QUANTITATIVE DETECTION IN GAS CHROMATOGRAPHY

A Thesis submitted for the Degree of Doctor of Philosophy of

Brunel University

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Brunel University, London, W.3. September, 1967.

ABSTRACT.

The difficulties encountered in quantitative analysis by gas chromatography are discussed, with particular reference to detection systems. The properties of an ideal detector for quantitative analysis are listed. A description is given of the mode of operation of existing detectors for gas chromatography, and the extent to which they are suitable for quantitative work is assessed. It was concluded that no one detector possessed all the properties required for an ideal detector. In particular a qualitative knowledge of the sample for analysis was required by all detectors, and calibration was required by the majority of detectors. The extent to which the Brunel mass detector overcomes these limitations was assessed. It is shown that the response of the mass detector depends solely on weight changes caused by adsorption of materials eluted from the chromatographic column thus completely eliminating the need for calibration and qualitative information. The response of the detector is integral, so that the problems associated with peak area measurement do not arise. The sensitivity of the detector is of a similar order to conventional hot wire detectors. The detector gave a quantitative response to all materials analysed, covering a wide boiling range: the upper limit was determined by the maximum column operating temperature, and the lower limit by the extent to which the detector was cooled. The detector responded quantitatively to water. At room temperature the detector responded on a qualitative basis to organic and inorganic gases. The detector was used for the calibration of other detectors, and was operated in conjunction with the Martin gas density balance, to determine the molecular weights of eluted materials.

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CONTENTS.

CHAPTER 1.

The Problems Associated with Quantitative Gas Chromatography.

1.1 Introduction.

Qualitative gas chromatographic analysis is a particularly valuable method of separating and detecting the constituents of mixtures. Quantitative gas chromatography has not reached the same state of refinement as qualitative analysis. The reasons for this situation will become evident on considering the errors which may arise. There are many inaccuracies in quantitative analysis, and these are discussed in the order in which they occur in an analysis. The materials for analysis are themselves subject to composition changes if not stored correctly: the taking of a sample and the method of injection can make an appreciable difference to the result if care is not taken. Irreversible adsorption of a proportion of the components of the mixture within the chromatographic column can occur and thus render the results valueless. One of the major difficulties encountered is the inability of all common detectors to give a response which is a simple function of a stoicheometric property. Since detection systems form the main part of this work, the properties of an ideal detector for quantitative analysis are discussed in detail in the following chapters.

The interpretation of results is often a source of difficulty in quantitative analysis. Even assuming that detector responses are accurately known, the measurement of peak areas obtained from a detector of differential response is both time-consuming and subject to errors.

1.2 Discussion.

An outline of the difficulties which may be encountered in quantitative analysis has been given. The means by which these difficulties can be overcome, and the resultant errors minimised are

now to be discussed.

1.2a Sample Storage.

The storage of a sample to be analysed by gas chromatography would not at first sight appear to be the concern of the analyst. But this is far from so, in that incorrect storage will lead to changes in the composition of a mixture with time. Consider a simple case in which a sample from a reaction product in an industrial process is monitored at daily intervals. If an analysis is carried out immediately after a sample is removed from the reaction vessel, and a second analysis performed on the same sample several days later, the results may not be the same. Such an occurrence with samples taken on different days from the same reaction vessel may lead to the erroneous conclusion that the composition of the product varies from day to day. Poor storage of a mixture in which the components differ in volatility will lead to preferential loss of the more volatile components. The percentage composition of the more volatile materials will thus decrease with time, and the amount of the less volatile materials present will appear to increase. Obvious methods of minimising this effect are to store the material in completely air-tight bottles or phials in a refrigerator. But losses of the more volatile components will still occur on opening the vessel to remove a sample for analysis. The recommended methods of minimising changes in composition are to have as little as possible air space in the sample bottle, to open the bottle as infrequently as possible, and for the minimum amount of time. A better method of minimising sample losses is to never open the bottle at all, but to fit the top with a rubber septum which can be pierced with the needle of the syringe used for injecting the sample into the chromatograph.

1.2b Sample Injection.

