# A method for studying air movement in complex occupied buildings such as hospitals: halocarbons as gas tracers using gas chromatography

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## 1 INTRODUCTION

Transport of infective particles by air movements in the environment could be an important factor in the spread of some infections. During a cross-infection survey in a new, fully mechanically-ventilated hospital a detailed study of the actual air movements which existed was made and the development of the method that was used is described below.

The most convenient method for a field study of ventilation and air movement is the gas tracer and a review of many gases and techniques which have ben used or suggested is given by Hitchin and Wilson.[1] An ideal tracer gas has physical properties similar to those of air, and is chemically and physically inert to anything naturally found in the environment—including human beings. It is undetectable by the human senses, not naturally present, able to be assessed accurately both at low concentrations and over a wide range of concentrations and easily obtained and dispersed.

Nitrous oxide has been extensively used in the hospital situation in conjunction with an infra-red gas analyser (e.g., Lidwell and Williams,[2] Baird[3]). Using this technique, the lowest measurable concentration is about 1 part by volume in $10^6$ parts air and although it is possible to measure concentrations up to 1 part in 2, concentrations much above 1 in $10^3$ introduce considerable problems in introduction and dispersion of the large quantities of gas needed. The range for one machine, however, is seldom more than 100:1, with an accuracy of 10 per cent. Working at maximum sensitivity, uncertainties arise since concentrations of this order of nitrous oxide may well be present naturally in a hospital. Both the sensitivity and the range are inadequate for more than adjacent room transfer measurements.

Radioactive tracers provide a much more sensitive method. Gaseous low energy $\beta$-emitters such as $^{41}$A (Collins and Smith[4]), $^{85}$Kr (Howland *et al.*[5]) and $^{133}$Xe (Cadiergues and Leveque[6]) have been used for ventilation and tracer experiments but their usefulness is limited by health hazards. Lundquist,[7] in an inhabited environment, was able to detect 1 part by volume $^{85}$Kr in $5 \times 10^{10}$ parts air with a probable range of 500:1. Even if this order of sensitivity and range is sufficient it is preferable to avoid the dis-

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*Table 1. A selection of possible tracer gases*

| Gas | Formula | Boiling point (°C) | Relative sensitivity to detection by electron capture detector |
|---|---|---|---|
| Sulphur hexafluoride | $SF_6$ | −68 (sublimes) | Most sensitive |
| BCF | $CBrClF_2$ | −3 | |
| Freon 11 | $CCl_3F$ | 24 | |
| Freon C318 | $CF_2.CF_2.CF_2.CF_2$ | −6 | |
| Freon 12 | $CCl_2F_2$ | −30 | |
| Freon 114 | $CClF_2CClF_2$ | 4 | |
| Halothane* | $CHBrCl.CF_3$ | 50 | |
| Freon 142B | $CH_3CClF_2$ | −10 | Least sensitive |

The relative sensitivity is based upon the peak height response of the detector and is meaningful only where the gas delay time resulting from the column is short (<5 minutes).

* Halothane is an anaesthetic and is included in this table as possibly being relevant in a hospital situation.

persion of any radioactive material within an occupied area because of the possibility or fear of a health risk.

Gas ionization detection techniques provide sensitivities of the desired order of magnitude matching those of radioactive tracer methods. Their use was demonstrated by meteorological tracer experiments over distances of up to 5 km (Collins *et al.*,[8] Saltzman *et al.*[9]). Several detectors exist which employ ionization techniques (Lovelock[10]) and the two most common are probably the flame ionization detector giving a maximum sensitivity of, for example, 1 part propane in $10^{11}$ parts air and the electron capture detector giving a maximum sensitivity of, for example, 1 part carbon tetrachloride in $10^{11}$ parts air. Use was made of the electron capture detector since it is selective and has a slightly higher sensitivity to a convenient group of possible tracer gases. Such a cell contains a $\beta$-emitter across which is applied a potential and the free electrons establish a current, termed the standing current, which is measured. The presence of a gas which absorbs electrons is detected by a drop in this current and this drop is related to the concentration of that gas. The exceedingly low concentrations which are required of an electron absorbing gas used as a tracer help to ensure that it meets almost all the criteria of the perfect tracer.

