The buffer containing 20% alcohol was chosen because of the shorter time period necessary for maximum color development.

When stronger buffers than 0.07*M* were employed, there was a tendency to obtain turbid solutions when 20% alcohol was added to the buffer.

Several other water-miscible solvents were compared with alcohol. The solvents and the results are shown in Table III. Isopropyl and *tert*-butyl alcohol both gave slightly higher absorbance readings than did ethyl alcohol with the same amount of ronnel. Thus, either isopropyl or *tert*-butyl alcohol could be used in the buffer in place of ethyl alcohol.

The effect of alcohol concentration on the maximum amount of ronnel which could be determined with the 0.07*M* phosphate buffer without precipitation was studied. The results are shown in Figure 4. All absorbance readings were made after 20 minutes. With no alcohol in the buffer, the maximum concentration of ronnel which could be determined without precipitation was 7 μg. per ml. With 10% alcohol in the buffer, the limit was increased to about 9.5 μg.; while with the 20% alcohol, the limit was increased to 15 μg. of ronnel per ml. The use of the 0.07*M* phosphate buffer containing 20% alcohol thus doubled the concentration of ronnel which could be measured and also increased the stability of the color complex. As pointed out by Emerson (*1–3*), the ratio of 4-aminoantipyrine to potassium ferricyanide is important in obtaining maximum color. The optimum ratio was determined by selecting a concentration of aminoantipyrine which would be in excess of the maximum amount necessary to couple with the phenol present and then varying the amount of potassium ferricyanide added. This was accomplished by using 0.25 ml. of 1% 4-aminoantipyrine and varying the amount of 1% potassium ferricyanide solution used. The results shown in Figure 5 indicate that 0.35 ml. of the 1% potassium ferricyanide solution gave maximum color formation. In this procedure, the yellow color of the potassium ferricyanide contributes to the final color. Under these conditions, a minimum amount of potassium ferricyanide should be employed to minimize the reagent blank (Figure 6).

In the procedure described above, it is more convenient to use the same volume of both the aminoantipyrine solution and the potassium ferricyanide solution. For this reason, 0.25 ml. of 1.4% potassium ferricyanide solution is employed which will add the same amount of compound as would the addition of 0.35 ml. of a 1% solution.

Specificity. In using an organic phosphate insecticide, there is always the possibility that the compound may be decomposed by chemical or biological reactions with the formation of a series of hydrolyzed products. If an analytical procedure is to be specific for the determination of ronnel, the ronnel must be separated from its possible degradation products, such as the phenol and those phosphates or thiophosphates still containing the phenol radical. All of these compounds will form sodium salts and should distribute in favor of the aqueous phase in the extraction procedure described above. To check this possibility, dilute acetone solutions of 2,4,5-trichlorophenol and various degradation products of ronnel were prepared and extracted by the procedure described above. The results of these studies are shown in Table IV.

Data indicate that all the ronnel can be extracted from either an acid or an alkaline solution while none of the trichlorophenol or other degradation products are extracted from an alkaline solution. From an acid solution, extraction of trichlorophenol was complete while various amounts of the other degradation products were obtained depending on the chemical nature of the compound.

By employing an alkaline extraction procedure, this method is then specific for the ronnel, and free phenols and other degradation products of ronnel do not interfere with the test.

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GRAIN FUMIGANTS

Inhibitors of Carbon Disulfide Decomposition during Gas Chromatography of Fumigant Vapors

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FUMIGATION RESEARCH has been facilitated by recent developments in gas chromatography, a useful method for qualitative and quantitative analyses of volatile chemicals.

In studies of differential sorption and distribution of the vapors of various fumigants when applied to stored grain and other commodities, gaseous samples are withdrawn from the interstices of fumigated material and analyzed (*4, 5, 8*). Compositions of liquid formulations used in such experiments are also verified by gas chromatography.

Carbon disulfide (CS_2) is one of the most common components of liquid fumigant formulations. To reduce fire hazards in commercial formulations, CS_2 is mixed with a large percentage of a nonflammable fumigant such as carbon tetrachloride (*2*) or chloroform (*7*). Fire hazards associated with CS_2 are often further minimized by addition of a small percentage of a fire inhibitor such as *n*-pentane, petroleum ether, or sulfur dioxide (*1, 3*).

Many common fumigants used in liquid formulations have low boiling points and therefore can be analyzed by gas chromatography at moderate or low column temperatures (e.g., 40° C.) and without a heated sample inlet. However, a few, such as ethylene dibro-

Chromatographic analyses were conducted to evaluate the relative efficacy of carbon tetrachloride, chloroform, *n*-pentane, and sulfur dioxide as inhibitors of thermal decomposition of carbon disulfide vapor in air. Decomposition of CS_2 occurred in concentrations ranging from 6 to 100 mg. per liter when chromatograph temperatures were 100° C. at the column and 207° C. at the sample inlet, but not when the column was 160° C. and the inlet was 70° C. Two chromatographic peaks were associated with decomposition. One was probably SO_2, since its t_R was identical with the t_R for SO_2. Nearly complete inhibition of CS_2 decomposition (at 25.3 mg. per liter) was obtained with 151.5 mg. of CCl_4 per liter, while the same result was achieved with 74.9 mg. of $CHCl_3$ per liter. Small quantities of C_5H_{12} were particularly effective when used in conjunction with a chlorinated hydrocarbon. SO_2 was also effective.

