NBSIR 73-259

A Gas Dilution System for Methyl Bromide

Eugene P. Scheide, Ernest E. Hughes, and John K. Taylor

National Bureau of Standards
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Final Report

Prepared for
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U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary

NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director

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ABSTRACT

A system capable of producing well-defined test atmospheres of methyl bromide in air (or any other desired diluent) and an analytical system for the analysis of these gas mixtures is described. Using a bulk mixture of 1000 ppm methyl bromide in nitrogen, and accurately blending this with a stream of clean, dry air, concentrations between 5 and 100 ppm can be produced. This system provides a means of calibration of the various analytical systems for methyl bromide now in use.

1. INTRODUCTION

This report describes a system capable of producing well-defined test atmospheres containing concentrations of methyl bromide for the calibration of analytical instruments and evaluation of analytical methodology. The system developed and described was designed to produce concentrations in the industrial hygiene important range of 5 to 100 ppm but other concentrations could be achieved by suitable adjustment of the operational parameters.

2. EXPERIMENTAL

Methyl bromide is a relatively stable substance so that little difficulty is encountered in preparing low concentration mixtures of it in air by dilution of high concentration mixtures. Furthermore, high concentration mixtures of methyl bromide in air prepared at high pressure in gas cylinders appear to have sufficient stability so that frequent re-analysis is not required. Consequently, the simplest system for providing a variety of concentrations of methyl bromide in air consists of a cylinder at high pressure containing a known concentration of methyl bromide and a system for diluting this high concentration with accurately measured volumes of air. Systems for the accurate blending of gas mixtures have been built and evaluated and it is intended that such systems will be used for the dilution of methyl bromide.

The dilution system is described in detail elsewhere [1] and is shown schematically in Figure 1. It consists of two controlled flow systems, one for the diluent air and one for the bulk mixture of methyl bromide, two flow meters for measuring the flow of each gas stream, a mixing chamber where the two streams are combined, and a manifold from which the mixture may be withdrawn for analysis or for calibration purposes.

2.1 Gases, Gas Mixtures

A pressurized cylinder containing a bulk mixture of methyl bromide in nitrogen was prepared manometrically to have a methyl bromide concentration of 1000 ppm. The cylinder was pressurized to a total pressure of 1200 psi corresponding to 3600 liters of the 1000 ppm mixture at standard conditions. The mixture also contained 350 ppm of propane as an internal calibrant.

The source of air for dynamic dilution of the bulk mixture can be either a pressurized cylinder of "breathing" air or "house" air from the bench. In either case, the air is pre-treated by passing through a silica gel-charcoal dryer to remove major contaminants.

2.2 Analysis

A gas chromatograph with a flame ionization detector can be used to analyze the concentration of either the bulk mixture of methyl bromide or any of the dilutions produced with the system. The dilution, sampling and analytical systems are shown diagramatically in Figure 2. Sampling is accomplished by inserting a Teflon tube, connected at one end to a gas sampling valve, into one port of the sampling manifold. Samples are drawn through the gas sampling valve by suction, and are then injected into the gas chromatograph by the carrier gas.

The recommended gas chromatographic operating parameters are as follows:

column	6 ft x 1/4 in Porapak Q, 80-100 mesh, #5750
column temp.	145 °C
detector	FID at 225 °C
He flow	50 ml/min
sample	10 ml
sampling rate	40 ml/min

Precautions should be taken to optimize the detector sensitivity before each set of analyses. A significant decrease in the detection signal for samples of the same concentration is an indication that the detector must be optimized again. The decline in detector response is not the same for methyl bromide and propane hence the need to optimize the detector each time it is used.

2.3 Calculation of Bulk Mixture Concentration

The bulk mixture concentration is calculated using the following equation:

$$C_b = \frac{\text{MeBr g.c. peak area}}{\text{Propane g.c. peak area}} \times R \times \text{propane concentration.} \quad \text{(Eq. 1)}$$

where,

C_b = bulk concentration of methyl bromide (ppm).

