

**INSTRUMENTATION FOR MEASUREMENT OF GAS PERMEABILITY
OF POLYMERIC MEMBRANES***

Billy T. Upchurch
NASA Langley Research Center
Hampton, VA 23681

George M. Wood
NASA Langley Research Center
Hampton, VA 23681

Kenneth G. Brown
Old Dominion University
Norfolk, VA 23529

Karen S. Burns
Old Dominion University
Norfolk, VA 23529

ABSTRACT

A mass spectrometric "Dynamic Delta" method for the measurement of gas permeability of polymeric membranes has been developed. The method is universally applicable for measurement of the permeability of any gas through polymeric membrane materials. The usual large sample size of more than 100 square centimeters required for other methods is not necessary for this new method which requires a size less than one square centimeter. The new method should fulfill requirements and find applicability for industrial materials such as food packaging, contact lenses and other commercial materials where gas permeability or permselectivity properties are important.

INTRODUCTION

The gas permeability of a polymeric material is an important physical property which helps determine whether or not a given material might be appropriate for a particular application. Some application examples are food packaging, beverage containers, gas separation processes and oxygen permeability in contact lens materials. The permeability depends upon two physical processes, the solubility of the gas in the material and the diffusivity (D) of the gas through the material. The solubility often follows Henry's Law behavior and can be represented by the Henry's Law constant k. If the thickness of the membrane (L) is taken into account then we can define the permeance or transmissibility by equation 1:

$$P = \frac{Dk}{L} \quad (1)$$

where P is the gas permeation rate through a known area and thickness of material per unit time.

Several analytical techniques have been applied to the problem of determining gas permeability. A few

*This research is a part of the Gas Permeable Polymeric Materials (GPPM) flight experiment, and is being carried out under the auspices of the Office of Commercial Programs, NASA Headquarters, Washington, DC. The GPPM experiment is manifested as part of the SPACEHAB payload on the STS-57 mission in April, 1993, and includes materials from both NASA and an Industrial Guest Investigator, Paragon Optical Co., Mesa, AZ.

are gas specific, such as polarography for oxygen determination¹, the application of platinum and silver electrodes for measurement of oxygen in living tissues¹, and the application of electron spin resonance (ESR) to oxygen permeation in polyethylene². Additional techniques involve the use of spectrophotometry but these involve the incorporation of photosensitive dyes into the materials^{3,4,5}. The American Society of Testing and Materials (ASTM) has adopted three standard test methods; a) a manometric technique, ASTM:D 1434-82⁶, b) a volumetric method, ASTM:D 1434-82⁶, and c) a coulometric method, ASTM:D 3985-81⁶. Each of these standard techniques requires large sample test areas (50 - 100 cm²) and is not capable of differentiating between gases when gas mixtures are being measured.

This paper describes a mass spectrometric technique that minimizes sample area and allows the determination of permeation rates for individual gases in gas mixtures. This technique, termed the "Dynamic Delta" method⁷, is a significant improvement upon standard mass spectrometric techniques. The technique is applicable for any gas and is easy to perform with good reproducibility. We shall demonstrate its appropriateness to be included as a standard industrial test for gas permeability.

METHOD

The "dynamic delta" measurement, is not specific for any particular pressure measuring device or mass spectrometer as long as the response is linear over the range of interest. The basic setup is illustrated in figure 1 with a standard X-Y plotter as the recording device. With this particular configuration we can simultaneously monitor the ion signal as a function of the inlet pressure. The ion signal I_A is proportional to the partial pressure P_A through an experimentally determined proportionality constant S_A . The magnitude of I_A is determined by the sum of the partial pressure of gaseous constituent A introduced into the ion source, the background pressure of A which may already exist in the ion source, and the contribution from an unresolved ion equivalent in mass to that of constituent A.

In general practice, the background signal is experimentally determined prior to introducing a sample into the mass spectrometer. This signal is then subtracted from the total signal prior to calculating the concentration. When the concentration of the sample is large with respect to the background, the quantitative analysis can be carried out with high accuracy. When analyzing at trace levels however, the signal from the sample may approximate that from the background and the accuracy is significantly reduced.

