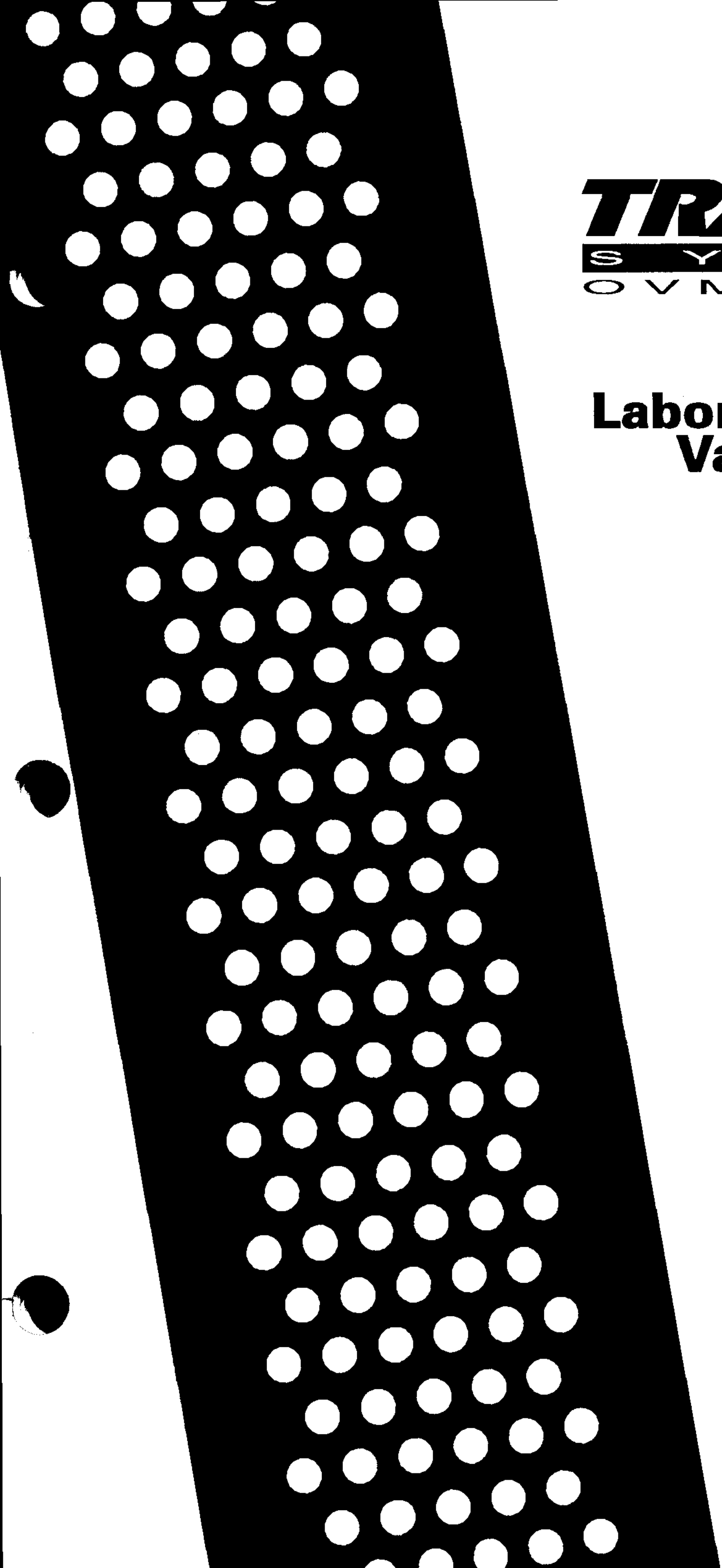

TRACEAIR™
SYSTEM
OVM BADGES

Laboratory and Field Validation Report February 1993

AROMATICS

- Benzene
- Ethyl Benzene
- Toluene
- Xylene

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Summary

This report describes in detail the procedures and results used by Gilian Environmental Corp. to evaluate the performance and operating parameters of the Gilian TRACEAIR^{TM} Organic Vapor Monitor Badge.

The laboratory protocol used Gilian TRACEAIR^{TM} OVM-2 badges and pump/charcoal tubes. Benzene, ethyl benzene, toluene, and xylene were used as the contaminant across concentration ranges of 0.5 ppm to 3.0 ppm in a dynamic laboratory exposure chamber. Benzene was generated from a temperature-controlled permeation oven. Ethyl benzene, toluene, and xylene were generated from a syringe pump. Permeation tubes were calibrated and verified daily using gravimetric techniques. An in-line gas chromatograph with an electronic gas sampling valve was used continuously to verify system concentrations. In every case, the true concentration was established when the predicted concentration and the measured concentration were within 5% agreement of each other.

These studies indicated that the overall accuracy for the Gilian TRACEAIR^{TM} badges were for benzene, +/- 9.4% with a mean coefficient of variation (M.C.V.) of 4.6% and a mean bias of 0.17%, for ethyl benzene +/- 3.8% with a mean coefficient of variation (M.C.V.) of 1.9% and a mean bias of 0.0%, for toluene +/- 7.9% with a mean coefficient of variation (M.C.V.) of 2.4% and a mean bias of -3.1%, for xylene +/- 4.7% with a mean coefficient of variation (M.C.V.) of 2.3% and a mean bias of -0.09%. This accuracy is across all conditions validated in this protocol. In summary, these results indicate that the Gilian TRACEAIR^{TM} OVM badges accurately predict concentrations of Benzene in ambient air well within the National Institute of Occupational Safety and Health (NIOSH) and the Occupational Safety and Health (OSHA) accuracy standards of +/- 25%.

Introduction

Passive diffusion monitors are air sampling devices that are very easy to use and require little technical expertise. They are used as an alternative to sampling pump and sorbent tubes to measure time-weighted average concentrations of certain airborne gases or vapors. Passive monitors, like any device, have limitations. It is the purpose of this protocol to determine suitable operating parameters for which the Gilian TRACEAIR™ monitors can function properly and yet meet the NIOSH and OSHA accuracy requirements.

