Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

Case Studies

Problems With NIOSH Method 2520 for Methyl Bromide

Dawn Tharr Column Editor , Yvonne Gagnon , Virginia Ringenburg & John Fajen

To cite this article: Dawn Tharr Column Editor , Yvonne Gagnon , Virginia Ringenburg & John Fajen (1994) Case Studies, Applied Occupational and Environmental Hygiene, 9:3, 165-167, DOI: 10.1080/1047322X.1994.10388290

To link to this article: https://doi.org/10.1080/1047322X.1994.10388290

Published online: 25 Feb 2011.

Case Studies

Problems With NIOSH Method 2520 for Methyl Bromide

Dawn Tharr, Column Editor

Reported by Yvonne Gagnon, Virginia Ringenburg, and John Fajen

Introduction

The National Institute for Occupational Safety and Health (NIOSH) publishes the NIOSH *Manual of Analytical Methods* (NMAM), a collection of analytical methods for characterizing exposures to environmental chemicals. When an industrial hygienist selects a method to monitor worker exposure, it is important to remember that not all the methods in the NMAM have undergone the same level of evaluation, as the following case demonstrates.

As part of an industrywide study of the health effects resulting from methyl bromide exposure in structural and agricultural applicators, NIOSH researchers conducted industrial hygiene monitoring for methyl bromide in Florida during July 1990. NIOSH Method 2520 was used. This method recommends use of two charcoal tubes (400 mg/200 mg) in series, desorption with carbon disulfide, and analysis by gas chromatography with a flame ionization detector. Sampling results from these surveys indicated a capacity problem.

A project was then initiated to determine the reason for the methyl bromide breakthrough that occurred during industrial hygiene monitoring. While conducting research to define and solve this problem, several other problems were identified: reduced adsorption capacity caused by high humidity, difficulty in preparing standard solutions, sample instability, change in recovery with loading, and insufficiently low quantitation limit. The addition of a drying tube to the sampling train, as well as changes to the analytical technique, to the desorption solvent, and to the time till analysis, resulted in an improved method for methyl bromide.

This case study demonstrates the importance of noting the conditions under which a method was evaluated and the benefit of testing method performance under conditions likely to exist at a field site.

Background

NIOSH researchers conducted a cross-sectional study of neurologic, neurobehavioral, and renal function in pesticide applicators exposed to methyl bromide and sulfuryl fluoride. As part of the industrywide study, in-depth industrial hygiene surveys were conducted at two structural fumigation facilities in Miami, Florida, during July 1990. The surveys were conducted to observe all aspects of structural fumigation using methyl bromide and to determine the range of potential occupational exposures to methyl bromide during these structural applications. Both area and personal samples were collected. During the monitoring period, the daily temperature ranged from 31°C (88°F) to 35°C (95°F), and the relative humidity (RH) ranged from 60 to 75 percent. The results indicated that breakthrough had occurred. Although the total loading was low, some backup tubes contained greater amounts of methyl bromide than the front sampling tubes. The total sample volume taken and the sampling rate were within the recommendations specified in NIOSH Method 2520 for methyl bromide.[1,2] Since additional monitoring was scheduled, researchers in the Methods Research Branch of the Division of Physical Sciences and Engineering (DPSE) were asked to investigate the source of the problem.

Methods

Initially, the capacity of the sampling tube for methyl bromide was investigated. As the investigation progressed, it became evident that preparing reproducible standards of methyl bromide was extremely difficult. Therefore, the standard preparation procedure from the original NIOSH method, S372, for methyl bromide was reviewed.[2] The instructions for calibration against gas standards were inadequate and the literature references were incomplete.

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 gas chromatograph (GC) equipped with an atomic emission detector (AED) was used to provide an independent determination of stock solutions of methyl bromide. This stock solution was calibrated against known concentrations of another bromine-containing compound, bromochloropropane, and analyzed by monitoring the bromine channel (478 nm) on the GC-AED.[3]

Eventually, because of difficulty in preparing reproducible standards by liquefying methyl bromide, all analyses were performed using the revised technique, GC-AED. This technique eliminates the need to prepare methyl bromide standards since other brominated compounds serve as standards. DPSE researchers used compounds similar to methyl bromide, and for these compounds the bromine response was not compound dependent.[3] The time required to obtain 5 percent breakthrough[4] of methyl bromide from a 400-mg petroleum charcoal tube was determined for the following conditions: flow rates of 0.010 to 0.100 L/min, humidity levels of 40 to 100 percent, and temperatures of 20° and 39°C (68° and 102°F).

