Original
9444

PB95179842

Research into Problems with NIOSH Method 2520 for Methyl Bromide

Y. T. Gagnon, V. L. Ringenburg and J. M. Fajen

Department of Health and Human Services,
U.S. Public Health Service
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health
4676 Columbia Parkway, Cincinnati, Ohio, 45226

DISCLAIMER
Mention of company names or products does not constitute endorsement by the Centers for Disease Control and Prevention.

AUG 1994

REPRODUCED BY:
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161
NTIS

50272-101

REPORT DOCUMENTATION PAGE	1. REPORT NO.	2.	PB95179842

4. Title and Subtitle Research into Problems with NIOSH Method 2520 for Methyl Bromide	5. Report Date 1994/08/00
	6.
7. Author(s) Gagnon, Y. T., V. L. Ringenburg, and J. M. Fajen	8. Performing Organization Rept. No.
9. Performing Organization Name and Address NIOSH, U.S. Department of Health and Human Services, Cincinnati, Ohio	10. Project/Task/Work Unit No.
	11. Contract (C) or Grant(G) No. (C) (G)
12. Sponsoring Organization Name and Address	13. Type of Report & Period Covered
	14.
15. Supplementary Notes National Institute for Occupational Safety and Health	

16. Abstract (Limit: 200 words) As part of an industry wide study in the fumigation industry, industrial hygiene evaluations were conducted at two structural fumigation facilities in Florida during July of 1990; difficulty was noted with (NIOSH) Method 2520 for methyl-bromide (74953). Sampling results indicated that methyl-bromide breakthrough had occurred. Some of the backup tubes contained greater amounts of methyl-bromide than the front sampling tubes. Several problems were discovered when reviewing the method. These included reduced adsorption capacity at high humidity, difficulty in preparing standard solutions, sample instability, decreasing recovery as the loading decreased, and insufficiently low quantitation limit. Several modifications were offered for methyl-bromide sampling. A maximum sample volume of one liter should be collected. The samples should be stored at minus 10 degrees-C or below until analysis. Samples should be analyzed within 6 days of collection. Methylene-chloride should be used as the desorption solvent rather than carbon-disulfide. Calibration should be against other brominated compounds. Before conducting air sampling, the conditions under which the analytical method was evaluated should be reviewed.

REPRODUCED BY:
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161
NTIS

17. Document Analysis a. Descriptors

b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Author, Air-quality-monitoring, Air-sampling, Analytical-methods, Chemical-analysis, Analytical-chemistry, Organo-bromine-compounds

c. COSATI Field/Group

18. Availability Statement	19. Security Class (This Report)	21. No. of Pages 26
	22. Security Class (This Page)	22. Price

Abstract

During an industry wide study of structural and agricultural fumigant applicators, air sampling results for methyl bromide indicated problems with Method 2520 of the NIOSH Manual of Analytical Methods (NMAM). Research was performed to identify and solve these problems. Capacity studies indicated that in the presence of high humidity, sample capacity was reduced from 11 liters to 1 liter. Addition of a sodium sulfate drying tube to the sample train extended sample capacity to 5 liters without affecting methyl bromide collection.

During the research, the procedure described in the original method for preparing standard solutions was found not to yield accurate, reproducible standards. To solve this calibration problem, other brominated compounds were used as standards to analyze for methyl bromide by monitoring bromine at 478 nm using a gas chromatograph with an atomic emission detector.

A storage study revealed that samples were not stable after one week at 0 °C. Changing the desorption solvent from carbon disulfide to methylene chloride improved recovery from 45% to 75.8% for the range from 14.5 to 57.8 μg per sample when samples were stored at 0 °C and analyzed within six days.

Method 2520 will not be included in the fourth edition of the NMAM. Further research might identify a better sorbent with

Preceding page blank

improved storage and recovery capacity. However, because of the anticipated ban on methyl bromide as an agricultural fumigant and our limited resources, further method development is not planned.

INTRODUCTION

Methyl bromide, a suspect occupational carcinogen,[1] is an alkylating agent and is used by the pesticide fumigation industry as a soil and spore fumigant. As part of an industry-wide study in the fumigation industry, industrial hygiene evaluations were conducted at two structural fumigation facilities in Florida during July 1990. The daily temperatures during monitoring ranged from 31 °C (88 °F) to 35 °C (95 °F), and relative humidities (RH) ranged from 60% to 75%. Both area and personal samples were collected in accordance with NIOSH Manual of Analytical Methods (NMAM) Method 2520.[2]

NMAM Method 2520 for methyl bromide recommends the use of two charcoal tubes, containing 400 mg and 200 mg portions, in series, desorption with carbon disulfide, and analysis by gas chromatography with a flame ionization detector. Sampling results indicated that methyl bromide breakthrough had occurred (breakthrough as defined on page 31, section 3.b.2. in the NMAM[2]). Although the total loading was low, some backup tubes contained greater amounts of methyl bromide than the front sampling tubes. The total sampling volume taken and the sampling flow rate were within the recommendations specified in NMAM Method 2520 for methyl bromide.[3],[4]

