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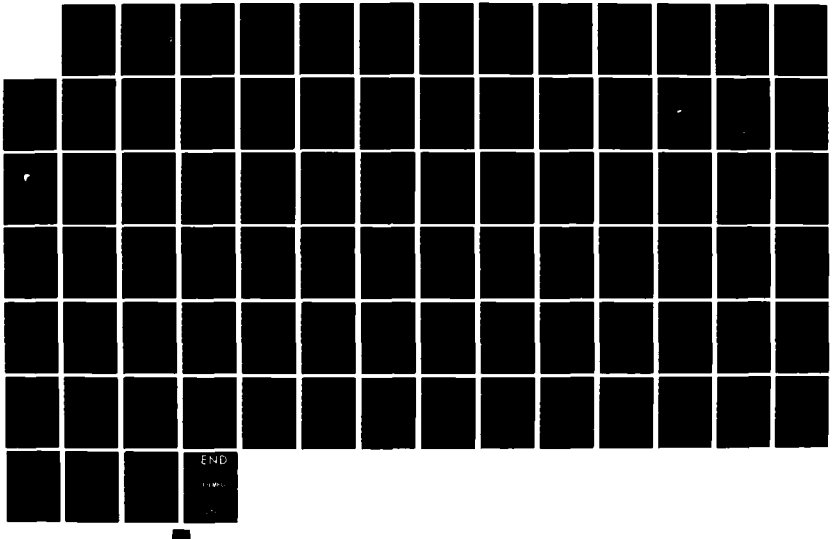

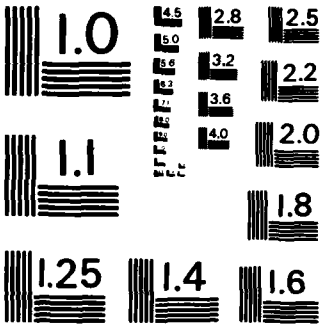

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1. Introduction

This thesis investigates the application of passive charcoal dosimeters to monitor concentrations of methylene chloride vapors. Monitoring the workplace air for methylene chloride vapors requires the collection of air samples in the worker's breathing zone during the work day. The work day exposure usually fluctuates and the air samples must be integrated over periods of several hours or more. This sample integration determines the time-weighted average (TWA) concentration. TWA exposures assist the industrial hygienist in assessing the healthfulness of the occupational environment and are used for compliance purposes by comparison with established 8-hour time-weighted average standards [1].

Evaluating personal exposure to methylene chloride traditionally has been accomplished by collecting air samples with charcoal tubes. This method requires the use of a small battery-powered air pump drawing air through a charcoal tube located in the worker's breathing zone, usually clipped to the shirt lapel. Even though collecting air samples by this method is accurate and accepted by the National Institute for Occupational Safety and Health (NIOSH) [2], the sampling apparatus is expensive, awkward for the worker, and requires constant care and calibration by a technically trained person.

A new method of air sampling has emerged which employs passive organic vapor dosimeters. Passive dosimetry relies on

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Methylene Chloride Sampling

with Passive Dosimeters

under Steady-State and Transient Conditions

by

Frank B. Liebhaber Jr.

A thesis submitted in partial fulfillment
of the requirements for the degree of

Master of Science

University of Washington

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the diffusion principle as the driving force in sample collection, not a mechanical pump. Passive diffusional monitors, like charcoal tubes, rely on adsorption of the contaminant onto a charcoal collection media. The diffusional driving force and subsequent charcoal capture is well explained theoretically, but is not without practical problems (3, 5, 11, 12, 15). Still, these recently introduced passive dosimeters offer significant advantages over the charcoal tube method for evaluating TWA exposures.

Methylene chloride is an organic solvent widely used in industry that epitomizes many of the problems associated with diffusional collection devices. It is a toxic chlorinated hydrocarbon that is very volatile. Due to its quasi-polar nature and low charcoal affinity, it does not adsorb well to activated charcoal and is easily displaced by competing hydrocarbons, moisture (19), and a reversed concentration gradient when the ambient concentration is lower than the dosimeter's internal concentration (11).

This study examined the methylene chloride sampling and retention abilities of passive dosimeters and their subsequent TWA determinations. To evaluate their performance, three commercially available dosimeters were exposed to known concentration profiles of methylene chloride. This comparison was done under laboratory conditions to minimize the differences in actual badge exposure.

There are five hypotheses to be tested. Each hypothesis tests the central issue: passive dosimetry is an accurate method

to sample fluctuating occupational exposures to methylene chloride. However, each hypothesis addresses a specific segment of this issue. The hypotheses are:

a. Passive charcoal dosimetry will sample a steady state concentration of methylene chloride and accurately reflect a time-weighed average (TWA) exposure.

b. Dosimetry will accurately reflect a TWA of short term, high concentration pulses superimposed on a steady state exposure.

c. Dosimetry will accurately reflect the TWA concentrations that bracket the established health standards.

d. No sampler bias exist under transient exposure conditions.

e. Dosimeters will not lose sample mass when a zero concentration exposure follows a steady state exposure.

2. Background

2.1 Methylene Chloride

a. Physical and Chemical Properties

Methylene chloride (dichloromethane, methylene dichloride) is a clear, colorless, volatile liquid with a mild ethereal odor. Though only slightly soluble in water, it is completely miscible with other chlorinated solvents, diethyl ether, and ethyl alcohol in all proportions. It dissolves in most other common organic solvents and is an excellent solvent for many resins, waxes, and fats. It alone exhibits no flash or fire point. Some physical properties are listed in Table 1. (20).

Table 1.

Physical Constants

Molecular Formula	CH_2Cl_2
Molecular Weight	84.94
Density	1.325 g/ml
Boiling Point	19.75°C
Diffusion Coefficient	0.1037 cm^2/sec
Molecular Radius	0.4754 millimicrons
Vapor Pressure	46.5 kPa at 20°C

b. Toxicology

Methylene chloride is one of the least toxic of the chlorinated methanes. The LD_{50} in rats is in the range of 1.6 - 3.0 g/kg body weight (9). The fatal human ingestion dose ranges from one ounce to one pint. This range is based on case histories and extrapolation from animal studies. Methylene chloride is painful and irritating if splashed into the eye. The ACGIH threshold limit value

(TLV) for methylene chloride is 100 ppm for an 8 hr. exposure and the 15 minute exposure limit (STEL) is 500 ppm (1).

Methylene chloride vapors act as a central nervous system (CNS) depressant. Its odor threshold is around 300 ppm. Exposure to concentrations between 310 and 800 ppm is clearly identifiable by the ethereal odor, but not unpleasant. In the range of 900 to 1200 ppm, the odor is pronounced and anesthetic affects with accompanying dizziness begin after 20 minutes exposure. Exposure to over 2300 ppm causes lightheadedness, dizziness, nausea, headaches, and tingling or numbness of extremities. Mental alertness and physical coordination may also be impaired (20).

Continuous exposure of dogs, monkeys, rats, and mice to methylene chloride at 500 and 1000 ppm concentrations produced the following severe toxic effects: dogs died after three weeks exposure to 1000 ppm and six weeks exposure to 500 ppm; 30% of the mice died after four weeks exposure to 500 ppm; rats survived 14 weeks exposure to 500 ppm but experienced subnormal weight gain. All three species exhibited significant liver growth and histopathological hepatic lesions after 14 weeks. In addition, the rats exhibited kidney histopathology. Continuous exposure to low-level methylene chloride concentrations of 100 ppm and 25 ppm for 14 weeks did not affect the spontaneous activity of mice (21). The fatal concentration in several species of animals for seven hours' exposure is given by many authorities as about 15,000 ppm (2). Other studies have shown it to be fetotoxic (9). Its carcinogenic

potential is unknown. Mutagenesis studies with Drosophila gave negative results (22).

c. Uses

Methylene chloride production (U.S.) began in 1940 at 1,500 metric tons (MT), and was up to 18,000 MT in 1950. Since 1950, production has experienced a growth of about 11% per year up to 1976 (23), and peaked in 1981 at 275,000 MT (24). The U.S. produces about 55% of the free world's methylene chloride, Europe about 30%, and Japan about 15%. This totals up to about 400,000 MT free worldwide (25).

Almost all of methylene chloride's uses are dispersive, i.e., the compound is lost directly to the environment through use. Most of its applications make use of its property as an excellent solvent for both polar and non-polar materials.

For use in paint strippers, about 40% of its total production, methylene chloride is blended with other chemical components to maximize its effectiveness against specific coatings. Typical additives include alcohols, acids, amines or ammonium hydroxide, detergents, and paraffin wax. Methylene chloride is used as an extraction solvent for the decaffeination of coffee, spices, and beer hops. It is used in the manufacture of photographic film and as a carrier solvent in the textile industry (26). Its use as a solvent for vapor degreasing of metal parts is increasing and accounts for about 10% of total production.

There is a rapidly growing market for methylene chloride as a vapor-pressure depressant and solvent in aerosol mixtures. Aerosol applications are expected to increase and now account for about 8% of production (24).

Other applications include low-pressure refrigerants, air conditioning installations, and as a low temperature heat transfer medium. There are several uses for methylene chloride in chemical processing, including the manufacture of polycarbonate plastic, the manufacture of photoresist coatings, and as a solvent carrier for the manufacture of insecticide and herbicide chemicals (20). Methylene chloride is also used by the pharmaceutical industry as process solvent in the manufacture of steroids, antibiotics, vitamins, and in the coating of tablets (27). Methylene chloride is used extensively in the urethane foam industry as an auxiliary blowing agent for flexible forms. Other uses include grain fumigation, oil dewaxing, inks, and adhesives (28).

d. Occurences

Measurements of methylene chloride have been made in various indoor atmospheres (29). Results range up to 23,400+ ppt for a beauty parlor, to 64 ppt inside a used car, and many areas such as TV repair shops, drug stores, restaurants, offices, air terminals, showing 500 to 600 ppt. In many cases, there were local sources of methylene chloride such as an aerosol hair spray in the beauty parlor, or the solvent section of a carpet store.

Outdoor measurements have found methylene chloride at concentrations of 35 ppt in the continental and marine backgrounds (30) which is about the same as the tropospheric background level of 20 to 50 ppt (25). Urban concentrations vary from a low of 20 ppt to a maximum concentration of 144 ppt found in St. Louis (30).

Methylene chloride has only been measured a few times in the atmosphere despite the fact of its huge emissions (31). The main reason for this is the relatively short atmospheric life and the fact that the GC-EC detector lacks the sensitivity needed for true assessment. The scarcity of atmospheric measurements makes it futile to attempt any sort of global mass balance despite its large emissions.

2.2 Passive Dosimeters

a. General

Historically, dosimeters have been around since Gordon and Lowe patented their carbon monoxide diffusion monitor in 1927 (41). Then it was not until 1968 that Plantz, et al, developed a dosimeter for measuring hydrazine. This was a semi-quantitative colormetric detector that had many interferences (42). Pioneering work by Palmes and Gunnison in 1973 led to the design of a dosimeter that relied on diffusion through a dead air space or cavity (43), such as in most dosimeters we see today.

In 1977, Abcor GASBADGE™ came to market as the first commercial passive dosimeters for monitoring organic vapors (37).

These dosimeters are still commercially available with slight modifications through National Mine Service Company. Others to follow were DuPont Pro-Tek™ Organic Vapor G-AA Air Monitoring Badge, 3M 3500 Organic Vapor Monitor, and SKC Gas Monitoring Dosimeter Badges. All of these dosimeters utilize activated charcoal in one form or another as the collection medium. All but the DuPont Pro-Tek use draft shields to maintain undisturbed air in the diffusional cavity, for this DuPont uses a grid plate with holes. All the other aspects of the dosimeter are similar with respect to actual physical dimensions.

Charcoal dosimeters were developed for the determination of the time-weighed average (TWA) concentrations of organic vapors (4). This type of monitor samples and collects the vapors by exploiting molecular diffusion and adsorption onto an activated charcoal wafer. Small and light weight in design, the dosimeter badges are to be worn in the breathing zone of the exposed worker for extended lengths of time, up to the full 8 hour work shift (43). They require no power, no air sampling pump, no calibration nor recharging, and no tubes. Their small lightweight design, without the trappings of the charcoal tube/pump samplers, are not likely to interfere with workers' movements. They are not fragile, but if rendered useless, they can be discarded, unlike expensive sampling air pumps with calibration and maintenance problems.

Simplicity of use is the dosimeter's basic appeal. Unlike the charcoal tube/pump sampling method which require elaborate set-up and calibration procedures, dosimeters do not consume the limited time of a technically trained person. They afford the single hygienist or technician more opportunity to sample through the dosimeter's ease of application. Dosimeters can even be placed on the worker by the shop foreman or the workplace health nurse in the same way x-ray film badges are used. The only difference is the need to record the exposure duration. Any reliable timepiece would work. They also can be used as area monitors.

