A new passive monitor for organic vapors has been developed for the determination of the time-weighted average (TWA) concentration of contaminants in air. This personal dosimeter type badge monitor collects the organic vapors through the mechanism of molecular diffusion and adsorption onto an activated carbon collection element. After exposure, the activated carbon is removed from the device and analyzed using gas chromatographic techniques outlined in NIOSH Physical and Chemical Analysis Method (P&CAM) 127. Current NIOSH standards for measuring the concentration of organic vapors in the atmosphere involve the use of charcoal tubes and sampling pumps for collection, desorption by carbon disulfide and subsequent analysis using gas chromatographic techniques. In comparative testing, the new passive monitor has demonstrated that its overall accuracy is at least equivalent to the charcoal tube method in determining ambient contaminant concentration. Several organic compounds were sampled over the range of 0.5 ppm - 1100 ppm exposure levels. Both field and laboratory tests were conducted and the results were compared. Environmental parameters such as temperature, relative humidity, and air movement were among the factors examined. Other factors considered were desorption efficiencies, sampling rates, sampling range, bias, and precision.

A new personal badge monitor for organic vapors

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introduction

Recent interest in sampling organic vapors with a passive sampling device in place of the pump/solid sorbent tube method has been growing.[1-8] In general these devices depend on permeation-controlled, diffusionally controlled, and permeation/diffusionally controlled mass transport sampling mechanisms. The new Du Pont PRO-TEK™ G-AA Organic Vapor Air Monitoring Badge has been developed with unique features which include immediate response, increased sensitivity, variable sampling rate, and wide sampling range without the need of draft shields, attenuating sheets, or permeation membranes.

Lightweight, small in size, and packaged fully assembled in a sealed pouch, the G-AA Badge has been designed to be worn near the breathing zone of personnel exposed to potentially hazardous environments.[9] To activate the badge for use, one simply removes the badge from the sealed pouch, removes the protective covers and clips the badge to the employee's shirt collar. Each badge can be individually numbered to facilitate accurate recordkeeping.

Throughout exposure, organic vapors are collected through a multi-cavity diffuser element and adsorbed onto an activated charcoal collection element. (See Figure 1.) After exposure, the badge is removed from use, deactivated by replacement of the protective covers, and resealed in the original pouch with the closure provided.

Analysis involves removing the activated charcoal collection strip from the badge and placing it directly into an automatic gas chromatography (G.C.) vial for desorption with 1.0 mL of desorbing solvent. The sample is now ready for G.C. analysis, similar to NIOSH P&CAM 127. When the sampling time, amount of material collected, and the badge sampling rate (determined by diffusion coefficient data supplied by Du Pont)[10] are ascertained, the TWA can be determined.

principle of operation
dynamic vs. diffusionally controlled

When the pump/solid sorbent method, i.e., charcoal tube, is used to sample for organic vapors, the mass of the vapor collected in the sorbent tube is a direct function of the sampling rate of the pump (cm³/min), the ambient (integrated TWA) concentration, C (mg/m³), and the sampling time, t (min). (See Equation 1.)

Mass, M (ng) =

Pump Sampling Rate (cm³/min) $\times$ C (mg/m³) $\times$ t (min)   (1)

When diffusionally controlled devices such as the PRO-TEK Badge are used for sampling, the mass uptake of the badge is controlled by the length and diameter of the badge cavities and the physical properties of the contaminant. Because of the existence of a concentration gradient between the outside of the badge and the activated charcoal strip, the gas diffuses through the cavities by molecular diffusion and is eventually adsorbed onto the activated charcoal strip. According to Fick's First Law of Diffusion, it can be shown that the amount of material or mass, M (ng), picked up on the charcoal is a function of the sampling rate, (DA/L) (cm³/min), times the ambient (integrated TWA) concentration, C (mg/m³), and the sampling time, t (min).[3,5,7,11-...]

M (ng) =   (2)

Badge Sampling Rate, DA/L (cm³/min) $\times$ C (mg/m³) $\times$ t (min)

The badge sampling rate is a direct function of the diffusion coefficient (D) of the organic vapor(s) being sampled and the total cross-sectional area (A) of the badge cavities. The rate is an inverse function of the diffusion path or length (L) of the cavities.
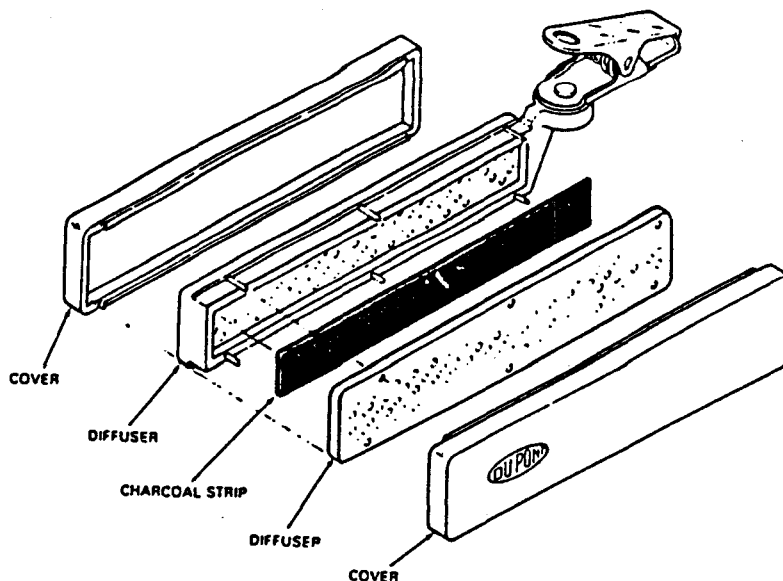
Figure 1 — PRO-TEK G-AA Badge components.

Sampling Rate, (cm³/min) = D(A/L) (3)

where: D, cm²/min = Diffusion coefficient at 25 °C, 760 mm Hg

A, cm² = Total cross-sectional area of the cavities or (number of cavities) × (πr^2)

L, cm = Length of cavities

The kinetic theory of gases[15] indicates that the diffusion coefficient, D, is a function of absolute temperature and pressure by Equation 4.

$$D = f(T^{3/2}/P) (4)$$

The mass collected, however, can be shown to be independent of pressure and only slightly dependent on temperature.[3,13] For example, since $M = f(D \times C)$ (Equation 2), $C = f(P/T)$ (Ideal Gas Law) and $D = f(T^{3/2}/P)$ (Equation 4), then $M = f(T)^{1/2} P^0$. ($P^0 = 1$.)

