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Author
Hodgson, A.T.

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A.T. Hodgson, K.L. Geisling, B. Remijn,
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DISCLAIMER

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A.T. Hodgson, K.L. Geisling, B. Remijn, and J.R. Girman

Building Ventilation and Indoor Air Quality Program
Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

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ABSTRACT

A passive sampling device based on the principle of diffusion has been developed specifically for the determination of formaldehyde in residential indoor air. The device, which is inexpensive and easy to use, is capable of measuring one-week time-weighted average concentrations of formaldehyde from as low as 0.018 ppm to over 1 ppm. The sampler was validated by a series of laboratory experiments and a field study conducted in occupied residences and an office. The parameters evaluated in the laboratory and field experiments were: sampling rate; sampling period; detection limit; relative humidity effects; chemical interferences; shelf life; sample stability; overall precision; bias; and overall accuracy. The performance of the passive sampler compared favorably to that of a reference pump/bubbler sampler.

Keywords: passive sampler, formaldehyde, indoor air, residences, method validation, field comparison

INTRODUCTION

It has recently been demonstrated that relatively low concentrations of formaldehyde (HCHO) in air have potential adverse public health effects (Gunby 1980, Swenberg et al. 1980). In addition, it has been shown that significant chronic exposures to HCHO can occur in residential indoor environments (NRC 1981). The perceived need to protect residential indoor air quality by maintaining low concentrations of HCHO and other air pollutants can conflict with energy conservation goals. The controversy over the use of urea-formaldehyde foam insulation was an example of this conflict until the use of the material was banned by the U.S. Consumer Product Safety Commission (Chemistry and Engineering News 1982). Other sources of HCHO are more prevalent in the residential environment since HCHO is used in many construction materials and consumer goods and is a combustion product. Consequently, residential weatherization programs, which achieve energy conservation by reducing building air exchange rates, have the potential to result in deleterious increases in concentrations of HCHO and other indoor-generated air pollutants. At present, data on HCHO in the residential environment, which are needed to evaluate this issue, are severely limited.

Investigations of the magnitude and extent of the potential HCHO problem in the residential environment have been inhibited, in part, by the lack of simple and inexpensive methods to accurately determine low concentrations of HCHO in air. In response to this need, several diffusion sampling devices, originally developed for industrial hygiene applications, are now being marketed for use in residences (e.g., DU PONT PRO-TEK, 3M Formaldehyde Monitor). However, the suitability of

these devices for this new application, where it is desirable to measure relatively low concentrations of HCHO over extended time periods, has not been adequately demonstrated.

Lawrence Berkeley Laboratory (LBL) recently has developed a passive sampling device based on the principle of diffusion specifically for the determination of HCHO in residential indoor air (Geisling et al. 1982a). The device, which is inexpensive and easy to use, is capable of accurately measuring time-weighted average concentrations of HCHO from as low as 0.018 ppm to over 1 ppm for a period of one week. The one week sampling interval is ideally suited for quantification of chronic HCHO exposures since HCHO concentrations vary in response to environmental factors such as temperature, humidity, and ventilation (Moschandreas and Rector 1981) which are influenced by occupant activity cycles, e.g., weekday/weekend changes in activities. Peak concentrations are not obtained; however, passive samplers respond quickly to transients, and peak concentrations are incorporated into the time-weighted average (Martin 1981).

This report presents the results of laboratory validation experiments conducted with the LBL passive sampler for HCHO, as well as the results of a field evaluation in which the performance of the passive sampler was compared to that of a reference pump/bubbler sampler. A description of the passive sampler and the results of the laboratory and field validation experiments are summarized in Table 1.

LABORATORY VALIDATION

Sampler Preparation

Passive samplers are prepared as described by Geisling et al. (1982a) with one modification. Sodium bisulfite impregnated filters are dried under vacuum for approximately 3 hr instead of under a constant stream of dry nitrogen. Sampling efficiency, as determined by sampling rate, is not affected by this change in procedure.

Sampler Deployment

Procedures for the deployment of the passive samplers in residences are simple. The date and time of initiation of sampling and identification data are recorded on the passive sampler labels and on a separate data sheet. The samplers are uncapped and attached with masking tape to a suitable surface out of the reach of children and pets. Samplers are hung with their open ends facing down to exclude dust. If replicate samplers are employed, samplers are spaced approximately 2 cm apart. Samplers are not attached directly to surfaces which are potential HCHO sources. In addition, an attempt is made to space samplers out away from walls so that wall effects (e.g., stratified air layers, temperature differentials) are avoided. At the end of a one-week sampling period, the samplers are tightly capped, and the date and time are recorded. The samplers are promptly returned to the laboratory for HCHO analysis.

