

PB94108123



DYNAFLOW, INC.

REPORT 92003_1

LIGHTER COMPACT RESPIRATORS FOR TOXIC VAPOR PROTECTION

C.E. Brown
K.M. Kalumuck
G.L. Chahine
G.S. Frederick
June 1993

DYNAFLOW, INC.
7210 Pindell School Road
Fulton, MD 20759

The work described in this report was conducted under SBIR Phase I
Grant No. 1 R43 OH03011-01 from the **National Institute Of Occupational Safety and**
Health, Centers for Disease Control, Atlanta GA.
Principal Investigator: Clinton E. Brown

REPRODUCED BY: **NTIS**
U.S. Department of Commerce
National Technical Information Service
Springfield, Virginia 22161

GENERAL DISCLAIMER

This document may be affected by one or more of the following statements

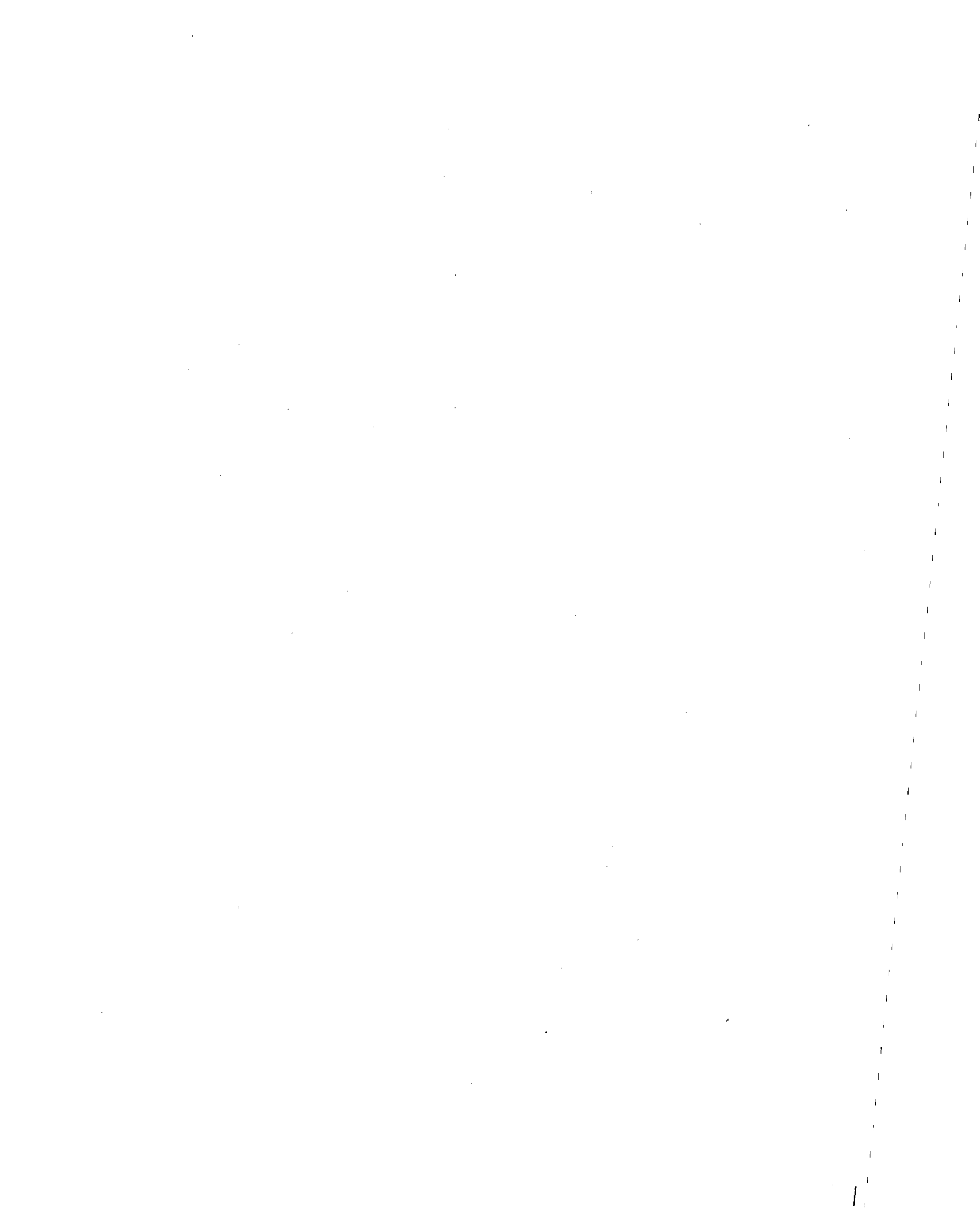
- **This document has been reproduced from the best copy furnished by the sponsoring agency. It is being released in the interest of making available as much information as possible.**
- **This document may contain data which exceeds the sheet parameters. It was furnished in this condition by the sponsoring agency and is the best copy available.**
- **This document may contain tone-on-tone or color graphs, charts and/or pictures which have been reproduced in black and white.**
- **This document is paginated as submitted by the original source.**
- **Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.**

Preceding page blank



PB94-108123

| | | | | |
|--|--|--|----|---|
| REPORT DOCUMENTATION PAGE | | 1. REPORT NO. | 2. | 3. |
| 4. Title and Subtitle Lighter Compact Respirators for Toxic Vapor Protection | | | | 5. Report Date 1993/06/00 |
| 7. Author(s) Brown, C. E., K. M. Kalumuck, G. L. Chahine, and G. S. Frederick | | | | 6. |
| 9. Performing Organization Name and Address Dynaflow, Inc., Fulton, Maryland | | | | 8. Performing Organization Rept. No. 92003-1 |
| 12. Sponsoring Organization Name and Address | | | | 10. Project/Task/Work Unit No. |
| | | | | 11. Contract (C) or Grant(G) No. (C) (G) R43-OH-03011 |
| 15. Supplementary Notes | | | | 13. Type of Report & Period Covered |
| 16. Abstract (Limit: 200 words) An attempt was made to reduce the size and weight of the canisters or elements in a respirator that remove the toxic vapors from the breathed air. The system studied involved substitution of the usual activated charcoal absorbent and its required valving with a specially selected and configured polymer absorbent material combined with bidirectional flow through the porous bed. Experiments were conducted with a high boiling point vapor typical of many toxic vapors found in industrial work places. An experimental loop which simulated the human breathing cycle was designed and constructed and a polymer absorbent test module with many fine air passage channels that simulated a section of the novel respirator was cast and used in the experimental loop. When two way oscillatory flow was compared with one way flow, a dramatic increase in breakthrough time and a decrease in the concentration after breakthrough were seen with two way flow. A parametric study conducted with a numerical simulation model indicated that using of the two way oscillating flow with polymer absorbents to substantially increase the breakthrough time for toxic vapors was feasible. | | | | 14. |
| 17. Document Analysis a. Descriptors | | | | |
| b. Identifiers/Open-Ended Terms NIOSH-Publication, NIOSH-Grant, Grant-Number-R43-OH-03011, Adsorbents, End-Date-03-29-1993, Respirators, Respiratory-protective-equipment, Personal-protective-equipment, Toxic-vapors, Filter-materials | | | | |
| c. COSATI Field/Group | | | | |
| 18. Availability Statement | | PROTECTED UNDER INTERNATIONAL COPYRIGHT ALL RIGHTS RESERVED. NATIONAL TECHNICAL INFORMATION SERVICE U.S. DEPARTMENT OF COMMERCE | | 21. No. of Pages 38 |
| | | | | 22. Price |



Contents

| | | |
|-----|---|----|
| 1 | List of Abbreviations | 2 |
| 2 | List of Figures | 3 |
| 3 | Significant Findings | 4 |
| 4 | Abstract | 5 |
| 5 | Background | 6 |
| 6 | Specific Aims | 8 |
| 7 | Procedures and Methodology | 9 |
| 7.1 | Concept Description | 9 |
| 7.2 | Physics of the Mass Transfer Process | 9 |
| 7.3 | Analysis of Oscillating Flow With Absorbent Walls | 10 |
| 7.4 | Experimental Setup | 12 |
| 7.5 | Polymer Partition Coefficients | 15 |
| 7.6 | Oscillatory Flow Test Procedures | 16 |
| 8 | Results and Discussion | 17 |
| 8.1 | Computational Study | 17 |
| 8.2 | Evaluation of Respirator Pressure Drop | 19 |
| 8.3 | Experimental Study | 20 |
| 9 | Conclusions | 21 |
| 10 | Acknowledgements | 22 |
| 11 | Literature Cited | 22 |
| 12 | Publications | 23 |
| 13 | Figures | 24 |

1 List of Abbreviations

c_a : toxic gas concentration in air

c_p : toxic gas concentration in the polymer

D_a : diffusion coefficient of toxic gas in air

D_p : diffusion coefficient of toxic gas in the polymer

DMMP: DiMethyl Methyl Phosphonate

f, H : numerical discretization parameters defined in equation (7)

K : polymer toxic gas pair partition coefficient

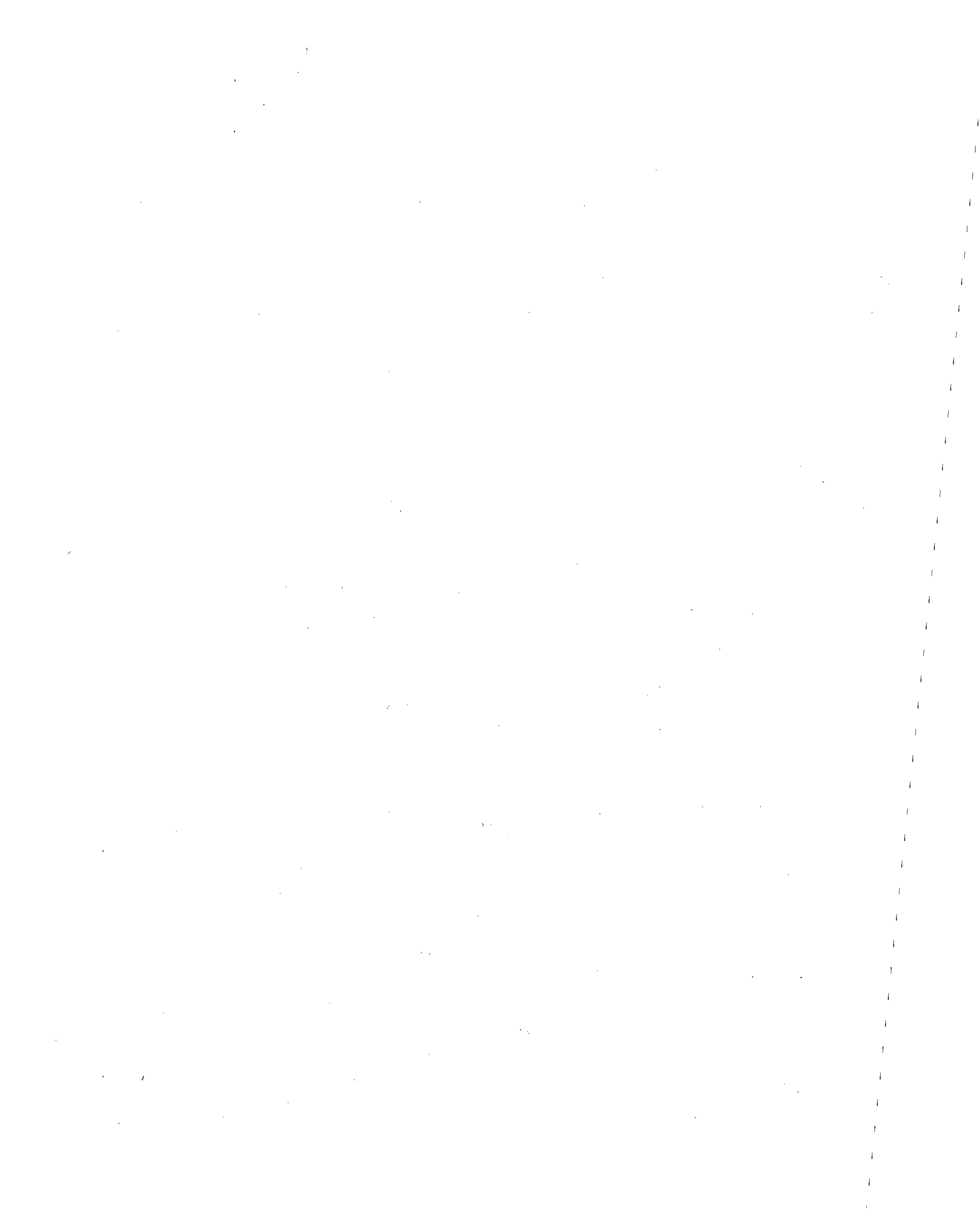
l : tube length

r_{mx} : tube radius

U_{mean} : mean velocity in tube

Δt : time step size for numerical model

μ : dynamic viscosity of air



2 List of Figures

- Figure 1. Respiratory Air Flow Characteristics.
- Figure 2. Schematic of Experimental Setup.
- Figure 3. Close Up Photograph of Test Module.
- Figure 4. Photograph of Experimental Setup.
- Figure 5. Flame Ionization Detector: Calibration and Photograph in Experimental Setup.
- Figure 6. Photograph of DMS Membrane.
- Figure 7. Comparisons of Concentration Ratios with and without Oscillatory Flow.
- Figure 8. Effect of Partition Coefficient on Concentration Ratios in the Channels.
- Figure 9. Effect of the Polymer/Gas Diffusion Coefficient on Channel Concentration Ratios.
- Figure 10. Effect of Velocity on Channel Concentration Ratios.
- Figure 11. Effect of Smaller Tubes and Partition Coefficients on Channel Concentration Ratios.
- Figure 12. Effect of Nondimensional Tube Length on Channel Concentration Ratios.
- Figure 13. Effect of Tube Length on Channel Concentration Ratios.
- Figure 14. Concentration Histories Under Oscillatory Flow Conditions.
- Figure 15. Comparison of Exit Flow Concentration Ratios for Oscillatory and One Way Flow.

