

A NEW PERSONAL ORGANIC VAPOR MONITOR WITH IN-SITU SAMPLE ELUTION

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I. ABSTRACT

This paper will describe a new monitor and method for monitoring personal exposures to organic vapors. The method consists of 1) attaching the monitoring assembly in the breathing zone for a measured interval of up to 8 hours, 2) terminating exposure and converting the monitor to an analytical device by interchanging one part, 3) adding a measured volume of eluent, and 4) analyzing by manual or automatic gas chromatography.

Environmental sampling is controlled by binary diffusion such that the rate of sample collection is a function of ambient concentration. Contact, handling, and extraneous exposure of the analytical sample is eliminated. Procedures qualifying the method for compounds of industrial hygiene interest will be presented along with results from evaluations comparing the method to charcoal tubes and known concentrations.

II. INTRODUCTION

In considering a new approach to monitoring personal exposures to organic vapors, the steps in an overall monitoring program can be individually addressed:

1. Development of Monitoring Plan
2. Purchase of Supplies
3. Preparation of Equipment
4. Sampling of Personal Exposures (includes recording data during sampling)
5. Preparation of Sample for Analysis
6. Analysis and T.W.A. Calculation
7. Report Communication and Follow-through

In examining and improving current methods for carrying out each of the above operations, we have evolved a monitoring system which simplifies the work while maintaining desirable objectives and monitoring requirements. The monitoring system which evolved is the 3M Brand Organic Vapor Monitor No. 3500.

3M BRAND NO. 3500 ORGANIC VAPOR MONITOR

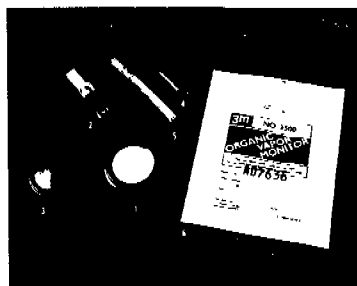


FIGURE 1

We can now consider the way in which this monitor interacts in each of the above seven areas.

Step one, monitoring planning, is simplified because the 3500 system allows the hygienist to work through trained aides in remote locations. It also helps increase the number of samples taken in the case where the hygienist is present for the monitoring, thereby lowering hygienist cost per sample. Purchase of supplies, step two, is reduced since only a single product is needed. Step three is virtually eliminated because the 3500 monitor needs no preparation or calibration by the user.

In the conduct of step four, or the actual exposure sampling, the monitor is readily accepted by employees wearing it. Monitors are individually identified, and the exposure time is recorded directly on the monitor. The package can be used to record comments and other data. A cap terminates sampling, and hermetically seals the sample.

Sorbent transfers and other analytical preparations normally comprising step five are eliminated because the capped monitor is already a discreet sample ready for elution. Step six, the actual analysis, is aided by in situ elution of the contaminants from the sorbent. Manual or automatic gas chromatographic analysis is also facilitated by the monitor design.

Efforts in preparation of reports, step seven, are reduced by having all the needed information concerning the sampling on the monitor package for calculation and reporting. In the next section, the objective is to technically describe the 3500 system.

III. PRODUCT DESCRIPTION

A pictorial representation of the monitoring and analysis method using the 3M Brand No. 3500 Organic Vapor Monitor is shown in Figure 2.

USE INSTRUCTIONS 3M BRAND NO. 3500 ORGANIC VAPOR MONITOR



FIGURE 2

Referring to the numbered steps as illustrated:

1. The monitor is removed from the package. Exposure start time is recorded on the back of the monitor.
2. The monitor is attached near the breathing zone of the worker. After exposure, the exposure end time is recorded on the back of the monitor.
3. The white face of the monitor is removed.
4. The elutriation cap is snapped on and the ports are sealed.
5. The sampling information is recorded on a package and the monitor is inserted. The package is sealed with the tubular closure.
6. The eluent is added through the center port, and the port is immediately resealed.
7. After 1/2 hour (with occasional gentle agitation) the eluent is decanted into the sampler vial, or an aliquot is removed from the center port for manual injection.
8. The gas chromatographic sample analysis is carried out by conventional means.

