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ETHYLENE DIBROMIDE AND CARBON TETRACHLORIDE  
IN ADMIXTURE IN AIR**

**Research Branch  
CANADA DEPARTMENT OF AGRICULTURE**

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IN ADMIXTURE IN AIR**

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# DETERMINATION OF METHYL BROMIDE, ETHYLENE DIBROMIDE AND CARBON TETRACHLORIDE IN ADMIXTURE IN AIR<sup>1</sup>

## ABSTRACT

Mixtures of methyl bromide, ethylene dibromide and carbon tetrachloride (MB, EB and CT) in air were quantitatively determined with an accuracy of 96 - 100 per cent by differential alkaline hydrolysis and amperometric titration of the ionic bromide and chloride in the hydrolysate. The method is based on kinetic differences in rate of hydrolysis with monoethanolamine: at 3° C. only MB reacts, and at 100° C. EB + CT can be measured by argentometric titration. EB in the presence of CT is determined by selective oxidation of Br<sup>-</sup> in the hydrolysate by a modified Kolthoff-Yutzy method, the iodine end point being measured amperometrically. The design and analytical applications of a fumigant testing chamber are described.

## INTRODUCTION

Investigations (1) on the distribution and persistence of methyl bromide, ethylene dibromide and carbon tetrachloride (MB, EB and CT) in grain treated with these fumigants required methods for measuring these gases, both separately and in mixtures. Methods based on alkaline hydrolysis (2-6, 13, 15-20, 23, 24) were considered more readily adaptable for the purpose than those based on pyrolysis, colorimetry, vapor pressure or thermal conductivity.

An outline for the differential alkaline hydrolysis of MB, EB and CT is given in Table 1. Differences in reaction rate made it possible to measure MB without interference from EB, CT or ethylene dichloride (EDC). Thus, as shown in Figure 1, MB was quantitatively hydrolyzed by monoethanolamine at 3° C. in 20 hours, whereas EB, CT and EDC were inert. (Though EDC could readily be measured in the presence of EB and MB, it could not be differentiated from CT by the methods described here, and was accordingly omitted. However, CT can be quantitatively differentiated from EDC by Ramsey's (14) modification of the Fujiwara reaction.) At 100° C. for 3 hours, 99.0 per cent of EB reacted, and when sodium methoxide was added to the monoethanolamine 99.7 per cent of CT reacted.

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<sup>1</sup>

Contribution No. 63, Research Station, Winnipeg, Manitoba.

Bromide and chloride ions in the hydrolysate were each titrated amperometrically by the method of Laitinen, Jennings and Parks (11) with modifications for bromide measurement as indicated by Kolthoff and Stock (9). Bromide in the presence of chloride was determined by oxidation to bromate with hypochlorite (10). At the final stage,  $10^{-3}$  N sodium thiosulfate solution was added in excess and back-titrated amperometrically with  $10^{-3}$  N potassium iodate solution. This was sufficiently sensitive to measure as little as 1.3 micrograms of bromide (equivalent to 0.1 ml. of  $10^{-3}$  N sodium thiosulfate) with no interference from chloride.

Table 1.— Outline for determination of MB, EB and CT in admixture in air samples by differential hydrolysis

Fumigant (s)	Minimum number of samples required	Comments
MB	1	Ionic bromide obtained by hydrolysis at 3° for 20 hr., or at 25° C. for 6 hr., is calculated as MB.
EB	1	Bromide resulting from hydrolysis at 100° C. is calculated as EB.
CT*	1	Chloride resulting from hydrolysis at 100° is calculated as CT.
MB + EB	2	1st sample, hydrolyzed for 20 hr. at 3° C., gives MB; 2nd sample, at 100° C., gives total bromide. Deduct 1st value from 2nd to get bromide as EB.
MB + CT*	2	1st sample, at 3° C., gives MB; 2nd sample, at 100° C., gives total halide. Deduct 1st value from 2nd to get chloride as CT.
EB + CT*	2	Both samples, at 100° C., give total halide. Bromide in hydrolysate of 1st sample is oxidized to bromate and calculated as EB. Deduct bromide from total halide to get chloride and calculate as CT.
MB + EB + CT	3	1st sample, at 3° C., gives MB; 2nd and 3rd samples, at 100° C., give total halide. Bromide in hydrolysate of 3rd sample is oxidized to bromate and calculated as MB + EB. Deduct latter from total halide to get chloride present as CT.

