Residues of Methyl Bromide in Fumigated Grapefruit Determined by a Rapid, Headspace Assay

Jimmie R. King,* Clarence A. Benschoter, and Arthur K. Burditt, Jr.

A rapid headspace assay for methyl bromide (MB) in grapefruit has been developed and used to determine the effect of fumigant dose and storage time on the residues of MB resulting from fumigation. Salient steps of the assay are the blending of a 50-g grapefruit sample with water and assay of the headspace by use of a gas chromatograph equipped with a gas sample injection valve and a nickel-63 electron capture detector. The sensitivity (twice the background for samples of unfumigated grapefruit) was ~0.002 mg/kg. The partitioning of MB into the headspace was determined by using samples of unfumigated grapefruit fortified with MB at various concentrations.

At the present time ethylene dibromide (EDB) is widely used to fumigate various fruits and vegetables as a quarantine treatment. The recent Rebuttable Presumption Against Registration (RPAR) by the Environmental Protection Agency (EPA) (1977) has resulted in an increased effort to find a suitable substitute for EDB. A possible substitute is methyl bromide (MB) (Benschoter, 1979). Because MB is more volatile than EDB, the residues of MB decrease more rapidly than EDB residues.

The analysis of fumigant residues has recently been reviewed by Malone (1971) and by Berck (1975). Early techniques usually separated MB by aeration and then used hydrolysis and titration of the liberated inorganic bromide for quantitation.

Extensive studies of MB residues in a wide variety of fumigated commodities were made by Scudamore and Heuser (1970) and Heuser and Scudamore (1969). Acetone–water (5:1) and acetonitrile–water (5:1) solvent systems were used for extraction of MB from the commodities. The extracts, after drying, were assayed by using gas–liquid chromatography with the following detectors: flame ionization (FID), electron capture (ECD), and β ionization. Sensitivities for various fumigants assayed by this method were generally better than 0.1 mg/kg. Grapefruit samples have a high water content which makes the drying step of the above method more time consuming. Futhermore, a more sensitive method was needed to obtain residues in fumigation and storage studies simulating commercial practices. Therefore, a headspace assay was developed which not only achieved sensitivities of 0.002 mg/kg but was rapid, required the use of no solvent except water for blending, and utilized widely available gas chromatographic equipment.

The method has been successfully adapted to different commodities (Hartsell, 1980) such as plums, bell peppers, nectarines, grapes, pistachio nuts, and cactus pears. At this laboratory the method has also been adapted to assay tomatoes, mangos, and avocados (King, 1980).

EXPERIMENTAL SECTION

In a typical assay a 50-g sample of grapefruit and 50 mL of distilled water were put into a 500-mL Eberbach blending container. The container was quickly sealed with a Teflon-lined screw lid which had been modified by use of a 0.25-in. Swagelok union to incorporate a silicone rubber septum. The sample was blended for 1 min on the low speed of a two-speed Waring blender (No. 70105). After ~20 minutes, 5 mL of headspace gas was removed with a 10-mL syringe (fitted with a stopcock) and injected into a 0.5-mL loop of the gas injection valve of a Hewlett-Packard 5730 gas chromatograph equipped with a linear nickel-63 electron capture detector. A glass column (6-mm o.d., 4-mm i.d. × 1-m length) packed with 100–120-mesh Proapak Q (Waters Associates) was used.

The GLC conditions were as follows: detector temperature, 300 °C; oven temperature, 140 °C; injection valve temperature, 100 °C; carrier gas, argon–5% methane at 60 mL/min flow.

Typical chromatograms obtained from grapefruit spiked with MB are shown in Figure 1. The sensitivity of the method depends on the conditioning of the column and the quality of distilled water used. Interfering impurities in the water were removed when necessary by charcoal absorption as previously described by King et al. (1980) to obtain a background interference of 0.001 mg/kg or less for control samples.

Two methods were tested to prepare standards and found to be equivalent. In both methods unfumigated fruit and water were placed in a blending container as previously described. In the first method, a solution of MB in benzene was prepared and sealed in a 30-mL vial with a Teflon-lined silicone rubber septum. An appropriate amount of this solution was removed by using a Precision Sampling gas-tight syringe (Series A-2) having a push-button valve. The benzene solution was then injected into a piece of fruit in the blender jar; the jar was quickly sealed, the fruit blended, and headspace samples were taken as described above.

