 8 HOURS AT 60° F.

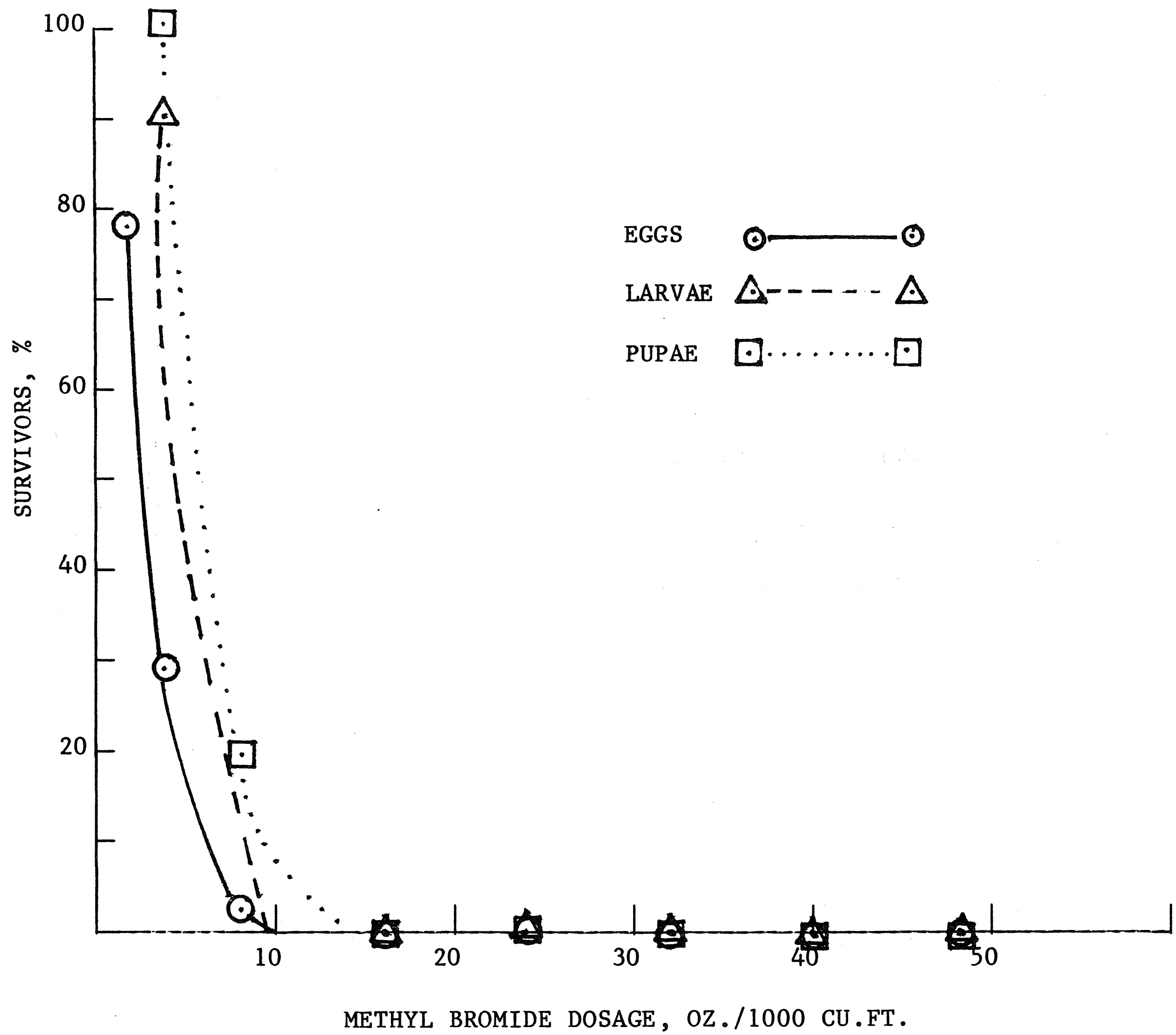


FIGURE 9 - EFFECT OF METHYL BROMIDE DOSAGE ON NAVEL ORANGEWORM MORTALITY. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF NONPAREIL KERNELS FOR 8 HOURS AT 60° F.

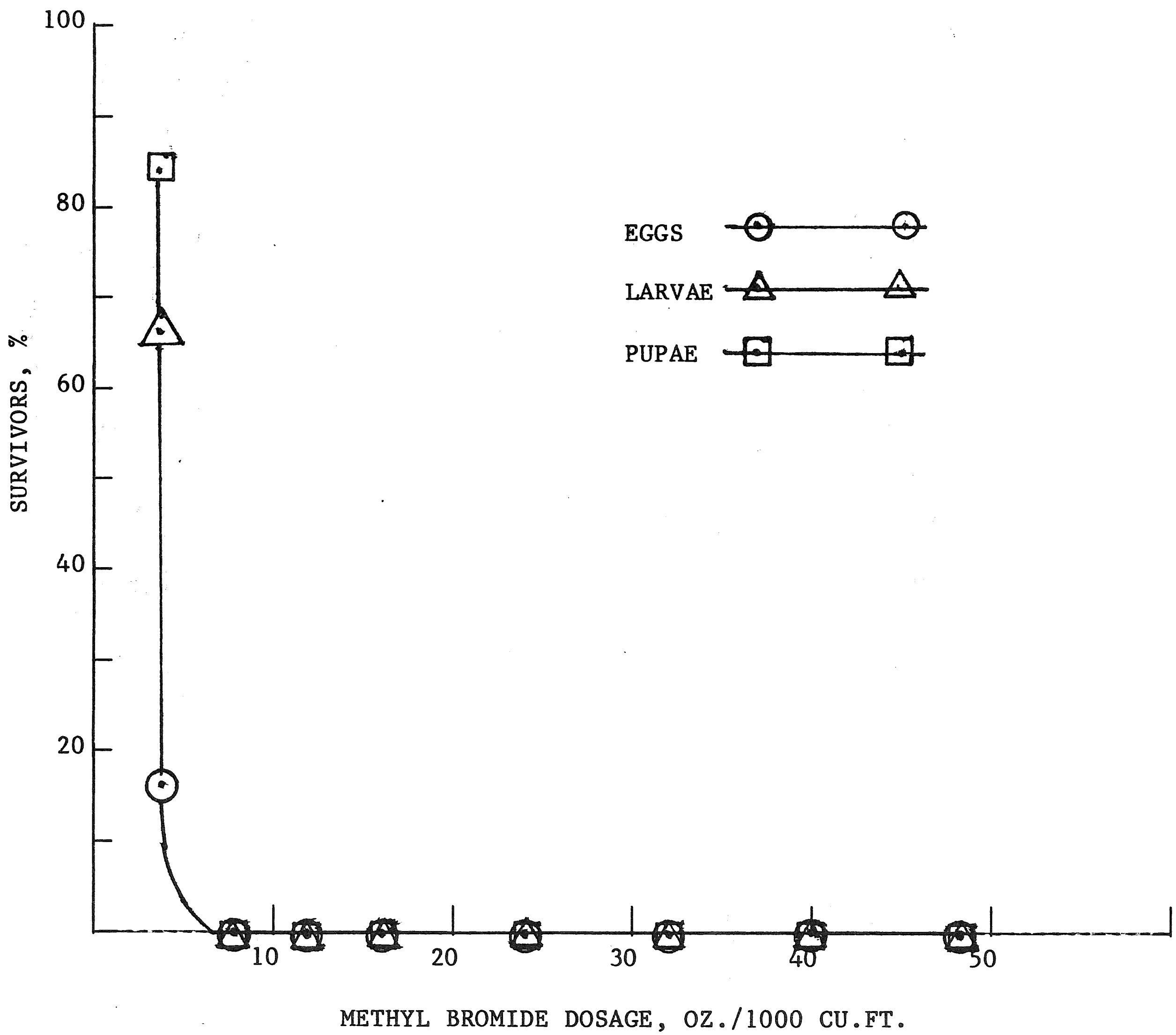


FIGURE 10 - KERNEL INORGANIC BROMIDE RESIDUES ASSOCIATED WITH MULTIPLE FUMIGATIONS OF NONPAREIL KERNELS IN 50 LB. CARTONS. 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