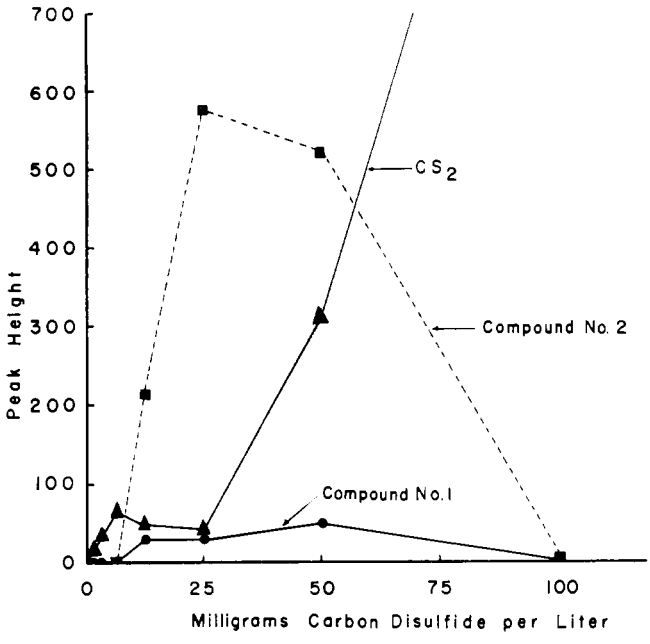

Figure 1. Gas chromatographic responses to a critical (i.e., decomposable) range of CS_2 vapor concentrations in air

(This is an enlargement of the first part of Figure 2 to illustrate the CS_2 decomposition more clearly)

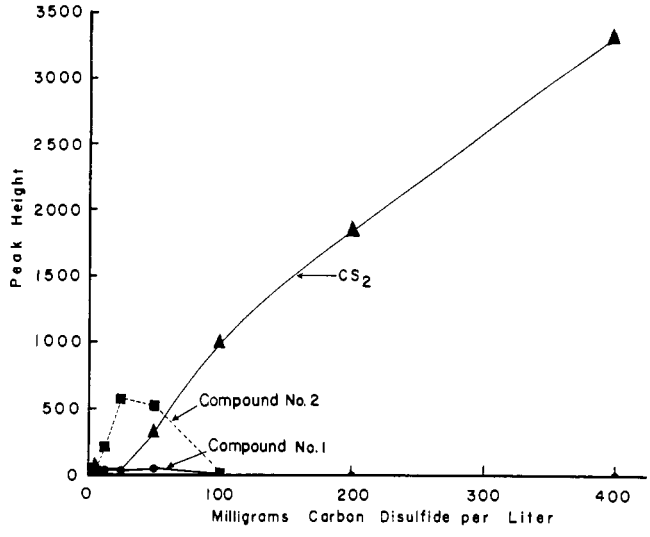

Figure 2. Gas chromatographic responses to a wide range of increasing CS_2 vapor concentrations in air

mide, have higher boiling points and require considerably higher chromatographic temperatures (e.g., 100° to 160° C.) and a heated sample inlet for efficient analyses. This frequently presents a problem because CS_2 and ethylene dibromide are quite commonly used in the same formulation and decomposition of a flammable or reactive chemical, such as CS_2, is generally enhanced by high temperatures.

In establishing standard curves for the chromatography of several fumigants, response from the thermal conductivity cell was found to be proportional to concentration, except for CS_2 vapor in air. An anomalous behavior was observed for CS_2-air mixtures in a critical (i.e., decomposable under conditions of these tests) concentration range of 6 mg. of CS_2 per liter to 100 mg. of CS_2 per liter. In this range, the conductivity cell response either decreased with increasing CS_2 concentrations or did not increase at the usual rate (Figures 1 and 2). Partial decomposition of CS_2 in the critical range was indicated qualitatively by the initial appearance of two additional chromatogram peaks at the time the CS_2 response trend changed from positive to negative. These peaks represented unidentified CS_2 decomposition products which, for convenience, are called Compound No. 1 and Compound No. 2.

No signs of decomposition were evident when the sample inlet heater was disconnected, even though column temperatures were as high as 160° C. Therefore, it is assumed that a catalyzed thermal decomposition in the inlet system was the cause of the anomalous results.

The purpose of this study was to evaluate the relative effectiveness of certain fire inhibitors which are commonly used in commercial fumigants.

Experimental Procedure

General. The general procedure was designed to determine chromatographic responses (recorder peak heights) to a graduated series of carbon disulfide vapor concentrations in air, simulating conditions found in practical fumigations. The effects of mixing CS_2 with nonflammable fumigants and of adding certain combustion inhibitors to critical CS_2 concentrations were studied. The chemicals (fumigants and inhibitors) used were anhydrous sulfur dioxide, *n*-pentane (practical grade), chloroform, carbon tetrachloride, and carbon disulfide (all analytical reagent grade).

