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**Atmospheric Sampling for Public Health Investigations  
Using Adsorption Tubes with Quantitative G.C. or  
G.C./M.S. Analysis**

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Air sampling techniques using Porapak Q and Tenax G.C. adsorption tubes are described for the collection of a wide range of organic pollutants. The sample is transferred by thermal desorption to a GC column followed by temperature programmed G.C. or G.C./M.S. analysis. The collection and sample recovery systems can be constructed without great expense or special expertise.

A method is reported for the measurement of retention volumes, and the estimation of collection efficiencies of organic compounds on the sample tubes. Such data are reported for ethanol, acetone, benzene, pyridine, toluene, styrene, furfural, naphthalene, nicotine and phenanthrene.

A method for the quantitative interpretation of routine analyses is illustrated by reference to some examples of the authors' work.

Many methods have been developed for the sampling and G.C. analysis of trace organic pollutants in air, but most have serious disadvantages if they are to be put to routine use in a non-specialised laboratory.

*Enclosure methods* are the simplest, the air being drawn into a glass or plastic vessel so that it can be transported to the laboratory where portions can be injected into the G.C. using a gas-tight syringe.<sup>1-3</sup> However, these methods lack sensitivity and there are difficulties in avoiding losses to, and contamination from, the walls of the containing vessel. In a review article, Robinson *et al.*<sup>4</sup> have suggested that terylene and nylon are the only suitable materials for plastic sample vessels. Perhaps P.T.F.E. could also be added to this list, but it is very expensive.

*Cryogenic trapping techniques* using dry ice or liquid nitrogen have been reported. The difficulties of accommodating the large amounts of water and carbon dioxide, which condense along with the pollutants, can be overcome<sup>5-9</sup> but these methods require rather bulky sampling equipment, trained personnel to operate it, and a regular supply of the coolant.

*Adsorption techniques*, in which a tube containing carbon,<sup>9-12</sup> or a polymeric adsorbent<sup>5,13-18</sup> is used to take up the pollutants as the air is drawn through it, have found the most widespread use, but these also have their defects. Pellizzari *et al.*<sup>13</sup> have reported poor collection efficiency on graphitised carbon and

there is a danger of catalytic decomposition with those techniques where thermal desorption is used to recover the sample from a carbon adsorbent. Perhaps the most elegant techniques are those using carbon with solvent recovery,<sup>9,10</sup> and those using polymeric adsorbent with recovery by thermal desorption. A certain amount of expertise is required with these, particularly in the use of carbon. The thermal desorption techniques mostly require facilities and services that are rarely available outside specialised laboratories, and modifications often have to be made to the G.C. which are a hindrance to the more routine usage of the equipment.

Three papers have recently appeared describing sampling methods with polymeric adsorbents which do not have these disadvantages. The simplest of these is that of Williams and Umstead.<sup>19</sup> The sample is collected by drawing the air under investigation through the G.C. column—the pollutants collect at the head of the column, and can be analysed by temperature programmed chromatography. This method has the advantage over most others that there is no need to transfer the sample from the sample tube to the column, since they are one and the same. However, the sampling rate is slow and the sample tube is bulky and expensive. In the method of Sickels and Stafford<sup>5</sup> the air pollutants are taken up on a short adsorption tube which is subsequently connected to the injection port of the chromatograph. A commercially available thermal flasher is used to vaporise the sample and then it is swept on the column. Mieure and Dietrich<sup>16</sup> describe two methods. In the first, the adsorption tube, containing the sample, is attached to the injection port of the G.C. column and the sample is discharged on to the column by lowering a hot, cylindrical oven around it. In their second method, the tube is attached to a modified column inside the G.C. oven so that it sits between the injection port and the column. Analysis is carried out by temperature programmed chromatography. There is difficulty with this last method in making a satisfactory tube to column coupling which will repeatedly survive the pressures and high temperatures employed on the chromatograph.

We have explored these methods and several modifications. We report here the three methods which we have found to be most satisfactory. All three are similar in essence to the first method of Mieure and Dietrich. They each have advantages and disadvantages depending on the type of work to be carried out.

In addition, we report a method for the quantitative interpretation of the results. Very little attention has been paid to this aspect of the work in the literature. Of those reviewed above, only the paper by Butler and Burke<sup>15</sup> gives serious consideration to the factors involved. They take a theoretical approach to the problem and demonstrate the method for determining the precise sample volume which would permit a minimum 99 per cent. sampling efficiency for a given compound on a given adsorbent. However, their work covers only a small number of compounds and needs to be extended if it is to be of general applicability. Our approach is based on a few simple assumptions which produce less precise results than those of Butler and Burke, but nevertheless permit sample volumes to be calculated for the sampling of a wide range of compounds with a high collection efficiency.

## Experimental

### APPARATUS

#### *Sample Tubes*

The sample tubes are prepared as illustrated in Figure 1 from Pyrex glass tubing packed with 0.5 g of 100–120 mesh, Porapak Q, or 0.25 g of 60–80 mesh, Tenax G.C. (both from Chromatography Services Limited, Merseyside).

