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ABSTRACT

In this preliminary study, we report on improvements made to a passive sampler for water vapor and on the results of tests to determine its suitability for studies of indoor air quality. Tests completed demonstrated precision, accuracy, linear response with exposure, sensitivity and capacity sufficient for use in large scale studies to determine absolute humidities inexpensively.

INTRODUCTION

Studies of indoor humidity are important for several reasons. Damage to building materials and furnishings can result from high humidity, and occupant comfort and health are affected by humidity, both directly and indirectly. Factors producing indirect effects include changes in pollutant levels with changes in humidity (e.g., emission of formaldehyde from building materials and, possibly, decay of nitrogen dioxide) and in the number of micro-organisms (e.g., mold and dust mites) with changes in humidity. In addition, humidity is a potential interferent in some analytical methods used to study indoor air quality (Hodgson et al., 1984; Srivastava et al., 1984).

Instrumentation available to measure humidity generally falls into two categories. There are expensive, real-time instruments producing electrical signals in response to humidity, e.g., lithium choloride (LiCl) and chilled-mirror hygrometers. While they produce detailed information, the cost of the instruments and associated data loggers precludes large scale studies of many indoor environments. The second category of instruments includes inexpensive sling and fan psychrometers and hair hygrometers. These devices are typically read visually, limiting the amount of information obtainable per unit effort and increasing the cost of studies.

A passive sampler for water vapor, similar to passive samplers employed to measure pollutant concentrations, offers many advantages, making it an attractive choice for studies of absolute humidity. These advantages include low cost, ease of deployment, lack of field calibration and maintenance, ruggedness and unobtrusiveness. Palmes et al. have described two designs for water vapor passive samplers: one based upon the use of a diffusion tube and silica gel or concentrated sulfuric acid (Palmes et al., 1973); the other based upon the use of molecular sieve (Palmes et al., 1976). With both samplers, the weight gain of the sampler and the time of exposure were related to the water vapor concentration sampled. In this preliminary study, we report on improvements to the Palmes water vapor sampler using molecular sieve and on tests of its suitability for studies of indoor air quality. For convenience and because much is known about face velocity effects for the Palmes NO_2 sampler (Girman et al., 1984; Palmes et al., 1976), we used, to the extent possible, the same sampler components and configuration as those used in the Palmes NO_2 passive sampler.

Theoretical Background

If a passive sampler contains a 100%-efficient sorbent for water vapor at the closed end of a diffusion tube, Fick's First Law of Diffusion can be solved for the sampler to obtain the following expression:

$$M = D \cdot A \cdot L^{-1} \cdot t \cdot C \qquad (1)$$

where: M = mass of water collected (mg),
D = diffusion coefficient of water vapor in air (cm^2 s^{-1}),
A = cross sectional area of the diffusion tube (cm^2),
L = length of diffusion tube (cm),
t = duration of exposure (s),
C = concentration of water vapor (mg cm^{-3}).

From the Kinetic Theory of Gases, D, equalling 0.239 cm^2 s^{-1} at 8°C (Weast, 1969a), is a function of the absolute temperature to the 3/2 power. Therefore, a value of 0.256 cm^2 s^{-1} at 21°C is substituted for D in the above expression. For the sampler, A is 0.71 cm^2, and L is 7.1 cm, yielding:

$$M(\mathrm{mg}) = 92.16\ (\mathrm{cm^3\ h^{-1}}) \cdot C(\mathrm{mg\ cm^{-3}}) \qquad (2)$$

The concentration, C, can be converted to the more familiar ratio, weight of water vapor to weight of air, by using the density of dry air at 21°C and one atmosphere, 1.201 mg cm^{-3} (Weast, 1969b), obtaining an expression relating the weight gain of sampler to the duration of sampling and the absolute humidity of the sampled atmosphere:

$$M(\mathrm{mg}) = 110.6(\mathrm{mg\ h^{-1}}) \cdot t(\mathrm{h}) \cdot C(\mathrm{g\ water} \cdot \mathrm{g^{-1}air}) \qquad (3)$$

Obviously the atmosphere sampled is not composed of dry air and the density should reflect this. However, over the typical range of humidities encountered, this causes an error of less than 2%.

