A New Multi-Tracer Gas Technique for Measuring Interzonal Air Flows in Buildings.

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KEY TO SYMBOLS USED

a = equivalent leakage area (m^2)

A = FID output at maximum sensitivity

c_o = concentration of tracer gas in incoming air (g m^{-3})

$c(t)$ = concentration of tracer gas in a decay rate experiment at time t (g m^{-3})

C = concentration of tracer gas at equilibrium during a constant emission rate experiment (g m^{-3})

C_p = specific heat capacity at constant pressure (J kg^{-1} K^{-1})

d = chart speed (cm min^{-1})

D = diffusion rate (ng min^{-1})

D_o = diffusion coefficient at T_o and P_o (cm^2 s^{-1})

e = flow exponent

E = area of building envelope (m^2)

$F_{i,j}$ = volume flow rate from zone i to zone j

G = matrix of interzonal flows from every zone to every other zone, normalised to the volume of destination zone

$G_i = F_{i,j}/V^j$ (volume flow rate from zone i to j normalised to volume of zone j)

h = peak height (mm)

H = rate of heat transfer (kW)

HETP = height equivalent to a theoretical plate

K = partition ratio of a solute between the mobile and stationary phases

l = length of diffusion path (cm)

L = length of chromatography column (cm)

m = mass of substance intering detector corresponding to respective peak (g)

M = molecular weight

n = number of theoretical plates

N = number of interconnecting zones

P = total pressure (mm Hg)

P_o = 760 mmHg

ΔP = pressure drop

q = rate of tracer gas supply (ng h^{-1})

Q = ventilation heat loss (W K^{-1})

r = peak resolution

R = air change rate (h^{-1})

ϱ = air density

s = detector sensitivity (Coulombs g^{-1})

S_j = total air flow rate in and out of zone j ($m^3\ h^{-1}$)

t_i = indoor temperature (°C)

t_o = outdoor temperature (°C)

t_M = time taken by an unretained solute to travel from the injector to the detector (min)

t_R = retention time (min)

t_R' = corrected retention time ($t_R' = t_R - t_M$)

T = temperature (K)

T_o = 273 K

u = average linear gas velocity ($cm\ s^{-1}$)

v = wind velocity ($m^3\ s^{-1}$)

V = volume of zone (m^3)

V_R = retention volume (ml)

W_b = width of peak at baseline (mm)

W_h = width of peak at half height

$\underline{x}(t)$ = vector transpose of tracer gas concentration in each zone at time t

$\underline{\dot{x}}(t)$ = rate of change of tracer gas concentration at time t

z = cross sectional area of diffusion path (cm^2)

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ABSTRACT

A method has been developed from first principles for following air movement in buildings using four perfluorocarbon tracer gases simultaneously.

The method may be divided into three well defined areas as follows:

1. Injection of gases at various points in a building
2. Sampling the tracer gases at several points in space and time
3. Analysing the tracer gas samples collected to yield curves of concentration against time at each sampling point

The tracer gases are injected remotely by flash evaporation from a small heater.

The sampling system employs the principle of gas adsorption on a solid. Tubes packed with adsorbent are connected by a system of manifolds and piping to a central pump. Solenoid valves at the front of each tube control the exposure of the packing material to the atmosphere. Tracer gas samples may be collected simultaneously at several locations, and in a timed sequence.

Tracer gas is liberated from the adsorbent by thermal desorption. The gases are then separated and analysed using a gas chromatograph fitted with a flame ionisation detector and a suitable column. The gas chromatograph was calibrated using standard gas mixtures made up on a glass vacuum line.

The work was carried out in two phases. During the first phase, the method was developed and prototype tracer gas release and sampling systems were built. Experiments carried out at the Polytechnic showed that the gases are not absorbed by room furnishings and that no stratification occurs at the concentrations used.

In the second phase, the sampling system was extended and all the injection, sampling and analysis procedures were automated by interfacing equipment to a BBC microcomputer. Experiments have been carried out using the new method to measure both single zone infiltration and interzonal air flows in several different buildings.

I INTRODUCTION

I.1 WHY MEASURE AIR MOVEMENT?

The study of air movement is of fundamental importance when considering building design. Over the last thirty years, researchers have paid particular attention to air movement as it affects the energy efficiency of buildings, the health and comfort of occupants and the cleanliness of special rooms such as operating theatres and ultra clean rooms, where high precision instruments are made from perfectly clean components.

Investigations (1,2,3,4) show how energy losses due to air infiltration in a building may account for up to 40 per cent of the total heating or cooling load. Work has been done to investigate the mechanisms of ventilation and infiltration in buildings and to relate the amount of infiltration or ventilation to other factors such as airtightness, weather conditions, temperature differences between rooms in the building and outside, open doors and windows.

Computer models are being developed to aid building design. These allow predictions to be made of energy consumption after various conditions such as structure, materials, leakage area, position relative to the sun and degree of shading have been specified. Air infiltration losses are much more difficult to model than other components such as energy loss through building components (5). As a result of this, building models often use very simplistic air infiltration routines.

The need to reduce energy losses by infiltration has led workers in cold climate areas such as Scandinavia and Canada to develop very highly insulated airtight buildings (6). These building designs have been highly successful in reducing heat losses but have presented problems of their own as far as maintenance of sufficient ventilation is concerned. Insufficient ventilation in airtight buildings gives rise to discomfort and health problems. It is important to maintain a low level of germs and odours for health and comfort. Even more important, ventilation should remove harmful substances such as radioactive radon daughters and formaldehyde which may be emitted from building materials (7), causing great harm to the building occupants (8).

Mechanical ventilation and air conditioning systems have been developed but there is concern over their efficiencies where building occupants have freedom to control ventilation by opening windows and internal doors. Such ventilation control is discussed by Gale (9). Reference is made to the Building Research Establishment claim that reductions of up to 0.5 air changes per hour are possible by ordinary weather stripping. Sandberg (10) writes about ventilation efficiency with regard to ventilation system design. Ventilation efficiency is defined in terms of the removal of indoor pollution. Three tracer gas methods are tried and compared. The treatment of results is based on the area under a measured tracer gas decay curve. Sandberg claims that this reduces errors caused by fluctuations in the data which are apparent when results are found by taking slopes of decay curves or measuring concentration ratios.

Another problem for ventilation efficiency is in the transport of toxic gases from a laboratory via a fume hood. Drivas et al (11) used sulphur hexafluoride (SF_6) to obtain quantitative data on contamination of laboratories and factories caused by re-entry of fume hood exhausts into buildings.

Specific internal air movement patterns are of great concern in hospitals where the transport of odours and germs must be kept to a minimum. Operating theatres must be given a constant supply of clean air in such a way as to minimise infection of patients by incoming air or by the air movement induced by theatre staff (12,13,14,15,16,17). In contrast to this, it is essential that air leaving isolation wards where highly contagious disease is present, does not make its way to other parts of the hospital.

Air movement patterns have to be followed to measure the efficiency of air conditioning systems installed in ultra clean rooms to make sure that as few particles as possible are available for contamination of precision instrument components (18,19).

I.2 TERMINOLOGY

The ventilation rate of a building is the rate at which air enters from outside. Natural ventilation results from natural forces such as the wind effect and the stack effect. Mechanical ventilation is that

obtained by mechanical means. Air infiltration is that part of the total ventilation due to unintentional gaps and cracks in the building structure (20,21). The air change rate of a single roomed building is synonymous with the ventilation rate. However, in a multi-roomed building the air in a room may exchange with air in another room as well as, or instead of, outside air (9).

I.3 MECHANISMS OF NATURAL VENTILATION

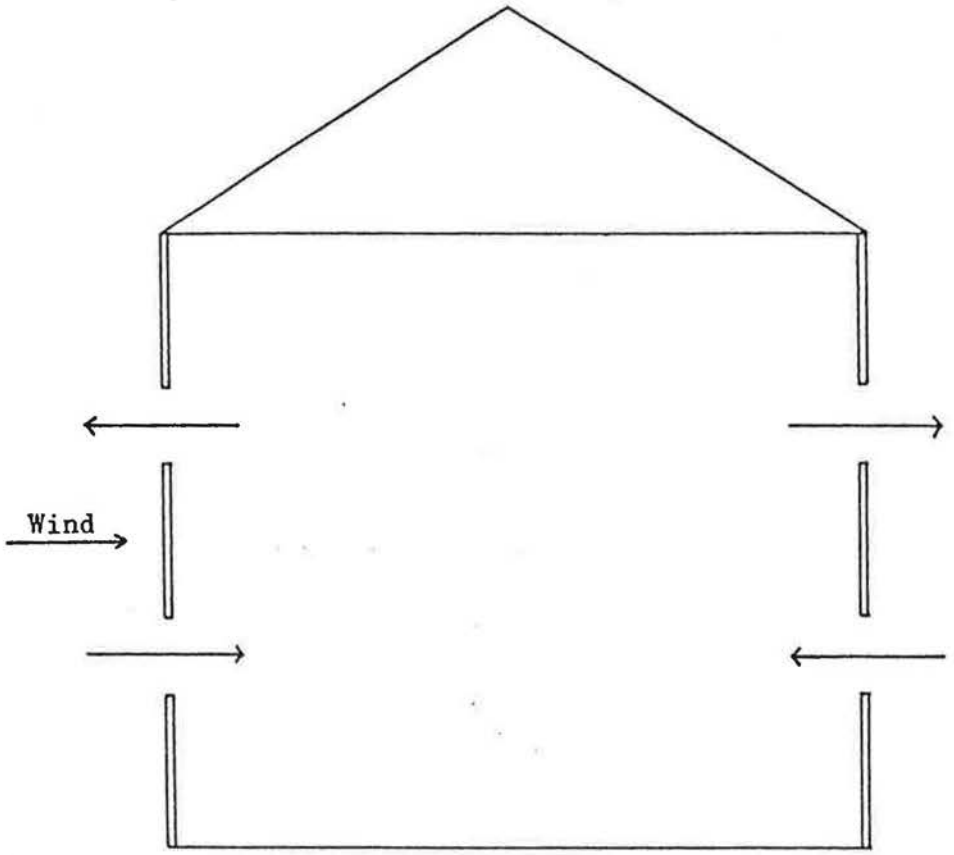
The process of natural ventilation of a building involves air entering at one place and leaving from another (Fig.1). The flow occurs due to a pressure difference between these places arising from two principal causes. Firstly, the wind effect; a pressure gradient is induced across a building when fast flowing air hits one of the surfaces. Air enters on the windward side and leaves from the leeward. Internal doors only act as obstructions if the gaps round them are small compared to those in the wall. Internal doors are usually a loose fit.

Laboratory tests show that air flow rate through ventilators and cracks round windows and doors is proportional to the square root of the pressure difference across the component (22). This relationship is only followed exactly if the hole is small and flow perfectly turbulent. For a large hole with laminar flow the relationship is that flow rate is proportional to pressure (8). In practice flow lies somewhere between these two extremes. The pressure drop across a building component may be expressed by the equation:

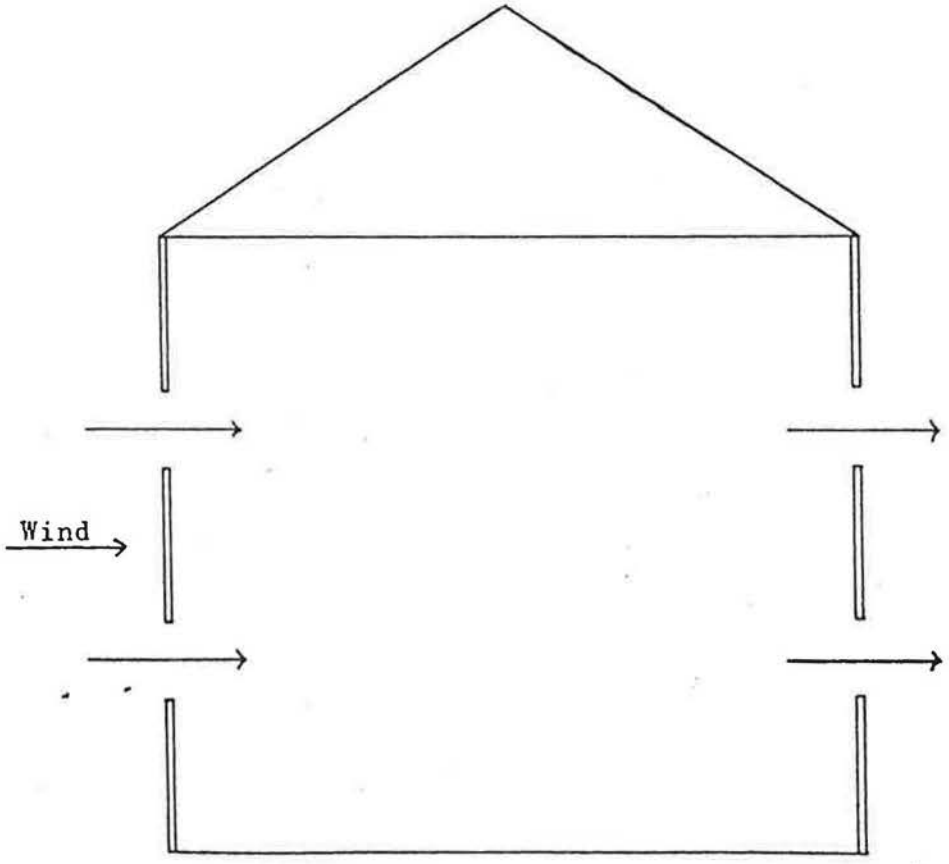
$$\Delta p = \left[\frac{F}{ka}\right]^2 \qquad \text{......} \quad 0$$

Δp = pressure drop (mm Hg)
F = volume flow rate ($m^3 s^{-1}$)
a = leakage area (m^2)
k = constant related to the discharge coefficient across leakage areas.

The stack effect is a buoyancy effect arising from a difference in



a) Stack effect predominant



b) Wind effect predominant

Fig.1 Patterns of air flow in a house

density between cold air outside and warm air inside. The generated pressure is a function of the temperature difference and the vertical distance between the lower (inlet) and upper (outlet) openings. The pressure due to the stack effect is given by the equation:

$\Delta p = H(t_i - t_o) \times 4.35 \times 10^{-2}$

H = height to the level where $\Delta p = 0$ (normally equal to half the height of the building).

t_i = indoor temperature

to = outdoor temperature

The wind and stack effects work together but in general the wind effect is dominant in controlling whole building ventilation rates where the temperature differences inside cause air movement from room to room (23). The only times when stack effect becomes dominant are in windless conditions or in the case of high rise buildings.

I.4 HOW IS VENTILATION MEASURED?

The two most common methods of determining infiltration and ventilation rates are the pressurisation and tracer gas techniques. The former is the simpler approach but only gives limited information from which infiltration rate has to be derived indirectly using some form of mathematical model. The latter approach enables ventilation rates to be determined directly, but requires more complex equipment and operating skills. Each method is considered more fully in the following sections.

I.5 THE PRESSURISATION TECHNIQUE

The air leakage rate of a building may be measured by creating a pressure difference between the interior and the outside by means of a fan fixed in place instead of an external door or window (Fig.2) (23a). The building leakage rate is evaluated by finding the flow rate of air into or out of the building required to maintain a given pressure difference. Both over pressure and under pressure can be created (Fig.3).

The pressurisation method is quick and reliable producing a quantitative measure of the airtightness of all the enclosing

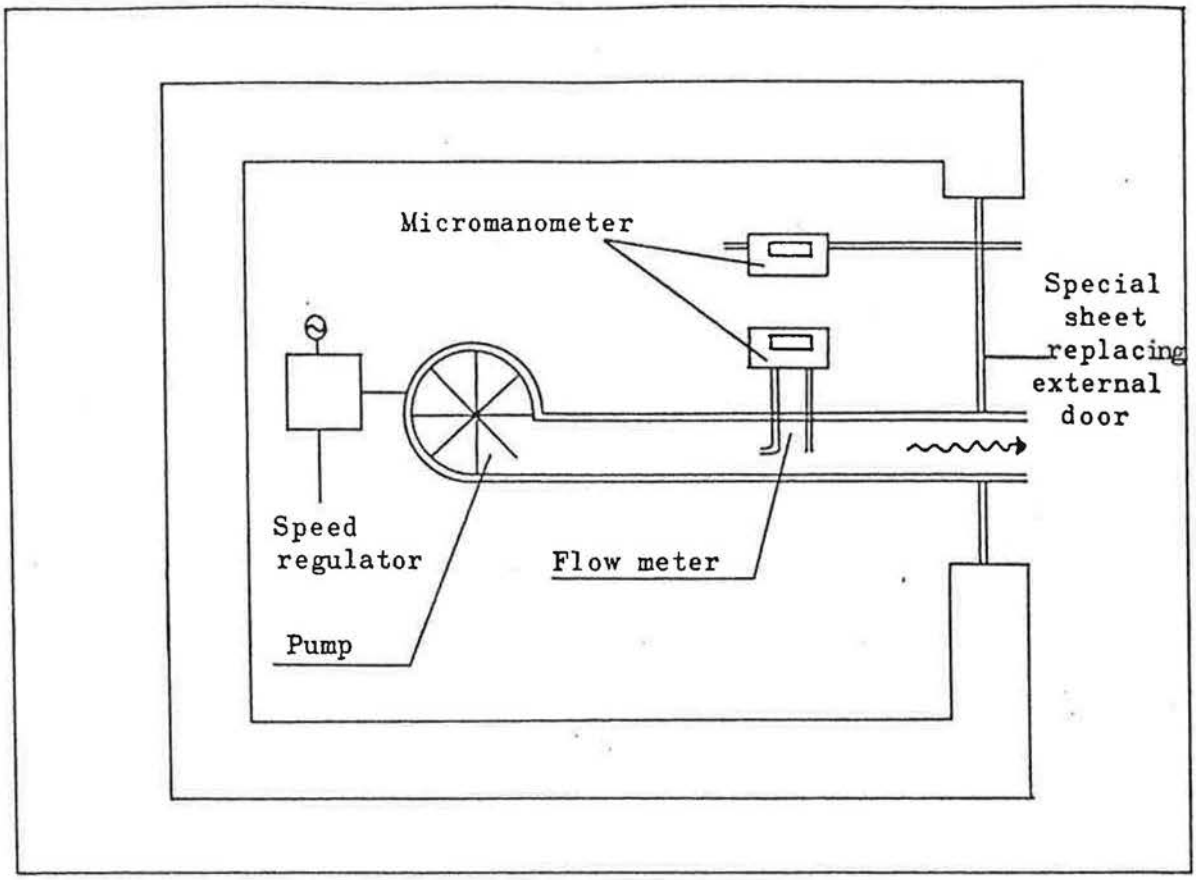


Fig.2 Measuring equipment: Schematic diagram

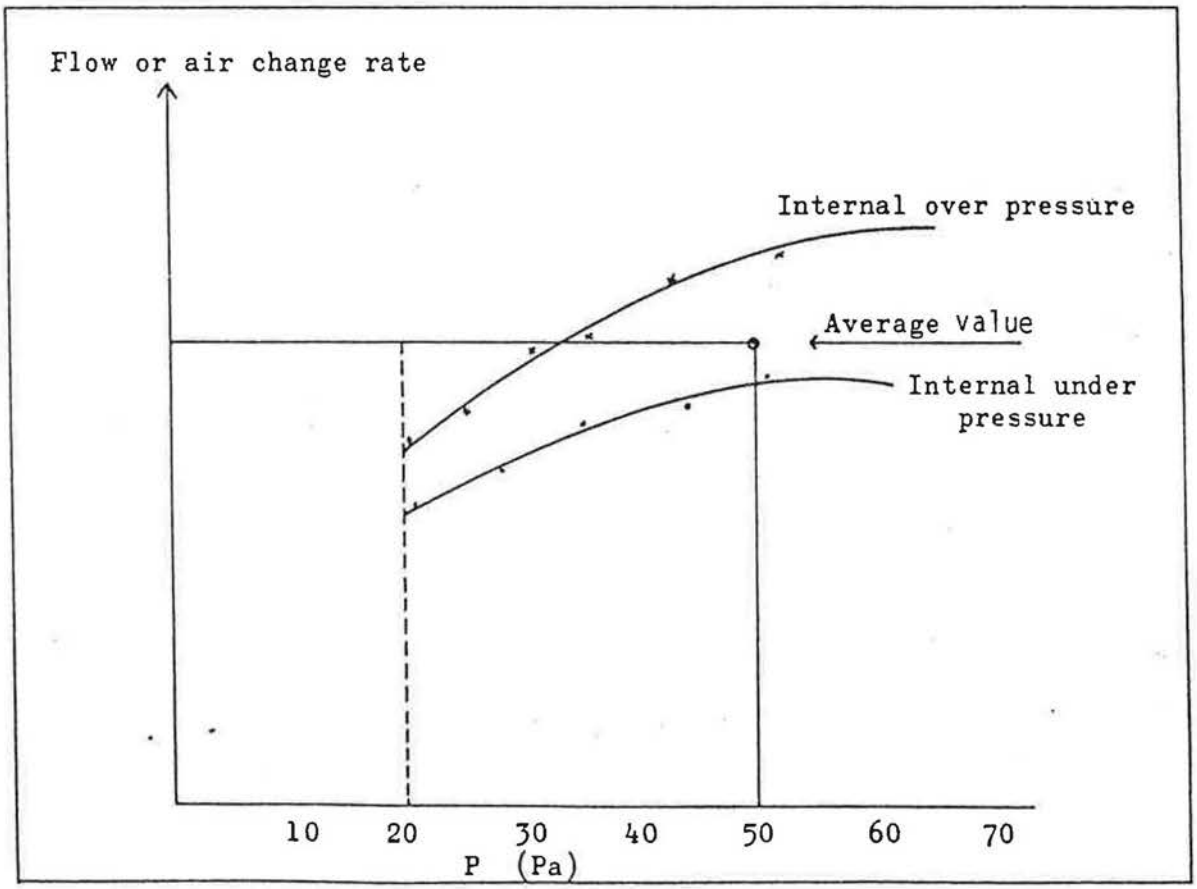


Fig.3 Example of test results in graph form

surfaces. However, the result is not directly useable for the evaluation of building air change under natural conditions. Normally the flows which arise from internal over pressure and under pressure are dissimilar. This is due to some leaks acting as non return valves. For instance, outward opening windows show a greater leakage with internal over pressure than with internal under pressure. The usual technique is to create a pressure difference of 50 Pa which itself causes problems in measuring the ventilation rate. Air flow is likely to be quite different under normal pressure conditions from that induced by a pressure difference of 50 Pa. However a number of mathematical models (24, 24a) are available, which enable infiltration rates to be derived for given wind speeds and temperature differences using the air leakage characteristics obtained from the pressurisation test.

This approach is not as accurate as direct measurement but may be useful for assessing, say, average infiltration rate of a building over a heating season or the effect of some air-tightening procedure such as weather stripping. Section III.8.2 describes leakage tests carried out on the PCL experimental houses at Peterborough.

I.6 TRACER GAS TECHNIQUES

I.6.1 MIXING THEORY

There are a range of tracer gas techniques. Each, however, requires that a gas with suitable properties (discussed in I.8.3) are injected and mixed within the space, or spaces, under consideration and its concentration measured over a period of time. In most cases it is assumed that the gas is uniformly mixed within the space at any instany of time. Departures from this condition can lead to errors in interpretation. Fig.4 illustates the main types of mixing pattern which can occur, ranging from perfect, instantaneous mixing to complete non-mixing, sometimes known as piston flow. In real sitiations an intermediate situation may be found, perhaps resulting from stratification, in which mixing is inhibited, or 'short-circuiting' occurs.

There are three distinct mixing proceses which combine to produce room air mixing. They do not contribute equally to the total mixing, but all play a part. Molecular diffusion takes place very slowly and

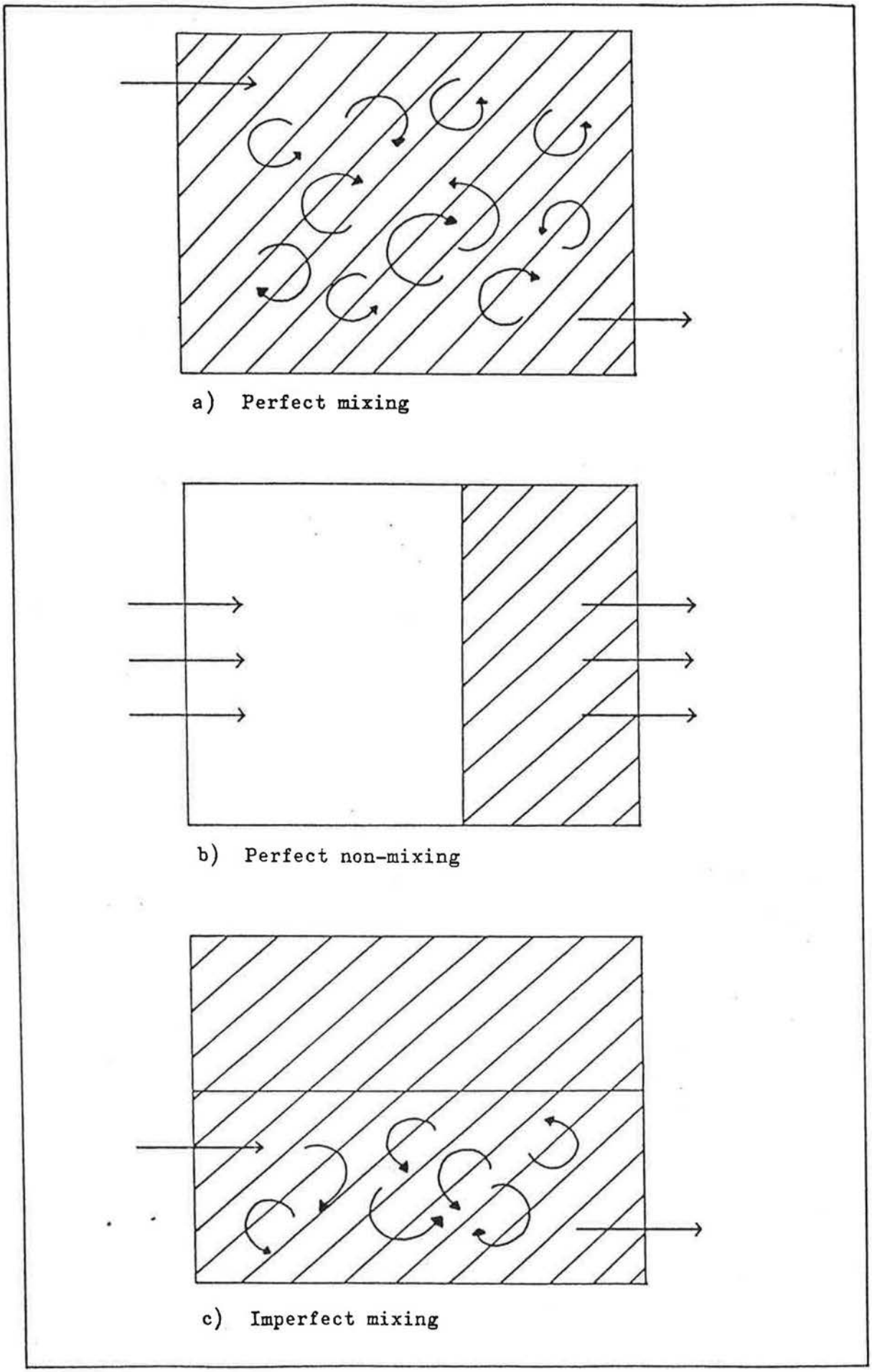


Fig.4 Three possible models of tracer dilution

calculations by Higgins et al (25) show that for the fastest diffusing gas hydrogen, a point 7.5 feet from the source reaches 95% of its final concentration more than one hour after the gas release. Comparing this with observed times of 20 minutes or less for a tracer gas to become uniform in a room without artificial mixing, it is clear that other mixing processes are at work which are at least three times faster. Hunt et al (26) have used helium (He) and sulphur hexafluoride (SF_6) simultaneously as tracer gases in a 4 bedroomed town house. The comparable results from the two gases show that molecular diffusion did not play a major part in the air infiltration process.

In calm stable atmospheric conditions the speed of mixing due to eddy diffusion (turbulence) is a factor of 10^3 greater than that due to molecular diffusion (27). However, even in Beaufort 1 winds (virtually calm by atmospheric standards) wind speeds are an order of magnitude greater than air speeds in a naturally ventilated room (24). A reduction of velocity by this amount must have a severe effect on the eddy diffusivity.

Thermally induced currents of high speeds have been measured in rooms where the ventilation rate is imeasurably small (27a). During the same experiments air speeds in other parts of the room were very low. Howland et al (28) found that in rooms of volume ~ 48 m^3, 6 minutes was sufficient time for uniform mixing in a similar situation. Lidwell et al (29) observed a circulation time of 4 minutes in an operating theatre, and found that it took about 20 minutes for acetone released as a tracer to reach a uniform concentration. At normal ventilaton rates the pattern is still followed, although 'high speed draughts' and 'through ventilation' at high ventilation rates give deviations from the uniform conditions resulting in a different airflow pattern.

A circulation of air currents resulting from convection or forced turbulence such as a fan or an occupant moving about, forms the dominant transport mechanism with eddy and molecular diffusion providing smaller scale mixing. Stratification of a tracer gas, ie. the formation of a relatively high concentration gradient towards the top or bottom of a room, arises from a difference in density between the tracer gas and the air. As a general rule the concentrations of very high or very low density tracer gases are limited to a maximum at which the density of the air and tracer mixture is within 1% of the

density of air. This prevents stratification (24).

Problems of imperfect mixing may be largely overcome by using fans or by taking several samples and averaging the contents either by physical mixing or by averaging concentration values.

I.6.2 BASIC EQUATION

In order to discuss the strategies available for using tracer gas to determine air exchange rates it is useful to consider the following simple, first-order differential equation which governs the rate of change of tracer gas concentration with time within a single space in which the tracer gas is well-mixed.

$$V \frac{dc}{dt} = q(t) - F(t).(c-c_e) \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

where,

V = volume of space (m^3)
$F(t)$ = volume flow rate of ventilating air
$q(t)$ = rate of injection of tracer gas ($g\ h^{-1}$)
$c(t)$ = concentration of tracer gas ($g\ m^{-3}$)
c_e = concentration of tracer gas in incoming ventilating air

I.6.3 THE DECAY RATE TECHNIQUE

A finite amount of tracer gas is injected into the space to give an initial concentration appropriate to the range of the instrument used to measure the gas concentration. After injection the concenttation is measured over a suitable period of time. Considering the terms in equation 1, $q(t) = 0$ and assuming that the flow rate of ventilatingh air remains constant over this period $Q(t) = Q$. Upon integration equation 1 gives the following expression for concentration, c;

$$c(t) = c(0).e^{-RT} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

where R is defined as (F/V) and is conventionally called the ventilation rate. The measured concentration may be plotted in the

form $\log_e(c)$ against time, t. This should yield a straight line whose slope gives the value of ventilation rate, R.

The decay rate technique is relatively simple to use and is suitable for discrete measurements of ventilation rates over periods when these would be expected to remain constant. One advantage is that provided that the response of the instrument used for measuring the concentration of gas is linear an absolute calibration is not necessary.

I.6.4 THE CONSTANT EMISSION METHOD

In this variation the tracer gas is injected continuously at a constant rate, q, starting at time t = 0. Assuming that the ventilation flow rate F is constant, equation 1 can be integrated to yield the following expression for concentration;

$$c(t) = \frac{q}{VR}(1 - e^{-Rt}) \qquad 3$$

After a suitably long period of time the concentration reaches an equilibrium value, c_E, equal to (q/VR). Provided that q is known R may be readily determined. More complex variations of this technique nave been used to obtain continuous measurements of changing ventilation rate over sustained periods of time (32,95).

It should be noted that the concentration measuring instrument requires absolute calibration and that the tracer gas injection rate needs to be measured with sufficient accuracy, making this method more susceptible to errors than the decay rate technique.

I.6.5 THE CONSTANT CONCENTRATION METHOD

This method requires more complex instrumentation than the two previously discussed methods. The instrument used to measure the tracer gas concentration is used to provide a signal in a feedback loop to a tracer gas injection device. Appropriate control equipment is used to ensure that the quantity of gas injected is sufficient to

ensure that the quantity of gas injected is sufficient to ensure the concentration in the space is maitained at constant concentration, c_{∞}, say. The solution to equation 1 becomes trivial, yielding,

$$F = \frac{q}{c_{\infty}} \qquad \ldots\ldots 4$$

It is usual to integrate the volume of tracer gas injected over a given period of time, say, 30 minutes and hence to obtain the average volume flow rate of ventilating air, F, over that period. Although requiring complex instrumentation, this method provides the best approach to measuring ventilation rates continuously over an extended period and, given an appropriate number of injection points, can be used in mutiple-celled and complex spaces, both to obtain local ventilation rates and whole building rates.

I.7 MEASUREMENT OF INTERNAL AIR FLOWS

Most buildings do not consist of a single-celled space but of a number of rooms and spaces connected by air flow paths. These paths restrict mixing between the individual spaces. The simple decay and constant emission techniques cannot generally be used in these conditions unless the mixing is enhanced. Although the constant concentration method is applicable it tells nothing about the actual inter-zone exchange rates. These are important in the context of the transfer of heat and indoor air pollutants.

In order to illustrate the approach to solving the problem of measuring interzonal flows, consider, instead of a single well-mixed space, two interconnedted well-mixed spaces, as shown in Fig.5. This could represent a house, with space 1 being the living area and space 2 the roof void. The concentration of a tracer gas injected into each of these spaces is now governed by two equations of similar form to equation 1;

$$V_1 \frac{dc_1}{dt} = q_1 + F_{01}.c_{\infty} - F_{10}c_1 - F_{12}c_1 + F_{21}c_2 \qquad \ldots\ldots 5a$$

$$V_2 \frac{dc_2}{dt} = q_2 + F_{o2}.c_o - F_{2o}c_2 - F_{21}c_1 + F_{12}c_2 \quad \text{.....5b}$$

Whereas equation 1 contained only one unknown these equations contain 6. Thus although two additional equations can be obtained by considering the conservation of mass for each space, it is clear that there is insufficient information to solve for all of the unknowns. One method of overcoming this is to use two gases, A and B, one injected into each space. Given appropriate equipment these can be measured, yielding results similar to those illustrated in Fig.6 The method of obtaining a solution, using measured data is discussed in depth in Appendix A for the more general case of an N-zoned space and the practical aspects of using more than one tracer gas are expanded on in the following sections.

I.8 THE DESIGN OF A MULTI-TRACER GAS SYSTEM

I.8.1 METHOD DESIGN

All tracer gas methods for following air movement in buildings require the solution to four problems:

1. The choice of a tracer gas.
2. A method of releasing the gas.
3. A sampler design to allow the collection of air mixed with tracer gas from different places over a period of time.
4. A method of separating a mixture of tracer gases and analysing them.

These problems are dealt with in turn below.

I.8.2 ADVANTAGES TO USING MORE THAN ONE GAS

It can be seen from the mathematical treatment of internal building air movement (Appendix A) that the number of data points required to reach solutions for all the flow equations is N^2 where N is the number

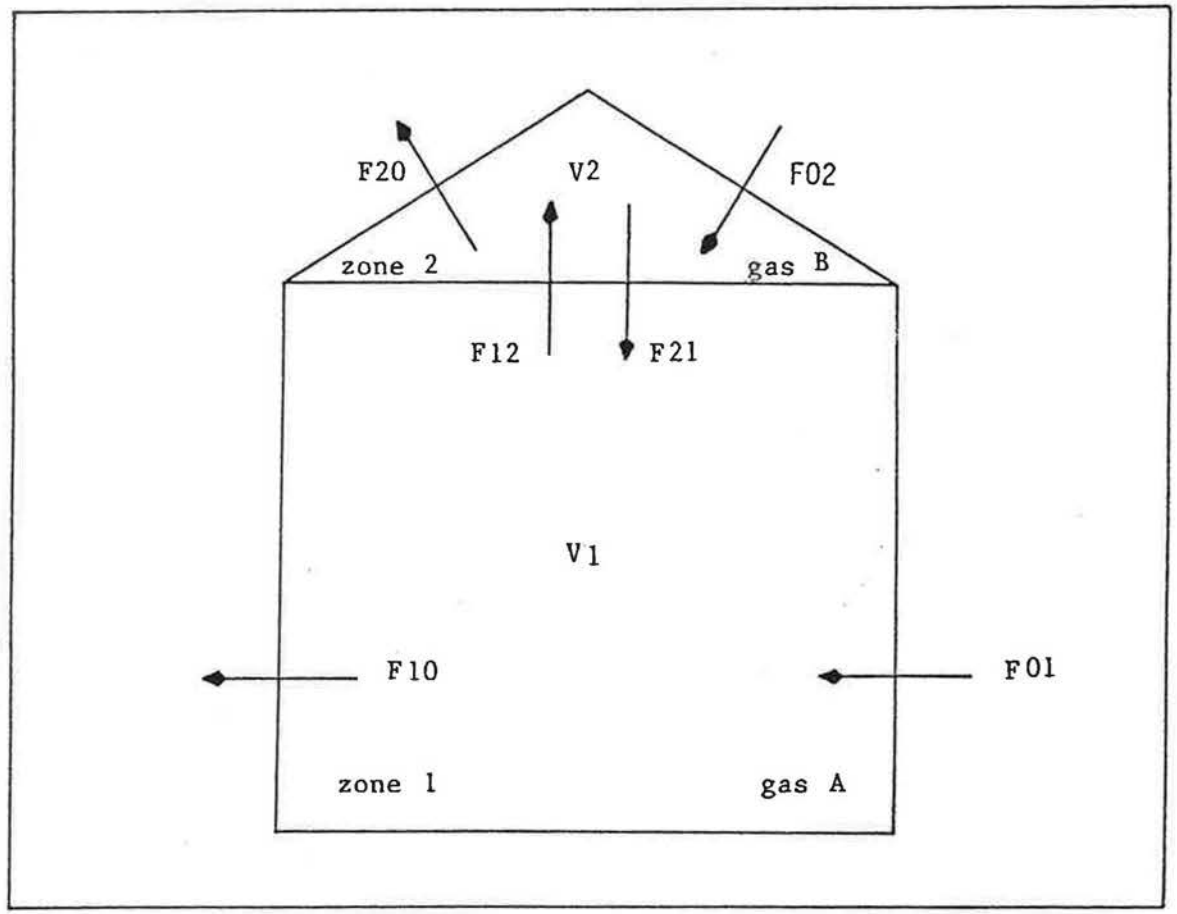


Fig.5 Two interconnecting chambers also connected to outside

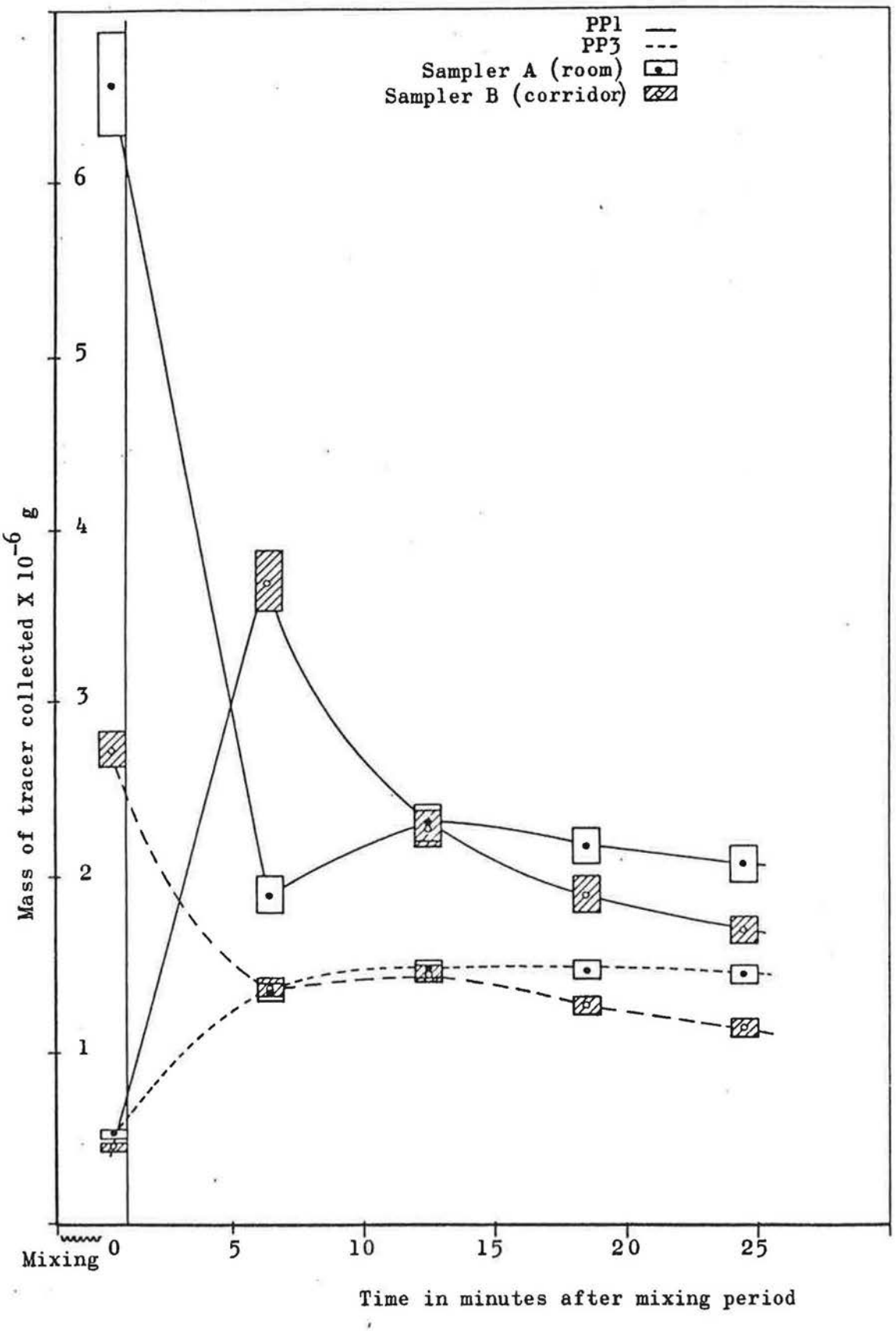


Fig.6. Two zone, two tracer test.

of interconnecting chambers. Using one tracer gas the N^2 equations would have to be generated by using N different time points. In principle it is simpler to use N different gases instead. By measuring concentrations of N gases in each of the N chambers, the necessary N^2 equations may be generated. Using N different gases, it is possible to keep the duration of the experiment short. A single gas measurement may pose considerable problems because of the relatively long time required to conduct it (4). Calculations based on single gas and multi-gas data collected during the work described here show that the use of several gases at once significantly improves the accuracy of interzonal flow rates calculated from measured data (see Appendix A).

I.8.3 TRACER GAS REQUIREMENTS

In order to be used as a tracer, a gas must satisfy the following conditions. It must be:-

1 non-toxic
2 chemically inert
3 of similar density to air to avoid stratification and condensation problems
4 not absorbed by test space materials
5 readily separated from any other tracers used simultaneously
6 easily quantified in low concentrations
7 of negligible background concentration
8 colourless and odourless; undetectable by occupants of the test space

The choice of a tracer gas or set of gases must coincide with that of a suitable analysis method. Some good reviews on tracer gases and their analysers have been published (3,5,24). Table 1 shows a summary from these collected reviews which illustrates the different systems which have been used and why in most cases they are unsuitable for the present application.

I.8.4 THE POPULAR DETECTORS

The three main detectors which have been used in tracer gas measurements are the katharometer, the IRGA (infra red gas analyser) and the ECD (electron capture detector).

Table 1 An historical summary of tracer gases and their analysers

ANALYSER	GAS	REFERENCES	COMMENTS
Katharometer (see below)	CO_2	24, 27, 30, 35, 36.	He, H_2 and CO_2 have very different densities to air. Maximum concentrations to avoid stratification are He 1.2%, H_2 1.1% and CO_2 2%. Minimum detectable concentrations are He 300 ppm, H_2 200 ppm and CO_2 0.15%. CO_2 has a high unstable background aggravated by building occupants and non-electric heating systems. Alone, the katharometer can only measure one gas at a time.
	He	9, 25, 30, 34, 39.	
	H_2	30, 38.	
	N_2O	37.	
IRGA (see below)	CO	42.	N_2O and CO are unpleasant because of their toxic properties. The IRGA is limited to measuring one gas at a time. Maximum concentration for N_2O to avoid stratification is 2%, for CO, toxicity is reached at 400 ppm. Detection limits are 1 ppm for N_2O, 1 ppm for CO_2 and 5 ppm for CO.
	CO_2	25, 32.	
	N_2O	93, 26, 32. 40, 41.	
Geiger Counter	^{85}Kr	43, 28.	Radiation is unpleasant in an occupied environment. Gas release is awkward and must ensure non-exposure of the operator. The detector cannot distinguish between different gases.
	^{133}Xe	44.	
	^{41}Ar	45.	
	^{82}Br	45.	
Photoelectric detector	Smoke	46, 47.	High tendancy for particles and smokes to cling on to walls and furnishings. A counter only measures particle size, further indentification requires chemical analysis. Difficult to set up a multiple tracer system with particles. Occupants may suffer allergic reactions.
	KI particles	15.	
Particle counters	Smoke	10.	