Background

Mass transfer occurs via one of three mechanisms, natural convection, forced convection or diffusion. An example of natural convection would be opening a window and allowing the components of the outside air to enter and travel across the room. If a mechanical device such as a fan were used, i.e. work, in the form of energy, is supplied and forced convection occurs.

Diffusion is defined as the random movement of individual molecules by virtue of their thermal (internal) energy. To be consistent with the above example, if a glass of a volatile substance such as acetone were placed in a dish on one side of the room the acetone vapors would diffuse into the surrounding air and eventually reach the other side of the room.

The mathematical models for convection are inherently complex differential equations which require sophisticated numerical solutions. In addition, many assumptions are required to reduce the equations to ones that can be solved. Diffusion can however, be described by Fick's first law to a high degree of reliability. For this reason, passive monitor sampling devices were designed to work on the principles of diffusion.

The diffusivity of a gas or vapor can be related to the concentration in the following manner:

$$Jx = DA\frac{\partial C}{\partial X} \qquad (1)$$

where

Jx = diffusive flux in the x direction (mg/min)

D = diffusion coefficient (cm^2/min)

A= cross sectional area (cm^2)

C = concentration (mg/cm^3)

X = length (cm)

$\frac{\partial C}{\partial X}$ = concentration gradient through the diffusion path

The above differential equation can be reduced to a simple algebraic expression by assuming that the concentration gradient is constant. Thus equation 1 above reduces to:

$$Jx = DA\frac{C-Ce}{L} \qquad (2)$$

Where C is the concentration at the surface of the diffusion path and Ce is the concentration at the interface of the sorbent. It can also be assumed that $Ce = 0$ at the surface of the sorbent. finally, the diffusive flux can be related to the concentration by the simple relationship:

$$Jx = \frac{DA}{L}C \qquad (3)$$

Integrating equation 3 over time gives us the more useful form:

$$Ma = \frac{DA}{L}Ct \qquad (4)$$

where Ma is the Mass adsorbed in mg.

It is apparent from an inspection of equation (3) that DA/L has units of (cm^3/min) and has been referred to as the sampling rate. Jx ,the diffusive flux, or the uptake rate, is a linear function of the concentration. If Jx is plotted versus dose, a straight line results and the slope of the line is DA/L. The diffusion coefficient is a function of the molecular structure of the molecule, the molecular weight, temperature. Since the sampling rate is proportional to the diffusion coefficient, each organic compound has a specific sampling rate.

There is a close analogy between the diffusion resistance in a diffusion path and the resistance in an electrical circuit. According to Ohm's Law, the Voltage varies proportionally to the current[1]. Setting this proportionality to an equality requires a proportionality constant which is, of course, the resistance. A plot of the voltage versus the current yields a straight line the slope of which is the resistance. Thus the sampling rate can be thought of as the resistance to mass transfer. The sampling rate is the most important variable which affects the efficiency of a passive sampler.

Determination of Sampling Rates Based on Estimated Diffusion Coefficients

If experimentally determined sampling rates are not available, sampling rates may be estimated from empirical equations, derived from the kinetic theory of gases that have been developed over the years to estimate diffusion coefficients [2]. The Wilke and Lee[3] modification of the equations developed by Herschfelder, Bird, and Spotz[4] is the most common method currently employed.

$$Dg = \frac{[22.03 - 5.07\sqrt{.0345 + \frac{1}{MW}}][\sqrt{.0345 + \frac{1}{MW}}]}{I_d(3.62 + 1.18V_2^{1/3})^2} \qquad (5)$$

MW = Molecular weight

I_d = Collision Integral

V_2 = Molal Volume

Dg = Diffusion Coefficient

Once the diffusion coefficient is known, the sampling rate may be estimated by knowing the A/L ratio of the dosimeter. A comparison of the experimentally determined sampling rate and the estimated values is shown in the Protocol section.

Validation Procedure

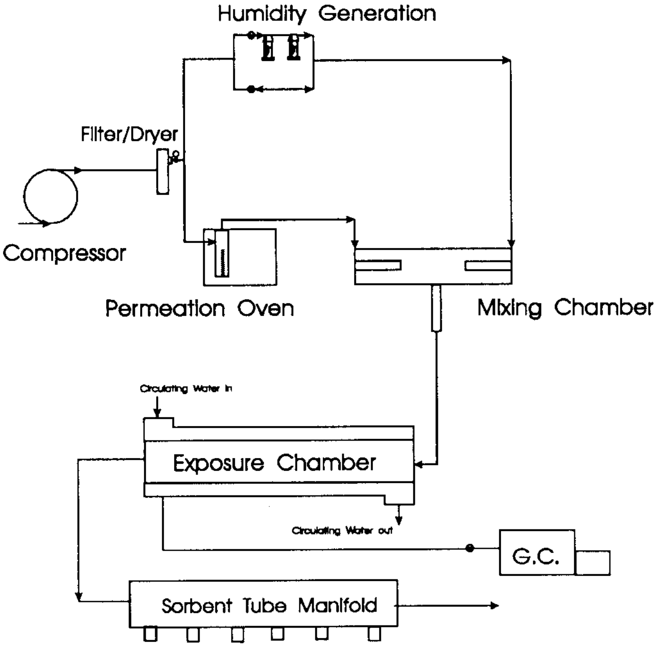
The experiments were based on the recommended procedures from the National Institute for Occupational Safety and Health[5] and on validation protocols developed from the experience of the researchers of Gilian Environmental Corp. The experiments were designed to characterize under controlled conditions the following: desorption efficiency, sampling rate and capacity, reverse diffusion, sample stability, temperature, and face velocity. It should be noted that all chamber experiments were performed at 80% relative humidity. Evaluation of the data was based on statistical tests using NIOSH criteria of +/- 25% accuracy at the 95% confidence level.

Experimental Section

The cornerstone of the validation work is the dynamic gas generating system. In order to determine sampling rates, measure performance parameters, and determine the accuracy of the badges, test atmospheres of known concentrations must be generated with a high degree of precision and accuracy.