Therefore:

$$M = f(T^{1/2}) (5)$$

This temperature effect can be corrected for by reducing the experimentally determined concentration in mg/m³ by 1.0 percent for every 10 °F above 77 °F and by increasing by 1.0 percent for every 10 °F below 77 °F. Dynamic pump/solid sorbent and/or impinger systems are normally corrected for changes in actual sampling volume conditions due to both temperature and pressure changes.

badge face velocity control
In many instances draft shields, attenuating sheets, and membranes have been used on the face of passive devices[3,16] to minimize the convective airflow as the rate determining step of mass transport.

The G-AA Badge does not need membrane-like draft shields for protection against windage effects. The elimination of convective airflow inside the badge is accomplished by minimizing the diameter size of the openings and maximizing cavity lengths while maintaining direct contact of the cavities with the collection element. In general the length to diameter ratio (L/D) of the cavities should be greater than 3.0 in order to eliminate convective airflow as the rate determining step to mass transport. The rate determining step of mass transport for the G-AA Badge is then simply the diffusion of the gas through the cavities to the collection element.

response time
An important function of any sampling device is the ability to integrate high peak concentrations. This function is directly related to the response time of the device. Previously described devices with draft shields or permeation membranes have been shown to have response times varying between 5 and 30 seconds.[4,17] A measure of the response time can be made by using Equation 6.[3]

$$\text{Response Time, } t = L^2/2D (6)$$

where: L = Diffusion length, cm
D = Diffusion coefficient, cm²/sec

For the G-AA Badge the calculated response time is found to be approximately 1/2 second. This short response time for the badge allows integration of rapidly changing concentration profiles, which ensures that the sample collected is a true TWA concentration.

dual sampling rate
With the G-AA Badge, one has the choice of two sampling rates of approximately 50 and 100 mL/min, determined by the removal of one or both protective covers. This choice affords the industrial hygienist the flexibility of sampling for low concentrations with improved sensitivity or high concentrations with little likelihood of saturation of the charcoal.

Generally the 100 mL/min sampling rate, both covers removed, should be used when exposure levels between 0.2 and 100 ppm-hrs are anticipated. This sampling range

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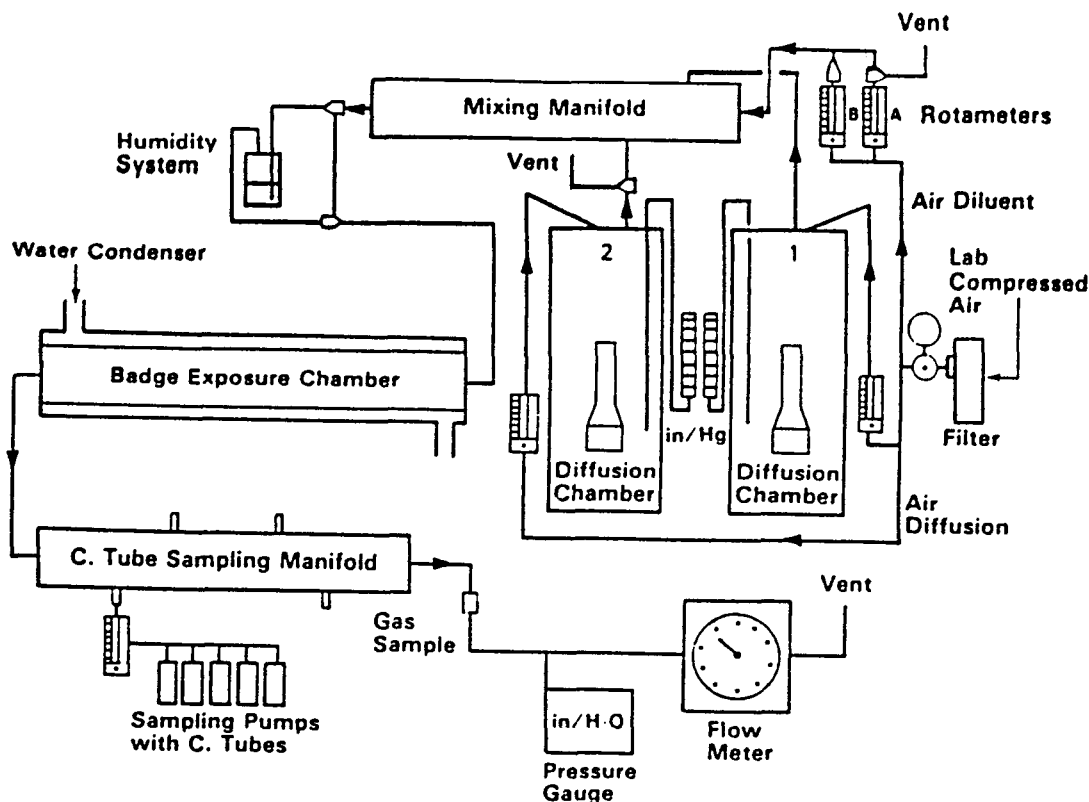*Am. Ind. Hyg. Assoc. J (41)*   October, 1980

Figure 2 — Laboratory test apparatus.

would exist for either short sampling times (15 minutes) or for measuring gases with low exposure levels (<12.5 ppm/8 hrs).

