Determination of Fumigant Gases by Gas Chromatography

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Analytical methods of improved accuracy, sensitivity, and specificity were developed with the aid of gas chromatography for microgram amounts of 34 fumigant gases. A single column (6-foot × 1/4-inch o.d. stainless steel, packed with 10% SE-30 on Diatoport S, 60- to 80-mesh) and a thermal conductivity detector were used. Relative retention times, typical calibration curves, and separations of multicomponent gas mixtures under isothermal and programmed temperature conditions are shown. Applications to determination of sorption of fumigant gases are described and additional research uses are listed. The fumigants investigated were: methyl chloride, methyl bromide, ethylene oxide, phosphine, hydrogen cyanide, acrylonitrile, methylene dichloride, carbon disulfide, chloroform, bromoform, chloropicrin, carbon tetrachloride, 1,1,1-trichloroethane, *sym*-tetrachloroethane, ethylene dichloride, ethylene dibromide, ethyl bromide, trichloroethylene, tetrachloroethylene, propylene dichloride, 1-bromopropane, 2-bromopropane, 1,3-dibromopropane, 3-bromopropane, 1-bromobutane, 2-bromobutane, 1-bromopentane, 2-bromopentane, chlorobenzene, bromobenzene, o-dichlorobenzene, *p*-dichlorobenzene, β,β-dichloroethyl ether, and hexachlorobutadiene.

Fumigant gases are used to control insects and fungi in stored grain, fruit, tobacco, textiles, and dairy products and to control plant diseases, anthrax organisms, and nematodes in the soil. Some are used as rodent killers and as sterilants for air, bags, surgical materials, and spices, and to bleach and preserve dried fruit. Representative problems which arise are measurement of gas concentrations to evaluate the physiological effectiveness of a particular gas or gas mixture, and determination of fumigant residues that may be retained by foodstuffs. The parent fumigant liquids are used extensively by chemical industries in organic syntheses and in the production of anesthetics, refrigerants, textiles, rubber, dyes, pharmaceuticals, petrochemicals, metals, plastics, and other products. The same chemicals may occur as air pollutants as well as fumigants, and the determination of occupational or health hazards by blood and air analyses is common to both. Thus, the potential uses in research for accurate, sensitive, and specific methods of fumigant gas analysis are considerable.

Lindgren and Vincent (*20*) used gas-liquid chromatography to determine the sorption by whole-kernel corn of eight fumigants applied singly, three binary mixtures, and one ternary mixture, but did not give details of analytical methods. Whitney and Kenaga (*31*) used mass spectrometry and a Gow-Mac thermal conductivity gas analyzer (air reference) to determine sorption by wheat of a mixture of ethylene dibromide, ethylene dichloride, carbon disulfide, and carbon tetrachloride. Other investigations (*1, 2, 7–9, 12–14, 16–18, 23–28, 32*) pertain to use of gas-liquid or gas-solid chromatography for particular gases that may be used as fumigants.

Berck (*5*) used gas-liquid chromatography to determine the sorption by 51 cereal products of ethylene dibromide, ethylene dichloride, and carbon tetrachloride applied in the vapor phase both singly and in admixture. In the course of this work (*5*), determination of other fumigant gases was explored on a variety of chromatographic columns. Among various liquid phases that were tested, SE-30 silicone gum rubber was the most generally useful liquid phase for partitioning the fumigant gases.

This report deals with the measurement of microgram amounts of 34 fumigant gases, some of which were injected in admixture, on a single column of SE-30. The objective was to assist identification of gas peaks of fumigant residues of unknown origin by their relative retention times, t_R, on a single chromatographic column.