Since additional monitoring was scheduled, NIOSH chemists were asked to investigate the source of the problem. During the

investigation, preparation of reproducible standards of methyl bromide was extremely difficult and storage stability of the samples was a problem. Therefore, the original NMAM Method, S372, for methyl bromide was reviewed.[2] The instructions for calibration against gas standards were inadequate, and the literature references were incomplete. Also the storage stability information indicated that the generated samples were not collected from an atmosphere containing humidity. This paper provides an expanded report of these problems, earlier outlined in a case studies report.[5]

EXPERIMENTAL DESIGN

Equipment

Analyses were performed on the following two systems: 1) a Hewlett-Packard (Palo Alto, CA) model 5890 gas chromatograph (GC) equipped with a flame-ionization detector (FID), a Hewlett-Packard model 7673A autosampler, and a Hewlett-Packard ChemStation; and 2) a Hewlett-Packard (Palo Alto, CA) model 5890 Series II GC equipped with an FID and an Atomic Emission detector (AED) model 5921-A, a Hewlett-Packard model 7673A autosampler, and a Hewlett-Packard ChemStation.

The generation system consisted of an air source, a flow monitor (NAV TEC Industries, Hauppauge, NY), mass flow controllers (Tylan Corp., Torrance, CA), a circulating cooling water bath (Forma Scientific, Marietta, OH), an in-line valved humidifier loop, two

mixing chambers, a multiport manifold, a Mason-type wet bulb and dry bulb hygrometer, a Total Ionizables Present detector (Photovac International Inc, Huntington, NY), and a strip chart recorder (Model 056, Hitachi, Ltd. Tokyo, Japan). (See Figure 1)

The sources of methyl bromide were two diffusion tubes made from 20-mL glass pipets sealed at the bottom of the bulb. Each diffusion tube neck was 8 cm long, with a diameter of 5 mm. Each tube contained about 5 mL of methyl bromide and was immersed in the -12 °C water and ethylene glycol bath equipped with a vented hood.

The generation system was set up to provide a steady concentration of 27 parts of methyl bromide per million parts of air (ppm).[6] An estimated diffusion coefficient of 0.0849 cm^2/sec was used initially to determine this concentration, but later a better estimate of 0.0646 cm^2/sec was determined.[7] Calculations using the estimated coefficient of 0.0646 cm^2/sec indicated a nominal concentration of 24 ppm. To generate methyl bromide vapor, clean, dry air was passed over the diffusion tubes at a flow rate of 0.67 L/min, and on to the mixing chambers and manifold. This vapor-containing air was diluted with 5.4 L/min of clean, dry air, and humidified air was added as needed before reaching the mixing chambers and manifold. The total air stream passed into a multiport sampling manifold. Air samples were collected from the manifold through sampling trains, using either

Model P-125 pumps (Dupont Co., Wilmington, DE) or Model FS-113 pumps (Gillian Instrument Corp., West Caldwell, NJ). Concentration and relative humidity were continuously monitored with a photoionization detector and a wet bulb/dry bulb hygrometer. The manifold was wrapped with heating tape so that elevated temperatures of 39 °C (102 °F) could be maintained in the manifold. The photoionization monitor indicated that the nominal concentration of 24 ppm did not vary significantly over time. The relative standard deviation was 4 percent over a 3-day period.

Reagents

Reagents were obtained from the following sources: glass distilled carbon disulfide from EM Science (Cherry Hill, New Jersey); methylene chloride from Baxter Healthcare Corp., Burdick and Jackson Div. (Muskegon, Michigan); bromomethane (methyl bromide), 1-bromoethane, 1-bromopropane, 1-bromobutane, dibromomethane, and 1-bromo-3-chloropropane from Aldrich Chemical Co. (Milwaukee, Wisconsin). Bromomethane (methyl bromide) in ethyl acetate solutions were obtained from both Accustandard (New Haven, Connecticut) and Supelco (Bellefonte, Pennsylvania). Petroleum charcoal tubes (400:200 mg, Lot 104 and 208, cat. #226-38-02) and sodium sulfate drying tubes (9 g, cat. # 226-44-02) were obtained from SKC, Inc. (Eighty Four, Pennsylvania). Drying tubes containing 400 mg of molecular sieve 5A with indicating material were obtained from Supelco.

Procedures

A 1-μL aliquot of a sample or standard was injected into the GC via an injection port, using the splitless injection mode. A DB-1 fused silica capillary column (J & W Scientific, Folsom, CA), 30 meters long by 0.32 mm internal diameter, with a 1.0-μm film thickness and connected to a deactivated (1 m x 0.53 mm i.d.) fused silica pre-column was used for all GC-AED analyses. The pre-column and analytical column were connected using a Supelco (Bellefonte, PA) GlasSeal capillary column connector. The same type of column was used in the GC-FID analyses, but no pre-column was necessary. The oven temperature program began at 30 °C for 3.5 minutes, increased at increments of 12 °C/minute to 130 °C, and was held at that temperature for one minute. GC injection port and detector temperatures were set at 150 and 200 °C. For the GC-AED system, the transfer line to the AED was set at 250 °C, and the bromine channel was set at 478 nm.