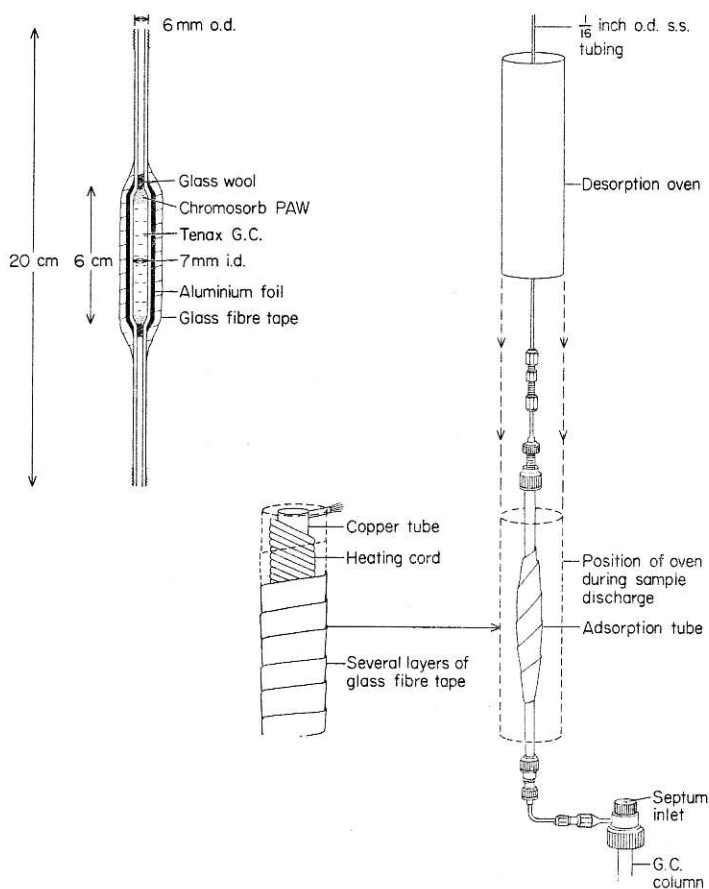


Fig. 1. The sample tube and its attachment to the G.C. in Method (1).

The two layers of Chromosorb PAW act as inert buffers to ensure that all of the Tenax G.C. remains in the centre of the tube. The resistance to air flow of each tube is fixed during its construction by adjusting the compaction of the glass wool plugs, so that the flow rate during sampling is 7 ml/sec. or less. The diameter of the adsorbent bed, 7 mm, is critical since it affects the efficiency of the thermal desorption process.

When not in use the tubes are sealed with  $\frac{1}{4}$  inch G.C. column caps and stored in 9 inch  $\times$  1 inch boiling tubes fitted with rubber bungs.

### *Sampling Equipment*

A Dymax Mk II A air sampling pump (Gallenkamp) fitted with a bubble flow meter on the pump outlet and  $\frac{1}{4}$  inch i.d. PVC tube on the pump inlet.

A Draeger hand pump.

### *Desorption Oven*

See Figure 1. A copper tube, 2 cm diameter and 15 cm long, wound with heating cord and glass fibre thermal insulation tape (the last two from Gallenkamp) and controlled by a V8HM variable transformer (Zenith Electric Co. Limited, Milton Keynes).

### *Adsorption Tube to G.C. Couplings*

Method (1): See Figure 1. Two Pye Unicam,  $\frac{1}{4}$  inch, O-ring couplings; one Pye Unicam 1/16 inch union; 1/16 inch o.d. stainless steel tube; 19 cm of 6 mm o.d. Pyrex glass tube with a 1 mm bore.

Method (2): A 1/16 inch o.d. stainless steel, carrier gas supply line connected to the adsorption tube through a  $\frac{1}{4}$  inch o.d. O-ring coupling; and the tube to column connection made with a  $\frac{1}{4}$  inch stainless steel Swagelok union, fitted with silicone rubber O-rings (the O-rings from Analabs).

Method (3): A Pye Unicam, six port, gas sampling valve is fitted in the G.C. carrier gas supply line between the G.C. needle valve and the septum inlet. The valve has two O-ring couplings arranged to take the adsorption tube in place of its sample loop.

### *Gas Chromatograph*

Oven Pye Unicam, Series 104 Chromatograph oven.

Columns A 2 metre  $\times$  2 mm, glass column packed with 60–80 mesh Tenax G.C.; a 2 metre  $\times$  2 mm, glass column packed with 100–120 mesh Chromosorb 101.

Carrier Gas Medical grade helium, purified by passage through a 13  $\times$  molecular sieve filter; flow rate = 20 ml/min.

### *Detection System*

A V.G. Micromass 16B mass spectrometer interfaced to the G.C. via a V.G. jet separator. Equipped for the fast scanning of a wide mass range, it can produce chromatograms and the associated mass spectra; also equipped with a selective ion monitoring system which is used for work requiring the greatest sensitivity and specificity (V.G. Micromass Limited, Altrincham).