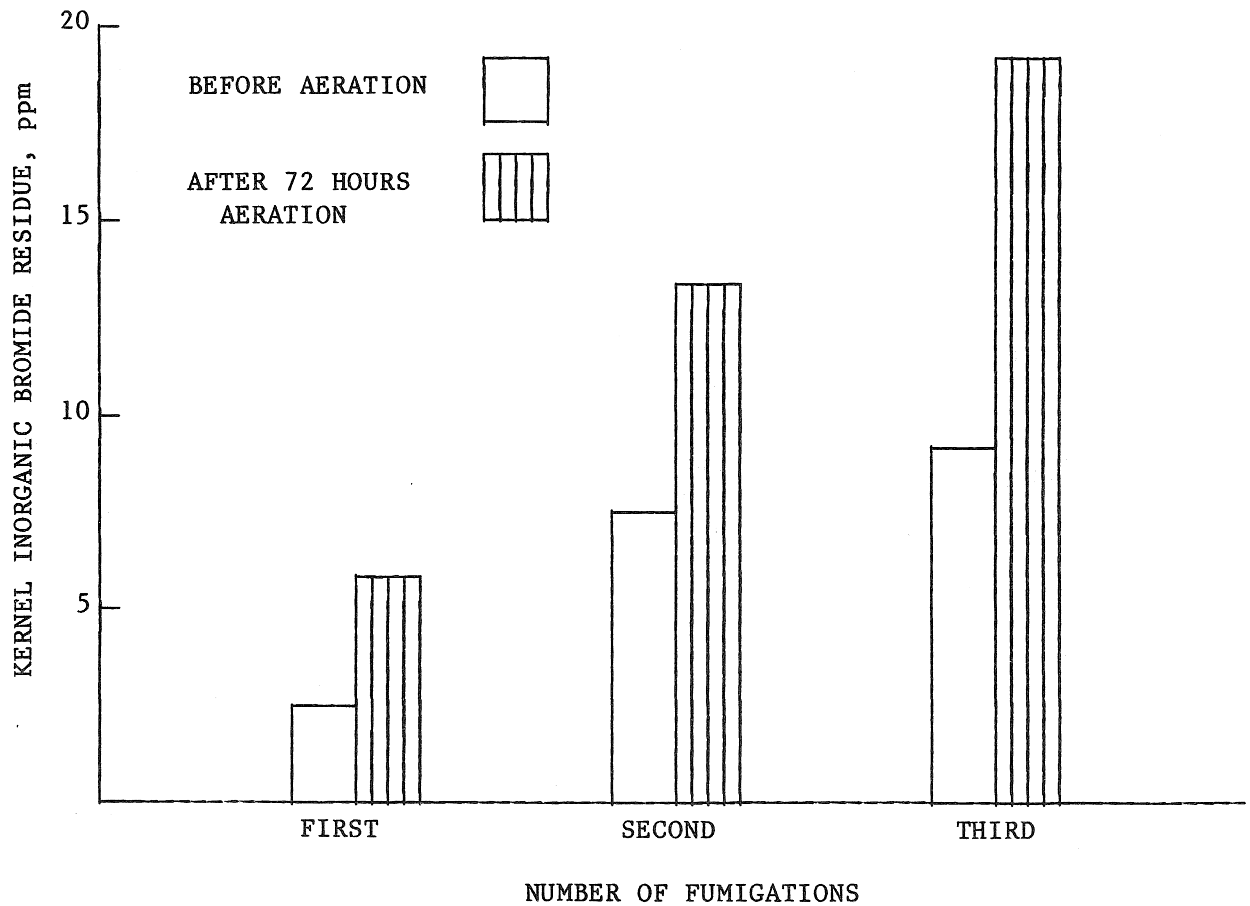


FIGURE 11 - KERNEL INORGANIC BROMIDE RESIDUES ASSOCIATED WITH MULTIPLE FUMIGATIONS OF INSHELL NONPAREIL ALMONDS IN SLOTTED WOODEN BINS 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

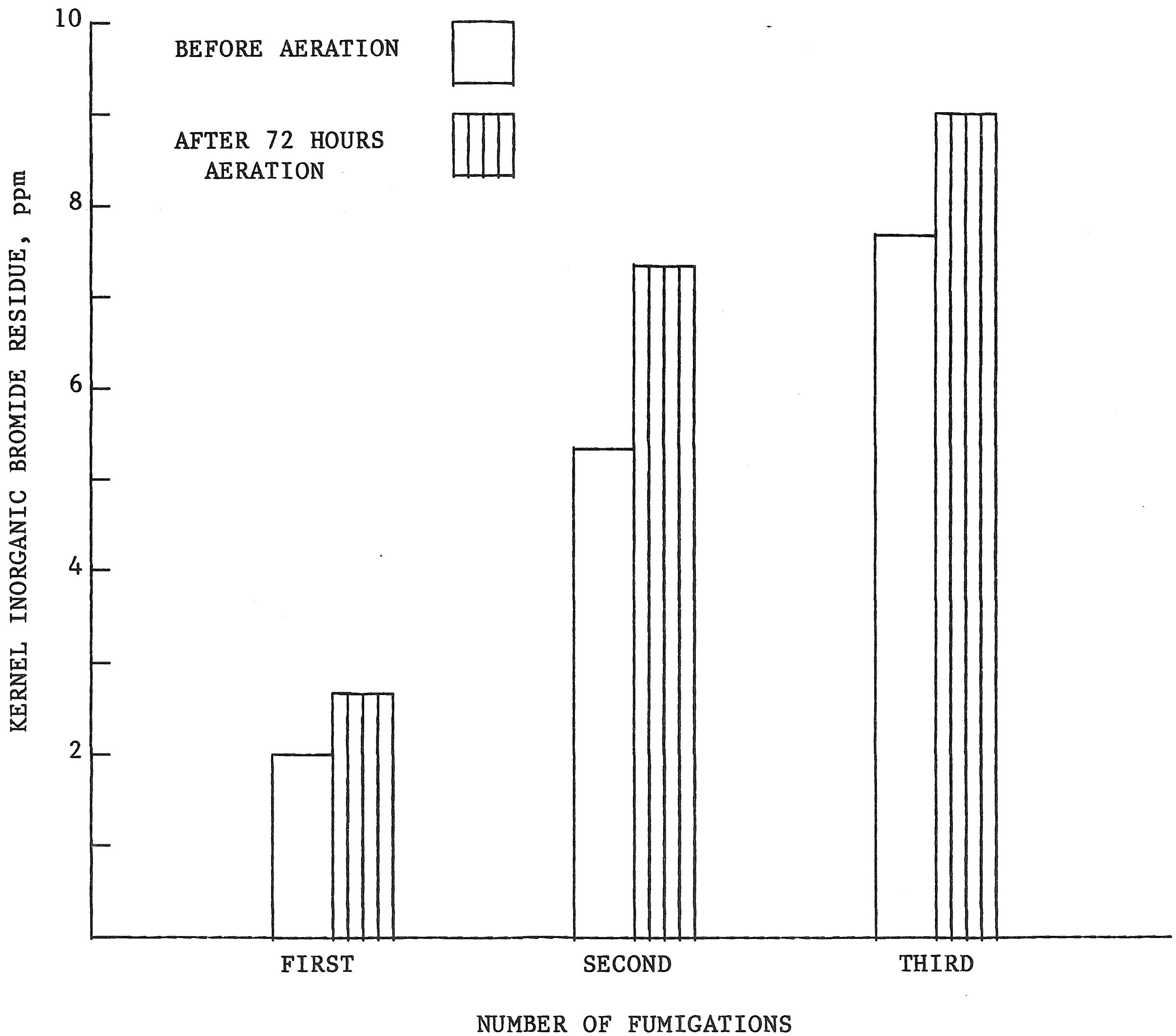


FIGURE 12 - SHELL INORGANIC BROMIDE RESIDUES ASSOCIATED WITH MULTIPLE FUMIGATIONS OF INSHELL NONPAREIL ALMONDS IN SLOTTED WOODEN BINS. FUMIGATION AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

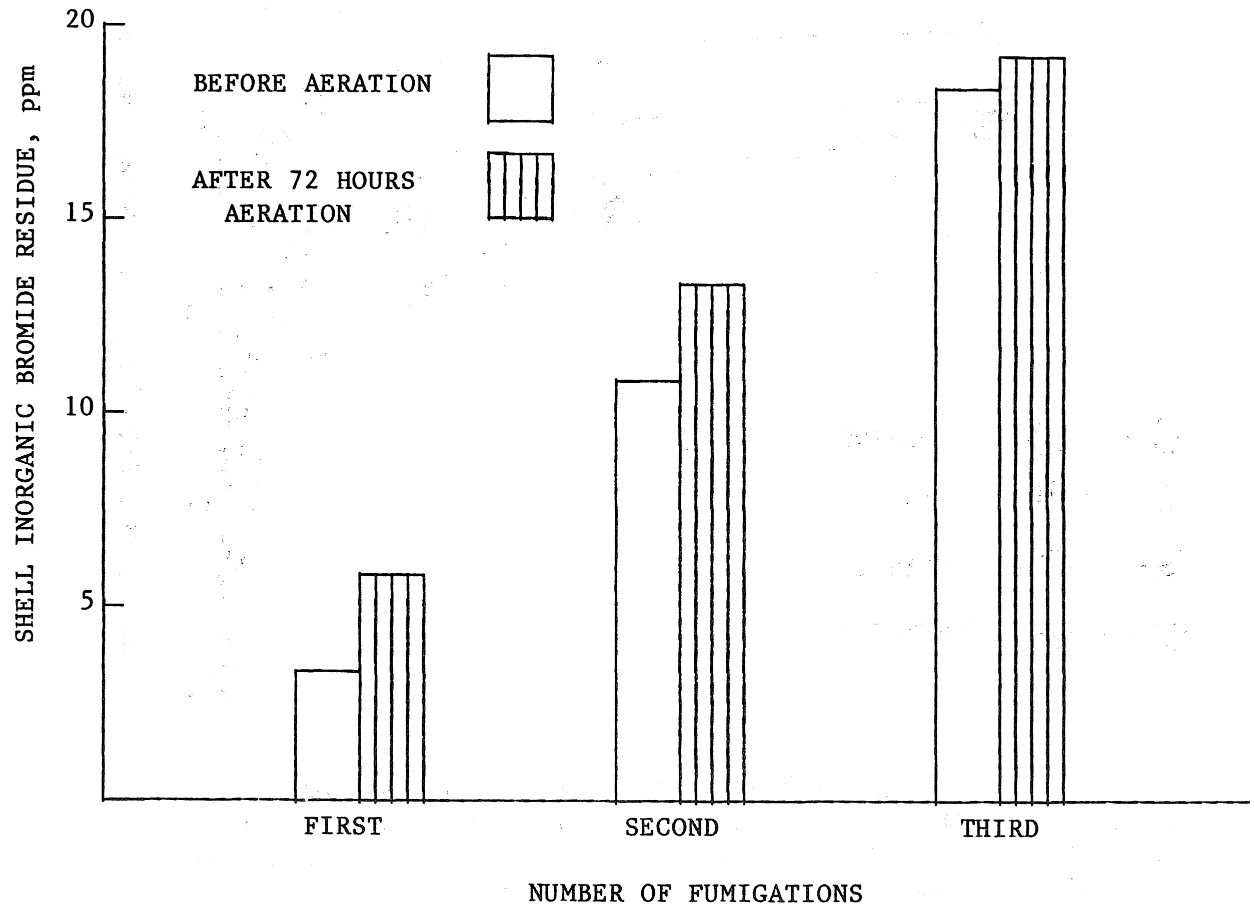


FIGURE 13 - DEPLETION OF METHYL BROMIDE FROM CHAMBER AIR DURING FUMIGATION OF FOUR DIFFERENT ALMOND VARIETIES. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF INSHELL ALMONDS AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

