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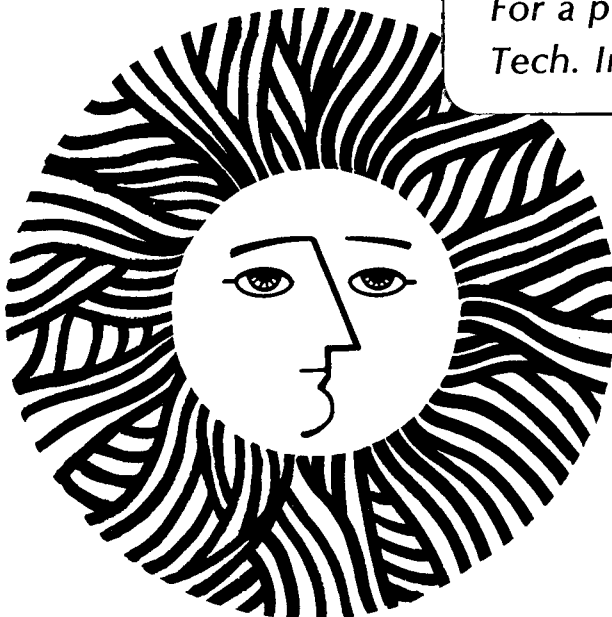
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ABSTRACT

A passive sampling device based on the principle of diffusion has been developed for the determination of formaldehyde in ambient air. The sampler consists of a capped glass tube (with approximate dimensions of 2.4 x 9 cm) containing a glass-fiber filter treated with NaHSO_3 . In the field the device collects a sample by being uncapped for a specified sampling time. After being recapped and returned to the laboratory, the filter is analyzed by the chromotropic acid (CTA) method. Laboratory validation studies were conducted by exposing the sampling devices for

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one week to dry formaldehyde gas generated by passing trioxane vapor over an acid catalyst bed. In these tests, formaldehyde concentrations ranged from 0.05 to 0.80 mL/m³. Reproducibility was excellent with relative standard deviations averaging 5.4% for five constant concentrations. The lower detection limit was determined to be 3.6 mL/m³-hr. In an occupational environment an 8-hr sample would be sufficient to detect compliance with the OSHA permissible exposure limit of 3 mL/m³; in a residential environment a one-week sample would allow detection of 0.025 mL/m³ for indoor air quality audits.

INTRODUCTION

Formaldehyde (HCHO) is a large-volume chemical used in the manufacture of building materials such as particleboard, plywood, fiberboard, and urea-formaldehyde foam (UFF) insulation. Recent concern that exposure to low levels of HCHO may cause a severe allergic response in 4 to 8% of the population (Gunby, 1980), and that it may be carcinogenic (NIOSH, 1981), have prompted many investigations of HCHO levels in homes and office buildings.

A serious obstacle to investigations of HCHO concentrations in indoor environments has been the lack of a simple, accurate, and inexpensive system for determining HCHO concentrations in air. At present, most sampling involves the use of water contained in bubblers through which air is drawn by means of a pump and flow-control device. These samplers are bulky, initial operating and maintenance costs are high, and samples must be collected and shipped under refrigeration to prevent HCHO loss through evaporation.

We have developed a passive sampling device that relies on the principle of diffusion for collecting HCHO. The sampler consists of a glass-fiber filter treated with NaHSO_3 which is contained in a glass vial. HCHO diffuses through the vial and reacts with NaHSO_3 to produce a stable addition product, sodium formaldehyde bisulfite. Passive sampling devices based on the laws of diffusion or permeation have already been shown to offer many advantages in sampling reactive gases in ambient air (Palmer et al., 1976; McCammon and Woodfin, 1977; and Nelms

et al., 1977). Most importantly, they obviate the need for pumps and flow-control systems. They measure integrated pollutant concentrations in any dynamic atmospheric environment in which contaminant concentrations are varying (Martin, 1981). The HCHO sampler reported here is lightweight and small, can be operated by untrained personnel, and is very inexpensive, thus making it particularly attractive for use in indoor air quality audits.