The dynamic generating system is shown in Figure 1. It consists of five major sections: 1)the generation section, in which the vapor is produced; 2) the mixing manifold in which the concentrated vapors are diluted; 3) the humidity generation section; 4) the exposure chamber and 5) in-line instrumentation to verify the concentrations. The details of the system have been described in detail by G.O. Nelson [6] and Woodfin [7].

Figure 1 - Gas Generation System



Pure air was delivered to the system using two oil-free compressors. In addition, an activated charcoal bed and a refrigerant dryer were used downstream to ensure that clean, dry air was introduced to the system. Air purity was verified with instrumentation prior to all experiments. The vapor contaminant can be generated via one of two methods: 1) permeation tube or 2) syringe pump. In the case of benzene, permeation tubes were used due to the low levels needed. All other compounds used a syringe pump. The permeation rate was determined by daily gravimetric calibration. All flow rates were monitored with high precision rotameters which were calibrated both before and after each experiment with a Gilian Gilibrator bubble calibrator.

The mixing manifold was constructed of inert glass and constructed in such a manner so as to ensure homogeneous mixing. This was verified by conducting a smoke test prior to use. All tubing was constructed using 1/2" inside diameter Teflon to minimize the pressure drop and ensure inertness.

The desired relative humidity was achieved by splitting the diluent air and passing one portion through two water scrubbers in series. The other portion was bypassed. Needle valves controlled the flow through both sections therefore allowing the desired relative humidity to be achieved. The humidity was monitored with an electronic hygrometer and a portable RH meter.

The badge exposure chamber was constructed of inert glass. Its size allowed the face velocity to be controlled by the insertion of Teflon plates to reduce the cross sectional area. Flow rates were in the range of 18-25 liters/min and the minimum face velocity was 20 cm/s. Five badges were inserted into the chamber at one time with a minimum of 4 inches between them in order to prevent starvation at the surface. Air velocities were verified with a hot wire anemometer (TSI Inc.). The temperature of the exposure chamber was kept constant by means of a constant temperature bath circulator.

The system concentration was verified with an SRI model 8610 portable gas chromatograph with an FID detector and a six foot stainless steel column containing porous polymer packing.

An electronic gas sampling valve was used to obtain four samples
each hour. The GC was calibrated daily. In addition six charcoal tubes were connected to the chamber via a tube manifold. Flow rates were maintained at 50 cc/min +/- 0.1 with constant flow orifices. In all cases, experiments were only conducted when the computed concentration, the concentration measured by the gas chromatograph, and the concentration measured by the pump/tube system all were within 5% agreement of each other.

The Protocol

Gilian TRACEAIR^{TM} model OVM-2 badges were used throughout the protocol to ensure breakthrough did not occur. In each experiment 5 badges were used. In each case, 80% RH was used. All testing was done at 25 C unless otherwise noted. The only influence that water vapor has on the TRACEAIR^{TM} badges are that they compete for active sites on the charcoal, or in other words, affect the capacity. Therefore performance parameters measured at 80% relative humidity will be valid or superior at any humidity conditions below 80%.

Desorption Efficiency

Desorption Efficiency (DE) values were determined by using the phase equilibrium method. DE values for many organic compounds using carbon disulfide as a desorbing solvent are in the literature. However, DE values can vary significantly as a result of several factors, such as charcoal surface activity, loading, temperature conditions, etc.

In determining the DE values, the charcoal strip was placed in a 4.0 ml GC vial. Into this vial were added 1.5 ml CS_2 and benzene. The benzene concentration of this solution was 5µl/ml. 1.5 ml of this solution was also placed in an empty 4.0 ml vial. The two vials were agitated for 30 minutes, and the solutions were injected into an HP 5880 gas chromatograph with an FID detector. The DE was determined by dividing the benzene peak area of the vial with the charcoal by the peak area of the benzene from the empty vial. Fourteen independent determinations were made. The results are listed below in Table 1.

TABLE -1 Desorption Efficiency Results

(Phase Equilibrium Method)

Spike #	DE
1	1.005
2	1.030
3	0.983
4	0.974
5	0.988
6	0.984
7	0.984
8	0.987
9	0.981
10	0.985
11	0.978
12	0.980
13	0.946
14	0.954
Average DE	0.98
Std Deviation	0.02
% CV	2.0

Sampling Rate

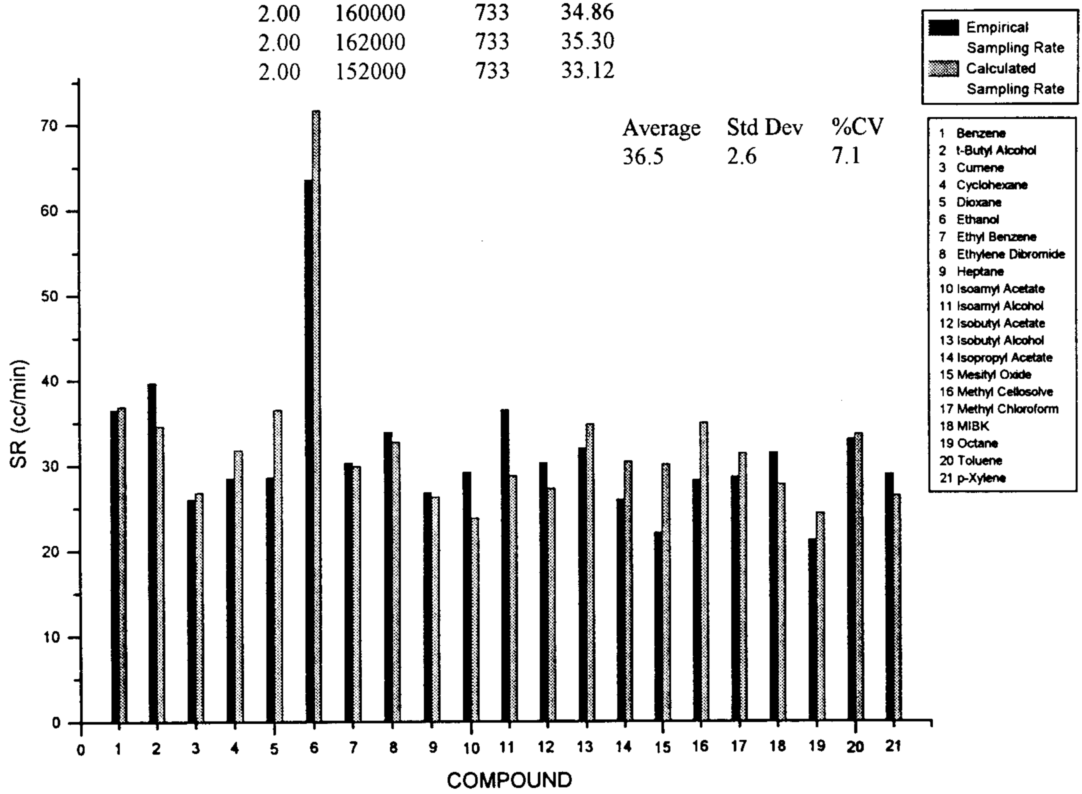
In order for Fick's law to apply, and for the passive monitor to be a useful device, the sampling rate must be constant across the range of concentrations expected during field application. In this experiment five monitors were exposed to four different concentrations, each at three different times. The concentrations tested were 0.5 ppm , 1.0 ppm, 2.0 ppm, and 3.0 ppm. The sampling rate for benzene was determined experimentally to be 36.5 cc/min. The results are listed below in table 2.

