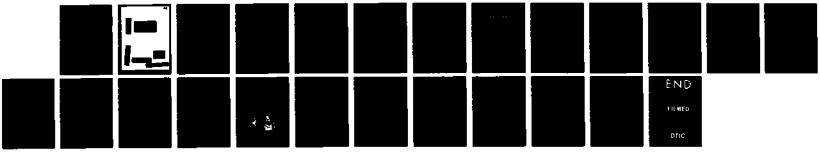
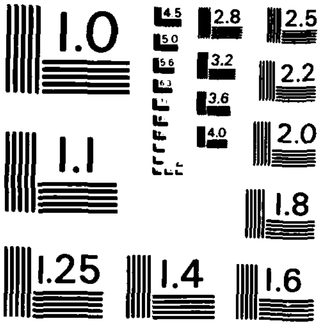
AD-A161 042 NEW MEMBRANE PRECONCENTRATION DEVICES FOR TRACE VAPOR 1/1
DETECTION SYSTEMS PHAS I(U) MEMBRANE TECHNOLOGY AND
RESEARCH INC MENLO PARK CA D ARMSTRONG ET AL. 1985
UNCLASSIFIED DAAK70-84-C-0078 F/G 7/1 NL





MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

(2)

NEW MEMBRANE PRECONCENTRATION DEVICES FOR TRACE VAPOR DETECTION SYSTEMS PHASE I

A Final Report to the
U.S. Army Belvoir Research
and Development Center

Contract No. DAAK70-84-C-0078

②

NEW MEMBRANE PRECONCENTRATION DEVICES FOR TRACE VAPOR DETECTION SYSTEMS PHASE I

A Final Report to the
U.S. Army Belvoir Research
and Development Center

Contract No. DAAK70-84-C-0078

MEMBRANE TECHNOLOGY AND RESEARCH, INC.
Menlo Park, California

Contributors to this report:

D. Armstrong
R.W. Baker
J. Mohr

I. SUMMARY

This report describes the results of a six month feasibility program to develop a membrane vapor concentration device. The device would be used to concentrate trace organic vapors in air prior to introduction to a detector instrument. In this way the complexity and cost of the instrumentation required to detect vapors emitted from hidden explosives could be reduced. The membrane concentrator involves the use of ultrathin silicone rubber composite membranes contained in a novel separation cell. Toluene was used as a model organic vapor for explosive vapors. The membrane system was able to obtain enrichments of as much as 50-fold with toluene at pressure ratios of less than 10 across the cell. However, the time to reach this degree of concentration was excessively long at 200 minutes. It appears that large amounts of the organic vapor are sorbed onto and into the membrane and adhesives of the membrane cell. It was not possible to overcome this sorption effect and reduce the system's lag time to a more useful value. Thus, this membrane concentration device does not appear to be a practical preconcentrator for a trace vapor detection instrument.

II. SIGNIFICANCE OF THE PROBLEM

A portable vapor detection system able to rapidly analyze organic vapors at very low concentration levels could be used to detect the presence of hidden explosives from the characteristic emitted vapors, such as trinitrotoluene (TNT). The system could also find an application as a chemical warfare alarm device, or in the monitoring of contraband drugs.

Current vapor detection systems are not suitable for widespread use. The principal problem is the complexity, and hence size, delicacy, and cost of detector instruments able to analyze organic vapors at the very low ppb concentration levels required. A possible solution to the problem is the use of a preconcentrator which would concentrate the organic vapor fraction in the air to the ppm level prior to introduction into the detector. The sensitivity required of the instrumentation could then drop significantly, and relatively robust (and small) GC or mass spectrometer instruments could be used.

Preconcentrators of various types are already used in several vapor analytical systems.(1-5) However, these systems are not amenable to routine field use. Also, the yield, i.e., the fraction of the vapor in the feed gas sample that is passed to the detector, is often low with current preconcentrators. This limits the instrument's sensitivity. The preconcentration system investigated in this program is based on a membrane separation system.

III BACKGROUND

A. Single Pass Membrane Concentrators

The preconcentration system we have investigated is based on a novel membrane separation cell. In this cell, a membrane separates a high pressure feed gas from a low pressure permeate gas. The membranes used are much more permeable to trace organic vapors than air, thus it is possible to produce a permeate enriched in trace vapors.

The degree of enrichment that can be obtained is dependent on two factors. First, the intrinsic selectivity of the membrane α, defined as

$$\alpha_{1/2} = \frac{\text{Permeability of component 1}}{\text{Permeability of component 2}} \tag{1}$$

and second, the ratio of the gas pressures across the membrane

$$\frac{P'}{P''} = \frac{\text{Pressure of feed gas}}{\text{Pressure of permeate gas}} \; . \tag{2}$$

As shown below, it is possible to find membranes with very high selectivities for explosive vapors, such as TNT, over air, and an αTNT/air of 1000 or more is possible. With these membranes, the pressure ratio P'/P" usually determines the enrichment obtained.

Consider the simple one stage membrane system shown in Figure 1. Let the feed pressure P' be 10 times the permeate pressure P". For the sake of calculation, let us assume that the selectivity of the membrane to organic vapor is extremely high, on the order of $\alpha \simeq 1000$ or more. In this case the organic will concentrate on the permeate side of the membrane until its vapor pressure is almost the same as the feed gas organic vapor pressure, i.e.,

$$P''C''_1 \longrightarrow P'C'_1$$

or

$$\frac{C''_1}{C'_1} \longrightarrow \frac{P'}{P''} \quad \text{as} \quad \alpha \longrightarrow \infty$$

It follows form the example given above that if P'/P" is 10, the maximum enrichment obtained is not more than 10 even with a very selective membrane. However, for an efficient trace vapor detector, we need enrichments of 100 or more. Such an enrichment

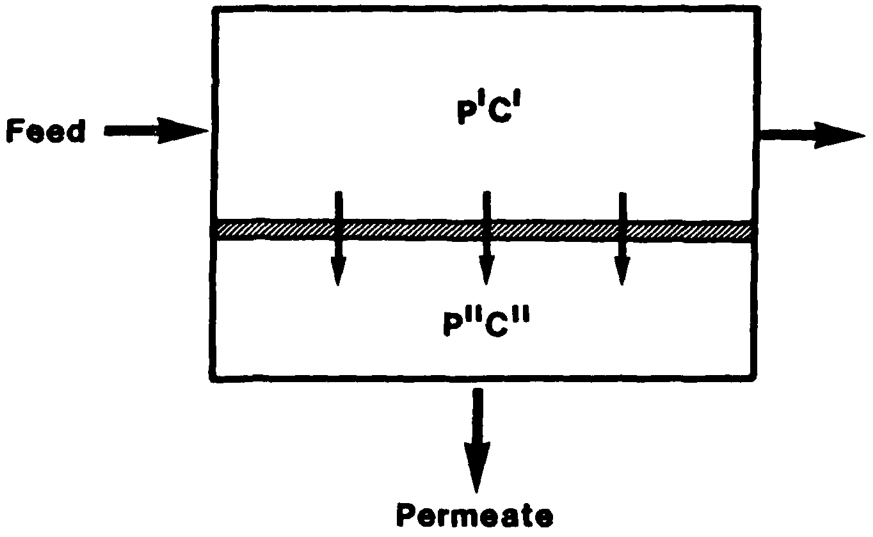


Figure 1. Single pass membrane system.

could be obtained by increasing the pressure rate P'/P", but there are practical limits. For example, the most efficient vacuum pumps cannot be used because the permeate gas is an organic vapor which is trapped in oil lubricated pumps. Therefore, diaphragm or bellows pumps must be used and it is difficult to generate pressure ratios of greater than 20 with these pumps. Single pass membrane preconcentrators cannot therefore generate the separation factors required for a vapor detector device.

