The Absorption of 1,2-Dibromoethane by Oranges and by Materials Used in Their Fumigation

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The absorption of 1,2-dibromoethane (ethylene dibromide) by materials used in fumigation chambers and the absorption and loss of ethylene dibromide by oranges was investigated using glass equipment. Copper, iron, and galvanized iron did not absorb, but iron and zinc oxides absorbed ethylene dibromide. Wood, rubber, petroleum grease, and concrete absorbed appreciable quantities. Of the paints tested, the polyurethane and epoxy resin types gave the lowest absorption and highest resistance. Of the plastic films, polyethylene gave the lowest absorption. Increasing quantities of ethylene dibromide were lost from oranges with increase in time of standing in air after fumigation. Both uptake and subsequent loss increased with time of storage of oranges before fumigation. The results partially explain the variable recoveries of ethylene dibromide after fumigation in chambers containing absorbing materials.

In experimental fumigation of oranges with ethylene dibromide at Gosford, N.S.W., to kill the eggs and larvae of the Queensland fruit fly (*Strumeta tryoni*), recoveries of the substance from the fruit were low and variable. To provide data which would assist in obtaining more reproducible absorption by the fruit, measurements of absorption by both oranges and materials used in fumigation chambers were made in an inert glass vessel. When this vessel contained no test material, a measured quantity of ethylene dibromide could be recovered quantitatively from the air 2 hours after introduction.

General Procedure

The glass fumigation apparatus is shown in Figure 1.

The quantity of ethylene dibromide required for fumigation was in excess of what could normally be held up in a glass tube of uniform bore by capillary action. Hence the micropipet was constructed so that the top of the capillary tube was of narrower bore, sufficiently small to hold up the column of ethylene dibromide after filling (Figure 2). The point of exit of the very fine capillary from the side of the micropipet was ground flat (*L*) so that plastic tubing could be butted to this surface and used for sucking in ethylene dibromide. The micropipet used in these experiments delivered 99.6 mg. of ethylene dibromide.

The sample to be tested for absorption of ethylene dibromide was placed inside the reaction flask, and the apparatus, shown in Figure 1, was assembled without the micropipet and shaft. The gas sampling bulb was evacuated to not more than 0.05 mm. Hg before assembly. The materials were placed in the reaction flask to give, as far as possible, free access of ethylene dibromide vapor. To reduce absorption of ethylene dibromide, a mixture of glycerol, dextrin, and

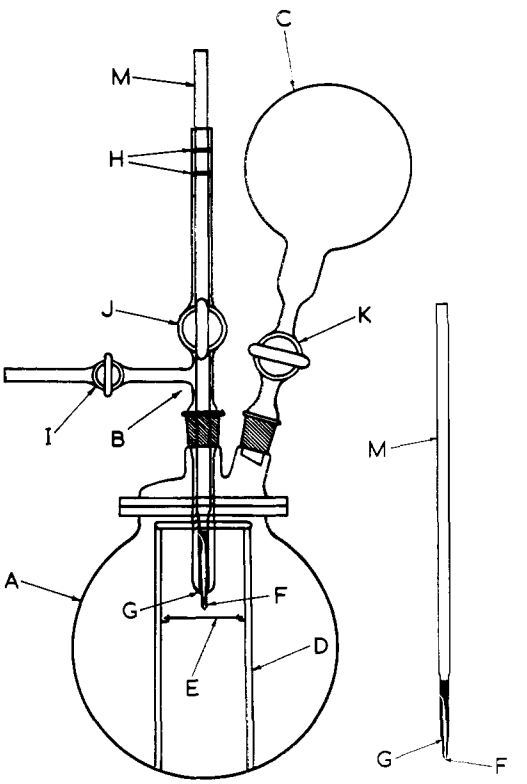

Figure 1. Fumigation apparatus

A, 5-liter reaction flask; *B*, sample introduction device with stopcocks *I* and *J* and standard cone; *C*, 1-liter gas sampling bulb with stopcock *K* and standard cone; *D*, glass tripod; *E*, asbestos paper circle held up by glass hooks attached to glass tripod; *F*, micropipet; *G*, carborundum powder-lapped surfaces giving seal between micropipet and end of sample introduction device; *H*, "O" rings separated by glass spacers attached to outer tube by araldite; *M*, glass tubing joined to micropipet to give airtight seal with "O" rings

D-mannitol (5) was used as lubricant where possible. However, the stopcock on the gas sampling bulb was lubricated with a silicone grease as the bulb was required to hold a vacuum for two hours.