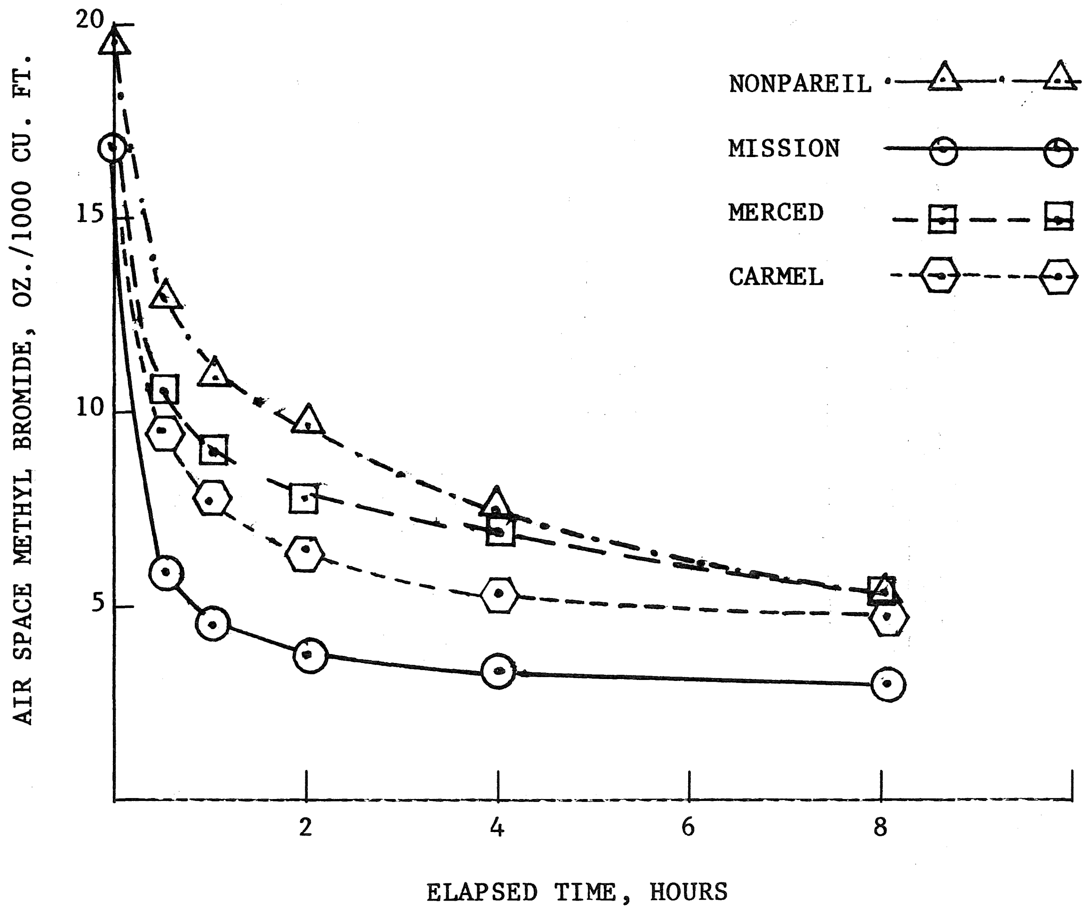


FIGURE 14 - INORGANIC BROMIDE IN KERNELS OF FOUR DIFFERENT VARIETIES. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF INSHELL ALMONDS AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

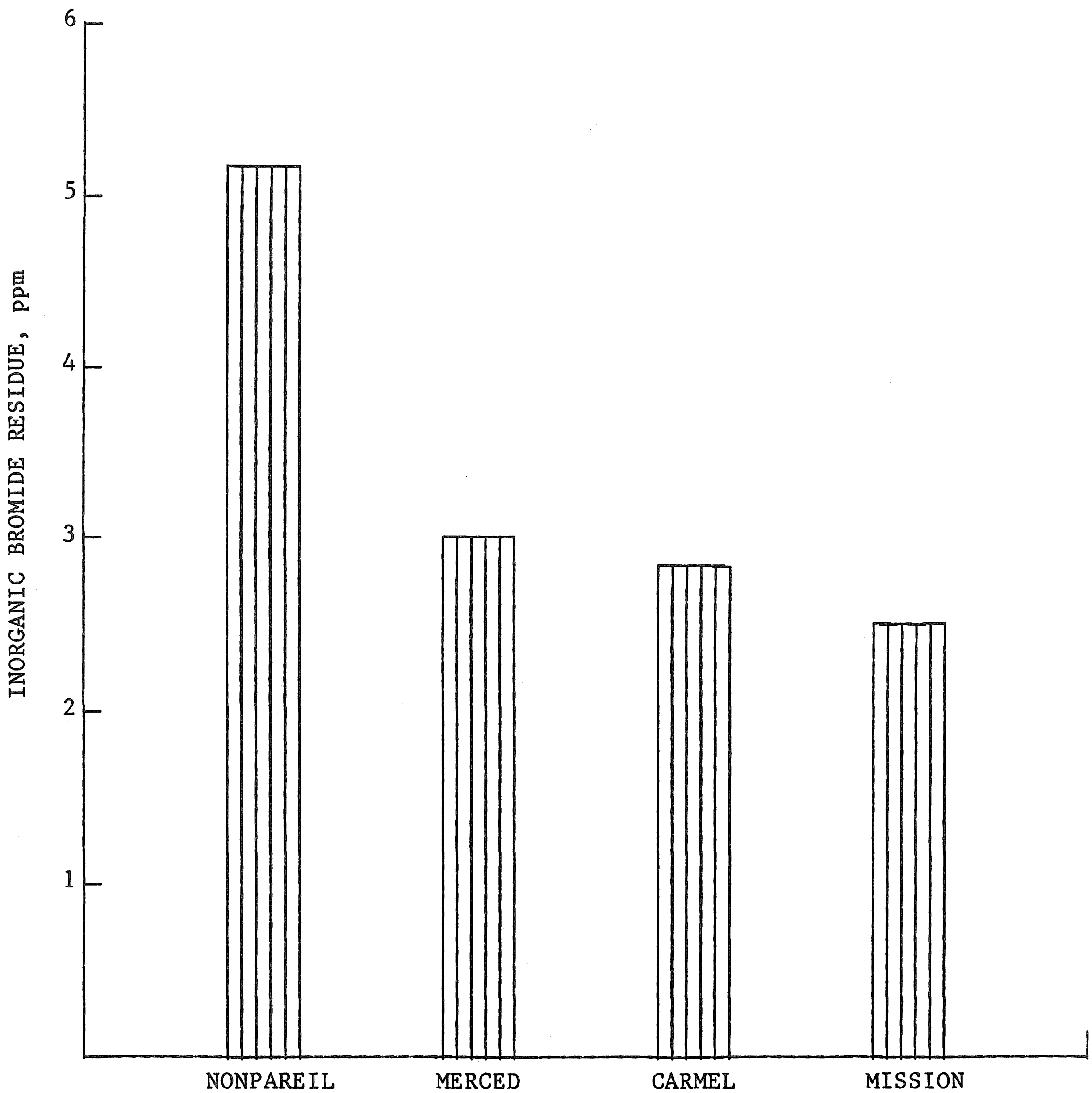


FIGURE 15 - METHYL BROMIDE DEPLETION IN CHAMBER AIR AT DIFFERENT TEMPERATURES. FUMIGATION OF INSHELL NONPAREIL ALMONDS IN WOODEN BINS AT 16 OZ. METHYL BROMIDE/1000 CU. FT.

