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Assessment of the Reliability of Backup Systems in Diffusive Sorbent Samplers

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Passive monitors that collect chemicals by molecular diffusion are a convenient means of assessing workplace exposures. The purpose of this investigation was to evaluate the ability of passive monitor backup systems to provide users with greater assurance of sampling reliability. Studies were made of backup systems in use by current manufacturers including Pro-Tek®, 3M, and SKC. Monitors were exposed to known concentrations of chemicals under differing challenge conditions and analyzed according to the manufacturer's recommendations. Data from these studies show that there are severe limitations to the usefulness of backup systems as a means of improving sampling reliability.

Industrial hygienists are concerned with the evaluation of chemical hazards in the workplace. Because worker health is at risk, it is important that the air samples collected accurately reflect airborne chemical levels. The sorbent tube has been documented as a reliable air sampling method for many chemicals. Sorbent tube methods have been extensively tested and their validity has been shown.

An alternative sampling method that has come into more widespread use is the passive monitor, which collects chemicals by molecular diffusion. Following the early work of Palmes et al.,[1,2] who developed a mathematical treatment of the factors involved in sample uptake, various types of passive monitors have been introduced.[3] One of the limitations of many commercially available passive monitors, however, is that they do not have a proven system that ensures a complete and quantitative uptake of airborne chemicals. With sorbent tubes, active airflow prevents sample loss caused by reverse diffusion, and a backup layer gives an indication of sample breakthrough. With passive monitors, however, the sorbent layer is directly exposed to the air in the absence of an active airstream and sample loss by reverse diffusion can be significant.[4–8] Some passive monitors do offer a backup layer whose operation has been paralleled to that in a sorbent tube.[9–12] There are some distinct differences, however, in the functions of backup layers in diffusive samplers and sorbent tubes.[13]

The objective of this paper is to consider methods for ensuring a reproducible and quantitative uptake of sample under given challenge conditions by using passive monitors. Such a study should assist in the design of passive monitors that could be used reliably for 8 hr under worst-case sampling conditions.

EXPERIMENTAL METHODS AND MATERIALS

Backup methods in use by current manufacturers were studied. The primary consideration was low and medium molecular weight chemicals where quantitative uptake is most often a problem. Methylene chloride was chosen as a representative chemical to evaluate quantitative uptake.

The two basic types of backup systems currently in use are a secondary layer of sorbent placed behind the main adsorbing layer and a dual-sample backup system previously described by Moore et al.[13]

The purpose of the secondary backup layer of sorbent is to capture sample not taken up in the primary adsorbing layer. In contrast, the dual-sample backup system has two separate monitors for each sample to be taken. The areas of the diffusion barriers, and thus the sampling rates, are usually fixed at a ratio of 10:1. After analysis, if the ratio of the uptakes is also 10:1, the monitor with the higher sampling rate is used. If not, the monitor with the lower sampling rate yields the acceptable sample. Theoretically, if nonlinear uptake begins to occur, it will occur on the monitor with the highest uptake rate first.

The apparatus used to conduct this study was designed to expose a known concentration of chemical to a passive sampler under controlled conditions of concentration, temperature, humidity, wind velocity, time, multicomponent interferences, and monitor orientation. The apparatus consisted of three major components: a chamber to condition the airflow stream, a chemical injection system, and an exposure chamber. The temperature of each of these components was closely controlled by using mercury thermoregulators and variable output controllers. Observed variation from the set temperature was less than ±0.3°C.

In the air-conditioning chamber, two streams of air flowed from a single air source through a purification train. One stream of air passed through a molecular sieve drier and the other through a water saturator. The saturated air was blended

with the dry air to provide a constant flow of air at known temperature and humidity.

The chemical injection system consisted of motor-driven syringes that allowed chemicals to be injected directly into the airflow stream. Air was delivered to the exposure chamber at a rate of 5.0 Lpm, thus supplying a large quantity of air at known concentrations of chemicals.

The exposure chamber used in the study was a stainless steel cylinder with a total volume of 2.85 L. At an air delivery rate of 5.0 Lpm, there were 1.75 air exchanges per minute. Wind velocity was controlled by placing the monitors on a rotating framework and varying the speed of rotation. Wind velocity within the chamber could be varied from 10 cm/sec to 900 cm/sec face velocity. The exposure chamber was equipped with a small hole (5.5-cm diameter), which was used to add or remove monitors during the experiment. This, in conjunction with a large air delivery rate, ensured consistent chemical concentrations within the chamber. The three independent concentration verifications used were injection rate, gas analysis of the chamber air, and sorbent tube sampling. Concentration verifications of the chamber air were done before, during, and after the monitors were in place. No decrement caused by the sampling devices was observed.