EXPERIMENTAL

Sampler Preparation & Analysis

The samplers were prepared as described by Palmes et al. (1976), with one exception: a cloth disk was inserted between the stainless-steel screen and the molecular sieve to prevent (1) loss of fine particles of sieve or (2) coating of the diffusion tube interior with fine particles of sieve. Figure 1 illustrates the design of the sampler. The sampler tested in this study employed a methacrylic diffusion tube. Molecular sieve (4A, 1/16 inch pellets, Linde Division, Union Carbide), is baked in either a vacuum oven for over 35 hours at 280°C or a muffle furnace for 16 hours at 375°C prior to use. (No significant difference between weight gains of samplers prepared with 3A and 4A molecular sieve has been detected, although samplers prepared from 4A have marginally better precision.) Between 1.7 to 2.0 g of dried sieve are placed in the bottom of a plastic cap (RCL-5, Caplugs Division, Protective Closures, Co., Buffalo, NY), and the cloth disk (50% polyester, 50% cotton) is placed on top of the sieve followed by the stainless-steel screen (Code ZWX, Newark Wire Cloth Co., Newark, NJ). Methacrylic tubes (3/8 inch ID, Tube

Sales, Cranbury, NJ) are cut and milled so that the cross sectional area-to-length ratio equals 0.100 cm. The removable plastic cap (EC-8, Caplugs Division, Protective Closures Co., Buffalo, NY) and the diffusion tube for a specific sampler are both scribed with the same number so that the two are always weighed together. After preparation, samplers are wiped clean with tissue paper and the individual samplers are weighed to the nearest 0.1 mg. (The overall weight of a sampler is less than 10 g.) Samplers are exposed to the sampled atmosphere by removing the plastic end cap for a measured length of time. For analysis, the samplers are again wiped clean with tissue paper and weighed to the nearest 0.1 mg.

Linearity, Precision & Accuracy Experiment

In a nine-day experiment, seventy-two samplers were exposed to ambient conditions in one of our laboratories while continuously recording ambient temperature and dew point temperature with a LiCl hygrometer (YSI Model 91). Spot checks of humidity were made with fan and sling psychrometers. Atmospheric pressure was monitored in a nearby laboratory. After 1, 3, 5, 7 or 9 days of exposure to humidities near 45% RH and temperatures near 21°C, 13 to 15 samplers were capped and their weight gains were determined. Five blanks (unexposed samplers) were given identical treatment except they were not uncapped.

Capacity Experiment

As a check of the capacity of the samplers, eight uncapped samplers were suspended in a sealed 500 ml glass vessel containing 35 ml of water in a watch glass. All samplers were weighted periodically to determine weight gain versus days of exposure near 100% RH at room temperature.

Blanks Experiment

To determine the cause of weight gain of blank samplers, capped samplers and individual sampler components were suspended in a sealed glass vessel containing either a Petri dish filled with water or silica gel dessicant. In the case of capped samplers, vacuum grease was applied to various surfaces of the plastic caps and seals to eliminate potential leaks. The weight gain or weight loss of samplers and sampler components with time was monitored.

RESULTS & DISCUSSION

Instantaneous hourly dew point temperatures measured by the LiCl hygrometer in the first experiment were converted to water vapor partial pressures and the partial pressures were averaged over intervals corresponding to sampler exposures.

The density of the dry air, calculated by inserting the average temperature and pressure during the appropriate intervals into the Ideal Gas Law, was used to convert vapor pressures to time-weighted average absolute humidities. Sampler exposures were calculated by multiplying the sampler exposure time by the appropriate absolute humidity.

During the course of the experiment, sampler blanks also gained weight with exposure. While the weight gain was much less than that of the uncapped samplers, it was nonetheless significant, averaging approximately 5 mg over nine days. Because of this, weight gains of the samplers were corrected by subtracting blank weight gains proportional to exposure.

