

GRAIN FUMIGANT DETERMINATION

Wheat as a Chromatographic Column toward Methyl Bromide, Ethylene Dibromide, Acrylonitrile, Chloropicrin, and Carbon Tetrachloride in the Vapor Phase

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Methyl bromide, ethylene dibromide, acrylonitrile, and chloropicrin were applied in the vapor phase, both singly and in admixture with carbon tetrachloride, to the surface of 7-foot columns containing wheat of 12, 16, and 20% moisture content, respectively. Air was used as a carrier gas and the composition of the gas-air mixture that emerged from the bottom of each column was assessed polarographically. Chloropicrin, acrylonitrile, and especially ethylene dibromide were strongly sorbed, particularly at 16 and 20% moisture. Even up to 13 days at 25° C., ethylene dibromide emerged only in small amounts and at 4.5° C. was consistently zero. Acrylonitrile showed an interesting delayed action. Carbon tetrachloride, which in itself is a mediocre fumigant, increased the peak output of each of the other fumigants at the various temperature and moisture levels under test. Carbon tetrachloride also extended the time when zero concentration was reached. The results were in agreement with earlier work with methyl bromide, ethylene dibromide, and carbon tetrachloride applied in the liquid phase. It is postulated that carbon tetrachloride vapor may act as an eluting agent, with wheat acting as a chromatographic column. The proportions of acrylonitrile-carbon tetrachloride, chloropicrin-carbon tetrachloride, etc., that emerged from the bottom vary with dosage, time, and the temperature and moisture content of the column, and in any event differ considerably from the proportions initially applied. It follows that biological evaluation of fumigants needs analytical data for correct interpretation of results.

THE CENTRAL THEME of this report is that a wheat pile may behave as a chromatographic column toward fumigants applied in the vapor phase to the surface of the pile. Kinetic differences in the rates and amounts of fumigant migration can be demonstrated analytically. Present data show that the temperature and moisture content of the wheat influence the amounts of gas that emerge from the bottom of a 7-foot column. Doubling the applied dosage increased, but did not double, the amounts of gas that emerged. Of considerable importance to the theory and practice of grain fumigation is the fact that the amounts of methyl bromide (MB), ethylene dibromide (EB), acrylonitrile (AN), or chloropicrin (CP) that migrated to the bottom of the column increased significantly when carbon tetrachloride (CT) vapor was applied in admixture. This effect is believed due to the eluting or "take-down" action of carbon tetrachloride vapor.

Results reported herein confirm those of earlier experiments wherein mixtures

of methyl bromide, ethylene dibromide, and carbon tetrachloride, including various commercial formulations, were applied in the liquid phase at 48° F. to the surface of 5-foot columns, each containing 5 bushels of wheat of 15.8% moisture content (7). The experiments were preceded by determination of the gas-air patterns of infested wheat storages in country elevator annexes that were treated with commercial fumigant mixtures. These showed that significant amounts of ethylene dibromide descended to the bottom of 30-foot piles of grain, even through "tough" grain (over 14% moisture content), when carbon tetrachloride was present in the formulation. This finding did not fit the prevailing concept (4) that fumigants in admixture penetrate individually to the same general levels as when applied singly. This concept is, in part, the basis for formulating fumigant mixtures for application to stored grain, wherein two or more fumigants of different penetration characteristics are combined to yield a balanced or "all-purpose" mixture capable of combating infestation

at all levels. Special potency or synergism is sometimes claimed for particular fumigant mixtures; it was found (7) that the original proportions in the formulation became unbalanced after passage through a grain column.

The factorial investigation reported herein was undertaken to obtain information about fumigants applied in the vapor phase, with particular emphasis