THEORETICAL CONSIDERATIONS

Fick's First Law of Diffusion has been used to describe the transport of a pollutant gas through a sampler tube open at one end (Palmer and Gunnison, 1973). The authors derived an expression relating the quantity of pollutant gas transferred through the sampler to its ambient concentration and the time of exposure under the condition that the concentration of the pollutant gas is maintained at zero at the closed end of the tube. The expression is given as:

$$Q = D \left(\frac{A}{L} \right) C t \quad (I)$$

where

- Q = quantity of gas transferred, μg
- D = diffusion coefficient of the pollutant gas in air, cm^2/sec
- A = cross-sectional area of the sampler, cm^2
- L = length of sampler, cm
- C = ambient concentration of gas, $\mu\text{g}/\text{cm}^3$
- t = time, sec

Time-weighted average pollutant concentrations are determined from the

amount of a contaminant collected by a passive sampler when the exposure time, geometry of the sampler, and the diffusion coefficient of the contaminant gas in air are known.

An important consideration in the design of the formaldehyde passive sampler was selection of the physical dimensions of the diffusion path. It has been suggested that an overall length to diameter ratio of 3 or greater minimizes the effects of turbulence (caused by air movement at the open end of the tube) on the diffusion of gas within the sampler (Lautenberger et al., 1980; Brown et al., 1981). The length to diameter ratio also determines the sampling rate of the diffusional passive sampler. We chose dimensions which allow sampling for one-week time periods at the concentrations commonly found in non-occupational indoor environments. Thus concentrations are averaged over the week-long activity cycle of occupants, a cycle which affects indoor air contaminants.

EXPERIMENTAL

To prepare the HCHO passive monitors, 24-mm glass fiber filters which contain no organic binders (Millipore, Bedford, MA.) were soaked in 5% solutions of NaHSO_3 (Mallinckrodt, St. Louis, MO.) and dried in a desiccator under a stream of N_2 for approximately three hours. Iodine titrations (Karchmer, 1970) indicated that from 4 to 6.5 mg of bisulfite remain on the filters after drying. Single filters were gently pressed into the bottom of glass vials 2.4 cm in diameter and 9.5 cm in length (area to length ratio of 0.455) and closed with polyethylene "Caplugs"

(#EC-16, Protective Closures Co., Inc., Buffalo, N.Y.). If the passive monitors were to be stored for more than one day prior to sampling, the vials were filled with dry N_2 .

Because the diffusion coefficient of HCHO in air is not well documented, it was necessary to perform a series of experiments to establish a calibration curve relating the amount of HCHO transferred through the passive sampler and trapped on the treated filters to the ambient air concentration.

The sampling devices were exposed to HCHO at five constant concentrations ranging from 0.05 to 0.8 mL/m³ for one-week sampling periods. Week long test-exposure periods were chosen to duplicate the field operating conditions for which the samplers were designed. Test atmospheres of HCHO gas were produced with a generation system in which trioxane, the cyclic trimer of HCHO, is decomposed over an acid catalyst to monomeric HCHO (Geisling et al., 1981). The apparatus for the exposure experiments is diagrammed in Figure 1. Streams of dilute HCHO gas of known concentration flowed in parallel through two cylindrical chambers 17.8 cm in depth and 16.5 cm in diameter, and then through pairs of midget bubblers in series. Each chamber contained five passive samplers allowing exposure of ten of the devices during each test run. Atmospheric pressure in the chambers was maintained by a vent in the generation system, and flow rates, controlled by critical orifices, were maintained such that the total rate at which the five passive samplers in a chamber sampled HCHO was less than 5% of the total flow rate of the gas stream through the chamber. The temperature surrounding the

chambers was held between 19 and 22° C and the air inside was mixed by fan-type magnetic stirrers operated with compressed air. Reference bubbler samples were collected daily to monitor the concentration of HCHO in the gas stream emerging from the generation system (see Figure 1).