\*Sodium methoxide is added to raise the hydrolyzing efficiency of monoethanolamine when measurement of CT is desired.



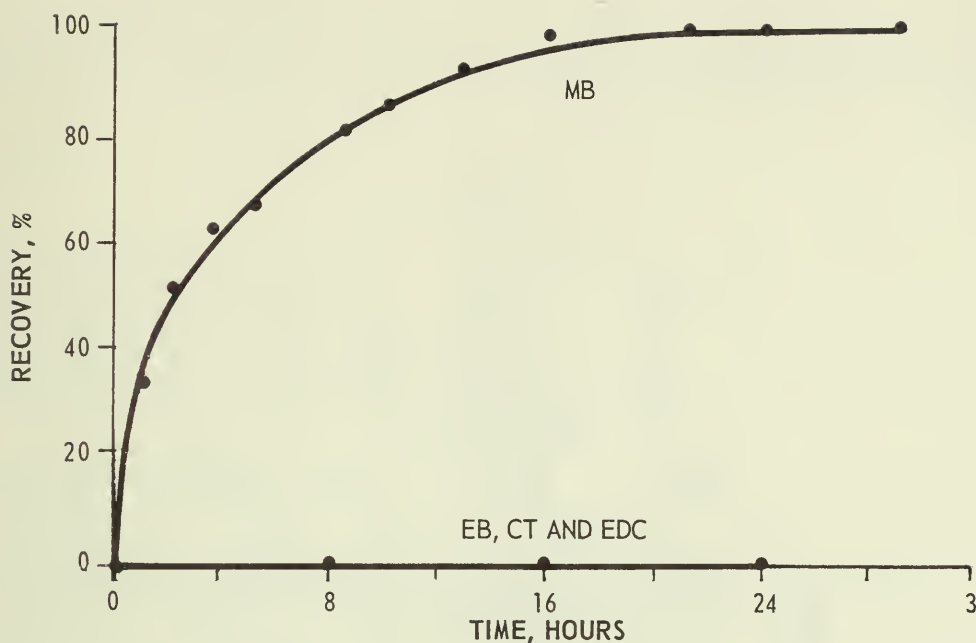


Figure 1.— Reaction rates with monoethanolamine at 3° C. of methyl bromide and of ethylene dibromide, carbon tetrachloride and ethylene dichloride.

## APPARATUS

### Amperometric Titration Assembly

The titration assembly consisted of a Sargent Model III polarograph (E. H. Sargent and Co., Chicago, Ill.), a platinum-wire electrode rotated at 600 r.p.m. and an H-type saturated calomel electrode (11) with a potassium nitrate–agar salt-bridge (8).

### Fumigant Testing Chamber

A steel drum with a removable cover and a capacity of 280 litres at 25° C. was improvised as a fumigant testing chamber (Figure 2).

### Sampling Bottles

Samples were taken with glass milk bottles, ranging in capacity from ½ pint to 1 quart.

### Dehalogenation Reaction Bottles

Two- and 4-ounce glass medicine bottles with metal screw caps were used for dehalogenation reactions. The caps were fitted with close-fitting disks cut with a cork borer from polyethylene sheeting about 0.025 inch thick.

### Titration and Pipetting Equipment

The following were used: a Gilmont combination micro pipette-burette, 1 ml., graduated in  $10^{-3}$ -ml. units (Emil Greiner Co., New York 13, N.Y.); a Koch micro-burette, 5 ml., graduated in  $10^{-2}$ -ml. units, with offset dispensing tip; and a pipette holder and micropipettes to deliver 0.125, 0.250, 0.500 and 1.000 ml. respectively (Microchemical Specialties Co., Berkeley, Calif.). Volumes were calibrated with mercury.