The effects of background on accuracy can be reduced if the measurements are carried out with several samples introduced into the ion source at incrementally increasing pressures and the concentration calculated from the differences in the resulting signals. Since the ion source background signal should not change, its effect will be reduced along with a reduced requirement for making highly accurate measurement of total pressure. Studies in the NASA Langley Instrument Research Division Mass Spectrometry Laboratory determined that the accuracy would increase with the number of difference calculations. If the ion source pressure were allowed to increase in a linear manner and the ion current from a single mass is simultaneously measured, this would be equivalent to obtaining an essentially infinite number of difference measurements and the concentration could be directly determined from a determination of the slope of the resulting line.

When the ion signal, representative of the gas species of interest, is provided as input to the Y axis of the recorder and the inlet pressure is provided as a signal to the X axis the resultant plot should be linear with any deviations from linearity indicating either experimental error or additional phenomena taking place elsewhere in the system. Typical experimental data, using oxygen as an illustration with argon as an internal reference gas are shown in figure 2. These data may be used to calculate the concentration of a particular species from the following relationship:

$$Vol \% = \frac{100 \cdot \tan\theta_1 \cdot \Omega_2 \cdot \mu_1 \cdot \alpha}{\tan\theta_2 \cdot \Omega_1 \cdot \mu_2} \quad (2)$$

where:

- $\tan\theta_1$ = the slope of the line for the analyte gas
- $\tan\theta_2$ = the slope of the line for the reference gas
- Ω_1 = the ion current amplifier resistance used for the reference gas
- Ω_2 = the ion current amplifier resistance used for the analyte gas
- μ_1 = the recorder attenuation used for the reference gas
- μ_2 = the recorder attenuation used for the analyte gas
- α = the relative gas sensitivity for the analyte and reference gases: identical gases $\alpha = 1$.

In the above expression everything but the angle measurements represents properties of the system and equation 2 may be rewritten as:

$$Vol \% = mol\% = 100 \cdot \frac{\tan\theta_1}{\tan\theta_2} \cdot K \quad (3)$$

where K is the experimentally determined proportionality constant for the analysis.

EXPERIMENTAL

Specimen holders, shown in figure 3, were designed to enable the study of both flat and curved surface specimens and were fabricated from brass. Samples were held tightly in place using an O-ring seal to prevent leakage around the polymer specimen. As shown in figure 4, the analysis system was designed to assure identical gas pressure and flow rates on both sides of the membrane. In this design the permeating analyte gas was allowed to flow by the upstream side of the membrane while the carrier gas, in this case argon, flowed by the membrane on the mass spectrometer side. Permeant gas then enters the argon gas stream and is carried to the capillary inlet of the mass spectrometer for analysis as discussed above.

All of the mass spectrometric measurements were made on a 180°, 12.7 cm radius magnetic sector mass spectrometer of the Dempster type. The instrument is equipped with a capillary inlet designed to permit continuous sampling from atmospheric pressure and to provide control of the pressure in the ion source. A representative sample of the gas is introduced directly into the ion source through a gold foil molecular leak and quartz tube. The entire assembly can be maintained at elevated temperature to prevent condensation of volatile gaseous constituents. The exit slit was adjusted to provide a flat top peak.

The gases used were argon, nitrogen, carbon dioxide with stated purities of 99.998% and research grade oxygen. The gravimetric primary standard calibration gas mixture was certified with the following concentrations: 0.4609% O₂; 0.5122% N₂; 0.8077% CO₂ and 98.23% Ar.

The standard reference material was purchased from the National Bureau of Standards (NBS). Fifteen sheets of a poly(ethyleneterephthalate) film were supplied. Three samples, 1.35 cm in diameter, were cut for the mass spectrometry measurements. Contact lens samples were provided by Paragon[®] Optical with a concave radius of 8.00 mm and a chord diameter of 10.00 mm. The center thickness was nominally 0.20 mm and was measured to ± 0.002 mm.