Materials and Apparatus

Gas Chromatograph. An F and M Model 500 linear temperature programmed gas chromatograph (F and M Scientific Corp., Avondale, Pa.) with thermal conductivity (four-filament tungsten) 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 (a silanized solid support available from F and M Scientific Corp.); helium flow rate, 50 cc. per minute; column temperatures, 50° to 180° C., depending on the gas investigated; injection port and detector block temperatures, 265° and 285° C., respectively; detector current, 200 ma. The instrument was fitted with a Minneapolis-Honeywell recorder (series Y 143, 0–1 mv., 1 second) used at a chart speed of 0.75 inch per minute. A Disc area integrator was used to record areas of the chromatograms and a soap bubble flowmeter to measure helium flow rate. Sample size ranged from 1 to 10 μl. for solutions and 1 to 10 cc. for air containing fumigant traces. Analysis time ranged from 3 to 10 minutes according to the nature of the sample.

"Gas Concentrate" Flasks. Precalibrated 6-liter all-glass Erlenmeyer flasks (Scientific Glass Apparatus Co., Bloomfield, N. J., Catalog No. JF-5230) fitted with custom ⅋ 55/50 flask heads (*5*), were used to contain fumigant-air mixtures for use as test atmospheres in micro fumigation chambers.

Syringes. Four types were used: Hamilton microliter syringes (Hamilton Co., Whittier, Calif.), 1.0- and 10-μl. capacity [10-μl. syringe calibrated for delivery (*11*)]; Hamilton Gas Tight syringes with Chaney (*10*) adaptor, in 5- and 10-cc. sizes; 20-cc. all-glass B-D (Becton-Dickinson) syringes; 100-cc. all-glass B-D syringes, with Luer stopcocks. The latter syringes were used as micro fumigation chambers, as in (*5*), and also as reaction chambers for the generation of HCN and PH_3 as described below.

Fumigants. Fumigant liquids were ACS reagent grade or nearest equivalent.

Methyl bromide, methyl chloride, and ethylene oxide were obtained in 98.5 to 99.5% purity as compressed gases in lecture-size bottles (Matheson Co., Inc., Whitby, Ontario). No attempt was made to purify the commercially obtained compounds further.

Fumigant Standards. A series of standard solutions of the fumigant liquids was made by serial dilution of 5.0% (w./v.) solutions in *n*-pentane or *m*-xylene down to 0.1% (w./v.) (1 μl. of solution = 1 μg. of gas). Methyl bromide, methyl chloride, and ethylene oxide were pressure-dispensed through a Hoke stainless steel needle valve (Matheson Co.) into precalibrated 20-cc. syringes fitted with Luer stopcocks, weighed, and discharged slowly through 22-gage 6-inch stainless steel B-D hypodermic needles into chilled *m*-xylene contained in 8-mm. o.d. glass test tubes. Standard solutions of HCN and PH_3 were prepared by discharging assayed aliquots of these gases into chilled 1-butanol.

Experimental

Determination of t_R. A helium flow rate of 50 cc. per minute and a detector current of 200 ma. were set at the start of each run. To locate the column temperature range in which a symmetrical elution pattern of a given liquid fumigant might be obtained, 0.2 μl. of the liquid was injected at an initial column temperature of 50° C. and was programmed at a moderate rate—e.g., 15° C. per minute. After the range was established, various column temperatures were tested isothermally at a helium flow rate of 50 cc. per minute and at 5° intervals below the temperature indicated by the initial temperature-programmed run, injecting for this purpose 2 μl. of a 0.1% (w./v.) solution of the fumigant in *n*-pentane or *m*-xylene. The peak areas of the different isothermal runs agreed within 10 Disc area units, and were essentially identical for the most part. The absolute t_R of each fumigant was measured from the point of injection of the fumigant solution to the apex of the gas peak, and was determined for each gas in triplicate at the temperature of choice, with agreement within 0.02 minute. Relative t_R was calculated as the ratio of the absolute t_R of the fumigant gas to that of *n*-pentane at a helium flow rate of 50 cc. per minute at the column temperatures listed in Table I.

Standard Curves. From standard solutions of fumigants as described above, separate calibration curves for the ranges 0 to 40 μg. (1, 2, 5, 10, 20, 30, and 40 μg.) and 50 to 500 μg. (50, 75, 100, 200, 300, 400, and 500 μg.), respectively, were prepared. The area-concentration relationships were plotted from duplicate determinations. The over-all agreement between replicates was within 6.5 Disc units, in which the area equivalence of 1 μg. of fumigant gas ranged from 70 to 120 Disc units, depending on the nature of the gas.

