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

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OFFICE OF
PESTICIDES AND TOXIC SUBSTANCES

MEMORANDUM

SUBJECT: Captan--Stauffer and Chevron Response to Data Call-In Letter - Validation Data for Market Basket Survey of 1977-78
Accession Nos. 259155 and 258851
RCB Nos. 5 and 1449

FROM: Lynn M. Bradley, Chemist
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Chevron Chemical Company and Stauffer Chemical Company have submitted responses to Section II-A, 1(b) of our April 29, 1985 Data Call-In (DCI) letter. Both Chevron and Stauffer have submitted validation data for the 1977-78 Captan Market Basket Survey, as required. These data will be tabulated and discussed below, and the methods used will be described.

Both companies also submitted several articles from the literature which indicate that captan residues dissipate with time and are destroyed by heat. These articles will be reviewed briefly--the amended program for residue reduction data for captan and tetrahydrophthalimide (THPI), as requested in the DCI letter, is expected to provide definitive data for use in dietary exposure assessment.

Chevron also resubmitted its goat metabolism study, which has been previously reviewed. Chevron's letter suggests that we reconsider the goat study as reason not to require analysis for 5-hydroxy tetrahydrophthalimide (5-OH THPI) in the large

animal feeding study which was also requested. Since we have reviewed and accepted the 1979 cow feeding study which was resubmitted in response to the DCI (memorandum of L.M. Bradley, November 15, 1985), we see no need to discuss the goat study here.

Conclusions

1. The validation data submitted as required by Section II-A, 1(b) of the Agency's April 29, 1985 DCI letter are adequate. These data indicate that analyses done for the Market Basket Survey are expected to be accurate.

2. The additional references submitted by Stauffer and Chevron generally indicate that captan residues are destroyed by any processing which involves high temperatures. These data will be further considered when the residue reduction data requested in that same DCI letter are reviewed.

Market Basket Validation Data

The analytical method given by Chevron is referenced as Method RM-1F-2. Samples are macerated with water added as necessary. Fortified samples are prepared by adding captan standard in acetone after maceration. The sample is then acidified with H_3PO_4 and extracted with ethyl acetate in the presence of Na_2SO_4. The ethyl acetate is then washed with water filtered through Na_2SO_4, and evaporated to dryness. Oily crop extracts are first reduced in volume prior to washing with water.

The residue from ethyl acetate extract is taken up in acetonitrile and hexane, then the acetonitrile fraction is retained and washed with hexane twice more. Hexane wash is back-extracted with acetonitrile which is combined with the original acetonitrile solution and evaporated to dryness. That residue is taken up in acetonitrile:hexane:water. The acetonitrile:water phase is separated and extracted three more times with hexane. Hexane extracts are combined, filtered through Na_2SO_4, and evaporated to dryness.

Oils are merely acidified with acetic acid, taken up in hexane, extracted with acetonitrile which is then washed with hexane, and evaporated to dryness.

At this stage, residue is taken up in hexane, chromatographed on Florisil by successive elution with hexane, benzene, then 1 percent methanol in benzene. The first 50 mL of methanol:benzene is discarded, and the remainder collected

and evaporated. Residue is taken up in hexane and subjected to gas chromatography (GC), using either electron capture (ECD) or flame photometric detection (FPD). For ECD, peak height is compared to reference standard; for FPD the square root of peak height is compared with that of a reference standard. Limits of detection are claimed as 0.01 part per million (ppm) for ECD and 0.03 ppm for FPD.

The type of detector used for individual analyses can most times be determined from the limit of detection associated with the recovery value for a given set of analyses, but is not specifically given. Since controls were not available, all recovery studies were performed by fortifying the purchased samples and correcting for captan found in the analysis of unfortified samples. By this method, we would expect a wider range of recovery values than usual, but the technique is acceptable for this type of study.

Although some THPI data are submitted, along with recovery data, no method for THPI analysis is presented by Chevron.

The method given by Stauffer for determining captan residues requires blending the sample with toluene, then filtering through Na_2SO_4. An aliquot of the toluene extract is evaporated to dryness, taken up in toluene, and subjected to GC. Certain oily crops are subjected to a hexane:acetonitrile partitioning, and the acetonitrile extract is dried, taken up in toluene, and injected into GC. FPD in sulfur mode is generally used as detector, with ECD in nitrogen mode used for confirmation of residues.

