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DEPOLYMERIZATION OF TRIOXANE

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Authors

Geisling, K.L.

Miksch, R.R.

Rappaport, S.M.

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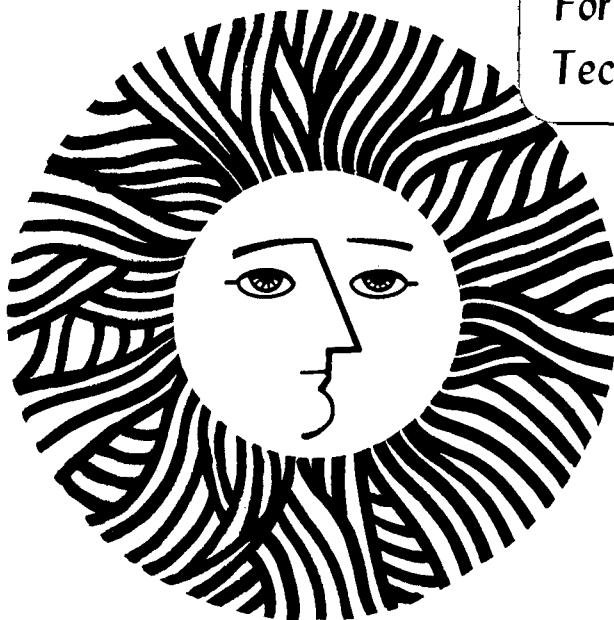
THE GENERATION OF DRY FORMALDEHYDE AT PPB-PPM LEVELS
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Kristin L. Geisling, Robert R. Miksch, and
Stephen M. Rappaport

May 1981

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THE GENERATION OF DRY FORMALDEHYDE
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Kristin L. Geisling and Robert R. Miksch

Building Ventilation and Indoor Air Quality Program
Energy and Environment Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

Stephen M. Rappaport

Department of Biomedical and Environmental Health Sciences
School of Public Health
University of California
Berkeley, CA 94720

May 1981

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ABSTRACT

A procedure is described for the generation of formaldehyde (HCHO) gas by the depolymerization of trioxane vapor emanating from a diffusion cell. The depolymerization is catalyzed by passing the vapor through a heated bed of Carborundum coated with phosphoric acid. Analysis of air samples collected downstream from the catalyst indicates that trioxane is stoichiometrically converted to HCHO and no interfering compounds are produced. Air concentrations of HCHO between 0.05 and 2 ppm have been produced.

Keywords: formaldehyde, gas generation system, trioxane

INTRODUCTION

Recent findings that low-level exposures to formaldehyde (HCHO) may produce allergic effects (1,2) and that HCHO may be carcinogenic (1,2) have led laboratories to undertake the measurement of ppb-ppm concentrations of HCHO in air. A serious obstacle to the development of sensitive sampling and analytical methods has been the lack of an absolute source of gaseous HCHO for generating dynamic, controlled test atmospheres of known concentrations.

Two types of methods have been reported for generating gaseous HCHO, those employing aqueous solutions of HCHO (3,4), and those based upon the depolymerization of various polymers of HCHO (5,6). Evaporation of aqueous solutions has several obvious shortcomings including: (1) the introduction of H₂O vapor and other impurities into the gas stream (e.g., CH₃OH would be generated if formalin was used); (2) the necessity of assaying the solution for its HCHO content, and; (3) the possibility that oligomers and other chemical forms of HCHO may be produced. For generating dry, gaseous HCHO by the depolymerization of various polymers of HCHO, two procedures have been reported. One involves the solid-phase depolymerization of paraformaldehyde or of alpha-polyoxymethylene (5,6), and the other involves the vapor-phase depolymerization of trioxane (7). Experience at Lawrence Berkeley Laboratory with the former technique has indicated that the generation rate of HCHO from paraformaldehyde was not constant and that other compounds were also released including water vapor, formic acid, and methyl formate. Accordingly, we turned our attention to the depolymerization of trioxane vapor which had been used by Schnizer et al to produce percent concentrations of HCHO in air (7). The reported procedure involves bubbling air through molten trioxane and sweeping the vapor through a catalyst. Conversions of trioxane to HCHO as high as 89% were reported. The authors suggested that higher yields were possible, but were not attained with their apparatus because of the repolymerization of HCHO. We report a modification of this technique to produce ppb-ppm air concentrations of HCHO. Trioxane vapor emanating from a diffusion cell is converted to HCHO with essentially 100% efficiency.

