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Concentrations of 80:20 Grain Fumigant (CCl_4-CS_2) in Handling Equipment During Transfers of Fumigated Wheat[1]

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ABSTRACT

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The composition and concentration of fumigant vapors in grain elevator-handling equipment were determined during transfers of wheat at four 32-h intervals after fumigation with a mixture of carbon tetrachloride (CCl_4) and carbon disulfide (CS_2) commonly known as 80:20. Fumigant concentrations present in the handling system were influenced by the temperature of the grain and the time interval between fumigation application and grain transfer. Concentrations of CS_2 were highest during transfers of wheat fumigated at 6.6°C, and concentrations of CCl_4 were highest during transfers of wheat fumigated at 27.7°C. Peak concentrations of each compound generally occurred during the transfer periods between 8 and 16 h after application of the fumigant. The highest concentrations of CS_2 and CCl_4 were found in air entrained with the grain as it passed from the storage bin into the drawoff. As the treated grain entered the elevator boot, the movement of air at dust collecting points in the bucket elevator effectively reduced most fumigant vapors to levels below 1 mg/liter. Concentrations of CS_2 and CCl_4 found in the handling equipment during transfer of fumigated grain generally exceeded threshold limit values established for these fumigant compounds but were often below minimum concentrations detectable by odor.

A mixture containing a 1:4 ratio of carbon disulfide (CS_2) and carbon tetrachloride (CCl_4), commonly known as 80:20, has been used for over 50 years to fumigate grain. The 80:20 formulation, developed to reduce the flammability and explosive hazards of straight carbon disulfide, has become the most widely used liquid fumigant for insect control in elevator terminals. In elevator storage, 80:20 is generally applied during bin loading with the layering method, in which 80:20 is pumped or poured over the grain between drafts from 3 to 7 m (10 to 20 ft) deep. Most 80:20 fumigant labels recommend treatment at temperatures >15°C (60°F) and suggest that the grain not be disturbed for a period of 3 to 7 days posttreatment. However, when marketing pressures to meet shipping deadlines are great, grain may be fumigated at temperatures below those recommended and transferred before the expiration of recommended exposure periods. With these modified schedules, high concentrations of fumigant could still be present in the grain when it is turned. During penetration of bulk grain in gravity fumigations, CS_2 and CCl_4 separate, particularly at low temperatures (Storey et al. 1970, Storey 1971). Under such conditions, the composition of fumigant vapors entrained by grain entering the handling system may be significantly different from the formulation originally applied to the grain. Therefore, a temporary fire or explosion hazard can be created that is not normally present (when grain is handled according to recommended procedures). Furthermore, transfer of recently fumigated grain may distribute hazardous amounts of fumigant vapors throughout the grain handling system. We report here results of studies conducted to measure the influence of grain temperature and length of exposure on the composition and concentration of fumigant vapors in grain handling equipment during transfer of 80:20-fumigated wheat.

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Materials and Methods

Test Facilities

Figure 1 is a schematic drawing of the grain-handling and dust control systems at the U.S. Grain Marketing Research Laboratory (USGMRL). Grain was allowed to fall by gravity through spouts, then entered the boot on the descending side of the bucket elevator. It was then

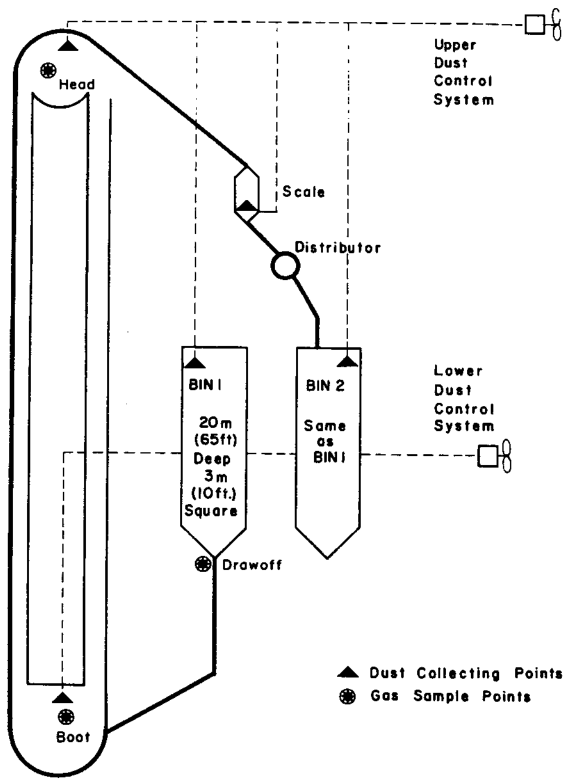

FIG. 1.—Grain-handling and dust control systems at the U.S. Grain Marketing Research Laboratory.

elevated 53 m (174 ft) and discharged into another spout, through which it descended 3 m (10 ft) into and through an automatic scale, 1.5 m (5 ft) to a hopper, 3 m (10 ft) to a distributor that directed the flow to a receiving bin, and finally another 4.6 m (15 ft) to the point where it entered the receiving bin. Both bins were ca. 20 m (65 ft) deep and 3 m (10 ft) square, with hopper bottoms that discharged from the center.

