



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
WASHINGTON, D.C. 20460

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OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Methyl Bromide Registration Standard. Protocols for Post Harvest Fumigation of Raisins, Prunes, Walnuts, and Almonds. (RCB #'s 4120, 4131, 4132, and 4134)

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In response to data gaps cited in the Methyl Bromide Registration Standard, the law office of Heron, Burchette, Ruckert, and Rothwell, representing the California Raisin Advisory Board (CRAB) has submitted protocols for the determination of methyl bromide and inorganic bromide levels on raisins, prunes, walnuts, and almonds after postharvest fumigation.

Summary of Deficiencies Relating to the Present Submission

- Numerous deficiencies have been cited in the submitted protocols. The protocols should take into account various fumigation temperatures, aeration temperatures, commercial packaging, cultivars, and fumigation intervals. CRAB also needs to explain how it determined the number of fumigations for each commodity; e.g., the protocol calls for 10 fumigations to raisins, and 2 for prunes. The protocol also employs a fumigation chamber with a capacity of 1 cu ft. No data have been submitted to bridge from this little chamber to the chambers used in commercial operations. RCB is concerned that after a 24 hr aeration period, residue levels in samples which can be contained in the small chamber may differ markedly from residue levels resulting in commercial operations, where several hundred pounds of a commodity are

fumigated and aerated. The protocols should also specify the preplant fumigation rate. Residue data reflecting the use of vacuum chambers are needed unless this use is removed or specifically excluded from the label.

### Recommendations

RCB recommends that CRAB should be sent a copy of this review as well as a copy of RCB's review of 7/14/88. The issues raised by RCB should either be incorporated into revised protocols or CRAB should explain why the protocols do not need revision. CRAB will need to support its arguments with documentation.

### Detailed Considerations

#### Data Gap Cited in the Methyl Bromide Registration Standard

##### Dried Fruit

The Registration Standard cited the need for additional data on dried fruits treated at 1.5 lb ai/1000ft<sup>3</sup> for 24 hours. Multiple applications are required, if appropriate. The data should reflect the use of several fumigation techniques, including vacuum chamber fumigation. Residue levels of MeBr and inorganic bromide (iBr) should be determined. Aeration should be continued until MeBr is nondetectable, and an aeration period should be proposed.

##### CRAB Response-Prunes

Fresh prunes grown in preplant fumigated soil will be dried by the process of tunnel drying. Three replicate samples of prunes grown on fumigated and nonfumigated soil will be analyzed for MeBr and iBr after drying.

The prunes grown in preplant fumigated soil will then be fumigated in one cubic foot atmospheric chambers located at the USDA-ARS station in Fresno. These chambers meet or exceed all performance requirements by USDA-APHIS. The prunes will be fumigated at a rate of 1.5 lb ai/1000 ft<sup>3</sup> for 24 hours at 50° F. The samples will be aerated for 24 hours, at which time samples will be taken for analysis for MeBr and iBr. Periodic samples will be taken for analysis until MeBr has declined to 0.01 ppm; at least 5 samples will be taken following aeration so that a decline curve can be generated.

After residues of MeBr in the prunes have decreased to 0.01 ppm, the prunes will be refumigated as before. A second decline curve extending to 0.01 ppm MeBr will be constructed.

Samples collected for residue analysis will be placed on dry ice immediately. If samples are not analyzed on the same day as collected, they will remain frozen until the analysis can be run.

The decline of MeBr residue levels in the frozen commodity will be followed. The storage stability study will extend beyond the sampling to analysis interval. Fortification/recovery data will be generated.

RCB's Comments/Conclusions, re: Prune Fumigation Study

The protocol should reflect the following modifications:

1. The protocol does not specify the preplant fumigation rate. The Methyl Bromide Registration Standard cited the need for residue data on plums grown in soil fumigated preplant at 870 lb ai/A. Fruit should be harvested 2 years posttreatment (or as soon as fruit are available).
2. The Registration Standard specified that commercial fumigation equipment should be used. RCB does not consider a one cubic foot chamber to represent commercially significant equipment. CRAB would need to demonstrate that use of the small chamber represents the worst case.

