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LUCAS HEIGHTS

# IMPERMEABLE GRAPHITE AS A FUEL CAN

# PART 2 – APPARATUS FOR THE MEASUREMENT OF PERMEABILITY

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ABSTRACT

An apparatus is described which is capable of measuring permeabilities of porous media down to $4 \times 10^{-11}$ cm$^2$ sec$^{-1}$ with a maximum error of ten per cent. The method, which uses a radioactive tracer technique, eliminates the errors due to gas leakage which are inherent in conventional apparatus for permeability measurement.

## CONTENTS

## 1. INTRODUCTION

To determine the permeability of relatively impermeable materials, it is necessary to measure very small gas flow rates. The methods used for measuring the gas flow rate by observing the rate of pressure rise in a vacuum system (Schwertz, 1949; O'Neill and others, 1959) suffer from the disadvantage that errors due to gas leaks in the system are difficult to estimate. This report describes an apparatus using a tracer technique for flow measurement, in which these errors are eliminated. The apparatus was developed for use in an investigation of methods of producing low permeability graphites.

## 2. THEORY

Carman (1956) gave the following correlation for the flow of gases through porous media:

$$K = \frac{q_m P_m L}{\Delta P A} = \frac{B_o}{\mu} P_m + \frac{4}{3} K_o \sqrt{\frac{8RT}{\Pi M}}$$

The values of the viscous flow permeability coefficient $B_o$ and the slip flow permeability coefficient $K_o$ may be determined by measuring the flow rate of a gas through the material over a range of mean pressures and then plotting K versus mean pressure $p_m$. $B_o$ is derived from the slope of the line and $K_o$ from the intercept on the K axis.

## 3. PRINCIPLE OF THE APPARATUS

The disadvantage of the conventional pressure rise method is that any air-leaks into the vacuum system are recorded as additional flow through the specimen. Therefore it is necessary to determine the "natural leak rate" of the system and to correct the flow measurements accordingly.

In the case of measurements on consolidated porous media, an additional source of error is gas-leakage from the upstream to the downstream side of the specimen through the seal used to mount the specimen in the apparatus. It is usual to test for such a leak by measuring the flow rate with an impermeable specimen mounted in the apparatus. It is assumed that an equally effective seal is obtained when the porous specimen is mounted but no positive test of this assumption is possible.

To overcome these disadvantages a tracer method was developed. This involves supplying radio-isotope labelled gas to the outside surface of a tubular graphite specimen at pressure, while the inside of the specimen is connected to a suitable evacuated radiation detector (Figures 1 and 2). With this system a leak of labelled gas from the pressure side to atmosphere through the seal is of no consequence. At the low pressure seal there is a pressure differential inwards and a concentration gradient of labelled gas outwards. The concentration gradient is quite small and unlikely to cause any diffusion of the labelled gas through the seal to the atmosphere. Any leak of air into the system, past the low pressure seal is not indicated by the radiation detector and only if its presence interfered with the performance of the radiation detector would it lead to incorrect measurement of the gas flow through the specimen.

W. R. Ellis of the A.A.E.C. Isotopes Section recommended the use of either Kr85 or C14-or tritium-labelled methane as the tracer gas. Since Hutcheon et al. (1958) had reported anomalous behaviour of methane in their study of gas flow through graphite, the use of krypton would have been

preferable. However the cost of inactive krypton which was required as a diluent was prohibitive and it was necessary to use methane instead. Counting techniques for both C14–and tritium–labelled methane were developed by Ellis and Fisher (1961).

## 4. APPARATUS

The general arrangement of the apparatus and the design of the specimen holder are shown in Figures 1 and 2 respectively.

The cylinder X delivered labelled methane to the pressure side of the five specimen holders at a selected pressure between 0 and 100 p.s.i.g. Gas passing through the specimens could be directed to either the vacuum manifold C or the counter F.

Gas collected in the counter was diluted to the optimum counting pressure with inactive methane admitted through G. A mercury bubbler safety valve in the inactive methane supply line protected the glass apparatus from excessive pressures. Manometer J was used to measure the pressure in the counting tube. The counter was a type GA.10M supplied by 20th Century Electronics Limited. It was shielded from background radiation by a 1¼ inch thick lead castle. A nichrome strip heating element and a chromel–alumel thermocouple were provided to facilitate outgassing of the counter.

The electronic equipment consisted of an A.E.R.E. cathode follower and pulse amplifier, type 1430A, feeding into an A.A.E.C. Scaler, type 2. The E.H.T. supply to the counter was from an Isotopes Development Limited E.H.T. unit, type 532/B. Continuous purging of the cathode follower and the electrical connections to the counter with dry nitrogen was found to be necessary to eliminate spurious counts resulting from stray electrical discharges.

The calibration flask K, of known volume, was used in conjunction with the manometer J to determine the volume of the counter and associated tubing. It also served as a reservoir for active methane during the determination of the concentration of radio–isotope in the labelled gas.

## 5. METHOD

### 5.1 Determination of Optimum Counting Conditions

Preliminary tests revealed that the characteristics of the counting equipment differed from those of Ellis and Fisher's equipment so it was necessary to determine the optimum counting conditions for the present apparatus.

The counter was first outgassed at 300°C for three hours at a pressure of 0.1 $\mu$ Hg. After the counter had cooled to room temperature, a small amount of tritium–labelled methane was admitted and the pressure was adjusted to 10 cm with inactive methane. The response of the counter to variations in the E.H.T. voltage was observed at various settings of the amplifier and scaler controls, and those giving the most stable count rate were selected for future operation.

The effect of variation in counting pressure on the count rate was then determined by observing the count rate for a given sample of active gas at pressures from 7 cm to 15 cm Hg.

Finally, the effects of small concentrations of air in the counter were determined.

5.2 Standardization of Labelled Methane

The sensitivity required in the permeability measurements determined the specific activity of the labelled methane fed to the specimen carriers. In most of the measurements made to date, a specific activity of 0.2 microcuries per free $cm^3$ (i.e. at atmospheric pressure) was used. This level of activity was obtained when the 2 litre active methane cylinder was charged with 4.5 millicuries of active methane and pressurised to 150 p.s.i.g. with inactive methane.

It was unnecessary to measure the specific activity as such, it being sufficient, each time the cylinder was freshly charged, to determine the count rate versus volume relationship which could be used directly in the flow measurements.