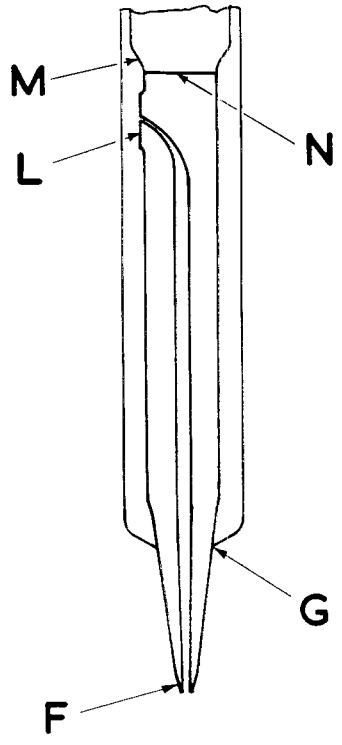

Figure 2. Lower part of sample introduction device with micropipet (enlarged)

F, micropipet; G, lapped surfaces giving seal; L, ground surface; M, glass tubing joined to solid glass top of the micropipet at N

With stopcock *J* closed, the pressure in the reaction flask was reduced by about 200 mm. Hg through stopcock *I*, which was then closed. The micropipet was filled with ethylene dibromide (purified by fractional distillation) and pushed through the "O" rings until its shaft engaged the "O" rings with the tip still clear of stopcock *J*. The shaft of the micropipet was smeared with the lubricant mixture to facilitate this movement. Stopcock *J* was opened and the micropipet was pushed down until the two lapped surfaces engaged.

On opening stopcock *I*, air entered and forced the ethylene dibromide out of the micropipet onto the circle of asbestos paper. Stopcock *I* was closed until the ethylene dibromide had evaporated from the asbestos paper during a period of 5 to 6 minutes and was then opened for 2 minutes to allow entering air to remove any residual ethylene dibromide from the micropipet.

The micropipet was withdrawn from the apparatus by reversing the procedure used for its introduction. Subsequently, stopcock *I* was opened and air rushed in,

Table I. Absorption of Ethylene Dibromide by Various Materials

(99.6 mg. introduced)

Material	Quantity or Surface Area Exposed	Ethylene Dibromide Absorbed, Mg.
Iron, clean	648 sq. cm.	0.9
rusty	648 sq. cm.	4.9, 3.9
Galvanized iron	1800 sq. cm.	0.7
Aluminum	324 sq. cm.	0.4, −0.6[a]
Copper	648 sq. cm.	−2.4
Ferric oxide	44 grams	88.7
Zinc oxide	44 grams	17.2, 23.0
Water	141 ml.; 22.9 sq. cm.	23.5, 23.5
Saturated NaCl solution	127 ml.; 22.9 sq. cm.	0.9, 0.9
Wood, Douglas fir (*Pseudotsuga taxifolia*)	198 sq. cm.	15.3, 14.9
blue gum (*Eucalyptus saligna*)	195 sq. cm.	28.1, 24.2
Rubber	178 sq. cm.	71.8, 73.8
Petroleum grease	173 sq. cm.	12.6, 13.5
Concrete	230 sq. cm.	27.2, 34.0
P.V.C.[b], clear (0.004 inch)	600 sq. cm.	57.0
opaque (0.004 inch)	600 sq. cm.	71.7
sun resistant (0.006 inch)	600 sq. cm.	76.0, 77.0
Polyethylene (0.004 inch)	600 sq. cm.	31.8
black (0.006 inch)	600 sq. cm.	34.3, 33.8
Pliofilm (0.0025 inch)	600 sq. cm.	43.7

[a] Ethylene dibromide absorbed = 99.6 − observed estimate of ethylene dibromide recovered from air; negative values occur if recovery exceeds 99.6.
[b] Polyvinyl chloride.