Stauffer also submitted a method for determining THPI residues in plants. Samples are blended in ethyl acetate and filtered through Na_2SO_4. An aliquot of the extract is evaporated to dryness, taken up in 20 percent ethyl acetate in toluene, and chromatographed on a silicic acid:Nuchar mixture topped with Na_2SO_4. After rinsing the column with more ethyl acetate:toluene, THPI is eluted with 15 percent acetone in toluene for GC analysis using flame ionization detector. The method writeup indicates that phthalimide may interfere, if present, but that lowering the GC column temperature improves separation. The claimed limit of detection is 0.05 ppm.

In the tables below, we have grouped together all data for each commodity. In fact, data are presented by variety and type of processing, as well as by crop. No significant differences in recovery values were noted among varieties, or type of processing (fresh, frozen, or canned).

Market Basket Survey, Captan

Commodity (S = Stauffer, C = Chevron)		Residue Range ppm	Fortification Level ppm	Recovery Range percent
Apricots	(C)	0.00-0.02	0.10	92
Apples, various types	(S)	0.00-0.82	0.1	90-125
	(C)	0.00-0.07	0.1-0.105	56-115
Applesauce	(S)	0.00-0.02	0.1	84-113
	(C)	0.00-0.07	0.105	72-99
Applejuice	(S)	0.00	0.1	77-110
	(C)	0.00-0.04	0.105	70-96
Almonds	(S)	0.00-0.05	0.1	72-107
	(C)	0.00-0.01	0.1-0.105	62-98
Cherries, sour	(S)	0.00-0.03	0.1	83-118
	(C)	0.00-0.01	0.105	70-91
Cherries, sweet	(C)	0.00-1.82	0.105	74
	(S)	0.08-5.30	0.1	75-100
Grapes				
juice & conc.	(S)	--	0.1	75-110
	(C)	0.00-0.10	0.1-0.105	67-99
jelly & jam	(S)	--	0.1	85-96
	(C)	0.00	0.10	104
Nectarines	(S)	0.00-0.36	0.1	100
	(C)	0.04-0.06	0.105	96
Oranges	(S)	--	0.1	80-122
	(C)	0.00-0.01	0.05	88-119
juice & conc.	(S)	--	0.1	88-108
	(C)	0.00-0.04	0.1-0.105	85-105
Peaches, all types	(S)	0.00-0.09	0.1	79-107
	(C)	0.00-0.14	0.05-0.105	74-111
Pears	(S)	0.00-0.04	0.1	92-109
	(C)	0.00-0.23	0.1-0.105	66-114
Plums	(S)	--	0.1	88-108
	(C)	0.00	0.105	98
Strawberries	(S)	0.00-22.3	0.1	80-120
	(C)	0.00-1.1	0.1-0.105	75-110
preserves & jam	(S)	0.00-0.09	0.1	74-120
	(C)	0.00-0.01	0.105	82-104
Raisins	(S)	0.00	0.1	88-100
	(C)	0.00-0.07	0.105	52-88

Market Basket Survey, THPI

Commodity (S = Stauffer, C = Chevron)		Residue Range ppm	Fortification Level ppm	Recovery Range percent
Apples	(S)	0.0-< 0.005	0.05	110
	(C)	0.00	0.10	64-105
Applesauce	(S)	0.00	0.05	90
Cherries, sweet	(S)	0.00	0.05	83
Grapes	(S)	0.005	0.05	95
	(C)	0.00-0.024	0.08-0.1	51-100
Peaches	(S)	0.00	0.05	100-118
	(C)	0.00	0.08	105-127
Pears	(S)	0.00	0.05	85
	(C)	0.00-0.16	0.08-0.1	51-100
Strawberries	(C)	0.00-0.35	0.08-0.1	63-112

The validation data submitted in support of the 1977-78 Market Basket Survey for captan residues are acceptable. The method is adequately described and the recovery data indicate that the analyses of samples collected in the survey are valid.

Articles From Literature

"Persistence of Captan on Apples, Grapes, and Pears in Ontario, Canada, 1981-83," Frank et al., J. Ag. Fd. Chem. 33, 514 (1985).

Apples, grapes, and pears grown in Ontario in 1980 received 1 to 15 applications of either 1.7, 2.8, or 3.4 kg/ha. The trials reported were part of a larger study to determine what PHIs would be needed to meet the 5 mg/kg Canadian Maximum Residue Limit (MRL).

The analytical method used was the multiresidue method described in PAM-I section 212 (1973). Recoveries reported ranged from 84 percent (mean) at 0.1 mg/kg fortification levels to 97 percent (mean) at 10 mg/kg.