Results and Discussion

Two trials for breakthrough were conducted for each set of experimental conditions with the generation system set to produce a theoretical concentration of 27 parts of methyl bromide per million parts of air. As the humidity levels were increased from 40 to 80 to 100 percent, the sample tube's capacity for methyl bromide decreased from 12.2 to 2.3 to 1.6 L, respectively. Since a total sample volume of 1 L is impractical and inadequate for many survey situations, an attempt was made to increase the sample tube capacity by placing a drying tube at the front of the sampling train. Capacity trials at greater than 80 percent RH indicated that a large, 9 g, sodium sulfate drying tube placed at the front of the sampling train resulted in an increased total sample volume of 5 L, without breakthrough. Flow rates, ranging from 0.010 to 0.100 L/min, did not appear to affect sample collection.

Because reproducible standards could not be prepared from liquefied methyl bromide, the GC-AED was used to analyze all subsequent field samples. 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 may also be used).

Storage stability was also studied over time, using methyl bromide solutions after the concentration was confirmed against the independent standards and GC-AED. After 8 days' storage at −10°C, less than 60 percent of the amount loaded (150 μg) was recovered (40% for 45 μg). However, samples stored less than 6 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. This indicated that recovery decreased as the quantity of methyl bromide adsorbed decreased and that storage stability deteriorated over 1 week. Analysis of samples after 3 through 7 days allowed determination of when the loss occurred. The percent of methyl bromide recovered was (averaged) 80.9, 81.3, 77.2, 79.0, and 67.1 percent for 3, 4, 5, 6, and 7 days' storage, respectively. While there was some gradual loss over the first 6 days, loss was greatest between day 6 and 7.

Because the concentrations of methyl bromide collected during sampling could be below this 58-μg limit of quantitation (LOQ) (75% recovery is a criterion for LOQ), and not accurately measurable due to this recovery limitation, methylene chloride and 2 percent acetone in carbon disulfide were studied, in addition to carbon disulfide alone. This was done to try to improve recovery at concentrations below 58 μg per sample. The use of methylene chloride improved recov-

ery of methyl bromide from petroleum charcoal to 75.8 percent for the range between 14.5 to 57.8 μg per sample.

Conclusions and Recommendations

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

If it is necessary to sample for methyl bromide, the following modifications are recommended: 1) collect a maximum sample volume of only 1 L, unless a 9-g sodium sulfate drying tube is used; then a maximum sample volume of 5 L can be collected; 2) store samples at −10°C or below until analysis; 3) analyze samples within 6 days of collection; 4) use methylene chloride rather than carbon disulfide as the desorption solvent; 5) calibrate against other brominated compounds, such as 1-bromopropane, dibromomethane, 1-bromobutane, bromochloropropane, or other brominated compounds; 6) analyze via GC/AED by monitoring the bromine channel at 478 nm.

While this modified method 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,[5] DPSE researchers do not plan further method development work on this compound. When planning any field sampling, it is important to review the conditions under which the method was evaluated. If these differ significantly from conditions at the chosen site, test the method performance under those conditions before proceeding with the survey.

References

1. 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. U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH, Cincinnati, OH (1984).
2. National Institute for Occupational Safety and Health: Methods S372, Methyl Bromide. In: NIOSH Manual of Analytical Methods, 2nd ed. Vol. 2, P.M. Eller, Ed. DHEW (NIOSH) Pub. No. 77-157-C. U.S. Department of Health and Education, and Welfare, Public Health Service, Center for Disease Control, NIOSH, Cincinnati, OH (1977).
3. Quantitative Characteristics of Gas Chromatography With Microwave-Induced Plasma Detection. In: Element-Specific Chromatographic Detection by Atomic Emission Spectroscopy, P.C. Uden, Ed. ACS Symposium Series 479, Washington, DC (1992).
4. Gunderson, E.C.; Smith, R.H.; Doemeny, L.J.: Development and Validation of Methods for Sampling and Analysis of Workplace Toxic Substances. National Institute for Occupational Safety and Health (Contract No. 210-76-0123). U.S. Department of Health and Human Services, Public Health Service, Centers for Disease Control, NIOSH, Cincinnati, OH (1980).
5. Zurer, P.S.: Proposed Ban on Methyl Bromide Opposed by Producers, Users. Chemical & Engineering News, Washington, DC (February 1, 1993).

Editorial Note: Yvonne Gagnon is with the Methods Research Branch, Division of Physical Sciences and Engineering, and Virginia Ringenburg and John Fajen are with the Industry-wide Studies Branch, Division of Surveillance, Hazard Evaluations and Field Studies, NIOSH. The authors can be contacted at 4676 Columbia Parkway, Cincinnati, OH 45226, or by telephoning (513) 841-4260.