Generation of Hydrogen Cyanide and Phosphine. PROCEDURE A. For the generation of HCN, the piston was removed from a 100-cc. syringe fitted with a Luer stopcock capped with a rubber serum cap. A 2½-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. NaCN crystals (0.1 to 0.2 gram) were transferred through a long-stemmed powder funnel into a corner of the syringe. The syringe piston was inserted and advanced to the 20-cc. mark, the air-vent needle was removed, and the syringe was placed horizontally in a fume chamber. One milliliter of H_2SO_4-H_2O solution, 1:2 v./v., was injected through the serum cap. After the piston stopped advancing from the expansion of the generated HCN, the serum cap was removed and a 2-inch glass tube containing granular magnesium perchlorate (*25*) as desiccant was attached. The other end of the drying tube was connected to a 100-cc. syringe acting as a receiver, into which the HCN gas from the generator syringe was slowly discharged. Duplicate aliquots of the HCN-air mixture were assayed by addition of 0.02*N* $AgNO_3$ solution and back-titration with standard KCNS solution (*3*). HCN standards, 0.1% (w./v.), were prepared by dispensing slowly calculated amounts of the assayed gas into tubes containing 1-butanol at ice-bath temperature, using a 6-inch 20-gage hypodermic needle for this purpose.

PROCEDURE B. For the generation of phosphine, 0.25 gram of Phostoxin was used (manufactured by the Degesch Co., Frankfort, West Germany). It is a registered grain fumigant available from Phostoxin Sales of Canada, Ltd., Montreal 24, Quebec, as 3-gram tablets containing 70% aluminum phosphide, and yielding 1 gram of PH_3 per tablet. The Phostoxin powder was transferred to a generator syringe, a serum cap was attached, and the syringe was placed horizontally in the fume chamber. One milliliter of water was injected to release PH_3, and 30 minutes was allowed for maximum gas volume to develop. The gas-air mixture was discharged slowly into a second syringe used as a receiver, and 5-cc. aliquots were assayed by the titration method of White and Bushey (*30*). A PH_3 standard of 0.1% (w./v.) was prepared in chilled 1-butanol. (*Caution.* Phosphine in high concentration in air will ignite upon injection into a hot injection port. This was experienced upon injection of 2 cc. of a phosphine-air mixture, 3:1 v./v., intended for reconnaissance tests.)

Results and Discussion

Figure 1 shows for comparative purposes the elution patterns for 2-μg. amounts of the 34 test fumigants listed in Table I. To conserve space in illustration, the air or solvent peaks are not shown, with the exception of fast-eluting

Table I. Absolute and Relative Retention Times of 34 Fumigants[a]

