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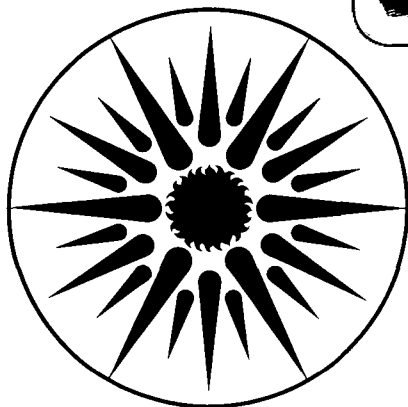
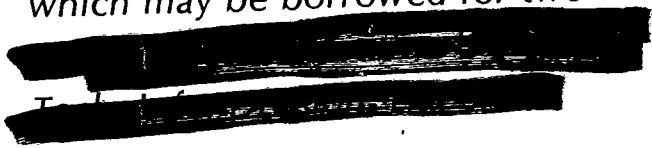
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LABORATORY STUDIES OF THE TEMPERATURE DEPENDENCE  
OF THE PALMES NO<sub>2</sub> PASSIVE SAMPLER

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## ABSTRACT

Passive samplers for air pollution measurement have been used in a variety of applications, e.g., the assessment of personal exposures to pollutants, the determination of area concentrations, and the comparison of indoor and outdoor pollutant concentrations. In some of these applications, samplers have been used under conditions for which they have been inadequately tested. Diffusion theory predicts only a 1.7% change in the sampling rate with a 10°C change in temperature at 21°C; however, triethanolamine, the NO<sub>2</sub> absorbent employed in the Palmes NO<sub>2</sub> sampler, has a liquid-solid phase transition at 21°C. Because this phase change occurs at a typical ambient temperature, the effect of temperature upon the performance of the sampler was investigated. During this investigation, the NO<sub>2</sub> concentration, exposure time, and face velocity were held constant while the temperature of the sampled air was varied from 7°C to 38°C. The collection efficiency of the Palmes NO<sub>2</sub> passive sampler was found to decrease by 15% when the temperature decreased from 27°C to 15°C. This study illustrates the need for careful evaluations of passive samplers under controlled conditions that closely approximate actual use conditions.

Keywords: air velocity, collection efficiency, face velocity, NO<sub>2</sub>, passive sampler, sampler starvation, temperature dependence.

## INTRODUCTION

The use of passive samplers for air pollution measurements has become widespread. Passive samplers have been used in a variety of applications, e.g., the assessment of personal exposures to pollutants (1), the determination of area concentrations (2) and the comparison of indoor and outdoor pollutant concentrations (3). In some of these applications, passive samplers have been used under conditions for which they have been inadequately tested.

The Building Ventilation and Indoor Air Quality Group at Lawrence Berkeley Laboratory has used an instrumented mobile laboratory (4), to study indoor air pollution in a variety of residences (3,5-9). These studies provided the opportunity to compare, under field conditions, the performance of the Palmes NO<sub>2</sub> passive sampler (10) with that of an accepted reference method, a chemiluminescent, continuous NO<sub>2</sub> analyzer. One anomaly became apparent during this comparison: agreement was better between the two methods for indoor measurements than for outdoor measurements. One obvious difference between indoor and outdoor conditions was the temperature at which the measurements were taken.

From diffusion theory, we know that temperature effects the sampling rate of a passive sampler. Because diffusion theory predicts only a 1.7% change in the sampling rate with a 10 °C change in temperature at 21 °C (10), temperature corrections have generally been ignored. However, the NO<sub>2</sub> absorbent employed in the sampler, triethanolamine (TEA), has a liquid-solid phase transition at 21 °C (11). Because this phase change occurs at a typical ambient temperature, the effect of temperature on the performance of the NO<sub>2</sub> passive sampler was investigated. We

anticipated one of two possible effects: constant collection efficiencies if the TEA phases have the same response to  $\text{NO}_2$ ; or a step function centered at  $21^\circ\text{C}$ , if their responses differ.

