Sorption of Ethylene Dibromide, Ethylene Dichloride, and Carbon Tetrachloride by Cereal Products

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The concept that wheat can behave as a chromatographic column toward fumigant gases was further explored by use of gas chromatography. Ethylene dibromide, ethylene dichloride, and carbon tetrachloride in the vapor phase were applied singly and in various admixtures for 5 hours at 27° C. in micro fumigation chambers to 51 cereals and cereal products that differed in species, moisture content, and particle size. The sorption equilibria showed that each substrate had a different affinity for the gases. The per cent sorption of each component was unaffected by changing the molar ratio of ethylene dibromide, ethylene dichloride, and carbon tetrachloride from 1:8:11 to 1:1:1, or increasing the applied dosage by 2× and 3×. Whether the gases were applied singly or in admixture, the order of sorption by most of the substrates was EDB > EDC > CT. Depending on the substrate, sorption of ethylene dibromide applied in admixture was 4 to 55% less, of ethylene dichloride was 0 to 14% less, and of carbon tetrachloride was 0 to 12% less than when applied singly. Increase in moisture content of wheat from 9.0 to 18.5% significantly increased the uptake of ethylene dibromide and ethylene dichloride, but not of carbon tetrachloride. Even moderate decrease in particle size by grinding very markedly increased the uptake of the three gases. The importance of assessing sorption characteristics prior to bulk fumigation, and the impact of chromatographic behavior of cereal products on fumigant residue data are discussed.

Although three-component fumigant mixtures are widely used to control insect and fungal infestations in stored grain, the only published data, to the author's knowledge, on their sorption by cereal substrates are those of Lindgren and Vincent (*18*) on whole-kernel corn. The sorption by wheat in recirculation chambers of a four-component mixture (ethylene dibromide, ethylene dichloride, carbon tetrachloride, and carbon disulfide) was determined by Whitney and Kenaga (*21*) by use of mass spectrometry and a Gow-Mac thermal conductivity gas analyzer (air reference). Such information was considered essential before undertaking the determination in stored wheat of fumigant residues of multicomponent mixtures.

This report deals with the sorption by 51 cereal substrates of ethylene dibromide, ethylene dichloride, and carbon tetrachloride (EDB, EDC, and CT) applied singly and in two admixtures in the vapor phase at 27° C.

Methods using gas chromatography (*5*) were developed which were more specific, sensitive, and rapid than the polarographic methods (*1, 4, 8*) used in previous investigations of fumigant behavior (*2, 3, 6, 9*) and enabled the use of 100-cc. syringes as micro fumigation chambers and smaller gas-air samples for analysis, and more rapid attainment of equilibria. The amount of each gas sorbed by each substrate, relative to that obtained in syringes used as experimental controls, was calculated from the drop in gas concentration in 4-cc. air samples taken $^1/_4$, 1, 2, 3, 4, and 5 hours after application. Some 2800 measurements of gas concentration were thus made.

Major emphasis was on wheat and on the use of Dowfume EB-5 (Dow Chemical Co., Midland, Mich.) as a commercially available three-component fumigant mixture. Dowfume EB-5 is widely used as a bulk grain fumigant and contains 7.2, 29.2, and 63.6% (w./w.) of ethylene dibromide, ethylene dichloride, and carbon tetrachloride. Other cereals and cereal products examined included flour mill fractions, screenings, poultry feed mixture, wheat gluten, wheat starch, and peas. The aim was to extend the range of observations in which wheat showed chromatographic behavior toward fumigant gases (*2, 6, 9*). Unlike the previous wheat column investigation (*9*) in which air was used as a carrier gas, the current investigation was confined to determination of sorption equilibria of cereal products, and no desorption (elution) was attempted.

Materials and Apparatus

Gas Chromatograph. An F & M Model 500 linear temperature-programmed gas chromatograph (F & M Scientific Corp., Avondale, Pa.) with a four-filament tungsten thermal conductivity detector was used. Operating conditions were: 6-foot × $^1/_4$-inch o.d. stainless steel column packed with 10% SE 30 (w./w.) on 60- to 80-mesh Diatoport S; helium flow rate, 50 cc. per minute; injection port and detector block temperatures, 265° and 285° C.; bridge current, 200 ma.; Minneapolis-Honeywell recorder (series Y 143, 0 to 1 mv., 1 second); chart speed, 45 inches per hour; Disc Integrator to record areas of the chromatograms; ethylene dichlorine and carbon tetrachloride determined isothermally at a column temperature of 60° C., and ethylene dibromide determined by programming temperature at 15° C. per minute after end of carbon tetrachloride peak.

Gas Concentrate Flasks. Precalibrated all-glass Strand flasks (Figure 1) were used to contain fumigant-air mixtures 10 to 20 times more concentrated than the amounts used in the test chambers. A minimum of silicone grease was used to lubricate the stopcocks. No lubricant was used for the ground-glass neck joints. Equivalent all-glass flasks can be used.

Micro Fumigation Chambers. A series of B-D Luer-Lok 100-cc. ground glass syringes (Becton-Dickinson Co., Ltd., East Rutherford, N. J.), precalibrated to 100-cc. volume with water at 27° C., served as micro fumigation chambers. Each syringe was fitted with a Luer stopcock, the end of which was capped with a silicone rubber serum cap (Figure 1).

Fumigant Standards. Ethylene dibromide, ethylene dichloride, and carbon tetrachloride standards in *n*-pentane were used to prepare standard curves in the range 0 to 200 μg.