Following exposure, distilled water was added to the passive samplers to dissolve the sodium formaldehyde bisulfite formed on the filters. Either 5 or 10 mL was added using volumetric pipettes to produce aqueous HCHO concentrations in the range of 0.2 to 2.0 µg/mL. The vials were gently shaken and the solutions centrifuged for 5 to 10 minutes to remove extraneous filter material. Four-mL aliquots of both the sample solutions and reference bubbler solutions were analyzed by the wet-chemical, spectrophotometric CTA method currently recommended by the National Institute of Occupational Safety and Health (NIOSH, 1977). The concentration of the chromotropic acid reagent was increased from 1 to 5% to insure complete color development. The absorbance of the solutions were read on a Cary Model 219 spectrophotometer (Varian Instrument Division, Palo Alto, CA).

Aqueous HCHO solutions were prepared and standardized following the procedure given by Miksch et al., 1981. At least five dilute HCHO standard solutions and a distilled water blank were analyzed with each sample batch. To investigate any effects that excess bisulfite may have had on the analytical method, NaHSO₃-treated filters were placed in the dilute HCHO standards and the solutions were then analyzed. No differences were observed in the slopes of standard curves generated with and without the filters and, therefore, standards were routinely analyzed

without the addition of treated filters.

RESULTS AND DISCUSSION

Results from the experiments described above allowed us to evaluate the performance of the passive samplers in relation to the theory of diffusion-based sampling, and provided the numerical constants necessary for field application. Data from the HCHO passive sampler exposure experiments are given in Table 1 and plotted as a calibration curve in Figure 2. With this curve, the user of the passive sampler can obtain time-weighted average concentrations of HCHO in air by measuring the amount of HCHO collected on a treated filter in a known exposure period. A linear regression analysis of the data also yields a mathematical expression relating the amount of HCHO collected to average concentrations of HCHO in air:

$$\mu\text{g HCHO collected} = [0.291 \times (\text{mL}/\text{m}^3)\text{-hr}] + 0.019 \quad (\text{II})$$

The correlation coefficient for this expression was 0.999, indicating that the rate at which HCHO was trapped by the NaHSO_3 -treated filters did not vary with concentration. It may be inferred, therefore, that the collection efficiency of the passive sampler for HCHO is high enough to assure performance over a wide range of HCHO concentrations.

The slope of the regression line ($0.291 \mu\text{g HCHO}/(\text{mL}/\text{m}^3)\text{-hr}$) reflects the rate at which the device samples HCHO in air. This rate can be converted

to the more familiar form of volume/time, thus allowing comparison with conventional air sampling methods that employ pumps. The sampling rate of the passive sampler reported here is $3.95 \pm 0.17 \text{ cm}^3/\text{min}$ and is specific for the collection of HCHO in air and for the exact geometry of the device.

The lower detection limit of the passive sampler (and the described analytical method) is $3.6 \text{ (mL/m}^3\text{)-hr}$. The device has been tested at exposures as high as $135 \text{ (mL/m}^3\text{)-hrs}$ and its capacity was not exceeded. In its present configuration the passive monitor can detect $.025 \text{ mL/m}^3$ in a one-week sampling period, (appropriate for indoor air quality audits in residential settings), and 3 mL/m^3 in an eight-hour sampling period, the legal permissible exposure limit for occupational environments (U.S. Occupational Safety and Health Administration, 1979).

An important requirement of any field sampling device is that it retain its capacity while being stored prior to exposure, and that the collected sample remain stable with no losses during storage and shipment after exposure. We performed tests to determine the pre- and post-exposure storage stability of the HCHO passive samplers for periods of one and two weeks. The data are presented in Tables 2 and 3. For the pre-exposure stability studies, passive samplers were stored after preparation and then, on the day they were to be exposed, another set of samplers was also prepared. By exposing the two groups of passive sampling devices simultaneously, we were able to compare the performance of the stored samplers with samplers exposed immediately after preparation. In the same manner, we compared the HCHO present in samplers stored

after exposure to that found on filters analyzed immediately after exposure. (These samples were also exposed to HCHO simultaneously).

