

Recapturing and decomposing methyl bromide in fumigation effluents

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Received 9 April 1997; accepted 31 August 1997

Abstract

Methyl bromide (CH_3Br) is an important fumigant for treating agricultural produce and structures, but emissions during fumigation may contribute to stratospheric ozone depletion and impose hazardous effects on human health. A method is described that uses activated carbon to recover CH_3Br from air streams, and sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$) to degrade the recovered CH_3Br to relatively nontoxic Br^- . Degradation of carbon-adsorbed CH_3Br in $\text{Na}_2\text{S}_2\text{O}_3$ solution was completed in less than 9 h at room temperature (20°C). In simulated pilot experiments, two coconut-based activated carbons trapped CH_3Br up to 15% of the weight of carbon, while an excessive molar amount of $\text{Na}_2\text{S}_2\text{O}_3$ in solution completely converted the CH_3Br to Br^- overnight. The reaction products, Br^- and sodium methylthiosulfate ($\text{NaCH}_3\text{S}_2\text{O}_3$), are freely soluble in water, non-corrosive, non-volatile and low in toxicity. Solutions containing 1% of these products may be disposed of directly into the drain according to current environmental regulations, which allows the spent carbon to be regenerated simply by rinsing in water and drying at a moderate temperature. Carbons recycled in this manner showed similar capacities in adsorbing CH_3Br as the unused carbons. The reported approach is environmentally-compatible and low in cost, and is especially suitable for on-site application. © 1998 Elsevier Science B.V.

Keywords: Methyl bromide; Fumigation; Activated carbon; Ozone depletion

1. Introduction

Methyl bromide (bromomethane, CH_3Br) is the most widely used fumigant for pest control in perishable produce (e.g. fresh fruits and vegetables, and cutflowers), en-

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durable produce (e.g. cereal grains, dry fruits and nuts, and timber), and structures. Fumigation with CH_3Br is mandatory for import and export of many agricultural products in international trade [1]. The worldwide use of CH_3Br for fumigating commodities and structures reached 1.8×10^7 kg, or 25% of its total use in 1992 [1]. Using current practices, however, as much as 51–88%, 85–95% and 90–95% of the applied CH_3Br escapes into the atmosphere during durables, perishables and structural treatment, respectively [1]. These emissions are primarily the result of intentional discharge of CH_3Br waste gases at the end of fumigation.

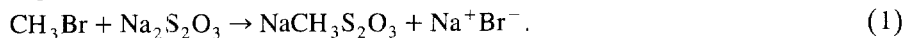
Emissions of CH_3Br during commodity and soil fumigation are reportedly contributing to stratospheric ozone depletion as well as imposing negative effects on human health [2–6], and thus the use of CH_3Br has been proposed to be discontinued in the USA by 2001, and in the other countries at 2010 [1,7]. However, as there are no effective alternatives, retaining CH_3Br for post-harvest and structural fumigation is of great economic importance [1,8]. Extension of CH_3Br usage may be permitted only if its emissions are sufficiently reduced. As commodity or structural fumigations are always carried out in closed environments, recovering unreacted CH_3Br is feasible. The fumigated products absorb little CH_3Br , leaving most of the applied chemical available for recovery [1].

Various methods have been proposed to recover and decompose CH_3Br from waste fumigation gases [9–15]. Among them, activated carbon-based methods have received the most attention because of its low cost and large capacity to adsorb CH_3Br (10–30% of the weight of carbon) [1,11,13,14]. After CH_3Br is trapped on carbon, heated N_2 (130–250°C) [9], methanol vapor (80°C) [10], or air (280°C) [11,13], is used to desorb CH_3Br . The desorbed CH_3Br is then incinerated at high temperatures (600°C) in a special furnace, and the HBr produced from the combustion is removed by scrubbing in a NaOH solution [11,13]. Although some of these methods are successful at the experimental and small production scales, none of them have found wide application. The lack of application may be attributed to the complexity of the detoxification steps, and the associated formidable cost and safety requirements. The stringent reaction conditions such as high temperatures require detoxification to be performed off-site in special facilities, but many safety regulations impose difficulties for off-site shipment of CH_3Br -contaminated carbons.