Standardization was done as follows:-

The whole apparatus was evacuated and active methane was admitted to the counter and calibration flask to a pressure of about 20 cm. Inactive methane was then admitted to a total pressure of about 60 cm and after allowing time for the gases to mix the pressure was pumped down to 20 cm. The dilution with inactive methane, followed by partial evacuation, was repeated, all pressures being measured accurately with a cathetometer.

The gas in the calibration flask was then isolated, the counter was outgassed, and a background count was taken with 10 cm pressure of inactive methane in the counter. The counter was evacuated again and the diluted active methane in the calibration flask was admitted into it. The pressure in the system was recorded, then adjusted, if necessary, to 10 cm by the addition of inactive methane, and the count rate observed.

The quantity of active gas in the counter was reduced in steps by further dilution with inactive methane followed by isolation of part of the gas in the calibration flask and subsequent expansion of this gas into the counter. The count rate was determined at each level. Background counts were taken prior to each active gas count. The volume of labelled gas in the counter at each dilution was calculated from the pressure measurements and plotted against the corresponding net count rate.

5.3 Permeability Measurement

The permeabilities of up to five specimens could be measured simultaneously in the apparatus. The specimens were mounted in the specimen holders and were outgassed to less than 0.1$\mu$ Hg. Active methane was admitted to the upstream sides of the specimens at a selected pressure while the downstream sides of the specimens were exhausted to the vacuum pumps A. The flow from each specimen was diverted in turn to the evacuated counter for a known time and the gas collected from each specimen was diluted to 10 cm pressure and counted. The flow rates were then readily calculated.

This cycle of measurements was repeated at suitable time intervals until equilibrium conditions were reached. All specimens were then outgassed again and the flow measurements were repeated at other upstream pressures. The permeability coefficients were determined in the usual manner from the equilibrium flow rates.

## 6. TYPICAL RESULTS

### 6.1 Determination of Optimum Counting Conditions

The response of the counter to variations in the E.H.T. voltage is shown in Figures 3, 4, and 5. Inspection of the curves shows that the most stable operation was obtained between 1,960 and 2,160 volts at 6 db attenuation with both differential and integral time constants at 0.8 microseconds. The variation in count rate with E.H.T. voltage under these conditions was 4 per cent.per hundred volts. Since the E.H.T. supply could easily be kept within ±20 volts of a set point, the maximum error resulting from voltage variation during operation would be ±0.8 per cent. The plateau is therefore satisfactory for the present application, although much lower plateau slopes are normally demanded for proportional counting.

The effect of counter pressure is shown in Figure 6. There was a negligible variation in count rate over the pressure range 9 cm to 11 cm.

On the basis of the above results the following operating conditions were selected:-

| | |
|---|---|
| Pressure | 10 cm Hg |
| E.H.T. Voltage | 2060 volts |
| Differential Time Constant | 0.8 $\mu$ sec |
| Integration Time Constant | 0.8 $\mu$ sec |
| Attenuation | 6 db |
| Discriminator | 5 volts |

The effect of the presence of air in the counter on the count rate is shown in Figure 7. At the normal operating voltage 10 per cent. of air caused a drop in the count rate of 3 per cent. and an additional 18 per cent. of air reduced the count rate by a further 4.8 per cent. Under normal operating conditions the amount of air entering the counter never exceeded about 2 per cent. and hence the maximum error expected from this source would be 0.6 per cent. assuming that the drop in count rate caused by air contamination is linear up to 10 per cent. air.

### 6.2 Standardization of Labelled Methane

The results of a typical standardization of the tritium-labelled methane supply are plotted in Figure 8. An excellent linear correlation with zero intercept was obtained, indicating that the extrapolation to small volumes could be used confidently.

### 6.3 Permeability Determination

The results of permeability measurements on a sample of furfuryl alcohol impregnated graphite are presented in Table 1. These results, together with results collected from repeat determinations are plotted in Figure 9. The results are well correlated by the Carman equation with the following coefficients:-

$$B_o = (1.18 \pm 0.02) \times 10^{-15} \text{ cm}^2$$

$$K_o = (1.32 \pm 0.05) \times 10^{-10} \text{ cm}$$

(5 per cent. limits)

## 7. DISCUSSION OF THE METHOD

### 7.1 Accuracy

The results above reveal that, at the confidence level chosen, the maximum random error in K to be expected is ±4 per cent. In addition there is one major source of systematic error as follows:

Since both C14- and tritium-labelled methanes have higher molecular weights than inactive methane, low results could be expected as a result of atmolysis with specimens in which a large proportion of the gas flow occurred by diffusion. The maximum error due to this effect would be 5.5 per cent. in the case of specimens in which only diffusional flow occurred. When part of the flow is viscous the error due to molecular separation would be less.

In the worst case, when the random error is in the same direction as the systematic error, the maximum error would be −9.5 per cent.

### 7.2 Sensitivity

The sensitivity which could be achieved with the apparatus is determined by the geometry of the specimen, the sampling time allowed,the level of the background count rate, and the specific activity of the labelled methane.

By suitable treatment of the counter, the background count rate could be limited to 200 counts per minute. If the minimum significant count rate for a sample of gas is taken as twice the background rate the apparatus would be able to detect a gas sample of 0.04 $cm^3$ when the active methane cylinder charge is one millicurie. If the sampling time is limited to 10,000 seconds the minimum detectable flow rate would be $4 \times 10^{-6}$ $cm^3$ $sec^{-1}$. With a standard specimen having the dimensions given in Table 1 and a pressure drop of 100 p.s.i. the minimum permeability which could be detected would be $4 \times 10^{-9}$ $cm^2$ $sec^{-1}$ when the active methane charge is one millicurie. The active methane charge could easily be increased to 100 millicuries, giving a sensitivity of $4 \times 10^{-11}$ $cm^2$ $sec^{-1}$.

## 8. CONCLUSION

The apparatus described is capable of measuring permeabilities of porous media down to $4 \times 10^{-11}$ $cm^2$ $sec^{-1}$ with a maximum error of 10 per cent. The method eliminates the errors due to gas leakage which are inherent in conventional apparatus for permeability measurement.

## 9. ACKNOWLEDGMENTS

The author wishes to express his gratitude to Mr. J.P. Chillag who built the apparatus and made the permeability measurements. Thanks are due also to Mr. C.L.W. Berglin and Mr. W.A.Lovell who offered many helpful suggestions.

