free aldehydes and ketones in plant tissue, though this application was not pursued for compounds other than acetaldehyde.

ACKNOWLEDGMENT

The authors thank Clay Reece for aid in obtaining spectra and Wray Winterlin for his helpful comments concerning the method.

LITERATURE CITED

Bowman, M. C., Beroza, M., Acree, F., Jr., *Anal. Chem.* **33**, 1053 (1961).
Craven, E. C., Jowitt, H., Ward, W. R., *J. Appl. Chem.* **12**, 526 (1962).
Giang, P. A., Smith, F. F., *J. Agr. Food Chem.* **4**, 623 (1956).
Hadden, N. G., *Garden Illus.* **58**, 255 (1936).
Kallio, H., Linko, R. R., Kaitaranta, J., *J. Chromatogr.* **65**, 355 (1972).
Karabatsos, G. J., Shapiro, B. L., Vane, F. M., Flemming, J. S., Ratka, J. S., *J. Amer. Chem. Soc.* **85**, 2784 (1963).
Kimura, Y., Miller, V. L., *J. Agr. Food Chem.* **12**, 249 (1964).
Mays, D. L., Born, G. S., Christian, J. E., *Bull. Environ. Contam. Toxicol.* **3**, 366 (1968).

Received for review October 26, 1972. Accepted January 24, 1973. This work was supported, in part, by U. S. Public Health Service Training Grant ES 00125.

Inorganic and Organic Bromide Residues in Foodstuffs Fumigated with Methyl Bromide and Ethylene Dibromide at Low Temperatures

Theodore Dumas

Fruit that was fumigated with methyl bromide over a range of temperatures had residues that diminished as the temperatures were lowered. When ethylene dibromide was used at a lower temperature (13°), the fumigant was highly adsorbed and retained for many days when stored at this temperature. Also, the inorganic bromide determination by ashing and bromate titration did not account for all the bromide resulting from ethylene dibromide present. Study of the distribution showed bromide in fruits was highest in the seed and skin and lowest in the pulp.

For the eradication of insects in harvested fruits, fumigants such as methyl bromide and ethylene dibromide are often used. The fixed residues formed as a result of chemical reaction between the fumigant and the tissue of the fruit are particularly important because they may tend to reduce quality of fruit or present a health hazard to the consumer. To avoid hazard to the consumer, residue limits are set by health authorities. When foodstuffs are treated with methyl bromide, some of the fumigant may react with the products to form inorganic bromide residue and the remaining fumigant is readily desorbed on aeration. However, with ethylene dibromide desorption is slow, especially at lower temperatures, and unreacted fumigant may remain for long periods after treatment (Heuser and Freeman, 1955). For this reason it is necessary to know the residual amount and the rate of desorption. Ethylene dibromide is very toxic and residues have been shown to affect the fertility of bulls (Amir and Volcani, 1965) and to cause biochemical changes in organs of chicks and rats that may affect growth, sexual development, and fertility (Alumot *et al.*, 1968; Nachtomi *et al.*, 1968). Also, it will affect the formation or release of hormones in hens (Alumot and Mandel, 1969).

Residue levels will vary with the temperature at which fumigation treatments are carried out. Many successful fumigations of various commodities have been conducted at temperatures down to 4° (30°F). With a decrease in temperature, the dosage of fumigant has to be increased to kill the insects and hence sorption of the gas by the commodity is increased. The question now arises as to whether the dosage of fumigant applied to foodstuffs at lower temperatures will lead to an increase of residues. This paper reports the levels of residues occurring in certain fruits and walnuts fumigated with methyl bromide and ethylene dibromide over a range of temperatures. Since early results showed that the "total bromide" method of determination ashing by Neufeld (1936), oxidation, and titration by Kolthoff and Yutzy (1937) failed to account for all of the bromide resulting from ethylene dibromide, the quantitative aspect of its conversion to inorganic bromide had to be investigated. The accuracy of the method used for the inorganic bromide determination was of ±10%.

Research Institute, Canada Agriculture, University Sub Post Office, London, Ontario N6A 3KO.

