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Determination of Methyl Bromide Used for the Preservation of Cultural Materials from Insects

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Abstract : A thermal desorption-gas chromatography/mass spectrometric method was developed for the determination of methyl bromide in fumes formed during preservation of cultural materials from insects. Methyl bromide in fumes was collected by drawing 10 *l* of air through the adsorbent tube filled with a solid adsorbent (Chromosorb). The air samples were analyzed by using a special thermal desorption device and GC/MS determination. The recovery of methyl bromide by air sampling was 88% and the detection limit of the assay was 0.1 pptv based upon assayed air of 10 *l*. The method was applied to the determination of fumed methyl bromide used for the preservation of papers in a library. The mean concentration of methyl bromide determined in a library was 280.2 ± 25.4 pptv.

Keywords : methylbromide, cultural material, determination, thermal desorption-gas chromatography/mass spectrometric method

Introduction

The control of plagues like mould or arthropods that damage paper in libraries and archives can be accomplished by methods such as ethylene oxide or methyl bromide sterilization. The use of methyl bromide for the simultaneous elimination of both plagues was proposed long ago and has been used successfully (Bell, 2000).

Methyl bromide is also the most widely used fumigant for pest control in perishable produce (e.g. fresh fruits and vegetables, and cutflowers), endurable produce (e.g., cereal grains, dry fruits and nut, and timber), and structures (Hayes, *et al.*, 1991; Gamliel, *et al.*, 1991). Fumigation with methyl bromide is mandatory for important and export of many agricultural products in international trade (UNEP, 1994). The worldwide use of methyl bromide for fumigating commodities and structures reached 1.8×10^7 kg, 25% of its total use in 1992 (UNEP, 1994). These emissions are primarily the result of discharge of methyl bromide waste gases at the end of fumigation.

Emissions of methyl bromide during commodity and soil fumigation are reportedly contributing to stratospheric ozone depletion as well as imposing negative effects on human health (Khalil, *et al.*, 1993; Singh, *et al.*, 1993; Butler, 1995; Yagi, *et al.*, 1995; Yang, *et al.*, 1995). As commodity or structural fumigations are always carried out in closed environments, unreacted methyl bromide in air is very harmful for human health. The fumigated products absorb little methyl bromide, leaving most of the applied chemical to the air. Methyl bromide was found to cause a wide tissue distribution of DNA methylation adducts after single or multiple administrations to rats and mice (Pletsa, *et al.*, 1995). Analysis of methyl bromide in indoor is, therefore, necessary, but it is not ease because the concentration of methyl bromide in air is relatively low.

Various methods have been proposed to detect methyl bromide from fumigation gases. The method utilizing gas chromatography-electron capture detector (GC-ECD) (Alge, *et al.*, 1984; Bassford,

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et al., 1998; Hughes, *et al.*, 1999) has been published, but ECD offers only a modest level of sensitivity for the detection of methyl bromide. Therefore, some improvement in ECD sensitivity to methyl bromide has been tried through the conversion to methyliodide, but this method was not distinguishable for all methylhalides such as methyl chloride, methyl bromide and methyl iodide. For the determination of part per trillion by volume (pptv) of methyl bromide in indoor air, the most frequently used method is gas chromatography-mass spectrometry (GC-MS) (Wingenter, *et al.*, 1998; Cicerone, *et al.*, 1998).

Desorption of the analytes after drawing air through the adsorbent tube filled with a solid adsorbent as air sampling can be accomplished in two ways namely: liquid desorption and thermal desorption. Very often, a liquid is used for desorption of the analytes from the adsorbent. The advantage of this approach is that analytes are desorbed under mild conditions and both polar and apolar compounds can be desorbed using an appropriate solvent. In most cases, however, at least 0.5-1 m*l* of solvent is needed.

Thermal desorption is increasingly being used as a sensitive to liquid desorption. Here, the trapping material is heated and the analytes are released at temperatures typically in range of 200-300°C and carried to the actual transfer onto the anlytical column by the carrier gas. Thermal desorption allows the complete transfer of the entire sample to the column which results in maximum sensitivity. Therefore, thermal desorption in many cases is far superior to liquid desorption.

This paper describes a thermal desorption-gas chromatography/mass spectrometric method for the determination of methyl bromide formed during preservation of paper from insects.

Experimental Section

Chemicals and Reagents

Methyl bromide gas was purchased from Sigma (St. Louis, MO, USA) and chromosorb adsorbent from Perkin-Elmer Ltd. Sodium sulfate (Junsei, Japan), methylene chloride, methanol (J. T. Baker, USA) and purified water (Millipore Corp., Milford, MA) were used as reagent and solvent.

Thermal Desorption-Gas Chromatography Mass Spectrometry

Thermal desorption of the sample tubes was carried out using a Perkin-Elmer Automatic Thermal Desorption System ATD400 (Perkin-Elmer Ltd). This apparatus contained a mechnism for holding the tubes to be desorbed while they were heated and purged simultaneously with inert carrier gas. The desorbed sample, contained in the purge gas, was routed to gas chromatography-mass spectrometry via heated transfer line. All mass spectra were obtained with a Agilent 6890/5973 N instrument. The ion source was operated in the electron ionization mode (EI; 70 eV, 230°C). Full-scan mass spectra (m/z 40-800) were recorded for analyte identification. Separation was achieved with an HP fused-silica capillary column with cross-linked methylsilicone (HP 1), ~30 m length, 0.2 mm i.d., 0.33 m film thickness. Samples were injected in the split mode with a splitting ratio of 1:8. The flow rate of the helium was 1.0 m*l*/min. The operating parameters were as follows: injector temperature, 200°C; transfer line temperature, 220°C; oven temperature, programmed from 30°C (held for 2 min) at 5°C/min to 200°C (held for 2 min). The ions selected in this study were m/z and.