The results of this nine-day experiment are illustrated in Figure 2, a plot of the sampler weight gain versus water vapor exposure. Because no systematic difference was evident when comparing weight gains of samplers prepared from sieve dried in the muffle furnace and those from sieve dried in the vacuum oven, weights from both types of samplers were averaged. The points correspond to 0, 24, 72, 120, 168 and 216 hours of exposure to an atmosphere with an average temperature of 21°C and an average absolute humidity of 0.0071 g water g^{-1} air (near 45% RH) over the nine-day period. The weight gain (minus blank weight gain) was 18.4 mg after 24 hours and 125.7 mg after 168 hours. The average precision was 3% with a worst case precision of 6% for the 72-hour exposure. While the results shown in Figure 2 exhibit some curvature, the weight gain is reasonably linear with exposures as shown by a linear regression giving the result

$$M(\mathrm{mg}) = 99.6(\mathrm{mg\ h^{-1}}) \cdot t(\mathrm{h}) \cdot C(\mathrm{g\ water} \cdot \mathrm{g^{-1}\ air}) + 2.7\ \mathrm{mg} \qquad (4)$$

with $R^2 = 0.998$. (The non-zero intercept is caused by the forced linearization.) The theoretical results based upon Equation 3 are also illustrated in Figure 2. Over the range of exposures for which the sampler was tested, the weight gains calculated from the Equation 4 differ from theoretical gains calculated from Equation 3 by less than 10%. The reference hygrometer used for comparison, which was not calibrated, has a manufacturer-rated accuracy of approximately 10% over the range of humidity measured. Spot psychrometer measurements supported this accuracy rating.

The results of the capacity experiment are illustrated in Figure 3. The dashed line represents the experimentally-derived regression line (Equation 4). The plot of results exhibits curvature caused by the decrease in sampling rate as the molecular sieve becomes saturated with water vapor and the diffusive path length increases. However, after seven days exposure to nearly 100% RH at room temperature, the weight gain of the sampler deviates by only 7% from the expected weight gain. While days-of-exposure is only a crude estimate of actual exposure, the results indicate that the capacity of the sampler is adequate for sampling times up to seven days.

Surprisingly, the major cause of the weight gain of blanks was not poor seals or permeation through the plastic caps but, rather, the weight gain of methacrylic tubing. Attempts to dessicate capped samplers or even the methacrylic tube to a reproducible dry weight failed. We are currently testing, with good results, samplers constructed from aluminum tubing dimensionally identical to the methacrylic tubes. Aluminum tubing has several advantages: lower material cost; greater durability; and greater dimensional stability. Moreover, the overall weight (less than 15 g) of samplers with aluminum is not appreciably greater than samplers constructed with methacrylic tubes.

Interferents were not tested. With one exception, indoor air contaminants that are trapped by molecular sieve are unlikely to be present in concentrations sufficiently high to produce measurable weight gain. The exception is carbon dioxide. As shown by Figure 4, under conditions of low humidity and high carbon dioxide concentrations, errors could be large if carbon dioxide is adsorbed by molecular sieve with high efficiency. If deployed under these conditions, a correction for the weight gain due to carbon dioxide must be applied.

CONCLUSIONS

We have improved the water vapor sampler initially designed by Palmes et al. (1976), and have conducted preliminary tests demonstrating the potential of the sampler to be a useful device for inexpensively obtaining time-weighted average absolute humidity with sufficient sensitivity for sampling periods as long as one week. Tests completed to date have also demonstrated good linearity, precision, and accuracy. Additional tests, currently under way, should result in the complete characterization of the sampler, making possible relatively inexpensive, large scale studies of absolute humidity in selected environments. Such a sampler could also be used to identify environments which warrant detailed study or could be used to measure humidity as a surrogate for other pollutants or micro-organisms.

ACKNOWLEDGEMENT

We would like to acknowledge the encouragement of Howard Ross. This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Building Energy Research and Development, Building Systems Division of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098. The mention of trade names, commercial products or organizations does not imply endorsement.