We report a simple and on-site applicable method for detoxifying CH_3Br captured on activated carbon. The method is based on a rapid nucleophilic substitution reaction between CH_3Br and $\text{Na}_2\text{S}_2\text{O}_3$. The reaction products are water soluble and very low in toxicity, and thus can be disposed of simply by rinsing in water, allowing the spent carbon to be regenerated at the same time. This method was successfully tested in simulated pilot experiments using two commercial carbons.

2. Theory

Degradation of CH_3Br adsorbed on carbon is based on the following reaction, in which $\text{S}_2\text{O}_3^{2-}$ acts as a nucleophile and $-\text{Br}$ on CH_3Br as the leaving group:



The above reaction is a well defined S_N2 -type nucleophilic substitution reaction [16,17]. Application of this reaction for detoxifying CH_3Br , however, has never been reported. $S_2O_3^{2-}$ is known as one of the strongest nucleophiles in S_N2 reactions [18]. The reaction rate of CH_3Br with $S_2O_3^{2-}$, at $3.24 \times 10^{-2} M^{-1} s^{-1}$, is 200 times that with OH^- [17,19]. The reaction is second order in kinetics, and when an excessive molar amount of $Na_2S_2O_3$ is present, the reaction completes within a few hours at ambient temperatures [16]. Unreacted substrate $Na_2S_2O_3$, and the reaction products sodium methylthiosulfate ($NaCH_3S_2O_3$), Na^+ and Br^- , are all non-volatile, non-corrosive, and freely soluble in water. $Na_2S_2O_3$, the fixing agent used in photo development, is inexpensive and low in toxicity (LD i.v. in rats: $> 2500 mg kg^{-1}$) [20]. According to the current environmental regulations, water solutions containing 1% of $Na_2S_2O_3$, $NaCH_3S_2O_3$ or Br^- are allowed to be disposed of directly into the drain.¹ The aforementioned characteristics of the reaction permit the reaction products to be safely disposed of, and at the same time, allow the spent carbon to be conveniently regenerated by rinsing the carbon in water and then drying at a moderate temperature (e.g. 80–120°C).

3. Experimental

3.1. Chemicals and activated carbons

Gaseous CH_3Br (99.5% purity) in a lecture bottle was purchased from Aldrich Chemical (St. Louis, MO). Before use, CH_3Br was filled into a deflated Teflon gas sampling bag. Methyl bromide in the sampling bag had a vapor density of $3.7 mg ml^{-1}$ at 20°C. Two types of activated carbon, a Sigma C (Sigma Chemical, St. Louis, MO) and a Calgon C (provided by Calgon Carbon, Pittsburgh, PA), were used in this study. The Sigma C was coconut-based, and had 8×20 mesh particle size, $600\text{--}800 m^2 g^{-1}$ surface area, and $800 mg g^{-1}$ iodine number; and the Calgon C was also coconut-based, and had 4×8 mesh particle size, $1150\text{--}1250 m^2 g^{-1}$ surface area and $1200 mg g^{-1}$ iodine number. Both carbons were dried in an oven at 105°C overnight before use. Sodium thiosulfate ($Na_2S_2O_3$, 99%) and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, 99%) were purchased from Fluka Chem. (Ronkonkoma, NY).

3.2. Degradation of carbon-adsorbed CH_3Br by $Na_2S_2O_3$

The reaction kinetics of CH_3Br and $Na_2S_2O_3$, with CH_3Br adsorbed on carbon and $Na_2S_2O_3$ present in excessive molar amount, was measured in solution at room temperature (20°C). Two g of Sigma or Calgon C were weighed into 21-ml headspace vials, and the vials were crimp sealed with aluminum caps and Teflon-faced butyl rubber septa. Twenty ml of gaseous CH_3Br was then injected through the septum into the vial using a gas-tight syringe. The amount of CH_3Br that each carbon sample adsorbed was

¹ Calculations made by Maggie Souder, Hazardous Waste Specialist, Univ. California, Riverside, based on current California Code of Regulation, Title 22, 66261.10–66261.113.

determined by weighing the sample to 0.1 mg before and after spiking. On average, each carbon sample received 71 ± 5 mg (0.74 ± 0.05 mmole) of CH_3Br .

