Sampling and Stability of Methyl Bromide on Activated Charcoal

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Monitoring methyl bromide (CH_3Br) emission into the atmosphere following soil fumigations requires sensitive and reproducible sampling methods. The factors affecting the sampling efficiency and stability of CH_3Br on activated charcoal sampling tubes were identified and evaluated in this study. The number of tubes required for accurate sampling using activated coconut and petroleum charcoal tubes was determined for various sampling flow rates and sampling intervals. Breakthrough of CH_3Br on both types of tubes increased with increasing flow rates and sampling intervals. CH_3Br hydrolyzed rapidly on moist charcoal, and the reaction was enhanced by temperature. At 40 °C and 21% moisture content, the half-lives of degradation were only 11 h on coconut charcoal and 17 h on petroleum charcoal. The rapid hydrolysis of CH_3Br on charcoal was caused by the high pH of the charcoal. To prevent degradation of CH_3Br bromide, charcoal samples should be always kept at low temperature and under dry conditions during transport and storage. Correction for loss due to degradation during sampling may be necessary if samples are taken from atmospheres with high temperature and humidity.

Keywords: *Methyl bromide; fumigants; volatilization; vapor sampling; activated charcoal; head-space analysis*

INTRODUCTION

Many crops, including strawberries, tomatoes, peppers, eggplants, tobacco, ornamentals, nursery stock, vines, and turf, are protected against soil-borne pathogens by preplant injection of methyl bromide (bromomethane, CH_3Br) into the soil at a depth of 30-60 cm (Albritton and Watson, 1992). Due to its extremely high vapor pressure (1420 mmHg at 20 °C), CH_3Br diffuses rapidly in the soil profile, and significant fractions (40-90%) may escape through the soil surface into the atmosphere (Yagi et al., 1993; Majewski et al., 1994; Yates et al., 1995a,b). Recent studies have indicated that CH_3Br has the capability of reacting with ozone, and the use of CH_3Br as a soil fumigant in agriculture has reportedly contributed to the ozone depletion in the stratosphere (Anderson and Lee-Bapty, 1992; Yung et al., 1980; Singh and Kanakidou, 1993). The environmental impact from the continuous use of CH_3Br as a fumigant has raised extensive concerns and may eventually lead to the phase-out of this chemical (Albritton and Watson, 1992). Since marine microorganisms also produce CH_3Br, direct measurements of CH_3Br emission into the atmosphere during and after soil application are important to estimate the contribution of agricultural practices to the overall accumulation of CH_3Br in the stratosphere. For monitoring CH_3Br in the atmosphere under natural environmental conditions, it is imperative to develop sensitive and reliable sampling methodologies.

Capillary glass tubing packed with various adsorbents has been used widely in collecting organic compounds in the air with active sampling devices (Ness, 1991). One of the most extensively used adsorbents is activated charcoal. Compared with many other adsorbents, such as the Tenax-GC series, charcoal tubes are inexpensive and easy to use. Sampling tubes containing charcoal made from coconut or petroleum are used widely for sampling a variety of organic compounds, including the monitoring of toxic vapor exposure at workplaces following NIOSH guidelines (Eller, 1984). In NIOSH method 2520, use of two petroleum charcoal tubes (400/200 mg) in series is recommended for collecting CH_3Br in work environments. However, conditions at a workplace and in an open field may be drastically different. For instance, the concentration of CH_3Br is usually higher in workplaces; therefore, a small sampling volume often is sufficient, which can be achieved by using a relatively low flow rate or a short sampling time. For sampling under field conditions, concentrations are usually at microliters per cubic meter or lower levels due to the enormous dilution, especially for off-site samples and samples taken several days after the CH_3Br treatment (Yates et al., 1995a,b). To obtain detectable samples, a large sample volume may be needed, which is usually obtained by extending sampling interval, increasing flow rate, or both.

When organic vapors are sampled, sampling tubes are connected in series to ensure complete recovery of the compound from the air stream. Depending on the type and the number of tubes used, as well as the sampling interval and flow rate, the distribution pattern of the compound along the tubes varies, and breakthrough might occur. Therefore, the number of sampling tubes necessary for accurate sampling of CH_3Br needs to be determined for different types of tubes and for different sampling intervals and flow rates. In addition, under field conditions, factors such as temperature and relative humidity are not as well controlled as in workplaces. In areas where CH_3Br is normally used, such as California, Florida, and Nevada, the air temperature may rise to 40-50 °C in the summer. During early morning hours, or during precipitation, or in closed flux chambers, the humidity near the soil surface may reach saturation and the water in the air may be absorbed

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1362 *J. Agric. Food Chem.*, Vol. *43*, No. 5, 1995

Gan et al.

on the charcoal. Therefore, the effects of temperature and moisture on the stability of CH_3Br on charcoal during sampling, transport, and storage need to be evaluated.

In this study, breakthrough of CH_3Br on both coconut and petroleum charcoal sampling tubes was determined for various flow rates and sampling intervals over a wide concentration range, and the optimum number of tubes in series for accurate sampling was determined for each situation. Degradation of CH_3Br on coconut and petroleum charcoal under controlled moisture and temperature conditions also was investigated. The information can be used as guidelines for sampling CH_3Br or similar organic vapors in the environmental atmosphere using activated charcoal tubes, as well as for appropriate handling during sample transport and storage prior to analysis.