Table II. Performance of Various Paints

(99.6 mg. of ethylene dibromide introduced)

		Absorption			Resistance	
Sample	Type	Weight fumigated, grams	Mean thickness on panels, inches × 10^3	Ethylene dibromide absorbed, mg.	Exposed to vapor	Immersed portion
A	Chlorinated rubber	2.94	1.8	13.6 (4)[a]	Dissolved in patches	Dissolved
B	Vinyl plastic	3.38	2.6	4.1 (3)	Unaffected	Dissolved
C	Phenolic varnish	1.01	1.2	−0.4 (3)	Unaffected	Unaffected
D	Phenolic varnish	0.91	0.9	0.1 (4)	Unaffected	Unaffected (developed greyish color on exposure to air
E	Epoxy	2.84	2.2	0.4 (3)	Unaffected[b]	Discolored with bubbling[b]
F	Polyurethane	2.26	1.8	−0.1 (2)	Unaffected	Unaffected
G	Polyurethane	5.74	4.7	1.3 (2)	Unaffected	Unaffected
H	Polyurethane	6.95	5.2	0.9 (2)	Unaffected	Unaffected (yellowed slightly on exposure to air)
I	Polyurethane	5.20	4.4	0.0 (3)	Unaffected	Unaffected (yellowed slightly on exposure to air)
J	Epoxy[c]	1.45	1.9	1.8 (2)	Unaffected	Severe crinkling and lifting (film still crinkled but re-adhered on exposure to air)
K	Epoxy	1.76	1.5	1.5 (2)	Unaffected	Unaffected
L	Polyurethane	1.66	1.8	1.8 (4)	Film blistered	Film lifted
M	Epoxy	4.34	3.5	0.6 (2)	Breakdown of bottom coat	Breakdown of bottom coat

[a] Number of determinations averaged in mean. Std. error of mean ethylene dibromide absorptions are ±0.77, ±0.63, ±0.55, on 25 degrees of freedom for means of 2, 3, and 4, respectively.
[b] This was achieved by using a ground glass surface. If plain glass was used, there was crinkling and lifting.
[c] This was an aluminum pigmented paint. The presence of the epoxy resin probably shields the aluminum from attack.

helping to disperse the ethylene dibromide vapor throughout the vessel. When atmospheric pressure was reached, stopcock I was closed. The sample was left in the fumigation vessel at 20° C. for 2 hours after the injection of ethylene dibromide.

After fumigation, stopcock K of the gas sampling bulb was opened for 15 seconds and the air sample taken was analyzed by the method of Kennett (*2*). The quantity of ethylene dibromide recovered from the air after fumigation was calculated by multiplying the quantity found in the sampling bulb by the factor $\frac{V_a + V_c - v}{V_c}$,

where V_a is the volume of the reaction flask,

V_c is the volume of the gas sampling bulb, and

v is the volume of the test material.

For an empty vessel, air recoveries of ethylene dibromide after 2 hours ranged from 99.1 to 100.5 mg., the mean being 99.7 mg. As loss in the all-glass system was negligible, the quantity of ethylene dibromide absorbed could be calculated by subtracting that remaining in the air from that originally introduced.

After the air sample had been taken in the fumigation of an orange, the apparatus was quickly dismantled and the orange removed and placed in a petri dish at 20° C. for a specific period of time. The orange was then cut into quarters and placed in a 1-liter, flat-bottomed flask. Ethylene dibromide was then determined by the method of Kennett and Huelin (*3*). Loss after fumigation was given by the difference between the quantity absorbed and that found subsequently by analysis of the orange.

Table III. Uptake and Loss of Ethylene Dibromide by Oranges

(99.6 mg. introduced)