MATERIALS AND METHODS

The kinds of fruit used in this investigation were peaches from the United States and Ontario, cherries (Bing and Schmidt varieties) from the United States, apples (Delicious variety from British Columbia, MacIntosh from Ontario), and plums and walnuts from the United States. They were treated with methyl bromide and ethylene dibromide at temperatures ranging from −4 to 25° (25° to 77°F) in 525-l. chambers described by Monro and Buckland (1956). The required dosage of methyl bromide was introduced as a gas from a pressure cylinder into the evacuated dispensers of the above mentioned chambers and then released into the main component of the chambers. Ethylene dibromide as liquid was placed in a shallow glass dish and evaporated by heat from a small hot plate in the chamber. A fan was employed to ensure uniform distribution of the fumigant. Dosage of fumigant and duration of the fumigation were selected according to the product treated.

Preparation of Fruits for Analysis. The fruits were purchased in local markets during the time that each was at its peak in the marketing season. As far as possible, boxes of fruit were left packed in normal shipping containers and placed in the chamber to simulate commercial conditions. The load for fruits was 40–50 lb and for walnuts was 5 lb per treatment. Following fumigation, indi-

Table I. Bromide Residues Found in Pulp and Skin of Fruits Fumigated with Methyl Bromide at Various Temperatures. Exposure at Normal Atmospheric Pressure (760 mm) for 2 hr

Temperature, °C	Dosage methyl bromide, mg/l.	Residues as bromide, ppm				
		Peach		Cherry		
		California	Ontario	California (Bing)	California (Schmidt)	Plum
25	0 (control)	0.3	0.2	4.1	3.0	0.3
25	16	3.5	4.9	11.4	6.7	1.9
25	24	4.5				
25	32	5.5				
21	24	4.0	4.2	11.0	6.1	2.6
21	32	4.6				
21	40	5.3				
15	32	3.5	3.2	8.2	5.9	2.9
15	40	4.0				
15	48	4.3				
10	40	2.7	2.3	7.2	4.6	
10	48	3.2	3.9	8.2		3.1
10	64	3.8				
4	48	1.9	2.4	4.2	3.5	
4	64	2.7	4.7	5.3	4.7	2.2
4	80	3.5				

vidual fruit samples were removed and sectioned so that various parts (*i.e.*, skin, pulp, pit, and seed) could be analyzed separately. For analysis of the edible portion (skin and pulp), sample sizes of 20 g for peaches, 40–50 g for plums, and 10 g for cherries were taken. The bromide residue also was determined for different parts of the fruits separately as follows. Peach: skin, 15–30 g; outer pulp, 50–60 g; inner pulp, 50–60 g; pit wall (hard woody exterior), 30–40 g; pit, 2–4 g. Plum: skin, 8–10 g; pulp, 40–60 g; pit (combined sample of wall and pit), 10–20 g. Cherry: skin and edible pulp combined, 10–11 g.

Methods of Analysis. Fumigant concentrations in the free air space were analyzed by gas chromatography to determine the concentration of the fumigant during the exposure time. The instrument used was the Burrell K7 with a flame ionization detector and 30% didecyl phthalate liquid phase on Chromosorb W 60–80 mesh. Column was stainless steel, ⅛ in. in diameter, 8 ft long, temperature was 115° and retention time was 7 min. Sensitivity was for 2 μg full-scale pen deflection on a 10 in. 1 mV recorder. Carrier gas was nitrogen, flow 40 cm^3/min. The organic bromide was extracted from fruits by steam distillation and analyzed by the method previously described by Dumas (1962).

Methyl Bromide Gas in Apples. At certain times after fumigation, two whole apples were placed in a 1-l. jar, and next to the apples was a 5-ml beaker containing 2 ml of 0.1 *N* sodium hydroxide in methanol; then the jar was held for 24 hr. The methyl bromide given off as a vapor by the fruit was absorbed, converted to sodium bromide, and titrated with silver ions by the coulometric method described by Dumas and Latimer (1962).

Inorganic Bromide Residue. Portions of fruits and nuts fumigated either with methyl bromide or ethylene dibromide were ashed (Neufeld, 1936), oxidized to bromate, and titrated iodometrically by the methods of Kolthoff and Yutzy (1937) and Meulen (1931). For these analyses a double amount of conversion reagent (sodium hydroxide) was used in the first ashing, and then for the other ashings the amount was reduced to ½ and 1/10, respectively. The results of the analyses are the average of three repeats for the total inorganic bromide.

