



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

SEP 8 1988

OFFICE OF  
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Follow-up to Methyl Bromide Registration Standard.  
Post Harvest Protocol for Herbs and Spices.  
RCB # 4152.

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TO: Jeffrey Kempter, Product Manager No. 32  
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and

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and

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In order to fulfill the requirement cited by the Methyl Bromide Registration Standard, the law offices of D.R. Thompson, on behalf of the American Spice Trade Association (ASTA), have submitted a protocol for generating residue data reflecting postharvest fumigation of herbs and spices.

An earlier submission from the Methyl Bromide Industry Panel (MBIP), which included proposed analytical methodology and storage stability studies, has already been reviewed. Many of the deficiencies cited in the review of that submission (memo of C. Deyrup, 7/14/88) also apply to the protocols in the present submission. DEB notes that the methodology for inorganic bromide (iBR) has been submitted three times, and

each submission has involved different equations for calculating ppm iBr. The registrant or ASTA will need to resolve these discrepancies and provide sample calculations which illustrate the construction and use of the standard curve and the determination of ppm iBr from the correct equation.

### Spices and Herbs

#### Domestic Herbs

Basil, chives, dill, marjoram, and sage (spice group 1) will be harvested from soil which has either been preplant fumigated with MeBr or which has not been fumigated. The 5 herbs grown in fumigated soil will be divided into 4 lots (a total of 20 lots). Control samples will be taken from each of the 4 lots grown in treated soil, and analyzed in triplicate for MeBr and inorganic bromide (iBr). Control samples will be taken from the top, middle, and bottom of each lot.

Each lot will be placed in an 885 ft<sup>3</sup> atmospheric chamber which has been certified by the California Department of Food and Agriculture. The dosage rate will be 3 lbs ai/1000 ft<sup>3</sup> for 24 hours at 80-90° F, followed by a 24 hour aeration period. The commodities will be fumigated and aerated two more times for a total of 3 fumigations and aerations.

The temperature will be monitored at 4 hour intervals during fumigation. Samples will be analyzed for MeBr and iBr in triplicate after each aeration period. Each sample will consist of sub-samples taken from the top, middle, and bottom of each lot.

Prior to analysis, samples will be collected and stored in one quart glass canning jars with screw top lids. The jars will be stored in a freezer at 0° F until analysis. All analyses for iBr and MeBr will be completed within 18 hours.

MeBr will be determined by the King headspace method, and iBr will be determined by the ion selective electrode (ISE) method. Spiked samples will be analyzed and compared to a sample curve.

#### Imported Herbs and Spices

Four different shipments of each of 7 spices will be secured as received and designated as lots. The herbs and spices chosen for investigation are black pepper, chilies, cassia, oregano, celery seed, sesame seed, and nutmeg. These spices were selected to represent spices derived from fruit, bark (cassia), leaf, and seed. Triplicate control samples of each lot will be analyzed for residues of MeBr and iBr.

The spices (excepting the portions set aside as controls) will then be fumigated and aerated 3 times as described above. Sampling, storage, and analysis will be carried out on the

imported commodities as described above for the domestic herbs.

DEB's Comments/Conclusions

1. The protocol does not specify the preplant fumigation rate for the domestic herbs. DEB notes that in PP #5F3198, pre-plant soil fumigation use was proposed on a crop group basis at 148-240 lbs ai/A. If it is ASTA's intent to fumigate soil at these rates, the herbs should be grown in soil fumigated at the maximum proposed rate.
2. The protocol should be modified to include analyses of samples grown in non-fumigated soil to determine background levels of MeBr and iBr.
3. The protocol does not specify whether the herbs (basil, dill, chives, marjoram, and sage) are to be dried before fumigation, although "dried leaves" are referred to at one point in the protocol.