After exposure, the charcoal wafer is removed from the badge and analyzed using lab techniques outlined in NIOSH Physical and Chemical Analysis Method (P & CAM) 127 (46). NIOSH requires an approved monitoring method be accurate within ±25% of the actual concentration or exposure (7).

b. Principles of Operation

Diffusional monitors, or dosimeters rely on permeation and diffusional mass transport through the badge dead space and adsorption onto the charcoal wafer (3). The mass uptake rate is controlled by the physical dimensions of the dosimeter cavities and the physical properties of the vapor being monitored. The force that drives this uptake is the concentration gradient between the ambient air and the charcoal wafer. Fick's first Law

of Diffusion shows that the mass of vapor (M), adsorbed by the charcoal is a function of the sampling rate [Diffusion coefficient (D) times the area of diffusion path (A), divided by the length of diffusion path (L)] times the ambient concentration (C) and the sampling time (t) (4).

$$M = \left[D \cdot \frac{A}{L} \right] C \cdot t$$

The dosimeter's sampling rate is a direct function of the diffusion coefficient (D) of the contaminant vapor being sampled and the dosimeter cavity's total cross-sectional area (A). Also, the sampling rate is an inverse function of the diffusion path or length of the dosimeter's cavity. The kinetic theory of gases (36) indicates that the diffusion coefficient is a function of absolute temperature and pressure. However, the mass collected can be shown to be independent of pressure and only slightly dependent on temperature (37). Correction for temperature can be done by decreasing the determined TWA by 1.0 percent for every 10°F above 77°F and increasing the TWA by the same percent per temperature drop. For this to work, the TWA must be in mg/m^3 (4).

Ideally, the uptake or collection rate is directly proportional to the ambient concentration and is stable. However, stability is a function of the concentration within the badge at the surface of the collection medium. For the uptake rate to remain proportional to ambient concentration throughout the

dosimeter's use, the concentration at the surface of the adsorbent must approach zero. This is assumed and is usually the case as long as adsorbent loading limits are not approached (39).

Other assumptions are implicit to dosimeter theory. All the mass transfer resistance is assumed to be internal to the dosimeter. On the face of dosimeters, above the diffusion cavity, are usually draft shields or membranes to minimize convection as the rate determining step of mass transport. Also, no concentration gradients should exist in the air above the face of the dosimeter. Airflow with some minimum velocity over the face of the dosimeter will insure this and prevent lower than established sampling rates.

c. Sources of Error

The greatest error when utilizing dosimeters arises from erroneous sampling rates. Sampling rates are determined in two ways: (1) experimentally for five or six compounds in a chemical family and (2) calculated for the rest of the chemical family based on the diffusion coefficient calculated from the Hirschfelder equation and the empirical relationship developed from the test compounds (3). It should be noted that sampling rates derived from empirical values may have a bias of $\pm$10 percent (4).

Another source of error becomes important as the dosimeter becomes loaded with contaminant. As the collected mass increases and approaches maximum capacity, the concentration gradient is

altered. Two events then take place: (1) the contaminant uptake decreases and (2) reverse sampling starts to occur with the off-migration of the collected contaminant. These problems were noted in several studies (3, 4, 12, 15).

Windage or face velocity may significantly contribute to error if airflow is less than 15 fpm causing starvation, or in excess of 400 fpm causing a reduced sampling rate by disturbing the concentration gradient in the dosimeter's diffusion cavity (16). With zero or low face velocities, the length of the diffusional path is effectively extended resulting in a decreased sampling rate, hence lower TWA. Workers wearing a dosimeter typically expose it to an average face velocity of 100 fpm (40) because of their movement. However, when used as an area monitor, minimum air velocities must be insured.

Other factors not unique to dosimeters may affect sampling accuracy. The most common are chemical interference, loss during storage, minimum levels of quantification, and competitive vapors to include humidity (11, 3). Air at 90% relative humidity is known to disrupt charcoal sampling (19), and sample loss has been reported at 70% RH (11).

Some of the sampling problems arise because of the charcoal used to capture the sample. Charcoal does not accept and release all chemicals with the same efficiency (4, 8, 11). More often than not, during analysis, some of the chemical is retained by the charcoal. This source of error is minimized by the deter-

mination of the desorption efficiency. A simple method has been developed to accurately determine desorption efficiencies of methylene chloride absorped on charcoal dosimeters. It involves phase equilibration between a spiked filter paper and the dosimeter charcoal wafer (10). Another charcoal consideration is the different performance of granulated charcoal, charcoal impregnated into a glass wool mat, or charcoal bound in an inert polymer wafer.

In summary, although numerous factors may affect the final TWA calculated, only face velocity and the accurate determination of the diffusion coefficient or sampling rate are unique sources of error for diffusional monitors. Therefore, if windage is within 15 to 400 fpm and the sampling rate has been accurately determined, dosimeters should meet NIOSH accuracy criteria and produce results comparable to traditional charcoal samplers.

3. Methods and Procedures

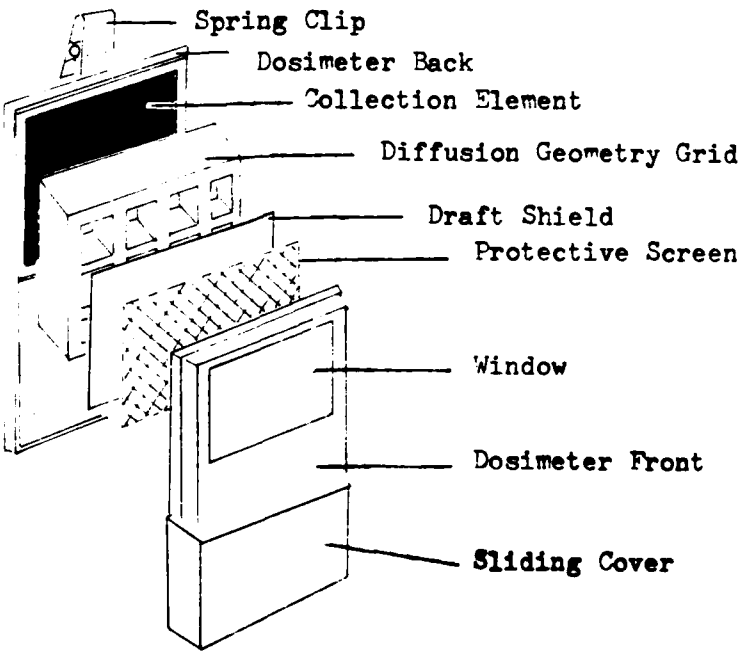
3.1 Samplers

There were three dosimeters used in this study:

a. National Mine Service Company, GASBADGE™, has an overall dimension of 5.7 cm x 7.9 cm x 2.6 cm not including the attachment clip. The ratio of cross-sectional an Area to Path length (A/L) is 7.28 cm, with a diffusion pathlength of 1.31 cm. An exploded view of the dosimeter appears in figure 1.

Figure 1.

GASBADGE Dosimeter



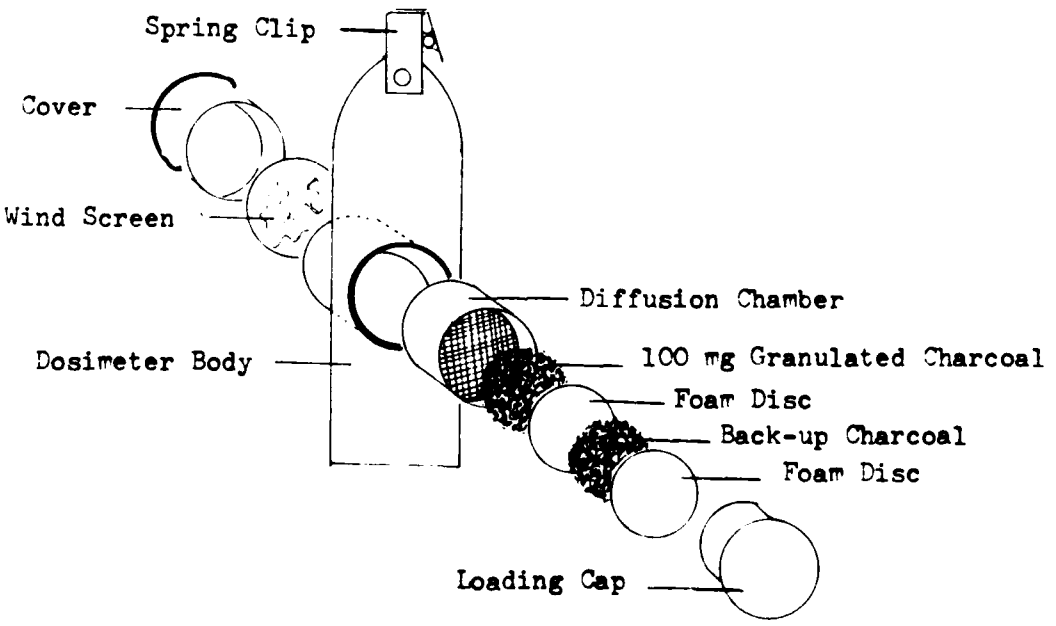
A sliding cover moves from top to bottom for exposure and back again for storage. The exposure window is protected with a plastic puncture screen. Behind this screen is a draft shield. An open grid supports the draft shield and establishes the path length of the diffusion layer. The top section houses a char-

coal impregnated glass wool pad as the collection media and in the bottom section another pad can be placed as a blank. The dosimeter housing is reusable, but the draft shield and charcoal pad must be renewed for each exposure. GASBADGE claims the useful range of their dosimeter is 0.20 to 200 ppm for an 8 hour exposure, with the range varying somewhat depending on substance being monitored, the sensitivity of the GC apparatus, and the length of exposure time. Its maximum collection load was stated as 10 mg, unspecified. The diffusion coefficient for methylene chloride in air was stated as being 0.1037 cm^2/sec at 760 mm Hg and 25°C (44).

b. SKC, Gas Monitoring Dosimeter Badges, Series 530 is modular in design. An exploded view of the dosimeter appears in figure 2.

Figure 2.

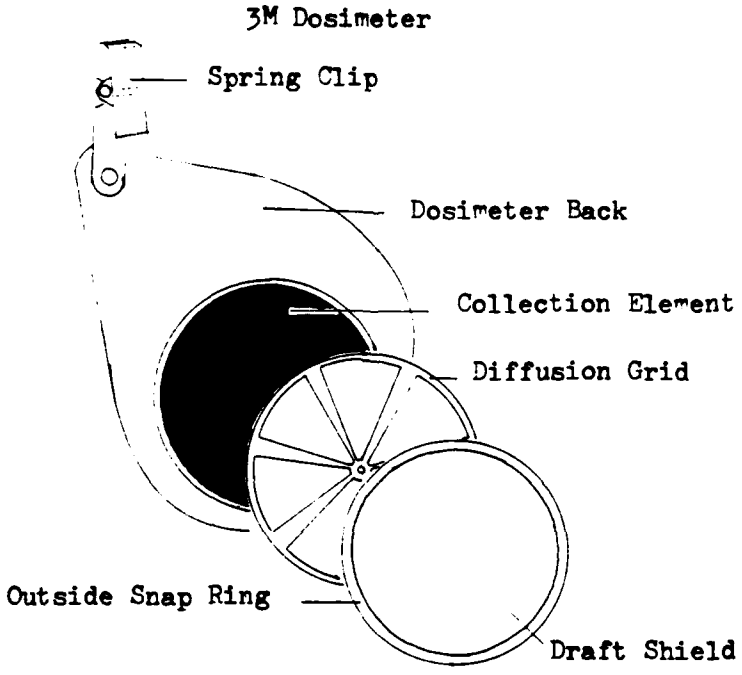
SKC Dosimeter



Its diffusional capsule has a diameter of 2.5 cm and an effective pathlength of approximately .03 cm. The A/L ratio is 125 cm. The pathlength is the thickness of the microporous polymeric material used as a combined wind screen/diffusional barrier. A plastic cap snaps off for exposure and on for storage. The collection medium consist of an aluminum cylindrical disk, 2.1 cm in diameter and 0.8 cm deep. It has a fine mesh screen at one end and a plastic cap at the other. Inside are two 100 mg charges of granulated charcoal separated by a porous foam pad. The dosimeter housing is reusable, but the aluminum charcoal capsule must be renewed with each exposure. SKC claims 23.3 mg capacity for methylene chloride based on NIOSH studies with 100 mg granulated charcoal (46). SKC claims a methylene chloride sampling rate of 13.72 cc/min accurate to ±5% (45).

c. 3M, 3500 Organic Vapor Monitor consists of a round nylon case of 4.5 cm diameter, excluding the attachment clip. Its A/L is approximately 5.9 cm. Over the diffusion cavity is a snap ring which holds in place a porous polymer membrane which acts as a draft shield. Under this shield is a star-shaped spacer which rests on top of the charcoal-impregnated polymer collection pad. An exploded view of the dosimeter appears in figure 3.

Figure 3.