The data show that passive samplers stored prior to exposure retained their ability to collect HCHO. (Samplers analyzed after storage without HCHO exposure gave a zero response.) No significant loss (within one standard deviation) of HCHO was detected for samples stored after exposure.

The most important potential interferent to the sampling system describe here is water vapor since it plays a role in both the oxidation of bisulfite and the release of HCHO in indoor environments. Initial experiments using bisulfite-treated filters in a different sampling configuration have shown HCHO collection to be unaffected at humidities as high as 85% RH (Geisling, 1980). Further tests are necessary to confirm that the filters used in this sampler remain unaffected by humidity.

Other potential interferents to this measuring system include phenols, some alcohols, and some aldehydes (especially acrolein) which have been identified as minor interferents to the CTA method (NIOSH, 1977). It is unlikely that (with the exception of acrolein) any of these compounds will be trapped by the bisulfite-treated filters in the passive samplers.

To investigate any possible interference from acrolein, treated filters were spiked with 10 μg HCHO (in the form of sodium formaldehyde bisulfite) and various amounts of acrolein, and analyzed by the CTA method. No interference was detected for filters on which the amount of

acrolein was 10 times greater than that of formaldehyde. Significant (negative) interference was observed only when acrolein exceeded HCHO by more than 50 times; however it is unlikely that acrolein would exceed HCHO to this degree in non-industrial indoor environments.

As part of a study to evaluate indoor air quality in energy-efficient houses in California, the passive samplers were used concurrently with bubbler samplers to measure HCHO levels within some houses with passive-solar designs. In the field, passive samplers were uncapped and taped, open end down (to prevent dust accumulation), to inert surfaces. Bubbler samplers were collected in a refrigerated unit (Lin et al., 1979) at flow rates between 150 and 250 cm³/min. All samples were taken over one-week periods in occupied houses under normal living conditions. The results of the field validation tests are given in Table 4.

Results indicate the passive samplers do have a slight (15%) positive bias when compared with the bubbler samples. Additional field measurements should indicate whether this difference is real or the result of a very limited number of measurements.

SUMMARY

We have developed an inexpensive, simple, and sensitive passive sampling device for measuring ambient HCHO concentrations in occupational and non-occupational indoor environments, and we have tested its storage stability both before and after exposure. Tests to date have demon-

strated excellent results for storage periods as long as two weeks, and we believe the samplers may be stored for much longer time periods. The passive sampler replaces devices currently in use which require a pump and skilled personnel to collect a sample. Ideally, the device can be used by the lay person in the field and shipped to a laboratory for analysis by a basic, familiar analytical technique. In addition, after initial investigation, no further calibration of the passive sampler is required since ambient temperature and pressure effects are minimal (see Palmes et al., 1976). With further development, the sensitivity range of this sampling system could be extended by modifying the geometry of the sampler or by alternating the sensitivity of the analytical method.

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REFERENCES

Geisling, K.L. (1981) "Impregnated filters for the determination of formaldehyde in indoor environments," LBL-12917, Lawrence Berkeley Laboratory, Berkeley, CA 94720.

Geisling, K.L., Miksch, R.R., and Rappaport, S.M. (1981) "Generation of dry formaldehyde at trace levels by the vapor-phase depolymerization of trioxane," Anal. Chem. 54, 140-142.

Gunby, P. (1980) "Fact or fiction about formaldehyde," J. Amer. Med. Assoc., 243, 1697-1703.

Karchmer, J.H., ed. (1970) "The analytical chemistry of sulfur and its compounds," Wiley-Interscience Publishers, New York, NY.