Following exposure, all samples were desorbed with 2.0 mL carbon disulfide and analyzed by gas chromatography. The gas chromatograph was equipped with a flame ionization detector and a column of 10% carbowax 20M on 80/100 mesh Chromosorb® W-AW (Johns-Manville Corp., Lompoc, Calif.). Column temperature was maintained at 70°C; injector and detector temperatures were maintained at 125°C.

Methylene chloride was chosen for study as a representative low molecular weight compound that has proven difficult to sample by passive monitors. In this investigation, identical monitors were exposed to known levels of methylene chloride for differing lengths of time under given challenge conditions. At specified time periods, a portion of the monitors was removed and analyzed. To study reverse diffusion, the concentration was reduced to zero at the maximum loading recommended by the manufacturers and a portion of the monitors was further exposed. The desorption efficiency of each badge for methylene chloride was determined according to manufacturers' instructions and corrections were made if necessary. Rybka et al.[14] have also reported on the validation of a passive monitoring method for methylene chloride.

RESULTS AND DISCUSSION

A series of experiments was conducted to evaluate the sampling accuracy of passive monitors for the collection of methylene chloride. Unless otherwise indicated, all experiments were conducted at 80% humidity, 25°C, and 20 cm/sec face velocity. Challenge concentrations are given as parts per million (ppm) as well as fractions or multiples of the current permissible exposure limit (PEL). The current PEL for methylene chloride is 500 ppm. Because the capacity and activity of the sorbent differs between brands of monitors, different challenge concentrations were used to induce nonlinear uptake. Results are reported as an average of at least two analyses of two monitors.

Experiment 1

This experiment was designed to examine sample uptake and reverse diffusion with single-layer monitors. Three types of monitors were used in this investigation: the 3M (St. Paul, Minn.) Model 3500, the Pro-Tek® (Middletown, N.Y.) Type G-AA, and the SKC (Eighty Four, Pa.) Model 530-01 with 500-mg Anasorb CA charcoal capsules. Challenge concentrations of 250 ppm (0.5 PEL) methylene chloride were used with the 3M and Pro-Tek monitors, and concentrations of 1000 ppm (2 PEL) were used with the SKC monitor.

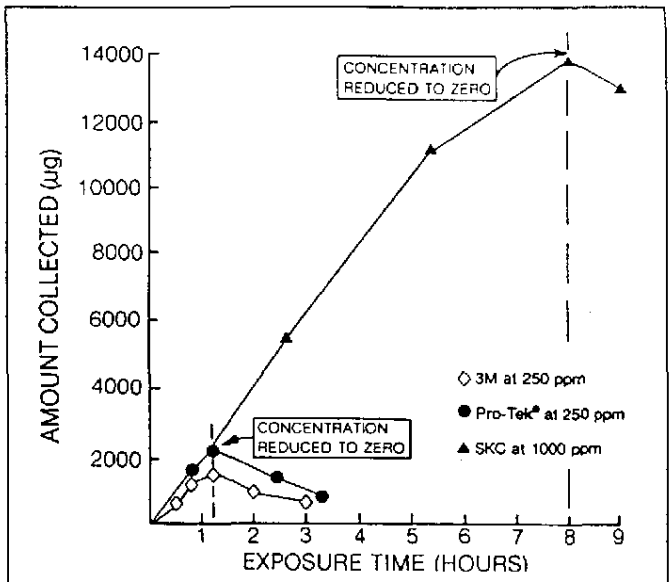

FIGURE 1. Uptake of methylene chloride on single-layer monitors

The results are shown in Figure 1, which shows that sample loss by reverse diffusion occurred on all monitors. With the Pro-Tek and 3M monitors, lower concentrations and shorter time periods were used to comply with the manufacturers' recommendations regarding capacity.

Experiment 2

This experiment was conducted to evaluate sample uptake and reverse diffusion on single-layer monitors in the presence of interfering compounds. The same monitors and concentrations of methylene chloride were used as in the previous experiment. Trichloroethylene was introduced as a challenge compound at 200 ppm (2 PEL).