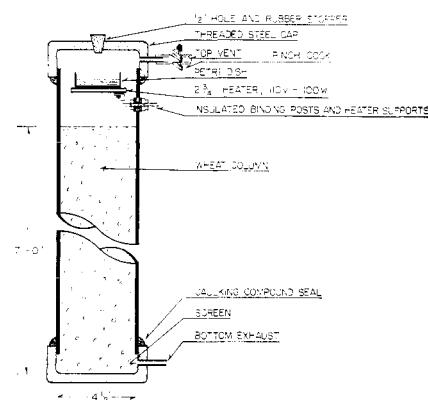


Figure 1. Cross section of steel column

on the interaction of the fumigant, dosage, temperature, moisture content of the wheat, and time. Although the trends shown by liquid phase applications (1) were significant, it was nevertheless possible under the conditions of the experiments to get localized sorption of liquid fumigant at the top of the open column, as well as "channeling"—i.e., rapid downward descent of gases, with little or no lateral diffusion. It was felt that these possible effects could be avoided by vaporizing the liquid fumigants within the column beforehand, and, after an arbitrary "rest" period of 1 hour, by using a constant air flow of 0.1 liter per minute (6 liters per hour) to help convey the diffusing gases through the interstitial spaces of the 7-foot wheat "filter stick" and out to the needle valve-controlled suction source. The investigation entailed a substantial analytical program that was expedited by the enhanced speed, accuracy, reproducibility, and specificity of polarographic methods using the dropping mercury electrode (2) and which, with improved methods of gas sampling, were developed for this investigation.

Materials and Apparatus

Wheat. The wheat was supplied for the investigation by the Canadian Government Grain Inspection Branch, Board of Grain Commissioners for Canada, Winnipeg, as No. 3 Northern "averages" containing about 1.5% dockage. The wheat was tempered to 12, 16, and 20% moisture ($\pm 0.1\%$) in 100-pound lots, using a mechanical end-over-end tumbler-mixer geared for 6 r.p.m. and operated for 2 hours. The tempered wheat was placed in heavy grade polyethylene bags (about 0.012 inch thick) that were specially made to fit within the original 2-bushel canvas bags in which

they were enclosed. The bagged wheat was stored in a "cold room" at 30° F. until required. At this temperature the wheat underwent no measurable change in quality and the moisture content remained remarkably constant.

Constant Temperature Rooms. These accommodated a three-column assembly at 25° and 4.5° C. (77° and 40° F.), respectively, and were equipped with power outlets and a suction source. The suction source was subdivided by a manifold and, by means of flowmeters (Fischer and Porter Co., Hattboro, Pa.) and stainless steel needle valves (Matheson Co., East Rutherford, N. J.), provided a constant air flow of 0.1 liter per minute to each of the three columns after loading. It was also a means of conveying the toxic gases in the effluent air to the outside atmosphere.

Columns. Steel columns, 7½ feet × 4 inches in I.D., were used to contain wheat of 12, 16, and 20% moisture for the 10- to 14-day duration of a given experiment. The columns were threaded at the ends to take screw-on steel caps that were fitted with air inlets and outlets (Figure 1). The plate heaters (2¾ inches in diameter, 110 volts, 100 watts) (Labconco Chromalox, Canadian Laboratory Supplies, Toronto) were demountable and fitted the insulated binding posts and heater supports. After each column was filled to the 7-foot mark with wheat (30 to 34 pounds were generally required), the plate heater was placed in position, an evaporating dish (borosilicate glass, flat-bottomed, 60 × 25 mm.) was placed on the heater, and the steel cap cover was screwed on tightly. The joints at the cap-column interface were sealed with caulking compound. Predetermined amounts of liquid fumigant, precalibrated by weighing, were dispensed through a rubber-

septum stopper located in the center of the steel cap by means of a Chaney-type syringe fitted with a 6-inch, 18-gage needle. The three heater cords were then plugged into a voltage-regulating transformer fitted with a three-way adapter, and the power was turned on (90 volts were generally used) long enough for complete evaporation of the amounts that had been dispensed (the time ranged from 4 to 10 minutes and was predetermined empirically by evaporating identical amounts under similar conditions). After an arbitrary gas-settling period of 1 hour, air as a carrier gas was allowed to come in through the top vent at a constant rate of 100 ml. per minute (6 liters per hour). Samples of the gas-air mixture that emerged from the bottom of the columns were taken at required intervals over a 10- to 14-day period.

Semiautomatic Gas-Sampling Assembly. The basic parts consisted of three machined, brass sampling heads (2) modified for this investigation to operate with a "side" feed, rather than with a "top" feed, for introduction of the air samples dispensed by three syringes. Figure 2 is a schematic diagram of the application and sampling setup for three columns operating concurrently.