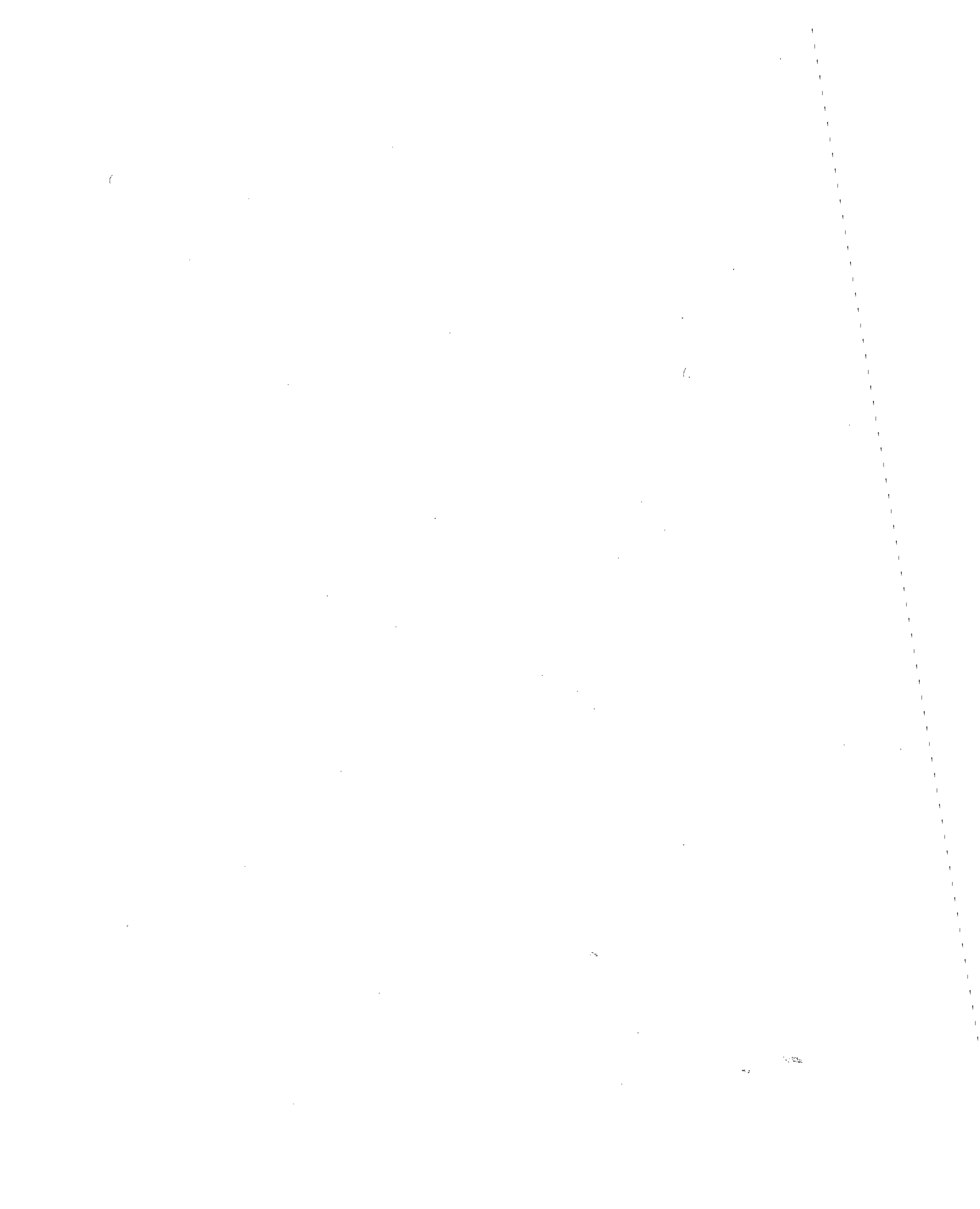


3 Significant Findings

The goal of the present research is to advance the technology for respirators used for protection against toxic vapors. The use of protective devices in the work place often depends upon worker acceptability which in turn is affected by the size, weight and general convenience of the devices to be worn. Specifically, the present work addresses the problem of reducing the size and weight of the canisters or elements in a respirator that remove the toxic vapors from the breathed air. The novel system studied involves substitution of the usual activated charcoal adsorbent and its required valving with a specially selected and configured polymer absorbent material that is combined with bidirectional flow through the porous bed. The Phase I effort has demonstrated the feasibility of utilizing such two way oscillatory flow to substantially increase the breakthrough time for removal of toxic gases with polymer absorbents. Respirators utilizing this concept would be of markedly reduced weight and volume compared with conventional systems. Alternatively, the new respirators could be designed to be of comparable size to conventional systems but with greatly extended lifetimes.

Experiments were conducted with a high boiling point vapor typical of many toxic vapors found in industrial work places. An experimental loop which simulates the human breathing cycle was designed and constructed and a polymer absorbent test module with many fine air passage channels that simulates a section of the novel respirator was cast and utilized in the experimental loop. Measurements were made of the concentrations of the toxic gas simulant exiting the module as a function of time. Comparison of results for operation with two way oscillatory flow - both inhaling and exhaling through the module - with those of conventional one way flow - only inhaling through the module - show a dramatic increase in the breakthrough time and a large decrease in the concentrations following breakthrough. These experiments demonstrated the feasibility of the new concept and its superior performance relative to conventional respirators such as those using charcoal. Results of the numerical simulation model developed show similar significant improvements in respirator performance using two way oscillatory flow over conventional one way flow.

Other findings important to future efforts were obtained from the results of a parametric study conducted with the numerical simulation model. The influence of various factors on oscillating flow polymer absorbent respirator performance was determined. Results were found to be most sensitive to the *partition coefficient* with air channel concentrations decreasing substantially with increasing values of the partition coefficient. Based on measurements and available data, candidate polymers were identified for future work having very large partition coefficients - up to three orders of magnitude greater than that used in the Phase I study. The parametric study results also indicate it is desirable to select a polymer with high *diffusivity* and to have *low flow velocities* through the air channels. The numerical model will prove a useful design tool in future work.



4 Abstract

A concept for greatly reducing the size and weight of respirators for removal of toxic gases was studied. A respirator based on this concept would employ many small tubes lined with an absorbent polymer through which both inhalation and exhalation would occur unlike conventional systems in which one way flow is utilized by means of valving. The two way oscillatory flow through the respirator element enables capture and expulsion of toxic vapors. Two way flow through activated charcoal is not generally used because of the adverse effect of moist breath on the charcoal efficiency. Absorption rather than adsorption is believed to be less subject to water vapor and other interferants and led to selection of several polymers for study. The absorptive capacity of these polymers was measured for a high boiling point vapor typical of many toxic vapors in the commercial work place. A test module using perforated DiMethyl silicone elements was designed, fabricated, and subjected to an oscillatory flow simulating a typical breathing cycle. Test results showed a large delay in toxic gas penetration over that obtained by conventional one way flow. The experimental testing was guided by analysis of the mass transfer in the perforated polymer bed. For this a numerical model was developed and utilized. Factors investigated include respirator element geometry, polymer and toxic vapor characteristics and flow through speed. The numerical model proved to be a useful design and evaluation tool. Results of the Phase I study demonstrate the feasibility of using the two way oscillating flow with polymer absorbents to substantially increase the breakthrough time for toxic vapors. This is thus a very effective means of toxic vapor removal.

5 Background

A wide variety of toxic vapors are present in industrial work places either on a normal operating basis or under an emergency situation such as due to a failure resulting in a sudden release or to leakage. It is desirable to make respirators as light, compact, and long lived as possible. This would increase the comfort to the user thereby making it easier to work while wearing a respirator and decreasing user fatigue. In addition, the pressure drop across the respirator should be minimal both to make breathing easy and to minimize leakage across the face seal. The novel technique that we have developed to achieve these objectives is to construct the respirator of tubes lined with a polymer that absorbs toxic gases. A respirator filter would consist of a large number of these short small tubes arranged in a parallel bundle. Breathing both in and out through these tubes sets up an oscillatory flow. On inhalation, the toxic gas is absorbed by the polymer. On exhalation, the toxic gas is desorbed into the initially contaminant free out-breath and expelled out of the respirator. Due to the physics of the mass transfer processes and the typical breathing cycle, not all of the gas is expelled from the respirator and a gradual increase in gas held in the polymer occurs which ultimately determines the effective life of the respirator element. This time, however is found to be substantially longer than that associated with a conventional one way flow respirator element such as activated charcoal.

Activated charcoal is currently used in many respirators, gas masks and air purification systems because of its excellent adsorption characteristics for many toxic gases. However, the presence of high concentrations of water vapor or other contaminants can seriously degrade the performance of activated charcoal. Adsorbent polymers are not subject to these interference effects as discussed below. Studies have been made in the past to treat carbons with chemicals designed to reduce the adverse effects of water vapor [8]; however, little progress has been made to date. It is probable that adsorbents that make use of a fine cracked structure will always find a competition between gases for the available spaces. This consideration is in accord with the hypothesis presented by Polanyi and Dubinin in [9]. It appears that water vapor at typical atmospheric conditions is of minor impact on respirator carbons but at the concentrations in exhaled air the degradation is enough to justify bypass valving. Furthermore, the bulk of the activated charcoal adds to the dead space in a respirator when used in an oscillatory breathing mode of operation. For cases where reverse flow would be acceptable, the charcoal unfortunately does not reversibly desorb the captured toxic substances. Thus the out-breath through the carbon bed cannot efficiently expel the adsorbed gases. Nevertheless, in some cases reverse flow through the charcoal bed can add to the break through time. An example of the behavior is presented in [1].

The research conducted originated from earlier theoretical studies at DYNAFLOW, INC. of oscillating flow through small diameter tubes having solid walls of high adsorptivity. Using experimental data as inputs, the mass transport in the tubes was calculated using a numerical

model. The results indicated that very large reduction in incoming toxic gas concentration could be achieved with small pressure drops. For high boiling point toxic gases the estimates for a sample non optimized case indicated a 97% reduction in mean incoming concentration. In other tests [1], even with activated charcoal, the life of a respirator used for vinyl chloride monomer protection was doubled by breathing back through the charcoal.

In these preliminary studies it was concluded that alternating flow filters using wall coatings of absorbent polymeric materials should be of greatest interest for respirators because the sorption process is much less sensitive to water vapor and other interferences than adsorption processes. In absorption, molecules of the substance being absorbed enter into a solution within the absorbing media. In adsorption processes, the molecules being adsorbed adhere to the surface of the adsorbing media. Furthermore, polymers have been identified having extremely high partition coefficients for high boiling point vapors and can thereby provide surface coatings significantly more effective than adsorptive surfaces. Thus the Phase I study was conducted utilizing absorbent polymers.

In selecting an absorbent polymer, it is desirable to have high solubility (large partition coefficient) as well as high diffusivity to provide for storage in the polymer film. This is verified in the results of the numerical simulations described below. (Here, solubility refers to the ability of the gas to enter into the absorbent polymer. The partition coefficient is a measure of this in that it is the ratio of gas concentrations in the polymer and the air at equilibrium. The diffusivity is a measure of the ability of the absorbed gas molecules to move through the polymer by diffusion. Thus, a large partition coefficient enables the concentration of toxic gas absorbed in the polymer at the air/polymer interface to be much larger than in the air. A large diffusivity allows the toxic gas to easily diffuse away from the interface into the polymer enabling more to enter from the air channel.) Some useful data are collected in [2] where silicone rubbers are seen to possess desirable characteristics as well as being polymers of good chemical stability and inertness. In [3] and [4], the polymer fluoropolyol was found to offer extremely high partition coefficients ($\approx 10^7$) for DiMethyl Methyl Phosphonate (DMMP) a relatively non toxic high boiling point compound related to the pesticides malathion and parathion as well as to dangerous nerve gases. Some caution must be used in selecting such polymers, however, because at vapor saturated conditions in the air, the absorption is so great that extensive swelling of the polymer will occur possibly producing changes in the diffusivity as well as in the partition coefficient. Useful data can also be found in [5-7, 10].

There has been extensive research into materials having high adsorptivity for toxic gases; however, activated charcoal is one of the best and most widely used in respirators. It is known that the presence of water vapor even at normal values of atmospheric concentration can sharply reduce the capacity of activated charcoal for gas adsorption. It is for this reason that charcoal canisters should be sealed from air contact until they are needed. Studies have been made of means to reduce the adverse effects of water vapor but no important

improvements have been found. In one in-depth study of activated charcoal adsorption of GB, GA, GF nerve gases and DiMethyl Methyl-Phosphonate (DMMP) [8], the charcoal was impregnated with siloxanes in an attempt to improve the adsorption in the presence of water vapor. However, little improvement was found. For this reason the present research is directed to the use of absorbent polymers rather than adsorbent surfaces along the air passage ways in the respirator. These remarks would also hold true for granular beds.

Useful data on human breathing can be found in [11]. In particular it is important to recognize the importance of respirator flow resistance on the respirator user as well as on its performance. There is, of course, a trade off between filter efficiency and flow pressure drop that must be considered in the design of respirators. Figure 1 taken from [11] shows the effect of increased respirator flow resistance on the flow rate histories for a human under moderate working conditions. Note the difference in duration of the inspiration and expiration portions. In the lower figure the effect of exertion on air flow rate is seen to be substantial. The table below, also reproduced from Reference [11], indicates the importance of low valve resistance in respirators in cases where the wearer may be unconscious. The table shows how much pressure can be exerted at the commencement of inspiration by the unconscious subject. Of 38 lightly anesthetized hospital patients, 40% exerted suction of 0.5 psi or more, but none would have been able to open an inspiratory valve requiring 1.0 psi differential.

| INSPIRATORY PRESSURE | MEAN | Std. Dev. |
|----------------------|-------|-----------|
| Inches of water | 12.5 | ±4.85 |
| mm Hg | 23.37 | ±9.31 |
| psi | 0.45 | ±0.18 |

As shown below, the flow in the absorbent polymer respirator tubes we are utilizing is laminar. The pressure drop in these tubes is easily and exactly computed using classical well substantiated equations. The use of small tube bundles for the respirator allows quite exact computations to be carried out for both pressure drop and the internal mass and heat transfer. However, the same favorable improvements in respiratory efficiency can be expected using particulate beds with oscillatory flow.

The results presented include an analytical approach to compute the oscillatory transfer within the perforated absorbent polymer bed and experimental test to demonstrate feasibility of the concept and to corroborate the analytical predictions.

6 Specific Aims

The primary aim of the Phase I research effort was to demonstrate the feasibility of utilizing polymer absorbers in conjunction with oscillatory flow for the removal of toxic gases enabling development of respirators of greatly reduced weight and size and/or of greatly increased life. The results clearly show that this aim has been achieved by demonstrating

both experimentally and analytically that substantial increases in the breakthrough time can be achieved.

A second aim was the identification of suitable polymeric materials for use in respirators. An initial identification of promising materials with high partition coefficients was made. These include Polyepichlorohydrin and Fluoropolyol. In addition a DiMethyl silicone polymer was utilized as an absorber for DMMP, a toxic gas simulant with properties similar to many pesticides. A more extensive identification effort is proposed for Phase II

The third aim was to develop methods for the design of respirators based on this concept. To this end both a numerical model and a laboratory experimental program were developed. The model, which includes the effects of diffusion in both the polymer and gas as well as convection in the gas, can be used for parametric studies. The experimental program included both a means of measuring the partition coefficient of a polymer/gas pair, and a flow system for simulating the breathing flow through a module that represents a section of a respirator. Both the modeling and experimental capabilities will be employed in future design studies.

7 Procedures and Methodology

7.1 Concept Description

In order to avoid some of the adverse characteristics of adsorbent systems and utilize the potential of breathing back through the sorbent bed, adsorbent polymers appear to have advantages. Rather than adsorb the toxic gases on surfaces or in cracks, polymers would absorb the gases forming solutions of the toxic gas in the polymer volume itself. The particular concept studied here provides for a respirator system in which the breath alternately passes through a sheet of porous polymer material. The conceptual analyses and experiments conducted made use of a polymer sheet having many parallel holes of small diameter. The mass transfer can be performed for a single tube of this sheet.

During oscillatory flow, toxic gas is absorbed during inflow and desorbed during out flow. However, an equilibrium state can be reached resulting in a constant outflow concentration. At this point the incoming mass must balance that being rejected during out flow.