With an electron capture detector it is necessary to use gas chromatographic techniques in order to separate the tracer gas from the oxygen of the air which is also electron absorbing. This is done by passing the air and tracer mixture in a non-electron-absorbing carrier gas through a chromatographic column. The column contains a suitable material which absorbs and desorbs oxygen and the tracer at different rates so that the mixture leaves the column separated and the response of each component can be observed. For a particular column under one set of conditions, the time a gas is delayed is characteristic of that gas and is the means of identification.

## 2 DEVELOPMENT OF THE ANALYSIS EQUIPMENT

Commercially produced gas chromatographic analysers are designed for laboratory use and the necessary versatility results in bulky and expensive equipment unsuitable for work in the field. The apparatus closest to our requirements was a 'SF6B Leak Detector' (Analytical Instruments Ltd). This is designed to detect very low concentrations of sulphur hexafluoride and consists of a sample tap to inject the mixture to be analysed into the carrier gas (nitrogen is recommended), a 300 mm stainless steel column packed with aluminium oxide used at room temperature, a pulsed electron capture detector with a tritium source, together with a control unit and an amplifier able to reverse the detector response and give a positive reading on a microammeter. The system, used in this sample mode, is capable of detecting 1 part of sulphur hexafluoride in $10^{11}$ parts air. This equipment is compact and relatively cheap.

The use of a gas chromatographic analysis system gives the added dimension to a tracer system that several tracer gases can be used simultaneously. Many suitable electron absorbing gases belong to the family of halogenated hydrocarbons the particularly inert and non-toxic ones which are commonly known as 'Freons' or 'Aretons'. Several gases from this family having suitable physical properties were tested, and work by Clemons and Altshuller[11] gave a guide to those which were worth trying. Table 1 shows the relevant selection of gases together with their chemical formulae and boiling points. The table is arranged in order of sensitivity with those to which the detector is most sensitive at the top. However, this relative sensitivity can only be taken as very approximate as it is determined on a peak height basis and not upon the peak area (see below) and so it is very dependent upon the delay times. It is meaningful in conjunction with the systems described where, for practical reasons, the delay times are kept to a minimum. The delay for most freons is substantially longer than that of sulphur hexafluoride on an aluminium oxide column at room temperature and is far too long to be feasible for estimating a series of samples in quick succession. There are two alternative approaches to this problem: (a) to vary the temperature of the column; and/or (b) to use a different column.



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*Table 2. Gas delay times (in seconds) over a range of column temperatures*

| | | Column temperature (°C) 0 — 50 — 100 |
|---|---|---|
| | $O_2$ | ← No delay → |
| Most sensitive | $SF_6$ | 16 — to — 6 Merged with $O_2$ |
| | Freon C 318 | 500 — to → 15 |
| | Freon 12 | 500 — to → 15 |
| Least sensitive | Freon 114 | 400 — to → 45 |

The column was 300 mm of aluminium oxide and the carrier gas was nitrogen flowing at 1·7 cm³/s. With this column freons C318 and 12 were undifferentiable at all temperatures.