The dosimeter is exposed by removing it from a sealed plastic bag and the exposure terminated by removing the draft shield/ diffusion membrane and snapping in place a tightfitting cap. This cap has two sealable ports with plugs that must be fitted, but these allow addition of the desorption solvent if the body is used as the desorption vessel. 3M has experimentally determined the sampling rate of methylene chloride to be 37.9 $\pm$ 3 cc/ min. 3M also claims that even though its dosimeter has a capacity of 25 or more mg for most organic vapors, for methylene chloride the capacity is only 2 mg. It also claims a 90% desorption efficiency (47).

3.2 Experimental Exposure

A controlled atmosphere test chamber was used for all exposures. Test atmospheres of reagent grade methylene chloride were generated at approximate levels of 40 ppm, 200 ppm, and 400 ppm. Over four hours' exposure these concentrations correspond to fractions of the 100 ppm 8-hour TWA dose (1) for methylene chloride of .2X, 1X, and 2X the TWA. Three exposure profiles were used at each concentration:

1) steady state
2) steady state for the first half of exposure and zero for the last half
3) steady state with superimposed short term, high concentration pulses

Figures 4, 5 and 6. illustrates these concentration profiles.

Figure 4.

Steady State Exposure

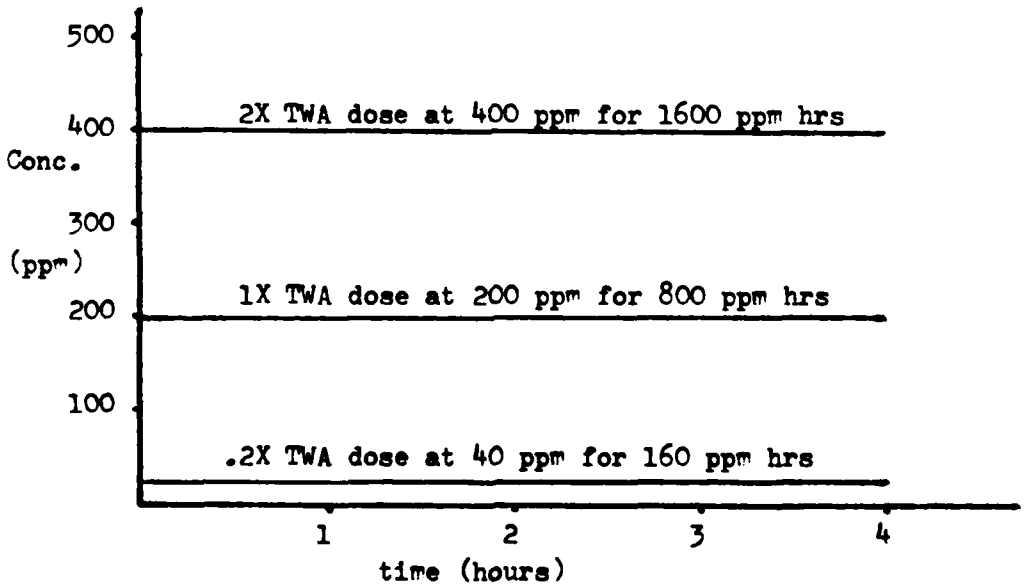


Figure 5.

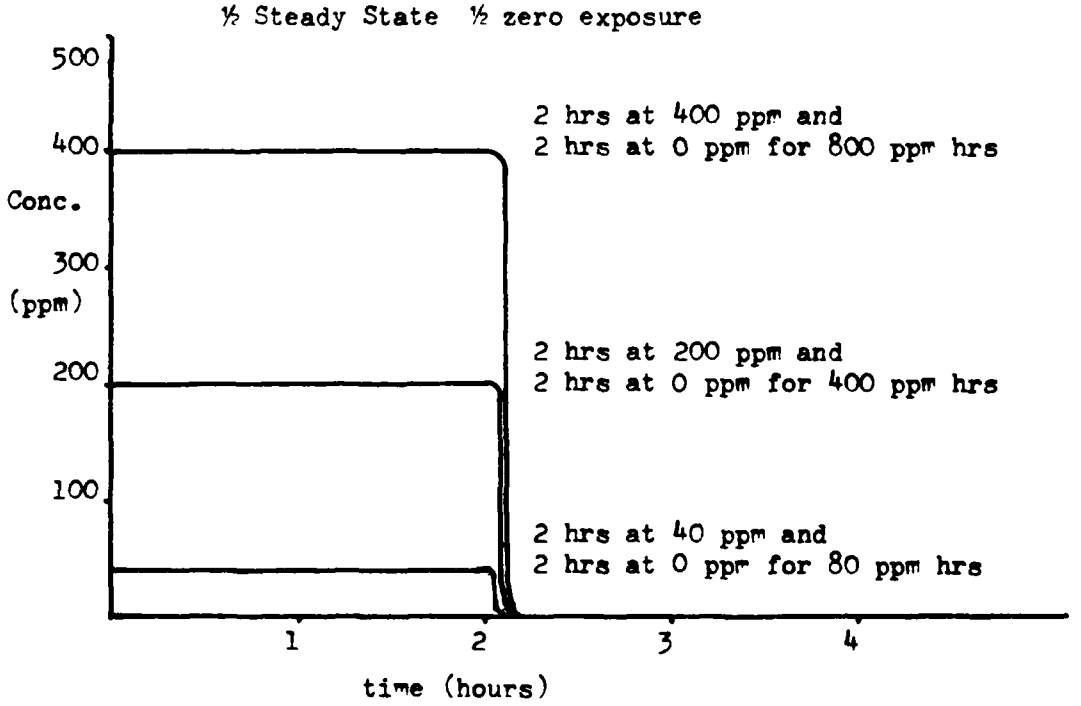
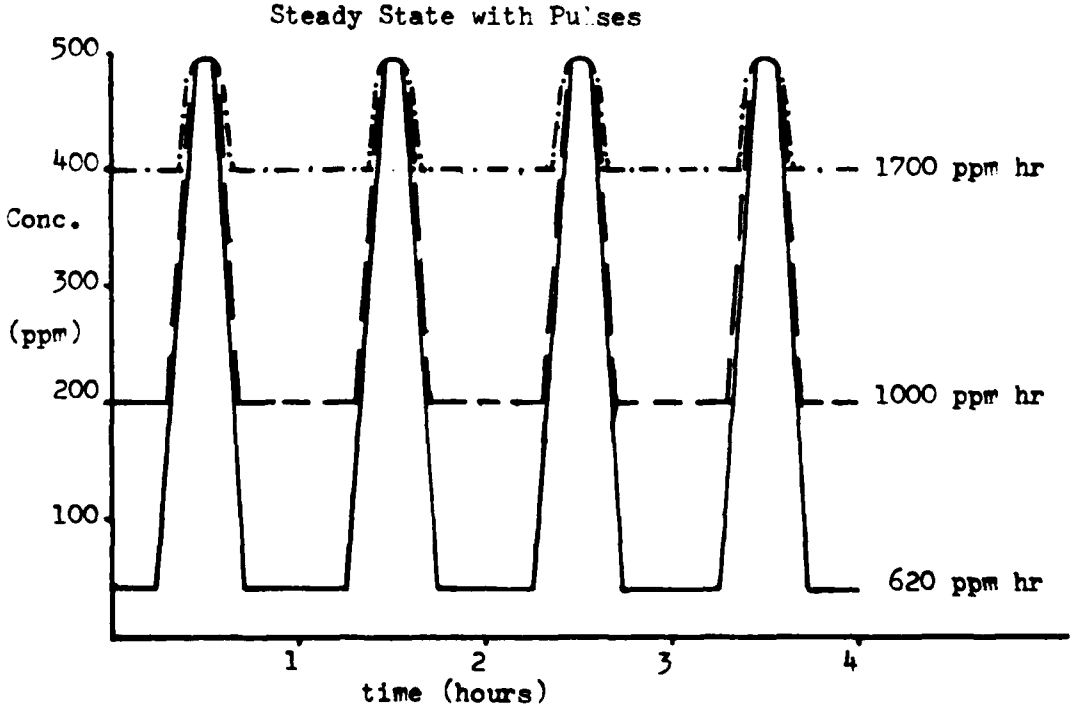


Figure 6.



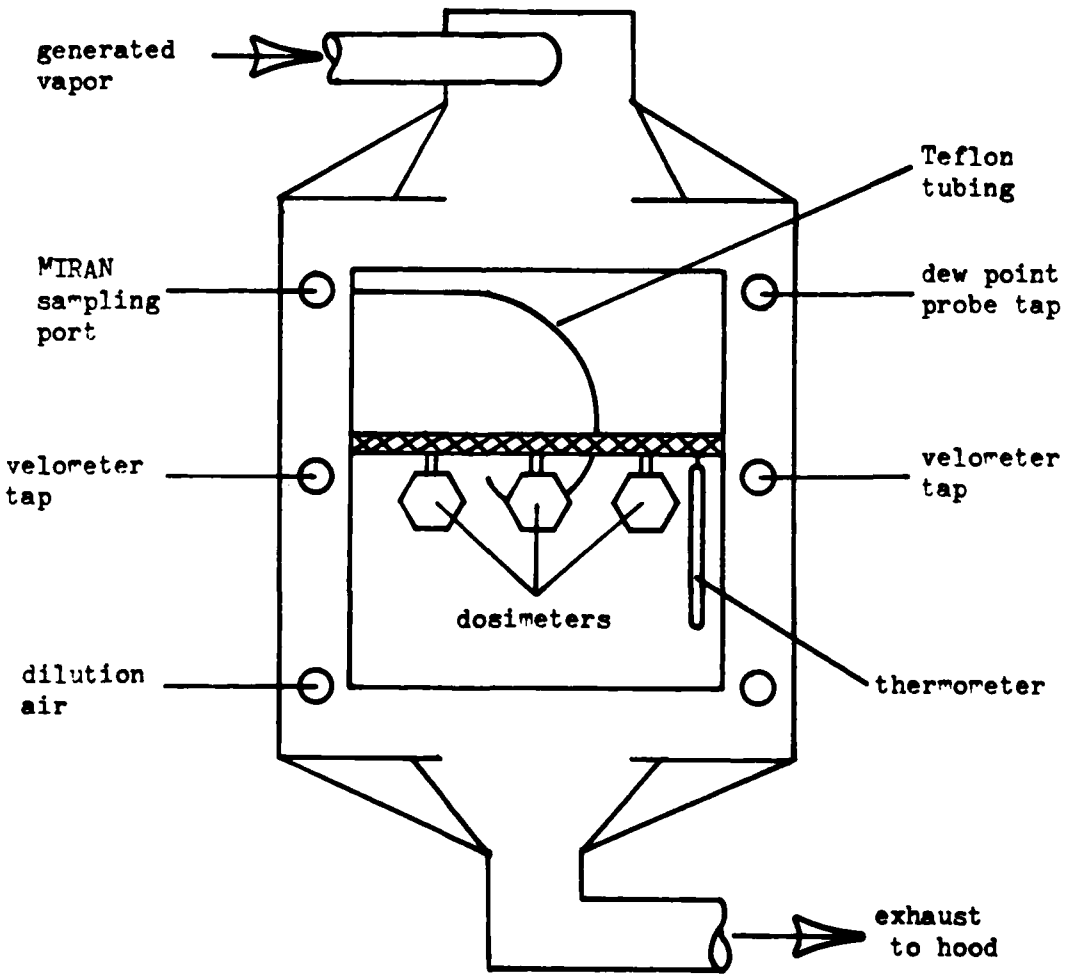
All exposures were done at an average room temperature of 21.9 ± 0.4°C and a relative humidity of 45 ± 3%.

3.3 Exposure Chamber

Exposures were carried out in a Young and Bertke Co. dynamic flow chamber constructed of stainless steel with two glass windows as shown in figure 7.

Figure 7.

Exposure Chamber



Characteristics of these chambers in term of uniform airflow and contaminant are known (48). A stainless steel 2.5 cm mesh grid was horizontally positioned center of the chamber on which the dosimeters were hung, spaced approximately 20 cm apart and from the chamber walls. The main chamber flow, tangentially introduced at the top of the chamber was in excess of 40 lpm and supplied by the vapor generator. A secondary flow of 10 to 40 lpm was introduced at mid chamber tangentially and opposite to the main flow. This flow insured turbulent mixing, dosimeter windage and dilution air for fine concentration control. Dilution flow consisted of compressed dry air.