7.2 Physics of the Mass Transfer Process

The absorption of vapors in a polymer is analogous to that of absorption in a liquid. For small vapor concentrations, the amount of vapor absorbed in the polymer at equilibrium is proportional to the contacting gas phase concentration, that is, it follows Henry's Law. However, for the analysis of the mass transfer between the gas phase and the polymer phase we introduce the partition coefficient, K , which is simply the ratio of volume concentration

in the contacting gas phase with that in the polymer at equilibrium. The value of K for the polymer/gas pairs of interest in the present study range from about 10^4 to 10^6 .

The mass transfer in the air channel occurs by both diffusion and convection along the tube. For the small tubes tested (and envisioned for use in actual respirators) the flow Reynolds numbers are so small that fully developed laminar pipe flow can be fully justified. In the tests conducted, the mean Reynolds number has a value of about 0.6. Thus the velocity is assumed to vary only in the radial direction, r , as given by the classical solution:

$$v(r) = 2U_{mean} \left(1 - \frac{r^2}{r_{mx}^2} \right), \quad (1)$$

where U_{mean} is the average speed and r_{mx} is the tube radius. The diffusion coefficients in the air channel and in the polymer are greatly different, that in the air being about $10^{-1} \text{ cm}^2/\text{sec}$ and in the polymer about $10^{-7} \text{ cm}^2/\text{sec}$.

7.3 Analysis of Oscillating Flow With Absorbent Walls

The parameters of importance in computing the mass and heat transfer in a polymer lined tube are as follows:

- (a) the polymer toxic gas pair partition coefficient, K ,
- (b) the diffusion coefficients of gas in air and in the polymer, D_a , D_p ,
- (c) physical dimensions: tube radius and length, r_{mx} , l ,
- (d) mean velocity, U_{mean} .

The assumptions made are as follows:

- (a) the flow is fully developed and laminar with time dependence,
- (b) the polymer lining in the tube has a thickness of one quarter of the open tube diameter,
- (c) the diffusion coefficients in the air and in the polymer as well as the partition coefficient are constant.

The differential equation governing the mass transfer in the air channel is then:

$$\frac{\partial c_a}{\partial t} = D_a \left(\frac{\partial^2 c_a}{\partial r^2} + \frac{1}{r} \frac{\partial c_a}{\partial r} + \frac{\partial^2 c_a}{\partial x^2} \right) - U(r, t) \frac{\partial c_a}{\partial x}, \quad (2)$$

where t is time, c_a the toxic gas concentration in the air, r and x the spatial cylindrical coordinates, and U the flow speed. In the polymer coating the mass transfer equation is similar except that the convection term is of course absent:

$$\frac{\partial c_p}{\partial t} = D_p \left(\frac{\partial^2 c_p}{\partial r^2} + \frac{1}{r} \frac{\partial c_p}{\partial r} + \frac{\partial^2 c_p}{\partial x^2} \right). \quad (3)$$

Here, c_p is the toxic gas concentration in the polymer. The boundary conditions for the problems are as follows.

(a) at the polymer air interface

$$D_a \frac{\partial c_a}{\partial r} = D_p \frac{\partial c_p}{\partial r}, \quad (4)$$

and

$$c_p = K c_a. \quad (5)$$

(b) at the polymer outer boundary,

$$D_p \frac{\partial c}{\partial r} = 0. \quad (6)$$

(c) at in-breath the upstream concentration is equal to the initial concentration, and on out-breath the return concentration is zero.

For the case of oscillatory flow, the velocity within the tube has been assumed to vary sinusoidally with an in-breath of 2.5 seconds followed by an out-breath of 3.5 seconds. This arrangement is an approximation to normal breathing as can be seen from Figure 1 taken from [11]. The total air flow mean value can be seen to vary from 10 to 40 liters per minute. In the present concept the flow area of the absorbent bed will be equal to the number of parallel tubes and their cross sectional area. This in turn is equal to the quotient of the total mean in-breath flow and the mean velocity in the individual tubes. It is clear therefore that to minimize size and weight of the absorbent bed, the tube velocity should be as high as possible. Against this is the desire to minimize the breathing resistance. More on this will be discussed later in this report.

The mass transfer equations with their boundary conditions are solved numerically with an explicit time stepping scheme. In space, a finite difference scheme is employed in which the airflow channel is divided into grids having a radial dimension of 1/3 of the tube radius and a length between 1 and 5 times the radial box size. Tube length and radius are variable and are input. Within the polymer, the first ten spacings are set finely enough and to a depth that will capture the complex distributions arising from oscillatory flow at a period of breathing of six seconds. A time stepping procedure is employed to compute the concentration at each grid point and time step. The numerical expression for the mass transfer equation

above with the concentration normalized by dividing through by the initial concentration is written:

$$\begin{aligned} \partial c(x', r', t) / \partial t = & \left(\frac{D_a}{r_{mx}^2 H^2} \right) c(x', r' + H, t) \left(1 + \frac{H}{2r'} \right) + \\ & + c(x', r' - H, t) \left(1 - \frac{H}{2r'} \right) + c(x' + fH, r', t) / f^2 + c(x' - fH, r', t) / f^2 + \\ & - \left(2 + \frac{2}{f^2} \right) c(x', r', t) - \frac{r_{mx} H U(r')}{2D_a f} (c(x' + fH, r', t) - c(x' - fH, r', t)) \end{aligned} \quad (7)$$

The primes on quantities r and x signify the ratio with r_{mx} the tube radius. H is the reciprocal of the number of boxes in the radial direction in the air channel and f is the aspect ratio of the boxes in the air channel, i.e. the box x-wise length over its radial length.

Stability of the explicit time stepping scheme requires that (see, for example, [13]):

$$\frac{D_a \Delta t}{r_{mx}^2 H^2} \leq 0.25. \quad (8)$$

If this requirement is not met, the solution is unstable and experiences unbounded growth with time. Below 0.25 the solution is stable and converges rapidly. However, this requirement causes the time step Δt to be quite small and long runs with a fast computer system are required. In the polymer, the above ratio contains the polymer diffusion coefficient, D_p , and because it is much smaller than that for air, D_a , the time step in the polymer region can be increased allowing a considerable speed up of the computation. This is done by keeping the values of the variables in the polymer constant over the polymer time step while the values in the air are updated at each air time step. Typically, a time step in the polymer 8 times that of the air was utilized. A comparison of results of computations made with these time step sizes to that utilizing the same time step in both the air and the polymer showed no significant difference.

7.4 Experimental Setup

The primary goals of the experimental program were to establish the feasibility of the oscillatory flow concept and to verify the predictions of the analytical work. A secondary goal was to identify polymers of high absorptivity that might be suitable for use in absorbers for high boiling point toxic compounds. The primary goals, we believe, are fully met by the data obtained and discussed below. The polymer used, however, was one of modest absorptivity and was chosen for its ease of molding the small diameter flow channels of the respirator test module (described below) and to provide for moderate length run times; that is, the time to equilibrium is shorter for polymers of reduced absorptivity. Tests with polymers of higher absorptivity will be carried out in the proposed Phase II program.

The feasibility tests were carried out using a DiMethyl silicone (DMS) polymer as absorber and DiMethyl Methyl Phosphonate (DMMP) as the toxic gas simulant. The DMS material was cast in a cylinder three eighths of an inch in diameter and one half of an inch long. 97 holes were formed parallel to the axis each being 0.020 inches in diameter. A sketch

of this test module is presented in Figure 2a, and a close up photograph is presented in Figure 3. Great care was exercised in casting of the test module. The 97 channels were formed using 0.02 inch diameter wires around which the DMS was poured. The wires were removed following curing of the polymer. This DMS filter element was then inserted into a plexiglass cylinder with a plenum at each end which fed or collected the flow from the channels. Tubing was connected to the two plenums to enable simulated inhalation and exhalation through the module and to allow for sampling of these gas streams.

The test loop into which the module was inserted is shown in Figure 2b and in the photograph of Figure 4. Nitrogen was used for the carrier gas for DMMP. Conducting experiments with high boiling point compounds is complicated because of the time needed to reach equilibrium caused by the considerable adsorption of the vapors on piping, meters, seals and crevices. Care was taken to minimize this time by employing short stainless steel short tube lengths for all lines carrying DMMP vapor. In addition the lines were wrapped with an electrically heated self limiting heat cable to warm them and thus minimize condensation of the DMMP on the walls. Tests were run to quantify these times to achieve equilibrium as described below. The entire system was purged with nitrogen between each experimental run.

All lines were of 0.25 inch (0.180 inch ID) or 0.125 inch (0.085 inch) stainless steel. The vapor bubbler was made of a length of 2 inch diameter stainless steel pipe filled with marbles to increase bubble rise time. The pipe and a trap were installed in a thermos container four inches in diameter and this was filled with water to provide thermal heat capacity and maintain a constant temperature. Breathing was simulated with a pair of bellows. The bellows were slaved together and pulsed by a motor driven cam. The inhalation and exhalation periods are equal. The motor speed is variable so that the breathing rate can be varied. In the experiments performed, The total in-breath/out-breath cycle time was set at 6 seconds and 5 seconds. The breath volume driven by the bellows was 7.1 cm³. Check valves having a very small opening pressure (less than 2 inches of water) obtained commercially were found to not possess an adequate seal for back flow. Consequently, a satisfactory design was obtained using a mercury seal. A small chamber utilizing a section of a stainless steel filtration cartridge with tiny pores was designed and fabricated. Mercury drops were placed above the pores and provided a seal when the gas flow forced the mercury against the pores. The mercury drop was lifted off the pores when the gas flow was in the opposite direction enabling flow to proceed in that direction. A vented pressure regulator was employed in the outflow line to provide sufficient back pressure to close the check valve.

Exhaled breath was simulated using a humid heated air supply free of DMMP. This was provided by bubbling nitrogen through a water reservoir heated and maintained at a temperature of 34 degrees C. The out-breath was thus a mixture of warm nitrogen and water vapor.

Measurements of DMMP concentrations were made using a GOW-MAC model 12-800

flame ionization detector (FID). The FID was operated at its design feed flow rates by using a pressure regulator and reservoir resulting in a constant pressure feed. The flow oscillations were thus highly damped allowing only slight variation of the FID meter readings. The FID was connected directly to a Hewlett Packard milliammeter providing by its own internal resistance a system measuring down to one picoampere at a reading of one millivolt. The range of concentrations used in the tests produced currents in the FID of up to four nanoamperes at DMMP concentrations of 3×10^{-6} gm/ml. Tests were made to determine the lag in FID measurements due to adsorption in the tubing between the exit of the respirator module and the FID. For this the feed was introduced to the FID piping, and the rise in the FID readings were noted. For the tests reported below, values of the order of 30 minutes were observed and the data corrected accordingly.

The simulated breathing experiments with two-way flow through the respirator test module proceeded as follows. A known concentration of DMMP in the nitrogen carrier gas is introduced to the system. Upon expansion, the lower bellows of Figure 2b draws in this mixture. As the bellows are compressed, check valves 1, 3, and 5 close while check valves 2, 4, and 6 open. This causes the DMMP mixture contained in the lower bellows to flow through the respirator test module from left to right with a mean velocity that varies sinusoidally with time. The amount of DMMP is reduced by absorption in the polymer in the module, and the resulting gas mixture exiting the module continues to flow on to the FID where the DMMP concentration is measured. As the bellows now begin to expand, check valves 1, 3, and 5 open while 2, 4, and 6 now close, and the out-breath portion of the cycle is simulated. The flow from the test module to the FID is cut off and a reverse flow (from right to left) of warm humid nitrogen (drawn from the heated reservoir) occurs across the module. DMMP is desorbed from the polymer in the test module into this stream. The stream is collected in the upper bellows and will be expelled from the system during the next bellows compression cycle.

The feasibility tests showing the experimental verification of the oscillatory flow concept did not require absolute values of the concentration, but only the ratios of output concentration to input concentration. This follows from the linearity of absorption with equilibrium concentration. Nevertheless, because of the bubbler design it is clear that the flow exiting the bubbler will be close to saturated. With this assumption, the concentration is computed from an equation developed by experiments at Edgewood Arsenal which give the following expression for the vapor pressure of DMMP:

$$P_o = 10^{(11.102 - 3310/T_o)}, \quad (9)$$

as a function of T_o , the absolute equilibrium temperature in degrees Kelvin. Concentration in gm/ml is obtained from the relation

$$C_0 = \frac{P_0 M_{DMMP}}{R T_0} \quad (10)$$

where R is the gas constant and M is the molecular weight. For other gas temperatures, T , under constant pressure conditions the concentration is simply

$$C = C_0 \times T_0/T. \quad (11)$$

The calibration of the FID was performed by varying the amount of nitrogen mixed with the DMMP feed from this bubbler. Figure 5a presents plots of FID meter readings versus percent of full saturated DMMP concentration. The calibration is quite sensitive to the bubbler temperatures as can be seen. Good correlation over much of the concentration range is obtained if the curves are corrected to a common temperature using the above equations as shown in Figure 5b. There is some scatter near saturated conditions.

Additional checks were made on the calibrations by varying the flow rate of nitrogen through the bubbler filled with DMMP between approximately 25 and 145 ml/min to check whether this flow rate over this range had any effect on the ability to obtain a gas mixture of nitrogen saturated with DMMP vapor from the bubbler. The mixture flow rate to the FID was maintained constant with any excess flow vented prior to feeding to the FID. Readings were found to be independent of flow rate over the ranges used in the experiments confirming that a constant concentration (saturated condition) was achieved. For most of the work, the feed flow rate to the FID was kept constant at 37.6 ml/min. Checks of the FID readings were made with varying feed flow rate by $\pm 4\%$. As expected, readings with a fixed feed concentration were directly proportional to the feed flow rate.

FID calibration was regularly checked by introducing a known concentration of DMMP. If the reading were not correct, the FID was recalibrated. Periodically, the FID was disassembled and cleaned of the powder residue due to combustion. This was accomplished with an acetone solvent, brushing, and blowing out of the powder.

A photograph of the FID in the experimental test loop is provided in Figure 5c. Also visible at lower left in this photograph is the absorbent polymer test module.

7.5 Polymer Partition Coefficients

Three polymers of interest were obtained for evaluation, a DiMethyl silicone rubber, polyepichlorohydrin and fluoropolyol. The silicone rubber material was a commercial two part potting compound made by Dow Chemical Company with the designation SYLGARD 184 Silicone Elastomer. While its partition coefficient was considerably less than that of the other two, it had excellent casting characteristics. This was important to being able to make a test module with a large number of small diameter parallel channels in a short period of time. The silicone rubber did, as hoped, cast the desired module easily. For measurement of the

partition coefficient of the DMS (silicone rubber) material, a thin membrane approximately 0.25 mm thick was cast on a flat surface giving a surface area of about 100 square centimeters total. This sample was then suspended in a jar that was flushed for 16 hours or more with a fixed feed concentration, C_0 . The partition coefficient, K , was then calculated by the relation

$$K = \frac{\text{Fractional weight gain}}{\text{DMMP feed concentration}} \times \text{polymer density} \quad (12)$$

Figure 6 presents a photograph of this membrane.

Tests for the poly-epichlorohydrin (PECH) from the Aldrich Chemical Company were made in a slightly different way. The polymer which is a tough elastic material was liquefied to a honey like consistency by dissolving it in dichloromethane, a very volatile compound. The solution was quickly poured over a flat sheet of aluminum foil and dried leaving a very thin coating of PECH. This foil was then joined with another sheet of foil to form a closed flat bag into which a tube carrying feed flow was inserted. This arrangement permitted rather good mass transfer to the polymer. All weights were recorded before and after permeation and this polymer provided a remarkable 38% weight gain as compared to 3% for the DMS membrane under similar conditions. Results are presented below.