	Fumigant	Formula	Col. Temp., °C.	Abs. t_R, Minutes	Rel. t_R[b]
1.	Methyl chloride	CH_3Cl	60	0.84	0.71
2.	Methyl bromide	CH_3Br	60	1.00	0.85
3.	Ethylene oxide	$(CH_2)_2O$	80	0.85	0.89
4.	Phosphine	PH_3	75	0.70	0.71
5.	Hydrogen cyanide	HCN	75	0.88	1.11
6.	Methylene dichloride	CH_2Cl_2	60	1.32	1.12
7.	Carbon disulfide	CS_2	60	1.52	1.29
8.	Chloroform	$CHCl_3$	60	2.22	1.89
9.	1,1,1-Trichloroethane	$CCl_3.CH_3$	60	2.40	2.04
10.	Ethylene dichloride	$CH_2Cl.CH_2Cl$	60	2.67	2.27
11.	Carbon tetrachloride	CCl_4	60	3.17	2.70
12.	Propylene dichloride	$CH_2Cl.CHCl.CH_3$	60	3.55	3.02
13.	Ethyl bromide	C_2H_5Br	70	1.17	1.11
14.	2-Bromopropane	$CH_3.CHBr.CH_3$	70	1.55	1.48
15.	3-Bromopropene	$CH_2:CH.CH_2Br$	70	1.80	1.71
16.	1-Bromopropane	C_3H_7Br	70	1.93	1.84
17.	2-Bromobutane	$C_2H_5.CHBr.CH_3$	70	2.63	2.51
18.	Trichloroethylene	$CHCl:CCl_2$	70	2.74	2.61
19.	Chloropicrin	$CCl_3.NO_2$	80	(3 peaks)	...[c]
20.	1-Bromobutane	$C_3H_7.CH_2Br$	80	2.58	2.71
21.	1-Bromopentane	$C_4H_9.CH_2Br$	100	2.38	2.83
22.	Ethylene dibromide	$CH_2Br.CH_2Br$	100	2.57	3.05
23.	Tetrachloroethylene	$CCl_2:CCl_2$	100	2.63	3.13
24.	Acrylonitrile	$CH_2:CHCN$	110	0.92	1.21
25.	2-Bromopentane	$C_3H_7.CHBr.CH_3$	110	2.28	3.02
26.	Chlorobenzene	C_6H_5Cl	125	1.88	2.64
27.	Bromoform	$CHBr_3$	125	2.33	3.28
28.	*sym*-Tetrachloroethane	$CHCl_2.CHCl_2$	125	2.57	3.70
29.	1,3-Dibromopropane	$CH_2Br.CH_2.CH_2Br$	125	2.78	3.90
30.	Bromobenzene	C_6H_5Br	125	2.85	4.00
31.	β,β'-Dichloroethyl ether	$(C_2H_4Cl)_2O$	125	3.03	4.26
32.	*p*-Dichlorobenzene	$C_6H_4Cl_2$	125	4.05	5.68
33.	*o*-Dichlorobenzene	$C_6H_4Cl_2$	125	4.20	5.90
34.	Hexachlorobutadiene	$CCl_2:CCl.CCl:CCl_2$	180	2.68	4.32

[a] 2 micrograms of fumigant; instrument attenuation = 1 *x*; flow rate = 50 cc. helium/min.
[b] Relative to *n*-pentane = 1.00.
[c] Three peaks for chloropicrin at 0.90, 2.75, and 3.62 minutes abs. t_R.

gases 1 to 3, 5 to 8, 13 to 15, 19, and 24, which show an air peak in close proximity to the numbered gas peak. With phosphine (gas 4) the air peak (t_R = 0.65 minute) is enveloped in the PH_3 peak (t_R = 0.70 minute at 75° C. column temperature). However, although the PH_3 peak was not separated from the air peak under the conditions described, the area of the air peak is small and constant for a given volume of 1-butanol, and correction for the air peak area is readily achieved. Dumas (*12*) recently developed a new method for the determination of PH_3 in air, in which the column packing was 30% Apiezon L on 40- to 60-mesh firebrick. Because of the proximity of the air and PH_3 peaks, 1-cc. air samples were recommended for PH_3 concentrations below 500 μg. per liter (*12*) in order to minimize interference from air. The present method, using 10% SE-30 as liquid phase and 1-butanol as trapping solvent, yields faster separation of PH_3 and considerable reduction in area of the air peak, concomitantly enabling increased sensitivity through use of larger air samples. In the latter regard, the maximum air-retaining capacity of 1-butanol is small, as is also the case with *n*-pentane and *m*-xylene, and the air peaks for 5 and 5000 cc. of air are identical. Semiautomatic sampling apparatus for dispensing large air samples containing trace amounts of fumigant gases into a chilled trapping solvent has been described (*4*).