The Eight Peak Index of Mass Spectra (MSDC, Aldermaston) used for the identification of the mass spectra.

Note: The more conventional G.C. detection systems such as FID are also used successfully for this type of work.<sup>4,6,13,16,19</sup>

### *Clean Air for Blank Analyses*

A supply of moist, clean air, i.e. air free from organic contaminants, is obtained by drawing air through a 30–60 mesh, activated charcoal filter, then

through a Dreschel bottle containing distilled water, and finally on to the adsorption tube. The suction can be provided either by the Dymax pump listed above or by a water pump.

#### *Additional Apparatus for Measuring Retention Volumes*

Tube measurements: A sample tube packed with a known weight of the adsorbent.

A commercial G.C. exit splitter (or one can be made as described under tube measurements, in which case the following are required to connect it to the G.C.:  $\frac{1}{4}$  inch o.d. Teflon tube (Phase Separations Limited), 1/16 inch stainless steel tube, a  $\frac{1}{4}$  inch o.d. O-ring coupling, and a Pye Unicam 1/16 inch union).

Column measurements: A 2 mm  $\times$  2 metre glass column packed with a known weight of the adsorbent.

#### SAMPLING

##### *With the Dymax Electrical Pump*

Connect the adsorption tube to the pump with the PVC tube and measure the flow rate on the bubble meter. Draw the air to be sampled through the tube for a measured period of time. Check the flow rate at the end of the sampling period, re-seal the tube with the rubber caps and store it in the boiling-tube.

##### *With the 100 ml Draeger Hand Pump*

Attach the sample tube to the pump in the same way as for Draeger tubes, and pump the required volume of air.

Caution: Allow at least 5 seconds at the end of each stroke for the passage of the full volume of air (100 ml).

#### SAMPLE DESORPTION TO THE G.C. COLUMN

##### *Method (1)—Tube to Column Transfer via the Septum Inlet*

See Figure 1. This is suitable for both the volatile and the less volatile components of the sample. Connect the tube between the carrier gas supply line and the column. Discharge the sample by lowering the cylindrical oven (preset to 200°C for Porapak Q tubes, or 250°C for Tenax G.C. tubes). After 5 minutes begin the temperature programme. For a sample being analysed for its more volatile components, the sample should be discharged on to the Chromosorb 101 column at room temperature and temperature programmed from 100°C to 235°C at 10°C per min. Discharge other samples on to the Tenax G.C. column and temperature programme from 50°C to 350°C at 10°C per min. The desorption oven should remain in position on the tube for the whole of the analysis period. At the end of the programme standardise the analysis by making injections of one or more standard solutions, e.g. 1  $\mu$ l of 0.2 per cent. ethyl acetate in methanol on Tenax G.C. at 130°C or on Chromosorb 101 at 200°C. The use of an internal standard is not practicable in this work. Report the preliminary results semi-quantitatively by quoting the chromato-

gram peak heights relative to the external standard as approximate concentrations in the original volume of air. For example:

| Compound                    | Peak height | Height relative to standard | Sample volume, litre | Approximate concentration <sup>†</sup> , $\mu\text{g/litre}$ |
|-----------------------------|-------------|-----------------------------|----------------------|--------------------------------------------------------------|
| Compound X                  | $x$         | $x/s$                       | $V$                  | $2x/sV$                                                      |
| Compound Y                  | $y$         | $y/s$                       |                      | $2y/sV$                                                      |
| 2 $\mu\text{g}$ of standard | $s$         | —                           |                      | —                                                            |

<sup>†</sup> Assuming similar, and linear, detector sensitivity for all compounds.

For quantitative work, calibrate the technique by injecting known amounts of the compounds of interest on to adsorption tubes, drawing the compounds into the tubes with about 1 litre of clean air, and analysing the tubes in the normal way. Draw the calibration graphs by plotting "peak height relative to the external standard" versus "amount injected".

#### *Method (2)—Tube to Column Transfer away from the Oven*

This is suitable for both volatile and less volatile compounds. It can be used with any model of G.C. Carry out the transfer as in method (1) but with the column and tube removed from the G.C. and connected to a separate carrier gas supply line. Heat the tube for 30 minutes to discharge the sample completely on to the column, then replace the column in the G.C. oven and analyse as above.

#### *Method (3)—Tube to Column Transfer via a Gas Sampling Valve*

This is suitable for the more volatile compounds only. Connect the adsorption tube to the sampling valve in place of the sample valve loop. Purge the residual air from the tube and switch the tube into the G.C. carrier gas supply line. Carry out the sample transfer and analysis in a similar way to method (1).

#### BLANK ANALYSIS

To confirm that the adsorption tube was completely purged of its sample during the analysis, carry out a blank by disconnecting the tube, drawing 5 litres or more of clean air through it, and repeating the analysis. The tube is usually found to be completely purged of its sample, in which case it is ready for its next assignment. Keep a record of the blank analysis with the tube as evidence that it is clean.