Table 1 continued:-

ANALYSER	GAS	REFERENCES	COMMENTS
Ultra-violet absorption	Ethylace-toacetate Acetyl-acetone	81.	At the concentrations necessary for a ventilation measurement, both gases have a detectable odour.
Colorimetric analysis	CS_2 TBH	81.	CS_2 is highly toxic and has an unpleasant odour. Tertiary butyl hypochlorite is a highly unstable, explosive substance. Lidwell and Lovelock have used it in 50% solution with the highly toxic solvent carbon tetrachloride.
Change of pH on absorption by hydroxylamine hydrochloride	acetone	31.	Highly quantitative absorption of gases in chemical media is essential. Problems arise if several gases are to be used simultaneously. They must all be trapped efficiently in the same medium and have different responses to say, ultra violet, or atomic absorption colorimetric analysis.
Colorimetric analysis	NH_3	48.	Ammonia is toxic with a maximum working concentration (OSHA value) of 50 ppm and a detection limit of 1 ppm.
Hygrometer	H_2O vapour	49.	H_2O vapour has high and variable background concentrations. It condenses and is absorbed by walls and furnishings. H_2O vapour concentration is difficult to measure accurately

Table 1 continued:-

ANALYSER	GAS	REFERENCES	COMMENTS
Gas Chromatograph and ECD (see below)	SF_6	2, 17, 25, 50, 51, 52, 53, 54, 56, 57, 58, 59, 60.	SF_6 is stable, inert and non-flammable. It can be measured in concentrations as low as 1 pp 10^{13}, and is commonly used in concentrations between 5 and 30 ppm. It is non-toxic even when a major constituent in air. The detector unit requires frequent calibration to maintain sensitivity. Minor leaks in regulator valves and connections which would go unnoticed with other gases are totally unacceptable when SF_6 is used as an indoor tracer. Problems with the detector are described below.
Gas Chromatograph and ECD (see below)	Freon 12 Freon 114 BCF SF_6 and Freon 12	1, 15, 16. 55.	Freon 12 (dichlorodifluoromethane) and Freon 114 (dichlorotetrafluoroethane) are commonly used as refrigerants and have a measureable background concentration. BCF (bromochlorodifluoromethane) is a fire extingusher.
Gas Chromatograph and ECD	PFCs PFCs and SF_6	61, 62. 63, 64, 65.	Perfluorocarbons were chosen to replace SF_6 as a meteorological tracer when SF_6 reached a measureable level in the atmosphere. The perfluorocarbons used, are chemically inert, non-toxic, of low background concentration and are readily detected by ECD. Several may be used simultaneously.
Gas Chromatograph and ECD	PFCs	66, 67, 68, 69.	Rubber plugs in the detonators of commercial explosives are impregnated with PFC which is then emitted slowly over a period of five to ten years. Special detection apparatus incorporating an ECD may be used in aeroplanes, at customs points and important meeting places to check for the presence of clandestine explosives.

I.8.4.1 THE KATHAROMETER

The katharometer measures the thermal conductivity of a mixture of tracer gas in air. The instrument is essentially a Wheatstone bridge circuit with arms consisting of platinum filaments in small gas-filled cells. Two of the cells are filled with a reference gas and two are open to the sample under examination. A current through the bridge raises the filament temperature by about 15 °C. The exact temperature, and so the resistance of the filament, depends on the rate of loss of heat in the cell. Clearly this depends on the thermal conductivity of the gas surrounding the filament, which is proportional to the gas concentration.

I.8.4.2 THE IRGA (INFRA RED GAS ANALYSER)

Most heteroatomic molecules absorb infra red radiation. By measuring the transmission of radiation at a suitable absorption frequency and through a fixed path length, the concentration of one gas in another may be determined. In practice, the transmission is compared with that of gas contained in a reference cell.

I.8.4.3 THE ECD (ELECTRON CAPTURE DETECTOR)

The electron capture detector was developed by Lovelock (70,71,72,73). It relies on the ability of certain molecules to absorb electrons. In the ECD, the carrier gas flowing constantly through the detector is ionised by a radioactive source which forms the cathode of an electrode pair. A small potential is applied between this and the anode in the form of a parallel plate or a cylinder surrounding the cathode. The applied potential is just sufficient to collect all the electrons and ions created and so a standing current is produced which is amplified and shown as the base line on a chart recorder. When an electron capturing substance enters the chamber, electrons are absorbed from the standing current by one of the reactions:-

$$AB + e^- \longrightarrow (AB)^-$$

$$AB + e^- \longrightarrow A + B^-$$

This results in a decrease in the ion current which may be observed as peaks on the chart recorder. In order to obtain positive peaks it is

necessary to change the polarity of the amplifier or the recorder.

The ECD is sensitive only to molecules containing atoms or groups of high electron affinity such as halogens, carbonyls, nitro groups and condensed ring aromatics. It has a low sensitivity for non aromatic hydrocarbons. The linear range is 1 : 1000 from the minimum detectable level which is 10^{-12} - 10^{-8} for chlorinated pesticides.

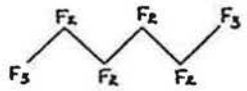
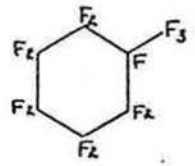
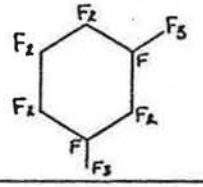
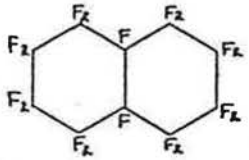
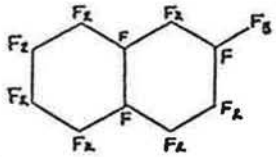
I.9 CHOOSING THE TRACER GASES

The major problem here is to find a set of gases which are all similar to air and each other in their transport properties but which differ sufficiently to allow their separation and measurement. The more gases which can be found, the greater the scope of the method.

Very few multi tracer studies have so far been done, and most of them have used only two or three gases. Foord and Lidwell (16) used Freon 12 (dichloro-difluoro-methane) and Freon 114 (dichloro-tetrafluoro-ethane) with BCF (bromo-chloro-difluoro-methane) to follow air flow in a hospital. Rubin and Gittins (17) used the same gases in a similar experiment. I'Anson et al (1) used these gases in a house. Alexander et al (32) used N_2O and CO_2 in a house. Clements (Ed) (63) used C_8F_{16}, C_6F_{12}, $^{13}CD_4$, $^{12}CD_4$ and SF_6 in a meteorological study.

Dietz et al (66,67,68,69) have developed a system where they can label certain types of explosives by impregnating the rubber seal incorporated as part of the blasting cap, with various perfluorocarbons (fully fluorinated hydrocarbons). The impregnated gas is then emitted at a rate proportional to its concentration in the rubber. The presence of desorbed gas may then be detected using a sensitive electron capture detector (71) and so clandestine explosives for use in terrorist activities, such as bombing important buildings and hijacking aircraft, may be found before any damage has been done. Several of these gases are available and they all exhibit suitable tracer gas properties as listed in I.3. The only problem which may arise would be due to the high densities of perfluorocarbons relative to air which may result in condensation, absorption by test space materials or stratification. However, it has been shown in the course of this work (section II.B) that these effects are negligable for the gases which have been chosen, at the concentrations used. Table 2

Table 2 Perfluorocarbons tested for use in this work

TRADE NAME	CHEMICAL NAME	FORMULA	MOLECULAR WEIGHT	BOILING POINT
PP1	Perfluoro-n-hexane		338	57°C
PP2	Perfluoromethylcyclohexane		350	76°C
PP3	Perfluorodimethylcyclohexane		400	102°C
PP5	Perfluorodecalin		462	142°C
PP9	Perfluoromethyldecalin		512	160°C

shows the gases which were donated by ISC Chemicals Ltd for testing. They are all liquids at room temperature which makes them convenient to transport.

All the compounds except PP9 obeyed the conditions of I.8.3. PP9 was discarded because it was not of sufficient purity to make it useful as a tracer gas. Due to the extreme conditions under which it is made, several impurities were found including a high concentration of PP5. A chromatogram (Fig 7) illustrates the separation of all five gases on a suitable column. PP9 consists of a mixture of small peaks which would be difficult to quantify. The other compounds were all sufficiently pure to allow their simultaneous use as tracers.

The two peaks which correspond to PP5 arise from its cis and trans isomers.

I.10 TRACER GAS RELEASE

The release can be made in one of two ways,either as a single injection for a measurement of concentration decay or as a continuous injection for the constant emission rate, transfer index and steady concentration methods (I.6). See sections I.6.2 to I.6.5.

The idea of impregnating a suitable rubber with tracer (66,67,68,69) is attractive because it would be a very elegant method of gas release. The rubber could be placed in the zone of interest and left to emit its contents at a measured and steady rate. There are two major problems associated with this. Firstly, there would be considerable difficulties in sizing rubber emitters to make sure that they all emit their tracer at suitable and similar rates (the amount of gas liberated within a given time is a function of the rubber surface area and temperature). Secondly, calculations using data extrapolated from Senum et al (69) indicate that even if the rubber were to be kept in contact with the liquid (ie saturated, and emitting at its maximum rate) the rate of emission is prohibitively slow where a flame ionisation detector is to be used in the analysis (see section II.A.5.2). An alternative method for continuous gas release would be to have a slow bleed from a pressurised container with a small fan to promote mixing of the gas with air (16). A major disadvantage is the need to run the fan continuously which may affect the flows being measured. Cylinders of the perfluourocarbons to be used here are not

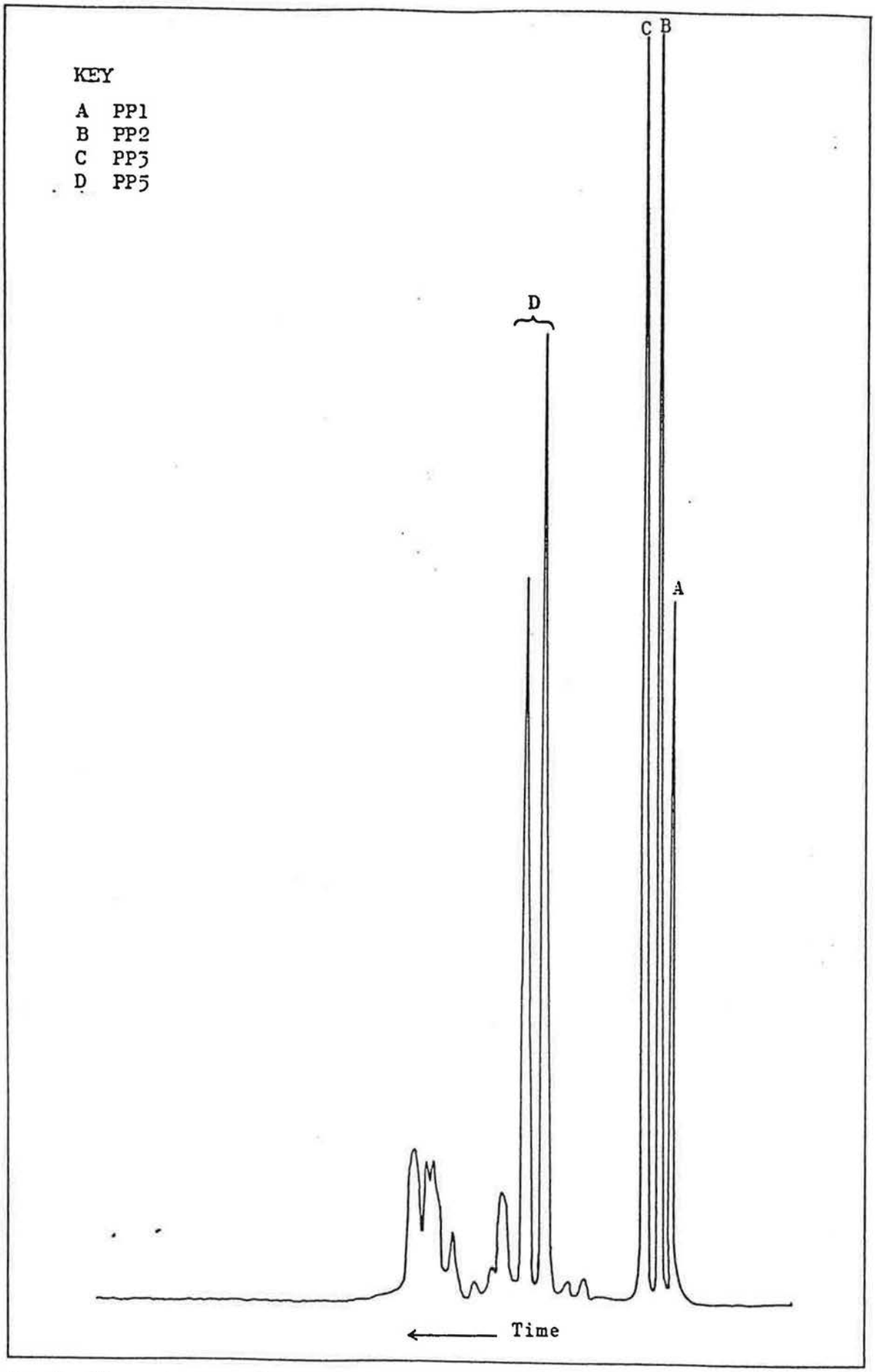


Fig.7 Chromatogram showing separation of PP1, PP2, PP3, PP5 and PP9

commercially available.

Another alternative is to drop each liquid on to a heated surface for an instantaneous release. The advantage to this method is that it is simple to set up and use. It is the method used most in this work although in section IV a constant emission rate method with equilibrium gas concentration measurement has also been developed and tested.

I.11 TAKING SAMPLES

A sampling system must be devised which will enable an accurate estimation to be made of tracer gas concentrations at different points in space and time. Many of the standard tracer gas measurements involve direct sampling and real time analysis. This requires analysis equipment to be portable and on site. In a multi-tracer experiment, constraint is put on the minimum interval between samples which will depend on how long each analysis takes. This may be as long as five minutes (1).

Several methods are available for non-real time experiments and these include collection in mylar sampling bags, in spring loaded, gas tight syringes (74), in evacuated glass bulbs or by the principle of gas adsorption on a solid adsorbent.

An important point here is that it should be easy to transport large numbers of samples from sampling points to the laboratory for analysis. The large volumes occupied by samples collected in bags, bottles, or syringes makes the use of these methods impractical. By contrast, a solid adsorbent is usually in the form of a high surface area powder which may be contained in a tube the size of a pen. This is not a new technique for collecting gases; activated charcoal for instance, has been used in gas masks for years. However, over the last 20 years more adsorbents have come on the market, most with affinities for particular classes of compound. They tend to be aromatic co-polymers many of which are familiar as support materials used in the packing of chromatography columns. Some workers have specifically investigated the sorption properties of several sorbents and compared their efficiencies (75,76,77,78,79).

There are two ways of liberating the gases from adsorbents for

analysis. The first is by dissolution in a suitable solvent such as CS_2 (carbon disulphide) followed by chemical analysis. The second is by thermal desorption. The main disadvantage of the CS_2 method is that the solvent itself is very poisonous, presenting a hazard to the analyst. It is also very difficult to make sure that solvent desorption is 100% efficient and so analytical errors are likely. Thermal desorption is much safer to carry out. Gas can be quantitatively desorbed from the adsorbent and swept directly into a gas chromatograph for separation and analysis.

Perkin-Elmer have recently developed an automatic thermal desorber ATD50 which is microprocessor controlled and may be programmed to desorb up to 50 samples unattended. The adsorber tubes which are used in this work are packed with ~ 440mg Chromosorb 102 which is a divinyl-benzene / styrene co-polymer.

I.12 ANALYSIS

Having desorbed the collected gases from the adsorber tubes, it is necessary to separate and analyse them. The best way to do this is to use a gas chromatograph. This should be fitted with a suitable column and detector. A column temperature programme and carrier gas flow rate have to be found which will separate the gases in a mixture and a detector must be chosen which will give a quantitative electrical response to be plotted on a chart recorder. Practical details and chromatographic theory are given in Section II.A.5.

I.13 SUBSEQUENT CHAPTERS

The rest of the work is divided into three main parts. This follows the form which the work took. In Section II the initial development of the new multi-tracer gas decay method is described with details of the prototype gas release and sampling systems. The experiments carried out using the prototype equipment in a Polytechnic office led to further funding and further development work. Part III describes modifications made to the sampler increasing its sampling capability and steps taken to automate the tracer release, sampling, analysis and data collection using a BBC microcomputer. Experiments carried out with the modified method are described for several buildings. Part IV describes a constant tracer gas release method with continuous passive sampling which was developed as a result of understanding gained from

working with the tracer decay method. Experiments carried out using the constant emission method in two different houses are described.

All the experiments are treated separately from each other. The description of each experimental method is accompanied by a discussion of its results which are presented in graphical and tabular form.

II DEVELOPMENT AND USE OF THE PROTOTYPE MULTI-TRACER GAS TECHNIQUE

II.A METHOD AND APPARATUS

II.A.1 PROTOTYPE TRACER GAS RELEASE

The tracer gases are liquids at room temperature (I.9 Table 2). They are released by dropping a measured volume from a syringe on to a 250W heater at 160°C (Photo 15).

II.A.2 THE SAMPLING SYSTEM DESIGN

Following the liberation of a set of tracer gases in a set of interconnecting zones, a sampling system must take air samples from which the concentrations of the different gases may be determined showing how they vary from place to place over a time period. To allow for collection of samples simultaneously at each sampling point and also in a sequence it is necessary to perform analyses at some time after all the samples have been taken. By using the principle of gas adsorption on a solid adsorbent it is possible to collect samples in a conveniently small volume which makes transport to the analytical equipment relatively easy. From this outline the essential features of the sampling system could be defined.

Stainless steel tubes packed with a known amount of adsorbent are of central importance in the design of the sampler. All adsorbents have the capacity to take up gases passively as well as actively when air is forced over them. It is thus essential to control the exposure of the tubes by sealing them into an airtight holder. The back end leads to a pump which allows for forced sampling. On the front there is a solenoid valve which remains closed at all times except when the tube is to take a sample. To allow concentrations to be measured over a period of time several tubes each with a control valve are placed at each sampling point.

II.A.3 PROTOTYPE SAMPLING SYSTEM DESIGN

Fig.8 shows a schematic of the prototype sampling system and Fig.10 shows a single sampling point. Five adsorber tubes were joined to a manifold by identical lengths of nylon tubing. The nylon was made as short as possible to keep the exposed ends of the tubes close

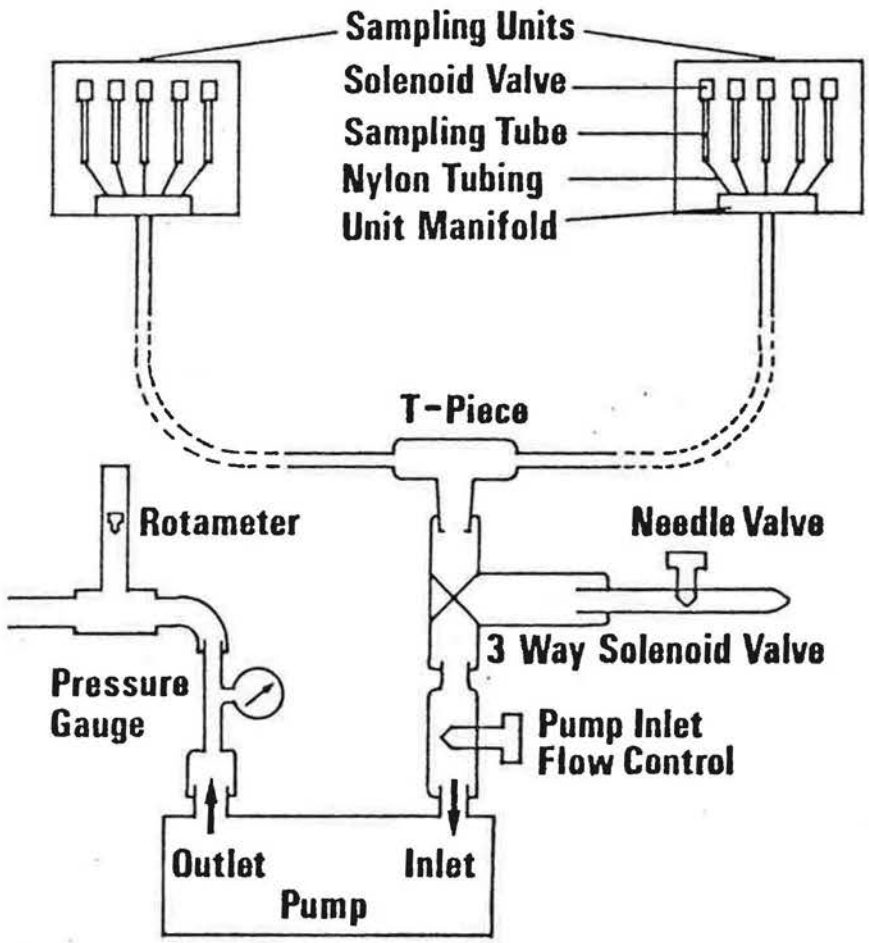


Fig.8 The prototype sampling system

together, minimising the area over which samples were collected. The lengths were the same to ensure that each adsorber tube would present the same resistance to sampling air flow as the others.

From the sampling unit manifold another piece of nylon tubing led to another manifold in the form of a T piece which joined the sampler to a second unit and the pump. The lines to the pump manifold were the same length as each other and long enough to allow the sampling units to be placed in any position required within the building. A three way solenoid valve between the pump manifold and the pump allows air to be drawn from atmosphere surrounding the pump when no sample is required. By placing a needle valve on the 'atmosphere' inlet to the three way solenoid valve the rate of flow of surrounding air into the pump can be made equal to the corresponding flow through the sampling tubes. By doing this, the pump may run continuously without the risk of a 'surge of air' being produced at the beginning of a sample due to the formation of a partial vacuum. This also should prevent the packing of a tube from being drawn too tightly against its retaining gauze which would seriously affect its gas flow and adsorption properties (Fig.9).

A pressure gauge and a rotameter were connected to the pump outlet to allow the sample volume and pump action to be monitored. Although the sample volume cannot be measured directly in this way, it may be obtained from a knowledge of the sampling rate and the time for which the sampling tube is exposed. An electric switch was connected to the solenoid valves so that the exposure of sampling tubes may be controlled.

II.A.3.1 CHOICE OF COMPONENTS

In this section all of the components making up the prototype sampling system are described in a logical sequence from the solenoid valves at the front of the adsorber tubes to the flow meter at the pump outlet.

<> Sampling point solenoid valves

Ten two port solenoid valves were supplied by Western Automation Ltd. at the following specifications: brass body; 24 volts DC; 1/8" orifice; Rc pipe fitting and urethane seat (to minimise absorption of perfluorocarbons). The valves are normally closed, opening when

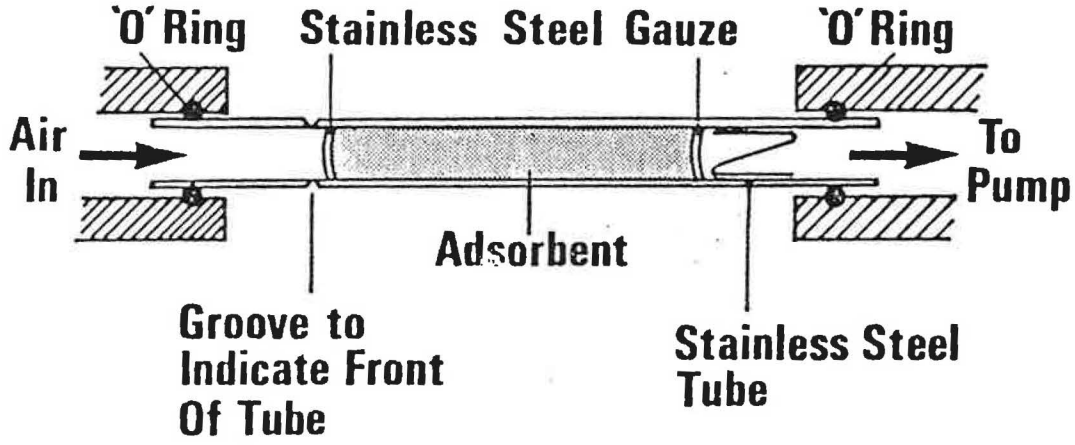


Fig.9 A single sampling tube

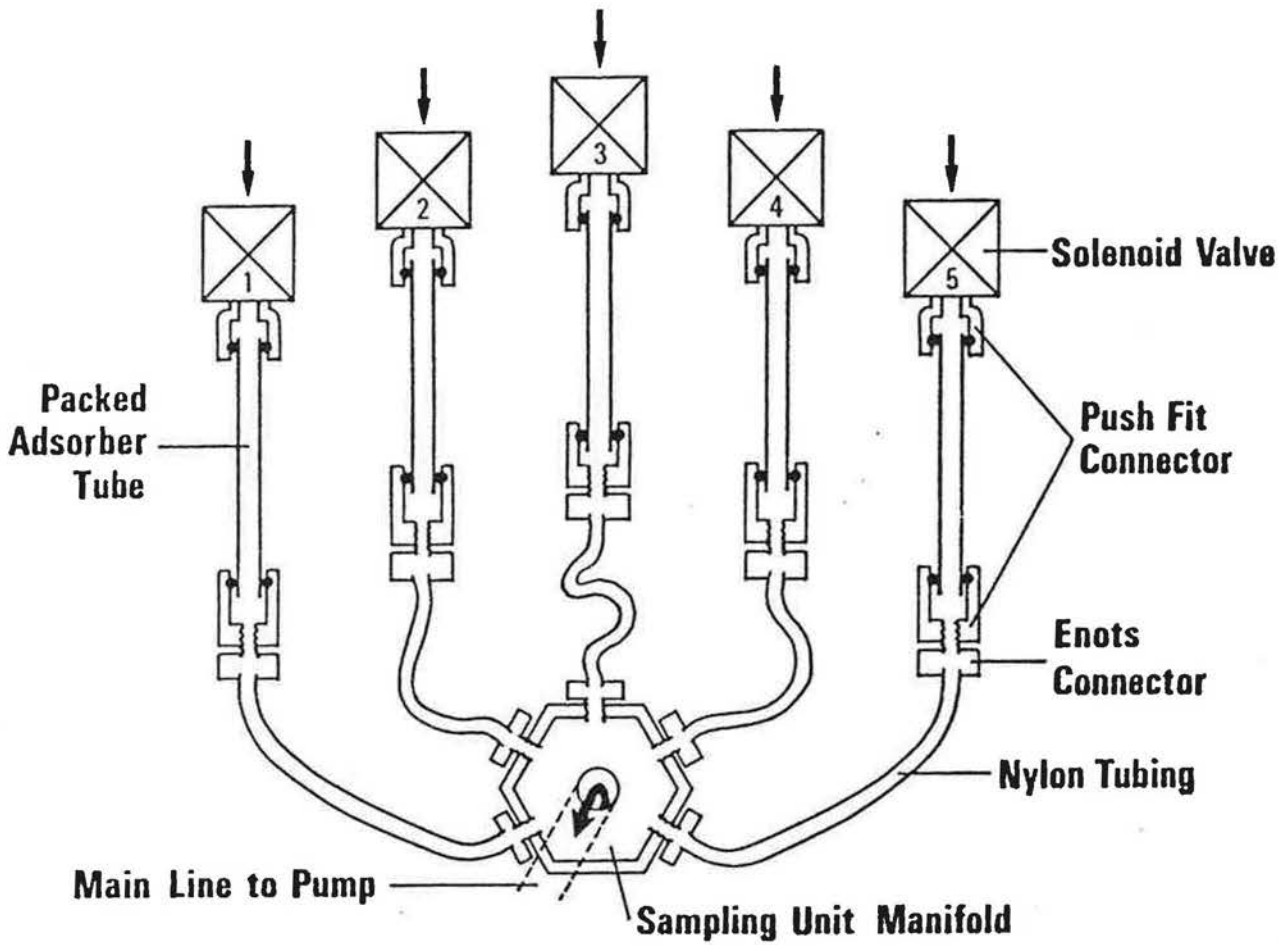


Fig.10 Detail of a sampling unit

energised.

<> Adsorber tubes

Adsorber tubes designed to be compatible with the Perkin-Elmer ATD50 automatic thermal desorber (Section II.A.3.1) were obtained from Perkin-Elmer Ltd. Each tube assembly consisted of an empty tube with a retaining gauze at the front end, a separate gauze for placing behind the packing material and two blank end caps for sealing when not in use (Fig.11). For a description of the packing method see Section II.A.3.5. The packing material used in this work was Chromosorb 102 60-80 mesh, supplied by Phase Separations Ltd.

<> The adsorber tube holders

The original design involved the use of a metal sleeve which was made in two parts and fitted tightly round the adsorber tube. The front joined the solenoid valve and the back led to the sampling unit manifold. The design was faulty and is described in more detail in Section II.A.3.3 with reasons for its failure. Modifications were made to the design until a satisfactory alternative was found. The new design took the form of push fit connectors working on the same principle as the sealing caps and the special caps for use during thermal desorption. The new design is also described in section II.A.3.4.

<> Manifolds

The sampling unit manifolds were made in the Polytechnic workshops from hexagonal steel bar drilled out to form a hollow centre and tapped and threaded at 1/8" bsp on five of the six sides (Fig.11). In the base a sixth hole was made and threaded. Finally a plate was cut from the same hexagonal bar and brazed on to form the closed manifold with inlets at five of the sides and one at the top so that the resistance to flow due to the presence of the manifold would be the same for each tube.

<> Nylon tubing and connectors

All the flexible connections between adsorber tubes, manifolds, the pump and the flow meter were made from nylon tubing 8 mm o.d and

5 mm i.d. There was some concern over choosing a suitable flexible

Table 3 Results of tests for adsorption of perfluorocarbons by plastics

PLASTIC	PERFLUOROCARBON	EXPOSURE TIME	% WEIGHT CHANGE
Nylon	PP1	12 weeks	-0.5
	PP2		-1.8
	PP3		0.4
	PP9		0.3
Polypropylene	PP1	12 weeks	0.1
	PP2		0.9
	PP3		0.0
	PP9		0.1
Polyethylene	PP1	12 weeks	0.0
	PP2		0.0
	PP3		-0.2
	PP9		0.3
Silicone rubber	PP1	12 weeks	3.0
	PP2		7.4
	PP3		1.5 - 3.9
	PP9		0.0

material because many, such as conventional rubber hose and silicone rubber have a high absorption affinity for perfluorocarbons. It is important that none of the perfluorocarbon tracers should be removed from the sampling point by any means other than air movement. The zone end of each sample tube is isolated by the solenoid valve, but the pump side remains open to the connecting pipework which is made of non-absorbing metal and nylon.

ISC Chemicals Ltd. (80) have carried out tests in which various plastic materials such as silicone rubber, polypropylene, polyethylene and nylon hae been observed during exposure to PP1, PP2, PP3 and PP9.

The PP9 used in this test is heavily contaminated with PP5. For this reason results of absorption tests using PP9 are regarded here as if only PP5 were present. ISC Chemicals Ltd. did not carry out tests on PP5 itself. Each plastic was immersed in all of the perfluorocarbon liquids at room temperature for twelve weeks. The extent of absorption by the plastic is expressed as a percentage weight change. Results are shown in Table 3.

The negative values for PP1 and PP2 indicate a leaching of the plastic by the perfluorocarbon. The small values for absorption and the severe conditions of the test compared to conditions during the use of the sampler, suggest that there should be no absorption losses detectable using either nylon, polypropylene or polyethylene. The tracer gas is always at a small concentration (of the order of a few ppm) in the air and the nylon tubing is usually only exposed to it for a few hours. The longest exposure used in this work was four days. (See Section III.B.4). Compared to the amount of gas collected during sampling by the tube packing material any passive absorption by the nylon tubing is negligible. Whatever the flexible tubing chosen, it is essential to have a reliable means of fixing it to the other parts of the sampling system. IMI Enots Ltd. have developed a brass push-in tube fitting (Fig.12) suitable for use with nylon tubing. The tubing is pushed into the brass collet where it is tightly held, sealing being achieved by a nitrile 'O'ring. The connectors have been designed for working at high pressures but the tubing is sufficiently rigid to allow their use under a modest vacuum. A set of brass connectors and compatible nylon tubing were supplied by John Tullis of London.

<> The T Piece

The T piece joining the two sampling lines consists of two rods of circular section drilled and tapped to fit Enots connectors. The upright of the T has been shaped to fit the bar and is brazed on (Fig.13). This was made in the Polytechnic workshops.

<> The Pump Solenoid Valve

A three port solenoid valve was obtained from Western Automation Ltd. to allow the pump to run continuously. Specifications: 24 volts DC; 3/64" orifice; 1/4" Rc pipe connection and a Buna N rubber valve seat.

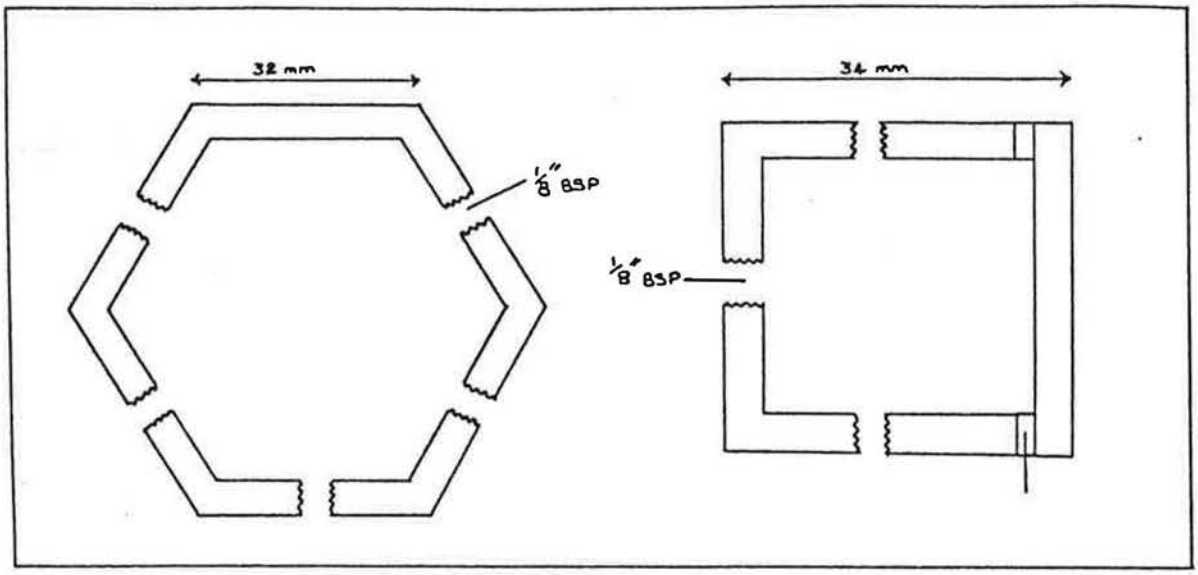


Fig.11 Sampling unit manifold

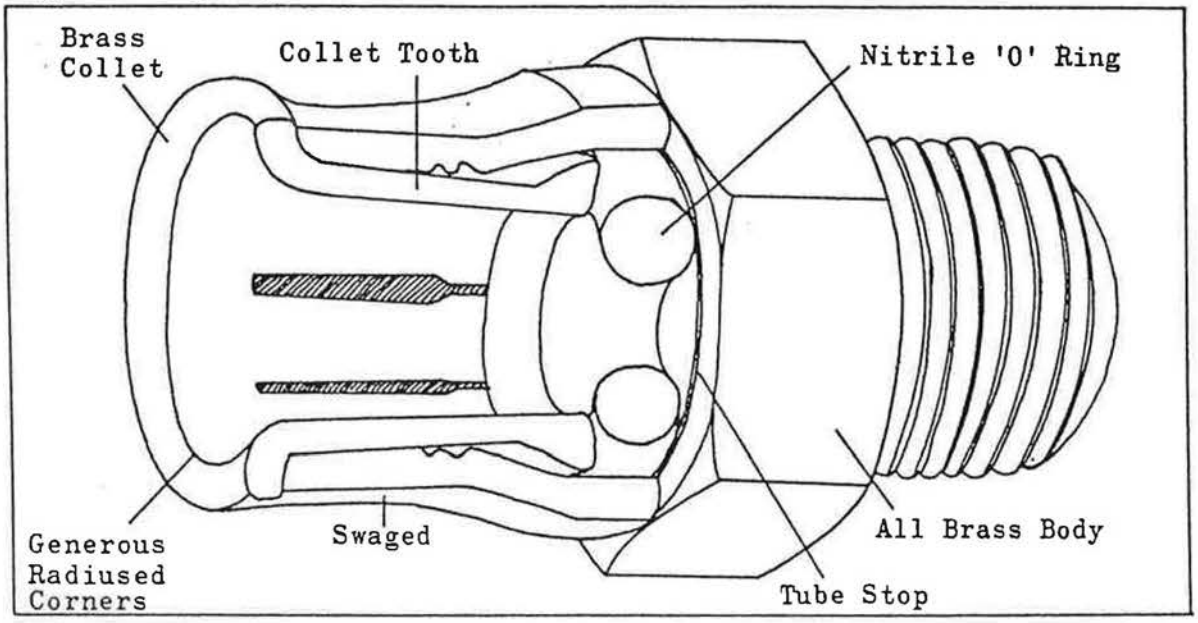


Fig.12 Enots brass connector

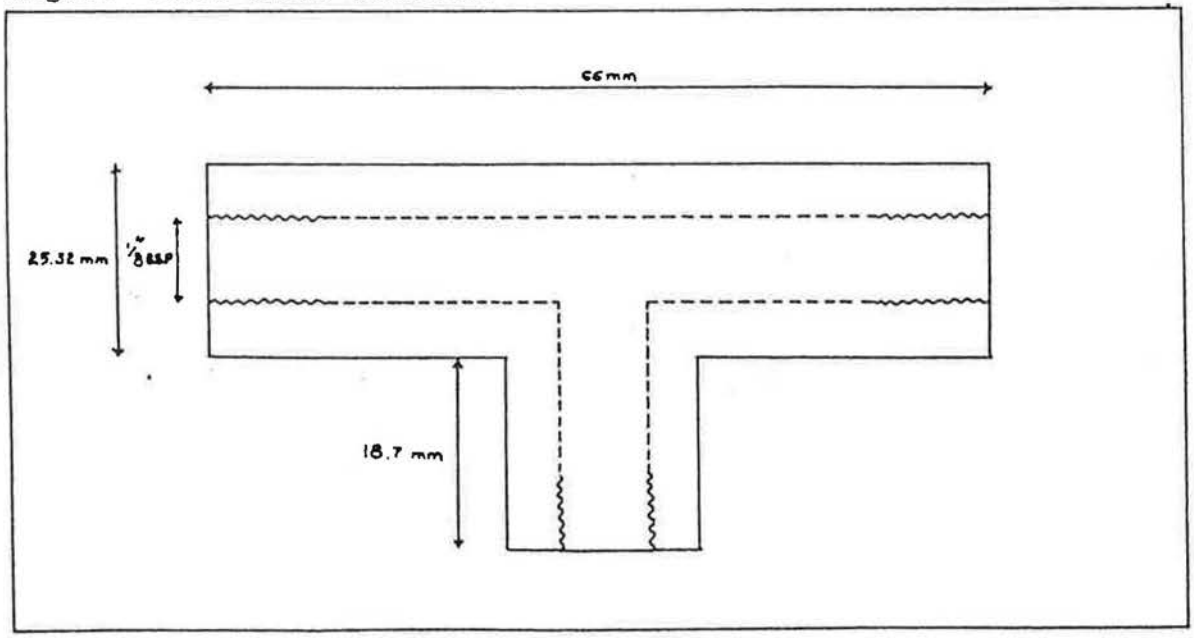


Fig.13 T piece

The valve works in the universal mode such that when energised, air is drawn from the sampling units and when de-energised air is drawn from the surrounding atmosphere. The needle valve placed on the atmosphere inlet to the valve is of unknown make.

<> Stopcock

A 3/8" bsp thread needle valve was supplied by W H Wilcox of London to cut down the excessive air flow into the pump (see Photo 3).

<> The Pump

A Compton Series 4 Type D/617 pump was supplied by Dawson McDonald and Dawson. It was thought at first that a powerful pump would be needed to overcome the large resistance to flow presented by the packed adsorber tubes during sampling. Initial tests however, showed that this pump was too big for the job to be done and a valve at the inlet (see stopcock) was used to cut down the flow. The tests involved pumping air through some typical packed tubes. It was found that without flow restriction, the packing was pulled hard against the retaining gauze and flow properties were disrupted.

<> Pressure Gauge

A 0-30 psi pressure gauge was obtained from C A Norgren Ltd. to measure the pressure build up in the pump during sampling (see Photo 4).

<> Flow Meter

A small needle valve was prepared in the workshops to aid the use of the flow meter. By using the fine control to build up a slight (1 psi) back pressure at the pump, irregularities of flow due to the action of the pump were smoothed out and an improved estimate of the true flow rate could be made (see Photo 1).

<> The Electronic Controller

The valves are operated manually from the electronic controller (Photo 2) to expose the tubes in pairs, one at each sample point. Samples are thus taken simultaneously at each point and in a timed sequence

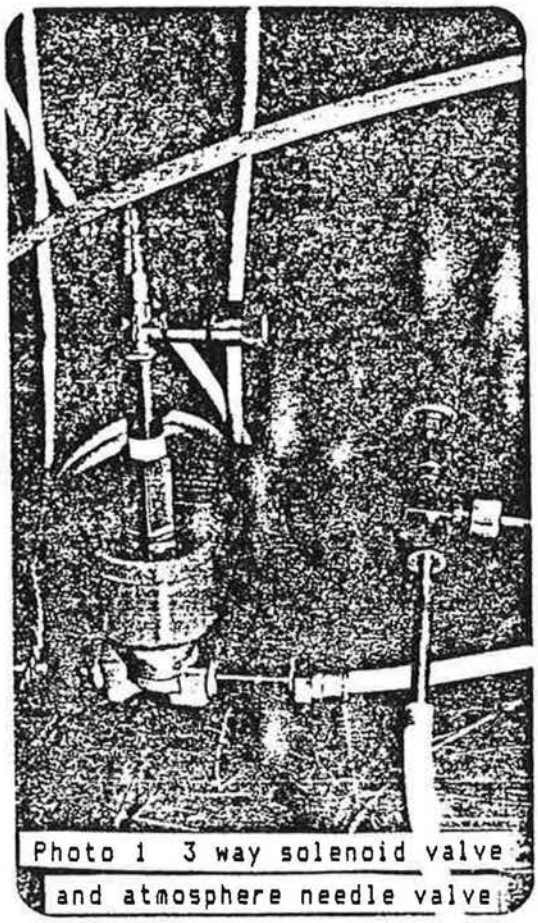


Photo 1 3 way solenoid valve and atmosphere needle valve

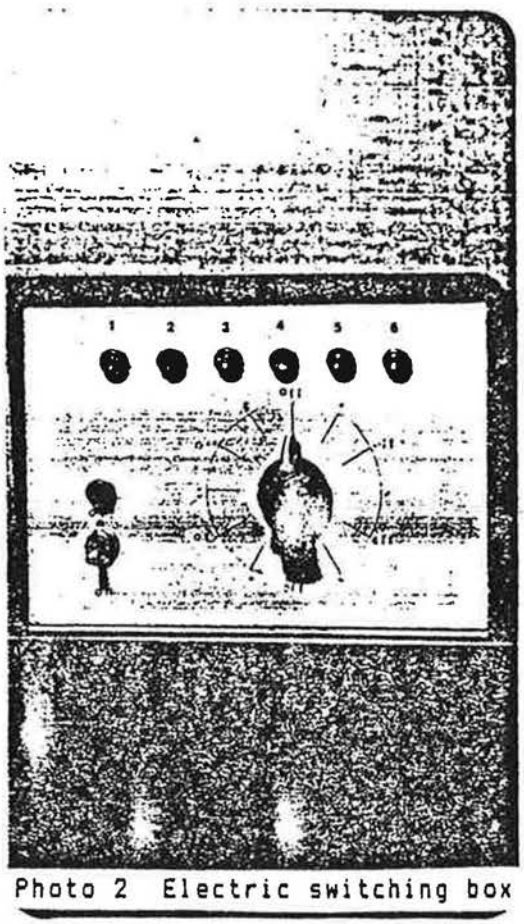


Photo 2 Electric switching box

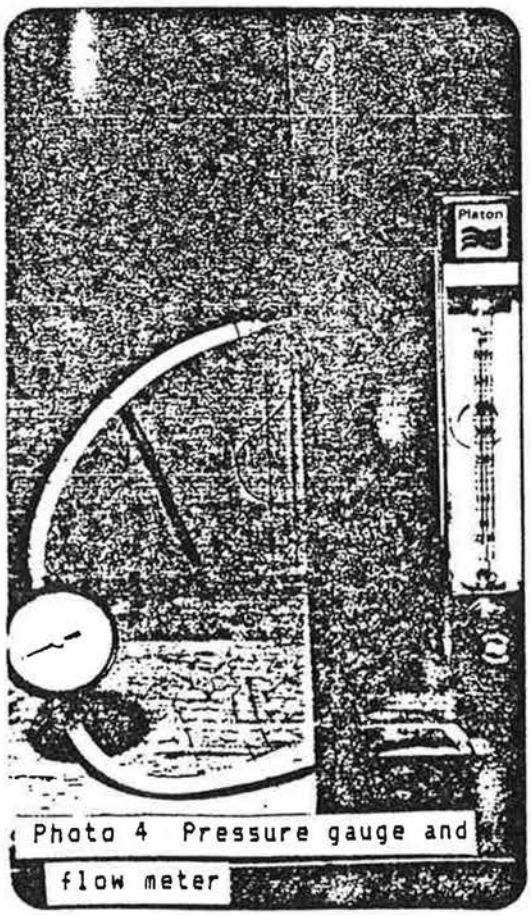


Photo 4 Pressure gauge and flow meter

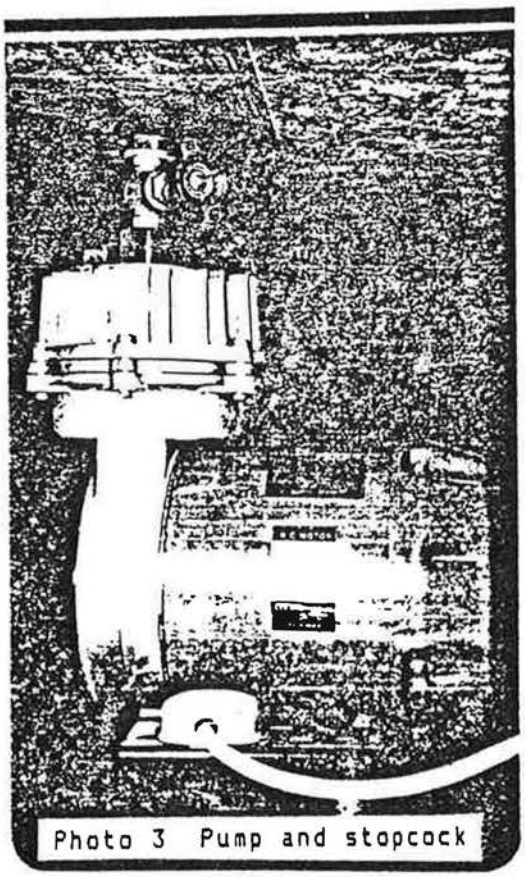


Photo 3 Pump and stopcock

from 1 to 5. Fig.14 shows a circuit diagram for the switch.