Gas Chromatograph and Operation. The gas chromatograph was a Beckman GC-2, equipped with a 6-foot × 1/4-inch O.D. stainless steel column (Beckman No. 17449) packed with 15 grams of crushed, 42- to 60-mesh (Johns-Manville C-22) firebrick coated with 8 ml. of Silicone 550 (Dow-Corning). Helium was the carrier gas. The helium flow

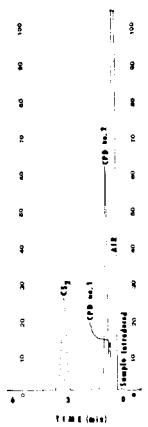

Figure 3. Typical chromatogram showing thermal decomposition of carbon disulfide vapor during analysis

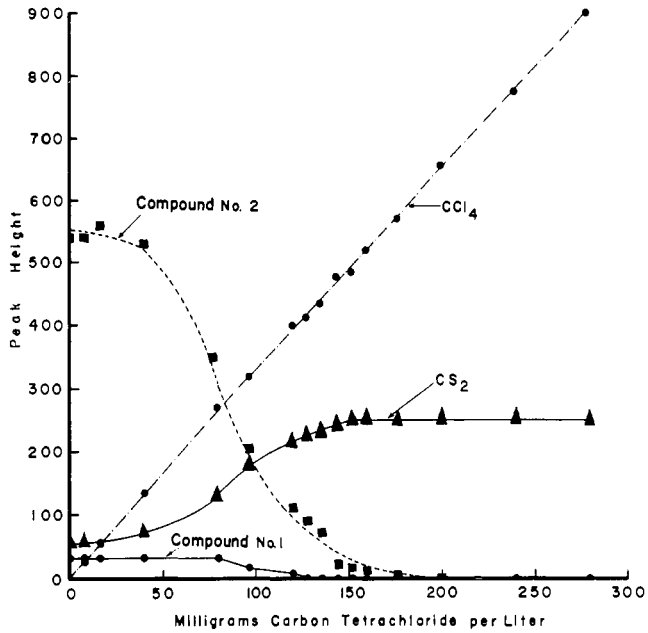

Figure 4. Inhibition of CS_2 thermal decomposition during gas chromatography by use of CCl_4, as shown by chromatographic responses to 25.3 mg. of CS_2 vapor per liter in air in mixture with increasing CCl_4 vapor concentrations

Table I. Gas Chromatographic Retention Time and Peak Width at Base for Fumigants, Air, and Two CS_2 Decomposition Products (Compounds No. 1 and 2)

Compound	Minutes t_R	Minutes Δt
Air	0.50	0.31
Compound No. 1	0.82	0.15
Compound No. 2	0.99	0.25
Sulfur dioxide	0.99	0.25
n-Pentane	1.78	0.37
Carbon disulfide	3.25	0.50
Chloroform	5.03	0.80
Carbon tetrachloride	6.02	1.00

rate (F_c) was 82 cc. per minute. Operating temperatures of the chromatograph were 100° C. for the column and detector and 207° C. for the sample inlet. The detector filament current was 300 ma. The chromatograph utilized a 10-ml. gas sampling valve which subsampled the larger samples as the gaseous fumigant was introduced into the instrument.

A Minneapolis-Honeywell 1 mv. high speed, strip chart recorder was used in conjunction with the chromatograph. Full scale (10 inches) pen travel time for this recorder was 1 second, and the chart speed was 0.5 inch per minute.

Techniques. Known concentrations of each fumigant (singly and in combinations) were established in air-filled, glass, 5-gallon bottles. Liquids (*n*-pentane, CS_2, $CHCl_3$, and CCl_4) were measured into the bottles by means of a 0.2500-ml. microsyringe with 0.0001-ml. graduations (*6*). Sulfur dioxide gas was measured into the bottles at atmospheric pressure by use of a 50-cc. glass syringe. Magnetic stirrers were used to facilitate the evaporation of liquid fumigants and helped mix gaseous fumigants with air in the bottles. The magnetic stirring bars were wrapped with tin foil in a way to cause a fanning effect inside the bottles.

Fumigant–air samples were usually withdrawn from the bottles by a 50-cc. glass syringe and introduced into the chromatograph by the same syringe. In a few tests, it was desired to study the effects of diluting the samples with room air to reduce the CS_2 concentrations below the critical level. When dilution was desired, samples were taken in evacuated 125-ml. borosilicate glass gas sampling tubes. Each tube was fitted with two capillary stopcocks. Sampling with the evacuated tubes was accomplished by attaching one end of the sample tube to the stem of a stopcock at the top of the 5-gallon bottle and opening the proper stopcocks. A mercury leveling bulb system was used to flush gaseous fumigant from the 125-ml. sampling tubes into the chromatograph. Only one half of the sample was introduced. Dilution of the remaining half occurred after the initial sample introduction when air was allowed to enter the tube as the mercury was removed. One half of the diluted sample was introduced for a subsequent chromatogram. A second dilution was made by once again removing the mercury and allowing air to enter the tube. Subsequent dilutions and chromatograms were made as many times as required to eliminate the CS_2 decomposition-produced peaks and to obtain a constant CS_2 reading after mathematical adjustment for dilution factors. Mathematical adjustment was accomplished by multiplying the observed reading by 2 for each dilution of one half. When samples contained $CHCl_3$ and CS_2 or CCl_4 and CS_2, it was not necessary to stop the mercury flow exactly at the halfway point in the 125-ml. sample tube because the chlorinated hydrocarbon served as an internal standard. Dilution factors and mathematical adjustments, when using internal standards, were based upon ratios between the original (undiluted) and subsequent (diluted) chlorinated hydrocarbon readings. If a sample containing CCl_4 and CS_2 vapor produced a CCl_4 reading of 424 units from the original sample and a CCl_4 reading of 203 units from the diluted sample, the CS_2 reading from the diluted sample would be multiplied by the factor $\left(\frac{424}{203}\right)$ to adjust for dilution (Table II).