After several experimental trials, the most reproducible procedure for standards preparation was to liquefy methyl bromide and transfer a "known" volume, chilled, to carbon disulfide, also chilled. A GC equipped with an AED was used to provide an independent determination of methyl bromide concentration of the stock solutions. These stock solutions were calibrated against known concentrations of another bromine-containing compound, 1-bromo-3-chloropropane, and analyzed by monitoring the bromine

channel (478 nm) on the GC-AED.[8]

Sample Treatment

After collection, all samples were stored at -10 °C until analysis, unless stated otherwise. The charcoal sample tubes were desorbed in 2-mL of carbon disulfide (or later, methylene chloride), which had been thoroughly chilled, using flaked dry ice. Each tube was broken open after scoring the tube with a file. The sorbent from the tube was added to the vial containing chilled solvent, and each vial was capped. The vials were allowed to sit at room temperature for at least 30 minutes with occasional agitation. Then the vials were chilled again and the sample was transferred to autosampler vials for analysis. The autosampler tray was not cooled.

Results & Discussion

Initially, the problem with NMAM Method 2520 was reported to be breakthrough which may have been effected by flow rate, temperature and/or humidity. To study this problem in depth, samples were collected from the generator and sorbent breakthrough was determined by monitoring the effluent of 400 mg charcoal tubes using the photoionization detector and a pump in line. When the concentration of the effluent was 5 percent of the full-scale concentration (no tube in line), breakthrough had occurred. The time required to obtain 5 percent breakthrough[9] of methyl bromide from a 400 mg petroleum charcoal tube was

determined twice for each of the following conditions: flow rates of 0.010 to 0.100 L/min, humidity levels of 40 to 100 percent, and temperatures of 20 to 39 °C (68-102 °F). The generation system was set to produce a theoretical concentration of 24 ppm methyl bromide in air. As the humidity levels were increased from 40 percent to 80 percent to 100 percent, the sample tube's capacity for methyl bromide decreased from 12.2 to 2.3 to 1.6 liters, respectively.

Since a total sample volume of one liter is impractical and inadequate for many survey situations, an attempt was made to increase the sampling tube capacity by placing a drying tube in front of the sampling train. Two types of drying tubes were tested: sodium sulfate, and 5A molecular sieve with indicating material. The generation system was set to deliver 44 ppm methyl bromide. Capacity trials at >80 percent relative humidity indicated that a large, 9-g, sodium sulfate drying tube placed in front of the sampling train resulted in an increased total sample volume of 5 liters, without breakthrough. When 10 liters of air was sampled, 50 percent of the methyl bromide was found on the back section. Flow rates ranging from 0.010 to 0.100 L/min did not appear to affect sample collection. The average concentration determined on these samples (which did not have breakthrough occur) was 33.2 ppm, and when this value was corrected for 75 percent desorption efficiency, the 44.2 ppm "corrected" concentration agreed with the calculated

concentration of 44 ppm (See Table 1). The molecular sieve drying tubes were unsatisfactory since they appeared to irreversibly adsorb the methyl bromide, and no analyte was recovered from the charcoal tubes.

Following the capacity work, eight sets of tubes consisting of one 400-mg section and two 200-mg sections were collected to check the concentration of the generation system. Because of difficulty preparing standards, these tubes were analyzed after they had been stored at -10 °C for two months. Stock solutions of methyl bromide were prepared and calibrated against another brominated compound by GC-AED, but the samples and standards were analyzed by GC-FID. The average concentration found, 11.4 ppm, was much lower than the theoretical concentration of 24 ppm, which raised questions about both standard preparation and storage stability. Since it was not clear whether the low results were due to standards' preparation or sample storage problems, all further analyses were done via GC-AED using several other brominated compounds as standards.

Although others[10] have successfully prepared methyl bromide standards by chilling, NIOSH chemists were not able to prepare accurate standards repeatedly for quantitation of methyl bromide samples. When chilled, syringes did not seal properly. Due to similar calibration problems, other researchers[11] have used headspace analysis to determine methyl bromide residue in

imported goods. Since NIOSH chemists did not have this headspace equipment, the technique was not pursued as an alternative. It also was not clear that this headspace technique could be applied easily to charcoal tube samples.

Use of the GC-AED system eliminated the need to prepare methyl bromide standards since other brominated compounds served as standards. NIOSH chemists used compounds similar to methyl bromide, and for these compounds the bromine response was not compound dependent.[8] With this detector, the bromine response was monitored, using the following three brominated compounds as standards: 1-bromopropane, dibromomethane, and 1-bromobutane (other brominated compounds also may be used). Figure 2 shows that the response observed for dibromomethane is approximately twice the size of the response of the monobrominated compounds. Figure 3 shows calibration data from three different days using these three brominated compounds. The regression coefficients from these three data sets were 0.984, 0.991 and 0.991.