EXPERIMENTAL

A schematic diagram of the generation system we developed is shown in Figure 1. The diffusion cell, with a diffusion path of 7.9 cm x 4.9 mm i.d., was maintained at 35.2 ± 0.05 °C in a thermostatically-controlled oven (Model 300, Analytical Instrument Development, Inc., Avondale, PA). Using a capillary funnel warmed with a heat gun, molten trioxane (Aldrich Chemical Co., purity = 98%, reported m.p. = 61-62.5 °C) was introduced into the reservoir of the diffusion cell where it was allowed to solidify at room temperature. Dry N₂ flowing at 0.2 L/min swept trioxane vapor from the diffusion chamber through the catalyst bed which was held at 160 °C in a tube furnace. The catalyst consisted of 18 g of Carborundum (Fisher Scientific Company), ground to 40 mesh and

coated to saturation with 85% phosphoric acid (Mallinckrodt Chemical Company), tightly packed into a 7.5 cm section of 1 cm i.d. quartz tubing. To prevent repolymerization of HCHO caused by high concentrations, the gas stream emerging from the catalyst was immediately diluted with air that had been purified with 13X molecular sieve to remove water vapor and any background HCHO. While connected to the vapor source it was necessary to continuously heat and purge the catalyst with N₂ to prevent the accumulation of HCHO.

Samples of the diluted gas stream were collected over 24 hours by bubbling the air through two distilled water bubblers which were connected in series and maintained at 2 °C. Air flow rates through the bubblers were controlled with critical orifices at 0.8 L/min. The collection efficiency of this sampling procedure, verified in our laboratory, has been reported to be approximately 95% (8,9). Aliquots of the bubbler solutions were analyzed simultaneously by two procedures which have been commonly used for the measurement of HCHO, the chromotropic acid (CTA) method (8,9) and the pararosaniline (PRA) method (10). We observed that the CTA method stoichiometrically responds both to trioxane vapor and to gaseous HCHO, whereas the PRA method responds only to gaseous HCHO (10). A gas sample collected from the effluent of the catalyst with a gas-sampling flask was analyzed by a mass spectrometer (CEC Model 21-103B) with a room temperature inlet system.

RESULTS AND DISCUSSION

The generation rate of trioxane from the diffusion cell was determined gravimetrically by weighing the cell periodically on a five place analytical balance. After one week, a constant rate of 740 ± 10 $\mu\text{g/hr}$ was observed. This rate was maintained for a period of five months until the reservoir became significantly depleted of trioxane whereupon it gradually decreased. We observed that an equilibrium exists between trioxane/HCHO absorbed on the catalyst and HCHO in the N₂ stream. A steady state was established relatively quickly (approximately one week).

The generation rate of HCHO from the catalyst, based upon the analysis of 18 samples by the PRA method (which does not respond to trioxane) was 769 ± 29 $\mu\text{g/hr}$. The corresponding rate based on 65 analyses by the CTA method was 761 ± 28 $\mu\text{g/hr}$. (These values were corrected for the collection efficiency of the sampling method, which was assumed to be 95%.) The close agreement between these two figures suggests that the conversion of trioxane to HCHO was essentially complete. This conclusion was supported by mass spectrometric analysis which failed to detect the presence of trioxane or of other anomalous compounds in amounts exceeding 2% of the total HCHO present in a gas sample taken downstream from the catalyst. The generation rate of dry HCHO from the catalyst, as indicated by all 83 analyses, was 103% of the gravimetrically determined generation rate of trioxane. The slight positive bias observed is well within the limits commonly achieved with the gas dilution apparatus used in this study (11).

By using the apparatus described above with the double air-dilution system shown in Figure 1, we have produced dynamic, controlled test atmospheres of HCHO at air concentrations between 0.05 and 2 ppm. The generation rate of trioxane vapor and, ultimately, of gaseous HCHO depends upon the temperature and geometry of the diffusion cell and, therefore, a virtually unlimited range of HCHO air concentrations may be produced by modifying these parameters.

This method constitutes a significant improvement over previous HCHO generation techniques. The apparatus is easily assembled and produces a dry gas stream, eliminating potential HCHO losses caused by interactions with water vapor. Most importantly, the generation system produces monomeric HCHO, free from impurities, at air concentrations that can be accurately predicted from gravimetric data and which remain constant for long periods of time.