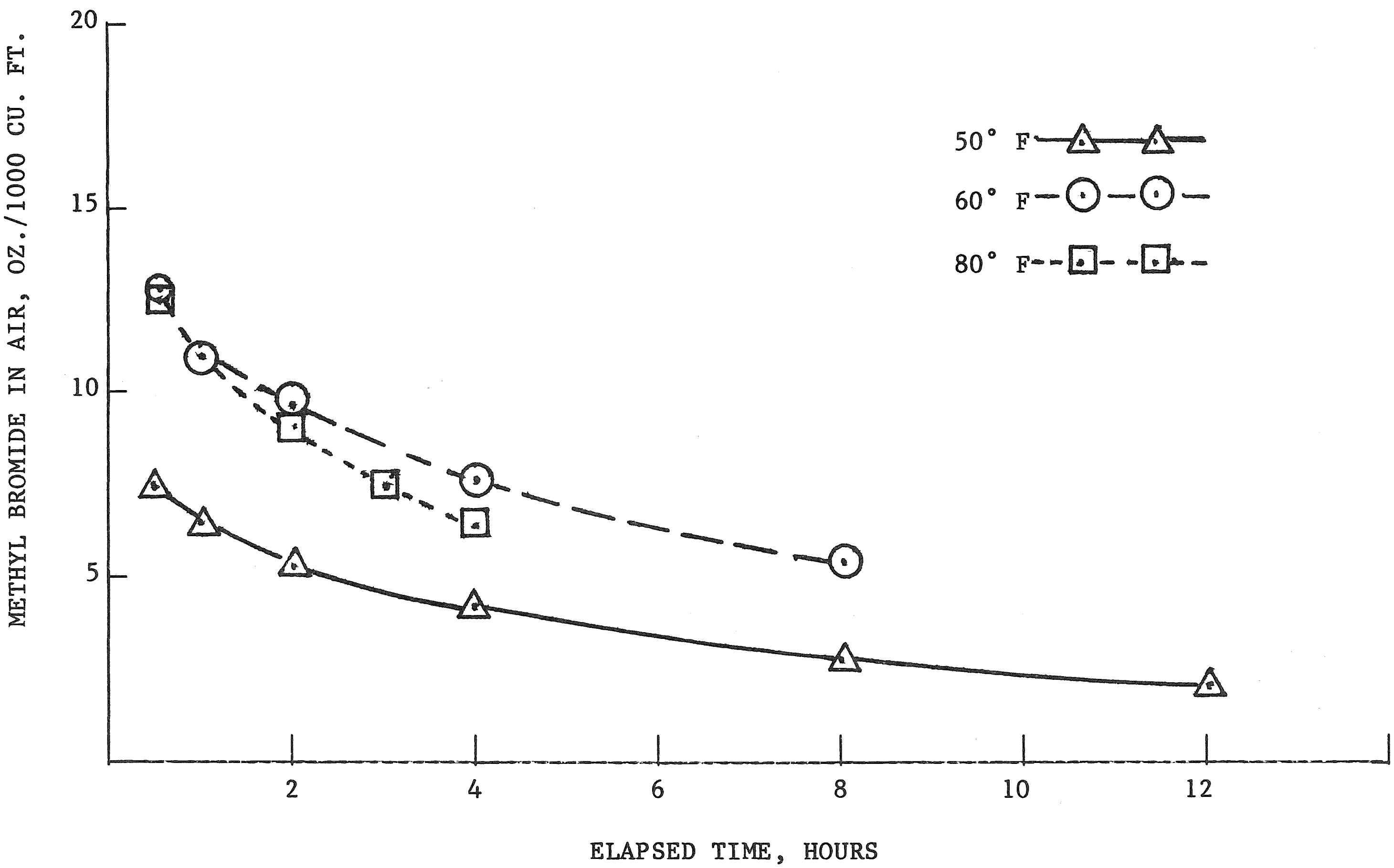


FIGURE 16 - METHYL BROMIDE DEPLETION IN CHAMBER AIR AT DIFFERENT TEMPERATURES. FUMIGATION OF NONPAREIL ALMOND KERNELS IN CARTONS AT 16 OZ. METHYL BROMIDE/1000 CU. FT.

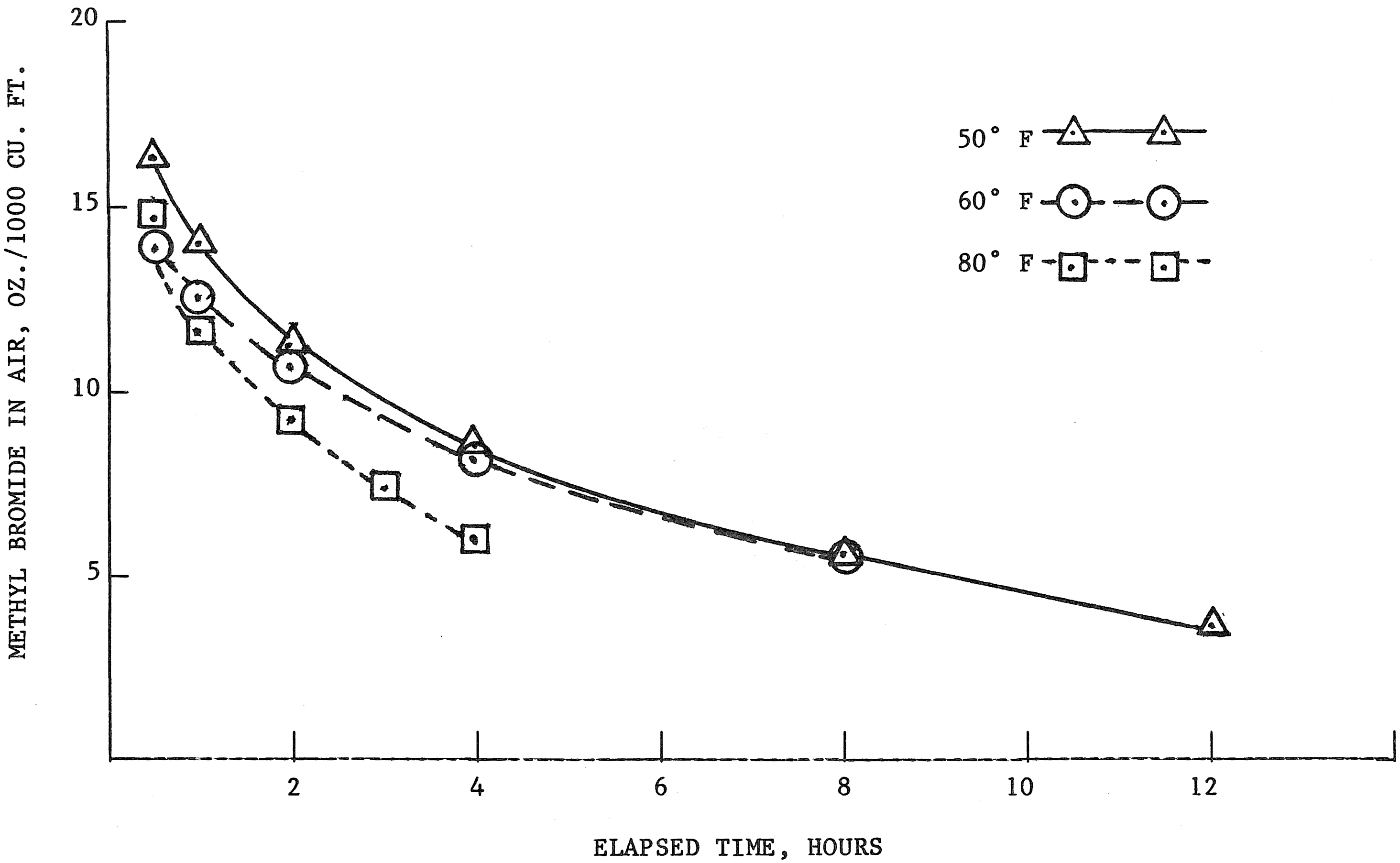


FIGURE 17 - EFFECT OF TEMPERATURE ON KERNEL INORGANIC BROMIDE RESIDUES. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF NONPAREIL KERNELS AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS

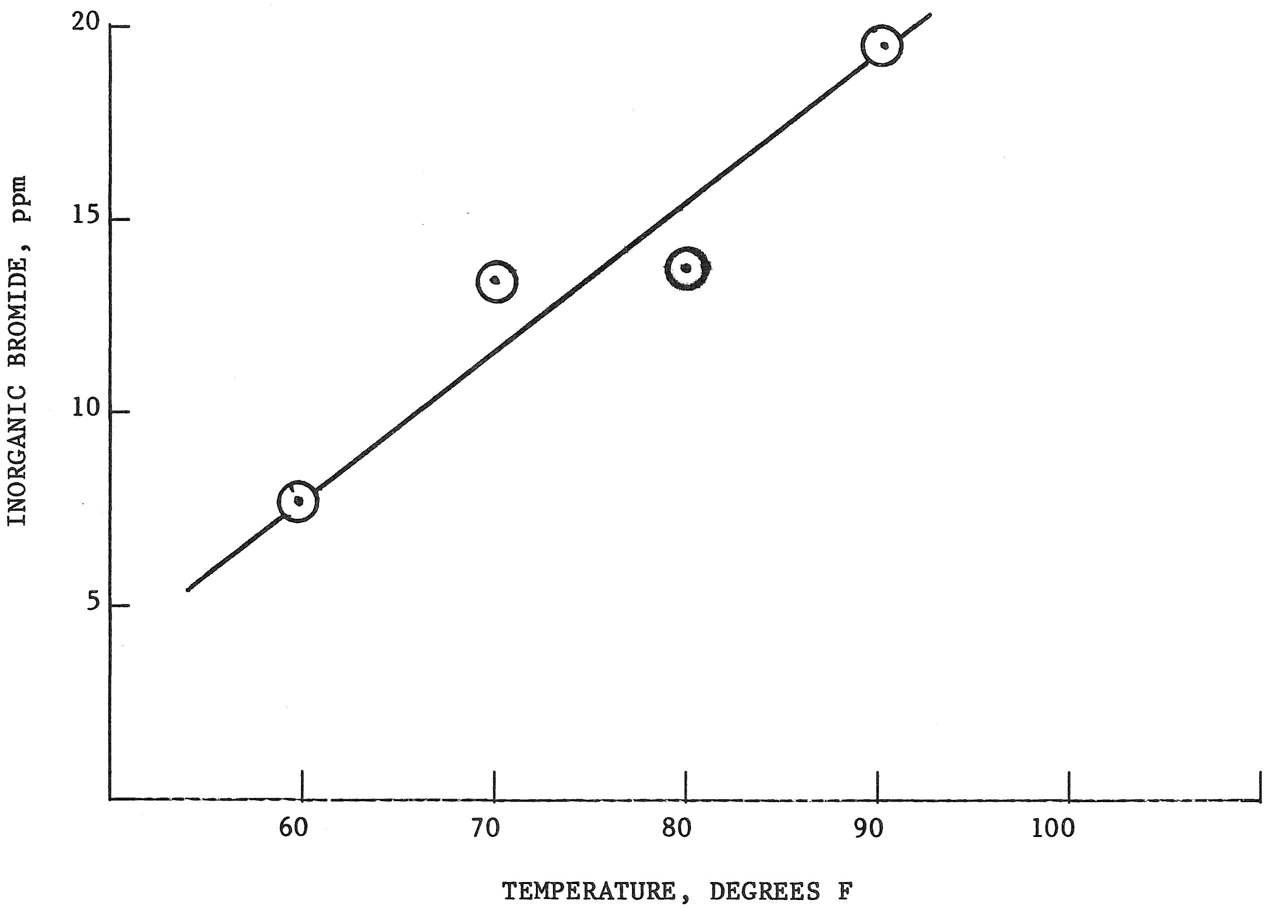


FIGURE 18 - EFFECT OF TEMPERATURE ON INORGANIC BROMIDE RESIDUES IN KERNELS. SMALL SCALE (1 CU. FT. CHAMBER) FUMIGATION OF INSHELL NONPAREIL ALMONDS AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS

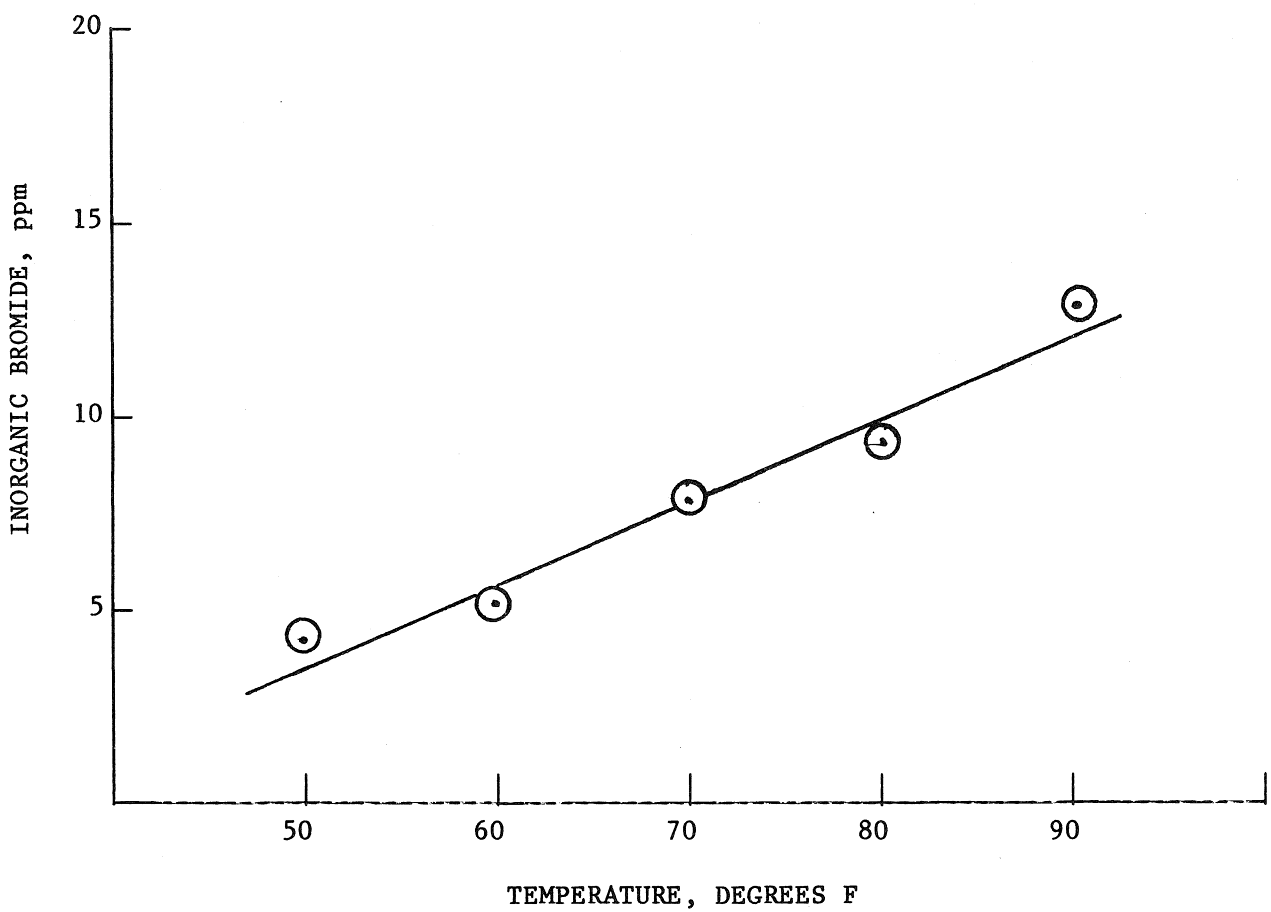


FIGURE 19 - METHYL BROMIDE DEPLETION IN CARTON AIR DURING FUMIGATION OF NONPAREIL KERNELS IN CARTONS. METHYL BROMIDE AT 16 OZ./1000 CU. FT. FOR 8 HOURS AT 60° F.

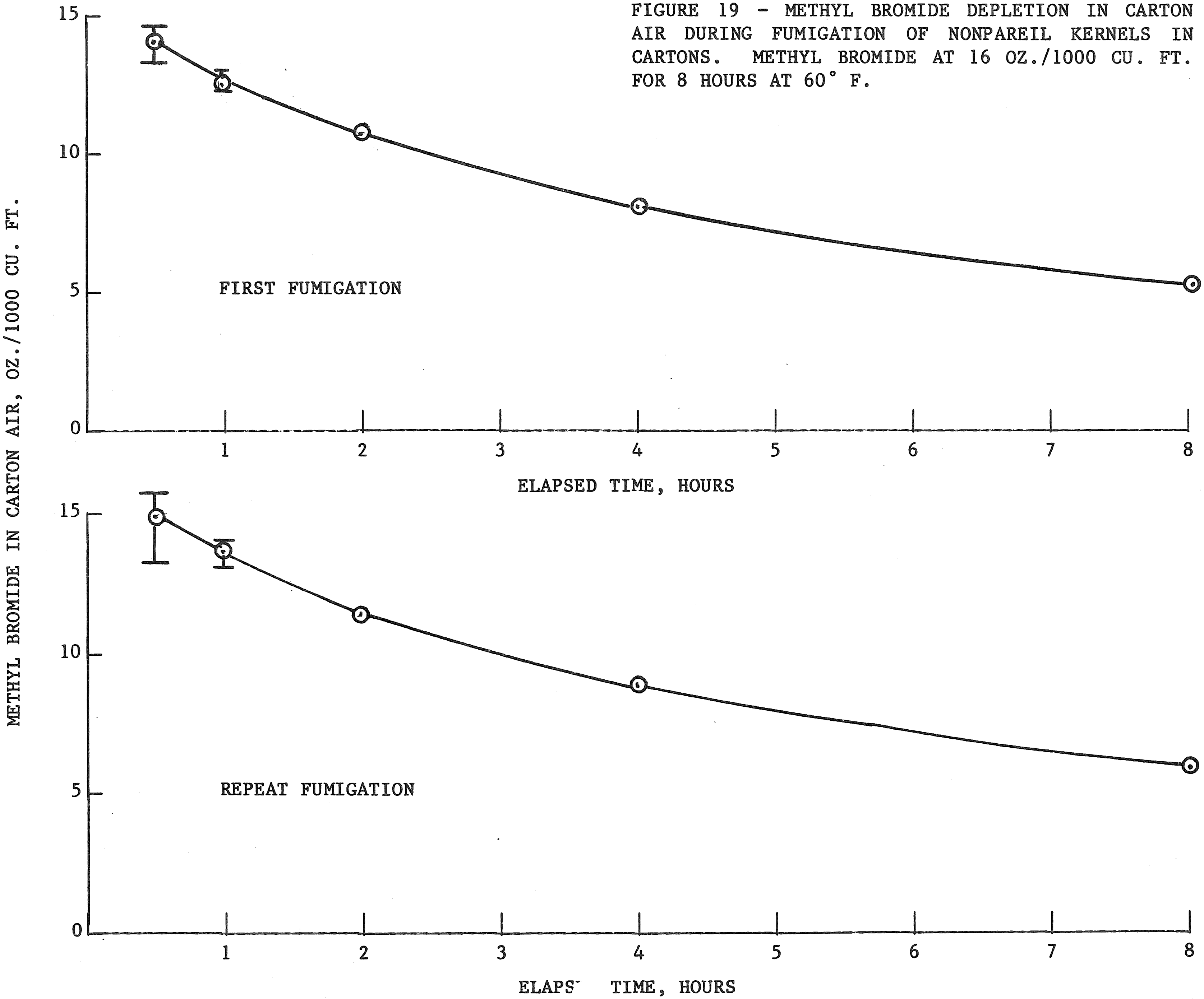


FIGURE 20 - METHYL BROMIDE DEPLETION IN CARTON AIR DURING AERATION OF NONPAREIL KERNELS IN CARTONS. SEE FIGURE 19 FOR DETAILS OF FUMIGATION