The suction source, *O*, draws air through the air inlets, *G*, of the columns, *A*, at a constant rate of 0.1 liter per minute that was controlled by stainless steel needle valves, *N*, and indicated on flowmeters, *M*. When sampling was not in progress, the absorption tubes, *K*, were replaced with empty tubes to permit the gas-air mixtures to pass directly into the vacuum line, *O*. During this period, the plungers of the 100-ml. glass syringes, *J*, were down. To obtain samples of the effluent gas, the vacuum source, *O*, was bypassed by opening T-tube *P* and absorption tubes *K* (containing "gas-trapping" solvent of choice), were fitted to the sampling heads, *L*. The syringe plungers were lifted to draw in predetermined volumes into the syringes, *J*, whereupon the pinchclamp valves, *I*,

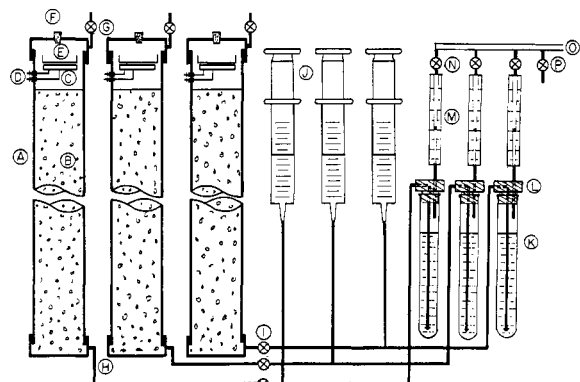


Figure 2. Schematic diagram of fumigant application and sampling setup for three columns operating concurrently

- | | |
|-----------------------------|----------------------|
| A. Steel column | I. Shutoff valve |
| B. Wheat | J. 100-ml. syringe |
| C. Heater plate | K. 15-ml. test tube |
| D. Insulated binding posts | L. Gas-sampling head |
| E. Petri dish | M. Flowmeter |
| F. Rubber stopper | N. Needle valve |
| G. Air inlet shut-off valve | O. Vacuum source |
| H. Effluent line | P. Bypass valve |

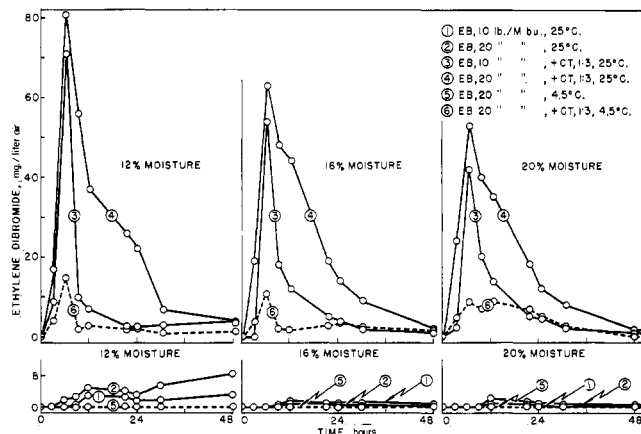


Figure 3. Concentration of ethylene dibromide in effluent air in absence and presence of carbon tetrachloride

were closed. After closing bypass valve *P*, the vacuum was readjusted by valves *N* to regulate the admittance of the air samples into tubes *K* at a rate of 30 to 35 ml. of air per minute. After the syringe contents were thus discharged, tubes *K* were removed and replaced by empty tubes as before, pinchclamp valves *I* were opened, and the flow rate was reset to 0.1 liter per minute with valves *N*.

Procedure

Three steel columns (Figure 1) were filled to the 7-foot mark with wheat of 12.0, 16.0, and 20.0 ± 0.1% moisture content, respectively. The liquid fumigants were introduced through the top of each column by weight-calibrated Chaney-type syringes, and were vaporized, as previously described. For methyl bromide, a 1-pound lecture bottle of the compressed gas (Matheson Co., East Rutherford, N. J.) was used to deliver predetermined volumes through the air inlet at the top of each column. After an arbitrary "rest" period of 1 hour in the closed system, a constant air flow of 0.1 liter per minute (6 liters per hour) was used to help convey the various gases downward and out (Figure 2). The effluent gas-air mixtures were sampled over a 10- to 14-day