NIOSH chemists did get "certified" solutions from several manufacturers, but upon analysis by GC-AED these solutions were found to be different in concentration from the labelled ones (i.e. labelled as 0.2 $\mu g/\mu L$, but determined via GC-AED as 14.0 and 14.9 $\mu g/\mu L$). One supplier indicated that shipping conditions could affect the concentration and that they had similar problems (as discussed above) when preparing standards of methyl bromide.

Since the calibration work had indicated a stability problem with NMAM Method 2520, sample storage stability was studied, using methyl bromide solutions after the concentration was confirmed against the independent standards and GC-AED. 400-mg portions of petroleum charcoal were loaded with aliquots of independently calibrated methyl bromide in carbon disulfide, as air was drawn through the tube. After eight days storage at -10 °C, less than 60 percent of the amount loaded (150 μg) was recovered. Forty percent was recovered at a loading amount of 45 μg. However, samples stored less than six days at -10 °C had 75 percent recovery when loaded with at least 58 μg per tube. For loadings of 233, 58, 44, 22, 11, and 5 μg per sample, the recoveries were 79, 80, 63, 53, 45, and 0 percent, respectively. Recoveries decreased as the quantity of adsorbed methyl bromide decreased, and storage stability deteriorated over one week. Analysis of samples after 3 through 7 days storage allowed determination of how much and on which day the losses occurred. Three sample tubes were loaded per level per day for this study. The percentages of methyl bromide recovered averaged: 79.2 ± 3.4, 81.0 ± 1.7, 77.2 ± 2.5, 79.0 ± 1.5 and 67.1 ± 10.0 for the 233 μg level and; 83.7 ± 1.2, 81.5 ± 1.3, 79.2 ± 0.6, 78.7 ± 1.5 and 73.6 ± 0.6% for the 58.2 μg level for 3, 4, 5, 6, and 7 days storage, respectively (See Figure 4). The data in Figure 4 are averages of three samples each. While some gradual loss was observed over the first six days, loss was greatest between days six and seven.

Because the concentrations of methyl bromide collected during sampling could be below the 58-μg limit of quantitation (LOQ) (75 percent recovery of the analyte from the sampler is a NIOSH criterion for LOQ) and not accurately measurable due to the recovery limitation, methylene chloride and 2 percent acetone in carbon disulfide were studied as desorption solvents, in addition to carbon disulfide alone. This study was done to try to improve recovery at concentrations below 58 μg per sample. With 2 percent acetone in carbon disulfide, the solvent partially coeluted with the methyl bromide during analysis and precluded accurate determination of the analyte. The use of methylene chloride improved recovery of methyl bromide from petroleum charcoal to 75.8 percent for the range of 14.5 to 57.8 μg per sample. (See Figure 5)

Another field survey was conducted after modification of NMAM Method 2520. Of the twenty air samples collected using sodium sulfate drying tubes and analyzed within six days, only four had quantities of methyl bromide above the LOQ of 14.5 μg per tube. No methyl bromide was observed on any of the backup tubes. Sampling volumes ranged from 0.9 to 8.2 liters, and the concentration from the samples above the LOQ ranged from 3.3 to 551 mg/m^3 (16.6 to 1796.9 μg per sample). The limit of quantitation, 14.5 μg per sample, is based on 75% recovery while the limit of detection (0.5 μg per sample) is an instrumental limit (both based on analysis within six days of collection).

Conclusions & Recommendations

NMAM Method 2520 has several problems which are important enough that it will not be included in the fourth edition of the NIOSH Manual of Analytical Methods. These problems included reduced adsorption capacity at high humidity, difficult-to-prepare standard solutions, sample instability, decreasing recovery as the loading decreases, and insufficiently low quantitation limit.

The following modifications are recommended for methyl bromide sampling:

(1) Collection of a maximum sample volume of one liter. When a 9-g sodium sulfate drying tube is used, then a maximum sample volume of five liters can be collected.

(2) Storage of samples at -10 °C or below until analysis.

(3) Analysis of samples within six days of collection.

(4) Use of methylene chloride rather than carbon disulfide as the desorption solvent.

(5) Calibration against other brominated compounds, such as 1-bromopropane, dibromomethane, 1-bromobutane, 1-bromo-3-chloropropane.

(6) Analysis via GC/AED by monitoring the bromine channel at 478 nm.

While the modified technique allows collection and analysis of

methyl bromide, further improvements in capacity and desorption efficiency (i.e., better sorbent materials or desorption solvents) would be appropriate. However, because of the anticipated ban on methyl bromide,[12] NIOSH chemists do not plan further method development work on this compound.

Before conducting air sampling, the conditions under which the analytical method was evaluated should be reviewed. If laboratory conditions differ from the expected environmental conditions at the proposed test site, the method's performance should be tested under the expected conditions before the air sampling survey is conducted.

