# Residues of Methyl Bromide and Inorganic Bromide in Fumigated Produce

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Several cultivars of sweet cherry, apple, nashi, and plum and red and green capsicums were fumigated with 40–45 g/m$^3$ methyl bromide for 2 h at 17 °C followed by 2 h of ventilation at 17 °C as a quarantine treatment for the export of Australian fresh fruit to Japan. After fumigation and ventilation, residues of methyl bromide decreased to less than the detection limit of 0.002 ppm while in storage at 1 °C. Residues of methyl bromide in most fruit took 12 or more days at 1 °C to reach this point except cherries and Sugar plums, which took 5–6 days. Inorganic bromide residues were less than the Japanese maximum residues limits of 20 ppm (60 ppm for capsicums) in all fruit. Of the fruit tested, cherries and Sugar plums have the greatest potential, with respect to both methyl bromide residues and value, for air freight shipment following fumigation with methyl bromide and storage at 1 °C.

## INTRODUCTION

Fruit exported from Australia to several overseas countries and that transported interstate must be free from infestations of Queensland fruit fly (*Bactrocera tryoni* Froggatt), Mediterranean fruit fly (*Ceratitis capitata* Wiedemann), and codling moth (*Cydia pomonella* L.). If fruit is to be exported to these regions, a quarantine treatment must be applied. At present, approved treatments against these insects are fumigation with methyl bromide (MeBr) or ethylene dibromide (EDB), cold storage, heat treatment, and dipping in insecticides (Commonwealth Department of Health, 1980; USDA, 1985). EDB has been banned in many countries including Japan (W. Horrigan, Australian Quarantine Inspection Service, Canberra, personal communication, 1991) and will effectively be banned in New Zealand in January 1994 (Export Inspection Circular Memorandum 1992/62, Australian Quarantine Inspection Service, Canberra).

Currently, at this laboratory, tests are underway to provide data to the Japanese Ministry of Agriculture, Forestry and Fisheries (MAFF) and the New Zealand Government confirming the efficacy of MeBr fumigation against one or all of these insects. In addition to efficacy data, MAFF must be supplied with details of MeBr and inorganic bromide (InBr) residues in fruit immediately after fumigation, and during and following the likely shipping time to Japan (All-Japan Union of Plant Quarantine Associations, 1979). The lowest likely carriage temperature for fruit during shipment to Japan is 1 °C and shipping time is about 21 days.

The proposed quarantine disinfestation schedule for the treatment of Australian-grown fruit against Queensland fruit fly, Mediterranean fruit fly, and codling moth is 40 g/m$^3$ MeBr at 17 °C for 2 h followed by ventilation for 2 h. This schedule is based on studies in progress at this laboratory (Jessup, unpublished data, 1993).

On the advice of the Bureau of Rural Resources, Chemical Residues Section, Barton, ACT (J. Walker, personal communication, 1993) no methyl bromide maximum residue limit (MRL) has been set by the Japanese authorities, so the objective is to show nil residue (i.e., less than the detectable limit) in the fruit by the time it arrives in Japan. The Japanese MRL for inorganic bromide in all fruit tested in the experiments reported here is 20 ppm, except for capsicums which is 60 ppm.

## MATERIALS AND METHODS

Upon arrival at the Gosford laboratory, fruit were stored at 1 °C until required for experimentation. A sample of unfumigated fruit was stored at −15 °C for later analysis of InBr.

**Fruit.** Fruit were purchased from the Flemington Produce Markets in Sydney, NSW, and stored at 1 °C until required for fumigation. Apple cultivars studied were Red Democrat, Golden Delicious, and Red Delicious. Cherry cultivars were American Bing and Ron's Seedling. Plum cultivars were Santa Rosa, Friar, and Sugar (Prune D'Agen). Nashi cultivars were Nijisseiki and Hosui. The capsicum cultivar was Green Giant, and green and red fruit were fumigated and analyzed separately to test for maturity differences in residues.

**Fumigation.** One to four cartons of each cultivar (depending on carton volume) was equilibrated overnight to 17 °C in 0.283-m$^3$ stainless steel gas chambers (Rigney and Wild, 1975). Liquid MeBr was bled into a long closed-off copper tube to evaporate. The gaseous MeBr was then allowed to flow through a graduated needle value into the gas chamber for a given time (in seconds) to give the nominated MeBr concentration in the chamber. Fruit were fumigated with a carton of apples to bring the chamber loading factor to 35%.

Using a gastight syringe (Rigney and Wild, 1975), samples of chamber atmosphere were taken at 15, 30, 60, 90, and 120 min after fumigant injection to monitor the MeBr dose received. These samples were analyzed using a Gowmac GC fited with a flame ionization detector. Conditions: column, 1 m × 3 mm stainless steel column packed with 100–120-mesh Poropak Q; injector temperature, 170 °C; column temperature, 135 °C; carrier gas, high-purity nitrogen at 30 mL/min; fuel gases, hydrogen at 30 mL/min and air at 300 mL/min. Standard fumigant samples were 0.18% MeBr in nitrogen.