If it is ASTA's intent to fumigate dried herbs only, this should be clear in both the protocol and on the label. If dried leaves are to be used, ASTA will need to describe the drying of the herbs so that DEB can determine whether the drying process reflects common commercial practice. Basil, dill, and chives are often used fresh; when tolerances are established on the herb and spice group, residue data on both fresh and dried herbs are required. Therefore, if it is ASTA's intent to limit fumigation to dried herbs, ASTA will need to notify MBIP so that the label can be revised to specify "dried herbs" and spices. Otherwise residue data reflecting the fumigation of fresh herbs would be required.

4. ASTA has not described the physical state of the spices. Residue data are needed on both ground and unground spices.
5. ASTA will need to support the argument that herbs and spices are fumigated up to 3 times. [DEB has received a protocol from MBIP which involves 4 fumigations of imported spices.] Fumigation practices in the country of origin should also be taken into account.
6. At the meeting of 8/27/87, representatives of the spice industry reported that the use of vacuum chambers resulted in consistently higher residue levels. Since vacuum chambers represented the worst case, they proposed using a vacuum chamber and foregoing other types of fumigation methods. DEB agreed that this approach was reasonable. The present protocol calls for the use of a normal atmospheric pressure chamber. Preliminary data on carrots, potatoes, wheat, and walnuts indicate that a fumigation vault represents the second worst case; this study also indicated that the vacuum chamber repre-

sented the worst case. As long as vacuum chamber fumigation is permitted on the label, residue data reflecting this use are required. If ASTA intends to use only chamber fumigation, MBIP should be notified so that vacuum chamber fumigation is deleted from the label.

7. The temperature during the fumigation is to be 80-90°F. The latest proposed label (submitted with PP #5F3300) allows fumigation at 250°F. ASTA will need to show that 80-90°F represents the worst case. If fumigations occur at lower temperatures, higher residues may result. Residue data reflecting the worst case are needed.
8. ASTA needs to further describe the aeration (i.e., whether forced or unforced) and should support the position that this type of aeration is used commercially.

The type of aeration used to generate the residue data should be specified on the label. Therefore, MBIP should be notified of the type of aeration used to determine a tolerance level.

9. The aeration temperature should be specified. Again, if cooler temperatures are used commercially than are observed in the residue study, higher residue levels may result. ASTA has the option of requesting MBIP to revise the label to specify a minimum aeration temperature (if lower temperatures lead to higher residue levels), if it can be demonstrated that such a label restriction is practical.
10. ASTA will need to describe the containers which hold the various lots. Since the size and composition of the containers may affect residue levels in/on the commodities, ASTA will need to support the position that the containers to be used are representative of containers used in commercial operations. If a variety of containers is used commercially, the most commonly used containers should be used to generate the residue data.
11. The residue tests should represent actual commercial fumigation events in all respects, such as MeBr introduction, temperature, humidity, air circulation, packaging, load factor, and aeration and storage conditions. These details should be provided.
12. After consulting with the FDA (telecon with D. Reid, 8/16/88), DEB recommends that the sample selection process should mimic the FDA sample selection process as much as possible. The FDA monitors samples as they move through commercial channels. Therefore, if several bins (or "lots") from the same fumigation travel together through commercial channels, the FDA would sample from several bins; in effect this practice would composite samples which originated from different

sections of the fumigation chamber. On the other hand, if it is possible that the lot could travel through commercial channels by itself, then, of course, sampling from only the one lot is possible.

If it is commercial practice for bins to travel together, samples should be drawn from different sections of bins (e.g., from the top, middle, and bottom) from different areas of the chamber. The samples should be composited before analysis. If it is possible that a single bin could travel through channels to a distributor, then samples should be drawn from different sections of the bins located in the areas of highest MeBr concentration in the chamber. Again, the samples should be composited before analysis.