Storage at 7.5° C., Days	Weight of Orange at Picking, Grams	Weight Loss before Fumigation, Grams	Standing Time at 20° C. after Fumigation, Min.	Ethylene Dibromide Absorbed by Orange, Mg.	Ethylene Dibromide Found by Analysis, Mg.	Loss after Fumigation, Mg.
			Washington Navel Oranges Picked May 15, 1961			
1	151.0	0.8	30	28.4	28.3	0.1
2	152.3	1.5	0	30.8	29.7	1.1
3	152.4	2.2	15	32.3	30.7	1.6
4	150.9	2.4	60	25.9	22.1	3.8
8	150.4	5.7	60	31.5	27.3	4.2
9	150.7	4.4	15	25.6	24.1	1.5
11	150.6	6.7	30	25.9	22.1	3.8
11	150.7	7.9	0	30.2	29.5	0.7
15	152.8	8.7	15	30.2	28.1	2.1
17	151.8	9.3	60	35.0	29.3	5.7
17	152.0	5.9	0	33.6	30.7	2.9
18	152.9	8.2	30	34.0	29.5	4.5
22	151.9	12.1	0	35.5	31.2	4.3
23	151.0	11.5	30	38.9	32.1	6.8
24	151.2	12.9	60	38.4	28.7	9.7
25	150.4	13.3	15	36.5	29.4	7.1
			Washington Navel Oranges Picked July 3, 1961			
1	152.9	0.6	0	31.2	29.8	1.4
2	151.1	1.6	30	32.1	26.7	5.4
3	154.9	2.1	15	30.7	27.1	3.6
4	153.8	2.2	60	31.2	26.5	4.7
9	154.8	3.3	60	36.3	29.8	6.5
9	154.4	3.5	15	33.0	28.0	5.0
10	151.2	6.6	30	36.3	30.6	5.7
11	152.8	6.0	0	35.8	33.6	2.2
15	152.2	4.4	15	34.6	30.2	4.4
16	151.3	6.9	60	40.3	32.7	7.6
17	150.1	6.4	0	35.0	28.1	6.9
18	152.4	8.4	30	38.9	31.5	7.4
22	150.5	10.2	30	38.5	32.1	6.4
23	154.4	13.0	0	37.5	34.2	3.3
24	153.1	8.9	60	36.6	28.9	7.7
25	154.4	12.6	15	34.6	30.9	3.7
			Valencia Oranges Picked October 30, 1961			
1	151.4	0.8	0	21.9	21.4	0.5
2	152.0	1.1	60	20.0	20.0	0.0
3	154.7	1.2	30	19.5	18.9	0.6
4	150.4	1.5	15	16.5	16.7	−0.2
8	153.6	2.6	60	20.0	18.8	1.2
9	151.2	2.7	30	20.9	20.0	0.9
10	152.2	2.6	15	20.0	19.5	0.5
11	151.9	1.9	0	16.6	15.5	1.1
15	152.9	2.7	30	17.2	...	...
16	150.6	4.3	15	21.1	21.7	−0.6
17	151.2	7.1	0	23.1	24.5	−1.4
18	150.0	4.2	60	21.6	21.7	−0.1
22	153.2	4.5	15	24.0	23.3	0.7
23	153.9	4.7	0	25.0	21.0	4.0
24	154.3	4.5	60	24.5	22.9	1.6
25	154.2	4.7	30	22.1	20.8	1.3

Absorption of Ethylene Dibromide by Various Materials

Various materials which had been or might be used in fumigation, including several types of paints and plastic films, were tested for their absorption of ethylene dibromide. They were cleaned of grease and other contaminants before the absorption tests. The results, with the exception of those for paints, are given in Table I.

The metals tested did not absorb appreciable quantities of ethylene dibromide (Table I). Although no corrosive effect of ethylene dibromide on aluminum was noticed after a 2-hour fumigation, its use is not recommended, for Grierson and Hayward (*1*) reported serious corrosion by liquid ethylene dibromide in 24 hours at 20° C. The oxides of iron and zinc, however, absorbed ethylene dibromide in appreciable quantities.

After fumigation, ferric oxide was placed in a distillation flask and ethylene dibromide determined by the method of Kennett and Huelin (*3*). Inorganic bromide was determined in the aqueous extract of the residue. Of the 88.7 mg. absorbed by 44 grams of ferric oxide, 78.4 mg. were recovered as unchanged ethylene dibromide and only 0.9 mg. as inorganic bromide. Probably most of the inorganic bromide of decomposition was recovered, but some of the volatile ethylene dibromide may have been lost in removing the oxide for analysis. Hence there was little chemical change in the absorbed ethylene dibromide.