References

1. National Institute for Occupational Safety and Health: Current Intelligence Bulletin 43: Monohalomethanes; Methyl Chloride, Methyl Bromide, Methyl Iodide. DHHS (NIOSH) Pub. No. 84-117. NIOSH, Cincinnati, OH (1984).

2. National Institute for Occupational Safety and Health: Method 2520, Methyl Bromide. In: NIOSH Manual of Analytical Methods, 3rd ed., P. M. Eller, ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).

3. National Institute for Occupational Safety and Health: Method S372, Methyl Bromide. In: NIOSH Manual of Analytical Methods, 2nd ed. Vol. 2, D.G. Taylor, ed. DHEW (NIOSH) Pub. No. 77-157-C. NIOSH, Cincinnati, OH (1977).

4. National Institute for Occupational Safety and Health: Method 2520, Methyl Bromide. In: NIOSH Manual of Analytical Methods, 3rd ed., P. M. Eller, ed. DHHS (NIOSH) Pub. No. 84-100. NIOSH, Cincinnati, OH (1984).

5. Gagnon, Y.T.; Ringenburg, V.L.; Fajen, J.M.: Problems with NIOSH Method 2520 for Methyl Bromide, a Case Study Report. Appl. Occ. Environ. Hyg. 9(3), March 1994, 165-167.

6. Nelson, G. O.: Controlled Test Atmospheres, pp. 126-134. Ann Arbor Science Publishers, Inc., Ann Arbor, MI (1971).

7. Nelson, G. O.: Gas Mixtures: Preparation and Control, pp. 263-264. Lewis Publishers: Chelsea, MI (1992).

8. Quantitative Characteristics of Gas Chromatography with Microwave-Induced Plasma Detection. In: Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy, P.C. Uden, ed. American Chemical Society Symposium Series 479, Washington, DC (1992).

9. Gunderson, E.C.; Anderson, C.C.; Smith, R.H.; Doemeny, L.J.: Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances. DHHS (NIOSH) Pub. No. 80-133. NIOSH, Cincinnati, OH (1980).

10. Woodrow, J.E.; McChesney, M.M.; Sieber, J.N.: Determination of Methyl Bromide in Air Samples by Headspace Gas Chromatography. Anal. Chem. 60:509-512 (1988).

11. Ford, J.H.; Legendre, M.G.; Ladner, D.L.; Dawson, J.A.; Raymond, C.: Automated Closed-System Headspace Determination of Methyl Bromide in a Variety of Raw and Processed Nuts. Journal of AOAC International 75(2) (1992).

12. Zurer, P.S.: Proposed Ban on Methyl Bromide Opposed by Producers, Users. Chem. Eng. News. pp. 23-24 (February 1, 1993).

Table 1. Results from Drying Tube Test (analyzed within five days)

Drying Tube Type	Total µg Found	% total on Back Section	Volume in Liters	Sample Flow Rate, mL/min	µg per Liter	ppm
M	ND	none	4.9	10.0	---	---
M	14.5	100%	5.3	10.6	2.7	0.7
M	ND	none	11.4	50.1	---	---
S	1278.2	53.8%	10.7	50.0	119.5*	30.8
S	642.4	1.5%	5.0	10.1	128.4	32.9
S	662.5	2.9%	5.2	10.5	127.4	32.4
S	1242.8	58.6%	11.2	51.1	110.9*	28.6
S	1521.0	53.8%	10.7	40.0	142.1*	36.7
S	1223.4	62.0%	13.5	50.0	90.6*	23.4
N	83.1	none	1.0	10.0	83.1	21.0
N	284.2	none	1.9	15.0	149.6	39.2
N	225.2	none	1.5	40.0	150.1	38.2
N	203.0	none	1.4	40.0	145.0	35.3
N	135.5	none	0.9	15.0	150.6	37.6
N	98.1	none	1.1	10.0	89.2	23.6
N	391.7	none	2.6	51.1	150.7	38.8

* = Breakthrough had occurred

Legend:

M = 5A Molecular Sieve drying tube
S = Sodium Sulfate (SKC # 226-44-02) drying tube
N = No drying tube used

Titles for Figures

Figure 1. Diagram of Methyl Bromide Gas Generation System

Figure 2. **Bromine Channel Response for Methyl Bromide and Other Bromine Standards at 478 nm**