MATERIALS AND METHODS

Chemicals. CH_3Br with a purity of better than 99.5% was purchased in a lecture bottle from Matheson Gas Products Inc. (East Rutherford, NJ). CH_3Br gas was first introduced into a 500-mL PTFE sampling bag (Fisher Scientific Inc., Fair Lawn, NJ) via a needle valve, PTFE tubing, and a hydraulic needle in a fume hood; this was used as the stock gas for preparing standards and spiking samples. The stock CH_3Br gas in the sampling bag had a vapor density of 3.90 mg/mL under normal atmospheric pressure at 25 "C. Benzyl alcohol was obtained from Fisher Scientific and used without further purification.

Charcoal Tubes and Activated Charcoal. Charcoal sampling tubes ORBO-32 (large) and ORBO-306 were purchased from Supelco Co. (Bellefonte, PA). Petroleum-based ORBO-306 is used in standard NIOSH method 2520 for sampling CHsBr at workplaces, while coconut-based ORBO-32 is used for many other organic vapors (Ness, 1991). Both tubes had the same configuration: 400 mg of charcoal granules (20-40 mesh, or 0.08-0.16-mm effective diameter, bed 1) packed into 8 x 6 x 110 mm (o.d. x i.d. x L) glass tubing, followed by a polyurethane spacer (ORBO-32) or glass wool plug (ORBO-306) and an additional 200 mg of charcoal (bed 2). Glass wool plugs were placed on both ends to hold the sorption beds in position. New tubes had both ends flame sealed. The ends of the ORB0 tubes were broken with a tubing cutter and smoothed with a grinder before use. Bulk samples of the activated coconut and petroleum charcoals used in the ORBO-32 and -306 tubes were obtained from Supelco.

Sampling Efficiency and Breakthrough. Sampling efficiency and breakthrough of CH_3Br on the activated charcoal was evaluated through laboratory experiments. Headspace vials (125 mL, Supelco) were sealed with PTFE-faced butyl-rubber septa and aluminum seals (Supelco) by using a hand crimper. Preliminary tests confirmed that the closed system was gastight, and less than 5% of the spiked CHsBr leaked over a 2-week period. Two hydraulic needles inserted through the septa were used as the inlet and outlet for air flow. Three prepared ORBO-32 or ORBO-306 tubes were connected in series using Teflon tubing connectors. One end of the tube series was installed on the outlet of the headspace vial and the other end to the manifold of a flow adjustor (SKC West Inc., Fullerton, CA). The tube series was placed in such a way that all of the no. 1 beds pointed toward the vial and no. 2 beds toward the manifold. Vacuum was then applied through the manifold, and the flow rate to each vial was adjusted independently to 100 or 200 mL/min at the inlet using a flowmeter. When the flow rate stabilized, CH_3Br gas (l-1000 μL) was introduced into each vial using gastight syringes. The spiked CH_3Br in the vials was sampled for different time intervals (l-4 h) at the specified flow rate. At the end of each sampling interval, the tube series was dismantled and each tube was analyzed individually to determine CH_3Br content. The tube nearest the CH_3Br source (vial) was considered tube A, the tube in the middle tube B, and the tube nearest the vacuum source tube C. Tube A was considered the primary

tube, and tubes B and C were the first and second backup tubes. Distribution of CH_3Br among the three tubes was calculated as percentage of the total CHsBr recovered. Four replicates were used for each concentration-sampling interval-flow rate combination.

Analyses of CH_3Br on both ORBO-32 and -306 tubes were carried out on a Hewlett-Packard 5890 GC coupled with a Tekmar 7000 headspace autosampler (Tekmar Co.: Cincinnati, OH). The method of headspace-GC analysis of CH_3Br on charcoal sampling tubes was reported previously (Gan et al., 1995). In brief, the charcoal from each ORB0 tube was placed into a 9-mL headspace vial (Tekmar), 1 mL of benzyl alcohol was added, and the vial was capped immediately with a PTFE-faced butyl septum and aluminum seal. The sample vials were then equilibrated in the headspace autosampler for 15 min at 110 "C, and 2 mL of the vapor phase in the vials was introduced into the GC injection port via a six-port valve and an interfacing line. The GC conditions were as follows: RTX-624 capillary column (30 m x 0.25 mm x 1.4 μm, Restek Corp., Bellefonte, PA); carrier gas, helium; column flow rate, 1.1 mL/min; detector gas, nitrogen; split ratio, 10:l; isothermal oven temperature, 35 °C; injection port temperature, 85 "C; and detector temperature, 240 "C. CH_3Br was eluted approximately 2.45 min after the injection. Calibration was made by analyzing a set of charcoal tubes spiked with known amounts of CH_3Br on the headspace autosampler-GC under the same conditions.

Stability of CH_3Br on Charcoal. To determine the uptake of moisture from moist air by activated charcoal, air was bubbled through water and then passed through ORBO-32 and ORBO-306 tubes at 100 or 200 mL/min. The uptake of moisture on charcoal was determined from weighing the tubes before and after sampling for different time periods.