Ethylene Dibromide Vapors in Fruits. The method of Kennett and Huelin (1957) was modified for the analysis of ethylene dibromide by using coulometric titration (Dumas and Latimer, 1962). Modification was desirable to eliminate the need for oxidation to bromate before the

Table II. Distribution of Residue in Peaches and Plums (ppm) Fumigated with Methyl Bromide at Different Dosages and Temperatures for 2 hr

		Dosage methyl bromide, mg/l.		
		0	16	64
		Temperature, °C		
	Fruit part	25	25	4
Peaches	Skin	4.3	10.4	3.4
Peaches	Pulp, outside half	2.0	1.8	1.9
Peaches	Pulp, inside half	2.0	5.2	2.3
Peaches	Pit wall	1.3	4.1	1.1
Peaches	Seed	15.0	47.0	15.7
Plums	Skin	4.7	7.1	8.6
Plums	Pulp	1.0	1.9	1.8
Plums	Pit	2.2	5.2	6.2

Table III. Residues of Ethylene Dibromide and Inorganic Bromide in Apples[a] after Fumigation with Ethylene Dibromide 12 mg/l. and 24 mg/l. for 4 hr at 13°

Concentration, mg/l.	Time after fumigation, days	Ethylene dibromide residue, ppm	Inorganic bromide[b] residue, ppm
12	1	36	
12	2	14	
12	3	4.5	3.5
12	6	1.2	
12	12		2.7
24	1	75	
24	2	40	
24	3	13	5.4
24	6	1.6	
Control nonfumigated apples		0	0.1

[a] Apples (Delicious variety) held in cold storage 10 months and kept at 13° after treatment. [b] This includes some bromide resulting from the ethylene dibromide.

Table IV. Residue of Ethylene Dibromide and Inorganic Bromide in Newly Harvested MacIntosh Apples after Fumigation with Ethylene Dibromide 12 mg/l. for 4 hr at 13°

Concentration, mg/l.	Time after fumigation, days	Storage temperature, °C	Ethylene dibromide, ppm	Inorganic[a] bromide residue, ppm
12	1	13	23	1.7
12	2	13	3.6	2.2
12	4	13	1.2	
12	6	13	0.17	2.4
12	9	13	0.14	
12	12	13	0.23	1.9
12	2	25	0.2	
12	3	25	0.15	
12	5	25	0	
Control nonfumigated apples			0	0.8

[a] This includes some bromide resulting from the ethylene dibromide.

Table V. Inorganic Bromide Residue in Shelled and "in-Shell" Walnuts after Exposure to Methyl Bromide at Various Concentrations for 24 hr

	Fumigation temperature, °C	CH_3Br dosage, mg/l.	Inorganic bromide residue, ppm
Without shell	25	0	2
	25	16	90
	21	24	81
	15	32	74
	10	40	67
	5	58	110
	2	64	45
	−1	64	65
	−4	64	72
In shell	25	16	22
	21	24	34
	15	32	24
	10	40	14
	5	58	17

iodometric titration. The ethylene dibromide was extracted by steam distillation and trapped in benzene, converted to inorganic bromide by hydrolysis, and subsequently analyzed by coulometric titration. For extraction, a 100-g sample size was used and the results of the analysis are averages of two samples. All samples were kept at the temperature of treatment in controlled cold rooms until the analysis time.

RESULTS AND DISCUSSION

The quantity of fumigant residue remaining in the fruit as represented by the combined skin and pulp (edible portion), after fumigation with methyl bromide for 2 hr at different dosages and temperatures, is shown in Table I. The data show that even when the amount of fumigant was increased from 16 to 80 mg/l., the amount of bromide residue did not increase when the temperature was decreased. Table II shows that the bromide residue for peaches, when separated into component parts (skin, pulp, pit wall, and seed) at different temperatures and dosages of methyl bromide for a 2-hr exposure period and at normal atmospheric pressure, was highest on the skin and seed and lowest on the pulp. At lower temperatures, although the concentration of fumigant was higher, the residue was greatly reduced. The distribution of bromide residues in skin, pulp, and pit of plums treated with methyl bromide at various temperatures is also shown in Table II. Here the low level of bromide residue was maintained on the pulp section and showed the same increase for skin and pit when the temperature was reduced, even when the amount of fumigant was increased fourfold.