Table 4 Flow Meter Calibration

FLOW SETTING	TIME TAKEN 500 ml	FLOW RATE
500	69.6 70.0 70.0	431 ml min^{-1}
400	91.2 90.8 91.2	320 ml min^{-1}
300	123 123 125	242 ml min^{-1}
200	193 196 196	154 ml min^{-1}

A six core cable joins the switch to each sampling unit.

<> Adaptors

Various adaptors have been made in the Polytechnic workshops to allow connections to be made between components of different sizes and to enable the further use of nylon tubing wherever necessary. All have been made from hexagonal or circular section which has been drilled out and threaded according to the connections required. In addition to these, a special tool was made to facilitate disconnection of nylon tubes from brass Enots connectors. All of the parts made in the Polytechnic workshops were made of mild steel. To prevent rusting they were all 'blued' by heating to 250 to 300°C followed by quenching in a bath of oil. Each piece was then cleaned by immersing it for fifteen minutes in a beaker of inhibisol in an ultrasonic bath.

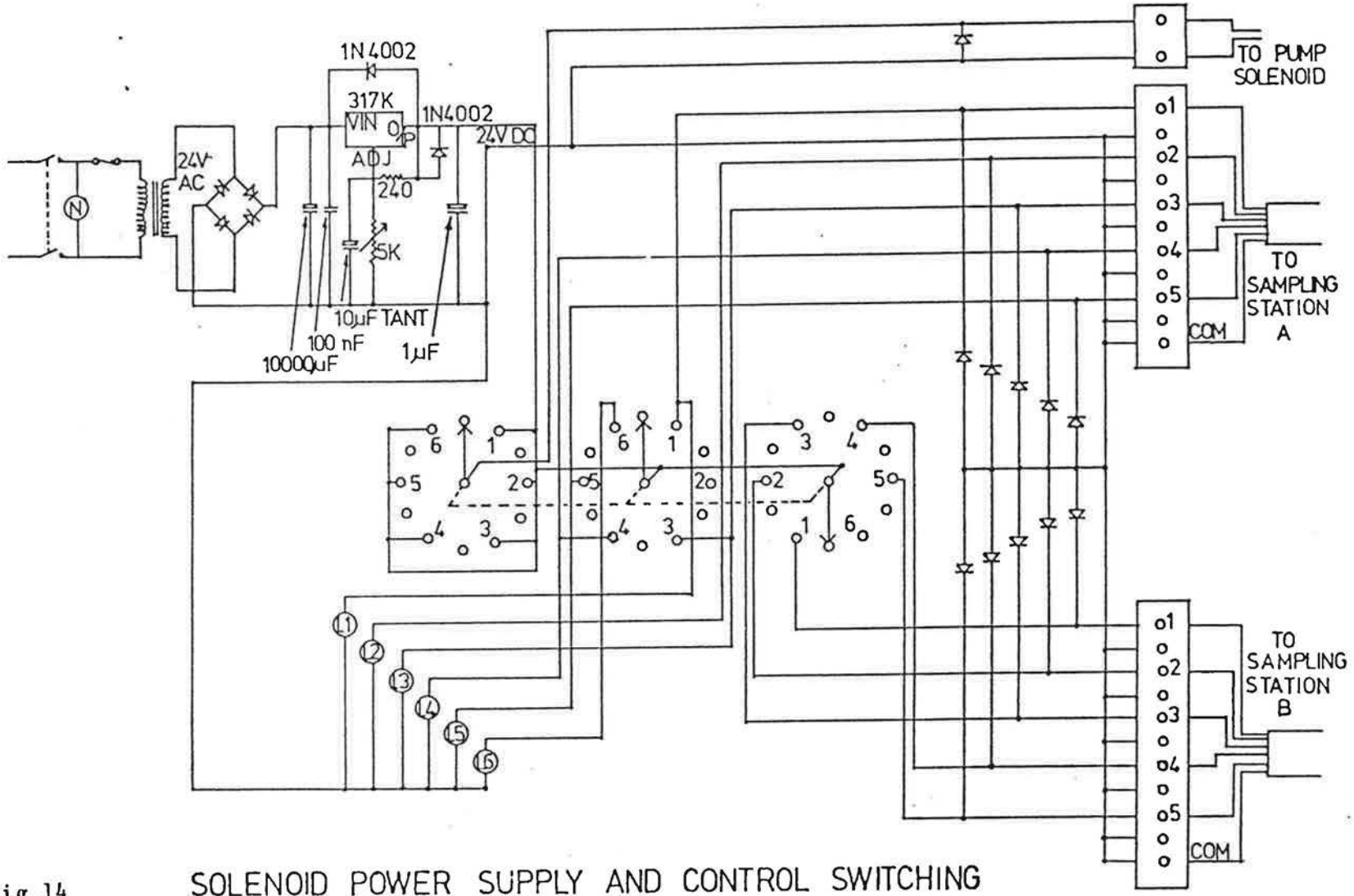


Fig.14 SOLENOID POWER SUPPLY AND CONTROL SWITCHING

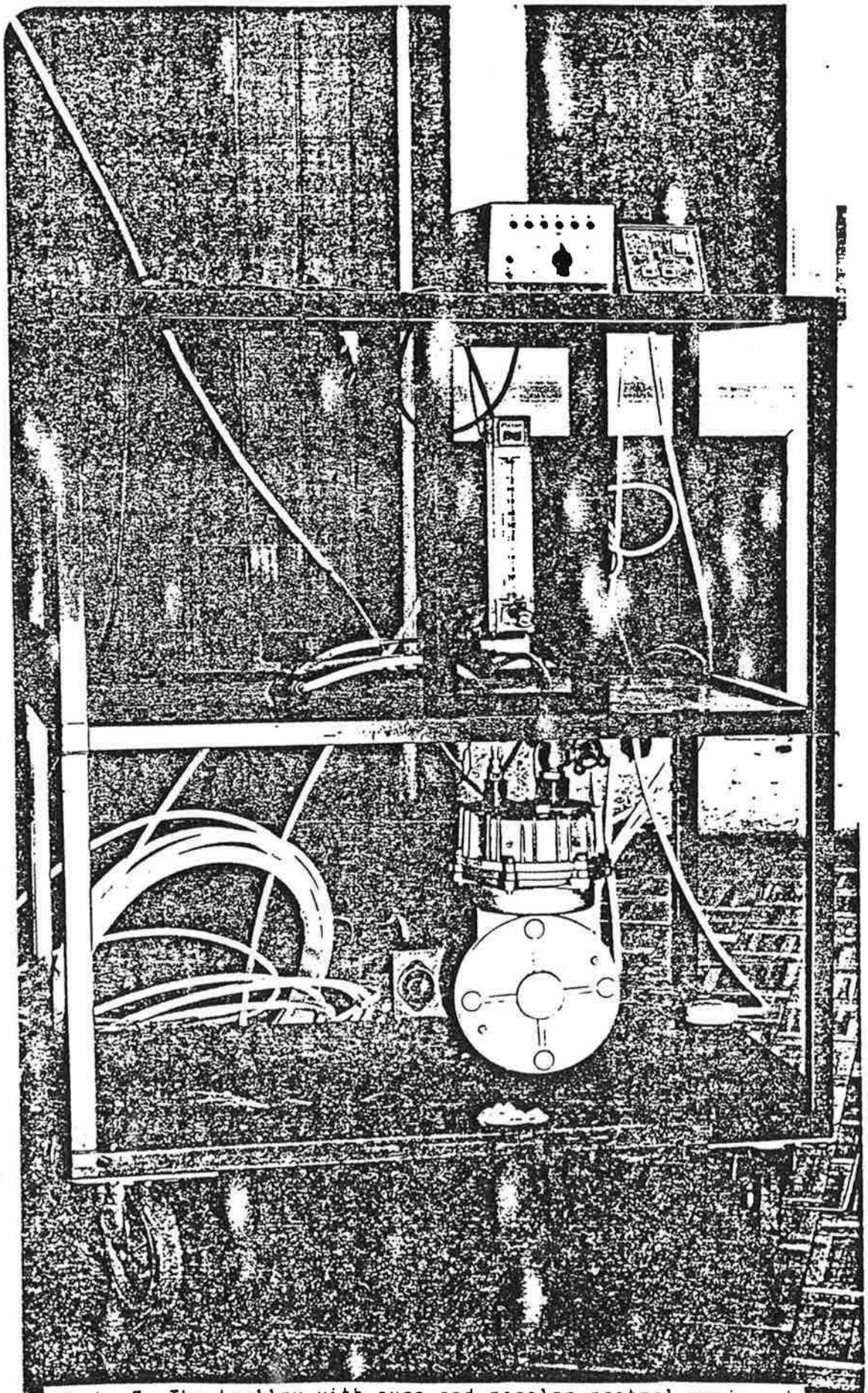


Photo 5 The trolley with pump and sampler control equipment

II.A.3.2 BUILDING THE PROTOTYPE SAMPLING SYSTEM

The sampling system was assembled piece by piece from the pump as a starting point with systematic leak checks at each connection until the sampling units were reached. These were built one at a time. Photo 5 shows the pump and control units on a trolley. The leak checks were made using the flow meter on the pump outlet. At each stage during the building of the sampler the new inlet point to the pump was carefully blocked and the reading on the flow meter noted with the pump on. When this registered zero flow, ie. when the float remained at rest the system was judged to be leak free.

<> Calibration of the Flow Meter

The flow meter was calibrated by measuring the length of time taken for 500 ml water in a volumetric flask inverted over a bucket of water to be replaced with air when the pump was running and the flow meter control valve was set to various flow readings. Time was measured in seconds by a stopwatch. Results are shown in Table 4.

II.A.3.3 THE ADSORBER TUBE HOLDERS

<> Sleeves

The original design consisted of a metal sleeve made in two pieces which fitted closely round the adsorber tube and connected it to the solenoid valve and the rest of the sampling system (Fig.15 and Photo 6). The larger of the pieces fitted into the solenoid valve and the smaller, knurled to make it easy to turn, was fixed to an Enots fitting and a nylon tube leading to the sampling unit manifold. Preparation for an experiment involved sliding an adsorber tube into the front sleeve and adding the second piece by forming a screw connection between them. At first the sleeves leaked at the join of the two parts. This was remedied by adding neoprene 'O' rings to the outside of the screw thread on the front section.

Tests were carried out in a sealed room described later (Section II.B.1). A uniform mixture of PP2 and PP3 was established with the aid of a mixing fan. Following the experimental procedure outlined in section II.A.3.5 samples of air were taken at a rate of 200 ml min^{-1} for a duration of 1 minute at half hour intervals. Four separate

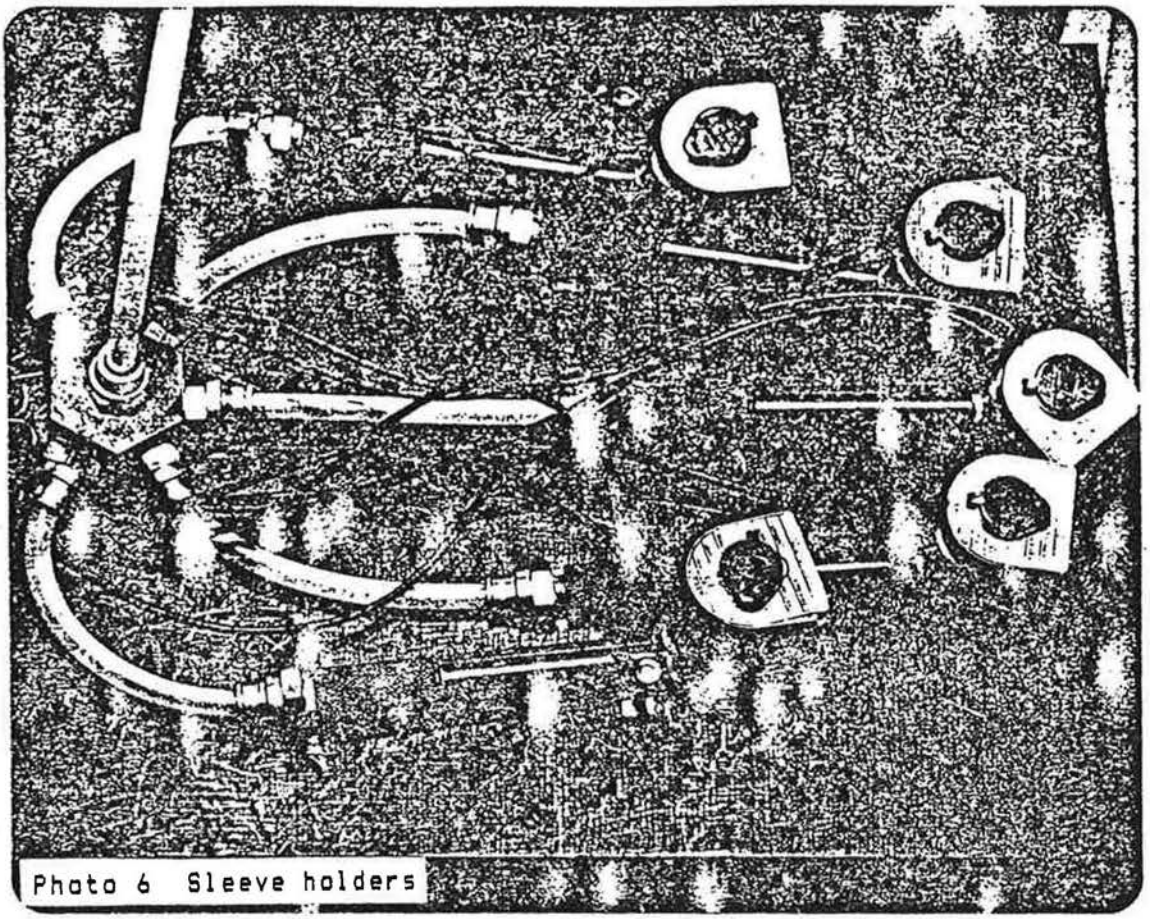


Photo 6 Sleeve holders

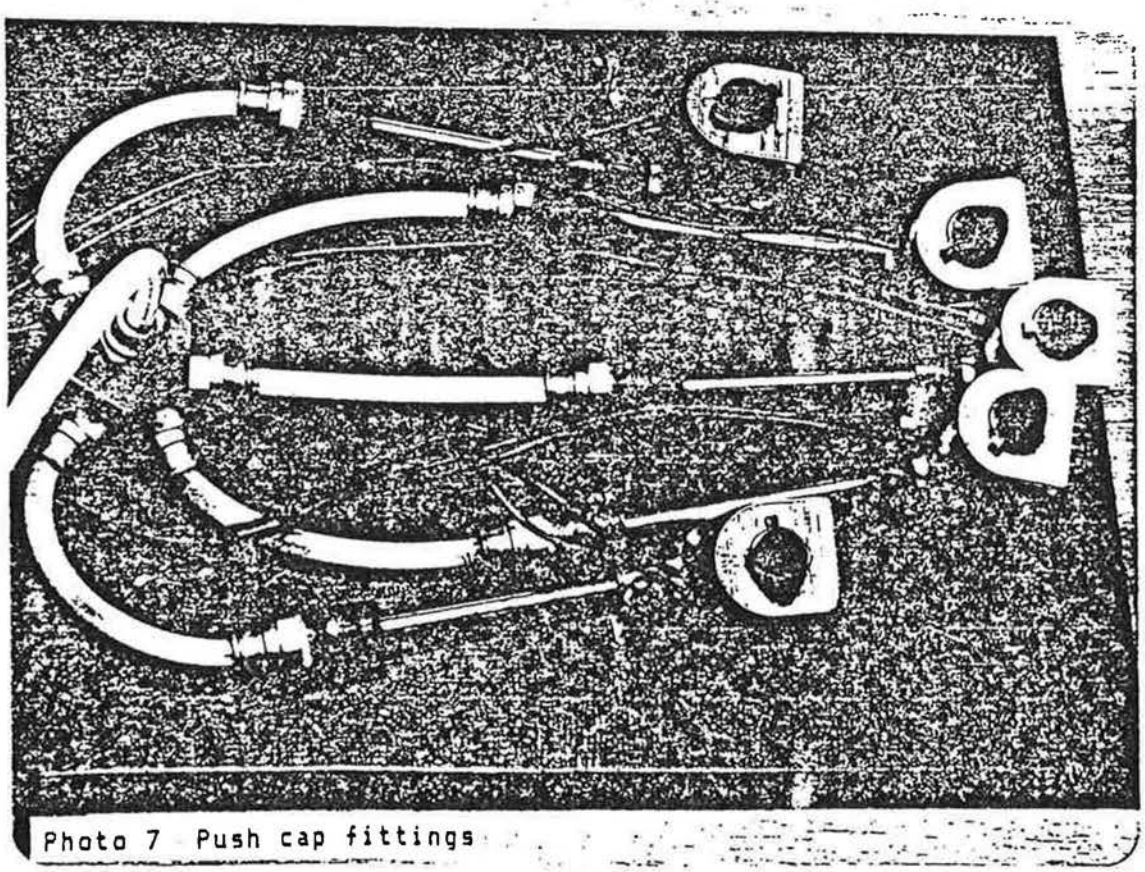


Photo 7 Push cap fittings

experiments were carried out in this way. For two of these, the samplers were placed at the same vertical level, one by the door and one by the window. For the other two, the samplers were placed one above the other in the attempt to observe a room profile. In each case the results show an apparent increase in concentration between the first and second samples (ie. a maximum appears an hour after the tracer gas release). The concentration then drops again at the third sample and in each case except the first profile measurement, remains about the same until the end of the experiment. The unexpected concentration versus time pattern shown by these results cannot be explained in terms of air movement. In a well sealed room with a mixing fan, a tracer gas should reach a uniform distribution very quickly. Any apparent changes in gas concentration would have to be due to one of the following causes:

1) Air leaking out of the room due to imperfect sealing.
2) Absorption by walls and furnishings
3) Chemical reaction with test space materials.
4) A fault in the sampler which results in different volumes of air being drawn through different tubes.

The first three possibilities may be dismissed immediately as they all involve a consistant removal of gas from the test space. If these were to have an effect, the result would be a continual decrease in concentration. Instead there is an apparently large increase in concentration as much as an hour after the gas release. This must be due to the sampling system drawing different volumes of tracer gas through different adsorber tubes. To test this theory an air movement experiment was carried out as before in the sealed room but this time the tubes were exposed in reverse order 5 - 1 instead of the usual 1 - 5. The concentration time pattern which resulted was the reverse of the pattern observed before. It was therefore concluded that the tubes must be imperfectly sealed in their holders.

<> Modifications to the Sleeve

An attempt was made to improve the sealing of the adsorber tubes by inserting cork rings at the back end of each sleeve. Laborious tests were necessary to ensure that each cork was acting as a seal before an experiment could be carried out. The results showed a considerable improvement, but the corks tended to be susceptible to damage during

insertion, and by the adsorber tube inside the sleeve. It would be very inconvenient to have to change and test some, or all of the seals after a test and it is not possible to test the quality of the seals once the adsorber tubes have been loaded.

A completely new design was required for the connection of the adsorber tubes to the rest of the sampling system which would give repeatable and high quality sealing of the tube and which would allow for the speedy installation and recovery which is required during tracer gas tests.

II.A.3.4 PUSH FIT CONNECTORS

During storage the packed adsorber tubes are fitted with blank sealing caps and during analysis they are fitted with special caps which have a spring loaded ball bearing in the end (see Photo 8). All of these caps form a push fit over the adsorber tubes and are sealed by an 'O' ring contained in a groove near the edge of the cap. The new connectors were to be designed on this principle. A cap to push on to the front of the adsorber tube was designed which would also connect to the solenoid valve. The cap to go on the back was designed to fit on to the brass Enots connectors (see Fig.16 and Photo 7). A groove was cut in each connecting piece to take an 'O' ring the same size as those used in the storage and analysis caps. A set of analytical end cap 'O' rings was bought from Perkin-Elmer Ltd. and these were placed in the new connectors.

The new design means that the adsorber tubes are reliably sealed into the rest of the system so that all the air drawn by the pump comes in at the solenoid valve and passes inside the adsorber tube. Another advantage of the new design is that it has made the insertion and removal of sampling tubes much easier and less time consuming than before.

II.A.3.5 GENERAL INSTRUCTIONS FOR THE SAMPLING SYSTEM

The stepwise setting up of the apparatus for an experiment is best described with a list of instructions:

1) Connect fresh adsorber tubes to the sampling system and note their positions with respect to the sampling unit and solenoid valve, both

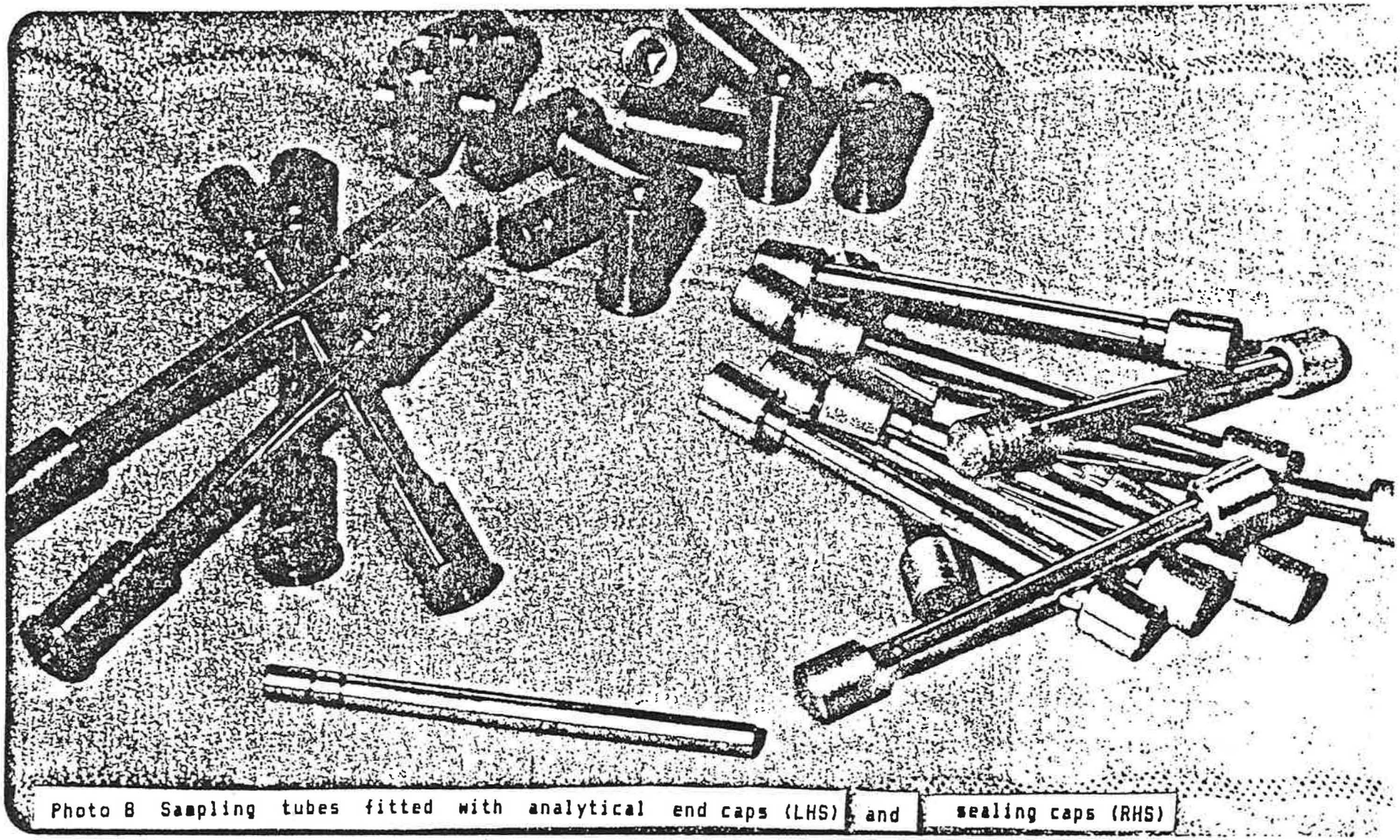


Photo 8 Sampling tubes fitted with analytical end caps (LHS) and sealing caps (RHS)

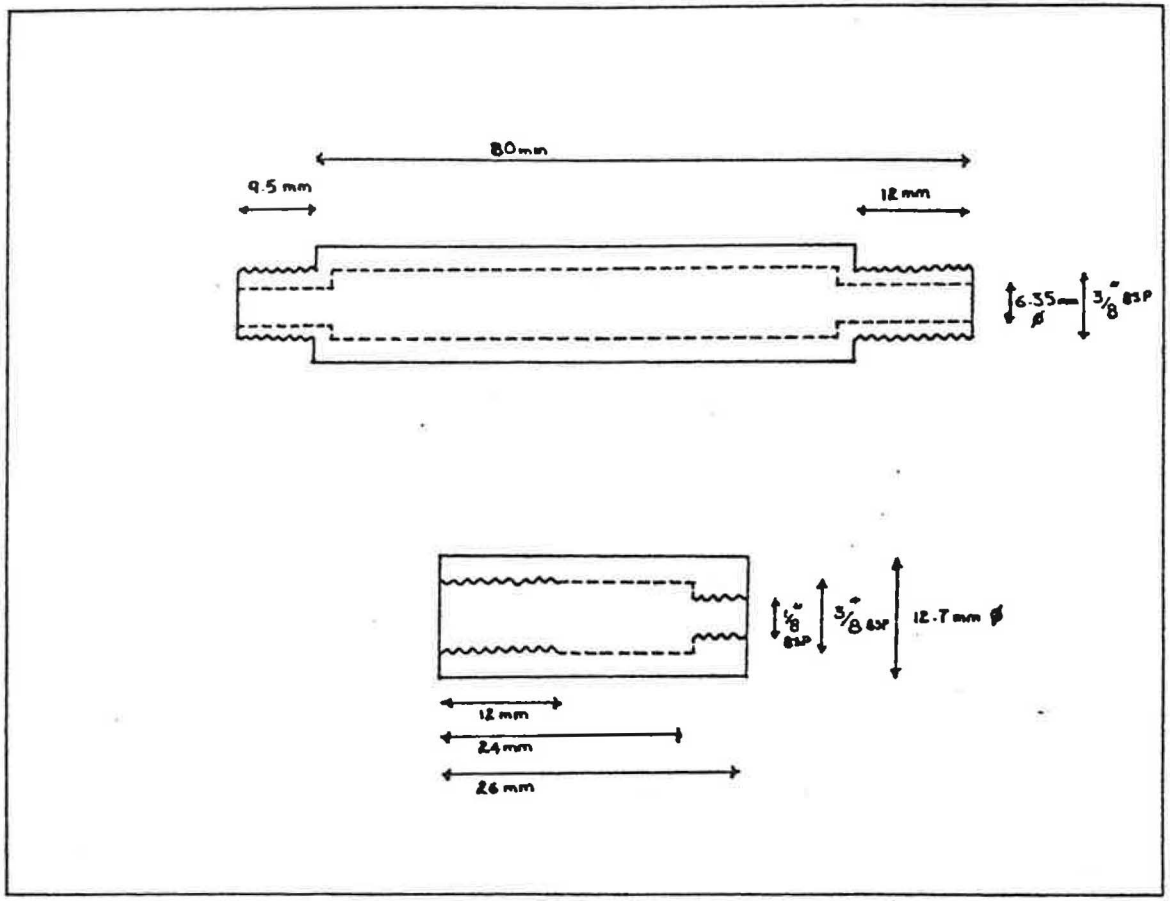


Fig.15 Sleeve Design

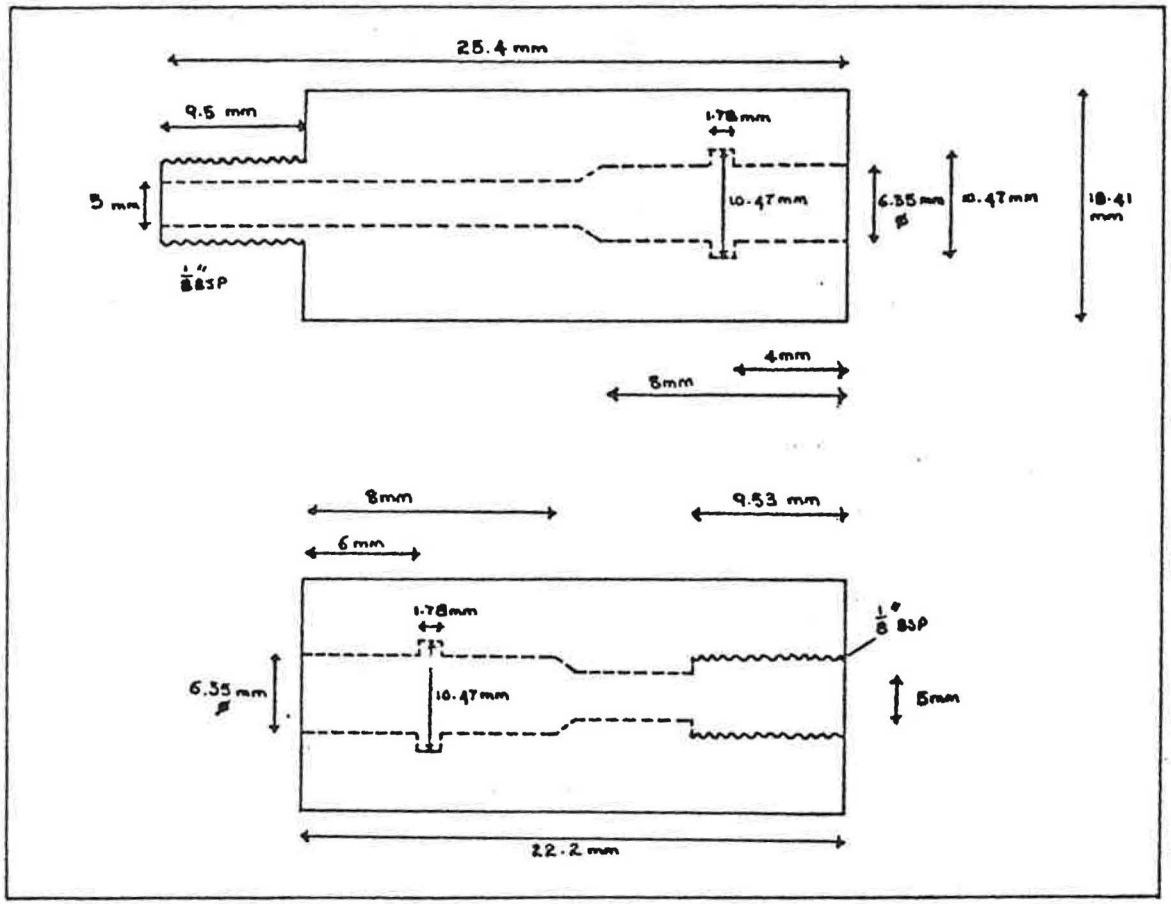


Fig.16 Push Cap Fittings

of which are identified by numbers.

2) Check that all the solenoid valves are working by energizing with the pump OFF.

3) Place sampling units at their sampling points and note their position in the zone.

4) Set up release heaters.

5) Lay sampling lines and power cable for the solenoid valves along the floor to the trolley housing the pump and switching gear.

6) Set up the trolley where it will not interfere with measurements.

7) Set the position of the needle valve on the pump solenoid to ensure that the same flow is drawn from atmosphere as is drawn from the adsorber tubes. To do this, select a typical packed tube for each sampler and keep them solely for this test. Install the chosen tubes in the number 1 position at each sampling unit. Energise the number 1 solenoid valves and switch on the pump. With the fine controller fully open, adjust the flow rate with the pump stopcock until it is about 50 ml min^{-1} higher than desired, then slowly close the fine controller until the flow meter gives a stable reading at the required level. The pressure gauge should now have a steady reading of about 1-2 psi. Now de-energise the solenoid valves and adjust the atmosphere needle valve until the flow obtained with the adsorber tubes has been reached. This procedure ensures that the pump can be allowed to run during an experiment when samples are not being taken without the risk of creating a partial vacuum in the system and disrupting the flow properties of the tubes.

8) Replace the flow balance tubes with fresh adsorber tubes and check that the solenoid valves are working.

9) Switch on the pump with solenoid valves de-energised and leave for a few seconds while the required flow is established.

10) To take a background sample, energise the number 1 solenoids and record the exposure time. Note also the flow rate.

The setting up and testing procedure is now complete. The next set of instructions describes how to carry out a complete air movement test using the prototype system:

1) Drop measured volumes of tracer liquid on to heaters at about 160°C and note the time. Switch off heaters.

2) With any interconnecting doors between measurement zones closed, mix the tracer with room air using a fan.

3) Switch the fan off and the pump on (with solenoids de-energised) about three minutes before taking a sample to allow room air to settle.

4) Take the first sample by energising the number 1 solenoids noting the time of adsorber tube exposure and the flow rate. De-energise the valves.

5) Take subsequent samples in the same way in a timed sequence.

6) At the end of an experiment, remove adsorber tubes from their holders and replace their sealing caps. Switch off electric power.

II.A.4 SAMPLE ANALYSIS

The analytical procedure has three main features, desorption of the gases from adsorber tubes, separation into components and quantitative analysis. A Perkin-Elmer ATD50 automatic thermal desorber is used to reclaim the tracer gases which are then swept into a Perkin-Elmer Sigma 3B gas chromatograph where they are separated and analysed. The gas chromatograph is fitted with a flame ionisation detector and a 4m glass column packed with 5% SE30 on Chromosorb W.HP 100/120 mesh. Each instrument is treated separately with an explanation of why it was chosen and how it was calibrated along with a description of the general operating procedure.

II.A.4.1 THE AUTOMATIC THERMAL DESORBER

The safest and most efficient way of desorbing gases adsorbed on solids is to heat the solid in the presence of a flowing, inert gas. This is done by heating the whole adsorber tube with the adsorbent

inside it. Once a tube has been packed with adsorbent, it may be used many times. Each time it is desorbed for analysis it becomes conditioned for a new test.

Thermal desorption can occur in one or two stages. In the single stage process an inert gas flushes adsorbed gases from the heated sample tube on to the chromatographic column. A heater is clamped round the tube and carrier gas is passed over the adsorbent until the gases of interest have been desorbed. A valve isolating the tube from the injector can then be turned allowing the desorbed gases to be flushed on to the column. In a two stage desorption, the gases desorbed from a tube are collected in either an empty or a packed U tube called a trap. This trap is cooled by placing round it a liquid N_2 bath or dry ice. As the cold trap is heated, the gases are swept on to the chromatography column. The cold trap is always of smaller volume than the adsorber tube and is heated much more quickly. This has the advantage that the sample is swept on to the analytical column as a sharp band of vapour. Thes results in higher resolution of peaks and so improved analytical efficiency.

II.A.4.2 MANUAL THERMAL DESORPTION

The technique of gas desorption by a solid followed by thermal desorption has been available for at least twenty years. Cropper and Kaminsky (82) describe the first experiment to collect a mixture of organic pollutants at room temperature on a solid contained in a glass tube. The tube was later connected directly to a gas chromatography column by silicone rubber tubing and heated with a flow of carrier gas to deposit the adsorbed gases on the column. Parsons (83) and Jarke (84) used manual single stage desorption in experiments to investigate the levels of organic pollutants in the atmosphere. Parsons connected his adsorber tube in place of the U shaped sampling loop of a conventional gas sampling valve attached to the injection port of a gas chromatograph. The adsorber tube was heated with an air bath at 200°C for some minutes and the sample was swept on to the column which was kept at room temperature for the first four minutes before being temperature programmed for separation and analysis. Jarke modified the injection port of a gas chromatograph and attached an adsorber tube. While heating the adsorber tube to about 240°C, carrier gas flushed the sample on to the column.

Other workers have developed two stage manual desorption techniques. Dravnieks (85,86) desorbed gases from an adsorber tube heated to 120°C, into a special low volume hypodermic injector needle which was cooled by liquid nitrogen. The needle was quickly transfered to the inlet of a gas chromatograph where it continued to be cooled by copper blocks immersed in liquid nitrogen. A bellows pump at the end of a line containing a manometer (serving as a system leak detector) and a U tube immersed in liquid nitrogen (previously cleaned by flushing with warm helium) was connected to the free end of the injector needle. The pump drew 1 ml helium from the gas chromatograph, over the sample tube and into its bellows. Sample injection occured when the bellows motor was activated. The cold blocks moved away from the needle to be replaced by preheated blocks at 250°C. The bellows movement pushed the 1 ml helium back along the needle thus flushing the sample into the gas chromatograph (Fig 17).

Zlatkis (87,88) modified the injector port of a gas chromatograph and placed his adsorber tube inside. Contained in the injector block of the gas chromatograph, the adsorber tube was heated with carrier gas flowing over it. A pre-column with a four port valve between it and the analytical column was attached to the injector port. The pre-column was cooled with dry ice whilst the sample was desorbed from the adsorber tube at 300°C for 20 minutes at a carrier gas flow rate of 20 ml min^{-1}. Chromatography was begun after warming the pre-column and transferring the sample to the analytical column.

Novotny (89) attached his charged adsorber tube to the modified injector port of a gas chromatograph and heated the injector block to 240°C, flushing the contents of the tube for five minutes on to the first 15 cm of the analytical column which was cooled by liquid nitrogen. The nitrogen was then removed and the temperature of the oven programmed for the separation required.

Versino (90) connected a charged adsorber tube with a pair of heating plates round it to a U tube connected to a flash heater but cooled in a liquid nitrogen bath. The U tube was connected directly to the inlet of a gas chtomatograph. Compounds were eluted at 250°C within 30 minutes at a carrier flow of 20 ml min^{-1} and collected in the cooled U tube. Flash heating allowed them to be swept on to the analytical column of the gas chromatograph.

Pellizzari (78) has designed a high resolution interface manifold for

thermal desorption of an adsorber tube into a gas chromatograph (Fig 18). In a typical desorption cycle, an adsorber tube was placed in the preheated chamber (225°C) and carrier gas passed through at 20 ml min^{-1} flushing vapours into a gold plated nickel capillary trap. This used valve position A. After the thermal desorption of the adsorber tube, the six port valve was put to position B and the capillary trap was flash heated to carry the sample on to the gas chromatograph column.

The quality of peak shapes and retention values obtained are highly dependant on the thermal transfer between the heaters and the primary and secondary desorption volumes. In general, two stage manual desorption gives a better injection to a gas chromatograph than single stage does. However, where large numbers of samples are involved, the increased number of essential manual operations increases the risk of operator induced errors.