## 10. NOTATION

| | | |
|---|---|---|
| $A$ | = | cross-sectional area for flow |
| $B_o$ | = | viscous flow permeability coefficient |
| $\mu$ | = | viscosity of gas |
| $K$ | = | permeability coefficient |

$K_o$ = slip flow permeability coefficient

L = length of porous medium in direction of flow

M = molecular weight of gas

$p_m$ = mean pressure of gas in porous medium

$q_m$ = volume flow rate of gas, measured at mean pressure

R = universal gas constant

T = absolute temperature of the gas

$\Delta P$ = pressure difference across specimen

## 11. REFERENCES

Carman, P.C. 1956 Flow of Gases through Porous Media, p. 70. London: Butterworth's Scientific Publications.

Ellis, W.R., and Fisher, M.E. 1961 The Development of a Radioactive Gas Counting Method for Measuring Diffusion of Gases Through Graphite for Permeability Studies. AAEC/TM 89.

Hutcheon, J.M., Longstaff, B., and Warner, R.K. 1958 The Flow of Gases through a Fine-Pore Graphite. Society of Chemical Industry, Conference on Industrial Carbon and Graphite, p. 259.

O'Neill, J.S., Hey, A.W., and Livey, D.T. 1959 Density and Permeability Relationships in Fabricated Beryllia, AERE-R3007.

Schwertz, F.A. 1949 Fluid-Flow Study of Porous Glass. J. Am. Ceramic Soc., 32: 390.

# TABLE 1

Flow of Methane at 22°C through Low Permeability Graphite

Sample H.S. -8*

| Upstream Pressure p.s.i.g. | Time from Start of Run min. | Sampling Time min. | Count Rate+ counts/min | | Volume Collected Free $cm^3$ | Gas Flow x $10^2$ Free $cm^3$ $sec^{-1}$ | K x $10^5$ $cm^2$ $sec^{-1}$ |
|---|---|---|---|---|---|---|---|
| | | | Total | Net | | | |
| – | Background | – | 340 | – | – | – | – |
| 90 | 30 | 1 | 145,280 | 144,940 | 3.42 | 5.70 | 5.02 |
| 90 | 60 | 1 | 145,880 | 145,540 | 3.45 | 5.75 | 5.06 |
| – | Background | – | 330 | – | – | – | – |
| 70 | 30 | 1 | 102,310 | 101,980 | 2.41 | 4.02 | 4.38 |
| 70 | 60 | 1 | 101,020 | 100,690 | 2.38 | 3.97 | 4.32 |
| – | Background | – | 330 | – | – | – | – |
| 50 | 30 | 1 | 65,330 | 65,000 | 1.53 | 2.55 | 3.63 |
| 50 | 60 | 1 | 64,860 | 64,530 | 1.525 | 2.54 | 3.62 |
| 30 | 60 | 2 | 69,250 | 68,920 | 1.626 | 1.36 | 2.79 |
| 30 | 90 | 2 | 69,250 | 68,920 | 1.626 | 1.36 | 2.79 |
| 10 | 30 | 2 | 27,800 | 27,470 | 0.649 | 0.54 | 2.02 |
| 10 | 60 | 2 | 27,720 | 27,390 | 0.647 | 0.54 | 2.02 |
| – | Background | – | 320 | – | – | – | – |

+ Mean of six 30-second counts

* Sample Dimensions:

Outside diameter ($d_o$) = 2.55 cm
Inside diameter ($d_i$) = 1.59 cm
Overall length = 15.19 cm
Length blind end = 2.55 cm
Length covered by O-ring = 0.64 cm
Effective length (E.L.) = 15.19 – (2.55 + 0.64) = 12.00 cm
Wall thickness (L) = $\frac{1}{2}(d_o - d_i)$ = 0.48 cm

Log mean area (A) = $\Pi \dfrac{d_o - d_i}{\log \frac{d_o}{d_i}}$ x E.L. = 77.0 $cm^2$