Similar tests for Fluoropolyol were not obtained because of time limitations. A sample of the material was kindly supplied by Dr. Snow of the U.S. Navy Research Laboratory. The polymer in the form received is an extremely viscous liquid that required 3 months to flatten out in a small jar about 3 centimeters in diameter. Partition coefficients for Fluoropolyol measured in [3] against DMMP vapors were found to be remarkably high and exhibited a variation with concentration. Values of K as high as 10^7 were reported at low concentrations and declined as concentration increased [3]. In view of the large amount of swelling that would occur even at modest concentrations, this result is not surprising. If concentrations of DMMP used in our present tests (10^{-6} gm/ml.) were equilibrated with Fluoropolyol at a K value of 10^7 , the weight gain would theoretically be one thousand percent! Measurements at concentrations much lower than those available for our present test system should be carried out and are planned for our Phase II research program.

7.6 Oscillatory Flow Test Procedures

The oscillatory flow test were performed as follows:

- 1) Before each run, the module was heated to approximately 50°C and flushed for several hours with pure nitrogen.
- 2) The DMMP feed bellows was saturated with DMMP feed vapor for 20 minutes to prevent any adsorption on the bellows walls during the run.
- 3) After start up flow meters were maintained at preset values; temperatures of the bubbler feed, test module and humidified return flow were measured at frequent intervals;

FID meter readings were taken and the test was allowed to run for two to three hours.

- 4) All tests were made in a chemical hood with fans running.

8 Results and Discussion

8.1 Computational Study

The mass transfer code was exercised for a group of input variables and the results are given as plots of the concentration in the air channel divided by the input concentration against axial position. Curves are shown at the end of in-breaths or out-breaths. The value of the concentration ratio, at the end of the tube at the end of in-breath, would be the maximum fraction of the input concentration breathed by the respirator wearer at the times indicated of one half hour and one hour of continuous breathing. The most interesting computation that relates directly to the feasibility of the oscillatory flow concept is shown in Figure 7a. Here a comparison is shown for the combination of a silicon rubber compound and a simulant toxic gas, DiMethyl-Methyl Phosphonate. The upper pair of curves represent use of the absorber in the conventional way with the out-breath diverted from the channel. The lower pair of curves show the concentration along the channel when the out-breath is passed back through the polymer. Both curves are for one hour of continuous breathing. Note that the oscillatory system provides much greater protection by producing much lower concentrations at the tube exit and that the one-way flow system would be inadequate. Realistic values of K , D_a , and D_p have been used in this calculation ($K = 10^5$, $D_a = 0.075 \text{ cm}^2/\text{sec}$, $D_p = 10^{-7} \text{ cm}^2/\text{sec}$). Figure 7b shows the exiting values of the mean concentration ratio for in-breath as a function of time for the oscillatory case and the one-way flow case. The advantage of oscillation is evident. In these figures, axial position is normalized on tube length.

Figures 8a and b show that the partition coefficient has a major effect on the system performance with the concentrations in the channel declining rapidly with increasing value of K . This is due to the fact that, as noted above, larger partition coefficients enable a greater amount of absorption by the polymer. Note that for $K = 50000$ which is an easily achievable value in practice (see below for K values of various polymers), breakthrough has not occurred for the conditions chosen. Figures 9a and 9b indicate that the polymer diffusion coefficient has a significant, but less dramatic effect than the partition coefficient on the final exiting concentrations. In this figure, the polymer diffusivity is varied over a factor of 10. Increasing polymer diffusivity is seen to decrease the channel gas concentrations but not as significantly as the five fold variation in K does shown in Figure 8. The polymer diffusivity controls transport within the polymer. Thus an increase in diffusivity should facilitate transport away from the tube wall and allow more gas to be absorbed. The results of these figures suggest that the mass transfer process is controlled more by K than by D_p .

Figure 10 presents the effects of a two fold variation in mean flow velocity through

the polymer lined channels. The concentrations in the channel are seen to decrease with decreasing mean flow velocity. Comparing this variation with that due to a ten fold variation in polymer diffusivity shown in Figure 9, it can be seen that the channel concentrations are more sensitive to mean velocity than to polymer diffusivity. One should also note that with a lower mean flow velocity and all other parameters kept constant, less total mass of toxic gas is being drawn through the channel (the total mass being given by the product of the mean velocity, inlet concentration, and channel inlet cross sectional area). However, referring to Figure 10, it can be seen that decreasing flow velocity lowers exit concentrations more than the amount of the decreased mass inflow. A decrease in mean velocity from 20 to 10 cm/s results in a decrease in the total mass inflow by a factor of 2. As seen in Figure 10, the exit concentration is decreased significantly more than this factor between the case of mean velocities of 20 and 10 cm/s at both 0.5 and 1 hour of breathing. Flow velocity is a design choice and controls the total frontal area of the respirator absorption element.

From these figures it can be seen that it is desirable to have high values of K and D_p and low flow velocities (in the absence of other design considerations such as respirator pressure drop discussed below). However, having a polymer with a large value of K is most important to obtaining good performance.

Computations were also carried out for a small tube of 0.0127 cm channel radius with the length again set at 50 radii. Figures 11a and 11b presents results of this calculation showing the effects of variation of K and of the mean flow velocity. In these figures, the concentration profiles are grouped into an upper pair and a lower pair. The upper pair correspond to $K = 10^4$ while the lower pair correspond to $K = 10^5$. The strong influence of larger values of K decreasing the channel concentration is again demonstrated. Within each pair of curves, the flow velocity has been varied from 30 to 20 cm/sec. The trend of Figure 10 of decreased velocities resulting in decreased concentrations is again shown.

Figures 12 and 13 show the effect of lengthening the channel. Shown are results for channel lengths of 50 and 100 radii. Figures 12a and 12b present the results plotted against axial position nondimensionalized on the tube length for each case. Figures 13a and 13b present the same results nondimensionalized on the length of the shorter tube. Thus in Figure 13 the exit for the shorter tube is at axial position 1.0 while that for the longer tube is at the axial position 2.0 while in Figure 12, the exits for both cases are at 1.0. For the conditions shown breakthrough has not occurred for the longer channel even after 1 hour of operation while breakthrough has already occurred for the shorter channel after only 0.5 hours of operation. It is perhaps more instructive to examine Figure 13 to assess the influence of channel length. In this figure, the axial concentration distribution for the two cases is nearly identical when plotted against actual distance, x . One can obtain a very good approximation to the concentration distribution for the shorter tube by simply taking the upstream half of the distribution for the longer tube. The influence of exit conditions causes a divergence from this similarity near the exit of the smaller tube. This is very small at

0.5 hours of operation while it is more significant after 1 hour. Clearly, from the standpoint of increased absorption and increased respirator life, it is desirable to have longer channels. However, this also increases respirator size and weight as well as the pressure drop across the respirator. This is a design trade-off discussed below.

The results presented above show the concentration distributions at particular points in time or the concentrations at a particular location over time but at the same point in the breathing cycle (e.g., end of in-breath). It is instructive, however, to enable better understanding of the process physics to examine the concentration history at a particular point over an extended time period. The process is inherently unsteady and cyclic. Figure 14a presents the calculated concentration ratio history at 3 points on the channel center line at $x/l = 0.2, 0.5, 0.8$ during the first 200 seconds of breathing for the case of a combined in-breath/out-breath cycle time of 6 seconds. The large cyclic variation due to absorption and desorption during the breathing cycle is apparent as is the gradual rise of the mean value of the concentration which will gradually asymptote to a "cyclic equilibrium" value. The concentration histories at these three stations are in phase and decrease in amplitude with x . Shown in Figure 14b is the concentration history in the polymer (at a location 4 grid points from the wall, $r/r_{mx} = 1.02$) at $x/l = 0.5$ together with the air channel concentration histories for the same case and at the same axial locations as in Figure 14a, but after one hour of breathing. The variation in concentration amplitude in the polymer is much less than that in the air channel at the same axial location, and it is approximately 90 degrees out of phase with the sinusoidal variation in the air channel. This phase shift is due to the mass absorption capacity of the polymer

8.2 Evaluation of Respirator Pressure Drop

In the design of a practical respirator there are several important parameters not yet discussed. Breathing resistance, that is, pressure drop through the absorber or canister is of primary concern. Pressure drop maximums have been established by NIOSH as a requirement for certification. These levels depend on the respirator's use but range from 20 to 70 millimeters of water. Without getting into an optimized design, we can obtain an estimate of pressure drop for the oscillatory system by making an educated guess as to geometry and flow speed in the polymer channels as:

$$\begin{aligned}r_{mx} &= .0127\text{cm} \\l &= 1.27\text{cm} \\U_{mean} &= 30\text{cm/sec}\end{aligned}$$

Using the well known relation for pressure loss in a channel with laminar flow we obtain using viscosity values for air

$$\Delta p = 8 \frac{\mu U l}{r_{mx}^2} \quad (13)$$

where μ is viscosity of air. Substitution of the above values in the equation provides a value of $\Delta p = 0.3mm$ of water (0.006 psi), a very small value.

8.3 Experimental Study

The results of our study of polymer partition coefficients described above are presented in the Table below and illustrate the potential for achieving high K values that in turn would result in excellent performance of an oscillatory flow system as indicated by the analysis presented above.

PARTITION COEFFICIENTS

| Source / Polymer | DMS | Polyepichlorohydrin | Fluoropolyol |
|------------------|---------|---------------------|---------------|
| DYNAFLOW Tests | > 7,000 | 100,000 | — |
| Reference 2 | 10,000 | — | — |
| Reference 3 | — | 100,000 | $10^6 - 10^7$ |

These data in conjunction with the predictions of the numerical model clearly indicate the desirability of using a polymer such as polyepichlorohydrin or fluoropolyol which have value of K 1 to 3 orders of magnitude greater than that of DMS.

The test runs made with the polymer module were designed to show the effectiveness of the oscillatory concept in reducing the influx of toxic gas into the breathing space. Figure 15 presents results of an experiment run with zero back flow and compares the results with predictions of the numerical model for this case. This simulates the condition in a valved respirator where the exhaust air is diverted to the outside. In this case, a 6 second breathing cycle is simulated with 3 seconds of in-breath flow through the respirator module followed by a 3 second period of no flow through the module. The comparison between experiment and prediction is very good with the model over predicting the experiment by a few percent. The disparity is somewhat larger at longer times.

Figure 15 also presents two sets of oscillating flow data - one each for 6 and 5 second breathing cycles. In each of these cases, the in-breath and out-breath periods are equal and flow occurs both in the forward and reverse directions. The earlier breakthrough for the 5 second period case is expected because the shorter period results in an increase of the mean flow velocity through the module by 20 percent.

The contrast between the zero back flow case data and that of the oscillating flow is striking. After 1 hour of operation, the exit concentration of the zero back flow case is in excess of 75% of the incoming concentration while there is no measurable contaminant concentration at the module exit for the 6 second period oscillating flow case. Even the

“plateau” value of the exit concentration is only 12% of the inlet concentration at over 2 hours of operation. It must be highlighted that these results were achieved with a DMS polymer which has a partition coefficient of 1 to 3 orders of magnitude less than candidate polymers for the actual respirator such as polyepichlorohydrin and fluoropolyol. These results clearly demonstrate the feasibility of the concept of using oscillatory flow in conjunction with absorbent polymers to greatly improve the performance of toxic vapor removal.

Also shown in Figure 15 is the prediction from the numerical model for the 6 second breathing cycle with oscillatory flow. The comparison between experiment and prediction in this oscillatory flow case is not good. The predicted “plateau” concentration level is about 70 percent that of the experimental data. The experimental data also show a substantial lag in reaching a plateau. The reason for this is believed to be the use of heated return air in the experiments that was not included in the numerical modeling. This heated air will increase the amount of gas desorbed from the polymer, and thus improve performance of the respirator over that obtained with exhalation flow at the same temperature as the inhalation flow. This is due to the polymer absorption coefficient decreasing with increasing temperature as shown for silicone rubber polymers in [2]. Such thermal considerations will be addressed in the Phase II effort by expanding the numerical model to solve the coupled heat and mass transfer equations.

9 Conclusions

We believe that the Phase I study has demonstrated that significant improvements in respirator efficiency can be made using the alternating flow concept. This effort has demonstrated both experimentally and analytically the feasibility of utilizing two way oscillatory flow to substantially increase the breakthrough time for removal of toxic gases with polymer absorbents. The technology would have application to respirators for many toxic gases and toxic gas mixtures found in commercial work places. The possible elimination of activated charcoal may make the filters reusable by simple air flushing procedures, and the polymeric materials should prove less sensitive to destructive interferences from benign pollutants such as water vapor and dust. Due to the improved performance, respirators utilizing this concept could be of markedly reduced weight and volume compared with conventional systems for the same useful operating life. Alternatively, the new respirators could be designed to be of comparable size to conventional systems but with greatly extended lifetimes. Preliminary estimates indicate respirators based on this concept can be designed to have very low pressure drops. This would both increase comfort, and, more significantly, decrease the amount of leakage around the face seal thus affording the wearer a greater degree of protection.

An initial identification of promising polymeric materials with high partition coefficients was made. In addition a DiMethyl silicone polymer was utilized as an absorber for DMMP, a high boiling point toxic gas simulant typical of many toxic vapors found in industrial work

places. Both a numerical model and a laboratory experimental test rig were developed. The model, which includes the effects of diffusion in both the polymer and gas as well as convection in the gas, can be used for parametric studies. Results of a parametric study demonstrated the importance of various factors on respirator design. The most significant factor found to affect performance was the partition coefficient. Toxic gas concentrations in the air channel decrease and breakthrough time increases significantly as the value of the partition coefficient is increased. Based on measurements made during the effort and available data two candidate polymers having partition coefficients one to three orders of magnitude greater than the DMS used in the current study were identified. The numerical simulations also showed that larger polymer diffusivities and lower flow velocities also decreased toxic gas concentrations in the air channel, although their influence is weaker than that of the partition coefficient.

The experimental program developed both a means of measuring the partition coefficient of a polymer/gas pair, and a flow system for simulating the breathing flow through a module that represents a section of a respirator. Both the modeling and experimental capabilities will be employed in future design studies. Experiments were conducted using flow of a mixture of nitrogen and DMMP through a test module cast of DMS polymer. Comparison of measurements of exit concentrations for the cases of one way flow (as in conventional respirators) and two way oscillating flow show dramatic decreases in the concentration at a given time and increase in the breakthrough time for the two way oscillating flow case.

10 Acknowledgements

The authors wish to thank Professor Timothy Barbari for his consultations particularly in the area of polymeric films. We would also like to acknowledge the assistance of our colleagues at DYNAFLOW. In particular, we would like to thank Dr. Ramani Duraiswami for assistance in the analysis and Mr. Pat Aley for assistance in the conduct of the experiments.

