Chloropicrin Residues in Food Commodities after Chamber Fumigations

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Field beans and peas, corn, broiler feed, flour, and toasted wheat flakes were fumigated with 2 and 4 pounds of chloropicrin per 1000 cu. feet in a chamber. Wheat flakes and flour were also fumigated at $1^1/_2$ pounds per 1000 cu. feet. Samples were analyzed for chloropicrin after no aeration and at intervals up to 30 days after fumigation. Chloropicrin residues are reduced to low levels by aeration. The residue in biscuits made from fumigated flour was much lower than in the flour from which they were made. No residue was found in biscuits made from flour treated with $1^1/_2$ pounds of fumigant per 1000 cu. feet.

LITTLE information appears in the literature on residues of chloropicrin resulting from fumigation of foods, although it has been proposed as a fumigant since Moore (*6*) suggested its use in 1918, finding it safer than CS_2. Several publications over the ensuing years (*1, 2, 4, 6–10*) have reported usage practices for effective control of rodents and insects under a variety of conditions. Because of the general applicability and effectiveness of the fumigant, this study was undertaken to determine the levels and persistence of residues in certain commodities following fumigation.

Two series of fumigations were carried out: at the Bioproducts Department, The Dow Chemical Co., and at the Agricultural Section, Morton Chemical Co. Samples were analyzed at the laboratories of Foster D. Snell, Inc., New York, N. Y.

Experimental

Fumigation Procedure. FIRST SERIES. The fumigations were carried out at 75° to 80° F. in a 27-cu. foot horizontal metal cylindrical chamber 44 inches long and 35 inches in diameter. One end is a door which can be sealed into place. At the other end is a 4-inch pipe with a gate valve, which leads through a fan to a hood stack, for rapid air exchange in the vault. On the upper side of the tank is a 4-inch pipe with a valve for admission of air when aeration is carried out. A gas-inlet valve is attached at the closed end. An electrically driven fan is mounted at the top of the chamber for circulation of the fumigant.

After the vault has been loaded to approximately 75% of capacity, a vacuum of about 300 mm. of Hg was drawn through the gas-inlet valve, with all other openings sealed. The calculated amount of Picfume (registered trade-mark of The Dow Chemical Co. for fumigant containing 99% chloropicrin and 1% inert ingredients) to be used was weighed into a small filter flask fitted with a one-hole stopper. A glass tube with a stopcock protruded through the stopper to near the bottom

Table I. Blank Values Found on Unfumigated Commodities

(Apparent p.p.m. chloropicrin)

Water (Reagent Blank)	Broiler Feed[a]	Field Corn[a]
0.49	0.37	0.39
0.41	0.68[b]	0.51
0.31	0.66	0.65
0.59	0.56	0.83
0.50	0.45	0.62
0.71	0.51	0.28
0.47		0.85
0.49		0.63
Av. 0.50	0.54	0.60

Flour[b]	Biscuits	Wheaties[b]
0.40	0.50	0.54
0.00	0.60	0.30
0.10	0.70	0.78
0.08	0.80	0.62[c]
0.12		0.30
0.24		0.90
0.44		0.36[c]
0.76		0.18[c]
0.26		
0.44		
0.22		
Av. 0.28	0.65	0.50

Beans[b]	Peas[a]
0.70	0.64
0.34	0.46
0.80	0.26
0.42	0.90
0.40	0.26
0.86	0.56
Av. 0.59	0.51

[a] 20-ml. aliquot analyzed.
[b] 10-ml. aliquot analyzed.
[c] 25-ml. aliquot analyzed.

Table II. Recovery of Known Amounts of Chloropicrin Added to Commodities

Added, P.P.M.	Recovered, %
BEANS AND PEAS	
0.8	102
1.05	83
	121
1.1	125
1.2	96
1.6	97
2.1	84
2.16	80
	104
2.3	84
2.4	98
3.15	82
	113
3.2	79
3.5	100
4.52	75
4.6	83
5.65	89
10.0	93
10.2	75
11.3	110
20.3	85
21.0	77
22.6	89
Av.	93

Added, P.P.M.	Recovered, %
WHEATIES	
1.0	92
	104
1.1	91
2.0	130
	95
2.2	97
2.9	82
	90
3.3	82
5.3	73
	100
10.6	81
	119
21.2	67
	81
	72
Av.	91
BISCUITS	
1.0	81
2.1	92
3.1	85
5.2	83
10.4	86
20.8	92
	87