period. Most of the samples were taken during the first 48 to 72 hours to plot the location and extent of the time period showing greatest change in gas concentration, as well as to determine the peak concentration. Samples were generally taken once every hour for the first 8 hours (except for methyl bromide, where 0.5-hour intervals were used), and then at 11, 14, 24, 28, 32, 38, 48, 56, 72, etc., hours. Gas concentrations were determined by polarographic methods (2), which enabled changes in concentration to be monitored rapidly. The concentration-time relationships, and the comparative areas of 114 different curves pertaining to them, were determined at 25° and 4.5° C., respectively, for wheat to which the fumigants were applied in the vapor phase singly and in admixture with carbon tetrachloride as a diluent and carrier.

Two rates of fumigant application were used—normal (*N*) and twice normal (*2N*), where *N* represented a dosage approximating that recommended by some manufacturers or that had been found empirically (7) to yield a measurable emergence of gas through a column of wheat of approximately 16% moisture content. The *N* rates for methyl bromide, ethylene dibromide, acrylonitrile,

chloropicrin, and carbon tetrachloride were 8, 10, 11, 10, and 32 pounds per 1000 bushels. The same *N* and *2N* amounts were used in the single fumigant applications as in their admixtures with carbon tetrachloride. In the latter regard, carbon tetrachloride was added as 3 to 1 (w./w.) of the methyl bromide and ethylene dibromide amounts, and as 4 to 1 (w./w.) of the acrylonitrile and chloropicrin amounts. At 25° C. both the *N* and *2N* dosages were used, whereas at 4.5° C. only the *2N* rates were applied because of the considerable increase in sorption due to the lower temperature.

Results and Discussion

Figures 3 to 6 show as a function of time and in terms of milligrams per liter of effluent air, the gas concentrations of ethylene dibromide, methyl bromide, acrylonitrile, and chloropicrin after their application in the vapor phase both singly and in combination with carbon tetrachloride to 7-foot columns of wheat. Figure 7 shows the concentration-time trends of carbon tetrachloride after it was applied alone. Some 40 curves pertaining to the concentration-time relationships of carbon tetrachloride when it was a concomitant of the various binary mixtures are omitted, since in general

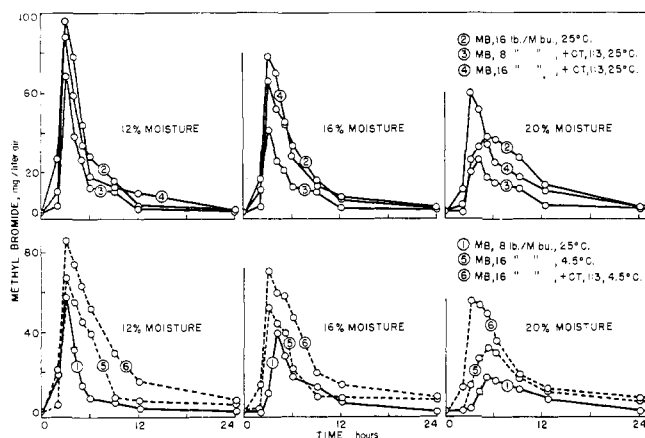


Figure 4. Concentration of methyl bromide in effluent air in absence and presence of carbon tetrachloride

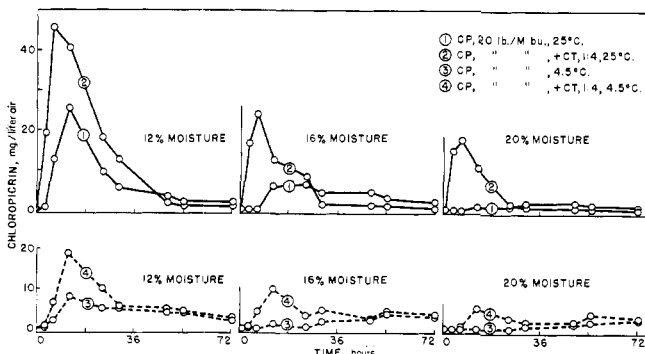


Figure 6. Concentration of chloropicrin in effluent air in absence and presence of carbon tetrachloride