Calibration and Quantification

Calibration curve for methyl bromide was established by adsorption and desorption after adding standard gas as concentration of 10, 20, 50 and 100 pptv in 10 *l* tedlar bag. The standard addition was spiked with a known amount (139 ppmv in nitrogen gas) of methyl bromide using a 1 m*l* gas-tight syringe. The peak area of standard was used in the quantification of the compound.

Results and Discussion

Mass Spectrometry

The mass spectrum of methyl bromide is shown in Fig. 1. The molecular ion at m/z 104 and the diagnostic ions at m/z 79, 81 and 93 and were obtained from standard of methyl bromide. The molecular ion was the base peak. The ions at m/z 79 were from the losses of one methyl group from the molecular ion.

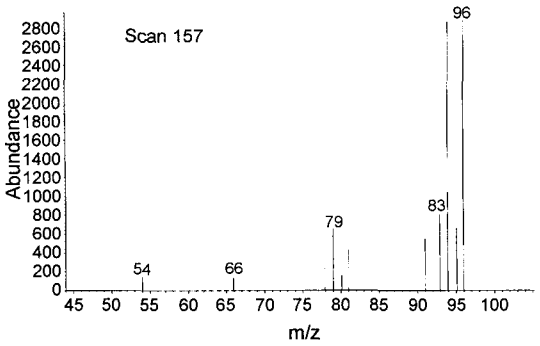

Fig. 1. The mass spectrum of methyl bromide.

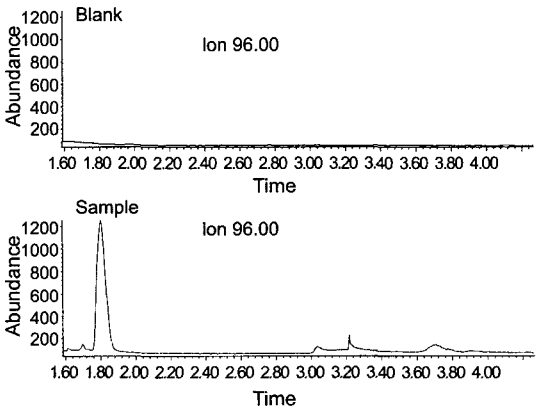

Fig. 2. The chromatogram of methyl bromide (above : blank, under : indoor sample quantified as 32 ppbv).

Chromatography

Fig. 2 also shows the chromatogram of methyl bromide. For the GC separation of the peaks, the use of the non-polar stationary phase was found to be efficient. The peaks are symmetrical and no tailing can be seen. The peak also do not show any adsorption effects in the GC system. The retention time of methyl bromide was 1.81 min. There were no extraneous peaks observed in a chromatogram of blank sample at the retention time of the analyte.

Linearity

Examination of typical standard curve by computing a regression line of peak area of methyl bromide on concentration using least-squares demonstrated a good fit with correlation coefficients being consistently greater than 0.999. The lines of best fit is $y = 262.1x + 188.9$ ($r^2 = 0.9998$) over a range of 10-100 pptv, where x is the analyte concentration (pptv) and y is the peak area of the analyte.

Table 1. Within-run precision and accuracy of methyl bromide in air (n=3)

Added concentration (pptv)	Found (pptv) Results	X ± D (RSD)
20	19.2, 22.6, 18.4	1.0 0.1 (7.1)
50	51.4, 46.5 49.7	5.0 0.2 (4.2)

X = mean value; SD = standard deviation ; RSD = relative standard deviation.

Adsorption and Desorption Yield

Several samples of varying composition were prepared in tedlar bag and the extraction yield was calculated by percentage of the methyl bromide recovered. The recovery was about 88% at the concentration of 10 pptv, and it was found to be nearly constant at several concentrations.

Precision and Accuracy

The reproducibility of the assay was very good, as shown in Table 1. For five independent determinations at 20 and 50 pptv, the coefficient of variation was less than 6%.

Sensitivity

The combination of adsorption yield and the high sensitivity of the analyte by EI-MS (SIM) permit the determination of methyl bromide at concentrations well below those reported previously. Method detection limits was 1.0 pptv based upon an assayed air of 10 *l*. Limits were defined by a minimum signal-to-noise ratio of 3 and coefficients of variation for replicate determinations (n=5) of 15% or less.

Application

10 *l* of air samples were taken into Chromosor adsorbent and transported to a laboratory for analysis by the method described here. The mean concentration of methyl bromide in background air was 11.3 pptv with uncertainty of 1.2 pptv and that of methyl bromide in a library was 280.2 pptv with uncertainty of 25.4 pptv. This result indicates that the concentration of methyl bromide in library is about 20 times greater than average back ground level. Also, it is expected due to use methyl

bromide for the control of plagues like mould or arthropods that damage paper in libraries.

Conclusion

We have demonstrated here a relatively simple and sensitive instrumental method by which the methyl bromide content of background air and indoor air could be directly adsorbed and detected as unchanged form. With ongoing refine-ments of adsorbents, additional improvements in the levels sensitivity and reproducibility demonstrated here are expected.

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