The 50 mL/min sampling rate, one cover removed, should be used when the anticipated sampling range is 100-4000 ppm-hrs. This sampling range would exist for either long sampling times, such as 16 hours, or for measuring gases with high exposure levels (up to 500 ppm/8 hrs).

experimental
badge construction
Initial work involved the use of prototype badges individually machined from Delrin ® acetal resin. Badges were cleaned by extraction with carbon disulfide in a Soxhlet extractor and then dried overnight in a forced air oven at 70 °C. The average A/L was found to be 15.6 cm ± 12 percent. Commercially produced badges are made from an injection molding process using high density polyethylene as the plastic of choice. Overall dimensional uniformity is substantially improved with an A/L of 14.8 cm ± 5 percent.

charcoal
Each charcoal strip in the badges contains approximately 300 mg of coconut-based activated charcoal impregnated in an inert polymer. This composite material is made by a proprietary process. Special cleaning and activation techniques, coupled with rigid quality control procedures, ensure that the activated charcoal strip is clean and active. This amount of activated charcoal increases the badge sampling range and allows for increased badge loading capacity and extended sampling times up to 16 hours.

test apparatus
The basic dynamic contaminant generation system used (see Figure 2) was originally developed by Du Pont[18] for the purpose of laboratory validation of sampling methods where an accurate measure of the true contaminant concentration could be determined. The system is constructed of glass and Teflon * FEP-fluorocarbon resin tubing.

This system uses the principle of vaporization and diffusion of an organic contaminant from a diffusion tube.[19] The diffusion tube is of a predetermined cross-sectional area (A) with ± 2 percent precision and length (L). The tubes are contained in a chamber in which constant temperature (± 0.1 °C) is maintained. The resulting vapor is diluted by mixing with dry or wet air to produce the desired contaminant concentration. The rate of diffusion can be determined by periodic weighing of the tubes (considered to be a primary standard).

Different diffusion rates and subsequently different concentrations can also be obtained by varying the A/L of the tube or by changing the temperature of the chamber surrounding the tube. Concentrations can usually be generated between 0.5-200 ppm for selected organic vapors. Total flow rate of the system is measured at the end of the apparatus train through the use of a dry test meter (Singer Model DTM115, calibrated with a soap bubble meter, a primary standard). If 1/2-inch tubing is used throughout the system to minimize pressure drop, flow rates can be varied between 1 and 20 liters/min, ± 5 percent. Teflon FEP-Fluorocarbon resin tubing was the material of choice because of its chemical inertness.

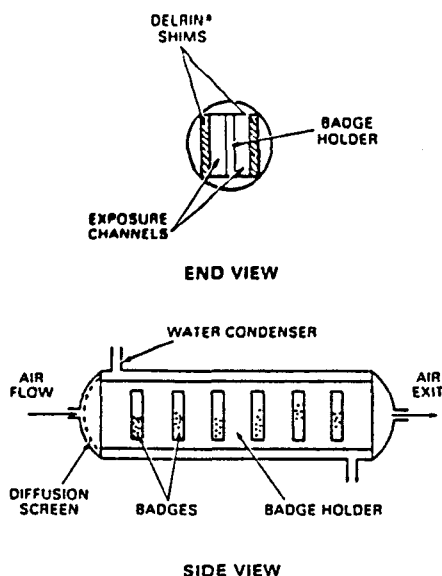For organic vapors with high exposure level (≥200 ppm), a 50 mL glass syringe with syringe pump (Harvard Model

END VIEW

SIDE VIEW

Figure 3 — Badge exposure chamber.

940) was connected to the test apparatus to generate the desired contaminant concentration. Mixture studies can also be performed by using more than one set of diffusion chambers, each containing a different organic solvent. Vaporization and diffusion from diffusion tubes can also be used to determine diffusion coefficients.[20] All organic chemicals used were Fisher Scientific Company spectro quality grade.

Additional secondary reference means for verifying the concentration of the organic contaminant being generated were determined by using calibrated on-line instruments such as a gas chromatograph (Hewlett-Packard Model 5840A equipped with an automatic gas sampling valve) and/or an infrared spectrophotometer (Wilks Model 80 equipped with continuous readout). These instruments permit continuous or periodic checks on the concentration. Other sampling methods, such as charcoal tubes connected to Du Pont Constant Low Flow Sampler pumps, were also used to verify the actual concentration.

Water vapor can be added to the system by passing part of the diluent air through an impinger. The actual humidity is measured with an electronic hygrometer (Panametrics Model 1000).

The badge exposure chamber, based on a design originally used by DuPont's Haskell Laboratories,[21] (see Figure 3) was actually a miniaturized wind tunnel made of glass rectangular tubing jacketed with a water condenser allowing for temperature control. The entrance port of the exposure chamber is equipped with an aluminum screen which acts as a diffuser and eliminates concentration gradients and turbulent flow patterns of the incoming contaminant(s)/air mixture. The width of the exposure channel can be varied by placement of Delrin acetal resin shims along the sides of the rectangular chamber walls. As the thickness of the shims used and the airflow rate are varied, the face velocity can be varied. Air velocities were calculated from the flow rate and the open cross-sectional area of the exposure channel. The calculated values were verified by the use of an anemometer probe (Thermo

Systems Model 1125). This probe was moved down the length of the exposure channel to determine the total velocity profile of the chamber. Through the use of shims and flow rate variation, face velocities between 5 and 400 ft/min could be obtained.

procedures
laboratory exposure testing
G-AA Badges are normally placed in the center of the exposure channel chamber and held in position so that the flow of air is parallel to the face of the badges. The exposure channel chamber was modified to permit variation of the angle of incidence of the incoming contaminant/air mixture. This modification involved making separate compartments (baffled by diffuser plates containing 1/8" diameter holes) in the chamber so that the badge's position could be changed relative to the flow of the incoming air.

The exposure chamber can hold up to eight badges. Most tests involved four to eight badges at face velocities of either 50 or 100 ft/min. A minimum distance of 3-4 inches between badges is recommended to minimize the formation of concentration gradients within the chamber. This chamber design permits easy exposure replication, which leads to accurate estimates of badge precision. Sampling times varied from 15 minutes to 72 hours. The badges exposed in series each remove a small fraction of the contaminant (less than 1 percent at flow rates $\geq$ 10 liters/min). One can correct for this reduction in concentration.

analysis
The activated charcoal strip, because of its tensile strength properties and elasticity, can be readily transferred to an automatic sampler G.C. vial for desorption and G.C. analysis without any loss of charcoal. The charcoal strips are then usually desorbed with 1.0 mL of spectro quality carbon disulfide and agitated for 30 minutes with a shaker (SKC Model Charcoal Developer). The desorbing solution is then analyzed by removing a 0.5 μL aliquot and injecting it into a Hewlett-Packard Model 5840A gas chromatograph equipped with an automatic sampler (Model 7672A) and flame ionization detector. The analytical column normally used was a 6-foot by 1/8-inch glass tube packed with 10 percent Carbowax ® 20M on 80/100 mesh Chromosorb W. The unit normally was operated isothermally with column temperatures ranging between 65 °C and 100 °C depending on the contaminant being measured. The carrier gas used was nitrogen at a flow rate of 30 cm³/min. Calibration standards were prepared daily to contain known quantities of the contaminant in the desorbing solvent. The weight of the desorbed contaminant is determined by comparison with peak areas of known calibration standards. This weight should be corrected by subtracting the concentration of any blank samples.