RESULTS AND DISCUSSION

This method is very amenable to computerization utilizing one channel of an A-D converter for the pressure signal and another channel for the ion signal. Computer programs have been written to process data of this type with highly precise results. Raw data is shown in table I to illustrate measurement precision obtained from duplicate runs on two samples of one contact lens material.

Table I: Raw data for oxygen from the Dynamic Delta method for contact lens specimen 5 at 35 °C.

Run	Sample 5a (L = 0.0186cm)	Sample 5b (L = 0.0192 cm)
Peak (ratio)	Slope or Slope Ratio	Slope or Slope Ratio
³⁶ Ar reference	0.7236 ± 0.0039	0.7257 ± 0.0202
³² O impurity	0.1377 ± 0.0099	0.1347 ± 0.0141
³² O/ ³⁶ Ar impurity	0.1903 ± 0.0137	0.1856 ± 0.0201
³⁶ Ar reference	0.7318 ± 0.0019	0.7321 ± 0.0083
³² O total	0.4677 ± 0.0052	0.4380 ± 0.0066
³² O/ ³⁶ Ar total	0.6391 ± 0.0073	0.5983 ± 0.0115
³² O/ ³⁶ Ar corrected	0.4488 ± 0.0155	0.4127 ± 0.0232

The results of the mass spectrometric analyses of some general polymer materials are presented in Table II. The measured value for the SRM 1470 represents the current detection limit of the system using this grade of Ar gas and the small sample size. This detection limit is due to the presence of oxygen in the argon carrier gas. This level of impurity was a problem in trying to determine the permeability of the standard reference material (SRM 1470). We determined the permeability at 23 °C to be $4.52 \pm 0.01 \times 10^{-12}$ mL O₂/cm s mm Hg, which corresponds to the level of oxygen in the argon gas, and is an order of magnitude greater than the NBS certified value of 2.67×10^{-13} mL O₂/cm s mm Hg. It should be noted that the SRM is a barrier material meant as a standard for the testing of barrier materials.

The SRM 1470 is a highly crystalline film, biaxially cold-drawn when it is made, and has a glass transition temperature T_g close to 90 °C or well above room temperature.⁸ These first two characteristics lead to constraints of the polymer chains to reorient.^{9,10} When a glassy polymer is below its glass transition, it is not in a state of true thermodynamic equilibrium, and the permeability and solubility coefficients are more dependent on gas pressure or concentration in polymers and on temperature.¹⁰ These types of materials generally exhibit dual-mode sorption behavior unless their "excess" free or void volume below T_g is small.¹⁰ Dual mode or type II isotherm can result when these glassy polymers absorb gases into pre-existing voids and then behaves as a true solution. With the exception of the silicone membrane, the other materials in Table II are known to have crystalline or semi-crystalline forms and a T_g well above room temperature. Subsequent literature review did not find oxygen permeability data on these materials for comparison. The oxygen permeability of the silicone membrane data is comparable to the product literature¹¹ and other data¹².

The gas permeabilities for the contact lens materials are summarized in tables III and IV for the temperatures 22 °C and 35 °C respectively. With the exception of the two materials of lowest permeability, 6 and 8, the permeabilities at 35 °C for oxygen, nitrogen, and carbon dioxide were significantly greater than permeation rates determined at room temperature.

Our measured carbon dioxide permeation rates are much greater than oxygen or nitrogen permeation rates which is consistent with trends reported in the literature. On average CO₂ permeabilities were five times greater than oxygen permeabilities and ten times greater than nitrogen permeabilities. Carbon dioxide permeation rates are least affected by increased temperature. The Nitrogen and Oxygen permeabilities for materials 2 and 3 are affected the most by increased temperature. At 35 °C these specimens have over a two fold increase in permeation rates. The remaining materials have nitrogen permeation rates only about 50% greater at 35 °C, while the oxygen permeation rates for the corresponding materials have a somewhat smaller increase. This can be explained by the fact that the Henry's law solubility constant of gases in liquids decreases with increasing temperature while the diffusion constant (D) increases with increasing temperature. Consequently, those materials affected least by temperature increases have lower temperature coefficients for a specific gas permeation rate.