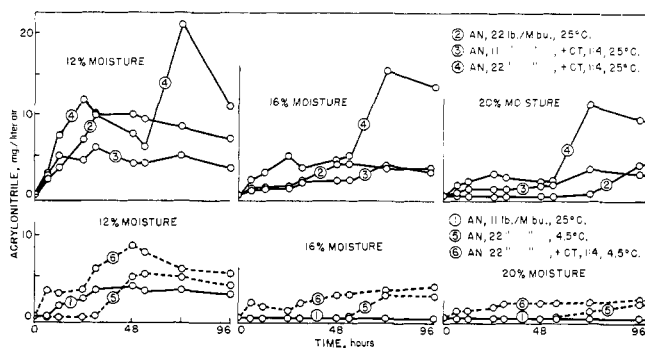


Figure 5. Concentration of acrylonitrile in effluent air in absence and presence of carbon tetrachloride

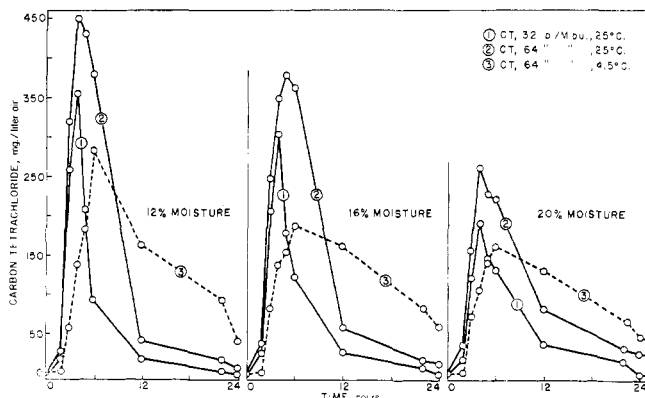


Figure 7. Concentration of carbon tetrachloride vapor in effluent air when carbon tetrachloride alone is applied

Table I. Increase in Elution of EB, MB, AN, and CP Due to CT Vapor in Columns Containing Wheat of 12, 16, and 20% Moisture at 25° C. (77° F.) and 4.5° C. (40° F.)

Fumigant	Dosage, lb./M Bushel	Wheat Moisture, %	% Elution	
			CT absent	CT present ^a
At 25° C.				
EB	10	12	15.7	31.1
		16	0.9	20.8
		20	0.4	19.4
EB	20	12	14.3	29.9
		16	0.3	25.8
		20	0.2	20.5
MB	8	12	88.0	94.5
		16	77.1	89.0
		20	74.0	79.8
MB	16	12	80.7	95.5
		16	72.5	88.4
		20	73.9	83.5
AN	11	12	13.0	21.1
		16	0.0	9.6
		20	0.0	9.0
AN	22	12	13.2	24.3
		16	8.3	25.8
		20	3.8	24.5
CP	20	12	10.8	37.7
		16	7.7	23.8
		20	2.7	21.5
CT	32	12	..	95.9
		16	..	98.9
		20	..	88.5
CT	64	12	..	98.0
		16	..	98.1
		20	..	86.2
At 4.5° C.				
EB	20	12	0.0	15.6
		16	0.0	11.0
		20	0.0	9.3
MB	16	12	60.0	93.3
		16	52.7	71.4
		20	51.5	69.2
AN	22	12	10.3	16.8
		16	4.1	9.4
		20	3.4	8.4
CP	20	12	6.9	20.4
		16	6.6	18.8
		20	2.8	9.4
CT	64	12	..	85.2
		16	..	70.0
		20	..	74.2

^a Formulation ratio, w./w., of CT to EB and MB = 3:1.
Formulation ratio, w./w., of CT to AN and CP = 4:1.

they were similar to that shown in Figure 7. The 75 curves encompassed by Figures 3 to 7 show only one third of the total number of plot points that were taken during the 10- to 14-day span of each curve, since it was felt that the protracted horizontal or "tapering off" portions of the curves should be omitted in order to illustrate more readily the period of significant change in concentration. For purposes of illustration, it was necessary to vary both the concentration and time scales, as may be seen. Curves pertaining to the gases applied at 4.5° C. are depicted with broken lines.

