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**The history of development and validation testing of passive dosimeters is reviewed. Theoretical considerations including possible limiting factors or interferences, are pr sented. Laboratory and fi ld validation tests are critically reviewed and results are pr sented for comparative purposes. Evaluation of available data indicates tha passive dosimetry, with some exceptions, is an acceptabl method for monitoring gasses and vapors. Mos importantly, passive systems appear to be as reliable as the now accepted active sampling syst ms.**

# Passive dosimetry — state of the art review

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## introduction

Recognition, evaluation and control are the cornerstones of the application of that mixture of science and art known as industrial hygiene. These three tasks, however, are no longer the eminent domain of the industrial hygienist. In the past decade, a proliferation of training in the recognition of workplace hazards has been made widely available to workers and management alike. At the other end of the spectrum has been the training of individuals highly specialized in the control of specific hazards, especially those involving noise and toxic air contaminants. These developments are welcomed because they contribute significantly to the ultimate goal of protecting the health of workers by providing safer and more healthful workplaces.

At the same time, professional industrial hygienists recognize that often the critical step in the process is not recognition of toxicity, but evaluation of hazard which leads to the subsequent development of the most effective means of control where warranted. This key step of evaluation is the unique domain of the industrial hygienist, often supplemented by other members of the occupational health and safety team. Where evaluation requires the determination of worker exposure to airborne toxic substances, the industrial hygienist has seen a revolution in the development of sophisticated techniques and equipment.

The "organ-grinder" impinger sampler is a relic, having been replaced by constant flow, eight-hour battery-operated pumps, light enough to be carried by the worker. The liquid bubbler and impinger have been replaced by the charcoal and chemical substrate sampling tube. The laboratory has come to the field in the form of the portable gas chromatograph and infrared monitor, albeit with a price rise directly proportional to the sophistication of the equipment. Even the once lowly, direct-reading detector tube has become legitimate with the establishment of government programs to certify accuracy and precision.

But while most evaluation techniques were reaching the point where the industrial hygiene staff required the addition of someone with a Ph.D. in electrical engineering, a new device has appeared which has the key of simplicity — the personal passive dosimeter: personal, because it can be worn by the worker in close proximity to the breathing zone; passive, because there is no pump to move the air over a collector, which equates to fewer calibration and maintenance problems. Some quarrel with the term dosimeter, with purists preferring to call them collectors, monitors, or samplers. While many of the devices are collectors and require the application of subsequent analytical procedures, others provide for a more direct measurement of "exposure dose." Their basic appeal, however, is simplicity of use. Theoretically, elaborate calibration procedures are unnecessary, and all that is needed is a fairly reliable timepiece to measure exposure duration. There is some recognition that temperature and humidity may affect the observations; therefore, most manufacturers advise the user to report these environmental conditions to the analytical laboratory processing the dosimeter.

Rather than viewing passive dosimeters as another way to replace the industrial hygienist, industrial hygienists must recognize and appreciate the potential of the dosimeters in helping to achieve the hygienists' goals. That potential is significant in that personal dosimeters, if properly used, offer the opportunity to revolutionize the evaluation step. The parallels with detector tubes, as well as with noise and ionizing radiation dosimeters, are obvious. Indeed, the parallel with radiation dosimeters, especially film badges, is striking. The opportunity to significantly expand the measurement of worker exposure to many toxic materials can provide a quantum leap in our ability to provide safe and healthful workplaces. With any sampling device, however, there also must be the understanding that use of such device is only one part of the evaluation step. The concepts of proper selection of workers at risk; the understanding of limitations, interferences and similar factors, and ultimately the proper interpretation of the results are still key ingredients in the evaluation step. The possibility of "false negative" decisions leading to erroneous assumptions of safety or "false positive" conclusions leading to unwarranted expenditures of resources for controls still exists regardless of the measurement device used.

With the rapid proliferation of passive dosimeters in the past several years, it is appropriate that industrial hygienists evaluate the "state-of-the-art" and, as professionals, become involved with the proper application of these monitoring devices.

## theories of operation

In that passive dosimeters by definition do not use an air moving device to transport contaminated air to a collector, natural forces are relied upon to ensure that a representative amount of contaminant is "seen" by the detector. To date, one of two principles has been applied in the design of dosimeters. The first, and most widely used, is the principle of *diffusion* of contaminant molecules through a stagnant gas (air) layer. The second principle involves the absorption in and subsequent *permeation* of contaminant molecules through a membrane.

*Diffusional* monitors rely on the movement of contaminant molecules across a concentration gradient which for steady-state conditions, can be defined by Fick's First Law of Diffusion:[1]

$$W = -DA\frac{dc}{dx} \qquad (1)$$

where: W = mass transfer rate, ng sec,
D = diffusion coefficient, $cm^2$ sec,
A = cross sectional area of diffusion path, $cm^2$, and
dc dx = the instantaneous rate of change in concentration over diffusion path, (ng $cm^3$)$cm^{-1}$.

Considering the change in concentration ($C_1 - C_0$) over the total diffusion path length ($X_1 - X_0 = -L$), equation (1) becomes:

$$W = D\frac{A}{l}(C_1 - C_0) \qquad (2)$$

where: L = length of the diffusion (static) path, cm,
$C_1$ = ambient concentration of contaminant, ng $cm^3$, and
$C_0$ = concentration of contaminant at collecting surface, ng $cm^3$.

If an effective collection medium is employed, the contaminant concentration at the surface of the collector ($C_0$) can be assumed to be zero, and multiplying both sides of equation (2) by time, yields:

$$M = D\frac{A}{L}(C_1)\,t \qquad (3)$$

where: M = total mass transferred, ng, and
t = time that the badge is exposed to the contaminated air, sec.

It is also interesting to note that the units of the product of D and A, divided by L, are $cm^3$ sec, which are the same units associated with active air-moving devices such as personal sampling pumps.

Rearranging equation (3) as follows:

$$C_1 = \frac{ML}{DAt} \qquad (4)$$

it becomes apparent that five factors affect the measurement of the ambient air concentration of a substance ($C_1$). Two of the factors (L and A) are physical parameters associated with the construction of the dosimeter, one (M) is provided by measuring the total mass of contaminant collected by the sampler, another is the duration (t) the sampler was exposed to the contaminated atmosphere, and the final factor (D) is an individual property of each vapor or gas. It also is known[1] that the diffusion coefficient is directly proportional to the absolute temperature (T) of the vapor, raised to three-halves power and inversely proportional to the atmospheric pressure (P),

$$D \propto \frac{T^{1.5}}{P} \qquad (5)$$

Dosimeters that rely on the principle of *permeation* through a membrane are especially useful where the contaminant of concern is usually found mixed with other interfering vapors or gases or when a liquid collecting medium is employed. The goal then becomes to identify a membrane material that is highly permeable to the contaminant of interest and impermeable to most other components in the atmosphere, and or the collecting media.

The determination of ambient concentrations of a contaminant using a permeation device can be determined from the formula:

$$C = wk\,t \qquad (6)$$

where: C = concentration of contaminant, ppm,
w = mass of contaminant collected, $\mu$g,
k = permeation constant, ppm-hours $\mu$g, and
t = exposure time, hours.

The permeation constant (k) is determined experimentally and is a function of the specific membrane material and contaminant of interest.[2]

## sources of measurement error

The most obvious sources of error for both types of passive dosimeters are apparent from equations (4) and (6). Common to both badges are determinations of the mass of contaminant collected and the time of exposure of the dosimeter to the contaminated atmosphere. For the diffusional monitor, accurate knowledge of the physical parameters associated with badge construction (length and cross-sectional area) and the diffusion coefficient of the contaminant are important. There are at least nine prediction methods for calculating the diffusion coefficient, and in one study comparing observed and expected values for more than 100 compounds it was not uncommon to have less than 50 percent of the calculated results within ± 5 percent of the observed.[3] Montalvo has described a procedure for limiting errors associated with computed diffusion coefficients.[4] At

least one manufacturer, the 3M Company, makes available its procedures for determining sampling rates (DA/L) for its badges.[5] Its approach has been to experimentally determine the sampling rate for five or six compounds in a chemical family to establish the relationship between the diffusion coefficient and the measured sampling rates. Sampling rates for other compounds are determined from the diffusion coefficients calculated by the Hirschfelder equation and the empirical relationships developed from the test compounds. The rationale for the selection of the Hirschfelder equation is not given, but in the study of the nine diffusion coefficient formulas, the author concluded that for higher molecular weight compounds the Hirschfelder, Biard and Spatz equations were in closest agreement with determined values.[3] For the permeation monitor, accurate determination of the permeation coefficient for each monitor is necessary for obtaining accurate results. Factors influencing permeation include: thickness and uniformity of the membrane, affinity of the membrane for the analyte, swelling or shrinkage of the membrane, and possible etching by corrosive chemicals.

The problems associated with accurate determinations of the mass of the contaminant collected are similar to those involved with other collection devices such as charcoal or silica gel tubes, or to those in which the collection of the contaminant involves a chemical reaction with the collection medium. Using known amounts or concentrations of contaminants to determine collection and or desorption efficiencies is as critical a step for passive dosimeters as it is for other methods of collection. Saturation of the sorbent as well as the subsequent accuracy of analytical techniques are also part of the total error associated with the measurement.

Another common concern in all types of environmental measurements is the potential for interferences, either positive or negative, from other contaminants in the sampled air. As the evaluation of passive dosimeters has matured, increased attention is being paid to possible interferences in multi-contaminant exposure situations, in both the laboratory and field. In evaluating such interferences it should be recognized that there are several potential sites for such interferences to appear, *e.g.*, effects on adsorption or absorption efficiency of the sampling medium, chemical reactions of two or more contaminants prior to analysis, and the multitude of interferences associated with analysis of complex mixtures of gases and or vapors. These problems also are found in the more classical sampling and analytical methods.