The chamber could be used in pilot studies; for instance, the chamber could be useful in determining which type of commercial packaging represents the worst case or the effect of fumigation temperature on MeBr residue levels. Once the worst case has been established, the protocol should include at least 3 "runs."

3. If it is CRAB's intent to permit fumigation in vacuum chambers, data reflecting the use of such chambers are required.
4. The type of packaging may affect the residue levels in the prunes; the residue levels should be determined in prunes packaged in common commercial containers to determine which type represents the worst case. Prunes should be sampled from different sections of the package. Residue data reflecting fumigation using that type of packing material should then be submitted. If it is practical, the label might be revised to permit fumigation of prunes in specific types of cartons; then the residue data should reflect the use of those types of cartons.
5. The temperature of the fumigation in the protocol is 50° F. The effect of temperature on residue levels from fumigation is very complex [See "Factors Affecting the Fumigation of Food Commodities for Insect Control," J. Econ. Entomol., 51 (6), 891-900 (1958)] If CRAB can show that a label restriction specifying a narrower range of fumigation temperatures is practical, residue data covering that range of temperatures would be adequate. The present label only restricts fumigation to temperatures ≥50° F. Otherwise, residue data covering the range of temperatures expected in commercial chambers and/or of the commodities themselves would be required.

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RCB needs to know the shortest fumigation intervals which can occur as prunes move through commercial channels. If this interval is shorter than that required for MeBr levels to drop to 0.01 ppm, the prunes should be refumigated after the shortest fumigation interval has elapsed, even if MeBr residues are >0.01 ppm.

6. The type of aeration (forced or unforced) should be specified. Residue data reflecting commercial equipment and aeration are required because the extent of residue removal following commercial fumigation and aeration could differ markedly from that following fumigation and aeration of the amount of prunes which can be contained in a 1 ft<sup>3</sup> chamber.

The temperature of the aeration should reflect the worst case, and CRAB will need to support its position that the temperature selected for aeration actually represents the worst case. If CRAB can show that a label restriction is practical, the label could be revised via MBIP to specify an aeration temperature and appropriate residue data could be submitted.

The revised label will also need to specify the type of aeration (forced or unforced) to be used.

7. CRAB will need to explain why 2 fumigations are adequate. If no more than 2 fumigations are expected as prunes move through commercial channels, this position should be supported by documentation or marketing experts.
8. After fumigation, MeBr levels should be monitored in various parts of the loaded vault before sampling. Load factors typical of commercial operations should be used.
9. Analyses should be run as soon as possible. The samples should be placed in airtight jars and kept at dry ice temperatures until analysis. Even under these conditions, data submitted by MBIP have shown that about 30% of the MeBr residues may be lost from certain commodities after 24 hours (Storage Stability of Fumigated Products, MRID No. 406185-01).

CRAB will need to describe in detail the precautions taken during sample handling (such as pit removal) to prevent the loss of the volatile analyte.

10. Individual results for each analysis should be submitted, rather than averages. Fortification/recovery data for MeBr and iBr should also be submitted, along with representative chromatograms, calculations, standard curves, etc.
11. If tolerances are proposed on the basis of residue levels following a period of aeration, CRAB will need to demonstrate that the aeration period is appropriate (i.e., that the com-

modity will not be available for sampling by the FDA before the aeration period has elapsed).

#### CRAB Response-Raisins

Three replicate samples of raisins from grapes grown on fumigated and nonfumigated soil will be analyzed for MeBr and iBr after drying. The raisins grown in preplant fumigated soil will then be fumigated and aerated as described under Prunes. Samples will be analyzed until MeBr residue levels drop to 0.01 ppm. At least 5 samples will be used to generate the decline curve. The raisins will then be refumigated as before, and a second decline curve will be constructed. The raisins will be fumigated a total of 10 times. Following the fumigations, aeration will proceed for 24 hours, and three samples will be taken from fumigations 1, 5, and 10. Sampling will continue until MeBr residue levels decline to 0.01 ppm. At least 5 samplings will be used to construct the decline curve. Analyses for MeBr and iBr will be carried out.