11 Literature Cited

1. McAlister, J.W., Ord, J.A., Anders, L.W. and Kohler, G.A. - U.S. Patent 4155358, May, 1979.
2. Hagal, D., Laverty, V.J., and Brown, C.E., *A Basic Research Study of Factors Affecting the Collection Efficiency and Power Use of High Volume Sampling Systems*. Hydronautics, Inc. Technical Report 7413-1, May 1977.
3. Grate, Jay; Snow, Arthur; Ballantine, David; Wohltjen, Hank; Abraham, Michael; McGill, R. Andrew; and Sasson, Prina, *Determination of Partition Coefficients from*

- Surface Acoustic Wave Vapor Sensor Responses and Correlation with Gas-Liquid Chromatographic Partition Coefficients.*” Anal. Chem. 1988, 60, 869-875.
4. Ballantine, D., Rose, P., Grate, J., and Wohltjen, H. “*Correlation of Surface Acoustic Wave Device Coating Responses with Solubility Properties and Chemical Structures Using Pattern Recognition.*” Anal. Chem. 58, 3058, 1986.
 5. Stamuet, V., et al., *Permeability of Plastic Films and Coated Papers to Gases and Vapors*, TAPPI Monograph Series No. 23, 1962.
 6. Tobb, W.L., *Thin Silicone Membranes - Their Permeation Properties and Some Applications*, Report No. 65-6-031, G.E. R&D Center, Schenectady, New York, 1965.
 7. Crank, J. and Paid, G.S., *Diffusion in Polymers*, Academic Press, New York, pp 46-56, 75-104, 1968.
 8. Tollen, E.D., *Sorption Properties of Activated Carbon*, Comprehensive Progress Report - Contract DA18-035-AMC-10953(A), Edgewood Arsenal, Maryland, 1968.
 9. Bering, P.P., Dubinin, M.M., and Serpendky, V.V., *Journal of Colloid and Interface Science* 21:378 1966.
 10. Brown, C.E. and Santo, J. E., *A Preliminary Investigation of the Adsorption and Desorption of Di-isopropylmethyl-phosphonate and Water Vapor on Several Metallic Substrates*, Chem. Sys. Lab. Contractor Report ARCSL-CR-80071, October 1980.
 11. *Bioastronautics Data Book*, NASA SP-3006, 1964.
 12. Hines, A.L. and Maddox, R.N. *Mass Transfer-Fundamentals and Applications*, Prentice Hall, 1985.
 13. Roache, P. J., *Computational Fluid Dynamics*, Hermosa Publishers, Albuquerque, NM, 1976.

12 Publications

“A Study of Oscillatory Absorptive Flow for Reducing the Size and Weight of Respirators,” Brown, C. E., Kalumuck, K. M., Chahine, G. L. and Frederick, G. S., in preparation for submission to the AIChE Journal.

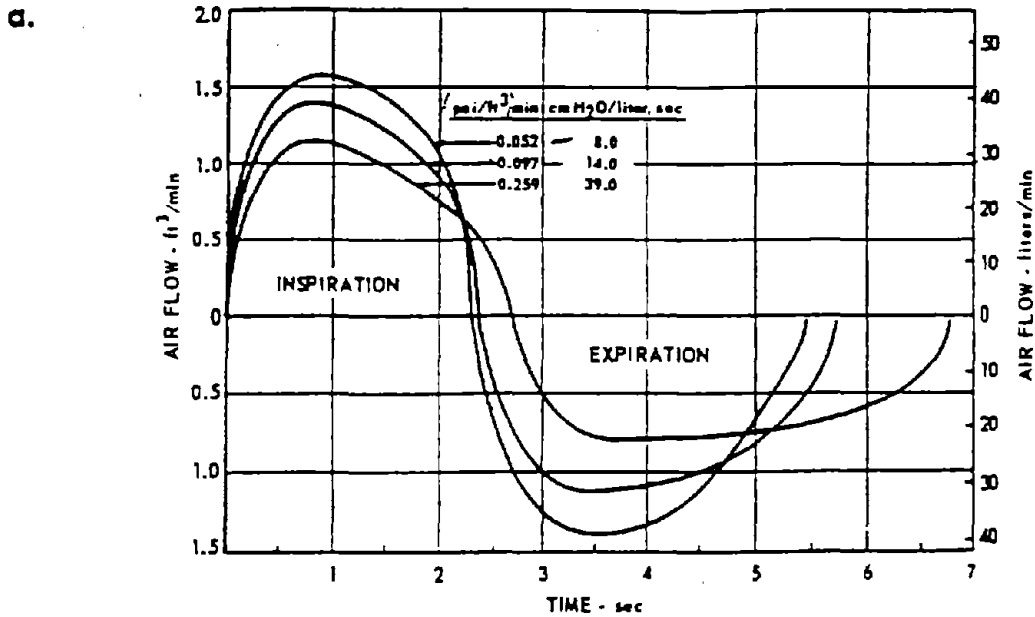


Figure a shows the reduction of peak flow rate at tidal volume of 1000 ml and the lengthening of the respiratory cycle produced by increasing the impedance to flow in protective equipment. Other effects are the increase in dead space and consequent changes in alveolar air. Figure b shows typical profiles for inspiratory flow at rest and in moderate exercise. The central light area, which represents the flow at or above 80% of the peak flow, shows that over 50% of the tidal volume is delivered at these high flow rates. The patterns of air flow during respiration are highly individual, and vary greatly at different activity levels.

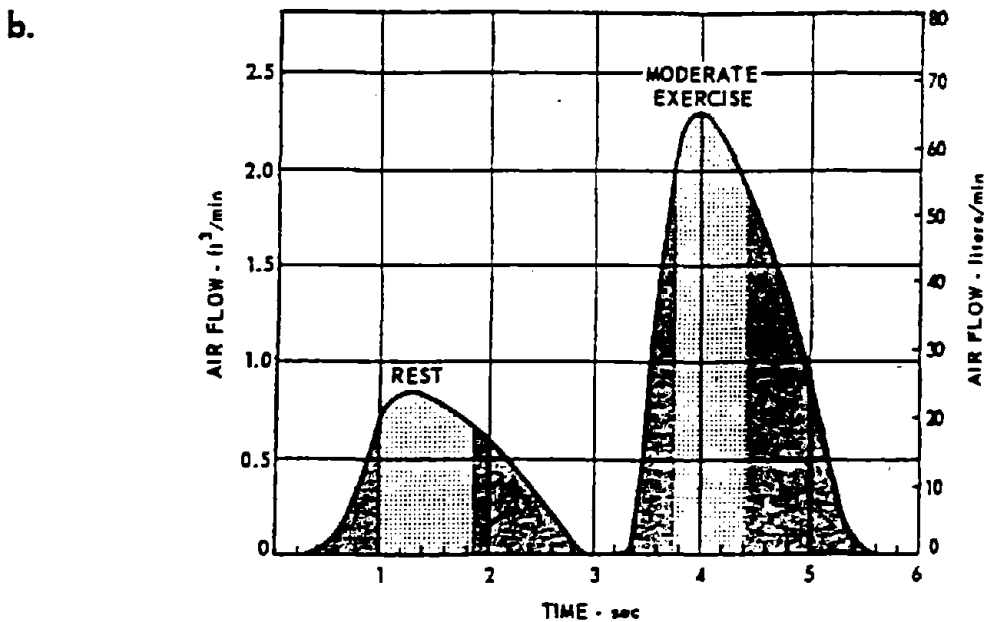


FIGURE 1: Respiratory Air Flow Characteristics (from [11]).

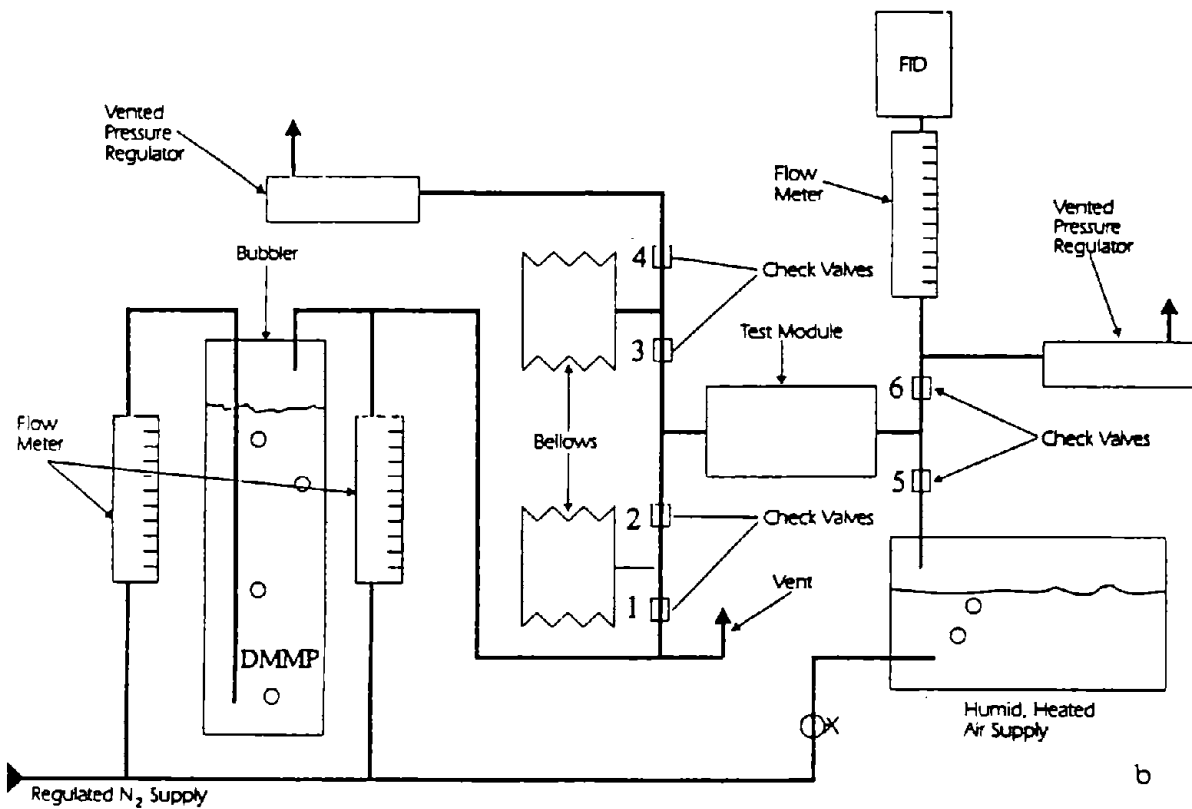
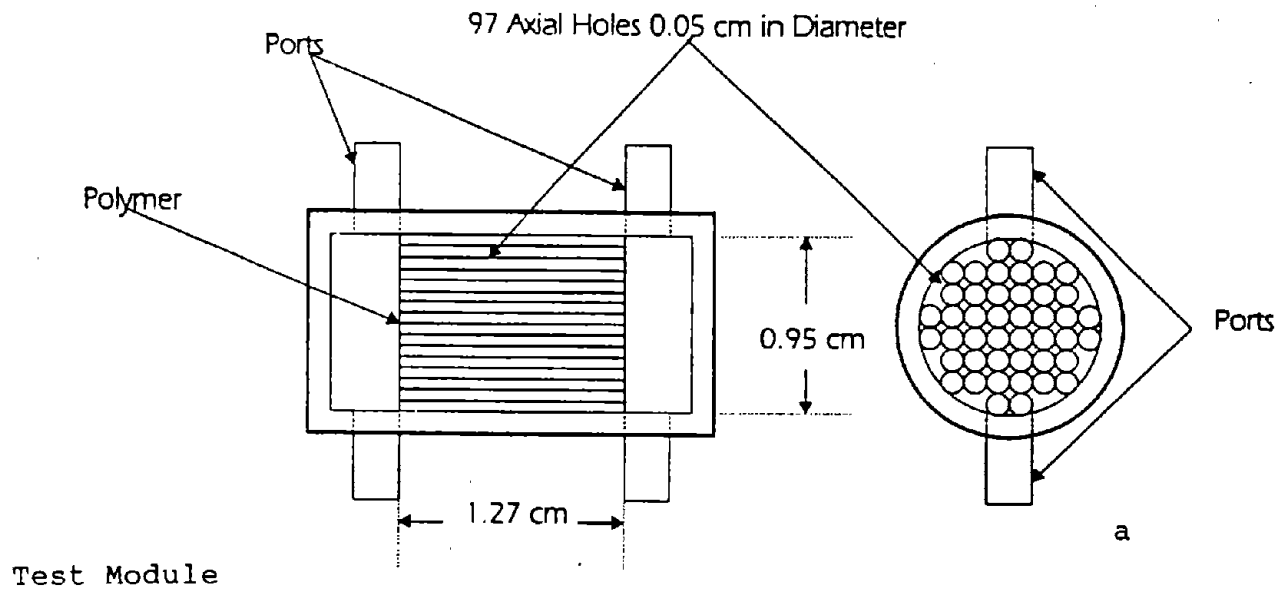


Figure 2. Schematic of Experimental Setup.

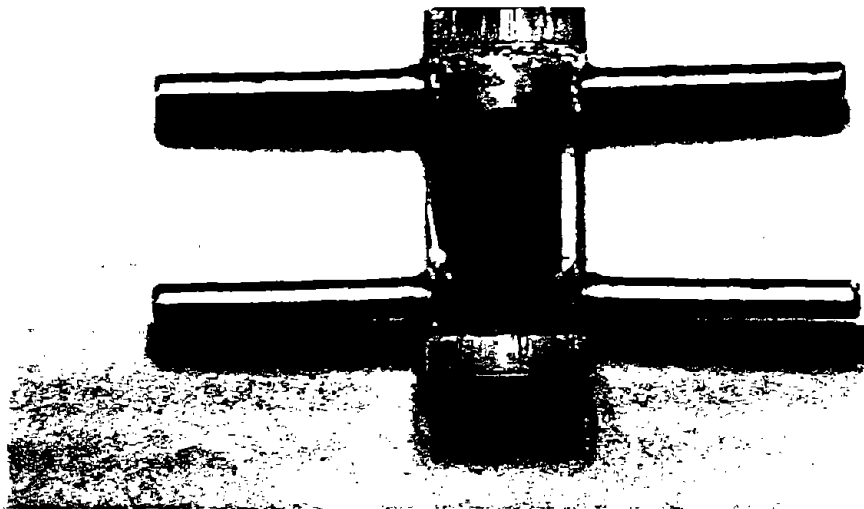


Figure 3. Close Up Photograph of Test Module.

