The Temperature Effect on Fumigant Desorption from Cereal Grain

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The more rapid desorption of fumigant residues from whole cereal grain at low (14–17°) rather than at high (30–37°) temperature was confirmed with several fumigants by two methods of analysis. The unchanged fumigant residues seem to be present in the fumigated grain in two forms: loosely and firmly bound. The desorption of the firmly bound residues from grain fumigated at room temperature is at least twice as fast at low rather than at high temperature of airing. Fumigation temperatures affect the relative amounts of the residues: at lower temperatures lower levels of firmly bound residues are present. This temperature effect may be responsible for faster desorption in winter than in summer as noted in field experiments. The low-temperature effect was abolished by grinding the grain and was not due to the fat fraction of the fumigated materials. It seems that the intact grain structure is responsible for this effect.

Unchanged residues of halogenated fumigants, except methyl bromide, persist in cereal grain several weeks after fumigation (Olomucki and Bondi, 1955; Bielorai and Alumot, 1966; Scudamore and Heuser, 1973). Efficient airing is therefore desirable to prevent harmful effects of residues, mainly on animals consuming cereal grain as such.

In a previous work with a fumigant mixture we demonstrated that airing at low temperature is more efficient than at high temperature (Alumot and Bielorai, 1969). In a recent work Scudamore and Heuser (1973), using carbon tetrachloride as sole fumigant, did not confirm our results. These authors also questioned the efficiency of carbon tetrachloride extraction by our steam-distillation method (Bielorai and Alumot, 1966), when compared with cold extraction (Heuser and Scudamore, 1969).

Our conclusion, that lowering the temperature speeds up the desorption of residues, was based mainly on experiments with trichloroethylene and chloroform, determined by the steam-distillation method. Several fumigation experiments were carried out with ethylene dibromide, carbon tetrachloride, and trichloroethylene on laboratory and commercial scale, using the above-mentioned two methods for residue determination. Experiments with extracted leguminous seeds and cereal grain were conducted in an attempt to explain the faster desorption at low rather than at high temperature.

METHODS

Fumigation. Laboratory fumigation experiments were carried out in special 20-l., hermetically sealed containers filled up to three-quarters of their volume with the fumigated commodity. After fumigation at room temperature the materials were divided into two equal parts and aired at two different temperatures. The fumigation and airing procedures were described previously (Alumot and Calderon, 1965). Most of the experiments were carried out with previously untreated local wheat.

The commercial fumigation was carried out with sorghum grain (local variety), fumigated in a silo with a cell capacity of 8 m^3. A commercial fumigant mixture, containing trichloroethylene (64%), carbon tetrachloride (10%), and carbon disulfide (26%), w/w, was applied at a concentration of 480 g/m^3 for 72 hr. The airing was carried out by transferring the grain twice from one cell to another through an elevator. In this procedure the grain was exposed to air for about 1 hr. Four samples were taken during the second transfer back to the original cell. About 12 transfers were performed during the 40 days of airing. Two fumigations were carried out, one in summer at 28° and the other in winter at 17°. Grain temperatures during the airing period fluctuated between 28 and 30° in summer, and between 11 and 17° in winter.

Residue Determination. The cold extraction method of Heuser and Scudamore (1969) was compared with steam distillation (Bielorai and Alumot, 1966).

In contrast to the report by Scudamore and Heuser (1973) that by our procedure prolonged boiling was necessary for maximum recovery, two extractions of 15 min each were sufficient for practical purposes. Less than 1% of the first extract was found in the third extract, and no increase in fumigant recovered occurred after prolonging the boiling time up to 3.5 hr.

However, fumigant levels obtained in fumigated grain by cold extraction were always higher than those determined by steam distillation. The levels of ethylene dibromide and trichloroethylene found with our method were 70–85% of those obtained by the cold extraction method. The carbon tetrachloride residues from whole grain were only 50% and from fumigated mash 75% of those obtained by the cold extraction method.

Since recoveries of standards by our method are always close to 100%, as confirmed by Scudamore and Heuser (1973), it is possible that the differences are due to some interaction between the fumigant and the cereal grain constituents during boiling.

The determinations of residues in the airing experiments were carried out by the two methods.