For stability experiments, 1.0 g of air-dried coconut or petroleum charcoal was weighed into 21-mL headspace vials, and appropriate amounts of deionized water were added to bring the moisture content of the charcoal to 1.1 (air-dried), 11,21, or 51% (w/w). One milliliter of CHsBr gas was spiked on the charcoal using a gastight syringe, and the vials were capped immediately with septa and seals. The treated charcoal samples were incubated at -4, 25, 40, and 60 °C in the dark. At predetermined time intervals after the treatment, duplicate vials were removed and Br^- was measured. The degradation rate was calculated as the percentage of CH_3Br degraded to Br^-. Bromide ion concentration was measured using a Br^- selective electrode (Fisher Scientific). Charcoal was transferred into a 125-mL beaker, and 50 mL of deionized water was added. The mixture was stirred, and measurements were taken 15 min after the addition of water. Calibration and reading were completed on an Accumet 25 pH meter (Fisher Scientific).

The pH of the charcoal-water mixture (1:l0 w/w) was measured using a pH electrode on an Accumet 25 pH meter. To determine the effect of pH on CHsBr degradation on charcoal, petroleum or coconut charcoal (200 g) was leached with 10 L of deionized water in a Büchner funnel and air-dried. One gram of the air-dried leached charcoal was spiked with 1.0 mL of CH_3Br in headspace vials after the moisture content was adjusted to 21% by adding deionized water, and the capped vials were incubated at 25 and 40 °C in the dark. The production of Br^- was analyzed at the predetermined intervals as described for nonleached charcoal samples.

RESULTS AND DISCUSSION

Breakthrough of CH_3Br on Sampling Tubes. CHsBr in the air stream was first adsorbed and then desorbed as the air continued to pass through the charcoal in the sampling tubes. After sampling, CH_3Br was distributed at different positions along the charcoal tube or among different tubes when a tube series was used. Types of charcoal tubes, flow rates, and sampling intervals all showed profound effects on the distribution patterns of CHsBr among the sampling tubes.

Stability of Methyl Bromide on Charcoal

J. Agric. Food Chem., Vol. **43**, *No. 5*, 1995 **1363**

Table 1. Breakthrough of CH₃Br on OBBO-32 Tubes (Percent of CH₃Br Recovered ± SE, *n* = 4)

CH₃Br spiked (µL)	sampling intervals								
	1 h			2 h			4 h		
	A	B	C	A	B	C	A	B	C
	Flow Rate, 100 mL/min								
10	99.55 ± 0.34	0.45 ± 0.34	ND"	99.95 ± 0.09	0.05 ± 0.09	ND	81.76 ± 0.08	18.24 ± 0.08	ND
30	99.99 ± 0.02	0.02 ± 0.02	ND	99.95 ± 0.06	0.05 ± 0.06	ND	64.18 ± 8.91	35.80 ± 8.89	0.02 ± 0.02
100	99.99 ± 0.01	0.01 ± 0.01	ND	97.72 ± 1.64	2.28 ± 1.64	ND	59.10 ± 4.25	40.89 ± 4.24	0.01 ± 0.01
300	99.90 ± 0.17	0.10 ± 0.17	ND	99.19 ± 1.01	0.81 ± 1.01	ND	54.51 ± 2.81	45.49 ± 2.81	ND
1000	99.86 ± 0.15	0.14 ± 0.15	ND	99.30 ± 0.10	0.70 ± 0.10	ND	36.47 ± 4.52	61.63 ± 4.12	1.90 ± 2.76
	Flow Rate, 200 mL/min								
10	99.71 ± 0.13	0.16 ± 0.09	0.13 ± 0.13	70.00 ± 5.25	29.95 f5.18	0.05 ± 0.06	17.15 i-4.35	64.45 ± 2.19	17.40 ± 4.29
30	98.80 ± 1.97	1.20 ± 1.99	ND	80.97 ± 6.98	17.78 ± 5.15	1.25 ± 1.96	8.56 ± 1.83	74.59 ± 5.21	16.86 ± 5.97
100	99.50 ± 0.77	0.50 ± 0.77	ND	83.98 ± 4.80	16.03 ± 4.80	ND	8.21 ± 1.23	78.19 ± 5.28	13.60 ± 6.31
300	98.70 ± 0.30	1.30 ± 0.30	ND	80.12 ± 1.97	19.761 2.08	0.12 ± 0.21	3.53 ± 1.48	72.21 ± 12.69	24.26 ± 13.71
1000	98.61 ± 0.39	1.39 ± 0.39	ND	38.56 ± 14.51	60.51 ± 13.32	0.93 ± 0.43	1.97 ± 0.43	49.14 ± 2.55	48.80 ± 2.92

ᵃ ND, not detected.

Table 2. Breakthrough of CH₃Br on OBBO-306 Tubes (Percent of CH₃Br Recovered ± SE, *n* = 4)