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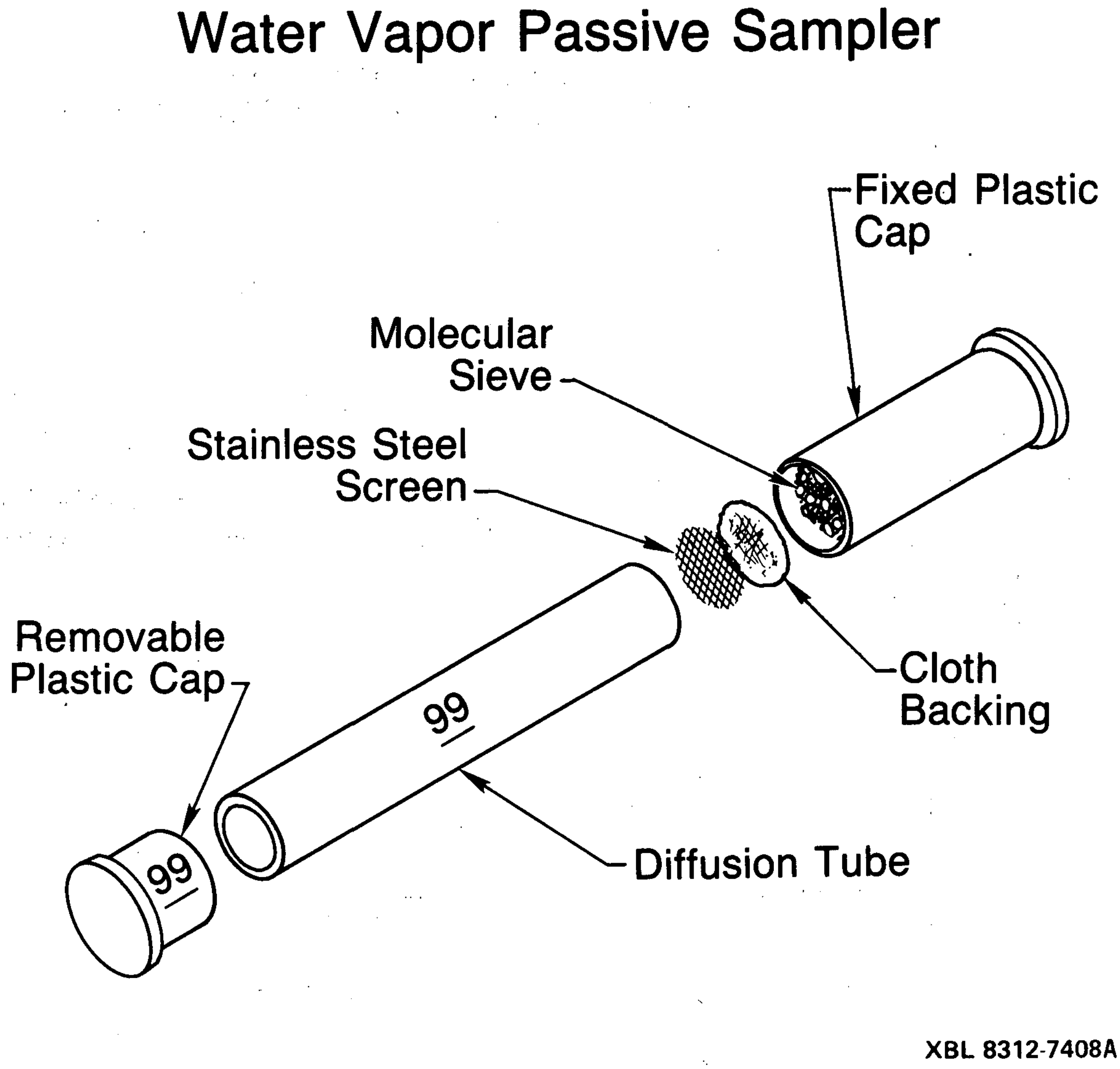

Figure 1. Exploded view of a passive sampler for water vapor.

