

AN EXPERIMENTAL STUDY OF OSCILLATING FLOW WITH ABSORBENT
POLYMERS FOR USE IN RESPIRATORS

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Abstract

A respirator system involving alternating flow (inhaling and exhaling) through a perforated polymer filter was examined to determine the potential for savings in weight and bulk of respirators. Experimental testing included measurements of breakthrough times and toxic vapor removal efficiencies of polymer modules constructed with multiple parallel channels having variations in length and radii. Flows through the channels were cycled sinusoidally and mean velocities as well as the cycle periods were varied. The entering air contained measured concentrations of vapor to be filtered while the return air contained none. Flame ionization detectors were used to measure exiting concentrations as functions of time. The oscillating flow system was found to reach an equilibrium state for which exiting mean concentration reached a steady value at a fraction of the entering concentration.

Measurements of partition coefficients and diffusion coefficients were made for various polymers using the vapors of dimethylmethyl-phosphonate and toluene. Partition coefficients were found to vary from one polymer to another by orders of magnitude and polymers tested showed decreases with temperature over the range from 20 to 37 degrees centigrade important for two way breathing systems. The reverse scavenging of absorbed vapors has been shown to be effective and offers potential for further development of more efficient systems.

Keywords: polymer, absorption, respirator, diffusion, partition coefficient, mass transfer

1 Introduction

This paper presents results of research carried out to improve workplace respirators by reductions in size and weight. The concept studied involves alternating flow (inhaling and exhaling) through the filter material allowing for ejection of a large fraction of the toxic material captured by the filter during intake. Systems using activated charcoal presently in use are valved because the charcoal degrades in adsorptive performance if exposed to humid breath on exhaling. Thus for two-way flow it is important to find filter materials that are not degraded by the presence of water vapor at concentrations found in human breath. To this end, the project concentrated on polymeric materials that *absorb* rather than *adsorb* toxic vapors.

Because polymers can have strength and flexibility, the respirator was conceived to be in the form of a surgical type mask for which the absorbent polymer itself made up the major portion of the mask area and weight. To obtain the necessary surface area for mass transfer the polymeric material could be perforated by various means such as fine parallel holes, or the material could conceivably be formed of polymer coated matted fine fibers or polymer coated open celled foams.

Experimental studies of simulated breathing were made using small modules of silicone rubber having parallel holes for which hole radius and length were varied. Face velocities into the filter were cycled sinusoidally and the mean velocities as well as the breathing period were varied. The choice of Silicone rubber for the tests was based on the ability to cast this polymer with fine parallel flow channels. It was considered important to select materials with high absorption for toxic vapors to minimize the weight of the filter. The partition coefficient is a measure of this characteristic, and is defined to be the ratio of concentration in the polymer to that in a contacting vapor at equilibrium conditions. High diffusion coefficients were also desirable to allow rapid mass transfer from the flow channels into the polymer. Analysis of this mass transport in small channels⁽¹⁾ has shown these two material properties to be of greatest impact.

2 Experimental Methods

Two vapors were used, dimethyl methylphosphonate (DMMP) and toluene, having vapor pressures at 25° C of 1 and 20 Torr respectively. Several rubbery polymers or mixtures were selected based on research carried out by Grate, et. al.⁽²⁾ and Hagel, et. al.⁽³⁾. They were selected primarily on the basis of having high partition coefficients, as corresponding data on diffusion coefficients were not found in the literature. The polymers investigated are tabulated below:

TABLE 1. Polymers Whose Partition Coefficients Were Measured.

<i>Polymer</i>	<i>Source</i>
DMS - dimethyl siloxane	Dow Corning Corp. Midland, MI
PECH - polyepichlorhydrin	Aldrich Chemical Co. Milwaukee, WI
Latex - natural rubber	Woodland Sconics, Lynn Creek, Mo.
ABACD ¹ - abietic acid	Aldrich Chemical Co. Milwaukee, WI
SEB ² -styrene/ethylene-butylene	Aldrich Chemical Co. Milwaukee, WI
(1) <i>Mixture with DMS, 50%DMS – 50%ABACD</i>	Dissolved in Chloroform, Cured at 150°C
(2) <i>Powder</i>	Dissolved in toluene, Cured at 150°C

2.1 Feed Vapor Generation

Test concentrations were prepared by use of a bubbler system in which nitrogen is saturated with vapor at a controlled temperature. The device consisted of a vessel partially filled with glass marbles one centimeter in diameter and the chemical liquid to be vaporized. Nitrogen gas was introduced at the bottom of the vessel and collected at the top. The saturated nitrogen was then mixed with a second diluting stream to obtain the desired vapor concentration and piped to the test apparatus. Flow rates were set and measurements were made using Cole Parmer variable area flow meters having accuracies of better than 5 percent of flow readings. Concentrations exiting the bubbler system were computed from equations for vapor pressure of DMMP and toluene as follows:

$$\log(p'_o)_{DMMP} = 11.102 - 3310/T_o \quad (1)$$

$$\log(p'_o)_{toluene} = 8.323 - 2050/T_o \quad (2)$$

where T_o is the temperature in Kelvin, and p'_o is the equilibrium vapor pressure in Torr. The DMMP relation was obtained from Schiff⁽⁴⁾ and that for toluene was obtained from Perry, et. al.⁽⁵⁾. The concentration, C_B , exiting the bubbler is then obtained from the ideal gas relation,

$$C_B = p'_o M / RT_o, \quad (3)$$

where M is the molecular weight of the vapor and R is the universal gas constant, 82 being proper for concentration in gms/cc and pressure in atmospheres. It has been assumed that the vapor closely approaches saturation and tests using variable flows through the bubbler system confirmed this result.

Concentrations in the feed and exit of test modules were measured using two calibrated Gow-Mac model 12-800 flame ionization detectors (FIDs). Concentrations for FID calibrations were prepared in two manners: by varying the amount of nitrogen mixed with the DMMP feed from the bubbler or by varying the temperature of the water bath in which the bubbler is immersed. The FID units were connected to a Gow-Mac 40-900 electrometer that supplied the polarization potential and measured the ionization current. The output was connected to a strip recorder.