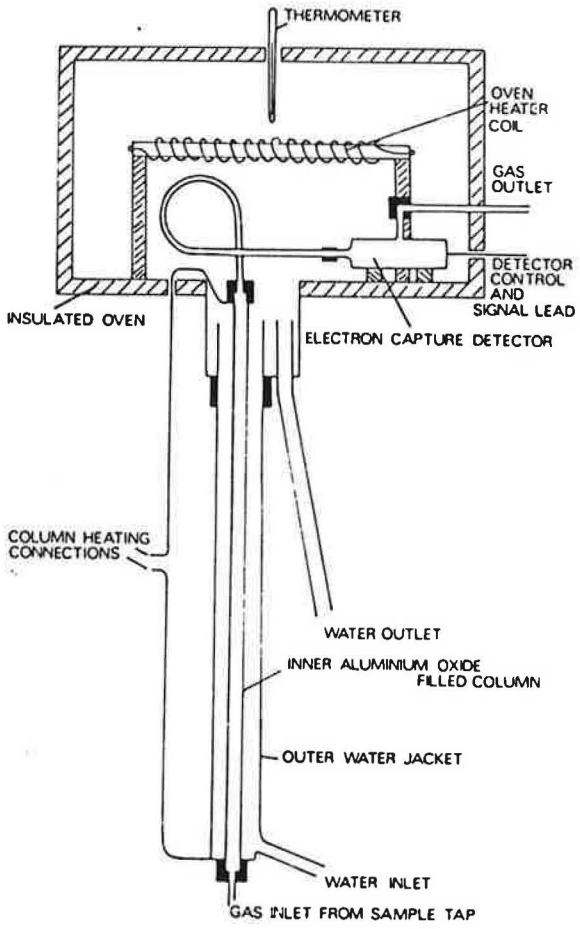



*Fig. 1. Section through temperature cycling column.*

## 2.1 The temperature cycling column

The delay times for several of these gases on the aluminium oxide column at different temperatures are shown in Table 2. The fact that there was no single column temperature that was able to combine sulphur hexafluoride satisfactorily with any of the other gases suggested the use of a temperature cycling column. As illustrated in Fig. 1 this consisted of a 300 mm vertical stainless steel tube packed with aluminium oxide for the column, electrical connections at each end for providing a heating current, an outer jacket to provide for water cooling and an oven situated at the top enclosing the detector which was connected to the exit of the column. The purpose of the oven was to prevent condensation in and poisoning of the detector cell by materials liberated from the column.

The procedure for the use of the column was as follows:

(i) Cool column with cold tap water and drain clear;
(ii) Inject sample;
(iii) Wait for appearance of sulphur hexafluoride as indicated by the response from the detector;
(iv) Connect high current through column and heat rapidly;
(v) Wait for appearance of other tracer gases;
(vi) Cool column with cold tap water ready for next sample.

The exact timing necessary for this procedure was very dependent on the conditions chosen. Fig. 2 illustrates a typical case. The carrier gas was nitrogen flowing at 1·7 cm³/s, the column heating current was 75 A at 1 V (a.c.), and the detector cell oven was kept at 100°C. The reversed detector response from the amplifier was recorded by a flat bed recorder giving a peak for each electron absorbing gas present.

For large concentrations of tracer gases (i.e., concentrations >0·5 parts SF6 or 200 parts freon C318 or 500 parts freon 12 or 2 000 parts freon 114 in $10^9$ parts air) the above system was found to be very satisfactory. However, when working near the limit of detectability the stability of the base line became an important factor. It was found that the sudden heating produced a correspondingly sudden rise in the base line (i.e., a drop in the standing current) and the sudden cooling an exactly opposite effect. The reason was thought to be that the column was insufficiently clear of impurities even after considerable baking out. The erratic nature of the base line effectively raised the lower limit of the system and reduced its range. No satisfactory solution was found to this problem which required either more extensive cleaning or a slowing down of the heating and cooling rates.

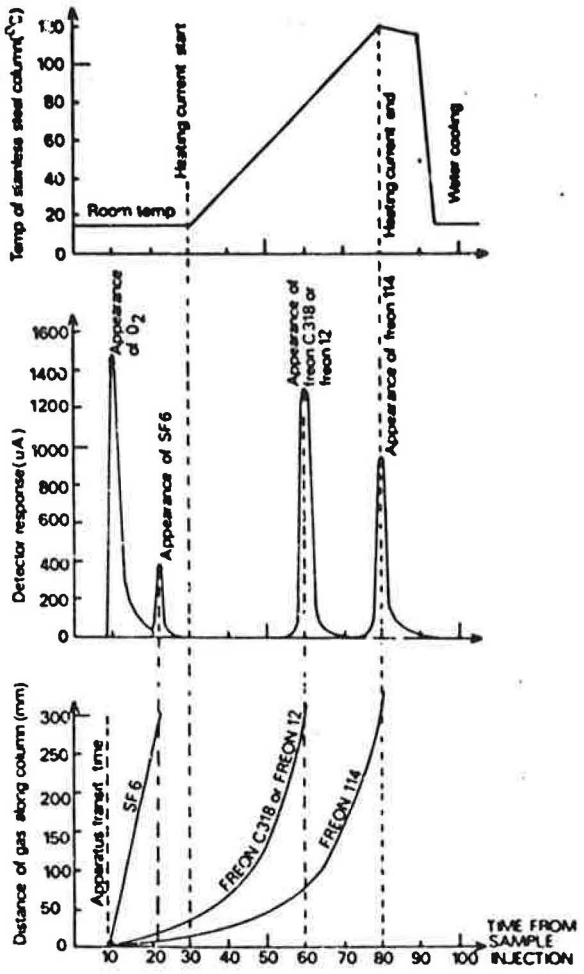
## 2.2 The squalane column

Columns packed with silica gel and molecular sieves were tried but none had practical delay times for a convenient group of tracer gases simultaneously. Upon a suggestion from the manufacturers of the equipment a suitable system was found in the form