To calculate the concentration of the contaminant to which the badge was exposed, one uses Equation 7:

$$mg/m^3 = \frac{\text{Corrected Weight, ng}}{\left(\begin{matrix}\text{Desorption}\\\text{Efficiency}\end{matrix}\right)\left(\begin{matrix}\text{Sampling}\\\text{Rate, cm}^3/\text{min}\end{matrix}\right)\left(\begin{matrix}\text{Sampling}\\\text{Time, min}\end{matrix}\right)} \quad (7)$$

TABLE I
PRO-TEK Prototype Badge Sampling Rates

Compound	Test Exposure (ppm-hrs)	Sampling Rate (cm³/min)	M.C.V.	M.W.
Acrylonitrile	30-1000	102.8	8.4	53.06
Benzene	2-20	90.3	6.1	78.11
Carbon Tetrachloride	8-60	69.7	4.4	153.84

If the badge sampling rate (DA/L) is known, the test concentration can be determined and compared with the true concentration, which is determined by the diffusion tube weighings (primary reference standard) or on-line instrument readings (secondary reference standard). Alternatively, if the concentration in mg/m³ is known along with the corrected weight and desorption efficiency, one can determine the sampling rate (DA/L) and then determine the diffusion coefficient D by knowing the A/L of the badge.

desorption efficiency

The method normally recommended by Du Pont for determining desorption efficiencies (DE's) is based on the phase equilibrium method previously described.[22,23] This method is considered to be not only easier but also more accurate than the NIOSH recommended procedure. However, this method should be compared for equivalency with NIOSH recommended procedures before being used during routine analysis of industrial hygiene samples. The Du Pont procedure involves adding a known concentration of contaminant to the desorbing solvent. Samples of this solution are injected into G.C. vials with and without charcoal strips. The vial contents are agitated gently and then allowed to equilibrate for one hour. A sample is then taken from each vial and the amount of contaminant present is determined using G.C. techniques. The DE at that particular loading level will be the relative peak areas of the solution with the charcoal strip divided by the relative peak area of the solution without the charcoal strip. At least three DE's should be determined at three different loading levels at concentrations expected during actual test exposures.

field testing

Field testing was performed for both personal and area monitoring. Generally the evaluation for personal monitoring involved placing a badge on one side of a worker's collar and another sampling device, such as a charcoal tube and pump, on the other side of the collar. The evaluation for area monitoring involved placing badges and pumps with charcoal tubes on an open rack in an area free of obstructions. Sampling times varied from 15 minutes to 10 hours.

statistics

overall accuracy

NIOSH recommends that the overall accuracy of a sampling method in the range of 0.5 to 2.0 times the environmental standard should be ± 25 percent for 95 percent of the samples tested.[24] OSHA's accuracy requirement varies from ± 25 to ± 50 percent depending on the individual standard. Other authors have discussed the implementation of these criteria into a possible statistical protocol involving the use of tolerance and non-parametric tolerance intervals or separate estimates of accuracy and bias.[25,26] A new statistical criterion based on NIOSH and OSHA recommended procedures has been defined. If sufficient samples are tested, an overall accuracy statement corresponding to the NIOSH criterion can be expressed by the use of Equation 8:

$$\text{OVERALL} \atop \text{ACCURACY} = \pm \left[{\text{Absolute} \atop \text{Mean Bias}} + \left(\frac{2 \times \text{Mean Coefficient}}{\text{of Variation}} \right) \right]$$

(8)

The term overall accuracy refers to the percent difference between a measured concentration and the true concentration of an air sample. Overall accuracy includes:

1. The difference between the average value resulting from the sampling method and the true value (estimated by the mean bias); and

2. The random variation of the sampling method about its own mean (estimated by the precision or mean coefficient of variation).

Equation 8 assumes that the mean bias is a known quantity not subject to random errors of estimation.

In general, six or more replicate samples are collected at three or more concentrations and analyzed for the mass collected. Samples are corrected for desorption efficiency (DE) values which should be greater than 50 percent. The NIOSH method recommends DE values of at least 75 percent.

The mean, standard deviation, and coefficient of variation are calculated at each concentration level. The
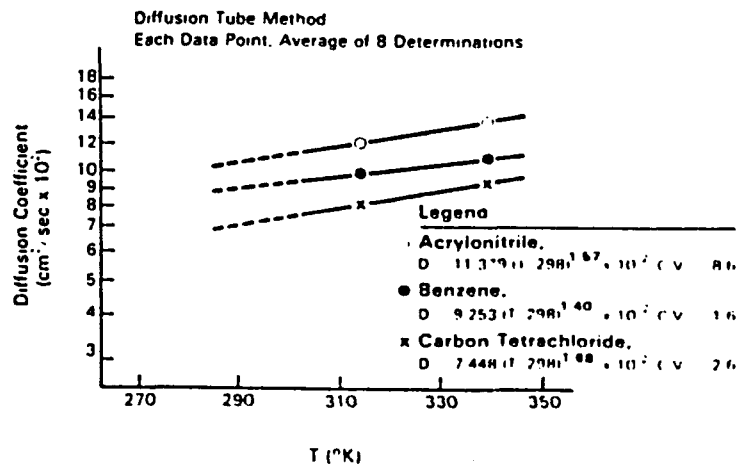

Figure 4 — Temperature dependency of diffusion coefficients.

