Optimization of Analysis of Methyl Bromide on Charcoal Sampling Tubes

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Analytical methods with low detection limits and large sample throughput are needed for environmental monitoring of methyl bromide emission into the atmosphere after fumigation. The effectiveness of the traditional solvent-phase analysis with carbon disulfide was compared with headspace analysis using a headspace autosampler on coconut-based ORBO-32 and petroleum-based ORBO-33 charcoal sampling tubes. Conditions for headspace analysis were optimized on the basis of the partition behavior of methyl bromide among the vapor, solvent, and solid phases in the closed system. Under optimum conditions, the detection limit using headspace analysis was 0.4 ng/tube, which was significantly lower than that for the solvent-phase analysis method (32 ng/tube). If 24 L of air is sampled, the equivalent detection limit in air concentration would be 17 ng/m^3 for the headspace method and 1300 ng/m^3 for the solvent-phase method. The headspace method is highly automated, and the number of samples that can be analyzed in 24 h is 300 under the proposed conditions, which is a significant improvement over all of the previously reported methods.

INTRODUCTION

Methyl bromide (bromomethane, CH$_3$Br) is used as a fumigant for soils, commodities, and structures. Currently its use is vital for the economic viability of certain agricultural crops, especially strawberries, tomatoes, peppers, eggplants, tobacco, ornamentals, nursery stock, vines, and turf, and for quarantine treatment of certain products in international trade (UNEP, 1992). The production of CH$_3$Br in 1990 was 63 000 tons, or 126 million pounds (UNEP, 1992). However, CH$_3$Br from these fumigation uses reportedly contributes to ozone depletion in the stratosphere, and extensive concerns about the environmental impact from the continuation of these practices have been raised (UNEP, 1992). Soil fumigation constitutes approximately 80% of the total use of CH$_3$Br. To quantitatively estimate the contribution of soil fumigation to the overall CH$_3$Br accumulation in the stratosphere, it is essential to monitor the emission of CH$_3$Br from soil into the atmosphere after application. The behavior of CH$_3$Br in the soil–air environment is influenced by numerous factors, including injection depth, tarping, soil texture, organic matter and moisture levels, temperature, air relative humidity, wind speed, and soil–air heat exchange (Arvieu, 1983; Kolbezen et al., 1974; Yagi et al., 1993; Yates et al., 1995a,b). The concentration of CH$_3$Br in the adjacent atmosphere decreases with time after application, as well as the vertical or horizontal distance away from the treated site. In a recent field study, the observed concentrations in all off-site samples, and most on-site samples, a few days after application were in the low parts per billion [ppb(v)] (μL/m^3 or 3.89 μg/m^3) range (Yates et al., 1995a,b). To be able to monitor CH$_3$Br at such a trace level, it was necessary to develop more sensitive sampling and analytical methods.

Both the National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health Administration (OSHA) specify the use of charcoal tubes for sampling a wide variety of organic gases and volatile compounds in the air, including CH$_3$Br (Eller, 1984; Ness, 1991). Before analysis, quantitative desorption of CH$_3$Br from the sorbent is essential. Extremely high affinity of CH$_3$Br on charcoal was observed in preliminary studies, and heating up to 180 °C alone did not desorb a significant fraction of spiked CH$_3$Br. Solvent extraction was found to be very effective in extracting CH$_3$Br from charcoal at both normal and elevated temperatures. Due to the very low boiling point (3.56 °C) and extremely high vapor pressure (1420 mmHg at 20 °C) of CH$_3$Br, solvent extraction must be carried out in gastight systems, such as capped headspace vials. Subsequent analysis may be conducted from either the solvent phase or the vapor phase in the headspace. In the NIOSH method, 2.0 mL of carbon disulfide (CS$_2$) is used for the extraction at room temperature, and an aliquot (5 μL) of the solvent phase is injected into GC for analysis (Eller, 1984). Limited applications of manual and automated headspace methods have been reported for analyzing CH$_3$Br and other volatiles on charcoal (Canela and Mühleisen, 1988; Jentsch et al., 1968; Kolb, 1976; Woodrow et al., 1988). However, all of the published methods for analyzing CH$_3$Br or other halocarbons on charcoal tubes are either poor in detection capability or low in sample throughput. Woodrow et al. (1988) reported an improved automated headspace GC method, and the sensitivity of analysis was significantly enhanced. However, due to the disruption of the carrier gas flow caused by vial pressurization, 32 min was needed for each run, which resulted in a limited sample throughput.

In this paper, conditions of a headspace autosampler were optimized on the basis of the distributions of CH$_3$-Br in vapor, solvent, and solid phases in headspace vials to achieve maximum sensitivity. The effectiveness of analysis from the solvent phase and headspace is compared on two commonly used charcoal tubes, ORBO-32 and ORBO-33.