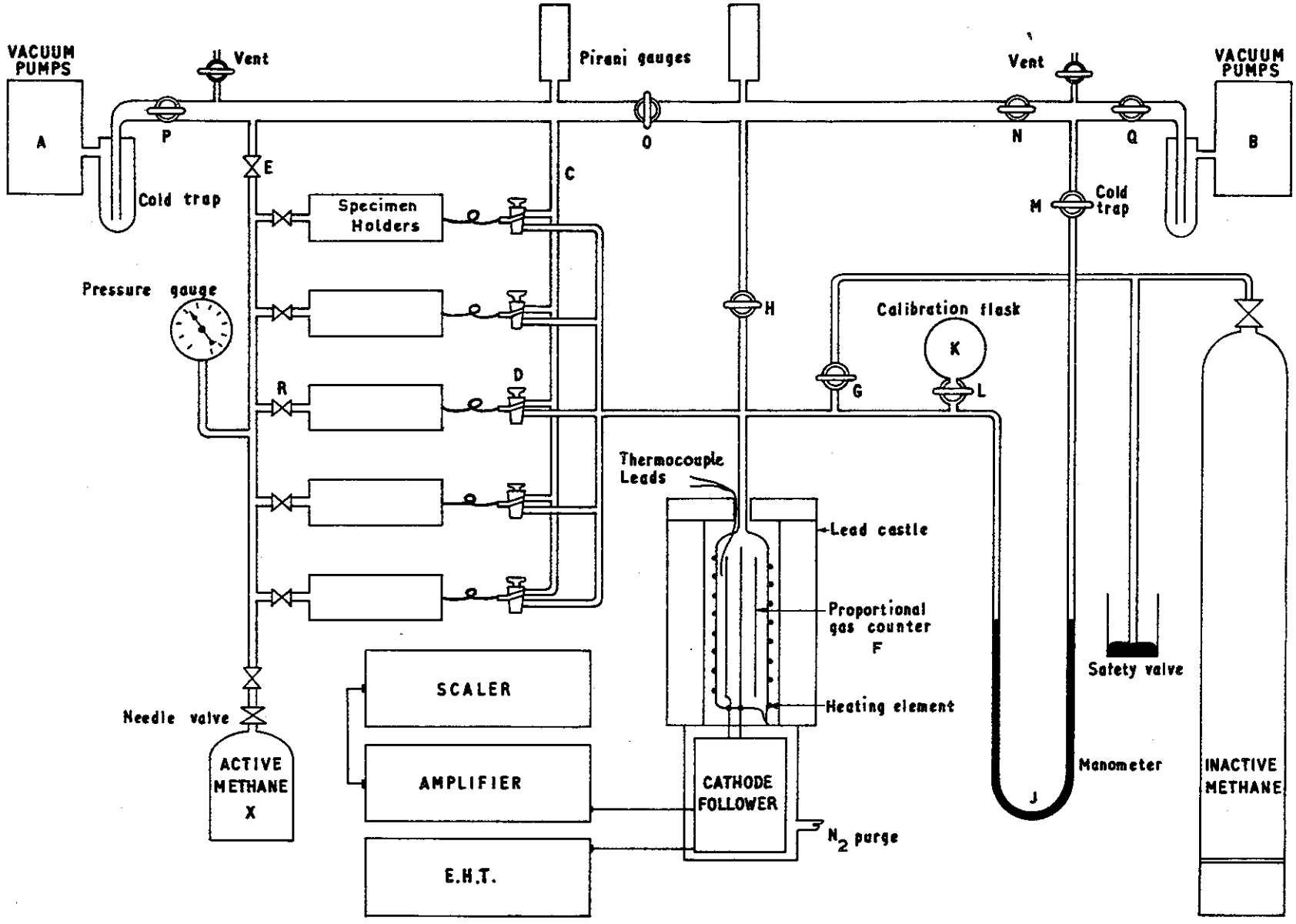


Fig. 1 APPARATUS

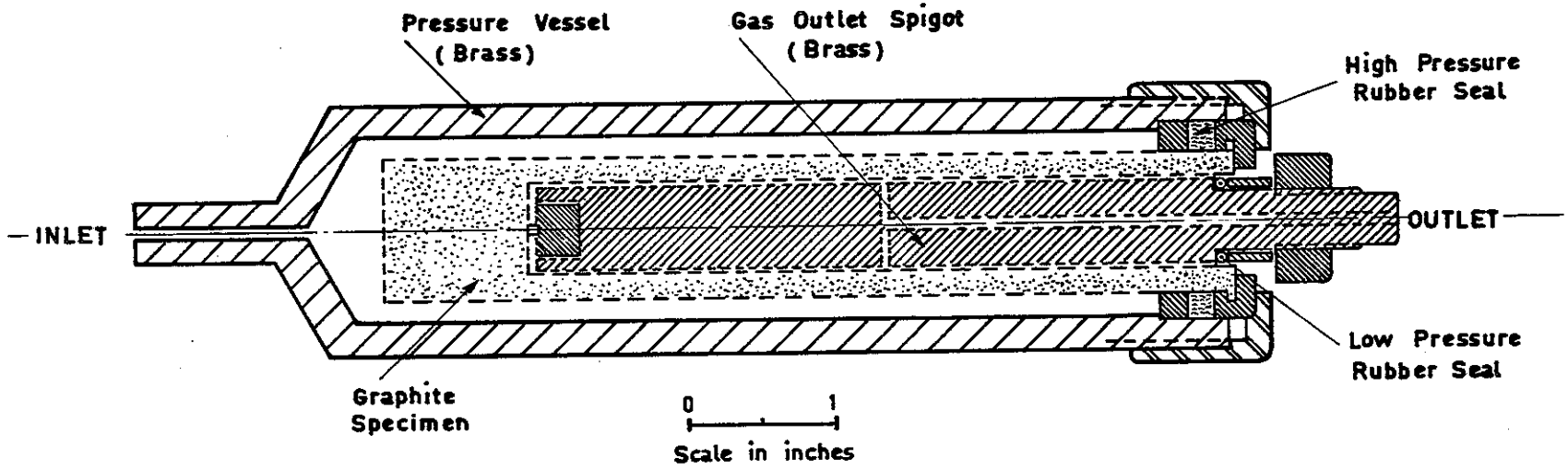


Fig. 2 SPECIMEN HOLDER

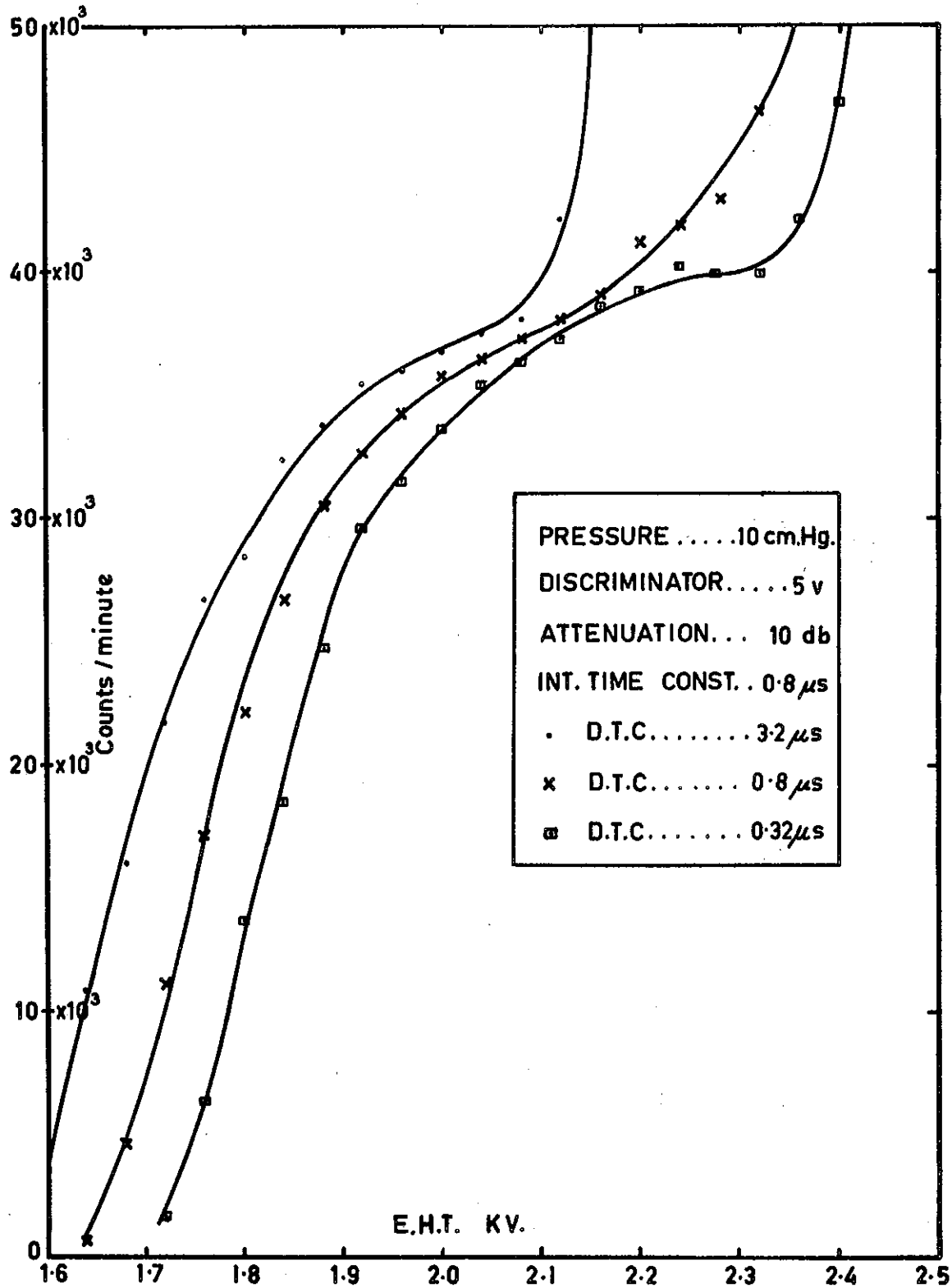