#### MEASUREMENTS OF RETENTION VOLUMES

##### *Tube Measurements*

Apply a high carrier gas pressure to the G.C. (50 p.s.i. or more) and control the flow rate with the G.C. needle valve. This will ensure a constant carrier gas flow rate during the measurements. Fit the tube into the G.C. oven at the septum inlet. Connect to the splitter and to the detector. (A splitter can be

made by drawing out one arm of a  $\frac{1}{4}$  inch o.d. glass, Y-tube into a jet. Connect one of the wider arms to the sample tube with  $\frac{1}{4}$  inch o.d. Teflon tubing and connect the other to the detector with a  $\frac{1}{4}$  inch o.d. Pye Unicam, O-ring coupling and  $1/16$  inch stainless steel tube. Shorten the length of the splitter jet until the flow of carrier gas to the detector, measured by a bubble flow meter, is about  $1/10$  that through the jet.) Measure the flow rates at the splitter jet and the detector ambient temperature and adjust the needle valve to give a total ambient flow which is similar to that which is used when sampling air.

Inject 2 ml of the headspace vapour from a reagent bottle containing the compound of interest and measure the retention volumes with respect to the peak maximum, over a range of temperatures. Note that the peaks resulting from these injections are much broader than the corresponding peaks obtained on a G.C. column (see Figure 2).

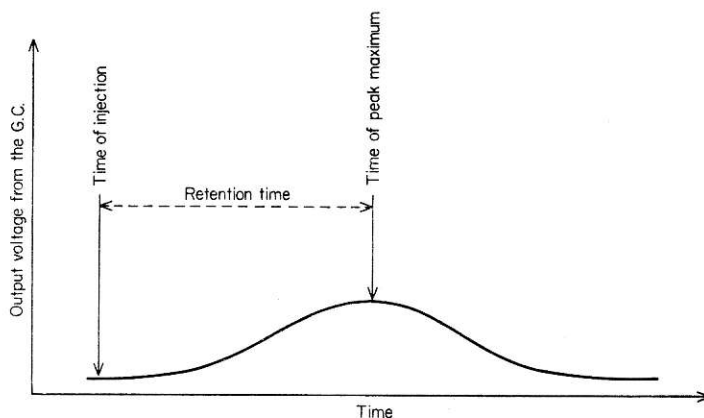


Fig. 2. The measurement of retention volumes.

The retention volumes are determined from the expression:

$$\text{Retention volume} = \text{retention time} \times \text{real flow rate.}$$

The real flow rate in the G.C. oven is greater than that which was measured externally at ambient temperature because of the expansion of the gas in the hot oven. Hence:

$$\text{Real flow} = \text{total ambient flow} \times \frac{\text{oven temperature (K)}}{\text{ambient temperature (K)}}$$

Plot  $\log(\text{retention volume})$  versus  $\frac{1}{T \text{ (K}^{-1}\text{)}}$  and extrapolate to determine the retention volume at  $20^\circ\text{C}$  (293 K).

#### Column Measurements

Retention volumes can likewise be measured on G.C. columns packed with a known weight of the adsorbent and using normal G.C. operating conditions. Report the results obtained by either method as specific retention volumes:

$$\text{Specific retention volume} = \text{retention volume/weight of adsorbent.}$$

## DIRECT MEASUREMENT OF OVERALL EFFICIENCY

Simulate the sampling operation in the laboratory by injecting a known amount of the compound of interest, in aqueous or methanolic solution, into the end of the sample tube and drawing it on to the adsorbent with clean air, using the same flow rate and sampling time as would be employed in practice. Afterwards measure the amount of compound remaining on the tube by one of the above techniques, and from this calculate:

$$\text{Efficiency} \geq \frac{\text{amount detected}}{\text{amount injected}} \times 100 \text{ per cent.}$$

The inequality in this expression arises because the compound is injected at the beginning of the simulated sampling period. In practice a large portion of the sampled material would probably be collected in the later stages of a real sampling operation and this portion would be retained with correspondingly greater efficiency because it is purged for a shorter length of time.

**An Application of the Method to the Measurement of Furfural Emissions from a Chemical Works**

Extracts from a survey of furfural measurements in the atmosphere are reported here to illustrate the sensitivity and accuracy which is achieved with these techniques. The survey was carried out to study the dilution in the atmosphere of certain emissions from a factory stack which contained a significant amount of furfural.

Most samples were collected continuously for a period of 3 hours on Porapak Q adsorption tubes. Method (3) was used for the analysis and furfural was detected by selective ion monitoring, scanning the characteristic 97, 96, 95 and 67 m/e ion fragments on the mass spectrometer.

The calibration plot of the peak height for furfural relative to the external standard (injections on to the G.C. after each sample, of 200 ng of furfural dissolved in ethyl acetate) is shown in Figure 3. The points on the plot were

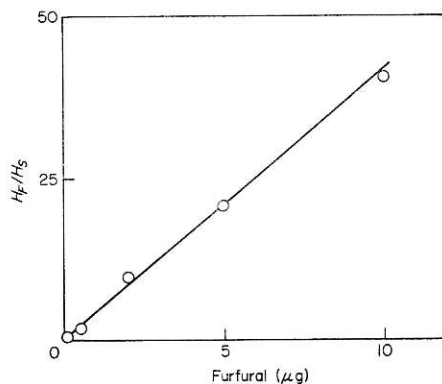


Fig. 3. Furfural calibration graph.  $H_F/H_S$  is the ratio of the furfural peak height of the sample to the peak height of a 200 ng furfural standard injected onto the Chromosorb column at 235°C.

mostly obtained on separate days over a period of one week and using three different adsorption tubes. The linearity and lack of scatter in the plot indicated that the technique was a reliable one.