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MATERIALS AND METHODS

Chemicals. Methyl bromide with a purity >99.5% was purchased in a lecture bottle from Matheson Gas Products, Inc. (East Rutherford, NJ). Methyl bromide gas from the lecture bottle was introduced via a needle valve, Teflon tubing, and a hydraulic needle into a Teflon sampling bag (500 mL) in a fume hood and used as stock gas for preparing standards and spiked samples. The pure CH_3Br gas in the sampling bag had a vapor density of 3.9 mg/mL under normal atmospheric pressure and room temperature (25 °C). Benzyl alcohol (BA, phenylmethanol), ethyl acetate (EA), and carbon disulfide (CS_2) were all purchased from Fisher Scientific (Fair Lawn, NJ) and used without further treatment.

Charcoal Tubes and Headspace Vials. ORBO-32 and ORBO-33 charcoal tubes were used to trap CH_3Br (Supelco Inc., Bellefonte, PA). In ORBO-32 tubes, 400 mg of 20/40 mesh activated coconut-based charcoal is contained in the front section and 200 mg in the backup section in an 8 × 6 × 100 mm (o.d. × i.d. × L) glass tubing. In ORBO-33 tubes, 700 mg of 20/40 mesh activated petroleum charcoal is contained in the front section and 390 mg in the backup section in an 8 × 6 × 150 mm (o.d. × i.d. × L) glass tubing. Unused tubes come with both ends flame sealed. The ends of the ORBO tubes were broken using a tubing cutter and smoothed with a grinder before use.

All tests were made in closed 9 (Tekmar, Cincinnati, OH) or 21 mL (Supelco) glass headspace vials. The actual inside volumes were measured as 8.76 ± 0.05 mL for the 9 mL vials and 21.6 ± 0.06 mL for the 21 mL vials. Teflon-faced butyl septa and aluminum seals (Supelco) were used to seal the vials by employing a hand crimper. Preliminary tests showed that the closed vials were gastight and CH_3Br did not leak significantly over a 2 week period.

Sample Analysis. A Hewlett-Packard 5890 gas chromatograph with electron capture detector was used for the detection of CH_3Br. GC conditions were as follows: RTX-624 capillary column (30 m by 0.25 mm by 1.4 μm, Restek Corp., Bellefonte, PA); carrier gas, helium; column flow rate, 1.1 mL/min; detector gas, 5% methane + 95% argon; split ratio, 20:1; oven temperature, 35 °C; injection port temperature, 85 °C; detector temperature, 240 °C. Methyl bromide was eluted approximately 2.30 min after hand injection and 2.45 min after injection from the headspace autosampler under the above conditions.

For solvent-phase analysis, all injections were made by hand. Gastight syringes (Hamilton Co., Reno, NV) were used throughout the preparation and injection of samples. For headspace analysis, injections were made from a Tekmar 7000 headspace autosampler (HSA) equipped with a 7050 sample carrousel. The headspace autosampler was operated in tandem with GC, and helium was supplied as the pressurization gas and carrier gas through two separate inlets. The sample loop was 1 mL, and the temperature for interface lines and valves was maintained at 150 °C for all analyses. The 12 platens in the HSA would allow multiple sample vials to be equilibrated simultaneously. Use of inserts allowed 21 and 9 mL vials to be interchanged in the equilibration platens. During injection, sample vials were pressurized, and the pressure (2–4 psi higher than the static pressure in a closed vial) drove a portion of the headspace vapor through the sampling needle into the sample loop. A switch in the six-port valve placed the sample loop in line with the carrier gas flow. The carrier gas then back-flushed the sample through the heated transfer line into the GC injection port. The use of a six-port valve avoided the disruption of carrier gas flow while pressurization and injection were in process. Baseline response remained stable throughout all steps of the headspace analysis, which is an improvement over a configuration reported previously (Woodrow et al., 1988). This assured a shorter GC cycle time and clean chromatogram when the HSA was used.

Optimization of HSA Conditions. Various factors influencing the distribution of CH_3Br in the headspace vials in the HSA were modified to obtain maximum detection response. ORBO-32 and -33 tubes were spiked with known amounts of

CH_3Br, and air was drawn through the tubes at 100 mL/min for 60 min to simulate samples taken from a real active sampling device. The glass tubing was broken at one end, and the charcoal, along with the glass wool plug and urethane spacers, was emptied into headspace vials. For all analyses, the sample loop was 1 mL and vial size was 9 mL unless otherwise specified. Samples in the headspace vials were analyzed on the HSA-GC using different conditions on the HSA as described below. Optimum HSA conditions for analyzing CH_3Br on ORBO-32 and ORBO-33 tubes were determined on the basis of the sensitivity of analysis.

Solvent Types. Two solvents, ethyl acetate (EA) and benzyl alcohol (BA), were compared as the extraction solvent. Benzyl alcohol was used as extraction solvent in the headspace method reported by Woodrow et al. (1988). When EA was used, each spiked sample (0.2–500 μL, or 0.78–1950 μg) was equilibrated with 1.0 mL of EA at 70 °C for 15 min. When BA was used, the spiked samples were equilibrated with 1.0 mL of BA at 110 °C for 15 min. The lower equilibrating temperature was chosen for EA because of its lower boiling point (77 °C). The selection of BA over other solvents is mainly because its relatively high boiling point (204 °C) allows the use of a higher equilibration temperature without the introduction of significant amounts of solvent vapor into the GC column.