Figure 2 shows the results of the study for the Pro-Tek monitor. The upper curve is a reproduction of Figure 1 and illustrates the results that would have been obtained if no other compound had been present. The lower curve is for the two-component mixture. The difference between the curves is the effect of competition and displacement by the other compound present. Similar results were obtained with the 3M and SKC monitors. It is important to note that 80% relative humidity represents a

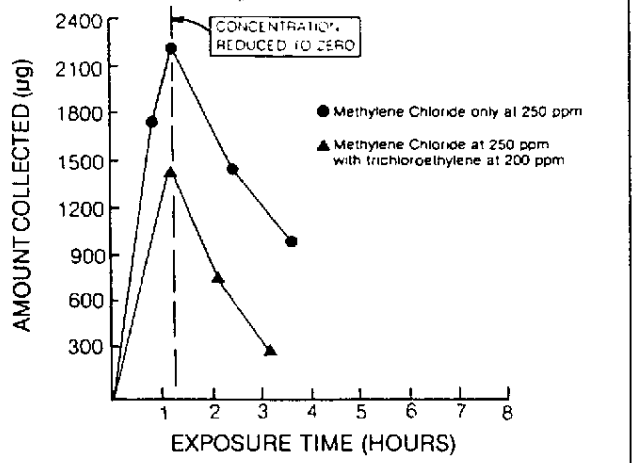

FIGURE 2. Uptake of methylene chloride on a Pro-Tek® single-layer monitor with the presence of an interfering compound

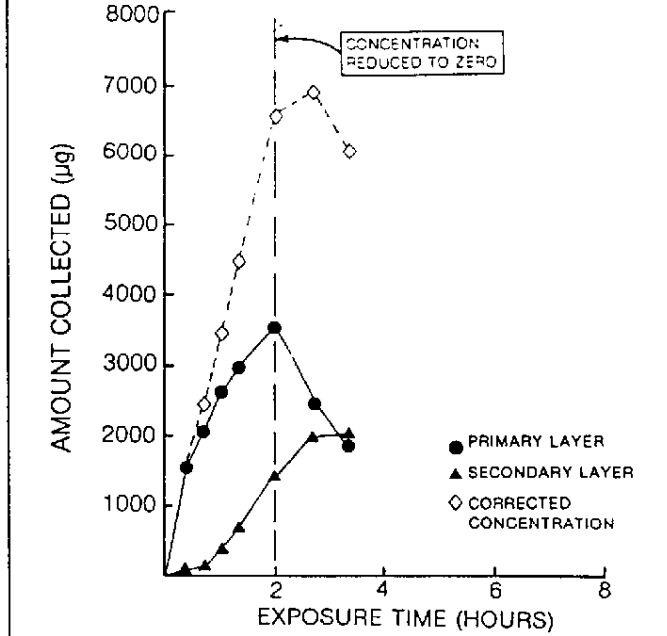

FIGURE 3. Uptake of methylene chloride on a Pro-Tek® dual-layer monitor

significant water challenge to the sample medium. The introduction of the interfering compound presents an additional challenge to the monitor.

Experiment 3

This experiment was conducted to evaluate sample uptake and reverse diffusion by using dual-layer monitors and applying corrections as recommended by the manufacturers. The Pro-Tek Type G-BB, 3M Model 3520, and SKC dual-layer monitor Model 530-01 with sorbent capsules containing two 200-mg layers of Anasorb CA charcoal were used in this study. A challenge concentration of 250 ppm (0.5 PEL) methylene chloride was used with the 3M and Pro-Tek monitors, and a concentration of 1000 ppm (2 PEL) was used with the SKC monitor. The temperature was elevated to 40°C with the SKC monitor to provide a maximum challenge as this monitor contains a larger amount of a more active sorbent.

Figures 3, 4, and 5 show the results from these studies. When the concentration was reduced to zero, the total amount of compound collected declined. This sample loss was caused by reverse diffusion from the face of the monitor and sample migration from the primary to the secondary layer. The degree of sample loss will depend upon the duration of zero exposure as well as the difference between the concentration levels when sampling and the zero exposure that follows. Applying the correction factor will partially correct this sample loss. This is evidenced in the fact that results obtained by using dual-layer monitors and applying correction factors produced results far superior to those obtained with single-layer monitors. One important requirement is to separate the two sorbent layers immediately after sampling; otherwise, chemicals will migrate between the primary and secondary layers and corrected concentrations will not be accurate. Furthermore, because the capacity of some monitors can limit the maximum sampling time to less than 8 hr, manufacturers' recommendations should be consulted and monitors replaced as necessary to assess full-shift exposures accurately.