TABLE II
Comparison of Diffusion Coefficients
(25 °C, 760 mm Hg) (cm²/sec × 10²)

Organic Vapor	Experimental		Literature
	Diffusion Tube	Badge	(Lugg)
Acetone	-	10.62	10.49
Acrylonitrile	11.40	10.98	10.59
Benzene	9.25	9.72	9.32
Carbon Tetrachloride	7.45	7.46	8.28
Toluene	-	7.90	8.49

mean coefficient of variation (M.C.V.) is determined by Equation 9:

$$M.C.V. = \sqrt{\frac{(n_1-1)(C.V._1)^2 + \ldots (n_i-1)(C.V._i)^2}{\sum_{i=1}^{n}(n_i-1)}} \times 100 \qquad (9)$$

The bias (b_i) at any one concentration is determined by Equation 10:

BIAS (b_i) =

$$\frac{X_i, \text{Average ppm (sample)} - X^0, \text{Average ppm (known)}}{X^0, \text{Average ppm (known)}} \times 100 \qquad (10)$$

The mean bias ($\bar{b}$) is determined by Equation 11:

$$MEAN\ BIAS\ (\bar{b}) = \frac{b_1 n_1 + b_2 n_2 + \ldots b_i n_i}{\sum_{i=1}^{n} n_i} \qquad (11)$$

where n is the number of samples run at any one concentration.

In order to satisfy the NIOSH requirement of ±25 percent for 95 percent of the samples, the sum of the absolute mean bias and 2 × M.C.V. should not exceed 25 percent. For example, with an absolute mean bias of 10 percent, one could not have a M.C.V. greater than 7.5 percent in order to meet the ±25 percent criterion. If initial data from an analytical method do not meet this criterion but the method is thought to be valid, increased sampling should be considered in order to obtain better estimates of the M.C.V. and the mean bias.

correlation coefficient

When paired comparisons between two different methods are to be made, it is useful to calculate the linear correlation coefficient, r.[27] This value determines the degree to which the paired results are associated with each other. High positive r values (up to +1.0) are a good indication that the two sampling methods are responding in the same way to the environment.

results and discussion
sampling rates

As previously stated, the sampling rate of the badge is (A/L) expressed in units of cm³/min. If A/L is assumed to be a constant, the sampling rate is a function of the diffusion coefficient of the gas which is related inversely to the molecular size of the contaminant. As the size of the molecule increases, the diffusion coefficient decreases and

T 298 K, RH 5%, P 760 mm Hg, Organic Vapor Benzene
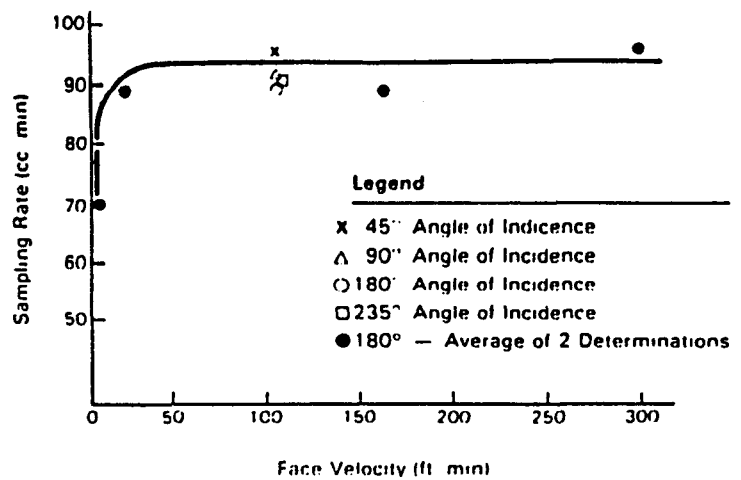Sampling Time 30 to 180 min, Concentration Range 3.2 to 35.8 ppm

Legend

X 45° Angle of Incidence
∧ 90° Angle of Incidence
◯ 180° Angle of Incidence
▢ 235° Angle of Incidence
● 180° — Average of 2 Determinations

Figure 5 — Face velocity effects.

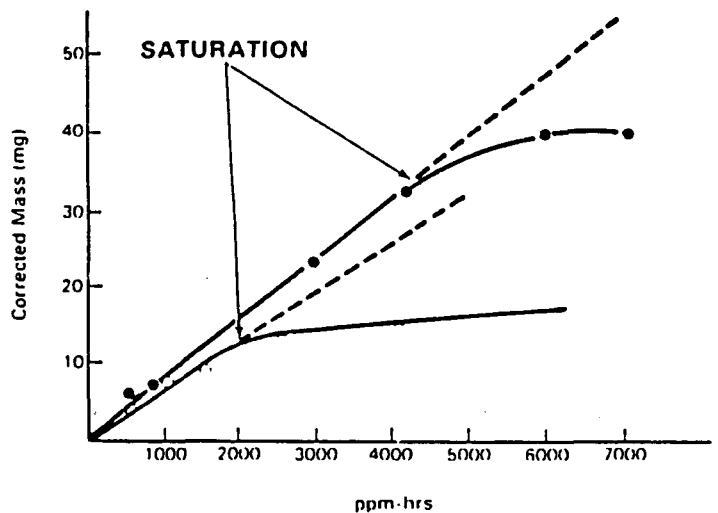| Organic Vapor | ● Toluene, Concentration | 150 ppm |
| | ◯ Acetone, Concentration | 1100 ppm |

T 298 K, RH 50%, P 760 mm Hg

SATURATION

Figure 6 — Maximum exposure limit.

TOLUENE

ACETONE
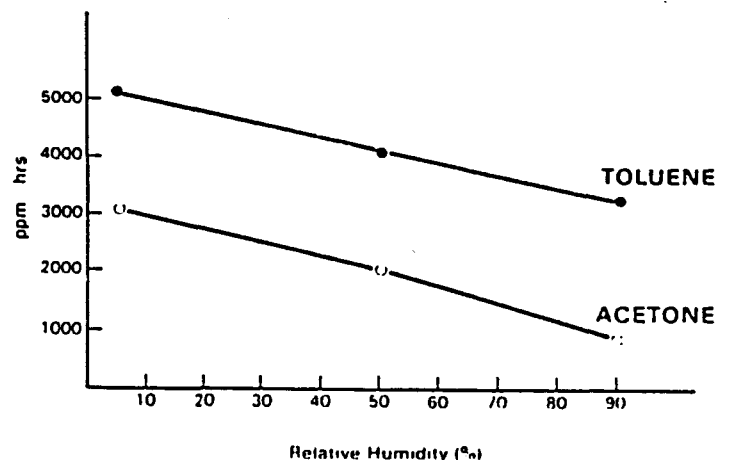
Figure 7 — Relative humidity effect on maximum exposure limit.