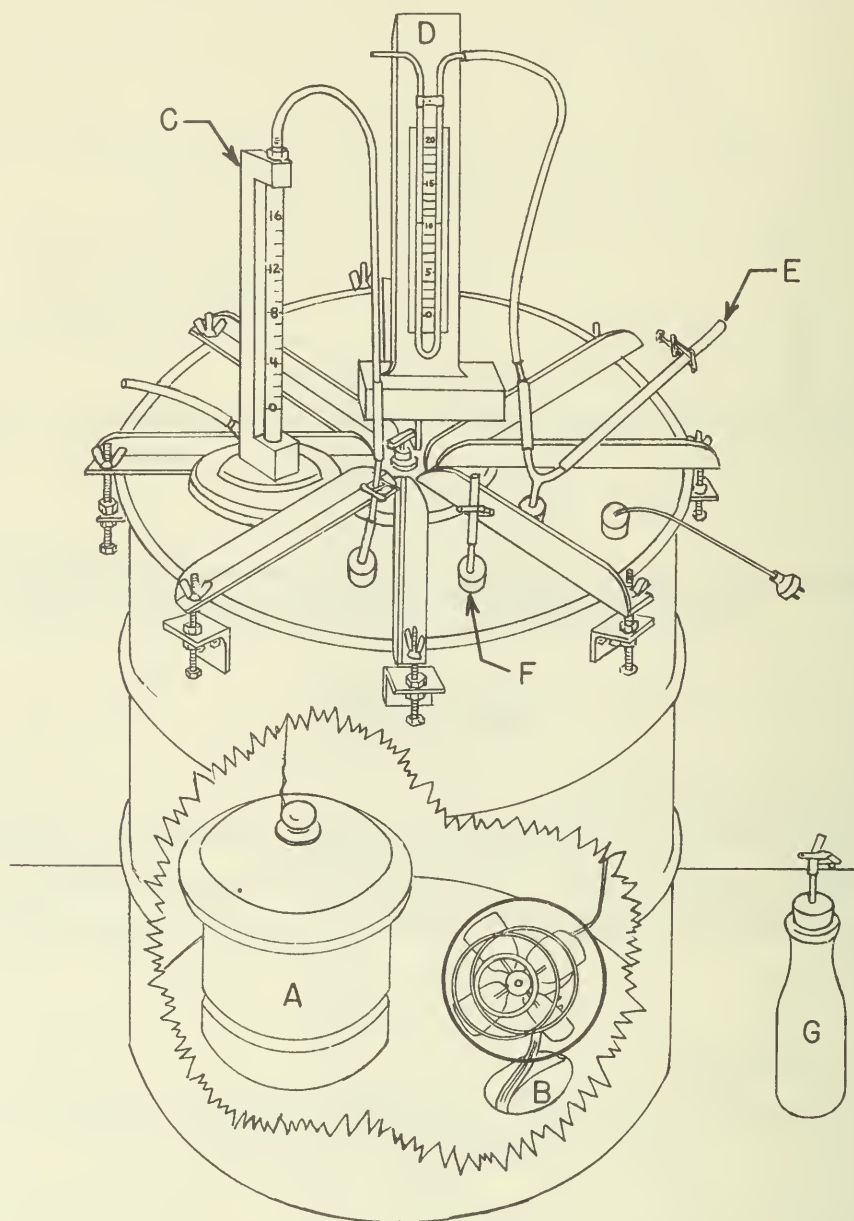


Figure 2.—Fumigant testing chamber. A. Desiccator fitted with wire to raise cover. B. Fan for circulation of fumigant. C. Rotameter (optional) for metering the fumigant gas or gases being introduced or for sampling gas-air mixtures in gas-absorption bottles. D. Manometer ( $H_2O$ ) for measuring atmospheric pressure in drum. E. Outlet for attachment to vacuum source. F. Outlet for gas-sampling purposes. G. Gas-sampling bottle, to which capillary tubing is attached before sample is taken.