After equilibrating the spiked carbon samples for 2 h at room temperature, 5 ml of 0.2 M $\text{Na}_2\text{S}_2\text{O}_3$ solution (1.0 mmole) was injected into the sample vials through the septum. All sample vials remained at room temperature to allow the reaction to proceed. The time of $\text{Na}_2\text{S}_2\text{O}_3$ addition was considered as time zero. Three replicate samples were removed at different times, and the carbon slurry was washed into a beaker with 20 ml deionized H_2O . Bromide in the solution phase was then determined using a Br-selective electrode on an Accumet-25 pH meter (Fisher Scientific, Pittsburg, PA) after proper dilution. The decomposition rate of CH_3Br was calculated as the percent of the spiked amount that was degraded to Br^- .

3.3. Simulated pilot experiments

Two small-scale experiments were conducted using a model system to demonstrate the application of the method. The system (Fig. 1) consisted of a fumigation enclosure (box) made of sheet metal ($60 \times 60 \times 30$ cm, or 106 l inside volume), a recirculating pump (Fisher Scientific), a moisture filter containing Drierite (Fisher Scientific), and an adsorption bed. The adsorption bed was constructed by packing a mixture of 325.0 g carbon (60%) and 216.0 g $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (40%) into a hollow brass cylinder [8 (i.d.) $\times 30$ cm (h)] with an inlet and an outlet. Glass wool was placed at both ends of the cylinder to hold the carbon particles in place. After all the components were connected with latex tubing, the recirculating pump was turned on, creating a flow of about 14 l min^{-1} circulating from the fumigation box through the carbon bed and then back into the fumigation box (Fig. 1).

Liquid CH_3Br (density = 1.73 g ml^{-1}) prepared by chilling gaseous CH_3Br on dry ice was injected into the fumigation box through the injection/sampling port. In

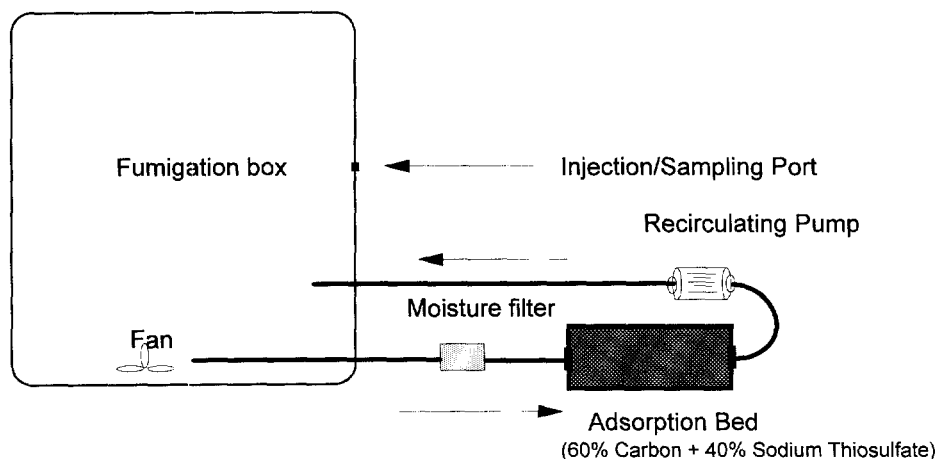


Fig. 1. Diagram of the model system used in the simulated pilot experiments for trapping methyl bromide from a closed environment.

Experiment I, the adsorption bed was packed with the Sigma C, and 50.0 g liquid CH_3Br was added. In Experiment II, the bed was packed with the Calgon C, and 60.0 g CH_3Br was introduced. After application, CH_3Br concentration in the box was periodically monitored by withdrawing an aliquot of air from the inside of the box and analyzing it by gas chromatography (GC) using an HP5890 GC (Hewlett Packard, Fresno, CA). The GC conditions were: RTX-624 capillary column ($30\text{ m} \times 0.32\text{ mm} \times 1.4\text{ }\mu\text{m}$, Restek, Bellefonte, PA), 1.1 ml min^{-1} helium flow rate, 35°C isothermal column temperature, 170°C injection port temperature and 240°C electron capture detector temperature. Recirculation was stopped when CH_3Br concentration in the fumigation box either decreased to a nondetectable level or became constant. The carbon cylinder was then dismantled, and the weight of carbon- $\text{Na}_2\text{S}_2\text{O}_3$ mix was measured to 0.1 g. Since the moisture filter placed in front of the adsorption bed removed any water in the air stream, net weight change could be attributed to adsorption of CH_3Br onto the carbon.