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thus the sampling rate decreases (see Table I). These diffusion coefficients are also a function of temperature (see Figure 4). The experimental diffusion coefficients shown in Figure 4 are based on the known A/L of a diffusion tube and the known rate at which the gas leaves the diffusion tube at a known temperature and pressure. The diffusion coefficient equations illustrate the fact that the temperature dependency is approximately $T(^\circ K)$ raised to the 1.5 power, which agrees well with the kinetic theory of gases. The diffusion coefficients of the gases at 25 °C (298 °K) can be estimated from these equations and are shown in the second column of Table II. The third column of Table II lists the experimental values based on actual badge exposure data. The values are obtained from the known A/L of the badge and the exposure concentration, C. The last column in Table II reflects experimentally determined literature values.[20,28] To date, we have found the Lugg literature values to be within 10 percent of experimentally determined diffusion coefficient values.

If experimentally determined sampling rates are not available, they can be calculated from the experimental literature values if the A/L of the badge is known.

For example:

D, Pentane, cm²/sec = 0.0842 (Lugg Value)

or

D, Pentane, cm²/min = 5.052

A/L, Badge = 14.8 cm

$$D(A/L) = 5.052 \text{ cm}^2/\text{min} \times 14.8 \text{ cm} = 74.8 \text{ cm}^3/\text{min}$$
(12)

It should be recognized that sampling rates derived from experimentally determined literature values may have a bias or systematic error of ± 10 percent. One should note, however, that if the total M.C.V. of the system is ≤5 percent, the overall accuracy of the method will still meet the NIOSH accuracy requirements of ±·25 percent for 95 percent of the samples. (See Experimental, Statistics.)

For compounds which do not have experimentally determined literature values but for which the activated charcoal solid sorbent method is recommended, one can determine sampling rates by using either:

1. Calculated diffusion coefficients and the A/L of the badge, or
2. Direct comparison with validated charcoal tube/pump methods.

face velocity effects

Windage or face velocity does not significantly affect the G-AA Badge at its maximum sampling rate (*i.e.*, both covers removed) unless it falls below 35 ft/min (see Figure 5). Below 35 ft/min, the badge will have a low reading because of starvation occurring at the face of the badge. Below 35 ft/min face velocities, the external resistance to mass transfer becomes a significant fraction of the internal diffusional resistance, and the mass of contaminant collected will be less than that predicted on the basis of Equation 2.[3] When the badge is used as an area monitor it

should not be placed in stagnant air areas, against walls, or in corners. This effect can be minimized by keeping one of the protective covers on the badge to reduce the sampling rate by one-half. Personnel wearing a passive dosimeter will be exposed to an average face velocity of 100 ft/min or higher because of the movement of the individual in his/her environment (see NIOSH Contract No. 210-78-0115-C000, Evaluation of Passive Organic Vapor Monitors). As a result, the air velocity requirements of the badge are considered minimal and are of no concern for personal monitoring. The badge was also tested at 100 ft/min face velocities where the angle of incidence of the incoming air was varied. No significant change in the sampling rate was observed with these variations.

Overall, the G-AA Badge has been tested to accurately measure between 35 and 400 ft/min face velocities (see Figure 5).

range and sensitivity

The badge sampling range for most organic vapors will vary between 0.2 and 4000 ppm-hours depending on the organic vapor being monitored.

The lower limit (sensitivity) of the sampling range is a direct function of:

1. The sampling rate of the badge.
2. The amount of contaminant desorbed from the charcoal strip.
3. The separation of that contaminant on a G.C. column.
4. Any blank correction for the charcoal strip.
5. The sensitivity of the G.C. detector for the contaminant.

For most organic compounds, the lower limit of detection ranges between 0.002 and 0.1 mg of contaminant per sample.

The maximum limit of the sampling range is a function of the saturation of the charcoal. Saturation is defined as the point at which sufficient contaminant has been adsorbed that the sampling rate of the badge is no longer constant and has decreased by more than 10 percent. This phenomenon will eventually occur for all organic vapors because a limited amount of organic contaminant can be adsorbed onto the charcoal. Figure 6 illustrates the saturation limit or maximum exposure limit of the sampling range of the G-AA Badge for toluene and acetone at 50 percent relative humidity (R.H.) with one of the protective covers on. The maximum limit occurs at approximately 4100 and 2020 ppm-hours, respectively, for toluene and acetone and represents the point at which:

1. The mass uptake is no longer a linear function of the amount of material to which the badge is exposed, or
2. The sampling rate is no longer constant and has decreased by more than 10 percent.

Saturation is also affected by coadsorption of other compounds, R.H. (adsorption of water), and temperature.
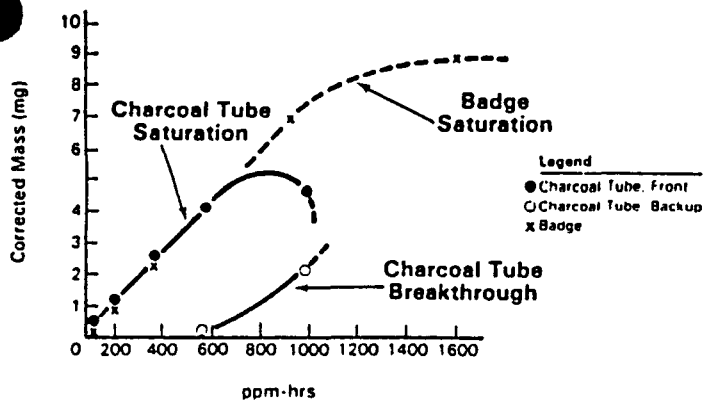
Figure 8 — Badge vs. charcoal tube saturation.