Solvent Volume. When BA was used as the solvent, solvent volume was changed while all of the other parameters were kept the same. ORBO-32 and ORBO-33 tubes were spiked with 100 μL (390 μg) of CH_3Br and then analyzed by equilibrating with 0.5, 1.0, 1.5, 2.0, or 3.0 mL of BA at 110 °C for 15 min in the HSA before injection to determine the effect of solvent volume.

Vial Size. Available vial sizes for Tekmar 7000 headspace autosampler were 21, 12, and 9 mL. Spiked samples were equilibrated with 1.0 mL of BA at 110 °C for 15 min in 21 or 9 mL headspace vials in the HSA before injection to determine the effect of headspace vial size.

Equilibration Temperature and Time. Equilibration temperature was modified while all of the other factors were kept the same. ORBO-32 or ORBO-33 tube samples spiked with 100 μL of CH_3Br were equilibrated with 1.0 mL of BA for 15 min at 60, 80, 100, 120, 140, 160, 180, or 200 °C in the HSA before injection to test the effect of equilibration temperature. Similarly spiked samples were equilibrated with 1.0 mL of BA at 110 °C for 5, 10, 15, 20, 25, 30, 40, or 60 min in the HSA before injection into the GC to determine the effect of various equilibration times on sensitivity of analysis.

Comparison of Solvent-Phase and Headspace Analyses. Known amounts of CH_3Br gas (0.2–500 μL) were spiked in the front sections of ORBO-32 and ORBO-33 tubes, and air was drawn through the tubes at 100 mL/min for 60 min. The spiked samples were analyzed either by solvent-phase or headspace methods under optimum conditions. In solvent-phase analysis, 3.0 mL of CS_2 was added, and the vials were sealed immediately and equilibrated at room temperature for 60 min, and an aliquot (2.0 μL) of the solvent phase was injected into the GC. In headspace analysis, 1.0 mL of BA was used and the sealed vials were thermostated for 15 min at 110 °C in the HSA for both ORBO-32 and ORBO-33; 1.0 mL of the pressurized headspace was introduced into the GC for analysis. Detector response in peak area was plotted against the amount of CH_3Br spiked for comparison of sensitivity.

Determination of Partition Coefficients K_H and K_d. One hundred microliters of CH_3Br gas was spiked on ORBO-32 and -33 tubes, and the samples were prepared as above. Blank vials and vials containing solvents only were also spiked with 100 μL of CH_3Br gas using a gastight syringe, and the vials were capped instantly. These two treatments were considered as solventless and solvent-only controls. Immediate capping was found to give good reproducibility for the amount of CH_3Br delivered into each vial. Vials containing the spiked charcoal standards and the controls were then prepared and analyzed using the solvent-phase or headspace methods under conditions described above.
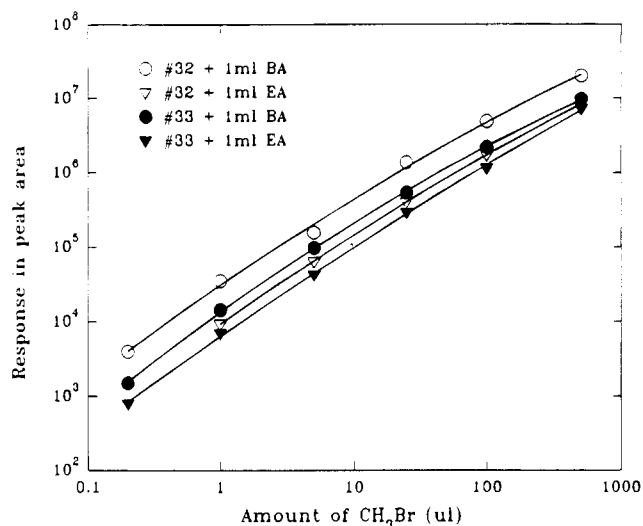
Figure 1. Effect of solvent types on sensitivity of headspace analysis of CH_3Br on ORBO-32 and ORBO-33 charcoal tubes (data points are averaged value of three replicates, and standard deviation is <5% in all analyses).

At equilibrium, the distribution of CH_3Br among the solvent, solid, and vapor phases in the headspace vials could be described by eqs 1 and 2, where C_a, C_l, and C_s are CH_3Br

$$C_a/C_l = K_H \qquad (1)$$

$$C_s/C_l = K_d \qquad (2)$$

concentrations in the vapor, solvent, and solid phases, respectively; K_H is the partition coefficient between the vapor and solvent phases, or the Henry's law constant; and K_d is the partition coefficient between the solvent and solid phases.