Fig. 3 COUNTER RESPONSE...EFFECT OF DIFFERENTIAL TIME CONSTANT

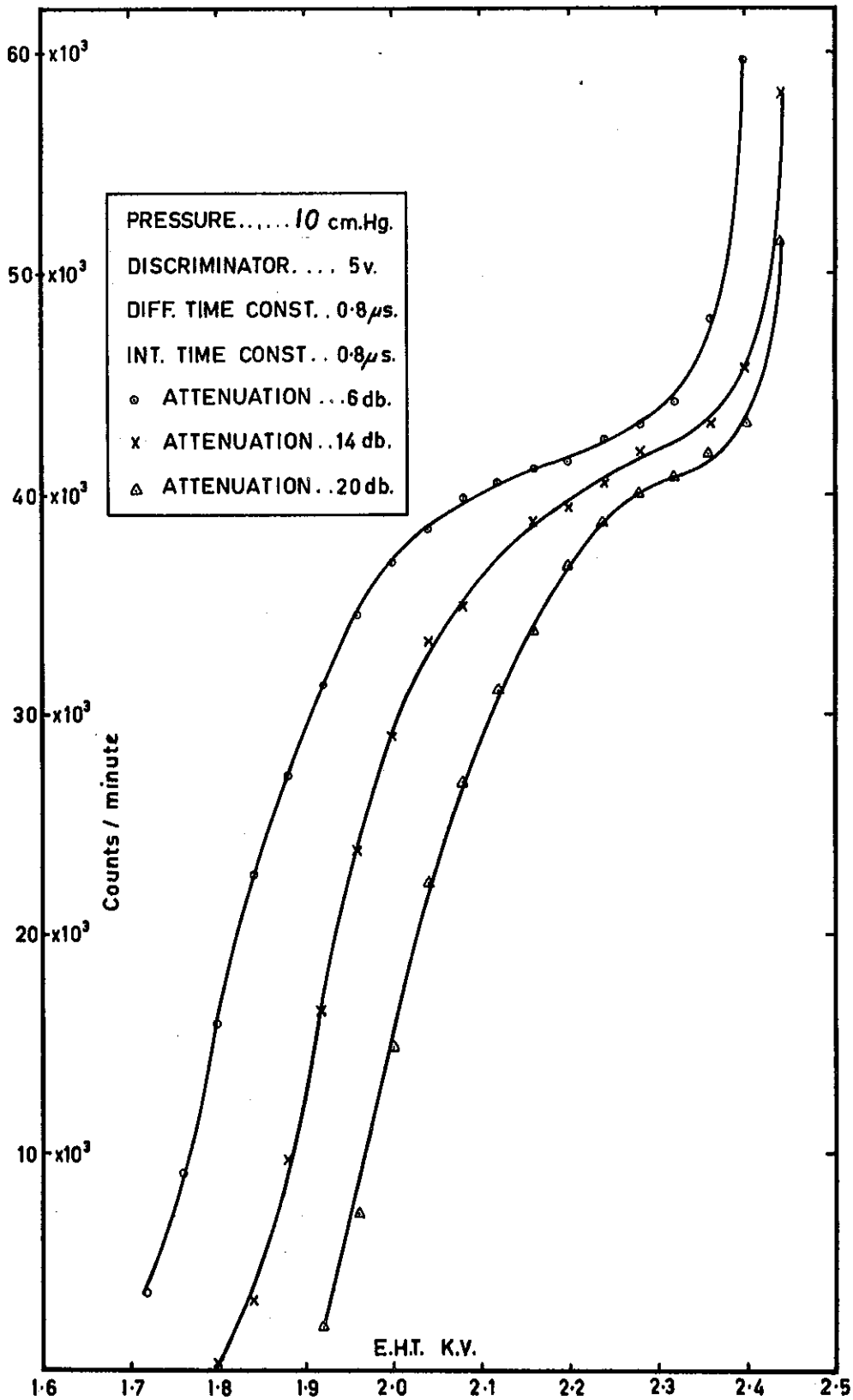


Fig. 4 COUNTER RESPONSE .... EFFECT OF ATTENUATION.