Residue decline rates varied inconsistently, sometimes correlated with rainfall or time, but sometimes not. Wine made from grapes containing 2.2 mg/kg captan contained no detectable captan (0.1 mg/kg) after fermentation (1 week). Residues in fruit declined to the 5 mg/kg MRL by day 5 for grapes, day 3 for pears, and day 7 for apples (except for one high dose, multiple application trial). The authors also concluded that the MRL residue levels are sufficient to protect against fruit rot.

"Removal of Captan from Treated Apples," Frank et al., Arch. Env. Contam. Toxicol., 12, 256 (1983).

McIntosh apples were dipped in 2.5 g/L captan solution, drained, dried, and stored for 60 to 120 hours. Apples were variously rinsed, washed, wiped, boiled (peeled and unpeeled), or processed in several combinations of these procedures, then refrigerated until analysis. Extraction of samples was completed in less than 24 hours; analysis followed the multi-residue procedure described in PAM-I, section 212 (acetonitrile: water extraction). Recoveries are reported as 84 to 97 percent for apple tissue and 91 to 106 percent for water (levels not specified), and the detection limits were 0.01 microgram/g for apples and 0.25 g/L for water.

The initial residue level was 9.9 microgram/g; rinsing removed 43 percent; rinsing and wiping, 75 percent; washing (with a brush) and wiping, 88 percent; boiling, 79 percent; washing and boiling, 91 percent; and wiping and boiling, 95 percent. Several other studies demonstrated similar results; dicing and cooling removed 94 to 98 percent of captan.

A study on captan hydrolysis rates in water at varying temperatures, and pH are also reported. Solutions containing 10, 100, or 1000 microgram/L were maintained at 5 or 22 °C and pH 5.5 or 8.5 for 1 to 96 hours. Higher temperature and alkaline pH gave consistently rapid disappearance of captan from solution. At 22 °C and pH 8.5, the half-life was less than 1 hour, whereas at 5 °C and pH 5.5, the half-life was 208 hours.

"Captan in Green Vegetables," Klayder, JAOAC, 46, 241 (1963).

This paper reports a collaborative study among eight labs to extend the official method for captan to vegetable crops. Purchased samples of fresh or frozen asparagus, green beans, or spinach were analyzed in duplicate as blanks, fortified controls, and fortified unknowns (unknown solution distributed to participants). Modifications to the colorimetric AOAC captan method for fruits which were used in this study are a slightly different procedure for benzene extraction, with admonition to repeat cleanup if extract is still colored.

Recovery values for controls (levels known to experimenters) were 84 to 110 percent for asparagus; 90 to 98 percent for beans, and 88 to 98 percent for spinach; fortification levels ranged from 50 to 105 ppm. Recoveries from unknowns were 90 to 112 percent for asparagus, 92 to 112 percent for beans, and 70 to 108 percent for spinach. Blanks were 0.00 ppm for asparagus and 0 to 0.4 ppm for both beans and spinach.

Further studies on the effect of canning into jars using pressure cooker (using preliminary blanching) were conducted on all three crops using water as control. Samples were fortified at 0, 10, 50, 100, and 120 ppm captan. The maximum remaining after canning was 4.6 ppm in asparagus. Levels remaining were roughly proportional to levels added for each crop.

"Magnitude and Stability of Captan Residues in Fresh and Preserved Plant Products," Koivistoinen et al., J. Ag. Fd. Chem. 13, 468 (1965).

Strawberries, gooseberries, tomatoes, plums, apples, and string beans were dipped in aqueous captan suspension. Application variables examined included uniformity of residue disposition, effect of dip concentration on initial deposits, effect of dip time on initial deposit, and effect of fruit size on residue deposition. The stability of residues during storage and processing or preservation was also examined.

Ten samples of strawberries and tomatoes were dipped in two concentrations of captan suspension and analyzed for captan residues. Strawberries dipped in 0.05 percent solution had 13.0 ppm mean residues; those dipped in 0.2 percent had 49.3 ppm mean residue levels. Successive batches of strawberries dipped in the 0.05 percent solution showed progressively lower residue levels. The difference was small but statistically significant. Tomatoes dipped in 0.05 percent had 1.5 ppm (mean) captan; 0.5 percent, 9.5 ppm.