B. Multiple Pass Membrane Systems

One method of increasing the separation factor would be to use a system in which several membrane stages are connected in series. However, this would require a separate interstage pump for each stage and would be too bulky for a practical unit. Our approach to this problem is to use a separation cell of the type shown in Figure 2. Two slightly different designs are shown. In both systems pressurized feed gas travels down the pressurized side of the membrane. The more permeable vapor permeates the membrane and thus the feed is depleted of vapor on the feed side of the membrane and is discarded. The vapor concentrate is circulated counter to the feed gas flow, pressurized, and recirculated. The two systems shown in Figure 2 differ in the point at which fresh feed air is mixed with the organic vapor permeate. However, in both systems organics concentrate at one end of the membrane cell and are removed as organic vapor concentrate. The advantage of these systems is that the average vapor molecule circulates through the membrane and compressor many times before finally leaving the system. On each pass through the membrane, a further separation is obtained until the final high separations characteristic of several passes through a membrane in series are obtained. Thus, high enrichments of organic vapor can be achieved even with modest P'/P" pressure ratios. The vapor concentrator we have developed is based on these two systems.

C. Membrane Materials

The ideal membrane for the separation systems shown in Figure 2 should have an extremely high selectivity, α, for trinitrotoluene and other organic vapors from air. The membrane should also have a high permeate flux so that the membrane cell can be made small and compact. In this program we have concentrated on silicone rubber composite membranes which meet these requirements.

The permeability of a number of gases through a silicone rubber membrane is shown in Figure 3. As shown, organic vapors such as toluene, hexane and carbon tetrachloride are 50 to 100

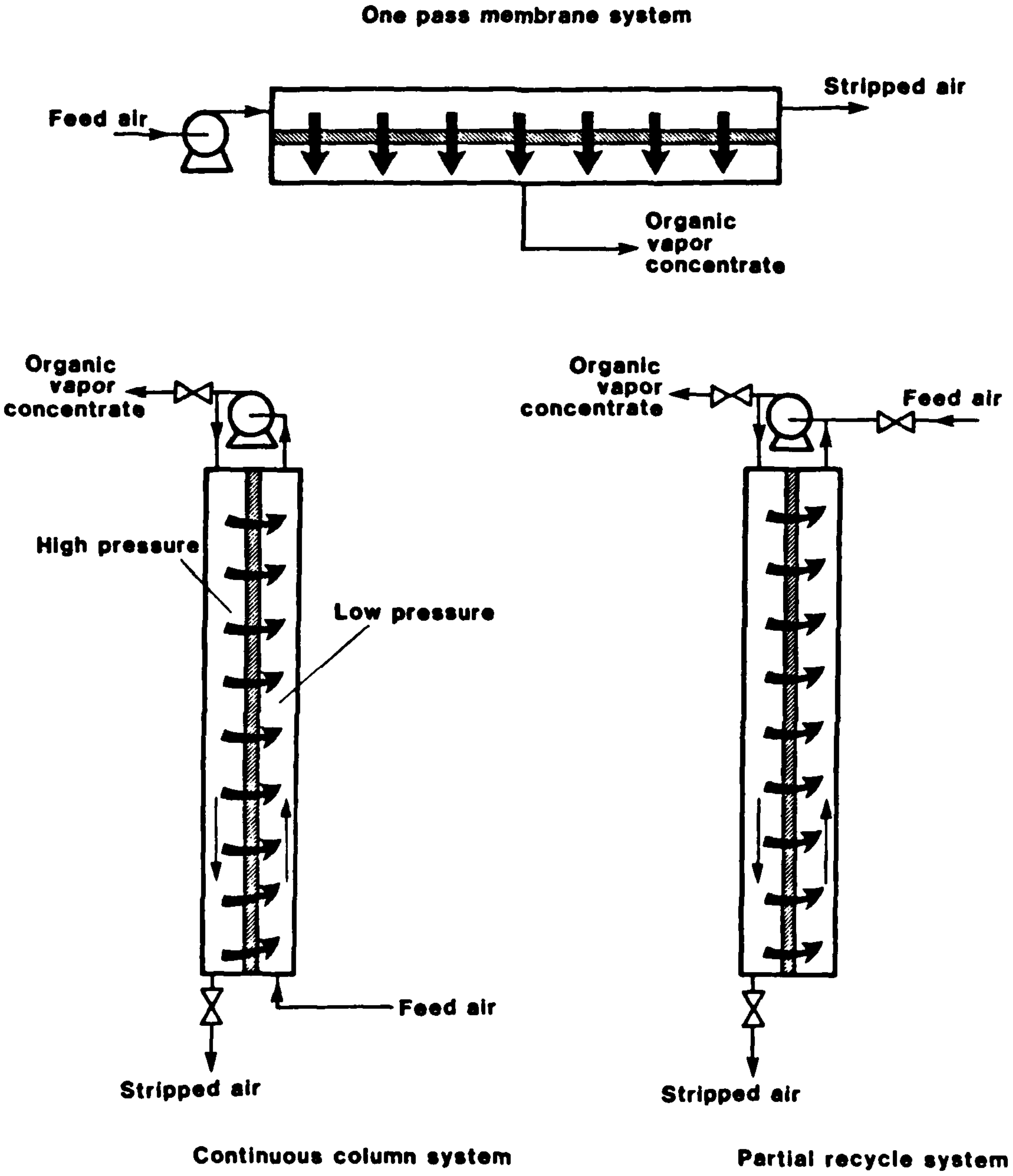


Figure 2. Types of membrane vapor concentration systems.