Lin, C.I., Anclerio, R.H., Anthon, D.W., Fanning, L.Z., and Hollowell, C.D., (1979) "Indoor/outdoor measurements of formaldehyde and total aldehydes," LBL-9397, Lawrence Berkeley Laboratory, Berkeley, CA.

Martin, J.E. (1981) "An intuitive approach to passive monitors," W.D. Kelley, ed., Annals of the American Conference of Governmental Industrial Hygienists-Dosimetry for Chemical and Physical Agents, American Conference of Governmental Industrial Hygienists, Cincinnati, OH, pp. 101-106.

McCammon, C.S. Jr. and Woodfin, J.W. (1977) "An evaluation of a passive monitor for mercury vapor," Am. Ind. Hyg. Assoc. J., 38, 378-386.

Miksch, R.R., Anthon, D.W., Fanning, L.Z., Hollowell, C.D., Revzan, K., and Glanville, J. (1981), "Modified pararosaniline method for the determination of formaldehyde in air," Anal. Chem., 53, 2118-2123.

Nelms, L.H., Reiszner, K.D., and West, P.W. (1977) "Personal vinyl chloride monitoring device with permeation technique for sampling," Anal. Chem., 49, 994-998.

National Institute of Occupational Safety and Health (1981) "NIOSH current intelligence bulletin #34 - Formaldehyde: Evidence of Carcinogenicity," National Institute of Occupational Safety and Health, Cincinnati, OH.

National Institute of Occupational Safety and Health (1977) "NIOSH manual of analytical methods, 2nd ed.", Publication no. 77-157A, National Institute of Occupational Safety and Health, Cincinnati, OH.

Palmes, E.D., Gunnison, A.F., DiMattio, J., and Tomczyk, C. (1976) "Personal sampler for nitrogen dioxide," Am. Ind. Hyg. Assoc. J., 37, 570-577.

Palmes, E.D., and Gunnison, A.F. (1973) "Personal monitoring device for gaseous contaminants," Am. Ind. Hyg. Assoc. J., 34, 78-81.

Spangenberg, C.D. (1951) "Nomograph for Gaseous Systems," Chem. Eng., 58, 170-171.

U.S. Occupational Safety and Health Administration (1979) "Occupational Safety and Health Standards, Hazardous Materials," 29 CFR 1910.1000,

July 1, 1979, published by Government Printing Office, Washington, D.C.

Table 1. Results of Calibration Experiments for the HCHO Passive Sampler.

Known HCHO Air Conc. ^a (mL/m ³)	Reference Method HCHO Air Conc. ^b (mL/m ³)	Duration of Sampling (hrs)	HCHO Collected ^c (ug)
0.058	0.060 ± 0.002	162.67	2.96 ± 0.22 (n = 10)
0.096	0.101 ± 0.003	154.52	4.39 ± 0.17 (n = 10)
0.201	0.204 ± 0.006	141.17	8.40 ± 0.26 (n = 9)
0.397	0.407 ± 0.008	158.84	17.5 ± 1.7 (n = 10)
0.839	0.871 ± 0.025	160.24	39.4 ± 2.4 (n = 9)

^aBased on gravimetrically-determined generation rate of HCHO

^bBased on 24-hr bubbler samples, average of 14 observations ± absolute standard deviation

^cAverage ± absolute standard deviation

Table 2. Pre-Exposure Storage Stability of Passive Samplers.

Storage Time	HCHO Concentration (mL/m ³)		Concentration Ratio Stored/Non-Stored
	Passive Samplers Stored Prior to Exposure ^a	Passive Samplers Exposed Immediately after Preparation ^b	
1 wk	1.42 ± .07 (n=7)	1.40 ± .05 (n=4)	1.01
2 wk	1.36 ± .10 (n=8)	1.33 ± .07 (n=4)	1.02

^aPassive samplers were prepared, filled with N₂ and capped, and stored at room temperature before exposure to HCHO. Average HCHO concentration ± absolute standard deviation for n samples.

^bAverage HCHO concentration ± absolute standard deviation for n samples. Non-stored and stored samplers were exposed to the same atmosphere.