In solvent-phase analysis, GC analysis gave a direct measurement of C_l. C_a was estimated from the difference between C_l in the solvent-only controls and the total CH_3Br in the solventless controls. C_s was then calculated by subtracting CH_3Br in the solvent and headspace phases in vials containing charcoal from the total spiked CH_3Br. In headspace analyses, GC analysis gave a direct measurement of C_a. C_l was estimated from the difference between C_a in the solvent-only and the solventless controls. C_s was then calculated by subtracting CH_3Br in the solvent and headspace phases in the vials containing charcoal from the total spiked CH_3Br. K_H and K_d were calculated using eqs 1 and 2.

RESULTS AND DISCUSSION

Optimization of Conditions in Headspace Analysis. *Solvent Type.* Solvent determines the desorption of CH_3Br from the charcoal phase and the partition of desorbed CH_3Br between vapor and solvent phases and thus affects the concentration in the headspace. In addition, a solvent should be chosen with the consideration that the equilibration temperature in the HSA should not exceed or approach the boiling point of the solvent. The effect of solvent type on sensitivity of headspace analysis for CH_3Br is shown in Figure 1. Because of the large range of CH_3Br used (0.2−500 μL), both the X-axis (amount of CH_3Br in microliters) and Y-axis (response in area) were transformed into logarithmic format and then plotted against each other (Figure 1). Headspace analysis using 1.0 mL of EA at 70 °C showed lower sensitivity compared to 1.0 mL of BA at 110 °C on both tubes, and the difference was more significant on ORBO-32 tubes. The correlation of response in peak area and amounts of CH_3Br was found to be slightly nonlinear and was best described with a
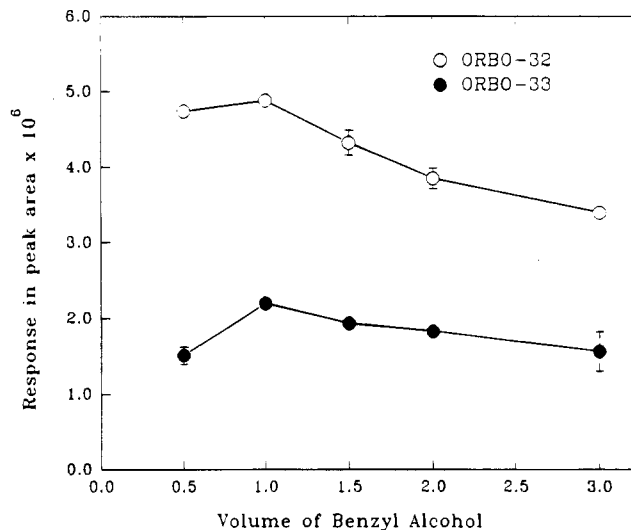

Figure 2. Effect of solvent volume on sensitivity of headspace analysis for 100 μL of CH_3Br on ORBO-32 and ORBO-33 charcoal tubes using BA as the solvent ($n = 3$).

second-order kinetics model (Figure 1). This could be caused by the very large range of CH_3Br volumes used in the experiment.

Solvent Volume. When more solvent is in a closed vial, partition of CH_3Br into the headspace decreases due to the increased dissolution of CH_3Br in the solvent phase. As shown in Figure 2, sensitivity increased when the volume of benzyl alcohol increased from 0.5 to 1.0 mL, but decreased gradually when the solvent volume further increased (Figure 2). The optimum amount of solvent was thus determined to be 1.0 mL for both ORBO-32 and ORBO-33 when BA was used as the extraction solvent.

Vial Size. Larger vial size increases the volume of headspace, causing more dilution of CH_3Br in the headspace. In the 9 mL headspace vials containing the contents from an ORBO-32 tube and 1.0 mL of solvent, the free headspace was determined to be 7.4 mL. In the 21 mL vials, the free headspace was 20.3 mL, which was 2.74 times larger than that in the 9 mL vials. Analysis of the same samples using the 9 mL vials consistently gave higher response compared to the 21 mL vials for both ORBO-32 and ORBO-33 tubes (Figure 3). Therefore, 9 mL vials were chosen over the 21 mL vials throughout this study.