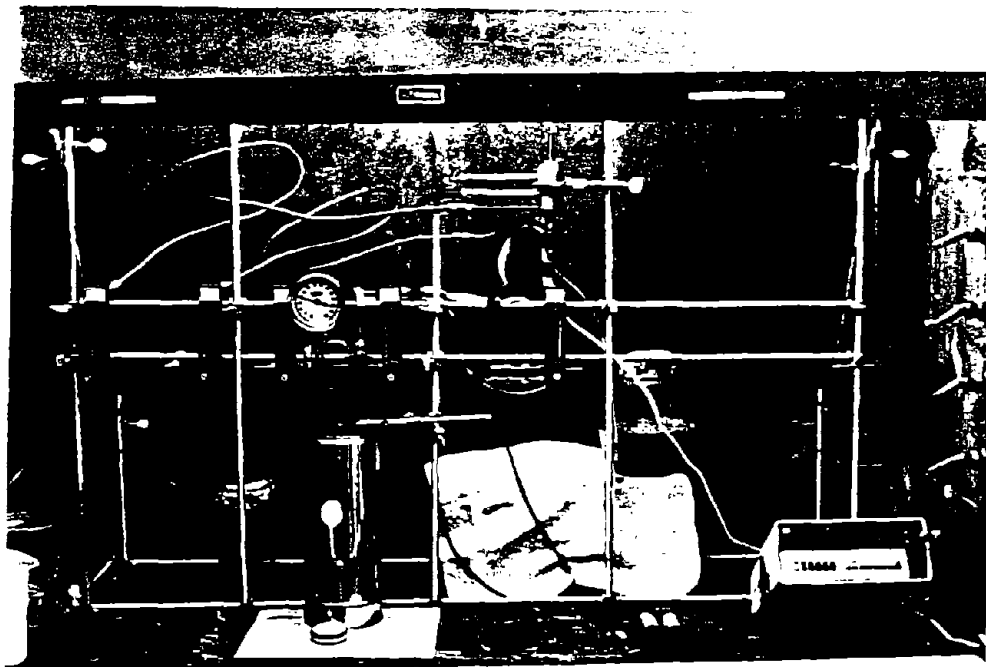
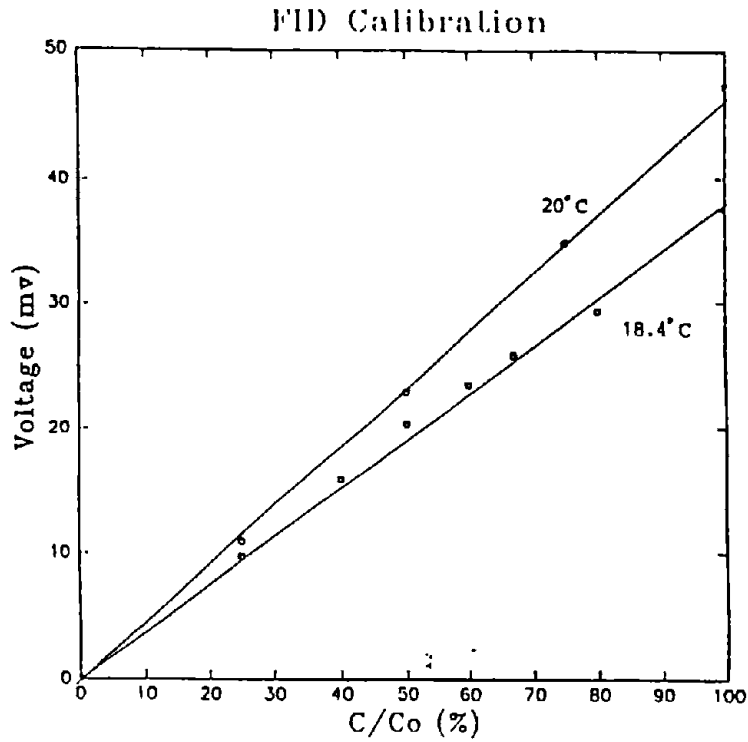
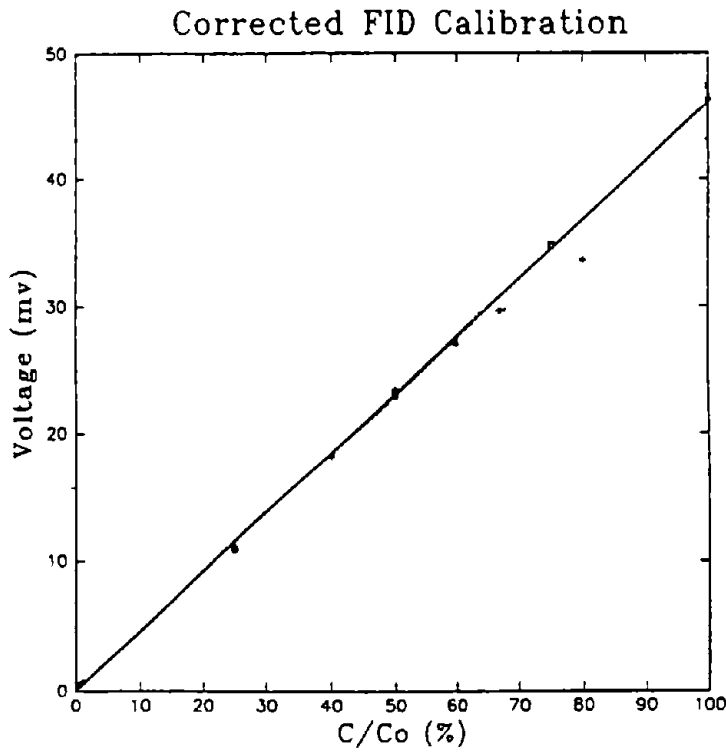


Figure 4. Photograph of Experimental Setup.



a. Variation With Temperature.



b. Corrected to 20°C.

Figure 5. Flame Ionization Detector Calibration

28

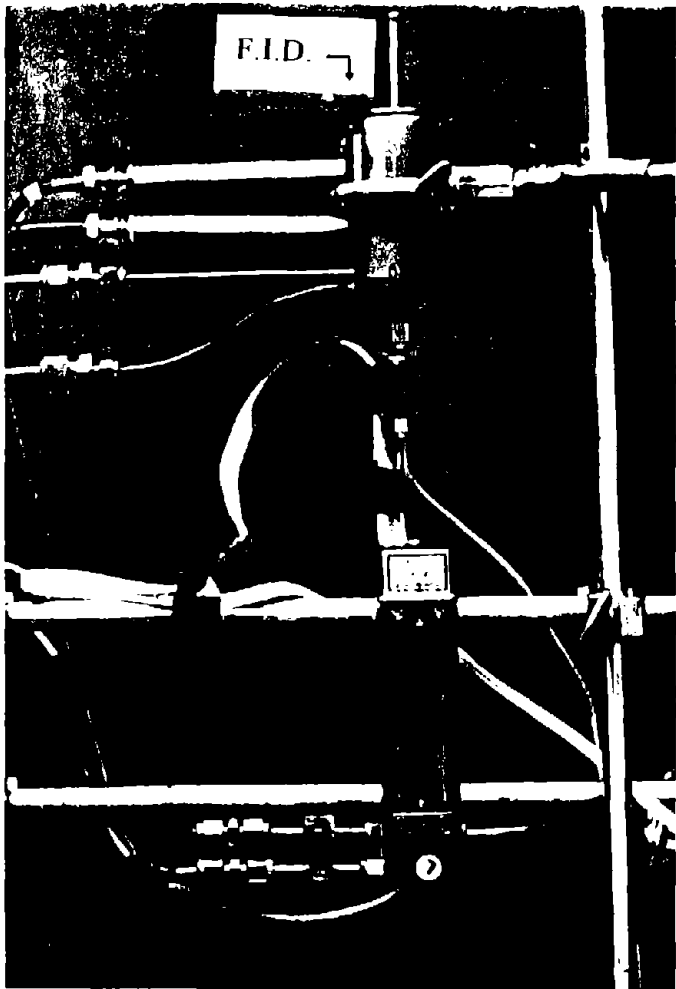


Figure 5c. View of Flame Ionization Detector in Test Loop. Test Module Visible at Lower Left.

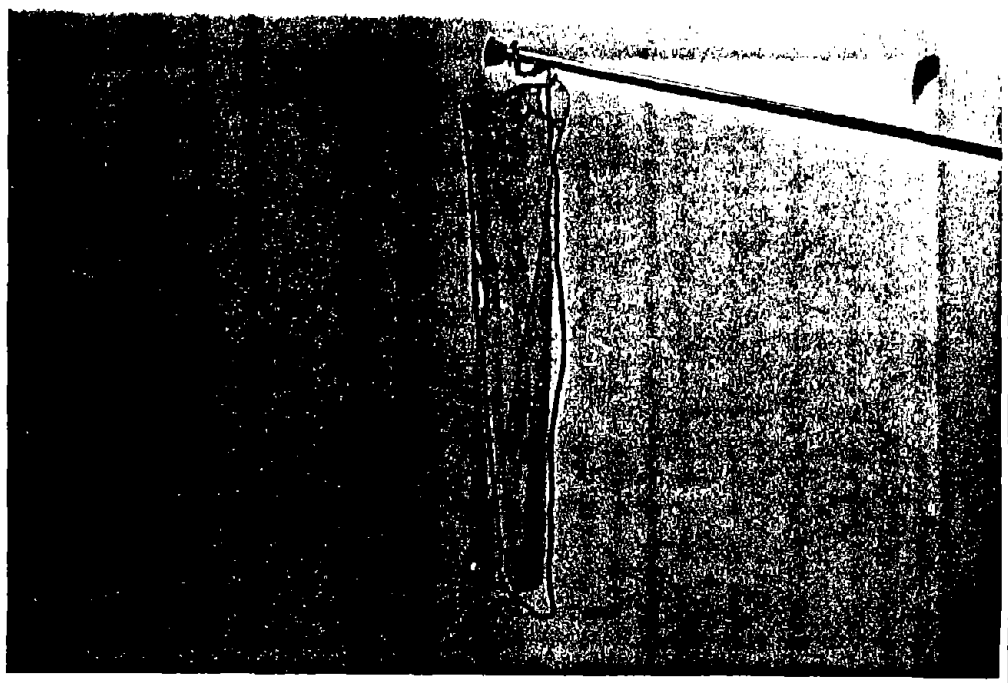


Figure 6. Photograph of DMS Membrane.

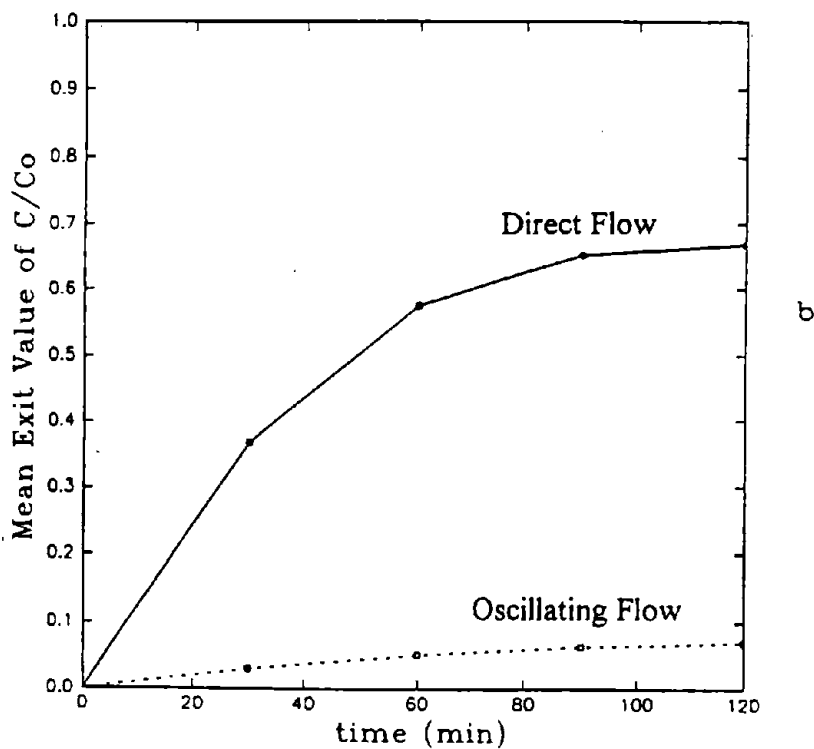
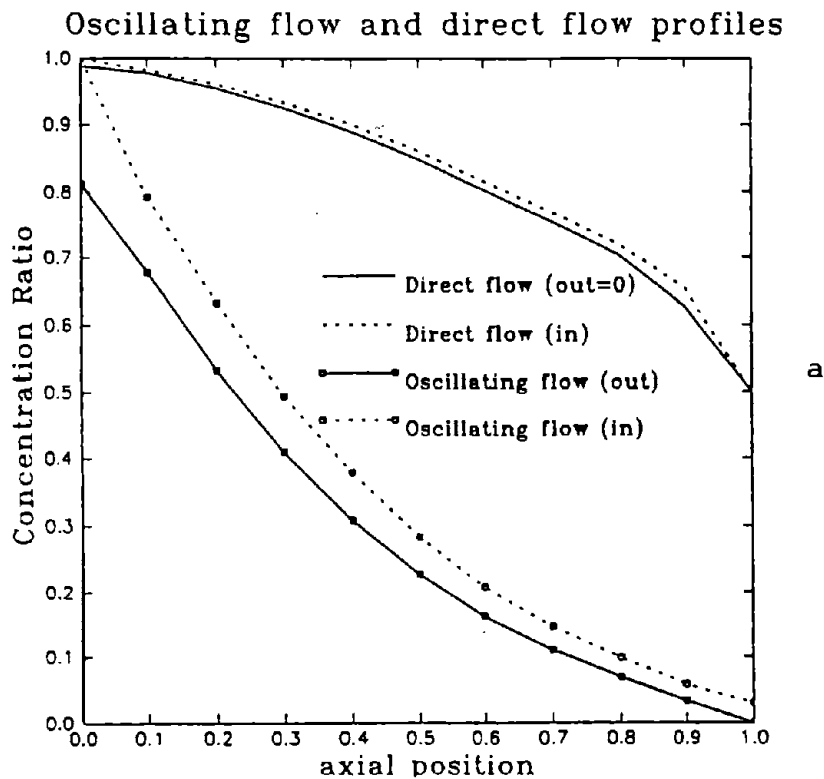
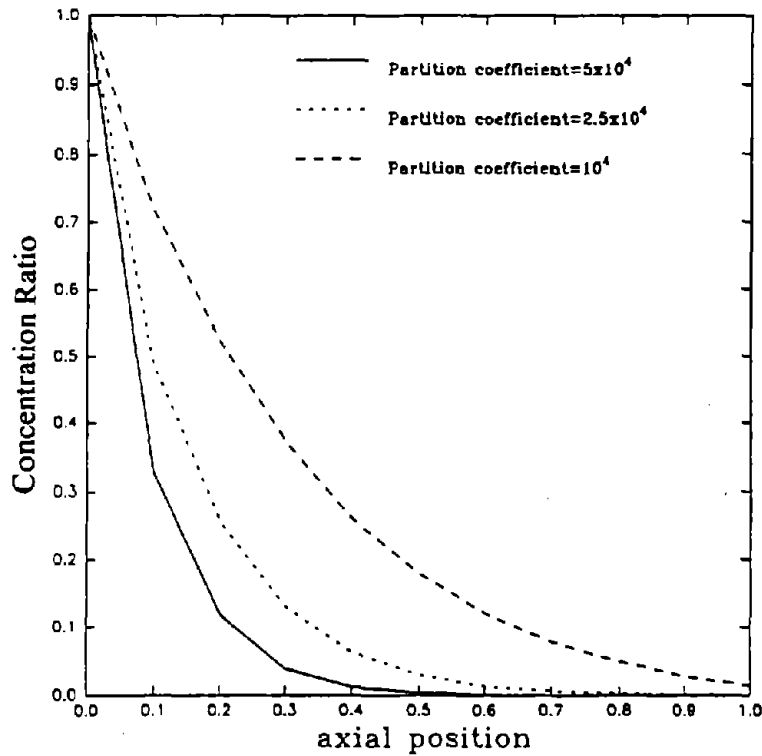