Added, P.P.M.	Recovered, %
BROILER FEED	
1.1	62
	100
2.1	59
	70
3.2	55
	60
9.6	70
19	60
38	52
Av.	65
FIELD CORN	
1.3	114
	112
2.6	95
	103
3.8	90
	92
5.3	81
10.2	87
20.5	81
Av.	95

Added, P.P.M.	Recovered, %
FLOUR	
1.0	103
	74
1.1	79
1.9	94
	86
2.1	99
2.9	80
	94
4.3	87
5.4	76
10.8	83
20.3	94
Av.	87

of the flask. The side arm of the flask was connected to the gas-inlet tube on the vault, and the valve was opened. By using a flame to heat the flask and opening the stopcock to sweep vapors in with air, all the fumigant was transferred to the chamber. Atmospheric pressure in the vault was achieved by allowing air to sweep through the flask. Gas in the chamber was thoroughly mixed by running the fan for several hours after addition of the fumigant. Because an airtight vault was used and the fumigant introduced under vacuum, the conditions for picking up a residue were much more severe than in a commercial fumigation at the same rate.

At the termination of a 24-hour fumigation period, the air-inlet and discharge valves were opened and air was drawn through the vault for several minutes to discharge the fumigant in the free air space, so materials could be handled without the use of a gas mask.

Immediately after the postfumigation airing, samples were taken and stored frozen in friction-lid cans until they were analyzed. For shipment each can was soldered at two points on the lid to keep it sealed and then placed in an insulated box with dry ice.

Following the first sampling, within 1 hour of the end of fumigation, the bags of samples were placed in a room and sampled at intervals.

The vault was loaded with the commodities in the quantities and packages given below. For each fumigation, the vault was approximately 75% filled with commodities.

Toasted wheat flakes (Wheaties, General Mills, Inc., Minneapolis, Minn.) in commercial 21-ounce boxes. About 30 holes were punched in each of 30 boxes with an ice pick to simulate packages that might be broken open.

Flour (Gold Medal, a first patent flour, General Mills, Inc., Minneapolis, Minn.) was in paper bags with the top taped shut. About 30 holes were made in each of 2 bags.

Broiler feed (from Cohoon Elevator, Midland, Mich.) was used in burlap bags. Two bags were used per fumigation, each containing about 50 pounds.

Field corn. One 100-pound burlap bag was used per fumigation.

Canadian field peas, dry, and Navy beans. Two 50-pound burlap bags of each were used per fumigation.

Second Series. Larvacide 100 (registered trade-mark of Morton Chemical Co. for fumigant containing 99% chloropicrin and 1% inert ingredients) was used for fumigation of flour (5-pound bags, Sunnyfield family enriched flour bleached, The Great Atlantic and Pacific Tea Co., New York, N. Y.) and wheat flakes (18-ounce packages of Wheaties, General Mills, Inc., Minneapolis, Minn.) at about 70° F.

The fumigation chamber consisted of a horizontal cylindrical container, 22½ inches in diameter and 69 inches in length (volume 16 cubic feet). Both ends of the container were removable. One end of the chamber was connected through a 4-inch duct to one end of a small fan. The other end of the fan was connected to a 3-inch duct which served as a return duct to the other end of the cylindrical chamber. Duct work and chamber had a total volume of 16.5 cubic feet. The rate of air flow could be adjusted by a damper in the duct leading from the fan.

The fumigation chamber was loaded to approximately 40% of its capacity with loosely stacked containers, while one end of the cylindrical vault was closed. The fumigant was pipetted on cotton wads suspended in the free air