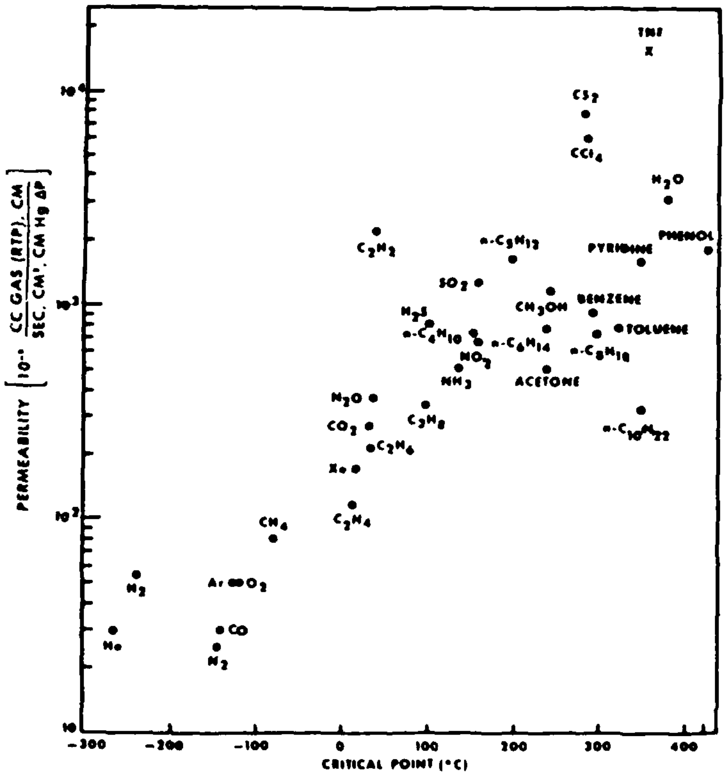


Figure 3. Vapor permeabilities in dimethyl-silicone membranes vs. critical point.(I)

times more permeable than oxygen and nitrogen, while TNT, the most volatile component of explosives, is 1-500 times more permeable than oxygen and nitrogen. Thus, silicone rubber membranes have the required selectivity.

High flux silicone rubber membranes have been prepared by making composite membranes of the form shown in Figure 4. These membranes have a three layer structure. A polyester web is first coated with a microporous ultrafiltration membrane to form a smooth, finely porous surface which can then be coated with an ultrathin layer of silicone rubber. The polyester web provides the mechanical strength for the composite while the silicone rubber layer performs the separation. Because the silicone rubber layer is very thin, very high fluxes can be achieved.

IV. PROGRESS UNDER THE PRESENT CONTRACT

A. Overall Approach

Our overall approach was to demonstrate the feasibility of this system by preparing small membrane modules incorporating silicone rubber composite membranes. Modules were made that could be used in a continuous column system and in a partial recycle system. A bench scale test loop was then constructed and the modules were evaluated first with O_2 and N_2 to test their integrity and then with dilute toluene feed solutions as a model for TNT-containing air.

B. Membrane Preparation

The composite membranes used in this program were made in a multistep process. First, a microporous support membrane was coated onto a fabric carrier web. In a second operation, the support membrane was coated with the permselective ultrathin silicone rubber layer. The casting machine used to prepare the support membrane is shown in Figure 5. The casting solution, consisting of a polymer solution dissolved in a water miscible solvent, is doctored onto a moving belt of the fabric web. The belt passes into a water bath which precipitates the polymer to form the membrane. The belt is then collected on a take-up roll, after which the membrane is washed overnight to remove any remaining solvent and dried to form the support membrane. Using this machinery, we have made support membrane from a number of polymers in our laboratory. These polymers include: polysulfone (Udel P3500®, Union Carbide, Danbury, CT), polyamide (Nomex®, DuPont, Wilmington, DE), polyetherether ketone (Victrex®, ICI Americas Inc., Wilmington, DE), and polyvinylidene fluoride (Kynar®, Pennwalt Corp., Philadelphia, PA). In this program polysulfone support membranes were used.

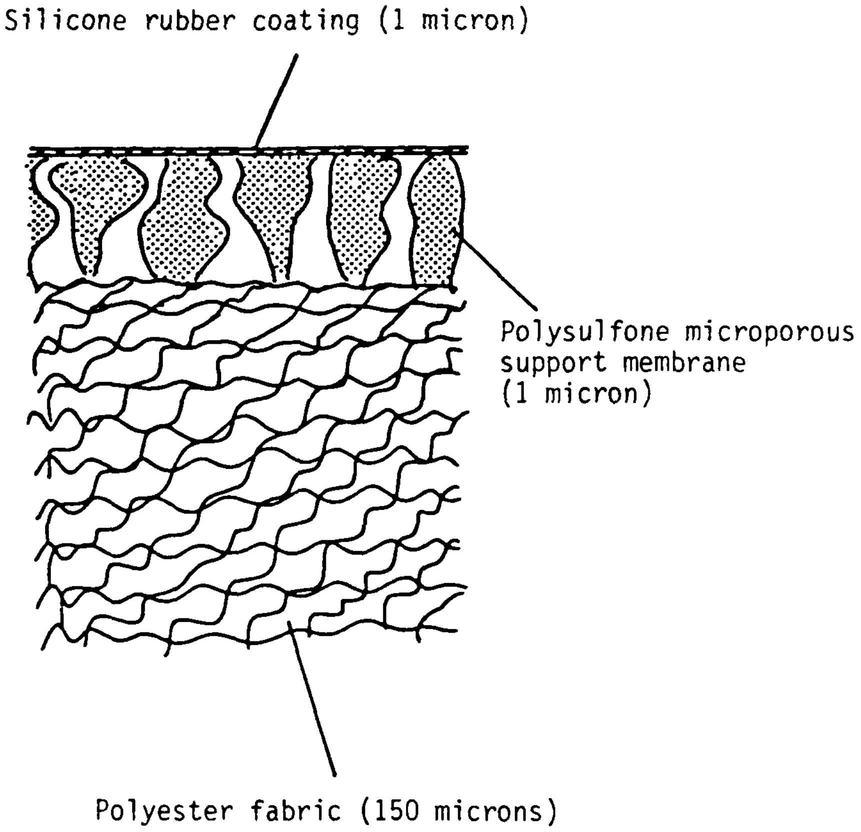


Figure 4. Structure of the three-layer composite membrane used.