R = g.c. response factor (ratio of signals for equal concentrations) = 3.309 (experimental value).

For example, using a bulk mixture of methyl bromide containing 350 ppm propane, if the propane g.c. peak area = 4220 and the methyl bromide peak area = 4045, then the bulk mixture concentration of methyl bromide would be 1110 ppm, e.g.,

$$C_b = \frac{4045}{4220} \times 3.309 \times 350 = \underline{1110} \text{ ppm.}$$

The methyl bromide concentration of the various dilutions is calculated using Equation (2).

$$C_x = \frac{F_b \cdot C_b}{F_b + F_{air}} \quad \text{(Eq. 2)}$$

where, C_x = methyl bromide concentration produced in the manifold (ppm).

F_b = measured flow rate of bulk mixture (cc/min).

F_{air} = measured flow rate of diluent air (cc/min).

C_b = concentration of bulk mixture (ppm).

For example, using a 1000 ppm bulk mixture of methyl bromide and a methyl bromide flow of 30 cc/min, an air flow of 5970 cc/min would be needed to produce a 5 ppm mixture in the manifold;

$$F_{air} = \frac{F_b \cdot C_b}{C_x} - F_b = \frac{(30)(1000)}{(5)} - (30).$$

$$F_{air} = 5970 \text{ cm}^3/\text{min}.$$

It is recommended that the sample flow rate be maintained at a fixed value and only the air flow be varied in producing various methyl bromide concentrations.

3. PERFORMANCE EVALUATION

3.1 Conditioning of Gas Cylinders

Pressurized steel cylinders containing gas mixtures of methyl bromide in nitrogen do not need to be preconditioned before use. The stability of the 1000 ppm bulk mixture is good showing less than 1 percent decrease per month.

3.2 Tank Stability

Figure 3 shows a plot of concentration of methyl bromide versus time. The bulk mixture contains propane in addition to the methyl bromide. The propane (350 ppm), serves as an internal standard by which changes in concentration of the methyl bromide may be recognized. Many measurements in this laboratory have shown propane mixtures to be stable.

3.3 Analysis of Bulk Mixtures and Dilutions

The bulk mixtures and dilutions were analyzed by gas chromatography as described earlier. Table 1 shows the results of replicate analyses of one of the dilutions taken from the sampling manifold. The precision of these analyses is very good indicating that the analytical system and sampling technique are reliable.

Various mixtures of methyl bromide in air between 5 and 100 ppm were prepared and analyzed by gas chromatography. Figure 4 shows a plot of g.c. signal versus methyl bromide concentration. The plot is linear and the g.c. sensitivity is sufficient to analyze all of the dilutions directly.

3.4 Calibration

Methyl bromide calibration mixtures were prepared by conventional manometric measurements.

4. CONCLUSIONS

The system described in this report is capable of producing well-defined test atmospheres of varying concentration of methyl bromide in air by blending a bulk mixture of methyl bromide in nitrogen from a pressurized cylinder with a stream of diluent air. Analysis of the bulk mixture and the dilutions can be easily performed by gas chromatography. This gas generation system should provide a means of calibrating the various analytical systems for methyl bromide now in use.

5. REFERENCE

1. E. E. Hughes, W. D. Dorko, E. Scheide, J. K. Taylor, Gas Generating Systems for the Evaluation of Gas Detecting Devices, NBS Report NBSIR 73-292, October 1973.

TABLE 1

Precision of Gas Chromatographic Analysis of Methyl Bromide[a]

Run	Propane signal	Methyl bromide signal	MeBr/propane
1	252,800	248,500	0.983
2	252,500	248,300	0.983
3	252,600	248,500	0.984
4	252,700	248,300	0.983
Ave.	252,650	248,400	0.983
Std. Dev.	129	115	0.00058
Rel. Std. Dev.	0.051%	0.046%	0.059%

[a]Successive measurements made on a 64 ppm mixture generated by dynamic dilution of the bulk mixture.