## EXPERIMENTAL

The passive sampler test facility employed in these studies is shown schematically in Figure 1. This facility allows for rapid set-up of a wide range of experimental conditions. The gas streams are temperature-preconditioned before entry into either of two temperature-controlled exposure chambers, each of which can hold up to 16 passive samplers. Extensive microprocessor control extends flexibility and allows automatic data logging.

For the temperature dependence tests, experimental conditions were as follows:  $\text{NO}_2$  concentrations were either 0.301 ppm or 0.349 ppm at 2 Lpm depending on which of two  $\text{NO}_2$  permeation tubes were used; face velocity was 0.25 cm/s; relative humidity was less than 20%; exposure time was 24 h; and temperature was varied from 7 to  $38^\circ\text{C}$ .

For each series of tests, a lot of samplers was prepared. Groups of 16 samplers were exposed to the  $\text{NO}_2$  test atmosphere at different temperatures until all samplers from a lot were exposed. All samplers from a lot were analyzed together.

For reasons explained below, an additional test to determine the effect of face velocity was conducted under the following conditions:  $\text{NO}_2$  concentration was 0.151 ppm; relative humidity was less than 20%; exposure time was 48 h; temperature was  $21^\circ\text{C}$ ; and flow rate through the chamber was varied from 0.25 to 4.5 Lpm to produce apparent linear face

velocities from 0.03 to 0.6 cm/s. Calculated velocities were confirmed by visually timing the progress of injections of "smoke" from Draeger smokesticks. When velocities were below 0.1 cm/s, the flow was well described as plug flow; when velocities were greater than 0.1 cm/s, there was some turbulence and a correspondingly greater uncertainty in face velocities.

## RESULTS AND DISCUSSION

The results of the temperature dependence study are illustrated in Figure 2. Each data point represents the mean value of 14 to 16 samplers with a relative standard deviation of the mean of approximately 1%. Each symbol type represents a different lot of samplers with the exception of the open circles and triangles which represent samplers from the same lot. All collection efficiencies were corrected for the temperature effect calculated from diffusion theory.

The NO<sub>2</sub> passive samplers have a storage stability of several months. Nevertheless, we were concerned that differences in the pre-exposure or post-exposure storage time (a single series of tests lasted up to twelve days) could introduce a small systematic bias which might diminish our ability to detect temperature effects.

To check for this bias, 16 samplers from a lot, represented by the open triangles in Figure 2, were exposed at successive temperatures from 7 °C to 38 °C. Next, 16 samplers from the same lot, represented by open circles, were exposed to successively decreasing temperatures from 38 °C to 7 °C. This same ordering was maintained during analysis. As is evident in Figure 2, no bias with respect to order of either exposure or



analysis was found.

While the data shows some scatter and some minor variation among sampler lots, the collection efficiency is fairly constant below 15 °C, averaging 82%, and then gradually rises to approximately 96% at temperatures above 27 °C. The overall change in collection efficiency from 15 to 27 °C is approximately 15% or 1% per degree C.

The temperature response occurred gradually over a larger temperature range than anticipated. TEA as actually used in the sampler, i.e., contaminated with residual acetone used as a solvent in sampler preparation, was found to melt over a wide range, 16 to 21 °C. This may, in part, account for the range of the sampler's temperature response. However, since TEA is hygroscopic, in humid atmospheres the liquid range of TEA may be extended, diminishing any temperature effects.

(The cause of the variation in collection efficiency with phase is unknown. If it is due to the kinetics of absorption, the possibility exists that the sampling rate is concentration dependent at low temperatures.)