13. The protocol states, "Each lot to be treated will be placed in a 885 cubic foot atmospheric chamber..." DEB needs to know whether each lot of a particular spice is to be fumigated separately, i.e., four separate fumigation runs per spice are proposed. If that is the case, DEB has no objection, because several fumigation runs are needed to determine residue levels in spices from the postharvest use. One fumigation run would not serve as an adequate data base for establishing residues arising from the proposed use.
14. RCB reiterates that if tolerances are proposed on the basis of residue levels following a period of aeration, ASTA will need to demonstrate that the aeration period is appropriate (i.e., that the commodity will not be available for sampling by the FDA before the aeration period has elapsed).
15. The nature of the residue in plants after postharvest fumigation is not yet adequately understood. If the metabolism studies underway identify other residues of concern, besides MeBr and iBr, additional residue data may be required.
16. A storage stability study is needed for each commodity. Data submitted by MBIP indicate that loss of MeBr during storage could depend upon the nature of the commodity. MeBr residues in rice declined by 22% after 8 hours of storage at dry ice temperature, -78°C, which is considerably colder than the storage temperature proposed in the current protocol. ASTA may want to store the commodities at dry ice temperatures instead of 0°F.  
  
Possibly residues declined faster in rice because of the finely divided nature of rice. Storage stability data are needed for spices because ground spices are even more finely divided than rice.
17. The following comment is from DEB's review of an MBIP submission which involved the analytical methodology described in

ASTA's current submission (memo of C. Deyrup, 7/14/88).

"In this latest revision, the oven temperature to be used and the amount of water to be added to the sample depend upon the commodity. Although MBIP has provided instructions on determining the water content of the sample, the analyst is not told what should be done with this information until the end of Procedure II, which describes inorganic bromide analysis. MBIP will need to provide a summary at the beginning to explain that methyl bromide and inorganic bromide (iBr) may be determined successively but that the water content of the sample must be known before the bromide content can be determined. MBIP will also need to submit fortification/recovery data and sample chromatograms to validate the residue data and describe any precautions taken during maceration of the sample to prevent loss of the volatile MeBr. RCB suggests that the loss of MeBr during maceration could be minimized by maintaining a temperature of  $<3.6^{\circ}\text{C}$  (MeBr bp) during this process; spiked samples should be macerated and analyzed to determine whether significant amounts of MeBr are lost during the maceration procedure which is used."

The present protocol does not call for any maceration; so loss of residues in this step may not pose a problem. However, if it is necessary to process whole nutmegs before adding them to the Waring blender, care should be taken to avoid loss of the volatile analyte, and ASTA should demonstrate that MeBr is not lost during this process.

18. The following comment is from DEB's review of an MBIP submission which involved the analytical methodology described in ASTA's current submission (memo of C. Deyrup, 7/14/88).

"The description of the methodology should specify if the selective ion electrode can be attached to an ordinary pH meter.

The description of the analysis of bromide should be rewritten so that the operations and calculations are more comprehensible.

The current instructions refer to both the standards and the test material as "samples." When standards are being measured, they should be referred to as standards. The current directions say to "Add 1 ml of working standard #1 to sample beaker;" confusion may arise because both standards and test materials are called samples.

The directions should clarify that the determination of bromide is carried out by first measuring the test sample, adding three consecutive aliquots of standard to the test sample, and plotting the 4 resulting points vs the concentration of added  $\text{Br}^-$ . RCB suggests that it would be helpful to provide an explanatory summary preceding

The limit of determination was not specified. MBIP should provide the limit of determination and should support the claimed limit of determination with appropriate fortification and recovery data. Without this information, RCB cannot judge the adequacy of the method for the collection of data."

DEB notes that the methodology for inorganic bromide has been submitted three times, and each submission has involved different equations for calculating ppm iBr. The registrant or ASTA will need to resolve these discrepancies and provide sample calculations which illustrate the construction and use of the standard curve and the determination of ppm iBr from the correct equation.

19. ASTA should heed RCB's comments contained in previous memos and in the Registration Standard regarding the generation of residue data for post harvest use.

#### Recommendations

DEB recommends that the spice protocol be modified to take into account the Comments/Conclusions delineated above.

Attachment 1: MBIP Postharvest Protocol Review, dated 7/14/88;  
to PM only

cc: Amy Rispin (EFED/SACS), PMSD/ISB, SF, RF, Reg. Std.  
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