All gases listed in Table I, except chloropicrin and hydrogen cyanide, yielded

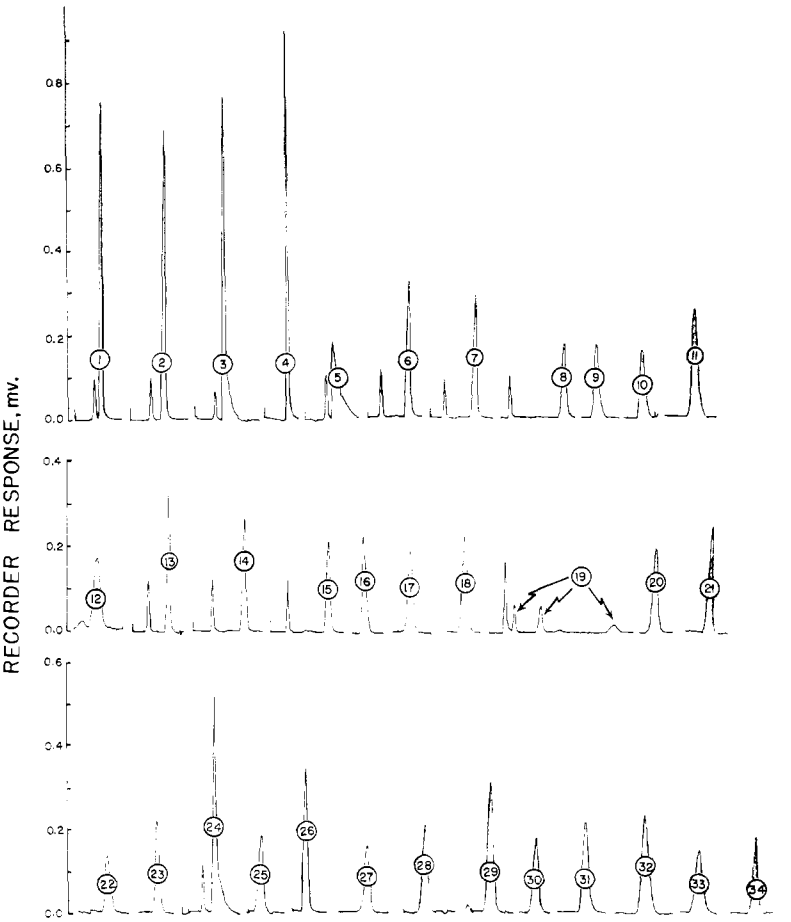

Figure 1. Elution profiles of fumigants listed in Table I

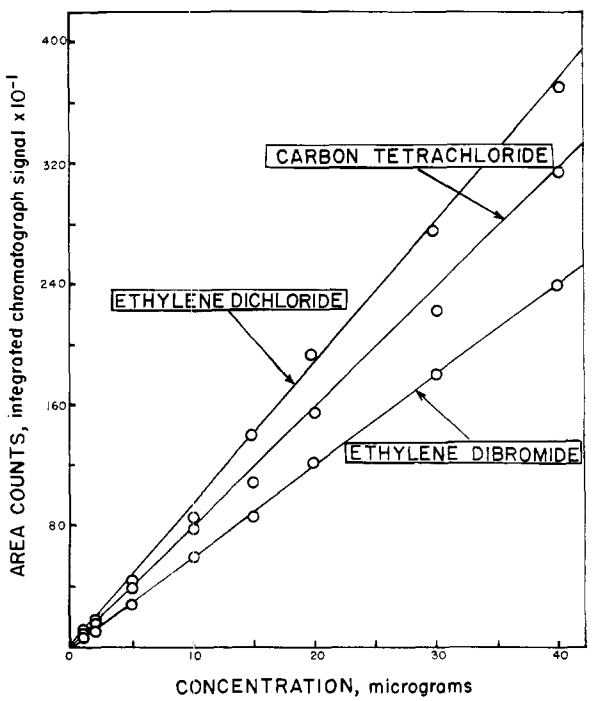

Figure 2. Standard curves for ethylene dichloride, carbon tetrachloride, and ethylene dibromide

Range 0 to 40 μg.