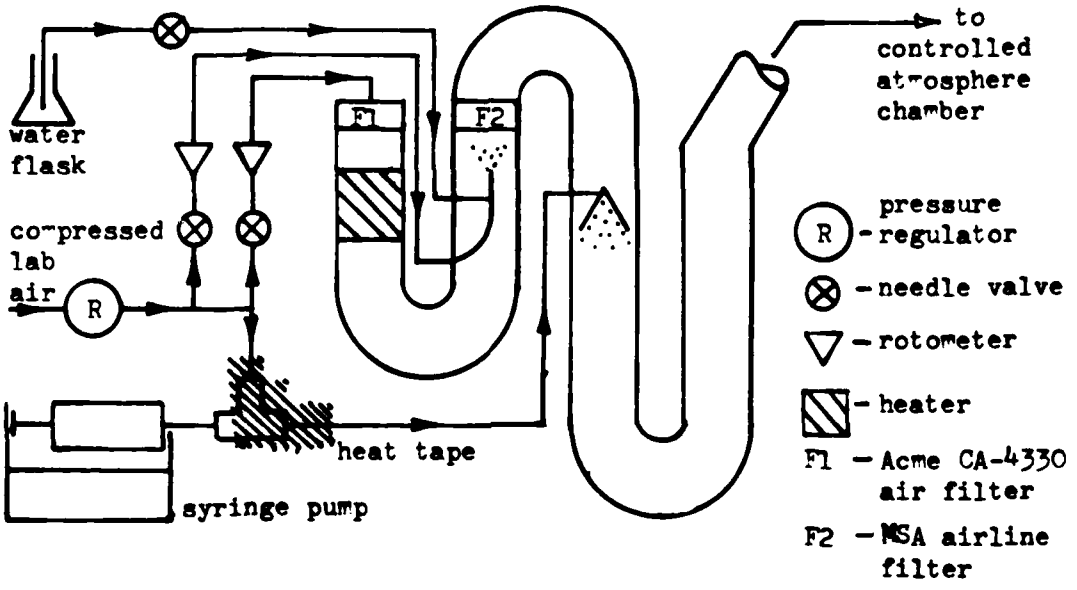
Air velocities within the chamber were constantly monitored with an Alnor Thermo Anemometer and averaged 34.5 $\pm$ 3 fpm at mid-chamber. Dosimeter locations were checked for uniform flows and found to be within the range specified. A General Eastern Dew-point Hydrometer, Model 1200A monitored the dew point in the chamber. A thermometer was suspended alongside the dosimeters and read through the glass window during exposures. The exposure concentration was continuously measured at mid-chamber using a MIRAN 1A spectrophotometer. All chamber monitoring tubing was Teflon . The exposure chamber was connected to the vapor generator with 3 in. OD PVC pipe.

3.4 Vapor Generation System

A dynamic vapor mixing system was used to generate the test atmospheres as shown in figure 8.

Figure 8.

Vapor Generation System



Filtered compressed air was metered through a calibrated flowmeter at a flow rate slightly above 40 lpm. Deionized water was aspirated from a bottle and then atomized into the system. A resistance heater was used to heat the air to approximately 30°C upstream of the humidifier. A Dewpoint Hydrometer (General Eastern Co., Model 1200A) and thermometer probe interfaced with a digital readout monitored the system's dew point and temperature.

A Harvard Apparatus Infusion/withdrawal pump fitted with a 10 cc glass syringe delivered constant rate liquid injections. Methylene chloride was injected at adjustable rates into a stainless steel tube through a Teflon septum. The tube, septum fitting, and some of the trailing Teflon tubing were wrapped in heat tape

(30°C) to assure vaporization of the injected liquid. The vaporized methylene chloride was then introduced into the mainstream of the mixing chamber, mixed uniformly, and then passed from the vapor generator at the desired concentration.

3.5 Atmosphere Validation

A MIRAN - 1A infrared gas analyser was used to continually monitor the exposure concentration. Prior to use, the MIRAN was checked in accordance with factory instructions (38). The MIRAN was calibrated weekly throughout the experiment by liquid injections of methylene chloride with a 5 ul Hamilton syringe into a circulating closed-loop calibration system of known volume. Liquid injections into the known calibration volume were converted to concentration (ppm) and plotted against absorbance for the calibration curve, appendix A. Lack of precision for injections less than 1 ul corresponded to absorbance values less than .035, hence concentrations less than 82 ppm were determined by extrapolation of the calibration curve. The MIRAN's calibration response was linear throughout the 82 to 606 ppm range. Additionally, absorbance and concentration were related in the linear expression: ppm = 2306.6 (Abs) - 7.03, r = 0.997. A Hewlett Packard Integrator Model 3390A was coupled with the MIRAN to plot the absorbance and integrate the area under the absorbance vs. time curve. Integrator counts were related to concentration with a calibration curve (Appendix A).

3.6 Analytical Procedures

All analytic determinations were performed on a Shimadzu Mini 2 Gas Chromatograph equipped with a 10 ft column, 1/8 in. OD, packed with 10% SP-1000, on 80/100 Supelcoport. The Shimadzu is a dual column gas chromatograph (GC) with a hydrogen flame ionization detector. The isothermal column temperature was 90°C, the detector temperature was 130°C, and the injection port temperature was 90°C. Chromatographic grade helium was used as the carrier gas and the flow was set at 44 cc/minute, the air flow was set at 380 cc/min., and hydrogen at 40 cc/min.

Methylene chloride standards were prepared throughout the study to assure proper GC calibration. Standards were made by pipetting 1 ml of reagent grade methylene chloride in to a volumetric flask and then adding spectral grade carbon disulfide (CS_2) to the 10 ml mark, resulting in a 132.5 ug CH_2Cl_2 per microliter (ul) of standard. This was serially diluted to a final standard of .01325 ug CH_2Cl_2 per ul of standard.

A 5 ul Hamilton syringe was used to make all GC injections. All injections utilized the solvent flush method as recommended in NIOSH P and CAM No. 127 (35). The Hewlett Packard Integrator Model 3390A was coupled with the GC for injection quantification. The GC displayed linear response over the range of standards. The linear expression relating counts to mass injected is:

$$(mg)mass = 1.307 \times 10^{-7} (counts) - .008, \; r = .99999$$

The calibration curve is shown in Appendix A.

3.7 Desorption

Desorption efficiencies were determined for each type of dosimeter at levels of loading corresponding to the mass each dosimeter was to collect during exposure. The phase equalibrium or vapor-state spiking technique was used because it is believed to be more representative of desorption after actual vapor sampling than liquid spiking (10, 39). For this technique, 2.0 sq cm of filter paper was placed in the desorption vial alongside the collection medium. Then the liquid spike was delivered through the septum, or the center elurtriation port in the case of the 3M #3500, and onto the filter paper. The vials were then left undisturbed for 16 - 24 hours before elution to give sufficient time for total transfer of the spike from the filter paper to the sorbent. The filter paper was removed and discarded. Then dosimeters were then desorbed following the same basic steps outlined in NIOSH P and CAM No. 127, subject to modifications by each manufacturer.

Concurrently with the vapor-state spiking, 2 ml of CS_2 was pipetted into vials, capped, and similar liquid spikes were injected through the septum into the CS_2. All spiking was done with a 5 ul Hamilton syringe. These spiked standards were then analyzed in parallel to the desorbed samples and efficiencies computed as follows:

$$\text{Desorption Efficiencies} = \frac{(\text{GC counts/ul injected sample})100}{\text{GC counts/ul injected standard}}$$

4. Results

4.1 Calculations

Mass collected on the dosimeters was computed with the GC analysis results, desorption efficiencies, and the volume of solvent used for desorption as follows:

$$\text{Analyzed Mass Collected} = \frac{\text{GC results } (\frac{\text{ug}}{\text{ul}} \text{ injected}) \times \text{desorption volume (ul)}}{\text{desorption efficiency (\% } \div 100)}$$

Sampling rates used for SKC and 3M dosimeters were those given by their manufacturers. The sampling rate for GASBADGE was calculated with the badge dimensions and methylene chloride's diffusion coefficient as follows:

$$\text{Sampling Rate} = \frac{\text{diffusion coefficient } (cm^2/min) \times \text{diffusional area } (cm^2)}{\text{diffusional Pathlength (cm)}}$$

Also, an empirical GASBADGE sampling rate was experimentally determined. Assuming 100% collection efficiency during the steady state exposure, the mean collected mass was used to calculate a new sampling rate. An asterisk denotes the experimental rate. Sampling rates are given in Table 2.:

Table 2.

Sampling Rates

Dosimeter	SKC	3M	GASBADGE	GASBADGE*
Rate (cm^3/min)	13.72	37.9	45.31	24.31

Desorption efficiency was computed with the desorbed sample GC count, blank count, and injection standard count as follows:

$$\text{desorption efficiency} = \frac{(\text{Sample count} - \text{blank counts}) \times 100}{\text{standard count}}$$

The desorption efficiencies were ther pooled for each dosimeter and the mean efficiencies are shown in Table 2.:

Table 2.

Desorption Efficiencies

Dosimeter	SKC	3M	GASBADGE
Efficiency Mean S.D.(%)	105 ± 6.8	94.7 ± 2.7	96.5 ± 2.8
Sample size, n	5	3	9

Time weighed averages were computed using the sampling rate, analyzed mass collected, mass on blank, if any, duration of exposure, and desorption efficiency as follows:

$$\text{TWA } (mg/m^3) = \frac{\text{Corrected Mass (mg)} \times 10^6 (CM^3/M^3)}{\text{sampling rate } (CM^3/\text{min}) \times \text{sample time (min)}}$$

TWA values can be corrected for temperature by considering them to be proportional to the square root of the temperature ratio (47).

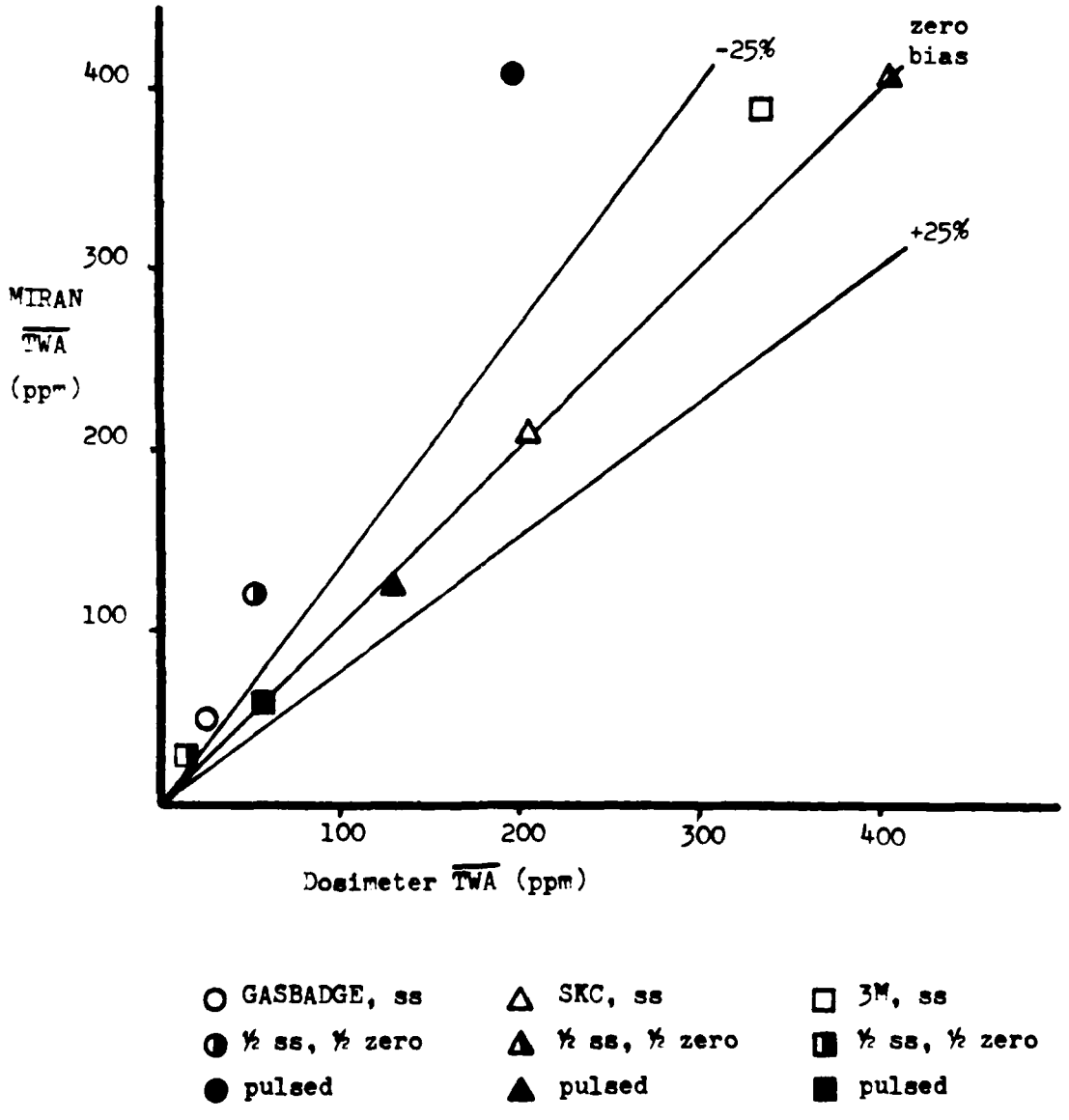
$$\text{TWA corrected} = \text{TWA} \times \left(\frac{298°k}{Ts}\right)^{1/2}$$

Where: Ts = Temperature at sample site in °k.