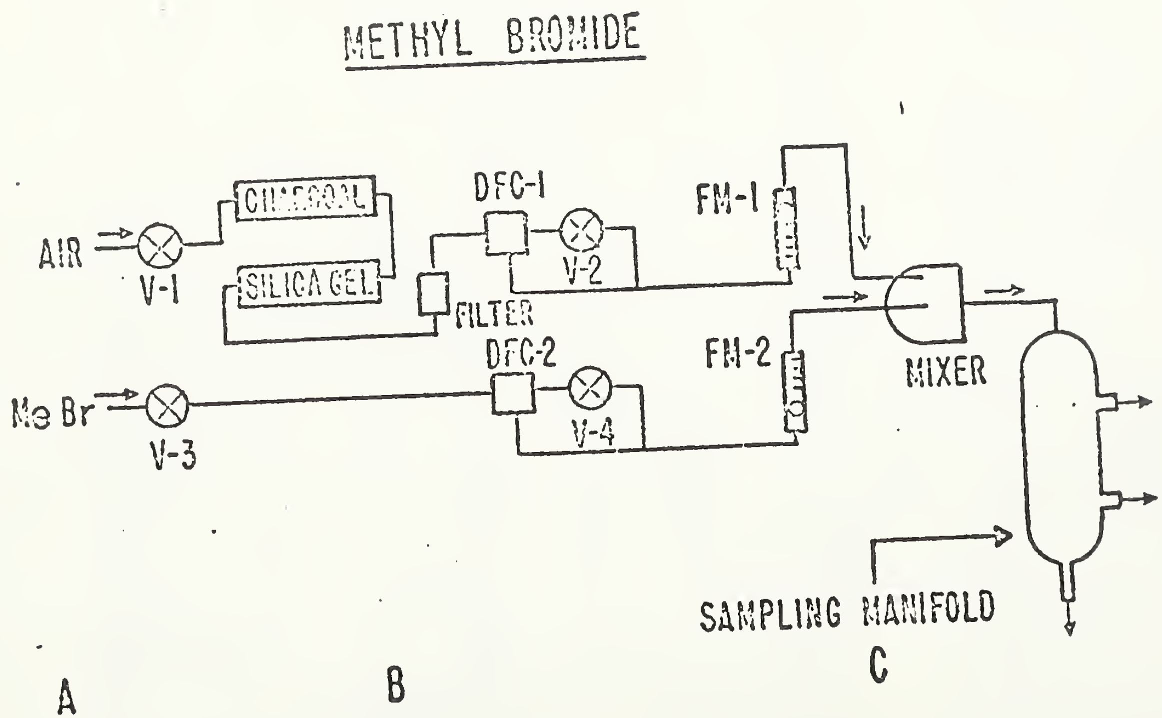

Figure 1. Schematic diagram of methyl bromide dilution system.