After the independent standard curves were constructed for fumigants and the critical CS_2 concentration range was determined, two of the critical CS_2 concentrations (12.6 and 25.3 mg. per liter) were used for inhibition studies. However, since results were similar with both concentrations, only data from the higher concentration are reported here.

Two procedures were followed in the studies of decomposition inhibitors. The first one (for CCl_4, $CHCl_3$, and SO_2) was as follows: the desired CS_2 concentration was uniformly established in an air-filled, 5-gallon bottle; a gaseous sample was withdrawn and analyzed; the magnetic stirrer was stopped (to minimize loss of gas in the next step); a measured quantity of the selected inhibitor (CCl_4, $CHCl_3$, or SO_2) was introduced into the bottle; the stirrer was operated for 5 minutes; a gaseous sample was drawn and analyzed; the

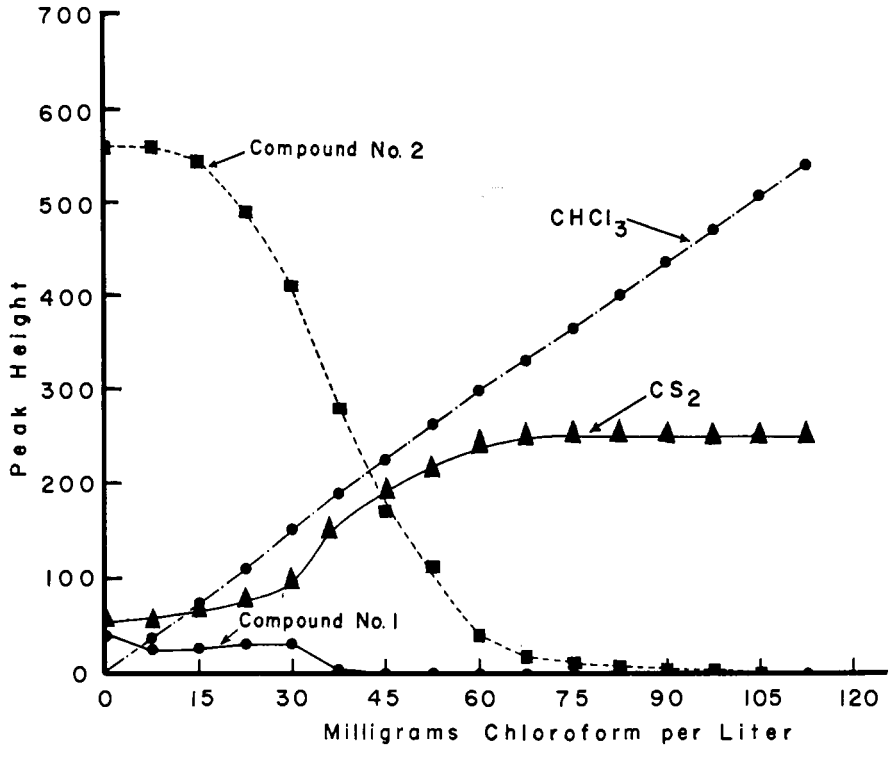

Figure 5. Inhibition of CS_2 thermal decomposition during gas chromatography by use of $CHCl_3$, as shown by chromatographic responses to 25.3 mg. of CS_2 vapor per liter in air in mixture with increasing $CHCl_3$ vapor concentrations

stirrer was stopped; a second addition of inhibitor was made; the stirrer was again operated for 5 minutes; a gaseous sample was drawn and analyzed; and so on, with subsequent additions of inhibitor until readings from the CS_2 decomposition products disappeared from the chromatograms and the CS_2 readings leveled off and remained constant.

The second procedure was used for *n*-pentane. When pentane is added commercially to liquid fumigant formulations (such as to the mixture of 80% CCl_4 and 20% CS_2 by volume, which is commonly called 80:20), the rate is usually about 1% by volume (*1, 3*). In this inhibited 80:20 formulation, the approximate pentane-CS_2 ratio is 1 part to 20 parts by volume in the liquid state. Pentane was used in these tests in a binary combination with CS_2 and in a ternary combination with 80:20. The CS_2 concentration in each 5-gallon bottle was established at 25.3 mg. per liter for both combinations. Two pentane-CS_2 ratios were used for both the binary and ternary combinations, viz., 1 to 20 and 1 to 10, representing, respectively, amounts of pentane which would be contained in liquid formulations containing 1% and 2% pentane by volume. Gaseous samples were drawn from the 5-gallon bottles and analyzed before and after additions of pentane so that inhibitory effects could be observed with CS_2 alone and in combination with CCl_4 and CS_2.

Results and Discussion

Chromatographic Retention Times and Peak Widths. Table I presents retention time (t_R) and peak width at base (Δ_t) for each of the fumigants, inhibitors, and observed decomposition products (Compounds No. 1 and No. 2). Values are in minutes and are not corrected for dead volume in the chromatograph. Dead volume can be estimated by multiplying the helium flow rate by the retention time for air.