Analytical Method

The passive samplers are eluted with 6 ml of distilled water upon arrival in the laboratory. If the samplers are not to be analyzed immediately, they are stored in their eluted state in a refrigerator at 5 °C.

Samplers are analyzed for HCHO by the spectrophotometric chromotropic acid (CA) procedure described in P&CAM No. 125 (NIOSH 1977). Specific details of the entire analytical procedure used for the samplers are presented by Geisling et al. (1982a).

Sampling Rate

The sampling rate for diffusion passive samplers is equal to the diffusion coefficient of the contaminant gas in air multiplied by the cross sectional area of the sampler divided by the diffusion path length. Mass uptake is the product of the sampling rate, the ambient concentration, and the sampling time. Sampling rate and the general theory of passive samplers are discussed in detail by Palmes et al. (1976) and Lautenberger et al. (1981).

Since the diffusion coefficient of HCHO in air has not been quantified, it was necessary to empirically determine the sampling rate in the laboratory by exposing the passive samplers to known HCHO concentrations. Test atmospheres at approximately 1 atm and 20 °C were produced with a HCHO gas generation/dilution system (Geisling et al. 1982b). With this system, the production of HCHO gas of known concentrations is achieved by catalytical decomposition of trioxane vapor emanating from a diffusion cell and subsequent dilution with clean air. A calibration

curve was constructed relating the mass of HCHO collected by the samplers to the HCHO exposure (the product of concentration and exposure time) from which the empirical sampling rate was calculated (Geisling et al. 1982a).

In initial tests, the sampling rate for a one-week (168-hr) sampling period was determined to be 3.95 cm^3/min with a standard deviation of 0.17 cm^3/min (Geisling et al. 1982a). Additional laboratory data on the mass of HCHO collected versus HCHO exposure have been collected for one-week periods over a wide range of HCHO concentrations (Table 2). The sampling rate determined from these data by a linear regression weighted for instrumental uncertainties (Bevington 1969) is 4.02 cm^3/min (0.296 µg/ppm-hr) with a standard deviation of 0.11 cm^3/min (Figure 1). The coefficient of determination (r^2) for the regression analysis is 0.996, demonstrating that sampling rate is independent of concentration.

Recent preliminary data indicate that the sampling rate may be moderately higher at sampling periods of less than one week. It is recommended that the passive samplers only be deployed for a period of one week until sufficient data have been collected to accurately quantify the relationship between sampling rate and time.

Detection Limit

The theoretical detection limit of the method is derived from the HCHO concentration that produces an analytical absorbance that is significantly different from the absorbance of the system blank. Passive sampler blanks have a mean absorbance of 0.037 with a standard deviation of 0.005 (Table 3). An absorbance of 0.05 is demonstrated to be signi-

ficantly different from this system blank ($p = <0.01$) by application of a one-tailed Student's t-test to determine whether a single variate sampled at random could belong to a given population (Sokal and Rohlf 1969). The absorbance of 0.05 is equivalent to a HCHO concentration of 0.07 µg/ml, and the absorbance of the system blank is equivalent to a concentration of 0.02 µg/ml (Figure 2). The difference, 0.05 µg/ml, is attributable to the sample. Since the analytical procedure calls for the elution of the samplers with 6 ml of water, the samplers must collect a minimum of 0.3 µg of HCHO to be at the limit of detection. Use of the 4.0 cm^3/min sampling rate and the recommended deployment period of one week results in a HCHO in air theoretical detection limit of 0.006 ppm.

Field experience with the sampler has shown that precision is often considerably reduced at the theoretical detection limit perhaps due, in part, to the relatively large contribution of the system blank error to the total error at this concentration. Therefore, we recommend the adoption of a lower quantification limit of 0.018 ppm (0.075 absorbance) which is three times the theoretical limit. Precision is considerably improved at 0.018 ppm, and the use of the sampler is not meaningfully restricted since this quantification limit is more than adequate for residential applications.

Upper Quantification Limit

A laboratory experiment demonstrated that the passive sampler has the capacity to collect at least 1500 µg of HCHO from air. However, since the passive sampler is designed specifically for use in residential and office environments, laboratory evaluation of the device has

been limited to a maximum concentration of 1 ppm for 168 hr (50 μg of HCHO collected).

Use of the prescribed analytical procedure results in an upper quantification limit of 0.56 ppm. This upper limit, which is established by the maximum linear range of the calibration curve, is sufficient for most residential applications. When the absorbance of the sample exceeds that of the highest aqueous HCHO standard, the upper limit can be extended to well over 1 ppm without loss of the original sample by reduction of the spectrophotometer cuvette path length. The upper limit can also be extended by dilution and reanalysis of the unused portion of the sample. These procedures can produce an upper limit of over 5 ppm for a 168-hr exposure; however, the sampler's linearity of response has not yet been determined for concentrations in excess of 1 ppm.