Table-2 Sampling Rate Determination

Conc. (ppm)	Mass (ng)	Time (min)	Sampling Rate	Average	Std. Dev.	%CV
0.50	14660	240	39.02	39.46	1.3	3.3
0.50	14730	240	39.21			
0.50	15240	240	40.56			
0.50	15370	240	40.91			
0.50	14120	240	37.58			
0.50	31730	493	41.11	38.39	2.7	7.0
0.50	30930	493	40.08			
0.50	26440	493	34.26			
0.50	30180	493	39.11			
0.50	28870	493	37.41			
0.52	43450	720	37.07	38.4	2.6	6.8
0.52	46290	720	39.49			
0.52	48150	720	41.08			
0.52	40480	720	34.53			
0.52	46700	720	39.84			
1.00	31280	250	39.96	38.99	0.6	1.5
1.00	30120	250	38.48			
1.00	30480	250	38.94			
1.00	30420	250	38.87			
1.00	30300	250	38.71			
0.99	51660	480	34.72	38.09	2.0	5.3
0.99	59500	480	39.99			
0.99	57250	480	38.48			
0.99	56750	480	38.14			
0.99	58170	480	39.11			

0.95	70890	720	33.10	33.25	1.7	5.1
0.95	68090	720	31.80			
0.95	67880	720	31.70			
0.95	72520	720	33.86			
0.95	76666	720	35.80			
3.35	86030	240	34.18	33.70	0.7	2.1
3.35	83620	240	33.22			
3.35	84430	240	33.54			
3.35	83010	240	32.98			
3.35	87090	240	34.60			
3.35	174000	480	34.56	33.89	0.7	2.1
3.35	173000	480	34.36			
3.35	169000	480	33.57			
3.35	165000	480	32.78			
3.35	172000	480	34.17			
2.00	164000	733	35.73	34.95	1.1	3.1
2.00	164000	733	35.73			
2.00	160000	733	34.86			
2.00	162000	733	35.30			
2.00	152000	733	33.12			

Average	Std Dev	%CV
36.5	2.6	7.1



Estimated Diffusion Coefficient

As previously described, the Wilke and Lee modification of the Herschfelder equation can be used to estimate diffusion coefficients.

$$Dg = \frac{[22.03 - 5.07\sqrt{.0345 + \frac{1}{MW}}][\sqrt{.0345 + \frac{1}{MW}}]}{I_d(3.62 + 1.18V_2^{\frac{1}{3}})^2} \qquad (5)$$

This equation has been simplified for a component in air (the diffusion coefficient of a species is a function of the medium). In the above equation *MW* is the molecular weight, I_d is the collision integral (and is a function of the molecular interaction), V_2 is the molal volume at normal boiling point. The reader is referred to Perry's handbook for an in depth discussion on estimated diffusion coefficients.

In the case of benzene, the collision integral is 0.5991, the molal volume is 96.0 cc/mole and the molecular weight is 78.11 g/mole. From equation (5), the diffusion coefficient for benzene is 0.0935 cm^2/s. The A/L ratio for the OVM-1 is 6.6 cm with one cover removed. After converting the diffusion coefficient to cm^2/min and multiplying by the A/L ratio of 6.7, the estimated sampling rate from equation (5) is 37.6 cm^3/min. Similarly, theoretical sampling rates are: ethyl benzene 30.4, toluene 34.1, xylene 26.9.

Capacity

Five OVM-2 badges were exposed to five times the TWA (5 ppm benzene) for eight and twelve hours. As shown in Table 3, analysis of the backup section showed that no breakthrough occurred. Therefore, the OVM-1 badge, with only one charcoal strip, is suitable for sampling at least five times the TWA for benzene.

Table 3-Capacity Determination

Conc. (ppm)	Mass(ng) (Front)	Mass(ng) (Bkup)	E. Time (min)	Average Mass	%CV
5.0	273000	ND	480	266800	5.0
5.0	254000	ND	480		
5.0	255000	ND	480		
5.0	266000	ND	480		
5.0	286000	ND	480		

Conc. (ppm)	Mass(ng) (Front)	Mass(ng) (Bkup)	E. Time (min)	Average Mass	%CV
5.0	466000	ND	720	444200	3.5
5.0	425000	ND	720		
5.0	447000	ND	720		
5.0	449000	ND	720		
5.0	434000	ND	720		

ND - None Detected

Reverse Diffusion

Reverse diffusion may be a significant problem when high peak exposures are followed by very low exposures, particularly for poorly retained species. Reverse diffusion can also become significant as the sorbent approaches saturation.