Table III shows the "inorganic bromide" residue in apples as a result of ethylene dibromide treatment at different temperatures and various dosages, as well as the organic bromide which is calculated as ethylene dibromide. By the method used for inorganic bromide determination only one of the bromides from ethylene dibromide is converted to inorganic bromide. These apples were treated at 13° (55°F) with 12 mg/l. and 24 mg/l. of ethylene dibromide for 4 hr and stored at this temperature to determine the rate of desorption and the length of time needed to reduce the content of fumigant to a safe level for consumption of the fruit. The amount of ethylene dibromide in the apples was high initially, especially for higher dosages of fumigant, but after 6 days it decreased to 1.2 and 1.6 mg of ethylene dibromide, respectively, per kg of fruit. The total inorganic bromide residue after 3 days aeration was 3.5 and 5.4 mg, respectively, as shown in Table III. Table IV illustrates that the determination of total bromide by treating the sample with alcoholic sodium hydroxide, followed by ashing as described by Neufeld (1936), then oxidation by the Meulen (1931) and Kolthoff and Yutzy method (1937), will not measure all the organic bromide because considerable organic bromide is lost by this method. The rate of desorption as shown in this table is three times faster at 25° than at 13°. The results in Tables III and IV show that newly harvested apples have lower residue levels compared to apples stored for several months. The accuracy of the method was tested by adding to apples ethylene dibromide in the range 0.75 to 30 mg per sample, and the recovery was 99.6 to 101%, as described by Dumas (1962).

The disappearance of methyl bromide from apples treated with this fumigant was determined at 40 mg/l. for 2 hr and 25° (77°F). After 5 min the methyl bromide residue was 3.5 ppm, at 30 min it was 0.5 ppm, and no fumigant was found after 1 hr. The desorption was tested at 25°, room temperature. The inorganic bromide values for walnuts after 24 hr of fumigation, with a range of methyl bromide concentrations and a range of temperatures, were found to decrease with the decrease of temperature, until the boiling point for methyl bromide (3.6°) was approached (Table V). At 5° the bromide residue increased and at 2 and −4° was lower again, probably due to increased sorption by condensation. The bromide residue was significantly lower when the walnuts were treated in the shell and the amount of bromide decreased with the decrease in temperature. The variability for three determinations was of ±7%.

The results of these experiments show that when fruits are fumigated with methyl bromide at a lower temperature, the bromide residue is significantly reduced. In the case of ethylene dibromide, the residue at a lower temperature showed some increase because the unchanged fumigant remained in the fruit for a long time after treatment. It also indicates that the "total bromide" determination for the estimation of ethylene dibromide does not represent the amount present. For this reason ethylene dibromide should be directly determined. Although the total amount remaining is small, the unchanged fumigant may be of some significance because of its toxicity. The residue of importance is the organic ethylene dibromide, which increased with the reduction of the fumigation temperature. Sufficient aeration time should be allowed for adequate desorption of this material.

ACKNOWLEDGMENT

The author thanks H. A. U. Monro for suggesting the

problem and E. J. Bond for help in preparing the manuscript.

LITERATURE CITED

Alumot, E., Mandel, E., *Poultry Sci.* **3,** 957 (1969).
Alumot, E., Nachtomi, E., Kemperich-Pinto, D., Mandel, E., Schindler, H., *Poultry Sci.* **6,** 1975 (1968).
Amir, D., Volcani, R., *Nature (London)* **206,** 99 (1965).
Dumas, T., *J. Agr. Food Chem.* **10,** 476 (1962).
Dumas, T., Latimer, R. A., *J. Agr. Food Chem.* **10,** 276 (1962).
Heuser, S. G., Freeman, G. E., "Residues in wheat fumigated with ethylene dibromide," *Pest Infest. Res. Slough, England* 40 (1955).
Kennett, B. H., Heulin, F. E., *J. Agr. Food Chem.* **5,** 201 (1957).
Kolthoff, I. M., Yutzy, M., *Ind. Eng. Chem. Anal. Ed.* **9,** 75 (1937).
van der Meulen, J. M., *Chem. Weekbl.* **28,** 238 (1931).
Monro, H. A. U., Buckland, C. T., *Annu. Rep. Entomol. Soc. Ont.* **86,** 58 (1956).
Nachtomi, E., Alumot, E., Bondi, A., *Isr. J. Chem.* **6,** 803 (1968).
Neufeld, A. H., *Can. J. Res. Sect. B.* **14,** 160 (1936).

Received for review November 13, 1972. Accepted February 22, 1973.