The measured collection efficiency at 21 °C, 87%, is lower than the efficiencies, 92 to 95%, reported or calculated from data in other reports (12-14). Since precision in our study was typically better than 1%, possible systematic causes for the discrepancy in collection efficiency were examined. The mass-flow controlled, permeation tube oven which serves as the NO<sub>2</sub> source was calibrated by an independent laboratory; the measured NO<sub>2</sub> permeation rate agreed with the manufacturer's rate to within 1%. Sampler preparation was checked by preparing and

sending samplers to researchers at the Agricultural University, Wageningen, the Netherlands. They exposed our samplers simultaneously with samplers they had prepared. Agreement was better than 4% between the two sets of samplers (15). Using our facility, we exposed samplers prepared by Columbia University and then returned half of the samplers to them for analysis. Collection efficiency of these samplers was 88% (16).

Having eliminated the  $\text{NO}_2$  source, sampler preparation and analysis as causes of the discrepancy, we next examined the effect of low face velocities. When face velocities are low, convective transport in the volume just external to the sampler opening is no longer very large with respect to diffusive transport. In effect the concentration in this volume becomes depleted of the pollutant being sampled and is no longer representative of the larger volume to be characterized. This condition, sampler starvation, was examined theoretically by Tompkins and Goldsmith (17).

The results of our preliminary study of the effects of low face velocity are illustrated in Figure 3. Each of the four points represents the mean of 16 samplers. The solid line is the solution of the Tompkins and Goldsmith equation for the  $\text{NO}_2$  passive sampler. While the results do not definitively prove the theory, they tend to support it, especially for plug flow conditions.

Because adequate instrumentation for measuring low air velocities is presently lacking, these velocities in residences are not well known. However, typical air velocities in residences are expected to be smaller than velocities encountered in industrial or outdoor environments. Air velocities were measured in 20 houses by Oak Ridge National Laboratory

(18). All houses were closed and the air conditioner fans were turned on to circulate air without cooling. Measurements were made by timing the movement of puffs of "smoke" from Draeger smokesticks. Most velocities were between 5 and 10 cm/s, though extremes of 1 cm/s and 20 cm/s were not infrequent. Since these measurements were made with mechanical fans circulating the air, it is possible that even lower air velocities often occur in house interiors.

Using Tompkins and Goldsmith's equation, correction for the theoretical sampling efficiencies caused by the low face velocities can be applied to the results of the temperature dependence study to obtain the results shown in Figure 4. When this correction is applied, the collection efficiency at 21 °C is 95%, in agreement with results of other researchers. At temperatures about 27 °C, the collection efficiency is greater than 100%. Possible causes of this could include the uncertainty in the theoretically-derived diffusion coefficient of NO<sub>2</sub> in air used to calculate the sampling rate (10) or a systematic bias of the experiment.

## CONCLUSIONS

This study illustrates that even simple devices such as passive samplers have the potential for error if not adequately evaluated for actual use conditions. We have measured a temperature dependence of the Palmes NO<sub>2</sub> passive sampler of 1% per °C over the temperature range of 15 to 27 °C. The overall variation of 15% is not large for a device with an accuracy of approximately 10%. However depending upon the resolution of the study, corrections for the variation with respect to temperature should be taken into account when comparing indoor and outdoor NO<sub>2</sub>

concentrations and, in certain cases, when comparing concentrations in different rooms of the same house, since e.g., bedrooms and kitchens are often at different temperatures. Because people have elevated surface temperatures relative to their surroundings, temperature corrections may also be warranted in comparisons of personal and area concentrations.

One factor for which we cannot establish appropriate test conditions is face velocity. At present we do not know the range of typical air velocities in residential environments. Without this knowledge the potential exists for deploying passive samplers, especially industrial hygiene samplers with high sampling rates, under conditions where sampler starvation can occur.