CH₃Br spiked (µL)	sampling intervals								
	1 h			2 h			4 h		
	A	B	C	A	B	C	A	B	C
	Flow Rate, 100 mL/min								
10	100	ND"	ND	84.43 ± 3.56	15.57 ± 3.56	ND	8.61 ± 1.20	90.17 ± 2.31	1.22 ± 0.23
30	100	ND	ND	99.7 ± 0.01	0.25 ± 0.06	0.05 ± 0.05	16.49 ± 3.51	83.5 ± 3.51	**ND**
100	100	ND	ND	97.48 ± 2.42	2.46 ± 2.41	0.06 ± 0.01	1.75 ± 0.20	63.28 ± 5.45	34.97 ± 5.65
300	100	ND	ND	96.44 ± 1.16	3.55 ± 1.17	0.01 ± 0.01	14.72 ± 0.43	83.30 ± 1.48	1.98 ± 1.91
1000	99.46 ± 0.51	0.54 ± 0.51	ND	82.01 ± 4.50	18.06 ± 4.50	ND	2.77 ± 1.27	74.01 ± 10.91	23.23 ± 12.17
	Flow Rate, 200 mL/min								
10	99.20 ± 0.30	0.80 ± 0.30	ND	41.96 ± 7.42	57.88 ± 7.24	0.18 ± 0.18	2.33 ± 0.37	8.87 ± 1.50	88.80 ± 1.86
30	99.73 ± 0.27	0.26 ± 0.26	ND	61.53 ± 2.99	38.28 ± 3.19	0.19 ± 0.19	0.99 ± 0.10	5.24 ± 0.97	93.77 ± 1.07
100	96.23 ± 1.02	3.75 ± 1.04	0.02 ± 0.02	43.28 ± 4.78	56.65 ± 4.78	0.07 ± 0.01	0.55 ± 0	9.21 ± 1.11	90.24 ± 1.11
300	98.24 ± 0.50	1.76 ± 0.50	ND	36.72 ± 1.85	63.27 ± 1.85	0.01 ± 0.01	0.91 ± 0.11	16.57 ± 3.81	82.52 ± 3.92
1000	76.59 ± 8.82	23.10 ± 9.12	0.31 ± 0.31	50.08 ± 2.31	47.01 ± 3.01	2.91 ± 1.09	1.17 ± 0.06	12.00 ± 0.11	86.84 ± 0.05

ᵃ ND, not detected.

On coconut-based ORBO-32 tubes (Table 1), CHsBr distribution shifted from tube A toward tube C as the sampling interval increased from 1 to 4 h at both flow rates. At 100 mL/min, no CHsBr broke through the first backup tube (B) when the 2-h sampling interval was used. However, when the interval increased to 4 h, the average CHsBr present in the first backup tube (B) was 40.4% and a small fraction was found in tube C. On the basis of distribution patterns of CHsBr along the tube series, two tubes should be used for 1- and 2-h samplings and three tubes for 4-h samplings. At 200 mL/min, CHsBr broke through the first backup tubes for all sampling intervals greater than 1 h. In 2- and 4-h samples at 200 mL/min, considerably more CHsBr moved into the backup tubes than at 100 mL/min. Since only three tubes were used, some CHsBr broke through tube C and an average of 8.8% of the spiked CHsBr was not recovered for the 4-h sampling. The recovery of spiked CHsBr in all of the rest of the treatments was 97-105% of the amount added. To ensure minimal breakthrough during sampling at 200 mL/min, two and three tubes should be used for 1- and 2-h samples, respectively, and at least four tubes should be used for sampling intervals at or longer than 4 h. CH₃Br concentration did not significantly affect the breakthrough, though more CHsBr was recovered from tubes B and C at the highest loading rate. For instance, when the flow rate and sampling interval were 200 mL/min and 4 h, respectively, 48.8% of the CHsBr was found in tube C for the spike of 1000 µL, compared to an average of 18.03% for the spikes of 1-300 µL.

CHsBr was retained less effectively on petroleum-based ORBO-306 tubes (Table 2) than on the ORBO-32 tubes, and at high flow rates or long sampling intervals a larger fraction moved into the backup tubes than with ORBO-32 tubes under the same conditions. At 100 mL/min, no significant fraction of CHsBr was found in tube C for the 1- and 2-h intervals. However, when the sampling interval was extended to 4 h, O-34.97% of the recovered CHsBr was detected in tube C and 0-15.1% of the spiked CHsBr was not recovered. For accurate sampling using ORBO-306, two tubes should be used for 1- and 2-h sampling and at least four tubes should be used for 4-h samples. At 200 ml/min, more CH₃Br moved into the backup tubes than at 100 mL/min. When the interval was 4 h, the majority (82.5-93.8%) of the recovered CHsBr was present in tube C and a large fraction (23.4-45.6%) of the spiked CHsBr was not recovered. The recovery of spiked CHsBr in the rest of the treatments was 98-105%. For accurate sampling at 200 mL/min, at least two tubes should be used for 1-h sampling, three tubes for 2-h sampling, and four or more tubes for 4-h sampling. It must be pointed out that sampling tubes packed with more charcoal may be either commercially available or custom made. In the case when larger sampling tubes are used, the number of tubes in series can be reduced and good trapping efficiency maintained.