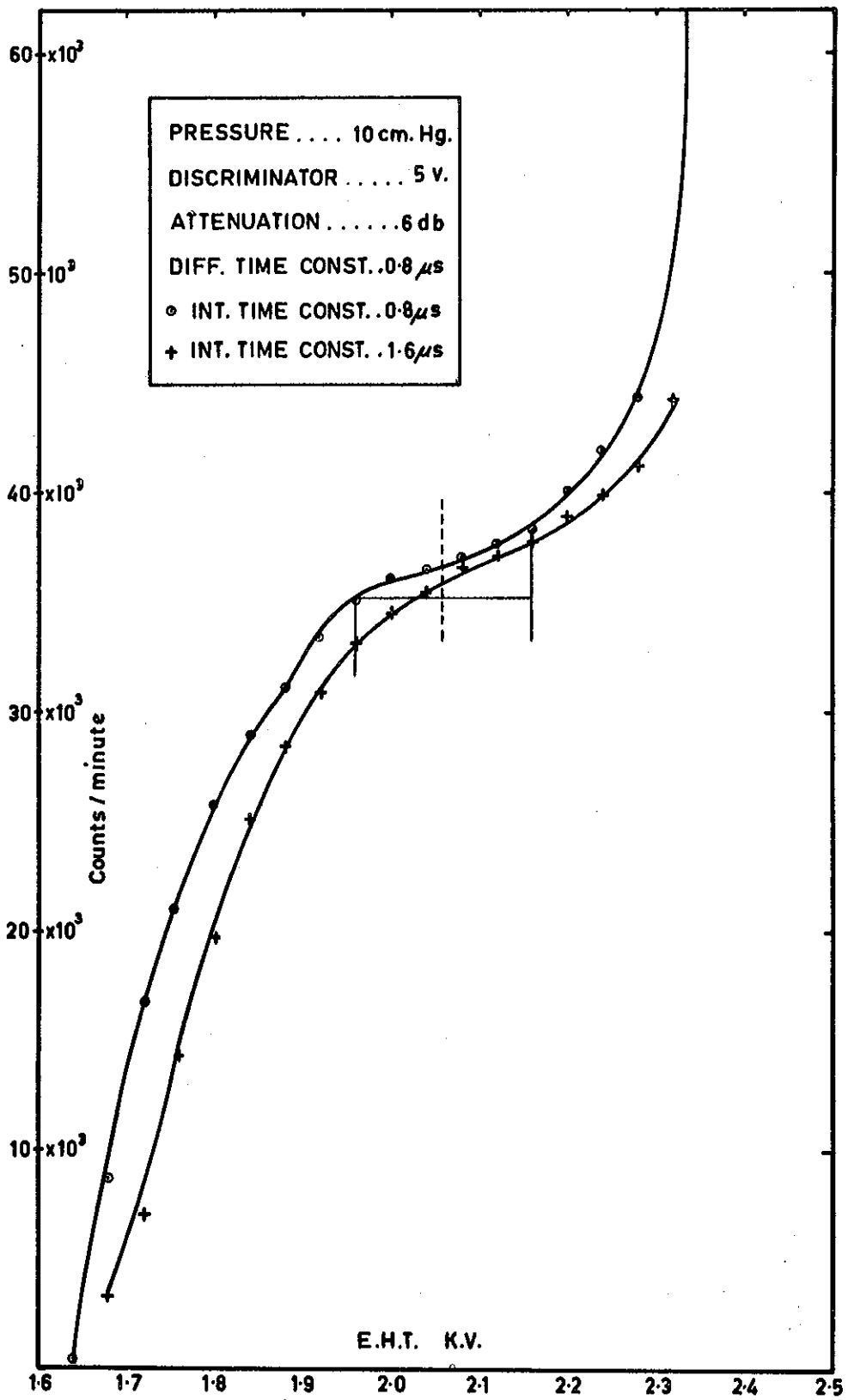


Fig. 5 COUNTER RESPONSE ...EFFECT OF INTEGRATION TIME CONSTANT.