To detoxify recovered CH_3Br , the carbon- $\text{Na}_2\text{S}_2\text{O}_3$ mix was transferred into a 2-l Erlenmeyer flask, and 600 ml deionized H_2O was added. The flask was then closed with aluminum tape, and kept at room temperature overnight. To determine the rate of CH_3Br degradation, the reacted carbon slurry was washed into a large pan with 10 l deionized water and the mixture was thoroughly stirred. An aliquot of the solution was sampled and the Br^- concentration measured after dilution.

3.4. Regeneration of spent carbon

The carbon used in the above experiments was rinsed in running tap water for approximately 10 min and then dried at 105°C overnight in a conventional laboratory oven. This process served two purposes: disposal of reaction products and unreacted $\text{Na}_2\text{S}_2\text{O}_3$, and regeneration of the spent carbon. To compare the capacity of regenerated and unused carbons for adsorbing CH_3Br , an air stream containing 150 mg l^{-1} CH_3Br was passed through a moisture filter and then through a cylinder packed with 325 g of the regenerated or unused Sigma or Calgon C at 2 l min^{-1} . Methyl bromide in the effluent was periodically monitored, and CH_3Br flowing into the adsorption bed was stopped at the first detection of CH_3Br in the effluent. The weight of carbon was measured to 0.1 g, and the increase in the weight of carbon was assumed to be due to adsorption of CH_3Br onto the carbon.

4. Results and discussion

4.1. Reaction of $\text{Na}_2\text{S}_2\text{O}_3$ with carbon-adsorbed CH_3Br

In water solution with the presence of an excessive molar amount of $\text{Na}_2\text{S}_2\text{O}_3$, CH_3Br adsorbed on carbon was rapidly decomposed to Br^- at room temperature (20°C) (Fig. 2). Approximately 80% and 92% of the CH_3Br adsorbed on Sigma and Calgon C was degraded to Br^- after 30 min of reaction. After 9 h of reaction, decomposition of CH_3Br measured as production of Br^- approached 100% for both carbons, indicating

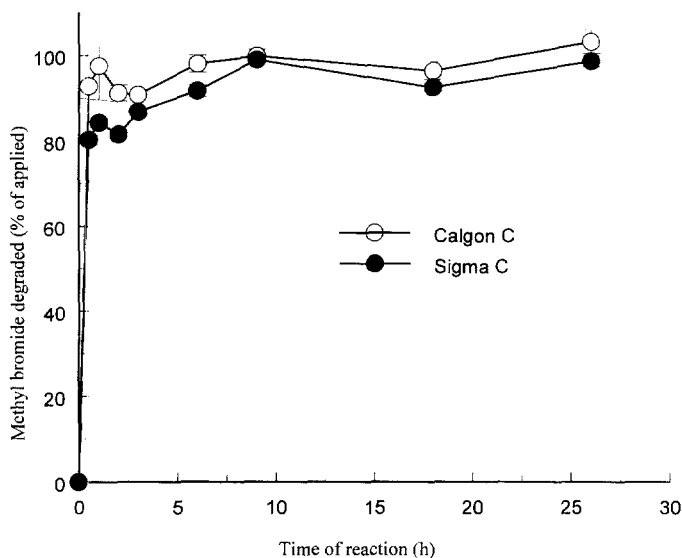


Fig. 2. Degradation of carbon-adsorbed methyl bromide in sodium thiosulfate solution at room temperature (20°C) to bromide ion.