After fumigant injection, the chamber's internal fan was turned on. Following the 2-h fumigation, the chamber lid was removed and the fan allowed to run for 30 min. Ventilation proceeded passively with the fan off for a further 90 min.

**Storage and Sampling.** Following fumigation and ventilation, fruit were placed in storage at 1 °C to simulate the lowest likely carriage temperature for exported fruit. Residues would be expected to be at their maximum under these conditions. A data logger monitored fruit core temperature to confirm adherence to a storage temperature of 1 ± 0.5 °C for the duration of storage.

Samples of fruit of each cultivar were taken at various intervals from day 0 or day 1 after fumigation, and subsequent storage at 1 °C, and analyzed for MeBr. A sample of fruit of each cultivar from the last day of sampling for MeBr residues were frozen to −15 °C for InBr analysis.

**MeBr Analysis.** Each fruit in the sample to be analyzed was removed from cold storage and immediately dissected and the

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seed (if large) removed. The skin and pulp were then weighed and blended at high speed for 1 min in a gastight 1260-mL blender goblet. To reduce MeBr loss, fruit (still at 1 °C) was dissected and contained in the goblet within 30 s. The mixture was allowed to stand for at least 5 min, and a sample of head space was withdrawn through a silicon septum in the goblet lid into a gastight syringe and injected into a GC.

MeBr residues were determined by head-space analysis using the method of King *et al.* (1981). In our experiment analytical conditions varied slightly in that we used a Varian 1400 GC with electron capture detector and a 1.8 m × 3 mm stainless steel column packed with 100–120-mesh Poropak Q. Detector temperature was 230 °C; column temperature, 140 °C; injector temperature, 170 °C; and carrier gas, high-purity nitrogen at a flow rate of 35 mL/min. Retention time for MeBr was 3 min 15 s, and the analytical detection limit was 0.002 ppm.

MeBr standards were prepared each day of analysis using a calibrated mixture of MeBr in nitrogen. Standards were prepared on unfumigated fruit homogenate of the variety being tested that day to minimize partitioning differences between standards and test fruit. This method was validated by testing for recovery of MeBr (from the calibrated MeBr mixture) from spiked unfumigated fruit homogenate. Recovery was 96 ± 2% depending on the fruit variety used.

**InBr Analysis.** Samples of fruit of each cultivar were analyzed for InBr following the methods of Gnanasunderam and Triggs (1983) and Austin and Phillips (1985) with a bromide selective electrode (BrSE). Our method differed slightly in that the standard curve was constructed on unfumigated fruit supernatant (prepared in the same way as the fumigated sample fruit) rather than on water. This method overcame any problems due to background interference that may have been imparted by the fruit.

Three 25-g samples were taken from each homogenate and were processed individually. An ionic strength adjuster (2 mL of 5 M sodium nitrate solution) was added and the sample diluted to 100 mL with distilled water. After mixing, the sample was allowed to stand for at least 15 min and then centrifuged at 1000*g* for 10 min. The BrSE measured the potential of a 50-mL aliquot of the sample supernatant. InBr concentration in the supernatant ($C_S$) was calculated from the standard curve. InBr concentration in parts per million in the fruit ($C_F$) was calculated from the equation

$$C_F = (C_S \times 100)/W$$

where $W$ is the weight (grams) of fruit in the sample. The analytical detection limit for InBr was 0.3 ppm. Recovery of InBr from preparations spiked with KBr was 98 ± 2% depending on the fruit variety tested.

**Replication.** On each day of analysis 3 apples, 3 nashi, 3 capsicums, 3 samples of 10 plums or 3 samples of 20 cherries were analyzed for MeBr and InBr residues. All fruit of each variety were homogenized together, and 3 samples of the head space (for MeBr analysis) or fruit supernatant (for InBr analysis) of each fruit variety were analyzed. Three replicate fumigations were done on each fruit variety. In addition, Red Delicious apples fumigated in 1990 were from Bathurst on the Central Tablelands of New South Wales, and those fumigated in 1991 were from Batlow on the Southern Highlands of New South Wales. This replication-in-time was done to test residue variations in fruit grown under different conditions.