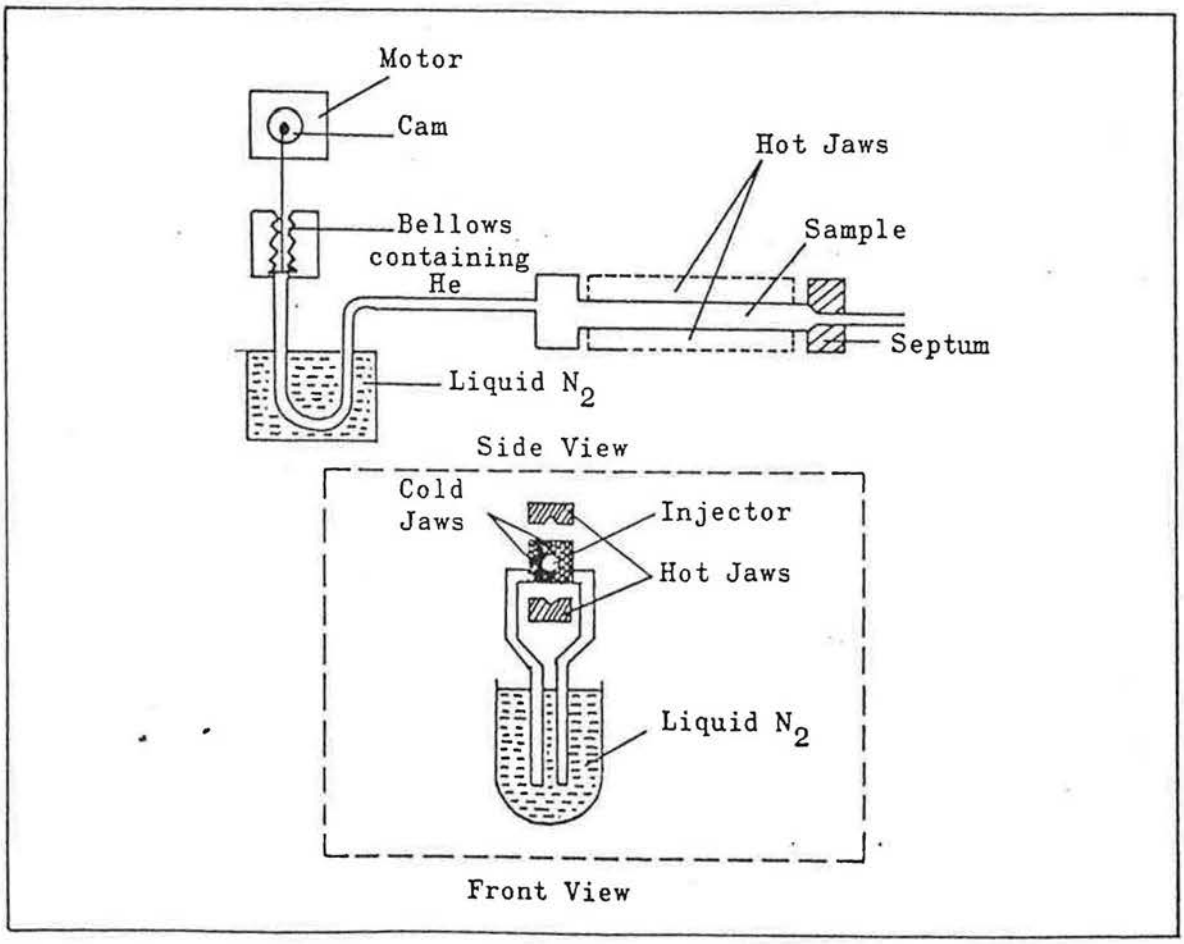


Fig.17 Sample injection apparatus of Dravnieks (85,86)

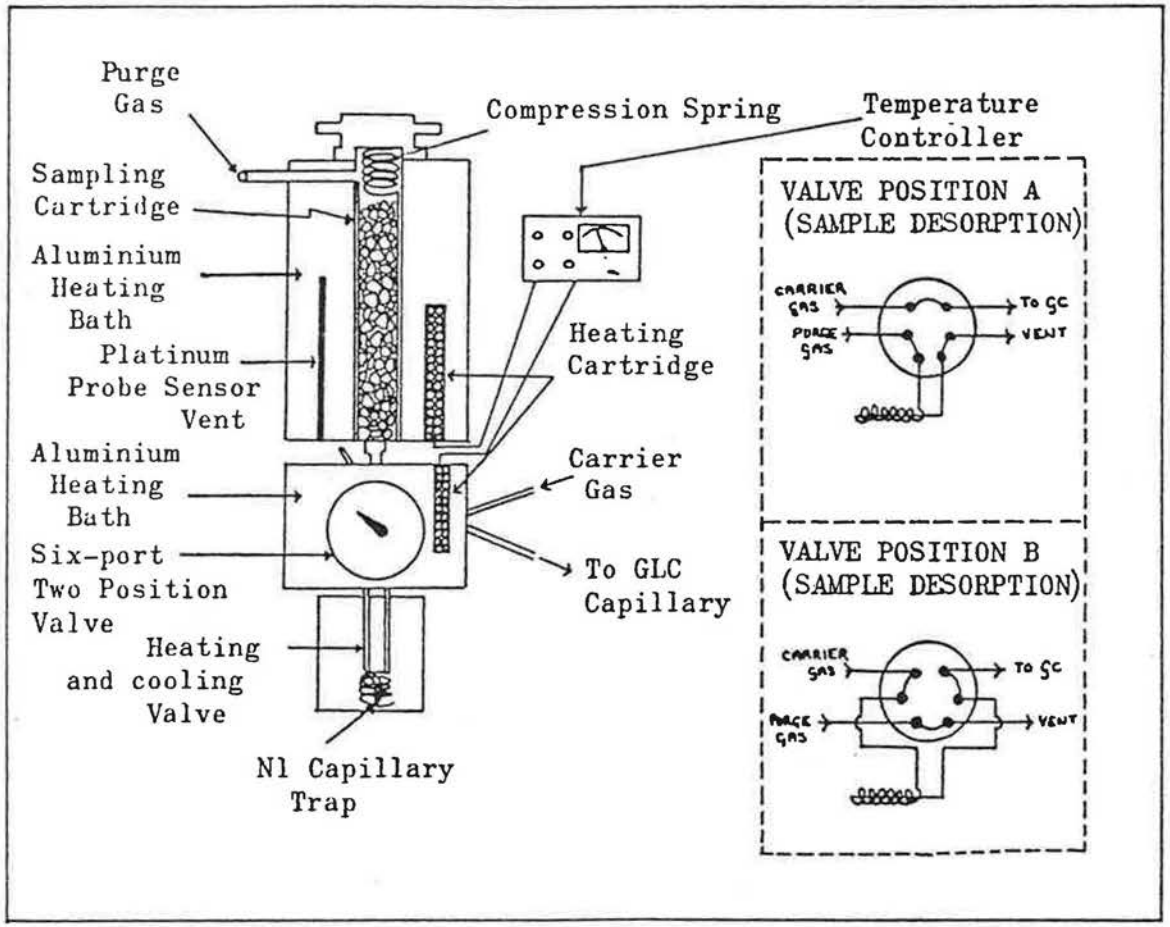


Fig.18 Thermal desorption/ high resolution interface manifold for gas chromatography (78)

II.A.4.3 COMMERCIAL THERMAL DESORBERS

There are now two thermal desorbers on the market which are more convenient than any of the manual methods so far described. The Foxboro Company Ltd. have produced an instrument called The Century Programmed Thermal Desorber PTD 132A. This machine can be programmed to desorb charged adsorber tubes one at a time under operator controlled conditions of desorption temperature and duration. It is essentially a single stage desorber (Fig.19) (91). The charged adsorber tube is placed in an oven which can be heated between 100 and 350°C. Purge gas is drawn through the adsorber tube by means of a sample pump. This works by pulling on a plunger fitted in a box, rather like a large syringe. The sample from the adsorber tube is thus diluted to a volume of 300 ml. Aliquots of this total volume may then be manually or automatically injected into a gas chromatograph for analysis. Several samples may be taken allowing for tests of repeatability. After the necessary number of samples have been put into the gas chromatograph the temperature of the PTD may be raised to 350°C to clean the oven and adsorber tube of any residual contaminants. The storage chamber may be cleaned by flushing automatically with the PTD pump or manually with the chamber piston.

An advantage of this system over all the others discussed so far is the facility for repeat analysis of effluent from a tube. However, the source of this advantage, the dilution to a 300 ml volume results in a severe disadvantage. This is the loss of the concentrating effect of the tube and so the loss of sensitivity of the analysis. If an adsorber tube is used to collect spot samples of air, drawing say 100 ml over 1 minute, dilution to 300 ml after desorbing the gas from the tube would present a sample to the gas chromatograph at one third of its ambient, sampled concentration. In the case of a tracer gas decay experiment this severely limits detection of tracer gases at low levels meaning that relatively large quantities of tracer would have to be released to produce reliable concentration decay data. This instrument would be much better suited to long term, time weighted average experiments where many litres of gas may be drawn through a tube over a period of hours. This is the only way in which the dilution to 300 ml of the tube would not have an adverse effect on the concentrating properties of the adsorber tube. The other commercially available thermal desorber is the Perkin-Elmer ATD50 chosen for this

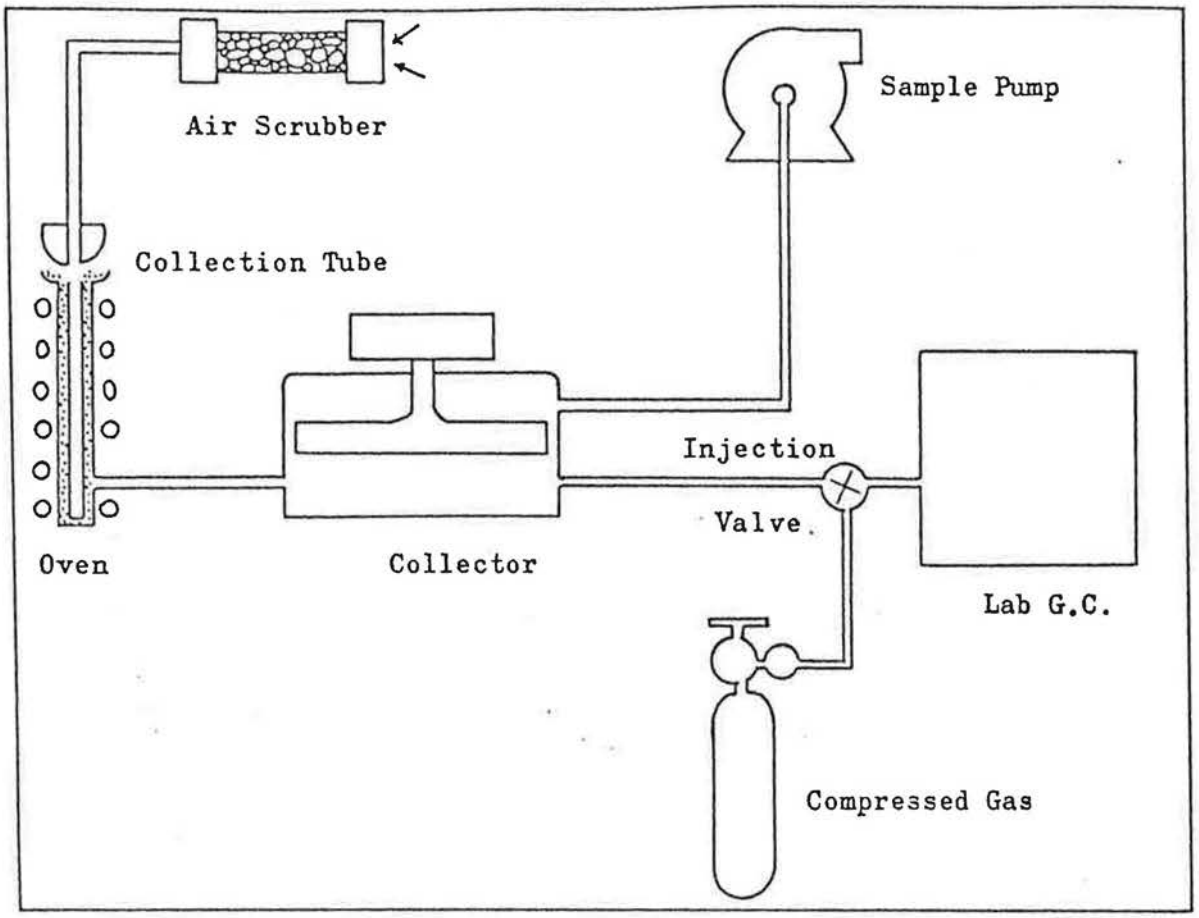


Fig.19 Foxboro Century Programmed Thermal Desorber.

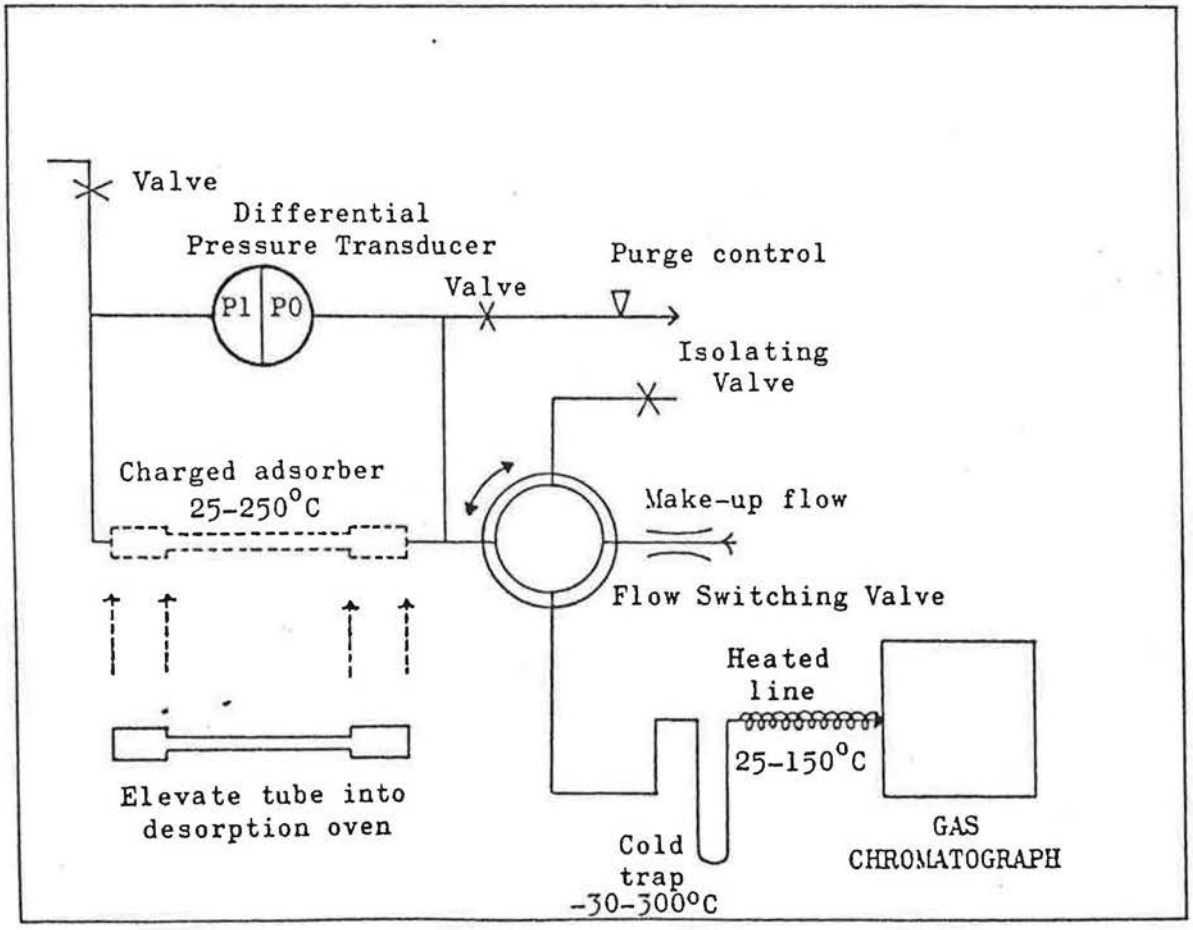


Fig.20 The Automatic Thermal Desorption Process

work and described below.

II.A.4.4 THE PERKIN-ELMER ATD50 AUTOMATIC THERMAL DESORBER

The instrument is a fully automatic, microprocessor controlled thermal desorber. It can desorb up to 50 adsorber tubes unattended and may be programmed for either single or two stage desorption (see Fig.20 and Photo 9).

The principal components of the instrument are a sample turntable which holds the sampling tubes and rotates, presenting them one at a time to a desorption oven; an electrically cooled cold trap (which may also be electrically heated); heated pneumatics and a heated line connecting the outlet from the cold trap to the inlet of the gas chromatograph column. A key pad on the front panel of the ATD50 allows the setting up of various desorption parameters and these are shown on a back lighted display (Fig.21). A battery inside the instrument allows the simultaneous storage of up to four sets of desorption parameters (known as methods) for as long as two months when mains power to the instrument is switched off.

When programming the ATD50, the keyboard requests information from the operator in a logical sequence. As each parameter is entered, the button coresponding to the next one in sequence lights up. Programmed and actual values of all parameters can be displayed at any time. All parameters are continuously monitored by the microprocessor and any illogical entry is indicated by an error signal display.

When setting up the ATD50 for a desorption run, the buttons light up in the following order:

METHOD A number from 1 to 4 should be entered to recall a method already in store, or to generate a new method.

MODE Several desorption modes are possible, entry of number 1 indicates a single stage desorption; number 2, a two stage desorption; number 5, a two stage desorption with repeated desorption of the adsorber tube; and number 6, which fires the cold trap alone.

OVEN The temperature for the primary desorption is set between 50°C and 250°C in 1°C increments.

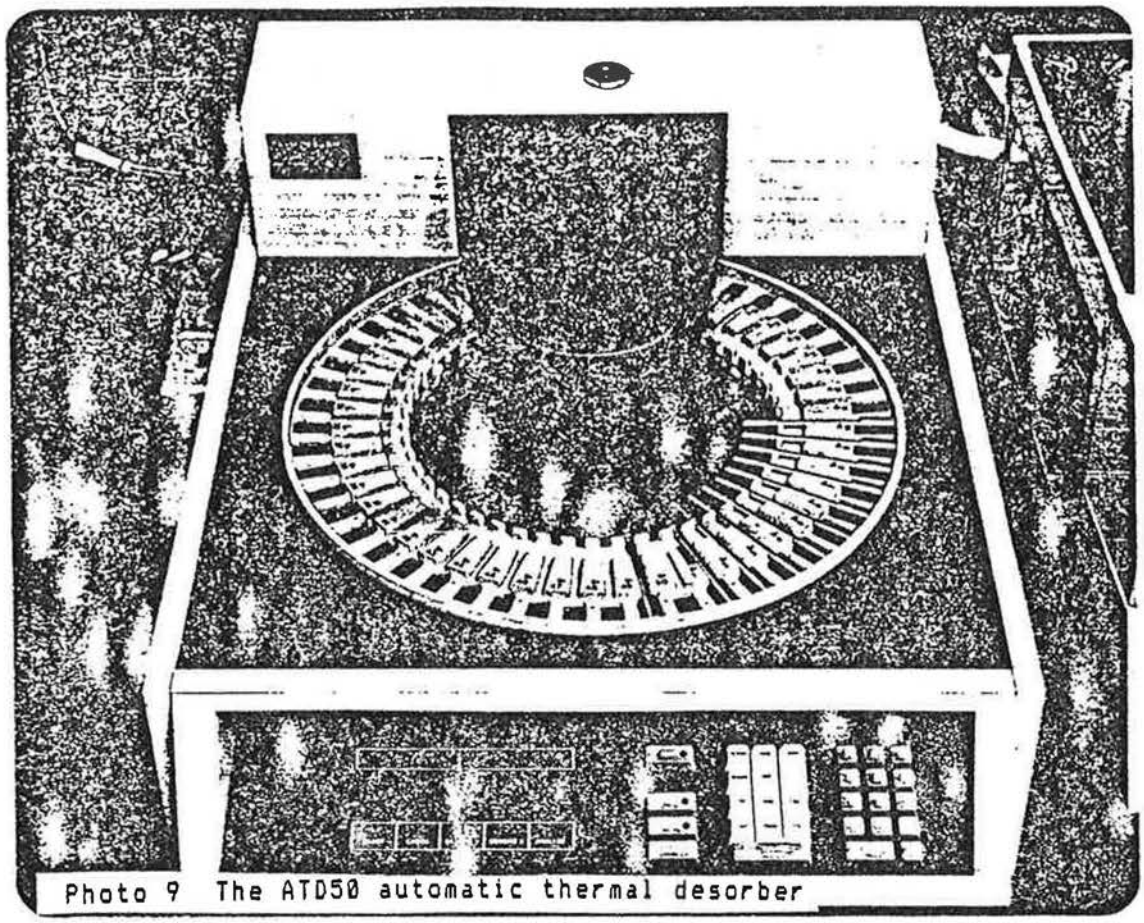


Photo 9 The ATD50 automatic thermal desorber

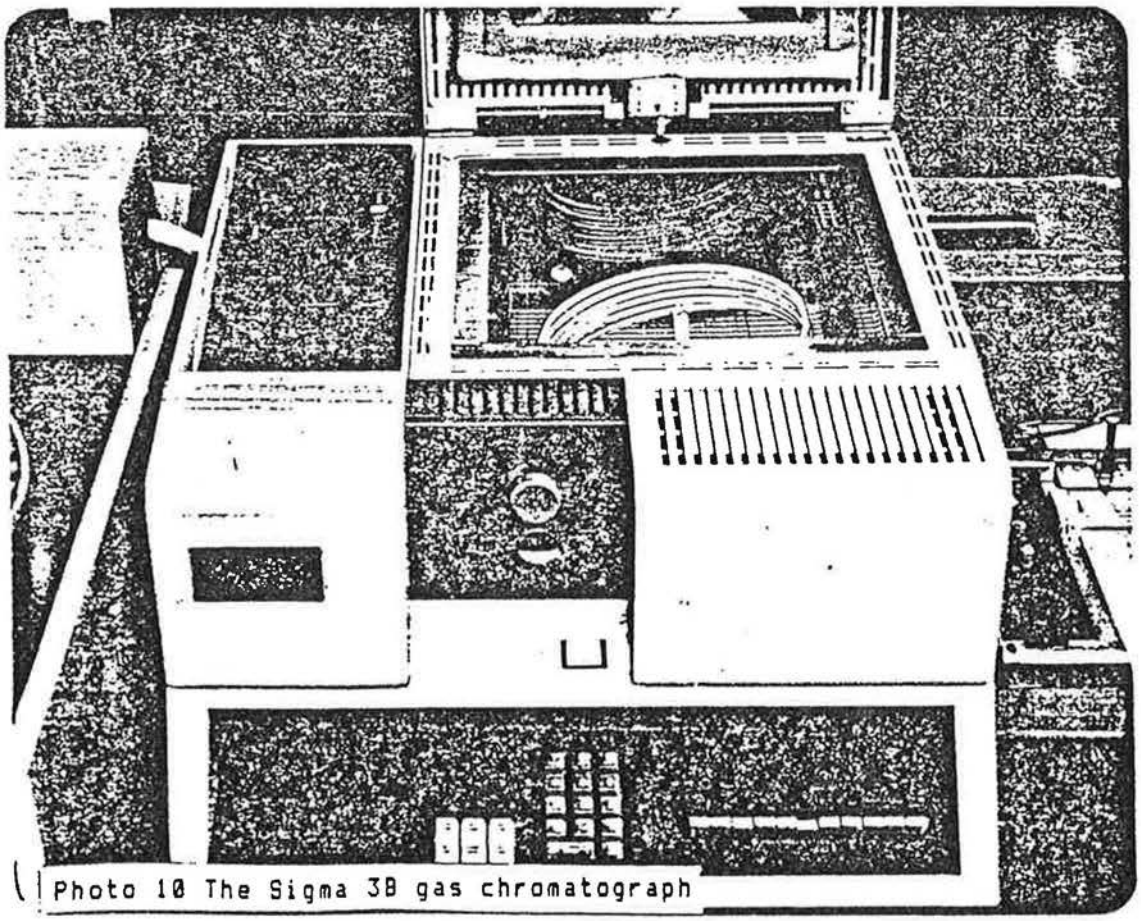


Photo 10 The Sigma 3B gas chromatograph

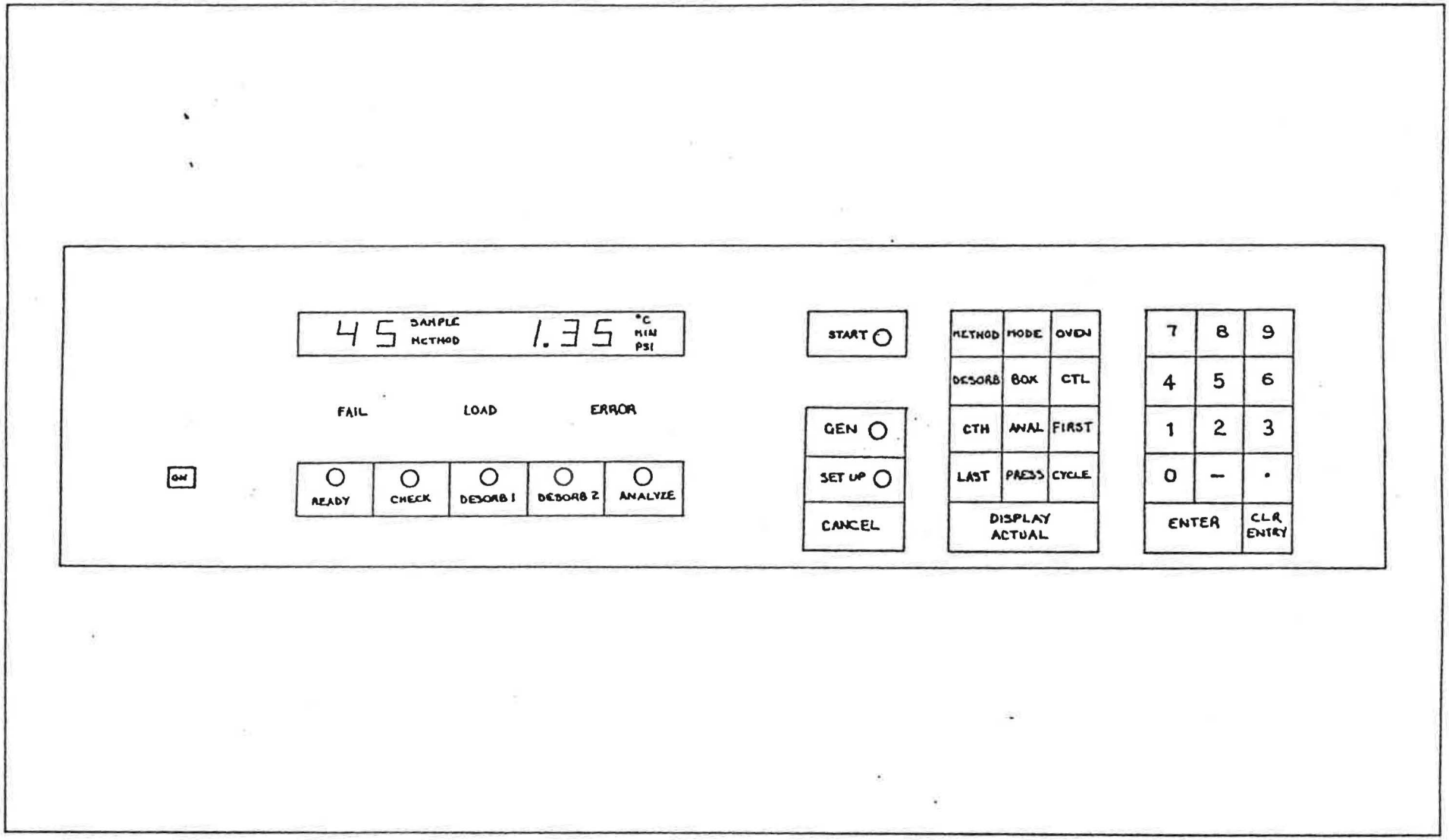


Fig.21 The Keyboard of the ATD50

DESORB The primary desorption time is set between 3 and 30 minutes in 1 minute increments.

BOX The temperature of the pneumatic box and heated sample transfer line to the gas chromatograph is set to between 50°C and 150°C in 1°C increments.

CTL The lowest temperature of the cold trap is set between -30°C and +30°C in 1°C increments.

CTH The highest temperature of the cold trap may be set between 50°C and 300°C in 1°C increments.

ANAL Between the completion of desorption from one tube and the selection of the next, time is allowed for the gas chromatograph to carry out its analysis. This is set between 4 and 99 minutes in 1 minute increments.

FIRST A number between 1 and 50 can be selected to indicate the position of the first tube to be analysed. In the case of mode 5 this number is the position of the tube being given a repeated desorption.

LAST This is the last tube to be desorbed. In mode 5 the difference between FIRST and LAST values gives the number of repeated desorptions.

PRESS This indicates the minimum useable carrier gas pressure. It is usually set at 90% of the column outlet pressure on the gas chromatograph. The pressure control is an important part of the tube safety check pressure described below. If the pressure in the line falls below the level set, the sampling cycle is interrupted, the pressure key lights, actual pressure is displayed and the Error legend flashes. When the pressure is restored to above this set value the sampling cycle is resumed.

CYCLE When this key is pressed, the total time required for any analysis is displayed. It is the sum of desorption time, analysis time and the check period time.

The ATD50 requires two gas supplies. Two lines from a gas

chromatograph carrier supply must be provided, one at the normal operating pressure of the column inlet and the other at 20 to 30 psi higher than this. If the gas supply is not connected before the power is turned on, a hardware failure indication will be given. In this case, power should be switched off before turning on the gas supply. With the gases on and the power on, a method may be generated using the key pad.

Charged adsorber tubes are then loaded radially on to the tuntable having first replaced their sealing caps with special desorption fittings (Photo 9). When all the desorption parameters have reached their programmed values a light comes on to indicate that the machine is ready to start on the desorption programme.

Pressing the 'start' button initiates a desorption run. The turntable moves round until it 'sees' an indicator which tells it where position 1 is. It then counts its way round the turntable until it reaches the first tube for desorption. The tube is lifted from the turntable and sealed ento a high pressure carrier gas line (Fig.22). Carrier gas is forced over the tube packing at room temperature to drive out any traces of air which may affect the adsorbed sample at high temperatures.

Next the tube is leak tested to make sure that none of the sample will be lost during the primary desorption sequence (Fig.23). High pressure gas continues to flow through the adsorber tube but instead of flowing to vent it is used to raise the pressure in the lines connecting the adsorber tube in the ATD50. When the desired pressure has been reached the system is left to stand for 1 minute. If during this period the pressure in the tube drops by more than 1/16 of the original value, the tube is defined as 'leaky' and the Fail legend lights. If a tube fails for this or some other reason (ie. it may not be present in its holder, or if present it may not be sealed correctly) the ATD50 replaces it on the table and proceeds to the next position. Only if it encounters three consecutive failures will the ATD50 cease to operate. At the end of an analysis experiment, or after three consecutive failures, the positions of the failed tubes on the turntable are displayed along with a failure code to indicate the cause of failure.

For the tube which passes the pressure and leak test, analysis may now

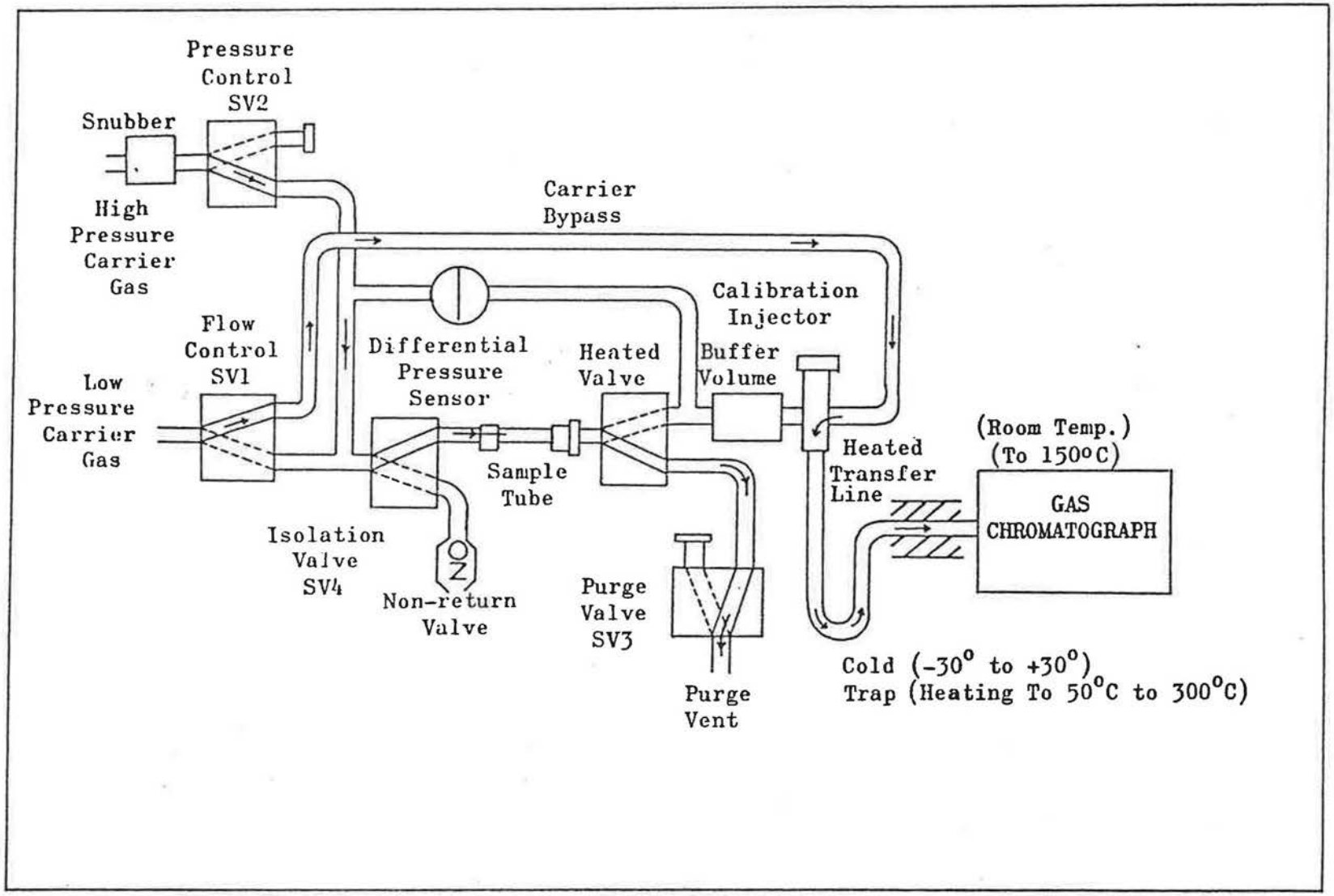


Fig.22 Tube Purge

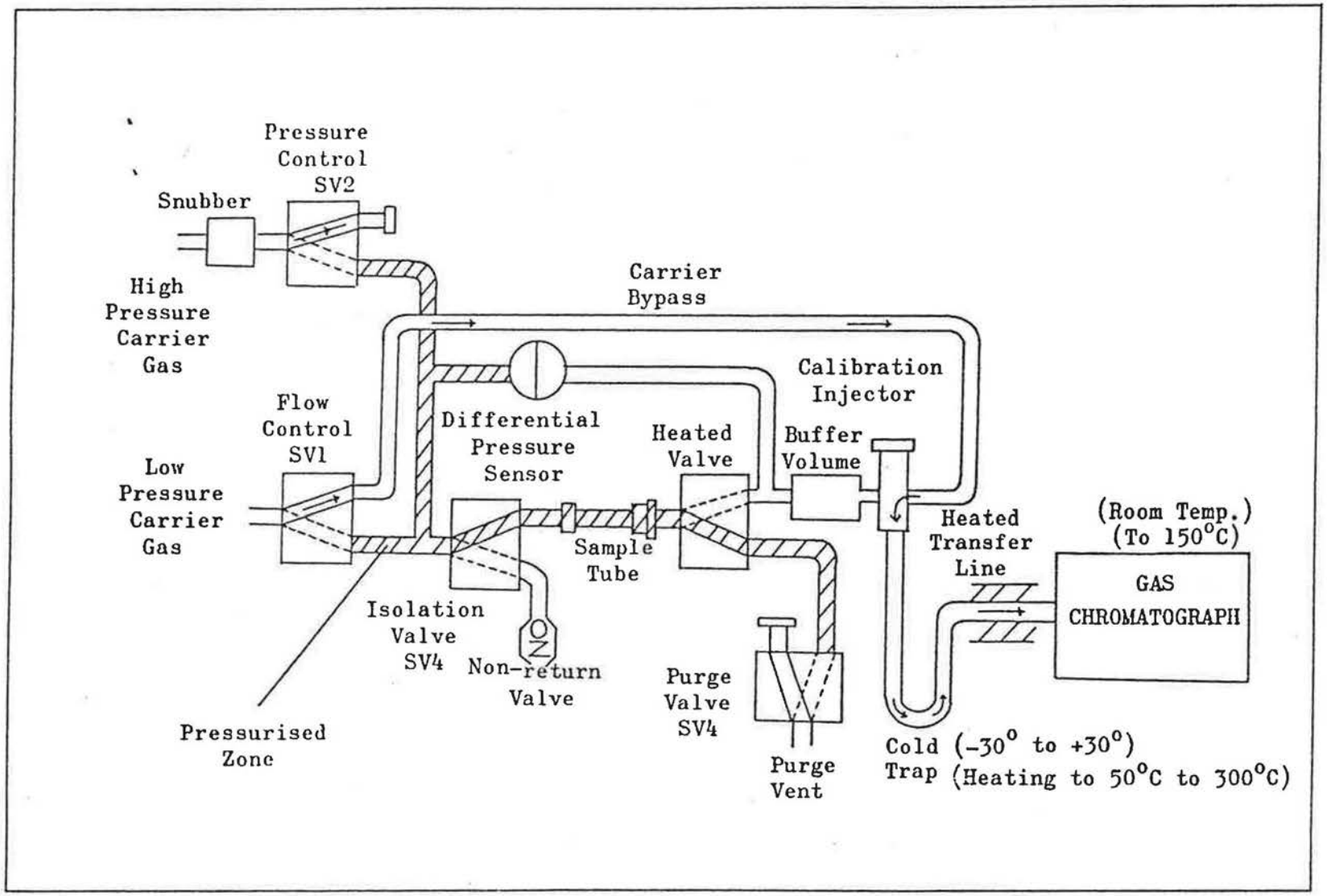


Fig.23 Leak Test

proceed (Fig.24a). The primary desorption oven is engaged round the tube and stays there for the programmed time. If for some reason the heater will not engage, a failure legend appears and the tube is returned to the turntable whilst the machine moves to the next tube to be analysed. During the primary desorption, carrier gas at the gas chromatograph operating pressure is passed over the adsorber tube at a rate controlled by the gas chromatograph flow controller. The carrier gas then passes through the cold trap and into the gas chromatograph. All the effluent from the adsorber tube remains on the cold trap. At the end of the primary desorption sequence the cold trap is automatically fired by flash heating it to its upper set temperature. The desorbed gases are then swept as a narrow band (1 ml is the cold trap volume) on to the gas chromatograph column (Fig.24b).

II.A.4.5 PACKING AND CONDITIONING THE ADSORBER TUBES

Each of the 50 adsorber tubes was labelled and weighed with its two sealing caps, the retaining gauze and retaining spring (Fig.11). Chromosorb 102 60/80 mesh packing was added until it reached the top of the tube. The tube was tapped to settle the contents and the retaining gauze and spring inserted. The sealing caps were replaced, weighing was repeated and the mass of Chromosorb 102 calculated. The packing weights for each tube are given in Table 5. The mean weight is 426 mg with a standard deviation of 8.5. The adsorber tubes were all conditioned before use in the field to remove spurious compounds from the packing material. This was done using the ATD50 itself. The column was removed from the gas chromatograph to prevent contamination from the tubes and the following parameters were set up on the ATD50 and in the gas chromatograph itself.

METHOD 1	ANAL 4 mins
MODE 2	FIRST 1
OVEN 200°C	LAST 51
DESORB 30 mins	PRESS 0 psi
BOX 145°C	CYCLE 36 mins
CTL -30°C	GC oven temperature 250°C
CTH 250°C	N_2 flow rate 50 ml min^{-1}

A reasonably high desorption temperature within the limits of the packing material was chosen (maximum temperature for Chromosorb 102 is 250°C) with the longest possible desorption time of 30 minutes. By

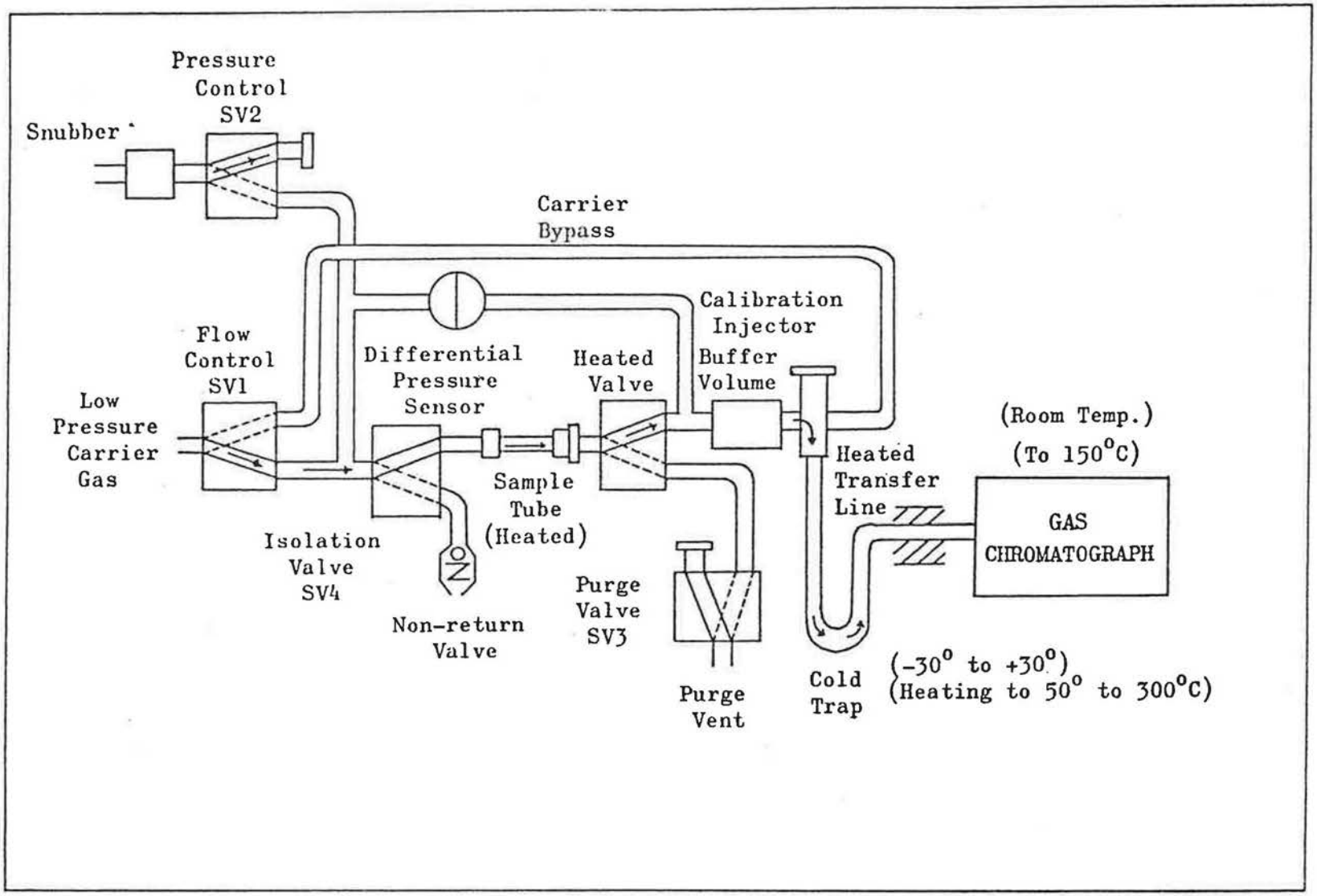


Fig.24a) First Desorption

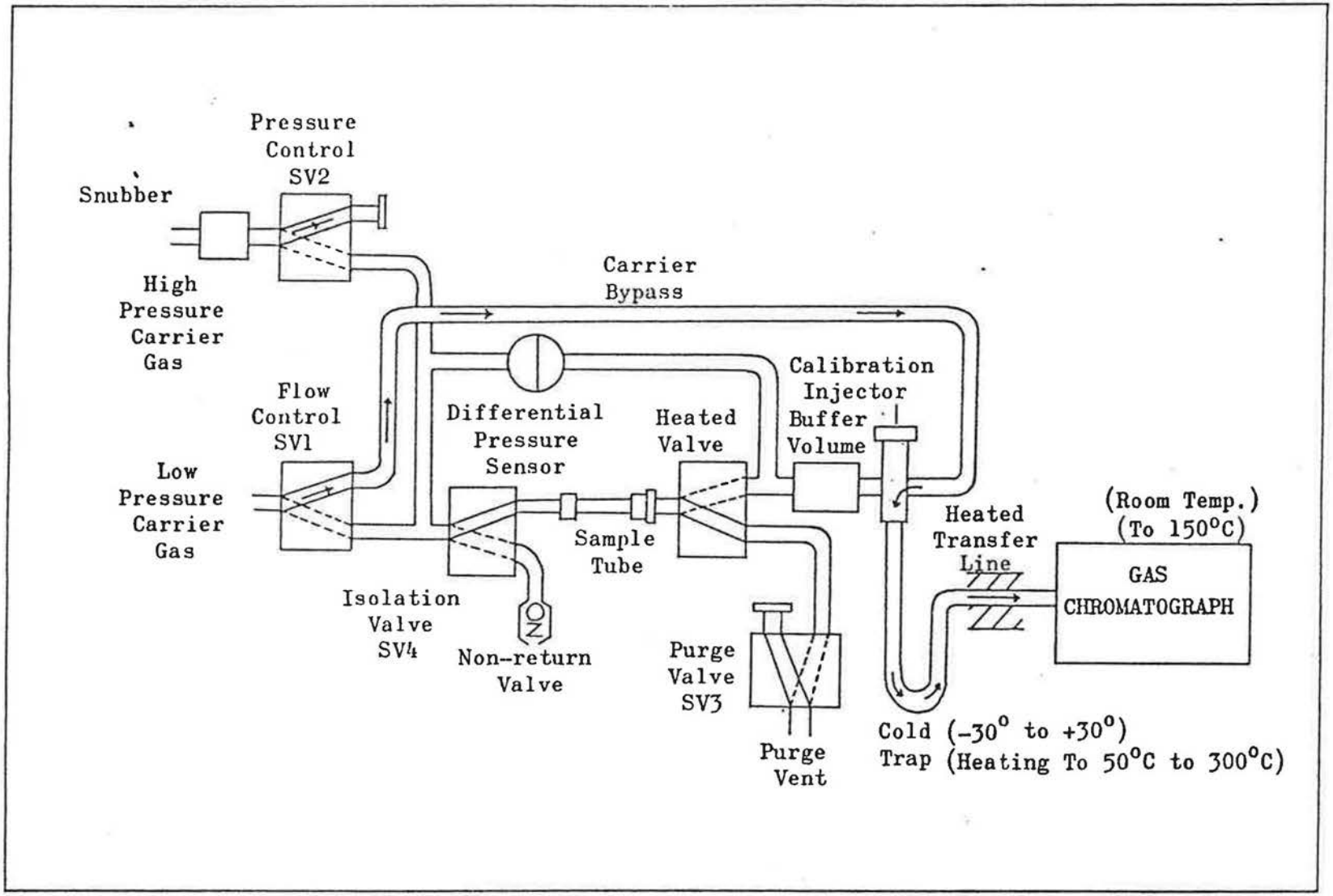


Fig.24b) Second Desorption

Table 5 Packing Weights in Adsorber Tubes (g)

TUBE NO.	WEIGHT OF TUBE EMPTY + 2 GAUZE + SPRING	WEIGHT OF PACKED TUBE	WEIGHT OF CHROMOSORB 102
1	14.3000	14.7438	0.4438
2	14.2824	14.7028	0.4204
3	14.2935	14.7085	0.4150
4	14.1817	14.6213	0.4396
5	14.0918	14.5102	0.4184
6	14.2504	14.6768	0.4264
7	14.3463	14.7772	0.4309
8	14.3100	14.7218	0.4181
9	14.1370	14.5692	0.4322
10	14.1033	14.5292	0.4259
11	14.1260	14.5495	0.4235
12	14.2748	14.6920	0.4172
13	14.1250	14.5566	0.4316
14	14.0478	14.4786	0.4308
15	14.3314	14.7542	0.4228
16	14.0784	14.5136	0.4352
17	14.1120	14.5536	0.4416
18	14.1590	14.5919	0.4329
19	14.1470	14.5833	0.4361
20	14.1472	14.5581	0.4109
21	14.3080	14.7275	0.4195
22	14.3186	14.7443	0.4257
23	14.2954	14.7116	0.4162
24	14.2872	14.7067	0.4195
25	14.2570	14.6775	0.4205
26	14.0716	14.4996	0.4280
27	14.1336	14.5733	0.4397
28	14.3157	14.7410	0.4253
29	14.2702	14.7027	0.4325
30	14.2541	14.6760	0.4219
31	14.2786	14.7115	0.4329
32	14.2293	14.6400	0.4107
33	14.2478	14.6755	0.4277
34	14.1875	14.6164	0.4289
35	14.1203	14.5493	0.4290
36	14.3515	14.7741	0.4226
37	14.3423	14.7646	0.4223
38	14.0964	14.5320	0.4356
39	14.3034	14.7296	0.4262
40	14.3265	14.7480	0.4215
41	14.2849	14.7162	0.4313
42	14.2732	14.6988	0.4256
43	14.2358	14.6646	0.4288
44	14.3238	14.7375	0.4137
45	14.0882	14.5268	0.4386
46	14.3310	14.7510	0.4200
47	14.3387	14.7480	0.4093
48	14.3120	14.7330	0.4210
49	14.2666	14.6913	0.4247
50	14.1432	14.5573	0.4141

setting the LAST value to 51 the turntable could continue to condition tubes several times before being stopped by the operator.