A review of the adsorption mechanism may be helpful to illustrate collection with dual-layer devices. In the adsorption mechanism, a dynamic equilibrium exists between the gas phase and the adsorbed phase. In an ideal sample collector, the equilibrium is shifted so far to the adsorbed phase that the concentration in the gas phase is near zero and no loss by reverse diffusion occurs. For poorly adsorbed compounds, loss by re-

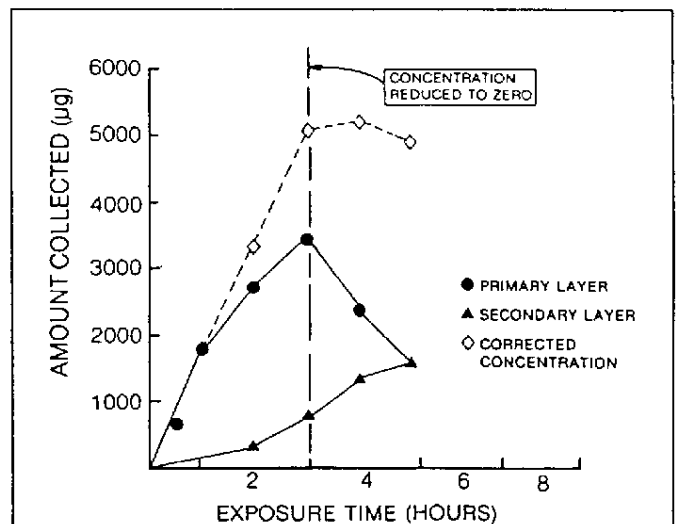

FIGURE 4. Uptake of methylene chloride on a 3M dual-layer monitor

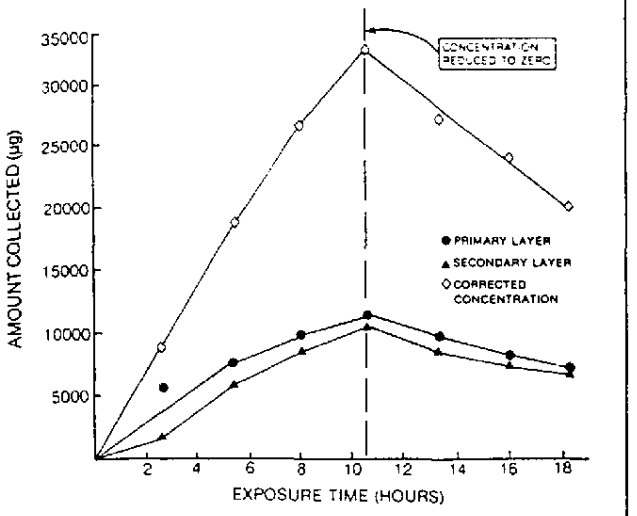

FIGURE 5. Uptake of methylene chloride on an SKC dual-layer monitor

verse diffusion is less a matter of saturation than the shifting of the equilibrium toward the gas phase. That is, as the concentration of the adsorbed phase increases, the equilibrium shifts toward the gas phase and sample loss by reverse diffusion is evidenced. Saturation of the primary sorbent layer is not required before collection begins in the secondary layer. Indeed, it became evident in this study that collection of chemicals in the secondary layer commences almost from the start of the exposure.

When a compound leaves the primary sorbent layer of a passive monitor, it can either escape from the monitor and be lost, migrate back onto the primary sorbent layer, or migrate back to the secondary layer. The amount of compound on the secondary layer, then, is a relative measure of the compound lost from the back surface of the primary layer. Because losses occur from both the front and back of the primary layer, the total sample loss from the primary layer must be at least two times the amount adsorbed by the secondary layer. Indeed, most manufacturers state that the total exposure is the amount in the primary layer plus 2.2 times the amount in the secondary layer.

It is, therefore, unfortunate that the term "backup layer" has been applied to passive monitors because it implies that compound not collected on the primary layer is collected on the secondary layer. This is only partially true. The terms "dual layer" or "correction layer" would be more appropriate because the amount of compound collected on this layer is more realistically a measure of nonlinear uptake and sample loss by reverse diffusion.

The mechanism of the dual-layer sorbent tube, however, is different from that of the passive monitor. When sampling with sorbent tubes, any compound leaving the surface is drawn back into the sorbent by the sample airstream. As the compound penetrates beyond the primary sorbent layer, it is quantitatively transported to the secondary layer, where it may be adsorbed. In this way, as long as the concentration in the secondary layer is low with respect to that in the primary layer, collection of all compound is assumed. Total exposure is obtained by combining the amounts in the primary and secondary layers.