Table 3. Post-Exposure Storage Stability of Passive Samplers.

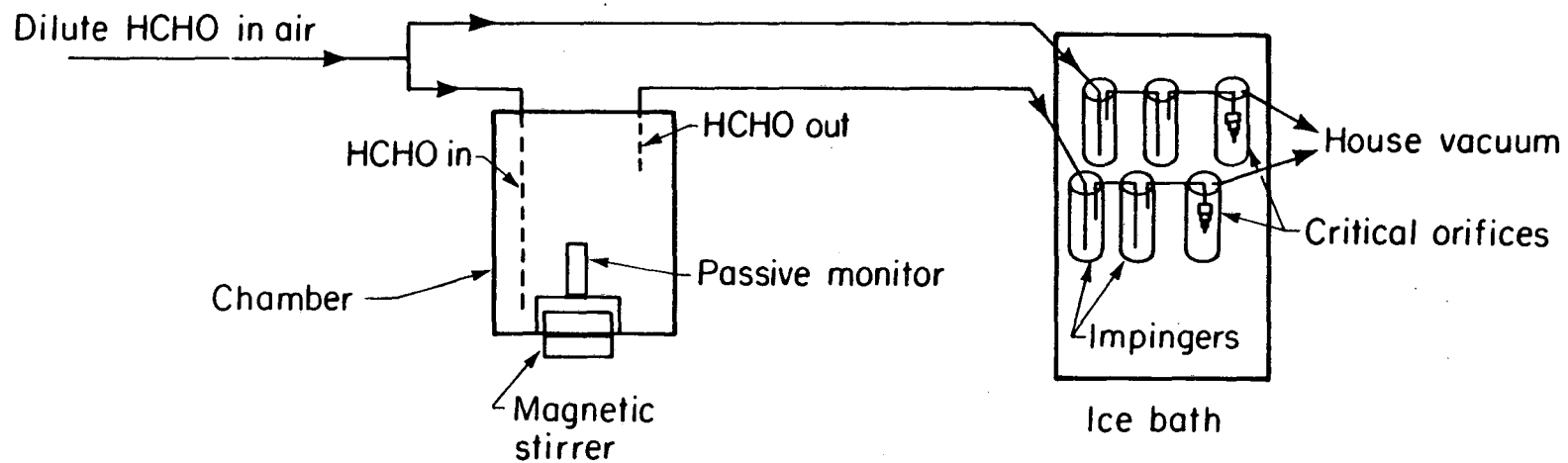
Storage Time	HCHO Concentration ^a (mL/m ³)		Concentration Ratio Stored/Non-Stored
	Passive Samplers Stored After Exposure ^b	Passive Samplers Analyzed After Exposure	
1 wk	1.24 ± .07 (n=7)	1.35 ± .09 (n=5)	0.92
2 wk	1.41 ± .06 (n=8)	1.36 ± .02 (n=4)	1.04

^a Average HCHO concentration ± absolute standard deviation for n samples.

^b Stored at room temperature.