The Influence of Fat on Desorption. To check the possibility of residue retention in the fat fraction at high temperatures, several experiments were conducted with cereal grain and oil seeds. Since the attempts to remove fat from whole grain were unsuccessful, the grain was ground to pass through a 2-mm sieve and fat extraction was carried out as usual, with petrol ether, in a large Soxhlet apparatus. Wheat and corn were fumigated at room temperature with 150 g/m^3 of the fumigant mixture for 24 hr. Airing was carried out at 15 and at 30°.

Dehulled sunflower seeds after partial fat extraction were compared with fat-containing seeds. The concentration of the fumigant mixture was 300 g/m^3 and the fumigation time was 48 hr. In the following trials ethylene dibromide was used at the above conditions; whole soybean seeds and corn were fumigated simultaneously and the desorption rates of residues compared at two temperatures. Lentils and chick peas were included in the investigations to test the desorption in whole leguminous grain with low fat levels.

RESULTS

Laboratory Experiments. The data presented in the first report on temperature effect (Alumot and Bielorai, 1969) were now analyzed for exponential desorption, plot-

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Table I. Constants of the Slow Residue Desorption Term from Cereals Fumigated and Aired at Two Temperatures[a]

	Chloroform		Trichloroethylene	
	17°	30°	17°	30°
	k_2, in %/Day			
Wheat	18.7	3.0	18.7	3.1
Barley	16.1	1.8	13.4	2.9
Corn	11.6	3.2	14.7	2.9
Sorghum	13.7	2.3	9.7	3.2
	C_b, in % of the Initial Value			
Wheat	55	70	55	65
Barley	33	42	23	45
Corn	52	57	29	47
Sorghum	42	50	37	62

[a] For fumigation conditions see the legend to Figure 1.

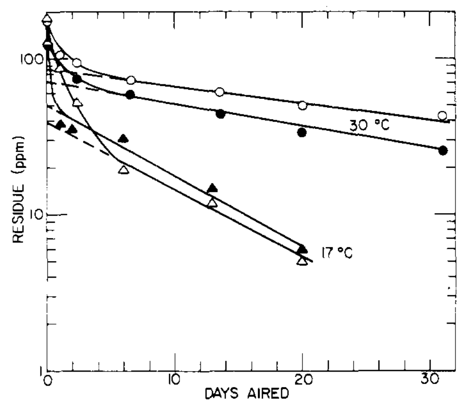

Figure 1. Residues of chloroform and trichloroethylene in sorghum fumigated and aired at two temperatures: (O, △) chloroform at 30 and 17°, respectively; (●,▲) trichloroethylene at 30 and 17°, respectively. The fumigant mixture contained carbon tetrachloride, carbon disulfide, chloroform, and trichloroethylene at 5, 26, 32, and 37 vol %, respectively, at a concentration of 300 g/m^3 for 48 hr.

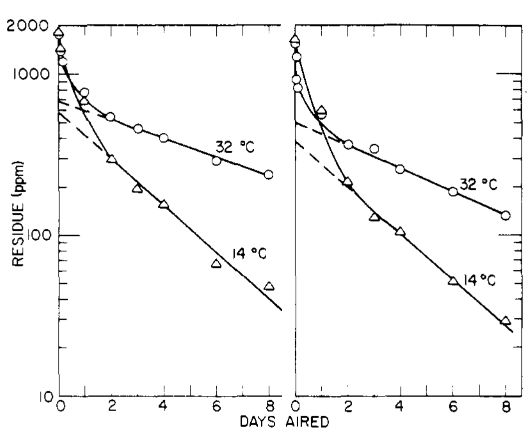

Figure 2. Desorption of ethylene dibromide residues from wheat aired at two temperatures: (left) cold extraction; (right) steam distillation; fumigation conditions, 200 g/m^3 for 48 hr at room temperature.

ting the fumigant residues on a logarithmic scale against time. Curves indicating a multiple exponential function with at least two terms, $C_t = C_a \exp(-k_1t) + C_b \exp(-k_2t)$, were obtained for each fumigant at a given temperature, as illustrated in Figure 1 for sorghum grain. The first term of the equation expresses the very rapid initial desorption; the second term expresses the subsequent slower desorption; C_a is the initial amount of rapidly desorbing, probably loosely bound fumigant, and C_b is the initial amount of slowly desorbing, probably more firmly bound fumigant. Since the determination of the first day constants was difficult due to the rapidity of the process, only the second term of the equation was analyzed (Table I). The values of k_2 (in percent/day) were 3–8 times greater at 17° than at 30° for all cereals and both fumigants tested. The initial amounts of firmly bound fumigants were always higher in grain fumigated at 30 than at 17°.