The time-weighted exposure level is then calculated using the following equations:

$$\text{mg/m}^3 = \frac{\text{Corrected weight on monitor (nanograms)}}{\text{Sampling rate (cm}^3/\text{min)} \times \text{sampling time (min)}}$$

$$\text{ppm} = \frac{\text{mg}}{\text{m}^3} \times \frac{22.4 \text{ /mole}}{\text{m.w. g/mole}} \times \frac{\text{T}^\circ\text{K}}{273^\circ\text{K}} \times \frac{760\text{mm Hg}}{\text{Pmm Hg}}$$

The corrected weight on the monitor is obtained from the sample analysis after corrections are made for blank samples and desorption efficiency. The sampling rate for each contaminant is determined and published by 3M Company as discussed in the next section.

IV. PRINCIPLES OF OPERATION

A. Diffusion Equation

The relationship between environmental contaminant concentration and the weight of material collected by the monitor is given by equation (1):

$$M = D \frac{A}{L} C t \quad (1)$$

M = total mass of contaminant collect (nanograms)

D = molecular diffusion coefficient (cm²/sec.)

A = diffusion path area (cm²)

L = diffusion path length (cm)

C = environmental contaminant concentration (mg/m³ = ng/cm³)

t = sampling time (sec)

Equation (1) assumes that the contaminant concentration at the face of the monitor closely approximates the environmental concentration, the monitor wall effects are negligible, and the collection efficiency of the sorbent element is unity.

In normal use, environmental concentration (C) is to be determined, mass collected (M) is determined via gas chromatography, and the monitoring time (t) is measured. Therefore, a value for the $D \frac{A}{L}$ term is needed to solve the equation. Substitution of the appropriate units for D, A, and L reduces to cm²/sec units which defines the sampling rate for the contaminant and shows the correspondence between diffusion-controlled monitors and conventional pump methods. The diffusion-controlled monitors do, in effect, sample the contaminants in air at a useful, calculable rate. The driving force for sampling is the concentration gradient between the collection face and the sorbent layer in the monitor.

B. Monitor Calibration

1. Parameters calibrated

Monitor calibration data is provided by 3M Company for many organic vapors of industrial hygiene importance. The items which are provided are:

- a. Sampling rate ($D \frac{A}{L}$ from equation)
- b. Recovery coefficient
- c. Exposure limit
- d. Environmental effects
- e. Sample storage recommendations
- f. Concise equations for calculation of results

2. Calibration Apparatus

Monitor calibration requires that accurately known exposures be made. Typical equipment for generating known time-weighted average contaminant concentrations is shown in Figure 3.

The compressed air from the gas cylinder is passed through a charcoal bed to remove any organic material which may be present. The air flow is integrated by a calibrated flow meter. The organic liquid to be studied is placed in the bottom of the diffusion column which is divided as shown by a porous membrane. The organic vapor diffuses into the dilution air stream at a calculable rate, and a wide range of contaminant concentrations are attainable by varying diffusion column diameter and length, dilution air flow rate, or diffusion column temperature. The

MONITOR CALIBRATION APPARATUS

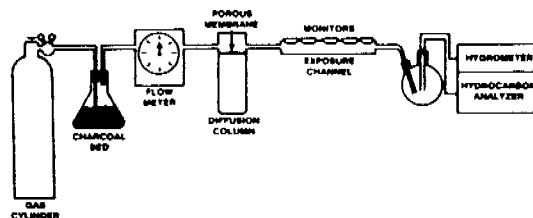


FIGURE 3

monitor exposure section is a metal conduit with a series of ports into which monitors fit snugly. The design permits easy exposure replication to give good estimates of monitor precision. A simple insert makes adaptation to charcoal tubes possible for comparison studies. The air stream finally enters a large collection chamber where the relative humidity is monitored and the contaminant concentration verified with a calibrated hydrocarbon analyzer. The monitors exposed in series each remove a small fraction of the contaminant, (usually less than 0.5 percent) but the amount removed is calculable and corrections are easily made. The dilution air stream can be humidified by several means between the flow meter and diffusion column.