The headhouse was equipped with two conventional dust control systems, one for the upper and one for the lower part of the handling system, in which cyclone separators separated dust from the air. Ducts in each system connected the many dust collection points to the appropriate cyclone. Dust collection points were located at the boot and head pulley covers of the bucket elevator. Valves located at dust collection points controlled the amount of air flowing into the dust collection system. Efficient performance of the cyclone separators required that most valves be open. Air entrained by the grain entered the elevator boot, and air from an outside vent entered the head cover. Air from the top of the bin overspaces was removed by other ducts and replaced by air entering through outside vents.

Test Procedure

The air control valves were set to control the airflow to the upper cyclone at 4.7 m^3/sec (10,000 ft^3/min) and to the lower cyclone at 7.1 m^3/sec (15,000 ft^3/min).

The wheat used in the test was no. 1 hard red winter wheat with a moisture content of 13.2%. We used a commercial formulation of 80:20 composed, by weight, of 82.82% CCl_4, 16.41% CS_2, and 0.77% inert ingredients in each of three fumigations conducted when average grain temperatures were 6.6°C (range 5 to 8.3°C), 16.9°C (range 16.7 to 17.2°C), and 27.7°C (range 27.2 to 28.3°C), respectively. The 80:20 mixture was poured over the grain surface at the rate commonly used in terminal elevators of 0.35 liters/metric ton (2.5 gal/1,000 bu). For testing, 8.16-metric ton (300-bu) lots of fumigated wheat were transfered at intervals of 4, 8, 12, 16, and 32 h posttreatment. During each transfer, air samples (125-cm) for CS_2 and CCl_4 analyses were drawn from 0.63-cm-diameter polyethylene tubing at the outlet spout of drawoff beneath the storage tank at the boot of base area of the bucket elevator, and at the top or elevator head of the bucket elevator enclosure. Each transfer consisted of 20 load and dump cycles (ca. 0.41 metric ton per cycle) of the scale at a flow rate of 24.5 metric tons/h (900 bu/h). The air-gas mixture was sampled for analysis of fumigant components during the interval between the 19th and 20th dump cycles of each transfer. The samples were collected in 125-ml glass tubes fitted with gas-tight stopcocks at each end. Samples were analyzed on a Miraon IA® IR spectrophotometer modified for small-sample analysis. For increased sensitivity in CS_2 analyses, samples also were analyzed by gas chromatography-photoionization.

Results

Concentrations of CS_2 and CCl_4 were highest in air entrained by the grain as it passed from the bin into the drawoff (Table 1). When the treated grain entered the elevator boot, the movement of air at dust collection

Table 1.—Fumigant concentrations (mg/liter) in grain-handling equipment at indicated times posttreatment and at indicated temperatures during transfers of wheat fumigated with 80:20 (four parts CCl_4 to one part CS_2), at a dosage of 0.35 liters/metric ton[a].

Temp (°C)	Location	4 h		8 h		12 h		16 h		32 h	
		CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4	CS_2	CCl_4
6.6[b]	Drawoff	0.33	0.25	9.68	5.75	15.69	10.0	14.35	11.50	8.68	0.65
	Elevator boot	0.33	0.125	0.33	0.125	0.33	0.125	2.00	0.63	0.33	0.125
	Elevator heat	0.33	0.125	0.67	0.125	0.33	0.125	0.67	0.50	0.33	0.125
16.9[c]	Drawoff	0.39	0.25	0.590	1.43	1.18	15.0	2.96	14.50	1.58	6.0
	Elevator boot	0.008	0.125	0.332	1.06	0.286	4.13	0.228	1.62	0.029	0.50
	Elevator head	0.0002	0.125	0.076	0.38	0.220	1.25	0.094	1.18	0.012	0.44
27.7[d]	Drawoff	0.018	0.22	0.005	51.0	0.005	48.0	0.005	35.0	0.005	16.0
	Elevator boot	0.005	0.15	0.213	0.810	0.193	0.580	0.196	0.66	0.119	0.73
	Elevator head	0.005	0.15	0.112	0.290	0.134	0.510	0.123	0.44	0.084	0.58

[a] Equivalent to ca. 2.5 gal/1,000 bu.
[b] Limit of detection for CCl_4 was 0.125 mg/liter, and for CS_2 it was 0.33 mg/liter.
[c] Limit of detection for CCl_4 was 0.125 mg/liter, and for CS_2 it was 0.0002 mg/liter.
[d] Limit of detection for CCl_4 was 0.150 mg/liter, and for CS_2 it was 0.005 mg/liter.

points at the boot and head pulley covers of the bucket elevator generally reduced concentrations to <1 mg/liter. Airflow in the dust control duct on the boot pulley cover was ca. 0.25 m^3/sec (550 ft^3/min).