In order to test for reverse diffusion, five badges were inserted into the exposure chamber and exposed for four hours. A second set of five badges were placed in the chamber and exposed for a total of eight hours. After the first four hours, the analyte flow was turned off and the badges were exposed to pure air for an additional four hours to see if reverse diffusion took place. The data were analyzed by a statistical test of differences for small samples (N<30)[8] to assure that the badge performance was not significantly affected by reverse diffusion. When the universe variances are not known and the samples are small, it is necessary to use the *t* distribution in testing the differences between two means. Assuming normal distribution with a common variance, then the statistic

$$t = \frac{d - d_0}{s\sqrt{\frac{1}{N_1} + \frac{1}{N_2}}} \qquad (6)$$

has the *t* distribution with n = $N_1 + N_2 - 2$, where d= $\overline{X_1} - \overline{X_2}$ and d_0 = the stated difference being tested. *s* can be determined by

$$s = \sqrt{\frac{\sum x_1^2 - \sum x_2^2}{N_1 + N_2 - 2}} \qquad (7)$$

where $x_1 = X_1 - \overline{X_1}$ and $x_2 = X_2 - \overline{X_2}$. If we employ this test and take $\alpha = 0.05$, the critical values will be $\pm t_{0.05}$ for n= N_1+N_2-2.

Tables 4 and 5 list the data from the reverse diffusion experiment. Table 4 lists the data that was exposed to the analyte for four hours. Table 5 lists the data for badges that were exposed to the analyte for four hours and to pure air for four hours.

Table 4-Reverse Diffusion (Analyte 4 hours)

Chamber Conc.	Mass (ng)	Time (min)	Average Mass	%CV
3.3	84490	240	82754	3.2
3.3	80660	240		
3.3	81470	240		
3.3	80600	240		
3.3	86550	240		

Table 5-Reverse Diffusion (Analyte 4 hours, Air 4 hours)

Chamber Conc.	Mass (ng)	Time (min)	Average Mass	%CV
3.3	78840	240	79516	3.5
3.3	82080	240		
3.3	76770	240		
3.3	77110	240		
3.3	82780	240		

Using a two-tailed t test and α=0.05, the critical values are ± 2.306. By applying equations (6) and (7) above, s =0.009 and t_{calc}=0.45. Since $t_{calc} < t_{crit}$ or 0.177<2.306, it can be stated that reverse diffusion was not observed within experimental error from this data.

Sample Stability

The purpose of the sample stability is to ensure that the sample will be valid by the time it reaches the laboratory. Three sets of 5 badges were exposed for eight hours. The first five badges were analyzed after 48 hours (unrefrigerated). The second set of badges were analyzed after 14 days unrefrigerated. The third set of badges were analyzed after 14 days, the last 12 of which were refrigerated (this was to simulate two days for a sample to be mailed to the laboratory, after which it would be immediately refrigerated). Table 6 below summarizes the data from the storage stability test.

Table 6 - Sample Stability

Chamber Conc (ppm)	Mass (ng)	Time (min)	Average Mass	%CV
1.01	47720	480	50128	5.1
1.01	50420	480		
1.01	54320	480		
1.01	48850	480		
1.01	49330	480		
0.99	46630	480	47510	6.2
0.99	52340	480		
0.99	44880	480		
0.99	47990	480		
0.99	45710	480		
1.00	52840	480	52210	2.6
1.00	51590	480		
1.00	53470	480		
1.00	52980	480		
1.00	50170	480		

Temperature Effects

According to the kinetic theory of gases, the diffusion coefficient D is a function of absolute temperature and pressure by the equation:

$D= f(T^{3/2}/P)$ (8)

The mass collected, however, can be shown to be independent of pressure. The mass flux is a function of the diffusion coefficient and the concentration, or $M=f(D,C)$. From the Ideal gas law, we know that the concentration is inversely proportional to the temperature, or $C=f(P/T)$.

Making the above substitution, the Mass flux, and the Mass collected are related to the temperature by the following correlation[9]:

$M=f(T^{1/2})$ (9)

This temperature effect is slight, resulting in approximately a 1% change per every 10oF and can be corrected for during the calculations.

The temperature effects portion of the protocol was conducted by exposing three groups of five monitors for four hours each at temperatures of 10°C, 25°C and 40°C. The data for the temperature effects are presented by showing their effect on the sampling rate and are presented below in Table 7.

Table 7 - Temperature Effects

Temp (C)	Conc. (ppm)	Mass (ng)	Time (min)	Sampling Rate (cc\min)	Average	Std Dev	%CV
10	1.1	26620	240	32.21	30.46	1.7	5.6
	1.1	25800	240	31.21			
	1.1	23000	240	27.83			
	1.1	25790	240	31.20			
	1.1	24690	240	29.87			
25	0.99	31280	250	36.98	36.08	0.5	1.4
	0.99	30120	250	35.61			
	0.99	30480	250	36.04			
	0.99	30420	250	35.97			
	0.99	30300	250	35.82			
40	0.99	35160	274	37.93	37.35	1.0	2.7
	0.99	33910	274	36.58			
	0.99	35420	274	38.21			
	0.99	33350	274	35.98			
	0.99	35250	274	38.03			

The above data have been normalized by applying the appropriate temperature correction.

Velocity Effects

Perhaps one of the most significant influences on passive dosimeters is the effect of face velocity. If the face velocity is too low, starvation occurs at the surface of the badge, and therefore a minimum velocity is required for mass transfer of the contaminant to the surface of the monitor. On the other hand, if the face velocity is excessive, convective mass transport mechanisms become significant and the diffusion models begin to break down.

Many badge manufacturer's control the rate of mass transfer by employing membranes to minimize or control the convective airflow. The Gilian TRACEAIR^{TM} monitors do not utilize membranes but control the convective transport properties by optimizing the L/D ratio of the diffuser. In general, the L/D ratio should be approximately 3.0. An L/D ratio of less than three does not reduce the velocity effects, while an L/D ratio above 3.0 increases the likelihood of the molecule exiting the diffuser rather than entering. This is cornerstone of the TRACEAIR^{TM} design which does not require membranes or shields which can become clogged and which can also reduce the response time[9].