that decomposition of CH_3Br was approximately completed. The decomposition of adsorbed CH_3Br was slightly slower than the reaction in pure $\text{Na}_2\text{S}_2\text{O}_3$ solution as estimated using the reported rate constant [17]. This might be caused by the heterogeneous nature of the reaction environment, i.e., the existence of solid (carbon), aqueous and gaseous phases. A few other reactions may also have occurred concurrently. One of these reactions is the $\text{S}_\text{N}2$ reaction with OH^- . Coconut-based carbons contain oxides, and their water supernatants were found to be basic in a previous study [21]. The pH in 1:10 (w/w) carbon–water mixture was measured as 11.4 for the Sigma C, and 11.2 for the Calgon C. However, as the rate of CH_3Br reaction with OH^- is > 2 orders of magnitude slower than that with $\text{S}_2\text{O}_3^{2-}$ [17,19], it should not contribute significantly to the rapid CH_3Br decomposition observed in the current study. The pH of the carbon– $\text{Na}_2\text{S}_2\text{O}_3$ solution was 10.8–11.0, and did not change significantly in the time course of the study.

4.2. Simulated pilot experiments

As the time of circulation increased, CH_3Br concentration in the fumigation box rapidly decreased (Fig. 3). The concentration decrease was especially fast at the beginning. For instance, about 78–82% of the added CH_3Br was removed within the first 20 min based on concentration differences. In Experiment I, CH_3Br in the fumigation box decreased to a nondetectable level after 60 min of circulation, while in Experiment II, it was depleted to less than 3% of the applied amount after 70 min. Weighing the carbon at the end of circulation showed that 49.5 g, or 99% of the added 50.0 g CH_3Br was trapped in the Sigma C adsorption bed in Experiment I, and 57.4 g,

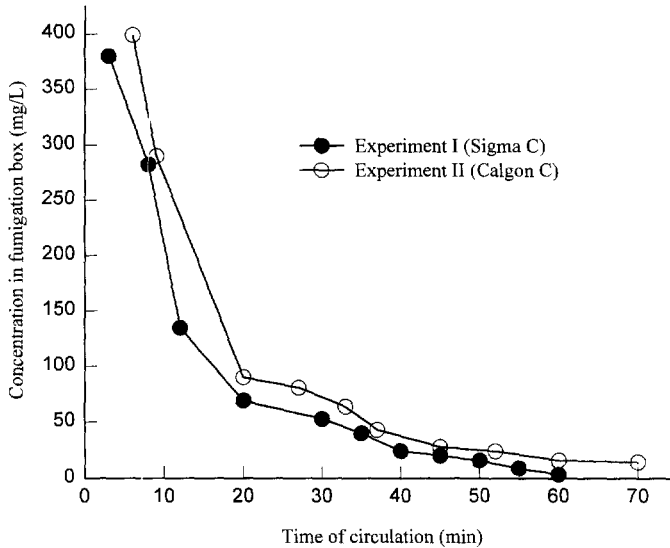


Fig. 3. Decrease in methyl bromide concentrations inside the fumigation box during the simulated pilot experiments.

or 95.7% of the added 60.0 g CH_3Br was trapped in the Calgon C bed in Experiment II (Table 1). The adsorption of CH_3Br was equivalent to 15.2 and 17.7% of the weight of carbon for the Sigma and Calgon C, respectively. Similar CH_3Br adsorption capacities have been reported for activated carbons by other investigators [11,12,14]. In practice, since the amount of CH_3Br to be applied is known beforehand, the amount of carbon that is needed to remove CH_3Br can be roughly determined.

After water was added to the carbon- $\text{Na}_2\text{S}_2\text{O}_3$ mix and the reaction continued overnight at room temperature, $101 \pm 3\%$ of the adsorbed CH_3Br on the Sigma C and $97.4 \pm 1.4\%$ on the Calgon C was decomposed to Br^- (Table 1). Based on Br^- production, only about 60–72% of the $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ was actually consumed in the reaction with CH_3Br . Since 1 g of CH_3Br (MW = 96) reacts approximately 2.6 g of

Table 1
Removal and decomposition of methyl bromide in simulated pilot experiments

	Experiment I (Sigma C)	Experiment II (Calgon C)
Amount of carbon (g)	325	325
Amount of $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ (g)	216	216
Flow rate (l min^{-1})	14	14
Total circulation time (min)	60	70
Amount of CH_3Br added (g)	50.0	60.0
Amount of CH_3Br removed (g)	49.5	57.4
% of CH_3Br removed	99	97.5
% of CH_3Br decomposed	101 ± 3	97.4 ± 1.4