TABLE II: Oxygen Permeability Coefficients for Selected Polymer Materials as Measured by Mass Spectrometry

Material	Dk ^a /10 ⁻¹²	T(°C)	Measured ^b P	Published ^b P
Polyamide (Kevlar)	2.41 ± 0.02	19	0.225	NA
Silicone	4410 ± 10	21	410	458 ^c 450-461 ^d
Polysulfone	43.8 ± 0.20	22	405	
Polyester 7d (SRM 1470)	4.52 ± 0.01	23	0.190	0.0113
7a	3.35 ± 0.80	23	0.141	0.0113
7b	3.37 ± 0.73	23	0.142	0.0113
7c	4.05 ± 0.73	23	0.170	0.0113
Polyimide ^e (ODPA/p-PDA) 2% offset	7.82 ± 0.20	22	0.724	N/A
ODPA-p-PDA	8.10 ± 0.20	22	0.750	N/A

a. The units are (cm²/s)(mL O₂/cm²·mmHg)

b. Correction to STP assumed pressure differences from one atmosphere or 760 mm Hg were negligible. The temperature was corrected using T₀ = 273 K and T_{measured(K)} by multiplying Dk by the factor T₀/T_{measured(K)}. The units are Barrer units mL O₂(STP)/cm²·s·cm Hg

c. From GE product literature after converting from room temperature of 25 °C to STP.

d. Rogers, C.E., In Polymer Permeability, Comyn, J., Ed.; Elsevier Applied Science Publishers, London, 1985; Chapter 2.

e. ODPA/p-PDA are acronyms for oxydiphthalic anhydride/ p-phenylenediamine.

TABLE III: Gas Permeability Coefficients^a for Contact Lens Specimens at 22 °C

Material	Oxygen	Nitrogen	Carbon Dioxide
1	15.4 ± 1.4	9.1 ± 1.6	89 ± 4
2	29.7 ± 1.8	9.2 ± 3.3	265 ± 4
3	43.5 ± 1.3	14.4 ± 1.9	357 ± 11
4	62.5 ± 1.8	34.2 ± 1.7	488 ± 13
5	36.5 ± 0.9	20.4 ± 0.9	227 ± 7
6	7.8 ± 0.8	10.2 ± 1.1	13.5 ± 5.0
8	10.4 ± 1.2	10.1 ± 1.1	5.2 ± 1.0
9	64.1 ± 7.1	27.3 ± 2.1	390 ± 9

TABLE IV: Gas Permeability Coefficients^a for Contact Lens Specimens at 35 °C

Material	Oxygen	Nitrogen	Carbon Dioxide
1	29.7 ± 3.6	13.2 ± 3.1	126 ± 5
2	70.2 ± 2.4	32.4 ± 2.4	297 ± 6
3	78.6 ± 2.8	34.4 ± 4.0	408 ± 8
4	99 ± 1	50.7 ± 4.0	555 ± 3
5	46.0 ± 1.5	27.2 ± 0.9	253 ± 7
6	10.7 ± 0.8	23.7 ± 2.4	18.2 ± 2.9
8	6.0 ± 2.1	11.4 ± 1.6	5.6 ± 1.3
9	90 ± 3.5	44.1 ± 1.6	435 ± 9

a. The units are $(\text{cm}^2/\text{s}) \times (\text{mL O}_2/\text{cm}^3 \cdot \text{mmHg}) \times 10^{-11}$

CONCLUSIONS

We believe that the method reported herein is the most accurate method for determining true or intrinsic gaseous permeabilities of any polymeric system. The "Dynamic Delta" method offers significant advantages over standard mass spectrometric techniques including, but not limited to, speed of measurement. By the design of the test cell that we have employed the total pressure gradient is eliminated. The technique permits the use of a very small sample size, 0.5 cm², is selective for specific gases or isotopes, and is sensitivity limited only by the impurity of the carrier gas and the sealing ability of the gasket material. We have been able to demonstrate a leak-free system by using a metal blank. It was determined that flat Teflon gaskets on both

sides of the flat membrane specimens sealed better than the Buna-N or Viton materials. The Buna-N O-ring, however, has the better sealing ability for the contact lens samples.