Accurate measurement of the time the sampling device is exposed, is essential to most industrial hygiene sampling procedures. For both short-term and full-shift exposure measurements, errors less than one percent, *i.e.* 9 seconds in 15 minutes and 4.8 minutes over 8 hours, are not unreasonable goals.

For the diffusion coefficient and possibly the permeation constant, it would appear that three factors have the greatest effect on variability. These factors are the two already identified, temperature and pressure, and, less readily apparent, the velocity of the air external to the badges.

Considering temperature and pressure, and referring to equation (5) it can be shown that a temperature rise from 5 to 35 °C would give a 16 percent increase in the diffusion coefficient, while a rise in barometric pressure from 710 to 810 mm Hg would cause a 14 percent decrease.[1] However, at the same time, the changes in temperature and pressure also are affecting the concentration (mass volume; actually, density is the proper term but most authors use concentration) of the contaminant in that concentration is inversely proportional to the temperature and directly proportional to the pressure. As a result, the total mass (M) collected by the dosimeter is only slightly affected by temperature ($M \propto T^{1.5}$) and is independent of the pressure.[1] Consequently, while at ambient temperatures, the diffusion coefficient will increase about 0.5 percent per °C, and the total mass collected by the sampler will increase less than 0.2 percent per °C. Therefore, a temperature change from 25 to 30 °C, if uncorrected, will introduce a measurement error of less than one percent, while a change from 5 to 35 °C, if uncorrected, would introduce an error of about five percent.

The final source of error to consider is the velocity of the air external to the dosimeter; often this is referred to as face velocity. In an early assessment of face velocity effects, especially the lack thereof, Tompkins and Goldsmith point out that the important consideration is to contain all resistance to contaminant transport within the stagnant air layer inside the device.[1] As Jonas *et al.* subsequently noted, the face velocity directly affects the concentration gradient $C_1 - C_0$ in equation (2), and $C_1$ can no longer be assumed to be the ambient concentration when the air external to the badge is stagnant.[6] With zero or low face velocities, the length (L) of the diffusion pathway is effectively extended, and there is a decrease in the measured ambient concentration. In Tompkins' and Goldsmith's work with the GASBADGE™, they determined experimentally that as long as face velocities were greater than 7.5 cm sec (15 fpm) there was "no significant effect on dosimeter response;" however, experimental results supporting this conclusion were not presented.[1] High face velocities may also affect the concentration gradient. Commercially available diffusion devices rely on either a large ratio of diffusion path length to diffusion tube diameter or a wind screen to limit errors from this condition.

One of the most comprehensive tests to document sources of error has been conducted under contract for the National Institute for Occupational Safety and Health, and although concluded, it is not yet available as a public report.[7] The study involved evaluation of the GASBADGE and 3M Organic Vapor Monitor™ (the DuPont badge not being available at the time the study was initiated) via challenge with several organic vapors. The factors investigated were precision, effects of storage, maximum and minimum levels of quantification, face velocity effects, effects of temperature and humidity, off-gassing (related to storage), exposure to mixtures, problems associated with applicable analytical methods, and adsorption of the contaminant by the badge itself with subsequent leaching to the sensing surface. The possibility of adsorption by the badge body, thus giving

higher results if the contaminant is subsequently released to the active medium, is of special concern in using passive dosimeters to measure very low ambient concentrations such as might be found in air pollution studies. Such interest and concern are evidenced by research on the subject being sponsored by the U.S. Environmental Protection Agency (EPA).[8] Because of the lower concentrations involved with air pollution studies as opposed to workplace environments, the EPA also is concerned with the background or post-manufacture contamination levels associated with the sensing medium. Initially, the focus concerns organics and activated charcoal.

In summary, although numerous factors may affect the final calculation of concentration, only face velocity and the determination of the diffusion coefficient are unique sources of error for passive collectors. Therefore, if face velocities are sufficient to prevent "starvation" (probably greater than 7.5 cm sec) and if diffusion coefficients have been accurately calculated or experimentally determined, passive dosimeters should give results comparable to those obtained with traditional active sampling systems.

## statistical considerations

In evaluating any new monitoring method, extensive laboratory and field testing is necessary. Interpretation of the results of these tests requires the application of appropriate statistical techniques. The use of statistical techniques which are meaningful and easily understood is important; consequently, a discussion of the techniques used to evaluate passive dosimeters is appropriate.

There are numerous statistical tests which can be applied to both field and laboratory validation data. The main difference between the two situations is the degree of certainty of the "true" concentration of the monitored environment. In the field, the true value is usually an estimate based on the results of a standard sampling and analytical method. In the laboratory, experimental "known" concentrations are evolved and are then used for comparison with the concentrations estimated from sampling and analytical methods.

What is often not stated is that a certain amount of error also exists in the determination of laboratory-evolved "known" concentrations. These errors are often difficult to estimate. The "known" concentration is often calculated by weighing a syringe before and after an injection period (mass balance) or simply by injecting or allowing to diffuse a measured volume. It is assumed that the aliquot delivered was vaporized or diffused into a test chamber of known size. Possible sources of error include adsorption to or leaks from the test chamber, absorption and adsorption to articles placed in the chamber, degradation of the analyte by air oxidation or hydrolysis at high relative humidities, and error in measuring the injected contaminant. A backup monitoring system may be used to ensure close proximity to the "known" concentration. For example, an infra-red (IR) analyzer or gas chromatograph may be used as a check on a known" concentration.

In other instances an IR analyzer or a direct reading instrument may be the only method for determining "known" concentrations. In this case the error in the instrument can be calculated or estimated. Charcoal tubes and critical orifices also have been used to measure "known" concentrations. If error in both the "known" concentration and the estimated concentration are considered, statistical tests used to validate the experimental method become considerably more complicated; hence, the error in measuring the "known" concentration is usually assumed to be small and unimportant.[9] Methods described above for determinint the "known" concentration vary in their accuracy, a fact which should be considered when evaluating validation data for any sampling and analytical method.

When one is validating a method in the laboratory, there are two main considerations: the variation of the samples or data points about their mean, and the deviation of the sample mean from the true mean or "known" concentration. The first consideration often is called precision and is probably the most important and reliable measure as it does not depend on the error in determining the "known" concentration. Precision is estimated by determining the coefficient of variation (CV) or relative standard deviation of the data set as follows:

$$CV = \frac{s}{X} \times 100 \qquad (7)$$

where: $s$ = Standard deviation of sample data set, and
$X$ = Mean of sample data set.

Where samples are taken at several concentrations, it is necessary to determine a pooled coefficient of variation which involves determination of number of levels tested.[10] It should be noted that determining the number of concentrations (or more appropriately, the number of statistical levels) is not always straightforward. For example, if 10 samples are taken at each of three concentrations, and if within each concentration five of the samples are collected over four hours while the other five are collected over eight hours, are there three levels or six levels? The important point to consider is whether the differentiation of a level is based upon an anticipated difference in the sample mean. Certainly if the investigator designs the experiment with different time levels, there is an anticipated effect of time on the mean. Unfortunately, when experiments are so designed, statistical analyses at the various levels usually are not performed.

The second statistical consideration, the difference between the sample mean and the "known" value, is sometimes called accuracy, but the term bias is more appropriate. It is defined as:

$$b = \frac{X - X_0}{X_0} \times 100 \qquad (8)$$

where: $X$ = mean of sample data set, and
$X_0$ = "known" value at level tested.

If more than one level is sampled, it is necessary to determine the pooled bias of the data set.[11]

The bias for a given set of data can sometimes be corrected. If the average bias (either the average of several samples at one level or the pooled bias for several levels) is large, one should note if the components of the bias value (either the individual samples or the levels) are consistently negative or positive. If the bias is large and varies consistently in one direction, the precision nevertheless may be quite small. In this case a physical or chemical variable may be consistently affecting the method (a systematic as opposed to random error), causing the experimental values to constantly fall short or long of the "known" concentration. This form of bias should be corrected.

In addition to these statistical tests, others have been used to assess the validity of passive monitoring systems. Overall system accuracy[11] has been defined as (2 × CV) + absolute bias, expressed as a percent. Others[12] have used the percentage of the "known" concentration accounted for by the sample mean ± two standard deviations as well as the term systematic error[13,14] which is equivalent to overall system accuracy. Relative standard deviation has also been used, and is defined as the equivalent of CV.[15] Additionally, some authors report only raw data while others report means without standard deviations or sample sizes, and various other combinations. While all of these statistical determinations have utility, it seems important for comparative purposes to consistently use those determinations which give the most information in the simplest form. Certainly, bias and precision meet these criteria.

Discussion of one other point seems necessary. NIOSH[10] has proposed as a guideline for their own internal purposes that sampling and analytical methods meet a minimum requirement of ± 25 percent accuracy; that is, the absolute total error of the method should be less than 25 percent in at least 95 percent of the sample population (assuming a normal distribution). NIOSH derives the maximum precision value for an unbiased method given the accuracy criteria stated. This value (12.8 percent) is the maximum precision value acceptable for an unbiased method. Although the 25 percent accuracy criterion has been criticized by some authors,[16] it was adopted for NIOSH's own internal use and is not meant as public policy. However, OSHA adopted the same criterion for the benzene standard, without a complete derivation or explanation. Consequently, this criterion has been criticized and alternatives have been proposed.[17] A second important point is that bias is also considered in the ± 25 percent criterion according to a somewhat complex statistical relationship,[10] but the overall system accuracy as defined earlier[11] is a fair approximation if the method has a true bias, *i.e.*, its mean is statistically different from the "known concentration." A final point is that as the number of samples at a level increases, the standard deviation and CV should decrease. These considerations are important when evaluating passive monitor validation data, especially in those cases where manufacturers have stated that they have met the 25 percent accuracy criterion.