The effect of dip concentration on initial deposits was studied for strawberries, gooseberries, plums, tomatoes, and apples. Results are reported graphically, and indicate a linear correlation of residue level with dip concentration up to 0.4 percent for apples and 1 percent for other fruit. Residue per surface area appeared to vary with the kind of plant material tested.

Strawberries, tomatoes, and plums were tested to see if dip time effected residue levels. The difference in residue levels between 5-second and 5-minute dip time was less than twofold.

Effect of size of fruit on initial deposit levels was studied with tomatoes. Although residue deposits per surface area were the same, residue levels were lower in larger fruit (residue levels varied inversely with weight).

Storage stability experiments were performed with strawberries, gooseberries, string beans, tomatoes, plums, and apples (fresh produce). Very little residue decline occurred at 4 °C during the first few days (strawberries, gooseberries,

and stringbeans) with higher losses occurring at 20 °C. Longer term experiments were done with tomatoes, plums, and apples some loss (up to 50%) occurred at 0 to 4 °C over 4 to 20 weeks, with higher losses at 10 to 20 °C. Reason for loss was not studied.

The same six commodities were preserved in various ways and the effect on residue levels studied. Results are summarized in the following table:

Commodity	Residue After Dipping, ppm	Preservation Technique	Residue in Preserved Product, ppm
Gooseberries	40.1	canned berry	< 0.1
		syrup	1.0
		mashed w/benzoate	32.4
		prepared for preserves	< 0.1
		prepared for jelly	< 0.1
		jam	< 0.1
		steam juice	0.2
		dried (heat)	80.9 (70% loss from theoretical)
		freezing, 1-8 mo. later	35.7-38.4
Strawberries	48.5	canned jam	0.2
		jam (stored overnite before cooking	27.1
		after cooking)	1.1
		freezing (1 mo.)	21.6
Tomatoes (green)	14.4	pickled (boiled) in vinegar and sugar	No trace
String beans	89.3	canned beans	< 0.1
			0.7
		freezing (blanched 1 to 8 mo.)	9.0-12.5
		salting 0 mo.	48.6 (steady
		8 mo.	8.6 loss)
Plums	23.7	canned	< 0.1
		jam	0.4
		dried	0.5
		freezing (1 mo.)	16.5
Apples	41.1	canned	< 0.1
		prepared for jelly	0.2
		steam juice	0.2
		pressure juice	7.5
		(pasteurized)	0.1
		freezing (1 mo.)	32

The effect of washing on residue levels was studied on five of the six fruits. One set of samples was washed immediately after the dip suspension dried, and another set was cold-stored for a week, then washed.

Captan Levels, ppm

Commodity	Immediate Wash Before	Immediate Wash After	Delayed Wash Before	Delayed Wash After
Gooseberries	40.1	11.3	38.3	14.7
Plums	23.7	7.6	18.3	8.2
Tomatoes	16.7	2.5	9.5	2.3
Apples	41.1	34.0	32.7	23.8
String beans	89.3	48.2	--	--

Washing reduces captan residues, and cooking destroys most captan. Drying, even with added heat, effects a residue concentration that, at least in these experiments, overtakes the destructive effects. Freezing without blanching reduces residues somewhat but not greatly.

"The Site and Fate of Captan Residues from Dipping Prunes Prior to Commercial Dehydration," Archu and Corbin, Food Technology, 23, 101 (1969).

Residues of captan were measured on "green fruit" (presumably fresh prunes) after postharvest dip in solution containing 1, 2, or 4 lb active per gallon, and then after dehydration (16 hrs at 190 to 195 °F). Fruits were stored for 3 weeks prior to analysis--the green fruit at 35 °F, and the dried fruit at 72 °F for 2 weeks and 35 °F for 1 week. The effect of "lye checking" on captan residues in both fresh and dried fruit was examined--fruit were dipped in a 2 percent KOH solution at 80 °C for 5 minutes. Fruits were also peeled, and the skin, flesh and pits examined for captan residue distribution. The removal of surface residues by benzene was also studied. Results are summarized below for the 4 lb captan per gallon dipped prunes:

Commodity	Captan, ppm Dry Weight Basis	Residue Loss, Lye Check	Dehydration
Green fruit	40.6	100%	61%
Dehydrated	15.9	92%	(higher % losses at lower dip concentrations)
Removed by benzene wash	28.4 (initial levels unspecified)		22.5 ppm
Green fruit			
Whole	30.6 measured (31.4 calculated)		
Peel (1-2mm)	87.2		
Flesh	2.0		

"Effect of Heat Processing and Storage on Pesticide Residues in Spinach and Apricots," Elkins et al., J. Ag. Fd. Chem. 20, 286 (1972).