#### ACKNOWLEDGEMENTS

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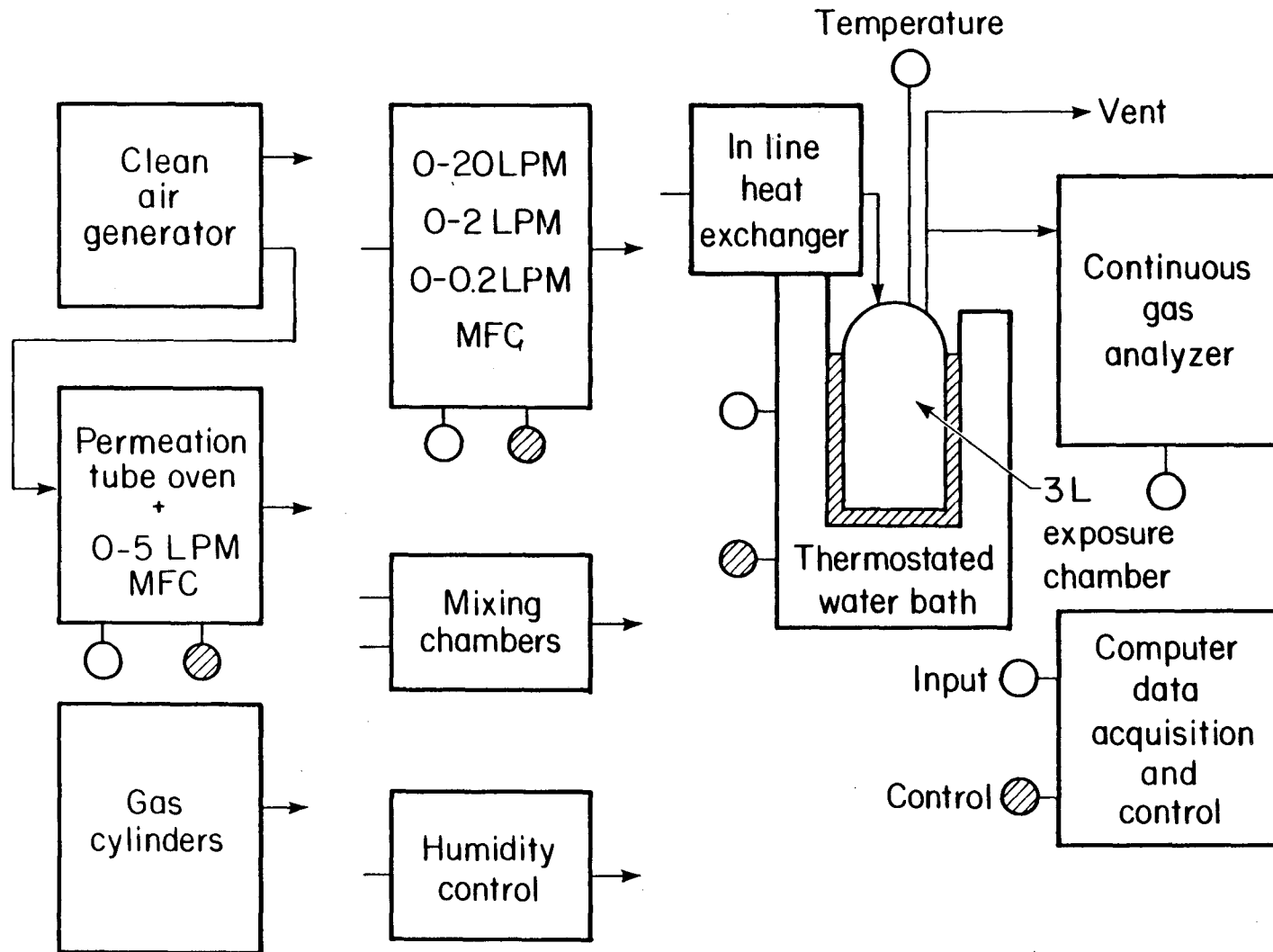