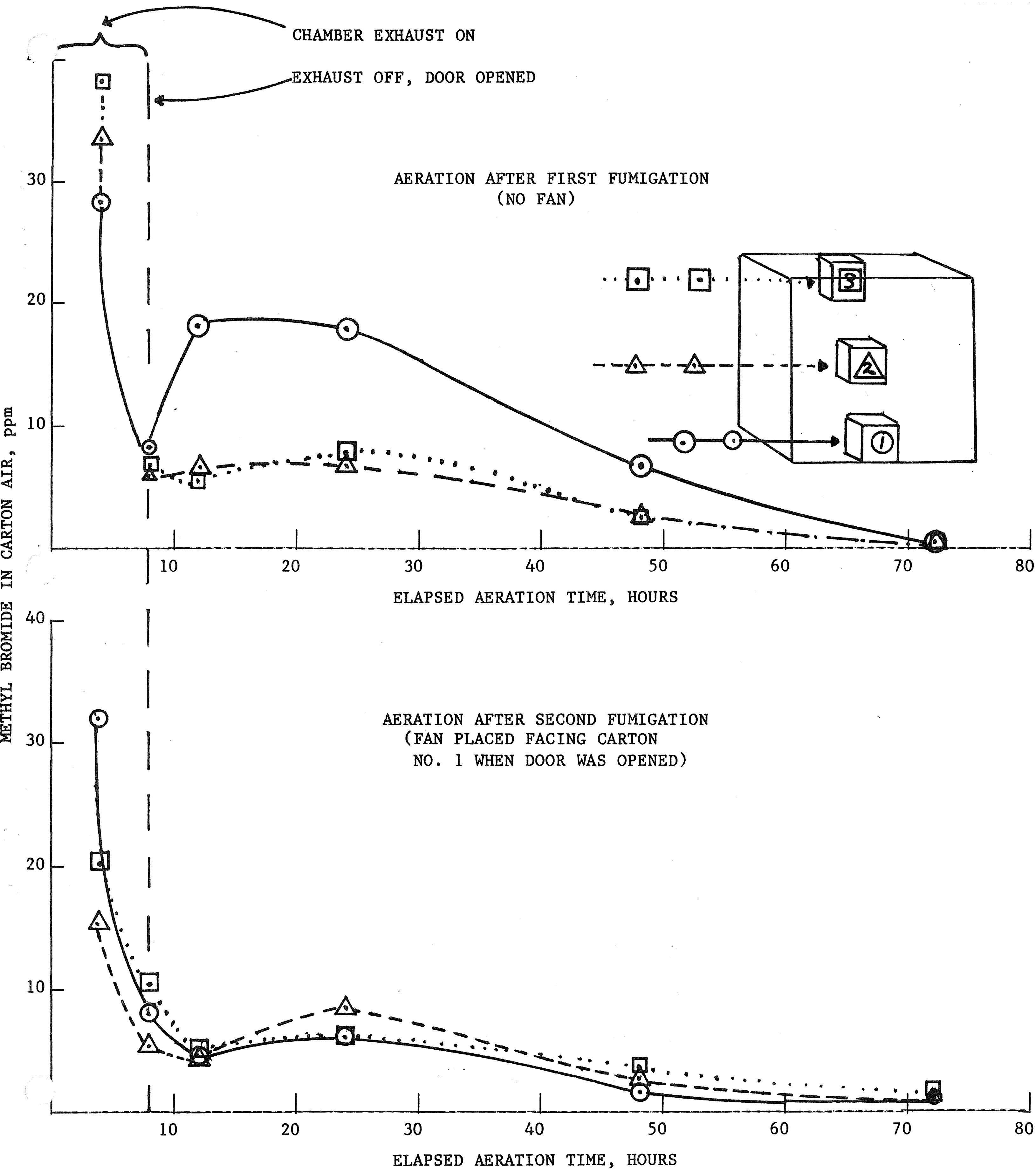


FIGURE 21 - CHANGE IN METHYL BROMIDE RESIDUES IN NONPAREIL KERNELS DURING AERATION. SAMPLES TAKEN FROM RANDOMLY SELECTED CARTONS AT FRONT OF CHAMBER, WITH A DIFFERENT CARTON SAMPLED EACH RUN. SEE FIGURE 19 FOR DETAILS OF FUMIGATION.

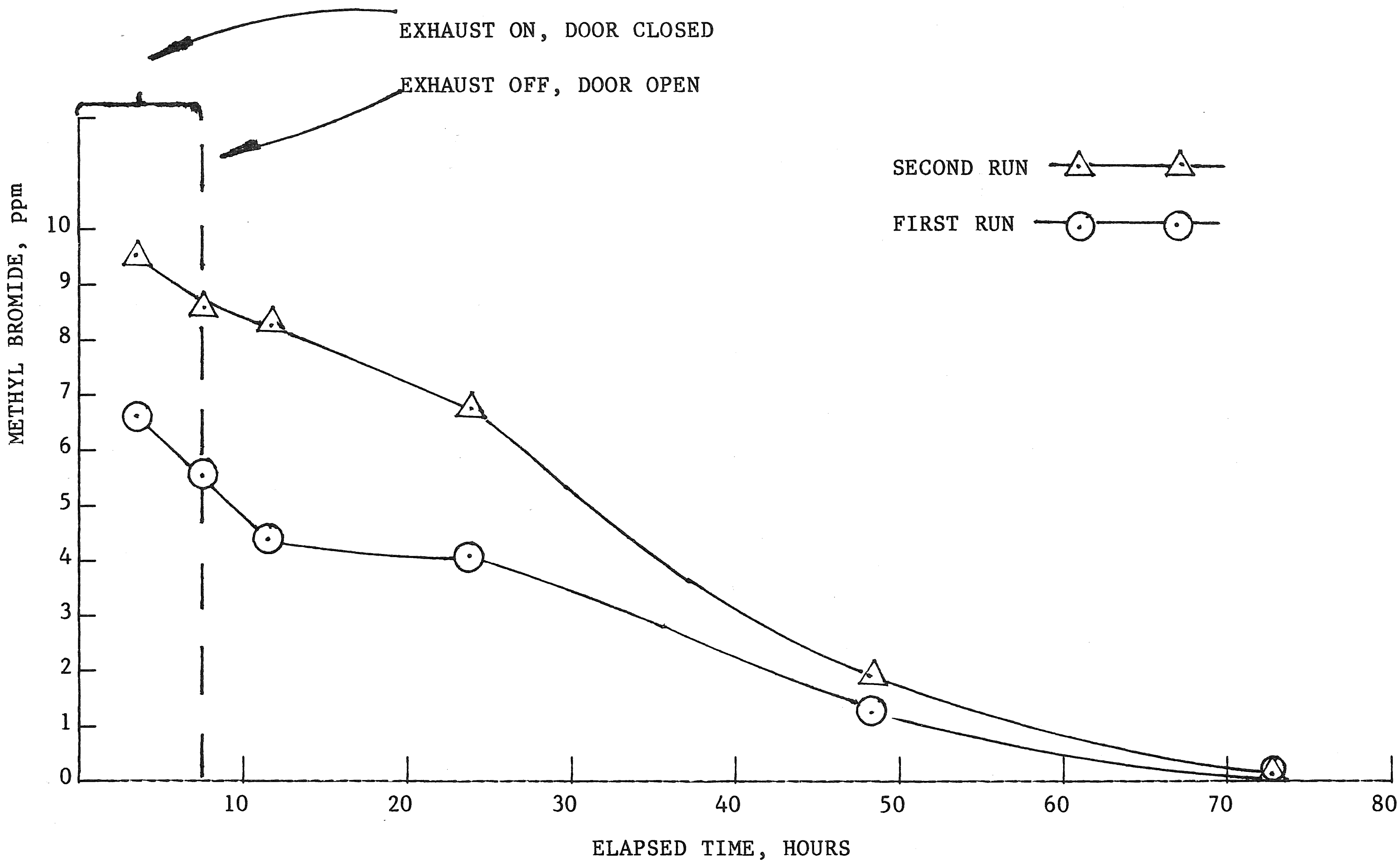


FIGURE 22 - FUMIGATIONS OF NONPAREIL KERNELS IN CARTONS - INORGANIC BROMIDE RESIDUES REMAINING AFTER 72 HOURS OF AERATION. SEE FIGURE 19 FOR CONDITIONS OF FUMIGATION AND FIGURES 20 AND 21 FOR CONDITIONS OF AERATION.

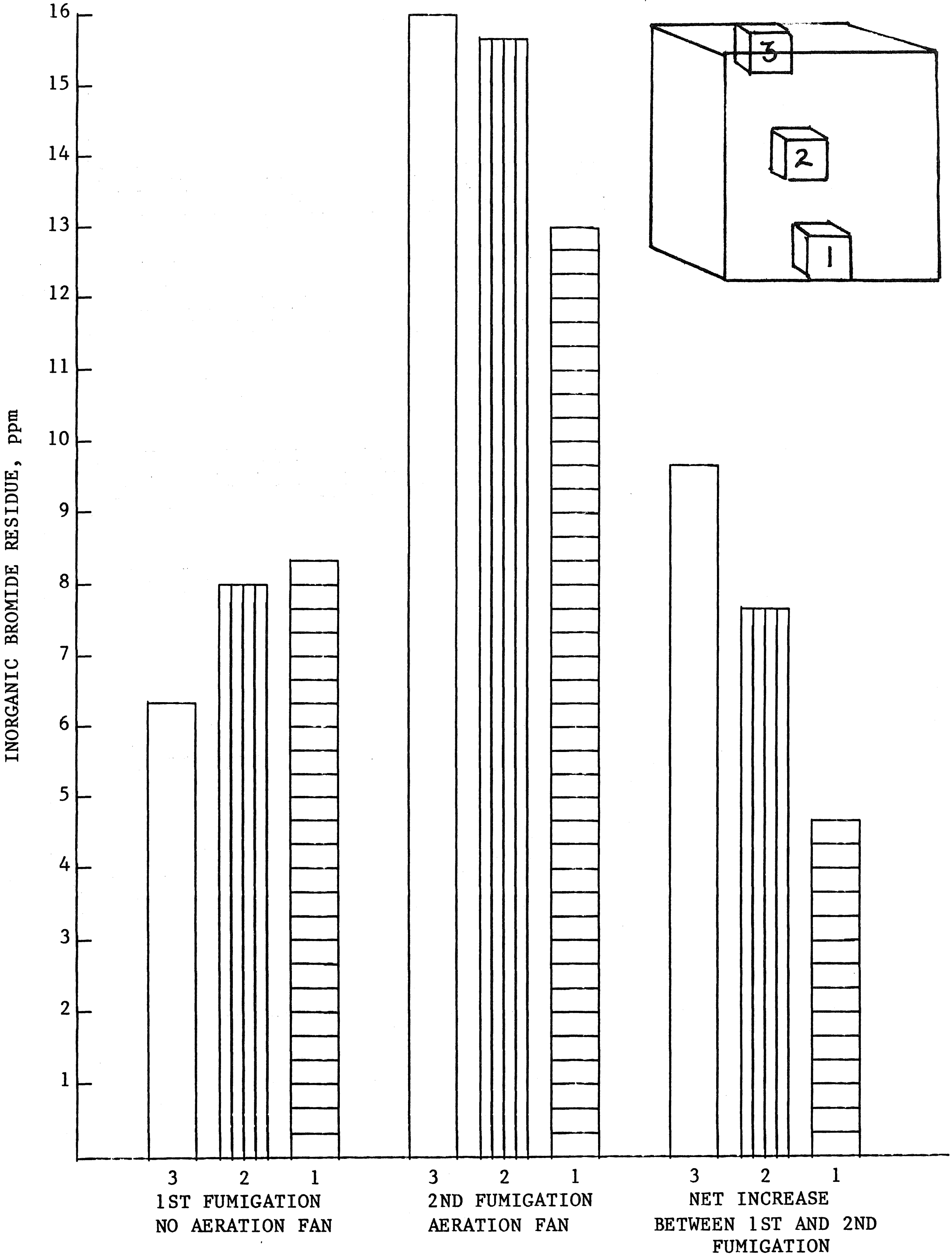


FIGURE 23 - INORGANIC BROMIDE RESIDUES REMAINING IN SHELLS AND KERNELS OF INSHELL NONPAREIL ALMONDS AFTER THREE SUCCESSIVE FUMIGATIONS IN SLOTTED WOODEN BINS. FUMIGATION AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