2.2 Property Measurements

Determination of the partition coefficients was made by exposing a measured volume of polymer to a known vapor concentration and measuring the weight gain of the polymer after an equilibrium had been reached. The partition coefficient was then obtained from the defining relation:

$$K = \frac{\text{weight gain}}{\text{polymer volume}} / \text{vapor concentration} \quad (4)$$

Two methods for measuring weight gain were employed, the first made use of a test module shown in Figure 1. A polymer membrane of 0.02 cm thickness was mounted in a rectangular aluminum frame allowing an exposed polymer surface of 14.9 by 4.7 cm. The polymer membrane remained fixed to this frame throughout the experiments. The polymer/frame assembly was sandwiched between two Plexiglas plates in which a series of flow channels was machined 0.16 cm deep. The grooved channels connected into small plenums machined in the Plexiglas at each end. The assembly was held together by clamping aluminum cover plates to the outside of the grooved Plexiglas plates. This arrangement enabled the module to be quickly disassembled to remove the polymer/frame assembly which was periodically weighed on a precision Mettler balance (0.1 mg precision) to determine the quantity of vapor absorbed. Because of the very short time required for disassembly relative to the time required to reach saturation, loss of vapor due to outgassing was insignificant. In order to saturate the polymer membrane feed concentration was introduced at ports 1 and 3 of Figure 1 until the exiting concentrations at ports 2 and 4 reached that of the feed.

A second weighing technique was also employed to provide a much larger polymer sample weight and hence for a given solubility a larger weight gain. In this method the polymer samples were prepared by applying a thin film of polymer to a sheet of aluminum foil. The polymer was fluidized by dissolving it in a solvent (Chloroform or toluene). After driving off the solvent by heating in an oven at 150°C, the foil sheet was folded to form a thin closed pocket about the polymer film. A tube was inserted into the foil pocket and a mixture of nitrogen and vapor of a measured concentration was introduced at a rate of approximately one liter per minute. A small hole was provided at an opposite end of the pocket to allow the mixture to escape. The lateral dimensions of the polymer on the foil were approximately 10 by 20 centimeters. To eliminate errors due to adsorption on the aluminum foil an uncoated dummy aluminum foil pocket of the same size was tested; however, the adsorption found was usually negligible. To obtain results at elevated temperatures the foil pocket was installed in an oven with controlled temperature.

For diffusivity measurement the experimental module of Figure 1 was operated as a counter

flow mass exchanger with one gas stream entering port 1 and flowing down the membrane to exit at port 2 and the second gas stream entering at port 4, flowing counter to the first stream and exiting at port 3. The gas stream entering port 1 contained a known concentration of vapor while that entering port 4 consisted of pure nitrogen. Thus, the vapor was absorbed by the membrane from the first stream, permeated across the membrane and was desorbed into the second stream. For steady flow with constant inlet conditions, such a system approached a steady state. For equal flow rates in each of the two streams and a constant thickness membrane, the steady state solution is well known⁽⁶⁾ and consists of a linear variation in concentration across the membrane and a constant concentration difference, ΔC , between the two channels that is independent of location along the channel. A mass flow balance for the vapor can be written

$$Q(C_1 - C_2) = Q(C_3 - C_4) = \Delta CKD_p A_M / \delta_p \quad (5)$$

Here, Q is the volumetric flow rate, D_p is the diffusion coefficient, A_M is the surface area of the polymer across which transfer occurs, and δ_p is the polymer membrane thickness. Note that the first term is the loss of vapor between ports 1 and 2 that must equal that between ports 3 and 4. The last term is the vapor transport across the membrane. Equation 5 provides for the calculation of the product KD_p from which, knowing K , D_p can be computed.

2.3 Polymer Test Modules

TABLE 2 Modules tested in simulated breathing experiments

		—	Module Tubes	—	
Polymer	Vapor	Number	Radius (cm)	Length (cm)	Module Diameter (cm)
DMS	DMMP	139	0.079	1.27	2.54
DMS	DMMP	139	0.079	2.54	2.54
DMS	DMMP	414	0.025	1.27	2.54
DMS	toluene	414	0.025	1.27	2.54
DMS	toluene	414	0.025	5.08	2.54
ABACD/DMS	DMMP	particles	~0.05	0.3	1.7

The modules of silicone rubber, DMS, listed in the table were cast with many closely spaced parallel holes. These modules were made by use of multiple rods of the desired diameter held in a drilled jig. The polymer was mixed with curing agent, poured around the rods and allowed to cure in place after which the rods were withdrawn leaving the open holes. A schematic drawing of such a module is shown in Figure 2. Attempts to form a module from PECH in this way were not successful. As a result only DMS was used for the parallel holed modules.

A module was also made of the prepared mixture of DMS and abietic acid by chopping it into stringy particles averaging 1/2 mm in diameter and 3 mm long and packing them loosely in a cylinder 17 mm in diameter and 25 mm long. The particles were held in place by fine screens at each end of the cylinder. The cylinder was provided with caps containing double ports for connection to the breathing apparatus. This polymer mix was not amenable to being cast in a parallel holed module.

Membranes of DMS and PECH for use in property measurements were cast on horizontal flat plates at final thicknesses of 0.2 and 0.05 mm respectively, DMS in a precured state and PECH dissolved in Chloroform. Both membranes were heated to 150°C for one hour following casting.

2.4 Breathing Test Apparatus and Test Procedures

The simulated breathing test loop is shown schematically in Figure 3. It contains a system to provide flow at a preset concentration to a bellows pump that in turn supplies flow to the test module on the inhale portion of the breathing cycle. On exiting the test module the majority of this flow is vented, but a small fraction is diverted to the flame ionization detector (FID #2) used to measure the exit concentration. On the exhale portion of the breathing cycle the second bellows sucks pure nitrogen gas through the test module. Six solenoid valves control the flows and are switched on or off to simulate breathing. The two bellows are driven by a motorized cam and provide for a sinusoidally varying flow through the test module. Before starting a test, the inbreath bellows and all piping leading to the test module are saturated with feed gas for one half an hour to assure full initial concentration to the test module. At the same time, the flow system to FID #2 is purged with pure nitrogen to remove any adsorbed or absorbed vapor. The system operates at atmospheric pressure by virtue of the vents provided. Flow pressure losses are small fractions of a centimeter of water; however, a pressure of about five centimeters of water is required to provide the flow through the FIDs. For FID#1 which measures the feed flow concentration this pressure is obtained by use of the throttle valve shown in Figure 3. A vacuum system provides flow to the FID #2, and allows a constant flow to the detector which is connected to a strip chart recorder. The recorded data thus shows a time evolution of the vapor concentration passing out of the test module.

In the tests using the apparatus of Figure 3 adsorption on the tubing walls and in the flow meter can be a problem resulting in a time lag in the concentration measurements exiting the test module. To provide a correct measure of this lag, a test was made to provide a step input of concentration at the module exit. A response time lag of only 3 to 4 minutes was found that is negligible for our respirator applications.