Constant temperature air oven.

Cereal Substrates. Five-gram samples of cereal substrates of various moisture contents were used. Selkirk wheat

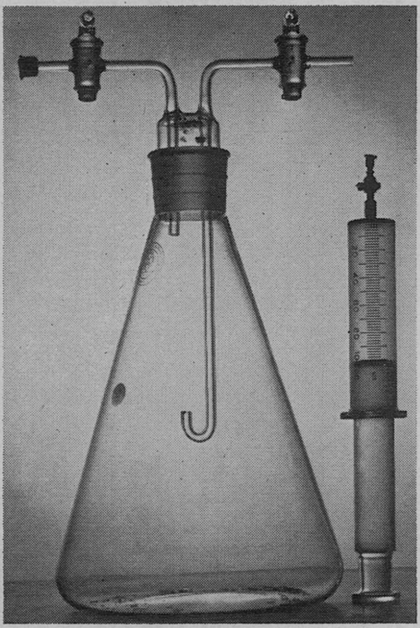

Figure 1. Strand flask containing ethylene dibromide, ethylene dichloride, and carbon tetrachloride gas mixture and 100-cc. precalibrated hypodermic syringe used as micro fumigation chamber

of 9.0, 13.5, and 18.5% moisture content was used. The particle size of each group was reduced by grinding with a Hobart grinder to a coarse size (>20-mesh, corresponding to broken kernels) and to a semifine size (<60-mesh, corresponding to a composite of flour and semifine wheat meal). The cereal substrates are listed in Table I.

Loading and Sampling Syringes. A weight-calibrated 20-cc. B-D syringe, fitted with a Chaney (*11*) adapter and a 1-inch 25-gage hypodermic needle, was used to load the fumigation chambers with the gas-air mixtures. A 5-cc. Gas Tight syringe (Hamilton Co., Inc., Whittier, Calif.), similarly fitted, was used in taking 4-cc. air samples from the chambers for determination by gas chromatography of the amount of fumigant not sorbed.

Fumigants and Rates of Application. Since a primary objective was to examine the affinities of cereal products for ethylene dibromide–ethylene dichloride–carbon tetrachloride mixtures, Dowfume EB-5 was applied to cereal products without regard to its suitability for practical control purposes. EB-5 was applied at a dosage of 0.1 *N*, where *N* is equivalent to the normal recommended dosage of 3 Imperial gallons (46.2 pounds) of EB-5 per 1000 bushels of wheat. When EB-5 is applied at a dosage of 0.1 *N*, the amounts of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in the vapor phase in the absence of sorptive materials are about 4.2, 16.8, and 36.8 mg. per liter of air, respectively, or in a 1:4:9 weight ratio. These amounts correspond to 0.54, 4.18, and 5.84 mmoles of ethylene dibromide, ethylene dichloride, and carbon tetrachloride, or a molar ratio of about 1:8:11, based on molecular volumes at 27° C. and 750 mm. of Hg.

To compare the effect on sorption of varying considerably the 1:8:11 molar ratio of ethylene dibromide, ethylene dichloride, and carbon tetrachloride present in EB-5, an equimolar mixture (EM) was made up in which ethylene dibromide, ethylene dichloride, and carbon tetrachloride were each at 1.0 m*M*, the corresponding (w./w.) amounts being 7.68, 6.28, and 4.04 mg. per liter of air. The EM mixture was applied at a nominal dosage of 3 mmoles. Thus, in the absence of sorptive materials, the initial amounts of ethylene dibromide, ethylene dichloride, and carbon tetrachloride applied in admixture were approximately 0.54, 4.2, and 5.8 times greater when EB-5 was applied at 0.1 *N* than when EM was applied at 3 m*M*.

In addition to comparing the two mixtures, ethylene dibromide, ethylene dichloride, and carbon tetrachloride were applied singly to some of the substrates in Table I, in amounts corresponding to those in EB-5 at a dosage of 0.1 *N*. The actual amounts present at time of application averaged about 12% less of ethylene dibromide, 6% less of ethylene dichloride, and 2% less of carbon tetrachloride. It was considered that the use of control chambers sampled at the same six periods as the test chambers would cancel out the per cent sorption contributed by the chamber walls.

To determine the effect on sorption equilibria of increasing the dosage of the three-component mixtures, EB-5 was applied at 0.05, 0.10, and 0.15 *N* to wheat of 13.5% moisture content. EM mixture was applied at a rate of 3, 6, and 9 mmoles.

Intercomparisons of three types of application, three moisture levels, and three particle sizes were made on wheat, as shown in items 1 to 9, Table I. The applications comprised EB-5 at a dosage of 0.1*N*, EM mixture at 3 m*M*, and the individual components corresponding to their amounts in EB-5 at 0.1 *N*. The wheat moisture levels were 9.0, 13.5, and 18.5%. The particle sizes were whole kernel, coarse ground (>20-mesh), and fine ground (<60-mesh) Selkirk wheat.