TABLE I  
OVERALL EFFICIENCY MEASUREMENTS FOR THE ADSORPTION OF FURFURAL ON A PORAPAK Q TUBE AND ITS TRANSFER TO THE COLUMN BY METHOD 3

| Furfural injected, $\mu\text{g}$ | Air flow rate, ml/sec. | Volume of air, litres | Efficiency of recovery, per cent. |
|----------------------------------|------------------------|-----------------------|-----------------------------------|
| 3.0                              | 6.1                    | 66                    | 87                                |
| 0.2                              | 4.1                    | 44                    | 100                               |

This survey was carried out before the methods for retention volume measurements had been developed and the sampling technique was checked by making efficiency measurements. The two results of 100 per cent. and 87 per cent. obtained under different sampling conditions are presented in Table I and they showed that confidence could be placed in the above procedures. During the course of the survey further confirmation of the reliability of the technique was obtained by giving several tubes repeated blank measurements after their analyses, to check that a high tube to column transfer efficiency was being maintained. The results are given in Table II.

The dilution of the factory emissions in the atmosphere was calculated with the expression:

$$\text{Dilution} = \frac{[F_S]}{[F_A] - [F_B]}$$

where  $[F_S]$  and  $[F_A]$  were the concentrations measured at source and at the sampling site, respectively.  $[F_B]$  was the background concentration, measured in an atmosphere independent of emissions from the factory. This background measurement was obtained by averaging the furfural concentrations for those samples which were taken when the wind was blowing the factory emissions away from the sampler. The concentration was very small, being in the range  $1\text{--}2 \mu\text{g}/\text{m}^3$ , and to check that the measurements were valid two tubes were connected in series and city air was sampled through both of them. Analysis of the first revealed a typical background concentration of  $1.9 \mu\text{g}/\text{m}^3$ . The second tube was found to contain no furfural (i.e. less than the limit of detection which was  $0.1 \mu\text{g}/\text{m}^3$  in that instance) and this effectively confirmed that the background measurements were genuine—and not a product of the analytical method.

TABLE II  
THE EFFICIENCY OF THE DISCHARGE OF FURFURAL FOR THREE AIR SAMPLES COLLECTED ON PORAPAK Q

|          | The quantities of furfural, $F(\mu\text{g})$ , measured in successive clean runs |       |       |        | Efficiency of initial discharge<br>$= (F_0/F_0 + F_1 + F_2 + \text{etc.}) \times 100$ ,<br>per cent. |
|----------|----------------------------------------------------------------------------------|-------|-------|--------|------------------------------------------------------------------------------------------------------|
|          | $F_0$                                                                            | $F_1$ | $F_2$ | $F_3$  |                                                                                                      |
| Sample A | 3.1                                                                              | 0.13  | 0.036 | 0.0002 | 99.5                                                                                                 |
| Sample B | 0.099                                                                            | 0.019 | 0.002 | —      | 83                                                                                                   |
| Sample C | 0.42                                                                             | 0.011 | 0.009 | 0.0000 | 95                                                                                                   |

Some typical measurements of furfural concentrations and the dilutions of the factory emissions are reported in Table III for a series of eight 3-hourly samples.

TABLE III  
FURFURAL CONCENTRATIONS AND STACK EMISSION DILUTIONS FOR A  
SERIES OF EIGHT 3-HOURLY SAMPLES

| Sample time | Sample volume,<br><i>litres</i> | Total furfural<br>concentration,<br><i>mg/m<sup>3</sup></i> | Dilution of<br>stack gas in<br>the atmosphere |
|-------------|---------------------------------|-------------------------------------------------------------|-----------------------------------------------|
| 15.50-18.50 | 85.3                            | 0.37                                                        | 600:1                                         |
| 18.50-21.50 | 55.0                            | 0.040                                                       | 5,800:1                                       |
| 21.50-00.50 | 77.7                            | 0.022                                                       | 11,000:1                                      |
| 00.50-03.50 | 47.0                            | 0.011                                                       | 25,000:1                                      |
| 03.50-06.50 | 66.4                            | 0.005                                                       | 71,000:1                                      |
| 06.50-09.50 | 74.3                            | 0.001                                                       | ∞                                             |
| 09.50-12.50 | 67.6                            | 0.001                                                       | ∞                                             |
| 12.50-15.50 | 60.8                            | 0.001                                                       | ∞                                             |

The sample site was 280 metres from the 52 metre high stack. Winds were 15 knots, varying from N.E. to E.N.E. overnight.