## RESULTS AND DISCUSSION

**MeBr Residues.** There were considerable differences in MeBr residues over time at 1 °C between fruit species and cultivars. Residues in Red Delicious apples (Table 1) and both nashi cultivars (Table 4) decreased to less than the detection limit (0.002 ppm) in 16–18 days, whereas those in Red Democrat and Golden Delicious apples (Table 1) took 12 days. Residues in Granny Smith apples fumigated with 32 g/m³ MeBr for 2 h at 17 or 10 °C and then stored at 1.5 °C were nondetectable (<0.05 ppm) after 7 days (Rippon *et al.*, 1982). MeBr residues in both cherry cultivars (Table 2) and in Sugar plums (Table 3) took only 6 days to reach the detection limit, capsicums (Table 5) took about 7 days, but Santa Rosa and Friar plums (Table 3) took 10 or 11 days. Tebbets *et al.* (1983) showed that MeBr residues in four plum cultivars did not differ in their rates of decrease over time. The cultivars they studied included Santa Rosa and Friar, and they were all of the Japanese type. The Sugar plum is a European type which may be the reason for MeBr residue differences between plum cultivars.

Replicate fumigations of different fruit from the same shipment showed no differences in MeBr residues or in rates of residue decline over time at 1 °C that may have been due to variability in fumigation procedures. This

**Table 1. Methyl Bromide (MeBr) Residues in Apples Fumigated at 17 °C for 2 h with 40–42 g/m³ Methyl Bromide, Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| time at 1 °C, days | mean MeBr concn,[a] ppm | | | |
|---|---|---|---|---|
| | Red Democrat | Red Delicious 1990 | Red Delicious 1991 | Golden Delicious |
| 1 | | 3.80 | 6.0 | |
| 2 | 2.04 | 2.085 | 3.2 | 0.52 |
| 4 | 0.39 | 2.07 | 2.07 | 0.21 |
| 5 | | | 0.88 | |
| 6 | 0.046 | 0.409 | 0.507 | 0.003 |
| 8 | 0.012 | 0.043 | 0.115 | 0.002 |
| 10 | 0.002 | 0.017 | 0.021 | 0.002 |
| 12 | nd | 0.016 | 0.009 | nd |
| 14 | nd | 0.006 | 0.004 | nd |
| 16 | nd | 0.004 | 0.004 | nd |
| 18 | | nd | nd | |
| 20 | | nd | nd | |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

**Table 2. Methyl Bromide (MeBr) Residues in Sweet Cherries Fumigated at 17 °C for 2 h with 39 g/m³ Methyl Bromide, Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| time at 1 °C, days | mean MeBr concn,[a] ppm | |
|---|---|---|
| | American Bing | Ron's Seedling |
| 1 | 11.0 | 4.6 |
| 2 | 4.59 | 3.54 |
| 3 | 0.479 | 0.165 |
| 4 | 0.002 | 0.004 |
| 5 | 0.002 | 0.002 |
| 6 | nd | nd |
| 7 | nd | nd |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

**Table 3. Methyl Bromide (MeBr) Residues in Plums Fumigated at 17 °C for 2 h with 38–40 g/m³ Methyl Bromide, Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| time at 1 °C, days | mean MeBr concn,[a] ppm | | |
|---|---|---|---|
| | Santa Rosa | Friar | Sugar |
| 1 | | 3.785 | 3.805 |
| 2 | 2.255 | 3.21 | 2.04 |
| 3 | 0.91 | 0.71 | 0.08 |
| 4 | 0.36 | 0.358 | 0.008 |
| 5 | 0.316 | 0.137 | 0.005 |
| 6 | 0.016 | 0.03 | nd |
| 7 | 0.011 | | nd |
| 8 | 0.004 | 0.003 | nd |
| 9 | 0.003 | nd | |
| 10 | nd | nd | |
| 11 | nd | nd | |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

**Table 4. Methyl Bromide (MeBr) Residues in Nashi Fumigated at 17 °C for 2 h with 41 g/m³ Methyl Bromide, Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| time at 1 °C, days | mean MeBr concn,[a] ppm | |
|---|---|---|
| | Nijisseiki | Hosui |
| 0 | 12.14 | 6.8 |
| 1 | 2.3 | 2.6 |
| 3 | 0.22 | 0.48 |
| 5 | 0.05 | 0.21 |
| 7 | 0.02 | 0.12 |
| 14 | 0.002 | 0.005 |
| 16 | nd | nd |
| 21 | nd | nd |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

**Table 5. Methyl Bromide (MeBr) Residues in Capsicums (Green Giant) Fumigated at 17 °C for 2 h with 39–40 g/m³ Methyl Bromide, Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| time at 1 °C, days | mean MeBr concn,[a] ppm | |
|---|---|---|
| | green fruit | red fruit |
| 0 | 24.2 | 28.3 |
| 1 | 1.83 | 7.9 |
| 3 | 0.31 | 2.7 |
| 5 | 0.015 | 0.005 |
| 7 | nd | nd |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