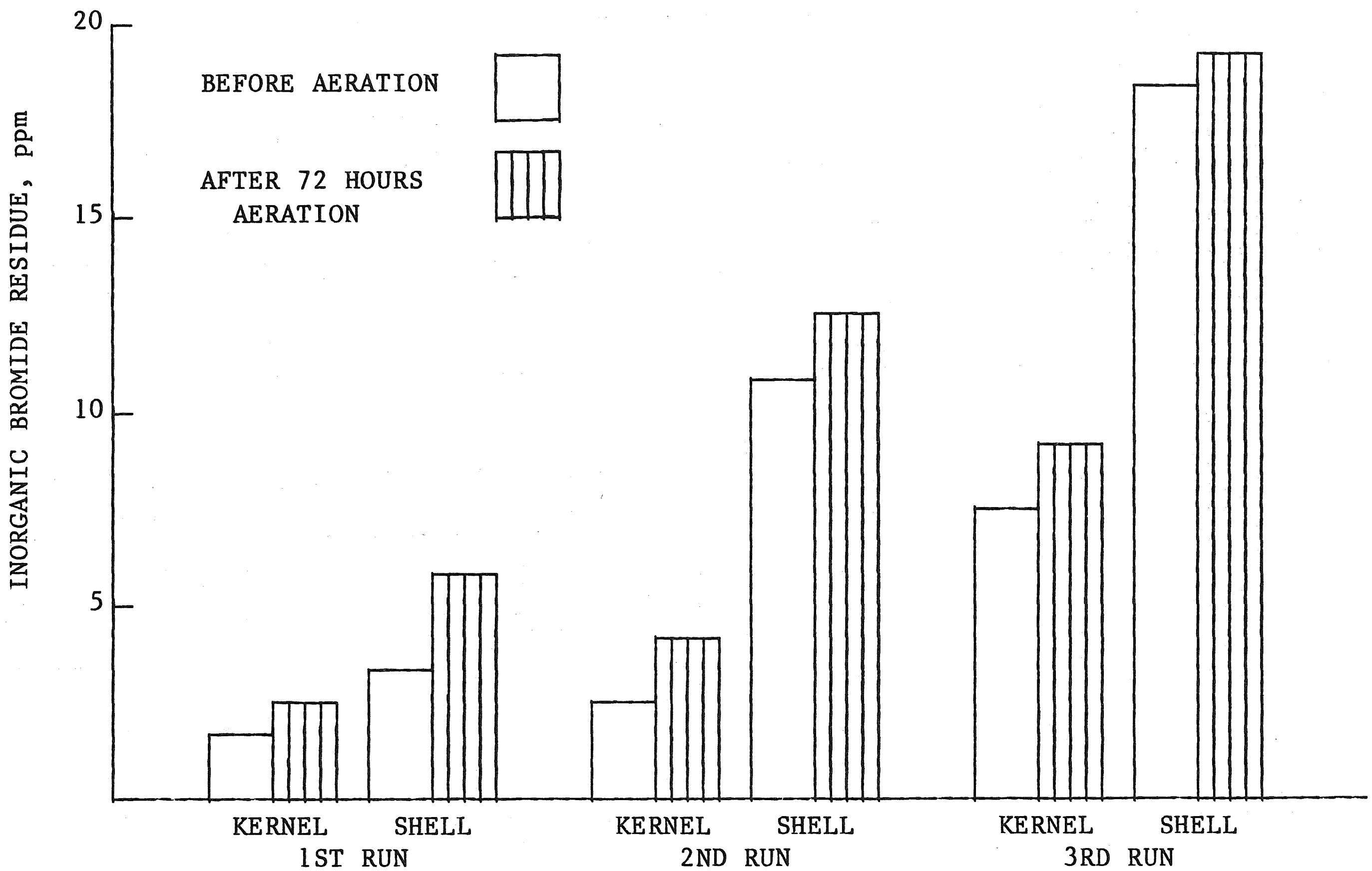


FIGURE 24 - COMPARISON OF METHYL BROMIDE DEPLETION IN AIR SPACE OF SLOTTED AND UNSLOTTED WOODEN BINS DURING AERATION OF FUMIGATED INSHELL NONPAREIL ALMONDS. FUMIGATION AT 16 OZ. METHYL BROMIDE/1000 CU. FT. FOR 8 HOURS AT 60° F.

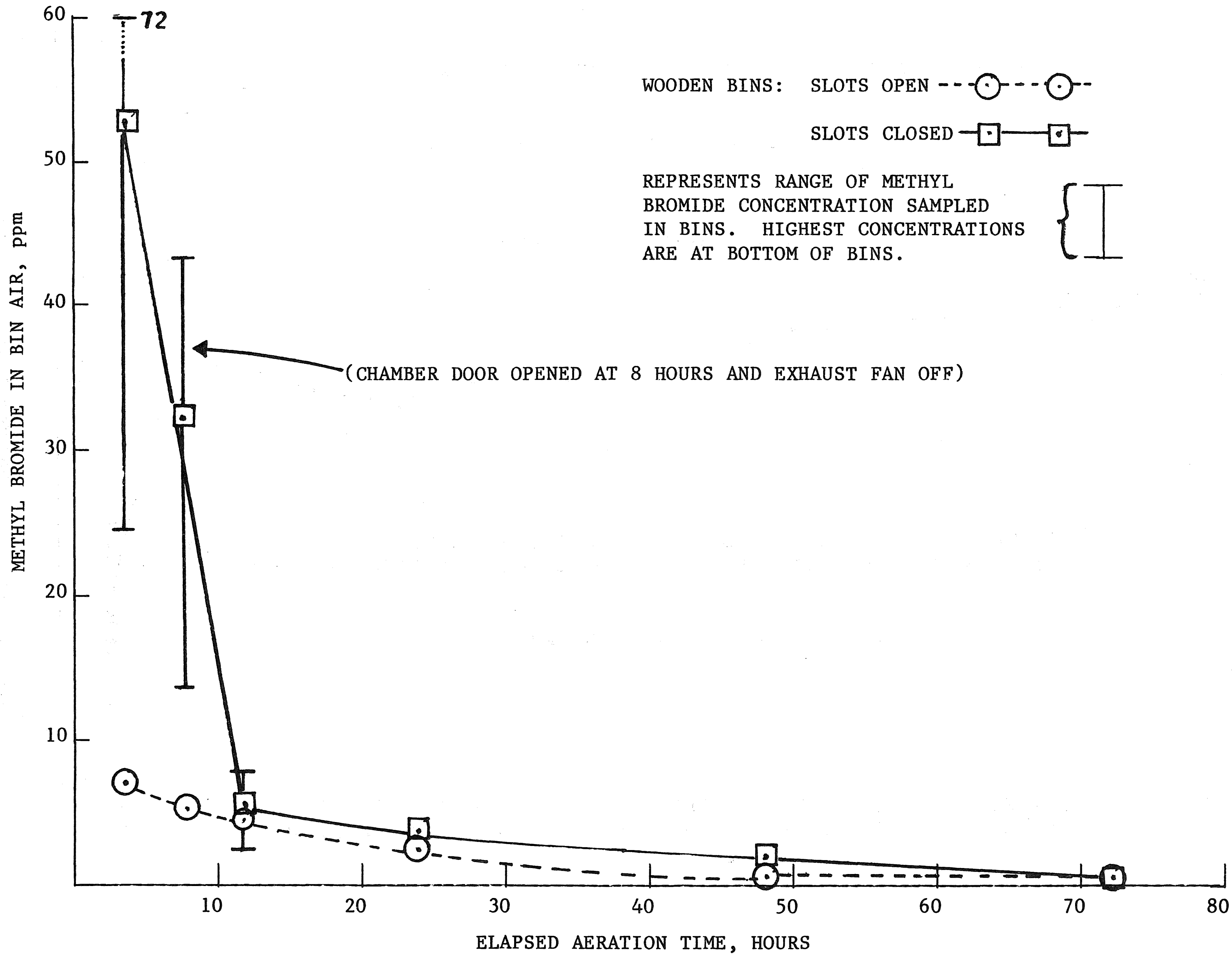


FIGURE 25 - COMPARISON OF METHYL BROMIDE DEPLETION IN CARTONS AND IN SLOTTED WOODEN BINS DURING AERATION. SEE FIGURE 19 FOR DETAILS OF CARTON FUMIGATION AND FIGURE 23 FOR DETAILS OF BIN FUMIGATION.

