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Final Report

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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 acrolein 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 9.0 ppm acrolein in nitrogen, and accurately blending this with a stream of clean, dry air, concentrations between 0.05 and 0.50 ppm can be produced. This system provides a means of calibration of the various analytical systems for acrolein now in use.

1. INTRODUCTION

This report describes a system capable of producing well-defined test atmospheres containing concentrations of acrolein ($CH_2{=}CHCHO$) 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 range of 0.05 to 0.5 ppm, but other concentrations could be achieved by suitable adjustment of the operational parameters.

2. EXPERIMENTAL

Acrolein 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 acrolein 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 acrolein in air consists of a cylinder at high pressure containing a known concentration of acrolein 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 acrolein.

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 acrolein, 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of each gas stream, a mixing chamber where the two streams are combined, and a manifold from which the mixture may be withdrawn for analysis or for calibration purposes.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 acrolein in nitrogen was prepared by the manometric method to have an acrolein concentration of 9.0 ppm. The cylinder was pressurized to a total pressure of 1200 psi corresponding to approximately 3600 liters of the 9.0 ppm mixture at ambient conditions. The mixture also contained 2.1 ppm of propane as an internal calibrant. The source of diluent air can be either a pressurized cylinder of "breathing" air or "house" air from the bench. In either case, the air is passed through a silica gel-charcoal dryer to remove major contaminants.

2.2 Analysis

A gas chromatograph equipped with a flame ionization detector can be used to analyze the concentration of either the bulk mixture of acrolein 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 applying a moderate vacuum, 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 gas chromatograph sensitivity before each set of analyses using the manufacturer's recommended procedure. A significant decrease in the detector signal for samples of the same concentration is an indication that the gas chromatograph must be optimized again.

2.3 Calculation of Bulk Mixture Concentration

The bulk mixture concentration is calculated using the following equation:

$$C_b = \left(\frac{\text{Acrolein g.c. peak area}}{\text{Propane g.c. peak area}}\right) \text{ x R x propane concentration} \qquad \text{Eq. (1)}$$

where,

C_b = bulk concentration of acrolein (ppm).

R = g.c. response factor (ratio of signals for equal concentrations) - 1.69 (experimental value).

For example, using a bulk mixture of acrolein containing 2.1 ppm propane, if the propane g.c. peak area - 1690 and the acrolein peak area - 4235, then the bulk mixture concentration of acrolein would be 8.9 ppm, i.e.,

$$C_b = \frac{4235}{1690} \text{ x } 1.69 \text{ x } 2{\cdot}1 = \underline{8.9} \text{ ppm.}$$

The acrolein concentration for various dilutions is calculated using Equation (2).

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

where,

C_x = acrolein concentration produced in the manifold (ppm).

F_x = measured flow rate of acrolein-N_2 mixture (cm^3/min).

F_{air} = measured flow rate of dilution air (cm^3/min).

C_b = concentration of bulk mixture (ppm).

Equation 2, rearranged, may be used to calculate the flow rates required to produce a given concentration of acrolein in the manifold. For example, using a 9.0 ppm bulk mixture of acrolein and a acrolein flow of 30 cm^3/min, an air flow of 5370 cc/min would be needed to porduce a 0.05 ppm mixture in the manifold: i.e.,

$$F_{air} = \frac{F_x \cdot C_b}{C_x} - F_x = \frac{(30)\ (9.0)}{(0.05)} - (30)$$

$$\underline{5370\ \text{cm}^3/\text{min}}.$$

It is recommended to maintain the sample flow at a fixed value and to vary only the air flow in producing various acrolein concentrations.

3. PERFORMANCE EVALUATION

3.1 Conditioning of Gas Cylinders

Mixtures of acrolein in nitrogen placed in pressurized steel cylinders will show a small but significant decrease in concentration with time. This decrease can be slowed down considerably by conditioning the cylinder by prior exposure to a high-concentration acrolein mixture. The cylinder is then evacuated and filled in the normal manner. This conditioning effect is shown in Figure 3.