## STANDARD SOLUTIONS AND REAGENTS

### Fumigant Standards

MB, EB and CT standards, 1 mg./ml. in chilled n-propanol, made from stock solutions of 25 - 50 mg./ml. MB standard prepared from weighed ampoules as described by Busbey and Drake (3). A full-face respirator used in preparing the stock solutions.

### Gas Sampling and Hydrolysis

N-propanol, reagent grade.

Monoethanolamine, reagent grade.

Sodium methoxide, approximately 2*N* in methanol.

### Argentometric Procedure

Acetone.

HNO<sub>3</sub>, 8*N* approximately.

Gelatin solution, 1.2 per cent. Chloroform added at 1 ml./100 ml. as preservative.

Standard solutions of KBr and KCl, 10<sup>-1</sup> *N*. Diluted to 10<sup>-2</sup> *N* and 10<sup>-3</sup> *N* as required.

AgNO<sub>3</sub>. Standard solutions 10<sup>-2</sup> and 10<sup>-3</sup> *N* prepared from 10<sup>-1</sup> *N* stock solution, and used as follows:

(a) 10<sup>-3</sup> *N* for MB and EB in amounts of 0.1 - 1.0 mg., or for CT in amounts 0.03 - 0.3 mg.

(b) 10<sup>-2</sup> *N* for MB and EB in amounts of 1 - 10 mg., or for CT in amounts of 0.3 - 3 mg.

(c) 10<sup>-1</sup> *N* for MB and EB in amounts of 10 - 100 mg., or for CT in amounts 3 - 35 mg.

### Oxidation Procedure

Saturated NaCl solution.

Sodium dihydrogen phosphate, 20 per cent solution.

Sodium formate, 50 per cent solution.

Ammonium molybdate, 1 per cent solution.

Sodium hydroxide, 2 *N*.

Potassium iodide, 30 per cent solution, freshly prepared as required.

Hydrochloric acid solution, approximately 6 *N*. Concentrated HCl diluted to 6 *N* and distilled, the first and last 10 per cent portions being discarded.

Sulfuric acid, 6 *N* approx.

Potassium iodate. Standard solutions 10<sup>-1</sup>, 10<sup>-2</sup> and 10<sup>-3</sup> *N*.

Sodium thiosulfate, 10<sup>-1</sup> *N*, standardized periodically against 10<sup>-1</sup> *N* KIO<sub>3</sub>. Chloroform, 0.1 per cent v/v, added as preservative. Standard solutions (10<sup>-2</sup> and 10<sup>-3</sup> *N*) prepared from stock solution as required.

## PROCEDURE

### Sampling

For routine sampling of fumigant gas in the interstitial air or above the surface of fumigated grain, evacuated flasks of known volume were used. Sample size ranged from 250 to 2,000 ml., the smallest volume possible being taken to obtain at least 0.25 mg. of gas per sample. The size of the sample was influenced by the kind and amount of fumigant applied, the time that elapsed after application of the fumigant, the distance of the sampling point from the area of application, and the moisture content and temperature of the grain.

Glass milk bottles were as accurate as conventional gas-sampling flasks, and were used to collect samples in field tests. The bottles were evacuated to 15 mm. of Hg after adding 10 ml. of 1:4 monoethanolamine in *n*-propanol. When CT was being determined, 2 ml. of 2 *N* sodium methoxide were also added. Temperature, atmospheric pressure and volume of reagents were considered in calculating net volume. Each bottle was calibrated by weighing before and after filling with water. As a precaution against implosion, each bottle was enclosed in a canvas bag during evacuation and until the gas sample was taken.