II.A.4.6 THE COLD TRAP

Like all the adsorber tubes the cold trap, a tiny U shaped tube with a volume of about 1 ml, is packed with a solid adsorbent. Initially the solid used in this word was Porapak Q (a styrene divinyl benzene co-polymer similar to Chromosorb 102). However, the packing was heated at some point to a temperature beyond its limit and it became charred. It was successfully replaced by some fresh Chromosorb 102, from a previously packed and conditioned adsorber tube which was subsequently re-packed, weighed and conditioned. Repeated firings of the cold trap always showed some spurious peaks at similar retention times to those shown by PP1, PP2 and PP3. An experiment using different intervals between firing times showed that there was a relationship between peak size and the amount of nitrogen (BOC white spot grade) passing through the trap. This nitrogen is oxygen free but it is possible that there are low levels of ambient organics present which on being passed through the cold trap are retained there and become concentrated sufficiently for them to appear as peaks. The manufacturer's instructions for connecting nitrogen to the gas chromatograph required a molecular sieve filter-drier to be fitted into the gas line at the outlet of the pressure reducing valve on the gas cylinder. Attempts were made to alleviate the problem of cylinder impurities by changing the packing material inside the filter. A packing of Chromosorb 102 was tried after inserting a conventional packed tube in series with the original filter. This showed a small improvement. A much greater improvement was seen when the filter was re-packed with activated charcoal. Spurious peaks at high amplifier sensitivity remained a slight problem. This is probably due to the slight deterioration of the cold trap packing (85). At the beginning of every analysis therefore, the cold trap was fired three or four times to remove as many contaminants as possible.

II.A.4.7 CHOICE OF ADSORBENT

The technique of concentrating small amounts of organic vapour in the atmosphere either cryogenically or on solid asdorbents was initially developed by workers interested in identifying and measuring low level hazardous organic vapour from the atmosphere depend primarily on the .

chemical properties of the gases being collected (77). Different adsorbents have different affinities for various organic vapours. They also differ in thermal stability and in the extent to which their performance is inhibited by the presence of water vapour. In general, the choice of an adsorbent for a particular task should be made according to the following criteria:

1 The sorbent should show a high quantitative efficiency in both collection and recovery of adsorbed gases.

2 The sorbent should demonstrate high breakthrough volumes (see Section II.A.4.8) for all adsorbed gases.

3 The sorbent should have little or no affinity for water vapour.

4 The sorbent should not undergo any structural or chemical change at the temperatures necessary for desorption.

The styrene divinyl benzene co-polymer Chromosorb 102 of Phase Separations Ltd. has been chosen as the adsorbent to collect PP1, PP2, PP3 and PP5 in this work, on the advice of Perkin-Elmer Ltd. It accords with the above criteria.

II.A.4.8 OPTIMUM SAMPLING VOLUMES

It is important to make sure that the air drawn through each adsorber tube in a field test deposits all its tracer gas on the adsorbent and that none breaks through to the other end of the tube (92). The optimum sampling volume of an adsorber tube is the maximum volume of air containing a given mixture of tracer gases which may be sampled over a variety of conditions such as humidity, temperature and sampling flow rate without significant breakthrough.

The breakthrough volume of an adsorber tube is the volume of air which when drawn through a tube laden with some tracer gas produces a just detectable amount of that tracer gas in the tube effluent. Breakthrough volume is strongly dependant on temperature and sampling flow rate, so the optimum sampling volume must have a safety margin to allow for changes in these parameters.

Breakthrough volumes can be measured directly (77) or indirectly (92).

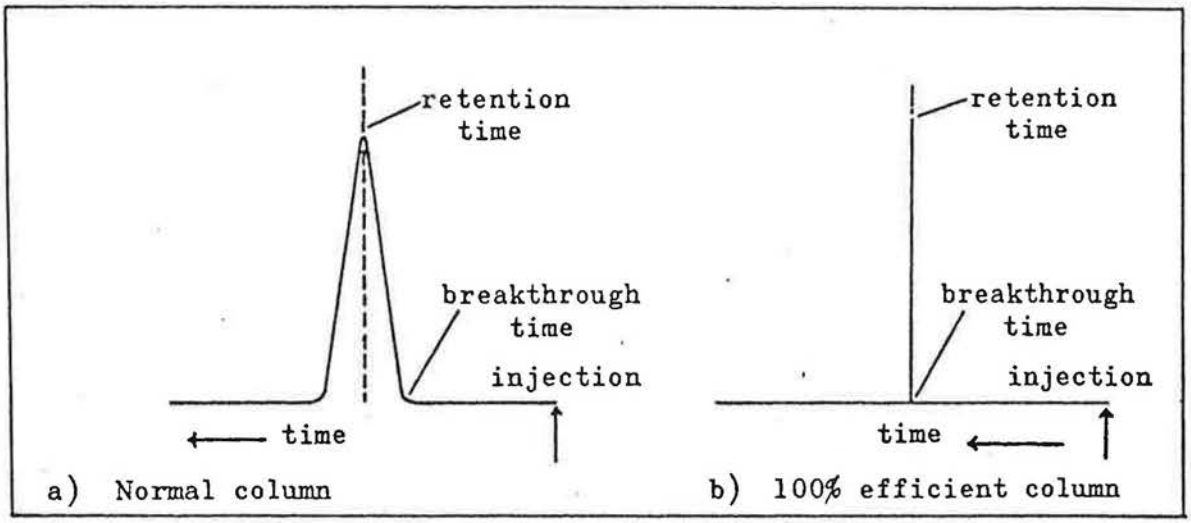


Fig.25 Illustration of retention time on a normal and a 100% efficient column

Pellizzari (77) created a gas mixture of known concentration in a flask connected on one side to a helium gas supply and on the other to a packed adsorber tube. Helium flowing through this reservoir swept the gas mixture over the adsorber tube. The effluent was monitored by a flame ionisation detector. The experiment was repeated for different sorbents, different gases and different purging rates. The effluent from the packed adsorber was monitored closely in conjunction with part of the same gas mixture diverted through an empty adsorber tube. The percentage collection efficiency for each sorbent and mixture of gases was estimated by comparing amounts of gases seen in the tube effluent for the packed and empty adsorber tubes.

Brown and Purnell (92) used a similar method to measure breakthrough volumes, the only difference was that they used a continuous atmosphere of constant concentration rather than allowing the concentration to decrease during sampling. Experiments were all

carried out on the sorbent Tenax GC for different gases and different sampling conditions. Because this method is awkward and time consuming, Brown and Purnell developed an indirect method for breakthrough volume measurement and used the direct method to confirm its validity.

The indirect method for measuring breakthrough volume is the one used in this work. Breakthrough volume and hence optimum sampling volume can be calculated from a measurement of the retention time of a tracer gas on the adsorber tube. The retention time (see Section II.A.5) is defined here as the point at which a single injection of tracer emerges from the tube. This is the value measured at the peak maximum in conventional gas chromatography. Retention volume is the carrier gas volume corresponding to the retention time of a component on a packed column (or adsorber tube).

$$V_R = t_R \times f_c \quad \text{.......................................} \quad 7$$

V_R = retention volume
t_R = retention time
f_c = volumetric flow rate at column outlet

Some authors (92) use retention volume synonymously with breakthrough volume. However, breakthrough volume is generally less than retention volume due to the column efficiency which is bound to be less than 100% (Fig.25).
Because all the principles of adsorption are the same for solid adsorbents, it is reasonable to extend the principles of evaluation shown by Brown and Purnell (92) with Tenax GC to other adsorbents such as Chromosorb 102.

From observations of breakthrough volumes of many different gases under greatly varying sampling conditions, the following conclusions were reached:

1 Changes in sampling flow rate have a marked effect on the theoretical plates and hence the collector efficiency of the tube. There is no corresponding effect on retention volume.

2 If the gases being sampled are at a concentration of 100 ppm or less, the actual gas concentration has no effect on the breakthrough

volume of the tube. If concentrations are higher than this, breakthrough may occur prematurely.

3 Temperature has only a small effect on theoretical plates but it has a much more serious effect on retention volume which varies inversely with temperature.

4 Polymeric adsorbents, if devoid of polar groups collect very little water while adequately collecting many organic substances (85). High ambient humidity does not therefore have an adverse effect on retention volumes.

Brown and Purnell (92) state a general rule for estimating optimum sampling volumes by the indirect method. The breakthrough volume of an adsorber tube (dimensions of 90 mm length and 5 mm id) is not less than 50% of the retention volume if the sampling conditions obey certain limits. The sample flow rate must be between 5 and 600 ml min^{-1}, vapour concentrations below 100 ppm, temperatures around 20°C and relative humidity up to 95% at 20°C.

It is thus only necessary to measure the retention volume of a gas on a tube at 20°C and within the sampling limits above; the safe or optimum sampling volume will be 50% of this value.

II.A.4.9 MEASUREMENT OF OPTIMUM SAMPLING VOLUMES

The front (grooved) end of an adsorber tube (packing weight 440 mg) was connected to the injector port by a 0.25" Swagelock nut and sealed with a graphite ferrule. The back was connected by a similar nut and ferrule to a short length of copper tubing which lead to the detector.

Retention volumes were determined for each of the four tracer gases PP1, PP2, PP3 and PP5 at three different temperatures. A plot of log retention time against the reciprocal of absolute temperature (Fig.26) gives a straight line in each case, which can be extrapolated to determine retention volume of the gases at room temperature.

With nitrogen carrier gas flowing at 20 ml min^{-1} and the flame ionisation detector gases at 16 psi for hydrogen and 30 psi for air, the retention volumes were measured by injecting about 0.1 ml volumes of gas and air mixtures taken from the headspace directly above the

liquids in their container bottles. Measured retention times were corrected for the time taken for a non-retained gas to pass through the column by taking samples of methane from a gas tap in the laboratory. Retention times were measured at three different temperatures for each gas and the results plotted as log retention volume (ml g^{-1} of adsorbent) against 10^3/ T °K (Fig.26 and Table 6). Extrapolated values of retention volumes at 20°C have been calculated and plotted from least squares fits to the experimental data points. The table gives the optimum sampling volume for each gas at 20°C to be collected on a tube containing 440 mg Chromosorb 102.

II.A.4.10 COLLECTION EFFICIENCY AND DESORPTION PARAMETERS

Before the collection efficiency of an adsorber tube could be measured the desorption parameters for the ATD50 had to be set up so that the whole sample from a desorption tube would always be desorbed in one firing of the adsorber tube and cold trap. Having determined the necessary desorption parameters it was then possible to carry out collection efficiency tests. These were done for high concentration standard gas mixtures of PP3 and PP5.

For optimum desorption efficiency it is necessary to have a high desorption temperature and long desorption time for the adsorber tube, and a high cold trap firing temperature. However, high temperatures bring problems with desorption of stray compounds which may have been adsorbed, and interference of the packing material itself arising from small scale deterioration. In choosing the desorption parameters for this work, the aim was to keep the primary desorption temperature as low as possible and to use a long time. Experiments with different CTH values (programmed cold trap firing temperatures) showed that it was necessary to use the maximum safe temperature for the packing to achieve a total desorption of PP5.

An arbitrary set of desorption parameters was set up on the ATD50 with a relatively low CTH value, oven temperature and short primary desorption time.

An adsorber tube was connected to the gas chromatograph with a Swagelock nut and graphite ferrule. With the oven and injector block at ambient temperature a 1 ml sample of PP3 mixed with air from a high concentration standard gas mixture (4000 ppm; see Section II.A.5.13)

Table 6 Optimum Sampling Volume Data for a tube containing 0.44g Chromosorb 102

PPX	TEMPERATURE ^{o}K	$10^3/K$	V_R (ml g^{-1})	log V_R	NO. OF THEORETICAL PLATES N	V_R PER TUBE	OPTIMUM SAMPLING VOLUME (ml)
PP1	398	2.51	22.7	1.36	7.5	10	
	363	2.75	68.2	1.83	3.4	30	
	343	2.92	145.5	2.16	2.0	64	
	293	3.41	1,318	3.12	-	520	290
PP2	398	2.51	27.3	1.44	2.5	12	
	388	2.58	40.9	1.61	2.3	18	
	373	2.68	95.5	1.98	3.5	42	
	293	3.41	20,417	4.31	-	8,983	4,492
PP3	423	2.36	36.4	1.56	6.8	94	
	398	2.51	81.8	1.9	4.2	36	
	373	2.68	213.6	2.33	3.1	16	
	293	3.41	12,589	4.10	-	5,539	2,770
	473	2.11	4.5	0.66	0.6	2	
	448	2.23	4.5	0.66	0.6	2	
	423	2.36	18.2	1.26	0.7	8	
	293	3.41	5,248	3.72	-	2,309	1,155

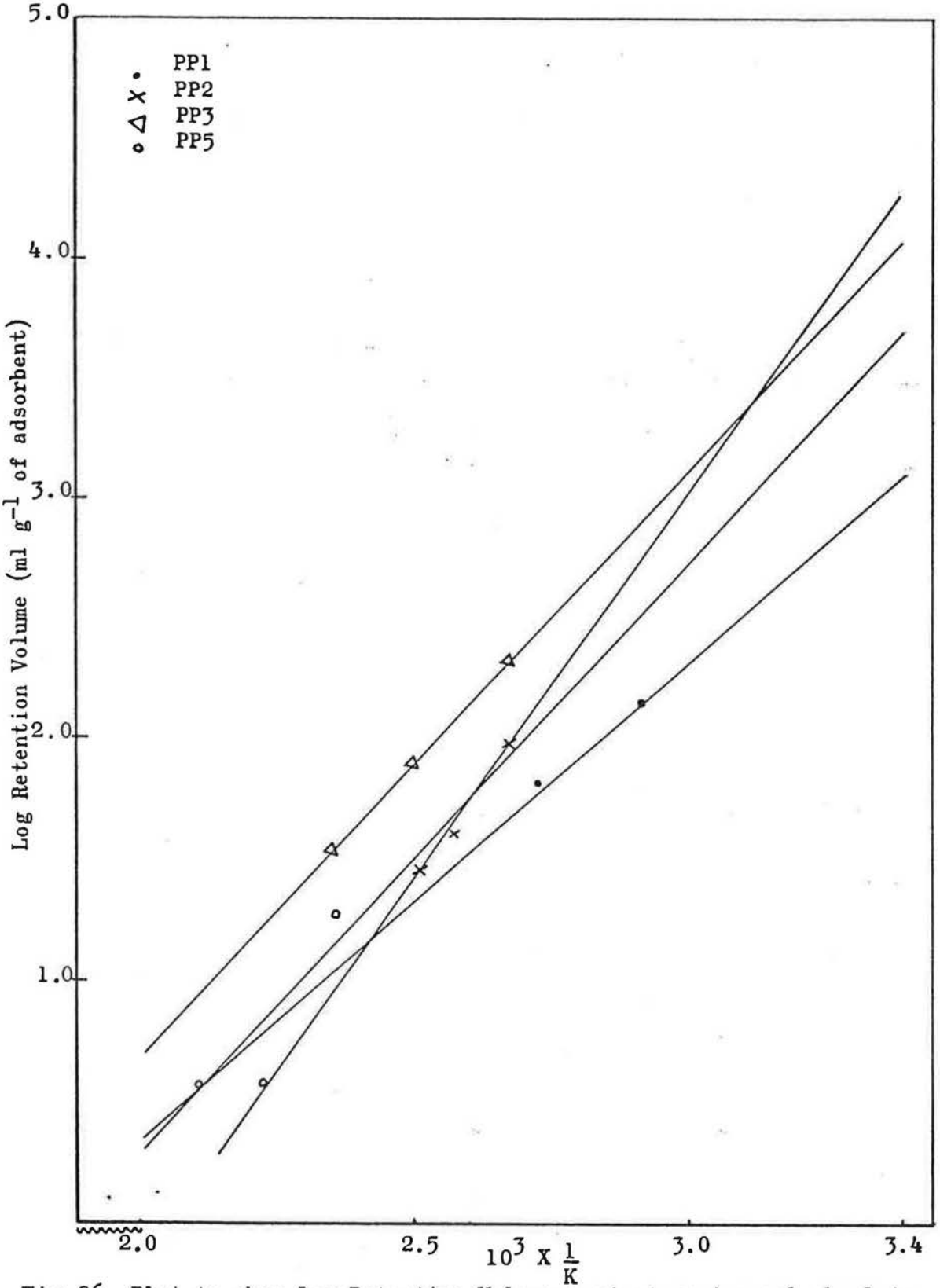


Fig.26 Plot to show Log Retention Volume against reciprocal absolute temperature

was injected using a 1 ml Hamilton gastight syringe. Carrier gas was allowed to flow at 20 ml min^{-1} until about 100 ml had passed over the tube and the gas sample was assumed to have been swept on to the adsorbent.

The charged adsorber tube was desorbed on the ATD50 using MODE 2. To check that all desorbed material from the tube had also come off the cold trap, MODE 6 was selected and the cold trap was fired alone. When a peak corresponding to PP3 appeared, the CTH value was raised by an arbitrary amount. When the cold trap was clear of residual PP3 from the primary desorption, the desorption process was repeated on the same tube to see if any PP3 remained. Desorption was repeated until all trace of PP3 had gone. From the number of desorptions necessary, a new set of desorption parameters was devised. Tests continued in this way with the same tube freshly charged with PP3 from the 4000 ppm standard gas mixture, for different values of the desorption parameters, until a suitable set was obtained.

The tests were then repeated for PP5 injecting 1 ml samples of a high concentration standard gas mixture (2500 ppm). The desorption temperature CTH was the only parameter which needed to be changed to ensure total desorption of the sample. The set of programmed desorption values was then defined:

OVEN	200°C
CTL	0°C
CTH	250°C
DESORB	15 mins
BOX	100°C

The collection efficiency of the tube for PP5 was measured by charging the tube with 1 ml of gas from the standard concentration gas mixture and desorbing on the ATD50. The whole procedure was repeated four times so that an average peak size for the amount of gas obtained from desorption could be compared to the peak size obtained by putting the gas directly on to the analytical column. The collection efficiency for PP3 was measured in the same way. Results of the experiments are shown in Table 7. A comparison of peak sizes between gas samples desorbed from an adsorber tube, and identical samples put straight on to the gas chromatograph shows that the collection efficiency for PP5 at 2500 ppm is about 100% and that for PP3 at 4000 ppm (this is about

Table 7 Results of Collection Efficiency Tests

TRACER	ADSORBER TUBE	PEAK HEIGHT (mm)	ATTENUATION	ATTENUATION X% DEFLECTION	LOG	LOG MASS	MASS 10^{-8}g
PP3	4	121	5120	3098	3.4910	3.6931	4,933 ± 197
		131	5120	3354	3.5255	3.7272	5,336 ± 213
		125	5120	3200	3.5051	3.7071	5,094 ± 204
		145	5120	3712	3.5696	3.7709	
		125	5120	3200	3.5051	3.7071	5,094 ± 204
						mean mass	5,272 ± 7%
	1ml sample from flask	158	5120	4037	3.4653	3.8062	6,400 ± 300
PP5	4	91	2560	1165	3.0663	3.6738	4,718 ± 189
		95	2560	1216	3.0849	3.6921	4,921 ± 200
		93	2560	1190	3.0757	3.6830	4,819 ± 200
		95	2560	1216	3.0849	3.6921	4,921 ± 200
						mean mass	4,845 ± 100
	1ml sample from flask	97	2560	2483	3.3950	3.6662	4,637 ± 200

1000 times more concentrated than tracer gas in a room at the start of a typical test) is 82%.
The incomplete adsorption of PP3 is due to the extremely high concentration of the standard gas mixture which has resulted in sample breakthrough. These values show that in spite of the low theoretical plate values obtained, Chromosorb 102 has a high affinity for these compounds and hence is a suitable adsorbent. The reason for working with high concentration gas mixtures was so that 100% desorption can always be guaranteed, even in cases of maximum sample loading.

The optimum sampling volume for PP1 (290 ml) is the limiting value for any tracer gas test in which a mixture of gases including PP1 is to be collected. The sampling volume chosen for use in this work was 100 ml. It provides an adequate volume for collecting low concentration tracer gases in the field and ensures that work is always carried out well within the breakthrough volume limits of the tube.

II.A.5 GAS CHROMATOGRAPHY

Chromatography is a physical technique for separating a mixture of compounds into its components. It relies on the distribution or partition of the mixture between a stationary and a mobile phase. In gas liquid chromatography (to be used in this work) the stationary phase consists of a thin layer of liquid bonded on to an inert solid support in the form of tiny beads giving a high surface area. This material is contained in a long, coiled tube of either steel or glass called a column. The mobile phase is an inert gas which passes through the column at a controlled rate.

Each compound has a different solubility ratio between the phases, some molecules being retained more firmly on the stationary phase than others. A process of repeated adsorption and desorption from the stationary phase occurs in which those components with low affinity for the stationary phase are retained by it to a lesser extent than those with a high affinity. Thus the compounds which are least soluble in the stationary phase leave the column first and those which are most soluble in the stationary phase leave last.

The mixture should be injected into the carrier gas at a temperature high enough to vapourize it, if it is a liquid, and for the duration

of the analysis the column must be kept at a temperature suitable to maintain the vapour. A suitable choice of column, operating temperature and mobile phase (carrier gas) flow rate ensures a complete separation of the mixture in the minimum time. One at a time as they emerge from the column, separated components pass into a detector which produces an electric signal proportional to the amount of material present. The signal is amplified and may be recorded in the form of a peak on a chart recorder.

The technique can thus be used for both qualitative and quantitative analysis. The retention time of a particular component under given chromatographic conditions will identify it, and the size of the peak from the detector indicates how much material is present.

A gas chromatograph consists essentially of three parts, a heated injector, a separating column in an oven and a heated detector. There are many differnt kinds of separating columns and detectors appropriate for a particular analysis. For instance there are some columns particularly suitable for analysis of alcohols and others for hydrocarbons, some particularly suitable for phosphorous containing compounds and others for inorganic gases. In short, the choice of a column and detector depends strongly on the particular analysis required.

II.A.5.1 FUNDAMENTAL TERMS AND RELATIONSHIPS

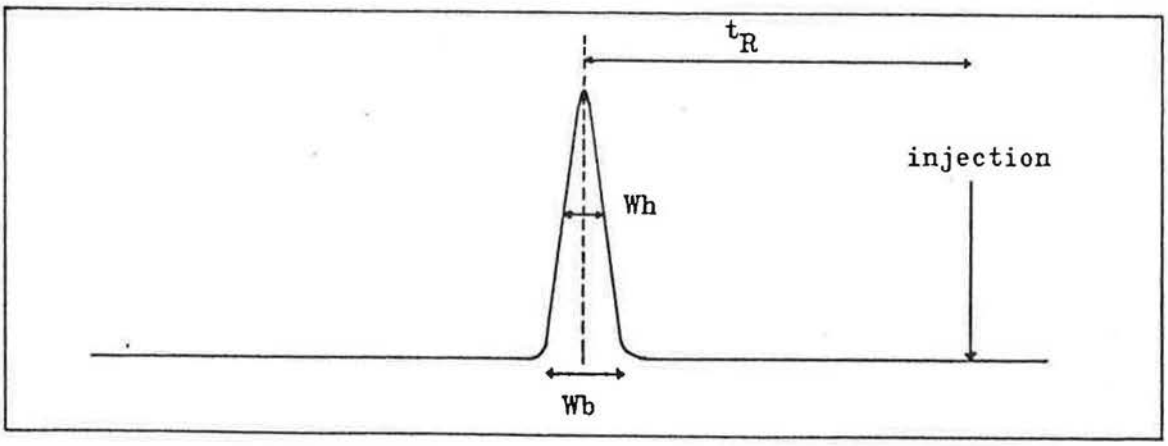


Fig.27 A Typical Chromatogram

All the information to be gained from the chart showing results of a chromatographic analysis may be obtained by measuring distances.

t_R = The retention time of a component measured as the distance between the point of injection and the peak maximum

t_M = The time taken for an un-retained solute to pass through the column

t_R' = The actual retention time ($t_R' = t_R - t_M$)

Wh = Peak width at half height

Wb = Peak width at baseline

H = Peak height

$$K = \frac{t_R'}{t_M}$$ = The partition ratio of a solute between mobile and stationary phases 8

The efficiency of a column to perform a given separation depends on the extent to which components are resolved. The number of theoretical plates, n of a column is a measure of separating efficiency. The height equivalent to a theoretical plate, HETP is the shortest length of column in which an equilibrium partition may exist between the mobile and stationary phases.

$$n = 5.54 \left[\frac{t_R}{Wh}\right]^2 \quad \text{..... 9}$$

$$HETP = \frac{L}{n} \quad \text{..... 10}$$

L = column length

The peak resolution r expresses the quality of separation between the two peaks,

$$r = \frac{\Delta t}{Wb_2} \qquad \text{.......... 11}$$

$\Delta t = t_{R2} - t_{R1}$

and the subscript 1 or 2 refers to the first or second peak to appear.

II.A.5.2 DETECTORS

Detectors show a high degree of specificity to certain groups of compounds. There are two detectors which respond particularly well to the perfluorocarbons used in this work. They are the electron capture detector (ECD) which has been described in section I.8.4 and the flame ionisation detector (FID).

In the flame ionisation detector, illustrated in Fig.28 (70,95), the column effluent is mixed with hydrogen and passed into a jet where it burns in air, producing a small flame. The jet forms one electrode in an electrode pair. A potential is applied between the electrodes and with just carrier gas flowing, a baseline current is established. When an analytical sample arrives at the jet, it is burned to form ions which increase the current flow. After suitable amplification, the signal appears as a peak on a chart recorder. The flame ionisation detector is sensitive to almost all organic substances but is insensitive to inorganic gases and water. It is a mass sensitive detector and its response is proportional to the total mass entering the detector per unit time independant of its concentration in the carrier gas. For each carrier gas flow rate there are optimum hydrogen and air flow rates which provide the optimum efficiency of the column and highest sensitivity of the detector. If the system is set up well, however, small changes in flow should not significantly influence the detector's operation (see section II.A.5.9)

II.A.5.2.1 ADVANTAGES AND DISADVANTAGES OF ECD AND FID

The electron capture detector has a much lower detection limit than

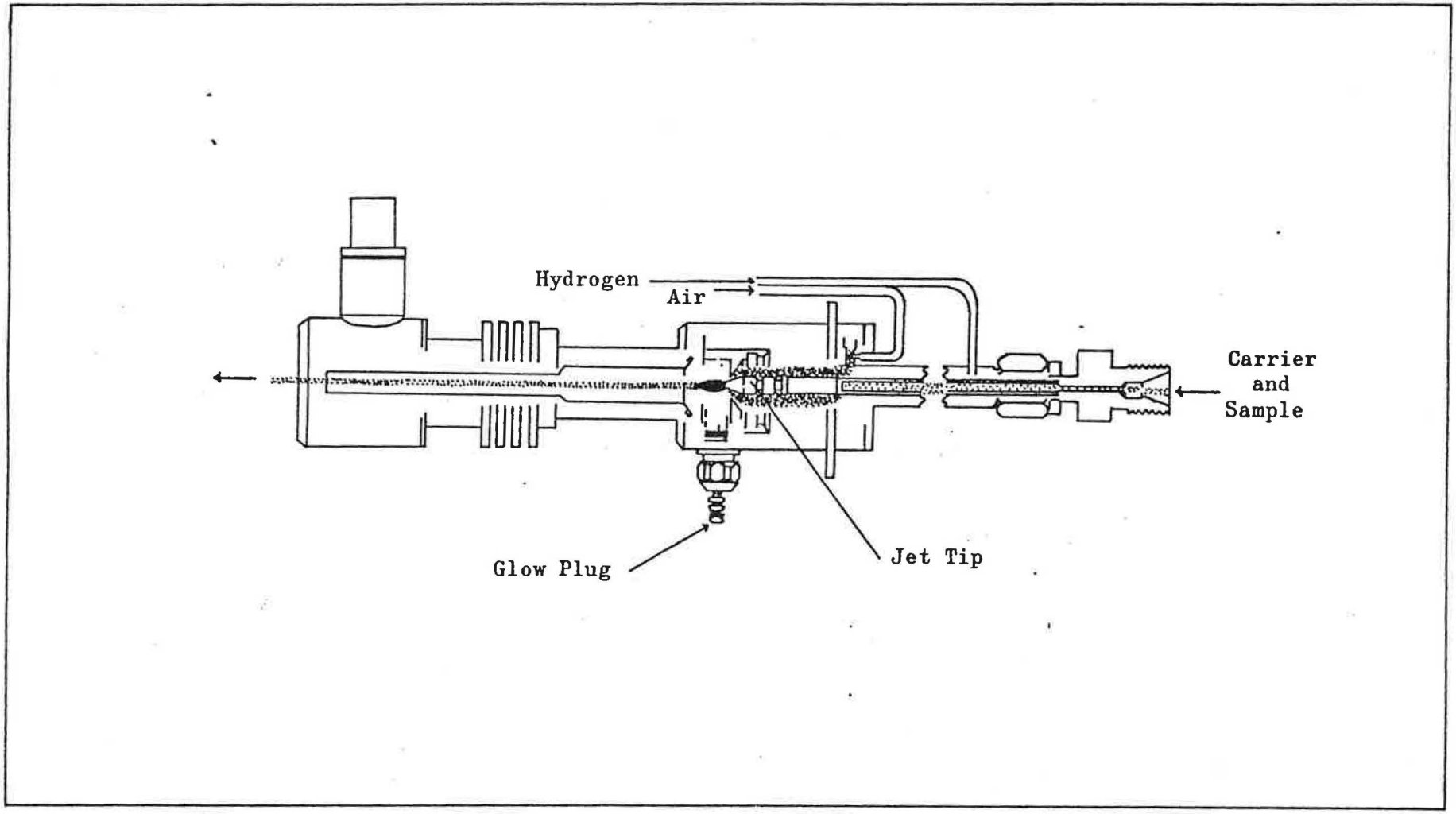


Fig.28 Flame Ionization Detector

the flame ionisation detector for halocarbons, which makes it ideal for use in meteorological tracing and tagging of clandestine explosives (68) where tiny concentrations of the order of one part in 10^{14} have to be measured. However, it is subject to problems in the way that water vapour and atmospheric oxygen may interfere with the detector operation. It is always necessary to make sure that all O_2 and H_2O vapour are removed before they reach the detector. Compared to the FID which has a linear range of $1:10^7$, the ECD linear range of $1:10^3$ is small. If samples are not presented to the detector in small amounts there is a risk of detector overload. In addition, the ECD response tends to drift with time particularly when first set up. To minimise errors caused by response drift, the detector response should be frequently checked against a reference standard.

In contrast to the ECD, the FID has a large range of response which is not subject to drift during measurements. It does not ordinarily suffer interference from O_2 or H_2O vapour. If these are present in large amounts, an electron capture phenomenon is observed in the form of a negative peak on the chart recorder. The detector is most sensitive to hydrocarbons but will respond to almost any organic compound. The sensitivity decreases with increasing substitution of electron absorbing hetero atoms as these tend to reduce the ion current produced in the flame by electron capture recombination effects. Such a reduction in sensitivity is most severe for molecules in which the hetero atoms are connected by labile bonds with low energies of dissociation. Examples of electron capturing elements are oxygen, nitrogen and the halogens. The ease of dissociation of halogens from halogen substituted hydrocarbons goes in the order I > Br > Cl > F. In spite of this problem, the FID maintains a high sensitivity to the perfluorocarbons PP1, PP2, PP3 and PP5 (section II.A.5.10).

II.A.5.2.2 REASONS FOR USING AN FID

1 The FID is cheaper and easier to use than the ECD.

2 Gases may be analysed at higher concentrations with an FID than they can with ECD, and so problems such as interference from background freons and accidental overloading of the detector are minimised.

3 The FID is more stable, and less subject to baseline drift and contamination than the ECD.

II.A.5.2.3 CARRIER GAS

The carrier gas to be used in an analysis depends on the type of column to be used. Typical examples are nitrogen, argon and helium. The function of the carrier gas is to carry the sample through the column and into the detector. The gas flows continuously through the detector producing a signal which gives rise to a baseline on the chart recorder against which sample peaks are compared. It is essential that the carrier gas should be free from contaminants such as O_2 or low levels of atmospheric hydrocarbons. If such contaminants are present they may interfere by reacting with the sample or the stationary phase giving rise to a high baseline, loss of detector sensitivity and anomalous peaks. The flow rate of the carrier gas has a profound effect on the speed of an analysis and the performance of the column.

II.A.5.4 CHOOSING A COLUMN

There are four important points to consider when choosing a column:

1 Column material.
2 Column type.
3 Column dimensions.
4 Stationary phase and its loading for a packed column.

Columns are usually made of stainless steel or glass. Glass columns are usually used for the separation of unstable compounds such as some biological samples and pesticides. In most cases either a stainless steel or a glass column may be used.

There are three main column types. There is the packed column and two types of capillary column. Firstly, the wall coated tubular column (WCOT), which has a coating of liquid phase on the column wall, and secondly, the support coated open tubular (SCOT), which has a liquid phase on a solid support just lining the inside of the column. In general, an analysis may be carried out more quickly and more efficiently with a capillary than with a packed column.

There are several disadvantages to using a capillary column which must be taken into account:

1 Capillary columns are much more expensive than packed columns.

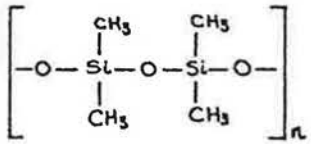
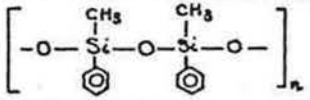
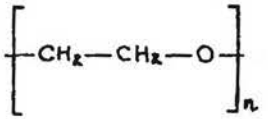
2 Due to the small diameter and great length of a capillary column, it is much more subject to the risk of accidental blockage than a packed column.

3 If a glass column is to be used, the glass capillary column is much more fragile than the packed column.

4 The smaller amount of stationary phase present on an open tubular column compared with a conventional packed column means that it is not usually possible to use standard injection techniques. There are three methods normally used to introduce the sample on to the column:
a A split injection technique allows a measurable volume of sample to be introduced by the operator. This is then split in the injector so that the majority is vented to atmosphere and column phase overload is avoided.
b The solvent effect injection allows the sample to condense at the front end of the column. A thick narrow band of liquid phase is formed which gives rise to very sharp resolution of peaks after rapidly raising the column temperature.
c With a few larger diameter columns it is possible to inject the sample without splitting but the volume needs to be kept very small, about 0.1 to 0.2 ul.

In general, if it is possible to achieve an adequate resolution with a packed column, it is cheaper and less troublesome than a capillary column. The selection of stationary phase is made according to the expression 'similis similibus solventur', in other words a solute for chromatography will dissolve in a phase of similar polarity. Other constraints which have to be considered when choosing a liquid phase are the temperature limits of operation. If a phase is heated to above its upper temperature limit it is liable to decompose giving rise to poor separation, high background and anomalous peaks. Below its minimum recommended temperature the phase may become viscous or even semi-crystalline and so column efficiency would be reduced. See Table 8 for a list of some of the common stationary phases with their temperature limits, activity and applications.

Table 8 Common Stationary Phases in Gas Chromatography

TYPE OF PHASE	NAME	CHEMICAL STRUCTURE	ACTIVITY	MAX. TEMP. OR TEMP. RANGE °C	APPLICATIONS
Hydrocarbon	Squalene		NP	-20 to 150	$C_5 - C_{10}$ Paraffins and cydo paraffins
Hydrocarbon	Apiezon L	Undefined mixture of hydrocarbons	NP	75 to 200	General purpose for high temps
Methyl silicone oil Methyl silicone gum	DC 200 or OV - 101 SE 30 or OV1		NP NP	-50 to 200 50 to 300	General purpose phase High boiling substances and steroids
Silicones (Phenyl 50% Methyl 50%)	DC - 710 or OV17 phenyl silicone oil		SP SP	-5 to 250 0 to 300	High boiling substances and steroids
Polyethylene glycols	Carbowax 1540 Carbowax 20M		P P	50 to 150 60 to 225	General purpose phases for lower & higher boiling polar samples respectively
Ester	Bis-2(2-methoxyethyl) adipate BMEA		P	65	$C_2 - C_{10}$ aliphatic hydrocarbons

P = polar NP = non polar

Most of the columns used in practice are partition columns in which the stationary phase is a liquid either coated on to a solid support (packed columns) or on to the inside of a capillary tube. Occasionally, adsorbents are used alone as column packings. They are most suitable for the ananlysis of permanent inorganic gases and light hydrocarbons (up to about C_3).
If a packed column is to be used in the analysis, support material must be chosen on which to load the phase. The most frequently used supports are made from specially treated diatomite.

Diatomite is a sedimentary rock composed of the skeletons of single celled aquatic plants called diatoms . The complete plant consists of the organism living inside two valves joined by a connecting band. The valve walls are made of opaline silica (95). These walls show complex patterns of chambers and partitions resulting in an internal structure which is highly porous on a microscopic scale.

The structure of the diatomite support essentially consists of a three dimensional lattice of:

O - Si - O - Si

with active hydroxyl and oxide groups on the surface. Thus the diatomite support material is not truly inert and active sites may interact with molecules which are polar or have labile bonds causing adsorption or decomposition. The activity is reduced by treatment with acid and, or base as well as silylation of the residual surface hydroxyl groups.

In general, to analyse non polar molecules, untreated, non acid washed diatomite support may be used. If polar samples are to be analysed, an acid washed and silylised support should be used. A silylised support must always be used for both polar and non polar samples if the phase loading is less than 5%.

Diatomite material is available in several grades in both treated and untreated forms. Several mesh sizes are available for each one. In choosing the correcct particle size for the support material it is necessary to make a compromise between the very small size required to maximise the theoretical plate efficiency of the column and the large size required to maximise the permeability. The permeability of a

column is proportional to the square of particle diameter and the pressure drop is inversely proportional to the square of particle diameter. Average particle diameter is specified by the mesh range of the material, a high mesh range meaning small particles. In general, the mesh range is usually selected according to the length and diameter of the column.

The stationary phase loading is expressed as a percentage by weight of stationary phase present in the column packing. The amount of liquid phase on a support influences the amount of sample which can be put on to the column and the theoretical plate efficiency. A high stationary phase loading means a high sample capacity. However for a fixed particle size an increase in phase loading means an increase in the thickness of the liquid layer and an increase in mass transfer (band spreading) of the sample. The higher the mass transfer, the poorer the column efficiency. A compromise therefore has to be reached in the selection of phase loading. The choice of column diameter depends on the detector selection and the minimum detectability of the sample. Usually small diameter (less than 4 mm) columns are used with FID and larger diameter (4 - 6 mm) columns are used with ECD. The column length depends on the efficiency necessary to achieve a particular analysis. The most frequently used packed columns have a length of between 2 and 4 m. The selection of carrier gas flow rate depends on the column diameter.

II.A.5.5 CHOOSING A GAS CHROMATOGRAPH

Tests were initially carried out on a Perkin-Elmer F11 gas chromatograph fitted with a flame ionisation detector and a variety of stainless steel, packed columns. Packing materials included 3% squalene on alumina, apiezon L on Chromosorb W and OV17 on chromosorb W-AW DCMS. Poor temperature control of the oven and low detector sensitivity made the instrument unsuitable for work with PP1, PP2, PP3 and PP5. The lowest working temperature of the F11 was 80°C which was too high to achieve a separation of the gases on any of the columns tried.

The Perkin-Elmer Sigma 3B (Photo 10) was chosen as a replacement for the F11 for several reasons. It is a microprocessor controlled instrument with a high degree of automation and a compatibility with the ATD50. It has a temperature programming function and will control

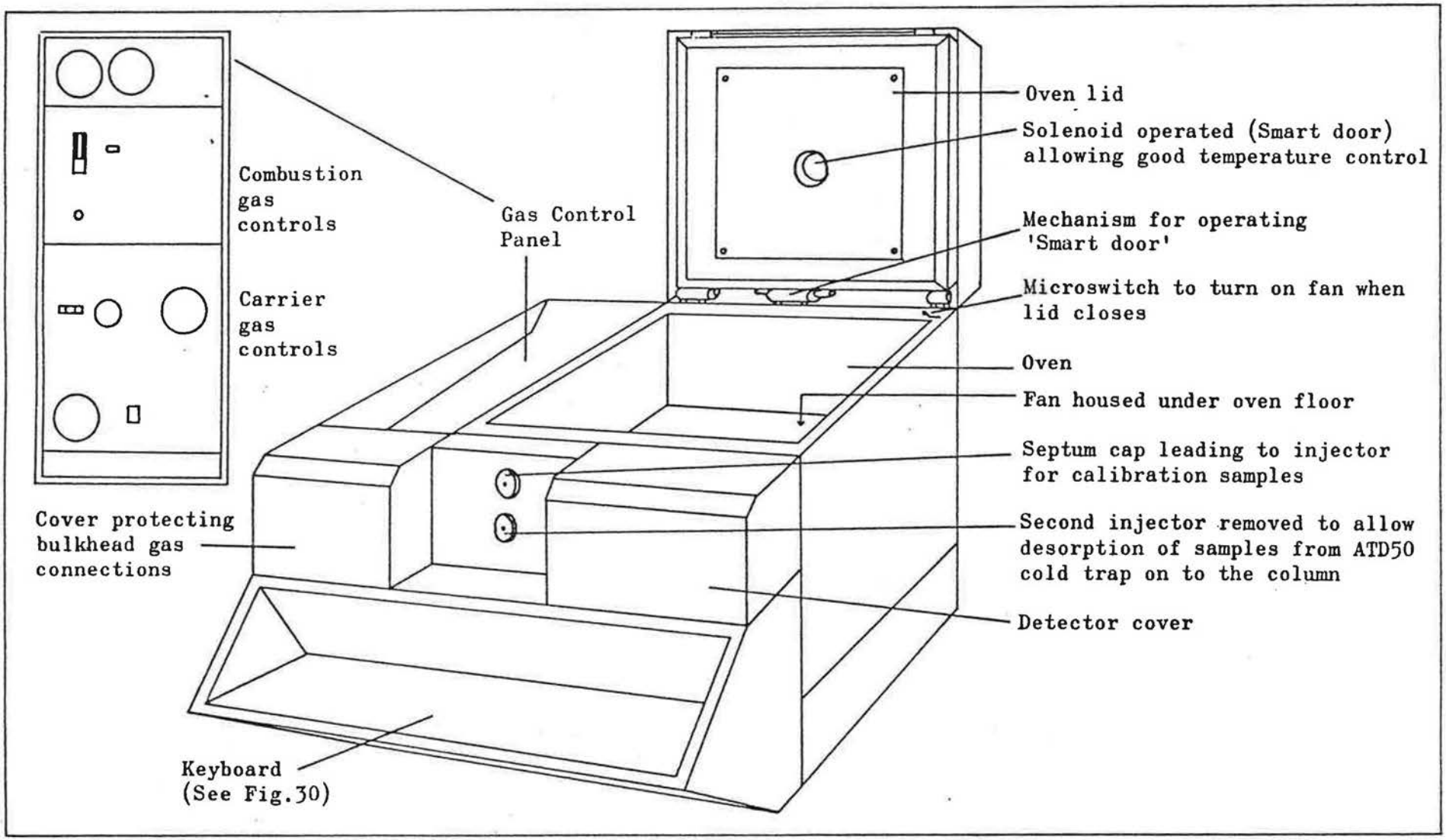


Fig.29 The Sigma 3B Gas Chromatograph

its oven temperature between 10°C above ambient and 449°C. All chromatographic parameters may be set using a key pad at the front of the instrument and set and actual values can be displayed at any time during an analysis (Fig.29).