For the face velocity step of the experiment, two groups of five badges were each exposed. The first group of five was exposed at 20 cm/s and the final group was exposed at 300 cm/s. A special chamber with a greatly reduced diameter was used in order to allow this magnitude of velocity to be achieved. The data for the velocity effects, and how it influences the sampling rate are presented below in table 8.

Table 8 - Velocity Effects

Velocity (cm/s)	Conc. (ppm)	Mass (ng)	Time (min)	Average	%CV
20	1.02	22800	240	25040	5.7
	1.02	25660	240		
	1.02	26430	240		
	1.02	25800	240		
	1.02	24510	240		
300	0.99	27160	240	26552	3.7
	0.99	27830	240		
	0.99	26320	240		
	0.99	25230	240		
	0.99	26220	240		

It is apparent from the data above that there is no significant difference between each group.

Overall Accuracy and Precision

As stated earlier, the accuracy and precision of passive monitors must meet the NIOSH and OSHA requirements of +/- 25% at the 95% confidence interval. In order for a device to be a viable, useful product, it must meet this criteria across the full spectrum of conditions which will be encountered in the field.

The results of the laboratory validation work are depicted in table 8. Exposure concentrations ranged from 0.5 ppm to 3.0 ppm. In summary, the data shows that the Gilian TRACEAIR^{TM} OVM badges show the mean coefficient of variation was 4.6% with an absolute mean bias of 0.17%. This results in an overall accuracy of 9.4%. The complete set of protocol data is shown below in Table 9.

Table 9 - Overall Accuracy

Chamber Conc (ppm)	Mass (ng)	Time (min)	Badge Conc	Average	%CV	Bias
0.50	14660	240	0.53	0.54	3.7	8.0
0.50	14730	240	0.54			
0.50	15240	240	0.55			
0.50	15370	240	0.56			
0.50	14120	240	0.51			
0.50	31730	493	0.56	0.52	7.7	4.0
0.50	30930	493	0.55			
0.50	26440	493	0.47			
0.50	30180	493	0.53			
0.50	28870	493	0.51			
0.52	43450	720	0.53	0.55	7.3	5.8
0.52	46290	720	0.56			
0.52	48150	720	0.58			
0.52	40480	720	0.49			
0.52	46700	720	0.57			
1.00	31280	250	1.09	1.06	1.9	6.0
1.00	30120	250	1.05			
1.00	30480	250	1.06			
1.00	30420	250	1.06			
1.00	30300	250	1.06			

0.99	51660	480	0.94	1.03	4.9	4.0
0.99	59500	480	1.08			
0.99	57250	480	1.04			
0.99	56750	480	1.03			
0.99	58170	480	1.06			
0.95	70890	720	0.86	0.86	4.7	-9.5
0.95	68090	720	0.83			
0.95	67880	720	0.82			
0.95	72520	720	0.88			
0.95	76666	720	0.93			
3.35	86030	240	3.13	3.09	1.9	-7.8
3.35	83620	240	3.04			
3.35	84430	240	3.07			
3.35	83010	240	3.02			
3.35	87090	240	3.17			
3.35	174000	480	3.16	3.10	2.3	-7.5
3.35	173000	480	3.15			
3.35	169000	480	3.07			
3.35	165000	480	3.00			
3.35	172000	480	3.13			
2.00	164000	733	1.95	1.91	3.1	-4.5
2.00	164000	733	1.95			
2.00	160000	733	1.91			
2.00	162000	733	1.93			
2.00	152000	733	1.81			
	Absolute Mean Bias				0.17	
	Mean Coefficient of Variation				4.6	
	Overall Accuracy				9.4	

Overall Accuracy Charcoal Tubes

The performance of the Gilian TRACEAIR OVM monitors were compared with charcoal tubes. This has been the accepted sampling method over the years. Five charcoal tubes (50/100 mg) were connected to a sampling manifold. The flow through each tube was maintained at 50 cc/min using critical orifices checked weekly for accuracy. The results are listed in Table 10. From Table 10 it can be seen that the charcoal tubes had an M.C.V of 1.8 and an overall accuracy of 14.4. The difference between 9.4 and 14.4 is that the experiments were conducted using critical orifices. In actual use, air sampling pumps would add +/- 5% error since this is the NIOSH accuracy requirements for personal sampling pumps.

Table 10 - Overall Accuracy Charcoal Tubes

Chamber Conc (ppm)	Mass (mg)	Time (min)	Tube Conc	Average	%CV	Bias
3.1	.150	348	2.7	2.8	3.9	-9.0
3.1	.161	348	2.9			
3.1	.157	348	2.9			
3.1	.147	348	2.7			
3.1	.157	348	2.9			
7.5	.360	312	7.3	7.3	2.6	-2.7
7.5	.374	312	7.6			
7.5	.354	312	7.2			
7.5	.349	312	7.1			
7.5	.360	312	7.3			
15.2	.891	348	16.3	15.9	2.9	4.6
15.2	.906	348	16.5			
15.2	.850	348	15.5			
15.2	.850	348	15.5			
15.2	.863	348	15.7			
24.5	.380	120	20.1	20.5	3.8	-16.2
24.5	.404	120	21.4			
24.5	.369	120	19.5			
24.5	.386	120	20.4			
24.5	.401	120	21.2			

Absolute Mean Bias	-5.8
Mean Coefficient of Variation	1.8
Overall Accuracy	9.4

Field Validation

A field test was set up to monitor for benzene vapor at a United States Gulf Coast Chemical plant. In the field tests, a Gilian TRACEAIR OVM-1 monitoring badge and a charcoal tube were exposed simultaneously. A total of 34 pairs of the monitoring devices were used in the procedure. Sampling times were varied between 13 minutes and 690 minutes. Benzene concentrations ranged from as low as 0.004 ppm to 6.62 ppm. The results are tabulated below in Table 11.