For field comparisons of conventional and passive monitors, different statistical tests are necessary. If passive monitor values, for example, are plotted against charcoal tube results (Y vs. X) and more than one concentration is sampled, one would expect an increase in X to cause an increase in Y. If the increase is linear, and the sample values lie on the regression line, the correlation coefficient (r) would have a value of one. If a change in X brings about an equal change in Y, then the slope would also have a value of one. If the individual values for the two devices are indeed equivalent, the line should intercept the origin. Each of these relationships is expected within reason. The difference of the slop from one, the correlation coefficient from one, and the intercept from zero can and should be tested.

In order to perform the regression analysis described above we must assume that X (active sampling data) is not subject to error. Of course, we know and can calculate under laboratory conditions the error of active sampling systems. There are at least three reasons why this error is often overlooked. First, it is assumed that consideration of the error in X would only cause small differences in regression analysis results. Second, in addition to laboratory demonstrated error, a range of errors introduced by varying environmental conditions must be considered. While difficult to assess, these errors may have a profound effect on X, and indeed the error in the X measurement may be as great or greater than that for Y. Finally, if the error in X is to be considered the statistical tests are complex. Such tests have been discussed for biological problems;[18] however, the theories apparently have not been applied to sampling and analytical methods even though their appropriateness has been recognized.[19]

## applications

From a historical vantage, one of the earliest reports of a "passive" monitor for evaluation of airborne contaminants was patented by Gordon and Lowe in 1927.[20] Their gas detector for carbon monoxide involved an "easily frangible vessel containing a solution of salts including palladium chloride, and a covering for said vessel of a light colored absorbent material." The principle involved breaking the vessel (a small ampule) and noting the subsequent color change of the solution as it reacted with the carbon monoxide on the light colored absorbent material. This type of semiquantitative device was certainly a forerunner of those that are available today, though it was undoubtedly affected by air velocity as a stagnant air layer was not employed.

An extension of Gordon and Lowe's concepts in the late 1960's provided the basis for Plantz *et al.* to develop a personal dosimeter for measuring hydrazine, unsymmetrical dimethylhydrazine and monomethylhydrazine.[21] The reaction of these compounds with a "colorimetric substance" (bindone) produced a purple color, the intensity of which was dependent on both concentration and duration of exposure. Color standards then were used to estimate the concentration as a function of the time the badge was exposed to the contaminated air; consequently, the method was only semiquantitative. In considering sources of error the authors noted that the purple color would also be produced by all volatile bases that were tested, including ammonia, aliphatic amines, aniline and cigarette smoke.

Of interest in this review, however, are *quantitative* devices based on the principle of either gas or vapor diffusion or permeation through a stagnant air layer. The first such device to be reported in the literature was described by Palmes and Gunnison in 1973.[22] Their device employed the principle of gas diffusion to determine airborne concentrations of sulfur dioxide and will receive further consideration subsequently. To gain the best overview of the various applications of these concepts, it is probably best to proceed by considering first the inorganic and then organic gases and vapors.

## inorganic gases and vapors

### *ammonia*

In 1978, Mazur *et al.* described the use of the Abcor GASBADGE to sample employee exposure to ammonia (this device currently is not marketed).[23] The investigators replaced the charcoal pad normally found in the GASBADGE with an acid impregnated absorption pad. Of three acids tested, phosphoric was most successful in providing the best approximation of theoretical concentrations. They determined, however, that volatile amines, specifically cyclohexylamine, could produce high readings, as high as 185 percent of the synthetic atmosphere. This led them to replace the glass fiber draft shield on the front of the GASBADGE with a "charcoal impregnated glass fiber filter which had been pretreated with alcoholic KOH containing 0.1 percent surfactant." The charcoal served to adsorb amines as they diffused into the dosimeter, while the KOH (aided by the wetting agent) eliminated irreversible ammonia adsorption by the charcoal, which would have caused underestimation of the ambient concentration. Additional laboratory experiments demonstrated that storage time of up to 47 days, prior to analysis, did not appear to adversely affect the results.

More recently, DuPont has developed a commercially available system for the measurement of several airborne contaminants including ammonia. In 1981, Kring *et al.* described DuPont's PRO-TEK™ system for ammonia, nitrogen dioxide and sulfur dioxide sampling analysis using a colorimetric readout instrument.[24] The ammonia badge relies on molecular diffusion of ammonia and subsequent chemical reaction with a solution of 0.3N boric acid and 0.03N sodium potassium tartarate (*sic*). After exposure, the reagent pack is removed from the badge holder and analysis is initiated by pressing reagent "blisters" which are adjacent to the absorbing solution. This action causes the release of a modified Nessler's reagent and the subsequent development of a colored solution. For ammonia, maximum color intensity is developed at 425 nanometers. The absorbance of the sample is then compared against a standard curve based on Beer's Law. After determination of the precision of the analytical method and verification of the linear range of the color chemistry, laboratory testing was conducted to establish the operational range as well as precision and accuracy of the overall method (see Table I). The minumum and maximum limits of the sampling range were found to be 50 and 500 ppm-hours, respectively. For an eight-hour time weighted average, these values correspond to one-fourth and two and one-half times the current ACGIH Threshold Limit Value of 25 parts per million.[25] In considering sources of error, environmental effects including temperature (10 to 40 °C), relative humidity (10 to 80 percent), pressure (730 to 790 mm Hg), and face velocity (2.5 to 125 cm/sec) were included. Of the environmental factors evaluated, temperature and the concentration of the contaminant were identified as being responsible for 98 percent of the data variation. For ammonia, a temperature correction factor of 0.6 percent per degree centigrade was suggested. Also investigated was the storage stability of both unexposed and exposed badges. Results indicated that refrigerated storage is necessary to extend the shelf life of unexposed badges. Once the badge is exposed to ammonia and before the reagents are mixed, the badges can be stored for one (room temperature) to three (refrigerated) weeks without losing any absorbed contaminant. Once the reagents are mixed and color formation is started, the badge should be read within 90 minutes. Additional testing results conducted by DuPont are shown in Table I.[26]

### *carbon monoxide*

Shor and Anders, of the 3M Company, have described the 3M "direct-read diffusional monitor" for evaluation of exposures to carbon monoxide.[27] The principle involves the reaction of the carbon monoxide and an unreported reagent(s) to give a visible color change from pink to tan. Theoretically, "if any pink color is observable at the end of the exposure period, then the exposure was less than the one time-weighted-average of 400 ppm-hours." They also state that noting the time to the endpoint allows for calculation of the average concentration of carbon monoxide during the exposure period. The authors present summary results of laboratory evaluations using an infrared radiation device to establish "known" concentrations (see Table I).

### *chlorine*

Hardy *et al.* have described a personal chlorine monitor (REAL, Inc.) which employs the principle of permeation of the gaseous contaminant through a silicone membrane and into 10 mL of a fluorescein-bromide solution.[28] Colorimetric techniques then can be applied to determine the chlorine concentration. The authors report a detection limit of 0.013 ppm chlorine for an eight-hour exposure, with a "working range" of 0.1 to 2.0 ppm. They also suggest that for shorter time periods, concentrations of up to five ppm can be determined. Other observations included effects of temperature, humidity, absorbent concentration, pH and response time, with all laboratory results presented graphically.

Moleculon Research Corporation has recently introduced a chlorine monitoring device which relies on plastic film impregnated with liquid reagents.[29] Exposure of the badge to chlorine gas gives a visible, "blue-purple," color change. Optical transmission measurements, and comparison with a standard curve, can then provide quantitative exposures in ppm-hours. The manufacturer's summary results indicating effects of temperature, humidity, wind velocity and concentration are reported as presenting an error at the 95 percent confidence level, which is "less than ± 15 percent."

TABLE I
Inorganic Gases and Vapors Laboratory Results

| Chemical | D simeter[A] | Bias[B] | Precision[C] | Range[D] (ppm) | Reference | Notes |
|---|---|---|---|---|---|---|
| Ammonia | DP | 0.5 | 7.4 | 20-50 | 24 | |
| | DP | 0.5 | 6.9 | 20-48 | 26 | |
| | GB | −3.2 | 9.3 | 6-62 | 23 | E,G |
| Nitrogen | GB | | 21.7 | 4-11 | 1 | H |
| Dioxide | DP | −3.2 | 7.5 | 4-11 | 38 | |
| | DP | −0.9 | 8.7 | 4-11 | 24 | |
| | MDA | −4.9 | 4.1 | 6-9 | 36 | E,G |
| Sulfur | GB | | 13.8 | 4.6-5.3 | 1 | H |
| Dioxide | DP | −1 | 5.8 | 4-11 | 38 | |
| | DP | −0.8 | 7.5 | 4-11 | 24 | |
| Hydrogen Sulfide | GB | | 15.3 | 1.6-2.2 | 1 | H |
| Mercury | 3M | 0.5 | 9 | 0.03-0.3mg/m³ | 32 | F |
| | 3M | 17 | 2 | 0.05-0.2mg/m³ | 33 | E,G |
| CO | 3M | 0.3 | 4.7 | 50-1830 | 27 | G |

[A]DP=DuPont Pro-Tek Colorimetric System Badges, 3M=3M Company Monitor, MDA=MDA Scientific, GB=Abcor GASBADGE

[B]See text, equation (8)

[C]See text, equation (7)

[D]Some values are rounded to nearest whole number

[E]Bias consistently negative

[F]Results derived from Table III of McCammon *et al.*[32]

[G]Results calculated from data provided in reference

[H]This product is not currently marketed

[I]Bias could not be calculated from data given

***hydrogen sulfide***

In 1977, Tompkins and Goldsmith described the development of the GASBADGE personal sampler.[1] Although later work with this device focused on the collection of organics on an activated charcoal substrate, initial studies researched sampling of both organic and inorganic compounds. (The GASBADGE for organic vapors is now marketed by National Mine Safety Company, and those for inorganic vapors are not currently marketed.) Applications involving inorganic gases relied on collective elements of an "appropriate substrate impregnated with a chemical medium specific for the contaminant of interest." Based on 60 observations, the authors' statistical summary is presented in Table I. Eighty percent of the measurements were within ± 25 percent of the "true" value. Challenge concentrations were established in a "well-mixed" environmental test chamber and were measured with an "independent wet-chemistry sampling train."