Figure 3. **Multicompound Calibration Curves from Three Different Days**

Figure 4. **Methyl Bromide Recovery over 3 to 7 Days Storage**

Figure 5. **Methyl Bromide Recovery Studies**

9444

Figure 1. DIAGRAM of METHYL BROMIDE GAS GENERATION SYSTEM

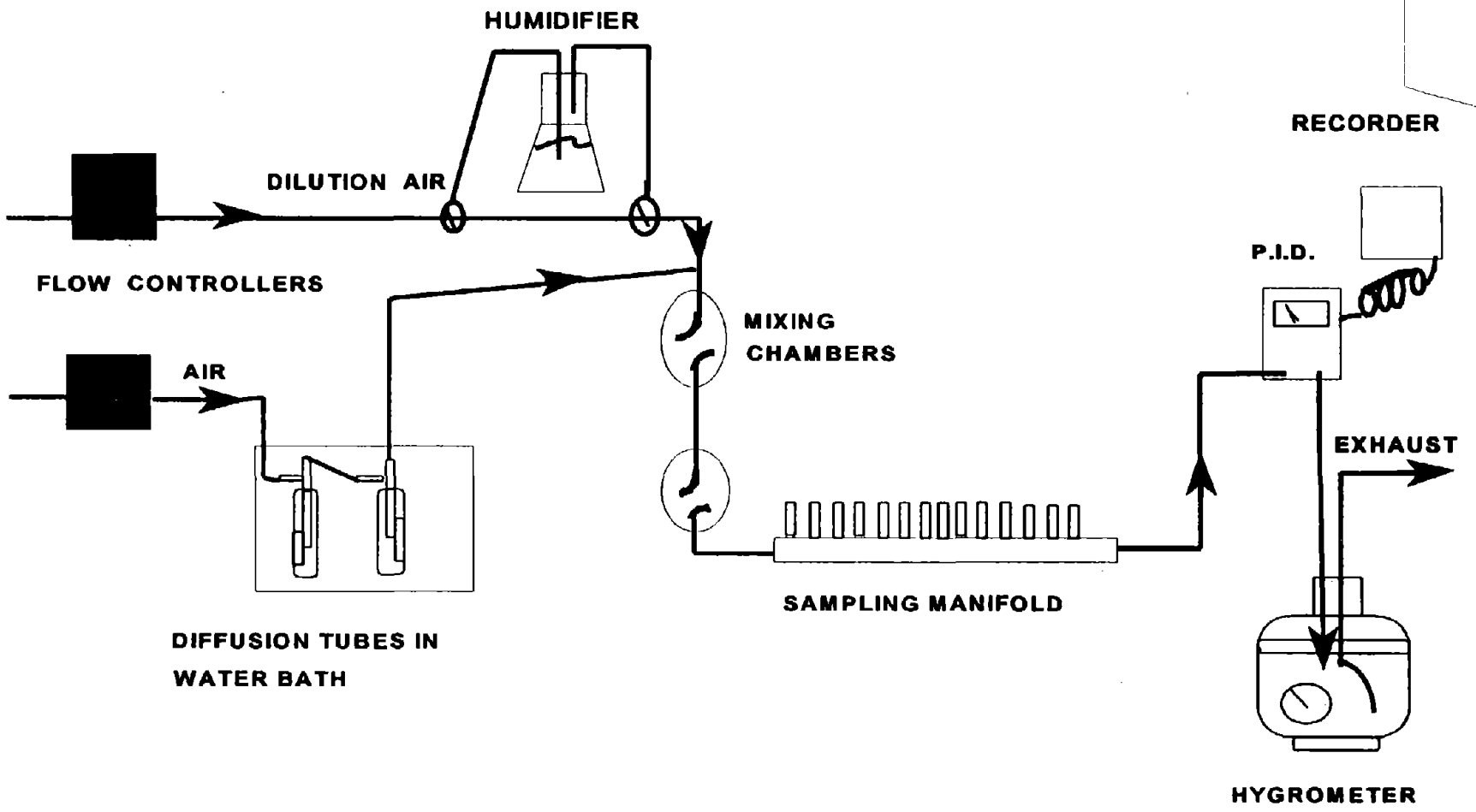


Figure 2. Bromine Channel response for Methyl Bromide and Other Bromine Standards at 478 nm.