When a substantial amount of liquid is introduced into the diffusion column, the system is capable of equilibrating to generate stable, known concentration environments for long periods of time. More typically, a known quantity of organic liquid is added into the diffusion column and allowed to evaporate to depletion as indicated by the hydrocarbon analyzer. Using this method, an accurate time-weighted average contaminant concentration can be determined by only two measurements: a gravimetric weight determination of organic liquid (mg) and a calibrated flow meter reading (m^3). As the organic liquid evaporates the concentration varies with time, but the time-weighted average concentration is known at the end of the experiment. Both diffusion-controlled monitors and pump methods are capable of integrating variable concentration, so this factor is of no consequence.

3. Calibration Techniques

a. Sampling Rate

The sampling rate of the 3M Organic Vapor Monitor is determined experimentally by generating known concentrations of each contaminant, exposing and analyzing the monitors, and solving equation (1) for the $D \frac{A}{L}$ term. The published sampling rate is generally based on three separate determinations in the 0.25-2 TLV, 8 hour exposure range. This experimental determination is considered necessary since desired diffusion coefficients D_1, D_2 are not always available and their accuracy is not usually known.

b. Recovery Coefficient

The recovery coefficient is determined by vapor-state spiking of monitors. This is accomplished by removing the white barrier film of the monitor, placing a filter paper on the diffusion spacer plate, snapping on the elutriation cap, and injecting a known quantity of the organic material onto the filter paper through the center port. The monitor is aged 16-24 hours before elution to allow total transfer of the organic material from the filter paper to the sorbent. The published number represents the mean ± 2 standard deviations from the tests conducted by 3M. It is, however, recommended that recovery coefficients be at least verified by the user, since techniques and presence of multiple contaminants can affect recovery coefficients.

c. Exposure Limit

The capacity of the monitor for each individual compound is based on molecular structure, vapor pressure, environmental conditions, etc. The exposure limit is specified in lieu of a need for a "back up" section. This is done by 3M by plotting the weight of the contaminant collected by the monitor vs. exposure.

ETHYL ACETATE EXPOSURE LIMIT

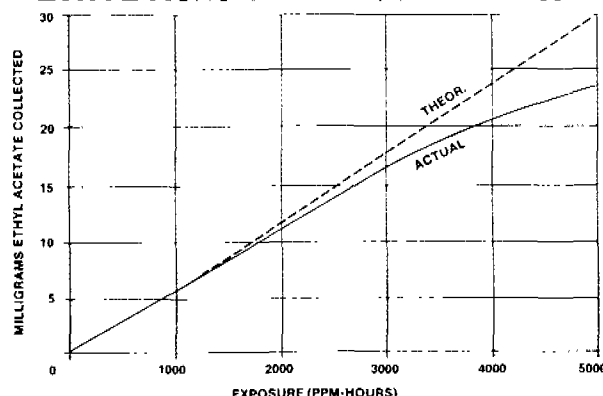


FIGURE 4

The exposure limit is specified as the weight of contaminant collected when significant deviation from linear adsorption is noted. For strongly-adsorbed materials, this limit is usually of the order of 15mg.

d. Environmental Effect

The ultimate vapor capacity of the monitor is sometimes affected by relative humidity. The exposure limit test described above is repeated at 80 + % relative humidity and deviations due to relative humidity are noted.

e. Sample Storage

Monitor samples which have received duplicate exposures are stored and analyzed after 1, 7, and 14 days. If deviations are noted, refrigerated storage is recommended.

Overall information and recommendations are published on qualification sheets. Figure 5 shows a representative qualification sheet for benzene.