In the second method, the fruit and water were first sealed in a blender jar and an appropriate sample of gaseous MB at ambient pressure and temperature was injected through the septum by means of a gas-tight syringe. The fruit was then blended and headspace samples were taken. Pure methyl bromide gas (1.5 lb; Dow Chemical Co., Midland, MI 48640) was used to prepare standards containing 1 ppm (which required 12.9 μL at 25 °C) or more. Dilutions of methyl bromide in air, usually 1 or 2%, were prepared for concentrations between 0.05 and 1.0 ppm.

Twelve boxes of "Marsh" seedless grapefruit (load factor of 80%) were fumigated for 2 h with a dose of 64 mg/L MB at 24 ± 1 °C in a 0.8-m^3 fumigation chamber as described by Benschoter (1979). The chamber was aerated ~15 min with forced ventilation, and the boxes of fruit were removed and stored at 24 ± 1 °C. A fruit was taken from each box after various intervals of time and assayed for MB.

For determination of the effect of the dose level of fumigant on the residue occurring in the fruit, grapefruit

Subtropical Horticulture Research Unit, U.S. Department of Agriculture, Science and Education Administration, Agricultural Research, Miami, Florida 33158.

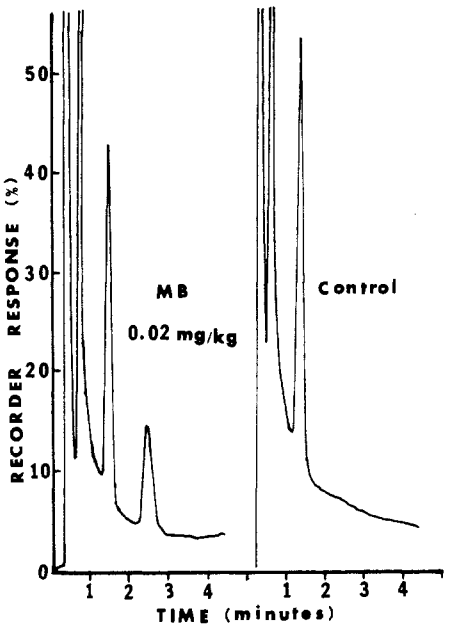

Figure 1. Typical gas chromatograms obtained from unfumigated grapefruit fortified to contain 0.02 mg/kg methyl bromide and an unfortified control. A 0.5-mL headspace sample was injected onto a 1-m glass column (4-mm i.d.) containing 100–120-mesh Porapak Q. A Hewlett-Packard linear electron capture detector was used at an attenuation of 8×.

were fumigated with 16, 32, and 64 g/m^3 of MB as described above except that three boxes of fruit were used per fumigation to give a load factor of 20%.

RESULTS AND DISCUSSION

If methyl bromide formed an ideal solution in the blended water and fruit mixed phase, the vapor pressure, and hence the concentration of MB in the gaseous phase, would be proportional to the total MB present, according to Henry's law when applied to a constant-volume system (Daniels and Alberty, 1956). Therefore, the fraction of MB partitioning into the vapor phase should be independent of the amount of MB present at constant temperature and pressure. So that the actual partitioning could be tested, samples of unfumigated grapefruit were fortified with MB at various levels in quadruplicate, and the headspace gas was assayed as described. The results (50.0 ± 1.5, 49.2 ± 1.4, 50.1 ± 0.4, and 50.1 ± 2.9% MB in the headspace for 20, 10, 5, and 1 mg/kg, respectively) indicate that partitioning is essentially concentration independent in the range measured. Although the partitioning of MB was reproducible during each fumigation and storage study, the partitioning did vary in studies conducted several months apart due, likely, to differences in age, storage time before fumigation, size, and water content of the fruit. Therefore, each time samples were assayed for residues, unfumigated control samples from the same lot of fruit were fortified to contain MB at levels that would bracket all the unknowns and the partition coefficients determined.

By use of the previously described method, three samples each of 50 g of grapefruit, 50 g of water, and mixtures of 45 g of water and 5 g of Mazola corn oil were fortified with MB at the 1 mg/kg level, and the headspace was assayed to determine the effect of water and oil content on the partitioning of MB. Values of 59.6 ± 1.4, 50.5 ± 1.1, and 23.8 ± 0.6% MB in the headspace were found for the grapefruit, water, and mixture of water and corn oil, respectively. The grapefruit had been stored at 10 °C for 12 weeks and therefore the water content may have been low. Water alone (100 mL) absorbs about as much MB as water plus grapefruit (50 mL + 50 g). The presence of oil greatly increases the fraction of MB partitioning into the liquid phase. The 5 g of oil was equivalent to 20% oil content which is much greater than that of most fruits and vegetables.