Other Substrates. The diverse cereal species tested are listed in Table I. Varieties are indicated when known. Oat "groats" (item 18) are an intermediate stage of oat milling and refer to "green" oats (raw, or as received) that have been kilned and dehulled. Pinhead oats (item 19) are groats that have been mechanically cut prior to processing as quick-cooking oatmeal. Rolled oats (item 20) are pinhead oats after partial cooking, followed by flaking or rolling. Pot barley (item 23) is essentially whole barley with the hulls ground off between mechanical emery plates. Pearl barley (item 24) is pot barley ground to somewhat smaller dimensions by longer grinding time. Refuse screenings (item 33) are mixed weed seeds, broken grain kernels, hulls, chaff, foreign matter, etc., resulting from grain cleaning. No. 2 mill screenings (item 35) are similar but with less foreign matter and a higher percentage of broken grain kernels, and thus with a higher value as animal feed. The screenings were ground by hammer mill. Wheatlets (item 45) are granular particles of purified endosperm from Hard Red Spring wheat. Vital gluten (item 48) is a commercial protein concentrate (more than 80% protein), and dried in a manner to avoid denaturation of the protein. Wheat starch (item 49) has a minimum of protein and fat (less than 1%) and is finer in particle size than flour. Poultry chick starter crumbles (item 47) has a high content of mixed cereal products and is an animal feed formulation that is pelletized and mechanically crumbled to yield small, reasonably uniform pellets of about $^1/_{12}$-inch diameter. Peas (items 50 and 51) come under the Canada Grain Act and were included mainly to help elucidate the relationship between increase in particle size of substrate and increased sorption of fumigant gas.

Procedure

Preparation of Gas Concentrates. Amounts of liquid fumigant that were calculated to yield "gas concentrates" 10 to 20 times stronger than required for testing were sealed into small soft-glass ampoules. Each sealed ampoule was scratched at the neck with a glass file and deposited in a Strand flask. With the flask head in place, a moderate vacuum was drawn, the stopcocks were closed, and the ampoule was broken upon several sharp shakes of the flask. The flask was warmed under a hot water tap to accelerate vaporization of the liquid, then cooled to ambient temperature and restored to atmospheric pressure by opening one of the stopcocks. A rubber serum cap was affixed to the short tube of the flask head. When used as a gas source, the flask was placed in a 40° C. water bath and shaken before it was sampled for constancy of gas concentration, the ampoule fragments serving as microstirrers in this regard. Preset volumes were analyzed and transferred to the test chambers. When 50 to 60 cc. of gas had been removed from a Strand flask (average volume 6300 cc.), air was admitted to restore atmospheric pressure, and the mixed atmosphere was reanalyzed and volumes were readjusted, if necessary.

Loading Micro Fumigation Chambers. The syringe piston of each precalibrated 100-cc. syringe was removed, a serum cap was attached to the Luer stopcock, and a $2^1/_2$-inch 20-gage hypodermic needle to act as an air vent was inserted through the cap center to extend about 1 inch past the bottom of the syringe. After 5.00 grams of substrate were transferred into the chamber through a long-stemmed powder funnel, the syringe piston was inserted and advanced slowly to the 30-cc. mark, and the 20-gage needle was removed. Required amounts of fumigant from the Strand flasks were transferred by Chaney syringe to each fumigation chamber. The Chaney syringe was detached from its needle, the chamber piston was further drawn up slowly to the 100-cc. mark, and the needle was removed. The chambers, including control chambers treated similarly, were placed in

Table I. Per Cent Sorption by 51 Cereal Substrates of EDC, CT, and EDB Supplied Singly and in Admixture in Vapor Phase for 5 Hours at 27° C.

Substrate Tested	*Moisture Content, %*	*EB-5 Mixture*[a]			*EM Mixture*[b]			*EDC, CT, and EDB Applied Singly*[c]		
		EDC	*CT*	*EDB*	*EDC*	*CT*	*EDB*	*EDC*	*CT*	*EDB*
Wheat, Hard Red Spring (Selkirk)										
1. Whole	9.0	0	0	18	0	0	18	8	0	31
2. Coarse ground	9.0	48	23	73	52	22	71	51	19	83
3. Fine ground	9.0	74	33	78	75	34	82	78	40	93
4. Whole	13.5	19	2	37	21	0	39	31	0	70
5. Coarse ground	13.5	58	21	80	62	26	81	66	18	92
6. Fine ground	13.5	69	28	84	74	34	88	77	31	97
7. Whole	18.5	45	8	73	42	4	68	50	20	91
8. Coarse ground	18.5	63	34	85	65	34	85	68	46	97
9. Fine ground	18.5	70	40	90	76	39	91	79	46	97
Wheat, Durum (Ramsey)										
10. Whole	13.2	15	3	35	11	0	36	22	7	79
11. Semolina, granular	14.2	61	30	84	60	29	81	66	30	87
12. Semolina, flour	13.9	72	42	89						
Wheat										
13. Soft White Spring	12.5	12	6	33	16	5	37			
14. Alberta Red Winter	12.2	13	0	27	12	3	32			
Oats										
15. (Garry), whole	11.0	22	0	40				21	3	41
16. (Rodney), whole	11.2	20	0	55				35	17	65
17. (Vicar), (hull-less), whole	10.8	44	23	71						
18. "Groats"	7.2	63	45	83						
19. Pinhead	7.6	80	62	89						
20. Rolled	9.5	86	71	92				85	72	99
Barley										
21. (Parkland), whole	9.6	9	0	28				8	0	32
22. (Parkland), malted, whole	3.8	15	8	15						
23. Pot	12.0	38	13	65						
24. Pearl	12.0	42	42	76				44	18	87
Rye										
25. Fall (Antelope)	9.5	8	0	20				4	4	34
26. Spring (Prolific)	9.8	10	0	32				2	8	51
Flax										
27. (Raja), whole	9.2	34	17	67	37	21	70	47	23	85
Corn										
28. Field (Falconer), whole	8.0	4	0	21	4	0	24	12	11	76
29. Cornmeal, yellow	12.5	74	21	88	65	22	86	66	26	88
Buckwheat										
30. Whole	14.0	19	1	34						
31. Grits, med. ground	13.8	66	16	81						
Screenings										
32. Mixed, dry, unground	12.0	51	19	76						
33. Refuse, unground	11.0	74	26	89				78	36	98
34. Refuse, ground	11.5	73	40	92				84	48	100
35. No. 2, mill, unground	12.0	65	28	85				60	18	89
36. No. 2, mill, ground	12.5	82	54	94				77	50	100
Flour										
37. First patent	13.0	74	23	89				74	29	95
38. Second patent	13.5	81	39	91						
39. Whole wheat	11.5	74	42	89				81	38	97
40. First clear	12.5	77	42	89						
41. Low grade	12.0	71	41	86						
Mill fractions										
42. Shorts	13.5	76	64	93				81	62	97
43. Bran	14.5	82	61	93				83	62	97
44. Feed middlings	11.5	78	61	94				75	62	98
45. "Wheatlets" (purified middlings)	14.0	67	18	87				79	18	92
46. Wheat germ, raw	12.5	85	81	94				87	79	99
Poultry feed										
47. Chick starter, pelletized, crumbles	11.5	79	60	82	77	60	86			
Gluten and starch										
48. Wheat gluten, "vital," powdered	5.0	53	23	73	52	21	75			
49. Wheat starch, powdered	12.0	16	2	27	19	2	30			
Dried peas										
50. Yellow (Creamette), whole	10.1	3	2	7	0	0	8	14	9	27
51. Yellow (Creamette), split	8.9	35	15	71	29	12	66	26	27	82