The bottles were attached within 5 minutes of evacuation to a hollow steel sampling probe that was inserted into the grain through 5/8-inch holes drilled at predetermined points in the walls of the granary. The holes were tightly corked between sampling periods. The probe consisted of 3-foot lengths of 1/8-inch steel pipe with threaded ends that were coupled together to the desired length, and was headed with a machined spear point near which was a ring of small holes to permit entry of the gas-air mixture. The other end of the probe was fitted with a copper stopcock. Before a sampling bottle was attached the probe was purged with a single draw of a rubber hand-bulb of about 80-ml. capacity. A 4-inch section of 0.5-mm. capillary tubing was fitted into the bottle inlet to give a gas entry rate of 30 - 40 seconds per liter. This rate gave better reproducibility of results than greater ones.

Samples were stored at room temperature until required, except that those allocated for differential analysis of MB in the presence of EB or CT were stored at 2 - 5° C. for at least 20 hours. The MB samples were swirled for a few seconds at three periods during their incubation.

### Hydrolysis

The time, space and equipment for hydrolyzing multiple samples of EB and CT by conventional refluxing for several hours after transfer of the samples to boiling flasks were considerably reduced by transferring the samples to ordinary 2-ounce medicine bottles fitted with metal screw caps. The sampling bottles were prechilled and the contents were quantitatively transferred, chilled *n*-propanol being used as the wash solvent. The screw caps were fitted with the polyethylene disks described in the previous section, each disk being used only once. The caps were tightened with pliers before the medicine bottles were placed in an air oven

to hydrolyze the contents at 100° C. for 3 hours. The hydrolysates were then transferred to 100-ml. beakers, hot water being used as the wash solvent.

### Argentometric Procedure

The argentometric procedure was adapted from those of other workers (9, 11, 12) as follows:

Neutralize the hydrolysate in tared 100-ml. beakers to a phenolphthalein end point by adding 1:1  $\text{HNO}_3$  dropwise. Add 6 ml. of the  $\text{HNO}_3$ , adjust the volume to approximately 30 ml. by adding distilled water and 1 ml. of gelatin solution and weighing each beaker on a trip balance to a net gain of 30 gm. Add 30 ml. of acetone and titrate amperometrically, using zero potential for  $\text{Cl}^-$  determinations and +0.15 volts for  $\text{Br}^-$ . Use the lowest galvanometer sensitivity commensurate with accurate results (1/10 - 1/20 of the full-scale sensitivity of 0.00635 micro-amperes per mm. was used), and a molarity of  $\text{AgNO}_3$  that is at least ten times that of the ionic halides present (7, Chap. 47).

Check the performance of the amperometric setup with the bromide and chloride standard solutions. Check the saturated  $\text{KNO}_3$  solution in the cell assembly (Figure 3) for chloride contamination caused by diffusion from the S.C.E. side of the H-cell and replace the nitrate as required. After use, immerse the titration cell arm of the  $\text{KNO}_3$ -agar bridge in a tube of saturated  $\text{KNO}_3$  solution.