On the advice of ISC Chemicals Ltd UK the gas chromatograph was fitted with a flame ionisation detector and a glass column 4 m long and of 3 mm id, packed with 5% silicone SE30 on Chromosorb W-HP (100 - 120 mesh). The flame ionisation detector and the phase SE30 are described above. Chromosorb W-HP is a high quality acid washed, silylised flux-calcined diatomite. Its special features include superior inertness, no catalytic surface activity and a short column conditioning time. The carrier gas chosen was nitrogen. The column was attatched to the injector by a swagelock nut and sealed by a graphite ferrule. With the detector end disconnected the column was conditioned according to the manufacturer's instructions.

II.A.5.6 USING THE SIGMA 3B

The gas chromatograph is placed next to the ATD50 (Photo 11).

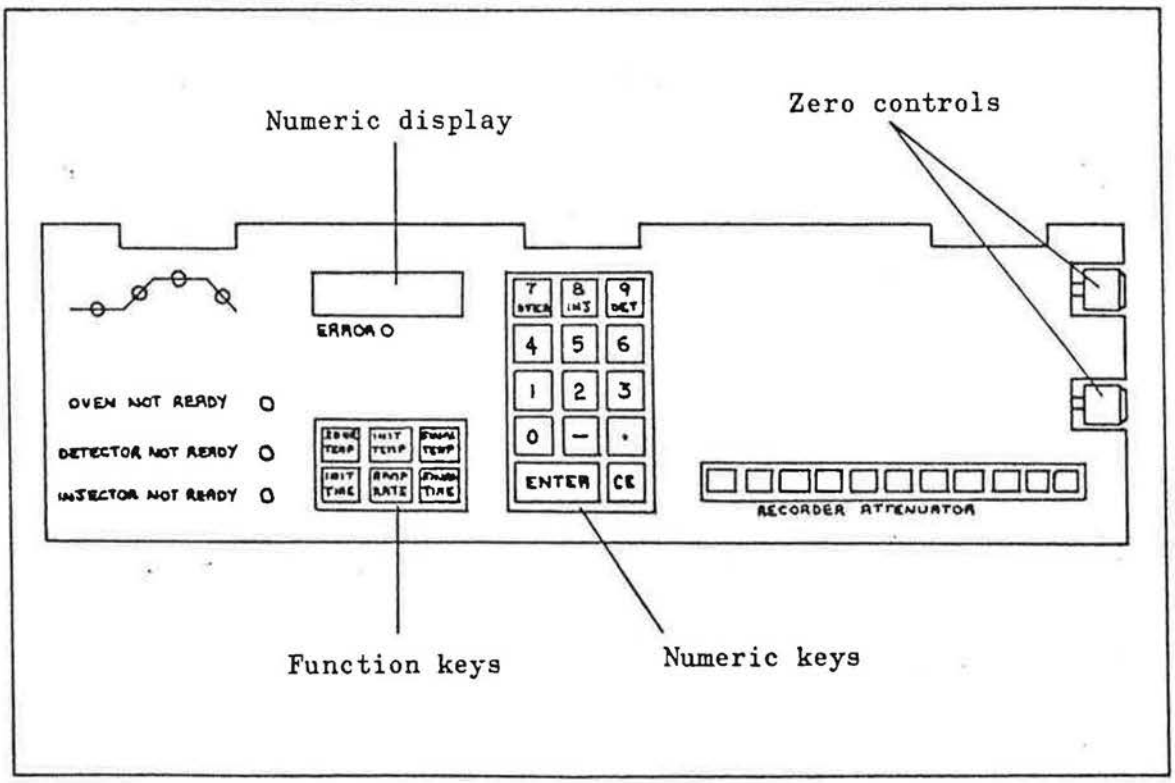


Fig.30 The Sigma 3B keyboard

Photo 11 The ATD50 and gas chromatograph in operation

The connections between them include copper piping, which handles nitrogen carrier gas and compressed air (for operating the pneumatics of the ATD50 and supporting the FID flame); two core wire to allow communication between the two, of states of readiness; and a heated line which passes directly from the ATD50 cold trap to a swagelock column fitting inside the chromatograph. The arrangement of the heated line column fitting is such that the inlet side of the column may be readily connected either to the ATD50 for analysis of the adsorber tube effluent or to the chromatograph injector for the injection of calibration standards. The inlet pressures of all three gases are controlled by regulator valves on the chromatograph. These pressures and also the column outlet pressure are monitored by a series of dials. The column outlet pressure dial serves as a useful indicator of leaks in the system.

A digital readout flow controller allows the carrier gas flow rate to be controlled anywhere between 1 and 100 ml min^{-1} at any column temperature. Before work was begun, the calibration of the flow controller was checked by comparing the digital read out with the actual flow rate as measured by a soap bubble meter.

II.A.5.7 SETTING CHROMATOGRAPHIC PARAMETERS

Keyboard controls are arranged in two groups with status displays at the left hand side. Keys below the numeric display are Function Keys and those to the right are Numeric Keys (Fig.30).
The displays light up to indicate instrument status. The set of 'not ready' lights at the left hand side are lit if programmed values have not been attained. Lights appearing on the temperature programme profile indicate the part of the programme which has been reached, such as the initial temperature, programmed increase, final temperature or cool down. The error display lights if an incorrect entry is attempted. The numeric display shows the set points or actual values for each function when the corresponding Function Key is pressed.

During a run the set oven temperature is displayed. A ready light at the top of the instrument lights about two minutes after the set values for oven injector and detector temperatures are reached. When this is pressed a run is initiated and the light extinguished.

To set up a programme, values for each function are selected using the numeric and function keys according to the operator's manual.

II.A.5.8 THE DETECTOR

The flame ionisation detector of the Sigma 3B is housed in a solid metal block which is heated to maintain the vapour state of the column effluent. The current produced by the sample molecules in an analysis is amplified and recorded by a Servoscribe chart recorder.

II.A.5.9 OPTIMISING THE HYDROGEN FLOW

In a flame ionisation detector, three different gases are always being used: the carrier gas, air and hydrogen. With each carrier gas flow rate there is an optimum hydrogen flow rate at which the response and linearity of the detector are at a maximum. The detector response for

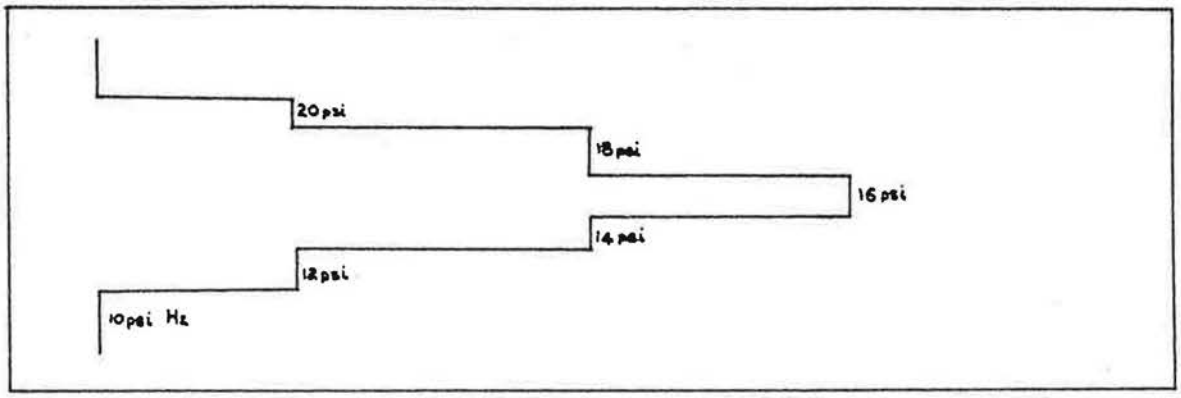


Fig.31 Hydrogen Optimisation Chart

the same amount of the same substance entering the detector first increases, reaches a maximum and then decreases as hydrogen flow increases.

Working close to optimum, slight fluctuations in the hydrogen or carrier flow rate result in a negligable change in relative response of the detector. However, if one is a long way from optimum, a small change in either hydrogen or carrier gas flow rate results in a significant change in the detector response (94). The flow rate of air is less critical. A plot of air flow rate against detector response shows a rising curve which levels off. It is thus only necessary to pick a flow rate corresponding to the plateau.

For this work a nitrogen flow rate of 15 ml min^{-1} was chosen on the advice of ISC Chemicals Ltd. An experiment was carried out to optimise the hydrogen flow rate at this carrier flow.

With all the gases switched on, the nitrogen at 15 ml min^{-1}, column inlet pressure of 69 psi and column outlet at 20 psi, air at 30 psi and hydrogen at 20 psi, the flame was ignited. The hydrogen pressure was then reduced to 10 psi. The oven temperature was modified to give slight column bleeding and a significant baseline deflection. Hydrogen pressure was then increased in 2 psi increments. At first, the detector output signal was increased more at each increment (Fig.31). It then reached a maximum level beyond which further increase in hydrogen pressure resulted in a smaller signal.

The pressure corresponding to the point of maximum detector output is the optimum hydrogen setting for the particular carrier gas flow rate used. For this work hydrogen was used at 16 psi.

II.A.5.10 EVALUATION OF THE GAS CHROMATOGRAPH

In order to make a total evaluation of the gas chromatograph, it was necessary to set up the machine and optimise operating conditions such as oven temperature, gas pressures and flow rates. Having done this, the quality of future routine analyses of the tracer gases could be established. The parameters determined were the retention times of the tracer gases, their partition coefficients, peak resolution, theoretical plate efficiencies and detector sensitivities.

ISC Chemicals Limited, who supplied the tracers, suggested that suitable analytical conditions would be a nitrogen carrier gas flow rate of 15 ml min^{-1} and a column operating temperature of between 50 and 135°C, depending on the boiling point of the tracer. Preliminary tests using headspace samples of all the tracers injected simultaneously, showed that complete separation was possible working isothermally at 50°C (the minimum working temperature of the column used). The flow rate of the carrier gas was then allowed to vary between 10 and 15 ml min^{-1}. It was noticed that retention time and peak widths were at a minimum and peak heights at a maximum for a 15 ml min^{-1} flow rate. At this flow rate the PP1, PP2 and PP3 emerge from the column very close together. At flow rates greater than 15 ml min^{-1} complete resolution of their peaks would not be possible.

The working conditions eventually chosen for the gas chromatograph are listed below:

Detector ..... Flame ionisation detector

Column ..... 4 m x 3 mm id glass packed with 5% SE30 on Chromosorb W-HP

Oven temperature ..... 50°C

Detector temperature ..... 120°C

Injector temperature ..... 120°C

Carrier gas ..... N_2 Inlet pressure .... 69 psi
Flow rate ..... 15 ml min^{-1}

Air pressure ..... 30 psi

Hydrogen pressure ..... 16 psi

The injector and detector temperatures were chosen arbitrarily to ensure that the sample would be maintained in the vapour phase at the beginning of an analysis and to prevent deposits accumulating in the detector at the end. The temperature had to be kept low enough to allow the oven controller to maintain the column temperature at 50°C. A volume of 1 ml was selected arbitrarily for the injection of gas samples on to the chromatography column. This was because 1 ml is a conveniently measured volume and because a syringe of this size is much easier to use than either a larger or a smaller one. 1 ml samples of gas mixture containing PP1, PP2, PP3 and PP5 were injected on to the column and analysed. Information gathered from resulting chromatograms is shown in Table 9.

The resolution, partition ratios, numbers of theoretical plates and length of column equivalent to a theoretical plate (HETP) are all column parameters. The detector sensitivity is the only quantity which describes the detector. The resolution of the peaks shows how completely the mixture is separated into its components. For any given pair of peaks the resolution between them is always described relative to the peak at longer retention time. In general, a value of

Table 9 · Evaluation of the Gas Chromatograph

TRACER	PP1	PP2	PP3	PP5
RETENTION TIME t_R (min)	2.5	2.8	3.2	5.6
CORRECTED * RETENTION TIME t_R' (min)	0.2	0.5	0.9	3.3
AVERAGE Wh (min)	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01
AVERAGE Wb (min)	-	0.17 ± 0.02	0.22 ± 0.02	0.36 ± 0.03
RESOLUTION r	-	1.8 ± 0.2	1.6 ± 0.2	6.6 ± 0.3
PARTITION RATIO K	8.70×10^{-2}	0.22	0.39	1.43
THEORETICAL PLATES n	3,463	4,343	5,673	4,343
HETP (mm)	1.2 ± 0.1	0.92 ± 0.09	0.71 ± 0.07	0.92 ± 0.09
DETECTOR SENSITIVITY (Coulombs g^{-1})	1.53×10^{-3} ($\pm 6.9 \times 10^{-5}$)	2.55×10^{-3} ($\pm 1.8 \times 10^{-4}$)	1.8×10^{-3} ($\pm 7.2 \times 10^{-5}$)	1.37×10^{-3} ($\pm 2.7 \times 10^{-5}$)

* The time taken for methane (an unretained solute) to pass through the column (t_M) is 2.3 minutes. The corrected retention time $t_R' = t_R - t_M$.

1.5 or more shows a complete separation of components (94). The efficiency of the column is normally expressed in terms of theoretical plates. A theoretical plate may be imagined as the smallest length of the column within which an equilibrium partition of the analyte may exist between the mobile and stationary phases. Usually one talks of the number of theoretical plates in a column (n) or the height equivalent to a theoretical plate (HETP). A typical value for HETP in a routine analysis carried out under optimum conditions is 0.6 - 1 mm.

The partition ratio is the fraction of analyte which is present in the stationary phase when an equilibrium exists between the analyte in the two phases.

The detector sensitivity has been calculated using the detector calibration lines (see section II.A.5.14).

The Sigma 3B operator manual claims a detector sensitivity of better than 0.015 Cg^{-1}. The values obtained for the perfluorocarbons show a sensitivity an order of magnitude less than this due to the electron capture effects of the fluorine atoms.

The general conclusion to be drawn from the evaluation study is that the column and operating conditions chosen for this work are good. Complete resolution of all the components can be achieved within 6.5 minutes and the detector sensitivity is perfectly adequate for the analysis required.

II.A.5.11 CALIBRATION OF THE FID

The detector was calibrated with standard concentration gas mixtures of each of the perfluorocarbons. Initially, an attempt was made to create standard gas mixtures by injecting a tiny measured volume of perfluorocarbon liquid into a 500 ml round bottom flask via an adaptor with a septum on it. Apart from the difficulty of measuring a tiny amount of perfluorocarbon liquid either by volume or by weight, problems were encountered due to absorption of the tracer into the septum and silicone lubricating grease. Standard gas mixtures were prepared instead on a glass vacuum line.

II.A.5.12 VACUUM LINE FOR PREPARING STANDARD GAS MIXTURES

A glass vacuum line (Fig.32 and Photo 12) was designed to allow the accurate measurement of a mass of perfluorocarbon liquid before mixing it with air in a vessel of known volume. This vessel could be detached from the rest of the vacuum line and samples extracted via a tap adaptor with a gastight hypodermic syringe. All the glass joints were sealed and lubricated with a special polar grease made up at the suggestion of ISC Chemicals Ltd who have found that it does not adsorb the perfluorocarbons to any great extent.

Polar lubricating grease

Material	Weight %
Dextrin	24.6
Glycerine jelly	63.2
Mannitol	12.2

The materials were weighed into a basin and heated gently with stirring until the mixture became clear. It was left to cool in a desiccator. All joints and taps on the vacuum line were greased with great care by heating the grease on a spatula and spreading in parallel lines on to the ground glass (also hot). Greased joints were assembled whilst still hot, and turned gently to give a smooth coating. The vacuum was obtained with an Edwards High Vacuum Speedivac ES55 pump. After assembly, the system was checked for leaks with a mercury manometer. Air was let into the line by heating and gently opening tap B. The volume of the vacuum line was measured by filling it with water from a burette. This was done in sections (see Fig.33).

II.A.5.13 PREPARATION OF PRIMARY SERIAL DILUTION STANDARDS

A small volume of perfluorocarbon liquid was placed in the introduction vial by means of a hypodermic syringe. The vial had previously been weighed accurately on an Oertling analytical balance. It was weighed again and the weight of perfluorocarbon calculated.

The vial was connected to the rest of the vacuum line (Fig.32). With taps A, C and E open and B, D and F closed, the pump was switched on

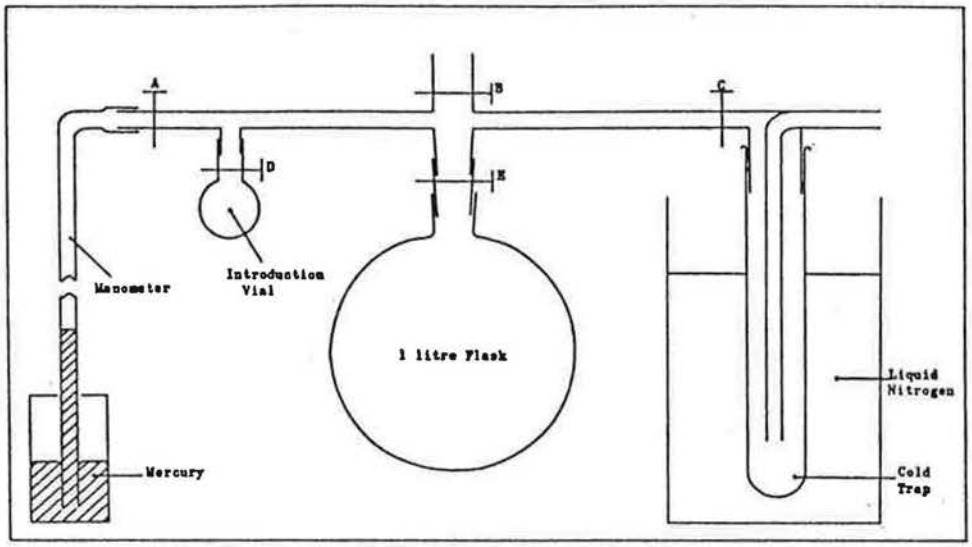


Fig.32 Glass Vacuum Line

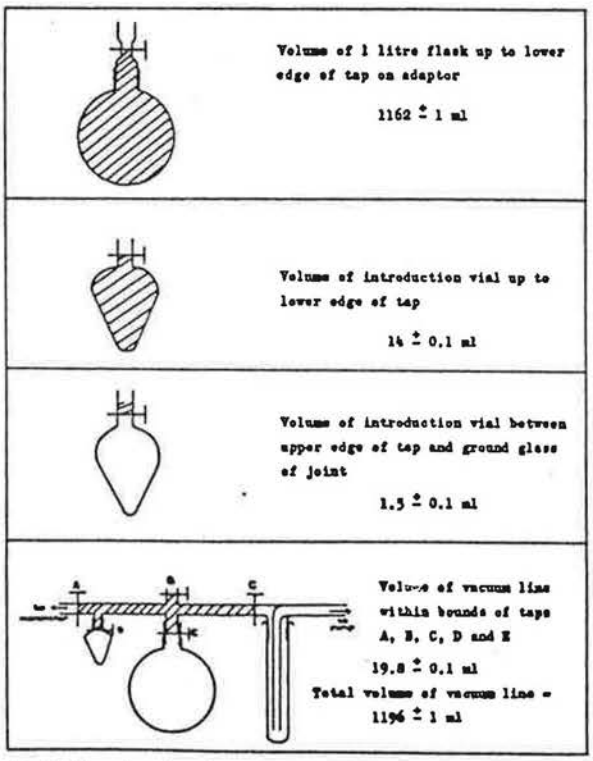


Fig.33 Measuring the volume of the vacuum line

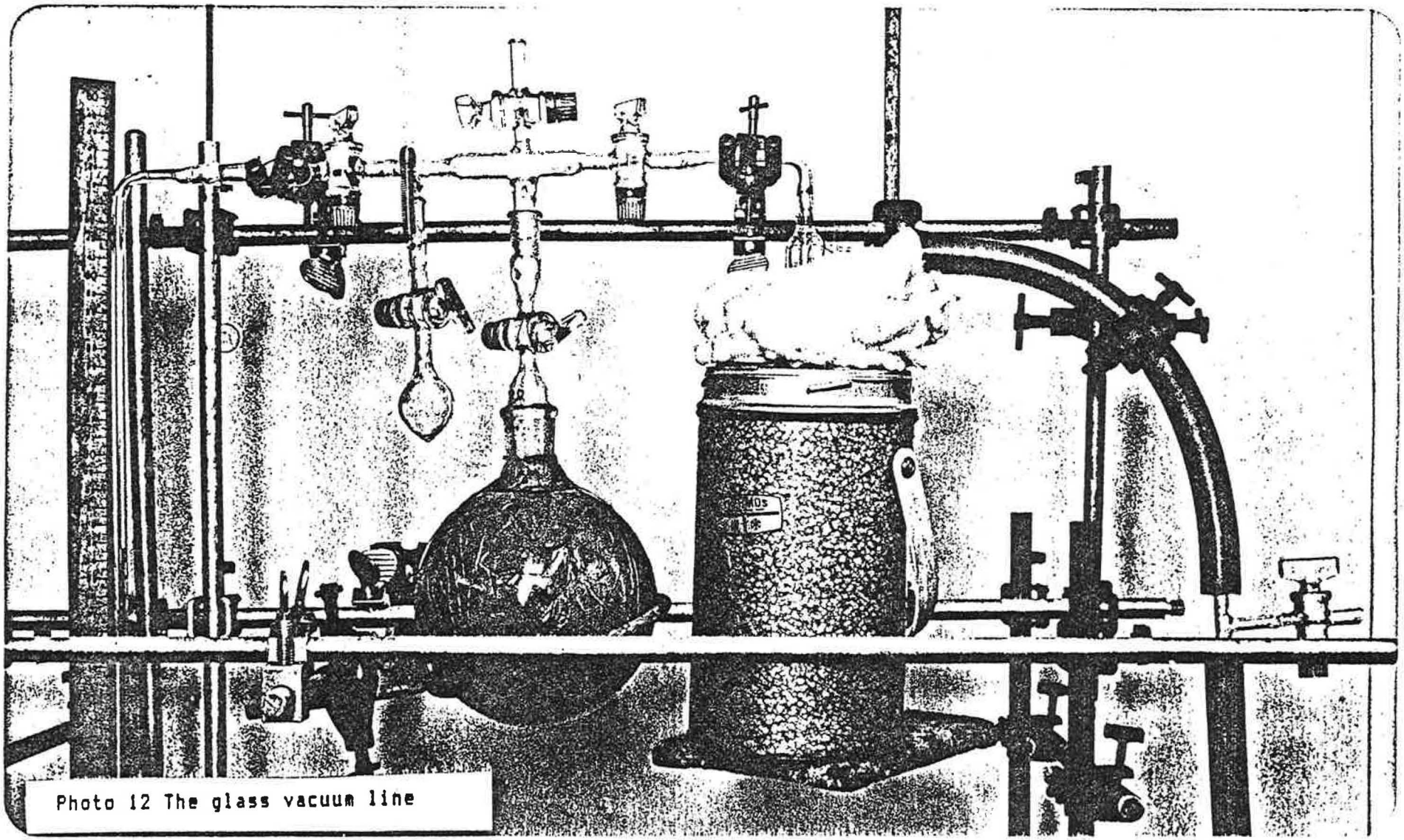


Photo 12 The glass vacuum line

until the mercury in the manometer stopped rising. Tap C was closed and the pump switched off. Tap F was opened to let air back into the pump. The line was left for a few minutes to make sure that the mercury level did not fall, indicating a leak free system. Then, tap A was closed and D opened to allow the weighed perfluorocarbon liquid to evaporate and fill the open volume of the vacuum line. The bottom of the vial was heated gently with a hair drier to encourage dispersion of the perfluorocarbon throughout the evacuated volume and the system left to equilibrate over a period of half an hour. Taps D and E were closed and tap B opened to allow air into the rest of the system. This made it possible to detach the litre flask and its tap adaptor from the rest of the system. Air was then allowed into the flask by slowly opening tap E.

Primary gas standards were made up in this way for each of the four tracer gases. However, in the case of PP5 it was necessary to heat the tiny vial for twenty mintes, leaving the system to equilibrate over a further forty minutes. A 1 ml volume Hamilton gas tight syringe with a luer fitting was used to take samples from the flask for analysis on the gas chromatograph, and for the preparation of serial dilution gas mixtures. The syringe was fitted with a 15 cm long, 24 gauge, stainless steel needle. Six of these were made by Central Surgical Ltd of Amwell Street, London EC1. An 8 cm collar was made in the Polytechnic workshops so that when fitted, only 7 cm of the needle entered the chromatograph injector. This was to protect the column. Serial dilutions of x 250, x 500 and x 1000 were made for each of the tracer gases by fitting tap adaptors to round bottom flasks of volumes 250 ml, 500 ml and 1000 ml respectively. In each case the total volume occupied by the gas mixture was measured by filling the flasks with water from a burette.

250 ml flask	total volume =	294 ml $\pm$ 1 ml
500 ml flask	total volume =	566 ml $\pm$ 2 ml
1000 ml flask	total volume =	1163 ml $\pm$ 1 ml

For each serial dilution mixture 1 ml of the primary standard mixture was taken with the gas tight syringe and injected into an appropriate dilution flask.

For PP2, extra serial dilution mixtures of x 50 and x 2000 were also made. In the first case, 5 ml of the primary standard were placed in

a 250 ml flask and in the second, 0.5 ml of the standard was placed in the 1000 ml flask.

For each gas, at each dilution, between 10 and 20 samples were analysed by the gas chromatograph. The results appeared as sharp narrow peaks on a Servoscribe chart recorder. It was decided that as peak widths at half height were always tiny (within 1% of peak height) a correlation between peak height and mass of tracer would be sufficient and so would remove the need to calculate peak areas by triangulation (ie calculation of h x Wh).

To test this assumption a Hewlett-Packard electronic integrator was connected to the detector with the chart recorder and some standard concentration samples of PP1 in air were tested. Results show that errors in measurement due to the use of peak heights instead of integrated areas were small compared to errors of reproducibility due to the gas tight syringe (Table 10). All the calibration data have been gathered using the peak height method.

II.A.5.14 CALIBRATION RESULTS

A calibration graph has been plotted for each of the four tracer gases. (Figs.34 to 37). Attenuation and mass data were entered into a plotting program which has made a least squares fit to the data producing the best fitting straight line for each gas. The data were processed on the BBC microcomputer and plotted on a Hewlett-Packard 7470 plotter.

Data were plotted as log Attenuation x % chart pen deflection against log mass of tracer in a 1 ml sample of the gas mixture under investigation. Log scales were used because of the large span of gas concentrations. In the case of PP5, all the measurements have been made with respect to the larger of the two isomeric peaks ie, the one at shorter retention time.

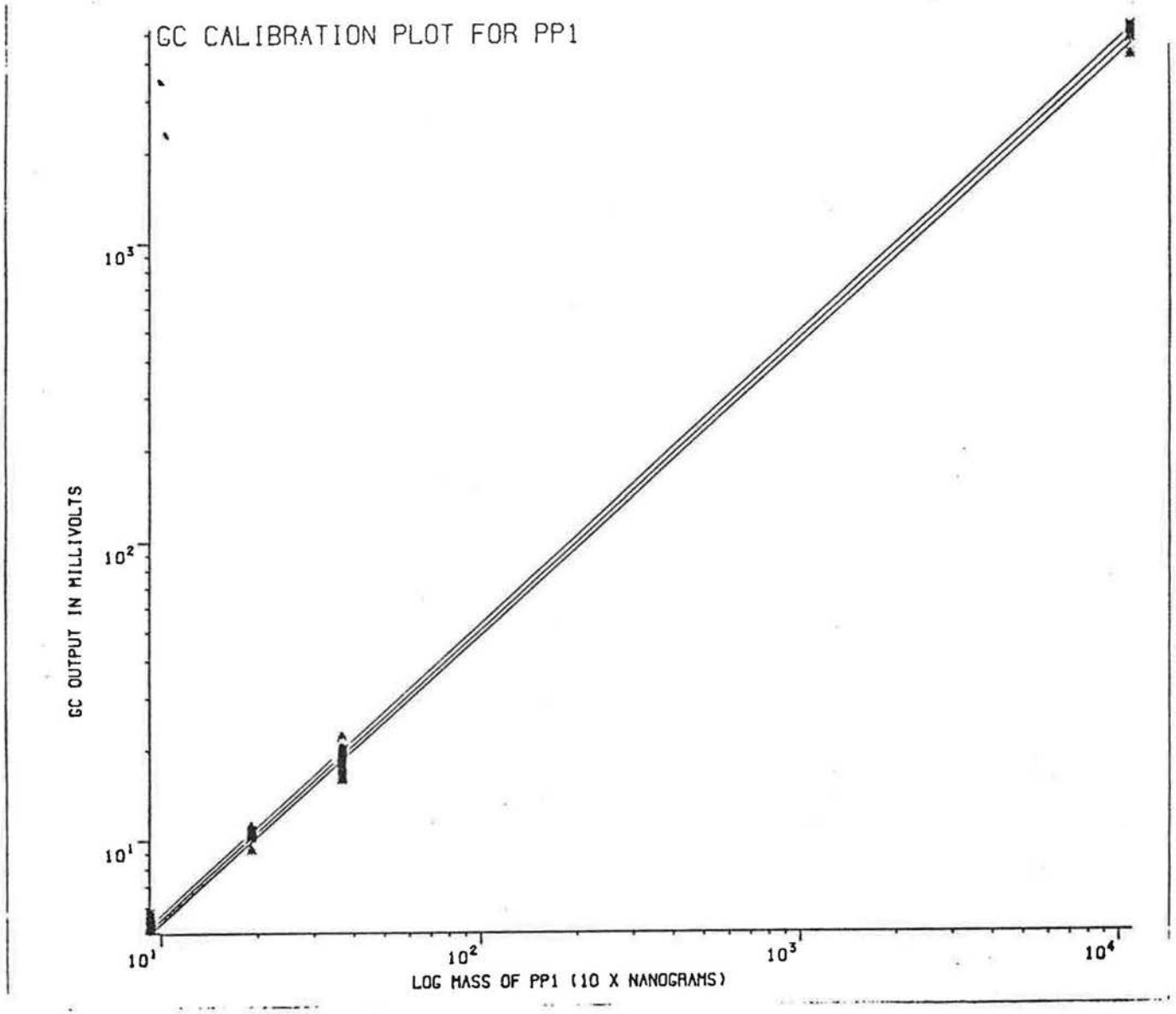
II.A.5.15 CHIEF SOURCES OF CALIBRATION ERROR

All the possible sources of calibration error may be listed:

1 Weighing the liquid perfluorocarbon.
2 Estimating the time to reach equilibration of perfluorocarbon in

Table 10 Comparison of reproducibility between peak heights and integrated areas

PEAK No.	RETENTION TIME (min)	INTEGRATED AREA	HEIGHT ON CHART mm	WIDTH AT ½ HEIGHT mm	TRIANGU-LATION AREA
1	2.5	471250	134	1.0	134
2	2.5	464990	136	1.0	136
3	2.5	464640	135	1.0	135
4	2.5	482811	139	1.0	139
5	2.5	487330	142	1.0	142
6	2.5	475320	136	1.0	136
7	2.5	527920	147	1.0	147
8	2.5	489550	141	1.0	141
9	2.5	498240	145	1.0	145
10	2.5	455370	134	1.0	134
11	2.5	493500	143	1.0	143
Mean	2.5	482811	139	1.0	139
σ		21196	5.6		5.6
σ as % of mean		4.4%	4.1%		4.1%



$y = mx + c$

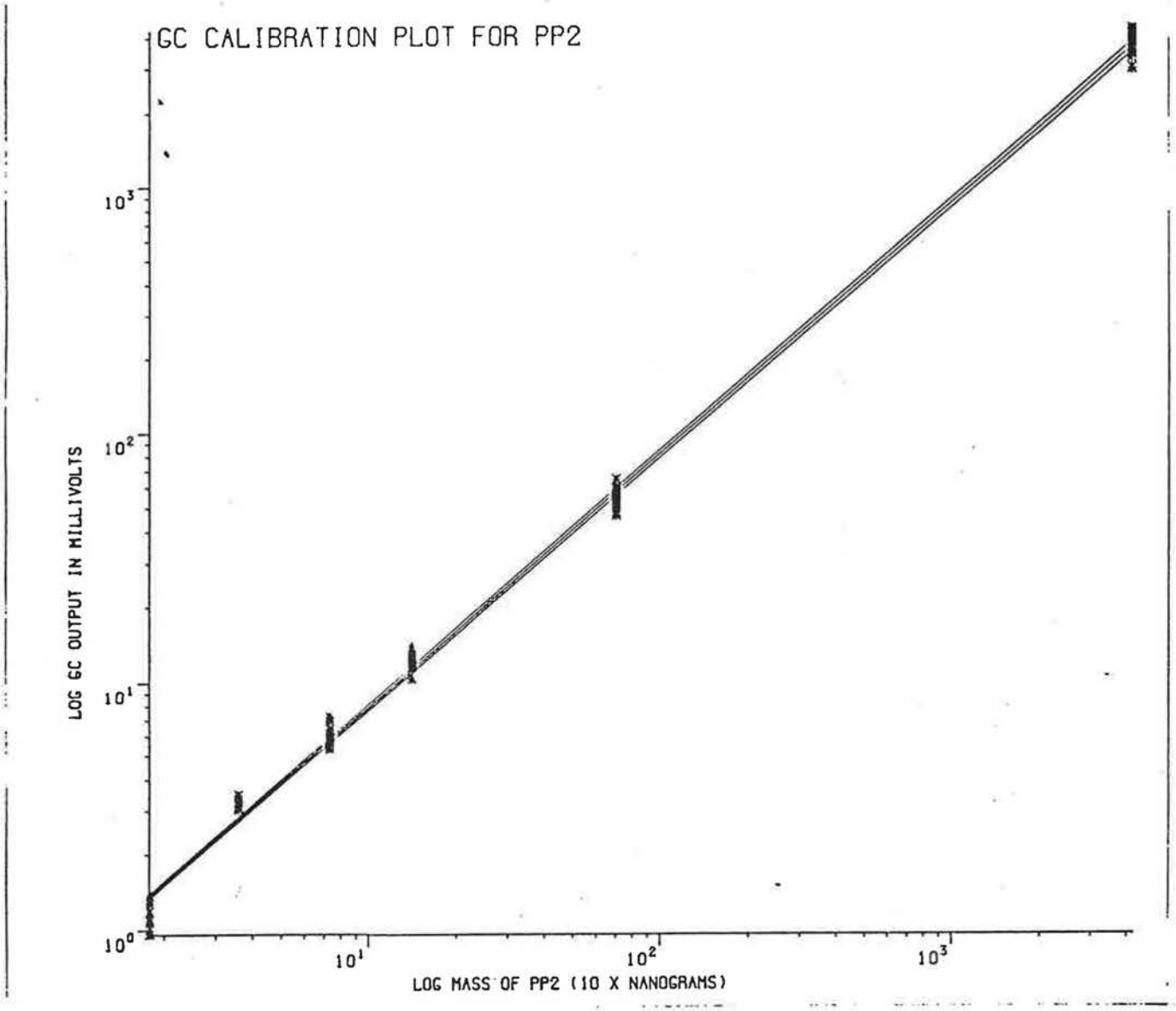
$m = 0.969$

$dm = 0.435 \times 10^{-2}$

$c = -0.230$

$dc = 0.944 \times 10^{-2}$

Fig.34



$y = mx + c$

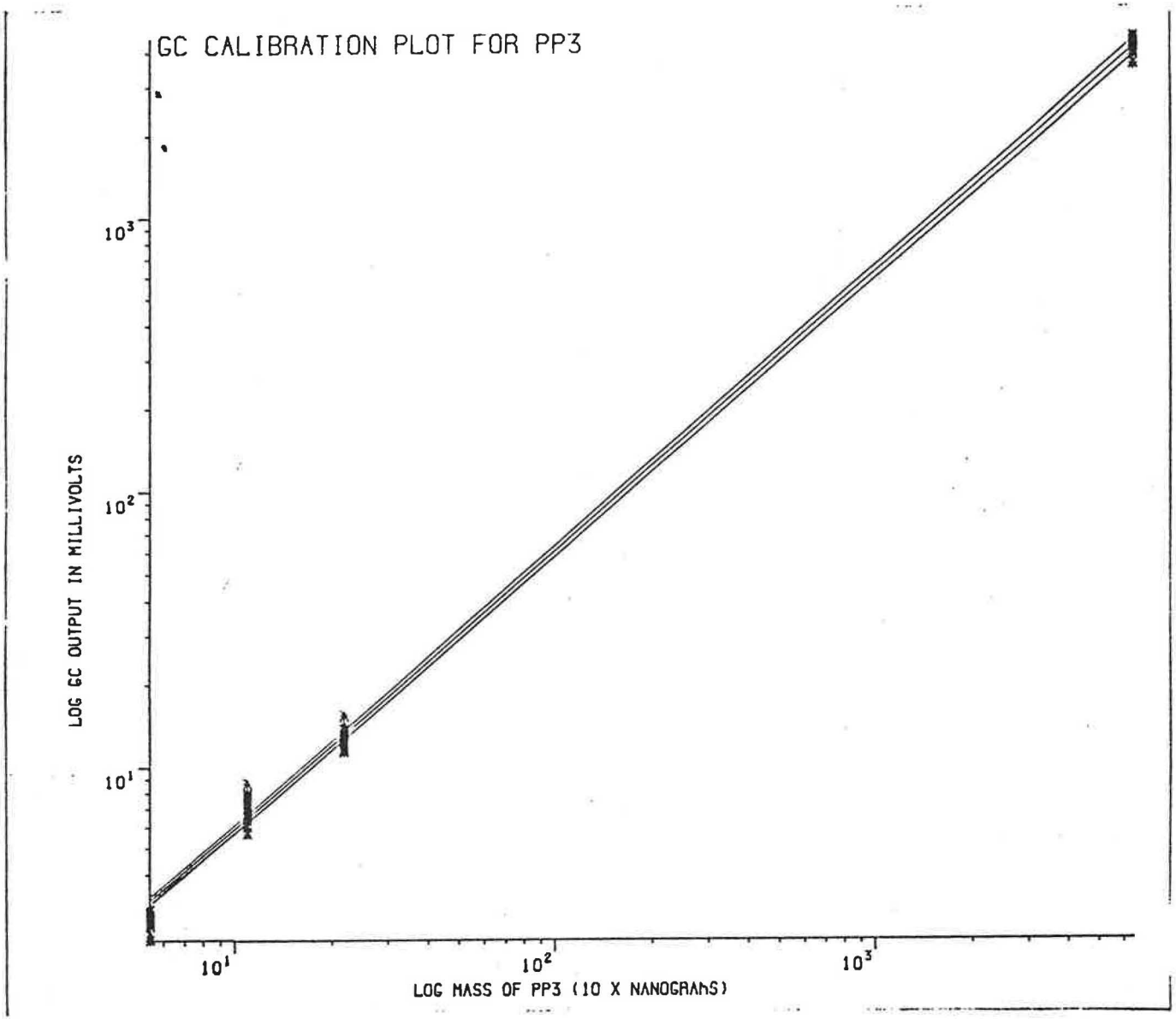
$m = 1.02$

$dm = 0.373 \times 10^{-2}$

$c = -0.115$

$dc = 0.811 \times 10^{-2}$

Fig.35



$y = mx + c$

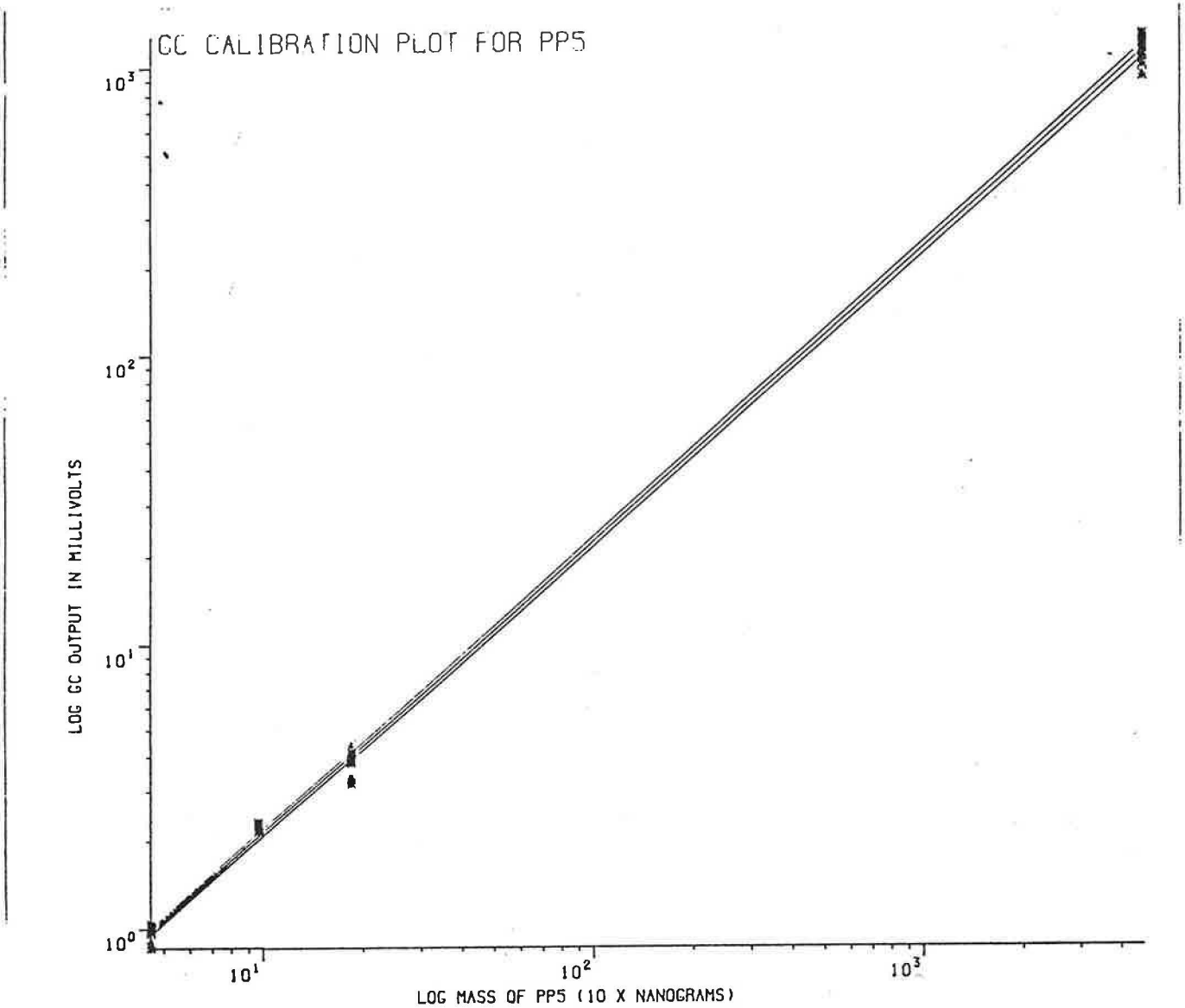
$m = 1.01$

$dm = 0.499 \times 10^{-2}$

$c = -0.239$

$dc = 0.111 \times 10^{-1}$

Fig.36



$y = mx + c$

$m = 1.02$

$dm = 0.412 \times 10^{-2}$

$c = -0.681$

$dc = 0.912 \times 10^{-2}$

Fig.37

the evacuated volume of the vacuum line.
3 Possible small losses incurred allowing air to enter the standard concentration flask.
4 Leaks on the gas tight syringe producing non-reproducible samples for analysis and unreliable serial dilution.
5 Losses while flask tap is open and samples are being withdrawn.
6 Possible absorption of the perfluorocarbons by the teflon plunger of the gas tight syringe.
7 Possible errors in detection.

Great care was taken in weighing the perfluorocarbon liquid. The flask was handled with medical gloves to avoid errors due to grease deposition. The sensitivity of the balance was to within $\pm$ 0.1 mg. After evacuating the volume to be filled by the tracer contained in the introduction vial, the top on the vial was heated and opened. The base of the vial was always heated and the system left for at least half an hour before allowing air into the system and detaching the litre flask. No measurements of the contents of the vial were made to see if equilibrium had been reached, because of its small volume. It was considered that such large errors would be incurred extracting several 1 ml samples of gas from only a 14 ml volume, it would be impossible to make a sensible comparison with the contents of the litre flask.