[a] EB-5 mixture applied at dosage of 0.1 N, where N = normal dosage of 3 Imp. gal. of EB-5 per 1000 bu. wheat.
[b] EM (equimolar) mixture applied at dosage of 3 mmoles.
[c] EDC, CT, and EDB applied singly in amounts corresponding to those in EB-5 at 0.1 N.

a circulating air oven at 27° C. Samples for analysis were taken at 1/4, 1, 2, 3, 4, and 5 hours after application, using the 5-cc. Hamilton syringe set for 4-cc. aliquots.

Results and Discussion

The end points of 105 sorption isotherms are given in Table I. Each value represents the per cent sorption at 5 hours of ethylene dichloride, carbon tetrachloride, or ethylene dibromide applied singly or in admixture as EB-5 or EM in the vapor phase at 27° C. to the cereal products indicated. Within the terms of reference of this preliminary investigation, the major emphasis was on wheat and on the use of EB-5 as a commercially available three-component fumigant mixture. Other substrates were not investigated to the same extent as was wheat; hence the unoccupied spaces in Table I.

Figure 2 shows nine series of sorption isotherms representing the interaction of three particle sizes of Selkirk wheat of 13.5% moisture content and three types of treatment (items 4 to 6, Table I). The particle sizes are whole kernel, coarse ground, and fine ground wheat. The formulations are Dowfume EB-5 applied at 0.1 *N*, EM applied at 3 m*M* and ethylene dibromide, ethylene dichloride, and carbon tetrachloride applied singly in the same proportions by weight as present in EB-5 at 0.1 *N*.

Figures 3 and 4 each show six series of sorption curves obtained with Selkirk wheat of 9.0% moisture content (Figure 3) and of 18.5% moisture content (Figure 4). Three particle sizes of wheat (whole kernel, coarse, and fine ground) and two types of application (EB-5 at 0.1 *N* and EM at 3 m*M*) were used in each instance.

Figure 5 shows six series of sorption curves to illustrate the effect of increasing the rates of application of EB-5 and EM. The substrate was Selkirk wheat of 13.5% moisture content. EB-5 was applied at 0.05, 0.10, and 0.15 *N*, and EM was applied at 3, 6, and 9 m*M*. Relatively dilute gas atmospheres were used because differences in sorption patterns could be more readily observed at lower gas concentrations with the gas chromatography methods (*5*) employed.

Figure 6 shows sorption isotherms for nine substrates other than Selkirk wheat. EB-5 was used at a dosage of 0.1 *N*. Space limitations do not permit showing all 237 sorption curves for the various substrates. However, Table I indicates the equilibria end points that were attained under the conditions stated.

Table I and Figures 2 to 6 indicate that each substrate had a different affinity for the three gases. Under these experimental conditions, sorption maxima were obtained within 3 hours. Reducing the particle size increases the amount of sorption. The sorption "speed lines" (*12*) thereby ascend faster

