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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Postharvest Fumigation of Cherimoyas with MeBr. Review of Protocol. RCB #4142.

FROM: Cynthia Deyrup, Ph.D., Chemist C. Deyrup
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THRU: John H. Onley, Ph.D., Section Head John H Onley
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TO: Jeffrey Kempter, Product Manager No. 32
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In a letter to J. Kempter (RD), dated 6/22/88, A.S. Marulli [president, Agricultural Trade Services (ATS)] has expressed the intent of seeking a tolerance for residues of methyl bromide on cherimoyas imported from Chile. Mr. Marulli said that the Methyl Bromide Industry Panel (MBIP) had informed him that data on analytical methodology and storage stability have already been completed and submitted. The ATS is relying on MBIP to complete the plant metabolism studies.

Preliminary residue data on cherimoyas were submitted with this letter. Mr. Marulli points out that treatment of Chilean cherimoyas with MeBr is required by the USDA. J. Kempter has requested DEB to review the protocol used to generate the preliminary residue data.

Recommendations

DEB recommends that ATS incorporate DEB's Comments/Conclusions into the protocol for generating residue data on cherimoyas fumigated with MeBr.

1

Detailed Considerations

According to Mr. Marulli, for quarantine fumigation, cherimoyas from Chile may be exposed to a maximum treatment rate of 3 lbs. MeBr/1000 ft^3 for 2 hours. The residue data reflect treatments at 3 lbs. ai/1000 ft^3 and 4 lbs. ai/1000 ft^3 for 2 hours. The fruit used in the trial was grown in CA. The fruit was divided into 3 equal lots. Lot 1 was not fumigated; Lot 2 was fumigated at the lower rate; and Lot 3 was fumigated at the higher rate. The fruit pulp temperature at the start of both fumigations was about 41° F. The chamber temperature in the fumigation at 3 lbs/1000 ft^3 was initially 46° F; after fumigation, the chamber temperature was 64° F. The chamber temperature used in the 4 lbs/1000 ft^3 study was initially 52° F. The final temperature was not recorded.

Each lot was sampled after aeration periods of 12, 24, and 36 hours. During the initial 12 hour period, the fruit were subjected to 3 hours of forced aeration, achieved by the use of the exhaust fan with the chamber door being open. At the end of 3 hours, the exhaust fan was turned off, and a small oscillating fan, set at a low speed, was placed in the chamber. At the end of 9 hours, the small fan was removed from the chamber. The fruit was stored at ambient temperature during aeration.

Three fruit were selected at random at the end of each aeration period. The fruit were peeled, the seeds were removed, and the fruit were cut up and mixed to form a composite sample. Four replicates were analyzed from each composite.

The levels of MeBr were determined by a modified King headspace method. Inorganic bromide (iBr) was determined with the use of an ion specific electrode (ISE). The modified King method and the ISE method were reviewed by DEB in its memo of 7/14/88 (memo of C. Deyrup). The following modification was made in the ISE methodology: "A 3.5 ml aliquot of 6 N HNO_3 was added to the samples with shaking prior to centrifugation. The addition of nitric acid to the sample caused the fiber to break down and be removed by centrifugation. The same amount of nitric acid was added to the standard solutions used."

The residue data are outlined below.

	Aeration time (hr)			
	0	12	24	36
MeBr (ppb)				
3 lbs/1000 ft^3		287-371	6.8-8.1	<3 ppb
4 lbs/1000 ft^3		59-175	<3 ppb	<3 ppb
Check	<3			

	Aeration time (hr)			
	0	12	24	36
iBr (ppm)				
3 lbs/1000 ft^3		21.5-28.4	13.9-24.4	13.6-19.8
4 lbs/1000 ft^3		19.9-38.8	25.9-28.0	28.3-30.5
Check	2.7-9.9			

RCB's Comments/Conclusions, re: Protocol

1. Fumigation Parameters

DEB's guidelines as put forth in its review of the almond protocol (memo of W. Hazel, 11/3/87), apply to all residue tests. The 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. For example:

a) DEB needs to know what sort of containers are used in the commercial fumigation of cherimoyas. If only one type is used, then residue data reflecting the use of this container only need be generated; however, the petitioner will need to support this position with documentation. Otherwise, residue data reflecting fumigation of fruit in the common commercial containers will be required. Samples should be drawn from various sections of the container; higher residue levels could result on the perimeters of the containers (due to release of MeBr by the container or in the middle (due to inefficient aeration).