Table III. Chloropicrin Residues Found in Fumigated Commodities

Commodity	Chloropicrin, Pounds/1000 Cu. Ft.	Net P.P.M. Chloropicrin[a] Found after Aeration, Days						
Flour		<1	1	2	4	10	20	30
Series 1	2	56	24	20	16		6	7
		56	24	18	15		6	7
	2	68	25	19	16			
		64	25	18	17			
	4	143	51	28	37		8	8
		150	50	29	39		8	9
	4	144	54	28	19			
		147	55	29	18			
Series 2	1½			3.8		2.8		1.3
				3.5		2.4		1.4
	1½			3.4		1.2		0.5
				3.9		1.4		0.4
	0			0.1				
				0.2				
				0.1				
				0.1				
Wheaties								
Series 1	2	54	9	3	4		0.5	0.9
		49	10	3	4		0.5	0.9
	2	55	15	5	3			
		54	14	5	3			
	4	121	16	13	8		0.6	1
		117	15	14	8		0.7	2
	4	60	21	12	5			
		59	22	12	6			
Series 2	1½	1.7				0.3		0.1
		1.7				0.2		0.2
	1½	1.6				0.4		0.3
		1.6				0.4		0.3
	0	0.2						
		0.1						
		0.2						
		0.2						
Beans	2	1.7	1.6	<0.5	1.1		1.5	0.8
Series 1		1.6	1.5	<0.5	1.3		1.8	0.7
	2	1.7	1.3	0.8	<0.5			
		1.5	1.1	0.7	0.5			
	4	2.5	2.4	1.5	1.2		1.5	1.0
		2.8	3.0	1.7	1.3		1.5	0.8
	4	3.4		1.1	1.5			
		3.9		1.3	1.8			
Peas	2	<0.5	0.5	0.5	0.8		<0.5	1.2
Series 1		<0.5	0.5	0.6	0.8		<0.5	1.1
	2	0.5	0.5	0.6	0.8			
		<0.5	<0.5	<0.5	0.5			
	4	1.4	1.0	2.0	0.6			
		0.6	0.9	1.8	<0.5			
	4	0.6	0.5	0.8	<0.5		<0.5	1.8
		<0.5	0.7	0.9	0.5		<0.5	1.8
Corn	2	9	8	6	6		4	1
Series 1		9	7	6	6		4	1
	2	9	4	4	3			
		9	4	4	4			
	4	20	11	8	6		4	3
		20	12	8	6		5	3
	4	22	14	10	8			
		23	14	9	9			
Broiler feed[b]	2	59	48	37	25		9	9
Series 1		57	51	35	25		9	8
	2	78	35	23	17			
		71	40	25	17			
	4	106	94	91	60		18	15
		106	97	97	66		18	16
	4	101	95	83	37			
		109	99	75	38			

[a] Residue of <0.5 p.p.m. below sensitivity of method.
[b] Values corrected for 65% recovery.

pace in the chamber. The other end of the chamber was closed immediately. The fan was started to facilitate evaporation and to recirculate the fumigant vapors to accomplish uniform concentration throughout the chamber. The damper was adjusted to give a rate of air flow equivalent to one complete exchange for every $2^1/_2$ minutes. Recirculation was continued during a 24-hour exposure period.

After 24 hours the recirculation duct was disconnected at the fan. The fan was thereafter operated at low speed for 24 hours; then the containers were removed from the fumigation chamber and placed in open air at room temperature. Duplicate fumigations were made using a dosage level of $1^1/_2$ pounds per 1000 cu. feet each time.

Samples of the fumigated products were removed 2, 10, and 30 days after the end of the exposure period, immediately transferred to tin cans with tight-fitting friction-type lids, and placed in a freezer. The samples for analysis were shipped in a well insulated package with dry ice.

Determinative Method. Chloropicrin was determined by a method based on the procedure of Feinsilver and Oberst (*3*), in which the chloropicrin is hydrolyzed to give nitrite ion which is determined colorimetrically by reaction with sulfanilic acid and subsequent reaction with *N*-(1-naphthyl)-ethylenediamine dihydrochloride.

Special Equipment and Reagents. Fumigant isolation apparatus as described by Mapes and Shrader (*5*) was used with two absorbers substituted for the combustion tube. Glass U-tubes packed with glass wool may be used for absorbers.

Beckman DU spectrophotometer, with photometric cells, 5-cm. optical path.

Sodium peroxide, 2% solution. Dissolve 2 grams of reagent grade sodium peroxide in 100 ml. of 1*N* sodium hydroxide. Prepare fresh daily.

Phosphotungstic acid, 20% solution. Dissolve 20 grams of phosphotungstic acid, $P_2O_5.24WO_3.25H_2O$, in 80 ml. of water.

Dow Corning Emulsion AF, defoaming agent.

Cylinder of nitrogen or clean compressed air.