3.2 Tank Stability

Once the cylinder is conditioned and allowed to reach equilibrium, the acrolein concentration will remain relatively constant. But, because a change may occur, analysis of the bulk mixture is advised before each day's operation.

Since the propane concentration has been found to be stable it serves as an internal standard by which the concentration of the acrolein may be determined at any time.

3.3 Analysis of Bulk Mixture and Dilutions

The bulk mixture 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 acrolein in air were prepared and analyzed by gas chromatography. Figure 4 shows a plot of g.c.

signal versus acrolein concentration. The plot is linear over the range of 0.05 to 0.5 ppm and the g.c. sensitivity is sufficient to analyze all of the dilutions directly.

3.4 Standards and Calibration

Calibration standards accurate to 1 percent were made volumetrically consisting of solutions of acrolein in benzene. These gave a linear plot from which the bulk mixture of acrolein in nitrogen was calibrated.

4. CONCLUSIONS

The system described in this report is capable of producing well-defined test atmospheres of varying concentration of acrolein in air by blending a bulk mixture of acrolein 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 analytical systems for acrolein now in use.

5. REFERENCE

1. E. E. Hughes, W. D. Dorko, E. P. 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 Acrolein

0.292 ppm Sample

Run	Propane signal	Acrolein signal	Acrolein/propane
1	1150	1304	1.134
2	1179	1212	1.028
3	1121	1203	1.073
4	1202	1302	1.083
Ave.	1163	1255	1.080
Std. Dev.	35	55	.043
Rel. Std. Dev.	3.01%	4.38%	3.98%

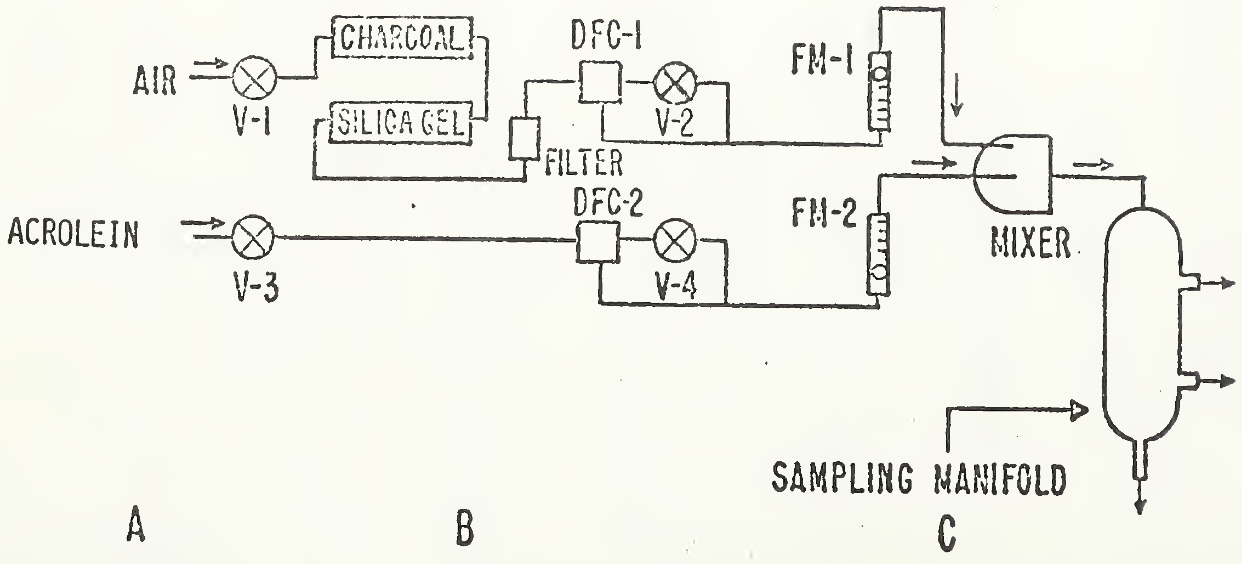

Figure 1. Schematic of dilution system for acrolein.