Hardy and associates have described a permeation device (REAL, Inc.) which relies on the permeation of $H_2S$ through a dimethyl silicone membrane and subsequent reaction with a solution of 0.2N sodium hydroxide and EDTA.[30] The colored product (methylene blue) is measured spectrophotometrically and compared with a calibration curve to determine ppm-hours. A knowledge of exposure time then allows for the determination of average exposure over the measurement period. The authors note that a critical step in the development of such a device is the experimental determination of the permeation constant (see Equation 6), which involves calibration of each monitor by exposure to known concentrations of the contaminant. The results of this laboratory research demonstrated a detection limit of 0.01 ppm for an eight-hour exposure, with a working range of 0.1 to 20 ppm and a linear response up to 200 ppm. The working range corresponds to one one-hundredth to two times the current eight-hour TLV of 10 ppm.[25] Evaluations of environmental effects indicated that neither temperature, over the range of −3 to 39 °C, nor humidity, from 0 to 99 percent relative, caused any significant variations in response of the device. Further research demonstrated a good response to high concentrations in less than one minute, adequate sample stability up to 10 days if EDTA is used in the absorbing solution, and negative and positive interferences, respectively, from chlorine gas and nitrogen dioxide. Precision and bias were not reported.

Another approach for the determination of gaseous hydrogen sulfide has been reported by Graedel and Franey.[31] Their research involved using a semiquantitative method without a stagnant air layer and relying on the discoloration of lead-stabilized polyvinyl chloride (PVC). The technique involves the diffusion of gas in a polymer and, at high $H_2S$ levels, the detection rather than the measurement of toxic levels of $H_2S$. Screening applications for low level exposures also are discussed.

***mercury***

In 1977, McCammon and Woodfin of NIOSH reported the results of a laboratory evaluation of 3M's mercury vapor monitor.[32] The monitor's operating principle involves molecular diffusion and deposition of mercury vapor on a gold substrate. The resulting change in electrical conductivity across the gold foil is related to the amount of mercury absorbed by the foil. Three other sampling methods, all of which involved the active movement of air, also were investigated and include the LASL tandum sampling tube, the hopcalite tube, and the iodine impregnated charcoal tube. For the passive monitor, precision and accuracy, the effects of face velocity and temperature, and potential interferences were investigated. Concentrations of mercury vapor in an exposure chamber were monitored with an ultraviolet mercury vapor meter, which in turn was calibrated by measurements using the LASL method. To determine precision of the monitors, 12 devices were exposed to a test atmosphere. Results from three measurements of the test atmosphere using the LASL method gave an "expected" concentration of 0.056 milligrams of mercury per cubic meter of air (mg $m^3$), with a standard deviation (SD) of 0.002 mg $m^3$ and a coefficient of variation (CV) of 0.037. Precision and bias calculated for the data given in Table III of McCammon *et al.*[32] is summarized in Table I. A least squares regression analysis of the combined precision and accuracy results for the passive dosimeters versus the "known" concentrations gave a Y intercept of −0.004 mg $m^3$ and a slope of 1.003. Tests for the effects of face velocities from 25 to 125 cm sec (50 to 250 fpm) did not appear to have any adverse effect on performance, while variation of temperature experimentally confirmed its effect on both the diffusion constant and the concentration of the contaminant. The potential effects of changes in relative humidity were not discussed by the authors. The other area of investigation in this study involved potential interferences of chlorine, sulfur dioxide, and hydrogen sulfide. Concomitant and sequential exposure to mercury and chlorine, the latter at high levels (5.8 ppm), produced a negative bias, but a similar effect was observed with the UV meter and the LASL system. The authors suggested that the mercury and chlorine may have been reacting to form mercuric chloride which was not being measured by any of the systems. The interference effects of sulfur dioxide and hydrogen sulfide, although less than chlorine, also were confirmed.

In 1980, McCammon and his NIOSH and OSHA coworkers conducted further tests of the four previously described mercury vapor sampling and analytical methods.[33] The design of this laboratory experiment involved intercomparison of four methods, and the findings suggested that the variability of the iodine charcoal tube method is significantly different from that of the other three methods. It was observed that the other three methods, including the 3M passive dosimeter, exhibited good precision over the concentration range of 0.05 to 0.2 mg $m^3$ as shown in Table I.

Recently SKC, Inc., introduced a gas monitoring badge (produced by GMD, Inc.) which uses the principle of molecular diffusion (without a stagnant air layer) to collect mercury vapor.[34] The sampling media is referred to as "Hydrar Sorbent," and "extensive" but unpublished field and laboratory testing are cited to show that "chlorine, moisture, etc., *do not interfere* with measurements. HYDRAR is developed from a "manganese dioxide catalyst material similar to 'Hopcalite.' " Quantitative determination is made by chemical desorption of the mercury and analysis with atomic absorption.

***nitrogen dioxide***

In 1976, Palmes *et al.* reported the results of their evaluation of a personal sampler for nitrogen dioxide ($NO_2$).[35] This work was an extension of their earlier pioneering efforts in developing a personal sampler, employing the principle of gas diffusion, for sulfur dioxide.[22] In their design, the sampling device was a 1.3 cm (0.5 inches) acrylic tube, 7.1 cm (2.8 inches) long. At the "closed" end of the diffusion path (tube) were placed three stainless steel grids coated with triethanolamine (TEA). TEA was selected because: 1) it captures $NO_2$ efficiently, 2) it provides a stable sampling surface, and 3) it yields a chemical complex with $NO_2$ that is very stable over time. Subsequent analysis yielded a colored complex whose absorption was measured at 540 nanometers. Results were then compared against a standard curve which obeyed Beer's Law. The experimental evaluation of the $NO_2$ sampler involved chamber measurements compared with "known" values determined by the volume of $NO_2$ introduced to the chamber or the weight loss of $NO_2$ from a permeation tube. Although neither individual nor summary results were presented, graphical comparison of the data indicated a close agreement between the passive sampler results and theoretical concentrations. The effects of wind velocity and direction as well as stability over time also were considered. In determining wind effects, the uptake of water vapor, rather than $NO_2$, was measured. The results indicated that there was an increase in average uptake with increased velocity and that the 45 degree incident angle gave the highest uptake (135 percent at 258 cm sec). Across all angles of exposure (0 to 180 degrees) the average uptake increased from 2 to 14 percent as the wind velocity increased from 50 to 258 cm sec (100 to 516 fpm). Stability studies indicated that the badges could be used for months both after preparation and before exposure as well as after exposure and before analysis.

In the previously described studies with the GASBADGE, Tompkins and Goldsmith also monitored for nitrogen dioxide.[1] Their summary results for 82 observations showed accuracies and precisions as summarized in Table I. Eighty-five percent of the observations were within ± 25 percent of the "true" value.

A commercial model of the Palmes passive sampler has been marketed by MDA Scientific, Inc., and additional laboratory testing demonstrated a linear collection efficiency for any given dose, *i.e.*, concentration × time (see Table I).[36] The sampler exhibited a consistently negative bias as compared to concentration determinations using a continuous monitor and the NIOSH wet chemical method.

As noted earlier, the DuPont PRO-TEK system includes a badge for nitrogen dioxide. Laboratory test results of this device are shown in Table I.[37]

### *sulfur dioxide*

As noted previously, pioneering work in 1973 on the design of a sampling device which relies solely on diffusion of gaseous contaminants through a stagnant air layer is attributed to Palmes and Gunnison.[22] Their initial studies involved experimental work on different tube lengths. The collecting medium was a complex of mercuric chloride and the final analysis involved colorimetric determination. The studies demonstrated that, except for very short diffusion paths (tube lengths), the diffusion monitor satisfactorily duplicated the results obtained by both wet chemical and conductrimetric measurements. Although this study did not go into the ramifications of environmental effects and interferences, it should be recognized as an important step in developing a new industrial hygiene technology.

The last of the three inorganic gases looked at by Tompkins and Goldsmith in their studies of the GASBADGE was sulfur dioxide.[1] Summary data for 23 observations on this gas are included in Table I. One hundred percent of the observations were within ± 25 percent of the "true" values.

The results from DuPont's tests on their sulfur dioxide badge also are shown in Table I.[38]

## organic gases and vapors

Most passive dosimeters designed to sample for organic gases and vapors use activated charcoal as the adsorbing medium. As we know from its extensive use in active systems, activated charcoal has an affinity for a wide range of organic compounds. Consequently, the discussion on the applications of passive dosimeters for the measurement of organic gases and vapors first will focus on devices using activated charcoal and then will turn to specific organics which rely on other collecting media.