Precision

Precision was quantified using the coefficient of variation which is simply the standard deviation expressed as a percentage of the mean. The coefficient of variation permits the comparison of the amount of variation in measurements having significantly different means.

The precision of the analytical method alone was determined from routine replicate analyses of aqueous HCHO standards on different days (Table 4). The sample-size-weighted, mean coefficient of variation for the analytical method is 3.2% and is not correlated with HCHO concentration which ranges between zero and 3.9 μg/ml.

The most realistic and useful estimate of the overall precision of the method is obtained from the field comparison (Table 5).

Replicate samplers used in the field comparison were initially clustered in a bundle until it was discovered that deployment of samplers in this manner results in relatively poor precision, perhaps due to starvation of several samplers. Precision was noticeably improved by spacing the samplers approximately 2 cm apart. This spacing is now incorporated into the recommended method of deployment. The six initial field samples with inadequate sampler spacing were excluded from the analysis of precision.

For the 15 field samples employing five or four (an occasional sampler was broken or otherwise lost) replicate samplers spaced 2 cm apart, the coefficient of variation for HCHO concentration ranges between 1.7 and 10.7%. The sample-size-weighted, mean coefficient of variation is 6.7%. The coefficient of variation is not correlated with HCHO concentration which ranges between 0.028 and 0.146 ppm.

Environmental Effects

Since the sampling rate of the passive sampler was established empirically at approximately 1 atm and 20 °C, the mass of HCHO collected by the sampler is standardized at these conditions. From kinetic theory, we know that in real gas diffusion processes the mass of a gas collected is a function of the square root of the absolute temperature and is independent of pressure (Palmes et al. 1976, Lautenberger et al. 1981). The temperature dependence of mass collected is small. For example, an increase in temperature from 20 °C to 25 °C increases the mass collected by only 1%. Therefore, the mass of HCHO collected by the passive sampler can be considered to be independent of both temperature and pressure for most residential applications.

The effect of relative humidity on the collection efficiency of the passive sampler was determined by exposing samplers to a range of relative humidities at 25 °C in a test atmosphere with 0.25 ppm HCHO. Sampling rate was not effected by a one-week exposure at 50-60% relative humidity. However, exposures at 70-85% relative humidity for one week resulted in a significant decrease in sampling rate. Consequently, the passive sampler should not be used in indoor environments where the average relative humidity exceeds 60% at 25 °C.

Interferences

Possible chemical interferences for the CA analytical method are listed in P&CAM No. 125 (NIOSH 1977). Ethanol, phenols, ethylene, propylene, and 2-methyl-1,3-butadiene are reported to produce negative interferences when in excess of HCHO. However, these compounds are normally present in air at lower concentrations than those of HCHO and are not considered to have a serious effect on the method (NIOSH 1977). The possibility that these compounds would interfere in the analysis of the passive samplers is even more remote since they are not expected to be collected by the samplers.

It is possible, however, that acrolein, an unsaturated aldehyde combustion product known to be present in indoor environments primarily as a component of cigarette smoke, could be collected. To test for the potential interference of acrolein with the CA analytical method, passive samplers were spiked with known volumes of aqueous HCHO and acrolein standard solutions. No significant difference in the amount of HCHO was observed between samplers with and without acrolein spikes when acrolein was in an approximate 10:1 excess of HCHO. Since acrolein

concentrations are unlikely to exceed HCHO concentrations in residential environments (NRC 1981), acrolein is not considered to be an interference.

Storage Stability

Pre-exposure storage stability (shelf life) of the passive samplers has been reported by Geisling et al. (1982a). Samplers were assembled, flushed with nitrogen, capped, and stored for one and two weeks. After storage, they were exposed to approximately 1.4 ppm HCHO in the laboratory test chamber along with freshly prepared samplers. No significant differences were detected with a Student's t-test ($p = 0.05$) between HCHO concentrations of stored and freshly prepared samplers (Table 6).

Post-exposure storage stability of the passive samplers was also reported by Geisling et al. (1982a). Samplers were exposed to approximately 1.4 ppm HCHO in the laboratory. Concentrations of HCHO determined from samples stored for one and two weeks before analysis were compared to concentrations determined from samples analyzed immediately after exposure. No significant differences were detected with a Student's t-test ($p = 0.05$) between stored and immediately analyzed samples (Table 7).