Equilibration Temperature and Time. Dissociation of bonds between CH_3Br and charcoal surface should increase with increased equilibration temperature, which leads to increased partitioning of CH_3Br into the solvent and headspace phases. A change of temperature in a closed system would also affect the Henry's law constant, and the partition should favor the headspace phase. However, at high temperatures, significant degradation may occur, which would decrease the CH_3Br concentration in all phases. On both ORBO-32 and ORBO-33 tubes, the response from the same samples increased when the equilibration temperature was increased from 60 to 100 °C and then decreased when the temperature was further increased (Figure 4). The optimum equilibration temperature was determined to be 110 °C for both ORBO-32 and ORBO-33 charcoal tubes when 15 min of equilibration time was used. The decrease of response on ORBO-32 tubes for temperature from 100 to 200 °C was more drastic than on ORBO-33 tubes, indicating that CH_3Br on petroleum charcoal might be more resistant to degradation than on coconut
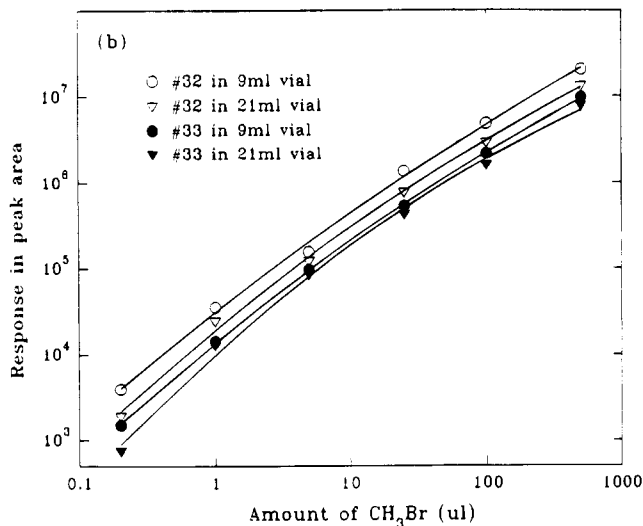
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Figure 3. Effect of vial size on sensitivity of headspace analysis of CH_3Br on ORBO-32 and ORBO-33 charcoal tubes using BA as the solvent (data points are averaged value of three replicates, and standard deviation is <5% in all analyses).
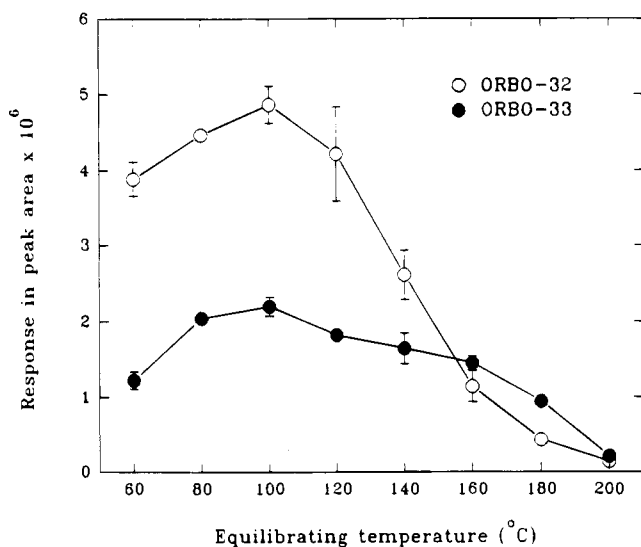

Figure 5. Effect of equilibration time on sensitivity of headspace analysis for 100 μL of CH_3Br on ORBO-32 and ORBO-33 charcoal tubes using BA as the solvent (equilibration temperature = 110 °C, n = 3).

Figure 4. Effect of equilibration temperature on sensitivity of headspace analysis for 100 μL of CH_3Br on ORBO-32 and ORBO-33 charcoal tubes using BA as the solvent (equilibration time = 15 min, n = 3).

Figure 6. Sensitivity of solvent-phase and headspace analysis of CH_3Br on OBRO-32 and ORBO-33 charcoal tubes (data points are averaged value of three replicates, and standard deviation is <5% in all analyses).

charcoal. Higher stability on petroleum charcoal was also observed for methyl isothiocyanate and 1,3-dichloropropene at elevated temperature in a headspace autosampler when equilibrated with benzyl alcohol (Gan et al., 1994). Poor storage stability was reported for 1,2-dichloropropane and 1,2-dibromo-3-chloropropane on coconut charcoal at room temperature (Albrecht et al., 1986). The higher reactivity of coconut charcoal toward CH_3Br might be attributed to the higher pH observed on this type of charcoal (Gan et al., 1995).