The ASTM methods have traditionally been done with large sample sizes in order to provide test areas of 50 - 100 cm². Such large sizes meant that the sample had to be placed upon a support. As a result the gas of interest had to permeate through both the sample and the support. In the "Dynamic Delta" method described in this paper the sample size is less than one square centimeter eliminating the need for the support. The permeability of the material can be measured directly. The new method should fulfill requirements and find applicability for industrial materials such as food packaging, contact lenses and other commercial materials where gas permeability or permselectivity properties are important.

REFERENCES

1. Clark, L. C., in Polarographic Oxygen Sensors, ed. Fatt, I, CRC Press, Cleveland, Ohio 1976.
2. Hori, Y, Shimada, S., and Kashiwabara, H., *ESR Studies on Oxidation Processes in Irradiated Polyethylene: I. Diffusion of Oxygen into Amorphous Parts at Low Temperatures*, Polymer Vol. 18, 151-154 (1977).
3. Shaw, G., *Quenching by Oxygen Diffusion of Phosphorescence Emission of Aromatic Molecules in Polymethylmethacrylate*, Trans. Faraday Soc., Vol. 63, 2181-2189, (1967).
4. Petrak, K., *Permeability of Oxygen Through Polymers. I. A Novel Spectrophotocatalytic Method*, J. of Appl. Polym. Sci., Vol. 23, 2365-2371, (1979).
5. Rooney, M. L., and Holland, R. V., *Measuring Oxygen Permeability of Polymer Films by a New Singlet Oxygen Technique*, Angew. Makromol. Chem., Vol. 88, 209-221, (1980).
6. Annual Book of ASTM Standards, 15.09, ASTM: Philadelphia, 1992.
7. Hughes, D. B. and Nowlin, T. D., *Trace Gas Analysis*, presented at the 19th Annual Conference on Mass Spectrometry and Allied Topics, Atlanta, Georgia, 1971.
8. *Standard Reference Materials: SRM 1470; Polyester Film for Oxygen Gas Transmission Measurements*, NBS Spec. Publ., (U.S.) No. 260-58 June, 1979.
9. Stern, S. A., and Trohalaki, S., in Barrier Polymers and Structures, Koros, W. J., ed., American Chemical Society Symposium Series No. 423, Washington, D. C., Chapter 2, (1990).
10. Weinkauff, D. H., and Paul, D. R., in Barrier Polymers and Structures, Koros, W. J., ed., American Chemical Society Symposium Series No. 423, Washington, D. C., Chapter 3, (1990).
11. General Electric Corporation Product Literature, *Permselective Membranes*, Medical Development Operation, Chemical and Medical Division, Membrane Products, Schenectady, N. Y.
12. Rogers, C. E., in Polymer Permeability, Comyn, J. ed., Elsevier Applied Science, London, chapter 2, (1985).