3M BRAND ORGANIC VAPOR MONITOR PRODUCT NO. 3500

Qualification Data For	<u>Benzene</u>
GENERAL INFORMATION	
Monitor Sampling Rate	<u>33.0 cm³/min</u>
Recovery Coefficient	<u>0.99 ± 0.03</u>
Upper Exposure Limit*	<u>> 1500 ppm-hours</u>
COMPOUND PROPERTIES & DATA	
Molecular Weight	<u>78.11</u>
Vapor Pressure (20°C)	<u>57.632 mm Hg</u>
Published Diffusion Constant†	<u>0.0932 cm²/sec</u>
Density	<u>0.8794 (20°C)</u>
T.W.A. (TLV)	<u>1.0 ppm</u>
CALCULATION PROCEDURE	
1. Determine mass of analyte in micrograms.	
2. Determine exposure time in minutes.	
3. Calculate concentration from:	
$\frac{\text{mg}}{\text{m}^3} = \frac{30.30 \text{ (micrograms)}}{(\text{recovery coefficient}) \text{ (minutes)}} = \frac{30.6 \text{ (micrograms)}}{(\text{minutes})}$	
$\text{ppm} = \frac{9.484 \text{ (micrograms)}}{(\text{recovery coefficient}) \text{ (minutes)}} = \frac{9.580 \text{ (micrograms)}}{(\text{minutes})}$	
1. The Upper Exposure Limit at 80% R.H. is 1500-ppm-hrs.	
2. Published diffusion constants are provided for general interest only. "Monitor Sampling Rate" data for each compound is determined by 3M Company.	
3. ppm based on 25°C, 760 mm Hg.	

FIGURE 5

V. PRODUCT USE DATA

A. Benzene Monitoring

Using equipment as pictured in Figure 3, known benzene vapor concentrations were generated in air and monitored using the published benzene sampling rate (33.0 cm³/min.) The analytical procedures outlined in Section III were followed. Table I is a summary of results comparing the 3M Organic Vapor Monitor to the known generated benzene concentrations. Tabulated values for the 3M monitor represent the mean of 4 separate determinations $\pm$ 2 standard deviations. The values fall well within the accuracy requirements contained in the O.S.H.A. standard.

TABLE 1
BENZENE MONITORING
TEST

3M ORGANIC VAPOR MONITOR
VS. TEST CONCENTRATIONS

Test Concentration (ppm)	3M Monitor No. 3500 Measurement (ppm $\pm$ 2 σ)
7.80	7.75 $\pm$ 0.43
4.13	4.12 $\pm$ 0.23
2.27	2.22 $\pm$ 0.06
1.32	1.23 $\pm$ 0.04
0.99	0.91 $\pm$ 0.06

B. Complex Mixture Analysis

It is recognized that in real field monitoring situations, combinations of organic vapor contaminants are typical, and that any feasible monitoring system must be capable of complex mixture analysis.

Gasoline was used to test the capability of the 3M Organic Vapor Monitor to sample complex hydrocarbon mixtures. It was reasoned that the high boiling components of gasoline would not be present during a typical exposure. To simulate a more likely field situation, a fraction of gasoline was distilled from a bulk sample. The fraction used was the first eighty per cent of distillate collected. The remaining twenty per cent was discarded. A syringe was used to inject 1.24529 grams of the light fraction through a septum capped port into a receiving vial. An air flow rate of 9.1924 liters per minute was allowed to pass over the open vial until all the gasoline had evaporated into the air stream. At the conclusion of the test, the total air volume was determined by the change in readings of a Model 175-S Rockwell flowmeter. A total of 11.581 cubic meters of air had passed during the 21 hours required for the gasoline distillate to evaporate. A flame ionization detector was used to verify the test end-point. Charcoal tubes were used to collect samples for comparison and correlation of test data. The tubes and 3M monitors were randomly selected but placed in a set pattern on a sampling channel. Two charcoal tubes were placed side-by-side in the first sampling port, followed by four 3M monitors in ports two through five. Port six contained two more charcoal tubes, again placed side-by-side (see Figure 6).