Equilibration time could influence the partitioning of CH_3Br among the three phases by affecting both the equilibrium and the extent of degradation. A longer equilibration time may result in more extensive degradation. As shown in Figure 5, when the equilibration time was increased from 5 to 15 min, the signal output increased for both ORBO-32 and ORBO-33 tubes. However, further increases in equilibration time resulted in a rapid decrease in sensitivity for ORBO-32 tubes and a relatively slower decrease for ORBO-33 tubes. Methyl bromide was again found to be more
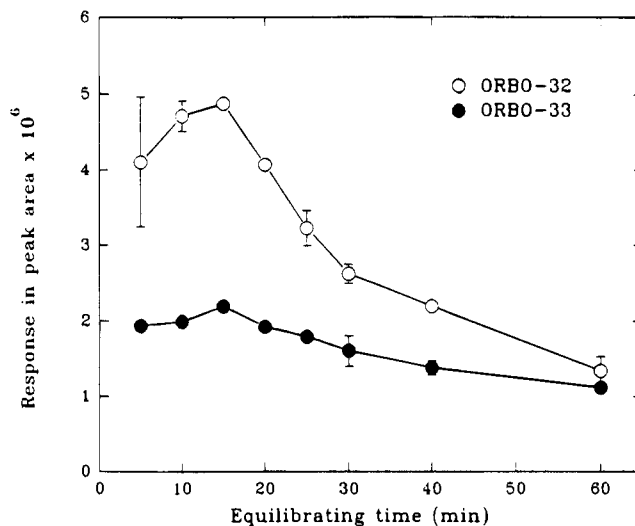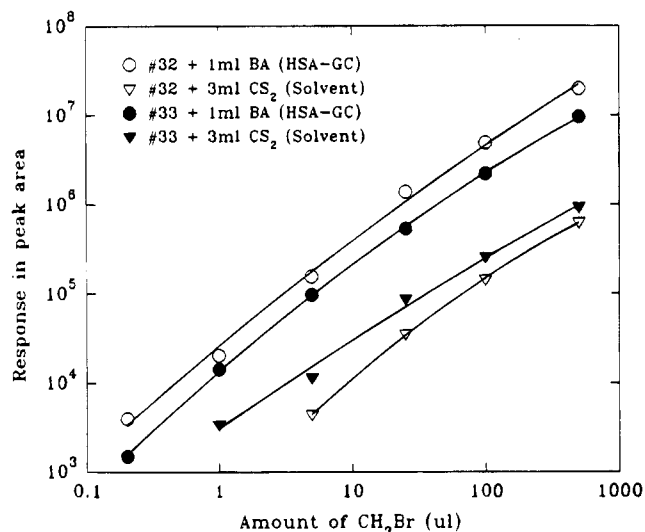
stable in vials containing petroleum charcoal rather than coconut charcoal (Figure 5).

Sensitivity of Solvent-Phase and Headspace Analyses. In solvent-phase analysis, 3.0 mL of CS_2 was found to be adequate for soaking all of the charcoal particles and forming enough free extract for sampling with a 10 μL syringe. Solvent-phase analysis of samples containing the same amounts of CH_3Br produced much lower response than the optimized headspace analysis (Figure 6). Response from headspace analysis under the optimum conditions was 30 times greater than that from solvent-phase analysis on ORBO-32 tubes and 10 times greater on ORBO-33 tubes when the slopes of the linearized calibration curves were compared. In headspace analysis, since no solvent (or only a trace amount) entered the column, no solvent peak was noted, and each analysis was completed in 4.0 min under the chosen GC conditions. In solvent-phase analysis, however, a large solvent peak (CS_2) was eluted 4.1 min after the injection under the same GC conditions, and thus a longer time (6.0 min) was required for each analysis. The minimum detection limit (MDL) was estimated

Table 1. Methyl Bromide Concentrations Measured in Air after Injection at 70 cm Depth in the Field

distance from soil surface (cm)	time after application			
	58 h		224 h	
	amt (μL)	concn[a] (ppb)	amt (μL)	concn (ppb)
5	0.442	36.83	0.0521	4.34
10	0.541	45.08	0.0347	2.89
30	0.333	27.75	0.00762	0.64
50	0.259	21.58	0.00505	0.44
70	0.178	14.83	0.00246	0.21
110	0.106	8.83	0.00398	0.33
150	0.0558	4.65	0.00147	0.12
200	0.0101	0.84	0.00069	0.06
260	0.0057	0.47	0.00137	0.11

[a] Sample volume was 12 L at 100 mL/min for 2 h; ppb = μL of CH_3Br/m^3 of air.

from the lower end of the calibration curves by assuming the detectable peak area to be 3 times the background noise. The MDL was estimated to be approximately 0.4 ng for the headspace method for either ORBO tube under the optimum conditions and 32 ng for the solvent-phase method. Assuming a total of 24 L of air is drawn through the tubes at 100 mL/min for 4 h, the corresponding MDL in air concentration would be 17 ng/m^3 for the headspace method and 1300 ng/m^3 for the CS_2 method. The MDL in the headspace analysis could be further improved by using a larger sample loop in the HSA or a smaller split ratio on the GC. In a recent field study, the atmospheric concentrations of CH_3Br were monitored for approximately 3 weeks by using ORBO-32 tubes installed on an active sampling mast after 325 kg/ha of the fumigant was injected at 70 cm in a Greenfield sandy loam. The charcoal samples were analyzed using the optimized headspace GC method under the optimum conditions. Measured concentrations at different heights along the mast 58 and 158 h after application were included in Table 1 to illustrate the sensitivity of the headspace method (Table 1).