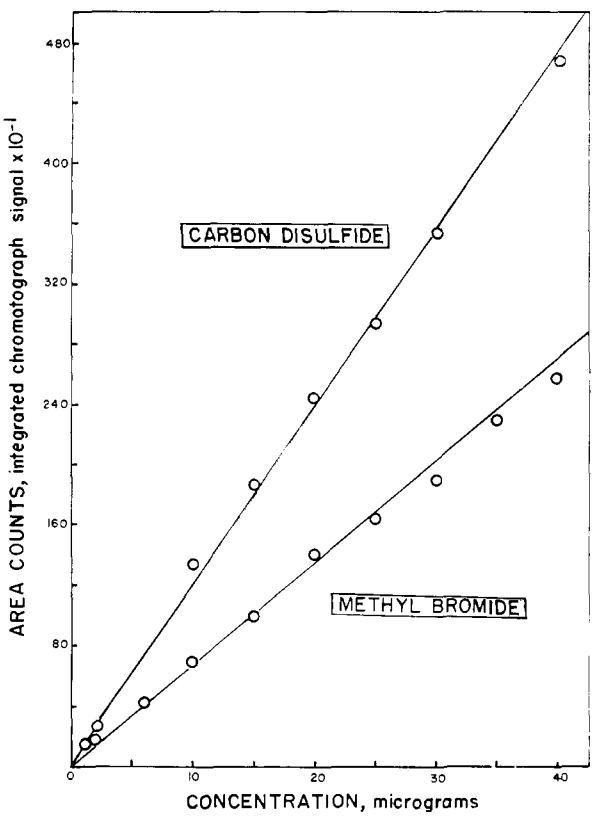

Figure 3. Standard curves for carbon disulfide and methyl bromide

Range 0 to 40 μg.

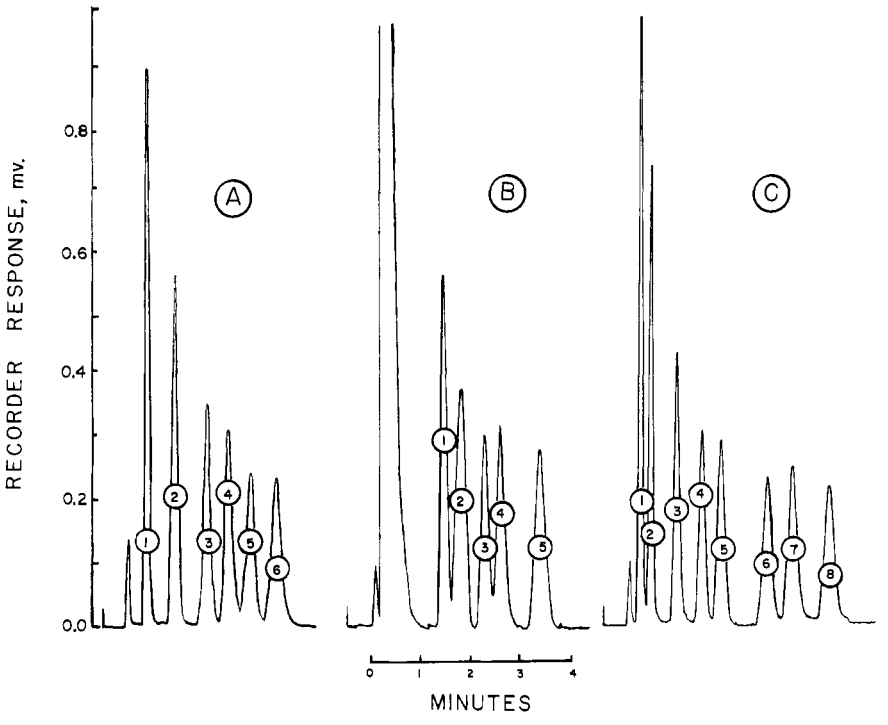

Figure 4. Elution of gas mixtures under isothermal and programmed temperature conditions

A. Isothermal separation of 6 gases at 60° C., attenuation 1 ×, abs. t_R (minutes)

1. Methyl bromide, 2.5 μg., 1.02 min.
2. Carbon disulfide, 4 μg., 1.55 min.
3. Chloroform, 4 μg., 2.23 min.
4. Ethylene dichloride, 4 μg., 2.65 min.
5. Carbon tetrachloride, 2 μg., 3.13 min.
6. Propylene dichloride, 3 μg., 3.58 min.