Samples collected for residue analysis will be placed on dry ice immediately. If samples are not analyzed on the same day as collected, they will remain frozen until the analysis can be run. CRAB also states, "In addition, analysis of organic bromide deterioration in frozen commodity exceeding the amount of time samples will be held will also be provided. A spike sample will be run to validate the standard curve each time a sample is analyzed."

#### RCB's Comments/Conclusions, re: Raisin Fumigation Study

The protocol should reflect the following modifications:

1. The protocol does not specify the preplant fumigation dosage rate. The Registration Standard cited the need for residue data on grapes grown in soil fumigated preplant at 600 lb ai/A.
2. After the first fumigation has been conducted, the protocol states, "The commodity will be refumigated at the same dosage after reaching 0.01 ppm organic bromide. Sampling will occur [from the second fumigation?] as noted above until 0.01 ppm organic bromide residue is obtained with a minimum of 5 sampling times. Refumigation of the same lot of fruit will occur for a total of 10 fumigations." Later in the protocol, CRAB states that samples will be drawn from fumigations 1, 5, and 10, yet the segment quoted above implies that samples will be taken from the second fumigation as well. CRAB should also specify whether samples will be refumigated directly after the 24 hour aeration period following treatments for which no decline curves will be generated.

CRAB will need to describe the protocol more clearly.

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3. CRAB intends to fumigate raisins 10 times and prunes 2 times, but has given no justification for the number of applications chosen. CRAB needs to explain why raisins need to be fumigated 10 times (why not 2, or 20?).
4. The following modifications cited by RCB for the prune protocol also apply to the raisin protocol. These modifications are described fully in RCB's Comments/Conclusions in the prune protocol section of this review.
  - a. Commercial equipment should be used; the protocol should include at least 3 "runs."
  - b. Residue data from vacuum chambers may be required.
  - c. The effect of packaging on residue levels should be investigated.
  - d. The effect of fumigation temperature (in the chamber or the stored commodity) should be investigated. The interval between fumigations should correspond to the shortest fumigation interval as the commodity moves through commercial channels.
  - e. The aeration type should be specified; the effect of aeration temperature should be investigated.
  - f. MeBr levels should be determined in various sections of the vault before sampling
  - g. The analyses should be run as soon as possible.
  - h. Individual results for each analysis should be submitted, rather than averages. Fortification/recovery data for MeBr and iBr should also be submitted, along with representative chromatograms, calculations, standard curves, etc.
  - i. If a tolerance is proposed based on an aeration time, CRAB will need to demonstrate that the aeration time is practical.

#### Data Gap Cited in the Methyl Bromide Registration Standard

##### Tree Nuts

Additional data are required for the representative commodities almonds, pecans, and English walnuts; these nuts are to be grown in soil fumigated preplant at 870 lb ai/A and then fumigated postharvest at 3.5 lb ai/1000 ft<sup>3</sup> for 24 hours as soon as ripe nuts are available from treated plots or 2 years later. Several commercial fumigation methods (such as vacuum chambers) should be

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tested. The maximum number of treatments used commercially should be tested. MeBr and iBr should be determined before and after the postharvest fumigation. Sampling should be continued until MeBr is undetectable (preferably approaching 0.001 ppm). Residue levels in almond hulls should also be determined.

#### CRAB Response

##### Almonds

Almonds grown on preplant fumigated soil and untreated soil will be obtained at harvest. The almonds grown on treated soil will be fumigated in one cubic foot atmospheric chambers which meet all performance requirements by the USDA-APHIS. The dosage will be 3.5 lbs ai/1000 ft<sup>3</sup> for 24 hours at 60° F. The chamber will be aerated for 24 hours, at which time sampling will begin. The decline of MeBr will be followed until residue levels of 0.1 ppm organic bromide are attained. At least 5 samplings will be used to define the rate of decline.