3 Test Results

3.1 Partition Coefficient and Permeability Measurements

There are considerable data in the literature for partition coefficients and diffusivities for vapors that are of commercial interest: O₂, N₂, CO₂, NH₃, etc. Data on organic vapors are sparse particularly for diffusivity. Grate, et al⁽²⁾ provide very useful data on relative absorptivity for several polymer/vapor pairs of interest but no listing of partition coefficients or corresponding diffusivities. As these parameters were considered to be of great importance in obtaining high absorption in a respirator, measurements were made of the polymers DMS, PECH, Latex, a mixture of DMS and Abietic Acid, and Styrene-Ethylene-Butylene (SEB) for the vapors DMMP and/or toluene. The results are tabulated in the following table.

TABLE 3. Room Temperature Partition Coefficients

VAPOR\POLYMER	DMS	PECH	LATEX	DMS/ABACD	SEB
DMMP	10 ⁴	10 ⁵	10 ⁴	4·10 ⁴	-
Toluene	10 ³	2·10 ³	-	-	1.5·10 ³

As anticipated roughly by Raoult's law⁽⁷⁾, the values for toluene are much lower than those for DMMP by virtue of its higher vapor pressure. The measured dependence of K on temperature is presented in Figure 4 for a range of temperature from 15-45° C. The values of K are seen to decrease with increasing temperature with the amount of decrease dependent on the polymer/gas pair. A factor of 2-3 is typical over this temperature range. These data were of interest as polymers used in a two way breathing system would encounter temperatures close to body temperatures on the outbreath portion of a respiratory cycle. This would seem to be a disadvantage; however, a favorable effect on diffusivity could offset the disadvantage. Such an increase in diffusivity was shown by Zellers and Sulewski⁽⁸⁾ for solvents in polymer membranes. The effect of temperature on the diffusion coefficients was not, however, addressed in this work.

The diffusivity of DMMP in PECH at room temperature was found to be two orders of magnitude lower than that in DMS. The value for DMS was $2.5 \cdot 10^{-7}$ cm²/sec., in rea-

sonable agreement with the results of Hagel et. al.⁽³⁾ whereas the value for PECH was $3.0 \cdot 10^{-9} \text{ cm}^2/\text{sec}$, surprisingly low for a rubbery polymer.

The selection of PECH for our studies was based on its measured high partition coefficient as indicated by the research of Grate, et. al.⁽²⁾. However, the very low diffusion coefficient found makes it questionable as a candidate for a high performance absorber in the system studied. Clearly, a combination of high partition coefficient and high diffusivity are desired.

3.2 Simulated Breathing Tests

A series of simulated breathing tests were conducted in the simulated breathing loop described previously (Figure 3). The modules tested (Table 2) provide for a variation in channel (tube) length, L , and radius, R_a . In addition to these geometric and property variations, the velocity through the tubes, U_{mean} , and half breathing period, τ , were varied. The term U_A is the approach velocity to the filter which must be smaller than the tube velocity because the holes represent only a fraction of the total filter volume. Figure 5 presents results of three repeated runs conducted over a period of hours for DMS and DMMP with the 414 tube 1.27 cm long module at a base breathing rate of 10/min, ($\tau = 3 \text{ sec}$). Data is presented as the ratio of the concentration measured at the mouth C_m to the input concentration, C_o , which was typically set at 10 to 15 percent of the saturated value. The simulated breathing was conducted continuously until the measured concentration at the mouth stopped showing any significant variations and thus attained a constant saturated value, in this case at 8 hours a value of approximately 10% of C_o . The test labeled number one was incomplete because of a power failure. The three curves provide a measure of repeatability of the experiment for this configuration. At 2 hours of breathing, the variation is about $\pm 15\%$ about an averaged value while at 8 hours, the variation is about $\pm 10\%$.

Figure 6 presents the measured influence of the velocity in the module tubes by comparing a test run at a mean channel velocity of 12.2 cm/s with a case run under identical conditions but with a mean velocity of 6.1 cm/s. The effect of velocity is seen to be substantial with the lower velocity case resulting in a measured concentration ratio of only 0.3% after 10

hours compared to over 9% for the higher velocity case. This is a 30 fold improvement for a reduction in the velocity by a factor of two. In addition, the lower velocity run has not achieved saturation after 12 hours while the higher velocity case saturates at about 8 hours.

Figure 7 presents the measured effect of breathing rate. In this case, the same total volume of air per breath was maintained, but the rate was varied from the base case of 10 breaths/min to higher rates of 12 and 15 breaths/min indicative of the effects of exertion. Thus, experimentally, the cycle period became shortened and the mean velocity increased. As expected because of the higher rate of vapor being introduced, higher concentrations were measured at the mouth. The nonlinear nature of performance prior to saturation is again evident. For example, breathing rates of 12 and 15 per minute represent increases in cycle mean velocity of 20% and 50%, respectively with proportional decreases in period. At 4 hrs of breathing, measured exit concentrations have increased by approximately 20% and 85%, respectively.

The effect of module tube length is shown in Figure 8. Here, data from DMS modules of tube radius 0.079 cm and lengths of both 1.27 and 2.54 cm are presented for DMMP and a mean velocity of 3.7 cm/s. Data from two runs with the longer module are presented and are seen to exhibit very good repeatability. The nonlinear nature of the response with tube length is apparent. At 4 hours of breathing the shorter module produces a concentration of 10% of C_o . However, doubling the module length cuts the measured concentration at 4 hours to 0.4% of C_o - a factor of 25 reduction in measured concentration.

Figure 9 presents results of simulated breathing tests with toluene for two different DMS modules with a value of $R_a = 0.025$ cm. In the first case, the same module and conditions are employed as used for DMMP in Figure 5 ($L = 1.27$ cm, $U_{mean} = 12.2$ cm/s). As can be seen in this figure, the measured concentration at the mouth rapidly saturates to a value of 20% of C_o after approximately 45 min. The second case ($L = 5.08$ cm, $U_{mean} = 6.1$ cm/s), as expected from discussions in the previous sections, produces substantially lower exit concentrations. After 2 hours of breathing, the exit concentration is only 0.1% of C_o (versus 20% for the first case) and at 3.2 hours, it is still only 0.3% of C_o compared with the saturated value of 20%

for the first case.

Figure 10 presents a comparison of performance of the two-way flow concept for the conditions of Figure 5 with that of a "one-way" flow configuration. In order to simulate this experimentally, the "outbreath" flow was disconnected from the module. Thus the module experienced an inbreath followed by a pause, but for both cases the same amount of vapor is presented to the module at each breath. This figure provides an illustration of the advantage of the two-way breathing approach. After two hours, the measured concentration is 80% of C_o for one-way breathing, but only 2.5% for the two-way mode. Of course, for one way breathing an adsorptive system would be the choice. This, however, does illustrate the advantage of two-way flow.