Fumigant concentrations in the grain handling system were influenced both by the temperature of the grain and the time interval between fumigant application and grain transfer. Concentrations of CS_2 and CCl_4 at each sample location generally peaked between 8 and 16 h posttreatment. The highest concentration of CCl_4 at each sample point appeared earlier as grain temperature increased. Concentrations of CS_2 in air samples from the drawoff duct were highest during transfers of wheat fumigated at 6.6°C, and most samples contained significantly more CS_2 than CCl_4. No CS_2 concentrations were greater than the lower explosive limit of 1.2% by volume (12,000 ppm or ca. 37 mg/liter) established for CS_2 (Coward and Jones 1952) alone, and no air sample contained only CS_2. In contrast, concentrations of CCl_4 in the drawoff were highest during transfer of grain treated at 27.7°C, and most of these samples contained only CCl_4.

Concentration variations in CS_2 or CCl_4 in the drawoff during transfer of the grain were not consistently reflected by corresponding concentration changes in the bucket elevator. For example, at 6.6°C, the concentration of CS_2 was highest in the drawoff (15.69 mg/liter) during the 12-h-posttreatment transfer, at which time concentrations of CS_2 on the boot and head were barely detectable. In contrast, also at 6.6°C, the concentration of CS_2 in the boot and in the elevator heat were highest (2.0 and 0.67 mg/liter, respectively) during the 16-h-posttreatment transfer, when the concentration in the drawoff was only 14.35 mg/liter. Similarly, CCl_4 concentrations in the drawoff, boot, and head during the 8-h transfer of wheat treated at 27.7°C were 51.0, 0.81, and 0.29 mg/liter, respectively. During the 12-h transfer of wheat treated at 17°C, the drawoff CCl_4 concentration was only 15.0 mg/liter, but it was 4.13 mg/liter in the boot and 1.25 mg/liter in the head.

In all locations, air samples generally contained CS_2 concentrations greater than those established for an 8-h, time-weighted average limit of 20 ppm (0.062 mg/liter) and greater than the acceptable ceiling concentration of 30 ppm (0.093 mg/liter)(Anonymous 1977). Furthermore, all drawoff samples at each interval at 6.6 and 16.9°C contained CS_2 concentrations of >100 ppm (0.311 mg/liter), the maximum peak above the acceptable ceiling concentration allowed for a duration of 30 min in an 8-h shift. The maximum allowable peak CS_2 concentration also was exceeded in the boot during the 16- and 32-h transfers at 6.6°C and at the 8-h transfer at 16.9°C. Concentrations of CS_2 were greater than the maximum allowable peak in the head during the 8-, 12-, and 16-h transfers at 6.6°C.

The minimum concentration of CCl_4 detected by the IR method of analysis of the samples was ca. 20 ppm (0.125 mg/liter), which is twice the level for an 8-h, time-weighted average limit of 10 ppm (0.063) established for $(Cl_4$. Nearly all samples analyzed during the grain transfers contained CCl_4 concentrations equal to or exceeding the established 20 ppm (0.125 mg/liter) limit.

Discussion

The results confirmed the presence of fumigant vapors in grain handling equipment during transfer of recently fumigated grain and emphasizes the potential hazards of moving grain too soon posttreatment. Atallah (1979) reported that the presence of 5 drops of a laboratory-prepared mixture of 80% CCl_4 and 20% CS_2 by volume, or the presence of just 1 drop of CS_2 alone, lowered the minimum explosible concentration of a commercial wheat flour dust in a 1-liter Hartmann apparatus from 0.17 to 0.085 g. Although no explosive concentrations of CS_2 were found under the conditions of our tests, the fumigant concentrations detected in the relatively confined area of the drawoff duct demonstrated the fumigant vapor load that might be expected when grain is moved after an "overnight" treatment. These results also showed the imbalanced ratio of CS_2 to CCl_4 that can result from differences in penetration and sorption characteristics of the two 80:20 components, particularly during fumigation of cold grain. Forced air movement for dust collection in the bucket elevator effectively dissipated most of the fumigant vapors entrained by the treated grain but did not reduce concentrations of CS_2 and CCl_4 in all cases to accepted safe levels for repeated or prolonged exposure.

Rowe (1957) estimated that the threshold concentrations for detection of odors of CCl_4 and CS_2 and 70 ppm (0.44 mg/liter) and 60 ppm (0.186 mg/liter), respectively, but cautioned that the odor of fumigants could not be relied upon to provide effective warning of the presence of hazardous amounts of vapor. We demonstrated the ineffectiveness of odor as a deterrent to fumigant exposure by applying Rowe's estimated odor threshold values to concentrations of fumigant detected in the elevator head during grain transfer. At this location, 40% of the samples contained CCl_4 and CS_2 concentrations greater than the recommended 8-h, time-weighted average but less than the estimated minimum concentrations for odor detection.

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