The TWA values of the dosimeters are compared graphically with the known MIRAN TWA in figure 9. This figure also indicates collection efficiencies.

Figure 9.

TWA Comparison



4.2 Statistical Considerations

For each group of five replicates of a particular dosimeter type and experimental condition, the bias and mean bias were computed as follows:

$$\text{Bias (B)} = \frac{(\overline{\text{TWA}}\ \text{sample} - \overline{\text{TWA}}\ \text{known}) \times 100}{\text{TWA known}}$$

Where the $\overline{\text{TWA}}$ sample is determined from a particular badge and the $\overline{\text{TWA}}$ known is the actual TWA as measured by the MIRAN, integrating continuous absorbance values over the exposure duration. Mean bias would then be the arithmatic mean of the individual biases.

The biases were analyzed in a Latin Square matrix due to the experiment's purposeful incomplete design. A more exhausting experiment would have tested each of the dosimeters under each of the exposure conditions. Testing one type of dosimeter would not fully test the sampling method due to the various dosimeter designs commercially available. Testing all the dosimeters under all the conditions would triple the time, cost, and resources consumed. This expansive scope was not feasible under current thesis guide lines. However, by testing in a Latin Square matrix, both completeness and resource conservation can be achieved.

The Latin Square matrix allows for analysis of three factors: (1) row variation, (2) column variation, and (3) variation within the matrix. Three levels of variation are to be chosen for each

factor. In this study's design, the factors were chosen to be:

1) Actual dosimeter loading; this is related to the exposure dose.
2) Time variation of the concentration; related to dosimeter response under transient conditions.
3) Manufacturer; related to physical dimensions and design.

Since the mean bias indicates the accuracy of dosimeter performance under the various exposure conditions, a Latin Square analysis was performed on the dosimeter bias values to determine significance. The mean bias of each exposure cell (n = 5 per cell), in the Latin Square matrix, are shown in figure 10.

Figure 10.

Latin Square Matrix of
Mean Bias $\pm$ S.D. (%)

TWA range Actual load	Low $<$ 1.54 mg	Moderate $<$ 2.31 mg	High $>$ 2.31 mg
Steady state	GASBADGE 48.2 $\pm$ 1.8	SKC -2.9 $\pm$ 7.6	3M -13.4 $\pm$ 4.5
½ Steady state ½ zero	3M -21.6 $\pm$ 3.7	GASBADGE 55.3 $\pm$ 1.1	SKC -0.5 $\pm$ 3.8
pulsed	SKC +5.9 $\pm$ 6.8	3M +4.2 $\pm$ 3.8	GASBADGE -45.8 $\pm$ 1.9

As stated previously, the matrix was arranged with dosimeter loading increasing left to right and exposure profile variation increasing from top to bottom. An exception was made for the 3M test at 400 ppm steady state due to its limited capacity of 2 mg, as follows: the high concentration and steady state exposure were maintained, but the time of exposure was cut short so as not to exceed the manufacturer's recommended capacity. The GASBADGE 400 ppm pulsed exposure was also cut short because of its 10 mg capacity, but its load never the less increased when compared to all other exposure cells. Therefore, no exception is noted. Table 3. shows the variance table.

Table 3.

Bias Variance Table

Source	Sum of Squares	df	mean square	F_n
1. Exposure profile	1103	2	552	13.79
2. Dosimeter loading	87	2	44	1.09
3. Dosimeter manufacturer	23,466	2	11,733	293.00
4. Variance residual	817	2	409	10.20
5. Variance within test cell	1442	36	40	

A variance factor (F_n) of 3.29 was determined from the tabulated distribution at $p = .05$. Comparing this value with the experimental values shows significance at $p < .05$ if F_n is greater than 3.29. Therefore, dosimeter load was not a significant factor, exposure profile was significant, and manufacturer was highly significant. The mean square of variance within the test cell, 40, indicates the

degree of random fluctuation relative to the influences of the identified factors.

Another Latin Square analysis was performed with this experimentally adjusted GASBADGE sampling rate. All else remained the same. The mean bias of each exposure cell (n = 5 per cell), with the effected biases denoted with an asterisk, are shown in figure 11.

Figure 11.

Adjusted Latin Square Matrix of
Mean Bias ± S.D. (%)

TWA range Actual load	Low < 1.54 mg	Moderate < 2.31 mg	High > 2.31 mg
Steady State	GASBADGE* -3.5 ± 3.8	SKC -2.9 ± 7.6	3M -13.4 ± 4.5
½ Steady state ½ Zero	3M -21.6 ± 3.7	GASBADGE* -16.5 ± 2.1	SKC -0.5 ± 3.8
Pulsed	SKC 5.9 ± 6.8	3M 4.2 ± 3.8	GASBADGE* 1.0 ± 3.6

Table 4. shows the computed variance.

Table 4.

Adjusted Bias Variance Table

Source	Sum of Squares	df	mean square	F_n
1. Exposure profile	2058	2	1029	24.0
2. Dosimeter loading	131	2	66	1.5
3. Dosimeter manufacturer	694	2	347	8.1
4. Variance residual	503	2	252	5.8
5. Variance within test cell	1541	36	43	

The same tabulated variance factor (F_n) was compared with the adjusted F values to show significance at p =.05. The results are very similar to the unadjusted analysis. Dosimeter load was not a significant factor, but exposure profile was significant. Dosimeter manufacturer was still significant, but much less so. The mean square of variance residual was halved, indicating less interaction among the identified factors.

4.3 NIOSH Criterion

NIOSH recommends that the overall accuracy of a sampling method should be ±25 percent of the true value for 95 percent of the samples tested in a range of 0.5 to 2.0 times the workplace air standard (40). This NIOSH criterion can be expressed by the following formula:

$$\text{overall accuracy} = \pm\left[\text{Absolute Mean Bias} + \left(2 \times \begin{matrix}\text{standard}\\ \text{deviation}\\ \text{of bias}\end{matrix}\right)\right]$$

Overall accuracy refers to the percent difference between the dosimeter measured concentration and the true TWA concentration. Absolute mean bias is the collective mean of the dosimeter biases. Twice the standard deviation of bias allows for a 95% confidence level. Together these indicate the overall accuracy of the various types of dosimeters to measure the TWA concentration of methylene chloride. Overall accuracy for the dosimeter brands studied are shown in Table 5. An asterisk denotes GASBADGE accuracy with the experimentally adjusted sampling rate.

Table 5.

	Overall Accuracy
GASBADGE	49.8 + (2 x 4.3) = 58.5%
GASBADGE*	6.3 + (2 x 8.1) = 22.35%
3M	8.3 + (2 x 11.8) = 31.9%
SKC	0.8 + (2 x 7.3) = 15.4%

5. Discussion

5.1 Concentration and Dose

Sampling performance between the various exposure doses (matrix columns) did not significantly differ among the dosimeters. Both the unmodified and the adjusted matrix analysis gave the same variance ratio, 1.09 vs. 1.5 respectively, when compared to f = 3.29 at p .05. These results indicate that for each manufacturer increasing loads, or dosimeter dose had no effect on badge performance.

This partially supports hypothesis 1d. that dosimeters will reflect the TWA concentration that bracket the established health standard. It seems then that dosimeter uptake or collection rates are proportional to the ambient concentration within the range tested.

It should be recognized that sampling rates derived from experiments may have a bias or systematic error of 10 percent (4), but are considered more accurate than those sampling rates calculated from literature values of the diffusion coefficient. Sampling rates for SKC and 3M dosimeters were experimentally determined by the manufacturers while the GASBADGE sampling rate was calculated from physical dimensions for the first analysis and experimentally determined for the adjusted analysis.

If it is assumed that starvation did not occur, then the methylene chloride dose was dependent on the ambient concentration and duration of exposure. Starvation would result if the concentration gradient was altered by insufficient dosimeter face velocity.

Windage was held relatively constant for all exposures. The duration of exposure was also constant except for the two exposures previously noted so as not to exceed rated capacities.

The maximum limit of the sampling range is a function of the collection media capacity. Exceeding capacity, sometimes called saturation, arises when sufficient methylene chloride is adsorbed so that the sampling rate is no longer constant. This phenomenon will eventually occur for all organic vapors because a limited amount of organic contaminant can be absorbed onto the sorbent. Upon saturation, the mass uptake is no longer a linear function of the methylene chloride concentration to which the dosimeters are exposed. Capacity is also affected by coadsorption of other compounds, including moisture, and by temperature. All of these were controlled in this case.

Approaching and exceeded capacities affect the dosimeter sampling rate by reducing the sampling rate with time as the collected mass increases. For a stable sampling rate to exist, the concentration of methylene chloride must be zero at the face of the collection medium. If the capacity is approached and exceeded, the partial pressure of methylene chloride within the sorbent becomes a significant fraction of the ambient partial vapor pressure at the face of the sorbent and the sampling rate is altered. Activated carbon, an imperfect sink for methylene chloride, exemplifies this behavior.

However, since probably starvation did not occur, exposure durations were constant and capacities were not exceeded, the only independent variable was exposure concentration. The manipulated concentration solely contributed to the various dosimeter loads which were shown not to significantly affect performance in each manufacturer's badge.

5.2 Exposure Profiles

Different concentration transient profiles did appear to influence dosimeter performance. The Latin Square row results when compared top to bottom, increasing transient variation, significantly differ for all manufacturers. Both matrices gave the same indication, 13.76 vs. 24.0, when compared to $f = 3.29$ at $p = .05$. The exposure profile then has some effect on badge performance.

The dosimeters were collectively challenged to three concentration profiles; (1) steady state, (2) a zero concentration following a steady state, and (3) short term, high concentration pulses superimposed over a steady state. Steady state tested only the dosimeter's linear response. One half steady state exposure followed by one half zero concentration tested the dosimeter's ability to remain a perfect sink and resist reverse sampling. Pulsed concentrations tested the dosimeter's response time under transient conditions, as well as resistance to reverse sampling. These tests seem to disprove the hypotheses 1e. and 1f. that no sampler bias exists under transient exposure conditions and that dosimeters will not lose sample

mass when a zero concentration exposure follows a steady state exposure.

Dosimeters exposed to a steady state concentration collect contaminant at a constant rate as long as the sorbent is not saturated. Steady state collection rate is proportional to the ambient concentration. If all independent variables are held constant and the dosimeter sampling rate is assumed accurate, no sampling bias should exist. In this study, there was a slight negative bias at medium and low dosimeter loads for SKC (-2.9%) and for GASBADGE with its adjusted sampling rate (-3.5%). 3M showed somewhat more bias (-13.4%), but it should be noted that 92% of its 2 mg capacity was used. These biases, together with their standard deviations, are acceptable performance under the ±25% NIOSH criteria.

Dosimeters all have transient response times unique to their particular design. This response time is directly related to the dosimeter's ability to integrate high peak concentrations. Response times are proportional to the (diffusion length)^2/diffusion coefficient ratio and may be modified by the dosimeter's draft shield or diffusion barrier. In this study, all the dosimeters showed similar response to the short term (15 min), high concentration (500 ppm) pulses that were superimposed over a steady state baseline exposure. This exposure variation had the only positive biases of the study, averaging +3.7% with the adjusted GASBADGE sampling rate.

Zero concentration following a steady state concentration produced the largest biases of the study; -21.6% for 3M, -16.5% for the adjusted GASBADGE, and -0.5% for SKC. When dosimeters are exposed to zero levels of contaminant following exposures, the resulting contaminant build-up on the sorbent produces an internal concentration at the face of the sorbent based on the partial pressure of the collected contaminant. Since the ambient concentration has reverted to zero, a reversal of the concentration gradient within the dosimeter is produced. Such a situation may produce back diffusion and sample loss. Variables which increase the concentration at or above the sorbent surface would also increase sample loss through reverse sampling. Such variables include competing solvents, high humidity, temperature, and probably the most important: the affinity of the contaminant for the sorbent, in this case activated charcoal. Since all mentioned variables were controlled, only methylene chloride's low affinity for activated carbon could explain the dosimeter's limited performance during the exposure mode in which concentration is reduced to zero.

Zero exposures following a steady state exposure have been shown in past studies to affect sample retention. Two types of dosimeters, one being GASBADGE, were found to demonstrate significant sample loss under this exposure profile and exposed to methyl chloroform or methylene chloride (11). Sample losses in this cited study were only significant for those compounds that were highly

volatile and had poor affinity for charcoal. Another study found a 17% sample loss from GASBADGE dosimeters that were exposed for one hour to 700 ppm methyl chloroform and then moved to a zero concentration for five additional hours (6). Therefore, in view of the similar bias exhibited by steady state and pulsed exposures, it is reasonable that the zero exposure following a steady state exposure contributed most to dosimeter bias.

5.3 Dosimeters

Differences in performance among manufacturers, or types of dosimeters, were highly significant in the unmodified matrix analysis. There still remained a significant difference in dosimeter performance when the GASBADGE sampling rate was experimentally determined and TWA values, hence bias, adjusted accordingly, but the variance ratio for this factor was markedly reduced, from 293 to 8.