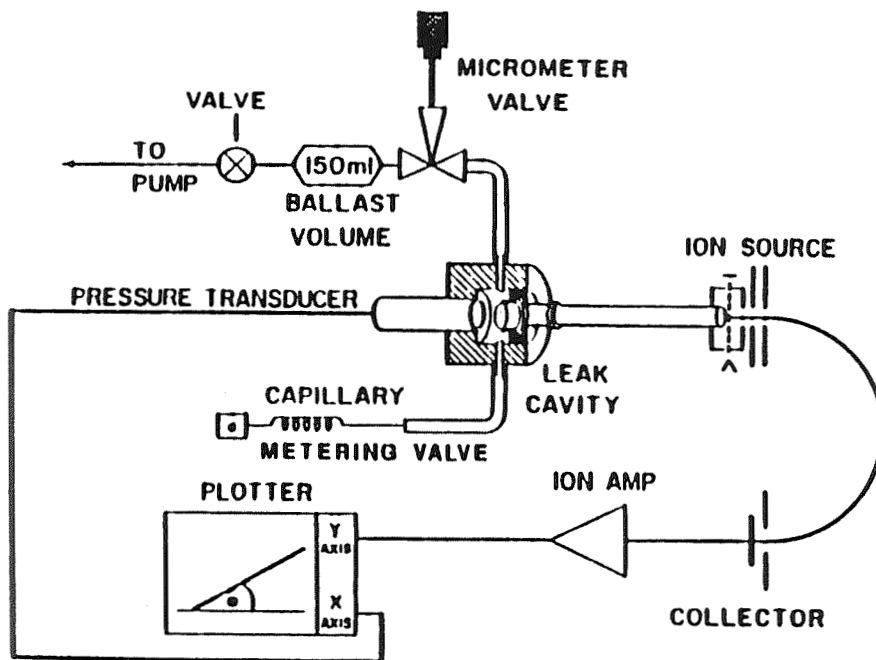


Figure 1. Schematic diagram of mass spectrometer analysis system.

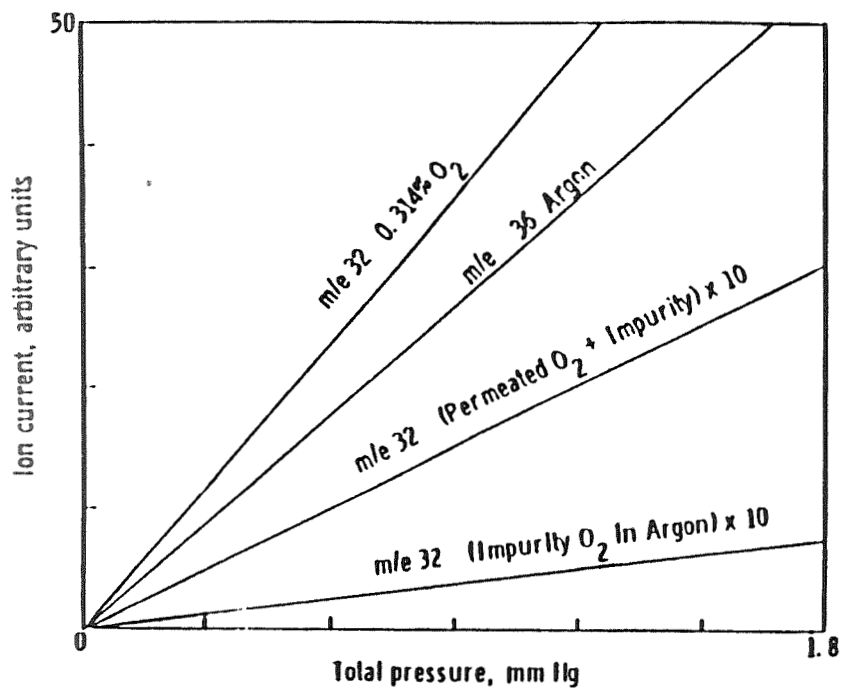


Figure 2. Typical "Dynamic Delta" for oxygen permeation system.

