

Effect of Temperature and Commodity on Distribution of CCl₄-CS₂(80:20) and EDC-CCl₄ (75:25) Applied by Gravity Penetration and Closed Recirculation¹

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ABSTRACT

Gravity penetration and closed recirculation fumigations were conducted in wheat, corn, and sorghum at 45, 65, and 85°F to investigate the effect of temperature and commodity on the distribution of 2 liquid fumigant mixtures, carbon tetrachloride-carbon disulfide (CCl₄-CS₂, 80:20) and ethylene dichloride-carbon tetrachloride (EDC-CCl₄, 75:25). The fumigations were conducted in 5-ft metal towers each containing 2 bushels of grain.

In the gravity fumigations the time required for the passage of a detectable concentration of fumigant through the commodity increased as grain temperatures decreased. Penetration time at each temperature tested was least

in corn and greatest in sorghum. Concentrations of each component were generally higher in the recirculation fumigations than in the gravity fumigations, particularly at 45°F fumigations. CS₂ was less affected by decreased temperatures or changes in commodity than CCl₄ or EDC. Comparison of the total component concentrations obtained in each commodity fumigation with the total obtained at each fumigation temperature indicates that the high sorption capacity of sorghum was a more limiting distribution factor than the slower rate of volatilization and penetration resulting from fumigation at 45°F in both gravity and recirculation fumigations.

Few studies have been published on the distribution of 80:20 and 75:25 mixtures and their components in bulk wheat, corn, and sorghum during fumigation. Strand (1927) was one of the first to measure penetration of fumigants. He found that, contrary to general belief at that time, the heavier fumigants such as CS₂ and chloropicrin did not sink very far in a mass of grain. He attributed this feature to sorption of the gases by the top layer of grain. Whitney and Kenaga (1960) conducted studies in which fumigant component distribution in small towers of wheat was determined by mass spectrometric analyses of air samples. They found that EDB was sorbed to the greatest extent during recirculation through wheat, followed by EDC, CS₂ and CCl₄. About 60-70% of the applied dosage was sorbed during the first 30 min of recirculation. It should be noted, however, that these tests were conducted at a rate of airflow far exceeding those used in the recirculation of fumigants in commercial applications. Berck (1961) reported on the distribution and persistence of CH₂Br, EDB, and CCl₄ applied in mixtures to 5-ft columns of wheat. He found that applied ratios of the mixture were altered appreciably during penetration through columns of wheat. Lindgren and Vincent (1959) measured concentrations of various single and multiple component fumigants recirculated through corn in small towers. They found that EDC in an EDC-CCl₄ mixture (75:25) disappeared within 15 min after application, and CCl₄ was reduced by 41% of its original concentration. In duplicate tests with CCl₄-CS₂ (80:20) the rate of sorption by corn was similar for both components.

The type and the temperature of grain are 2 factors considered in nearly all fumigant-dosage schedules that affect the amount of fumigant recommended (Anonymous 1968, Monro 1961). Dosages are generally increased with decreasing grain temperatures and with commodity changes from wheat to corn to sorghum. The study was conducted to investigate the effect of temperature and commodity on the distributional behavior of 2 commonly used liquid fumigant mixtures, carbon tetrachloride-carbon disulfide (CCl₄-CS₂, 80:20), and ethylene dichloride-carbon tetrachloride (EDC-CCl₄, 75:25), applied by gravity penetration and closed recirculation.

PROCEDURE.—Gravity penetration and closed recirculation fumigations were conducted in wheat, corn, and sorghum at grain temperatures of 45, 65, and 85°F in 5-ft metal towers 10-in. diam each containing 2 bu of grain. Tests with each temperature and commodity combination were replicated twice. The temperature of the air surrounding the towers was the same as the grain temperatures. Two liquid fumigant mixtures were used in the test, 1 composed of 4 parts CCl₄ to 1 part CS₂ (80:20) and the other composed of 3 parts EDC to 1 part CCl₄ (75:25).

Concentrations of the individual fumigant components were determined by gas chromatographic analyses.³

RESULTS.—*Gravity Fumigations.*—In the gravity fumigations air samples in the bottom of the towers were monitored continuously with a thermal conductivity unit following application of the fumigant in the top of the tower. Samples for analysis were taken as soon as the 1st signal was detected and again 30 and 45 min after the 1st concentration had penetrated through the grain mass.