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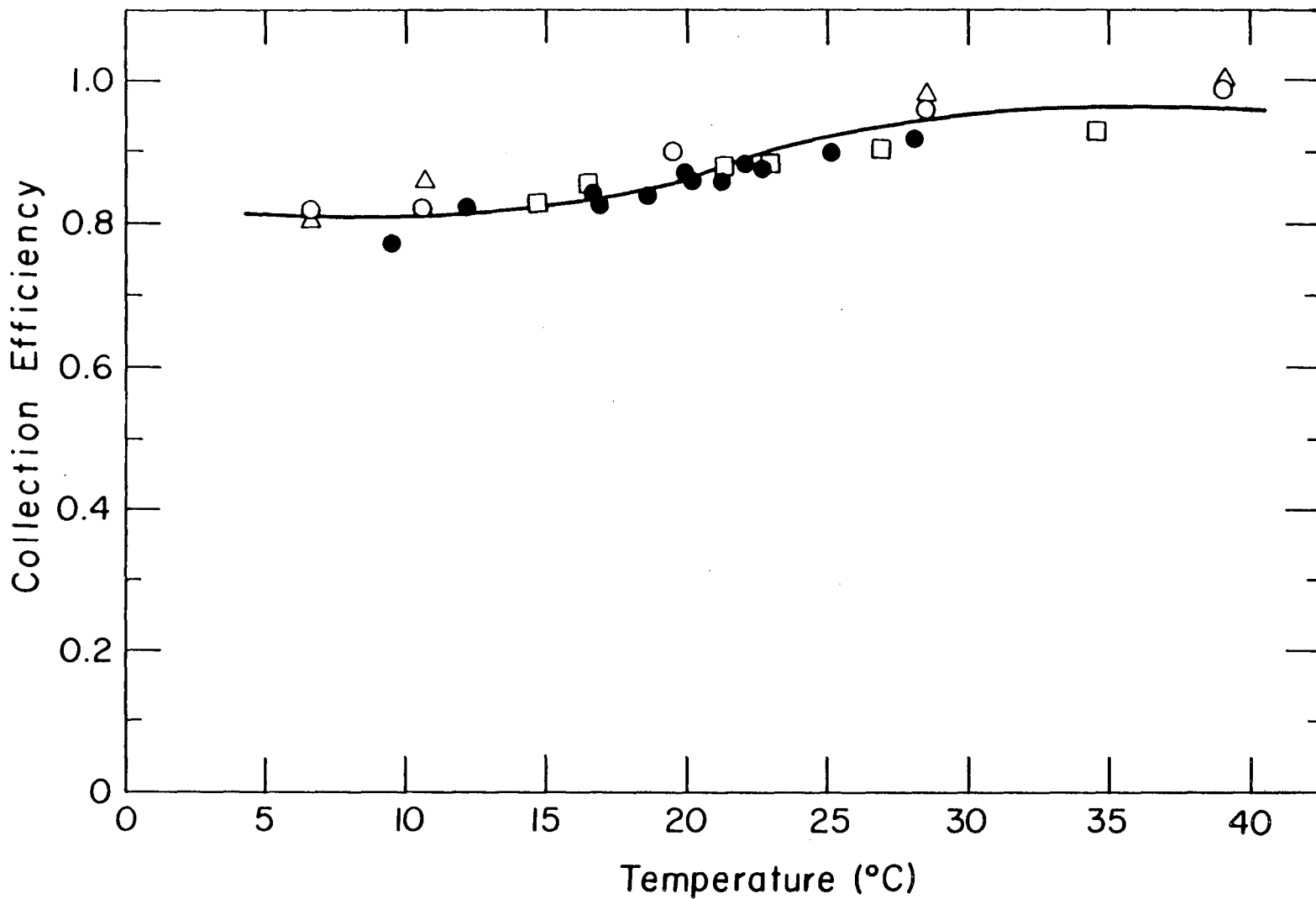
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XBL 834-1567