**TABLE II**
**Organic Gases and Vapors Laboratory Results**

| Chemical | Dosimeter[A] | Bias[B] | Precision[C] | Range[D] (ppm) | Reference | Notes |
|---|---|---|---|---|---|---|
| Carbon Tetrachloride | DPA | 0.4 | 4.4 | 3-18 | 10 | E |
| Toluene | DPA | 0.3 | 5.25 | 57-228 | 45 | |
| | NMS | −1.7 | 1.7 | 12-47 | 13 | F,J |
| Formaldehyde | DP | 1.5 | 6.3 | 0.2-4.2 | 55 | |
| Benzene | DPB | 3.3 | 4.7 | 3-24 | 46 | |
| | NMS | −4.1 | 1.7 | 0.8-5.4 | 13 | F,J |
| | NMS | 1.8 | 17 | 13-13.5 | 1 | E,G,J |
| Ethylene Oxide | 3M | −1.4 | 3.2 | 300 | 53 | J |
| Halothane | 3M | 3 | 7.4 | 0.5-20 | 44 | J |
| Enflurane | 3M | −2.8 | 4.8 | 0.5-20 | 44 | J |
| Acrylonitrile | NMS | 0.03 | 8.7 | 0.7-19 | 39 | |
| Hexane | NMS | −1.2 | 2 | 10-37 | 13 | F,J |
| Vinyl Chloride | R | −0.2 | 3.7 | 1.5-14 | 2 | H,J |
| Methyl Chloroform | 3M | −5.9 | 4.7 | 160-840 | 48 | I,J |
| | DPA | −10.6 | 4.5 | 160-840 | 48 | E,I,J |
| | NMS | 2.4 | 2 | 15-65 | 12 | F,J |
| Trichloro-ethylene | 3M | −3.9 | 7.6 | 20-200 | 48 | I,J |
| | DPA | −6.9 | 7.7 | 20-200 | 48 | E,I,J |
| | NMS | −0.5 | 1.9 | 15-67 | 12 | F,J |

[A] 3M = 3M Company Organic Vapor Monitor, DPA and DPB = DuPont PRO-TEK G-AA and G-BB Organic Vapor Badges, NMS = National Mine Safety GASBADGE, R = Real, Inc. MINIMONITOR, DP = DuPont PRO-TEK System Colorimetric Badges

[B] See text, equation (8)

[C] See text, equation (7)

[D] Some values are rounded to nearest whole number

[E] Small sample size

[F] Knowns were calculated using charcoal tubes with critical orifices. This could affect the bias measure

[G] Preliminary results

[H] Permeation dosimeter

[I] Bias consistently negative

[J] Results calculated from data provided in reference

***activated charcoal devices***

As of March, 1982, there were four manufacturers of passive dosimeters which rely on diffusion and subsequent adsorption on to activated charcoal: National Mine Service Company (GASBADGE), 3M Company (Organic Vapor Monitor), DuPont Company (PRO-TEK, G-AA and G-BB Organic Vapor Air Monitoring Badge), and the Mine Safety Appliance Company (Vaporgard Badge).

In 1977, Tompkins and Goldsmith described the first commercial passive dosimeter for monitoring organic vapors.[1] The GASBADGE relied on molecular diffusion of the vapor into the badge and subsequent adsorption onto activated charcoal. The authors developed the theoretical principles of the badge's operation, and discussed sensitivity to temperature and pressure, face velocity effects, and response time. Preliminary results showing the badge's response to benzene, ethyl acetate, methyl ethyl ketone, and styrene also were presented and were described as "very encouraging" (see Table II).

In the same year, Silverstein reported results of laboratory and field testing of the GASBADGE for acrylonitrile.[39] The results of the exposure of 33 badges to known concentrations in the laboratory are presented in Table II. The results indicate the acceptability of the GASBADGE for measurements of acrylonitrile over the range of 0.75 to 19 ppm. The time of exposure in the laboratory was not given, however, field measurements did cover periods of up to seven hours. Although temperature and relative humidity ranges were reported, data analysis to determine the effects of these variables was not presented. Silverstein also looked at desorption efficiencies and determined that the best results (94 percent) were obtained with four mL of two percent acetone in carbon disulfide.

In 1978, Bamberger *et al.* conducted a series of laboratory tests to evaluate the GASBADGE.[12] Their approach involved the generation of known concentrations of solvents and subsequent evaluation with charcoal tubes (active sampling) and the passive dosimeter. To evaluate the applicability of the dosimeter over a wide range of compounds, the investigation included seven different organic compounds each representative of a different functional group. Included in this study were: benzene (aromatic), n-butanol (alcohol), n-butyl acetate (ester), isooctane (alkane), methyl chloroform (halogenated alkane), methyl isobutyl ketone (ketone), and trichloroethylene (halogenated alkene). The diffusion coefficient (D) used was that supplied by the badge manufacturer, except in the case of isooctane which was reported as having an unknown coefficient. Computations involving this compound relied on the coefficient for n-octane. A variety of experiments was conducted to look at a wide range of questions. Their findings corroborated dosimeter concerns similar to those of active systems using charcoal tubes, *e.g.*, minimum and maximum loadings are important, post-sample contamination and loss can occur if the exposed absorbent is not adequately sealed, percent recovery for mixtures is consistent with percent recoveries for single compounds, and differences in charcoal lots can give different results. Other tests confirmed the need for some air movement across the badge face and the lack of effect of temperature changes over a small range (11 °C). The results of the simultaneous sampling with the badges and the charcoal tubes indicated that the badges had a consistent negative bias. The authors suggested that, because the results were so reproducible, corrections for adsorption desorption efficiencies less than 100 percent can be accomplished just as is done for charcoal tube data.

In 1979, Hirayama and Ikeda evaluated the application of the GASBADGE for monitoring exposures to mixed solvents.[40] Their research involved different preparations of activated carbon "felt" in place of the supplied collection medium and exposure to mixtures of n-hexane, ethyl acetate and toluene. Summary (graphical) data indicated that the amounts of contaminant absorbed by the dosimeter were proportional to both the vapor concentrations and time of exposure.

Halliday and Anderson reported on the use of the GASBADGE in monitoring for halothane.[11] Six observations indicated a range of measurements from minus nine to plus ten percent of the test atmospheres. Unfortunately, the authors did not report their procedure for determining the concentration of halothane in the test atmospheres.

In 1981, Evans and Horstman reported evaluations of desorption efficiencies of charcoal tubes and the GASBADGE for styrene.[42] For liquid dosing they found the dosimeter to be similar to the tube, while for vapor dosing the badge was superior. The authors suggested that the differences in results may have been related to the use of coconut shell carbon in the tubes and petroleum derived carbon in the badge. They did not explain why this difference would affect one method of dosing and not the other.

In 1980, Anders and Mullins of the 3M Company presented results comparing the 3M passive monitor with charcoal tubes in sampling for mixtures of organic compounds.[13] The laboratory tests included a binary mixture of toluene and methyl ethyl ketone; a tertiary mixture of benzene, toluene and xylene; and complex mixtures of unleaded and leaded gasoline containing various alcohols. Although the investigators cited "excellent" precision and accuracy for the diffusional monitor, sample sizes were small, and the complicated study design and lack of raw data preclude the determination of precision and bias statistics.

Mazur and his co-workers[14] conducted side-by-side laboratory and field tests with charcoal tubes and 3M organic vapor monitors to measure concentrations of halothane (2-bromo-2-chloro-1,1,1-trifluoroethane) and enflurane (2-chloro-1,1,2-trifluoroethyl difluoromethyl ether). The results of the laboratory studies are presented in Table II and support the authors' conclusions that the dosimeters are a reliable method for the collection of enflurane and halothane.

In 1980, Lautenberger *et al.* described DuPont's passive monitor for organic vapors.[11] Each charcoal strip in the PRO-TEK G-AA Organic Vapor Badge contains approximately 300 mg of coconut-based activated charcoal impregnated in an inert polymer. A dual sampling rate of approxi-

mately 50 or 100 ml · min is determined by the removal of one or both of the dosimeter's protective covers. One aspect of their research involved experimental determination of the diffusion coefficient of several gases and vapors. They reported that values calculated by Fuggi[49] were within 10 percent of their experimentally determined diffusion coefficient values. Preliminary experimental results were used to discuss face velocity effects, range and sensitivity, maximum and minimum sampling times, vapor retention, storage stability, desorption efficiency, and overall badge efficiency. The overall accuracy determinations were limited to four observations at each of two concentrations of carbon tetrachloride (see Table II). However, the presentation of raw data, as well as an explanation of the statistical tests applied, is most useful. This same detail of information is also found in DuPont's validation reports for toluene and benzene (see Table II).[45,46]

In the benzene report, DuPont also describes its PRO-TEK G-BB badge. This badge has a backup section of charcoal, which serves the same purpose as the second section in a charcoal tube, *i.e.*, to aid in determining if the sampler has been overloaded. The 3M Company also markets an Organic Vapor Monitor with a backup section.[47]

In studies of the measurement of waste anesthetic gases with passive dosimeters, Jonas *et al.* evaluated the GASBADGE, 3M Organic Vapor Monitor and DuPont Pro-Tek in measuring enflurane.[9] Unfortunately, the badges were not identified in the presentation of the results although interpretation of the reported sampler geometry would indicate that A was the DuPont badge, B was the 3M badge, and C was the GASBADGE. The results of their laboratory studies indicated that badge B had the lowest coefficients of variation (CV was not calculated as described in this text) as compared to concentrations determined by infrared analysis. Badge A had a low CV (9 percent) at 5 ppm and a much higher value (CV=34 percent) at 20 ppm. The C badge had consistently high CV's ranging from 23 to 30 percent. It should also be noted that the charcoal tube CV's ranged from 11 to 27 percent, that desorption efficiencies for the badges ranged from 0.81 to 1.17, and that IR analyses of tank concentrations were constantly lower than expected. If badge B was the 3M device, the results of Jonas *et al.* support those reported by Mazur *et al.*[44] Further testing of badges A and C seems necessary, however, to confirm their seemingly low precisions.