The concentration of furfural at source [*F*<sub>s</sub>] was 220 mg/m<sup>3</sup>, and the background concentration, [*F*<sub>B</sub>] was 0.0019 mg/m<sup>3</sup>.

The sampling site was set up at street level, 280 metres S.W. of the stack. The height of the stack was 52 metres and the winds were 15 knots N. Easterly varying E.N. Easterly overnight. This change in wind direction can be seen to coincide with the progressive fall in furfural concentrations.

### Retention Volumes and Collection Efficiencies

In the air pollution survey outlined above, a considerable amount of time was spent in checking the reliability of the analytical techniques. Being a large survey, the cost of the time spent in confirming the techniques was only a small fraction of the total cost. Not all surveys are large enough to justify, on a cost and time basis, such extensive checking of the reliability of the techniques, especially as much of the work encountered is localised to one household or business premises. With an understanding of how a sample tube works and some experimental groundwork it is possible to predict the sampling conditions which will permit the sampling of any pollutant with a high collection efficiency.

The adsorption tube described in this paper can be looked upon as a very short chromatography column for which the air being sampled is the carrier gas. The organic pollutants in the air are adsorbed on the packing but, as with a chromatography column, they gradually travel through the tube and eventually the pollutants are purged out of it. If the subsequent analysis of the retained compounds is to be made quantitative, in terms of concentrations in the original sample, some knowledge of the retention volumes of the pollutants on the adsorbent packing is necessary. Using the methods described above, the specific retention volumes for styrene and pyridine on a Tenax G.C. adsorption tube were found to be 400 and 60 litre/g, respectively. These tube measure-

TABLE IV  
SPECIFIC RETENTION VOLUMES AND ESTIMATED 75 PER CENT. RETENTION VOLUMES FOR 60/80 MESH TENAX G.C. OBTAINED FROM MEASUREMENTS ON A G.C. COLUMN

| Compound     | Specific retention volume,<br>litres carrier gas/<br>gramme adsorbent | 75 per cent.<br>retention volume†, litres/0.25 g |
|--------------|-----------------------------------------------------------------------|--------------------------------------------------|
| Ethanol      | 1                                                                     | 0.2                                              |
| Acetone      | 5                                                                     | 1                                                |
| Benzene      | 25                                                                    | 3                                                |
| Pyridine     | 70                                                                    | 9                                                |
| Toluene      | 120                                                                   | 15                                               |
| Styrene      | 500                                                                   | 60                                               |
| Furfural     | 650                                                                   | 80                                               |
| Naphthalene  | 2,000                                                                 | 250                                              |
| Nicotine     | 15,000                                                                | 2,000                                            |
| Phenanthrene | 15,000,000                                                            | 200,000                                          |

† The 75% retention volume of a compound on a Tenax G.C. tube is the maximum volume of a carrier gas which can be passed through the tube at 20°C and still leave at least 75 per cent. of the compound retained in the tube.

ments show agreement within experimental error of the corresponding measurements on the G.C. column (Table IV). From this we have concluded that the retention volumes measured on a column can be used to estimate the retention volumes for an adsorption tube. This is a valuable conclusion since column measurements can be made more quickly and easily than can the direct measurements on the adsorption tube.

All of these results were based on measurements of the volume of carrier gas that flowed from the time of injection to the time of the G.C. peak maximum, which corresponds to the passage through the packing of approximately 50 per cent. of the compound injected. In a similar study, Pellizzari *et al.*<sup>13</sup> measured the specific retention volumes of compounds on Tenax G.C. They also found close agreement between the results obtained on a Tenax G.C. column and on a Tenax G.C. tube.

The collection efficiency of a sample tube, defined as:

$$\text{Collection efficiency} = \frac{\text{amount retained}}{\text{amount in original sample}} \times 100 \text{ per cent.}$$

depends for any given compound on the retention volume of that compound, and it is affected by the length of the sampling period. The longer the sampling period, or the smaller the retention volume, the more the compound elutes from the tube, and the collection efficiency is reduced.

Although it would be difficult to determine accurate collection efficiencies for a particular sampling operation, it is possible to calculate the minimum collection efficiencies. Butler and Burke<sup>15</sup> have demonstrated precise, but complex methods for determining the maximum sampling volume which would ensure at least 99 per cent. recovery of any given compound. But such data is available for only a few compounds. We have taken a simpler, if less precise, approach for estimating the maximum sample volume for each compound which still

ensures a high collection efficiency for that compound. The figure of 99 per cent. collection efficiency, chosen by Butler and Burke, is rather high in view of the other errors involved in most practical air sampling exercises and we choose to aim for a minimum collection efficiency of 75 per cent. For the purpose of the calculations, first assume that the specific retention volumes reported in Table IV correspond to the passage of 50 per cent. of each compound over 1 g of Tenax G.C. in a tube. Further assume that the tube is only a very poor chromatography column such that if a compound is injected on to it while air is being drawn through, then the compound would be purged off the tube at a virtually constant rate. After the passage of one half of its specific retention volume, therefore, 25 per cent. of the compound would have been eluted and 75 per cent. would have been retained on the 1 g tube. For a tube containing not 1 g but 0.25 g, the 75 per cent. retention volume would be one eighth of its specific retention volume. The 75 per cent. retention volumes calculated in this way for the 0.25 g tubes are shown in the third column on Table IV.