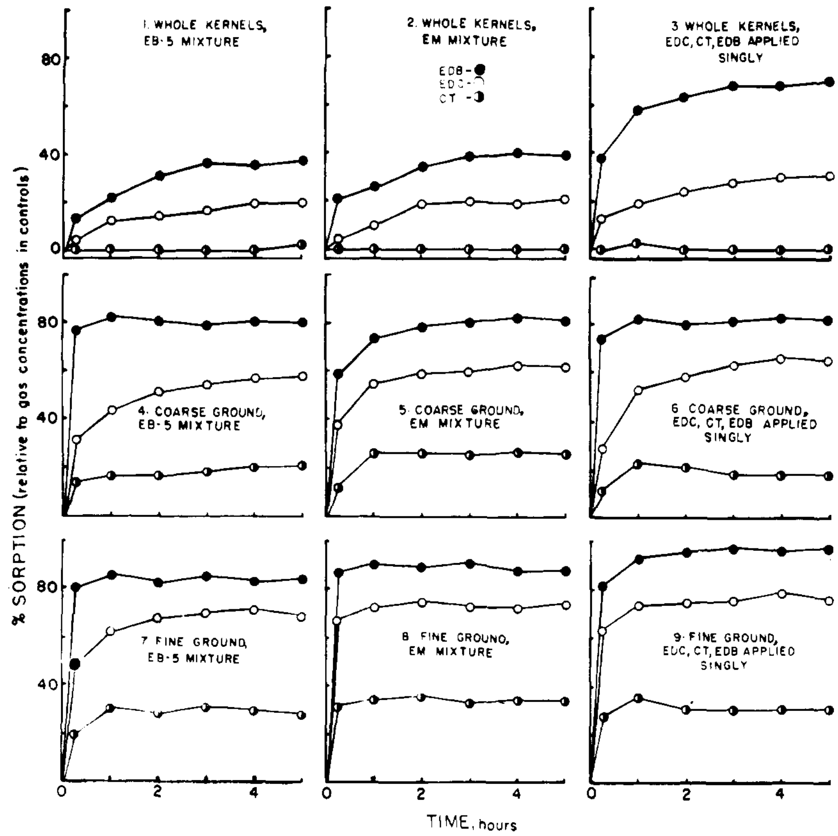

Figure 2. Sorption of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in vapor phase at 27° C. by Selkirk wheat of 13.5% moisture content of three particle sizes and after three treatments

Particle sizes. Whole kernel, coarse ground (>20 mesh); fine ground (<60 mesh)
Treatments. EB-5 at 0.1 N; EM mixture at 3 mM; and EDC, CT, and EDB applied singly in amounts corresponding to those in EB-5

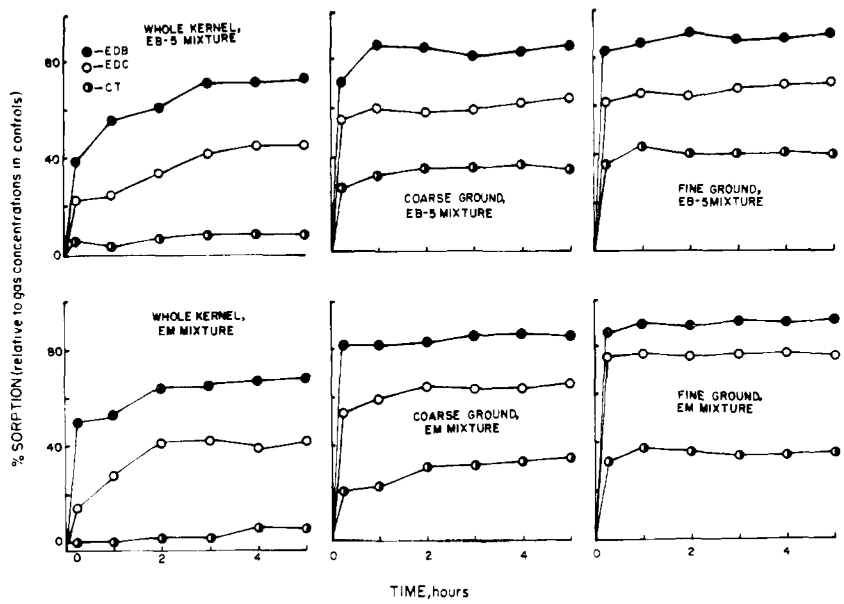

Figure 3. Sorption of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in vapor phase at 27° C. by Selkirk wheat of 9.0% moisture content of three particle sizes and after two treatments

Particle size. Whole kernel, coarse ground (>20 mesh); fine ground (<60 mesh)
Treatments. EB-5 at 0.1 N, and EM mixture at 3 mM

and equilibrium is reached sooner than is the case with whole grain. The same effect can be achieved by raising the moisture content (Figures 2 to 4). Nevertheless, the increased gas uptake is not a simple or direct function of decrease in particle size or increase in moisture content, as is discussed below.

Whether the three gases were applied singly or in admixture, the order of sorption by most of the substrates tested was EDB > EDC > CT. Relatively minor exceptions to this general order of sorption affinity for mixtures and single applications may be seen in Table I (items 1, 22, 25, 26, 50, and 51). Depending on the substrate, sorption of ethylene dibromide applied in admixture was 4 to 55% less, of ethylene dichloride was 0 to 15% less, and of carbon tetrachloride was 0 to 17% less than when applied singly. The reduction in sorption was greatest with whole cereal—e.g., corn, wheat, oats, and peas—and least when the moisture content was increased or the kernels were fractured or milled. Interestingly, ethylene dichloride and, to a lesser extent, carbon tetrachloride showed somewhat more sorption when applied in admixture as EB-5 or EM to split peas, screenings, and cornmeal.