Preparation of Standard Curve. In a sealed ampoule weigh accurately a small amount (2 to 4 mg.) of chloropicrin and break the ampoule under isopropyl alcohol in a 100-ml. volumetric flask. Make the solution to volume with isopropyl alcohol and mix. Place a 10-ml. aliquot of the solution in a 100-ml. volumetric flask and make to volume with isopropyl alcohol. Calculate the number of micrograms of chloropicrin per milliliter of isopropyl alcohol. From a 10-ml. buret add 0-, 1.0-, 2.0-, 3.0-, 4.0-, 5.0-, 6.0-, and 7.0-ml. portions of the standard chloropicrin solution to 125-ml. boiling flasks which contain, respectively, 11.5-, 10.5-, 9.5-, 8.5-, 7.5-, 6.5-, 5.5-, and 4.5-ml. portions of isopropyl alcohol. To each flask add 5.0 ml. of 2% sodium peroxide solution and 3.5 ml. of water. Place two or three glass beads in each flask.

Reflux each solution for 30 minutes at a fast rate of boiling using a small amount of glycerol to seal the glass joint between the condenser and the boiling flask. Use gas burners for refluxing the solutions because of the positive control of heating afforded by the gas flame. The condensation point of the vapors must be well up in the condensers. Wash the condenser with 5 ml. of isopropyl alcohol and remove the flask from the condenser. Cool the flask and solution to room temperature and transfer the solution to a 50-ml. volumetric flask. Rinse the boiling flask with small portions of water, adding the rinse water to the volumetric flask. Keep the total volume below 45 ml. Add 1 drop of phenolphthalein indicator and neutralize the solution with concentrated hydrochloric acid, added dropwise, with 1 drop in excess. Cool to room temperature. Add 1 ml. of sulfanilic acid solution and mix the solutions with a gentle swirling motion. Wait 2 minutes and add 1 ml. of *N*-(1-naphthyl)ethylenediamine dihydrochloride solution. Make the solution to volume with water and mix. Allow 15 minutes for color development and determine the absorbance at 550 mμ, using water as the reference solution.

Correct the observed absorbance by deducting the value of the reagent blank. Plot the corrected absorbance against the weight of chloropicrin on linear graph paper. Draw the line of best fit between the points on the standard curve.

Procedure for Analysis. Place 2.5 ml. of isopropyl alcohol and 2.5 ml. of sodium peroxide solution in each absorber tube, or 7.5 ml. of each if U-tubes are used. Connect the isolation apparatus, except the aeration flask, using a small amount of glycerol to seal the glass joints. With the constant temperature bath at 85° C., start the pump to circulate water through the condenser. Introduce 100 ml. of water, 10 ml. of 6*N* sulfuric acid, 10 ml. of 20% phosphotungstic acid solution, and a small amount (about 0.5 gram) of defoaming agent into the aeration flask, making sure that the stopcock of the flask is closed. Weigh a 200-gram sample of the material and place it immediately in a Waring Blendor. Add 200 ml. of water to the blender and make a slurry of the sample and water mixture. Smaller samples may be used when large chloropicrin residues are present. Granular materials, such as wheat need not be made into a slurry, but may be introduced directly into the aeration flask. Transfer the slurry to the flask and rinse the blender with 100 ml. of water, adding the rinse water to the flask. Connect the flask to the condenser and to the supply of nitrogen or clean compressed air. Open the stopcock of the flask to permit a slow stream of nitrogen or air to pass through the sample and water mixture. By means of a heating mantle controlled with a variable transformer, bring the contents of the aeration flask to boiling (15 to 20 minutes at a setting of 100 on a Powerstat). Turn the current

Table IV. Chloropicrin in Biscuits from Fumigated Flour

Fumigation Rate, Lb./1000 Cu. Ft.	Aeration, Days	Chloropicrin, P.P.M. In flour	In Biscuits Gross	In Biscuits Net[a]
		Series 1		
4	0	146	7.4	6.7
			6.8	6.1
			7.6	6.9
			7.6	6.9
			6.9	6.2
			6.0	5.3
			5.8	5.1
			4.6	3.9
4	0	147	26.4	26
			28.4	28
			27.4	27
			28.6	28
2	4	16	6.4	5.7
			6.4	5.7
			5.8	5.1
			4.5	3.7
2	4	17	3.0	2.3
			2.7	2.0
			2.6	1.9
			2.5	1.8
		Series 2		
$1^1/_2$	2	3.7	0.1	0
			0.2	0
$1^1/_2$	2	3.7	0.2	0
			0.2	0
0		0	0.3	
			0.3	
			0.3	
			0.2	
			0.2	

[a] Net = gross − blank.