The effect of flow rate and sampling interval on the distribution of CHsBr along the tube series can be compared with the behavior of a solute on a packed solid-phase GC column. On a GC column, the volume of mobile phase (carrier gas) flowing through the column determines the position of the solute on the column or its elution. The maximum volume of air that can be passed through charcoal tubes which does not result in
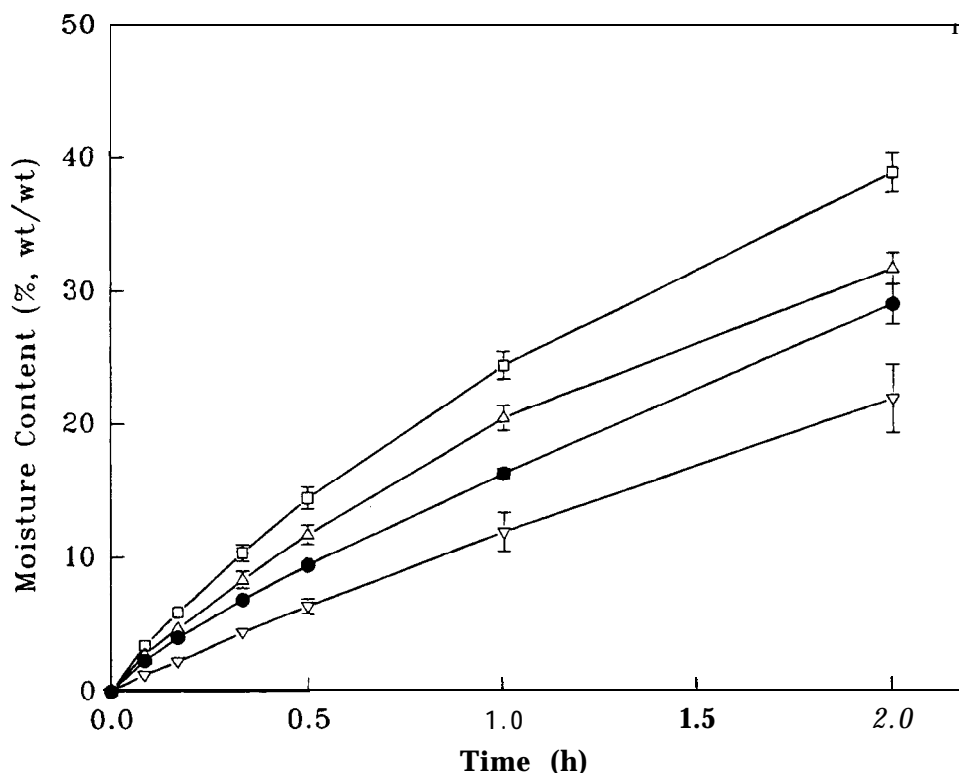
1364 J. *Agric. Food Chem.,* Vol. *43,* No. *5,* 1995

Gan et al.

Figure **1.** Absorption of moisture on activated coconut and petroleum charcoal from saturated air flow: (●) ORBO-32 at 100 mL min⁻¹; (□) ORBO-32 at 200 mL min⁻¹; (▽) ORBO-306 at 100 mL min⁻¹; (▲) ORBO-306 at 200 mL min⁻¹.

a significant elution of CH_3Br from the last backup tube is a factor of the flow rate and sampling interval. Breakthrough can be measured by mass recovery or by the ratio in the last backup tube when mass recovery is unknown. For instance, if more than 25% of the total trapped CH_3Br appears in the last backup tube, then the concentration in the air must be reported as a "greater than" number (Woodrow et al., 1988). Therefore, when a long sampling interval is needed, such as overnight sampling, low flow rates should be used. On the other hand, when a high flow rate is used for rapid sampling, the sampling interval should be kept short. With both ORBO-32 and ORBO-306 tubes, sampling intervals longer than 4 h should be avoided when the flow rate is higher than 100 mL/min. The type of charcoal may affect the resident patterns of CH_3Br in sampling tubes by affecting its distribution coefficient, K_D, between the air and charcoal phases. It appears that CH_3Br is retained more on coconut charcoal than on petroleum charcoal.

The effect of temperature and air humidity on CH_3-Br breakthrough and trapping efficiency needs to **be** further determined. It has been estimated that for every 10 °C increase in temperature, breakthrough is decreased by l-10% (Nelson et al., 1976). Polar compounds, such as dioxane, are very susceptible to water adsorbed on charcoal (Rudling and Bjorkholm, 1986).

Stability of CH_3Br on Charcoal. Both coconut and petroleum charcoal absorbed substantial amounts of water from the moist air, and the uptake increased with increase in sampling interval (Figure 1). After saturated air passed through the ORBO tubes at 100 mL/min for 2 h, the coconut charcoal in ORBO-32 tubes contained 28.7% water and the petroleum charcoal in ORBO-306 tubes contained 21.6%. When the flow rate increased to 200 mL/min, the water content on ORBO-32 and ORBO-306 tubes after a 2-h sampling further increased to 38.5 and 31.4%, respectively.

CH_3Br was not stable on wet charcoal and was readily subject to hydrolysis. The hydrolysis rate (release of Br^-) was dependent on the moisture content of the charcoal, temperature, and the origin of the charcoal (Figures 2 and 3). Hydrolysis of CH_3Br on wet charcoal apparently followed first-order kinetics when the temperature of incubation was above -4 °C, with all of the r values greater than 0.95 (Table 3). Significantly less degradation was observed on petroleum charcoal at all moisture contents and temperatures.

The mechanisms of CH_3Br degradation on charcoal have not been reported. According to Schwarzenbach et al. (1992) and Gentile et al. (1989), hydrolysis of CH_3-Br in water includes nucleophilic substitution with H_2O and hydroxyl group OH-:

$$CH_3Br + H_2O \rightarrow CH_3OH + H^+ + Br^- \qquad (I)$$

$$CH_3Br + OH^- \rightarrow CH_3OH + Br^- \qquad (2)$$
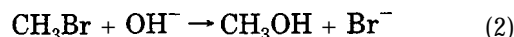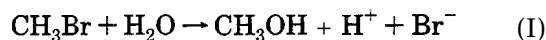
From (1) and (2), the overall reaction rate of CH_3Br can be written

$$-d[CH_3Br]/dt = d[Br^-]/dt = (k_{H_2O}[H_2O] +$$
$$k_{OH^-}[OH^-])[CH_3Br] \quad (3)$$

where $[CH_3Br]$, $[H_2O]$, and $[OH^-]$ are concentrations and k_{H_2O} and k_{OH^-} are rate constants for reactions 1 and **2,** respectively. At high pH or low CH_3Br aqueous concentrations, an effective overall rate constant (k_{eff}) *can* be written

$$k_{eff} = k_{H_2O}[H_2O] + k_{OH^-}[OH^-] \qquad (4)$$

and consequently, (3) can be treated as pseudo first order. The reported k_{H_2O} is 5 x 10^{-9} M^{-1} s^{-1}, and k_{OH^-}