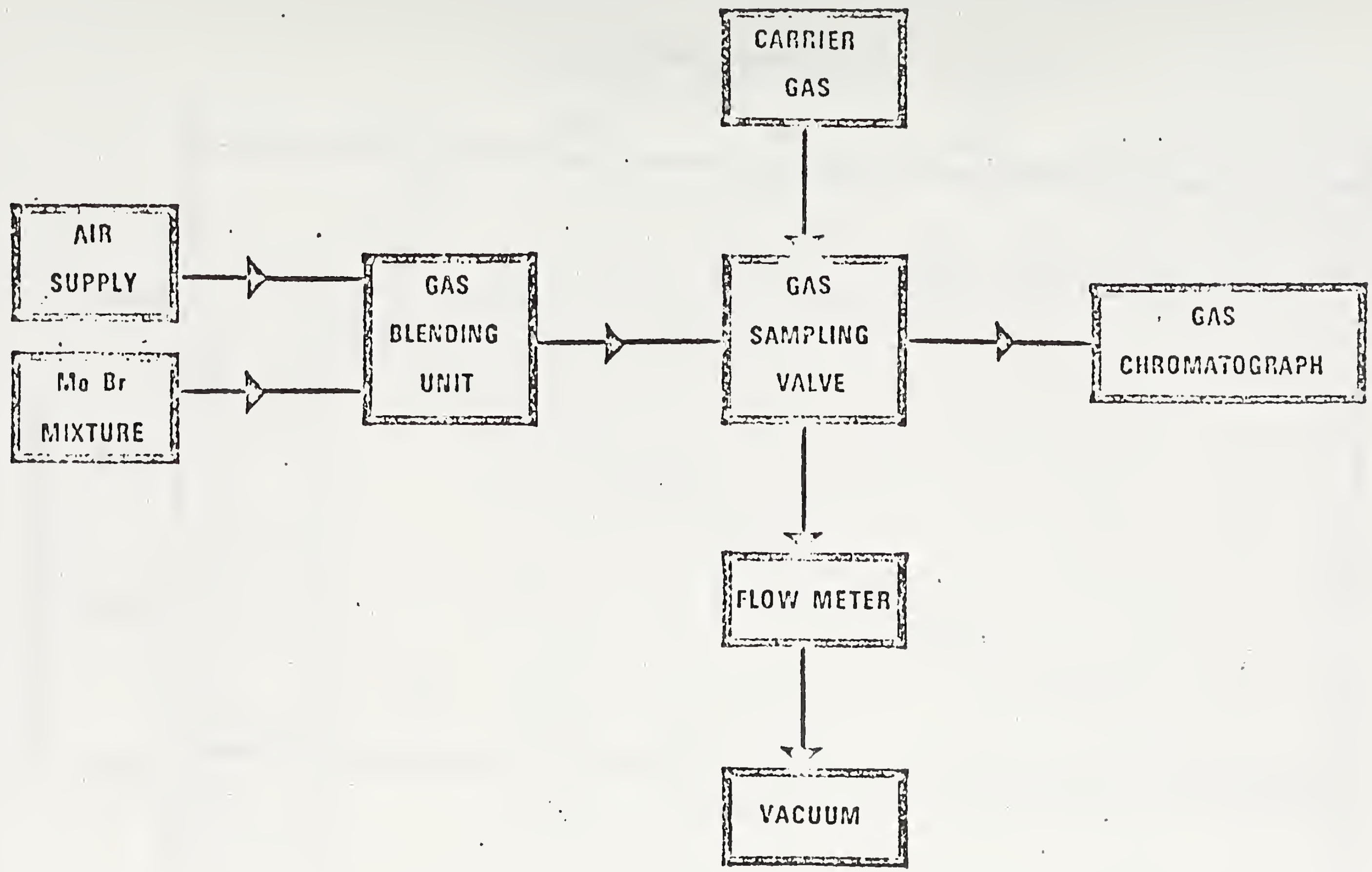

Figure 2. Schematic representation of the methyl bromide dilution and analysis system.