D14

*Fig. 2. Time sequence of temperature cycling column.*




*The response shown is for 18 parts $SF_6$, $2 \cdot 10^4$ parts freon 318 and $4 \cdot 10^4$ parts freon 114 in $10^8$ parts air.*

of a column using squalane as the stationary phase at room temperature. With this system the three gases freon 12, freon 14 and BCF could be satisfactorily separated in a convenient time.

Figs 3 and 6 show the practical set-up that was used for analysis. The carrier gas was oxygen-free nitrogen, usually flowing continuously at 1·7 $cm^3/s$ through the sample injection tap, the column, the detection cell and a flowmeter before being vented to the outside. The tap was a Pye gas sampling valve with a sample loop volume of about 0·5 $cm^3$ but this could easily be altered by interchange of loops. The column was made by filling a 2 m · 5 mm i.d. stainless steel tube with 20 per cent squalane on a 60-70 mesh celite base (supplied by J. J.'s (Chromatography) Ltd.). This was coiled twice and held vertical to prevent any settling which might lead to tracking of the gases. The electron capture detector was placed in an electrically heated oven maintained at 90 C in order to prevent any evaporated squalane from condensing in the cell. A pump was used to create a flow through the sample loop and upon operation of the tap the volume of air in the loop was inserted into the nitrogen flow for analysis. The amplified reversed response from the detector cell was recorded on a battery operated flat bed recorder (Servoscribe M. Smith Industries Ltd.).

Oxygen was undelayed by this column and the peak due to this gas was used as a time marker. The delay time of each tracer was known and used for identification. A typical read-out from the recorder is given in Fig. 4 showing the tracers and some other gases. Although this recording was made with a nitrogen flow of 1·3 $cm^3/s$, the delay times at 1·7 $cm^3/s$ were only slightly less about 6-18 s in the case of the three tracers. Freon C318 was not sufficiently clearly separated from oxygen for use as a tracer and freon 142B had insufficient sensitivity for use. Halothane is an anaesthetic which might be found naturally within a hospital. A small peak (not shown) with a five minutes delay was also often observed. This was probably due to accumulated freon 11 in the atmosphere (Lovelock[12]), the delay time being identical to that found with this substance.

It is common practice to relate the area under a peak to the concentration of the substance under test. However, assessment of peak area in the field was not easy and instead the peak heights were calibrated using mixtures of known concentrations. Although peak heights do not bear a linear relationship to concentration, with the particular instrument in use which had a stepped output range from 1 to 1 500 $\mu A$, a good working range of peak heights between 3 and 1 000 $\mu A$ could be estimated, and extended at the expense of accuracy. The relationship was approximately linear at the lower end of the range. Typical responses together with the errors involved are given in Table 3.

## 3 USE OF TRACER SYSTEM

Although in the hospital studies the ventilation rate of a particular room was important, the primary purpose of the tracer system was to evaluate the transfer of air between rooms sometimes quite remote. In practice it was found that the air movements changed rapidly so that the same situation could not be said to exist even on two consecutive days. The use of multiple tracers was thus imperative if two or more transfers were to be compared under identical conditions.

In view of the fact that a nitrogen supply was needed, it was decided to fix the analyser and make pipe connections from it to each room under observation and use a large common pump to provide suction (Fig. 7). The cylinders of tracer gases were made into portable dispersers (Figs. 5 and 8). These consisted of a three wheeled trolley upon which was a pyramidal shaped housing enclosing the cylinder. Connected to the cylinder was a valve and flow meter to control the output and the gas was released from a jet just below a battery fan in a cylindrical housing situated on top, which thoroughly mixed the gas with air. The gases were supplied liquified under pressure so that their own vapour pressure was suffi-