Stability of Methyl Bromide on Charcoal
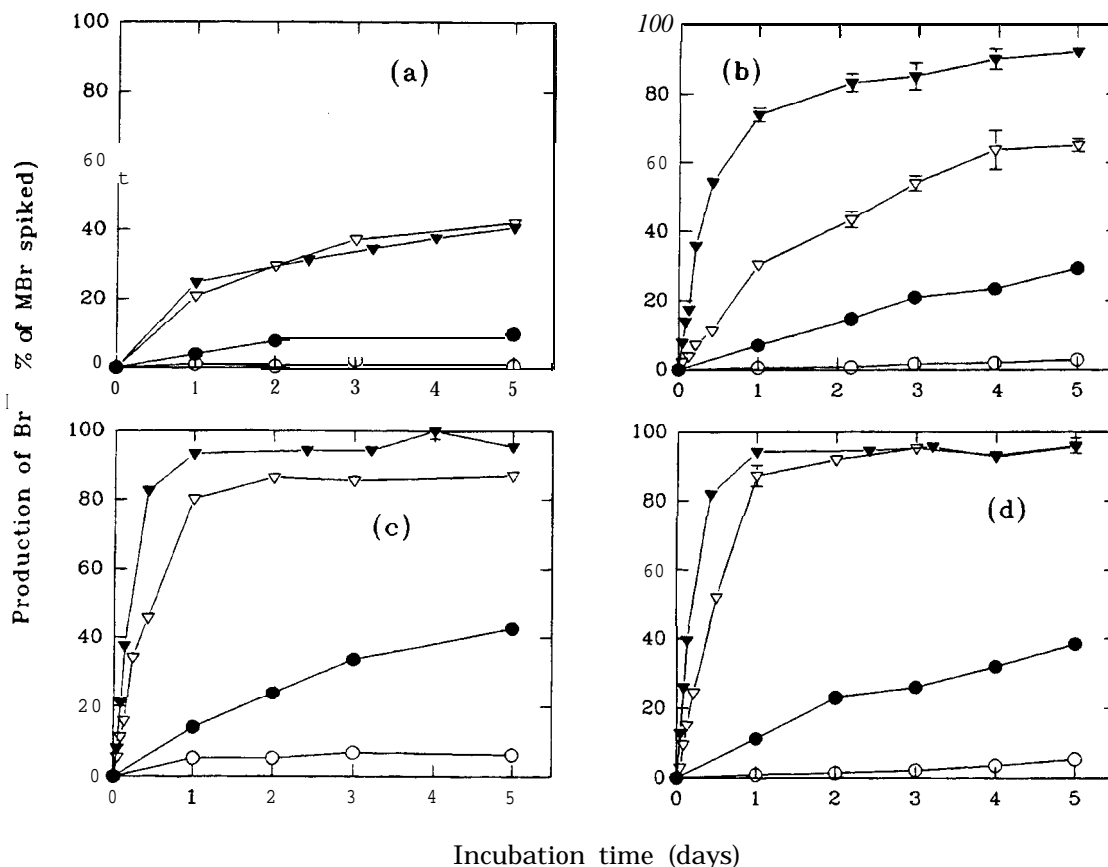
J. Agric. Food Chem., Vol. 43, No. 5, 1995 1365

Figure 2. Degradation of CH_3Br on coconut charcoal as influenced by moisture content and temperature: (a) moisture content = 1.01%; (b) moisture content = 11%: (c) moisture content = 21%; (d) moisture content = 51%; (○) -4 °C; (●) 25 °C; (v) 40 °C; (▼) 60 °C.

is 10^{-4} M^{-1}s^{-1} (25 °C) (Schwazenbach et al., 1992). The relative importance of reactions 1 and 2 to overall CH_3-Br loss is dependent on [OH$^-$] or the pH of the solution. The estimated [OH-] concentration required to contribute 50% of the overall hydrolysis at 25 °C is 55.5 M(5 x 10^{-9} M^{-1} s^{-1})/10^{-4} M^{-1} s^{-1}= 2.8 x 10^{-3} M, which corresponds to pH 11.4.

The measured pH in charcoal-water mixtures (1:10 w/w) was 10.5 for coconut charcoal and 10.1 for petroleum charcoal. If the basicity is due to the dissolution of oxides (e.g., CaO), then the pH at various moisture levels can be extrapolated. On coconut charcoal at a moisture content of 51%, the estimated pH is 11.8, and at 21%, the pH is 12.2; on petroleum charcoal, the estimated pH is 11.4 for 51% moisture and 11.8 for 21%. Under these pH conditions, reaction with OH- could contribute significantly to the overall hydrolysis of CH_3-Br. From eq 3, it is estimated that 85.1 and 69.5% of the hydrolysis should be caused by reaction with OH-on coconut charcoal for moisture contents of 21 and 51%, respectively, and 69.5 and 50% of the observed hydrolysis should be caused by reacting with OH- on petroleum charcoal for moisture contents of 21 and 51%, respectively. Substituting the reported k_{H_2O}, k_{OH^-}, and the measured pH in eq 4, the degradation rate constants k_{eff} for CH_3Br on coconut charcoal with 21 and 51% moisture content at 25 °C are calculated to be 0.16 and 0.078 day-l, respectively, which are close to the experimental observations (Table 3).