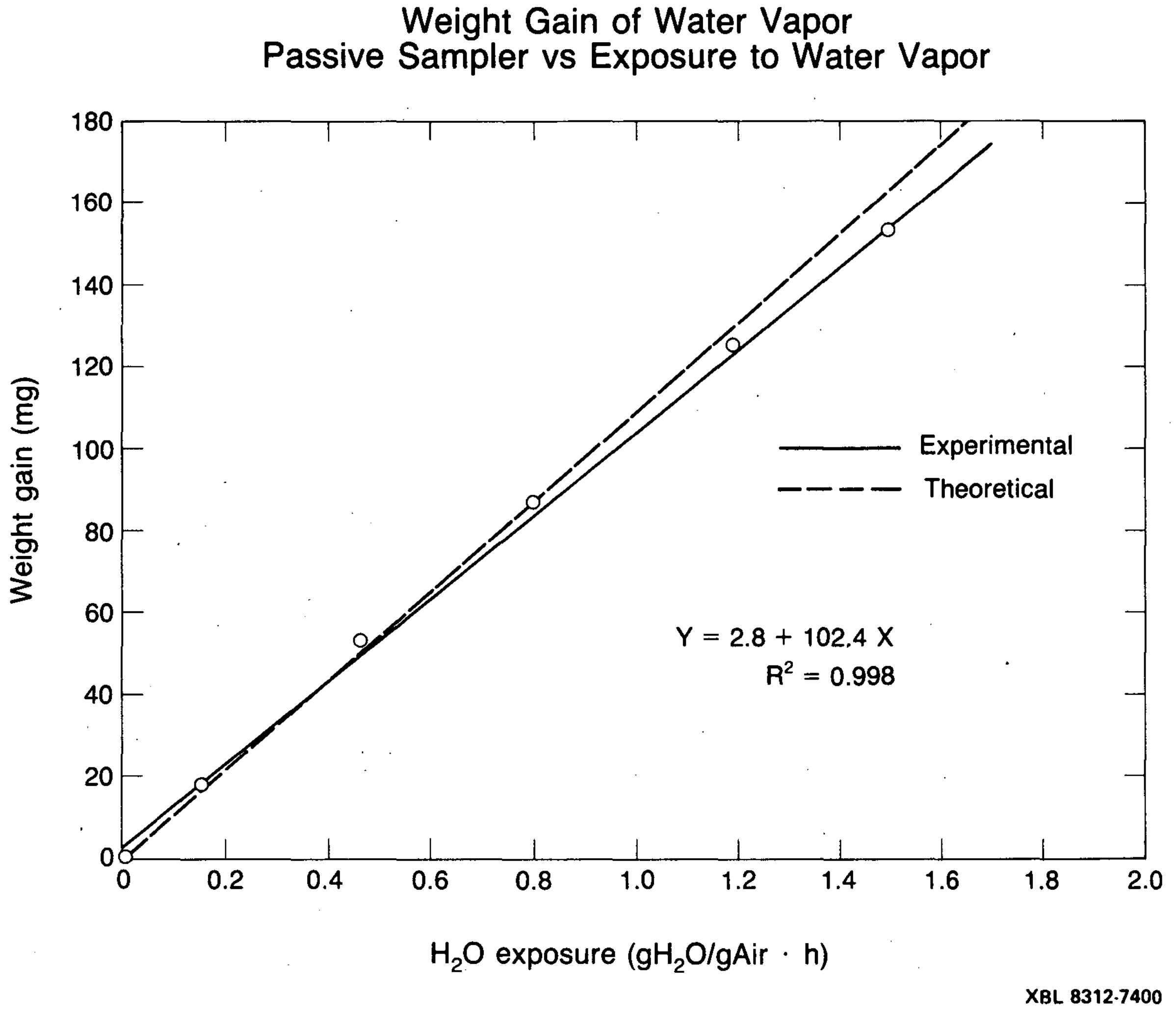

Figure 2. Weight gain of a passive sampler for water vapor versus exposure to an atmosphere near 45% RH at 21°C. Points represent 0-, 1-, 3-, 5-, 7- and 9 days exposure.