Similar results were obtained after absorption on zinc oxide. After the first absorption (17.2 mg.), only 0.1 mg. was found as inorganic bromide. No figure for ethylene dibromide could be obtained by the method of Kennett and Huelin (*3*) because of severe frothing, which was not controlled by the silicone antifoam recommended. After the second absorption (23.0 mg.), the ethylene dibromide was removed from the zinc oxide, heated to 100° C. in a stream of nitrogen, absorbed in ethanol cooled in solid carbon dioxide, and determined by the method of Kennett (*2*). The recovery of ethylene dibromide was 10.5 mg.

In experimental fumigation at Gosford, galvanized iron tanks were sealed by lids fitting into water-filled channels.

Table IV. Loss of Ethylene Dibromide from Oranges in Relation to Time of Storage before Fumigation

Date Picked	Mean Uptake, Mg. (n' = 16)[a]	Mean Loss from 4 Fruits (Mg.) after Storage Time (Weeks) 0	1	2	3
May 1961	32.0	1.65	2.55	3.80	6.98
July 1961	35.2	3.78	4.85	6.58	5.28
Oct. 1961	20.9	0.22	0.92	−0.52[b]	1.90

[a] n' denotes sample size.
[b] n' = 3 fruits; standing times 0, 15, and 60 minutes. Std. error of mean loss over four fruits: 0.44 on 17 degrees of freedom. Changes in mean loss per day of storage were homogeneous over experiments and standing times after fumigation and gave an over-all value of 0.130 mg. per day with std. error ± 0.026 based on 34 degrees of freedom.

Table V. Loss of Ethylene Dibromide from Oranges in Relation to Time of Standing after Fumigation

Date Picked	Mean Uptake, Mg. (n' = 16)[a]	Mean Loss from 4 Fruits (Mg.), Standing Time after Fumigation (Min.) 0	15	30	60
May 1961	32.0	2.25	3.08	3.80	5.85
July 1961	35.2	3.45	4.18	6.22	6.62
Oct. 1961	20.9	1.05	0.10	0.93[b]	0.68

[a] n' denotes sample size.
[b] n' = 3 fruits. Std. error of mean loss over 4 fruits: ±0.44 on 17 degrees of freedom. Change in mean losses were 0.060, 0.055, and 0.001 mg. per min. for May, July, and October, respectively (over-all mean, 0.039).

Absorption of ethylene dibromide by water (Table I) was probably a source of loss. However, this difficulty could be overcome by the use of a saturated sodium chloride solution. All other materials gave appreciable absorption and could give rise to serious loss. The materials which could cause a serious loss of ethylene dibromide in fumigation chambers should be kept to a minimum. Absorption could be reduced by covering with a resistant and nonabsorbing paint.

Performance of Various Paints

Nine glass panels, each 9 cm. square, were sprayed on one side with the paint to be tested, and two samples, each of four panels, were chosen for each paint. The number of coats of paint applied to the panels was as recommended by the manufacturer for use in ethylene dibromide fumigation chambers. After the specified curing time, each sample was fumigated for 2 hours. The surface area of paint exposed was 324 square cm. for each sample.

Besides absorption tests, the paints were also subjected to resistance tests on glass strips, according to the method described by Grierson and Hayward (*1*). These tests were carried out at 20° C.

The results of both the absorption and resistance tests are shown in Table II. Sample F is an undercoat for use with samples G, H, and I, all of which were applied to panels already coated with sample F. Sample M is also a two-coat system, having a bituminous-type epoxy resin as the undercoat and a pigmented epoxy resin as the top coat. The other paints were applied without undercoat.

In absorption tests, paints A and B were significantly different from each other and from the rest of the paints tested (at P = 0.05). Paints C to M were not significantly different from each other, and their mean did not represent a significant absorption. On absorption tests alone, paints A and B could be rejected.

If the resistance tests are taken into consideration, paints L and M would also be rejected. The other paints (C to K) appeared sufficiently inert for application to ethylene dibromide fumigation chambers.

Absorption and Loss of Ethylene Dibromide by Individual Oranges

Preliminary measurements of absorption and subsequent loss over short periods were made with Valencia oranges in 1960. When the measurements were repeated with oranges of the same picking, the period of storage before fumigation appeared to increase both uptake and subsequent loss. This effect was investigated systematically in the following year.