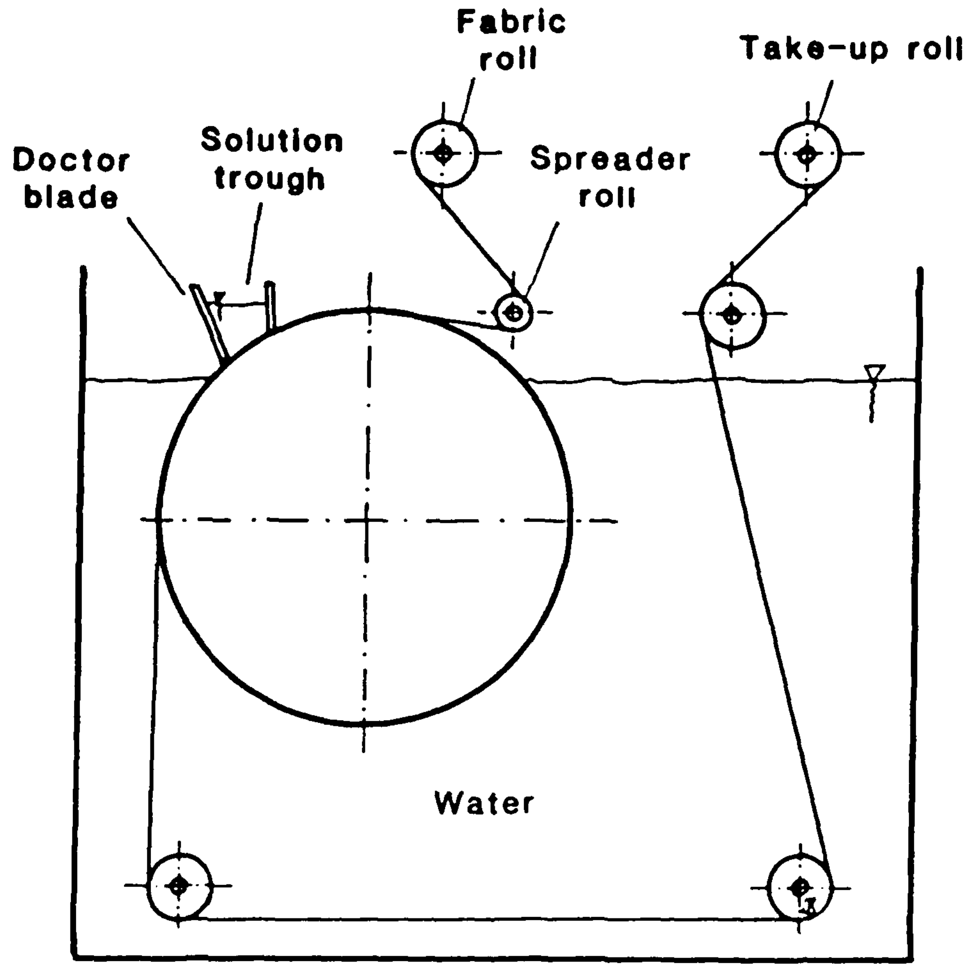


Figure 5. Schematic diagram of the membrane casting machine used to prepare the microporous membrane support.

The apparatus used to coat the silicone rubber layer is shown in Figure 6. The support film from a feed roll first passes through the coating station containing the coating solution and then through a drying oven before being wound up on a product roll. The simple dip coating tank shown contains a dilute solution of the polymer. This tank coats the traveling support film with a liquid layer 50-100 microns thick. After evaporation of the solvent, a polymer layer one to two microns thick remains.

The thickness of the polymer layer in these composite membranes is measured by comparing their nitrogen flux with values obtained with isotropic membranes of known thickness. The presence of membrane defects can also be detected by measuring the oxygen and nitrogen permeability ratio, α. Thick membranes of silicone rubber, for example, have a ratio of approximately 2.2, but even a small membrane defect will reduce this value. We consider a membrane to be defect-free if its O_2/N_2 permeability ratio is greater than 2.0. The apparatus used to obtain this permeability data is shown in Figure 7. We have found that the thickness and number of defects in a membrane (as measured by the O_2/N_2 permeability ratio) vary widely depending on the concentration and viscosity of the coating solution used and the nature of the microporous support film. The method of applying the coating solution is also important.

C. Module Preparation

The membrane modules used in this program were made of a modified spiral wound configuration. Both continuous and partial recycle modules were made. These modules are prepared on a winding table. As the first step the membrane is cut to size and folded around the polypropylene mesh feed spacer material and then folded around the central tube. The central tube is perforated with a number of holes and is divided into two halves by a central plug. The central tube is then placed in the jaws of a clutch and slowly wound up and simultaneously glued. Figure 8 shows the construction of the simpler partial recycle module. This figure also shows the flow of feed and product air across the membrane surface. The wound up and glued module is then potted in a PVC pipe as shown in Figure 9. The construction of a continuous column module is similar.

D. The Module Test System

The module test system is shown schematically in Figure 10. Nitrogen or compressed air feed gas and solvent are mixed and passed to a membrane module which separates the mixture into a stripped gas stream which is discharged and a concentrate stream containing the bulk of the solvent in the gas. The feed gas is at a pressure of 45-55 psia while the concentrate stream is maintained at a pressure of 5-10 psia by a diaphragm pump.

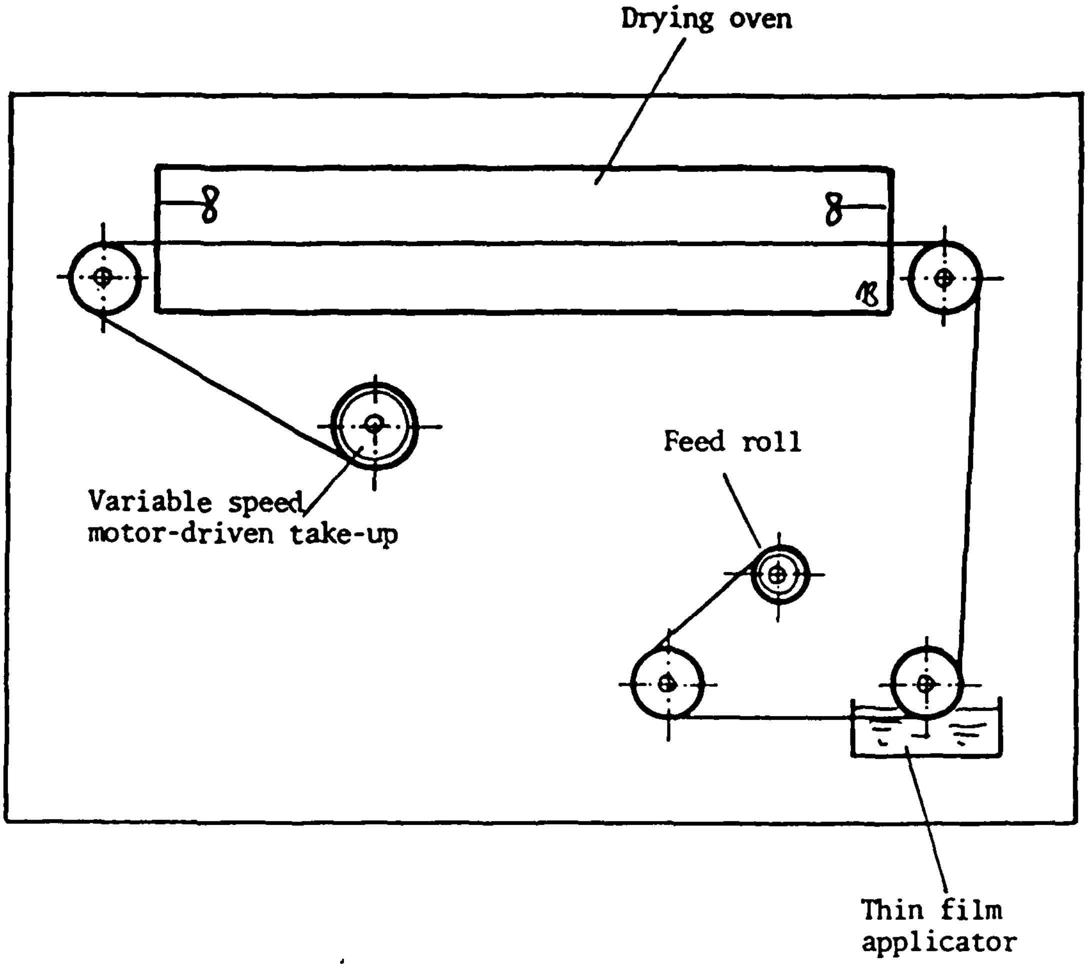


Figure 6. Schematic of thin film coating apparatus used to coat the microporous support film with a 0.5 to 2.0 micron thick silicone rubber layer.