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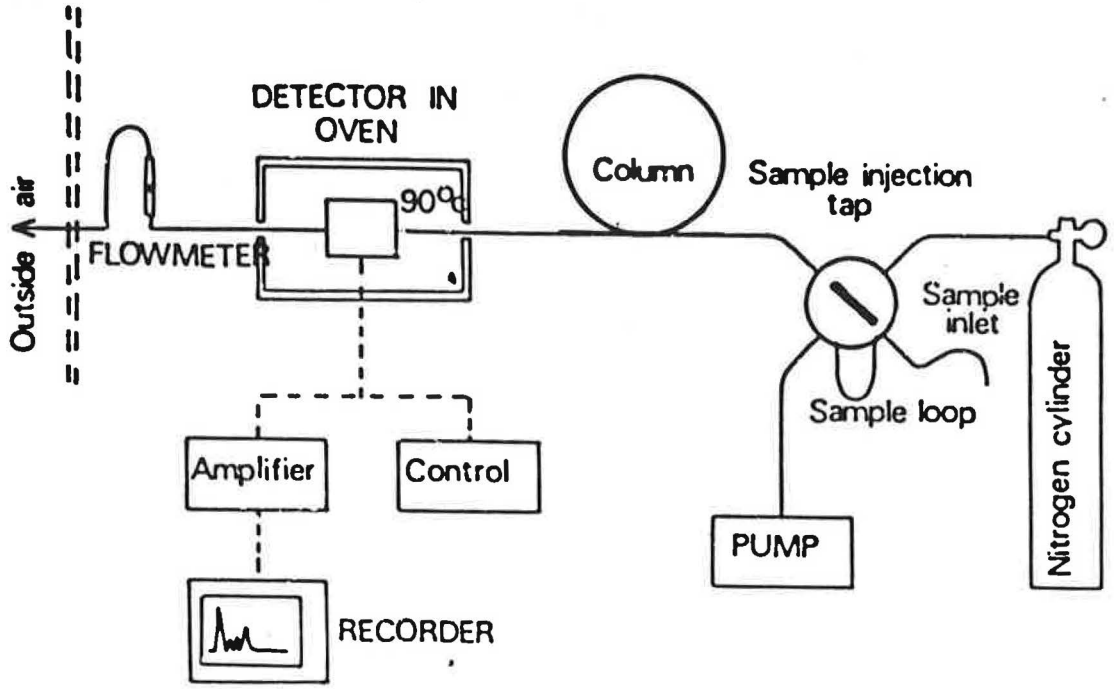
*Fig. 3. Schematic diagram of analyser set-up with a squalane column.*



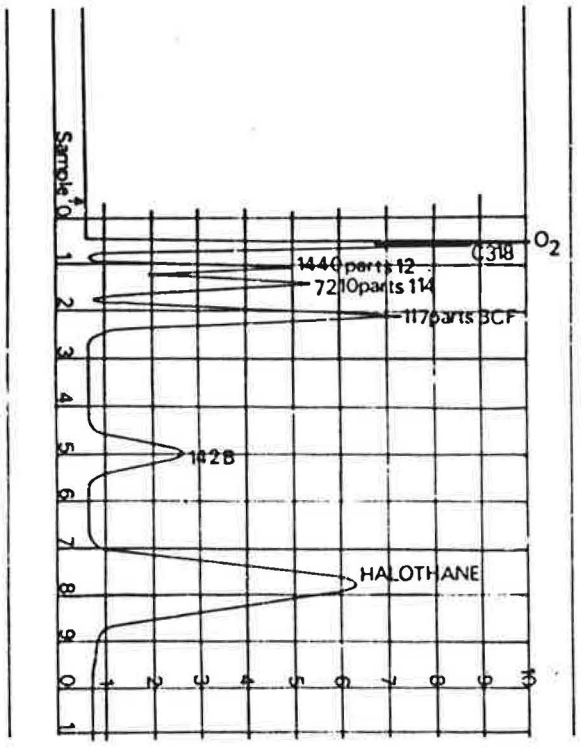




*Fig. 4. Recording of detector response for several gases. The column was 20 per cent squalane, the nitrogen flow 1·3 cm³/s and the paper speed 1 cm/min. 6.7.70: Detector E.C. cell (2) at 99° C; Column 2 m 20 per cent squalane at 20° C; Flush Oxygen-free hydrogen at 1·3 cm³/s; Amplifier sensitivity range 10 (R = 10); Recorder sensitivity 19 mV/cm (S = 10); paper 1 cm/min; Gas concentration in parts per 10⁹ parts by volume of air.*

cient to provide the flows required (Table 4). This system ensured that even over prolonged periods of dispersal the flow stayed constant without any attention. The mixing fan was essential because of the high density of the gas compared to air but, once mixed, the concentrations were well below the accepted upper limit which alters the density of the air by 1 per cent.