Although ethylene dibromide was quantitatively the smallest of the three gases that were applied singly or in admixture, it nevertheless exhibited the highest per cent uptake. Its marked affinity in binary mixtures for wheat or flour as substrate was noted by Berck (*2, 6, 9*), Bondi, Olomucki, and Calderon (*10*), Heuser (*14*), Kenaga (*15*), and Majumder, Muthu, and Narasimhan (*20*), and is shown here with ternary mixtures applied over a considerably wider range of substrates. Lindgren and Vincent (*18*) found that ethylene dibromide was more strongly sorbed than ethylene dichloride or carbon tetrachloride by whole kernel corn after applying a formulation essentially similar to the EB-5 mixture used here. Whitney and Kenaga (*21*) also found selective sorption by wheat of a four-component fumigant mixture, the decreasing order of sorption being ethylene dibromide, ethylene dichloride, carbon disulfide, and carbon tetrachloride.

The comparison between EB-5 and EM mixture, each applied to wheat at three different dosage levels (Figure 5), is interesting. The remarkable similarity of the various sorption curves shows that the absolute amounts of gas sorbed by the wheat increased in proportion to the amounts applied, since the relative amounts were essentially unchanged for the three dosage levels that were used. The most striking feature, however, is that marked changes in molar ratio of EDB:EDC:CT from 1:8:11 in EB-5 to 1:1:1 in EM mixture produced no significant effect on the per cent sorption maxima (Figures 2 to 4). Thus a relative limit appears to exist for wheat with regard to the per cent uptake of ethylene dibromide, ethylene dichloride, and carbon tetrachloride applied in admixture. The relative limit reached is independent of applied concentration (at least up to 0.15 *N* of EB-5 and 9 m*M* of EM mixture) and is not affected by change in molar ratio of the components. The similarity of sorption patterns between applications of EB-5 and EM mixture is not confined to wheat but is also shown by other substrates (Table I). Replicate determinations with EB-5 and EM mixtures on eight substrates made 3 to 5 weeks after the initial determinations yielded sorption values within ±3.5% of the original values. This relative constancy of uptake has fundamental implications. It extends to cereal products other than wheat the previously reported concept (*2, 6, 9*) of chromatographic behavior shown by selective retardation of the passage of fumigant gases. Differential sorption was also

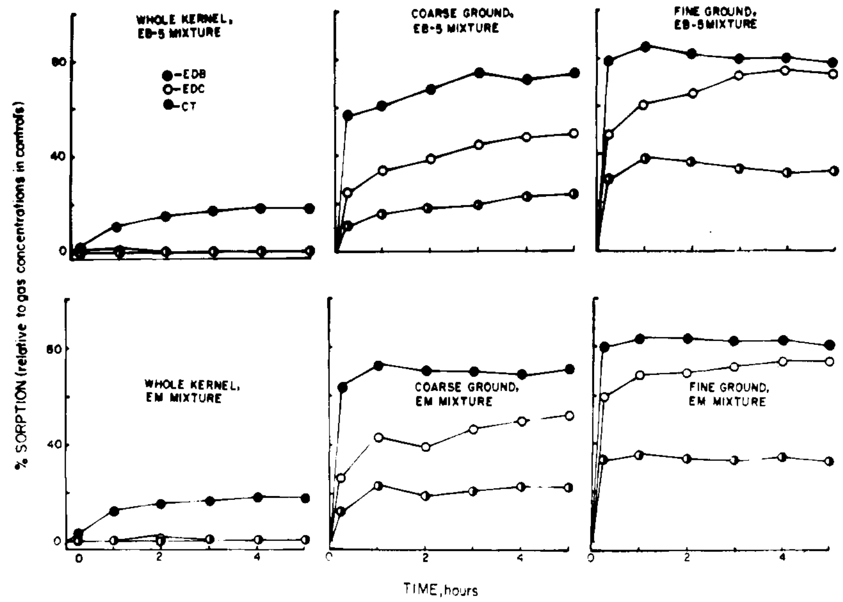

Figure 4. Sorption of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in vapor phase at 27° C. by Selkirk wheat of 18.5% moisture content of three particle sizes and after two treatments

Particle sizes. Whole kernel, coarse ground (>20 mesh); fine ground (<60 mesh)
Treatments. EB-5 at 0.1 N, and EM mixture at 3 mM

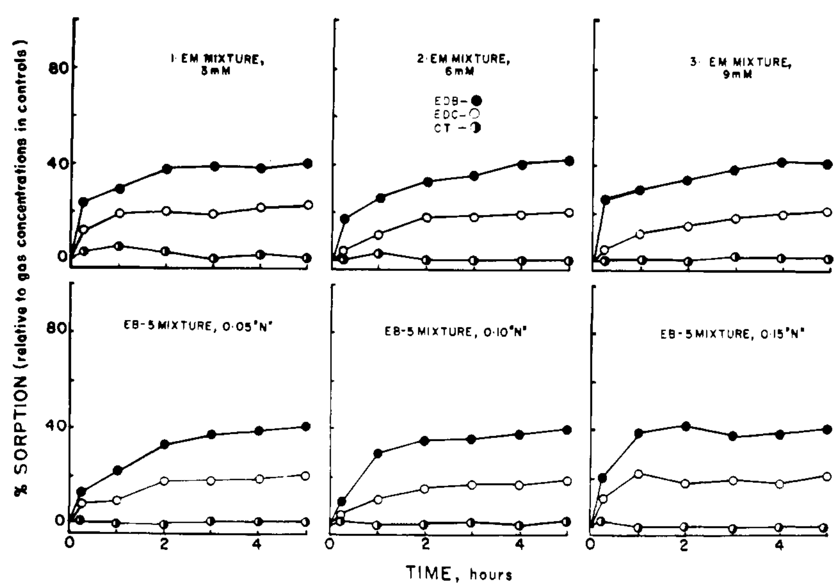

Figure 5. Sorption of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in vapor phase at 27° C. by whole-kernel Selkirk wheat of 13.5% moisture content after application of (*upper*) EM (equimolar) mixture at dosages of 3, 6, and 9 mmoles and (*lower*) EB-5 at dosages of 0.05, 0.10, and 0.15 *N*