Figures 3 to 7 show that significant changes in concentration occurred mainly during the first 24 to 96 hours,

and that these varied with the nature of the fumigant, dosage, moisture content, and temperature, and were influenced by the presence of carbon tetrachloride when binary mixtures were applied. The inhibiting effects on gas concentration of increased moisture content and lower temperature are evident from the various families of curves. Acrylonitrile showed an interesting "delayed action" that is discussed further, and ethylene dibromide, as well as chloropicrin to a lesser extent, exhibited a protracted period of low, but readily measurable amounts in the effluent air, particularly when in combination with carbon tetrachloride. In any event, in view of the clear-cut evidence of the assisting action of carbon tetrachloride on the

migration rate of the other gases, as shown by the increase in peak height and area of the pertinent concentration-time curves, the authors attempted to derive a quantitative approximation of what appeared to be elution development by carbon tetrachloride vapor, with the wheat column as a coarse-grained solid support with surface active properties that are manifested by differential sorption of the various gases. A comparative scale was accordingly used to estimate the per cent of fumigant eluted by carbon tetrachloride with the aid of air as a carrier gas, and was based on the following steps:

The area under each curve (concentration-time product) was measured by planimeter and calculated as total milligrams per liter-days, by means of a variable graph scale where 1 sq. inch = 1 mg. per liter-day.

The time in days in which the gas migrated into the effluent air in relatively significant amounts was designated as the "effective duration," and with the latter as denominator, the average milligram per liter per day was calculated in terms of "mg. recovered."

The total fumigant load applied was converted to milligrams per liter per day by dividing the milligrams applied by 144 (the product of 24 hours X the constant air flow rate of 6 liters per hour that was used in this investigation).

The ratio of milligrams per liter recovered to milligrams per liter applied was determined and from this the per cent of migration was readily derived. This was the basis for Table I, which attempts to show quantitatively the increase in elution of ethylene dibromide, methyl bromide, acrylonitrile, and chloropicrin due to carbon tetrachloride vapor in the wheat columns at 25° and 4.5° C., respectively.

The concept that wheat could behave as a chromatographic column toward fumigants was advanced by Berck (3), based on differential sorption of fumigants applied in the liquid phase, and by Kenaga (6). In general, and with due allowance for differences in methods of application and in dosage, temperature, and moisture content, the trends obtained here for ethylene dibromide and methyl bromide applied in the vapor phase with and without carbon tetrachloride are similar to those in which liquid phase applications were used (7). In both instances, downward migration increased when carbon tetrachloride was present. The increased emergence was shown by all fumigants that were thus evaluated.

As shown by Figures 3 to 7, sorption of the various fumigants was increased by higher moisture content, lower temperature, and higher dosage, and was in any event influenced by the nature of the fumigant. The term "chromatographic column" as applied to wheat is used herein in a wide sense to connote differential migration through a porous

medium which selectively retards some substances. Whether wheat kernels are sufficiently small in size and uniform in quality to separate other liquids and gases would be worth exploring, because starch and cellulose are used as solid supports in column chromatography (8). In the meantime, the specific adsorption forces are not clearly understood, nor whether the fractional elution observed is due to increased solubility, to displacement, or to both. Although the fumigants were applied in the vapor phase, nevertheless subsequent condensation of unknown amounts of the vapors onto the wheat kernels, particularly at 4.5° C., could not be prevented. It is thus probable that mechanisms pertaining both to gas-liquid and to gas-solid chromatography were involved. It is conceivable that frontal analysis (7) may occur, although the asymmetric character of many of the curves of Figures 3 to 7, showing a steep front with a long, drawn-out "tail," and also the relatively small amounts of fumigant used, suggests that elution development is the major mode of action.