Decomposition of Carbon Disulfide. Decomposition occurred only in certain

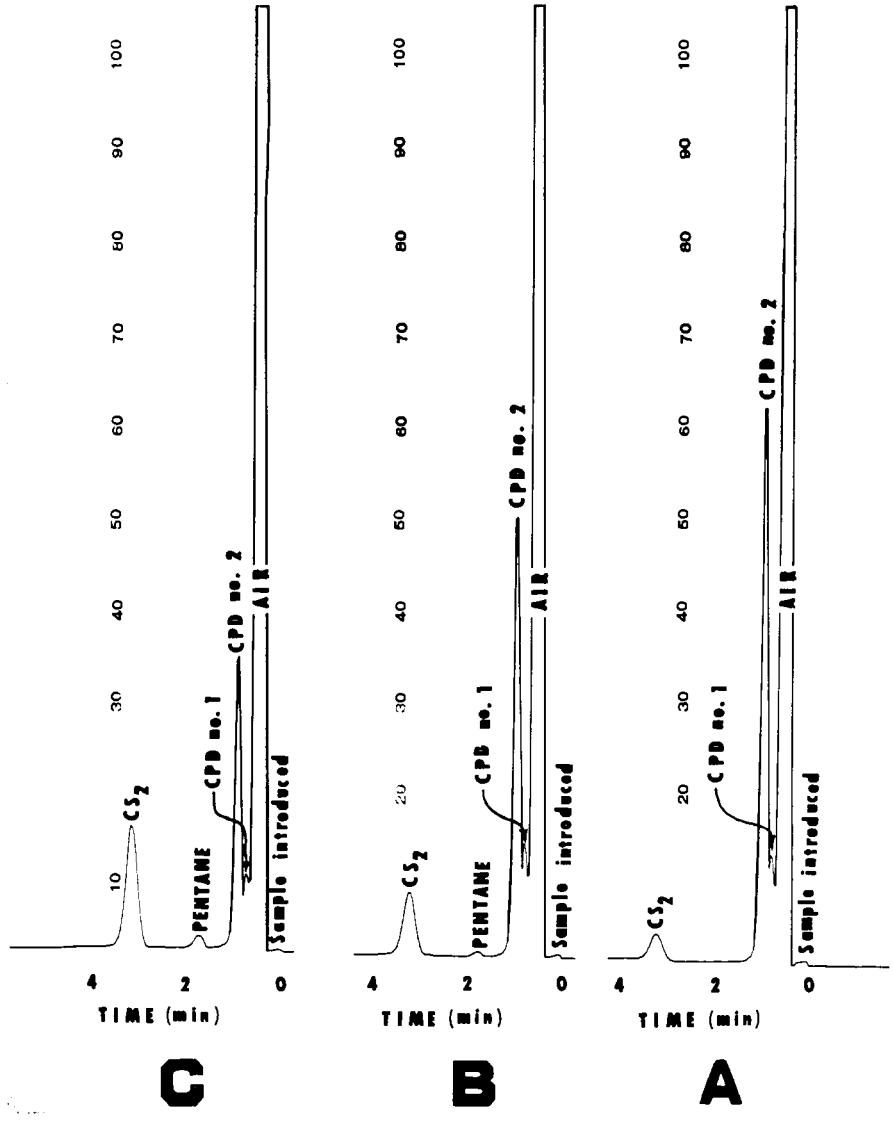

Figure 6. Inhibitory effects of *n*-pentane vapor on thermal decomposition of 25.3 mg. of CS_2 vapor per liter in air

Chromatogram *A*, no pentane; chromatogram *B*, 1 part pentane to 20 parts CS_2 by volume; chromatogram *C*, 1 part pentane to 10 parts CS_2

critical CS_2 concentrations (Figures 1 and 2) as shown by the concurrent appearance of anomalous CS_2 responses and of chromatogram peaks from two unidentified decomposition products (Compounds No. 1 and No. 2). Figure 3 represents a typical chromatogram (attenuation 10×) obtained from analysis of a 10-ml. gaseous sample containing 25.3 mg. of CS_2 vapor per liter in air. The two peaks marked Compound No. 1 and Compound No. 2 appeared from analyses of CS_2-air mixtures only when CS_2 concentrations were between 6 to 100 mg. per liter inclusive (Figures 1 and 2). The dotted lines in Figure 3 indicate increased CS_2 response and the lack of decomposition when the same CS_2 concentration was analyzed in the presence of sufficient CCl_4 or $CHCl_3$ vapor to completely suppress decomposition.

Figure 2 shows the over-all CS_2-air response for a wide range of CS_2 concentrations (through 400 mg. per liter, a concentration rarely exceeded in practical fumigations). A pronounced sag or dip appears in the first part of the CS_2 curve. The details of this portion of the graph are shown more clearly in Figure 1. Examination of Figure 1 reveals that the CS_2 curve starts in a positive and linear manner, but becomes negative in the same CS_2 concentration where the decomposition products appear. Furthermore, the lowest point in the sagging part of the CS_2 curve correlates with the highest point in the major decomposition product (Compound No. 2) curve.

Inhibitory Effects of CCl_4 and $CHCl_3$. Figures 4 and 5 illustrate the inhibitory effects of various increasing concentrations of CCl_4 and $CHCl_3$ vapors, respectively, when mixed with a constant critical CS_2 concentration (25.3 mg. per liter) in air. The concurrent decreases of Compounds No. 1 and No. 2 and increases of CS_2 and CCl_4 or $CHCl_3$ indicate that as more chlorinated hydrocarbon was added, less CS_2 was decomposed. Nearly complete inhibition of CS_2 decomposition is indicated in Figure 4 by the start of the CS_2 plateau of 250 peak height units when the CCl_4 concentration reached 151.5 mg. per liter. Chloroform (Figure 5) was about twice as efficient as CCl_4 in suppressing decomposition, since only 74.9 mg. of $CHCl_3$ per liter was required to achieve this same CS_2 plateau.