3.3 Respirator with Supplemental Air

In oscillatory breathing the return air acts to remove toxic vapors from the absorbent material, and it would appear that an increased backflow at some value could completely prevent the entrance of toxic vapor to the breather. If this were possible a system using much less supplied air could be built. For example, if the back flow was twenty percent of the air required for breathing, a tank of air would last five times as long as when breathing directly from the tank without the absorbent mask. To investigate this possibility experimental tests were performed using a module of DMS and ABACD described previously (Table 2). The test used 9.4 % supplemental air and the results are presented in Figure 11. It can be seen that a substantial reduction in equilibrium concentration is obtained and as well as a lengthened time to reach a given concentration before equilibrium.

4 Respirator Design Considerations

The goal of the research presented here was to develop respirators that are lighter and more compact than those presently available that use activated charcoal as the filter medium. The concept envisioned a porous absorbent polymer material formed in the manner of a surgical

mask through which breath is both inhaled and exhaled. The absorbent polymer would constitute the major weight of the respirator as it would not have to be constrained in a cannister or other support. Its value can be expressed by the relation:

$$\text{PolymerWeight} = \rho_p LA(1 - \epsilon) \quad (6)$$

where ρ_p is the polymer density, L the polymer thickness (channel length), A the total face area of the filter and ϵ is the fraction of A occupied by the channel holes. For a given mean respiration volumetric flow rate during inbreath, Q , (typically 30 to 40 liters per minute) the face area and the mean apparent flow velocity U_A are related by

$$Q = U_A A, \quad (7)$$

and in terms of the channel velocity,

$$U_{mean} = U_A / \epsilon \quad (8)$$

Combining the above relations we get for the polymer weight.

$$\text{PolymerWeight} = \frac{\rho_p QL}{U_{mean}} \left[\frac{1 - \epsilon}{\epsilon} \right] = \frac{\rho_p QL}{U_A} [1 - \epsilon] \quad (9)$$

For a desired performance specified by the breakthrough time to reach a limiting exit concentration of toxic vapor, the tests described above show the desirability of low mean velocity and long channel lengths whereas low weight as seen from Equation 11 requires just the opposite. In the design of a respirator this clearly constitutes a trade-off problem. The selection of L and U_A must be made to ensure an adequate performance in removing toxic vapors from the entering air. The performance of the filter is also dependent on the polymer and vapor partition coefficient and diffusivity, as well as the channel hole radius and spacing.

4.1 Breathing Resistance

The favorable effect of small channel dimensions in providing large surface area is limited by the requirements of low breathing resistance. For the channels of interest in respirators, the

Reynolds numbers of the flows are so small (less than 10) that fully developed laminar flow is to be expected. The pressure loss in breathing can therefore be expressed by:

$$\Delta p = 8\mu U_{mean} L / R_a^2 \quad (10)$$

in which μ is the viscosity of the air. For values of U_{mean} as high as 24 cm/sec, R_a of 0.0254 cm and channel lengths L of 5 cm, a pressure loss of approximately 3 mm of water is predicted. (Since the velocity is sinusoidal in time, the peak velocity, and thus the peak pressure drop, will be larger than the mean values by a factor of $\pi/2$.) Somewhat higher pressure loss can easily be sustained and would allow reductions in channel radii producing a favorable effect on performance.

4.2 Ambient Atmosphere Concentration Effects

In order to design a respirator for use in hazardous environments the levels of concentrations of the toxic vapors must be specified. Thus NIOSH approves respirators for use under specific conditions such as a liquid spill in a room where nearly saturated conditions may prevail or for more usual cases where only a fraction of saturation occurs. For example, NIOSH approval for cartridges filtering carbon tetrachloride vapors requires a maximum concentration at breakthrough of 5 ppm when breathing in an atmosphere of 5000 ppm⁽⁹⁾. This is a value of $C_m/C_o = 0.001$, but other values both higher and lower, will be of interest for other toxic vapors and other ambient workplace conditions. The 5000 ppm value is only 12% of saturated vapor concentration at 25°C and the performance in terms of C_m/C_o of a respirator for more fully saturated conditions would have to be correspondingly better. Thus it is clear that the size and weight of the respirator will depend on the conditions imposed.

For the present oscillating system using polymers as absorbers, the performance of the system measured by the ratio of intake to breathed toxic vapor concentrations will be independent of concentration levels when the absorption isotherms of the vapor in the polymer are linear obeying Henry's law.

4.3 Design Examples

To provide preliminary estimates of the size and weight of respirators designed for a particular application, two cases have been considered. The first makes use of the toluene/DMS data of Figure 9 that provides an estimate for C_m/C_o of 0.008 at four hours of use. Equations 6 through 9 together with the channel parameters allow the dimensions of the filter to be calculated. Typical values for the mean inspirational flow rate and the breathing period have been used. TLV values for toluene were taken from exposure indices published by the American Conference of Governmental Industrial Hygienists⁽⁹⁾. They represent acceptable concentrations for a forty hour per week work regimen.

TABLE 4. Design Example for a DMS/Toluene Respirator

TLV-toluene	100 ppm
Maximum workplace concentration	12500 ppm
Duration to breakthrough	4 hours
Mean inspiration air flow	30 liters/minute
Pressure drop	0.72 mm H ₂ O
Frontal area of filter	238 cm ²
Filter thickness	5.1 cm
Polymer filter weight	778 grms

This respirator design would consist of a single formed slab of the perforated polymer held in place over the nose and mouth with suitable straps. The filter would constitute the major part of the weight. Clearly the weight for this example is excessive and would not be an acceptable product except perhaps for emergency use as in a spill clean up operation. The analytical studies of Kalumuck et. al.⁽¹⁾ indicate that substantial reductions in size and weight may be expected if modules having much smaller holes can be constructed of polymers with higher partition and diffusion coefficients. Note the very low pressure drop incurred for breathing.

For a second case using the results shown in the lower curve of Figure 6, a duration of 8 hours was achieved with a C_m/C_o value of less than 0.005 for the DMS/DMMP combination.

The TLV values for DMMP unfortunately are not available but many other toxic vapors having vapor pressures equal to or lower than that of DMMP are listed. Since one would expect absorption for these low vapor pressure compounds to be similar to that for DMMP, we have taken, as an example, phenol with a vapor pressure of 0.8 Torr at 25°C and a TLV value of 10 ppm⁽⁹⁾.