The higher MDL of the CS_2 method might be sufficient for monitoring CH_3Br exposure at workplaces, where high concentrations of CH_3Br are usually present. However, it may fail to meet the sensitivity required for environmental sampling under open field conditions. Since gastight conditions need to be maintained during sample preparation, solvent-phase analysis would be also difficult to automate on current instruments. The HSA used in this study is highly automated with many adjustable features, and the use of a sample loop on the HSA generally assures good reproducibility between injections. Under the described conditions, the cycle time for each analysis for headspace analysis is only 4 min, and up to 300 injections can be made in 24 h. In a previously reported headspace method, a MDL of 50 ng was reported for CH_3Br when a 32 min run time was used for each analysis (Woodrow et al., 1988). In our headspace method, the baseline response was not interrupted by the HSA operations, and the very short run time was permissible.

Partition of CH_3Br among Vapor, Solvent, and Solid Phases in Headspace Vials. In a closed system, the partition coefficients K_H and K_d and headspace volume (V_a, in cm^3), solvent volume (V_1, in cm^3), and amount of charcoal (M_s, in g) determine the partition of CH_3Br among the three phases:

$$V_aC_a + V_1C_1 + M_sC_s + D = P \qquad (3)$$

Here D is the amount degraded and P the total amount of CH_3Br present in a closed vial.

Table 2. Partition Coefficients K_H and K_d for CH_3Br under Various Experimental Conditions ($\pm$ Standard Error, $n = 3$)

conditions	ORBO tube	K_H	K_d
CS_2 extraction	32	0.071 ± 0.006	20.12 ± 0.18
(25 °C, 60 min)	33		6.72 ± 0.26
ethyl acetate headspace	32	0.026 ± 0.002	1.14 ± 0.10
(70 °C, 15 min)	33		2.47 ± 0.18
benzyl alcohol headspace	32	0.075 ± 0.003	3.29 ± 0.82
(110 °C, 15 min)	33		6.87 ± 0.03
benzyl alcohol headspace	32	0.074 ± 0.001	5.83 ± 0.21
(110 °C, 60 min)	33		10.76 ± 1.66
benzyl alcohol headspace	32	0.146 ± 0.012	25.19 ± 4.47
(160 °C, 15 min)	33		10.55 ± 0.81

Combining eqs 1—3 would give

$$C_1 = \frac{P - D}{K_HV_a + V_1 + K_dM_s} \qquad (4)$$

$$C_a = \frac{K_H(P - D)}{K_HV_a + V_1 + K_dM_s} \qquad (5)$$

To optimize solvent-phase analysis, partition should favor the solvent phase, or a large C_1. From eq 4, this can be achieved by reducing V_a, V_1, M_s, or D or choosing solvent or solid material which gives a low K_d or K_H. To optimize the headspace method, partition should favor the vapor phase, or a large C_a. From eq 5, reducing V_a, V_1, M_s, K_d, or D or increasing K_H will maximize the presence of CH_3Br in the headspace and thus the sensitivity of analysis. Therefore, decreasing vial size, solvent volume, and charcoal mass increases the sensitivity of analysis for both methods. However, charcoal mass (M_s) is usually selected on the basis of trapping efficiency, and a large mass often ensures better recovery. The amount of solvent (V_1) should be sufficient to completely wet the charcoal granules in headspace analysis or result in sufficient free extract for solvent-phase analysis. Increasing equilibration temperature shifts the partition of CH_3Br from solvent phase into vapor phase and therefore will enhance C_a and sensitivity of analysis. However, at higher temperature, degradation may be accelerated, which results in a larger D or a smaller C_a.

Partition coefficients K_H and K_d were calculated in this study to explain the observed effects of various factors on sensitivity of analysis and to provide a rationale for optimizing HSA conditions (Table 2). It must be pointed out that since no effort was made to determine the degradation rate, the values of K_d in Table 2 are apparent values and may include the contribution from degradation. Substituting the measured V_a, V_1, M_s, K_H, and K_d in eqs 1—3, the proportion of CH_3Br in each phase was calculated (Table 3). Dilution factors were calculated as the ratio of the total amount of CH_3Br in samples vs the actual amount of CH_3Br being introduced into the GC for detection.

In the solvent-phase analysis, the high K_d value greatly favored the partition of CH_3Br into the charcoal phase (Table 1). Coconut-based charcoal from ORBO-32 had a higher K_d than petroleum-based charcoal from ORBO-33. Only 20 and 28% of the CH_3Br in the closed vial was dissolved in the CS_2 phase, respectively, in vials containing ORBO-32 and ORBO-33 samples. Since only 2 μL of the 3.0 mL of CS_2 extract was actually injected into the GC, the final dilution factors were determined to be 7500 for ORBO-32 and 5400 for ORBO-33. High