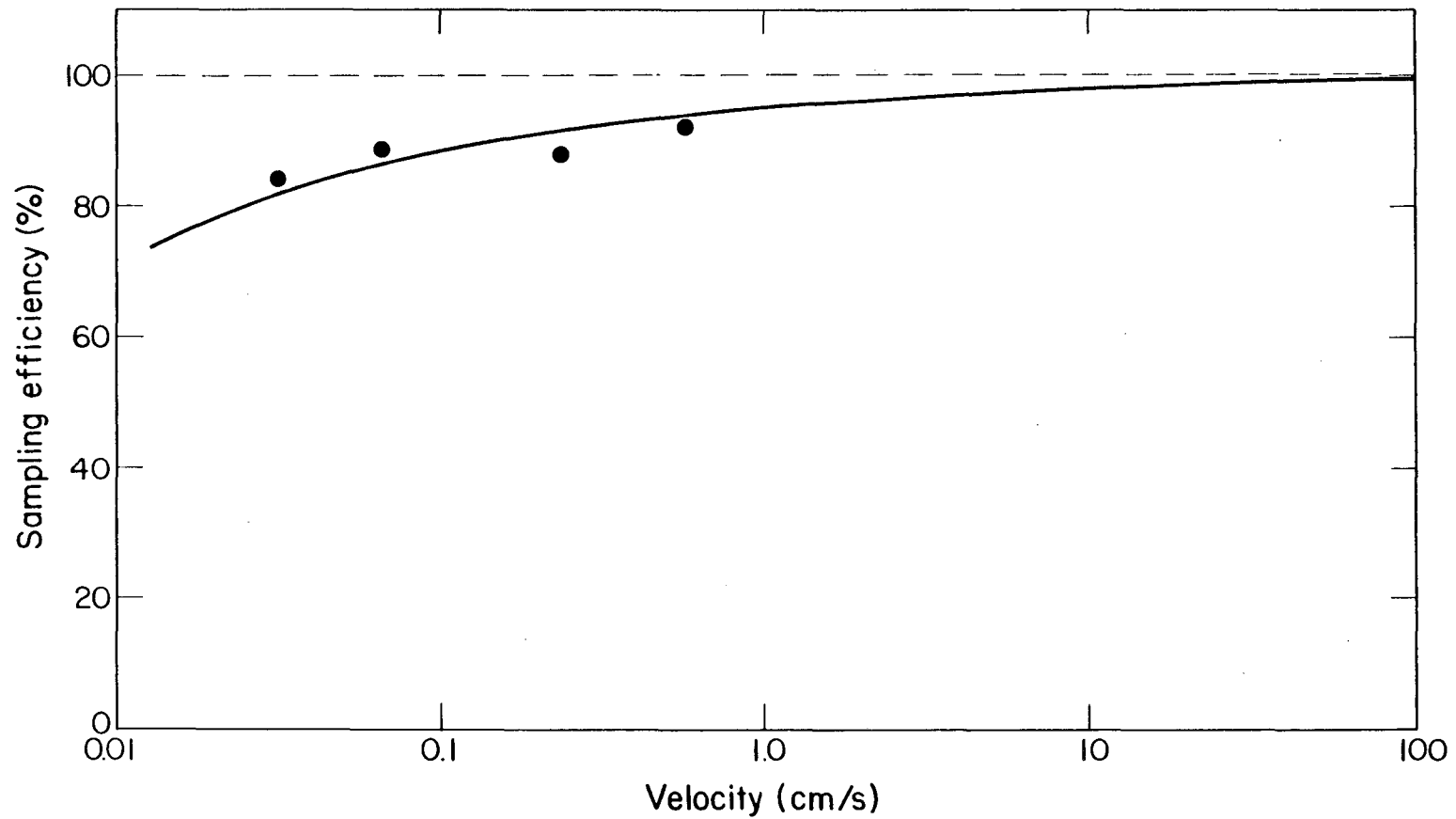
Figure 1. The passive sampler test facility is composed of modular components which are connected with teflon tubing and quick disconnect couplings.





