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

APR 10 1989

OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Follow-up to Methyl Bromide Registration Standard. Permeability of Fumigation Bags to Chloropicrin and Methyl Bromide. (DEB #4864) MRID. No. 408543-01

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Background

On Dec 15, DEB attended a meeting in Fresno CA with representatives of the Dried Fruit and Nut Association (DFA), the MBIP, and the USDA (see C. Deyrup and N. Dodd memo of 1/5/89). The possible effect of packaging on the MeBr levels of the contents was discussed at this meeting. DEB learned that poly bags were used by the dried nut and fruit industry, which needs to fumigate bagged commodities. Whenever lots are returned, the returned stock must be refumigated before it can be stored with the rest of the stock. Dr. White of the MBIP did not think that MeBr would penetrate poly bags, but the DFA pointed out that infested packages are sometimes fumigated to kill insects within the package. Dr. White argued that if MeBr went into the packages, it could come out. DEB was concerned that higher levels could result in bagged commodities, if MeBr residues

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diffused slowly from the bags.

The MBIP has therefore submitted a study aimed at determining the permeability of fumigation bags toward MeBr and chloropicrin.

Summary of DEB's Comments/Conclusions on the Permeability Studies

DEB commends the registrant on the design of the experiments examining the permeability of the bags toward MeBr and Pic and the diffusion of these residues from the bags.

The comments below are given in full at the end of this review.

1. DEB's concern that MeBr may be slow to diffuse from the bags has been borne out.

2. Residue data reflecting the fumigation of bagged commodities are needed to determine whether bagged or unbagged commodities represent the worst case. The commodities should be bagged according to commercial practice.

3. Although residue data reflecting the worst case may be needed to establish a tolerance, residue data reflecting more commonly encountered commercial practice are needed to estimate dietary exposure.

4. DEB has several questions relating to the conduct of the study examining residue levels in bagged commodities. These issues involve the storage time, possible discrepancies in data reporting, and recovery data and are discussed in full at the end of this review.

Present Consideration

The studies examined the permeability of various bag types (single or double bagged) toward methyl bromide and chloropicrin (Pic) and determined the levels of these residues and inorganic bromide (iBr) in bagged food samples which had been fumigated.

A. Permeability of Bags

In this study the MeBr and Pic levels were measured in the air within the bags.

Three types of bags were investigated: polyethylene bags with a thickness of 2.5 or 4 mil and Fumebags™ (1 mil). The composition of the Fumebags™ is proprietary.

The tests involved single Fumebags™, 2.5 mil poly bags, and 4 mil poly bags, as well as double-bagged Fumebags™ and 2.5 mil poly bags. Crumpled paper was placed within the inner bag to create an air space. The bags were sealed by tightly twisting the neck, folding the twisted neck back upon itself, and wrapping the folded neck with duct tape. For the sake of comparison, a 15 sq.

in. piece of Saran wrap was placed over the open end of the twisted neck prior to folding the neck back and wrapping it with duct tape.

The bags were placed in a fumigation chamber constructed of wood which had been sealed with epoxy paint. The chamber (capacity, 885 ft^3) had been certified by the state of California.

The bags were placed on wooden shipping pallets, and the chamber was fumigated at a rate of 3.0 lb/1000 ft^3 for 18.5 hours. The fumigation mixture was composed of 99.5% MeBr and 0.5% Pic. The chamber was then aerated for 1.75 hours to clear the chamber of MeBr (type of aeration not specified). The chamber concentrations were measured about 45 minutes after sample introduction.

The plastic bags were pierced with a lubricated syringe, and a 15 ml aliquot was withdrawn. Half the sample was injected into the injection port of the gas sampling valve, and levels of MeBr and Pic were measured by GLC with flame-ionization detection. The levels of determination for MeBr and Pic were 0.5 ppm.

The residue levels found within different types of bags are tabulated below. The data represent eight replicates of each bag type.

MeBr Concentration within Fumigation Bags (PPM, V/V)

MeBr Concentration during Fumigation: 12240 PPM

4 Mil Poly	2.5 Mil Poly		1 Mil Fumebag™	
	Outer	Inner	Outer	Inner
4914-6027	5814-6881	444-4202	874-2118	ND-115
Avg: 5474	Avg: 6301	Avg: 2993	Avg: 1499	Avg: 1.8

Pic Concentration within Fumigation Bags (PPM, V/V)

Pic Concentration during Fumigation: 13 PPM

4 Mil Poly	2.5 Mil Poly		1 Mil Fumebag™	
	Outer	Inner	Outer	Inner
5.7-7.8	3.9-4.5	0.4-3.0	0.1-1.6	ND
Avg: 6.7	Avg: 4.3	Avg: 2.4	Avg: 0.5	ND

B. Residue Levels in Bagged, Fumigated Food

Residue levels in the Fumebags™ differed markedly between different batches of bags. Upon closer examination of the bags, it was noted that the bottom seal of some of the bags may not have been intact. When the bottom of these bags had been folded up and sealed with duct tape before fumigation, residue levels within these bags

were much lower. Therefore, all the bags in the following experiments were folded twice across the bottom and sealed with duct tape. The tops of the bags were sealed by tightly twisting the neck, folding the twisted neck back upon itself, and wrapping the folded neck with duct tape.

Raw shelled almonds, long grain rice, and sliced American cheese were placed in 4 replicate bags of each type (4 mil poly bags and doubled Fumebags™). The rice and cheese were left in their commercial wrappers during fumigation; the sliced cheese was not individually wrapped. The almonds were loose.