The length of time required for the passage of the 1st detectable concentration of fumigant in the gravity penetration fumigations increased as grain temperatures decreased. Penetration time at each temperature tested was least in corn and greatest in sorghum. Penetration time in the 80:20 gravity fumigations (Table 1) ranged from 2 min 45 sec in 85°F corn to 57 min in 45°F sorghum. Delayed penetration of CCl₄ was evident in each of the 80:20 gravity fumigations regardless of temperature or type of commodity. In the 45°F sorghum fumigation the 1st concentrations were very low and were composed entirely of CS₂. Carbon disulfide concentrations still exceeded CCl₄ concentrations after 30 min and were in only a 1:1 ratio after 45 min. In 85°F corn the initial concentration of each component was fairly high; however, 30 min after 1st detection (100 mg/liter) the CCl₄ concentration increased to 417 mg/liter, but the CS₂ concentration remained nearly unchanged.

Penetration of the 75:25 components in the grav-

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³ Loren I. Davidson, of the Manhattan Laboratory, conducted the gas-chromatographic analyses.

Table 1.—Fumigant concentration obtained in gravity penetration fumigations in 5-ft towers of grain with a liquid fumigant mixture containing 4 parts of CCl₄ to 1 part CS₂ (80:20). Dosage rate: 3 gal/1000 bu.

Commodity	Grain temp °F	Penetration time (min)	Fumigant concentrations (mg/liter)					
			First signal		Plus 30 min		Plus 45 min	
			CS ₂	CCl ₄	CS ₂	CCl ₄	CS ₂	CCl ₄
Wheat	45	12	2.8	5.4	38.0	95	38	115
	65	16	4.6	12.0	48.0	271	41	290
	85	10	26.0	70.0	52.0	428	46	408
Sorghum	45	57	1.9	0*	23.0	14	25	26
	65	31	2.0	8.6	6.4	23	32	53
	85	20	5.1	8.7	32.0	241	29	249
Corn	45	9	13.0	15.0	37.0	150	33	161
	65	4	39.0	66.0	48.0	322	40	318
	85	3	51.0	100.0	56.0	417	44	384

* 0 indicates reading less than sensitivity level of 0.1 mg/liter.

ity fumigations (Table 2) ranged from 8 min in 85°F corn to 165 min in 45°F sorghum. The average penetration time of 75:25 was ca. 3 times longer than 80:20 for comparable temperatures and commodities. Initial concentrations were predominantly CCl₄ in all tests. No EDC was detected in the sorghum at 45 and 65°F, 45 min after the 1st CCl₄ signals were detected. The only significant concentrations of EDC detected at the bottom of the towers were found in the 65 and 85°F corn fumigations. All but one of the samples taken during the 3 sampling intervals in each of the gravity fumigations contained significantly more CCl₄ than EDC. This figure is in sharp contrast to the 3:1 ratio (EDC-CCl₄) of the 75:25 mixture when applied.

Recirculation Fumigations.—In the closed recirculation fumigations, samples were taken at the top of the towers after completion of 5, 10, and 25 min of recirculation at an airflow rate of 0.1 ft³/min per bushel. The fumigants were applied at the base of the towers and circulated upward through the grain mass.

Results obtained in the 80:20 recirculation fumi-

gations (Table 3) were similar to those obtained in the 80:20 gravity fumigations. Concentrations of CS₂ recorded after 5-min recirculation showed only minor increases after 10- and 25-min recirculation, whereas CCl₄ concentrations increased substantially in the samples taken after 10- and 25-min recirculation.

Concentrations of EDC and CCl₄ were generally much higher in the 75:25 recirculation fumigations (Table 4) than those obtained in the gravity fumigations. Recovery ratios were about 1 part EDC to 1 part CCl₄ in the recirculation fumigations.

DISCUSSION.—Carbon disulfide, which has the lowest boiling point and highest vapor pressure of the 3 components used in the 2 mixtures, was the least affected by decreased temperatures or the commodity treated. In contrast, EDC, which has a relatively high boiling point and low vapor pressure, virtually disappeared in low-temperature gravity fumigations in sorghum.

The amount of CCl₄ obtained in each 80:20 and 75:25 fumigation was influenced also by the grain temperature, commodity, and method of distribution. Within each of the 2 mixtures the amount of CCl₄

Table 2.—Fumigant concentration obtained in gravity penetration fumigations in 5-ft towers of grain with a liquid fumigant mixture containing 3 parts of EDC to 1 part CCl₄ (75:25). Dosage rate: 3 gal/1000 bu.