Experiment 4

This experiment was conducted to evaluate sample uptake and reverse diffusion by using a dual sample rate monitor. An SKC Model 530-04 containing two 500-mg Anasorb CA charcoal capsules was used. With this monitor two samples are collected simultaneously at sampling rates that differ by a ratio of 10:1. Challenge concentrations of 1000 ppm methylene chloride (2 PEL) were used.

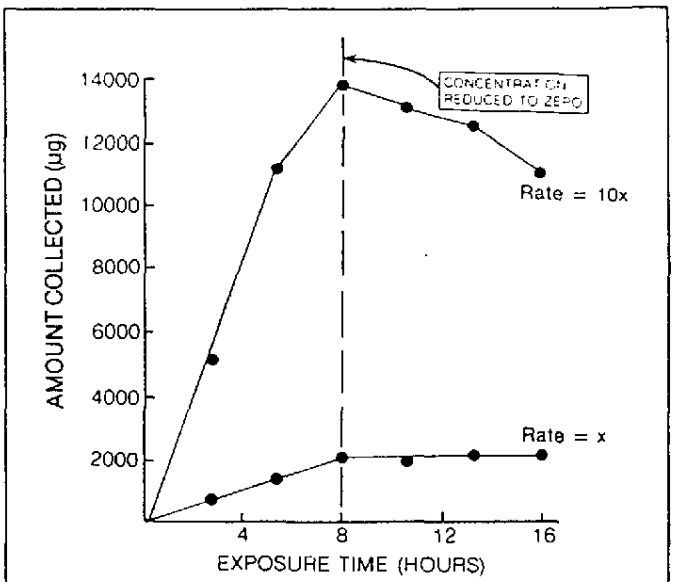

FIGURE 6. Uptake of methylene chloride on an SKC dual-rate monitor

Figure 6 shows the results of this study. Nonlinear uptake and losses occurred from the monitor with the higher uptake rate, but linear uptake and no significant sample loss occurred from the monitor with the lower sampling rate.

Overall, the results of these four experiments indicate that under challenge conditions, current monitors with backup systems may have the following drawbacks: sampling time is limited to less than 8 hr, requiring several samples for full-shift monitoring; field separation of sorbent layers or two separate analyses is required; significant errors may result if the manufacturer's instructions for proper use and sampling times are not followed.

CONCLUSIONS

This study shows that gross sampling errors can result when passive monitors with single sorbent layers are used for the collection of methylene chloride. Similar results may be expected when other poorly adsorbed compounds are monitored. Errors in sampling results are largely caused by the

effects of reverse diffusion, which are enhanced by the presence of interfering compounds.

Sampling reliability can be improved somewhat by using dual-layer monitors under constant concentration conditions and applying correction factors recommended by the manufacturer. Under most circumstances, however, dual-layer monitors yield reliable results only when used for short sampling times in the absence of interfering compounds. These monitors should be most suitable for survey work or for measuring short-term exposure limits or ceiling values.

The dual sampling rate system is advantageous in that it provides the user with two separate monitors sampling at different known rates. The ratio of the uptakes can be compared to the ratio of the sampling rates to give an indication of quantitative uptake. In most cases, the monitor with the lower sampling rate will yield quantitative uptake over a longer sampling time. Each chemical being monitored requires independent study at both sampling rates, however, to provide the desired assurance of sampling reliability.

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Ed. Note: A prepublication copy of this manuscript, "Assessment of the Reliability of Backup Systems in Diffusive Sorbent Samplers," was forwarded to the manufacturers for review and comment. A response from Pro-Tek follows.

Dear Sir:

Thank you for the opportunity to review and comment on "Assessment of the Reliability of Backup Systems in Diffusive Sorbent Samplers." The following is the consensus opinion reached by a committee I assembled specifically for this review project. Members of the committee included a certified industrial hygienist with more than 20 yr of industrial air monitoring experience and a senior chemist with more than 10 yr of analytical experience including serving as the laboratory director of a major analytical lab.

We feel that some clarification is required regarding the subject paper by L.V. Guild, D.F. Dietrich, and G. Moore.

The authors provide data that call into question the ability of the "backup systems" used by Pro-Tek® and 3M to accurately collect methylene chloride under what the authors call "worst-case conditions." The authors state in the Experimental Methods and Materials section:

> Backup methods in use by current manufacturers were studied. The primary consideration was low and medium molecular weight chemicals where quantitative uptake is most often a problem. Methylene chloride was chosen as a representative chemical to evaluate quantitative uptake.