FIELD COMPARISON

A field comparison was conducted in occupied residences and an office to determine the accuracy of the passive sampler method relative to the results obtained with a reference pump/bubbler method. Twenty-one individual sampler comparisons were made over a period of three

in a variety of locations which included new energy-efficient houses, weatherized houses, urea-formaldehyde foam insulated houses, conventional houses, and a prefabricated office. The data from these comparisons are summarized in Table 5.

LBL pump/bubbler samplers, which consist of a vacuum pump, flow controller, and refrigerated bubbler trains (Fanning et al. 1981, Miksch et al. 1981) were modified to collect four replicate samples over a period of one week using individual sampling rates near 0.14 L/min. These devices were installed in residences and an office with the sample tube inlet located 10-20 cm from five passive samplers. Sampling was conducted concurrently with both active and passive devices. Pump/bubbler sampler air flow rates were determined at the beginning and end of each one-week sampling period, and average flow rates were used in the calculation of HCHO concentrations. Initial and final flow rates typically varied less than 10% at a sampling location. Total volumes of air passed through the bubblers were corrected to standard pressure; no temperature corrections were made since the measured variation in indoor temperatures around 25 ^{o}C would only result in an approximate ± 1% variation in sample volume. The HCHO collection efficiency of the bubblers was assumed to be 95% (NIOSH 1977). Bubbler and passive monitor samples were analyzed concurrently using the CA method.

The results obtained by the two sampling methods were statistically compared using a two-way analysis of variance with replication (Sokal and Rohlf 1969). This test demonstrated that there is a significant difference ($p = <0.001$) between the sets of concentrations measured by the two methods.

In laboratory comparisons, concentrations of HCHO in air determined from bubbler samples collected for periods up to one week are typically within 2% of theoretical concentrations produced by the HCHO gas generation/dilution system. Consequently, we currently accept the bubbler sampler data as the best estimates of the true HCHO concentrations in indoor air for the field comparison. However, the possibility that the pump/bubbler sampler produces biased field results can not be ruled out and is currently being investigated.

The passive sampler concentrations versus pump/bubbler sampler concentrations from the field comparison are plotted in Figure 3. The relationship between the two variables is quantitatively defined by the use of Bartlett's three-group method for regression (Sokal and Rohlf 1969). This regression technique, rather than the standard linear regression, is appropriate when both variables are subject to measurement error. As can be seen in Figure 2, the fit of the data to the regression line is good. We recommend the use of the equation, $Y = 0.87X$, to convert passive sampler concentrations (X) to bubbler sample concentrations (Y) until the discrepancy between the two methods is resolved. With the conversion, the overall accuracy for the passive sampler method is equal to the true concentration with a 95% confidence interval of ± 14%.

SUMMARY

The LBL passive sampler for determining HCHO concentrations in residential indoor air has been validated in laboratory experiments and in a field comparison conducted in occupied residences and an office. The sampler is designed to measure time-weighted average concentrations of HCHO for a period of one week. The quantification range for the one-week period of 0.018 ppm to over 1 ppm is more than adequate for residential applications. The sampler is currently restricted to use in indoor environments where the average relative humidity is 60% or less. Acrolein, the only compound considered to be a significant potential interference, has no effect on the analytical method even when in a 10:1 excess of HCHO. Product shelf life and post-exposure sample stability of two weeks minimum are sufficient for residential survey applications. The overall precision obtainable with the sampler in the field is approximately 7%. When a correction factor is applied to compensate for presumed bias, the overall accuracy of the method in the field is equal to the true concentration plus and minus a 95% confidence interval of 14%.

The passive sampler is now developed and tested to a stage where it can be used with confidence to determine HCHO concentrations in residences; however, method validation efforts are continuing. The relationship between sampling rate and time for sampling periods shorter than one week is being characterized. The effect of high relative humidity on the performance of the sampler is being defined more rigorously. Finally, the source of the discrepancy between results obtained with the passive sampler and the pump/bubbler sampler is under investigation.

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Table 1. Description and specifications of the LBL passive sampler.