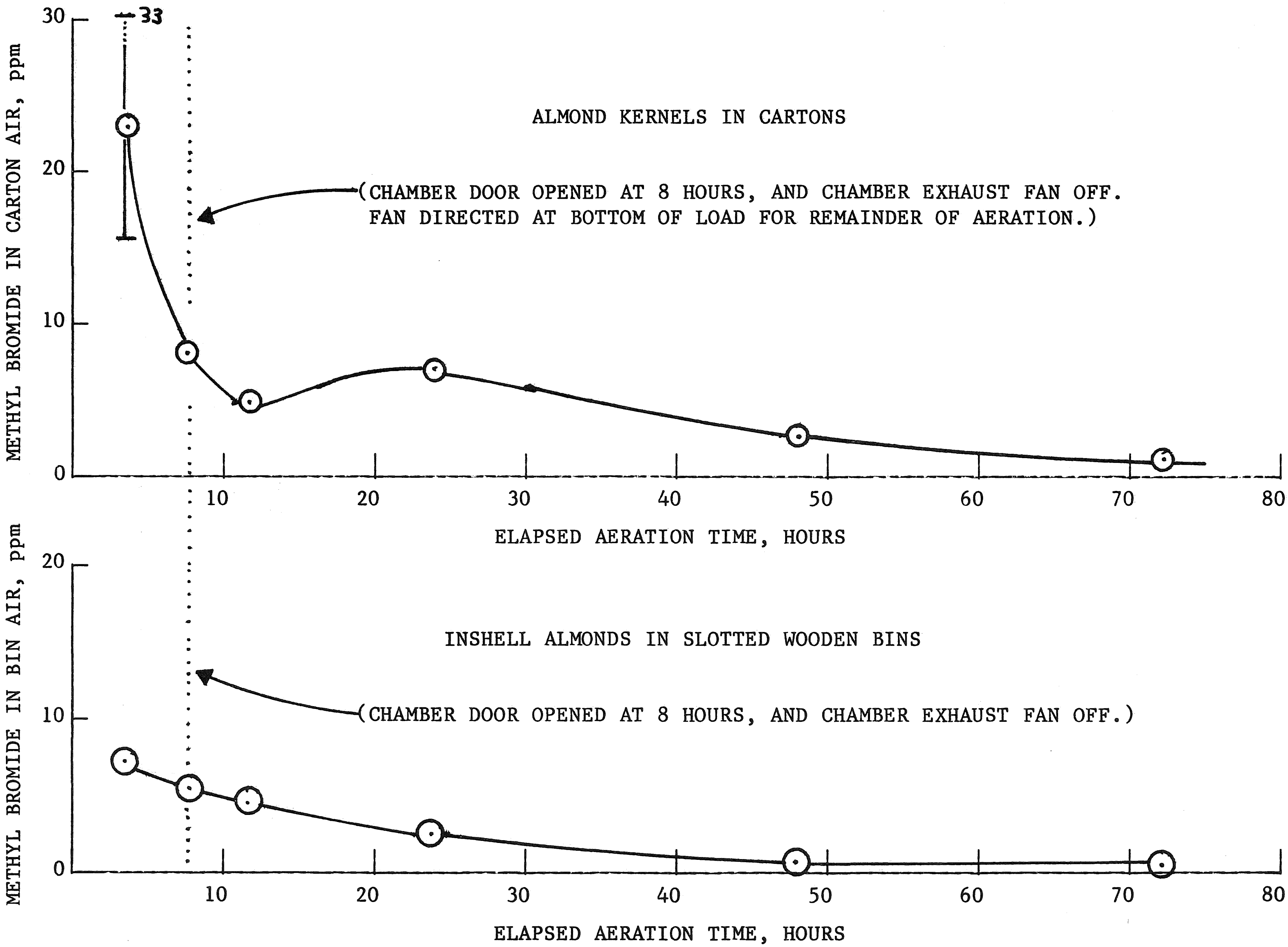


FIGURE 26 - EFFECT OF INCREASING METHYL BROMIDE DOSAGE ON INORGANIC BROMIDE RESIDUES IN KERNELS OF INSHELL NONPAREIL ALMONDS. SMALL SCALE (1 CU. FT.) FUMIGATION FOR 8 HOURS AT 60° F.

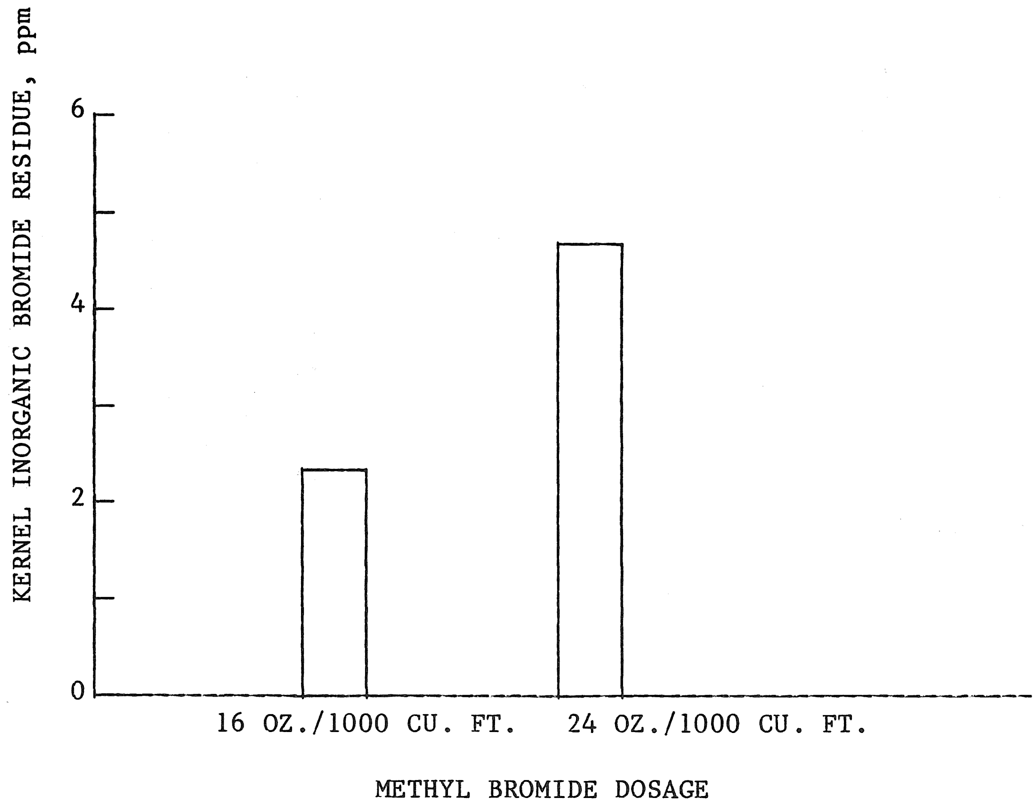


FIGURE 27 - INORGANIC BROMIDE RESIDUES IN ALMOND PRODUCTS DURING A SERIES OF THREE FUMIGATIONS. FUMIGATION AT 3 1/2 POUNDS METHYL BROMIDE/1000 CU. FT. FOR 12 AND 24 HOURS AT 80° F.

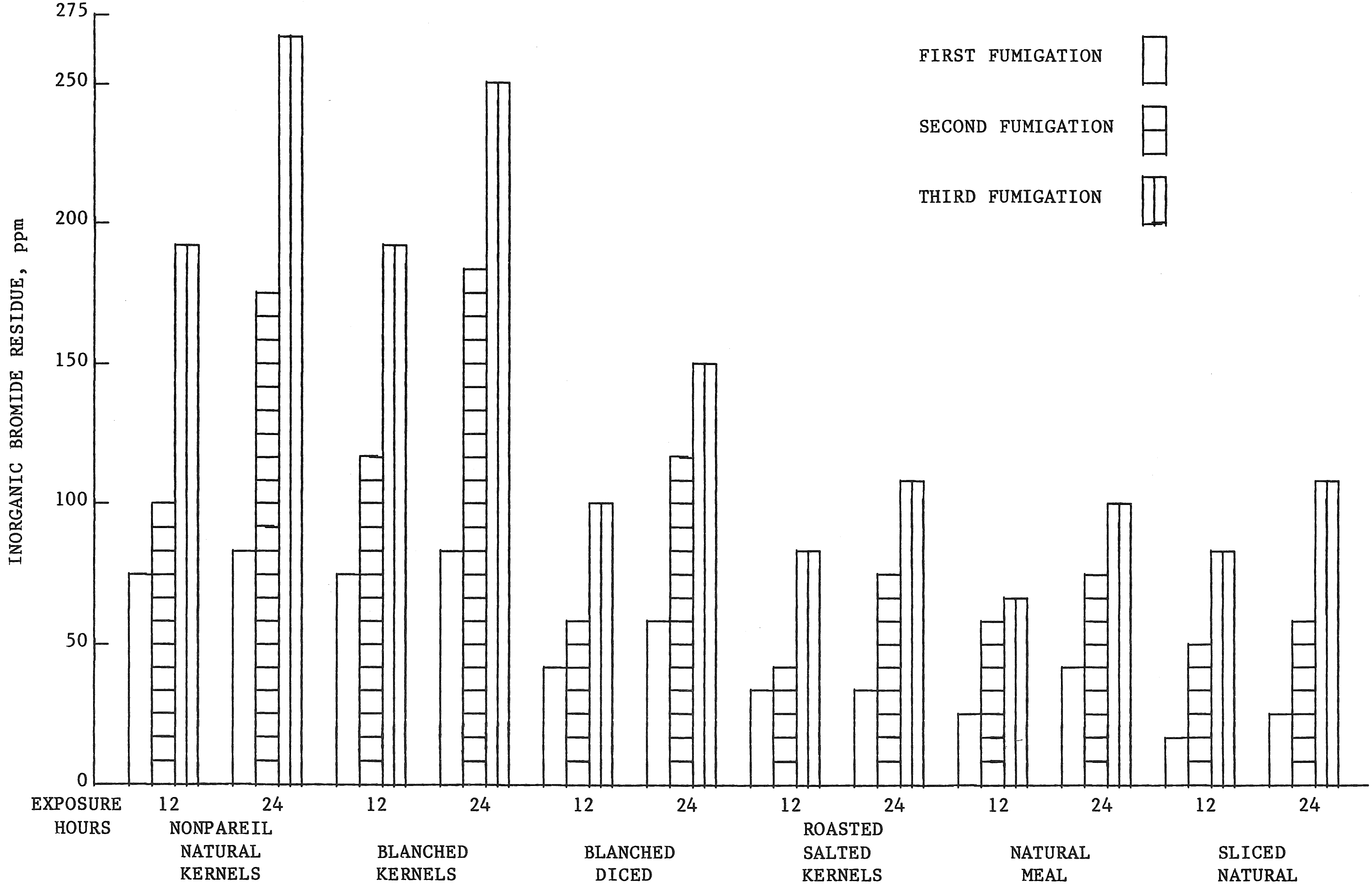


FIGURE 28 - DEPLETION OF METHYL BROMIDE FROM CHAMBER AIR DURING FUMIGATION OF ALMOND PRODUCTS. FUMIGATION AT 3 1/2 POUNDS METHYL BROMIDE/1000 CU. FT. FOR 24 HOURS AT 80° F.