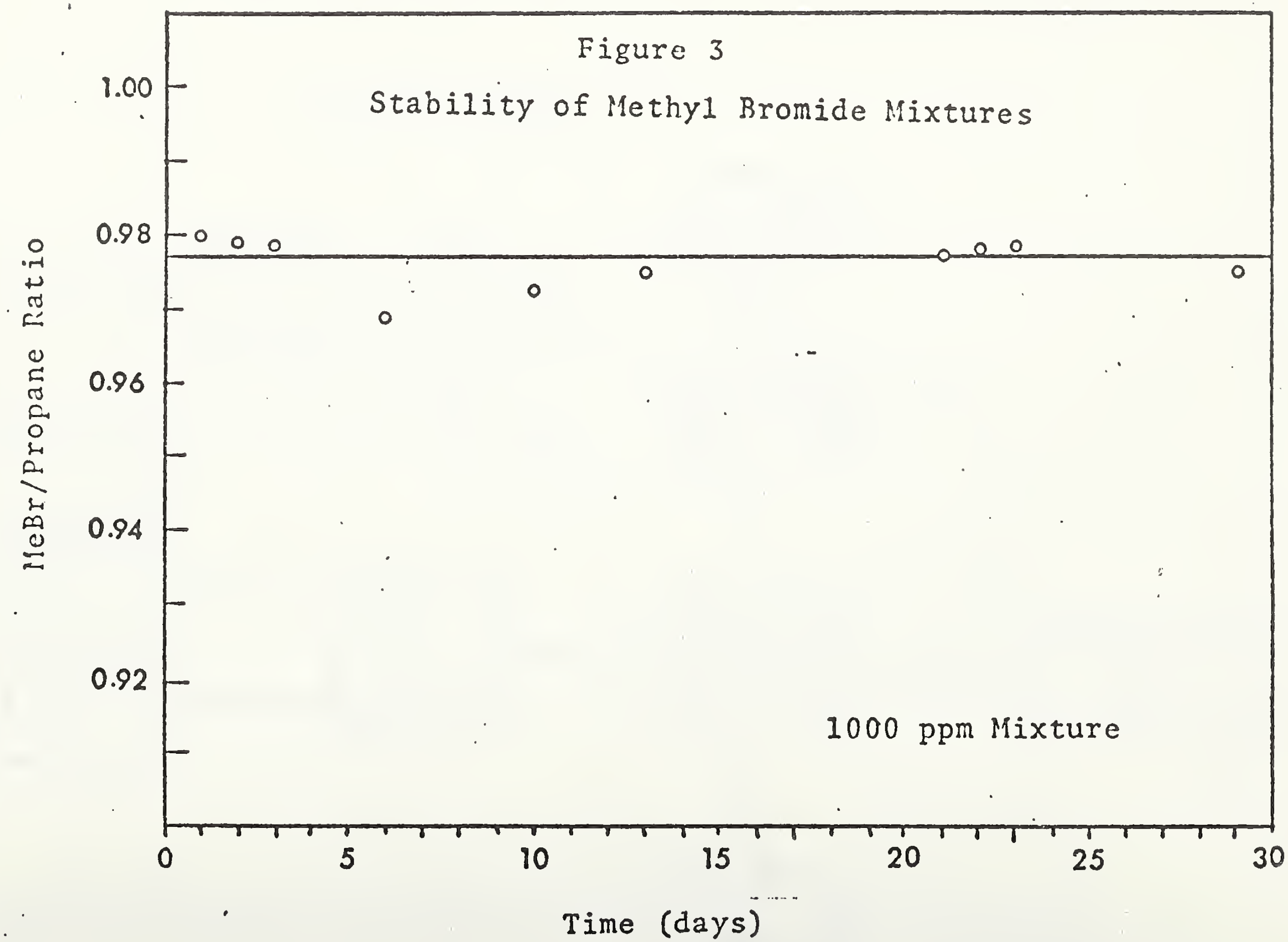

Figure 3. Stability of methyl bromide mixtures.