CONTAMINANT:	Formaldehyde (HCHO)
SAMPLER:	Passive diffusion sampler; area, 3.98 cm^2; path length, 9.4 cm; collection medium, $NaHSO_3$ impregnated glass fiber filter
ANALYSIS:	Chromotropic acid spectrophotometric analysis, NIOSH P&CAM No. 125
SAMPLING RATE:	4.02 cm^3/min (0.296 µg/ppm-hr) at 1 atm and 20 °C
SAMPLING PERIOD:	1 week (168 hr)
SAMPLING RANGE:	0.18 ppm to more than 1 ppm for 168 hr
ENVIRONMENTAL EFFECTS:	Independent of pressure, only slightly dependent on temperature
	Accuracy reduced when average relative humidity exceeds 60% at 25 °C
INTERFERENCES:	No identified significant interferences in residential environments
SHELF LIFE:	2 weeks minimum
SAMPLE STABILITY:	2 weeks minimum
OVERALL PRECISION:	Mean coefficient of variation = 6.7%
BIAS:	+15% based on field comparisons with reference method; true concentration = 0.87 x passive sampler concentration
OVERALL ACCURACY:	True concentration ± 95% confidence interval of 14%

Table 2. Mass of HCHO collected by passive samplers versus HCHO exposure.

HCHO Exposure Conc. (ppm)	Exposure Time (hr)	Exposure (ppm-hr)	n*	Mass of HCHO Collected (μg) x ± s.d.†
0.058	163	9.45	10	2.96 ± 0.218
0.096	154	14.8	10	4.39 ± 0.173
0.201	141	28.3	9	8.40 ± 0.265
0.211	169	35.7	10	9.59 ± 1.04
0.397	159	63.1	10	17.5 ± 1.75
0.839	160	134	9	39.4 ± 2.40
1.00	165	165	10	49.2 ± 1.79
1.00	166	166	12	55.5 ± 3.42

*Number of samplers.

†s.d. = standard deviation.

Table 3. Absorbances of passive sampler blanks.

Date Analyzed	Lot. No.	Absorbance
3-31	A	0.034
		0.038
4-14	B	0.045
		0.029
		0.047
4-21	C	0.040
		0.041
		0.039
4-26	D	0.036
		0.035
		0.037
5-3	E	0.042
		0.023
		0.036
5-17	F	0.033
		0.030
		0.037
5-17	H	0.038
		0.032
		0.036
5-19	G	0.035
		0.039
		0.040
	x =	0.037
	s.d. =	0.005
	CV* =	13.5%

*Coefficient of variation.

Table 4. Precision of analytical method as measured by the coefficient of variation. Routine analysis on different days.

HCHO Concentration (μg/ml)	n	Coefficient of Variation (%)
0	6	4.2
0.194	6	5.6
0.388	6	3.1
0.766	7	3.1
1.55	8	3.1
1.94	7	1.5
2.32	7	1.8
3.10	5	1.3
3.88	6	3.0
		Weighted mean = 3.2

Table 5. Field comparison of the performances of the LBL passive sampler and a reference pump/bubbler sampler.

	Bubbler	Passive	Bubbler	Passive	Bubbler	Passive
Location	S-6		S-10		S-15	
n	4	4	4	5	4	5
x (ppm)	.127	.146	.100	.107	.117	.140
± 95% c.l.	.035	.014	.019	.002	.053	.009
s.d. (ppm)	.022	.009	.012	.002	.033	.007
CV (%)	17.3	6.2	12.0	1.9	28.2	5.0
Location	S-16		S-17		CS-11	
n	4	4	4	5	4	4
x (ppm)	.102	.124	.098	.105	.065	.060
± 95% c.l.	.022	.018	.024	.004	.003	.024
s.d. (ppm)	.014	.011	.015	.003	.002	.015
CV (%)	13.7	8.9	15.3	2.8	3.1	25.0*
Location	CS-13		CS-14		CS-17	
n	4	5	4	5	4	5
x (ppm)	.063	.081	.074	.087	.065	.069
± 95% c.l.	.019	.020	.006	.011	.010	.024
s.d. (ppm)	.012	.016	.004	.009	.006	.019
CV (%)	19.0	19.8*	5.4	10.3*	9.2	27.5*
Location	CS-20		CS-23		CS-31	
n	4	4	4	5	4	5
x (ppm)	.026	.031	.042	.053	.033	.042
± 95% c.l.	.003	.011	.022	.005	.005	.004
s.d. (ppm)	.002	.007	.014	.004	.003	.003
CV (%)	7.7	22.6*	33.3	7.5	9.1	7.1

*Excluded from analysis of precision - see text, page 8.

Table 5. Field comparison of the performances of the LBL passive sampler and a reference pump/bubbler sampler. (cont.)