The fumigants varied with respect to the location of the peak (analogous to retention time in gas chromatography) in the concentration-time curves of Figures 3 to 7. Thus, when methyl bromide was applied to wheat of 12 and 16% moisture content at 25° and 4.5° C. (Figure 4), the peak was located at 3 hours. At the 20% moisture level, however, the methyl bromide peak had shifted to 4 to 5 hours when carbon tetrachloride was absent, but reverted to 3 hours when carbon tetrachloride was present. At 25° C., the peak concentration of carbon tetrachloride at all three moisture levels (Figure 7) was at 4 hours approximately, but at 4.5° C. this was displaced to 6 hours. In the absence of carbon tetrachloride, the peaks for chloropicrin (Figure 6) varied considerably as a function of moisture content and temperature, but in the presence of carbon tetrachloride the chloropicrin peaks were reasonably replicable at about 6 hours at all three moisture levels at 25° C., and were located at approximately 12 hours at 4.5° C. When carbon tetrachloride was absent, ethylene dibromide (Figure 3) under the experimental conditions had either a small and poorly defined peak in an extended and shallow curve, or none at all—e. g., the concentrations were consistently zero at 4.5° C. However, the presence of carbon tetrachloride stimulated a remarkable upsurge of ethylene dibromide, yielding a sharp peak at 6 hours at 25° C. at the three moisture levels. In contrast, acrylonitrile concentrations (Figure 5) fluctuated from zero to relatively small amounts and a characteristic peak location could not be estimated.

The concentration-time patterns of

acrylonitrile were characterized by an interesting delayed response—i.e., a protracted period of zero concentration followed by a fluctuating resurgence of small, but significant amounts of acrylonitrile. In this regard, many zero concentrations showed anomalous polarographic waves that resembled those for acrylonitrile, except that their $E_{1/2}$ values were about 0.15 volt more negative and the slopes of the discharge portion of the waves were more horizontal than true acrylonitrile waves. It is postulated that acrylonitrile formed a volatile sorption product with the wheat moisture. Sinclair and Lindgren (14) offer a somewhat similar explanation for the loss of fumigant when hydrogen cyanide is applied, particularly since HCN is readily soluble in water. In addition to absorption, chemisorption of fumigants may also occur, as shown by Page and Lubatti (12) with hydrogen cyanide and by Lewis (9, 10) with methyl bromide. In any event, investigation of the concentration-time patterns of acrylonitrile resulting from its combination with amounts of carbon tetrachloride greater than 1 to 4 may show whether anomalous acrylonitrile waves would be reduced in frequency. On the practical side, Ruppel, Bravo, and Hatheway (13) found acrylonitrile-carbon tetrachloride in 1 to 6 and 1 to 8 (w./w.) proportions to be effective against insect pests of stored corn.

Evaluation of the insecticidal effectiveness of the various treatments or of their effects on the germination and milling and baking properties of the wheat was not undertaken in this investigation, since the main aim was to determine experimentally and on a wider scale whether the postulated "chromatographic" behavior of fumigants applied in the liquid phase (7) would hold true for fumigants applied in the vapor phase. The evidence of the current investigation corroborates earlier findings and shows also that doubling the dosage increases, but does not double, the gas concentration in the wheat, and the ratios of the components of a fumigant mixture containing carbon tetrachloride change considerably from the proportions initially applied as a result of their differential sorption in the wheat pile. In the latter regard, similar conclusions are reached by Harein and Krause (5), although their results and those of Lindgren and Vincent (11) cannot be directly compared with results of this investigation because of differences in experimental conditions, such as fumigant dosage, methods of application, etc. However, in view of changes in fumigant proportions that can be "chromatographically" induced by wheat, and the possibility of chemisorption or of delayed development of peak concentration (cf. acrylonitrile), it is clear that evaluation of fumigants by bioassay procedures

alone is inadequate. Thus, conclusions may be misleading if, for instance, mortality of insects is attributed to a given gas mixture without prior confirmation that the composition of the mixture, in terms of component ratio, is constant throughout the treatment. The corollary of this criticism is that biological evaluation of fumigants needs analytical data to ensure correct interpretation of the results.

On the basis of indications herein that carbon tetrachloride may act as an eluent gas, it is conceivable that new fumigant mixtures with improved penetration or longevity of gas concentration may be developed by using eluting agents other than carbon tetrachloride. Thus, chloroform, dichloroethane, trichloroethylene, and possibly other eluents more polar (higher dielectric constant) than carbon tetrachloride may enhance the distribution and persistence patterns of more toxic components. Lederer and Lederer (8) give a partial list of eluents. Pilot experiments with grain columns as polyphase systems should yield useful information in this regard.

Acknowledgment

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