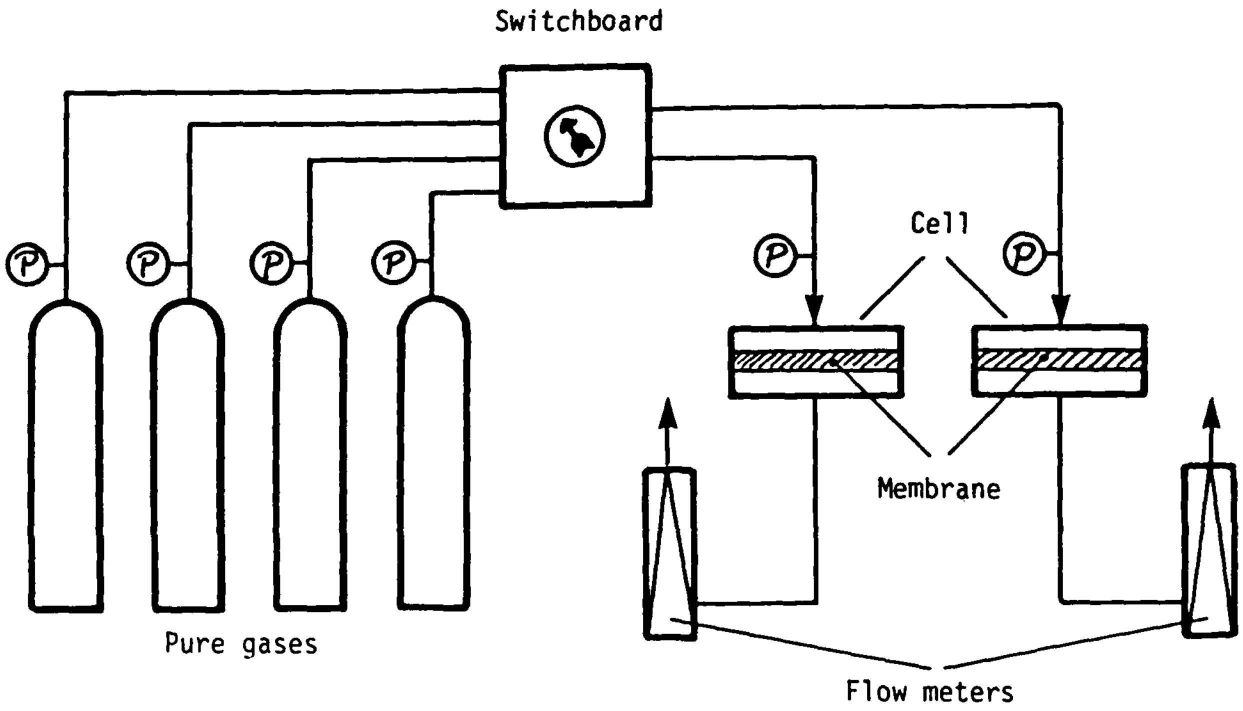


Figure 7. Gas permeability apparatus.

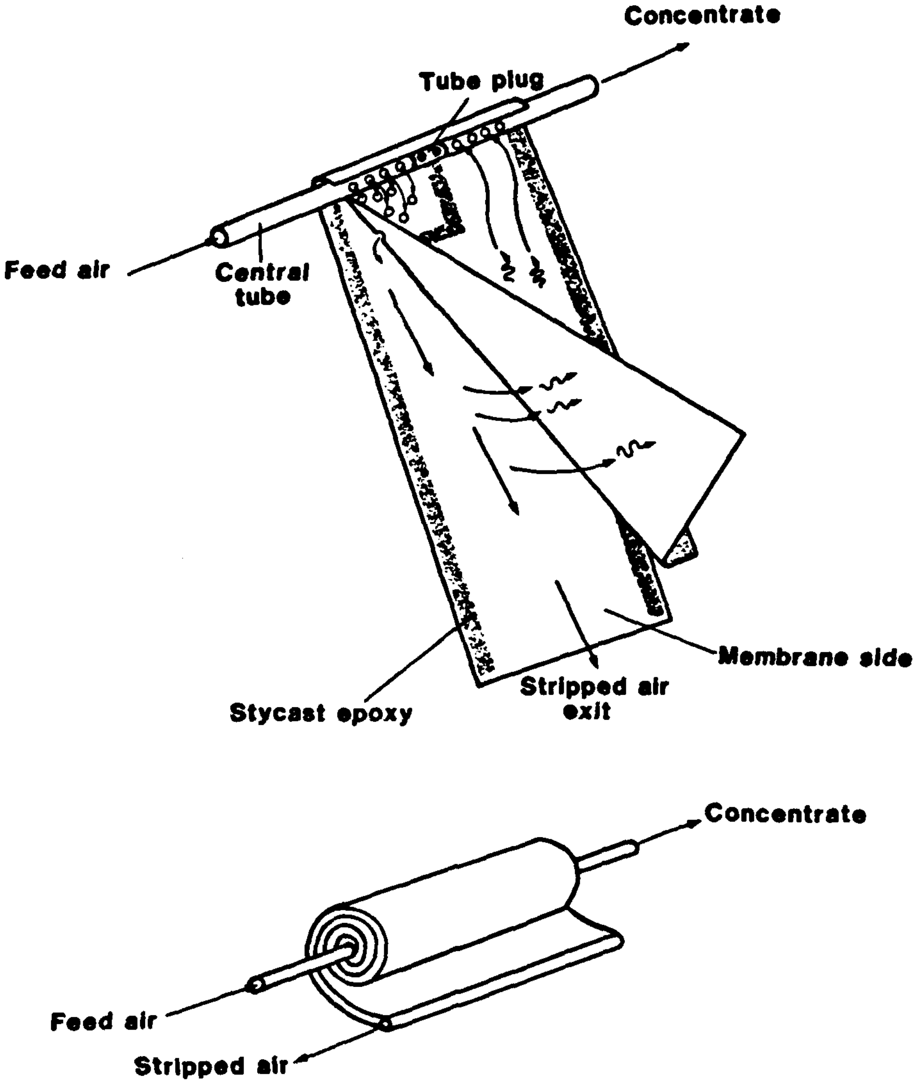


Figure 8. Schematic of glueing and winding operation used to prepare a partial recycle module.