Small decomposition-product readings (Compound No. 2) were still present in chromatograms although the CS_2 readings had leveled off; however, the CCl_4 + CS_2 mixture gave a higher decomposition product reading under these conditions than did the $CHCl_3$ + CS_2 mixture (15 *vs.* 9). To eliminate completely Compounds No. 1 and No. 2 from the chromatograms, considerably more CCl_4 than $CHCl_3$ was required.

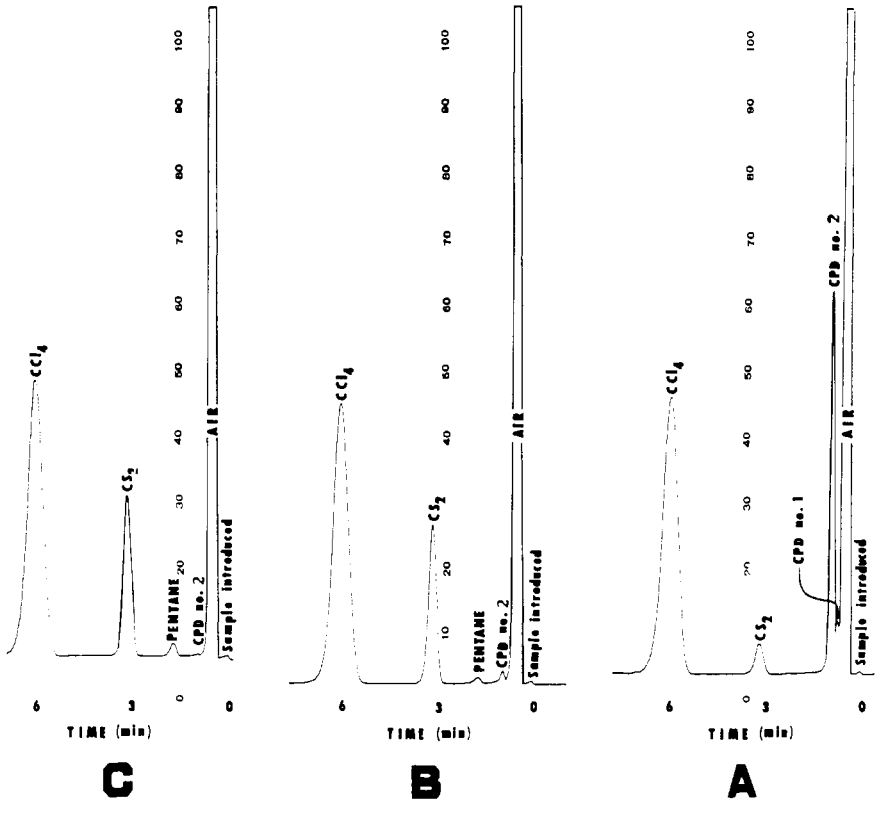

Figure 7. Combined inhibitory effects of *n*-pentane and CCl_4 vapor on thermal decomposition of 25.3 mg. of CS_2 vapor per liter in air

Chromatogram A, no pentane in 80:20; chromatogram B, 1 part pentane to 20 parts CS_2 by volume in 80:20; chromatogram C, 1 part pentane to 10 parts CS_2 by volume in 80:20

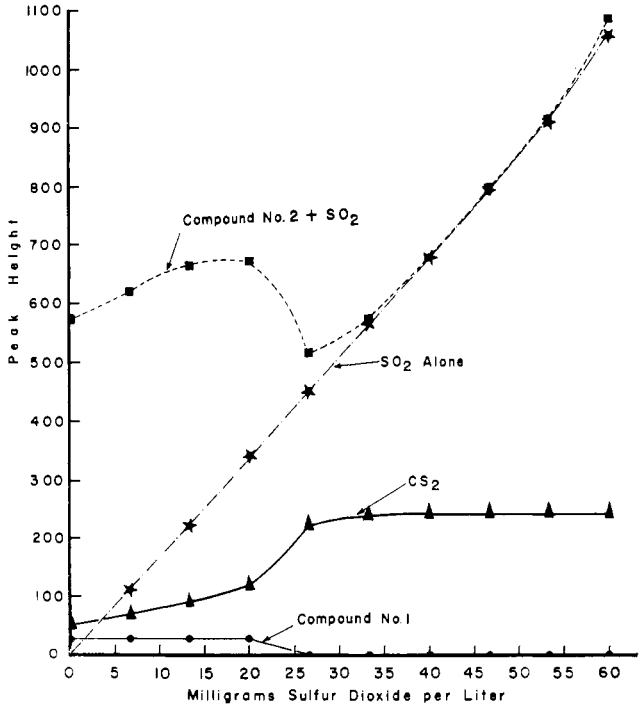

Figure 8. Inhibition of CS_2 thermal decomposition during gas chromatography by use of SO_2, as shown by chromatographic responses to 25.3 mg. of CS_2 vapor per liter in air in mixture with increasing SO_2 concentrations