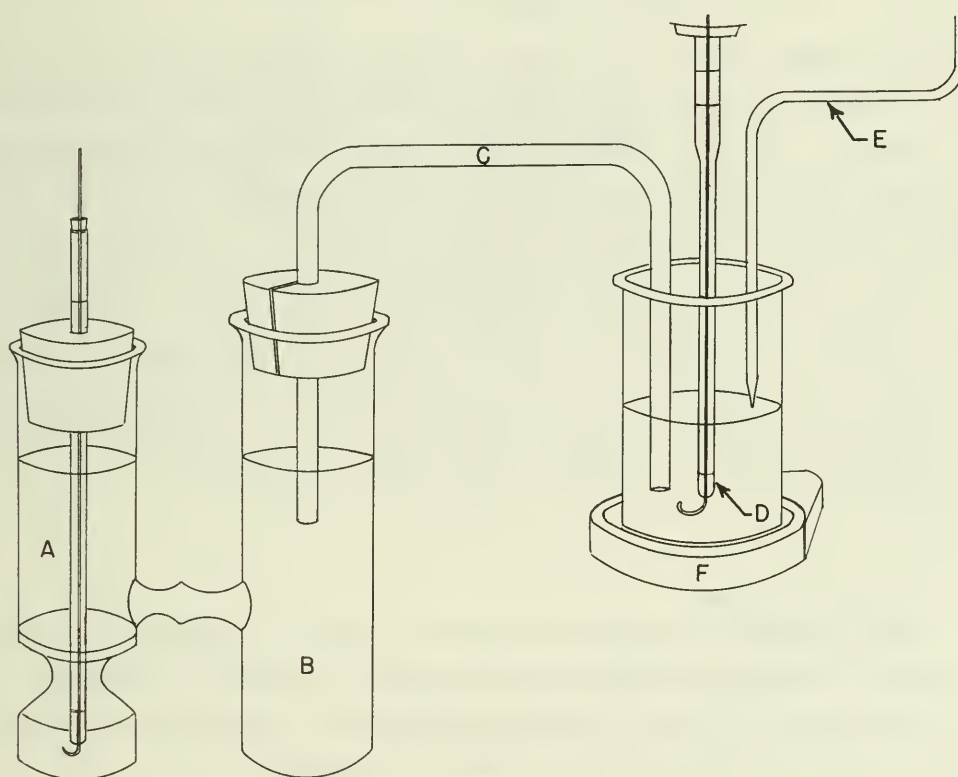


Figure 3.— Amperometric titration cell. A. Saturated calomel electrode used as a reference cell. B. Saturated  $\text{KNO}_3$ . C. Saturated  $\text{KNO}_3$  - 3 per cent agar bridge. D. Rotating platinum electrode. E. Offset tip of burette for introduction of titrant. F. Swing titration table.



### Determination of Ethylene Dibromide in Presence of Carbon Tetrachloride

The argentometric method (12) was unsatisfactory for  $\text{Br}^-$  in the presence of  $\text{Cl}^-$ , and accordingly the Kolthoff-Yutzy method (10) was adapted for determining EB in the presence of CT after alkaline hydrolysis of the gas sample. Preliminary tests of the Kolthoff-Yutzy method for that purpose based on the adaptation suggested by Stenger, Shrader and Beshgetoor (20) occasionally gave low and erratic recoveries. Traces of organic matter were suspected, and confirmed in testing the procedure as suggested by Winnek and Smith (22). Nearly quantitative (98.0 - 99.5 per cent) recoveries were obtained when the Winnek-Smith method for removing organic traces was combined with Willard and Heyn's (21) suggestion of adjusting the pH to 6.0 - 6.5 before adding the phosphate buffer and hypochlorite. The method finally used was as follows:

Add 2 ml. of 2 *N* NaOH and a glass bead or boiling chip to the hydrolysate in a 100-ml. beaker, place a cover glass on the beaker and evaporate to dryness. For smooth evaporation, use an overhead infra-red heater or place the beaker and contents in a heavy cast-aluminum cooking pot. If the residue is colored, add 10 ml. of water and 2 ml. of 30 per cent hydrogen peroxide and evaporate to dryness, using a cover glass. Rinse the sides of the beaker and cover glass, evaporate again and then heat the beaker in a muffle furnace at 450 - 500° C. for about 20 minutes. Cool, add 15 ml. of water and filter with washing through Whatman No. 40 filter paper. If the filtrate is not colorless, repeat the peroxide treatment and heating.

Redissolve the residue in 15 ml. of water, adjust the pH to approximately 6.0 with 6 *N* HCL, using methyl red as external indicator, and add 5 ml. of 20 per cent  $\text{NaH}_2\text{PO}_4$  solution. Add 3 ml. of saturated NaCl solution for amounts of bromide greater than 4 mg., but omit for lesser amounts (10). Add 4 ml. of the hypochlorite solution, and bring to a boil within 5 - 10 minutes. Cool slightly, rinse the beaker sides, and add 5 ml. of 50 per cent sodium formate. Boil gently for a few seconds, cool, dilute to about 35 ml. with water, and add 3 ml. of 30 per cent KI solution. If free iodine is liberated at this stage, discard the test. Add 1 drop of 1 *N* ammonium molybdate, 12 ml. of 6 *N*  $\text{H}_2\text{SO}_4$  and an excess of standard sodium thiosulfate solution. Back-titrate with potassium iodate solution, using the rotating platinum electrode, and subtract the blank.