The main mode of use was that of establishing as nearly as possible equilibrium conditions. The tracer gases were placed at selected sites, dispersing at known rates until the concentrations of all the gases reached approximately constant levels at each sampling site. A series of samples was then taken from which the mean values of these concentrations were estimated. Either a transfer index between each source and sample site was then calculated, i.e., the concentration which would have existed at the site if there had been dispersal at unit rate (Lidwell[11]) or the results were expressed as the relative concentration between the recovery site and the source room. Measurements from sites not piped to the analysing equipment could be made by collecting a sample in an ungreased glass syringe. Other modes of use such as releasing a cloud of gas over a short period and either collecting at each site an integrated sample to be analysed later or taking many discrete samples over a long period have been used. Ventilation rates were easily assessed by producing a gas concentration within a room and taking several samples from that room at known times during the subsequent die-away.

Although the tracer system was not compared with another type, consistent results were obtained from all three gases and of the same order as would be



E2

*Table 3. Concentrations (in parts per $10^9$ of air) of tracer gases used with squalane column which produced different detector responses*

| Response (uA peak height) | | Freon 12 | Freon 114 | BCF |
|---|---|---|---|---|
| 3 | Concentration | 5·0 | 17 | 0·2 |
| | Absolute error (a) | ±0·7 | ±3 | ±0·03 |
| | Relative error (%) | 14 | 18 | 15 |
| 100 | Concentration | 250 | 800 | 8 |
| | Absolute error (a) | ±5 | ±10 | ±0·1 |
| | Relative error (%) | 2 | 1 | 1 |
| 1 000 | Concentration | 10 000 | 30 000 | 200 |
| | Absolute error (b) | ±200 | ±1 000 | ±5 |
| | Relative error (%) | 2 | 3 | 2·5 |
| Max. | Concentration | 40 000 | 100 000 | 2 000 |
| | Absolute error (c) | ±5 000 | ±20 000 | ±500 |
| | Relative error (%) | 12·5 | 20 | 25 |
| | Working range | 2 000:1 | 1 750:1 | 1 000:1 |
| | Maximum range | 8 000:1 | 6 000:1 | 10 000:1 |

(a) Limited by detector noise level; (b) limited by calibration accuracy; (c) limited by detector saturation.

*Table 4. Properties of tracer gases used with squalane column*

| Gas | Boiling point (°C) | Saturated vapour pressure at 20°C (kN/m² gauge) | Maximum flow used at 20°C (cm³/s) | Relative vapour density at 20°C (air=1·0) | Concentration required to change air density by 1% (%) |
|---|---|---|---|---|---|
| Freon 12 | −30 | 460 | 8·0 | 4·2 | 0·313 |
| Freon 114 | 3·6 | 80 | 15·0 | 5·8 | 0·209 |
| BCF | −3·4 | 160 | 1·5 | 5·8 | 0·209 |