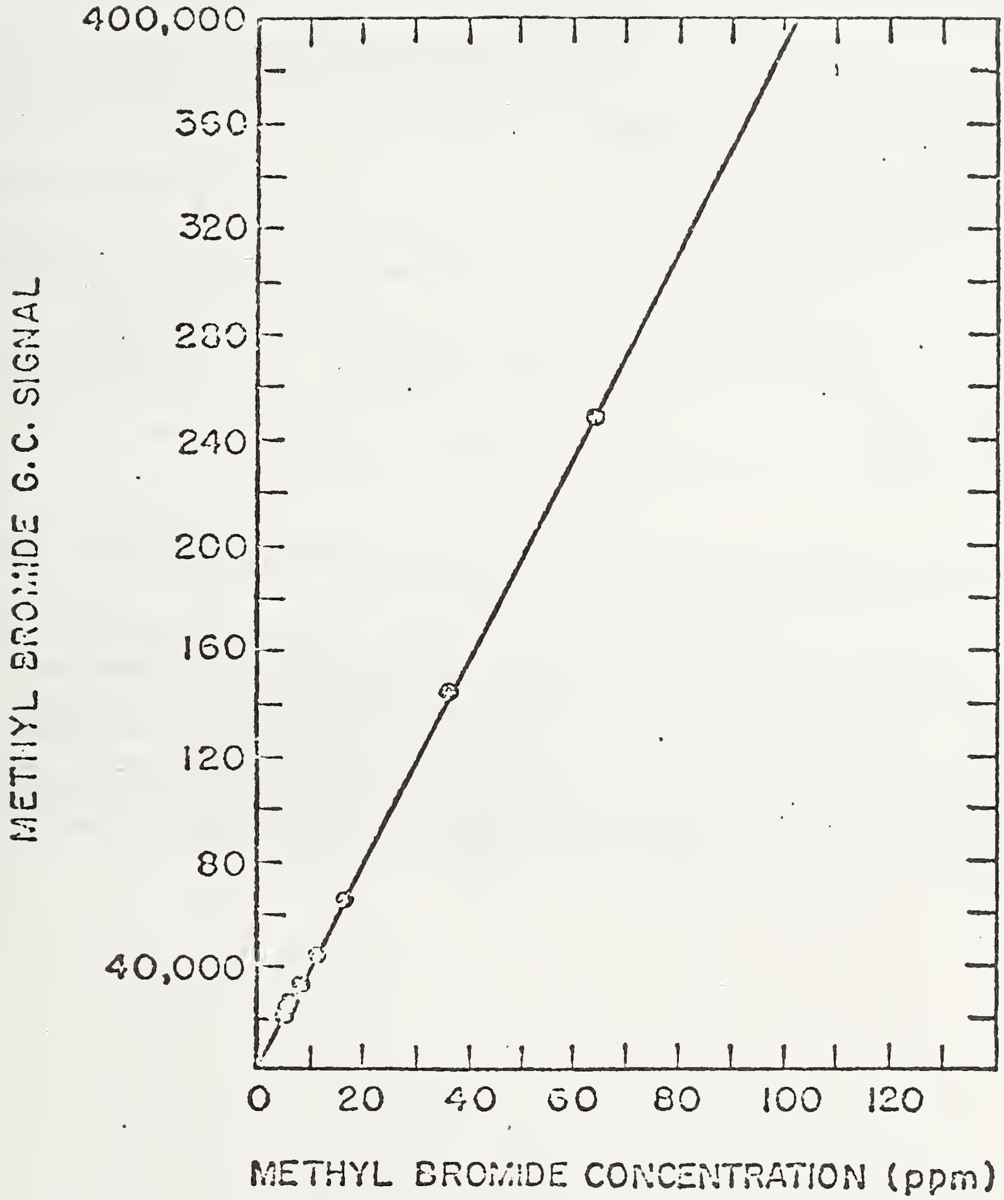

Figure 4. Response of gas chromotagraph to various concentrations of methyl bromide.

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15. SUPPLEMENTARY NOTES

16. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here.)

A system capable of producing well-defined test atmospheres of methyl bromide in air (or any other desired diluent) and an analytical system for the analysis of these gas mixtures is described. Using a bulk mixture of 1000 ppm methyl bromide in nitrogen, and accurately blending this with a stream of clean, dry air, concentrations between 5 and 100 ppm can be produced. This system provides a means of calibration of the various analytical systems for methyl bromide now in use.

17. KEY WORDS (Alphabetical order, separated by semicolons) Gas Chromatography Analysis; Gas Dilution System, Methyl Bromide; Occupational Safety.

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