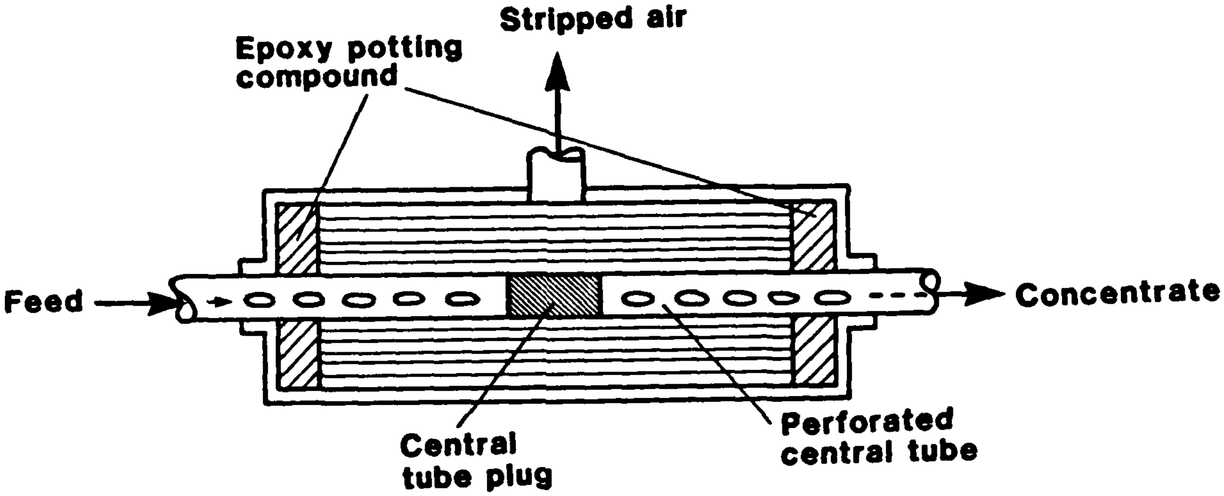


Figure 9. Schematic of partial recycle module.

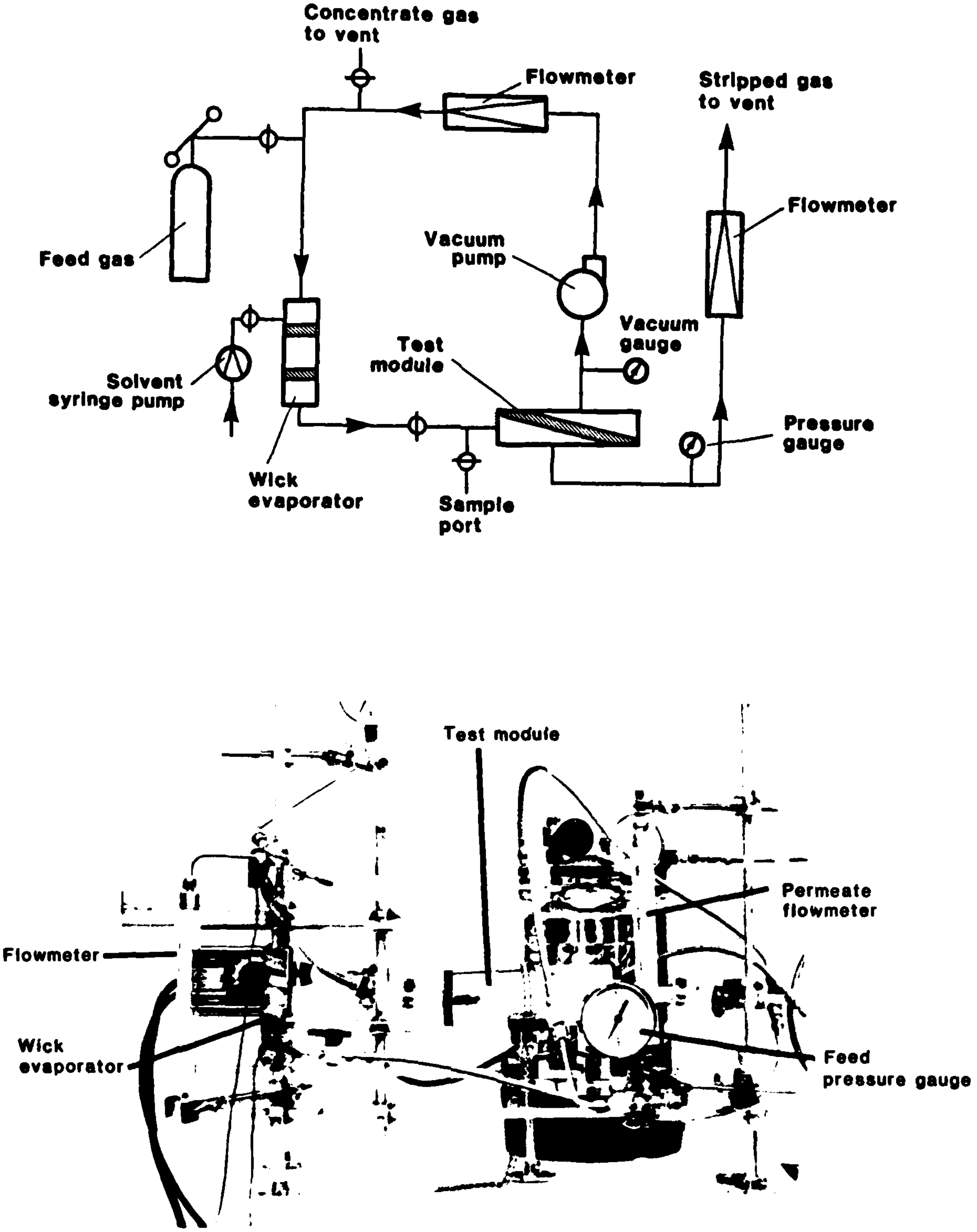


Figure 10. The module test system.

Thus, the P'/P" pressure ratio is approximately 5 to 10. The concentrate stream is mixed with the feed air stream and recycled continuously through the system.

E. Module Evaluation with Simple Gases

More than 60 modules were produced during the program. Many of these modules had membrane defects or seal leaks which were detected by measuring the module's ability to separate oxygen and nitrogen from air. A typical experiment illustrating the separation that can be obtained with a leak free module is shown in Figure 11. As this figure shows, when the product flow is a small fraction of the feed flow, the more permeable oxygen is significantly enriched in the product gas and the oxygen concentration reaches a maximum value of 62% compared to the feed air oxygen concentration of 21%. The CO_2 concentrate of the air also increased from a feed concentration of 0.028% to a permeate concentration of 0.31%. On the other hand, when the product flow is a large fraction of the feed flow, the oxygen content of the product gas approaches the concentration of the feed. However, the oxygen content of the strip gas becomes as low as 2-3%.

In another experiment the time required for the oxygen to reach its maximum enrichment at a product-to-flow ratio of almost zero was determined. These results are shown in Figure 12. As shown, it takes almost 15 minutes for the oxygen concentration to reach its maximum value of 62%. This time is only slightly longer than the system's dead volume of 2-3 liters would suggest.