Table II. Residues of Carbon Tetrachloride (ppm) in Sorghum after Commercial Fumigation in Summer and Winter[a]

Days of airing	Summer	Winter	Days of airing	Summer	Winter
0	31.7	45.0	15	11.2	12.2
1	23.9		17	11.2	11.9
2		24.0	20		10.6
3	18.3		23	7.7	
6		16.2	31	6.1	8.1
7	15.7		36	5.6	
10	13.7	14.3	44		5.0

[a] For fumigation conditions see legend to Figure 4.

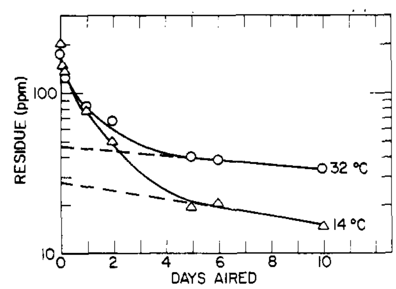

Figure 3. Desorption of carbon tetrachloride, determined by cold extraction, from wheat aired at two temperatures; fumigation conditions, 160 g/m^3 for 48 hr at room temperature.

In the above experiments the grain was fumigated at the same temperature as it was aired, i.e., there was a temperature difference not only during airing but also during sorption of the fumigant. Since different initial amounts of firmly and loosely bound residues could influence the desorption process, fumigation in the subsequent laboratory experiments was conducted at room temperature (about 22°) and only the airing temperatures differed. Wheat was fumigated with ethylene dibromide or carbon tetrachloride at 200 and 160 g/m^3, respectively, and aired at 32 and 14°. Several analyses by two methods were carried out during the first day and frequent determinations during the most intense desorption—up to 2 weeks of airing.

The results (Figures 2 and 3) show that airing of grain proceeds more rapidly at low than at high temperature. With grain fumigated at room temperature, the intercept of the slow desorption term, indicating the firmly bound fumigant, is similar at both airing temperatures.

The process of ethylene dibromide desorption (Figure 2) was similar to that observed previously with chloroform and trichloroethylene; the differences in desorption rate become evident after most of the loosely bound fumigant has disappeared, i.e., after about 2 days of airing. The rate constants of the slow term chosen as illustrated (Figure 2) were independent of the method of residue determination: 30.5%/day at 14° and 17%/day at 32° for ethylene dibromide analyzed by cold extraction and 32.2%/day and 17.3%/day, respectively, when analyzed by steam distillation.

Table III. Fumigant Residues (ppm) in Fat-Containing and Defatted Ground Wheat Aired at Two Temperatures[a]

	Trichloroethylene				Carbon tetrachloride			
	Fat containing		Defatted		Fat containing		Defatted	
Days of airing	15°	30°	15°	30°	15°	30°	15°	30°
0	133		130		21		15	
4	36	6	50	11	2.7	0.7	5.1	1.5

[a] For fumigant mixture, see legend to Figure 1; at a concentration of 150 g/m^3 for 24 hr at room temperature.

Table IV. Residues (ppm) of the Fumigant Mixture in Partially Extracted and in Intact Dehulled Sunflower Seeds, Aired at Two Temperatures[a]

	Trichloroethylene				Carbon tetrachloride			
	16% oil		48% oil		16% oil		48% oil	
Days of airing	15°	30°	15°	30°	15°	30°	15°	30°
0	1605		652		180		58	
1	514	426	326	309	53	45	18	16
2	333	174	275	204	22	20	17	8
5	198	59	194	174	16	11	8	8

[a] For fumigant mixture, see legend to Figure 1; at a concentration of 300 g/m^3 for 48 hr at room temperature.