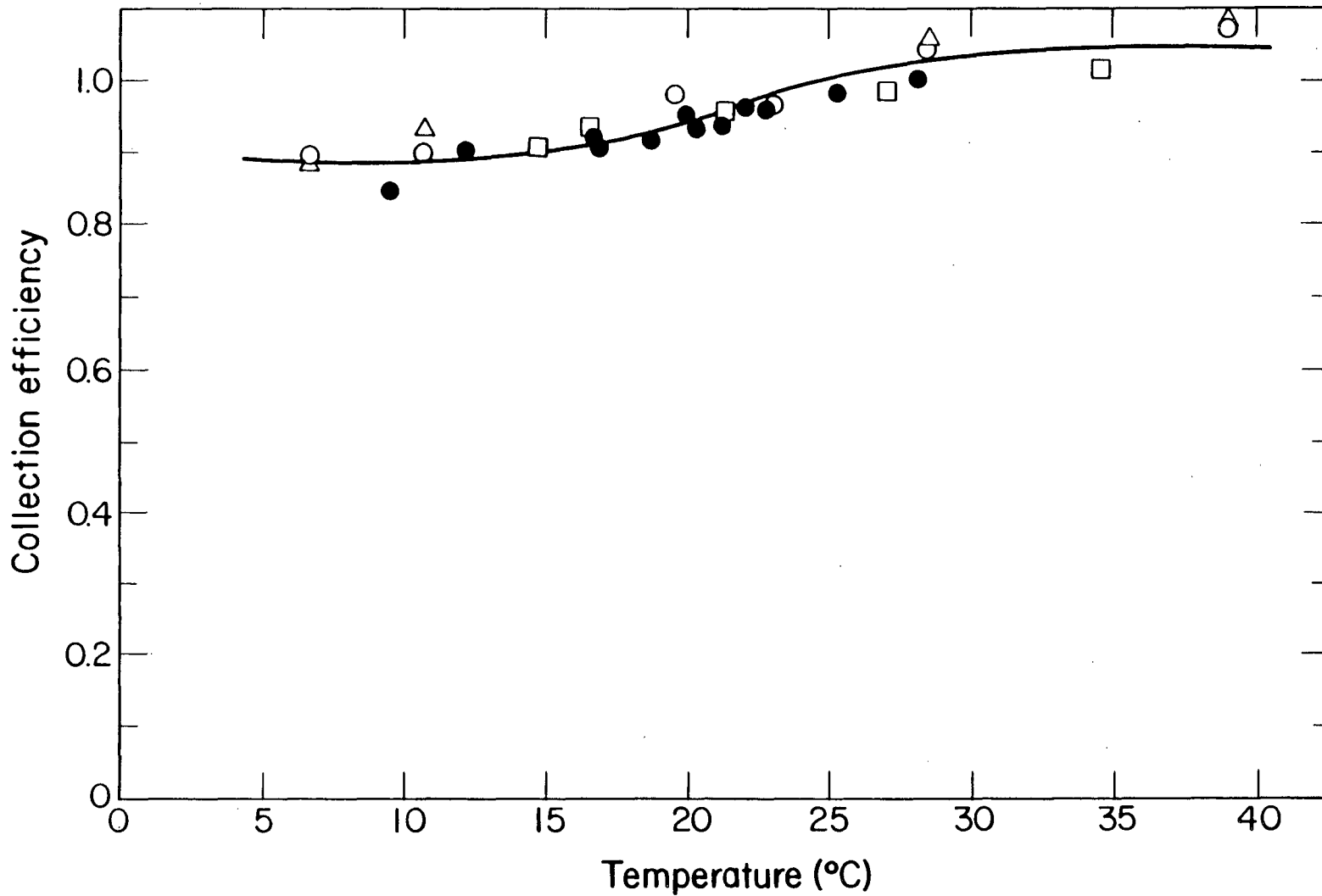
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Figure 2. Measured collection efficiencies of the Palmes NO<sub>2</sub> passive sampler versus temperature. Efficiencies are corrected for theoretical temperature dependence. See text for explanation of symbols and experimental conditions.



XBL 834-1569

Figure 3. Theoretical and measured sampling efficiency of the Palmes NO<sub>2</sub> passive sampler versus face velocity. See text for explanation of symbols and experimental conditions.



XBL 834-1570

Figure 4. Collection efficiencies versus temperature of the Palmes NO<sub>2</sub> passive sampler after correction for face velocity effects. Efficiencies are also corrected for the theoretical temperature dependence. See text for explanation of symbols.

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