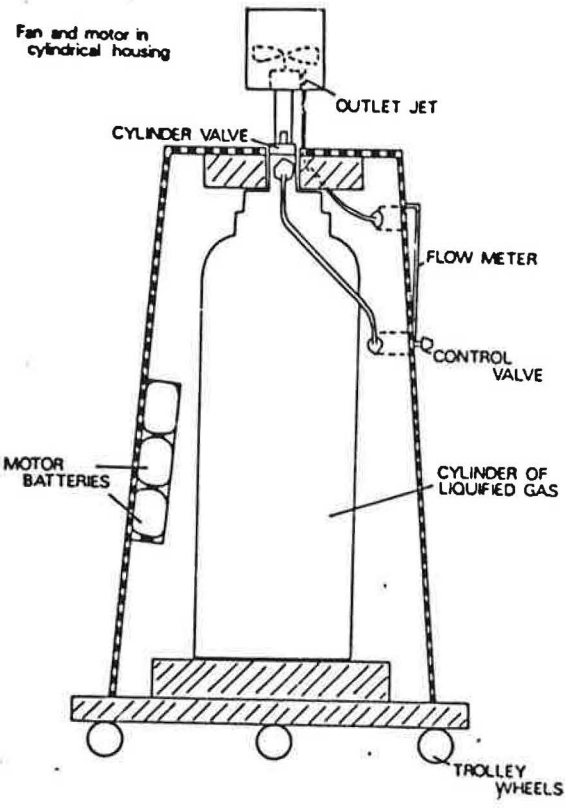



*Fig. 5. View of gas disperser with front panel removed.*

expected from calculations based upon the limited information about the ventilation plant that was available. Some very limited absorbtion by plastics did occur but any small effect this might have had was eliminated by the equilibrium mode of use.

## 4 PROBLEMS

Contamination of the analyser components was the major problem. All components and pipe work had to be thoroughly cleaned of all grease, most types of which seemed to produce a vapour which affected the detector. The solvents used for this had to be non-electron-absorbing, e.g., pure acetone or benzene. Components like reducing valves, etc., had been supplied by the manufacturers grease free but even then were not found to be completely satisfactory. The carrier gas supply was another possible source of contamination but most supplies of medical grade oxygen-free nitrogen (e.g., BOC's white spot) were found to be sufficiently clean for use although it was advisable not to use the gas when near the end of a cylinder. No effective way was found to clean contaminated nitrogen. It is standard procedure to clean chromatographic columns from material absorbed on to them by baking overnight while passing carrier gas through. In the case of the aluminium oxide column the procedure did not produce a sufficiently clean column for rapid temperature cycling while with the squalane column, too much squalane was lost by evaporation and it was better to replace the material rather than attempt to clean it. The electron capture detector was more difficult to deal with. It seemed likely that the sur-



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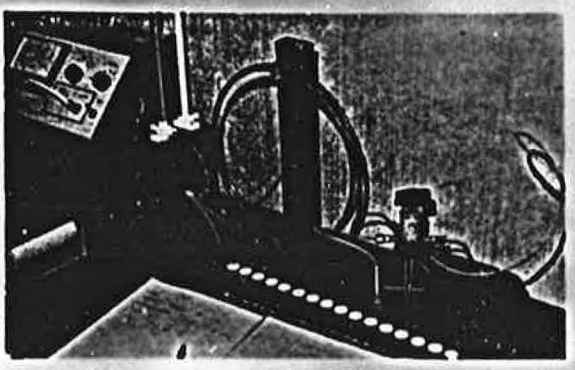

*Fig. 6. View of the gas chromatograph. The nitrogen line runs from the right to the sample injection tap and then into the coiled up column. The oven, containing the detector, is on the left with the amplifier and control unit standing on it together with the flowmeter for the exit gas. In front of the column and sample tap are a row of sockets from any of which gas may be drawn through the sample tap from the sampling lines installed below floor level. The recorder can be seen in front of the oven.*