	Bubbler	Passive	Bubbler	Passive	Bubbler	Passive
Location	CS-34		CS-44		CS-49	
n	4	5	3	3	4	5
x (ppm)	.046	.042	.100	.117	.034	.043
± 95% c.l.	.002	.007	.027	.007	.002	.004
s.d. (ppm)	.001	.006	.011	.003	.002	.003
CV (%)	2.2	14.3*	11.0	2.6	5.9	7.0
Location	CS-62		O-2		44B-1	
n	4	5	4	5	4	5
x (ppm)	.026	.028	.072	.082	.049	.056
± 95% c.l.	.008	.002	.019	.006	.006	.007
s.d. (ppm)	.005	.002	.012	.005	.004	.006
CV (%)	19.2	7.1	16.7	6.1	8.2	10.7
Location	44B-2		44B-3		44B-4	
n	4	5	4	4	4	5
x (ppm)	.046	.052	.051	.060	.052	.055
± 95% c.l.	.006	.002	.010	.002	.010	.004
s.d. (ppm)	.004	.002	.006	.001	.006	.003
CV (%)	8.7	3.8	11.8	1.7	11.5	5.5

*Excluded from analysis of precision - see text, page 8.

Table 6. Pre-exposure storage stability (shelf life) of passive samplers.

Storage Time (wk)	HCHO Concentration (ppm)		Ratio Stored/Non-stored
	Stored Prior to Exposure* x ± s.d.	Exposed Immediately after Preparation+ x ± s.d.	
1	1.42 ± 0.07 (n=7)	1.40 ± 0.05 (n=4)	1.01
2	1.36 ± 0.01 (n=8)	1.33 ± 0.07 (n=4)	1.02

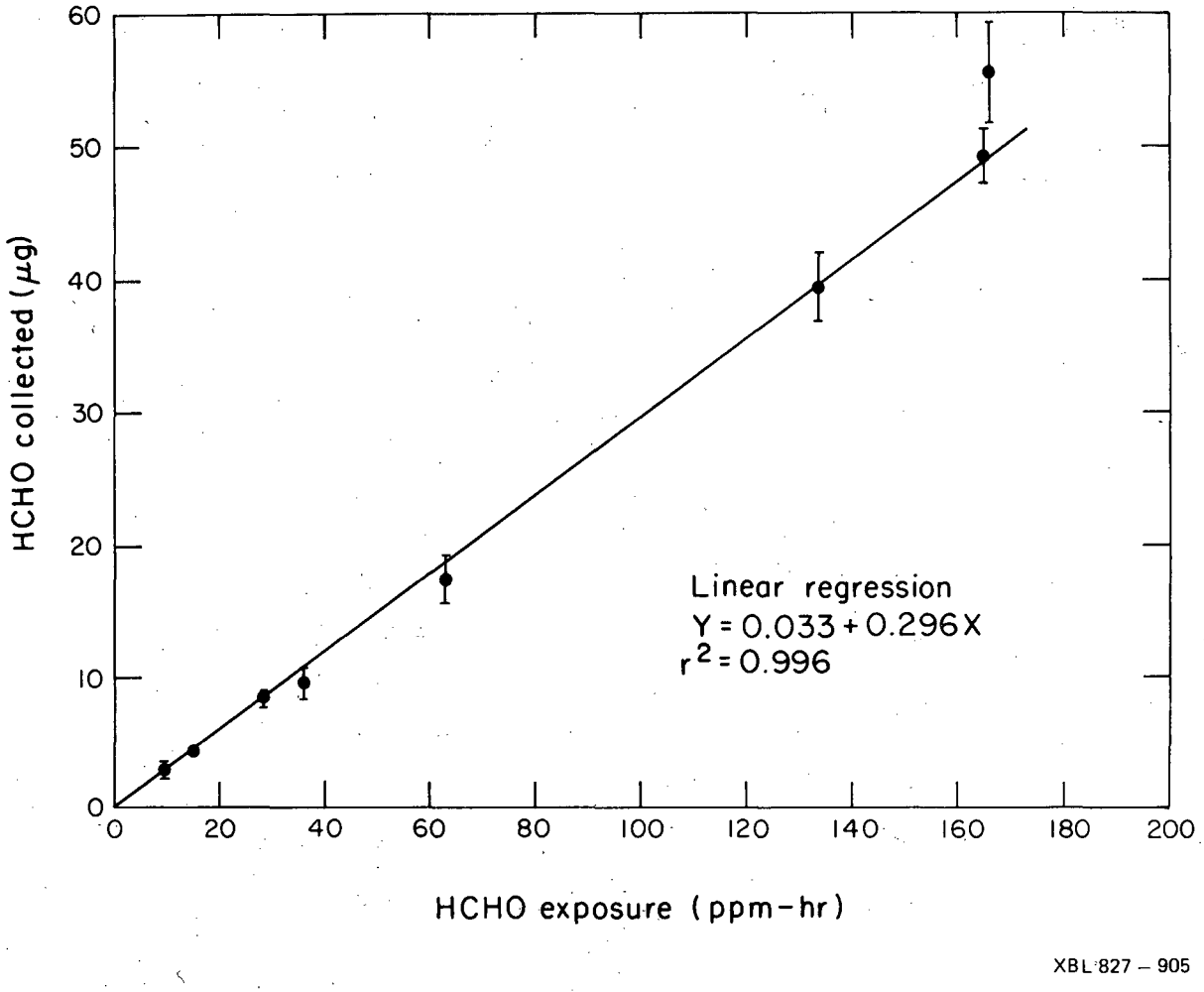
*Passive samplers were prepared, flushed with N_2, capped, and stored at room temperature before exposure to HCHO.