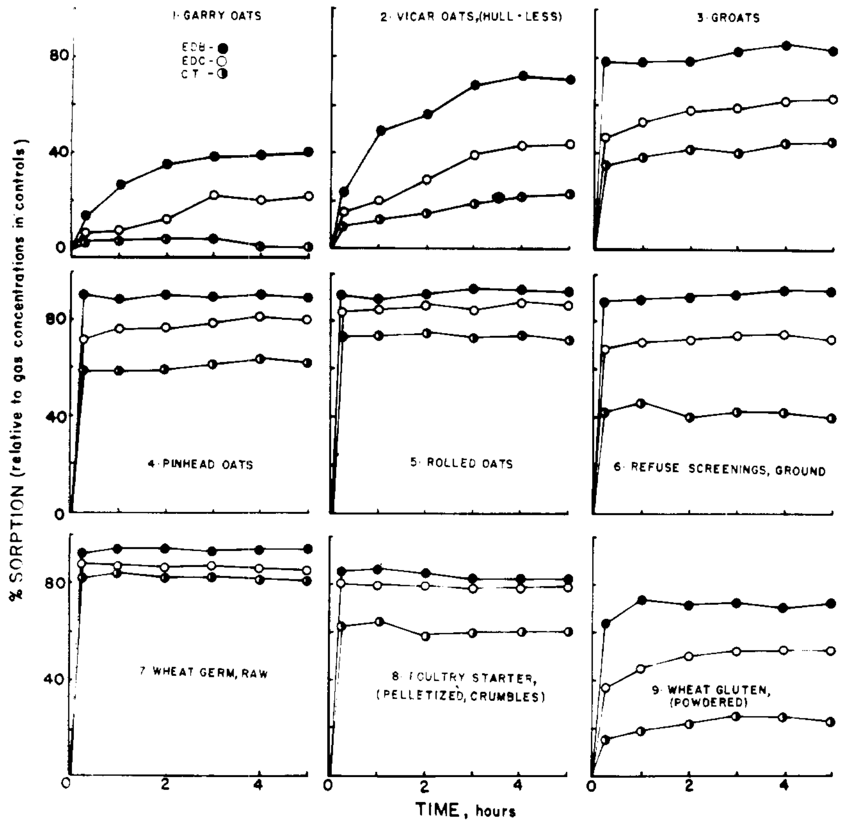

Figure 6. Sorption of ethylene dibromide, ethylene dichloride, and carbon tetrachloride in vapor phase at 27° C. by nine cereal substrates after application of EB-5 at 0.1 *N*

1. Garry oats
2. Vicar oats (hull-less)
3. Groats
4. Pinhead oats
5. Rolled oats
6. Refuse screenings, ground
7. Wheat germ, raw
8. Poultry starter, crumbles
9. Wheat gluten, powdered

shown by Harein and Krause (*13*), Heuser (*11*), Kenaga (*15*), Lindgren and Vincent (*18*), Majumder *et al.* (*20*), and Whitney and Kenaga (*21*) under different experimental conditions.

Relatively small differences in physicochemical properties may induce marked differences in retention characteristics of chromatographic columns (*12, 16, 17*). Cereals, like other natural products, are polyphase systems composed of diverse combinations of polar and nonpolar substances such as water, carbohydrates, proteins, and lipids. Differences in constitution or composition would account for differences in sorption patterns. Grinding and milling of cereals greatly multiply their sorption area and concomitantly create more sorption sites. The sites may be activated, all or in part, by additional moisture. Nevertheless, the increased gas uptake is not due entirely to multiplication of the surface area of whole kernel wheat by 800 to 1000 times, as in milling [based on work of Lyon, Pennington, and Boley (*19*)]. Thus, even moderate decrease in particle size by coarse grinding of wheat very markedly increased the uptake of the three gases (Figures 2 to 4). This was further confirmed by coarse cracking of wheat of 9% moisture content with an ordinary steel hammer before fumigation with EM mixture; the resultant EDC-CT-EDB end points of the manually cracked wheat were 49–17–66% (*cf.* item 2, Table I). To get a sizable increase in sorption, if suffices to fracture the protective seed coat, as with wheat or dried peas, or to remove the protective hull, as with oats in various stages of processing (items 18 to 20).

Fracture or removal of the seed coat enables the physicochemical complex of cereal endosperm to interact with ethylene dichloride, carbon tetrachloride, and ethylene dibromide, as shown by their increased uptake. An indication of chemical forces applicable to wheat endosperm may be seen by comparing wheat gluten with wheat starch (items 48, 49, Table I). The sorption of all three gases was considerably greater by wheat gluten, despite its lower moisture content of 5% and its coarser particle size, than by wheat starch (moisture content, 12.0%). This may be due to the high protein content of wheat gluten or to qualitative protein factors. In this regard, interesting behavior is shown by peas. Thus, the higher sorption end points of split peas (item 51, Table I) in contrast to those of whole peas show perhaps better than the end points of coarsely cracked wheat that exposure of reactive endosperm has a greater influence on sorption than multiplication of surface area, since the increase in surface area upon splitting of peas is comparatively small. Pea hulls are mechanically removed before split peas are commercially packed. In confirmatory tests with green split peas (Idabelle variety, 9.8% moisture content), EDC-CT-EDB sorption end points of 42–20–74% were obtained with EM mixture, and with split lentils (unknown variety from Lebanon, 9.2% moisture content), end points of 26–27–82% were obtained.