Washington Navel oranges from one tree were picked in May 1961 and graded by weight. To reduce variability due to weight, sufficient fruit for an experiment was selected in the range of 150 to 155 grams. The oranges were double-wrapped in diphenyl wraps (to reduce rotting) and stored at 7.5° C. Before fumigation of each orange, the selected fruit was allowed to come to the required temperature overnight and then removed from the wrap. Each orange was weighed again before fumigation, as the increased permeability to ethylene dibromide after storage might be associated with loss of water.

The design of the experiment allowed for time of storage before fumigation and time of standing in air after fumigation. As only one fruit could be dealt with on any day, one was taken for each of 4 days of each week during a period of four successive weeks. In this way, time of storage by weeks and days of the week was controlled by making them correspond to the rows and columns, respectively, of a Latin square of order four—the times of standing after fumigation (0, 15, 30, and 60 minutes) being treatments. The individual fruits for the various positions in the Latin square were allocated at random. Similar experiments were carried out with Washington Navel oranges in July 1961 and Valencia oranges in October 1961. The results are given in Table III.

Analysis of the data showed that uptake was linear on storage time in weeks and significant at P = 0.05 or better in all experiments. The effect of increase in uptake with increase in storage time has also been summarized by using regression of uptake on time of storage, and over all experiments this gave a rate of increase of 0.285 ± 0.045 mg. per day per fruit (the std. error having 44 degrees of freedom). The actual uptakes in the individual experiments differed greatly, the means being 32.0, 35.2 and 20.9 mg. (with std. error ±0.61 on 18 degrees of freedom) for the May and July Navel and October Valencia experiments, respectively. Lindgren and Sinclair (*4*) found that Navel oranges absorbed more ethylene dibromide than Valencia oranges.

Study of uptake in relation to weight loss by the method of serial correlation showed that, after eliminating the linear time trends in each experiment, there was no correlation significant at P = 0.05. However, during storage both weight loss and uptake of ethylene dibromide appeared to change more rapidly in Washington Navel than in Valencia oranges.

Examination of the data for loss subsequent to fumigation showed that loss increased with time of storage before fumigation. This effect was significant at P = 0.05 or better in each experiment but there was some differential effect among experiments. Mean values are shown in Table IV. During storage, the permeability of the rind to ethylene dibromide apparently increases, allowing more rapid uptake during fumigation and more rapid subsequent loss.

Losses of ethylene dibromide increased with time of standing after fumigation in the May and July Navel experiments (significant at P = 0.01). Loss from Valencia oranges did not change significantly with time of standing. Apparently in these oranges the ethylene dibromide remaining after the initial

loss, which occurred as a result of handling even for "zero" standing time, was held more firmly and lost comparatively slowly. Losses for the various standing times are shown in Table V.

Losses of ethylene dibromide in these experiments were more likely caused by evaporation rather than by chemical decomposition. Loss from the short-stored Valencia oranges of October 1961 was negligible immediately after fumigation (Tables III and IV). The small loss in other experiments was probably due to evaporation of ethylene dibromide near the surface during the unavoidable handling in preparation for analysis. Sinclair, Lindgren, and Forbes (*6*) found ethylene dibromide to be quite stable and nonreactive with orange tissues for 10 days at room temperature.

Discussion

The data given here help to explain the low and variable recoveries of ethylene dibromide obtained in experimental fumigation of oranges. They also suggest means of increasing these recoveries and reducing their variation. Absorption by the walls and equipment of the chamber can be reduced by suitable choice of materials and by covering absorbing materials with nonabsorbent and stable paints. As a result of the variation in uptake and loss by the oranges themselves, any procedure can still give a range of concentration in the fumigated fruit. But, if other sources of variation are reduced to a minimum, there is more chance of keeping the ethylene dibromide concentration between the upper limit to avoid fruit injury and the lower limit for fruit fly sterilization.

In the authors' experiments, each orange was fumigated separately in nonabsorbing equipment. Greater variation in uptake would be expected in large-scale fumigation where air movement and concentration of ethylene dibromide may not be uniform throughout the chamber. Increase in uptake after storage is of theoretical interest but probably of little practical importance in fumigation, as increased uptake is balanced by greater subsequent loss, and there may be much less difference in concentration in the fruit after loss has continued for several days.

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