SAMPLING SEQUENCE GASOLINE EXPOSURE

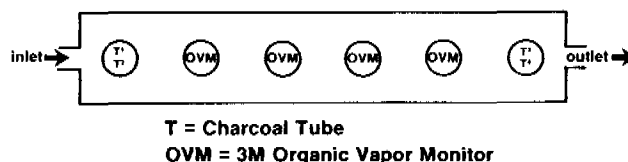


FIGURE 6

The charcoal tubes were positioned vertically to prevent channeling, and the 3M monitors were positioned so the air stream would be flowing parallel to the face of the monitor at approximately 100 fpm air velocity. One and one-half milliliters of spectroquality carbon disulfide was used to desorb the collected gasoline vapors. The samples were allowed to set for 30 minutes with occasional agitation, then transferred to a vial. Withdrawal of a 2 microliter aliquot from the sampling vial, and injection into a Hewlett Packard 5840A gas chromatograph was accomplished by using a Hewlett Packard automatic sampler (Model 7671A). The analytical column was a 7.5 ft. x 1/8 in. S.S. tube packed with 15% Carbowax 20M on 80/100 mesh Chromosorb W. A temperature program was used, starting at 70°C for 5 minutes and increasing to 125°C at the rate of 4°C per minute. A hold of 8 minutes was used on the final temperature. Helium (30cc/minute) was used as the carrier gas.

Quantification of pentane, heptane, octane, benzene, toluene, and xylenes was accomplished by preparing four calibration standards for each component. Each standard was individually prepared by injecting a known volume of each component into a known volume of carbon disulfide. The four data points were used to establish a best fit line from the linear regression method. The weight of each component was determined by comparing the peak area of the sample to the calibration line. This weight was corrected for desorption efficiency and the time-weighted exposure level was calculated in milligrams per cubic meter and converted to ppm. Figure 7 shows a replication of the chromatographic analysis made of the parent, 3M monitor, and charcoal tube samples.

CHROMATOGRAPHIC ANALYSIS GASOLINE EXPOSURE

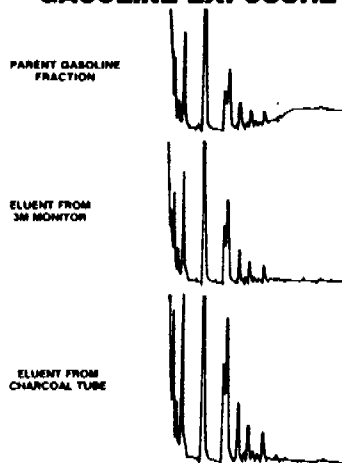


FIGURE 7

The chromatographs are identical except for peak amplitude, which illustrates that both monitoring techniques sample each vapor as if it were present individually.

The desorption efficiencies for components of gasoline were determined in the presence of one another. The recovery tests were done on both the charcoal tubes and the 3M monitors. A known amount of each component was injected onto 100mg sections of the charcoal tubes or onto a piece of Whatman filter paper 2.5cm in diameter in the 3M monitor as described earlier.

The analytical results of the charcoal tubes and 3M monitors agree very well with each other, and the actual test concentration (Table 2).

TABLE 2

**RESULTS OF GASOLINE
EXPOSURE TEST**

Components of Gasoline	Test Concentration (PPM)	3M No. 3500 Concentration (PPM $\pm 2\sigma$)	Charcoal Tube Concentration (PPM $\pm 2\sigma$)
Pentane	5.602	5.832 $\pm .408$	5.053 $\pm .500$
Heptane	0.573	0.570 $\pm .045$	0.578 $\pm .082$
Octane	0.294	0.307 $\pm .047$	0.329 $\pm .056$
Benzene	0.928	0.892 $\pm .160$	0.873 $\pm .180$
Toluene	1.768	1.710 $\pm .119$	1.552 $\pm .220$
Xylenes	1.153	1.230 $\pm .086$	1.034 $\pm .160$

In all cases, the 3M monitors gave lower standard deviations and better agreement with the challenge environment. The concentration of the selected components in gasoline was determined by injecting known volumes of the light gasoline fraction into known volumes of carbon disulfide and analyzing in the same manner as the monitor samples.