**Table 6. Inorganic Bromide (InBr) Residues in Fruit Fumigated at 17 °C for 2 h with Methyl Bromide (MeBr), Ventilated for 2 h at 17 °C, and Then Stored at 1 °C**

| fruit cultivar | MeBr dose, g/m³ | time at 1 °C, days | mean InBr concn,[a] ppm | | |
|---|---|---|---|---|---|
| | | | unfum fruit | fum fruit | increase in InBr |
| apple | | | | | |
| Red Democrat | 42 | 14 | 0.78 | 4.9 | 4.1 |
| Golden Delicious | 42 | 14 | 0.68 | 5.41 | 4.7 |
| Red Delicious | 40 | 20 | 0.87 | 4.9 | 4.0 |
| cherry | | | | | |
| American Bing | 39 | 7 | 0.71 | 10.6 | 9.9 |
| Ron's Seedling | 39 | 7 | 0.42 | 10.4 | 10.0 |
| plum | | | | | |
| Santa Rosa | 38 | 11 | 0.49 | 3.45 | 3.0 |
| Friar | 40 | 12 | 0.99 | 4.15 | 3.2 |
| Sugar | 40 | 7 | 0.55 | 7.00 | 6.4 |
| nashi | | | | | |
| Nijisseiki | 41 | 21 | 0.79 | 1.85 | 1.1 |
| Hosui | 41 | 21 | 1.25 | 2.38 | 1.1 |
| capsicum | | | | | |
| green | 43 | 7 | 2.09 | 24.0 | 21.9 |
| red | 40 | 7 | 2.60 | 30.1 | 27.5 |

[a] Each mean was obtained from three samples analyzed from each of three replicate fumigations.

was done for cherries (Table 3) and Santa Rosa and Sugar plums (Table 3).

Fumigation of fruit from different shipments of Red Delicious apples (Table 1) showed the number of days in storage at 1 °C to reach <0.002 ppm was 18 days for the 1990 fruit and 15 days for the 1990 fruit. The rate of decline in MeBr residues was 1.3 ($R^2$ = 0.94) and 2.0 ppm of MeBr/$\log_e$ (days at 1 °C) ($R^2$ = 0.88), respectively.

**InBr Residues (Table 6).** Background InBr levels (i.e., those occurring prior to fumigation with MeBr) were similar in all fruit (ranging from 0.40 to 0.99 ppm) except in Hosui nashi (1.25 ppm) and capsicums (2.01 ppm). Nonfumigated California-grown cherries contained 4.1 (American Bing) and 3.0 ppm (Schmidt) InBr (Dumas, 1973). The background level may be due to natural occurrence of bromides in fruit or in the particular soil type of the growing area or due to soil or air contamination with bromides.

Final InBr concentrations were less than the Japanese maximum residue limits for inorganic bromides (20 ppm for most fruit and 60 ppm for capsicums). Capsicums took up InBr to a greater extent than other fruits tested—21.9 ppm in green fruit and 27.5 ppm in red fruit. Getzendaner and Richardson (1966) and Seo *et al.* (1970) obtained InBr residues of 20 ppm.

The increase in InBr concentrations due to fumigation was similar for each fruit within species. Both cherries cultivars took up ≈10 ppm of InBr. Nashi cultivars took up 1.1 ppm. Apple cultivars took up ≈4.5 ppm of InBr. These apple results are in general agreement with results obtained by Singh *et al.* (1976) and Rippon *et al.* (1982) from fumigated Granny Smith apples. The exception was that Sugar plums (small European type plums) took up ≈6 ppm of InBr and the other (larger Japanese) plums took up only ≈3 ppm. The four Japanese type plums fumigated by Tebbets *et al.* (1983) contained 4.8–5.6 ppm of InBr, but the background concentration of InBr in nonfumigated plums was not given. Plums fumigated by Getzendaner and Richardson (1966) contained 3–4 ppm of InBr after storage.

## CONCLUSION

A dose of 40–45 g/m³ MeBr for 2 h at 17 °C followed by 2 h of ventilation at 17 °C is proposed as a quarantine treatment against Queensland fruit fly, Mediterranean fruit fly, and codling moth. Following storage at the lowest likely carriage temperature of 1 °C, residues of MeBr will decrease to less than the detection limit of 0.002 ppm over time in storage. Depending on the type of fruit, up to 18 days at 1 °C could be required to reach this level. In such cases fruit that is air-freighted to arrive at its destination shortly after fumigation will have high MeBr residues. A solution would be to store fruit at higher temperatures for 3–4 days to ensure volatilization of MeBr vapors prior to cold storage, but problems with fruit quality may occur with perishable produce such as plums. Apples may be suited to these conditions, but because of their low value to volume ratio and their relatively long storage life, they would probably not be economically feasible to freight by air. Of the fruit tested, cherries and Sugar plums have the greatest feasibility, with respect to both MeBr residues and value, to be air-freighted.

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