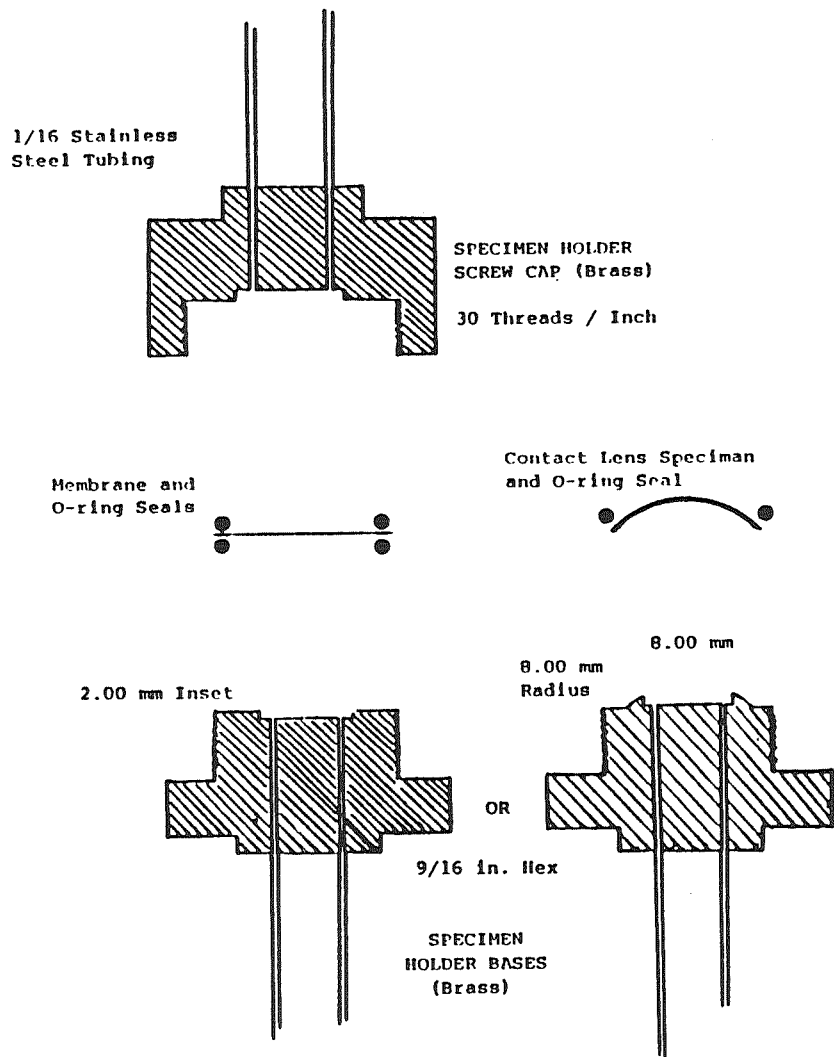


Figure 3. Mass spectrometer sample holder accommodating flat Specimens and contact lens specimens.

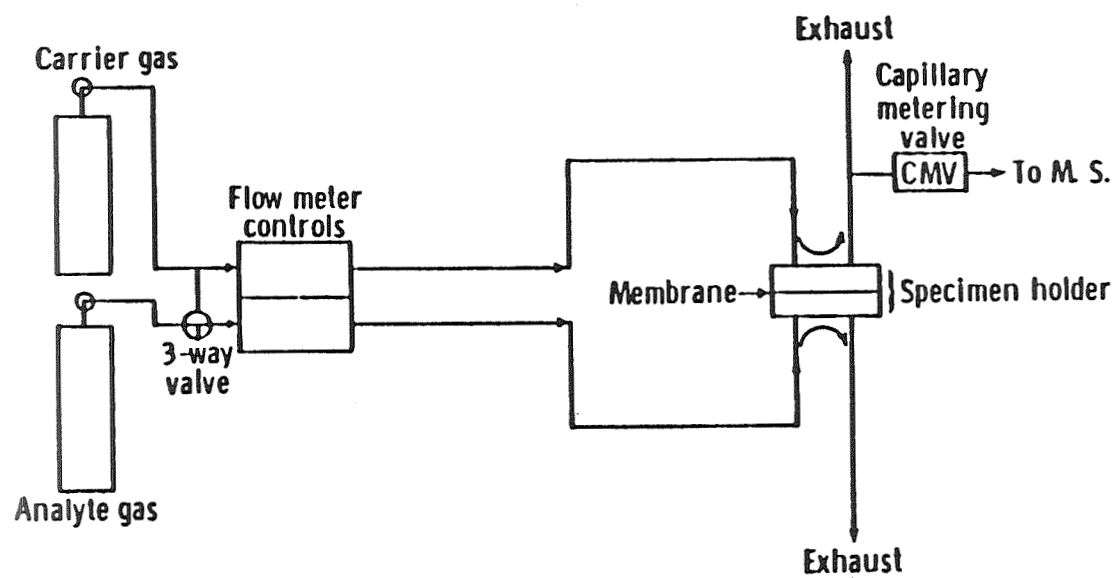


Figure 4. Gas flow schematic for mass spectrometric permeation measurement.