Table II. Effects of Air Dilution, Carbon Tetrachloride, and *n*-Pentane on Decomposition and Accuracy of Carbon Disulfide Vapor Analyses by Gas Chromatography

		Peak Height Units					
					Carbon disulfide		
Fumigant	Dilution	Compound no. 1	Compound no. 2	*n*-Pentane	Observed[a]	Corrected[b]	Carbon tetrachloride
CS_2[c]	Original sample	20	620	...	28	...	...
	1st $\left(\frac{1}{2}\right)$[d]	15	280	...	28	56	...
	2nd $\left(\frac{1}{4}\right)$[d]	0	0	...	56	224	...
80:20[c,e]	Original sample	15	580	...	46	...	424
	1st $\left(\frac{203}{424}\right)$[f]	0	5	...	117	244	203
	2nd $\left(\frac{70}{424}\right)$[f]	0	0	...	40	242	70
Fire inhibited[c,g] 80:20	Original sample	0	21	9	233	...	424
	1st $\left(\frac{196}{424}\right)$[f]	0	0	5	114	245	196
	2nd $\left(\frac{96}{424}\right)$[f]	0	0	2	55	242	96

[a] Actual chromatogram reading, after adjustment for chromatograph attenuation.
[b] Adjusted mathematically for dilution factors.
[c] CS_2 concentration = 25.3 mg./liter in air.
[d] Dilution approximated volumetrically.
[e] 80% CCl_4 and 20% CS_2 by volume.
[f] Dilution factors from CCl_4 readings (CCl_4 served as an internal standard).
[g] 1% *n*-Pentane by volume in the liquid formulation.

The response curves for CCl_4 and $CHCl_3$ from fumigant mixtures (Figures 4 and 5, respectively) are identical with their individual standard curves; therefore, separate graphs are not presented ofr these.

Inhibitory Effects of *n*-Pentane. Figures 6 and 7 illustrate the effectiveness of *n*-pentane in presenting CS_2 decomposition. Each figure contains chromatograms of three different fumigant-air mixtures; however, the CS_2 concentration (25.3 mg. per liter) was the same in each. The chromatograph attenuation was 10×. Figure 6 shows the effects of pentane on analyses of CS_2 in air without the presence of CCl_4. Figure 7 shows the combined inhibitory effects of pentane and CCl_4.

Chromatogram *A* in Figure 6 represents the response from 25.3 mg. of CS_2 per liter in air without an inhibitor. The initial slight rise above the baseline was associated with sample introduction. Since air was the major component of the sample, its peak is very large and no attempt was made to keep the air peak under 100 by attenuation. The third and fourth peaks are responses from the CS_2 decomposition products and the last peak represents the portion of CS_2 which did not decompose. Chromatograms *B* and *C* (Figure 6) illustrate partial inhibition (by *n*-pentane) of CS_2 decomposition. The appearance of smaller decomposition-product peaks and a larger CS_2 peak in each subsequent chromatogram indicates the inhibitory effect.

Each of the three chromatograms in Figure 7 resulted from analysis of gaseous 80:20. The CCl_4 and CS_2 concentrations were 127.6 and 25.3 mg. per liter, respectively, in each analysis. Chromatogram *A* is from analysis of 80:20 without pentane. Partial decomposition of CS_2 is indicated by presence of Compounds No. 1 and No. 2 and the relatively small CS_2 peak of 50 units (compare with 240 units in chromatogram *B* and 245 units in chromatogram *C*). When pentane was added in the amount usually found in commercial "inhibited" 80:20 (chromatogram *B*), one decomposition product (Compound No. 1) did not appear, the other (Compound No. 2) was quite small, and the CS_2 peak was much larger than from the same concentration of 80:20 without pentane (240 *vs.* 50 units). Chromatogram *C* (Figure 7) resulted from analysis of 80:20 which contained twice the usual commercial amount of pentane. The results show that only a slight amount of decomposition occurred and the CS_2 peak was 5 units greater than in chromatogram *B*.

Inhibitory Effects of Sulfur Dioxide. Figure 8 presents a standard curve for SO_2 alone, illustrates the effectiveness of SO_2 in preventing CS_2 decomposition, and gives circumstantial information regarding the identity of one decomposition product.

Prevention of decomposition is shown in two ways. The first and most obvious illustration is the achievement of CS_2 plateau (250 peak height units from 25.3 mg. of CS_2 per liter, as found with other inhibitors) when the SO_2 concentration reached about 35 mg. per liter.

The second illustration of inhibition is the disappearance of readings from Compounds No. 1 and No. 2 concurrently with the start of the CS_2 plateau. This is obvious for Compound No. 1. However, since retention time (t_R) for Compound No. 2 was identical with t_R for SO_2, it is not possible, using the described chromatographic arrangement, to distinguish between the two materials (if they really are different). In Figure 8, the curve designated SO_2 + Compound No. 2 is the integral of the two materials—i.e., the added SO_2 and Compound No. 2 from CS_2 decomposition. A curve for Compound No. 2 alone can be obtained by measuring the distance between the curves which are designated SO_2 + Compound No. 2 and SO_2 Alone. With this in mind, it becomes apparent that the first point on the SO_2 + Compound No. 2 curve resulted from CS_2 decomposition only. The next five points resulted from the combined effects of added SO_2 and CS_2 decomposition. When the SO_2 concentration was between 35 and 40 mg. per liter, decomposition was inhibited and the decomposition products completely disappeared from the graph.