GASBADGE, with its calculated sampling rate, exhibited a mean bias of -49.8%; this was 6 times that of 3M and 62 times that of SKC.

An explanation for poor performance of the GASBADGE could be erroneous sampling rate. The sampling rate was calculated using literature values for the diffusion coefficient. Literature diffusion coefficients have been shown to vary from empirical coefficients by as much as 12% (44) and it is not uncommon for manufacturers to adjust their sampling rates as empirical data become available. However, a 12% discrepancy is not enough to explain the average

-49% GASBADGE bias found in this study, nor the -28% mean bias found in another study. An inappropriate sampling rate, calculated from literature values for GASBADGE exposed to ethyl benzene, was suspect for the bias range of -79% to -63% in the cited study (51).

GASBADGE, with an experimentally determined sampling rate based on its steady state exposure, had an adjusted mean bias of 6.3%, which was less than 3M and only 5.5% more than SKC. This is an acceptable bias and indicative that an experimentally determined sampling rate for methylene chloride would enhance the GASBADGE performance.

The calculated GASBADGE sampling rate is the highest rate at 45.31 ml/min. High sampling rates are most affected by low face velocities. Starvation can occur if windage is not sufficient to feed the concentration gradient. While literature indicates an absolute minimum of 15 fpm (3) face velocity is needed, it is conceivable that with the GASBADGE high sampling rate, a higher windage may be required. Tompkin's work with GASBADGE determined that as long as face velocities were greater than 15 fpm there was no significant effect on dosimeter performance, but he did not present results which supported his conclusion (37). Two other studies recommend a minimum of 35 fpm for the dosimeters they studied, each having a lower sampling rate than GASBADGE, but neither supported their recommendations with data (14, 4).

3M dosimeters performed well under steady state and pulsed conditions. This seems to imply that the badge is sized correctly

for its sampling rate, it is not starved by windage, and its transient response is adequate. However, its performance during the zero exposure following a steady state exposure was marginal. Reverse sampling may have occured to produce the exhibited negative bias. This seems reasonable in light of 3M's reduced capacity for methylene chloride. This clearly defined capacity of 2 mg limits 3M's use with methylene chloride as a STEL monitor and care must always be exercized to withdraw and cap the badge immediately following the exposure.

SKC dosimeters clearly outperformed the other badges. This may be due to several factors. SKC's use of a microporous polymeric diffusional barrier to provide diffusional resistance instead of a diffusional cavity allows for the sorbent to be placed directly behind the barrier. This affords two advantages; (1) increased response time under transient conditions, and (2) minimized windage effects. Low face velocity performance is enhanced beyond any static air diffusional pathlength design. Also due to the short pathlength, response time can be reduced to approximately 0.08 second, where most badges operate in the range of .5 to 8 seconds. A measure of response time can be made by using the equation: (37)

$$\text{Response time} = \frac{\text{Diffusion length (CM)}^2}{2 \times \text{diffusion coefficient (cm}^2/\text{sec)}}$$

The sampling rate was empirically determined for SKC. It was also the lowest sampling rate. This has a distinct advantage

when combined with an increased sorbent capacity. It should be clear that approaching the capacity increases the chance of reverse sampling. Therefore, to minimize reverse sampling, it is important to use the maximum practicable sorbent mass coupled with the lowest practicable forward sampling rate. SKC achieves this with its low sampling rate and a capacity of 23.3 mg methylene chloride per 100 mg section.

A 46.6 mg capacity is not a practicable capacity because SKC uses the second section of charcoal as a back-up section. For results to be considered valid, the back-up section should not contain more than 25% of the front section contaminant load, as was the case in this study. However, this does not negate the advantage of increased capacity capable of maintaining a forward diffusional driving force.

5.4 Overall Accuracy

Any evaluation of the general dosimeter applicability must consider both bias and random error. As mentioned, NIOSH recommends that concentration measurements by a particular method should be within 25% of the true value 95% of the time. This approach assumes that the absolute mean bias is known without error and that individual measurement are normally distributed about the mean.

Overall accuracy for the dosimeters studied were GASBADGE 63.9%, 3M 31.9%, and SKC 15.4%. GASBADGE, with an adjusted sampling rate, had an overall accuracy of 22.4%. Only SKC meets

the NIOSH criterion for the conditions of this study. However, 3M is thought to be a valid dosimeter, but its mean coefficient of variation is too large to qualify it for NIOSH. GASBADGE certainly has a problem qualifying. An empirically determined sampling rate would rectify this.

5.5 Error

Other sources of error may contribute to disqualification. Certainly the assumption of normality seems proper since many errors in chemical analysis are normally distributed. The mean biases are in essence estimates of the true mean biases because a much larger number of replicates are needed for a true mean and the measurements of the MIRAN must be error free. The most significant possible MIRAN measurement errors are related to calibration and drift. Calibration error would result if the exact volume of the closed loop calibration system was not accurately determined and if a fraction of the methylene chloride liquid was lost to the interior walls of the system (17). Calibration volume errors are estimated to be 1% (39). When interior system loss occurs, the concentration within the system is lower than the expected concentration within the MIRAN and consequently lower absorbance readings result. Then when assessing the methylene chloride levels within the exposure chamber, the effect of vapor loss due to wall adsorption is minimized due to the continuous flow through the MIRAN. Therefore, overestimation of the methylene chloride concentration the dosimeters are exposed to may result, producing a negative bias

error. While the adsorption for organic solvents with vapor pressures higher than 16 mm Hg at 25°C was shown in a study to be insignificant (17), it was noted in this work that within-MIRAN adsorption did occur. After each 2 to 4 hour TWA exposure, the MIRAN was put on filtered lab air and was noted not to zero until hours after the exposure. Typical non-zero absorbance values were .003 to .007, or 2 to 3% of preceeding absorbance TWA value. However, the MIRAN did return to zero between 15 min. calibration runs. There was no data correction performed for non-zero phenomenon.

The variance residuals, 10.2 and 5.8 adjusted, were greater than the variance factor 3.29 indicating a significant effect due to unknown factors. Interaction between two factors was obvious in the case of SKC dosimeters outperforming GASBADGE and 3M dosimeters in the steady state exposure followed by zero exposure. This deviation from other badge behavior shows up as factor interaction. Other factor interactions may have contributed to the residuals but are too subtle to be identified in this work. The variance within the test cells, 40 and 43 adjusted, is an indication of the random fluctuation. This was assumed normally distributed thereby unaffecting the mean bias, but increasing the standard deviations and confidence intervals. More replication or better lab technique could lower the variance within the cells. Both numbers being about equal indicate the adjusted sampling rate of GASBADGE did not affect the random error.

A slight error in determining desorption efficiencies may have been introduced when the filter paper used in the vapor spiking was discarded without regard to its residual methylene chloride. Based on methylene chloride's high volatility it was assumed that all of the liquid spike was totally vaporized and was completely absorbed onto the collection charcoal. This assumption should be valid as long as the spike did not exceed the capacity of the sorbent.

A difference between the desorption samples and the experimentally exposed dosimeters was that the desorption dosimeter adsorbents had no exposure to water vapor. It took a few minutes to transfer the adsorbents from their sealed pouches to the desorption vial when exposure to ambient lab humidity was unavoidable. The significance of this has not been determined, but is thought to be minuscule.

6. Conclusions and Summary

This study has led to a number of conclusions concerning the performance of commercial passive dosimeters when monitoring methylene chloride vapors.

1. Some sampling bias exists under transient exposure conditions; this may be serious when zero exposure follows a steady state exposure.

2. Concentrations that bracket established health standard TWA do rot bias sampling as long as dosimeter capacities are not approached.

3. Capacities are a limiting factor in dosimeter performance and must be considered when sampling methylene chloride vapors.

4. Dosimeter performance adequately samples pulsed concentrations and integrates the pulses over time.

5. The performance of passive dosimeters was different for different manufacturers. Sampling rates and design were the major influences in performance.

   a. Sampling rates based on actual badge test, not diffusion coefficient data, should be used to compute TWA.
   b. Lower sampling rates seemed to enhance performance.
   c. Shorter diffusional pathways seemed to enhance performance.
   d. Larger capacities, especially if coupled with a back-up section, seemed to enhance performance.

6. Only one type of dosimeter met NIOSH specifications for the

organic compound, conditions, and TWAs used in this study.

a. GASBADGE performance was the least accurate with inappropriate sampling rate and possible windage starvation being suspected sources of error.

b. 3M would have met NIOSH specifications if the coefficient of variation were lower. The results for the half steady half zero exposure significantly contributed to this conclusion. More precise testing, or more replication would probably qualify this dosimeter.

c. SKC performance was clearly superior to the other dosimeters in reflecting accurately TWAs. Three factors which are thought most to influence its performance were:

1. The micro-porous polymer diffusion barrier limiting the diffusional path necessary, hence increasing response and allowing for a lower sampling rate.

2. Increased capacity and availability of a back-up section validation.

3. A design which combines the lowest practicable forward sampling rate with the maximum practicable sorbent mass, hence minimizing reverse diffusion losses.

Thus summarizing, it may be stated that passive dosimeters can accurately reflect TWA of non-uniform exposures to methylene chloride if proper care to select or design the dosimeters is used. Questions concerning dosimetry for methylene chloride in the presence of competing solvents, such as in a commercial paint stripper, may have significance and require further research.

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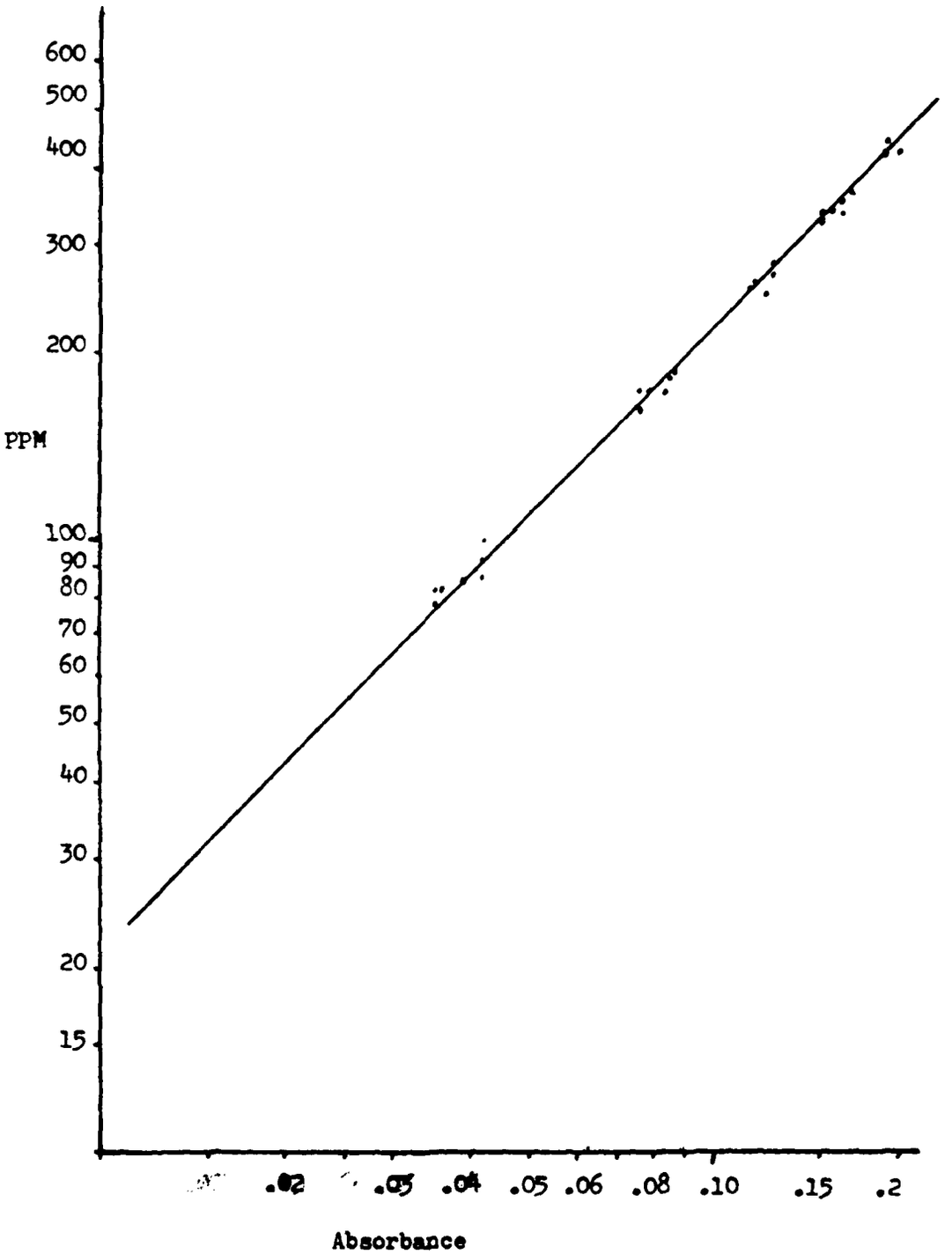
Appendix A: Calibration Curves