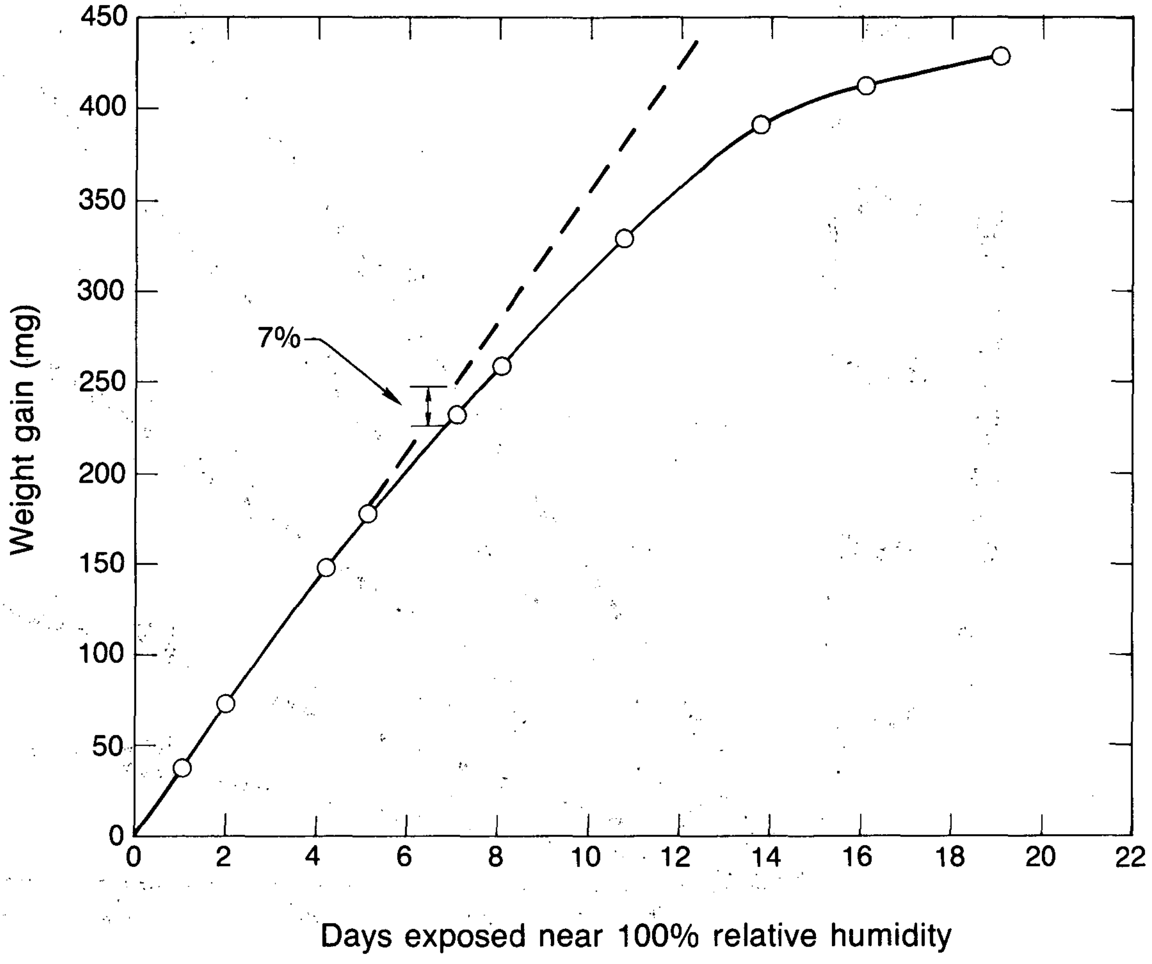

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Figure 3. Weight gain of a passive sampler for water vapor versus days of exposure to an atmosphere near 100% RH at room temperature. Solid line illustrates departure from linearity as the capacity of the sampler is exceeded.