down to maintain the mixture at a brisk rate of boiling (setting of 60) and increase the flow of gas to approximately 40 ml. per minute. Distill for 1 hour, collecting the distillate in the absorber tubes. At the completion of the distillation, disconnect the aeration apparatus and transfer the contents of the absorber tubes to a 100-ml. volumetric flask. Wash each absorber with 10 ml. of water and 15 ml. of isopropyl alcohol. Make the volume to 100 ml. with isopropyl alcohol. Mix well and transfer a suitable aliquot to a 125-ml. boiling flask. Calculate the amounts of water, sodium peroxide solution, and isopropyl alcohol contained in the aliquot taken and add sufficient amounts of each to the flask to make 3.5 ml. of water, 5 ml. of sodium peroxide solution, and 11.5 ml. of isopropyl alcohol in the flask. The stipulated ratio of 11.5 ml. of isopropyl alcohol to 8.5 ml. of total water is critical. For a 10-ml. aliquot add 1.1 ml. of the 2% sodium peroxide solution and make up to 20 ml. with a mixture of 5 parts of Na_2O_2 solution, 3.5 parts of water, and 11.5 parts of isopropyl alcohol. Place two or three glass beads in the boiling flask and proceed as in the second paragraph in "Preparation of Standard Curve." Run a blank on the reagents and subtract it from the sample reading. Determine the chloropicrin content of the sample from the corrected absorbance and the standard curve.

Volatile substances which act as buffering agents are obtained from some agricultural products during the distillation. Add sufficient hydrochloric acid to neutralize these materials, to prevent interference with the normal color development in the determinative step. The formation of a yellow or orange color at this step usually indicates the presence of such materials.

Run a blank with each batch of samples.

Results and Discussion

Blank values from reagents and untreated food products are given in Table I, which shows that the reagent blank accounts for most, if not all of the food blanks found.

All recovery values are high (Table II) except for the broiler feed, where no great effort was expended to improve the recovery. Although this increases the uncertainty of residue found in the broiler feed, the values reported are consistent. Because of this lower recovery, the values reported for residue content are corrected for 65% recovery, but other residue values are not corrected (Table III).

The residues of chloropicrin found after fumigation and aeration are given in Table III, which shows that, other conditions being equal, the physical state of the material may be an important factor in the amount of initial residue. Flour, toasted corn flakes, and broiler feed in Series 1 all have about the same initial content, while corn, beans, and peas, all large particles, are very much lower. Table III shows that aeration removes most of the chloropicrin.

The fumigations reported here are much more rigorous than fumigations of warehouses in which these commodities might be stored. In these laboratory tests, there was no chance for the fumigant to escape. In Series 1, where the chemical was vaporized into the chamber at reduced pressure, all of the fumigant was present from the beginning of the 24-hour period. In most fumigations, more nearly simulated by Series 2, the fumigant is applied as a liquid on an absorbent pad and allowed to vaporize during fumigation. Under actual space fumigation conditions, the fumigant is likely to leak from the building, so residues would probably be still lower than those found in Series 2. In Series 1, an effort was made to produce conditions giving high residue, such as puncturing packages to allow free access of the fumigant. This is reflected by the fact that residues found are higher than in Series 2.

Biscuits were made from flour samples, to determine if the fumigant would persist in baked food, using the formula: 2 cups of flour, 3 teaspoons of baking powder, 1 teaspoon of salt, 6 tablespoons of shortening, and $^3/_4$ cup of milk. They were baked in a 450° F. oven for 15 minutes. In Series 1, where the initial residue values were high, a residue of chloropicrin remained in the biscuits (Table IV). Biscuits from Series 2 showed no residue.

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FALLOUT DETERMINATION

Separation and Recovery of Fallout Cs^{137} from Zr-Nb^{95} in Forage Samples

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Forages provide a means of monitoring environmental fallout contamination and also provide data on one of the important steps in the passage of Cs^{137} through the dairy food chain of man. During periods of fresh fallout deposition this radionuclide cannot be determined directly by gamma-ray spectral analysis because of interference from gamma-rays of shorter lived nuclides, principally Zr-Nb^{95}. Since it is of importance to have rapid values of Cs^{137} contamination levels for predictive purposes, a chemical separation method applicable to environmental forage samples is necessary. This method was developed immediately after the 1961–1962 nuclear testing series and became of value again in the summer of 1965 to separate Cs^{137} from Zr-Nb^{95} caused by the spring Chinese nuclear test.

Experimental Methods

Forage samples were harvested from the University Farm near Fort Collins. Grass samples were cut from pasture and hay samples consisted of alfalfa