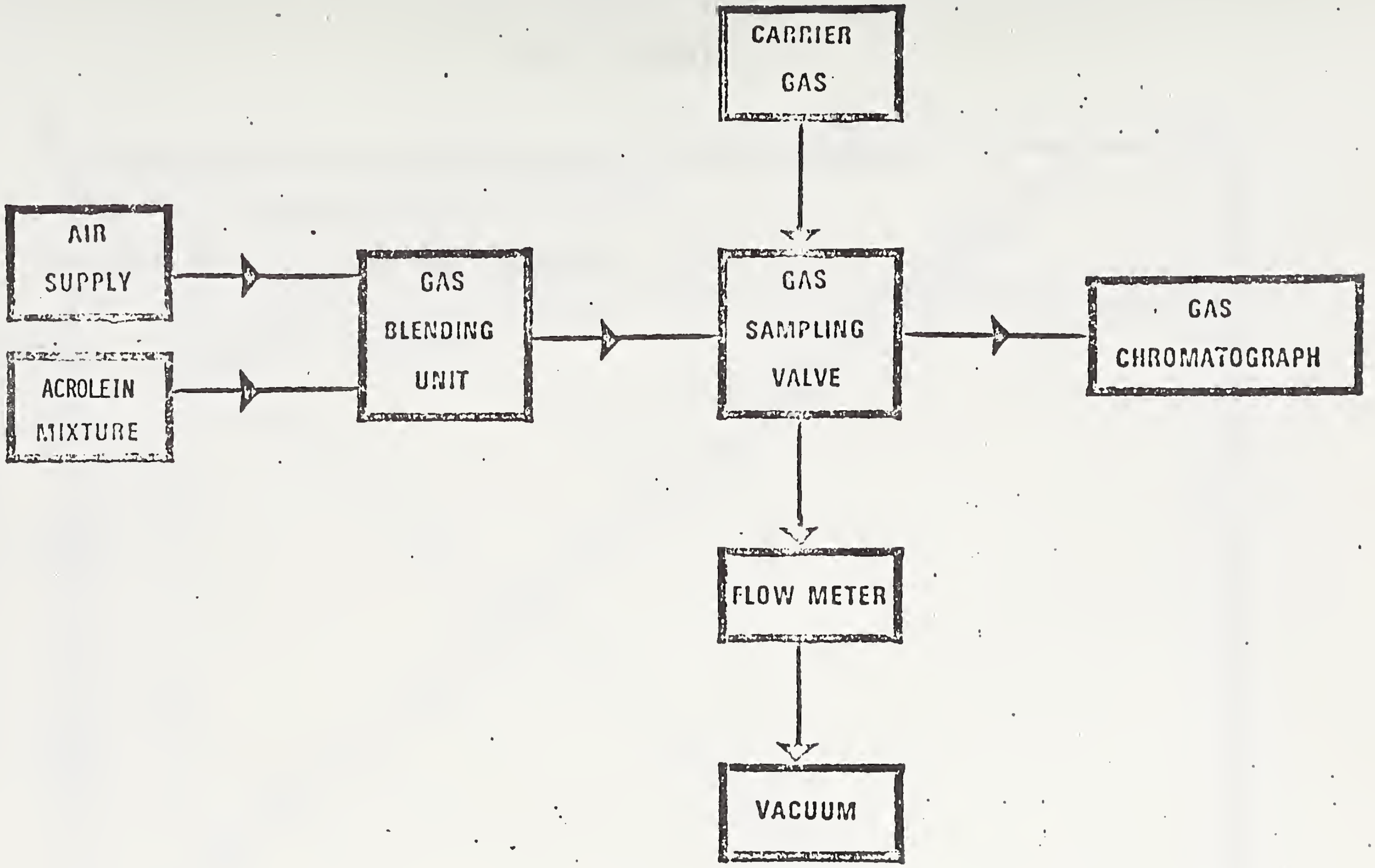

Figure 2. Schematic representation of dilution and analysis system for acrolein.