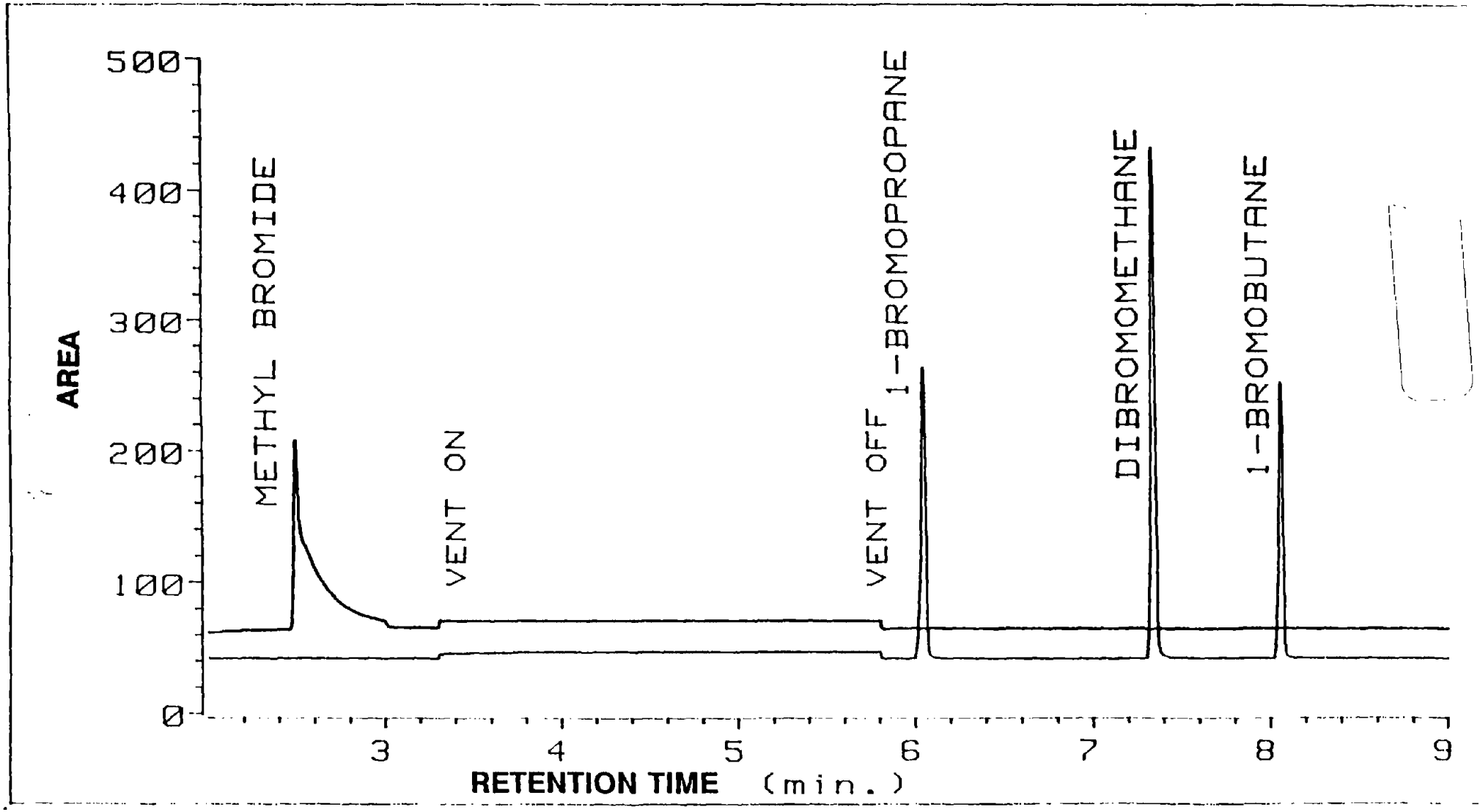


Figure 3. Multicompound Calibration Curves from Three Different Days

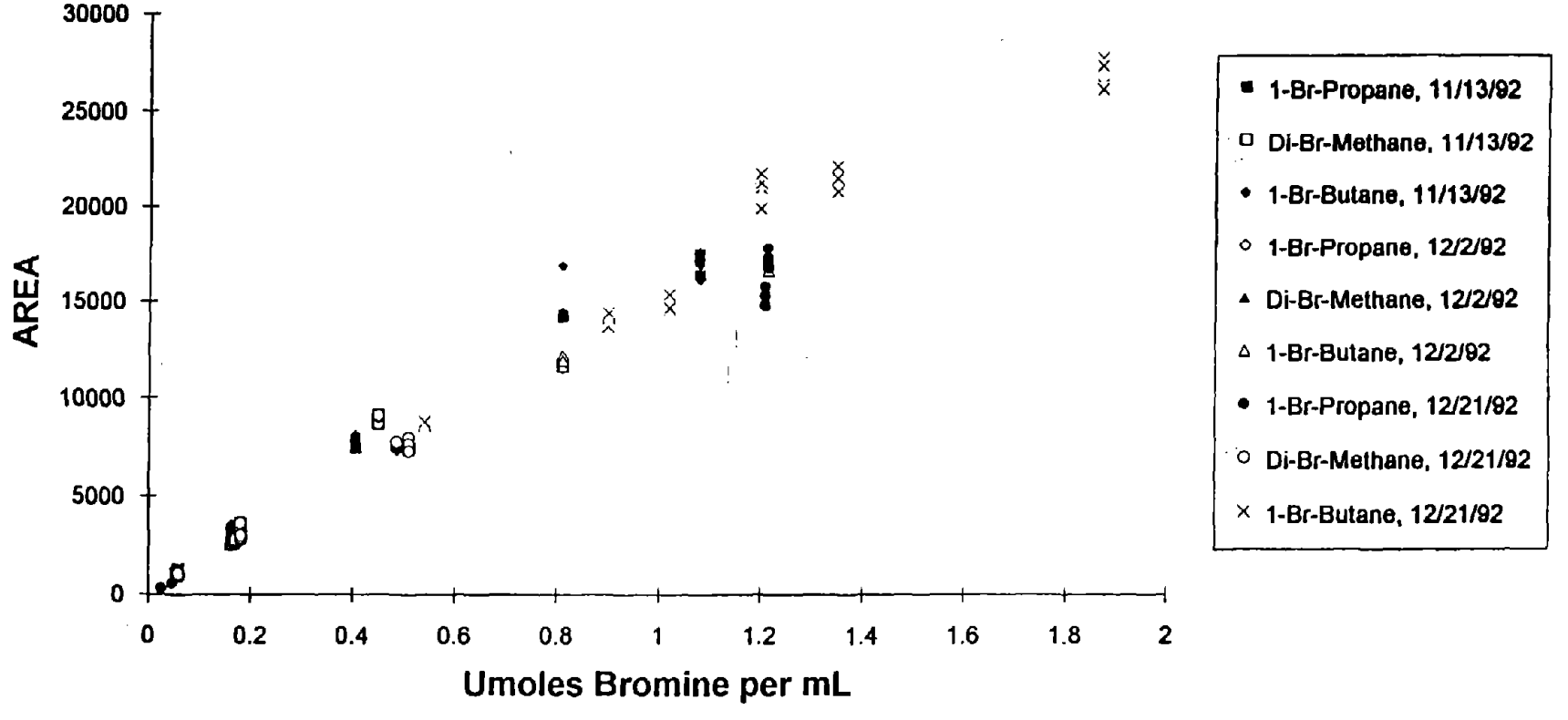