For example, increases in the R.H. to 90 percent can reduce the sampling range maximum limits by as much as 50 percent, especially for polar compounds (see Figure 7).

maximum and minimum sampling times

It is useful to determine what the minimum and maximum sampling times are for the anticipated exposures in order to determine if the badge will give a valid estimate of the actual TWA exposure. Determination of the minimum and maximum sampling times will depend on the upper and lower limits of the sampling range. For example, the lower exposure limit for benzene is estimated at 0.2 ppm-hour (based on the sampling rate and sensitivity of benzene to a flame ionization detector). If the expected exposure level is 1.0 ppm, then the minimum sampling time is 0.2 hour or 12 minutes (see Equation 13). The lower exposure limit occurs with *both* covers removed.

$$\text{Minimum Sampling Time (hr)} = \frac{\text{Maximum Exposure Limit (ppm-hr)}}{\text{Expected Exposure Level (ppm)}} \quad (13)$$

$$\frac{0.2 \text{ ppm-hr}}{1.0 \text{ ppm}} = 0.2 \text{ hr or 12 min}$$

This minimum sampling time would allow the user to determine the 15 minute ceiling exposure level for benzene. To determine the maximum sampling time, one divides the

maximum ppm-hour exposure by the expected exposure level in ppm. The maximum exposure limit occurs with *one* cover removed.

For example:

1. Toluene with a maximum ppm-hour exposure limit at 80 percent R.H. of 3500 ppm-hours at an expected exposure level of 200 ppm would have a maximum sampling time of 17.5 hours (see Equation 14).

$$\text{Maximum Sampling Time} = \frac{\text{Maximum Exposure Limit (ppm-hr)}}{\text{Expected Exposure Limit (ppm)}}$$

$$\frac{3500 \text{ ppm-hrs}}{200 \text{ ppm}} = 17.5 \text{ hrs} \quad (14)$$

2. Acetone with a maximum ppm-hour exposure limit at 80 percent R.H. of 1200 ppm-hours and an expected exposure level of 300 ppm would have a maximum sampling time of four hours. To determine an eight-hour TWA for acetone under these conditions, one would need to do consecutive four-hour sampling. In general, those contaminants which will be sampled at high exposure levels ($\geqslant$500 ppm) or have high vapor pressures and/or are polar compounds will require consecutive sampling over an eight-hour exposure period.

vapor retention

If one exceeds the maximum exposure limit of the badge any time during an exposure, material will be lost from the device. For example, four badges (each with one cover on) were exposed to 1200 ppm acetone at 50 percent R.H. for one hour. Two of the badges were analyzed immediately and two were left in the sampling chamber exposed to 50 percent R.H. air (no acetone present) for an additional three hours. The average mg adsorbed for the four-hour experiment was essentially the same (actually 7.13 mg vs. 7.44 mg) as the average for the one-hour experiment. The experiment was repeated, but in this case the initial one-hour exposure was 3538 ppm acetone at 50 percent R.H. The average mg adsorbed for the four-hour experiment was 35 percent lower (9.61 mg vs. 14.75 mg) than the average for the one-hour experiment. This implies a maximum exposure limit of <2300 ppm-hours (*i.e.*, 65 percent of 3538 ppm-hours) which agrees closely with the maximum exposure limit of the badge for 50 percent R.H. found in Figure 7. These data

TABLE III
Desorption Efficiency

Organic Vapor	Average Desorption Efficiency*	M.C.V. (%)	Desorbing Solvent
Acetone	0.67	4.1	1.0 mL CS₂
Acrylonitrile	0.71	5.9	1.0 mL MeOH
Benzene	0.96	3.7	1.0 mL CS₂
Carbon Tetrachloride	1.00	8.3	1.0 mL CS₂
Toluene	0.97	1.1	1.0 mL CS₂

*Average of at least 2 determinations over at least 3 concentrations (1/2–2 × TLV).

TABLE IV
Overall Accuracy
Prototype Badge vs. Charcoal Tube*

Chamber Concentration (ppm)	PRO-TEK	Charcoal Tube
18.2	20.5	21.8
18.2	18.3	20.7
18.2	18.1	20.8
18.2	18.8	23.9
Average =	18.8	21.8
2.76	2.73	2.57
2.76	2.68	3.08
2.76	2.68	2.67
2.76	2.66	2.76
Average =	2.69	2.77
M.C.V. =	4.38%	7.42%
Mean Bias =	0.4%	10.1%
Overall Accuracy =	± 9.2%	± 24.9%

*Test conditions:

T = 298 °K	Face velocity = 100 ft/min
R.H. = 5%	Pump flow rate = 100 cm³/min
Organic vapor = carbon tetrachloride	Badge sampling rate = 69.7 cm³/min
Sampling time = 3 hrs	

illustrate the fact that if a worker is exposed for a short time early in the workday to a high concentration which exceeds the maximum exposure limit of the badge, some adsorbed vapor will be lost before the charcoal strip is analyzed. If such a condition is expected in the field, the use of a passive device which contains a backup section of charcoal would be appropriate. Such capability currently exists with the pump/charcoal tube method where 100 mg of charcoal is present in the front section and 50 mg in the back (see Figure 8). The G-AA Badge does afford additional protection against saturation by using 300 mg of charcoal vs. 150 mg found in the standard charcoal tube (see Figure 8). Protection against saturation is also increased by leaving one of the covers on the badge, thus reducing the sampling rate by 50 percent.

storage stability
After an actual exposure, it is recommended that the covers be replaced on the badge and the badge resealed in the pouch with the resealing closure provided. This will minimize sample loss or further collection of material. As with standard charcoal tubes, it is also recommended that the samples be refrigerated, if possible, when they cannot be analyzed immediately. Particular attention should be given to highly volatile or reactive contaminants. Initial storage stability tests with methylene chloride, acrylonitrile, and benzene show no significant change in mass adsorbed after four weeks, with and without refrigeration. Tests were run on both charcoal tubes and G-AA Badges which had been exposed to a total ppm-hours exposure of approximately one-half the TLV.

desorption efficiency
Average DE's determined by the phase equilibrium method

are shown in Table III. The use of 1.0 mL of desorbing solvent will in general produce DE's of ≥0.90 for non-polar compounds and ≤0.75 for polar compounds. When DE's are found to be less than 75 percent, it may be advisable to use an increased amount of, or different, desorbing solvent. For removing polar compounds, improved DE's can be obtained by doing one of the following:

1. Using 2 mL desorbing solvent rather than 1 mL.[29]
2. Using mixed solvents such as 1.0-2.0 percent solution of methanol, propanol, butanol, or acetone in carbon disulfide.[30,31]
3. Using a two-phase (water-carbon disulfide) desorption mixture.[32]

DE's can vary with the following:[29,31,33]

1. The amount of material on the charcoal.
2. The amount of charcoal.
3. The amount and type of desorbing solvent.
4. Coadsorption of other polar compounds.
5. Temperature conditions at the time of desorption.
6. Chemical reactivity of the contaminant before analysis.
7. Collection rate of the sampling device.