Table I. Methyl Bromide Residues in Grapefruit after Fumigation and Storage at Ambient Temperature[a]

time, h	MB residue, mg/kg[b]
0	33.5 ± 1.2
1	26.9 ± 3.2
3	19.7 ± 1.7
5	13.5 ± 1.0
24	2.80 ± 0.42
48	0.52 ± 0.07

[a] Fruit fumigated for 2 h with methyl bromide at a dose of 64 mg/L, aerated 15 min with an exhaust blower, and stored at 24 ± 1 °C. [b] Mean ± SD. Sensitivity (twice the background) was ~0.002 mg/kg. Four samples, each from a different box, were analyzed separately.

Table II. Methyl Bromide Residues in Grapefruit following Fumigation at Various Dose Levels[a]

time, h	MB dosage, g/m^3		
	16	32	64
2	3.94 ± 0.17	8.99 ± 0.42	18.8 ± 1.5
24	0.45 ± 0.04	0.99 ± 0.06	2.75 ± 0.28
48	0.15 ± 0.01	0.23 ± 0.03	0.60 ± 0.07

[a] The mean ± standard deviation of MB residue, expressed as mg/kg, was determined by using three replicates (one fruit from each of three boxes) for each value. The fruit, contained in commercial fiberboard cartons, was fumigated 2 h, aerated 15 min with an exhaust blower, and stored at 22–24 °C.

Residues determined in grapefruit from a 12-box load fumigated with MB at a 64 g/m^3 dose level are shown in Table I. The observed rapid decrease in residue of MB is probably due primarily to desorption plus a small amount of hydrolysis to yield inorganic bromide. There is evidence that a small amount of MB is actually converted to methyl chloride (Dennis et al., 1972) which would probably involve hydrolysis as an intermediate reaction step. For the data at 2 h after fumigation, a plot of residue vs. dosage is linear (correlation coefficient = 0.99997, slope = 0.309, and intercept = −0.965 by linear regression), but the residue is not proportional to the dosage because the intercept is nonzero.

Interpolating the data in Table I for residue at 2 h gives a value of 22.4 mg/kg for an 80% load factor, which is only slightly more than the 18.8 mg/kg obtained with a 20% load factor.

Linear regression was used to fit the data of Table I to

$$t = m \ln C + b \quad (1)$$

where t is the time in hours, ln C is the natural logarithm of the MB residue concentration expressed as mg/kg, m is the slope, and b is the intercept. Values of −11.8, 38.7, and −0.992 were obtained for m, b, and the correlation coefficient, respectively. Thus, ln C as a function of time is fairly linear, which indicates that the rate of loss of MB is proportional to the amount present at any time, i.e.

$$dc/dt = kC \quad (2)$$

where k is a constant equal to $1/m$. Equation 1 can also be written in the exponential form

$$C = C_0 \exp(-kt) \quad (3)$$

where C_0 is the initial concentration of residue, k is a

constant depending on the rate of loss of residue, and C and t are as previously defined.

Applying a linear regression to the data in Table II for MB residues at 2 h after fumigation gives a correlation coefficient of 0.99997, which indicates excellent linearity of residue vs. applied dose. However, the line obtained does not pass through the origin, and consequently the residue is only approximately proportional to the applied dose.

LITERATURE CITED

Benschoter, C. A. *J. Econ. Entomol.* **1979**, *72*, 401.
Berck, B. *J. Chromatogr. Sci.* **1975**, *13*, 256.
Daniels, F.; Alberty, R. A. "Physical Chemistry"; Wiley: New York, 1956; pp 199, 200.
Dennis, N. M.; Eason, G.; Gillenwater, H. B. *J. Econ. Entomol.* **1972**, *65*, 1753.
Environmental Protection Agency *Fed. Regist.* **1977**, *42* (240), 63134–63161.
Hartsell, P. L., USDA-SEA-AR, Stored-Products Insects Research Laboratory, Fresno, CA 93727, personal communication, 1980.
Heuser, S. G.; Scudamore, K. A. *J. Sci. Food Agric.* **1969**, *20*, 566.
King, J. R., USDA-SEA-AR, Subtropical Horticulture Research Station, Miami, FL 33158, unpublished data, 1980.
King, J. R.; von Windeguth, D. L.; Burditt, A. K., Jr. *J. Agric. Food Chem.* **1980**, *28*, 1049.
Malone, B. *Residue Rev.* **1971**, *38*, 21.
Scudamore, K. A.; Heuser, S. G. *Pestic. Sci.* **1970**, *1*, 14.