Mazur and his coworkers conducted additional tests comparing the 3M and DuPont badges against charcoal tubes.[48] Methyl chloroform and trichloroethylene, two solvents widely used in vapor degreasing operations, were sampled. In the laboratory phase of the study, the badges and charcoal tubes were exposed to chamber concentrations over the range of 160 to 840 ppm of methyl chloroform and from 20 to 200 ppm of trichloroethylene. Exposure times varied from two to six hours for methyl chloroform and from four to six hours for trichloroethylene. The laboratory work indicated that the percent recoveries of the various doses (concentration × time) were in good agreement except for one exposure of the 3M badge which involved a five hour exposure at 700 ppm. The authors noted that this exposure of 3500 ppm-hours exceeded the upper exposure limit provided by the manufacturer. The overall mean recovery value for each type of sampler was used to correct all subsequent field data. In addition to the recovery measurements, the laboratory phase of this study also involved determination of storage stability. The authors found no significant losses of methyl chloroform or trichloroethylene from either badge following storage of exposed badges for up to three weeks.

In 1978, West and Reiszner reported on the field tests of the MINIMONITOR™ (REAL, Inc.) permeation personal monitor for vinyl chloride.[2] This monitor was a modified version of one previously described by Nelms *et al.*[19] The collecting medium was activated charcoal, but rather than relying on molecular diffusion, the badge design involved a polymeric membrane and the permeation of vinyl chloride through the membrane and adsorption onto the charcoal. Initial laboratory calibration was used to determine the permeation constant of the device. Laboratory results indicated good accuracies as summarized in Table II.

During the same period that Tompkins and Goldsmith[1] were describing the GASBADGE, Bailey and Hollingdale-Smith of Great Britain were presenting their ideas for a personal passive sampler for organic gases and vapors.[50] Their design involved the use of either one of two types of membrane and subsequent adsorption onto activated charcoal. They found two membranes to be satisfactory: one of thin silicone rubber which acted as a permeation barrier, and the second a porous polypropylene film which allowed for molecular diffusion of the gas and vapor. They conducted laboratory tests using carbon tetrachloride, styrene and dichlorodifluormethane. Their test results do mix some terminology, *e.g.*, permeation rates for both the permeation device and the diffusional device, but did provide an early demonstration of the feasibility of such a device for monitoring certain organics. The device, the Porton Diffusion Sampler, seems to see its greatest use in Great Britain.

***acrylonitrile***

One of the newest applications of passive dosimetry involves the use of a porous polymer (Porapak® N) as the collecting surface with subsequent thermal desorption and gas chromatographic analysis. Benson and Boyce have described such a device and its utility in sampling for acrylonitrile.[51] Laboratory testing for acrylonitrile involved comparison of the dosimeter values with concentrations measured on a gas chromatograph. Initial experimentation indicated that the dosimeter can be used for acrylonitrile concentrations in the range of 4 ppm, but at concentrations of 2 ppm a 40 percent error is reported.

***aniline***

In addition to activated charcoal, another widely used adsorbent medium is silica gel. To study the utility of this material, Campbell and Konzen constructed passive dosimeters from glass culture tubes (1.05 cm inside diameter) with 40 60 mesh silica gel as the collecting surface.[52] Laboratory testing involved exposure of the dosimeter to aniline, with exposure concentrations determined by gas chromatographic analysis of ethanol gas scrubbers. Three different

size (length) dosimeters were evaluated, with the best results obtained with the intermediate length tube (L = 3.0 cm; A/L = 0.3 cm). The authors present raw data and clearly described their statistical techniques.

***ethylene oxide***

Mullins and Anders have recently described the 3M diffusional monitor for sampling ethylene oxide in air.[53] In this badge the collecting surface is described as a "chemically impregnated charcoal surface, (where) a reaction occurs producing a stable compound with a vapor pressure substantially lower than the parent compound." The authors present statistically summarized data describing the linearity and capacity of the monitor, the recovery of absorbed ethylene oxide, environmental effects, sample stability, and the effects of potential interferences. Precision and bias are presented in Table II.

***formaldehyde***

Rodriguez *et al.* have described another 3M diffusional monitor for sampling formaldehyde.[54] In this diffusional monitor, the collecting surface is an "impregnated sorbent" which can then be desorbed *in situ* with water and the concentration of formaldehyde determined colorimetrically. Laboratory evaluation first involved determination of recovery coefficients, which at eight ppm-hours (19.5 micrograms) were found to be $1.00 \pm 0.04$ over six tests. The next step involved determination of the dosimeter's "sampling rate" (DA/L) by exposing the dosimeters to "known" concentrations of formaldehyde as generated by a permeation tube. The effect of relative humidity on the sampling rate also was investigated, and evaluation of the data did not indicate any statistically significant differences between the rates at 50 and 85 percent relative humidity. The study protocol then involved simultaneous exposures of impingers (modified chromotropic acid method) and dosimeters. The authors concluded that "the measured values by both methods lie within ± 25 percent of the expected response" and that "less variation is observed in the monitors than in the impingers." However, neither precision nor bias were reported. The authors also investigated effects of storage and determined that at elevated temperatures (38 °C) losses up to 11 percent occurred after one week, however no significant loss was seen for samples stored at 23 °C. The authors briefly discussed the potential for a negative interference from phenol and described the use of modified calibration curves to address this problem.

DuPont's PRO-TEK series of colorimetric Air Monitoring Badges, includes a badge for formaldehyde. The collection principle involves a chromotropic acid-sulfuric acid reaction. Laboratory evaluation (42 samples) of the device at seven exposure levels revealed results as shown in Table II.[55] Additional studies also were conducted on temperature and storage effects. The raw data and statistical analysis procedures are presented.

Kriesel[56] has described a new passive dosimeter for formaldehyde which is a modified version of the Palmes tube. At the present time experimental data concerning this device are not available.

***phosgene***

Matherne *et al.* have recently described the GMD, Inc. "passive dosimeter" which provides a semiquantitative measurement of phosgene exposure.[57] The badge involves direct contact between the contaminated air and a chemically impregnated tape and therefore does not rely on a stagnant air layer. The treated paper stain intensity is reported to be logarithmically proportional to the phosgene dose over a range of 2 to 100 ppm-minutes. For quantitative measurements the badges can be read colorimetrically.

## other methods

Hill and Fraser have described the use of commercial detector tubes modified to act as passive dosimeters.[58] In their research, common length-of-stain detector tubes were modified by cutting off the conical end of the tube and removing some of the indicator column material. This leaves an orifice with a cross-sectional area equal to that of the inside of the tube and a path length determined by the distance from the end of the tube, to the beginning of the indicator material. One would expect, however, that as the sorbent material becomes exposed, *i.e.*, the length of stain increases, the diffusion path length will also increase, thereby changing the sampling rate. Their evaluation of these devices involved separate laboratory exposures to toluene, ethanol and isopropanol. The results of their work, although presented only in graphical summary, demonstrate the potential for the use of modified commercial detector tubes as passive dosimeters.

## field validation

Relatively few studies have been published in which passive dosimeters have been compared side by side with charcoal tubes or other conventional sampling methods under actual field conditions. For inorganic compounds only two studies, involving nitrogen dioxide[59] and chlorine,[25] have been identified. For organic compounds, eight studies[2,9,39,44,48,51,60,61] have involved field comparisons, with the number of compounds per study ranging from one to 22. In three of these studies, statistical analyses of data were not presented and cannot be performed because of small sample size or insufficient presentation of data.

Jones *et al.*[59] conducted a field evaluation for $NO_2$ in a salt mine, which contained diesel equipment as the $NO_2$ source. At each of 16 different fixed area locations, two Palmes dosimeters and two TEA tubes with pumps were used to sample the atmosphere. The active sampling (pump) method gave a coefficient of variation (CV) of 8.7 percent while for passive tubes the CV was 5.8 percent. Regression analysis (where the active system was the X variable) of their data gives a correlation coefficient of 0.69, a slope of 0.59, and an intercept of 2.05 ppm for data over the range of 3.7 to 5.5 ppm as sampled by the active method. This indicates that the dosimeter gave consistently higher readings which is reflected in the means for the two methods: 4.51 ppm for passive and 4.14 ppm for active sampling. The authors did not report wind velocities, but low velocities, as would be expected with area samples, should have caused passive

values to be low as compared to active values; this was not the case. On the other hand, high face velocities could have led to the observed positive (passive versus active) bias.

Hardy *et al.*[28] reported the raw data results from a field evaluation of a permeation chlorine monitor (REAL, Inc.). Thirteen comparisons were made in which the results from a battery operated pump and an impinger sampler were compared with the measurements from either two or three permeation samplers. To further evaluate their results, the investigators performed a regression analysis using their permeation sample means for each comparison as the dependent variable. The results are quite good with a correlation coefficient of 0.95, a regression slope of 0.85, and an intercept of 0.15 over a range of 0.03 to 1.1 ppm as detected by the impinger. It should be noted that with five impinger samples of less than 0.1 ppm, the corresponding permeation devices detected considerably higher concentrations (0.16 to 0.4 ppm).