The bags were fumigated with 99.5% MeBr at a rate of 3.0 lb/1000 ft^3 for 17 hours (almonds) and 20 hours (rice and cheese). Following fumigation, the chamber was aerated for 1.5 hours after the almond trial, and for 2 hours after the rice and cheese trials. Commodities were also fumigated with Pic alone (1 oz/10,000 ft^3, 17 hour exposure, 1.5 hour aeration)

The air inside the bags was analyzed for MeBr and Pic. The bag was then opened, and the commodity was transferred to a glass canning jar. The jars were sealed with a metal lid and placed on dry ice until the sample was analyzed (no storage time given).

The modified King Headspace method, which has undergone a successful validation at the EPA lab, was used to determine levels of MeBr.

Inorganic bromide (iBr) was determined by the ion selective electrode (ISE) method. In its review of 11/3/88, DEB had concluded on the basis of recovery data that this method was too imprecise. In a subsequent meeting with the registrant (12/16/88), DEB suggested that the registrant use a GLC method, if erratic recoveries are encountered with the ISE method.

The method used to determine Pic residue levels is described briefly below.

The chopped commodity is boiled for about 45 minutes in a mixture of water/isooctane. During this time, a slow stream of nitrogen sweeps volatile residues to a distillation trap maintained at 0° C. The content of the trap is partitioned with brine; the isooctane phase is retained, dried with sodium sulfate, and analyzed by GLC with a ^{63}Ni electron capture detector. Separation was achieved on a 10% OV 101 column. The Pic level is calculated by comparing the sample response to an appropriate standard response.

Recoveries of MeBr and iBr were not provided. Though not specified, the registrant characterized the recoveries of iBr from cheese as "low."

Recovery data for Pic are given below. The fortification level was not given.

Commodity	% Pic Recovery
Almond	92-104
Cheese	98-107
Rice	95-106

The concentrations of MeBr, Pic, and iBr in these commodities are tabulated below. Because of low recoveries, the registrant does not believe that the ISE method yielded reliable results for the cheese samples.

	Residue Level in Almond		Rice		Cheese	
Residue	4 Mil Poly	Double Fumebag™ (1 Mil)	4 Mil Poly	Double Fumebag™ (1 Mil)	4 Mil Poly	Double Fumebag™ (1 Mil)
MeBr (PPM W/W)	3.68-4.00	<0.005	2.59-2.81	<0.005	1.88-3.60	<0.008
iBr (PPM W/W)	114-152	54.5-83.0	24.1-30.0	5.5-9.0	75.4-91.9	67.1-117
Check	44.2		4.3		118	
Pic (PPB)*	0.60-0.87	<0.20	1.44-3.52	<0.86	<0.52	<0.30
Pic (PPB)**	0.52-0.63	<0.10	0.81-1.23	<0.20	<0.10	<0.10

* Fumigated with 99.5% MeBr/0.5% Pic (3 lb/1000 ft^3)
** Fumigated with Pic (1 oz/10,000 ft^3)

DEB's Comments/Conclusions, re: Permeability Studies

Although the MeBr levels in the air within the poly bags was 24% (inner bag, 2.5 mil thickness) to 51% (outer 2.5 mil thick bag) of the MeBr chamber concentration during fumigation, these levels were measured after 1.75 hours of aeration. That is, the average MeBr levels in the poly bags ranged from 2993-6301 ppm, and the MeBr levels in the chamber were presumably <5ppm. Therefore, DEB's concern that MeBr may be slow to diffuse from the bags has been borne out.

MeBr levels in Fumebags™ were substantially lower than in poly bags, although levels within a single Fumebag were still higher than in the fumigation chamber after aeration. However, DEB doesn't know whether double-bagged Fumebags™ (twisted, folded, and sealed with duct tape) are generally used commercially.

In any case, since the registrant has shown that MeBr levels are slow to diffuse from the bags, it is apparent that residue data reflecting the fumigation of bagged commodities are needed to determine whether bagged or unbagged commodities represent the worst case. The commodities should be bagged according to commercial practice.

DEB reminds the registrant that residue data reflecting the worst

case may be needed to establish a tolerance, and residue data reflecting more commonly encountered commercial practice are needed to estimate dietary exposure.

According to the description of the study examining residue levels in food, "The air inside the bags was analyzed for MeBr and chloropicrin...After the air sample was removed, the bag was opened and the commodity transferred...." The registrant should explain why the MeBr levels within the bags containing food samples were the same for all the commodities, namely 7193, 7164, 6954, and 6944 ppm.

Although the methodology used to generate the data was adequate for these preliminary studies, DEB reminds the registrant that recovery data should be submitted in order to validate any residue data. Recovery data were given only for Pic.

The method for Pic apparently assumed a linear standard curve, since the residue levels were calculated by comparison of the sample response to a standard response. DEB has no objection to this method. However, in future submissions, the registrant should submit the relevant standard chromatograms in order to validate residue levels calculated in this fashion. The responses of the sample and standard shouldn't differ by more than 10-20%.

The storage time on dry ice was not specified. In future submissions, the storage time between sampling and analysis should be specified.

DEB notes that the application of the ISE method has once more led to problematic results, this time with cheese. In the actual generation of residue data, this method, if used at all, must be applied with caution. Whenever recoveries indicate that problems exist, another method should be used.

Although the residue levels in almonds, rice, and cheese are of limited use, DEB commends the registrant on the design of the experiments examining the permeability of the bags toward MeBr and Pic and the diffusion of these residues from the bags.

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