No special attempt was made to identify the decomposition products; however, the limited circumstantial information available (i.e., identical chromatographic retention times for SO_2 and Compound No. 2) suggests that Compound No. 2 was SO_2.

Effects of Air Dilution on CS_2 Analysis. Another means of preventing CS_2 decomposition during gas chromatography was to dilute each gaseous sample to a concentration below the critical level. Accurate analyses can be conducted this way in the event high inlet temperatures are necessary, if dilution factors are known and mathematical adjustments are made to correct the results for dilution. Examples of this procedure are shown in Table II.

Table II shows that when 25.3 mg. of CS_2 per liter in air was diluted approximately one half, the decomposition product readings were significantly reduced and the CS_2 reading (after correction for dilution) was doubled. A second dilution (to approximately one fourth the original concentration) eliminated the decomposition product readings and raised the corrected CS_2 reading to 224, or nearly nine times the original readings. When 80:20 was diluted and analyzed, the combined CCl_4 inhibition and air dilution effects

were quite pronounced. The first dilution almost eliminated decomposition and produced a corrected CS_2 reading of 244 units, approximately the reading which would be expected from 25.3 mg. of CS_2 per liter when inhibition is complete (Figure 4). The first dilution of "Fire inhibited" 80:20, which contained 1% *n*-pentane, completely eliminated decomposition and produced a corrected CS_2 reading of 245 units. The joint inhibitory effects of CCl_4 and pentane apparently raised the lower limit of the critical CS_2 concentration range above that for CS_2 in 80:20 without pentane.

Acknowledgment

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FUMIGANT RESIDUES

Determination of 1,2-Dibromo-Ethane in Air and as Residue in Fruits

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Since low dosages of 1,2-dibromo-ethane are effective as a fumigant, an accurate, simple, and rapid method was needed for its determination in air or as residue. The method presented is based on conversion to bromide followed by coulometric titration. The conversion to bromide from mixtures with air and extraction and conversion from fruits was achieved by the Kennett method. The accuracy of the method was determined using standards of 1,2-dibromo-ethane–air mixtures in the range selected from 0.75 mg. to 30 mg. Recovery was 101 to 99.6% in the above range. Examples from practical application are given for residual 1,2-dibromo-ethane and bromide.

THE FUMIGANT 1,2-dibromo-ethane (ethylene dibromide) is especially toxic to certain dipterous insects in fruits. It is also used in grain fumigation, alone (*3*) or in mixture with other fumigants (*1*). It is effective in small amounts but desorbs slowly from fumigated foodstuffs because of comparatively low vapor pressure.

1,2-Dibromo-ethane can be analyzed by several methods using monoethanolamine and Volhard titration (*8*), amperometric titration (*1*), or iodometric titration (*5, 6*), and the residual fumigant, by extraction and iodometric titration (*4*). Since low dosages of the fumigant are effective, an accurate, simple, and rapid method for the determination of small amounts was needed. In previous work for methyl bromide analysis (*2*), the coulometric method was found to satisfy the above requirements, and was used for the determination of this compound in air and as residue from small samples, after extraction and conversion to bromide (*4*).

Apparatus

The apparatus used was the Fisher Coulomatic Titrator with modifications (*2*).

Procedure

A special flask (*2*) was used for sampling of the 1,2-dibromo-ethane–air mixtures. The flask was evacuated to 0.2 mm. of Hg and the sample drawn in. Methanolic sodium hydroxide reagent was introduced for absorption and conversion, and the contents boiled under reflux for 15 minutes on a steam bath. This was sufficient time for complete conversion of one bromide from 1,2-dibromo-ethane (*4*) using 1 ml. of 0.5*N* sodium hydroxide. However, 1*N* was used to ensure complete reaction.

The flask was then cooled to about 25° C., and nitric acid was added to neutralize the excess sodium hydroxide. The resulting sodium bromide was determined by coulometric titration (*2*).

The residual 1,2-dibromo-ethane in apples was determined by extracting, absorbing, and converting to inorganic bromide by the Kennett method (*4*), and the resulting bromide determined by coulometric titration.

The total bromide residue was determined by treating the sample with alcoholic sodium hydroxide, followed by ashing as described by Neufeld (*7*). The procedure was modified to reduce the number of ignitions from five to three by using a larger amount of sodium hydroxide for the first ignition and progressively less for the following two—for the first ignition 1 ml., for the second 0.5 ml., and 0.05 ml. of 10*N* NaOH for the third. The fourth filtrate was titrated by the coulometric method, and no halide was found.

Since chloride content was higher than bromide in the ash, the latter was determined by oxidation to bromate and subsequent iodometric titration based on the method of van der Meulen (*6*), as modified by Kolthoff and Yutzy (*5*).

Known amounts of 1,2 - dibromo-ethane were used as standards to determine the accuracy and range of the method for 100% conversion. Thin-wall capillaries of small diameter and 20 to 30 mm. in length were used, depending on the amount required. The capillaries were filled by immersing one end in 1,2-dibromo-ethane. The liquid was then moved to the center of the capillary by tilting. The relatively high vapor pressure and the very short time between weighing and introduction into the flask made the sealing of capillaries unnecessary.

The amount of 1,2-dibromo-ethane was found by weighing the capillary before and after filling. The capillary