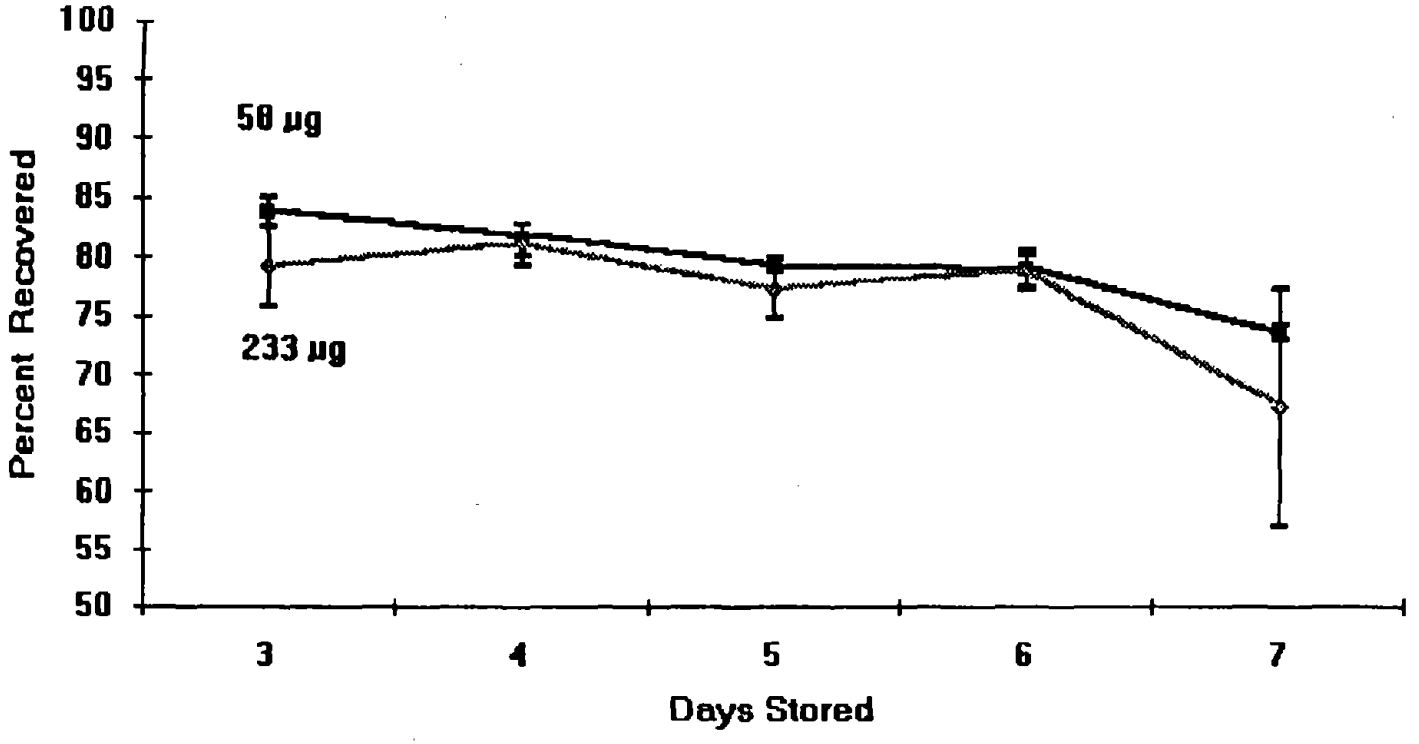


Figure 4. Methyl Bromide Recovery over 3 to 7 Days Storage



35

Figure 5. Methyl Bromide Recovery Studies