Determination of Heavy Metals in Foods

Richard A. Baetz[1] and Charles T. Kenner*

The proposed method utilized a V_2O_5-catalyzed $HNO_3/H_2SO_4/H_2O_2$ digestion followed by pH adjustment to 7.0 ± 0.5. If a precipitate formed, it was filtered and analyzed separately after being dissolved in acid. Heavy metals were removed from the digest with a column of Chelex 100 chelating ion-exchange resin in the sodium form. The metals were eluted from the column with 1 *N* H_2SO_4 and were determined by atomic absorption. Sensitivity varied from 20 ppb for Zn to 0.20 ppm for Pb, and recoveries of added standards varied from 91.4% for Pb to 100.5% for Zn, with an overall average recovery of 95.2% and an average standard deviation of 3.03%. The heavy metal content of eight different types of foodstuffs has been determined. The proposed method can be used to determine Pb, Cd, Cu, Co, Mn, Ni, and Zn in biological materials in the ppm and ppb range on a single sample.

The concern with possible heavy metal contamination of foods has created a need for analytical methodology to detect these metals in trace amounts since existing methods can not be used as a general screening method. The methods for the determination of individual metals in foods usually are not satisfactory for the analysis of several metals in a single sample. The present official method of the Association of Official Analytical Chemists (1970) for cadmium in foods, for example, utilizes either wet or dry ashing of organic material, followed by pH adjustment, organic solvent extraction, and colorimetric determination. If this method is applied to a scheme for multimetal determination, the extraction of the different metals involves differential pH adjustment and is tedious, lengthy, and subject to a vast number of interferences. A method is needed to determine several metals in a single sample charge which will be sensitive, precise, and accurate as the direct determination of each single element.

Previously published methods (AOAC, 1970; Flann and Bartlet, 1968; Hoover *et al.*, 1969; Thiers, 1957) for heavy metal determination have utilized either wet or dry ashing techniques for the destruction of organic material. Dry ashing has been reported (Thiers, 1957) to cause loss by volatilization, adsorption on unburned carbon, or formation of insoluble silicates. Hoover *et al.* (1969) have investigated several methods for lead and conclude that the method of Flann and Bartlet (1968), which involves wet digestion followed by coprecipitation of lead with strontium sulfate, offers the best solution to the problem of isolation and concentration of lead.

Volatilization is offset in wet ashing with acids, since the oxidation takes place at relatively low temperatures. One problem with wet ashing using H_2SO_4 arises from the presence of various metals, since lead coprecipitates with calcium and other sulfates. Wet oxidation using H_2SO_4 and 50% H_2O_2 has been used for the destruction of organic material in the determination of metals for many years. The procedure does not cause loss of cadmium by volatilization (Analytical Methods Committee, 1969) and has been proven to be a rapid and smooth oxidation with low blank values in the determination of heavy metals (Analytical Methods Committee, 1967).

The most common methods of separation and concentration include volatilization, electrodeposition, liquid–liquid extraction, precipitation, and ion exchange. Galle (1971) used the chelating ion-exchange resin, Chelex 100, to remove and concentrate manganese, iron, cobalt, nickel, copper, zinc, and lead in oil field brines. He effectively separated the metals from the brine after adjusting the pH of the solution and resin to 4.5. The metals were eluted from the column with 1 *N* HCl. Biechler (1965) used Chelex 100 to separate trace amounts of copper, lead, zinc, cadmium, nickel, and iron from industrial waste waters. He found it necessary to use 8 *N* HNO_3 to remove cadmium quantitatively from the resin and that the resin could not be regenerated after this treatment. Freudiger and Kenner (1972) separated trace amounts of cobalt, copper, iron, manganese, nickel, lead, and zinc from the high sodium ion concentration resulting from the basic fusion of ore samples by the use of Chelex 100 after adjustment of the pH to 7 ± 1. The metals were eluted with 3 *N* HCl and determined by atomic absorption. They observed that elimination of the high concentration of the alkali metal ions before measurement by atomic absorption resulted in greatly improved reproducibility and accuracy. Dingman *et al.* (1972) have used polyamine–polyurea resins to study the effects of pH, equilibrium time, and resin cross-linking in a batch equilibrium study on the chelation of Cu, Ni, Zn, and Co.

Department of Chemistry, Southern Methodist University, Dallas, Texas 75275.
[1] Food and Drug Administration, Dallas District, Dallas, Texas 75204.