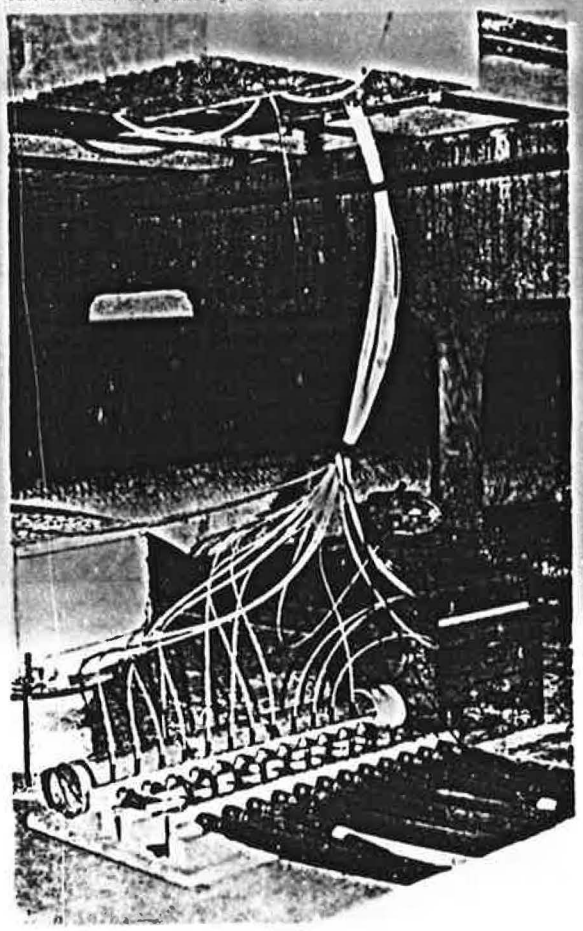

*Fig. 7. The sampling manifold below the floor. Twelve 25 mm diameter black polythene tubes lead from the sampling positions in various parts of the hospital. Air is drawn through these into a cylindrical manifold by a suction blower contained in the wooden box on the right. From each of the polythene tubes a 6 mm nylon tube leads to one of the sockets shown in Fig. 6. One of the sample is drawn from the selected line by the small pump shown on top of the blower. Nylon sampling tubes also run to sockets from the underfloor space [illegible] air ventilation ducts and from the outside air.*

*Fig. 8. A tritium gas chromatograph. The carrier gas after passing through the flowmeter on the side of the cylinder housing is discharged through the small tube just below the fan blades within the cylindrical guard.*

face of the tritium source became coated so that some electrons were absorbed and the standing current was reduced together with the working range of the instrument. Associated with this was the appearance of reverse peaks immediately following a large normal peak, e.g., from oxygen. By comparison with work done by Lovelock[12] this might have been caused by contact potentials set up between a contaminant and an electrode. It was sometimes possible to clean the cell by flushing with acetone or benzene but if this failed it was usually returned to the manufacturers. A method suggested by Holder and Wheatley[13] whereby the cell was dismantled and a metal cleaning paste used on the radioactive surface was found to be effective but required great care to avoid possible hazard to the worker.

The sensitivity of the instrument was affected by several factors. Time was the most important and although the sensitivity was stable over its use on any one occasion there was a long term drift. Once the system was set up it was left running continuously, changing the nitrogen supply every two months. The sensitivity increased relatively quickly



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during the first 10 days of installation and slowed to a much less rapid rate of change after 40 days. There was always a marked change in sensitivity when beginning a new nitrogen supply. The nitrogen flow rate also affected the sensitivity. With freons 12 and 114 a 1 per cent increase in the flow rate produced a 0·3 per cent decrease in sensitivity. The effect of altering the detector cell temperature was variable depending upon the gas. With freons 12 and 114 there was a distinct increase in sensitivity as the cell temperature was raised from room temperature to 85°C. Above this temperature there was little variation. In contrast, the sensitivity of BCF fell continuously as the temperature was raised. The mechanisms leading to such responses are discussed by Devaux and Guichon[16] and it seems likely that freons 12 and 114 were at maximum sensitivity when the cell was in the 90°C region.

As is often done in practice (e.g., Jeltes *et al.*[17]) the instrument was calibrated before each occasion it was used. A known diluted mixture of the gases was made and most of it injected manually into the sampling tap and analysed. The remainder of the mixture in the syringe was diluted 10 times with fresh air and the process was repeated. In this way a calibration curve was constructed over the whole workable range of the instrument. Satisfactory and reproducible results were easily obtained provided an ungreased glass syringe was used and the mixture was kept in the syringe for only a short time.

Interference from other materials present in the experimental area did occasionally occur. The most widespread source of such substances was the content of aerosol air fresheners and flysprays. This often contained a 50:50 mixture of freons 11 and 12 as the propellant which gave the usual freon 12 peak followed after about four minutes by a larger freon 11 peak. The second large peak interfered only with rapid sequential samples and its presence removed almost all the ambiguity which might have arisen about a freon 12 peak.

## 5 SUMMARY

A description is given of a gas tracer system which uses three halogenated hydrocarbons—freon 12 freon 114 and BCF as simultaneous tracers and detects and measures them by gas chromatographic techniques using a squalane column and electron capture detector. The system is capable of detecting down to 1 part tracer in $10^{10}$ parts air and measuring a range of concentrations greater than 1 000:1. Although many difficulties were encountered in the development of the system an account is given of how these were dealt with and in use it has been completely reliable.

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