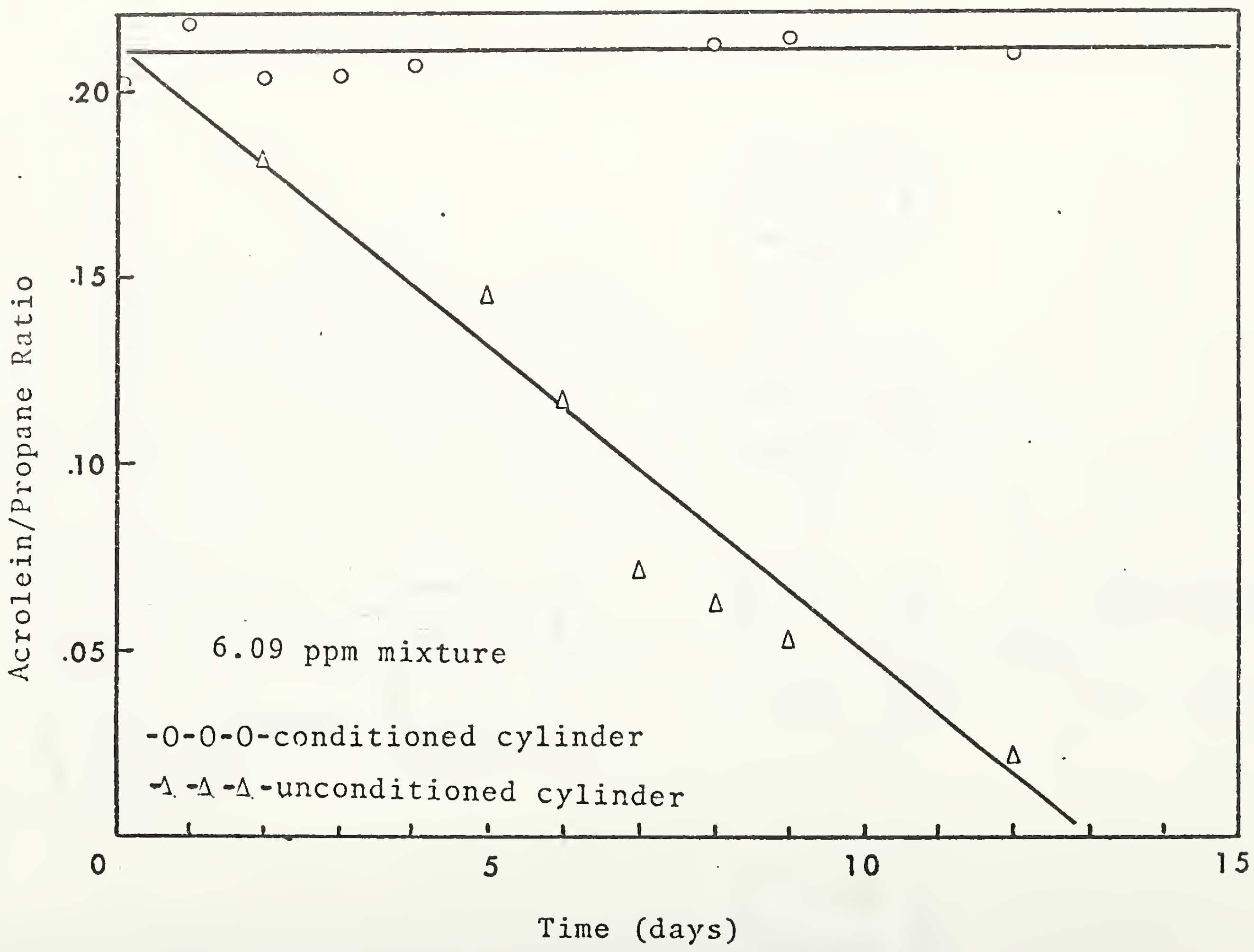

Figure 3. Effect of cylinder conditioning on the observed concentration of acrolein.