Leakage of the gas tight syringe proved to be a major source of difficulty and sampling errors. The Hamilton gas tight syringe consisted of a glass barrel accurately calibrated to a volume of 1 ml. The plunger was made of teflon and had a special, self-lubricating tip. This worked due to the regular flaking away of the tip material on to the inside of the barrel. While it fitted tightly, the plunger sealed well. This was tested by immersing the luer end of the barrel in a beaker of water and drawing it into the syringe with the plunger. The formation of any bubbles was an indication of leakage past the plunger.

The manufacturer recommends periodic boiling of the teflon plunger in water for five minutes to restore the tight fit. This was found to work well. The most difficult leaks to overcome were those resulting from a poor connection between needle and luer fitting on the syringe.

By spreading the polar grease, described above, thickly round the

outer joint between needle and barrel, leaks could be largely overcome. However, it was necessary to clean and regrease frequently as they tended to form again.

A further point of concern involved the possible absorption of perfluorocarbons by the teflon plunger. To test for this possibility, the syringe was filled with perfluorocarbon from a high concentration standard mixture. The syringe was then emptied and flushed with air by rapidly moving the plunger in and out of the barrel. With the detector amplifier at high sensitivity, the syringe was filled with air and the air injected into the gas chromatograph. No peaks appeared, showing that there was no measurable absorption (and subsequent desorption) effect. Any errors due to the detector are likely to be negligably small compared to syringe reproducibility errors and may be ignored.

II.B DEMONSTRATION OF THE METHOD

Experiments were carried out using the modified prototype sampling system to evaluate the method in terms of the suitability of the chosen gases, the sampler design, and the chemical analysis of collected samples. These tests were carried out in an office in one of the PCL buildings.

Four distinct experiments were necessary to evaluate the sampling system, the tracer gases in use and the method as a whole. The first involved testing to see whether or not the gases are absorbed by walls and furnishings (see section II.B.1). The second investigated the possibility of stratification occurring over a period of time both with and without a mixing fan (see Part II.B.2). The third observes the degree of mixing of the tracers in room air, under the influence of the release heater and no fan (see section II.B.3). Finally, some experiments were carried out to show first with one gas and then with two simultaneously, how the air between two adjacent zones mixes when a door between them is opened (see section II.B.4).

II.B.1 TESTS FOR ABSORPTION INTO WALLS AND FURNISHINGS

Method

An office of volume 33 m^3 with a false panelled wall, carpeted concrete floor, concrete ceiling and large sliding double glazed windows was sealed with tape over joints in the wall, gaps in the ceiling, the window frame and the skirting board (Photo 13 and 14).

The sampling system was set up and checked for leaks and flow equality through the sampling tubes and the 'atmosphere inlet' needle valve. The tracer release system (Photo 15) was set up in the middle of the room with an oscillating fan to ensure good mixing. One sampling unit was placed at each end of the room (Fig.38) and the trolley with the pump and switching equipment was positioned outside the door. 1 ml of each tracer was released into the room air by dropping the liquid from a syringe on to the heater at 160°C. The door was then closed and sealed from the outside. The fan was switched on. After 27 minutes the fan was switched off and the pump switched on. After a further 3 minutes, the first sample was taken. A further four samples were taken at intervals of 30 minutes. The test was repeated using

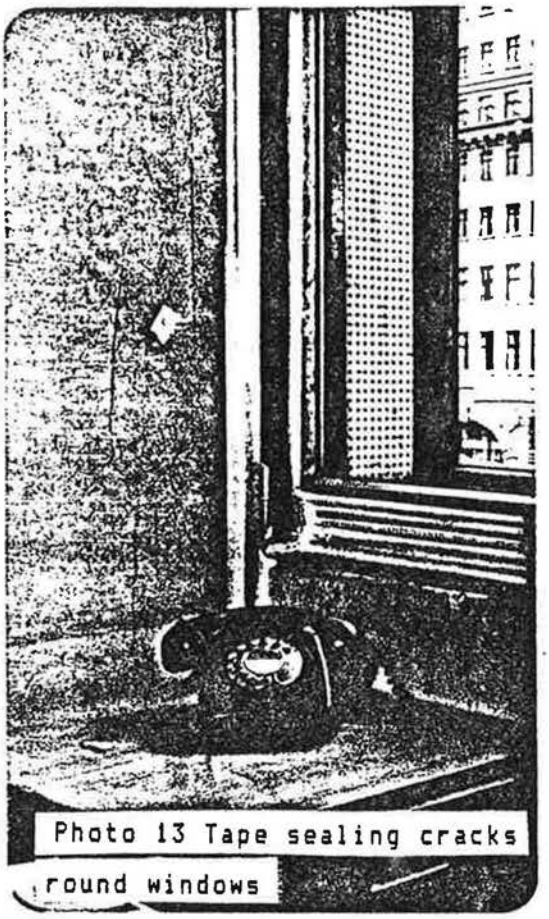


Photo 13 Tape sealing cracks round windows

Photo 14 Tape sealing joints in false wall

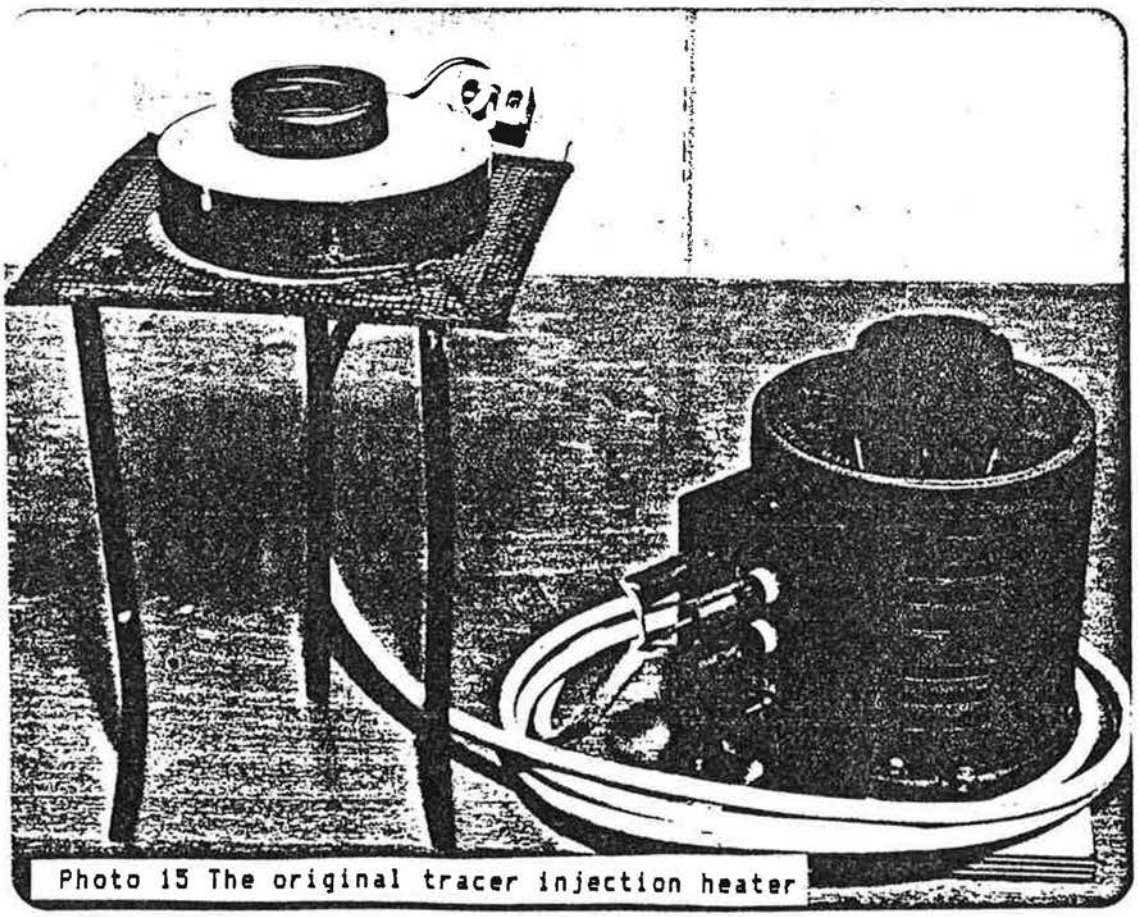


Photo 15 The original tracer injection heater

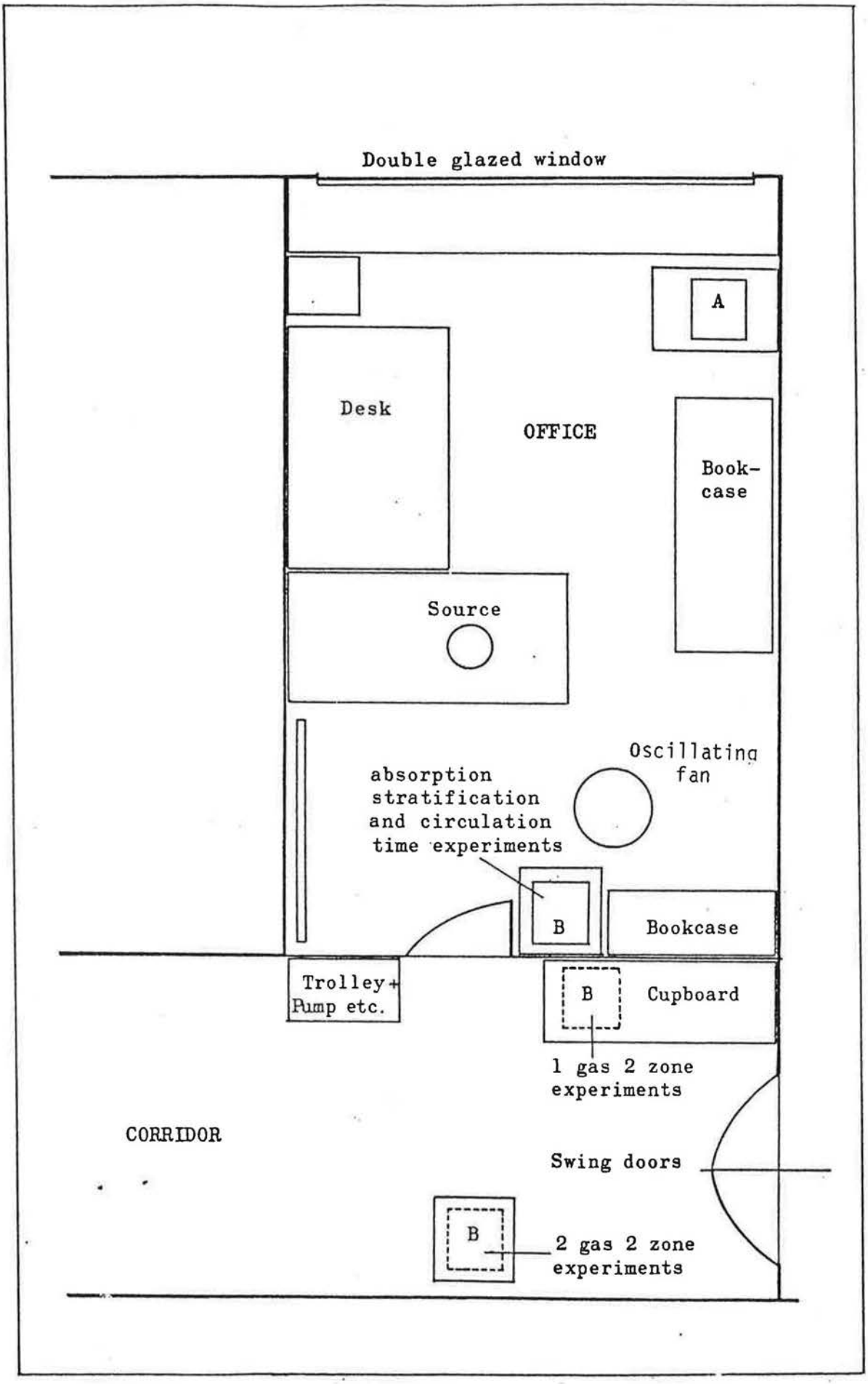


Fig.38 The office and corridor used for air movement tests.

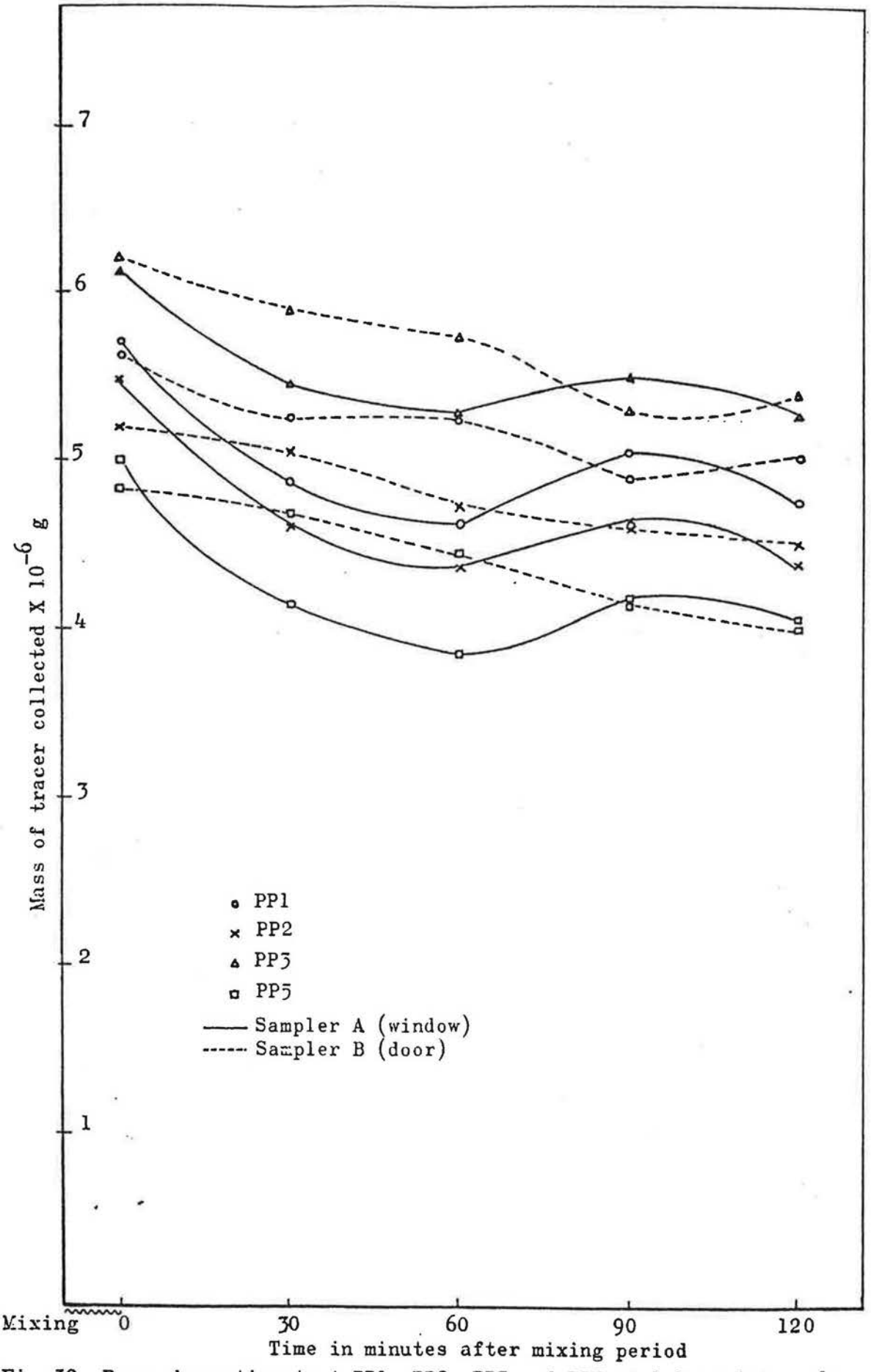


Fig.39 Room absorption test PP1, PP2, PP3 and PP5 at 1 hour intervals

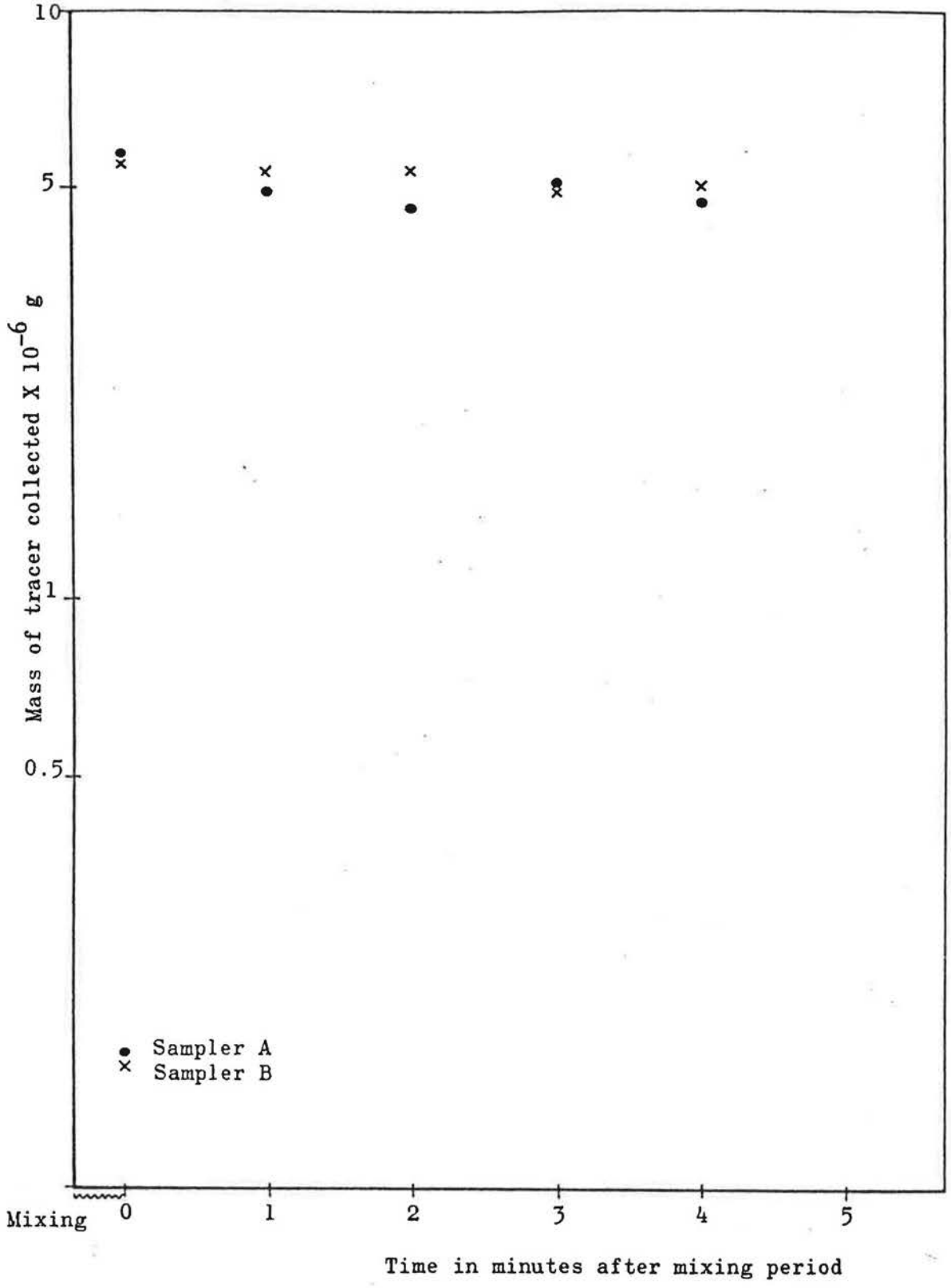


Fig.40 Semi-log plot of PP1 data from 1 hour interval absorption test

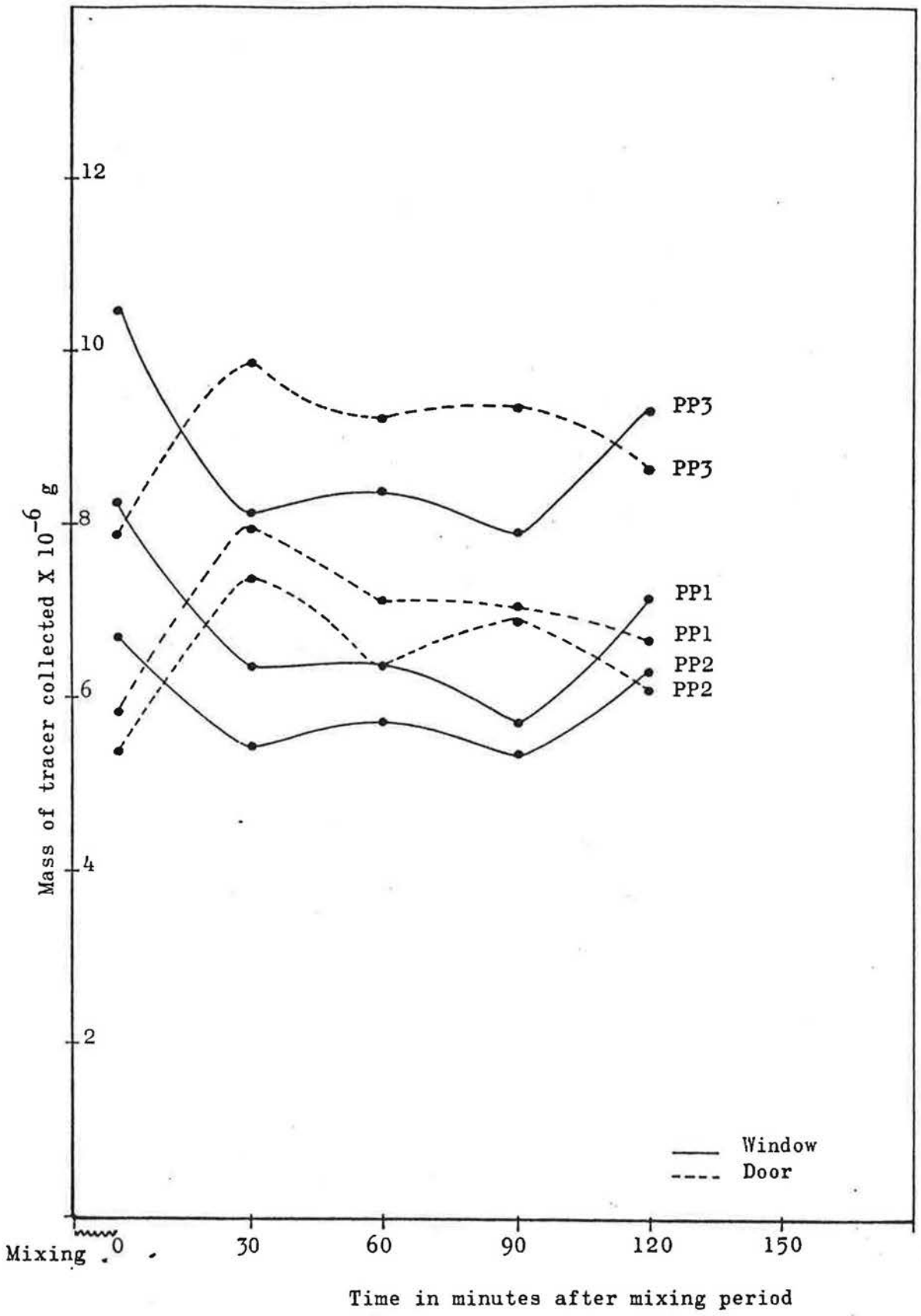


Fig.41 Room absorption test, sample intervals 30 minutes.

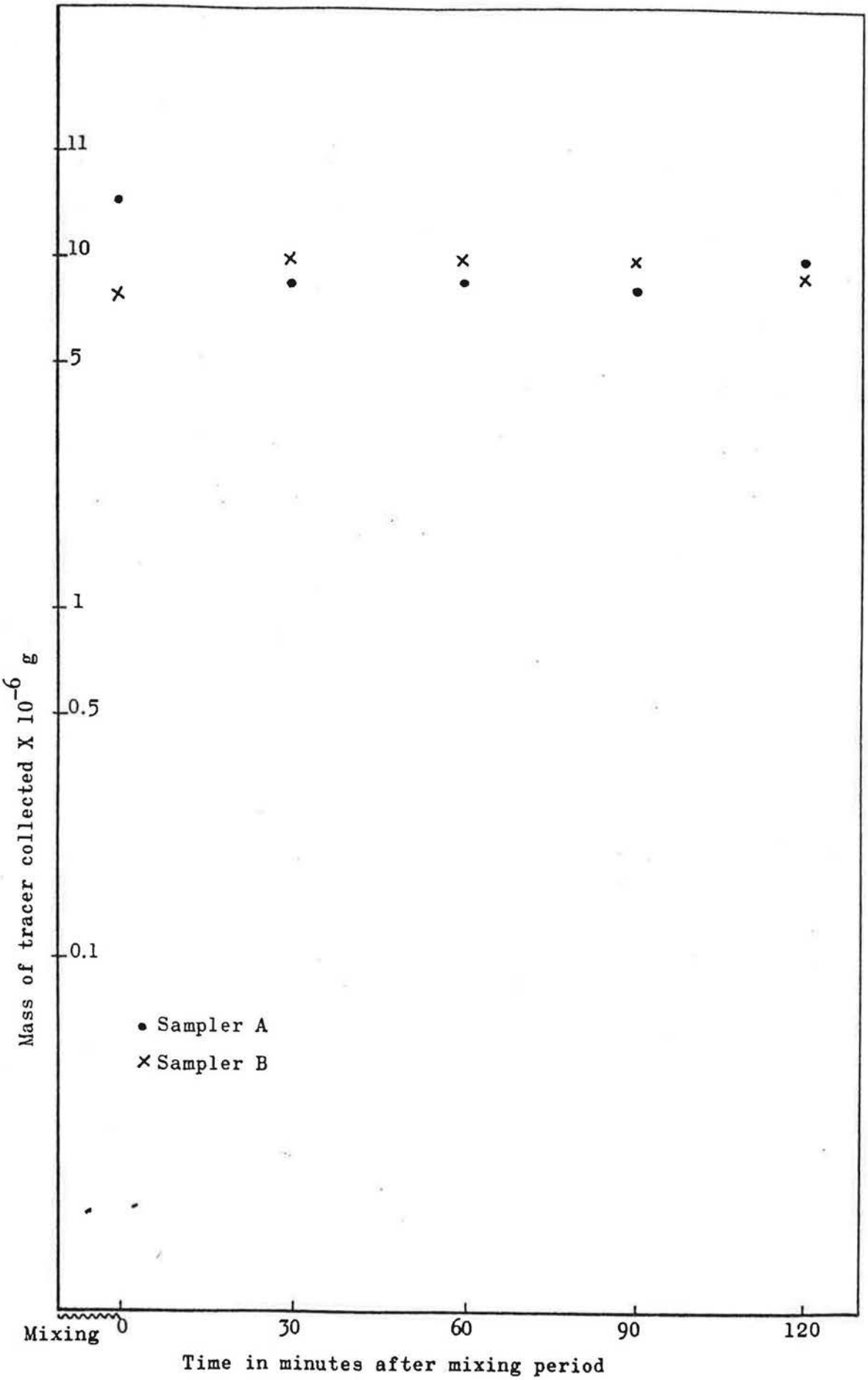


Fig.42 Semi-log plot of PP1 data from absorption test using $\frac{1}{2}$ hour sampling intervals.

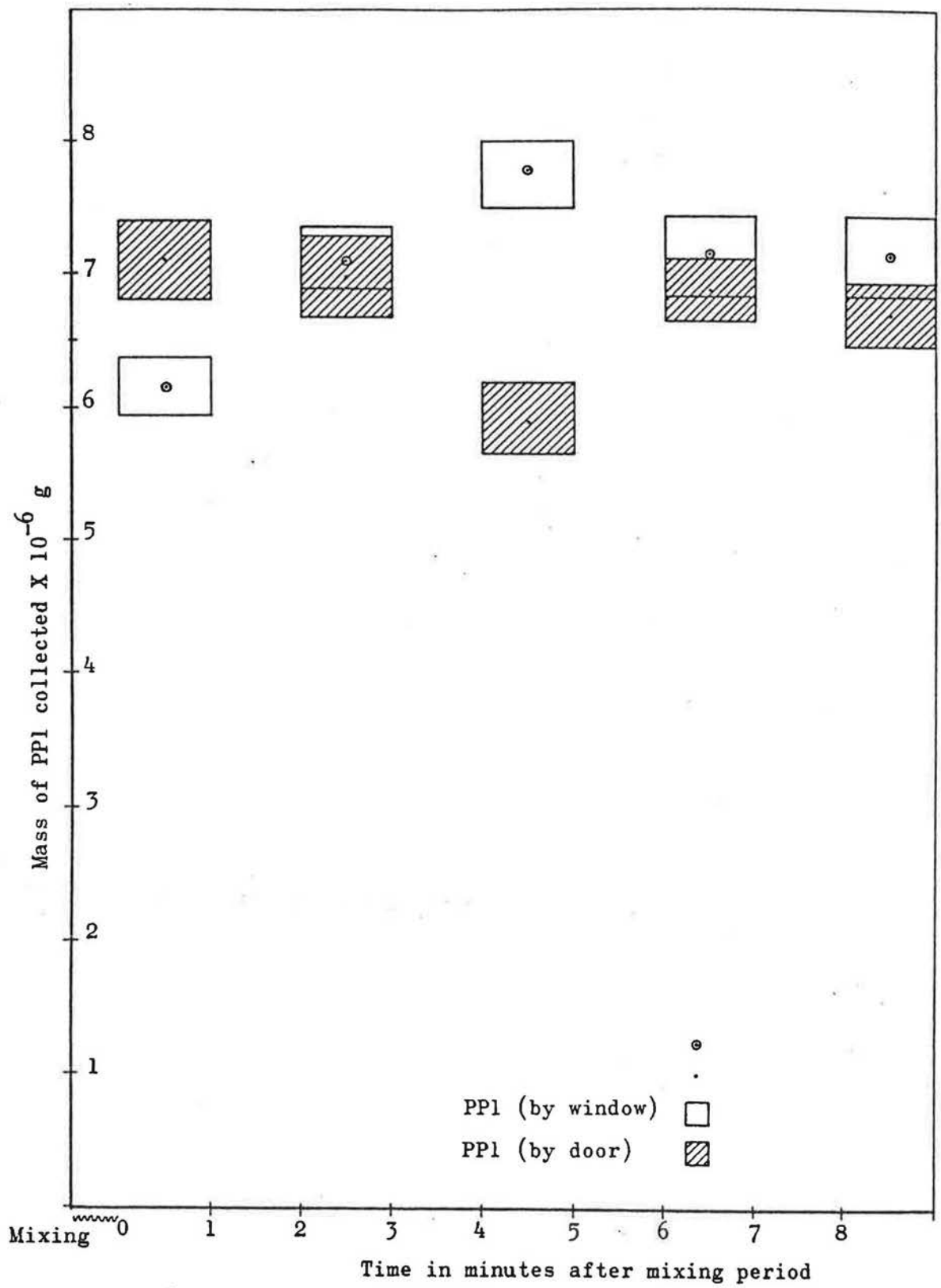


Fig.43 Room absorption test, sample intervals one minute.

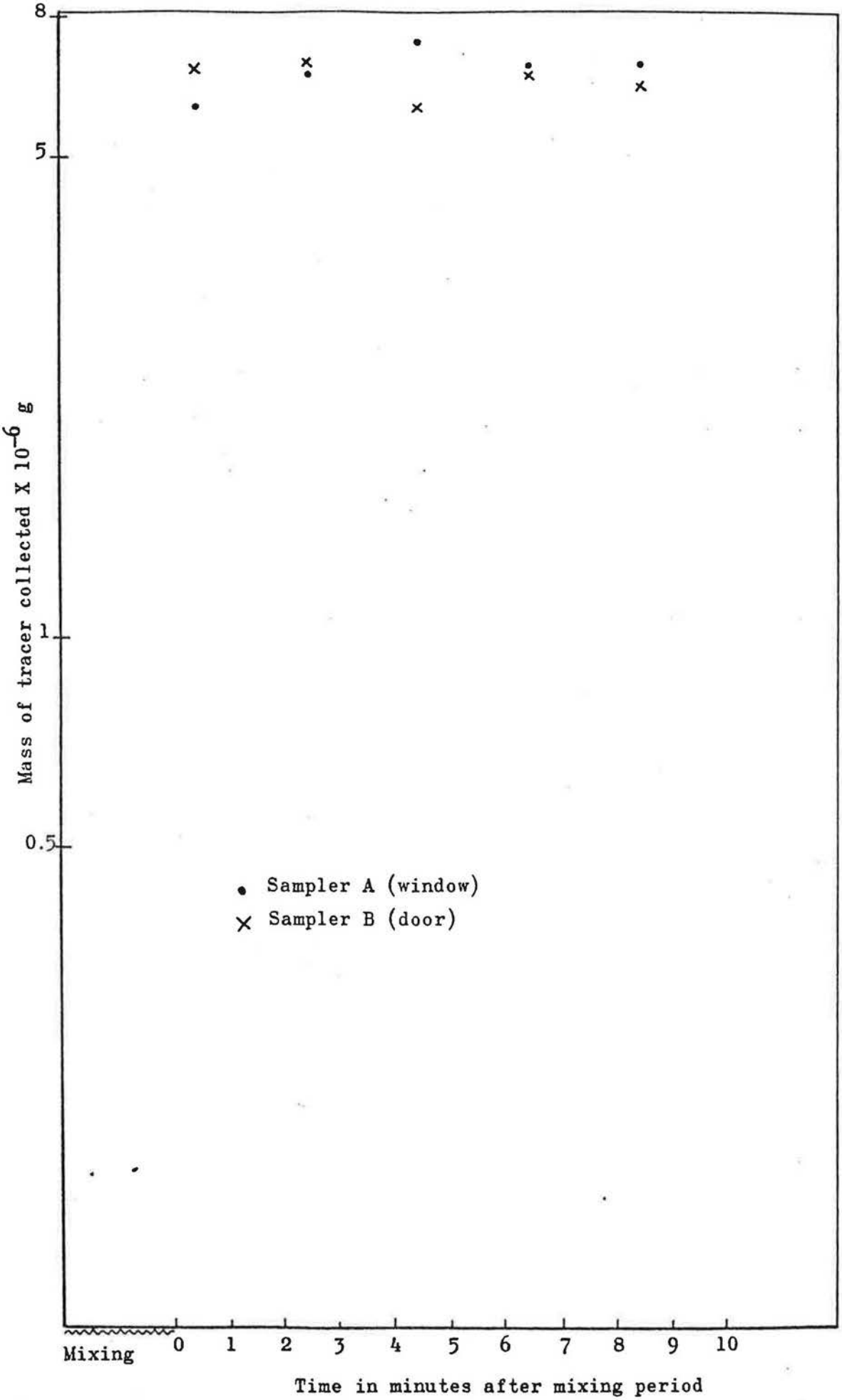


Fig.44 Semi-log plot, room absorption test at 1 minute intervals

intervals of one hour and intervals of one minute between samples. The sampling intervals were chosen arbitrarily. If it could be demonstrated that no significant absorption takes place over a relatively long time such as 5 hours, it would be safe to assume that experiments taking place over a shorter time would not carry the risk of losses by absorption.

The experiment carried out at sampling intervals of one minute, after a 30 minute mixing interval, aims to show that the small tracer gas losses observed during the 0.5 hour and 1 hour interval experiments were not an artifact of the sampling equipment.

Results

In each adsorption test experiment, all four tracer gases were released and observed. Fig.39 shows a plot of concentration against time for PP1, PP2, PP3 and PP5 where samples were taken at hourly intervals. The plot clearly shows that some decay of all the gases occurs in this time and that the concentration versus time patterns are similar for all the gases. Equation 1 (see section I.6.1) has been used to calculate the air change rate with respect to each gas in turn (see Table 11). Plots of log concentration versus time yielded straight lines whose slopes, calculated from a least squares fit give a direct estimation of the air change rate. The semi-log plot of PP1 data is illustrated in Fig.40. The average air change rate indicated was only $(1.7 \pm 0.3) \times 10^{-2}\ h^{-1}$. The small loss of gas is probably due to residual infiltration occurring in the room even though it was carefully sealed.

On a different day, the experiment was repeated with half hourly sampling intervals. Fig.41 shows the concentration versus time pattern displayed. Again plots of log concentration against time yielded straight lines indicating an air change rate of $(0.7 \pm 0.3) \times 10^{-2}\ h^{-1}$. Fig.42 illustrates the for PP1.

Data from the 1 minute interval experiment is illustrated for PP1 only in Figs.43 (concentration versus time) and 44 (log concentration versus time). Some scatter is present but there is no firm pattern of results to indicate an artifact of the sampling system.

The conclusion is that none of the perfluorocarbons is absorbed by the

test space materials. This is in keeping with results of tests for absorption of perfluorocarbons by test space materials carried out by Dietz and Cote (95).

Table 11 Least squares fits to data from absorption tests

FIG.	EXPERIMENT	SAMPLER	TRACER GAS	SLOPE LOG MASS / TIME $= -h^{-1}$
41	Absorption test ½ hour intervals 2 hour duration	A	PP1	-3.36×10^{-2}
			PP2	-2.34×10^{-2}
			PP3	-2.48×10^{-2}
		B	PP1	1.36×10^{-2}
			PP2	1.49×10^{-2}
			PP3	1.17×10^{-2}
		A + B	PP1	-1.00×10^{-2}
			PP2	-4.26×10^{-3}
			PP3	-5.47×10^{-3}
39	Absorption test 1 hour intervals 5 hour duration	A	PP1	-1.08×10^{-2}
			PP2	-1.92×10^{-2}
			PP3	-1.48×10^{-2}
			PP5	-1.82×10^{-2}
		B	PP1	-1.31×10^{-2}
			PP2	-1.61×10^{-2}
			PP3	-1.65×10^{-2}
			PP5	-2.24×10^{-2}
		A + B	PP1	-1.36×10^{-2}
			PP2	-1.76×10^{-2}
			PP3	-1.56×10^{-2}
			PP5	-2.03×10^{-2}

II.B.2. TESTS FOR PERFLUOROCARBON STATIFICATION

Sampling point A was placed 2.89 m above the floor and point B was placed 1.36 m above the floor and directly beneath point A (Fig.45). The four tracer gases were released as before and the door sealed from the outside. An oscillating fan was used to mix the gases for 27 minutes before the collection of the first sample at 30 minutes after the gas release. Further samples were taken at 30 minute intervals.

Two experiments were carried out. In the first, the fan was switched

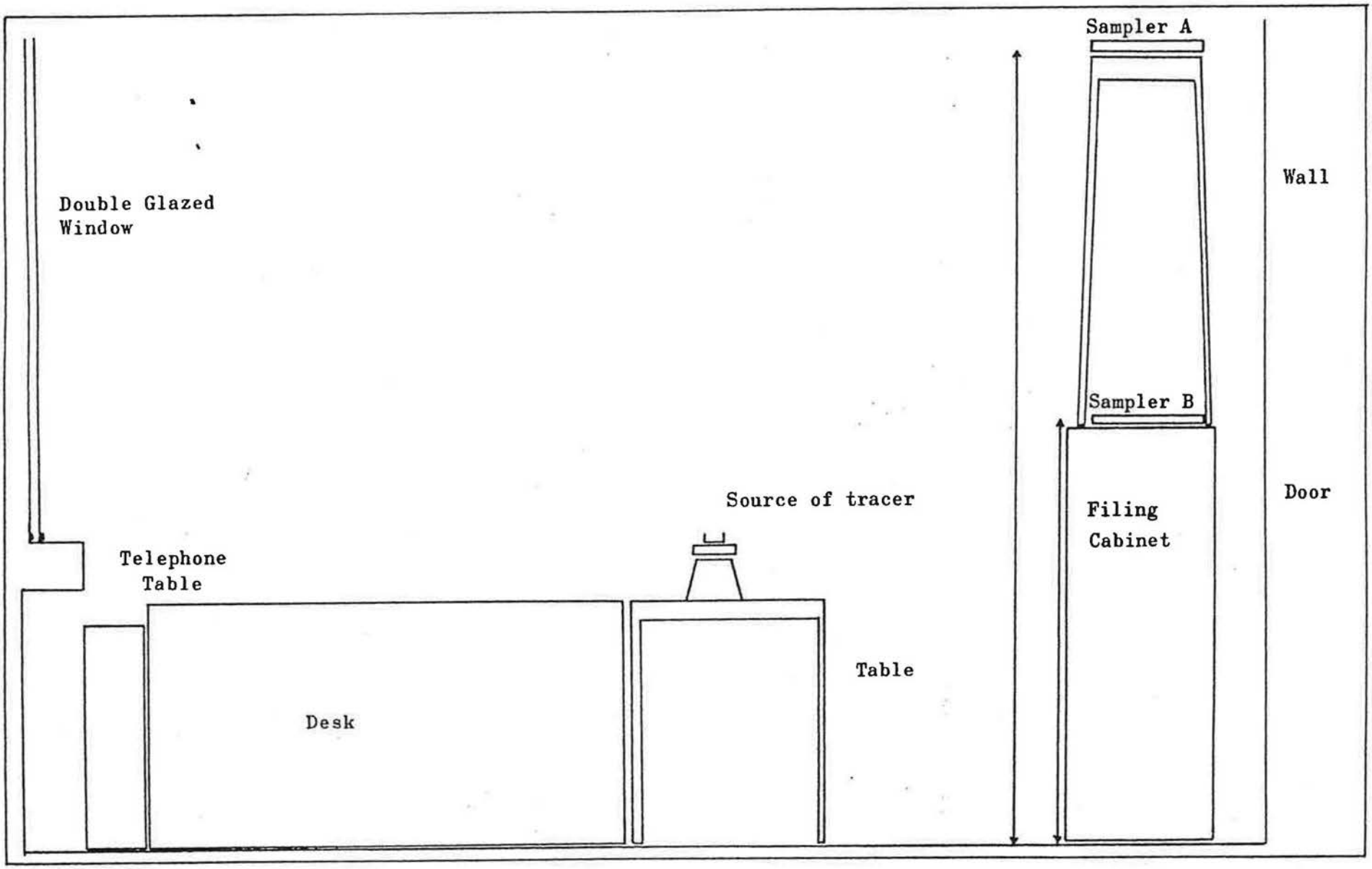


Fig.45 Arrangement of samplers for the stratification tests.

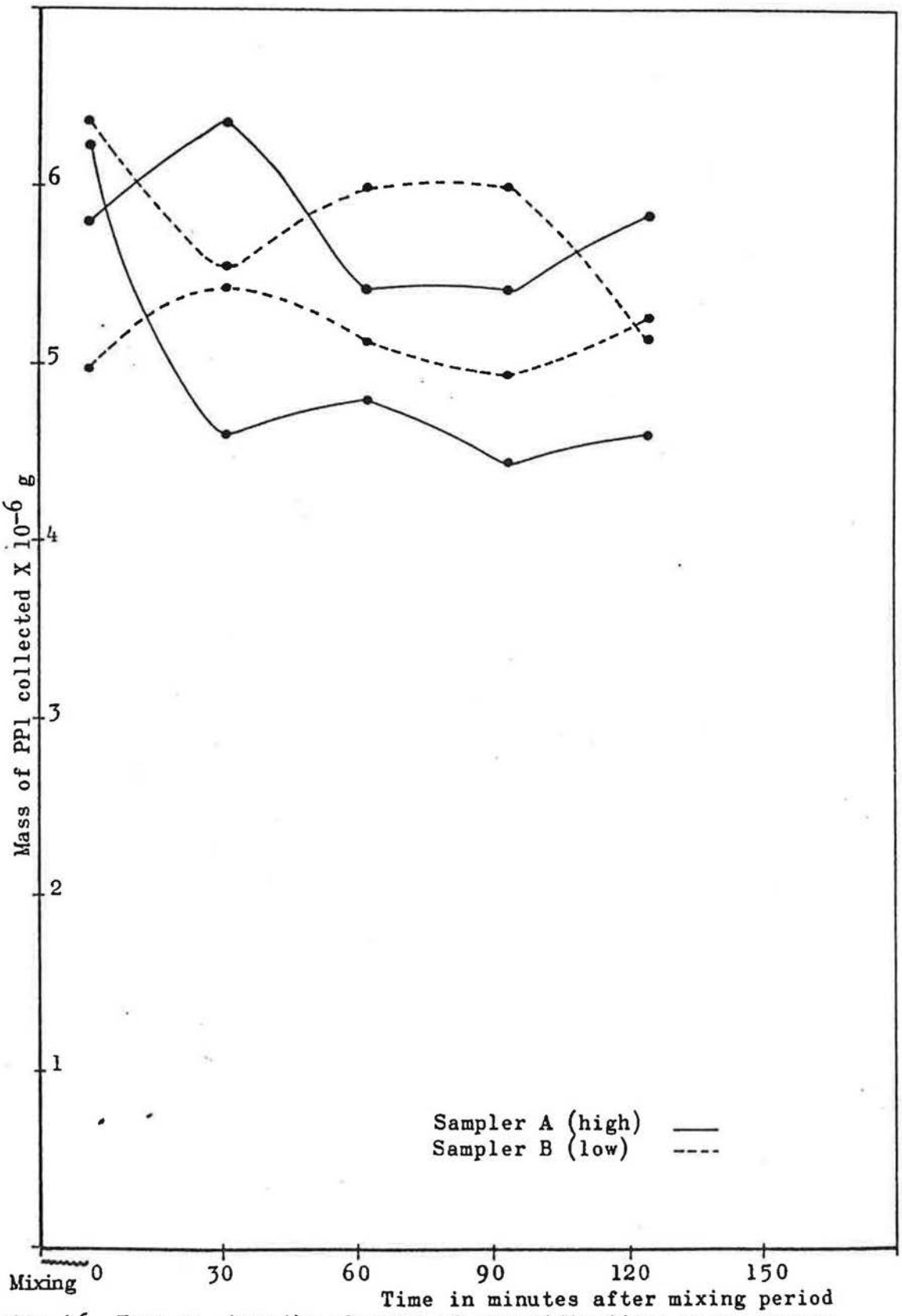


Fig.46 Test to show the absence of stratification: upper curves mixing fan on, lower curves fan off.