B. Isothermal separation of 5 gases at 125° C., attenuation 1 ×, abs. t_R (minutes)

1. Chlorobenzene, 4 μg , 1.97 min.
2. Bromoform, 4 μg., 2.37 min.
3. *sym*-Tetrachloroethane, 3 μg., 2.72 min.
4. β,β′-Dichloroethyl ether, 3 μg., 3.10 min.
5. *p*-Dichlorobenzene, 4 μg., 4.02 min.

C. PTGC separation of 8 gases, started at 50° C. column temp. and attenuation 1 ×. After air peak (0.68 min.), programmed at 7.9° C./min.

1. Methyl chloride, 3 μg., 0.90 min.
2. Methyl bromide, 2 μg., 1.10 min.
3. Methylene dichloride, 3 μg., 1.65 min.
4. 2-Bromopropane, 3 μg., 2.20 min.
5. Chloroform, 3 μg., 2.60 min.
6. Carbon tetrachloride, 2 μg., 3.53 min,
7. Propylene dichloride, 3 μg., 4.05 min.
8. 1-Bromobutane, 2 μg., 4.80 min.

satisfactory chromatograms for the 2-μg. amounts that were injected. One-microgram amounts were readily measured. Chloropicrin in *m*-xylene (gas 19, Figure 1) yielded three peaks after the air peak, indicating the presence of at least two concomitant compounds or impurities. The same three peaks were found in technical grade chloropicrin. This poses the question of which peak or peaks indicate substances that would exert greater physiological effectiveness. The existence of associated compounds was not indicated by the author's polarographic method (*6*) for chloropicrin.

HCN in 1-butanol (5, Figure 1) showed a sharp front with tailing that was not appreciably reduced by raising the column temperature. Comparative tests with the more polar column packing for HCN of Schneider and Freund (*25*) were not undertaken because methods for HCN measurement in particular were not required in this study. Comparisons among the comparatively few methods available for some of the other fumigants were also omitted. In this regard, a principal objective was to examine the possibility of separating a wide range of gases in microgram amounts by use of a single column packing—namely, 10% SE-30 on a solid support of 60- to 80-mesh Diatoport S. The results (Table I and Figure 1) show that various admixtures can be separated.

Methyl bromide, ethylene dibromide, ethylene dichloride, carbon tetrachloride, and carbon disulfide were of particular interest for the author's research program. Standard curves for their quantitative determination were made for the ranges 0 to 40 and 50 to 500 μg., respectively, in the manner described. The peak area–concentration relationships of these gases in the range 0 to 40 μg. are shown in Figures 2 and 3.

Figure 4 shows elution profiles recorded in the separation under isothermal and programmed temperature conditions of various gases in admixture, each in microgram amounts. Groups *A* and *C* were in solution in *m*-xylene, and group *B* in *n*-pentane. As may be seen from the absolute t_R values (Figure 4), rapid separation was achieved. In the investigation of sorption of three-component gas mixtures by cereal products (*5*), ethylene dichloride and carbon tetrachloride in 4-cc. air samples were determined isothermally at a column temperature of 60° C., and ethylene dibromide was determined by programming the column temperature at 15° C. per minute after carbon tetrachloride was eluted. Direct injection of more than 10 cc. of air impaired the reproducibility obtained with the thermal conductivity detector.

Peak area as a quantitative parameter was more reproducible than peak height and did not change with column temperature. This was particularly useful at different column temperatures used isothermally to improve the resolution of particular gas mixtures. Flow rate was checked frequently for constancy, since it affected significantly the reproducibility of peak areas. In pro-

grammed temperature (PTGC) runs, the 50-cc. flow rate applied only to the initial column temperature.

With 10% SE-30 as stationary phase, the t_R of the various fumigant gases were shorter, the sensitivity was higher, and the peaks were sharper and more symmetrical than those obtained with a loading of 30% SE-30. However, smaller aliquots must be used with the 10% loading.