Because of these effects, actual DE's should always be determined at the time of the analysis. DE's should be verified by the user under those charcoal loading conditions expected during test exposure.

overall accuracy
As illustrated in Table IV, the G-AA Badge method meets both OSHA and NIOSH accuracy requirements for sampling organic vapors. The table compares the performance of the G-AA Badge vs. the charcoal tube method. In chamber tests using carbon tetrachloride as the organic vapor and using Equation 8, the G-AA Badge has an overall accuracy of ± 9.2 percent vs. ± 24.9 percent for the charcoal tube method. This overall accuracy allows the G-AA Badge to meet the criterion that 95 percent of the samples will be within ± 25 percent of the true value.

field testing
Although laboratory validation can consider many parameters that might influence adsorption and desorption properties of the passive dosimeter, it is not often possible or feasible to simulate actual field sampling conditions. One technique for personal monitoring evaluation is to compare the method in the field with a previously established valid method. An example of such a technique is shown in Figure 9 where a significant correlation (r = 0.97, 8 samples) without significant bias was found between badges and charcoal tubes sampling at 80 cm³/min under actual field sampling conditions.

A more convenient validation in the field may involve area monitoring in which two methods are compared. Figure 10 illustrates the ability of the G-AA Badge and the charcoal tube method to give a true TWA value. Duplicate
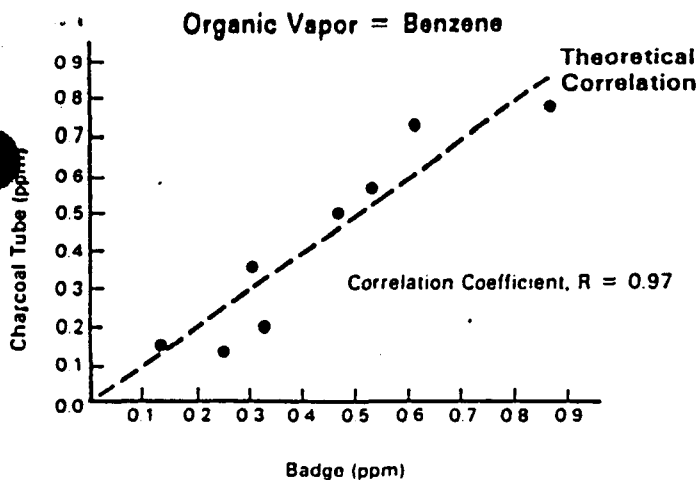
Figure 9 – Field testing – personal monitoring charcoal tube vs. PRO-TEK Badge.

Figure 10 – Field testing – area monitoring.

badges and charcoal tubes with Du Pont Constant Flow Sampler pumps were placed in an area and allowed to sample for six hours. These results were compared with the TWA calculated from the average of three sets of duplicate badges and charcoal tubes: each set was allowed to sample for a two-hour period, was removed, and was replaced with another set of fresh badges and charcoal tubes during the six-hour sampling period. The calculated TWA of the badges and the charcoal tubes was essentially the same as the TWA determined by the duplicate six-hour test. These experiments were repeated for a second day with similar results. The overall M.C.V. for badges was 8.1 percent vs. 15.0 percent for charcoal tubes with pumps.

conclusion

To date, laboratory tests and field trials of the PRO-TEK G-AA Organic Vapor Air Monitoring Badge have confirmed the new passive personal monitor's ability to:

1. Determine the TWA contaminant concentration well within the overall accuracy requirement contained in the OSHA and NIOSH standards.

2. Sample from 15 minutes to 16 hours for most organic vapors.

3. Be easy to use, small, and lightweight.

appendum

badge with backup capability

Currently under development at Du Pont is a passive badge with a backup section. This badge will allow the industrial hygienist to determine when charcoal capacity has been exceeded in the field.

mixtures

All testing described in the laboratory procedures deals with single component analysis with the exception of water vapor, which is a competing analyte. Field test data in general deal with multiple components. Mixture testing is currently being conducted and preliminary results indicate that the badges are able to accurately measure the TWA of
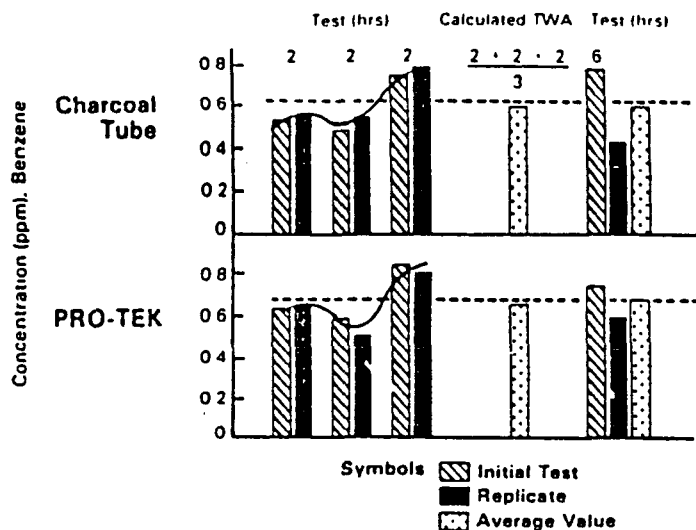
mixed vapors of organic solvents as long as the total weighted ppm-hour exposure of the solvent mixture is not exceeded. In a mixed solvent system, individual component sampling rates do not change, but careful attention must be given to DE's.

acknowledgments

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