TABLE 5. Design Example for a DMS/Phenol Respirator

TLV-phenol	5 ppm
Maximum workplace concentration	1000 ppm
Duration to breakthrough	8 hours
Mean inspiration air flow	30 liters/minute
Pressure drop	0.18 mm H ₂ O
Frontal area of filter	238 cm ²
Filter thickness	1.27 cm
Polymer filter weight	198 grms

This example illustrates the reduction in weight and size for case of low vapor pressure toxic compounds. As the filter element here represents the major part of the weight, the respirator when worn as a surgical type mask may be competitive with more conventional adsorptive systems. Again a more absorptive polymer constructed with smaller holes would lead to a smaller and more compact system.

5 Conclusions

Breathing forward and backward through polymer lined channels has been studied experimentally and the following general conclusions have been reached:

1. Relative to direct one way flow through the channels there is a large increase in the time to reach any specified exiting concentration.

2. The oscillating flow system is found to reach a final equilibrium value of the exit concentration at a fraction of the entering concentration. This is not possible with a one way flow system.
3. Performance of the channeled polymer filters was nonlinear with regard to increases in length or decreases in apparent velocity, particularly at times well before reaching an equilibrium. Halving the apparent velocity or doubling the length was found to result in an order of magnitude decrease in concentration at the mouth.
4. The concept of using two way breathing through a polymer respirator in conjunction with a supplemental air supply was shown to be able to extend the life of the air supply by exhaling the additional supplemental air back through the respirator.

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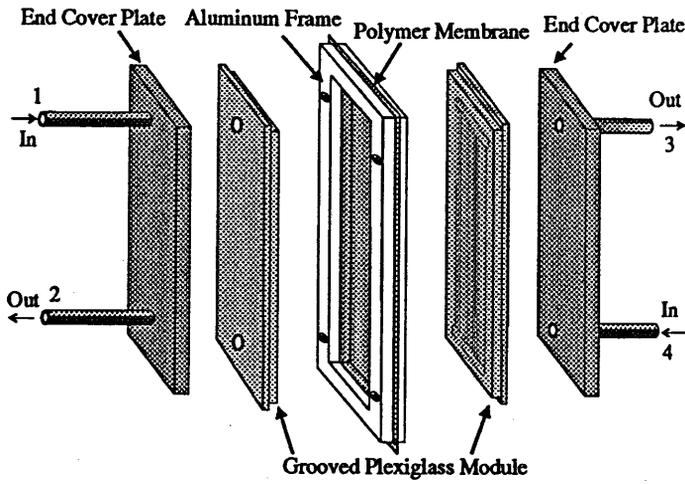


Figure 1: Schematic of Polymer Property Measurement Module Employing a Polymer Membrane of 14.9 x 4.7 cm Exposed Surface Area.

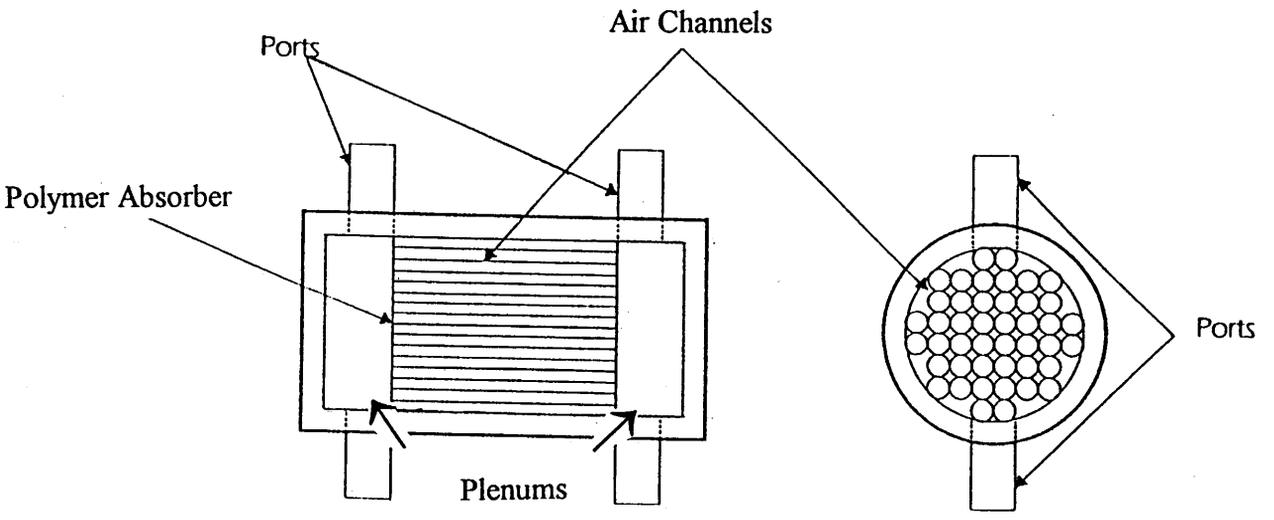


Figure 2: Polymer Absorber Test Module for Simulated Breathing Loop. Geometric Characteristics for the Various Modules Employed are Given in Table 2.