The two assumptions that were made for these calculations permit a considerable margin of error since:

- (a) the discharge of adsorbed material from the tube during sampling does not occur at a constant rate but approximates to the form of a very broad Gaussian peak, so that the calculations tend to underestimate the collection efficiencies;
- (b) these calculations apply only to the pollutants adsorbed at the beginning of the sampling period—material adsorbed at later stages of sampling would suffer correspondingly less elution, and the overall efficiency would again tend to be greater than calculated.

In view of the limited accuracy being aimed at in this approach (i.e. a possible error of up to 25 per cent. in the least retained compound) it is not necessary to carry out an independent determination of the retention volume for every pollutant not listed in Table IV. Knowing the position of the pollutant in the sequence of elution from Tenax G.C., it is possible to estimate its retention volume by comparison with those compounds in Table IV which elute before and after it.

The significance of these considerations can be understood by reference to an air sample data sheet. One such is illustrated in Table V for a sample of household air which was taken following complaints from the occupants of bad smells and a feeling of nausea. The problem was of a spasmodic nature and the sampling equipment was left with the householder for her to collect the sample. The sample volume was approximately the same as the 75 per cent. retention volume of toluene, for which the collection efficiency would therefore have been 75 per cent. or more. The concentrations of toluene and the compounds eluting after it were calculated by the method described in the experimental section and are listed in the 4th column of Table V. It is important to note that these concentrations are only approximate in absolute terms, since they were derived by assuming a similar and linear calibration for all compounds with respect to the external standard. Nevertheless, it was possible to make a reliable comparison of the results with those of other air samples analysed by the same procedure. When this was done, the sample was found to have had an un-

TABLE V  
A LABORATORY DATA SHEET

Type of Sample: Domestic air  
 Peculiarities: Occupants complained of "petrol-like fumes" which begin to appear in the evening and then disappear by lunchtime the following day. Smell disappears in damp weather but is worst during long hot spells.  
 Adsorbent: Tenax G.C. Weight: 0.25 g Tube: T.G.C. 2  
 Volume: 8.6 litre Date: 28 August 1977 Time: 9.55 a.m.  
 Column: Tenax G.C. 2 m x 2 mm Flow: 20 ml/min  
 Temperature program: 50-350°C, 10°C/min Sensitivity: 2, 10<sup>-6</sup>/1, 20 mV  
 Upper quantitative limit: † Peak 25A Lower quantitative limit: † Peak 9  
 Standardisation relative to: the peak height of a 10 µg injection of ethyl acetate. The results are reported as (mg/metre<sup>3</sup>)‡ in the original sample.

| Peak | Temperature, °C | Compound                                                    | Approximate concentration†, mg/ml |
|------|-----------------|-------------------------------------------------------------|-----------------------------------|
| 3    | 117             | <i>n</i> -pentane                                           | —                                 |
| 4    | 121             | <i>cis</i> -2-pentene or <i>trans</i> -2-pentene            | —                                 |
| 6    | 141             | Hexane                                                      | —                                 |
| 8    | 158             | Benzene and <i>n</i> -heptane                               | —                                 |
| 9    | 176             | Toluene and a paraffin, C <sub>8</sub> H <sub>18</sub>      | 3.9                               |
| 10   | 196             | Xylene                                                      | 2.7                               |
| 11   | 203             | Xylene                                                      | 0.49                              |
| 12   | 213             | 1-methyl-3-ethyl benzene                                    | 1.2                               |
| 13   | 219             | Trimethyl benzene                                           | 0.46                              |
| 14   | 224             | Probably 1,2-diethyl benzene                                | 0.14                              |
| 14A  | 228             | 1,4-dimethyl-2-ethylbenzene                                 | 0.09                              |
| 16   | 255             | Naphthalene and a paraffin, C <sub>14</sub> H <sub>30</sub> | 0.040                             |
| 18   | 270             | Paraffin, mol. wt. 226, C <sub>16</sub> H <sub>34</sub>     | 0.061                             |
| 20   | 300             | Diethyl phthalate                                           | 0.11                              |
| 21   | 307             | Unidentified, mol. wt. 212                                  | 0.12                              |
| 23   | 315             | Paraffin, mol. wt. 256, C <sub>18</sub> H <sub>40</sub>     | 0.22                              |
| 24   | 323             | Paraffin                                                    | 0.86                              |
| 25   | 328             | Paraffin, mol. wt. 338, C <sub>24</sub> H <sub>50</sub>     | 1.7                               |
| 25A  | 332             | Phenanthrene                                                | 0.06                              |
| 27   | 335             | Paraffin, mol. wt. 352, C <sub>25</sub> H <sub>52</sub>     | 2.8                               |
| 28   | 341             | Paraffin, mol. wt. 366, C <sub>26</sub> H <sub>54</sub>     | 3.5                               |
| 29   | 348             | Paraffin, mol. wt. 380, C <sub>27</sub> H <sub>56</sub>     | 3.4                               |
| 30   | 350 (+0.6 min)  | Paraffin, mol. wt. 394, C <sub>28</sub> H <sub>58</sub>     | 3.0                               |
| 31   | 350 (+1.2 min)  | Paraffin, mol. wt. 408, C <sub>29</sub> H <sub>60</sub>     | 2.0                               |
| 32   | 350 (+1.9 min)  | Paraffin, mol. wt. 422, C <sub>30</sub> H <sub>62</sub>     | 1.5                               |
| 33   | 350 (+2.8 min)  | Paraffin, mol. wt. 436, C <sub>31</sub> H <sub>64</sub>     | 0.63                              |
| 34   | 350 (+3.8 min)  | Paraffin, mol. wt. 450, C <sub>32</sub> H <sub>66</sub>     | 0.20                              |
| 35   | 350 (+4.6 min)  | Paraffin, mol. wt. 464, C <sub>33</sub> H <sub>68</sub>     | 0.09                              |
| 36   | 350 (+6.1 min)  | Paraffin, mol. wt. 478, C <sub>34</sub> H <sub>70</sub>     | 0.02                              |