Table 11-Field Validation Data

Sampling Time (min)	Badge Results (ppm)	Tube Results (ppm)	Variance
76	.05	.01	.04
30	6.62	8.89	-2.27
30	3.46	3.64	-.18
153	.59	.52	.07
158	.16	.17	-.01
18	.54	.21	.33
17	2.87	3.26	-.39
16	5.36	5.73	-.37
195	.30	.22	.08
360	.05	.06	-.01
510	.04	.02	.02
360	.03	.01	.02
610	.009	.004	.005
690	.03	.04	-.01
570	.03	.02	.01
525	.03	.03	0

600	.03	.02	.01
690	.01	.03	-.02
630	.01	.04	-.03
540	.02	.005	.015
390	.02	.01	.01
360	.04	.03	.01
690	.06	.12	-.06
510	.05	.01	.04
660	.04	.02	.02
660	.004	.02	-.016
690	.05	.10	-.05
15	2.91	3.23	-.32
205	.65	.37	.28
310	.13	.10	.03
310	.13	.10	.03
300	1.37	1.43	-.06
300	1.06	1.23	.17
13	.38	.24	.04

The data were analyzed by a statistical test of differences to determine if the badge performance was significantly different than the pump/tube performance. A t distribution is used to test the null hypothesis that the two means are the same within +/- 95% confidence. By using equations (6) and (7) and an $\alpha = 0.05$, the calculated critical value is t_{calc}= 0.45 (s=1.77). With t_{crit} = 2.0, it can be stated that the null hypothesis is accepted, i.e. no noted differences between the two population means was noted.

Toluene Data

Gilian TRACEAIR OVM-2 monitors were used to empirically determine the sampling rate for toluene and is listed in table 12. Refer to the Gilian Technical Reference guide for calculations using OVM-2 badges with backup charcoal strips. In addition, the desorption efficiency for Toluene was also determined and is listed in Table 13. From this data, i.e. DE and sampling rate, the overall accuracy for Toluene was determined and is listed in Table 14.

Table 12 -Toluene Desorption Efficiency

Spike #	DE
1	.994
2	.985
3	1.008
4	1.032
5	.974
6	.973
7	.882
8	.883
9	.991
10	.983
11	.980
12	.980
13	.976
14	.982
Average DE	.973
Std. Dev.	.04
%CV	4.2

Table 13 - Toluene Sampling Rate

Conc. (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Sampling Rate (ccm)	Average	Std. Dev.	%CV
42	570000	11960	120	32.37	32.24	1.3	4.0
42	605000	5151	120	33.45			
42	544000	4797	120	30.10			
42	584000	6805	120	32.51			
42	589000	6536	120	32.75			
50	2700000	26610	480	33.19	32.51	2.0	6.2
50	2732000	109000	480	31.74			
50	2521000	29770	480	2939			
50	2486000	43940	480	34.47			
50	2671000	28760	480	33.76			
96	1365000	12660	120	33.08	32.45	1.3	4.0
96	1345000	45820	120	34.33			
96	1293000	11200	120	31.29			
96	1332000	11260	120	32.22			
96	1291000	12890	120	31.33			
194	2414000	89370	120	30.68	31.55	0.9	2.9
194	2662000	36080	120	32.21			
194	2548000	26100	120	30.62			
194	2681000	46550	120	32.71			
194	2618000	29650	120	31.53			
					Average	Std. Dev	%CV
					33.1	2.8	8.6

Table 14 - Toluene Overall Accuracy

Chamber Conc. (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Badge Conc. (ppm)	Average	Bias.	%CV
42	570000	11960	120	40.94	40.78	-2.91	3.90
42	605000	5151	120	42.32			
42	544000	4797	120	38.07			
42	584000	6805	120	41.12			
42	589000	6536	120	41.43			
50	2700000	26610	480	47.35	46.80	-6.39	5.80
50	2732000	109000	480	51.01			
50	2521000	29770	480	44.40			
50	2486000	43940	480	44.33			
50	2671000	28760	480	46.93			
96	1365000	12660	120	95.63	93.82	-2.27	4.0
96	1345000	45820	120	99.26			
96	1293000	11200	120	90.47			
96	1332000	11260	120	93.15			
96	1291000	12890	120	90.58			
194	2414000	89370	120	179.24	192.39	-0.83	9.80
194	2662000	36080	120	188.21			
194	2548000	26100	120	178.88			
194	2681000	46550	120	191.10			
194	2618000	29650	120	224.53			
			M.C.V	2.4			
			Mean Bias	-3.1			
			Accuracy	7.9			

Xylene Data

Gilian TRACEAIR OVM-2 monitors were used to empirically determine the sampling rate for Xylene and is listed in table 15. Refer to the Gilian Technical Reference guide for calculations using OVM-2 badges with backup charcoal strips. In addition, the desorption efficiency for Xylene was also determined and is listed in Table 16. From this data, i.e. DE and sampling rate, the overall accuracy for Xylene was determined and is listed in Table 17.

Table 15 -Xylene Desorption Efficiency

Spike #	DE
1	.997
2	1.020
3	.942
4	.951
5	.973
6	.966
7	.958
8	.956
9	.955
10	.961
11	.9799
12	.9743
Average DE	.973
Std. Dev.	.04
%CV	4.2

Table 16 - Xylene Sampling Rate

Conc. (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Sampling Rate (ccm)	Average	Std. Dev.	%CV
46.9	636231	7522	122	27.0	28.1	2.2	7.8
46.9	678478	10643	122	29.1			
46.9	703178	4108	122	29.5			
46.9	591066	3154	122	24.8			
46.9	708053	7977	122	30.1			
95.7	1328939	24136	120	28.6	28.6	1.7	6.1
95.7	1220839	10963	120	25.7			
95.7	1406334	12484	120	29.6			
95.7	1355050	26484	120	29.2			
95.7	1432654	10805	120	30.1			
103.2	2889317	32177	240	29.6	31.3	1.4	4.3
103.2	2854615	33031	240	30.6			
103.2	2698075	30607	240	31.2			
103.2	2833573	24577	240	31.9			
103.2	2945838	28087	240	33.2			
190.8	2798632	26034	120	28.4	27.9	0.9	3.2
190.8	2845567	45840	120	28.1			
190.8	2936484	31512	120	26.5			
190.8	2963096	50654	120	27.7			
190.8	3149517	24399	120	28.8			