After MeBr levels have declined to 0.1 ppm, the commodity will be refumigated as above, and the decline to a level of 0.1 ppm MeBr will again be followed.

The almonds will then be shelled, and the nutmeats will be re-fumigated twice more (a total of 4 fumigations). The decline of MeBr will be followed as above after each fumigation.

Three replicate samples of almonds grown on fumigated and untreated soil will be analyzed as received after drying to determine background levels of MeBr and iBr.

Samples collected for residue analysis will be placed on dry ice immediately. If samples are not analyzed on the same day as collected, they will remain frozen until the analysis can be run. The decline of MeBr residue levels in the frozen commodity will be followed. The storage stability study will extend beyond the sampling to analysis interval. Fortification/recovery data will be generated.

#### RCB's Comments/Conclusions, re: Almond Fumigation Study

1. The protocol did not specify the preplant fumigation dosage rate. The Registration Standard cited the need for residue data on almonds grown in soil fumigated at a rate of 870 lb ai/A.
2. The treatment rate for almonds (in the husk) in the Plant Protection and Quarantine Manual (PPQ) is given as 2 lbs/1000 ft<sup>3</sup> for 3.5 hours at 70° F or above. RCB concludes that the protocol conditions of 3.5 lbs/1000 ft<sup>3</sup> for 24 hours at 60° F adequately reflect the PPQ fumigation schedule. However, since the protocol calls for a 24 hour aeration time, residue

levels arising from application of the proposed protocol may not adequately predict levels of MeBr in imported almonds which have been fumigated according to the PPQ, which does not stipulate a 24 hour aeration period.

3. No residue data on almond hulls are provided for in the protocol. Since the PPQ includes a use on almonds with the hulls, residue data on almond hulls are required.

Also, residue data reflecting treatments of in-hull almonds are needed to determine whether in-shell fumigation represents the worst case.

4. RCB has learned from D. Fiskaali, of the California Department of Food and Agriculture, that commercial fumigation of nuts is sometimes carried out in vacuum chambers. (The PPQ does not include vacuum chamber fumigation of almonds.) Therefore, residue data reflecting fumigation in vacuum chambers are needed. CRAB has the option of requesting MBIP to revise the label to limit fumigation to normal atmospheric pressure chambers.
5. The protocol calls for 2 in-shell fumigations followed by 2 fumigations of nutmeats. The protocol specifies that refumigations will be conducted only after residue levels have dropped to 0.1 ppm MeBr. RCB needs to know the shortest fumigation intervals which can occur as almonds move through commercial channels. If this interval is shorter than that required for MeBr levels to drop to 0.1 ppm, the almonds should be refumigated after the shortest fumigation interval has elapsed, even if MeBr residues are >0.1 ppm.
6. CRAB needs to explain why 2 in-shell fumigations and 2 nutmeat fumigations are adequate. RCB needs to know how often almonds may be fumigated as they move through commercial channels.
7. In its review of the almond residue postharvest fumigation protocol, RCB (memo of W. Hazel, 3/24/88) concluded that any almond cultivar could be used in the studies, provided that data were submitted to document that the oil content of the different almond cultivars is similar. This information has not yet been received. Also the almond cultivar to be used in the current protocol has not been specified. CRAB will need to specify the cultivar used; if the oil content of the various cultivars differs, residue data reflecting treatment of almond cultivars with the highest oil content are required.
8. The following modifications cited by RCB for the prune protocol also apply to the almond protocol. These modifications are described fully in RCB's Comments/Conclusions in the prune protocol section of this review.