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Table 3. Distribution (Percent) of Methyl Bromide among Vapor, Solvent, and Solid Phases under Various Experimental Conditions (± Standard Error, $n = 3$)

conditions	ORBO tube	vapor	solvent	solid + degradation	dilution[a]
CS$_2$ extraction	32	2.45 ± 0.23	19.88 ± 0.54	77.67 ± 0.41	7500 ± 150
(25 °C, 60 min)	33	3.54 ± 0.31	28.02 ± 0.19	68.44 ± 0.47	5400 ± 210
ethyl acetate headspace	32	10.01 ± 0.15	53.46 ± 1.02	36.53 ± 0.98	160 ± 5
(70 °C, 15 min)	33	4.72 ± 0.42	25.84 ± 0.87	69.44 ± 0.78	320 ± 8
benzyl alcohol headspace	32	15.59 ± 0.52	28.39 ± 0.79	56.02 ± 1.03	100 ± 5
(110 °C, 15 min)	33	5.92 ± 0.12	11.09 ± 0.39	82.99 ± 1.96	256 ± 19
benzyl alcohol headspace	32	10.79 ± 0.37	19.82 ± 0.62	69.39 ± 1.52	145 ± 8
(110 °C, 60 min)	33	3.99 ± 0.09	7.61 ± 0.23	88.40 ± 2.53	385 ± 26
benzyl alcohol headspace	32	4.44 ± 0.84	4.10 ± 0.82	91.46 ± 2.96	359 ± 71
(160 °C, 15 min)	33	5.60 ± 0.55	7.95 ± 0.51	86.45 ± 1.07	274 ± 27

[a] Dilution: dilution factor = ratio of total CH$_3$Br in sample to the amount of CH$_3$Br injected into the GC.

dilution factors were apparently responsible for the observed low sensitivity in this solvent-phase method (Figure 6).

When EA was used as the solvent and equilibration temperature set at 70 °C in headspace analysis, very small K_H and K_d values were obtained (Table 1). Small K_d favored the distribution of CH$_3$Br into the solvent phase, and as much as 53.5% of the CH$_3$Br was present in 1.0 mL of EA extract when ORBO-32 tubes were used. The large proportion of CH$_3$Br in the solvent phase partially countered the unfavorable partition between the solvent and headspace as determined by the small K_H, and the proportions of CH$_3$Br in the headspace phase reached 10% for ORBO-32 and 4.7% for ORBO-33 (Table 2). Since 1.0 mL of the pressurized headspace (equivalent to 0.47 mL of the headspace prior to pressurization) was introduced into the GC for analysis, the final calculated dilution factors were 160 for ORBO-32 and 320 for ORBO-33, indicating a great improvement over the solvent-phase analysis. A smaller dilution factor with ORBO-32 tubes can be attributed to the smaller mass or the different nature of the contained charcoal.

With BA as the solvent and the equilibration temperature increased to 110 °C in the HSA, both K_H and K_d were enhanced. Increased K_H favored the partition of CH$_3$Br into the headspace, which countered the unfavorable increase of K_d. As a net result, the proportion of CH$_3$Br present in headspace increased to 15.6% for ORBO-32 and to 5.9% for ORBO-33. The dilution factors concurrently decreased to 100 and 256 for ORBO-32 and -33, respectively. Increasing the equilibration temperature from 110 to 160 °C caused 1.95 times increase of K_H and 7.66 and 1.54 times increase of K_d for ORBO-32 and ORBO-33 tubes, respectively. For ORBO-32 tubes, the proportion of CH$_3$Br present in the headspace decreased from 15.6 to 4.4%, and the dilution factor consequently increased from 100 to 359. The effect of temperature on the distribution of CH$_3$Br in vials containing ORBO-33 samples was not as significant, and the dilution factors remained almost unchanged (Table 3). This could be explained by the observed stability of CH$_3$Br on petroleum-based charcoal. Equilibrating for a longer time in the HSA did not change the partition of CH$_3$Br between the headspace and solvent phases but did increase the partition into the charcoal phase and/or degradation (Table 2). The final dilution factors increased to 145 and 385 for ORBO-32 and ORBO-33, respectively. It seems that enhanced degradation during the longer equilibration time contributed to the apparent increase of partition into the solid phase.

In summary, headspace analysis of CH$_3$Br in charcoal tubes showed significantly higher sensitivity than the

traditional solvent-phase analysis. The lower sensitivity of the solvent-phase method could be attributed to the higher dilution factor, which was nearly 2 orders of magnitude larger than that in the headspace method. In headspace analysis, calibration can be made directly on the HSA-GC by analyzing a set of charcoal samples fortified with known amounts of CH$_3$Br. A highly sensitive optimized method for analyzing CH$_3$Br on ORBO tubes includes the following: ORBO-32 or similar coconut-based charcoal tubes; headspace analysis; 9 mL headspace vials; 1.0 mL of BA as the extraction solvent; 110 °C as the equilibration temperature; and 15 min as the equilibration time. In two field studies recently completed in this laboratory, over 10 000 ORBO tube samples were analyzed using the described method (Yates et al., 1995a,b). The potential of applying the headspace method to some other volatile compounds including other fumigants needs to be further explored. The suitability of headspace analysis for a specific analyte is determined to a great extent by the K_H, which in turn is greatly influenced by the analyte's vapor pressure and solubility in the chosen solvent. For compounds with low vapor pressure, headspace analysis may not be as sensitive as solvent-phase analysis.

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