1. MIRAN calibration with liquid methylene chloride injections

2. MIRAN absorbance values plotted against integrator counts per minute

3. GC calibration with methylene chloride injections in known volumes of carbon disulfide

1. Miran Calibrated With
Liquid CH_2Cl_2 Injections



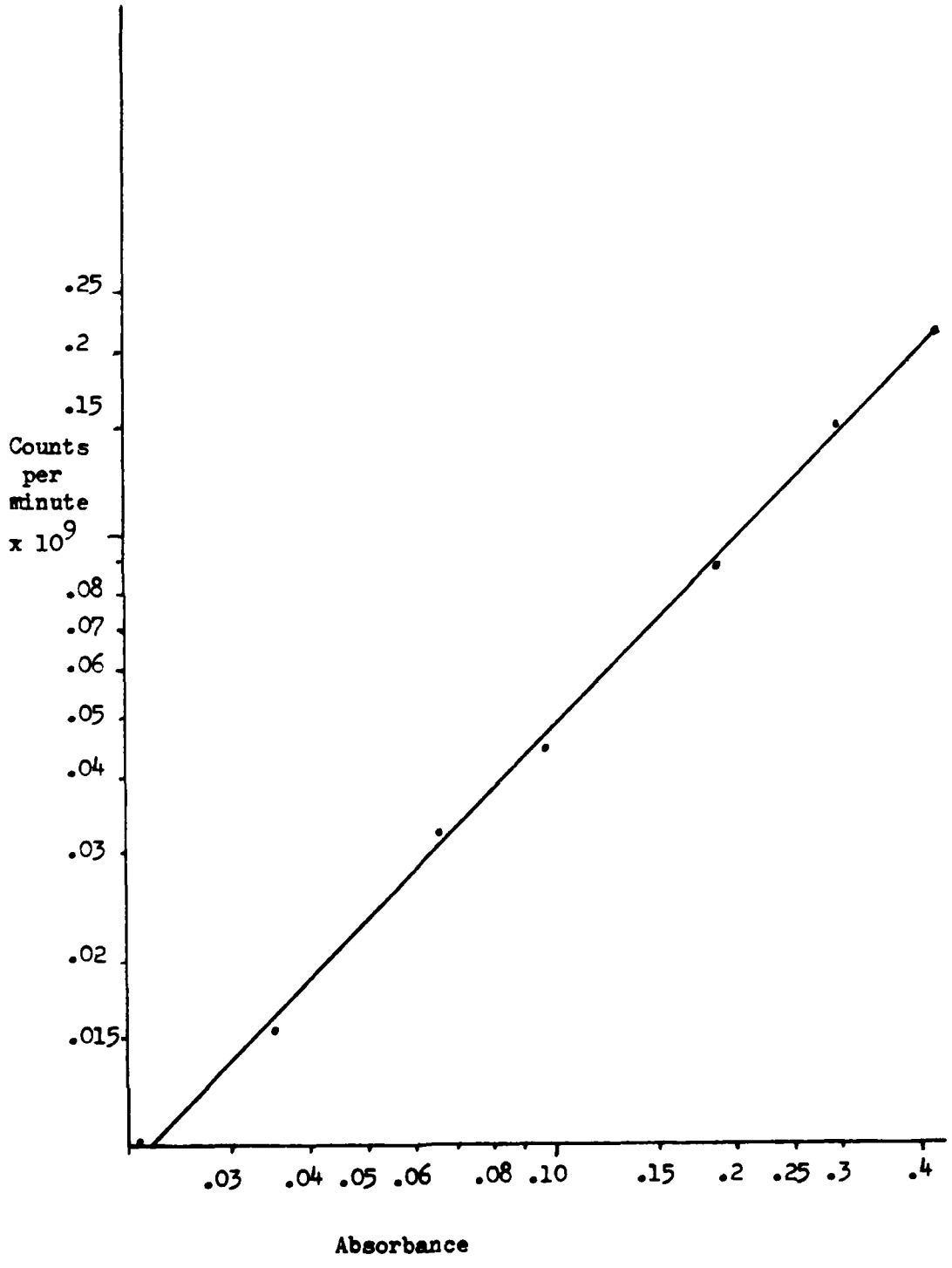
MIRAN Calibration with Liquid Injections

ul injected	Conc. ppm (y)	Abs (x)	ul injected	Conc. ppm (y)	Abs (x)
1.25	82.8	.035	5.20	344.4	.154
1.25	82.8	.036	5.25	347.7	.150
1.30	86.1	.039	5.20	344.4	.164
1.30	86.1	.042	5.40	357.6	.159
1.40	92.7	.041	5.65	374.2	.165
1.50	99.3	.044	5.85	387.4	.165
2.50	165.6	.075	6.45	427.2	.190
2.65	175.5	.075	6.50	430.5	.204
2.65	175.5	.078	6.80	450.4	.190
2.80	185.4	.084	6.55	433.8	.191
2.60	172.2	.084	7.05	466.9	.206
2.80	185.4	.084	7.10	470.2	.204
2.85	188.8	.085	7.55	500.0	.216
3.80	251.7	.122	7.85	519.9	.226
3.90	258.3	.122	7.85	519.9	.223
4.00	264.9	.115	7.95	526.5	.230
3.90	258.3	.114	7.90	523.2	.246
4.15	274.9	.123	8.45	559.6	.245
4.20	278.2	.125	8.45	559.6	.246
4.25	281.5	.125	8.95	592.8	.250
5.10	337.8	.150	9.15	606.0	.258

at 23°C & 760 mmHg 1 ul of $MeCl_2$ equals
66.228 ppm/ul $MeCl_2$

Linear regression ppm = 2306.6(Ab) - 7.03
r = .997

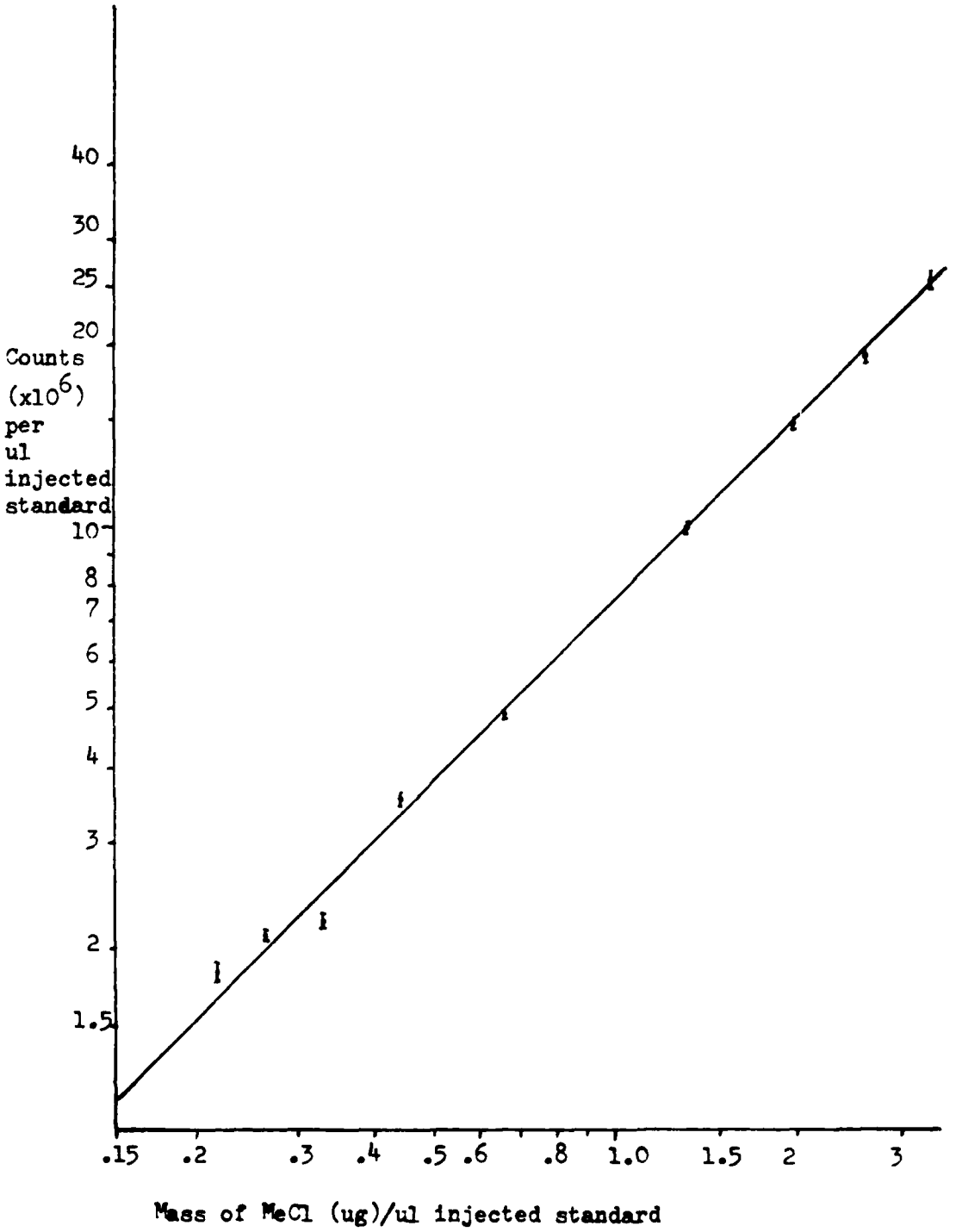
2. MIRAN (Ab) vs. Integrator (cts/min x 10^9)



MIRAN Calibrated against Integrator

MIRAN Ab	PPM	Counts (10^9)	Time	Cts/min
.011	18.3	.0894	17.19	.00520
.021	41.4	.2749	25.37	.01084
.037	78.0	.3949	25.59	.01519
.066	145.0	.7817	24.10	.03243
.100	220.0	.5340	12.20	.04377
.191	427	1.1958	13.65	.08662
.240	538	1.1316	11.55	.11397
.300	675	1.6742	11.25	.14881
.500	1130	2.4386	10.35	.23562

3. GC Calibration Curve



Desorption Data: Liquid MeCl Injections into 2 ml CS_2

Mass (ug)/GC injection / (ul) Volume / Solution Standard	Volume /2 ml (ul) of/ CS_2 MeCl /	Counts ± S.D./ul injection
.221 ug/ul	.3 ul/2 ml	$\bar{x}_4$ = 1,829,096 ± 89,582
.265	.4	$\bar{x}_4$ = 2,102,229 ± 59,129
.331	.5	$\bar{x}_{18}$ = 2,185,702 ± 178,942
.442	.6	$\bar{x}_4$ = 3,526,933 ± 21,349
.662	1.0	$\bar{x}_{12}$ = 4,809,152 ± 313,599
1.324	2.0	$\bar{x}_{13}$ = 9,774,348 ± 293,637
1.985	3.0	$\bar{x}_4$ = 14,529,280 ± 149,704
2.645	4.0	$\bar{x}_4$ = 18,874,629 ± 778,589
3.308	5.0	$\bar{x}_6$ = 25,477,760 ± 489,705
4.950	7.5	$\bar{x}_5$ = 36,408,730 ± 462,925

GC Calibration with Serial Dilution Standards

Counts	MeCl mass (ug)/ul injection of standard
$\bar{x}_{23}$ = 140,925 ± 19,895	.01325 ug
$\bar{x}_{38}$ = 1,099,511 ± 75,867	.1325
$\bar{x}_{39}$ = 10,196,358 ± 424,846	1.325
$\bar{x}_{10}$ = 98,325,733 ± 4,438,400	13.25
$\bar{x}_{14}$ = 929,894,857 ± 60,723,336	132.5

Appendix B: Dosimeter Data

1. GASBADGE exposures
   a. steady state
   b. ½ and ½
   c. pulsed

2. 3M exposures
   a. steady state
   b. ½ and ½
   c. pulsed

3. SKC exposures
   a. steady state
   b. ½ and ½
   c. pulsed

4. Desorption Efficiencies

GASBADGE 40 ppm Steady State

Temp	: 21.5°C	Lot	: A04
DP	: 44 - 46°F	Batch:	5003B
Pressure	: 29.9 in Hg		
Airflow	: 28 - 36 fpm		
Time	: 245.15 min		
Exposure	: 48.3 ppm		
Dose	: 197.5 ppm hr		
Mass expected	: 1.86 mg/1.00 mg*		
Mass collected	: 1.00 mg		

GC Counts ± S.D. (x 100)	TWA sample (ppm)	Bias (%)
1. 36760 ±2085	25.3/47.16*	-47.5/-2.3*
2. 36279 ±3707	25.1/46.8*	-48.2/-3.1*
3. 37139 ±1984	25.6/47.7*	-46.9/-1.2*
4. 37180 ± 860	25.6/47.7*	-46.9/-1.2*
5. 33911 ±1526	23.4/43.6*	-51.6/-9.7*