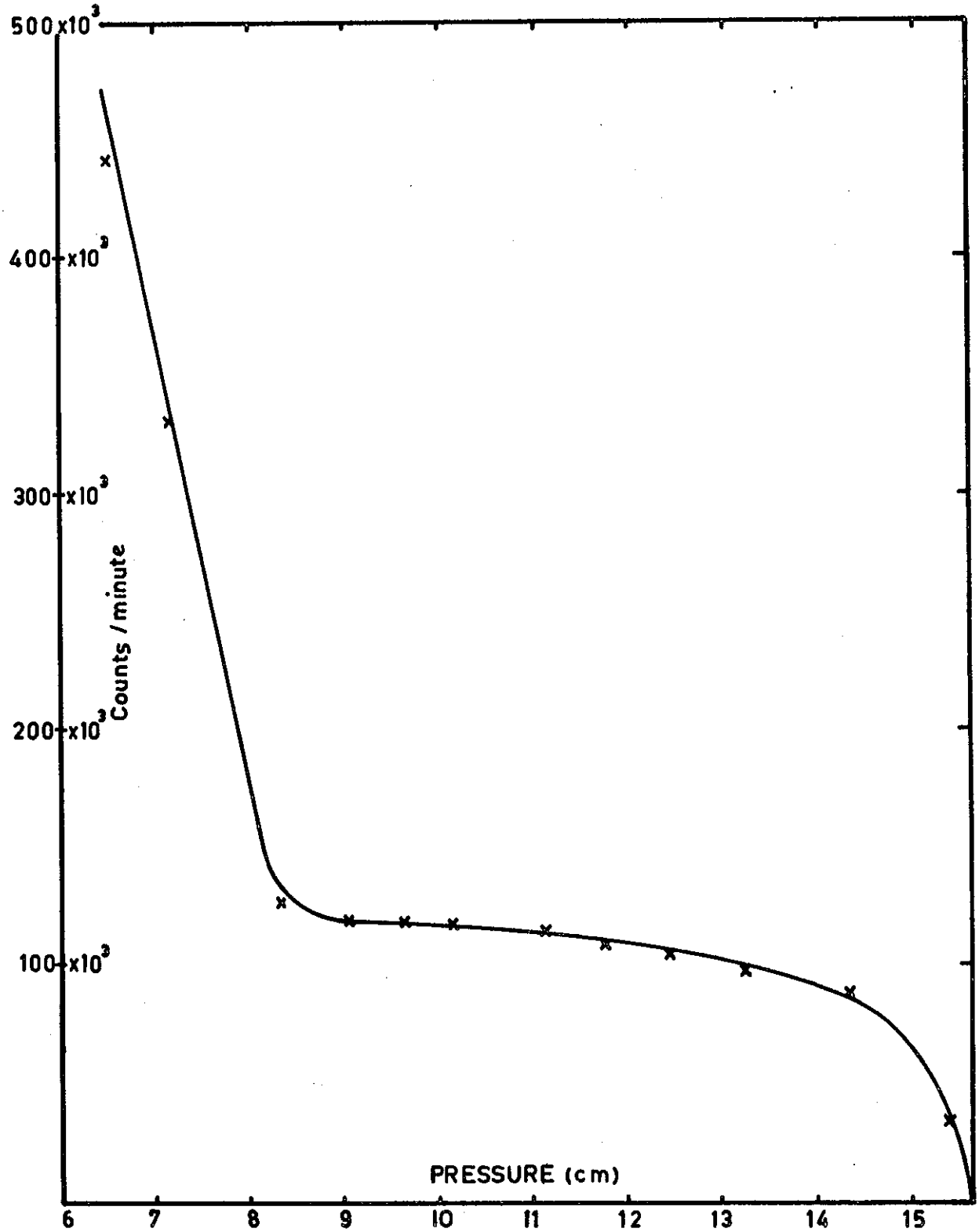


Fig. 6 COUNTER RESPONSE . . . EFFECT OF PRESSURE

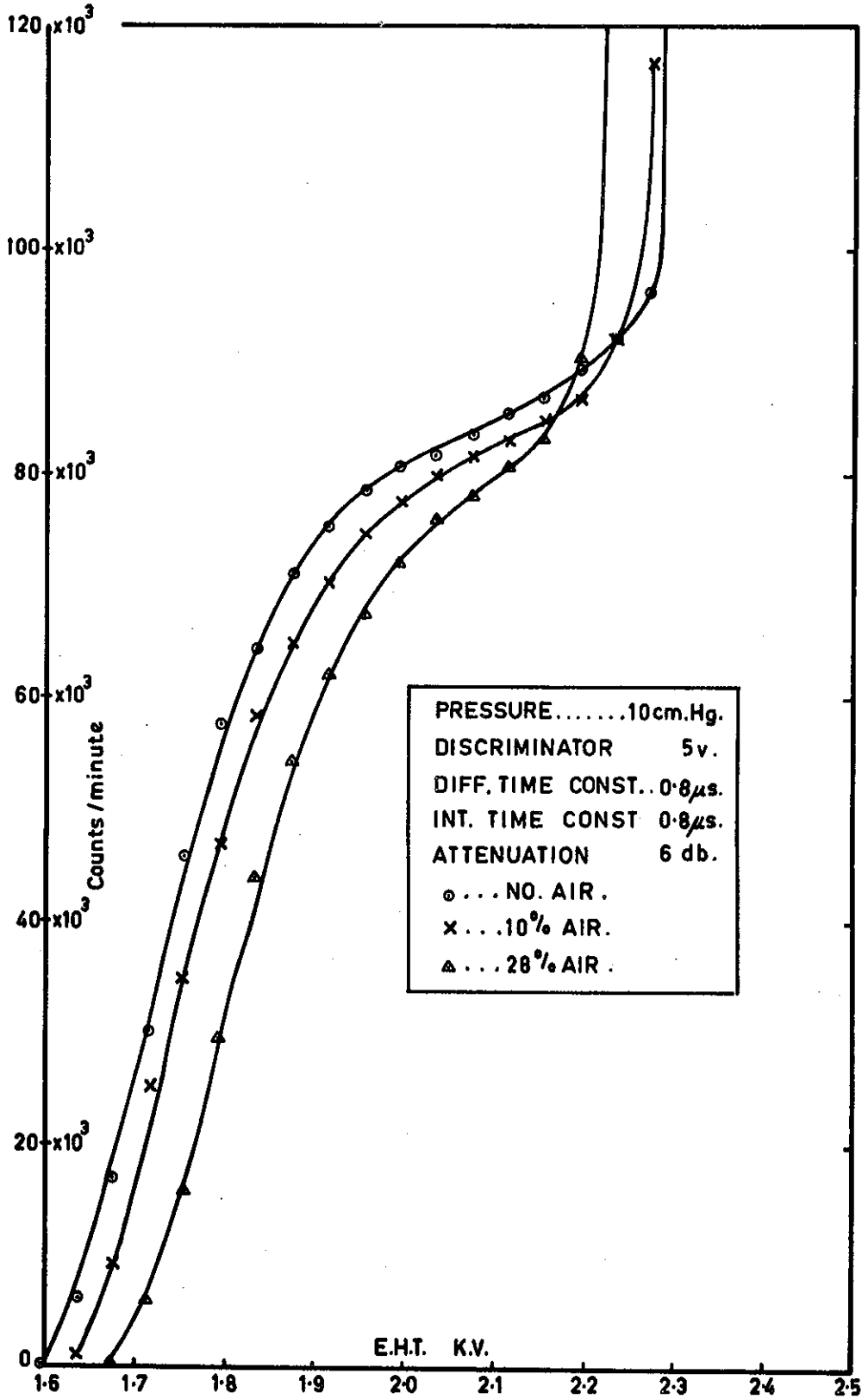


Fig. 7 COUNTER RESPONSE .... EFFECT OF AIR