C. Integration of Concentration Spikes

To verify the ability of the No. 3500 Organic Vapor Monitor to integrate high peak concentrations, several test exposures of 1, 3-butadiene were made using an exposure system as described in Figure 3, except an injection septum was placed in series between the flowmeter and exposure channel. In each case, charcoal tubes were used to collect samples for comparison and correlation of test data. During sampling, a randomly selected charcoal tube was positioned vertically and upstream of a 3M Organic Vapor Monitor. The 3M monitor was positioned in such a way that the air flow was parallel to the face of the monitor. The charcoal tubes had a sampling rate of 52cm³ per minute. The sampling rate of the 3M monitor is 41.3 cm³ per minute for the collection of 1, 3-butadiene.

Three different concentration levels were used to challenge the tubes and 3M monitors, and each level was replicated three times. The first concentration used was a single spike generated by injecting 5 ml of butadiene vapor into the air stream at a flowrate of 9.774 liters per minute, thus giving a TWA of 528 parts per million as determined by the total air volume (flowmeter) and the weight of 1, 3-butadiene injected. The next concentration (1585 ppm) was generated by three injections of 5 ml each. The last test concentration (3170 ppm) was produced by three injections of 10 ml each. The spike generations were monitored by a total hydrocarbon analyzer equipped with a flame ionization detector. The signal output from the detector was connected to a millivolt recorder to give a chromatogram of each injection. The sampling probe for the total hydrocarbon analyzer was placed downstream from the charcoal tubes and 3M monitors such that no interferences would be caused during the sampling. It was noticed from the recorder chart that each spike was generated in approximately six seconds. This means that the actual peak concentration was in the range of half a percent (5000 ppm) for 5 ml injections, and one percent (10,000 ppm) for 10 ml injections. The results are shown in Table 3.

TABLE 3

**INTEGRATION OF
VARIABLE
CONCENTRATION**

1,2 Butadiene Generated Concentration (PPM)	3M No. 3500 Concentration (PPM $\pm 2\sigma$)	Charcoal Tube Concentration (PPM $\pm 2\sigma$)
528 	527 ± 44	546 ± 78
1585 	1690 ± 74	1687 ± 127
3170 	3502 ± 223	3489 ± 179

Clearly, both the 3M monitors and the charcoal tubes with pumps effectively integrated the abrupt concentration changes to give a good estimate of the time-weighted average concentration.

D. Air Velocity Effects

Diffusion-controlled environmental monitors require a slight air movement across or impinging upon the face of the monitor. Use of equation (1) assumes that the contaminant concentration at the face of the monitor is representative of the overall environment. In stagnant air, the contaminant is removed from the atmosphere by the monitor. This results in a depleted zone at the face of the monitor and an underestimation of the true contaminant concentration. Previous work³ studied air velocities above 50 fpm.

Experiments were conducted to determine the air velocity requirements for the 3M No. 3500 Organic Vapor Monitor. The exposure apparatus shown in Figure 3 was employed, but the monitor exposure channel was designed as shown in Figure 8.