Mean Bias ± S.D.: -48.2 ± 1.8%/-3.5 ± 3.8 *

Avg. Collection Efficiency: 54%/96.8% *

*Adjusted values based on 24.31 ml/min Sampling Rate

GASBADGE ½ 200 ppm ½ Zero

Temp : 21.5°C

DP : 47 - 49°F

Pressure : 29.9 in Hg

Airflow : (½) 35 - 40 fpm/(2/2) 80 fpm

Time : 120 min at 236 ppm and 120 min at zero

Exposure : $\overline{118}$ ppm

Dose : 472 ppm hr

Mass expected : 4.45 mg/2.39 mg*

Mass collected: 1.995 mg

GC Counts ± S.D. (256), $\bar{x}_3$	TWA sample ppm	Bias %
1. 14130 ± 85	51.0/95.0*	-56.8/-19.4*
2. 15224 ±179	55.0/102.5*	-53.4/-13.1*
3. 14458 ±277	52.2/97.3*	-56.0/-17.5*
4. 14709 ±108	53.1/99.0*	-55.1/-16.1*
5. 14626	52.8/98.4*	-55.1/-16.6*

Mean Bias ± S.D.: -55.3 ± 1.1%/-16.5 ± 2.1% *

Avg. Collection Efficiency: 45%/83% *

*Adjusted values based on 24.31 ml/min Sampling Rate

GASBADGE 400 ppm Pulsed

Temp : 21.5°C Lot: A04

DP : 48 - 51°F Batch: 5003C

Pressure : 29.9 in Hg

Airflow : 32 - 38 fpm

Time : 150 min total with 4, $\overline{10.13}$ min pulses

Exposure : 366 Base line with 4, $\overline{147}$ ppm pulses: 405.6 ppm avg

Dose : 1014 ppm hr

Mass expected : 9.57 mg/5.14 mg*

Mass collected: 5.181 mg

GC Counts ± S.D. (x 256) $\bar{x}_3$	TWA sample ppm	Bias %
1. 38359 ± 524	228/425*	-43.7/+4.8*
2. 35563 ±1007	212/395*	-47.7/-2.6*
3. 37984 ± 301	226/421*	-44.3/+3.9*
4. 35154 ± 628	209/390*	-48.5/-4.0*
5. 37775 ± 566	224/418*	-44.8/+2.9*

Mean Bias ± S.D.: -45.8 ± 1.9/+1.0 ± 3.6%*

Avg. Collection Efficiency: 54.1%

*Adjusted values based on 24.31 ml/min Sampling Rate

3M 400 ppm Steady State

Temp : 22°C

DP : 45 - 50°F

Pressure : 29.9 in Hg

Airflow : 33 - 37 fpm

Time : 36.25 min (limited because of 2 mg capacity)

Exposure : 383 ppm

Dose : 231 ppm hr

Mass expected : 1.83 mg

Mass collected: 1.583 mg, blank none

GC Counts ± S.D. (x 256), $\bar{x}_3$	$\overline{TWA}$ sample (ppm)	Bias (%)
1. 29055 ±483	320.0	-16.4
2. 28299 ±224	311.6	-18.6
3. 30956 ±728	340.9	-11.0
4. 29561 ±486	325.5	-15.0
5. 32686 ±866	359.9	- 6.0

Mean Bias ± S.D.: -13.4 ± 4.5%

Avg. Collection Efficiency: 86.5%

3M ½ 40 ppm ½ Ø ppm

Temp : 22.5°C Lot : YF

DP : 50°F Batch: 4900
5000

Pressure : 29.9 in Hg

Airflow : 30 - 35 fpm

Time : 127 min at 41.4 ppm and 120 min at Ø ppm

Exposure : $\overline{21.9}$ ppm avg

Dose : 87.6 ppm hr

Mass expected : .692 mg

Mass collected: $\overline{.539}$ mg, blank none

GC Counts ± S.D. (x 64), $\bar{x}_3$	$\overline{\text{TWA}}$ sample (ppm)	Bias (%)
1. 42498 ±1496	32.9	-20.5
2. 43014 ± 929	33.3	-19.6
3. 41660 ± 446	32.2	-22.2
4. 43066 ± 756	33.3	-19.6
5. 37957 ± 90	29.3	-29.2

Mean Bias ± S.D.: -22.2 ± 3.6%

Avg. Collection Efficiency: 77.9%

3M ½ 40 ppm ½ Ø ppm (rerun)

Temp : 21.8°C Lot : YF

DP : 47 - 51°F Batch : 4800
5100

Pressure : 29.9 in Hg

Airflow : ½, 30 - 36 fpm 2/2, 80 fpm

Time : 121 min at 43 ppm and 119 min at Ø ppm

Exposure : $\overline{21.7}$ ppm avg

Dose : 86.7 ppm hr

Mass expected : .685 mg

Mass collected : $\overline{.540}$ mg, blank none

GC Counts ± S.D. (x 64), $\bar{x}_{3-5}$	TWA sample (ppm)	Bias (%)
1. 38923 ±1029	31.5	-26.7
2. 41014 ± 862	33.2	-22.8
3. 41724 ± 732	33.8	-21.4
4. 43984 ±1503	35.6	-17.4
5. 44342 ± 352	35.9	-16.5

Mean Bias ± S.D.: -20.9 ± 3.8%

Avg. Collection Efficiency: 78.9%

3M 40 ppm Pulsed

Temp : 22.0°C Lot : YF

DP : 39 - 44°F Batch: 5000s
5300s

Pressure : 29.9 in Hg

Airflow : 38 - 40 fpm

Time : 244.5 min with 4, $\overline{18}$ min pulses

Exposure : 37.5 ppm baseline with 4, $\overline{165.6}$ ppm peaks: $\overline{59}$ ppm avg

Dose : 240.4 ppm hr

Mass expected : 1.9 mg

Mass collected : $\overline{1.32}$ mg, blank none

GC Counts ± S.D. (x 256), $\bar{x}_3$	$\overline{TWA}$ samples (ppm)	Bias (%)
1. 34950 ±671	57.2	-3.1
2. 37499 ±418	61.3	+3.9
3. 38453 ±134	62.9	+6.6
4. 38151 ±273	62.4	+5.7
5. 38941 ±462	63.7	+7.9

Mean Bias ± S.D.: +4.2 ± 3.8%

Avg. Collection Efficiency: 104%

SKC 200 ppm Steady State

Temp : 21.5°C

DP : 50°F

Pressure : 29.9 in Hg

Airflow : 32 - 38 fpm

Time : 240.75 min

Exposure : 206.6 ppm

Dose : 829 ppm hr

Mass expected : 2.37 mg

Mass collected : 2.188 mg front and .116 mg back - $\overline{2.304}$ mg, blanks none

GC Counts ± S.D. (front x 256), $\bar{x}_3$	(Back x 64), $\bar{x}_3$	$\overline{\text{TWA}}$ sample (ppm)	Bias (%)
1. 31890 ± 72	7252 ±165	184.6	-10.6
2. 37665 ±519	8840 ±211	218.4	5.7
3. 37809 ±130	9995 ±407	220.7	6.8
4. 33597 ±445	7212 ±190	194	- 6.1
5. 31842 ±568	8167 ±505	185.5	-10.2

Mean Bias ± S.D.: -2.9 ± 7.6

Avg. Collection Efficiency: 97.2%

SKC ½ 400 ppm ½ Ø ppm

Temp : 22°C

DP : 47 - 50°F

Pressure : 29.9 in Hg

Airflow : 28 - 36 fpm

Time : 125.75 min at 409 ppm + 120 min at Ø ppm

Exposure : $\overline{209.3}$ ppm avg

Dose : 857 ppm hr

Mass expected : 2.45 mg

Mass collected: 2.24 mg front and .198 back = $\overline{2.438}$ mg total
Blanks none

GC Counts ± S.D. (front x 256), $\bar{x}_3$	(backs x 64), $\bar{x}_3$	$\overline{\text{TWA}}$ sample (ppm)	Bias (%)
1. 35579 ±994	12283 ±559	207.8	-0.7
2. 37648 ±233	13829 ±287	221.0	5.6
3. 36324 ± 70	12448 ±103	212.0	1.3
4. 33867 ±470	14624 ±725	201.4	-3.8
5. 33547 ±825	13818 ±125	198.8	-5.0

Mean Bias ± S.D.: -0.5 ± 3.8

Avg. Collection Efficiency: 99.5%

SKC 200 ppm Pulsed

Temp : 21.8°C

DP : 47 - 49°F

Pressure : 29.9 in Hg

Airflow : 32 - 36 fpm

Time : 243.41 min with 5, $\overline{12.5}$ min pulses

Exposure : 85 ppm baseline with 5, $\overline{100}$ ppm peaks: $\overline{125}$ ppm avg.

Dose : 500 ppm hr

Mass expected : 1.45 mg

Mass collected: 1.494 mg front + .38 mg back, Blank none

GC Counts ± S.D. (front x 256), $\bar{x}_3$	(Back x 64), $\bar{x}_3$	$\overline{\text{TWA}}$ sample (ppm)	Bias (%)
1. 22640 ±235	2826 ±109	126.0	0.8
2. 24819 ±186	4103 ±169	138.9	11.1
3. 24554 ±306	2902 ± 16	136.2	10.7
4. 21243 ±306	3320 ±241	118.7	-5.0
5. 25072 ±354	3350 ± 67	139.6	11.7

Mean Bias ± S.D.: +5.9 ± 6.8%

Avg. Collection Efficiency: 106%

Desorption Efficiencies

Vol MeCl injected onto badge (ul)	Mass MeCl per ul GC injection	Counts ± S.D.	Expected Counts	Desorption Percentile
GASBADGE				
.35	.231	1,810,709 ± 83,721	1,936,750	93%
.50	.331	2,166,944 ± 24,224	2,185,702	99%
1.00	.662	4,776,576 ± 88,205	4,809,152	99%
2.00	1.324	9,513,024 ± 88,224	9,774,348	97%
2.53	1.670	11,717,333 ±342,069	12,770,278	91%
3.75	2.480	18,090,666 ±464,662	18,844,443	96%
5.00	3.380	25,059,200 ±174,080	25,477,760	98%
7.50	4.950	35,210,922 ±576,336	36,408,730	97%

$\bar{x}_8 = 96.5\% \pm 2.8$

Desorption Efficiencies (cont'd)

3M

.05	.4415	2,961,450 ± 26,932	3,127,491	95%
1.0	.882	5,891,754 ± 62,102	6,450,029	91%
2.0	1.764	12,794,880 ±224,336	13,088,469	98%

$\bar{x}_3 = 94.7 \pm 2.7$

SKC

.10	.0662	970,575 ± 48,289	900,000	107%
.20	.1324	1,280,249 ± 25,878	1,200,000	107%
1.0	.662	5,436,757 ±118,109	4,809,152	113%
0.5	.331	2,273,237 ± 69,143	2,185,702	104%
5.0	3.308	24,033,200 ±218,000	25,471,760	94.3%

$\bar{x}_5 = 105.0\% \pm 6.8$

Appendix C: Latin Square Summary Matrix

Result Summary Matrix

Dosimeter	Gasbadge	SKC	3M (*38 min)
exposure $\overline{TWA}$	48.3 ppm	206.6 ppm	383 ppm
Dose	195 ppm hr	829 ppm hr	231 ppm hr
actual load	1.00 mg	2.30 mg	1.58 mg
expected load	1.86 mg	2.37 mg	1.83 mg
Mean Bias ± S.D.	-48.2 ± 1.8%	-2.9 ± 7.6%	-13.4 ± 4.5%
*Adjusted value	-3.5 ± 3.8%*		
Meets NIOSH?	no yes*	yes	yes

Dosimeter	3M	GASBADGE	SKC
exposure $\overline{TWA}$	21.8 ppm	118 ppm	209.3 ppm
Dose	87.2 ppm h4	472 ppm hr	857 ppm hr
actual load	.540 mg	1.995 mg	2.44 mg
expected load	.689 mg	4.30 mg	2.45 mg
Mean Bias ± S.D.	-21.6 ± 3.7%	-55.3 ± 1.1%	-0.5 ± 3.8%
*Adjusted value		-16.5 ± 2.1%*	
Meets NIOSH?	no	no yes*	yes

Dosimeter	SKC	3M	GASBADGE
exposure $\overline{TWA}$	125 ppm	59 ppm	405.6 ppm
Dose	500 ppm hr	240.4 ppm hr	1014 ppm hr
actual load	1.54 mg	1.98 mg	5.18 mg
expected load	1.45 mg	1.90 mg	9.57 mg
Mean Bias ± S.D.	+5.9 ± 6.8%	+4.2 ± 3.8%	-45.8 ± 1.9%
*Adjusted value			+1.0 ± 3.6%*
Meets NIOSH?	yes	yes	no yes*

END

FILMED

12-85

DTIC