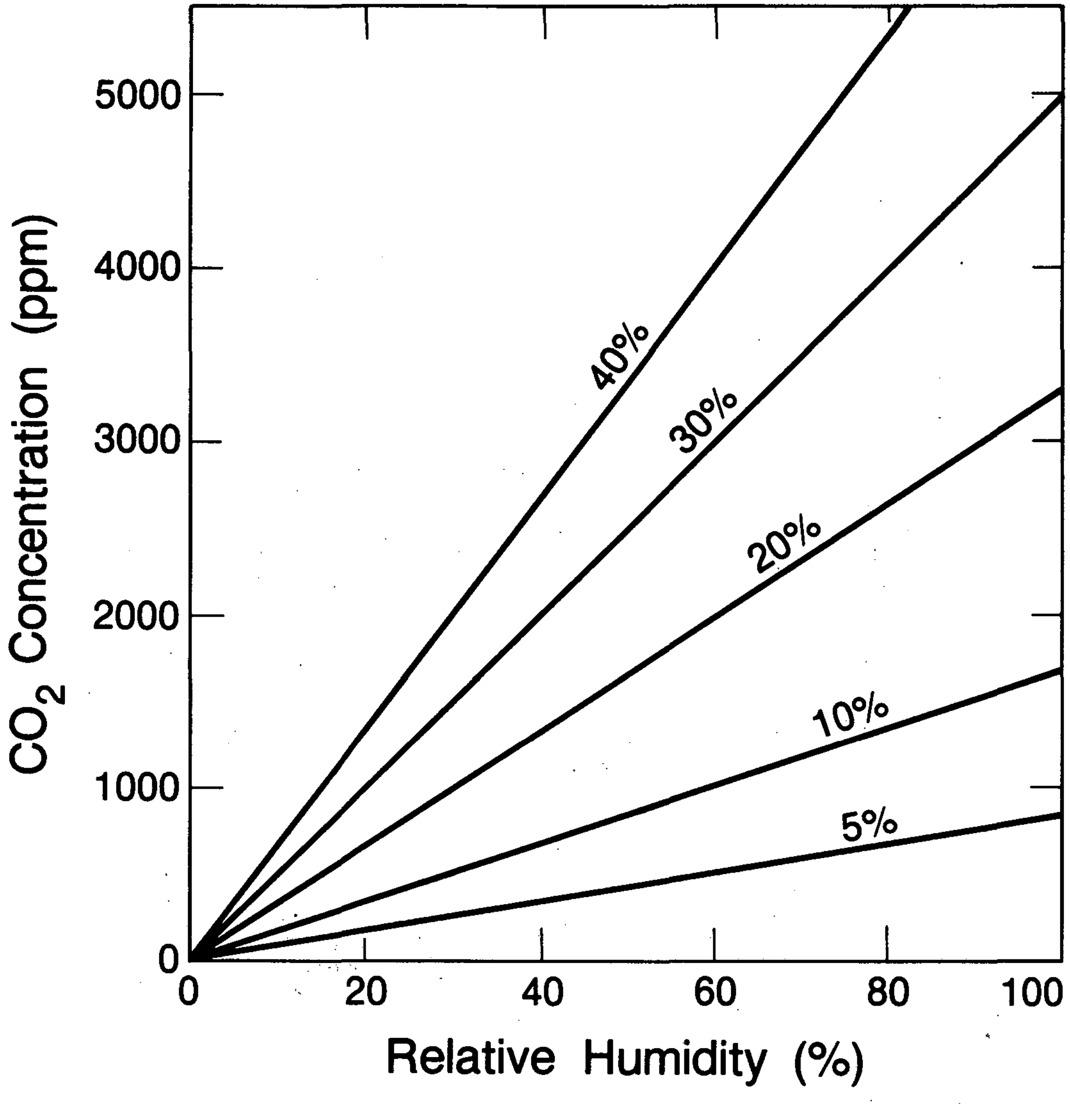

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Figure 4. Percent error of a water vapor passive sampler exposed to a range of carbon dioxide atmospheres and relative humidities at 21°C.