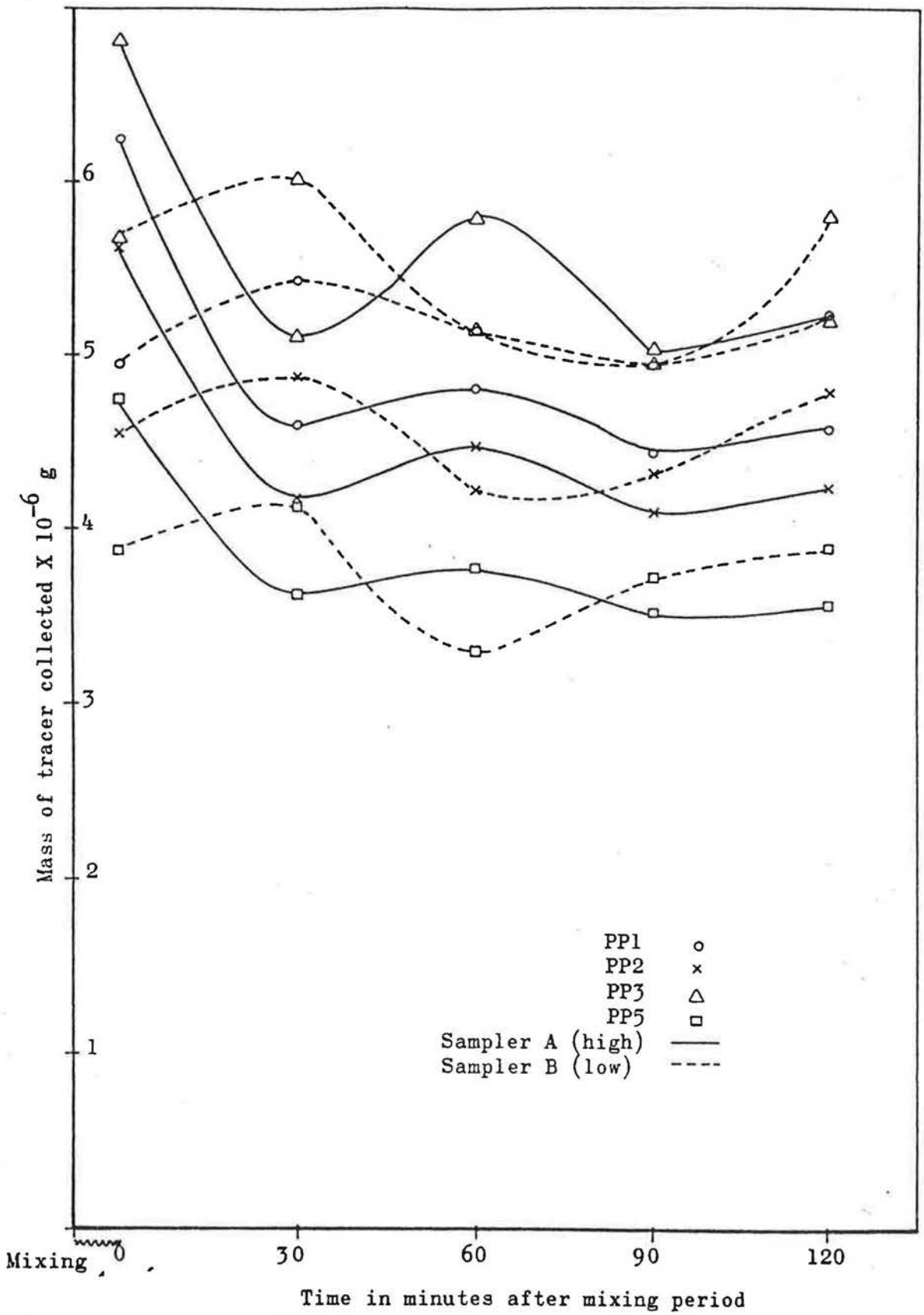


Fig.47 Test to show the absence of stratification with the heavier tracers.

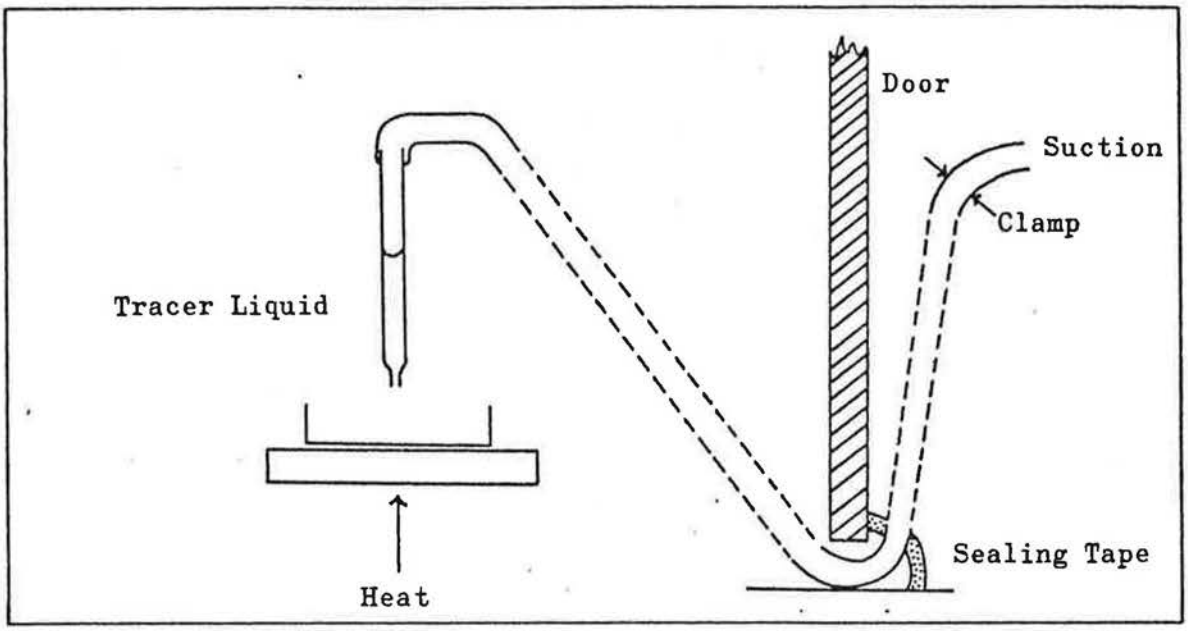


Fig.48 The Remote Release System

on and off between taking samples. In the second, the fan was left switched off. The aim of this test was to see if continuous mixing would be necessary to prevent stratification occurring over the 2.5 hour period of the experiment.

Results

Fig.46 illustrates the results of the two profile tests for the lightest tracer gas PP1 (molecular weight 338). The top curves show behavior with the fan on and the lower curves show behaviour with the fan off. If stratification should occur in either case, the results would indicate a gradual increase in concentration at the lower sampling point and a corresponding decrease at the higher one. In neither case does this happen.

Fig.47 shows the behaviour of all four gases together in the fan off experiment. Again it can be seen that there is no tendancy for any of the gases to stratify over the 2.5 hour duration of the experiment even without the influence of continuous mixing.

II.B.3 THE EFFECT OF THE HEATER ON THE MIXING OF THE TRACERS WITH ROOM AIR

An attempt was made to assess the effect of the release heater on the quality of tracer gas mixing with air in the sealed room in the absence of a mixing fan. The sampling units were set up as in the absorption test experiments with A by the window and B by the door. Samples of PP1, PP2 and PP3 were released remotely into the sealed room using the scheme shown in Fig.48. The fan was not used.
A plastic syringe was suspended over the tracer release heater and supported by a clamp and retort stand. Flexible rubber tubing was attatched to the syringe and this was lead underneath the door to the corridor outside. A mixture of PP1, PP2 and PP3 was sucked into the syringe and a clamp on the rubber tube was closed to hold the liquid in place until release was required. The door was sealed as usual from the outside and the perfluorocarbon mixture was released by opening the clamp. After two minutes the first sample was taken, the other samples following at one minute intervals. The experiment was repeated using PP2 only, and again with PP1, PP2 and PP3 released by hand.

Results

Results from all the tests show that initially, air flows from the heater to the relatively cold window surface. Fig.49 illustrates the concentration changes for each gas at each sampler, beginning two minutes after the remote release of the gases. The relatively high concentrations at the window (A) and low concentrations at the door (B) are evened out to equilibrium within 10 minutes of taking the first sample.

A comparison of Fig.49 with Fig.50 for PP1, PP2 and PP3 (released by hand before sealing the door) shows that the effect of the heater on the tracer gas air mixing is much more significant than that of a person walking into and out of the room.

The conclusion drawn from this experiment is that in the absence of a mixing fan, the time required by the gases to form a uniform distribution across the 33 m^3 room is only ten minutes.

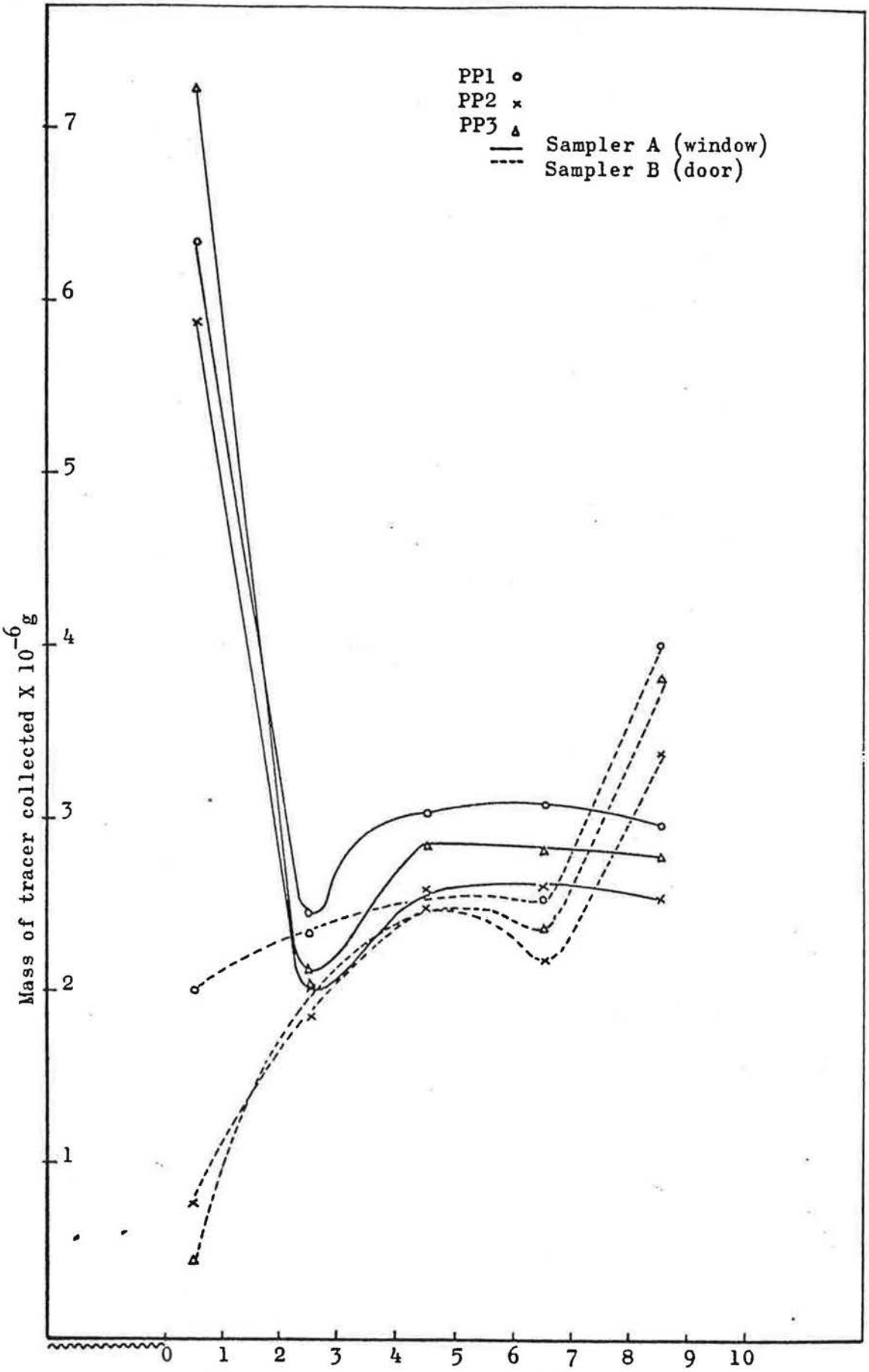


Fig.49 Effect of heater on circulation time - Remote release

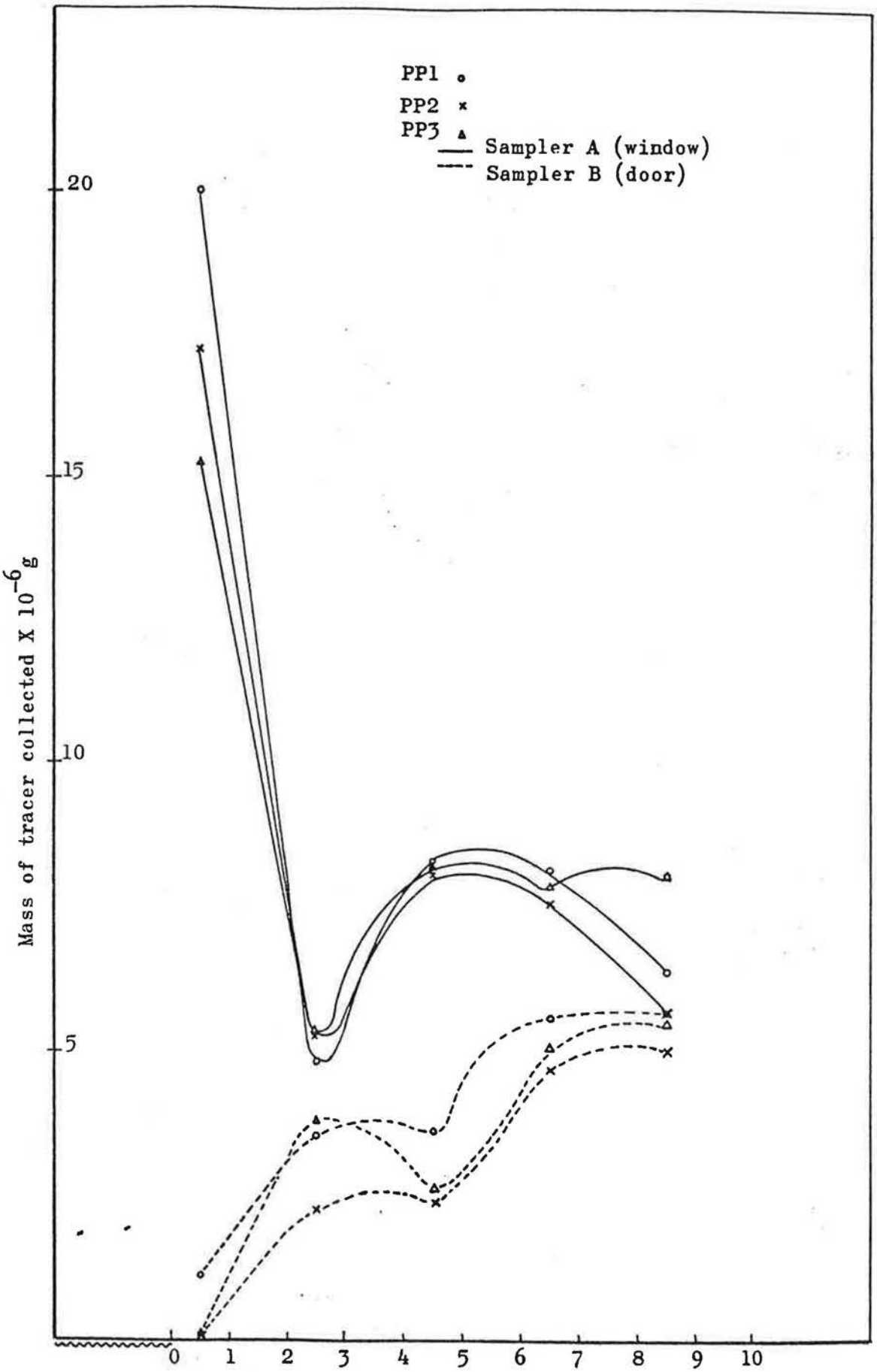


Fig.50 Effect of heater on circulation time - Release by hand

II.B.4 EXPERIMENTS TO SHOW AIR MOVEMENT BETWEEN ZONES

II.B.4.1 AIR EXCHANGE BETWEEN ROOM AND CORRIDOR: AIR SWEPT OUT BY OPENING DOOR

In these tests, PP2 was released into the office which was then sealed for 20 minutes whilst the air was mixed with a fan. The door was opened and samples taken at intervals of one, five and ten minutes. Two configurations each with two sample points were used. Configuration one: two samplers, one inside the room by the window and the other one just inside the doorway. Configuration two: one in the room and the second in the corridor just outside the door (Fig 38).

Both samplers in the room

Fig 51 shows that opening the door causes a large exchange of air, so that the concentration of tracer falls uniformly throughout the room by a factor of 3 within 10 minutes. similarly, Fig 52 illustrates the same behaviour with higher time-resolution. In the first 2.5 minutes the mean tracer concentration falls from 5.2×10^{-9} g l^{-1} to 3.5×10^{-9} g l^{-1}, indicating that roughly 0.4 of the air in the room, or 13 m^3 is swept out into the corridor.

One sample point in the room and one in the corridor

During the daytime, although the room was sealed (apart from its open door) the internal corridor was not. There was some movement of people through the corridor, opening and closing the doors at either end.

Fig 54 illustrates the rapid drop in room tracer when the room door is opened, accompanied by a rapid rise in corridor concentration. The two equalise in about 2.25 minutes in spite of the fact that the spaces are isothermal. The overall decay is caused by air movement out of the corridor at the rate of 1.5 air changes h^{-1} (see Fig 55). At night, (Fig 56) when no use is made of the corridor, an identical experiment shows an airchange rate very close to zero. Fig 56 also illustrates the rapid equalisation of tracer concentration in room and corridor after only 25 minutes, at night.

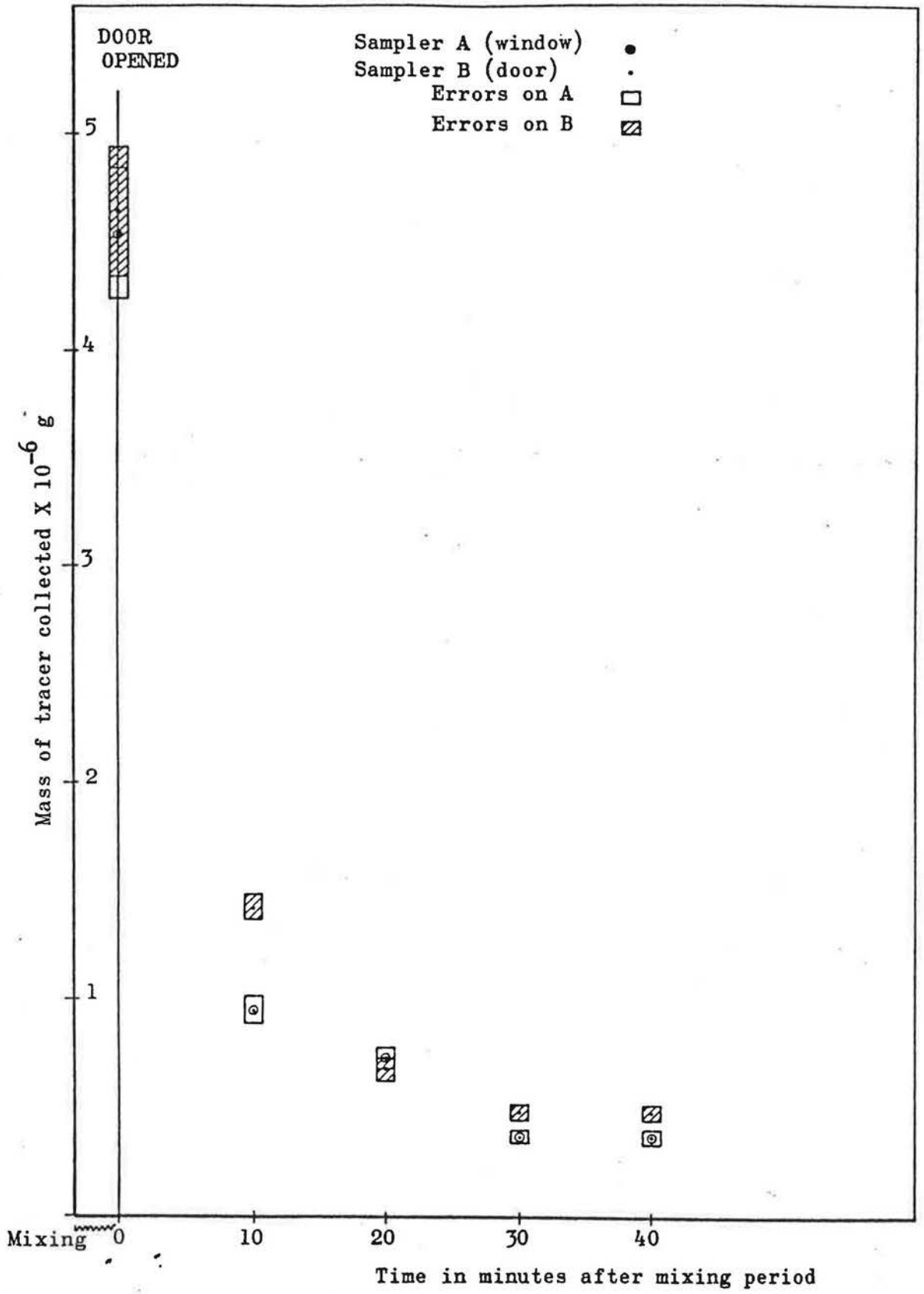


Fig.51 Loss of room air to the corridor on suddenly opening the door. – 10 minute sampling intervals.

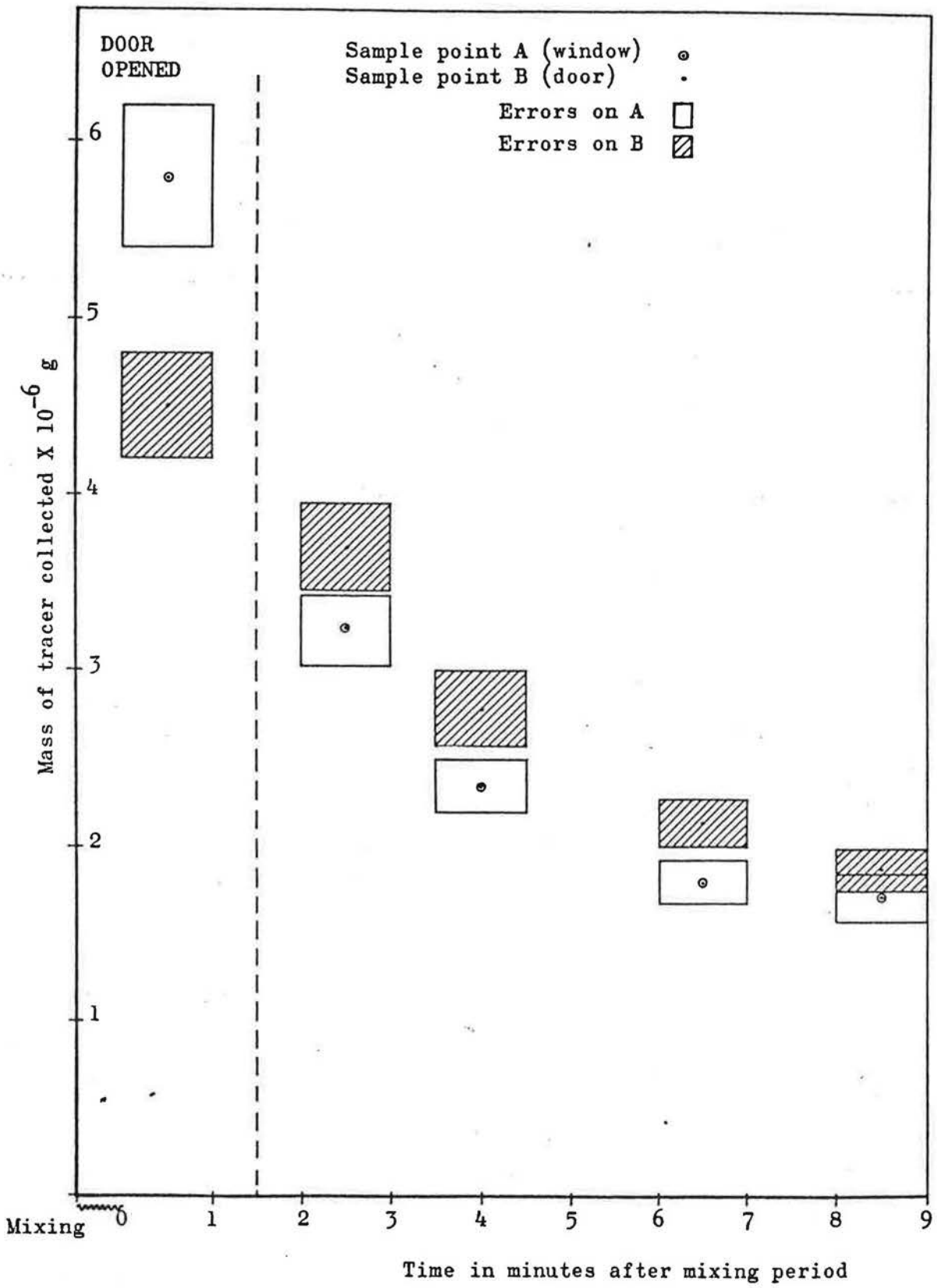


Fig.52 Loss of room air to the corridor on suddenly opening the door - sample rate 1 minute intervals

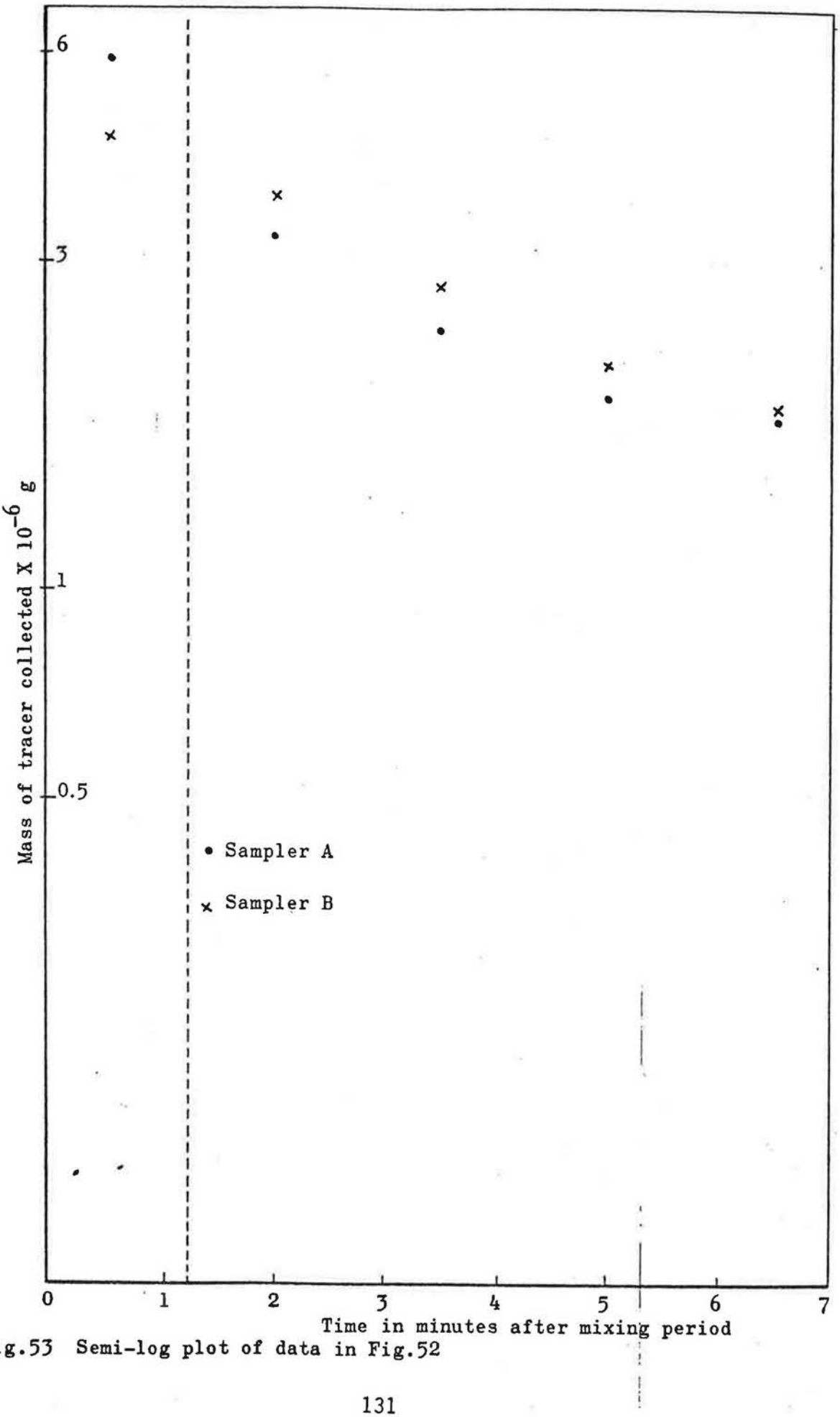


Fig.53 Semi-log plot of data in Fig.52

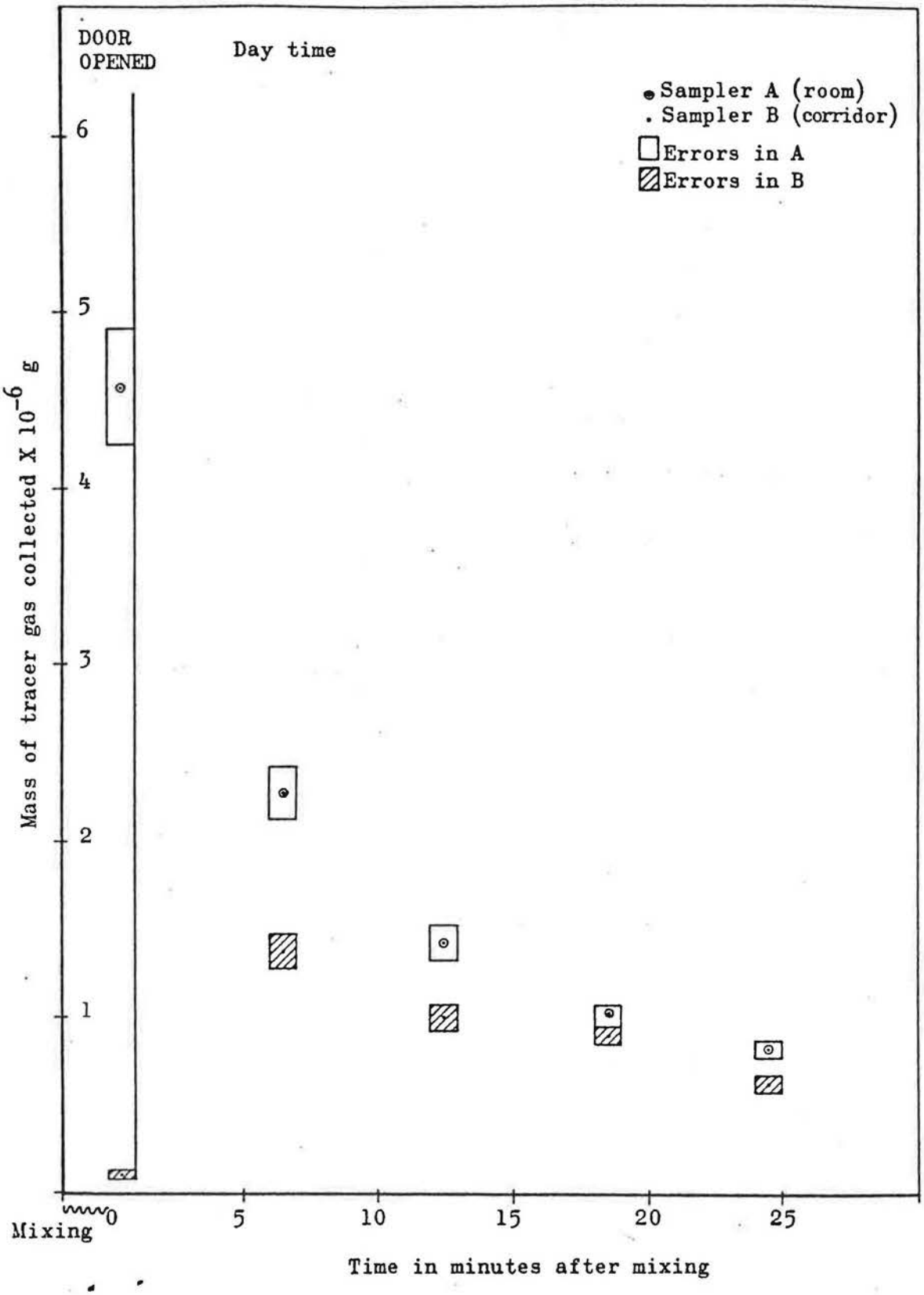


Fig.54 One tracer, two zone test showing air movement between the room and the corridor during the day.

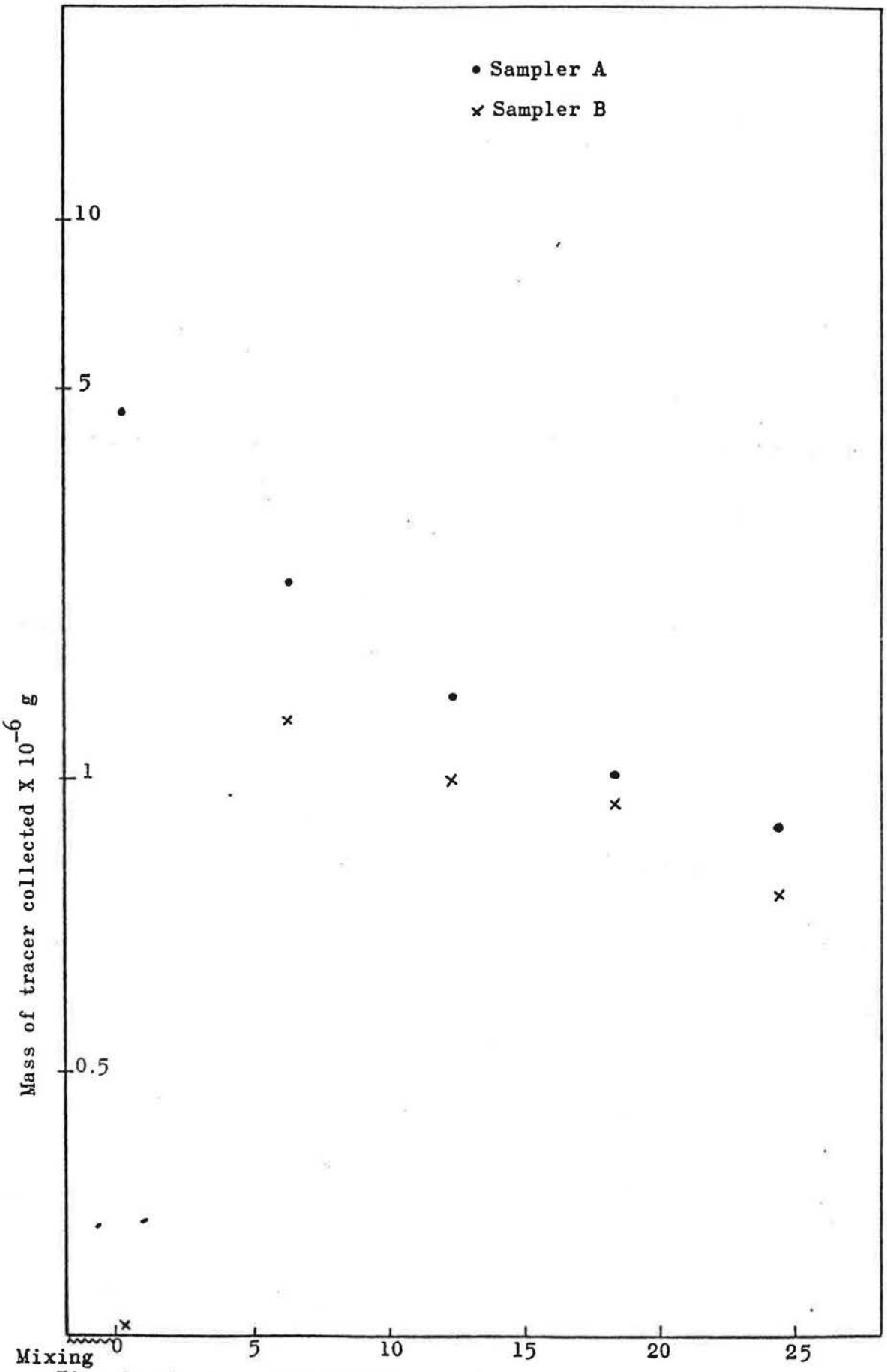


Fig.55 Semi-log plot of data in Fig.54

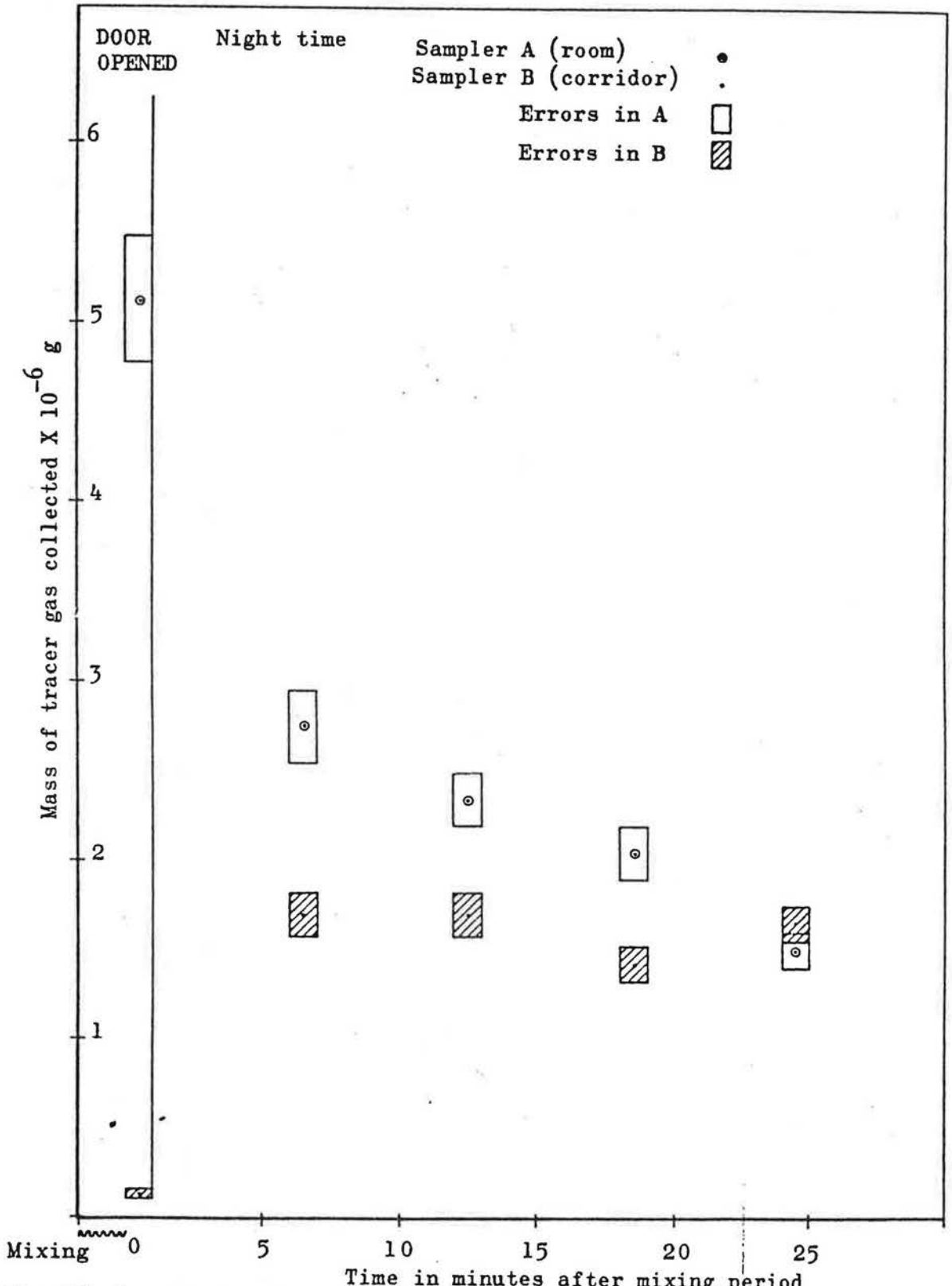


Fig.56 One tracer, two zone test showing air movement between the room and the corridor at night.

II.B.4.2 USING TWO TRACERS TO SHOW AIR MOVEMENT BETWEEN ZONES

Two sampling points were set up, one in the sealed room used in the previous tests and one in the corridor outside the room. Two gases, PP1 and either PP2 or PP3 were released, one in each zone. Air in each zone was mixed, with the communicating door closed. Samples were taken before opening the door, and at 5 minute intervals after it was opened. Fig 57 shows some of the results. PP1 (full line) is released in the sealed room, and after mixing reaches a concentration of 4.60×10^{-9} g l^{-1} (about 4 ppm). Its concentration in the corridor is very small (less than 0.2×10^{-1} g l^{-1}). PP3 is released in the corridor and after mixing reaches a concentration of 2.35×10^{-9} g l^{-1}. Its concentration in the room is zero.

When the door is opened, PP1 is swept into the corridor, leading to a fall in room PP1 and a rise in corridor PP1. Similarly, PP3 is swept into the room, with a concomitant fall in the PP3 concentration in the corridor.

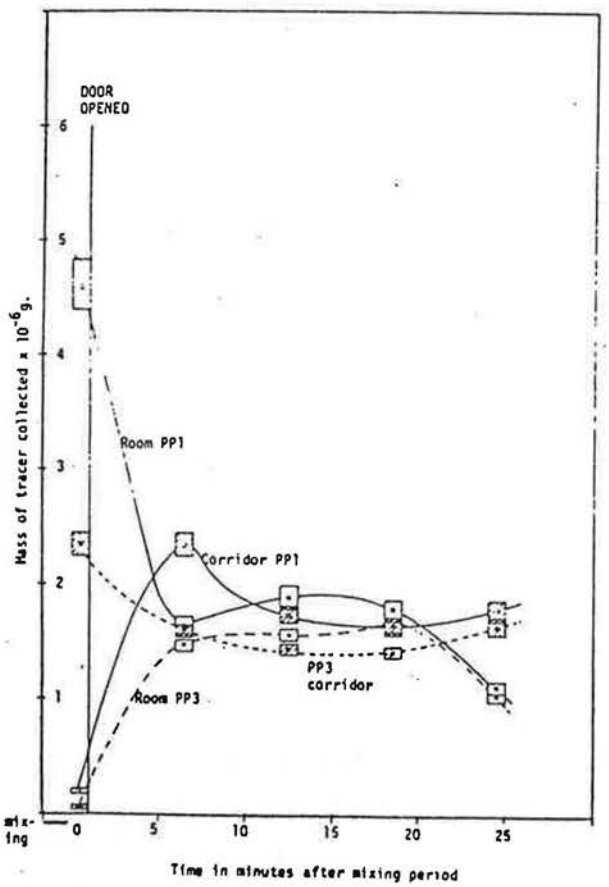


Fig.57 Two zone, two tracer test