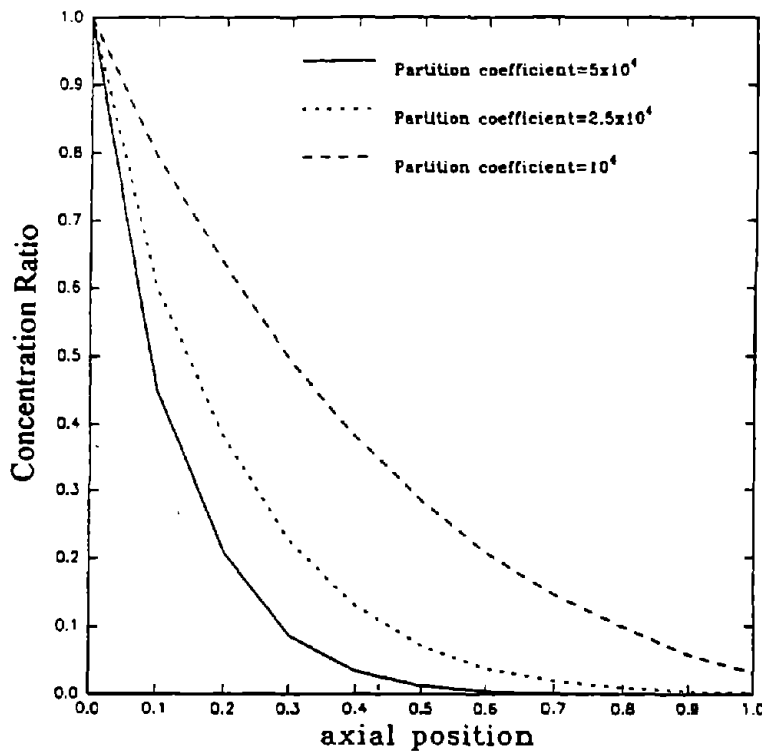
Figure 7. Comparison of Concentration Ratios with and without Oscillatory Flow After 1 hour of Continuous Breathing. $r_{mx} = .0254\text{cm}$, $l = 1.27\text{cm}$, $K = 10^5$, $U_{mean} = 15\text{cm/sec}$. $D_p = 10^{-7}\text{cm}^2/\text{sec}$, $D_a = .075\text{cm}^2/\text{sec}$. a) Along Tube b) At Tube Exit

Effect of Partition Coefficient, inbreath at 0.5hr.



a

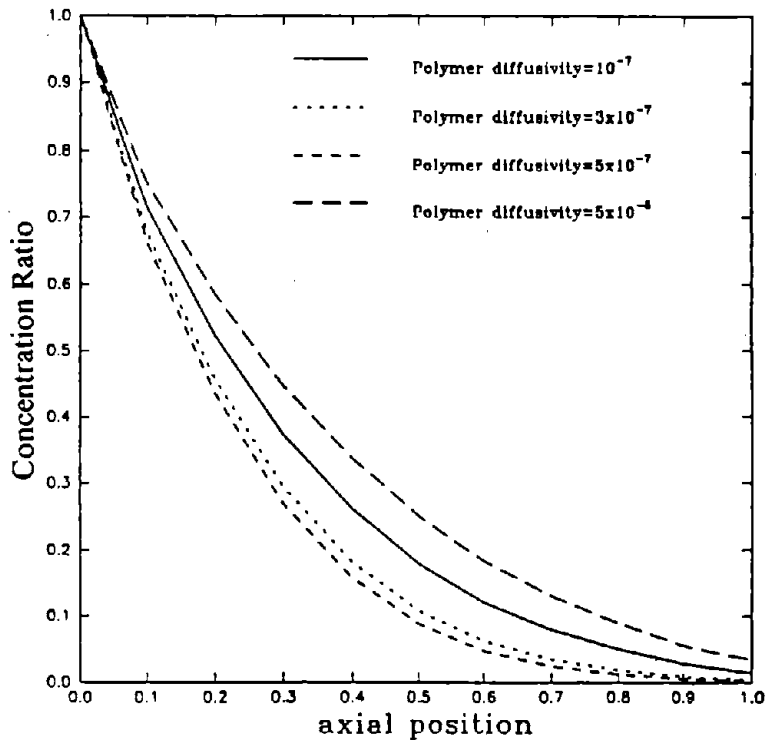
Effect of Partition Coefficient, inbreath at 1.0hr.



b

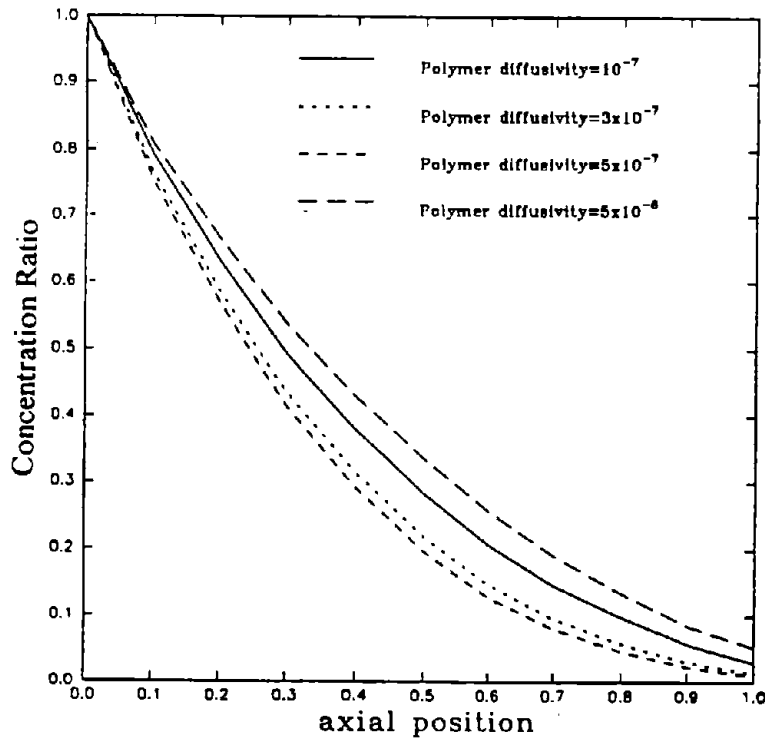
Figure 8. Effect of Partition Coefficient on Concentration Ratios in the Channels.
 $r_{mx} = .0254cm$, $l = 1.27cm$, $U_{mean} = 15cm/sec.$, $D_p = 10^{-7}cm^2/sec.$,
 $D_a = .075cm^2/sec.$

Effect of Diffusivity, inbreath at 0.5 hr.



a

Effect of Diffusivity, inbreath at 1 hr.



b

Figure 9 . Effect of Polymer/Gas Diffusion Coefficient on Channel Concentration Ratios.
 $r_{mx} = .0254cm$, $l = 1.27cm$, $K = 10^5$, $U_{mean} = 15cm/sec.$, $D_p = 10^{-7}cm^2/sec.$,
 $D_a = .075cm^2/sec.$

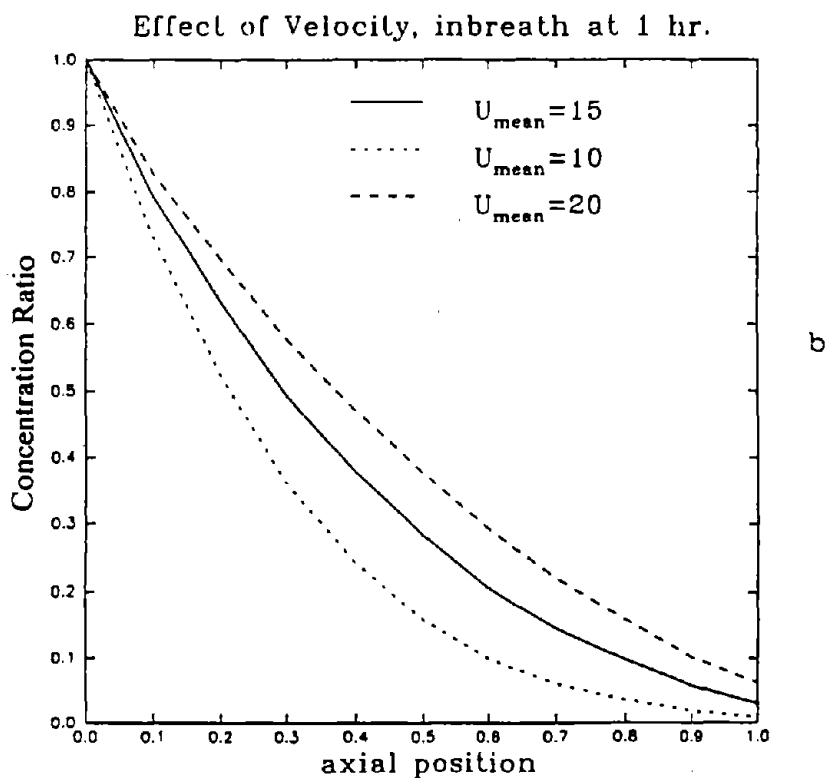
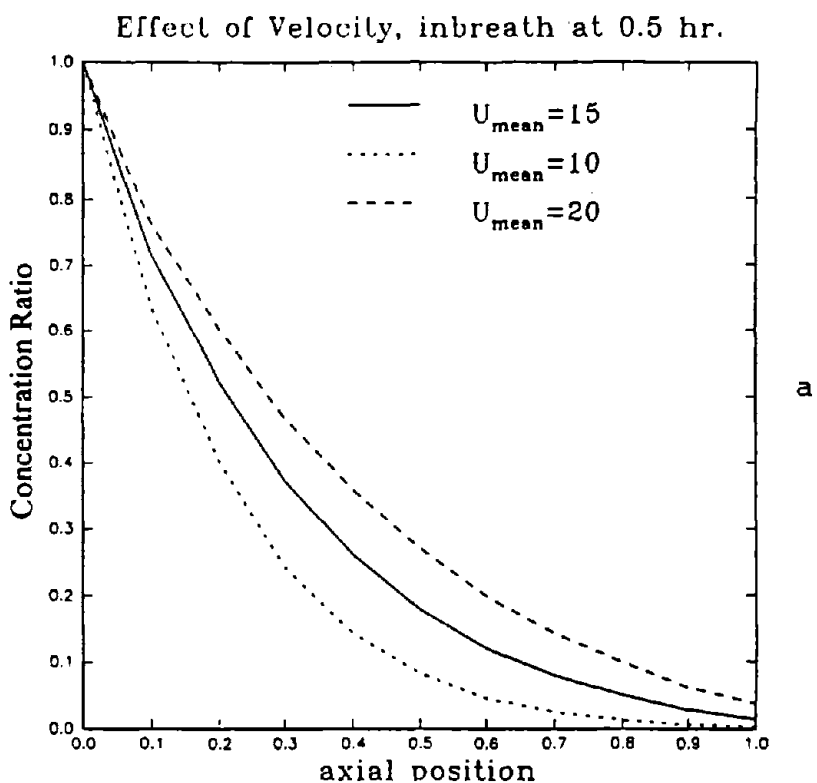


Figure 10. Effect of Velocity on Channel Concentration Ratios. $r_{mx} = .0254\text{cm}$, $l = 1.27\text{cm}$, $K = 10^5$, $D_p = 10^{-7}\text{cm}^2/\text{sec}$, $D_a = .075\text{cm}^2/\text{sec}$. U_{mean} in cm/sec .

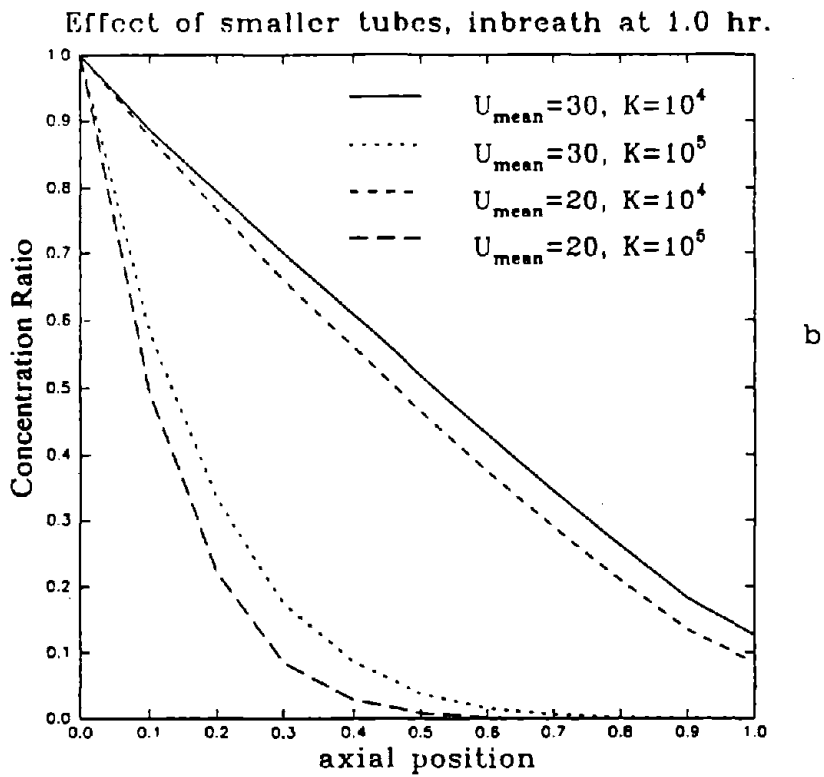
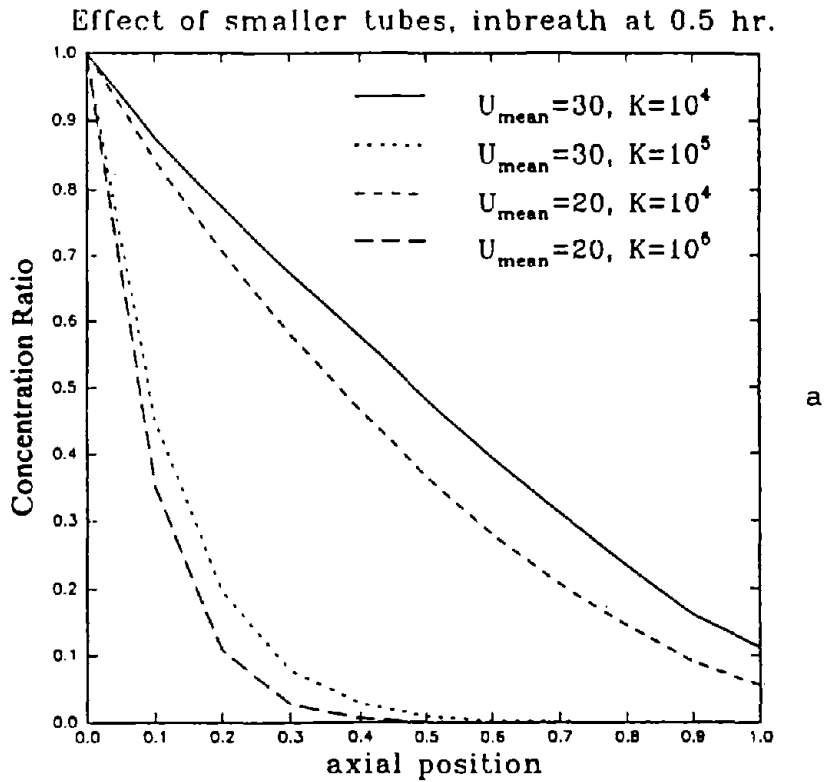


Figure 11. Effect of Smaller Tubes and Partition Coefficients on Channel Concentration Ratios. $r_{mx} = .0127cm$, $l = .635cm$, $D_p = .075cm^2/sec$. U_{mean} in cm/sec .