Although the physicochemical nature of the protein-starch-lipid-water complex influences endosperm reactivity, a more exact delineation of the forces that affect sorption of fumigant gases by cereal substrates is needed. It was not possible within the confines of this exploratory survey to attempt to determine whether chemisorption was involved in the endosperm reactivity. Investigation toward this end is planned.

Nine sets of sorption isotherms to illustrate points of discussion are shown in Figure 6. The substrates represented are Garry oats, Vicar oats (a hull-less variety), groats, pinhead oats, rolled oats, ground refuse screenings, raw wheat germ, pelletized poultry starter as "crumbles," and wheat gluten (items 15, 17 to 20, 34, 46 to 48, Table I). Vicar oats *vs.* Garry oats clearly demonstrates that absence of protective hull promoted greater uptake of gas by the Vicar oats. Groats, pinhead oats, and rolled oats show progressive uptake of each component, and illustrate the combined effects of dehulling, cracking of endosperm, and processing. Unground refuse screenings and raw wheat germ both show high amounts of sorption, as might perhaps be expected from their greater fat and protein content. Screenings are of interest, since they may constitute up to 15% of the harvested grain as delivered by farmers to grain elevators. Pelletized poultry chick starter "crumbles" demonstrate very interesting and rapid sorptive properties. Wheat gluten powder (80% protein) has been discussed. These examples as well as others shown in Table I—e.g., flour mill fractions, items 11 to 12, and 35 to 46—indicate that the "chromatographic character" of a cereal substrate is complex and can be varied, with resultant differences in gas sorption characteristics.

In conventional bulk fumigation of stored grain, liquid fumigant is applied at the top of a grain bin, the treated grain is covered with plastic sheeting, and the evolving vapors in their downward migration help to control mold and insect infestation. On the basis of these and previously reported data (*2, 9*), it is clear that components other than the grain itself—e.g., screenings, foreign matter, broken kernels, localized high moisture or low temperature areas, etc.—will compete with molds and insects for toxic gases. The heterogeneous grain bin components, each with its own chromatographic character, assist in altering the vapor composition of multicomponent mixtures after their application to the bin surface. Thus, in a recent trial with a 40-foot bin of oats containing about 20% of screenings, the gases that reached the bottom consisted largely of carbon tetrachloride, small amounts of ethylene dichloride, and no ethylene dibromide (*7*), and insect infestations were not controlled at the bottom of the bin. Variable results in our past experience with field fumigation may now be explained on the basis of differential sorption of the gases. Field tests of such laboratory-developed postulates are planned.

The amount of fumigant residue remaining in or on cereal products after a prescribed treatment with multicomponent mixtures is of practical interest. "Natural" desorption—i.e., after "normal" aeration *in situ*—followed by accelerated desorption of the residues by thermal stripping is used in the analytical determination. Exploratory tests on oats (*7*) show that residue levels after EDC-CT-EDB mixtures are applied are small but, interestingly, in a similar intercomponent ratio as was shown by experimental isotherms described herein. Such work will be reported more fully.

Syringes used as micro fumigation chambers were convenient both for introduction of gas mixtures and in sampling. Gas chromatography enabled rapid, sensitive, and specific measurement of small changes in gas concentration that resulted from the interaction of gas and substrate. The use herein of gas levels considerably smaller than are applied in grain elevators and warehouses expedited the observation of changes in gas concentrations and attainment of equilibria.

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PESTICIDE EFFECTS ON VITAMIN METABOLISM

Carotenoid and Vitamin A Concentrations in Serum and Liver of Steers Fed Forages Treated with DDT or MCPA

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When yearling beef steers were fed for 83 days with forage sprayed at the rate of 1.5 pounds per acre with DDT, terminal liver vitamin A stores (micrograms per gram of liver) were significantly decreased ($P < 0.05$) and blood serum vitamin A levels were increased. No deleterious effect resulted when MCPA-treated forage was fed under similar conditions. In view of the high rate of application of DDT and MCPA and minimal demonstrable effect on vitamin A concentrations, it is unlikely that use of these chlorinated compounds in normal agricultural practice has contributed to the increased incidence of vitamin A deficiency observed in bovines in Canada.

VITAMIN A deficiency of beef cattle occurs in Canada (*9*) and several observers believe the incidence has increased during the past decade (*6*). Changing agricultural practices may contribute to this. Toxic substances in the diet can impose stress conditions that alter nutrient requirements. The use of chlorinated hydrocarbons has increased markedly in North America during the last decade: bovine hyperkeratosis has been produced experimentally through administration of chlorinated naphthalene compounds (*12*) or topical application of an oil-based insecticide carrier (*5*). In both cases an influence on vitamin A metabolism has been demonstrated (*3*). These facts have led us to study the effect of ingested chlorinated agricultural chemicals on vitamin A and carotenoid utilization by animals.

In previous studies with the rat (*11*) it was demonstrated that the feeding of over 10 p.p.m. of DDT in the diet for periods up to 72 days decreased utilization of orally administered carotene and vitamin A. Hepatic storage of vitamin A was also reduced when a diet containing both DDT and carotene or

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