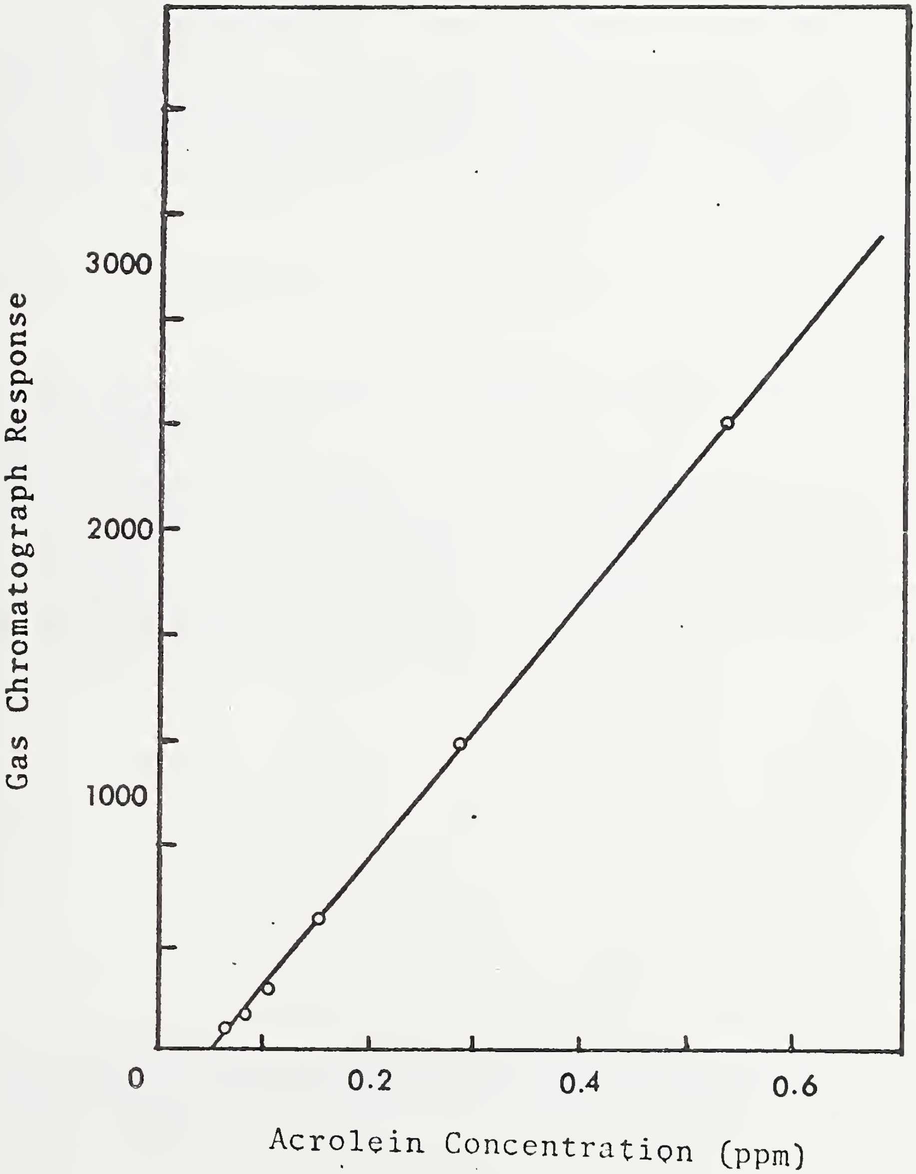

Figure 4. Measured response of gas chromatograph to various concentrations of acrolein.

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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 acrolein 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 9.0 ppm acrolein in nitrogen, and accurately blending this with a stream of clean, dry air, concentrations between 0.05 and 0.50 ppm can be produced. This system provides a means of calibration of the various analytical systems for acrolein now in use.

17. KEY WORDS *(six to twelve entries; alphabetical order; capitalize only the first letter of the first key word unless a proper name; separated by semicolons)* Acrolein; gas chromatography analysis; gas dilution system; occupational safety.

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