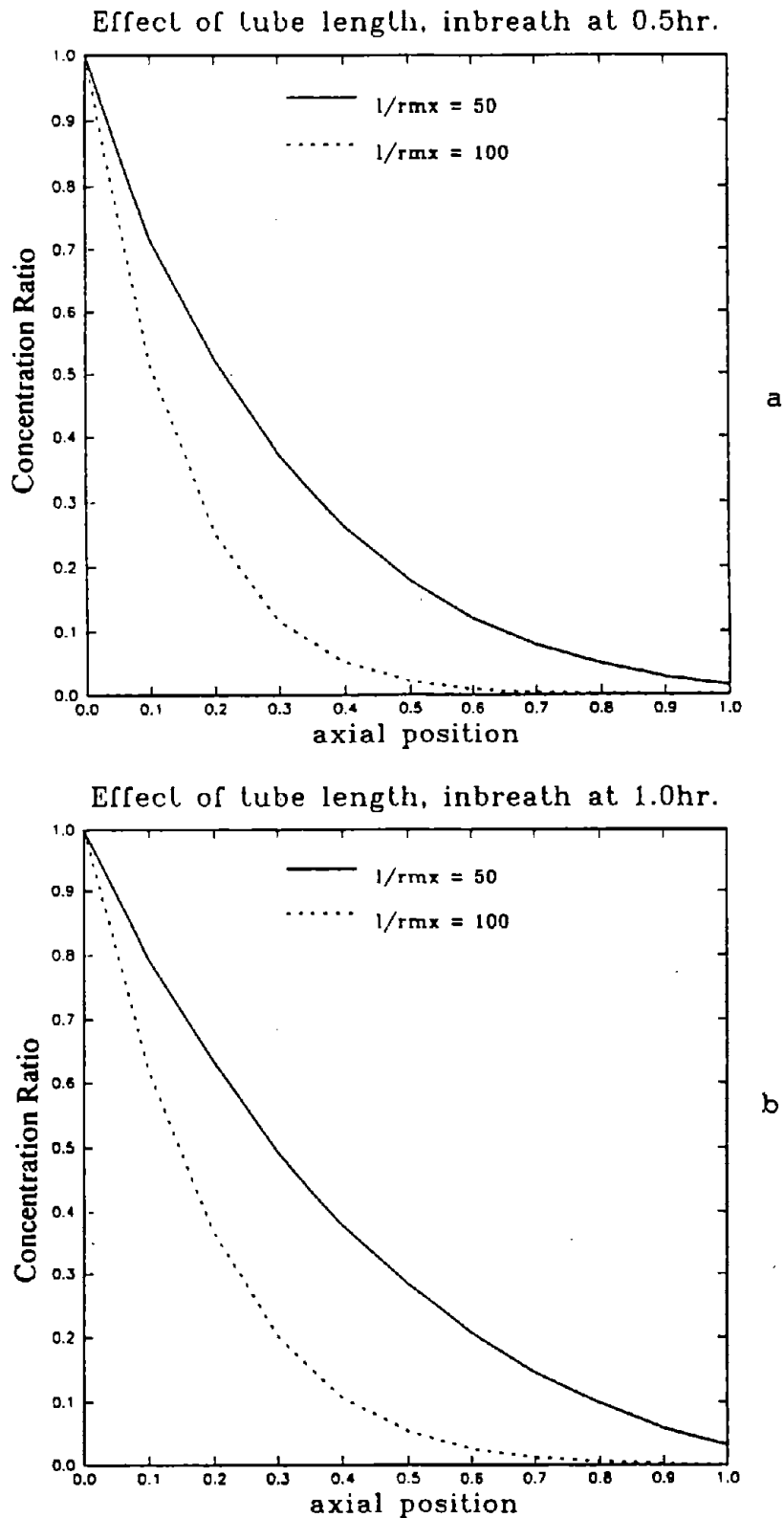


Figure 12. Effect of Nondimensional Tube Length on Channel Concentration Ratios.
 $r_{mx} = .0254cm$, $l = 1.27cm$, $K = 10^5$, $U_{mean} = 15cm/sec$. $D_p = 10^{-7}cm^2/sec.$,
 $D_a = .075cm^2/sec$.

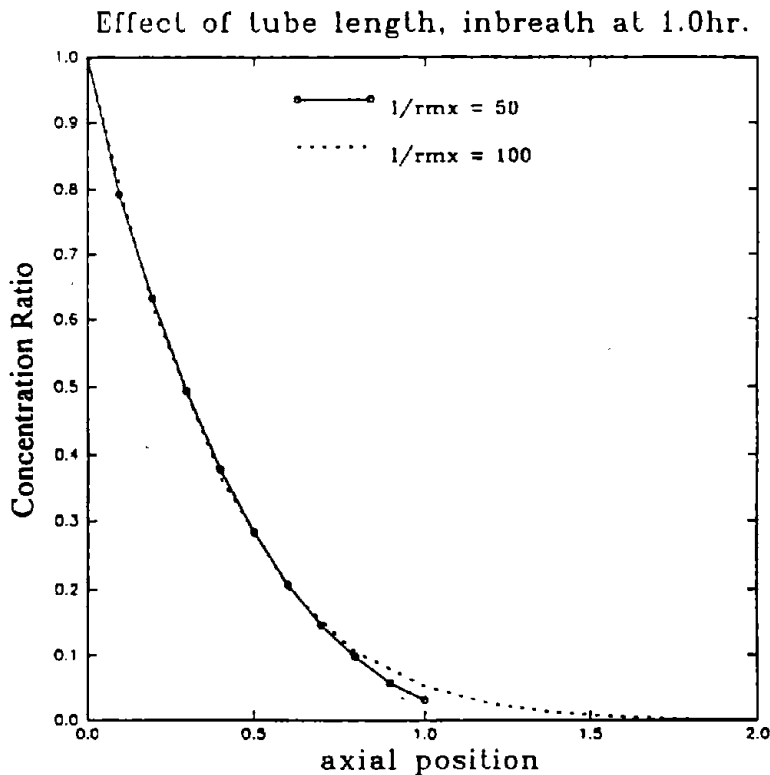
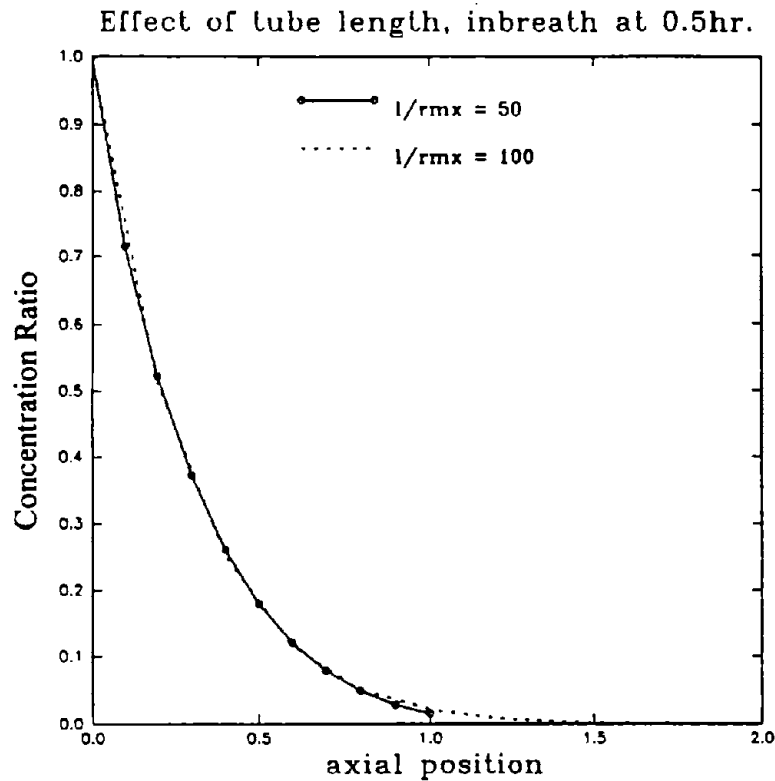
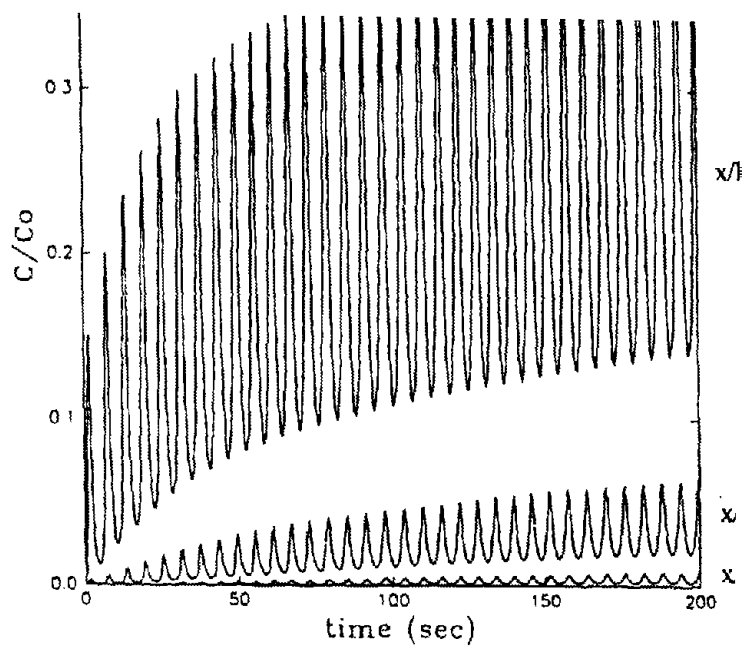
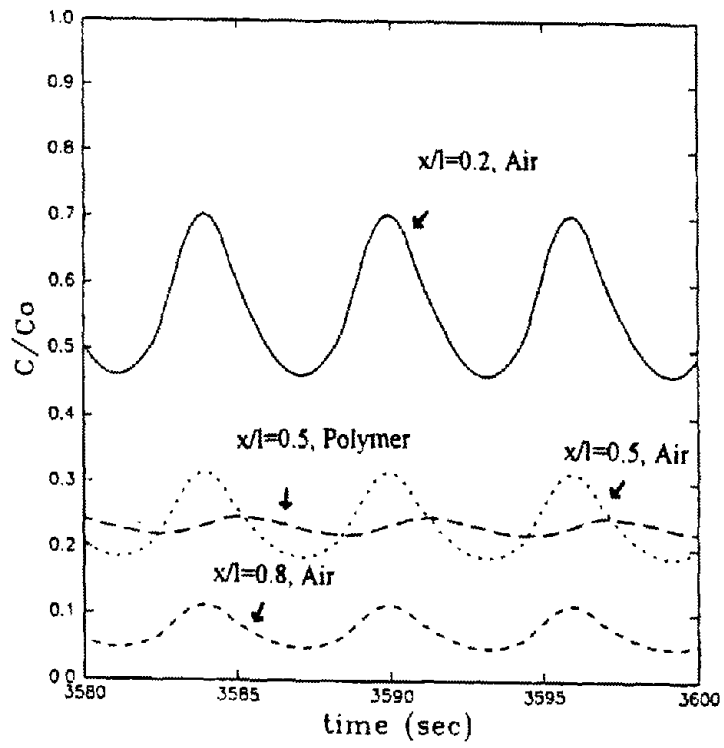


Figure 13. Effect of Tube Length on Channel Concentration Ratios. $r_{mx} = .0254cm$, $K = 10^5$, $U_{mean} = 15cm/sec$. $D_p = 10^{-7}cm^2/sec.$, $D_a = .075cm^2/sec$.



a. Initial in Air Channel



b. At 1 hour of Breathing. Note Concentration in Polymer is out of phase with that in the Channel.

Figure 14. Concentration Histories Under Oscillatory Flow C_0

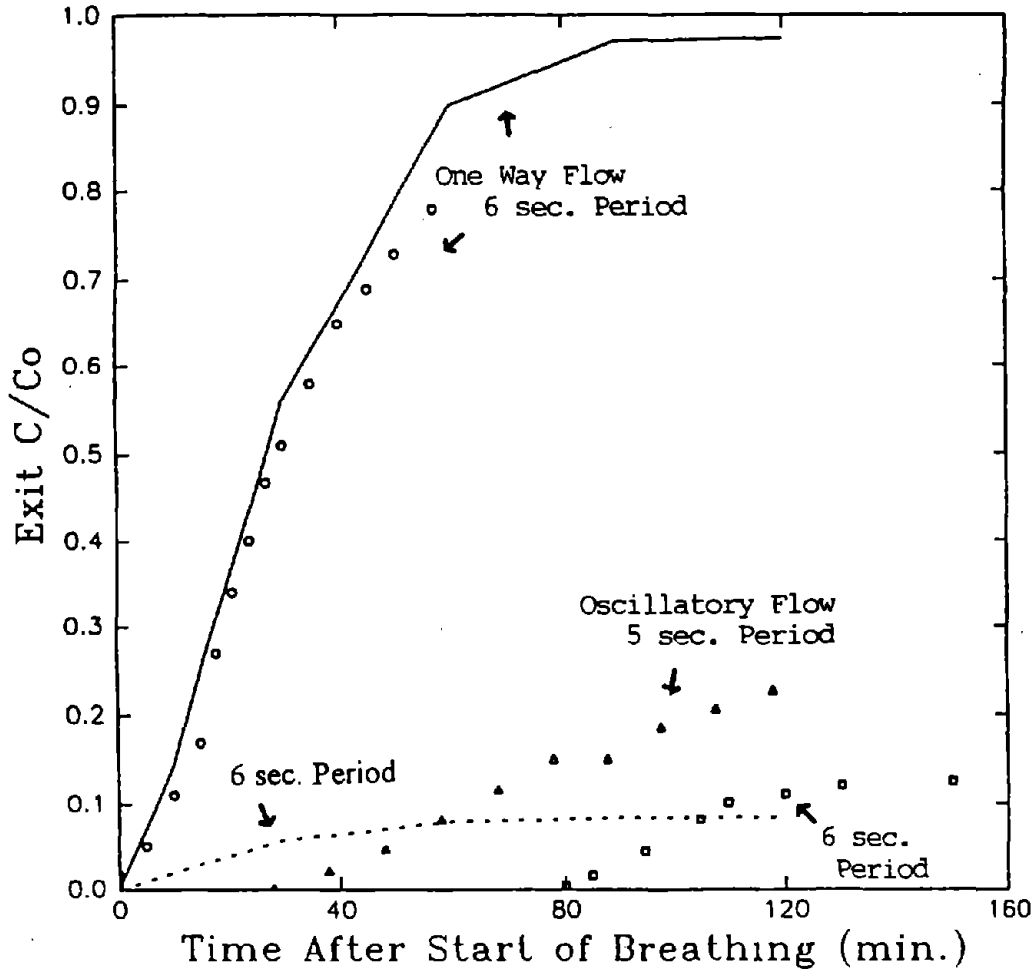


Figure 15. Comparison of Exit Flow Concentration Ratios for Oscillatory and One Way Flow. Silicone Rubber Test Module - $r_{mx} = .0254cm, l = 1.27cm$. Return Air Heated and Moistened to 33°C. Solid and Dotted Lines Show Calculated Results for 6 sec. Period. Symbols Show Measured Data.