**MONITOR EXPOSURE CHAMBER
AIR VELOCITY STUDY**

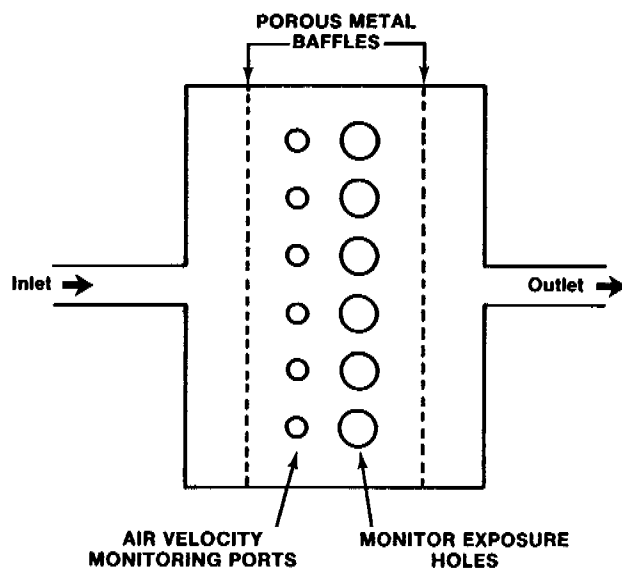


FIGURE 8

The air velocity in the exposure channel was controlled by adjusting air flow rate.

Air velocity was calculated from the flow rate and the exposure channel cross-sectional area. Uniformity of air velocity was also measured using an anemometer probe in the ports indicated. Several exposures to known benzene concentrations were made and the sampling rate was determined. A total of six monitors were exposed at each air velocity level. Elution and analysis was done following standard procedures outlined previously. Figure 9 is a plot of the results.

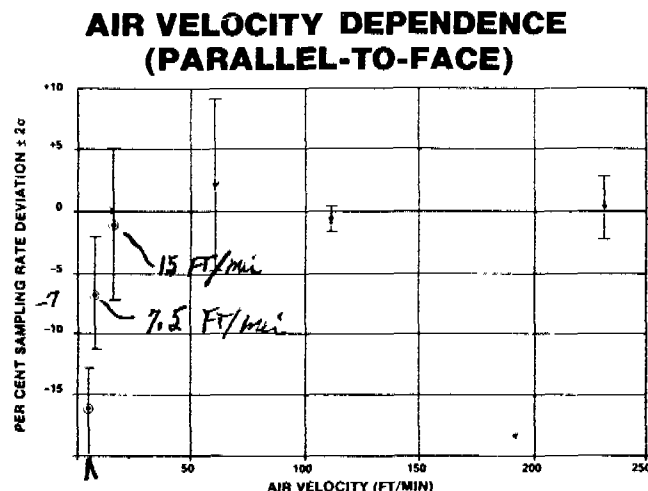


FIGURE 9

The plot shows a significant drop in benzene sampling rate below 10 ft/min face velocity. The ± 2 standard deviation error bars indicate considerable variability at low air velocity. This reflects the difficulty in achieving reproducible, uniform, low velocity in the exposure channel. The mean values do, however, conform well to the published sampling rate for benzene at the higher velocities and the results are believed to be valid. It should be noted that this experiment tested only parallel-to-face air velocity effects which is the worst-case situation.

As a result of these data, it is believed that the air velocity requirements of the 3M Organic Vapor Monitor are minimal and of no concern for personal monitoring. When used as an area sampler, however, placement of the monitor should be considered so that stagnant air areas be avoided. This situation could potentially exist against walls, in corners, etc.

E. Temperature and Pressure Effects

Both temperature and pressure affect the diffusion rate of gaseous contaminants in air. This could, in principle, lead to substantial monitoring errors using diffusion-controlled monitors. However, the net effects of temperature and pressure are offset to some degree by corresponding changes in contaminant concentration.⁴ In the case of atmospheric pressure, the change in diffusion rate and concentration offset each other exactly and no correction is required. The effect of temperature on diffusion coefficient and concentration is given by equations (2) and (3).

$$D = f(T^{3/2}) \quad (2)$$

$$C = f\left(\frac{1}{T}\right) \quad (3)$$

Therefore,

$$\text{Weight collected} = f(T^{1/2})$$

The net temperature effect can be compensated if desired by increasing the experimentally determined concentration in mg/m³ units by 1.08% for every 10°F above 70°F (and reducing by 1.08% for every 10°F below 70°F).

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