Silverstein[39] reported field results for acrylonitrile monitoring using 18 paired samples of GASBADGE passive monitors and active systems (charcoal tubes and pumps) over a range of 0.8 to 3.8 ppm as determined by the active method. The differences in results using the active system as a reference ranged from −0.7 to 1.5 ppm. The difference in means, 2.18 for the passive versus 2.73 for the active system, was 25 percent. Further data were not presented.

West and Reiszner reported five sets of field results for vinyl chloride sampled with permeation dosimeters (REAL, Inc.) and charcoal tubes.[2] Further interpretation of their results is presented in Table III. In each case data for the active system are the X values. Four of the correlation coefficient values are very near one, reflecting good correlation; however, the slopes show quite a large degree of variability (0.69 to 1.31), indicating that badge values may fall either well below or above charcoal tube values. In those cases where the slopes were less than 1.0, very high humidities (67 to 91 percent) were reported by the authors. This factor may have interfered with permeation, although the authors reported that humidity had no effect in laboratory validations; hence the variation in slope remains unexplained. The authors noted that the overall field results showed that the badges had a slight positive bias.

Hickey and Bishop exposed 78 pairs of side-by-side charcoal tubes and 3M Organic Vapor Monitors to complex mixtures of organic chemicals in tire manufacturing operations.[9] Generally the sampling period ranged from three to

**TABLE III**
**Regression Analysis of Vinyl Chloride Field Data[2]**

| N | Range (ppm) | r | Slope | Y-Intercept |
|---|---|---|---|---|
| 7 | 0 02-1 | 0 99 | 1 19 | 0 03 |
| 8 | 0.08-1.8 | 0 99 | 0.69 | 0.05 |
| 12 | 0.02-6.9 | 1.0 | 1.31 | 0.01 |
| 39 | 0 05-1.8 | 0.82 | 0.81 | 0.11 |
| 24 | 1 48-16 7 | 0 96 | 1.08 | 0 43 |

five hours, and most observations consisted of one monito and the time weighted average concentration from tw sequentially exposed charcoal tubes. Sixty-four of the se were personal samples, while the remaining 14 were are samples. The samples were collected in two separate plan (30 sample pairs in one plant and 48 in the other). Of the 2 organics potentially available for analysis, 10 were detecte over a sufficiently wide range of concentrations to allow fo appropriate statistical analysis by linear regression. Th results are interesting in that in the first plant, 9 of the 1 organics measured by the dosimeters showed higher vapo concentrations as compared to the charcoal tubes, while i the second plant only three substances had a regression slop greater than one. The combined data for both plants did no indicate that the passive system was consistently biase when compared to the active system. The authors did poin out that generally the Y-intercepts (Y=passive dosimete data) were slightly negative, a finding which may indicate lack of sensitivity on the part of the dosimeters at lo concentrations. For the remaining 12 compounds, paire t-tests revealed no significant difference between the cha coal tube and passive monitor means at the 95 percen confidence level. The use of t-tests to analyze such data ha been questioned since the means of the two methods may b very similar but the components of paired values can b considerably different.[19] This condition can only be reveale through regression analyses.

In 1980, Mazur *et al.*[44] reported limited field data fo halothane and enflurane measurements using both 3M Organic Vapor Monitors (OVM) and an active syste (charcoal tubes and pumps). For halothane three paire samples were reported. The mean concentration for th active system was 2.01 ppm while 1.9 ppm was reported fo the OVM, a difference (relative to the active system) of fiv percent. Only one data pair was reported for enflurane: 0.4 ppm for the OVM and 0.52 ppm for the active systen Obviously, more data are needed to draw conclusion regarding a comparison of the two methods for these agent.

A second study by Mazur *et al.*[48] reported field comparisons of passive dosimeters and active systems (pumps and charcoal tubes) in sampling for trichloroethylene (TCE) and methylchloroform (MC). Both DuPont PRO-TEK and 3M Organic Vapor Monitors were used for the passive systems Personal samples included exposure of one each of all thre monitors. Area sample results involved three average value one was the average of three charcoal tubes, and the othe two, the average of two of each type of dosimeter. For MC 11 personal and 7 area data points collected over time per ods of 1 to 5 hours at 15 to 21 °C and 35 to 40 percent relativ humidity were reported. For TCE, 22 personal and 7 are data points collected over periods of about 1 to 6 hours at 1 to 24 °C and 30 percent relative humidity were reported. regression analysis in which the charcoal tubes were th independent variable was reported by the authors. In each o the following data sets the presented values involve TC personal and stationary sampling followed by MC person and stationary sampling. For the DuPont badge, regressio

slopes of 1.0, 0.99, 0.99, and 0.98, and correlation coefficients of 0.98, 0.98, 0.94, and 0.94 were obtained. For the 3M badge, regression slopes of 1.08, 1.06, 1.07, and 0.90, and correlation coefficients of 0.98, 0.98, 0.98, and 0.90 were determined. These values appear to be quite good; however, the authors did not report if they tested the statistical significance of these values. They also did not report average of face velocities associated with stationary samples.

Evans *et al.*[60] of Great Britain reported field validation data for the Porton diffusion device while measuring methyl ethyl ketone. In this case the conventional sampler was a pump and a cassette fitted with a charcoal cloth similar to that used in the Porton device. A regression analysis performed with their data showed good correlation (0.9) and good slope (0.9); however, the intercept value (4.69) indicated that, at low concentrations, the "home-made" device gave lower values than those determined with the conventional monitor. Concentrations reported for the conventional device ranged from 11 to 189 ppm.

Benson and Boyce[51] field tested the Monsanto Poropak N device in Great Britain. Conventional samplers consisted of pumps and Poropak N polymer tubes. Sixty-five pairs of samples were obtained, and the range of acrylonitrile measured by the tubes was 0.13 to 21.65 ppm. Regression analysis of their data indicates only fair correlation (0.63), a low slope (0.46), and a negative intercept (−2.06). These values appear to result from the apparent inability of the passive device to accurately detect concentrations less than 0.5 ppm. Also, comparisons between values over the lower half of concentrations sampled showed considerable scatter.

The final field study to be discussed suggests perhaps the most serious discrepancies resulting from use of charcoal passive dosimeters.[61] This study was performed by NIOSH personnel in conjunction with industry-wide studies of the dry-cleaning, screen printing, and boat manufacturing industries, and also included one viscose rayon and one cellophane plant. Carbon disulfide, perchloroethylene, toluene, methylisobutyl ketone (MIBK), styrene, and acetone were sampled using the 3M OVM, the GASBADGE, and active systems with charcoal tubes. The presentation of the study design is not clear, but it appears that area samples involved all three devices while personal samples involved charcoal tubes and only one of either passive device. In that this study involves six compounds in 64 plants, the volume of data is quite large. In addition to regression analysis, paired t-tests and Wilcox signed rank tests were performed by the authors to determine equivalence of data sets. As noted earlier the use of t-tests for determination of equivalence has been questioned.[19]

Table IV shows the primary results of this study. As can be seen, the range of correlation coefficients (r) for most compounds was quite large. Although 12 plants were surveyed for toluene and MIBK, the data were grouped together, and therefore ranges of the correlation coefficients could not be determined. For carbon disulfide, one plant was surveyed with the OVM and GASBADGE, and one was surveyed with the GASBADGE only. For the ranges of r reported in Table IV, the upper values are quite acceptable, with the exception of carbon disulfide using the GASBADGE. However, the correlation coefficient for carbon disulfide using the OVM was 0.95. The correlation data can be summed up as being extremely variable. Table IV also reveals that concentration had an effect on the correlation coefficient for three of the compounds, though this was true for both monitors only when measuring acetone concentrations. Regression slopes were as variable as the correlation coefficients. The authors tested the slopes to see if they were significantly different from zero, and for acetone and carbon disulfide a difference could not be demonstrated for several of their data sets. This indicated that there was no relationship between the results obtained with the active system and those obtained with the passive dosimeter. For other compounds, it would have been useful to test the difference of the slope from one, which if not significantly different would indicate agreement of the two methods.

In tests of equivalence of data sets, the authors noted that for all plant data combined, only toluene showed equality, and this for the charcoal tube-GASBADGE (CT-GB) comparison. However, when results from individual plants are used, the comparison outcomes are quite variable. For perchloroethylene, equality was reported for one of three CT-BG comparisons and for one of two CT-3M sets. For styrene, two of six CT-GB and no CT-3M comparisons showed equality. For acetone, three of five CT-3M comparisons and one of six CT-GB data sets showed equality. In addition, GB-OVM comparisons showed equality in 6 of 17 comparisons. It is obvious that repeatability was not demonstrated in this study. Whether the problem involves the dosimeters, investigative or laboratory techniques, and or environmental conditions cannot be determined. In the only other field study of more than one plant, Hickey and Bishop[9] also reported some problems with the consistency of observations. These limited results clearly demonstrate the need for additional field studies of passive dosimeters as compared with standard monitoring techniques.

## discussion

Passive dosimetry (monitoring) is a rapidly developing technology as witnessed by the proliferation of devices and applications since Palmes and Gunnison introduced their concepts just under ten years ago.[22] The latest entry into the field comes from the MSA Company and involves an adaptation of their length-of-stain direct reading tubes for inorganic gases[62] which incorporates the application of molecular diffusion and a chemically impregnated paper as the sampling medium. Although research results are not available, as a first approximation one might assume that these devices have precisions and biases similar to those of conventional detector tubes.