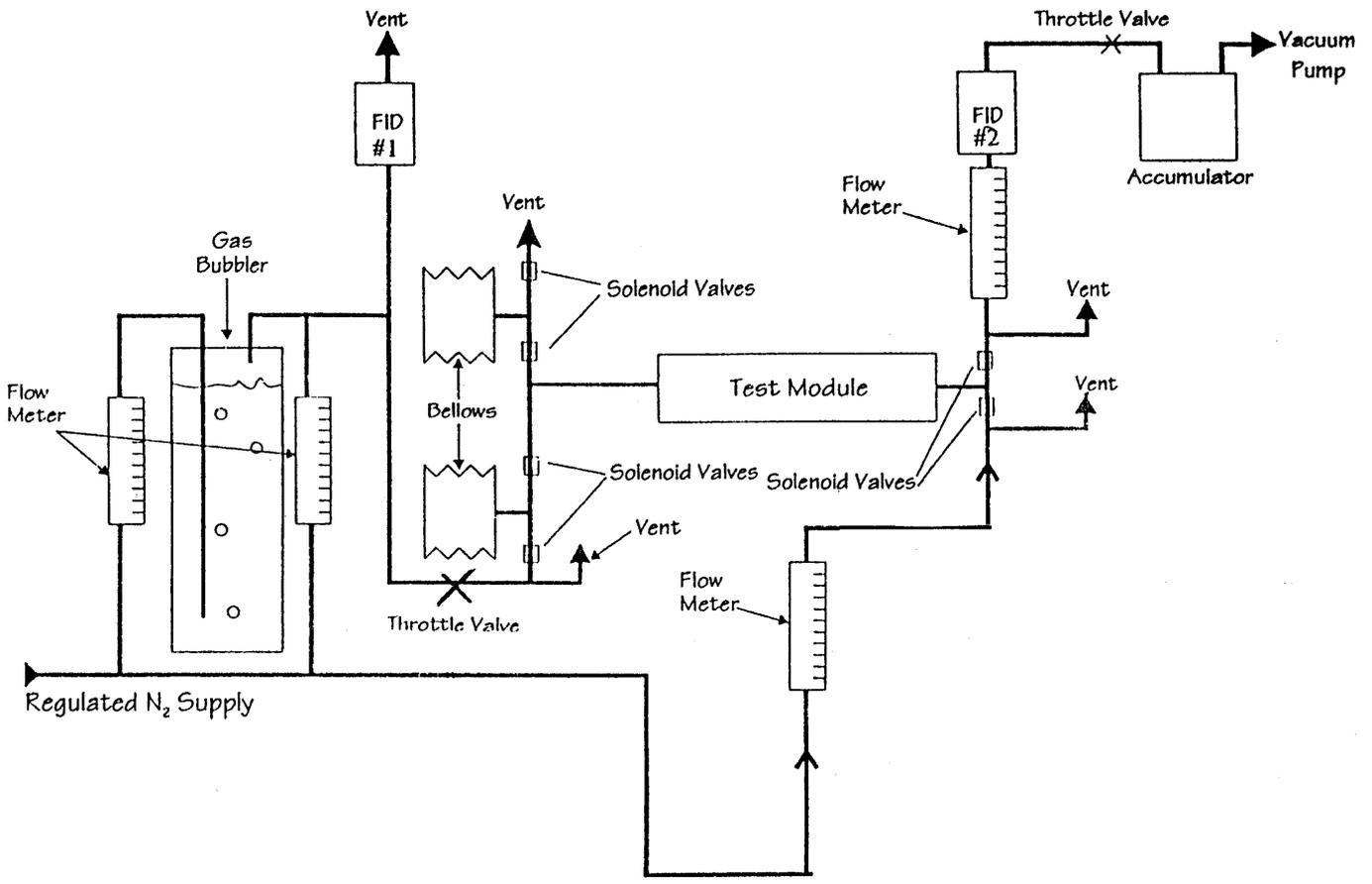


Figure 3: Schematic of Simulated Breathing Test Loop.

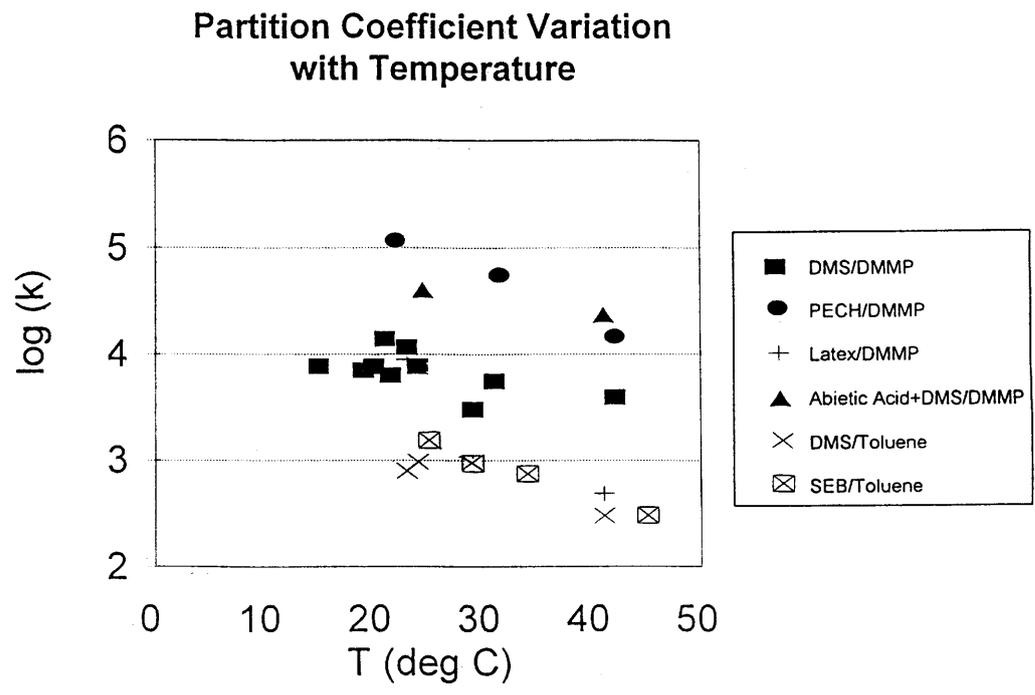


Figure 4: Measured Partition Coefficients and Their Variation with Temperature.

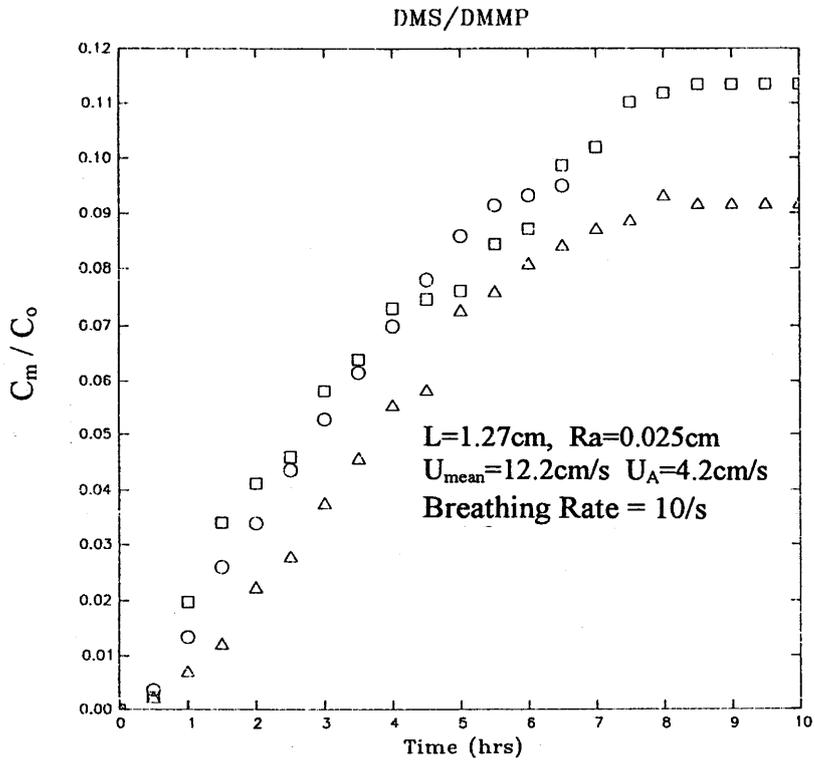


Figure 5: Results of a Simulated Breathing Test Repeated Three Times for a DMMP/DMS Module Showing Data Repeatability.