To separate the solvent peaks from the fumigant peaks, *m*-xylene was used as trapping solvent when the boiling points of the fumigants were below 80° C., and *n*-pentane was used for fumigants boiling above 80° C. The t_R of *m*-xylene (8.75 minutes at 60° C.) was sufficiently long to permit the separation from relatively large amounts of air of fast-eluting gases such as methyl bromide, methyl chloride, and ethylene oxide that normally would be encompassed in the air or *n*-pentane peak. The use of trapping solvent can be omitted for methyl bromide (t_R = 1.00 minute at 60° C.) if the methyl bromide concentration is greater than 1500 μg. per liter of air, in which case 1 cc. of air can be injected directly into the injection port.

Levadie (*18*, *19*) had previously used *m*-xylene as a trapping solvent for organic vapors. As indicated above, *m*-xylene was not suitable for HCN and PH_3, which are relatively polar, and 1-butanol was found to be better suited for these gases.

The determination by gas chromatography of parts per billion amounts in air of fumigants, air pollutants, organic solvents, etc., is expedited with trapping solvents, such as *n*-pentane, *m*-xylene, or 1-butanol, to aggregate the trace amounts and to reduce the air peak and the interfering effect of water vapor. Trapping solvents are particularly useful in sampling room or outside atmospheres, where sample sizes of 15 to 20 liters of air or more may be taken, and are relatively simpler and more convenient to use in this regard than by collecting the trace constituents on cold activated charcoal or in cold traps (*29*). However, where sample size must be limited by practical considerations, as in the determination of fumigant residues of foods or soil, cold traps may be preferred, since they permit analysis of the total volatiles trapped, rather than of an aliquot as with trapping solutions. Nevertheless, by increasing the sensitivity of detection, such as can be achieved with a hydrogen flame ionization (*1*) or an electron-capture detector (*15*, *21*, *22*), the advantages of trapping solvents can be extended to problems in which sample size is limited. An additional advantage of use of a hydrogen flame detector is the elimination of the air peak that is normally "seen" with a thermal conductivity detector.

Applications for the methods as indicated herein are abundant. Examples such as assessment of physiological effectiveness, toxic hazards, comparative efficiency of different methods of application, reaction kinetics, chemisorption, photodecomposition, fumigant residues, synergism or potentiation, air pollution, efficiency of respirator canisters, gas permeability of materials, chromatographic properties of cereal crops, etc., illustrate the many potential areas of use. In this regard, gas chromatography will play an increasingly important role in the identification and microdetermination of fumigant gases.

Acknowledgment

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CORRECTION

Nutrient-Conserving Agents. Loss of 2-Chloro-6-(trichoromethyl)-pyridine from Soil

In this article by C. T. Redemann, R. W. Meikle, and J. G. Widofsky [J. AGR. FOOD CHEM. **12,** 207 (1964)] the following corrections should be made.

Under the subheading, "6-Chloropicolinic-C^{14} Acid," the preparation of this acid is described. When we attempted to repeat this synthesis, we discovered that it was necessary to use 2-bromo-6-chloropyridine instead of 2,6-dichloropyridine and that the starting material for our first synthesis was the 2-bromo- derivative, at that time erroneously identified as 2,6-dichloropyridine. We have now demonstrated to our satisfaction that the dichloropyridine does not react with *n*-butyllithium under the conditions described.

2-Bromo-6-chloropyridine was prepared by means of a Sandmeyer reaction employing 2-amino-6-bromopyridine, cuprous chloride, and 6*N* hydrochloric acid (m.p. 87–88°).

ANALYSIS. Calculated for C_5H_3BrClN: C, 31.31; H, 1.57; N, 7.28. Found: C, 31.62; H, 1.45; N, 7.02.

The source of *n*-butyllithium used in this reaction was critical. The commercially available reagent dissolved in *n*-hexane or heptane will not react with 2-bromo-6-chloropyridine. However, a butyllithium preparation in ether, stored in a refrigerator and only a few days old, reacts very readily. Presumably, a small amount of lithium ethoxide is a necessary adjunct for a successful halogen-metal interconversion in this case. The obvious experiment in which lithium ethoxide is added to a butyllithium preparation in hexane was not carried out because the preparation in ether solved our problem.

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