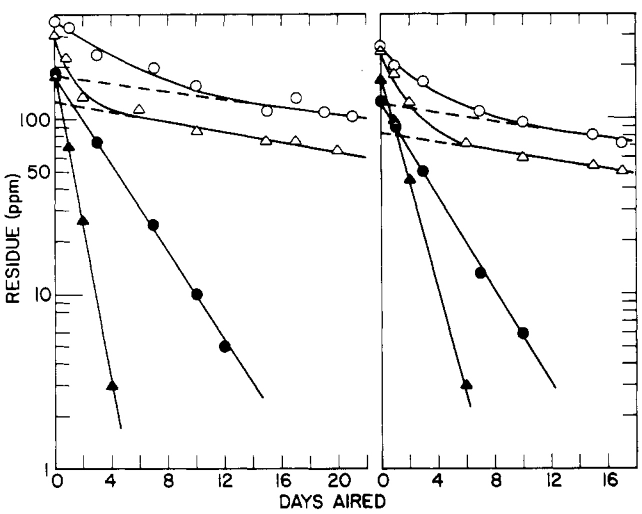

Figure 4. Desorption of trichloroethylene from sorghum fumigated in summer (O) and in winter (Δ); (● and ▲) the respective calculated values for the rapid desorption (the first term); (left) cold extraction; (right) steam distillation. The fumigant mixture contained trichloroethylene, carbon tetrachloride, and carbon disulfide at 64, 10, and 26 wt %, at a concentration of 480 g/m^3 for 72 hr.

The desorption of carbon tetrachloride (Figure 3) was in general slower than that of the other fumigants and therefore the temperature effect appears less pronounced. It seems that the process of rapid desorption is slower and longer with carbon tetrachloride than with other fumigants. After airing for 10 days, the residues at 32° were more than twice those at 14°. The rate constants could not be calculated precisely due to several possibilities of the exponential curves; when calculated from tangents chosen arbitrarily, the rate constants at a low temperature were in each case twice as great as at a high temperature.

Commercial Fumigation. The disappearance of the main constituent of the fumigant mixture, trichloroethylene, determined by two methods, is shown in Figure 4. There is a clear difference between the desorption rate in the two seasons, the faster desorption occurring at the lower temperature, in winter. The desorption process was expressed by a two-term exponential. The values for the first term were calculated by subtracting the values of the second, slow term from the total (Riggs, 1970). The rate constants for the rapid desorption, determined by cold extraction, were 4.0%/hr in winter and only 1.2%/hr in summer and by steam distillation, 3.0%/hr in winter and 1.4%/hr in summer. Thereafter, the process slowed down with the same rate constant of about 4%/day in winter and in summer.

Carbon tetrachloride residues were small and the trend of faster desorption at low temperature (winter) was noted only in the first week of airing. The results, determined by the cold extraction method, are given in Table II. As previously observed with wheat, the carbon tetrachloride desorption rate was less temperature dependent than that of the other fumigants.

The main difference between these and laboratory results is probably in the mode of airing: constant airing was carried out in the laboratory and airing during several short periods of time was done in the silo. This may be the cause of the slower desorption of loosely bound residues (first term) in the silo than in the laboratory. Since the "real" airing period in the silo was relatively short, the effect of temperature came to full expression only in the case of trichloroethylene and was less evident with carbon tetrachloride.

Influence of Fat on Airing at Different Temperatures. One of the possible causes of the unexpected slower desorption of residues at high than at low temperature could be better solubility and retention of the residues by the fat fraction of the grain, at the higher temperature. Experiments were conducted with defatted and fat-containing ground wheat fumigated with the fumigant mixture.

The desorption process of ground grain was not similar to that of whole grain. The disappearance of the fumigants was more rapid at 30 than at 15° (Table III). The presence of fat did not result in longer retention of the fumigants.

When whole, dehulled sunflower seeds were fumigated after partial fat extraction (no total extraction was possible from whole grain), the results (Table IV) were similar to the ground grain: the rate of residue disappearance was in all cases greater at 30 than at 15°. This trend was more marked in the extracted than in the nonextracted seeds. In the latter, the desorption rate was generally slower than in extracted seeds and only very slightly faster at 30 than at 15°. Although this may have been due to the presence of fat, it seems that the unchanged structure of the grain plays a more important role in this process.

The dehulling may eliminate the characteristic effect of low temperature on desorption. This is further accentuated by fat extraction, which probably affects the internal structure of the grain.