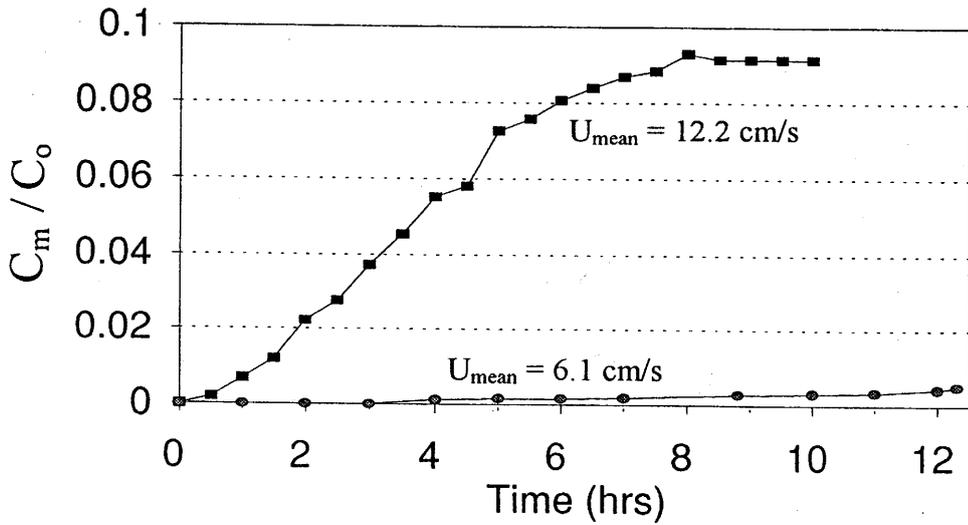


Figure 6: Influence of Velocity on Measured C_m / C_o Values for DMMP/DMS. $R_a = 0.025\text{cm}$, $L = 1.27\text{cm}$, Breathing Rate = 10/s.

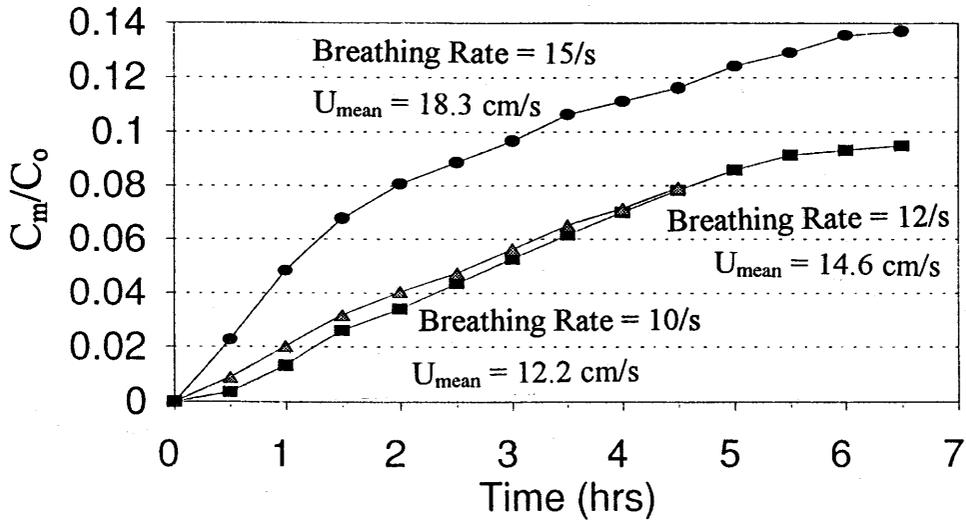


Figure 7: Influence of Breathing Rate on Measured Concentrations at the Mouth for DMMP/DMS.

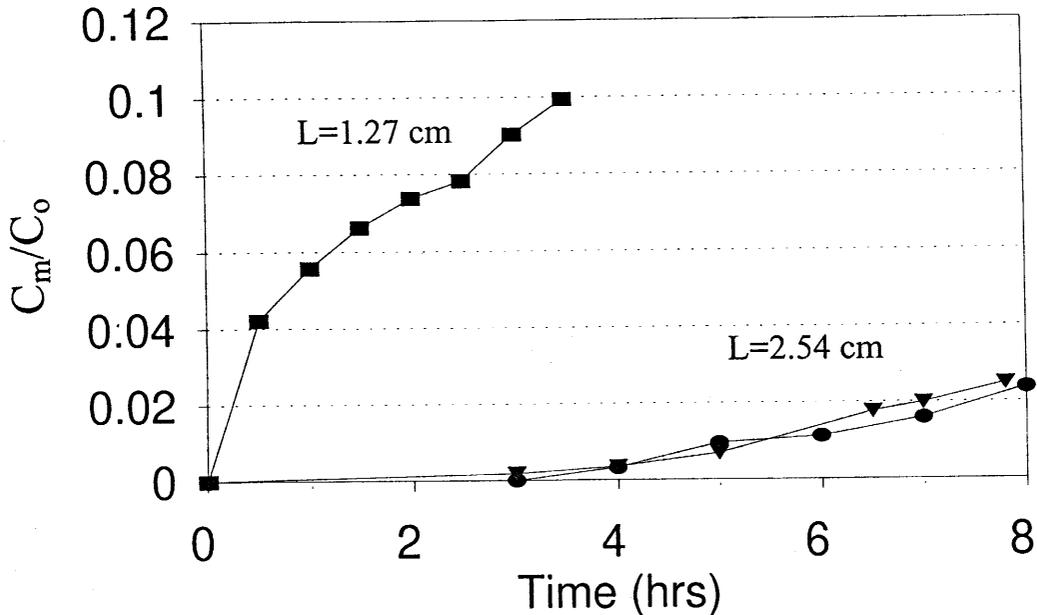


Figure 8: Influence of Module Length for DMS/DMMP Showing Order of Magnitude Decrease in Concentration at the Mouth with Doubling of Module Length. $R_a = 0.079$ cm., $R_p/R_a = 1.38$, Polymer Diffusivity = 2×10^{-7} cm²/s, Air Diffusivity = 0.075 cm²/s, Breathing Rate = 10 /s, $U_{mean} = 3.72$ cm/s, $U_A = 1.95$ cm/s.