+Stored and non-stored samplers were exposed to the same test atmosphere.

Table 7. Post-exposure storage stability of passive samplers.

Storage Time (wk)	HCHO Concentration (ppm)		Ratio Stored/Non-stored
	Stored after Exposure* $\bar{x} \pm$ s.d.	Analyzed Immediately after Exposure $\bar{x} \pm$ s.d.	
1	1.24 ± 0.07 (n=7)	1.35 ± 0.09 (n=5)	0.92
2	1.41 ± 0.06 (n=8)	1.36 ± 0.02 (n=4)	1.04

*Passive samplers were stored at room temperature.



XBL 827 – 905

Figure 1 Mass of HCHO collected by the passive sampler versus HCHO exposure. Data are from Table 2.

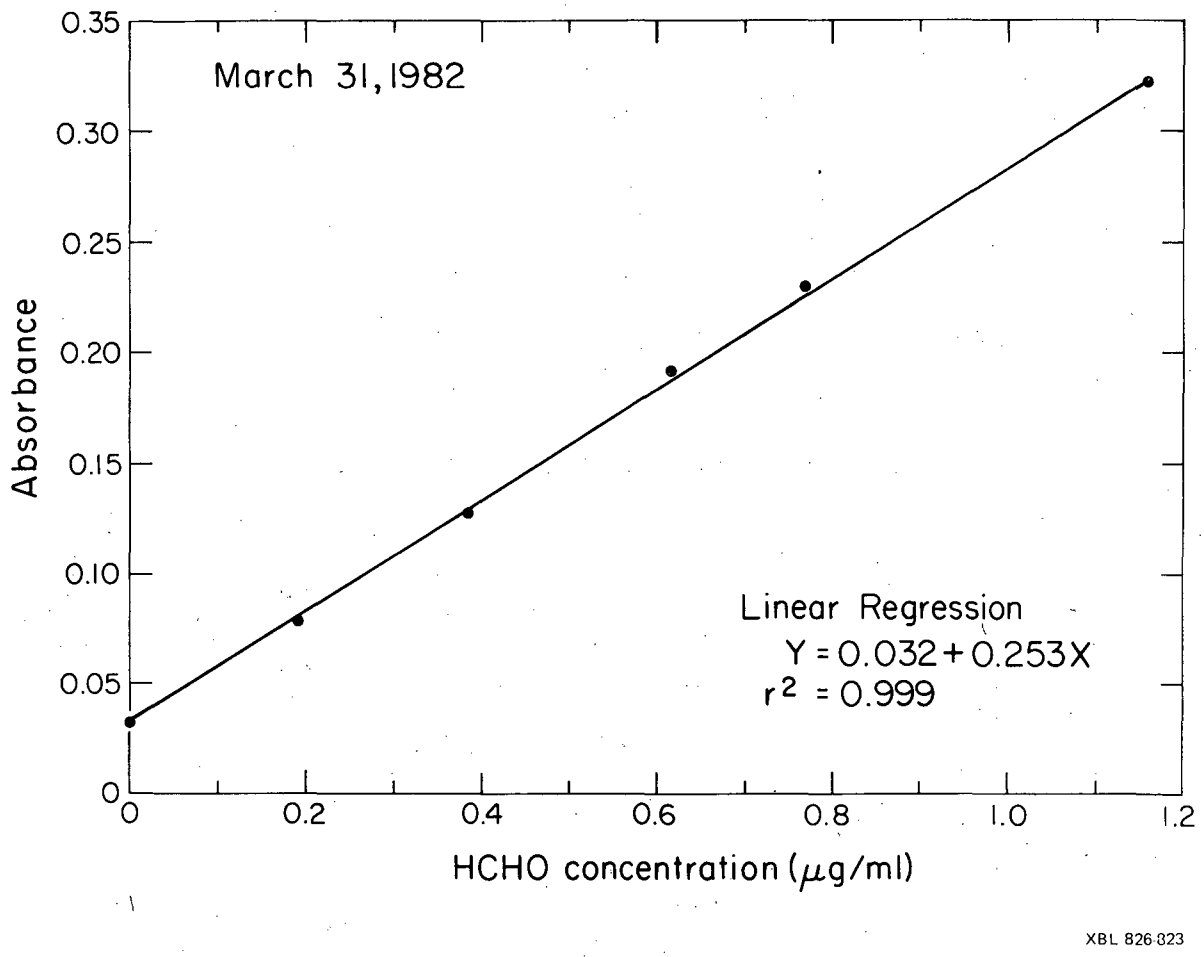


Figure 2 Calibration curve for chromotropic acid method of HCHO analysis. Absorbance versus concentration of aqueous standards.