Table 2

Methyl bromide adsorption capacities of regenerated and unused carbons

Carbon type	Sigma C		Calgon C	
	Regenerated	Unused	Regenerated	Unused
Amount of carbon (g)	325	325	325	325
Influent CH ₃ Br concentration (mg l ⁻¹)	150	150	150	150
Flow rate (l min ⁻¹)	2	2	2	2
Time to reach breakthrough (min)	190	180	200	190
Total CH ₃ Br adsorbed on C (g)	44.3	40.8	49.4	47.8
CH ₃ Br/Carbon (% wt./wt.)	13.6	12.5	15.2	14.7

Na₂S₂O₃ · 5H₂O (MW = 248), in practice the use of Na₂S₂O₃ · 5H₂O at 4–5 times the mass of CH₃Br is necessary to assure complete decomposition of CH₃Br. Since the decomposition is based on the reaction between CH₃Br and S₂O₃²⁻, the amount of H₂O is not critical, as long as it is sufficient to soak the carbon and dissolve Na₂S₂O₃ salt.

4.3. Regeneration of spent carbon

Since activated carbon adsorbs 10–30% of CH₃Br by weight, a high carbon-to-CH₃Br ratio is needed to achieve a complete recovery of CH₃Br. Even though carbon is relatively inexpensive, the overall cost to use carbon to remove CH₃Br will be high unless the spent carbon can be regenerated in a cost-effective manner. The used carbons from the above studies were regenerated by rinsing with water and then drying at 105°C overnight. The capacity of the regenerated carbons to adsorb CH₃Br was compared with unused carbons. The regenerated Sigma or Calgon C adsorbed similar amounts of CH₃Br as unused carbon under the same conditions (Table 2), indicating that the water-rinsing and oven-drying did not affect the carbon's capacity to adsorb CH₃Br.

5. Conclusions

Methyl bromide is an important fumigant, but emissions during the fumigation process may contribute to the stratospheric ozone depletion as well as cause health concerns. We have shown that it is economically feasible to remove CH₃Br from air streams by adsorption on activated carbon and to detoxify the CH₃Br in an environmentally friendly way using the simple and well characterized reaction with thiosulfate salts. Our study shows that this reaction can be applied to the decomposition of CH₃Br recovered on activated carbon. The reported method is more cost-effective than other existing methods. The main expendable cost of this method is Na₂S₂O₃, but technical grade Na₂S₂O₃ is very inexpensive. In lieu of Na₂S₂O₃, other thiosulfate salts, such as ammonium thiosulfate and potassium thiosulfate, can also be used. The latter two thiosulfate products are commercial fertilizers, and are therefore readily available at very low cost. Activated carbon is a nonhazardous and easily available material. Activated carbon is inexpensive, but since several parts (5–10) of carbon are required to trap one

part of CH_3Br , recycling carbon becomes economically necessary. As shown in this study, spent carbon may be reactivated in a very safe and energy-efficient manner, which should further lower the overall cost of this technique.

The steps for carrying out detoxification are also simple and safe enough to be applied at or near the fumigation site. The system for removing and decomposing CH_3Br , as illustrated in Fig. 1, is simple to construct, and the requirement for materials is insignificant since the same system may be reused. For large fumigation enclosures, multiple systems may be used simultaneously to expedite CH_3Br removal. Recovery and destruction of CH_3Br using this method can be expected to be completed within 24 h, and minimal personal attendance is needed once the circulation is established or water is added into the carbon– $\text{Na}_2\text{S}_2\text{O}_3$ mix. Considering the need for off-site treatment of CH_3Br -loaded carbons required by other methods, the on-site applicability of this method offers an important advantage.

Acknowledgements

The authors wish to thank Q. Zhang for obtaining some of the experimental data and M. Souder for calculating allowable disposal concentrations of sodium thiosulfate, bromide and sodium methylthiosulfate under California regulations. The authors also wish to express their gratitude to Dr. W.F. Spencer for his suggestions at the early stage of the work.

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