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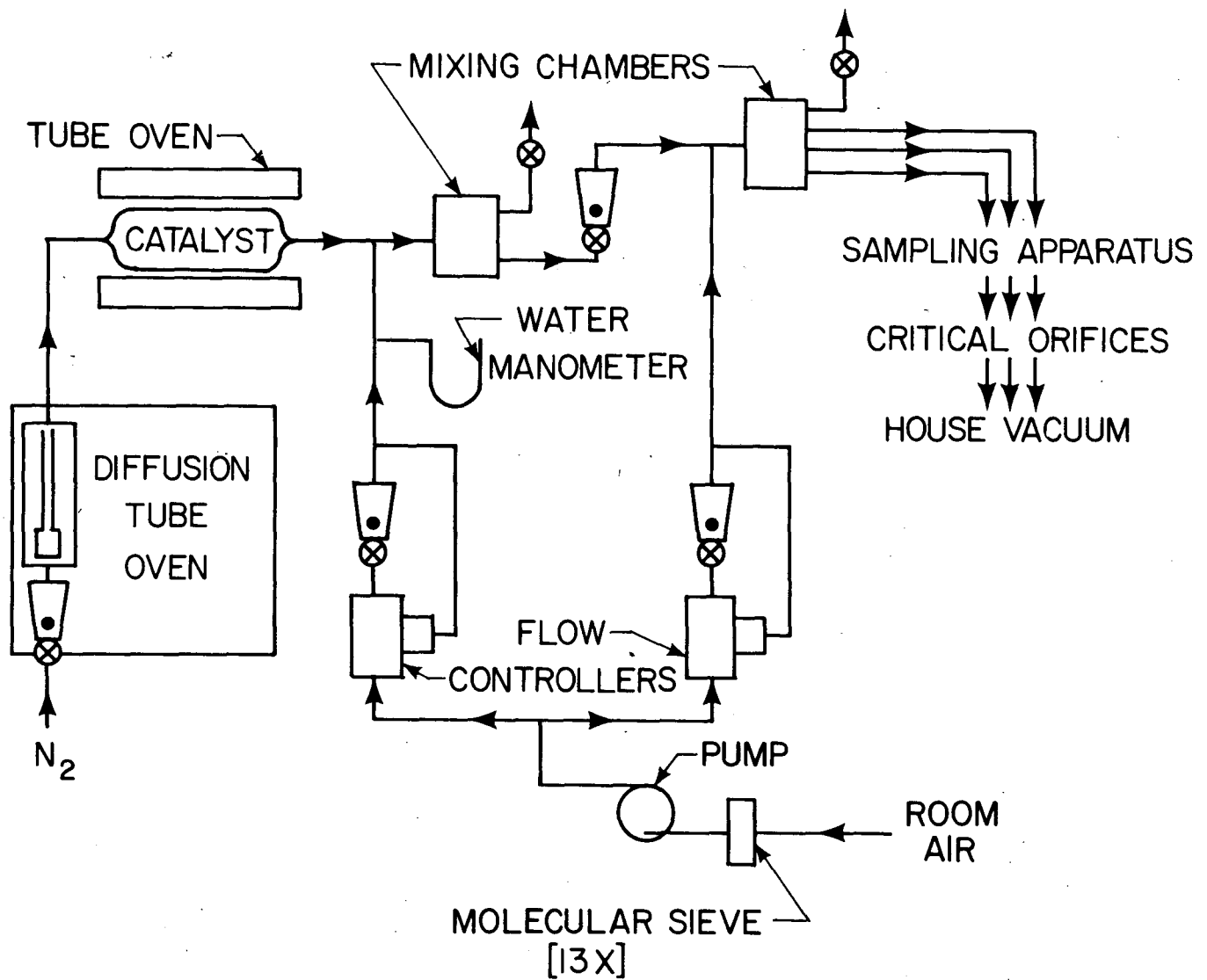
FIGURE CAPTION

Figure 1. Apparatus for generating ppb-ppm levels of formaldehyde gas. Trioxane vapor emanating from a diffusion cell is swept over a catalyst bed, and the resultant formaldehyde gas is diluted to the desired concentration using clean room air.

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Figure 1



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