Hydrolysis of CH_3Br on charcoal with lower moisture content was considerably slower than on more moist charcoal. On charcoal with low moisture content, the absence of a large water phase may have limited the

dissolution of CH_3Br into the aqueous phase and consequently lowered the hydrolysis of CH_3Br. On the other hand, when the water content increased from 21 to 51%, the hydrolysis rate did not change, or decreased slightly in some cases, which could be attributed to the reduced pH due to dilution at the higher moisture level. Therefore, a moisture level at which maximum degradation occurs may exist for each type of charcoal.

The hydrolysis rate of CH_3Br on wet charcoal increased rapidly with increasing temperature on both coconut and petroleum charcoal. The hydrolysis rate constants at 40 and 60 °C on coconut charcoal containing 21% water were 142 and 405 times greater than that at -4 °C and 14 and 39 times greater than that at 25 °C, respectively. On coconut charcoal with 21% moisture content, within the first day after treatment, 80.1% of the CH_3Br was hydrolyzed to Br$^-$ at 40 °C and 94% at 60 "C. From the Arrhenius equation

$$k = A\, e^{-E_a/RT} \qquad (5)$$

the activation energy, E_a, *can* be derived for the hydrolysis of CH_3Br on charcoal at different moisture contents by linear regression of a plot of ln k versus l/T(K):

$$\ln k = \ln A - E_a/RT \qquad (6)$$

The calculated E_a values for CH_3Br hydrolysis, using the k values in Table 3, are 72.9 and 73.1 kJ mol^{-1} for moisture contents of 21 and 51% on coconut charcoal and 64.6 and 66.4 kJ mol^{-1} for the same moisture contents on petroleum charcoal, respectively. From
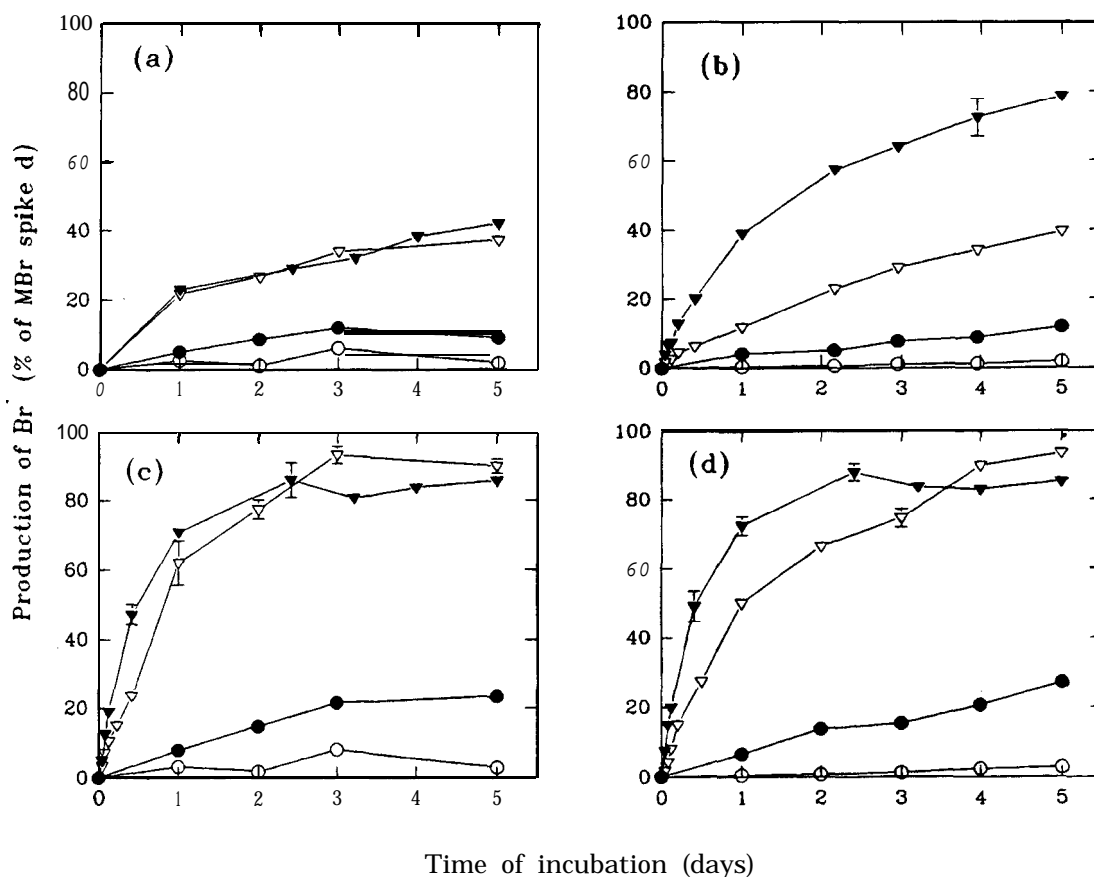
Figure 3. Degradation of CH_3Br on petroleum charcoal as influenced by moisture content and temperature: (a) moisture content = 1.01%; (b) moisture content = 11%: (c) moisture content = 21%; (d) moisture content = 51%; (O) -4 "C; (●) 25 °C;(▽) 40 °C; (▽) 60 °C.