Table 4. Field Validation of HCHO Passive Sampler

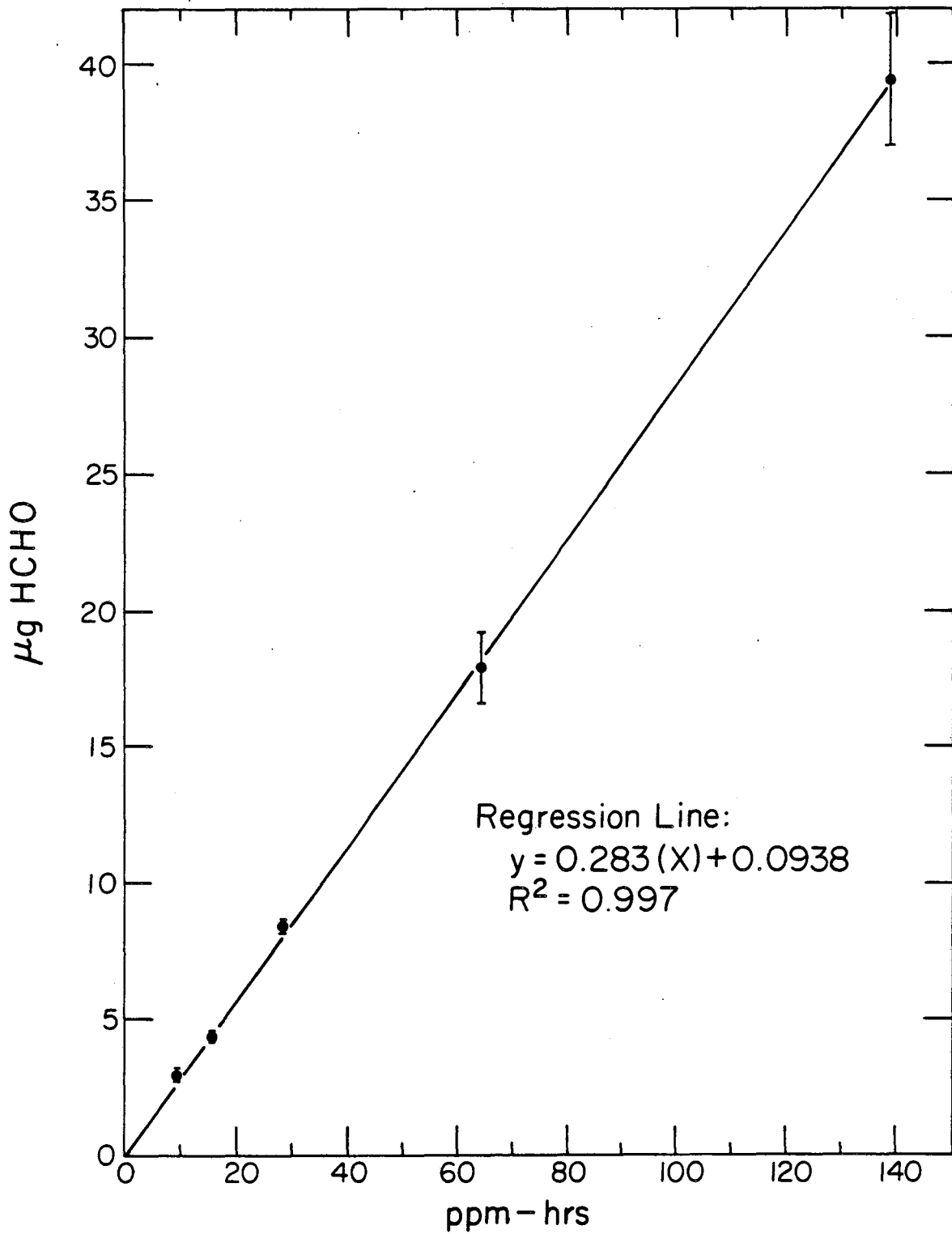
Location #	Exposure time (hr)	HCHO Concentration	
		Bubbler (mL/m ³)	Passive Sampler (mL/m ³)
1	167.8	0.102 ± 14% (n = 4)	0.126 ± 8.5% (n = 4)
2	169.2	0.117 ± 28% (n = 4)	0.142 ± 5.0% (n = 5)
3	168.8	0.127 ± 18% (n = 4)	0.147 ± 6.4% (n = 4)
4	170.2	0.100 ± 12% (n = 4)	0.108 ± 2.1% (n = 5)
5	168.0	0.098 ± 15% (n = 4)	0.106 ± 3.2% (n = 5)



XBL 816-2374

Fig. 1. Schematic diagram of the apparatus used for evaluating the passive monitor.

For our study, the apparatus was constructed in duplicate, and the two chambers were placed in an insulated box.



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Fig. 2. Amount of HCHO captured by the passive monitor plotted as a function of HCHO exposure level.

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