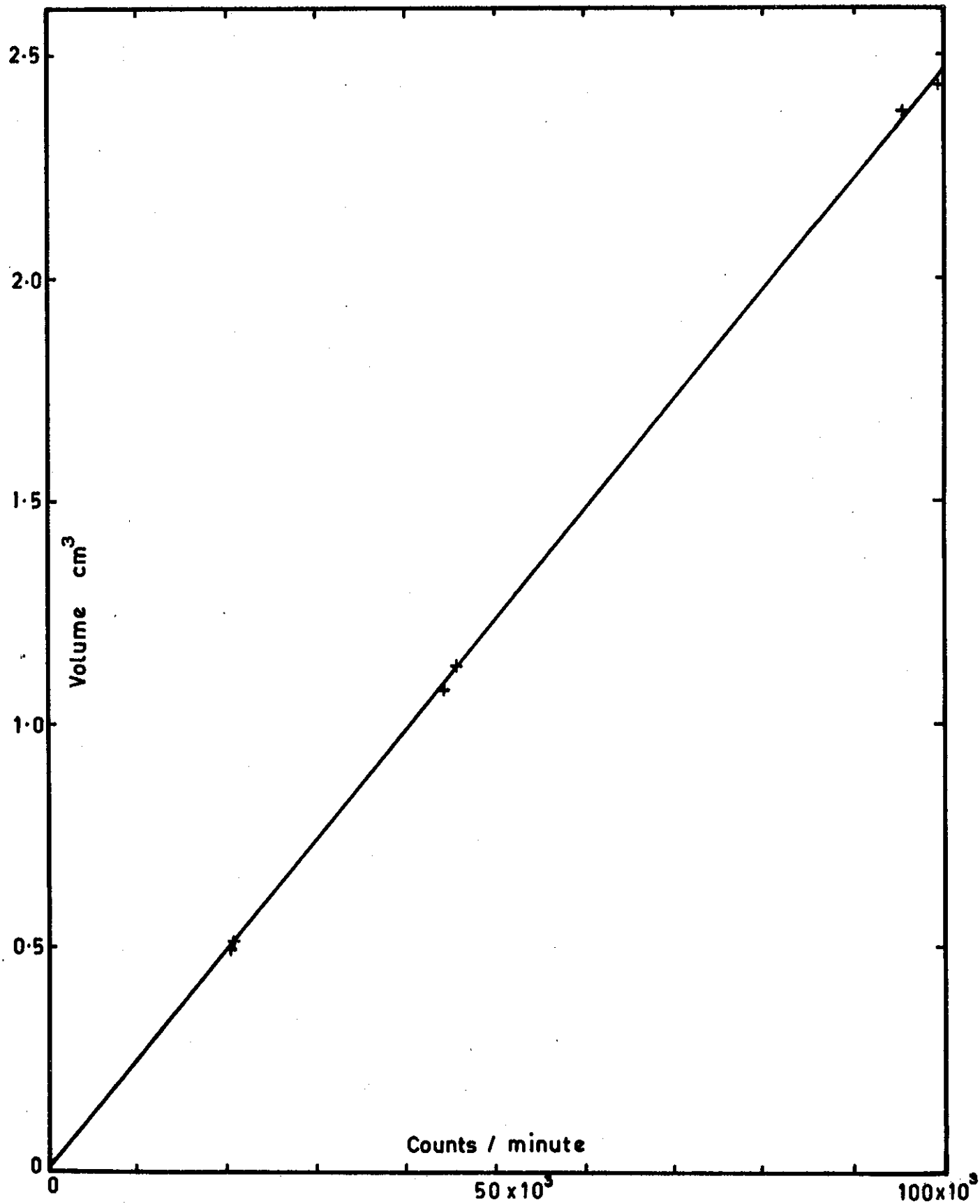


Fig. 8 ACTIVE METHANE STANDARDIZATION CURVE.

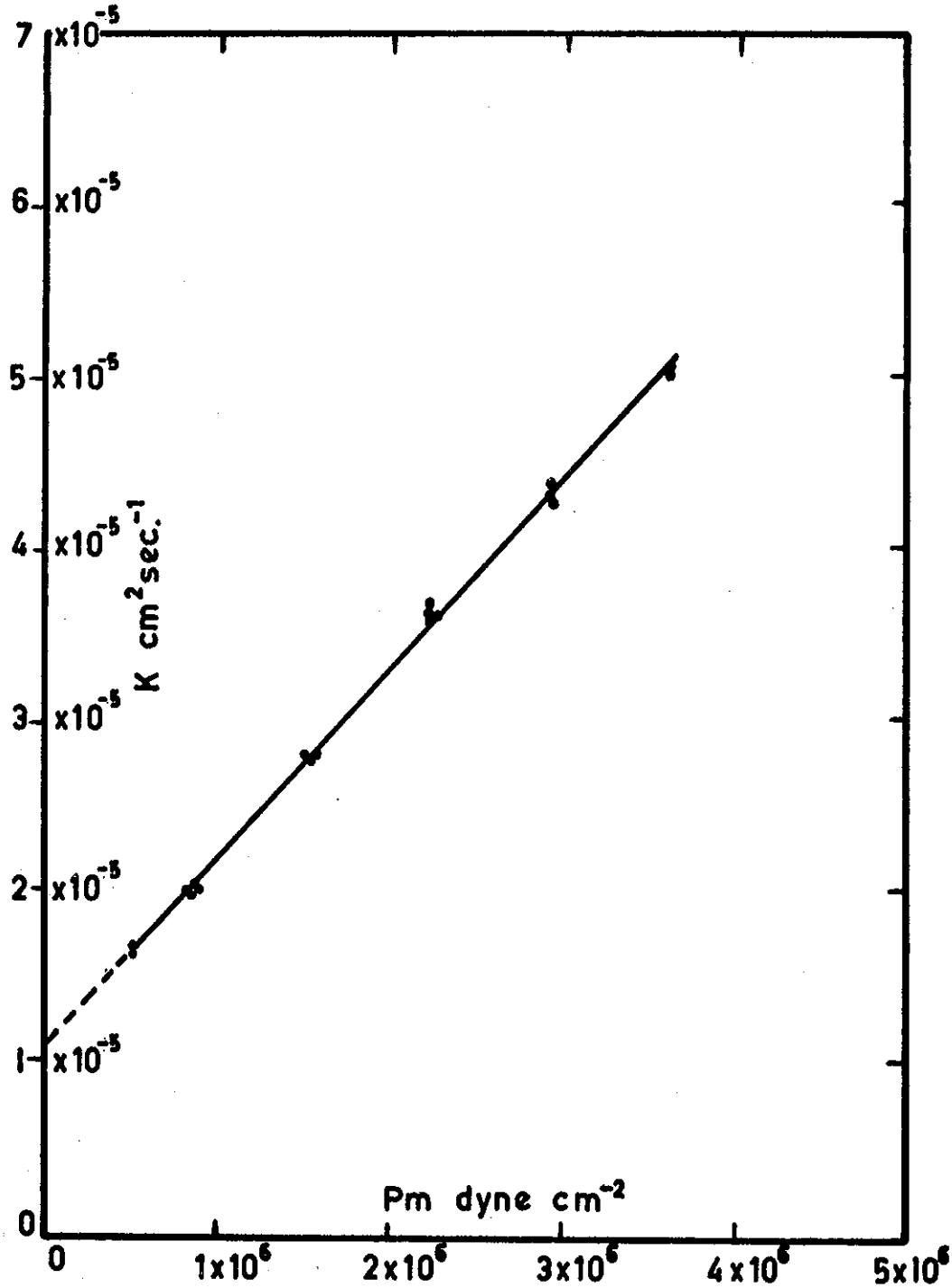


Fig. 9 RESULTS OF PERMEABILITY DETERMINATION