F. Module Evaluations with Toluene

A typical early test of the system with toluene as a model organic vapor feed is shown in Figure 13. In this experiment, the feed concentration was maintained at approximately 0.1% and the toluene concentration in the strip and permeate streams was monitored. The toluene concentration in the strip gas was undeterminable, i.e, below 0.02% toluene. The concentration of toluene in the feed rose steadily until after 50 minutes it had reached 1.1% toluene. At this point there was evidence that the toluene was condensing in the loop and the experiment was stopped. These early experiments showed the system was capable of significantly enriching toluene, more than 10-fold in this case, but that the feed concentration of toluene would have to be reduced if the maximum degree of toluene enrichment was to be determined. Lowering the toluene feed concentrations would also more closely model the situation with very low TNT concentrations. The GC detector used in the early experiments was replaced with a more sensitive thermal conducting flame ionization detector and the experiments repeated with toluene feed concentrations of 0.013%. The results of these experiments are shown in Figure 14. As shown, the toluene concentrations in the product gas rose steadily until the toluene concentration in the product was 20 to 50 times the concentration

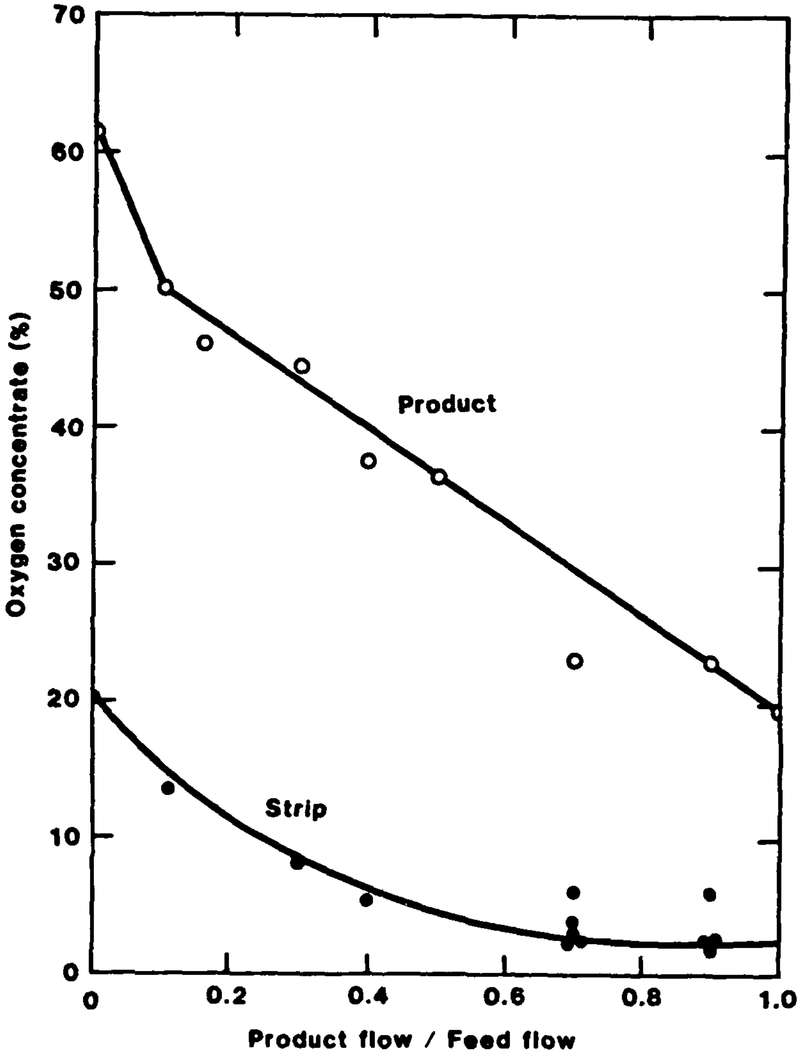


Figure 11. Separation of O_2 and N_2 in air using a partial recycle module. The experimental conditions were: Feed pressure, 50 psia; permeate pressure, 5 psia; feed flow, 0.5 liters/min; membrane area, 2.9 ft^2; membrane thickness, 1.5 microns.

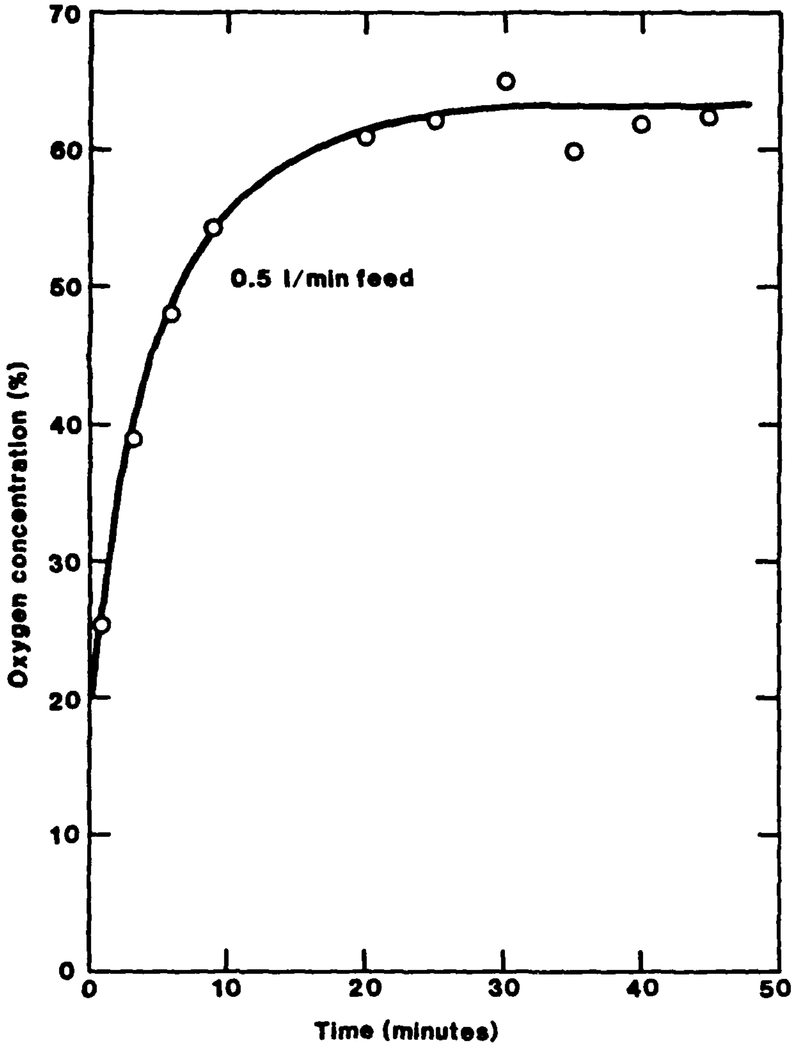


Figure 12. A plot of the time required to reach the steady state in an O_2 separation test. The experimental conditions were: Feed pressure, 50 psia; permeate pressure, 5 psia; feed flow, 0.5 liters/min; membrane area, 2.9 ft^2; membrane thickness, 1.5 microns.