Table 3. Calculated First-Order Hydrolysis Rate Constant of CH_3Br on Coconut- and Petroleum-Based Charcoal at Various Temperature and Moisture Conditions (in Day^{-1}, Numbers in Parentheses Are r Values of Correlation)

moisture content (%)	temperature			
	-4 °C	25 °C	40 °C	60 °C
		Coconut Charcoal		
1.01	0.0021 (0.44)	0.0211 (0.92)	0.1046 (0.94)	0.0940 (0.93)
11.0	0.0057 (0.98)	0.0688 (0.99)	0.2266 (0.98)	0.5079 (0.95)
21.0	0.0107 (0.74)	0.1115 (0.99)	1.5227 (0.99)	4.3337 (0.99)
21.0"	NM[b]	0.0582 (0.98)	0.3086 (0.99)	NM
51.0	0.0103 (0.97)	0.0933 (0.99)	1.5030 (0.99)	4.1637 (0.99)
		Petroleum Charcoal		
1.01	0.0048 (0.40)	0.0195 (0.76)	0.0865 (0.91)	0.0994 (0. 96)
11.0	0.0034 (0.98)	0.0232 (0.98)	0.1007 (0.99)	0.3097 (0.99)
21.0	0.0073 (0.45)	0.0547 (0.95)	0.9502 (0.99)	1.2374 (0.99)
21.0[a]	NM	0.0365 (0.99)	0.1680 (0.99)	NM
51.0	0.0058 (0.98)	0.0597 (0.99)	0.6935 (0.99)	1.2743 (0.99)

[a] Figures in this row are from water leached charcoal. [b] NM, not measured.

these E_a values, the average increase (decrease) of hydrolysis rate per 10 °C increase (decrease) in temperature is 2.5-2.9 times (Schwazenbach et al., 1992), which tended to agree with the experimental observations (Table 3), though other physical and chemical processes confound direct interpretation.

Coconut charcoal is derived from coconut shell, while petroleum charcoal is refined from coal. Both charcoals have a plant origin, which may account for the high pH observed. The difference in hydrolysis rate of CH_3Br between wet coconut and petroleum charcoal may be attributed to the difference in the amount and types of bases they contained. 1,2-Dichloropropane and 1,2-

dibromo-3-chloropropane were reported to be unstable on coconut charcoal at room temperature, and a daily loss of 7% for a 10-μg spike of 1,2-dibromo-3.chloropropane was observed (Albrecht et al., 1986). At elevated temperatures, more degradation of methyl isothiocyanate and (Z,E)-1,3-dichloropropene isomers was noticed on coconut charcoal than on petroleum charcoal (Gan et al., 1994).

To prevent CH_3Br hydrolysis prior to analysis, charcoal sampling tubes should always be kept at low temperature during transportation and storage. When sampling is performed under conditions where water can diffuse into the sampling tube, such as sampling in the ram or fog or sampling from a closed flux chamber over exposed soil, loss of CHsBr due to degradation during sampling should be considered, especially at warm temperatures. If the high pH is responsible for the hydrolysis of CH_3Br on charcoal, washing the charcoal with a weak acid or water in a pretreatment should reduce the hydrolysis rate by lowering the PH.

In a preliminary experiment, both coconut and petroleum charcoals were washed with water, and hydrolysis of CH_3Br in the leached charcoal was then determined. Hydrolysis of CHsBr in charcoal with 21% moisture content decreased 50% for coconut charcoal and 40% for petroleum charcoal at 25 °C and decreased 80% for coconut charcoal and 85% for petroleum charcoal at 40 °C (Table 3). The measured pH in the 1:lO charcoal/water mixtures decreased to 8.6 and 6.6 for leached coconut and petroleum charcoal, respectively, which would extrapolate to pH values of 10.3 and 8.3 in the water phase when the moisture content was 21%. From eq 4, when the pH in the solution on charcoal is

Stability of Methyl Bromide on Charcoal

J. Agric. Food Chem., Vol. 43, No. 5, 1995 1367

lowered to <10, the contribution from reaction with OH⁻ is <3.4% and the overall hydrolysis rate can theoretically be reduced 80-85%, consistent with the experimental results (Table 3). However, the trapping efficiency of prewashed charcoal may differ from that of unwashed charcoal due to the removal of impurities and therefore needs to be further investigated.

Conclusions. Breakthrough of CH_3Br on charcoal sampling tubes showed typical chromatographic behavior, with flow rate and sampling interval determining the distribution patterns of CH_3Br among the tubes. For long interval sampling, low flow rates should be used; high flow rates can be used for short intervals. CH_3Br rapidly degraded on moist charcoal, and the degradation rate increased with temperature from -4 to 60 "C. The high pH of charcoal is likely the cause for the observed rapid degradation. More hydrolysis occurred on coconut charcoal than on petroleum charcoal, which may be attributed to the higher pH in the former. Charcoal samples containing CH_3Br should always be transported and stored at low temperature before analysis. Loss of CH_3Br caused by degradation on charcoal tubes containing water should be corrected for the actual concentration. Washing charcoal with acid in a pretreatment procedure, or choosing petroleum charcoal over coconut charcoal, would likely reduce the hydrolysis and improve the recovery for CH_3Br in sampling.

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