### Fumigant Testing Chamber

The testing chamber (Figure 2) was used (a) to contain gas-air mixtures of which aliquots were taken to test the adequacy of sampling techniques, as well as to dilute fumigant with air in bioassay trials with insects and (b) to determine by the fall in gas concentration the amount of fumigant that was sorbed by wheat and flour (1). The main features of the testing chamber were as follows:

The cover had holes to accommodate rubber stoppers having outlets for

sampling tubes, a manometer, a thermometer, a tube connected to a vacuum pump, an inlet for introduction of fumigant, and wiring for a fan at the bottom of the drum. A molded neoprene gasket was cemented with a rubber-base gasket shellac to the inner surface of the concave rim of the cover. An 8-arm "spider" made of 1¼-inch angle iron was superimposed on the cover and was tightened on the lug-bolts with wing nuts, with a speed wrench having a slotted head machined to accommodate the wing nuts.

With the cover in position and all connections closed, the drum was considered to be sufficiently gastight when a pressure of 200 mm. of water (15 mm. Hg) less than the prevailing atmospheric pressure could be maintained for 10 minutes. At this pressure the fumigant gas was introduced through the gas-inlet tube by fitting snugly into the Tygon tubing (U. S. Stoneware Co., Akron 9, Ohio) the neck of a sealed ampoule containing a known weight of the fumigant liquid; the tip of the ampoule was cracked with pliers at a file-scratch mark. With the fan in continuous operation, the evaporation of the liquid was accelerated by heating the ampoule walls. When evaporation was visibly complete, the ampoule was detached and air was admitted to balance the gas-air mixture to atmospheric pressure, after which the tube was clamped off with a screw clamp. Gas samples were taken in evacuated bottles to compare the different sampling methods in efficiency and also to determine the concentration-time relationships in sorption experiments. Air was readmitted after each sampling in order to "zero" the internal pressure in the drum. The extent of the resultant dilution of the gas concentration in the drum was known at all times and was applied as a correction factor in the calculations. For small samples (200 - 300 ml.) taken at the outset of a given series the correction factor was negligible.

An alternative method of introducing MB involved use of a lecture-type cylinder of methyl bromide, 99.5 per cent pure (Olin Mathieson Co., East Rutherford, N.J.), in conjunction with a precalibrated rotameter (Fischer and Porter Co., Hatboro, Pa.) and a needle valve to control the rate of flow.

In sorption experiments, wheat or flour was placed in a large, ungreased desiccator. The knob of the desiccator cover was attached to a steel wire that passed through a tight Tygon plastic sleeve set in a rubber stopper in the cover of the drum. The drum was sealed and evacuated to a pressure of about 150 mm. of water less than the prevailing atmospheric pressure. After the fumigants were introduced, air was admitted to equalize the pressure. The gas-air mixture was continuously circulated by the fan shown in Figure 2, and a series of samples were taken at four intervals during a 1-hour period to confirm the constancy of the fumigant concentration. The desiccator cover was then raised by lifting the wire, and gas samples were taken at predetermined intervals. In any experiment, the effect of sorption of fumigant gases by the surfaces of the drum and desiccator were, for practical purposes, cancelled out on the assumption that the amount of gas thus captured was constant throughout the balance of the experiment.