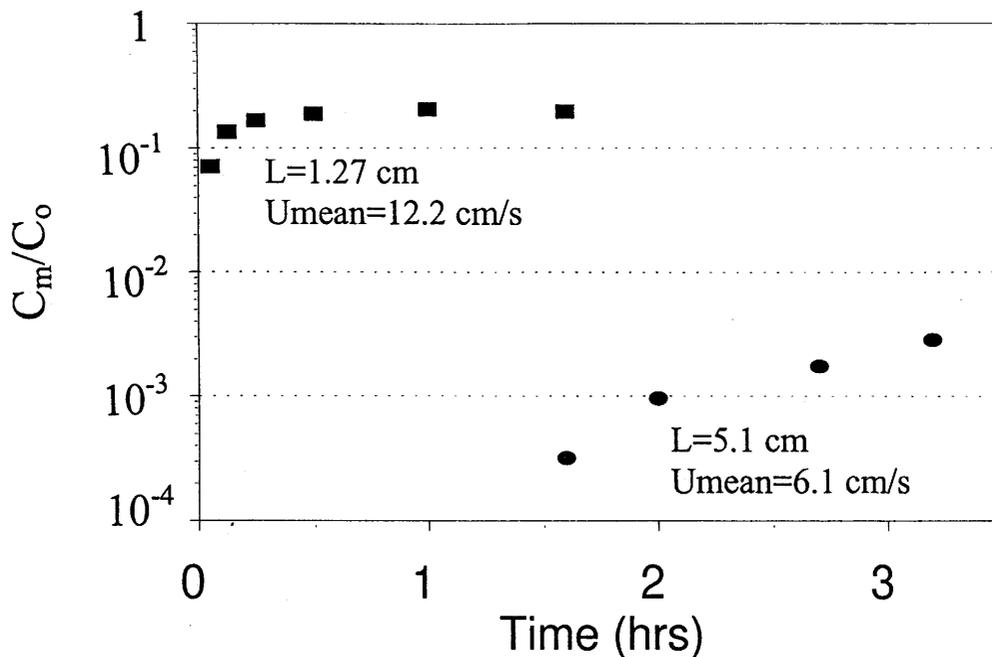


Figure 9: Experimentally Measured Performance of 1.27 and 5.08 cm Long DMS Modules with Toluene Showing More than Two Orders of Magnitude Difference in Concentration at the Mouth. $R_a = 0.025\text{cm}$, Breathing Rate = 10/s.

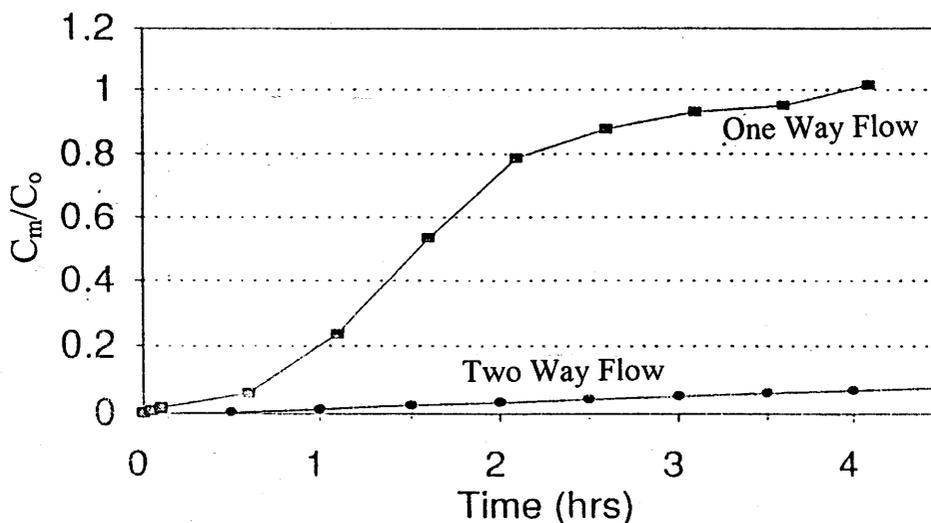


Figure 10: Comparison of Measured Concentrations in Two-Way Oscillatory Flow with Those of Conventional One-Way Flow for DMMP/DMS. $R_a = 0.025\text{cm}$, $L = 1.27\text{cm}$, $U_A = 4.7\text{cm/s}$, $U_{\text{mean}} = 12.2\text{cm/s}$, $R_p/R_a = 1.7$, Breathing Rate = 10/s.

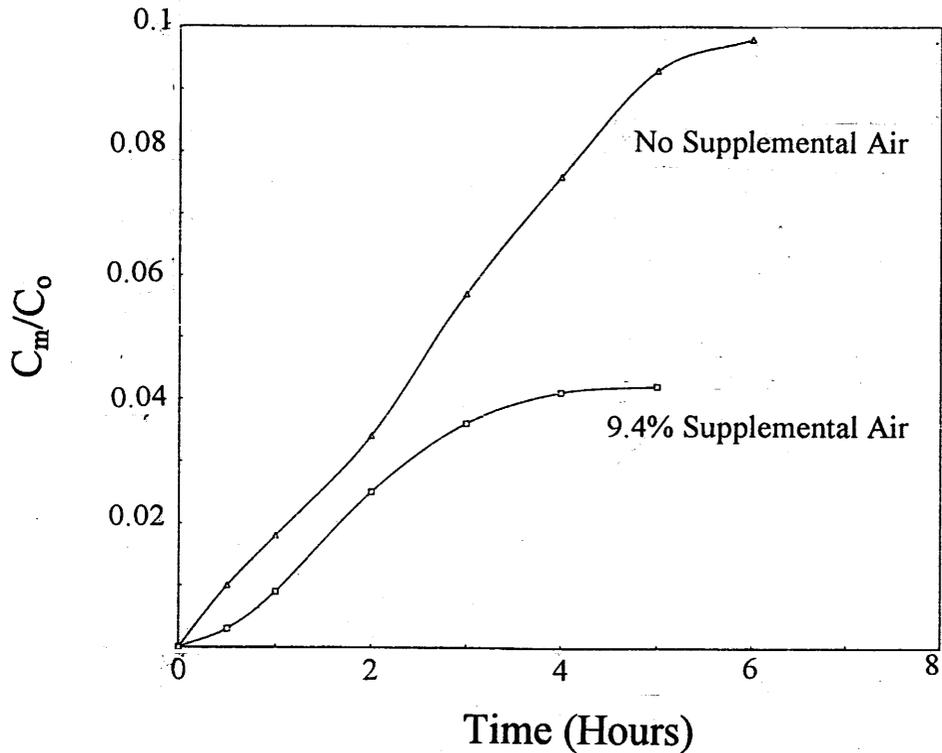


Figure 11 Measured Effect of Supplemental Air on C_m/C_o for DMMP and a DMS-Abietic Acid Polymer Module. $L = 2.5\text{cm}$, Breathing Rate = $10/\text{s}$, $U_A = 4.8\text{cm/s}$.