For any new technology to be accepted and used by practicing professionals, the development of a body of knowledge demonstrating efficacy is necessary. With environmental monitoring techniques, the determination of the efficacy usually starts in the laboratory and culminates in the field. In the case of passive monitors, a body of knowledge based on laboratory testing is rapidly being developed. Of the vari-

TABLE IV
Major Results of a Field Study for Organic Vapors[61]

| Substance | Comparison | Overall r | Range of r | Concentration Dependency |
|---|---|---|---|---|
| Perchloro-ethylene | CT-GB | 0 62 | 0 62-0.99 | |
| | CT-3M | 0.86 | 0.84-0.94 | |
| Styrene | CT-GB | 0 82 | 0.65-0.97 | |
| | CT-3M | 0.76 | 0.48-0.86 | |
| Acetone | CT-GB | 0 38 | 0.36-0 86 | Yes |
| | CT-3M | 0.45 | 0.25-0.83 | Yes |
| Toluene | CT-GB | 0 80 | NA | |
| | CT-3M | 0 91 | NA | Yes |
| MIBK | CT-GB | 0.88 | NA | |
| | CT-3M | 0 79 | NA | |
| $CS_2$ | CT-GB | 0 30 | 0.03-0 38 | |
| | CT-3M | 0 95 | NA | Yes |

ables that have been studied, three appear to uniquely affect a diffusion monitors accuracy in measuring airborne concentrations of gases or vapors. The most important factor appears to be determination of the contaminants' diffusion coefficient (or the sampling rate when the dosimeter's geometry is also considered), the wind velocity at the dosimeter face, and the relative humidity of the sampled air. As discussed earlier, there are also a variety of potential sources of error, such as interfering contaminants, sorbent capacity and problems associated with analytical determinations, which are common to both passive and active measurement techniques.

Laboratory determination of sampling rates (DA L) for a specific monitor and a specific contaminant are important and are being provided by several dosimeter manufacturers for an ever increasing number of compounds. Once an appropriate sampling rate has been determined, corrections for field use, specifically for temperature variations, can be made. The main problem would involve situations where the environmental temperature fluctuated widely (more than 25 °C) and went unnoticed, a very unlikely condition.

The research on effects of face velocities demonstrate that few problems should be encountered where dosimeters are worn by workers as personal monitoring devices.[1,12,24,25,32] Their use as area monitors should be carefully evaluated to ensure that stagnant atmospheres (velocities less than 7.5 cm sec) are not involved. High wind velocities (at least what would normally be encountered in the workplace) or wind direction do not appear to have adverse effects on dosimeters with wind screens.

Of greatest concern as a result of reviewing the literature on laboratory testing of passive dosimeters is not the results but rather the thoroughness of their presentation. As demonstrated in Tables I and II, where statistical analyses are presented by researchers, or where sufficient data are presented to allow the reader to determine bias and precision, the results are very encouraging. Unfortunately the presentation of experimental design, as well as sufficient data and or statistical analyses, are often lacking. This is true for some individual researchers as well as for several manufacturers o the devices, especially those for inorganic compounds. If on recommendation regarding laboratory testing is made, i would be that those researchers involved in the evaluation o passive dosimeters in the laboratory take the time to repor the conditions of their experiments, especially equipmen used and procedures for determining "known" concentra tions, and as much detail about their results as possible. I summarized data are presented, the author should presen the known concentration at each level, where levels ar determined by concentration and time, the number of obser vations made with passive dosimeters, and the average valu and standard deviation of the results. Statistical analyses again at each level tested, should involve determination o the coefficient of variation (precision) and the bias a described in equations (7) and (8), respectively. Once th evaluations are made at the various test levels, the determi nation of a pooled precision and bias is appropriate. I addition to these measurements, researchers may als choose to present an overall system accuracy. To develop a better understanding of appropriate statistical technique and their application to passive dosimetry, a review o Lautenberger *et al.* is recommended.[11]

For most active monitoring systems used in industria hygiene the random sampling error is usually associate with the pump and is traditionally set at ± 5 percent.[10] I many cases, especially for the measurement of organi vapors, the analytical procedures and consequently thei associated errors are equivalent for both passive and activ systems. Nevertheless, both systems have random error consequently, one should not expect perfect agreement o the results of comparisons obtained under field test condi tions. Another factor complicating the evaluation of fiel results is the greatly increased possibility for the introduc tion of operator, or systematic, errors. Since active system require mechanical pumps, the potential for operator erro would seem to be greater than for passive systems.

Overall, it is apparent that existing field observations comparing passive dosimeters with standard monitoring methods are highly varied. While some studies demonstrate good correlation and slope,[9,25,48] others show only good correlation,[2] or are extremely varied for both categories.[61] Collectively, these references neither support nor refute the use of passive dosimeters. Certainly environmental factors affect active systems as well as passive systems. In theory, a case can be made that environmental factors (wind and humidity) affect passive systems to the greatest extent, while temperature and pressure variations most greatly affec active systems. On the other hand one can also state that poor experimental quality control may affect such factors a contamination, time measurement error, and analytica error. Of course, chemical interferences may affect both systems.

As with laboratory experimentation, recommendations regarding the field testing of passive dosimeters involve a plea for better reporting of both field conditions and results of analysis. First, for both personal and area monitoring, the estimation and or measurement of face velocity is impor-

tant. Of equal importance is the reporting of airborne contaminants other than the one(s) of interest and environmental variables including temperature, pressure, and relative humidity along with information as to their variation over the period of observation. Again, if raw data cannot be presented, the reported results for each level tested (X value as determined by the standard method) should include the number of observations made with passive dosimeters, and their associated mean and coefficient of variation. Statistical evaluations also should include a regression analysis of the data as outlined earlier. Undoubtedly, additional research is needed on the effect of not considering the error associated with the supposedly independent (X) variable.

In summary, passive dosimeters show great promise as an important tool. The results presented in Tables I and II indicate that the precisions of the dosimeters are essentially equivalent to conventional techniques and in many cases the additional five percent error associated with mechanical pumps makes passive dosimeter systems even more attractive. This, coupled with their ease of use, lack of required maintenance, acceptance by workers due to light weight, and unnecessary calibration make passive dosimeters extremely advantageous. Certainly they will not replace conventional methods, as these have their place, especially for area sampling. The continued and growing use of passive dosimeters, however, should generate additional data documenting their reliability and eliminating doubts about their usefulness.


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# 3M FORMALDEHYDE MONITOR

## Summary

### Analytical Method

The NIOSH P&CAM 125 Chromotropic Acid Method has been modified to reduce analytical interferences and give an expanded linear response of absorbance as a function of formaldehyde solution concentration. The procedure uses 1 milliliter of 1% chromotropic acid and 5 milliliters of sulfuric acid for sample aliquot volumes ranging from 0.1 to 2.5 milliliters. For the modified method, using a 2.0 milliliter aliquot, the formaldehyde analytical detection limit is 0.5 ug/ml. The precision as measured by the coefficient of variance for the analytical method only is 0.023 and for the overall analytical method is 0.030.

### Sampling Parameters

The formaldehyde recovery from the 3M Formaldehyde Monitor is 1.01 as determined from samples spiked with a range of weights equivalent to sampling 0.1 to 4 ppm for 8 hours. For the 3M Formaldehyde Monitor, the formaldehyde sampling rate is 65.9±3.7 cc/min. The concentration sensitivity is dependent on the length of the sampling period. For a 4 hour sampling period, a concentration of 0.2 ppm can be quantified, for an 8 hour sampling period, 0.1 ppm and for a 24 hour sampling period, 0.03 ppm. Sampling performance is maintained with air movement as measured by a face velocity as low as 15 linear feet per minute. The 3M Formaldehyde Monitor has a capacity of 850 micrograms (174 ppm-hr). With this capacity, a concentration of 22 ppm can be sampled for 8 hours. The 3M Formaldehyde Monitor can sample accurately formaldehyde in ambient atmosphere with relative humidity ranging from 20 to 90%. From the sampling performance of product stored at 70°F and 100°F, the shelf life has been document to six months and can be extrapolated to be in excess of one year. The sample stability has been demonstrated to be at least 90 days when stored at temperatures as high as 100°F.

### Analytical & Sampling Interferences

The modified chromotropic acid method has eliminated the ethanol interference for samples collected by either the bisulfite impinger or the 3M Formaldehyde Monitor. With ethanol concentrations as high as 200 ppm and 4 hour sampling periods both sampling techniques measured a 1.21 ppm formaldehyde challenge with accuracy greater than ±5%. In the presence of phenol at concentrations as high as 10 ppm, the 3M Formaldehyde Monitor measured a 0.99 ppm formaldehyde challenge within ±4%. The bisulfite impinger meaured the formaldehyde concentration with a minimum of

interference at phenol concentrations as high as 1 ppm. For the bisulfite impingers at higher phenol concentrations, the phenol interference decreased the accuracy even when using 10% chromotropic acid concentration in the analysis procedure. If high phenol concentrations are encountered with the bisulfite impinger method, the solution concentration of phenol can be quantified with a GC analytical technique and the formaldehyde absorbance from the chromotropic acid method can be corrected for phenol interference.

## Sampling Performance

In the laboratory, the 3M Formaldehyde Monitors have sampled known challenges at various concentrations as low as 0.059 ppm with sampling periods ranging as long as 46 hours. The 3M Formaldehyde Monitors measured the concentrations with excellent precision and an accuracy of ±10% or greater. In the field, the formaldehyde concentration levels were measured with both the 3M Formaldehyde Monitor and the standard bisulfite impinger. These evaluations were conducted in a variety of ambient conditions, ranging from a coating/sizing of sandpaper operation to a mobile home. There was excellent correlation between the two techniques as well as extremely good precision when replicated samples were collected.

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