b) The residue data reflect 3 hours of forced aeration and 9 hours of circulation aeration prior to unaided aeration. The petitioner will need to document that this pattern of aeration is commonly practiced or will be employed in Chile.

c) DEB needs to know how cherimoyas are stored in Chile prior to fumigation. If temperatures <41° F are used, then residue data reflecting the cooler storage temperatures will be required.

d) The petitioner will need to supply details on the chamber, which should be of commercial size and type, the means of MeBr introduction, the humidity, load factor, the usual storage conditions for cherimoyas before fumigation, and the aeration temperature (described as "ambient."

e) DEB needs to know whether the aeration and fumigation temperatures reflect the worst case expected to arise in commercial practice.

It has been reported in the literature that the storage temperature prior to fumigation may effect the amount of fumigant absorbed by the commodity [W. B. Sinclair and D.L. Lindgren, "Factors Affecting the Fumigation of Food Commodities for Insect Control," J. Econ. Entomology, 51 (6): 891-900 (1958).]

2. Samples should be taken from containers located in various sections of the chamber. Analyses should be done on composites.

3. According to United Fresh Fruit and Vegetables, many commodities are sometimes waxed. If cherimoyas may be waxed before fumigation, residue data on waxed and unwaxed cherimoyas should be generated.

4. If the size of different cultivars of cherimoyas differ by a factor of 2 or more, residue data reflecting the smallest varieties should also be generated. Surface residues could result in higher residue levels in the small varieties because of the larger surface to volume ratio.

5. Residue data reflecting multiple applications are required when appropriate. DEB needs to know whether cherimoyas will be refumigated after they enter the US (by the USDA or anyone else). If so, residue data reflecting the maximum number of fumigations should be submitted. The petitioner should document his position.

6. If cherimoyas are generally stored before fumigation, some of the residue data should also reflect representative storage periods.

7. If cherimoyas are generally picked and fumigated when still green, the residue data should reflect residues in both green and mature fruit. Sinclair and Lindgren (see above) also reported that the amount of fumigant sorbed by the commodity could depend upon its stage of maturity.

8. Once the worst case conditions have been defined, the petitioner should submit residue data from at least 3 fumigation runs.

9. Since cherimoyas bruise very easily (Uncommon Fruits & Vegetables, Elizabeth Schneider, Harper & Row, New York City, NY, 1986), the cherimoyas traveling through commercial channels may not all be in perfect condition. Therefore, the samples should include a representative proportion of bruised commodities.

10. Analytical Methodology

    a. The analytical methods submitted with the cherimoya protocol are similar to the methods reviewed in RCB's memo of 7/14/88 (memo of C. Deyrup, "Follow-up to Methyl Bromide Registration

Standard. Post Harvest Protocol, Interim Plant Metabolism Report, Analytical Methods, and Storage Stability." RCB's comments on the method for the determination of MeBr are repeated below.

"Although MBIP [the Methyl Bromide Industry Panel] 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 deter mined. 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°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."

In addition to chopping the sample, the seeds are also removed from the cherimoyas. The petitioner should determine whether a significant amount of MeBr is lost during chopping and removing the seeds; such a loss during sample work-up could result in grossly underestimating the levels of MeBr.

b. "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 re-written 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 Br^-. RCB suggests that it would be helpful to provide an explanatory summary preceding the step-by-step instructions. A sample calculation of Br^- should be included in the revised version to illustrate

the use of the graph and the equation. The MBIP should verify that the submitted equation is correct." [The equation in the present submission appears to have been corrected; the petitioner should verify whether the revised equation is correct.]

"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."

c. The petitioner reports that the ISE method was modified by adding 3.5 ml of 6N HNO_3 to the samples and standard solutions. Was the HNO_3 added to the Standard KBr (1 L of solution), working standards (100 ml of solution), or to the working standards in the beakers (50 ml of solution)?

11. A storage stability study is needed for <u>each raw agricultural commodity</u>. Data submitted to DEB indicates that loss of MeBr during storage could depend on the nature of the commodity.

12. The petitioner needs to specify the storage period from sampling to analysis and should also specify the storage conditions.

13. DEB notes that the average MeBr residue levels are <u>3 times higher</u> for the <u>lower</u> fumigation rate. The petitioner should explain these apparently paradoxical results; these results cast doubt on the protocol used to generate the preliminary residue data.

14. 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.

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