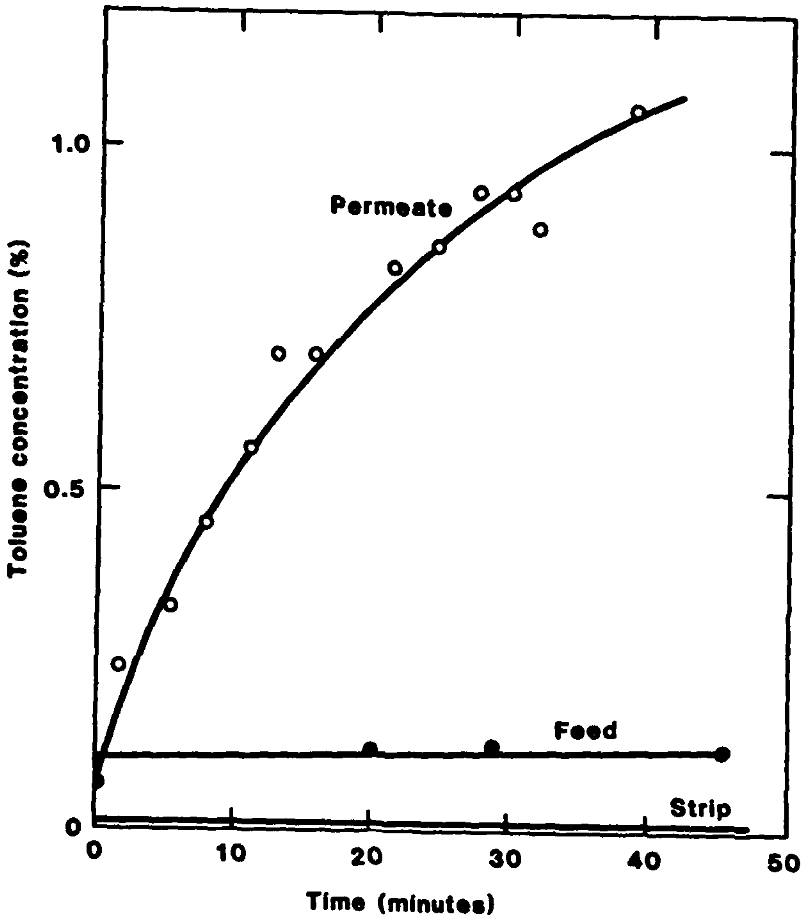


Figure 13. An early toluene enrichment experiment. The feed pressure was maintained at 45 psia and the permeate at 5 psia.

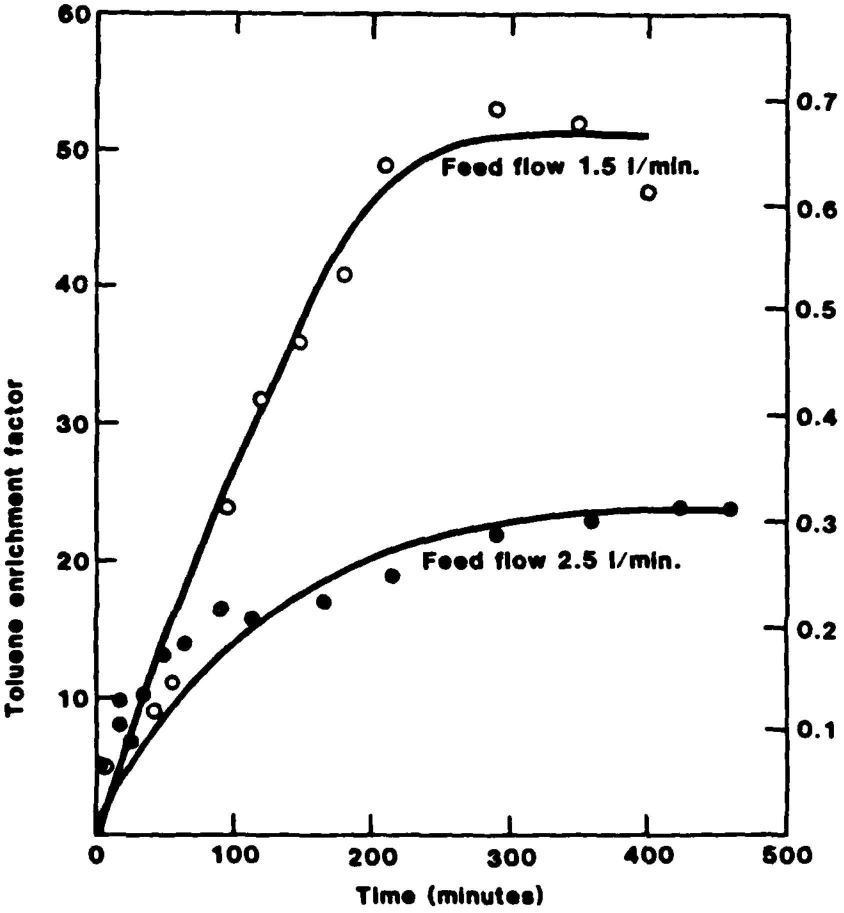


Figure 14. Toluene enrichment experiments with very dilute toluene feed streams of 0.013%. The feed pressure was 45 psia; the permeate pressure, 0.5 psia; the membrane area, 2.9 ft^2; the membrane thickness, 1.5 microns.

of the feed gas. However, it took almost 200 minutes to reach this concentration factor. This amount of time to reach the steady state is far too long for a practical detector system. Simply based on the dead volume of the system, the time to steady state should have been only 10 minutes or less and could have been reduced by reducing the dead volume of the pump, piping, and module. A 200 minute time lag, however, reflects absorption of toluene in the adhesive and membrane from which the system is made.

During the final weeks of the program modules were constructed using less absorbent adhesives and with reduced dead volumes, but we were not able to significantly reduce the time lag of the system.

IV. CONCLUSIONS

Membrane vapor concentration systems based on silicone rubber membranes and a modified spiral wound module design are able to concentrate organic vapors such as toluene more than 50-fold. However, it takes almost 200 minutes for the vapor concentration to build up to its maximum value. This long time lag appears to be due to absorption of the organic vapor onto and into the membrane and adhesive in the membrane module. There appears to be no easy way of overcoming this problem. As a result this type of membrane vapor concentration system does not seem suitable for use in a rapid response trace vapor detection system.

REFERENCES

1. G.E. Spangler, "Analysis of Two Membrane Inlet Systems on Two Potential Trace Vapor Detectors," *American Laboratory*, *7*, 36, (1975).

2. For example, the Elscint GC (Palisades Park) gas concentrator uses adsorption onto charcoal or aluminum cartridges, while the Universal Monitors Corporation's Olfax mass spectrograph uses a dual stage membrane unit. Similar equipment is sold by several other suppliers.

3. W.H. McFadden, *Techniques of Combined Gas Chromatography/Mass Spectrometry*, John Wiley, New York (1973).

4. F.W. Karasek, R.E. Clement, and J.A. Sweetman, "Reconcentration for Trace Organic Analysis," *Anal. Chem.* *53*, 1050A (1981).

5. T.A. Bellar and J.J. Lichtenberg, "The Determination of Volatile Organic Compounds at the g/l Level by Gas Chromatography," EPA Report EPA-670/4-74-009, November (1974).

END

FILMED

12-85

DTIC