The effect of canning, freezing, and storage on a number of pesticides was studied. Captan was determined by the official AOAC method. Four samples of each commodity were prepared and analyzed for each pesticide studied: thermally processed and unprocessed product with and without pesticide fortification. Unprocessed samples were kept frozen.

Commodity	Captan Residue Level, ppm
Spinach, fortified at 100 ppm unprocessed	36
processed at 252 °F for 66 min (immediately analyzed)	2
stored 1 yr ambient temperature	ND (< 0.01)
stored 1 yr at 100 °F	ND (< 0.01)
Apricots, fortified at 100 ppm unprocessed	89
processed at 217 °F for 50 min (immediately analyzed)	3
stored 1 yr ambient temperature	1.1 ppm
stored 1 yr at 100 °F	ND (< 0.01)

"Response of Stauffer Chemical Company to the Consultative Committee on Industrial Bio-Test Pesticides. CAPTAN. February 12, 1982."

This document was prepared to answer the question "What influence does cooking have on captan residues in or on food?" Most of the data discussed are from journal articles which are reviewed in original form in this memorandum--these will not be further discussed.

Stauffer developed data (submitted in Response to the RPAR Notice) showing that the solubility of captan in water is <0.5 ppm, and that the half-life varies from 32-hours at pH 4, 20 °C to < 2-minutes at pH 10, 40 °C. A study by Wolfe (J. Ag. Fd. Chem., 24:5, p. 1041 (1976)) is cited to say the maximum half-life of captan in water is 710 minutes and that at pH 2 to 6, hydrolysis reaction is independent of pH, but that at pH > 7, it is pH dependent.

Data from R. Frank of Ontario Provincial Pesticide Residue Testing Laboratory are presented to show that 68 to 94 percent of captan residue on peaches, cherries, and strawberries is removed by washing (treatment method not specified).

Data on the effect of baking treated potatoes are discussed--reference given is Petition #15 (Chevron). Potatoes were dipped in captan slurry and skin and pulp were analyzed before and after baking and boiling. Initial captan levels were 29 ppm on skin and 0.3 ppm in pulp; after baking, 0.5 ppm captan was found on potatoe skin. No residues were found in baked pulp on boiled skin or pulp.

Stauffer alone submitted a collection of three documents regarding captan residues in various citrus commodities. The first, identified as "Summary, Captan Residues on Processed Citrus By-Products, Moorestown, NJ, 11/20/59" describes a study of grapefruit treated at 2 lb active/100 gal. Grapefruit analyzed 6 to 9 days after treatment had 0.56 to 1.68 ppm captan. Oranges treated with 1.25 to 10 lb active/100 gal had 1.24 to 8.13 ppm, and normal washing reduced residue levels to approximately 0.2 ppm. Raw pulp fortified to the equivalent of 10 ppm after washing showed no detectable captan in finished pulp or molasses. Method of analysis is not specified.

A memorandum from A.A. Whipp to Dr. T.W. Reed dated April 3, 1958, Orlando, Florida, concerning "Captan Residues in Citrus Pulp" describes the processes used for making citrus pulp and molasses. The only mention of captan is that treated fruit will be sent to Moorestown.

A third document dated April 28, 1958, with the name Donald L. Davis, Chemist typed as a signature line refers to "described studies," and gives raw data for washing of sprayed fruit, (unspecified) which may be that summarized in the "Summary" (discussed above). Method of analysis is mentioned as "Kittleson's" (a colorimeteric method).

Effect of Washing on Captan-Treated Citrus (Oranges?)

Spray Used on Trees	Residue Level, ppm Before Washing	After Wash
10 lb ai/100 gal	8.3	0.19
5 lb ai/100 gal	4.8	0.10
2.5 lb ai/100 gal	2.6	0.22
1.25 lb ai/100 gal	1.2	0.12

Laboratory simulation of citrus processing was performed on untreated oranges, the pulp fortified, further processed, and analyzed. Residue levels in pulp and molasses are reported as 0 ppm.

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Stauffer also submitted copies of several slides concerning captan levels in crops presented at a meeting somewhere by Dick Frank with dates of December 1982. These data, as presented, are meaningless and will not be discussed further.

cc: Circu, S.F. (Captan), L.Bradley, R.F., PMSD/ISB

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