Received for review January 27, 1981. Accepted June 9, 1981.

Photohydrolysis of Methyl Bromide and Chloropicrin

Charles E. Castro* and Nao O. Belser

The rate of hydrolysis of methyl bromide and chloropicrin can be markedly enhanced by light. An ~7-fold increase in the rate for methyl bromide results from irradiation with a small pen-ray UV lamp (k_λ = 2.0×10^{-6} s^{-1}). At least 99.6% of the reaction proceeds quantitatively to methanol, bromide ion, and protons. A trace of methane (<0.4%) is produced. The lack of any significant oxidation product of methanol or bromide ion along with the very small yield of methane is interpreted to indicate the reaction is the result of the direct hydrolysis of photoexcited methyl bromide. Chloropicrin is decomposed even more rapidly by light ($k_\lambda = 1.4 \times 10^{-4}$ s^{-1}). In neutral aqueous solution without irradiation, no hydrolysis is detected in 10 days. With irradiation, a 10^{-3} M solution is dissipated in hours. The products of the aqueous photo reaction in air are carbon dioxide, chloride ion, nitrate ion, and protons. Nitrite ion can be detected in small amounts (~2–3%) when the reaction is conducted under argon. The nitrite to nitrate conversion is *not* fast enough to accommodate the kinetics under aerobic conditions.

Methyl bromide mixed with chloropicrin is a widely used combination for preplant soil sterilization. While the volatility of these halides suggests that significant amounts of them would escape the soil matrix, very little is known of their actual environmental chemistry.

In the course of our general studies of the microbiological and chemical transformations that haloorganic biocides may undergo [for summaries, cf. Castro (1977) and Castro et al. (1978)], we have learned that the hydrolysis of methyl bromide and chloropicrin can be markedly enhanced by light. The results show that photohydrolysis can be an important means of environmental detoxification for substances of this class.

EXPERIMENTAL SECTION

Materials and Methods. Chloropicrin, Eastman White Label, and methyl bromide, Matheson, were used without purification. Flame ionization gas chromatographic analysis of methyl bromide, chloropicrin, methanol, and methane was accomplished with a Varian 2440 gas chromatograph by direct injection of the aqueous solution and gas phase. The columns employed were all $^1/_8$ in. i.d. Porapak P columns of varying length: methyl bromide and methanol (18 in.; 160 °C), methane (6 ft; 100 °C), and chloropicrin (6 in.; 120 °C). Except for methane, quantitation of these substances was accomplished by sequential injection of reaction mixture and known amounts of standard. Calibration curves constructed from analysis of solutions of known composition of one of the above and standard were identical with those obtained by sequential injection of the components. The sequential injection procedure was then used to eliminate the complexities associated with the reaction of the standards during photolysis. The standards employed were 1-butanol, for chloropicrin, and acetone, for methyl bromide and methanol. Methane was quantitated by spiking with known amounts of methane. Reproducibility was ±7% in all cases. Chloride and bromide ions were determined by direct potentiometry employing Orion specific ion electrodes and a calomel reference electrode (Castro and Bartnicki, 1965; Castro and Belser, 1966). Nitrate ion was assayed by nitrating toluene and determining the amount of nitrotoluene in toluene by the absorption spectrum of the molecular complex (Bhatty and Townshend, 1971). Nitrite was determined in two ways: by using the above procedure, with a prior oxidation to nitrate and by diazotization and coupling of sulfanilic acid with *N*-(1-naphthyl)ethylenediamine (Feinsilver and Oberst, 1953).

Carbon dioxide was qualitatively established as the only gaseous product by mass spectrometric analysis of the gas produced by a photolysis of chloropicrin in water run in an argon atmosphere. In addition, a run with $Cl_3C^{14}NO_2$ (the synthesis will be reported elsewhere) yielded $BaC^{14}O_3$

Department of Nematology, University of California, Riverside, Riverside, California 92521.

0021-8561/81/1429-1005$01.25/0