Calculation of fumigant concentration in air involved the following:

A. Equivalents of 1 ml.  
of  $10^{-3}$  N AgNO<sub>3</sub>

0.0950 mg. MB  
0.0940 " EB  
0.0385 " CT  
0.0800 " B̄r

B. Equivalents of 1 ml.  
of  $10^{-3}$  N Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

0.0158 mg. MB  
0.0157 " EB  
—  
0.0133 " B̄r

To convert mg./l. to ppm (as volumes of gas per million volumes of air), use the gram-molecular volume relationship, namely, that a gm.-mol. wt. of gas has a volume of 22.4 l. at s.t.p. or of 24,450 ml. at 25° C. and 760 mm. of Hg. Thus, at the latter *t* and *p*, we have:

$$\text{ppm} = \frac{24,450 \times \text{mg.}}{\text{M.W.}}$$

The appropriate M. W. being substituted, the following conversion values apply at 25° C. and 760 mm. of Hg.:

1 mg. methyl bromide / 1. air = 257 ppm  
1 " ethylene dibromide / 1. " = 130 ppm  
1 " carbon tetrachloride / 1. " = 159 ppm

## ADEQUACY OF METHODS

Figure 1 shows how the reaction kinetics of MB clearly differ from those of EB, CT and EDC with respect to alkaline hydrolysis by monoethanolamine at 3° C. MB reacts quantitatively after 16 hours at 3° C. (although hydrolysis for 20 hours is recommended here for certainty), whereas EB, CT and EDC do not react even up to 48 hours. At 23° C. for 20 and 44 hours respectively, CT and EDC still did not react but EB reacted to the extent of 26.0 and 39.5 per cent. After sodium methoxide was added to the monoethanolamine, CT and EDC reacted quantitatively at 100° C. after 2½ hours. However, since CT and EDC both yield chloride upon hydrolysis at 100° C., it was not possible to distinguish between them by the methods described.

With amounts of fumigants to simulate some that were present in field tests (0.25 to 2.0 mg.), the mean percentage recovery from triplicate determinations of aliquots of standard solutions of MB, EB and CT, singly and in various admixtures, varied from 96.5 to 100.1 per cent, the coefficient of variation (C.V.) ranging from 0.8 to 3.3 per cent. The determination of amounts of gas above 1.5 mg. was generally reproducible to within  $\pm 2$  per cent. Occasionally, however, differences between replicates as large as 25 per cent were found in field samples. These were considered to be due to variations in distribution of the individual gases before equilibrium had become established in the fumigated grain (1).

The oxidative (10, 21) and argentometric (9, 11) methods of recovering bromide were compared. In the range 0.08 - 1.0 mg. of bromide, the percentage recovery of KBr from triplicate determinations was 98.4 - 99.5 with C.V. of 0.7 - 2.1 per cent by the oxidative method, and 97.0 - 99.2 with C.V. of 1.1 - 4.1 per cent by the argentometric method. The oxidative method was adequate for determining 0.01 mg. of bromide (95 per cent recovery with C.V. of 4.8 per cent) and surpassed the argentometric method both in sensitivity and in specificity for  $\text{Br}^-$  in the presence of  $\text{Cl}^-$ . However, it was more time-consuming and was mainly used for determining EB in the presence of CT or EDC.

The oxidative method coupled with amperometric titration gave a sharp end point for  $\text{Br}^-$  (as  $\text{BrO}_3^-$ ) with no interference from proportionately large amounts of CT. The determination of the iodine-thiosulphate end point by back titration with potassium iodate was more readily reproducible and more sensitive by the rotating platinum electrode than by the conventional use of starch indicator. It was important to have enough  $\text{H}_2\text{SO}_4$  solution in the titration cell since inadequate acidity decreased the speed at which the reaction was completed.

Screw-cap medicine bottles were durable and economical as reaction vessels, and eliminated considerable space and equipment in refluxing large numbers of samples. They were of particular value in studies of reaction rate.

Where MB is the sole fumigant gas under investigation, and where MB concentrations allow use of  $\frac{1}{2}$ -pint bottles for obtaining small samples, the hydrolysis and the amperometric titration both may be done directly in the sampling bottle, without the transfer step.

The hydrolysis of EB with monoethanolamine in screw-cap bottles at  $100^\circ\text{C}$ . yielded  $\text{Br}^-$  corresponding to two bromine atoms. This is in agreement with the results of Sinclair and Crandall (19).

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