These statements imply that compounds with low and medium molecular weights are inherently difficult to collect with passive monitors. The statements also imply that methylene chloride is considered "a representative chemical" because it possesses a "low molecular weight." The reader is led to believe that all compounds with a similar molecular weight to methylene chloride will behave the same as methylene chloride when being sampled by a passive dosimeter. This, of course, is *completely false.*

Methylene chloride is *not* "representative" with regard to collection efficiency on activated charcoal. It is well known and documented that methylene chloride *is* difficult to collect on both charcoal tubes and charcoal-based passive devices.

Occupational Safety and Health Administration (OSHA) method 59 recommends the use of a three-section charcoal tube, each section containing 350 mg of activated charcoal, for the collection of methylene chloride. The National Institute for Occupational Safety and Health (NIOSH) recommends two charcoal tubes connected in series for the collection of methylene chloride. NIOSH also recommends that the charcoal tubes be separated after sampling to prevent migration of the methylene chloride between the charcoal tubes.

If one compares the OSHA and NIOSH sampling methodologies for methylene chloride to compounds with similar molecular weights and boiling points (i.e., chloroform, trichloroethylene, methyl chloroform, benzene, toluene, or acetone), one easily recognizes that methylene chloride is not representative.

The readers who understand the unique qualities of methylene chloride will, hopefully, recognize that the data generated in this study can only be used to draw conclusions about the Pro-Tek, 3M, and SKC devices relative to methylene chloride. These readers may also recognize that the data presented should not be used to draw conclusions about the performance of these devices when monitoring for any other compound, even those with similar molecular weights or boiling points to methylene chloride. For readers who are not intimately familiar with the unique characteristics of methylene chloride, we believe the data is presented in a way that will facilitate their jumping to false conclusions.

In further defense of this point we cite DuPont's 1981 study, which tested the backup capability of the Pro-Tek G-BB passive dosimeter.[1] The compounds tested in this study were toluene, acetone, methyl chloroform, and trichloroethylene. The results of this study demonstrated that:

1. For all four compounds, breakthrough to the backup section occurred only after the front section was saturated.
2. For all four compounds, quantification was possible as long as the *backup section* was not saturated. This result was shown to be valid to 9000 ppm/hr for each compound.
3. Migration was only observed for acetone and trichloroethylene, but only if the backup and front sections remained together for 1 to 2 days after sampling.

In actual use, Pro-Tek (and 3M) recommend separating the backup and front sections immediately after sampling to prevent migration. Migration will also occur in charcoal tubes if the front and back sections are allowed to remain in the same tube for too long.

The authors' final conclusions, which attempt to narrow the scope of application for passive dosimetry, is completely unjustified by the data provided in their paper. Pro-Tek brand passive dosimeters are specifically designed to be used for short- and long-term sampling of many compounds, including methylene chloride.[2] Pro-Tek Systems, Inc. provides clear instructions on the proper sampling strategies for all compounds. As with any valid sampling methodology, proper usage and application will yield accurate quantitative results.

The generalizations presented by the authors from the very specific tests they conducted is quite unscientific. If this information is published in a respected publication such as the AIHA Journal, it would be an injustice to passive dosimetry in general and to all those who will be misled into believing that many of their sampling needs cannot be done with this marvelously simple technique. For example, the authors state that:

> . . . under challenge conditions current monitors with backup systems may have the following drawbacks: sampling time is limited to less than 8 hr, requiring several samples for full-shift monitoring . . .

We're not sure what the universally accepted definition of "challenge conditions" is, but at threshold limit value levels (published by the American Conference of Governmental Industrial Hygienists) a single Pro-Tek passive dosimeter can be used for full-shift monitoring for 80% of the most commonly used compounds.[3] At Action Level (50% of the permissible exposure limit), a single Pro-Tek monitor can be used for full-shift monitoring for more than 90% of those compounds.

The Pro-Tek brand passive dosimeter has been used in thousands of environments for over a decade. Although it is not appropriate for all sampling situations, it is considerably more versatile than Guild, Dietrich, and Moore infer from their very specific experiments.

Passive dosimetry provides an opportunity to inexpensively, accurately, and precisely monitor a wide variety of compounds. We believe it would be as unscientific to indict passive dosimeters based on data generated from experiments with methylene chloride as it would be to indict automobiles based on data generated from experiments with kerosene.

Sincerely yours,

Jeffrey R. Balancio, Ph.D.
President
Pro-Tek Systems, Inc.

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