Another experiment was therefore carried out with intact soybean seeds (17% oil) and corn (4% oil). Ethylene dibromide was used as the fumigant. It was assumed that the influence, if any, of fat on desorption should be more accentuated in soybean than in corn. The results, presented in Table V, show clearly that this is not the case. The initial sorption of ethylene dibromide was similar in soybean and corn, despite the much greater oil percentage in the soybean. Significantly more rapid desorption at the lower temperature occurred only in the case of corn. Ethylene dibromide disappeared from the soybean seeds at a

Table V. Residues (ppm) of Ethylene Dibromide in Corn and Soybean Aired at Two Temperatures[a]

Days of airing	Corn		Soybean	
	17°	37°	17°	37°
0	1565		1115	
1	462	903		
2			625	700
7	205	673	320	500
14	156	581	242	334

[a] Fumigation conditions, 300 g/m³ for 48 hr at room temperature.

Table VI. Residues (ppm) of Ethylene Dibromide in Lentils and Chickpeas Aired at Two Temperatures[a]

Days of airing	Lentils		Chickpeas	
	17°	37°	17°	37°
0	295		623	
1	247	244		
2			270	275
8	43	142	213	307
14	28	112	125	207

[a] For fumigation conditions see Table V.

slightly higher rate at the lower temperature, the effect of temperature being rather negligible.

In the third experiment of this series (Table VI), lentils (containing less than 1% oil) and chickpeas (5% oil) were fumigated with ethylene dibromide. Both of these leguminous seeds, but lentils in particular, showed more rapid desorption at the low temperature.

It seems that the whole (not dehulled) seed retains the fumigant residues longer at high temperatures. This effect is most characteristic in cereal grain and apparently does not depend on the presence of fat but rather on some features of the grain structure.

DISCUSSION

The more rapid desorption of fumigant residues from whole cereal grain aired at low rather than at high temperature was confirmed in several experiments by two different methods of analysis. Despite differences in absolute values, due to lower recovery by our method than by cold extraction, the calculated desorption rates were practically identical.

The results of desorption of fumigants from oil seeds indicate that fat is not the factor preventing desorption at high temperatures. Soybean oil seeds did not retain ethylene dibromide longer at 37 than at 17°, despite the presence of 17% oil. On the other hand, the desorption from lentils—leguminous seeds with a low fat content—was affected by temperature similarly to cereal grain. Grinding the cereal grain annulled the low-temperature effect, indicating that grain structure is the principal factor involved.

It seems that the fumigants are retained in whole grain in two forms: loosely and firmly bound. It is probable that the differentiation into the two forms occurs during sorption. The relative amounts of each form initially sorbed, calculated from the desorption curves, depend on temperature during fumigation. Less firmly bound residues were found in grain fumigated at low than at high temperatures (C_b, Table I). When fumigation was carried out at one temperature and only the airing was conducted at different temperatures, the distribution of the loosely and firmly bound fumigants was similar (Figure 2). The loosely bound residues disappear very rapidly during the first and second days of airing. The desorption rate of the firmly bound residues increased several times by lowering the temperature, contrary to what had been expected from the physical laws of sorption. The firmly bound residues are probably retained by the whole grain more strongly at high than at low temperatures.

There are, therefore, two components of faster desorption at low than at high temperatures: (1) faster desorption of firmly bound residues when airing is carried out at low temperature and (2) lower initial levels of the above residues when fumigation is carried out at low temperature.

The first component of temperature effect was distinct with ethylene dibromide, trichloroethylene, and chloroform (Figures 1 and 2), but less sharp with carbon tetrachloride, whose desorption is generally slower than that of the other fumigants. The first step of rapid desorption with carbon tetrachloride (Figure 3) seems to last several days, possibly influencing the levels of firmly bound residues.

In the field experiments (Figure 4) the second component seems to be of principal importance. This assumption is confirmed by the results of Scudamore and Heuser (1973): grain fumigated at 10° and aired at 25° loses the carbon tetrachloride residue faster than grain fumigated and aired at 25°. However, contrary to our results, after fumigation at the same temperature, the desorption rate was faster at 25 than at 10°. It is possible that some of the differences result from the experimental design. We measured the desorption rate frequently during the first 2 weeks of the most extensive airing. Scudamore and Heuser extended their experiments to 1 year, with few determinations during the first period. After several weeks of airing, when only traces of the residues are present, desorption may again follow the known physical laws. However, during the most important (early) period, there is a clear indication of temperature effect, as reported by us.

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