- a. Commercial equipment should be used. The protocol should include at least 3 "runs."
- b. The effect of packaging on residue levels should be investigated.
- c. The effect of fumigation temperature (of the chamber or of the stored commodities) should be investigated.
- d. The aeration type should be specified; the effect of aeration temperature should be investigated.
- e. MeBr levels should be determined in various sections of the vault before sampling.
- f. The analyses should be run as soon as possible.
- g. Individual results for each analysis should be submitted, rather than averages. Fortification/recovery data for MeBr and iBr should also be submitted, along with representative chromatograms, calculations, standard curves, etc.
- h. If a tolerance is proposed based on an aeration time, CRAB will need to demonstrate that the aeration time is practical.

#### Data Gap Cited in the Methyl Bromide Registration Standard

The data gap regarding walnuts was described under Tree Nuts on page 6.

#### CRAB Response

CRAB has submitted a walnut postharvest fumigation study. This study is identical to the almond protocol with one exception: the walnuts will be subjected to two in-shell fumigations (as with almonds), but the nutmeats from these samples will only be subjected to one fumigation, for a total of 3 fumigations, instead of 4.

#### RCB's Comments/Conclusions, re: Walnut Fumigation Study

1. The protocol did not specify the preplant fumigation dosage rate. The Registration Standard cited the need for residue data on walnuts grown in soil fumigated at a rate of 870 lb ai/A.
2. The treatment rate for walnuts (in the husk) in the PPQ is given as 2 lbs/1000 ft<sup>3</sup> for 3.5 hours at 70° F or above. RCB concludes that the protocol conditions of 3.5 lbs/1000 ft<sup>3</sup> for 24 hours at 60° F adequately reflect the PPQ fumigation schedule. However, since the protocol calls for a 24 hour aeration time, residue levels resulting from application

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of the proposed protocol may not adequately predict levels of MeBr in imported almonds which have been fumigated according to the PPQ, which does not stipulate a 24 hour aeration period.

If the protocol is intended to cover residues in/on imported walnuts, the protocol should include treatments of walnuts in the husk in order to determine the worst case (in-shell or in-hull fumigation).

3. CRAB needs to explain why the walnuts are to be subjected to 2 in-shell fumigations and one shelled fumigation. How did CRAB decide upon the number of fumigations?
4. CRAB needs to specify the type of cultivar used in the walnut study. The cultivar with the highest oil content should be used in the fumigation study, unless CRAB can document that commercially important cultivars have similar oil contents.
5. The protocol specifies that refumigations will be conducted only after residue levels have dropped to 0.1 ppm MeBr. RCB needs to know the shortest fumigation intervals which can occur as walnuts move through commercial channels. If this interval is shorter than that required for MeBr levels to drop to 0.1 ppm, the walnuts should be refumigated after the shortest fumigation interval has elapsed, even if some MeBr residues may be >0.1 ppm.
6. RCB has learned from D. Fiskaali, of the California Department of Food and Agriculture, that commercial fumigation of nuts is sometimes carried out in vacuum chambers. (The PPQ does not include vacuum chamber fumigation of walnuts.) Therefore, residue data reflecting fumigation in vacuum chambers are needed. CRAB has the option of requesting MBIP to revise the label to limit fumigation to normal atmospheric pressure chambers.
7. The following modifications cited by RCB for the prune protocol also apply to the walnut protocol. These modifications are described fully in RCB's Comments/Conclusions in the prune protocol section of this review.
  - a. Commercial equipment should be used. The protocol should include at least 3 "runs."
  - b. The effect of packaging on residue levels should be investigated.
  - c. The effect of fumigation temperature (of the chamber and in the stored commodities) should be investigated.
  - d. The aeration type should be specified; the effect of aeration temperature should be investigated.

- e. MeBr levels should be determined in various sections of the vault before sampling.
- f. The analyses should be run as soon as possible.
- g. Individual results for each analysis should be submitted, rather than averages. Fortification/recovery data for MeBr and iBr should also be submitted, along with representative chromatograms, calculations, standard curves, etc.
- h. If a tolerance is proposed based on an aeration time, CRAB will need to demonstrate that the aeration time is practical.

cc: Amy Rispin (SIS), PMSD/ISB, SF, RF, Reg. Std. File-Boodee,  
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