† The quantitative limits indicate the part of the analysis for which more than 75 per cent. of the sample was recovered.

‡ For the method of calculation see the experimental section.

usually high level of organic contamination. Several sources of pollution were suggested to the Environmental Health Officer, namely tar fumes from building operations, leakage of fumes from oil fired central heating, or fumes from a garage. The investigation is continuing.

This semi-quantitative approach is adequate for many investigations, but if necessary more accurate data can be provided by calibrating the compounds of interest against the external standard. We have found that the approximate measurements do not differ from their calibrated concentrations by more than a factor of 3 and usually by less than a factor of 2, provided that the chromatogram peak heights are not excessively broad and do not suffer severe tailing.

The discussion so far has been concerned with the problem of estimating sampling efficiencies for volatile compounds. It is also possible that this efficiency may be reduced for the less volatile material because of poor transfer efficiency from the sample tube to the G.C. column. The efficiency of the Tenax tubes was tested for 43  $\mu\text{g}$  of phenanthrene (B.P. = 340°C) and the transfer efficiency with Method (1) was 90–100 per cent. It can be assumed that more volatile compounds would be transferred with this or greater efficiency. The exceptions to this would be unstable or reactive compounds which may suffer thermal decomposition or reaction during the transfer stage, but using the methods described here, this should be no more of a problem than it is in the gas chromatographic analysis itself.

Phenanthrene is the most strongly retained compound for which the efficiency of sample recovery has yet been checked. If more strongly retained compounds need to be measured quantitatively their transfer efficiencies must also be measured.

#### GENERAL COMMENTS

Tenax G.C. has advantages over Porapak Q because of its thermal stability and lack of column bleed, and it has been the most widely used adsorbent in our work. However, Porapak Q has the better sampling capacity<sup>15</sup> and is considerably cheaper. The bleed from Porapak Q consists of ethyl-styrene and related compounds and these can sometimes cause difficulty during chromatographic analysis if they overlap with the compounds of interest. There were no such difficulties in the use of Porapak Q for the furfural survey.

Of the transfer procedures, Method (1) is preferred since it permits the transfer of a wide range of compounds with a minimum of procedure; but with other G.C. systems Methods (2) and (3) may be more appropriate.

The sample tubes were designed to fit into Pye Unicam  $\frac{1}{4}$  inch couplings, which we find particularly convenient. However, they do require a certain amount of glass-blowing expertise in their construction. Where this is not available it should be possible to construct a similar sample tube from a straight length of glass or stainless steel tube, and make the attachment to the G.C. via Swagelok couplings.

These techniques are not limited to use with a mass-spectrometer. More conventional G.C. detectors have been used extensively in this type of work,<sup>4,6,13,16,19</sup> and they are particularly suited to investigations where there are only a few major compounds of interest. Halliday<sup>17</sup> has found that adsorption tubes of similar design to those described here were suitable for the G.C. analysis of anaesthetic vapours in hospital operating theatres. The compounds of interest included low molecular weight alcohols and halothane and they were analysed on a Pye Unicam 104 G.C. with a flame ionisation detector. Conventional G.C. systems can also be used where there is one major source of pollution which gives a characteristic chromatogram on the G.C.

#### Conclusions

The techniques described in this paper permit the taking of time-averaged air samples and spot samples for a wide range of compounds, and can be used for

monitoring air pollution to test for compliance with the Government Guidance Note on Threshold Limit Values.

They do not require trained personnel for the sampling operation itself, and in the event of spasmodic complaints of air pollution the equipment can be loaned out to a member of the public to take the sample.

The apparatus costs relatively little to construct and is suitable for use with any G.C. system.

When necessary the techniques can be made very accurate and sensitive.

For nearly all of public health work, which does not require extremes of accuracy, we have established simple procedures for the quantitative assessment of the analyses with an adequate level of accuracy.

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