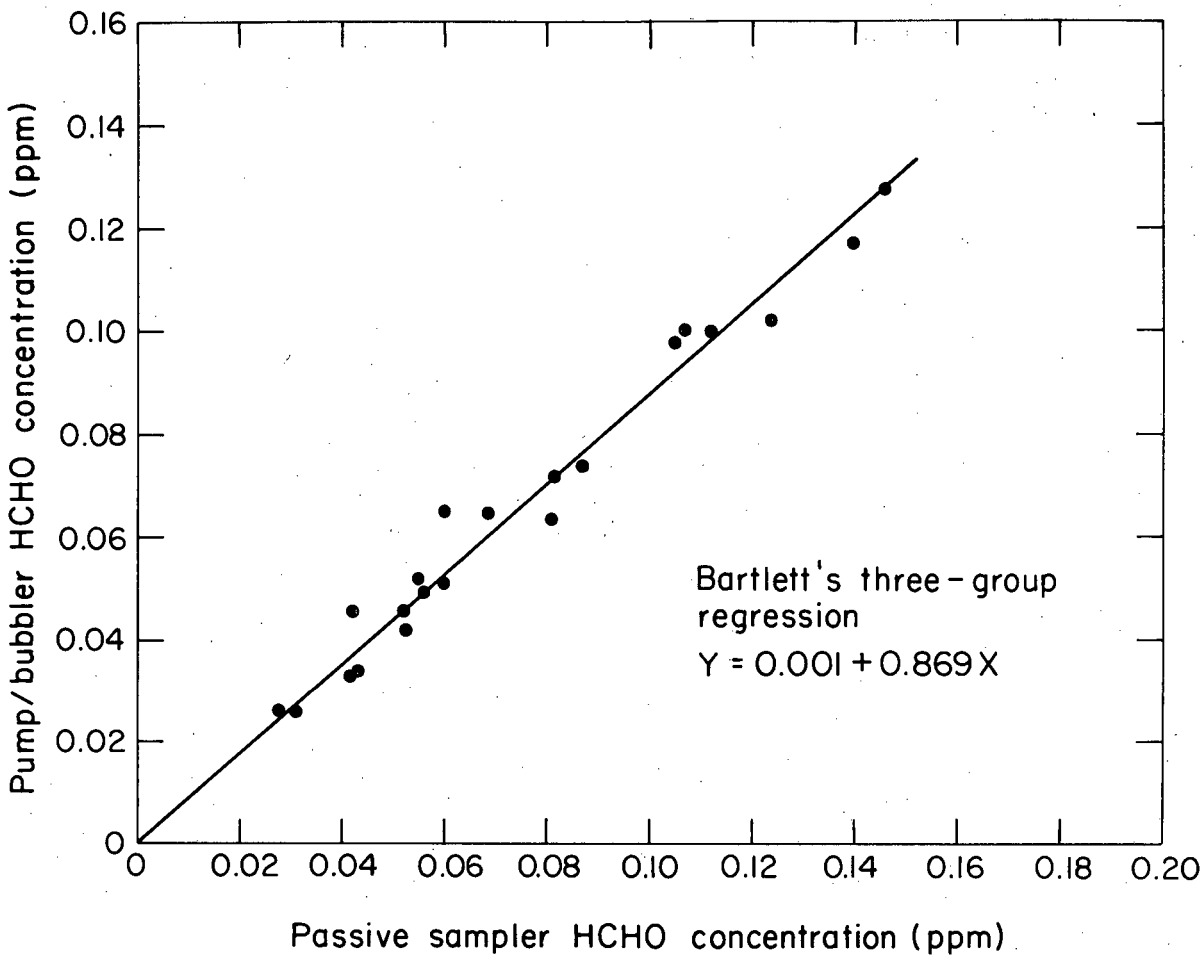


Figure 3 Passive sampler HCHO concentrations versus pump/bubbler sampler concentrations for 21 field comparisons.

TECHNICAL INFORMATION DEPARTMENT
LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIFORNIA 94720