Commodity	Grain temp °F	Penetration time (min)	Fumigant concentrations (mg/liter)					
			First signal		Plus 30 min		Plus 45 min	
			CCl ₄	EDC	CCl ₄	EDC	CCl ₄	EDC
Wheat	45	35	6.6	1.9	30.0	9.2	36	9.2
	65	27	0.3	0.7	32.0	0.8	62	1.6
	85	25	9.9	6.8	127.0	11.0	124	12.0
Sorghum	45	165	2.3	0*	10.0	0	14	0
	65	138	2.4	0	1.6	0	15	0
	85	65	4.5	0	19.0	0	35	1.4
Corn	45	27	1.8	.2	40.0	.5	46	.8
	65	11	15.0	2.1	79.0	18.0	68	20.0
	85	8	27.0	.5	95.0	29.0	97	36.0

* 0 indicates reading less than sensitivity level of 0.16 mg/liter.

Table 3.—Fumigant concentration obtained in closed recirculation fumigations in 5-ft towers of grain with a liquid fumigant mixture containing 4 parts CCl₄ to 1 part CS₂ (80:20). Dosage rate: 3 gal/1000 bu. Rate of airflow: 0.1 ft³/min per bu.

Commodity	Grain temp °F	Fumigant concentrations (mg/liter)					
		After 5 min recirculation		After 10 min recirculation		After 25 min recirculation	
		CS ₂	CCl ₄	CS ₂	CCl ₄	CS ₂	CCl ₄
Wheat	45	19	43	33	83	45	140
	65	22	62	36	110	49	228
	85	32	110	54	228	55	394
Sorghum	45	12	23	23	47	18	57
	65	22	19	25	50	34	111
	85	25	71	29	104	34	199
Corn	45	35	102	46	143	49	212
	65	49	149	62	219	63	372
	85	54	197	64	301	59	455

recovered increased with each increase in fumigation temperature. Between commodities the lowest concentrations were found in sorghum, with the highest concentration generally recorded in corn. In tests at 45°F the highest concentrations of CCl₄ from both 80:20 and 75:25 fumigations were found in the recirculation fumigations. Distribution of the CCl₄ portion of the 2 mixtures was also similar at 65°F; however, unlike the tests at 45°F, somewhat more CCl₄ was recovered in the gravity than in the recirculation fumigations in wheat. In fumigations at 85°F the CCl₄ concentrations were highest in recirculation fumigations in corn and in the gravity fumigations in wheat. In the sorghum fumigations at 85°F the CCl₄ concentrations in the 80:20 fumigations were highest in the gravity method, but in the 75:25 fumigations the CCl₄ concentrations were highest in the recirculation method.

Similar results were obtained during field fumigations (Storey et al. 1970) in corn stored in 3250-bu bins during summer, fall, and early winter. In these gravity tests it was observed that 80:20 components

volatilized and penetrated the grain fairly rapidly in both warm and cool grain. In contrast, volatilization of the EDC in 75:25 applied at grain temperatures below 60°F was delayed and distribution was limited to the upper half of the corn mass.

A comparison of the total component concentration obtained in each commodity fumigation versus the total obtained at each fumigation temperature indicates that the high sorption loss in sorghum was a more limiting distribution factor than the low rate of volatilization resulting from fumigation at 45°F in both gravity and recirculation fumigations. Poor distribution of 75:25 in gravity fumigations at low temperatures in each commodity and lack of penetration of EDC in sorghum fumigations regardless of temperature suggest that recommendations for gravity application of 75:25 under these conditions are of questionable value even at elevated dosages. In addition, these data suggest that the recommended dosage of 80:20 or 75:25 for wheat is adequate also for corn at a nominal moisture level of 12 to 12.5%, and that an increase in dosage for corn is not justified.

Table 4.—Fumigant concentration obtained in closed recirculation fumigations in 5-ft towers of grain with a liquid fumigant mixture containing 3 parts EDC to 1 part CCl₄ (75:25). Dosage rate: 3 gal/1000 bu. Rate of airflow: 0.1 ft³/min per bu.

Commodity	Grain temp °F	Fumigant concentrations (mg/liter)					
		After 5 min recirculation		After 10 min recirculation		After 25 min recirculation	
		CCl ₄	EDC	CCl ₄	EDC	CCl ₄	EDC
Wheat	45	32.0	44.0	42	47	60	67
	65	4.3	0.3	27	20	60	46
	85	31.0	39.0	58	48	95	78
Sorghum	45	11.0	7.0	16	14	28	22
	65	6.7	3.8	16	14	32	26
	85	25.0	15.0	36	30	67	58
Corn	45	28.0	28.0	40	35	58	45
	65	51.0	39.0	67	50	94	70
	85	71.0	70.0	107	102	128	114

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