Average	Std. Dev	%CV
29.0	1.6	5.4

Table 17- Xylene Overall Accuracy

Chamber Conc. (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Badge Conc. (ppm)	Average	Bias.	%CV
46.9	636231	7522	122	43.8	45.5	-3.15	7.7
46.9	678478	10643	122	47.1			
46.9	703178	4108	122	47.8			
46.9	591066	3154	122	40.1			
46.9	708053	7977	122	48.7			
95.7	1328939	24136	120	94.3	94.6	-1.2	6.0
95.7	1220839	10963	120	84.9			
95.7	1406334	12484	120	97.8			
95.7	1355050	26484	120	96.4			
95.7	1432654	10805	120	99.4			
103.2	2889317	32177	240	100.9	99.3	-3.8	3.2
103.2	2854615	33031	240	99.9			
103.2	2698075	30607	240	94.3			
103.2	2833573	24577	240	98.5			
103.2	2945838	28087	240	102.6			
190.8	2798632	26034	120	19.39	205.7	7.8	4.5
190.8	2845567	45840	120	201.0			
190.8	2936484	31512	120	205.1			
190.8	2963096	50654	120	209.8			
190.8	3149517	24399	120	218.5			
			M.C.V	2.30			
			Mean Bias	-0.09			
			Accuracy	4.70			

Ethyl Benzene Data

Gilian TRACEAIR OVM-2 monitors were used to empirically determine the sampling rate for Ethyl Benzene and is listed in table 18. Refer to the Gilian Technical Reference guide for calculations using OVM-2 badges with backup charcoal strips. In addition, the desorption efficiency for Ethyl Benzene was also determined and is listed in Table 19. From this data, i.e. DE and sampling rate, the overall accuracy for Ethyl Benzene was determined and is listed in Table 20.

Table 18 -Ethyl Benzene Desorption Efficiency

Level 1	Level 2	Level 3
101.2	102.5	100
101.2	102.5	100
102.4	102.5	100
102.4	102.5	100
102.4	102.5	100
102.6	102.5	100
Avg. 102.2	Avg. 102.5	Avg. 100.0
St.Dev 0.9	St.Dev 0.0	St.Dev. 0.0
%CV 0.9	%CV 0.0	%CV 0.0

Avg DE	101.6
St. Dev	0.2
%CV	0.2

Table 19 - Ethyl Benzene Sampling Rate

Conc (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Sampling Rate (ccm)	Average	Std. Dev.	%CV
31	1530000	ND	376.2	29.6	29.2	2.9	10
31	1380000	ND	376.2	26.7			
31	1390000	ND	376.2	26.9			
31	1470000	ND	376.2	28.5			
31	1540000	ND	376.2	29.8			
31	1780000	ND	376.2	34.5			
65	3120000	30000	376.2	29.4	30.5	1	3.2
65	3180000	40000	376.2	30.2			
65	3430000	30000	376.2	32.3			
65	3220000	30000	376.2	30.4			
65	3150000	40000	376.2	29.9			
65	3210000	40000	376.2	30.5			
124	6150000	90000	376.2	30.7	31.4	0.6	1.9
124	6200000	80000	376.2	30.9			
124	6240000	110000	376.2	31.4			
124	6340000	70000	376.2	31.4			
124	6440000	110000	376.2	32.4			
124	6310000	80000	376.2	31.4			

Average	Std. Dev.	%CV
30.3	1.1	3.6

Table 20 - Ethyl Benzene Overall Accuracy

Chamber Conc. (ppm)	Mass Front(ng)	Mass Back(ng)	Time (min)	Badge Conc. (ppm)	Average	Bias.	%CV
31	1530000	ND	376.2	30.3	29.9	-3.7	10
31	1380000	ND	376.2	27.3			
31	1390000	ND	376.2	27.5			
31	1470000	ND	376.2	29			
31	1540000	ND	376.2	30.5			
31	1780000	ND	376.2	35.3			
65	3120000	30000	376.2	63.1	65.3	0.5	3.2
65	3180000	40000	376.2	64.8			
65	3430000	30000	376.2	69.3			
65	3220000	30000	376.2	65.1			
65	3150000	40000	376.2	64.2			
65	3210000	40000	376.2	65.3			
124	6150000	90000	376.2	125.8	128.4	3.5	1.8
124	6200000	80000	376.2	126.3			
124	6240000	110000	376.2	128.4			
124	6340000	70000	376.2	128.7			
124	6440000	110000	376.2	132.4			
124	6310000	80000	376.2	128.5			

M.C.V.	6.2
Mean Bias	0.1
Accuracy	12.5

Accuracy Calculations

The overall accuracy is a measure of the total error of the sampling device and the analytical procedure. The overall system accuracy is calculated from the equation:

Overall Accuracy = 2 M.C.V. + $|\overline{b}|$ (10)

where M.C.V. is the mean coefficient of variation, and b the absolute mean bias.

$$M.C.V = \sqrt{\frac{\sum_{i=1}^{n}(n_i - 1)CV_i^2}{\sum_{i=1}^{n}(n_i - 1)}} \qquad (11)$$

where n_i = the number of badges exposed

$CV_i = \frac{s_i}{x_i}$ = coefficient of variation at concentration i.

$s_i = \sqrt{\frac{\sum_{i=1}^{n}(x_i)^2 - \frac{(\sum_{i=1}^{n} x_i)^2}{n}}{n-1}}$ = the standard deviation at concentration i where x_i = badge-determined concentration at concentration i.

and $$|\overline{b}| = \frac{\sum_{i=1}^{n} b_i n_i}{i = 1\sum_{i=1}^{n} n_i} \qquad (12)$$

where $$b_i = \frac{\overline{X_i} - X_c}{X_c} x100 \qquad (13)$$

n_i = the number of badges exposed

$\overline{X_i}$ = the average concentration of n_i badges

X_c = the known chamber concentration

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