Methods of sample injection. There are two common methods of injecting a liquid sample into a gas chromatograph, the first using a glass micropipette, and the second a syringe fitted with a metal hypodermic needle. The micropipette can be discharged on to an open column[2], through which the carrier gas supply has momentarily been shut off. Losses of the more volatile components of the mixture can readily occur after discharge on to the column, prior to reconnection of the carrier gas supply. Alternatively a closed system may be used[3], in which the carrier gas is not shut off. The pipette is fitted with a piece of soft iron, and is introduced into a sealed chamber via a system of stopcocks, such that there is no interruption of the carrier gas supply. The pipette is then lowered on to the column by means of a permanent magnet attached to the outside of the chamber. In general the disadvantages of the micropipette system are that the pipette is usually designed to hold only a fixed sample size; lower boiling components are preferentially lost by evaporation: there is an inherent delay between removing the sample from the bottle and introducing the sample to the column; sample bottles fitted with septa cannot be employed; the outside surface area of the pipette is large compared with the bore and hence the pipette may hold an excess charge unless carefully wiped. Lastly, it is not possible to inject into the column packing, but only on to the column. Hence back diffusion into the space above the column can occur.

A syringe has several advantages over the micropipette. Injection can be accomplished simply by piercing a rubber septum[4] at the top of the column with the syringe needle. There is no interruption of the carrier gas supply and stopcocks are not required. There need be virtually no delay between filling the syringe and injecting the

contents on to the column. It is possible to inject the sample into a flash vaporization chamber (see below), or on to the column. For quantitative analysis, injection into the column packing is the most satisfactory procedure. Several precautions must however, be taken when using a syringe. The outside of the needle should be wiped free of excess sample before injection, and all air should be excluded between the sample top and the syringe piston. Since all materials exhibit a finite vapour pressure, any air trapped in the syringe will result in part of the sample entering the vapour phase, thus changing its composition. Injection must be deliberate and rapid, retaining the needle in the injection port for the same short time for all injections. The septum must not be permitted to leak and should be renewed as necessary.

A syringe is capable of giving reproducible and representative sample injections provided the precautions noted above are taken. However, for accurate quantitative work it is advisable to check the syringe calibration. The author has found on a particular syringe that although calibration was necessary, the performance of the syringe, and the reproducibility of the injected sample size did not deteriorate at all over a period of nine months continual use. Details of syringe performance are discussed in Chapter 4.

A method of sample injection has been proposed in which the need to calibrate detector response with respect to sample size is eliminated[5]. The sample is introduced into a chamber, maintained at the temperature of the column, and is held in this chamber until thermal equilibrium between the sample and the operating temperature is reached. Only then is the sample allowed to pass on to the column. This ensures that a fixed volume of vapour is always introduced to the column. It is claimed that peak parameters, reduced to unit weight, are independent

of sample weight, which is not the case with direct injection. Hence calibration of a detector at only one sample size, suffices for all other sample sizes, provided that the vapour pressure in the chamber does not exceed the saturated vapour pressure. The alternative method of preheating a sample is to inject the sample into a chamber at a temperature such that vaporization of all the components of the mixture occurs immediately, and they are swept without delay as vapours on to the column. This method must be used with care since fractional distillation of the components can occur before reaching the column, and isomerisation or decomposition may occur if too high a temperature is used.

The injection of samples which are solids at room temperature introduces additional difficulties. Any method which involves the direct removal of a solid sample from the bulk will not give a representative analysis of the bulk, due to fractional crystallisation which must have occurred during the preparation of the solid. Samples must be taken in the liquid phase, either by melting the solid, or dissolving the solid in a solvent. Care must be taken to choose a solvent which does not form one of the constituents of the mixture, does not react chemically, and is well separated chromatographically from all the constituents. The sample should be injected directly into the column using a syringe.

The analysis of gaseous samples may be carried out using a syringe, but adsorption on to the walls of the syringe can lead to erroneous quantitative results. A syringe for gas analysis must be exceptionally clean, and should contain no lubricant. It must of course be gas tight. For accurate quantitative analysis, injection by means of a gas sampling valve is more satisfactory, but lubricants and rubber or PTFE fittings must be avoided. The analysis of the contents of a

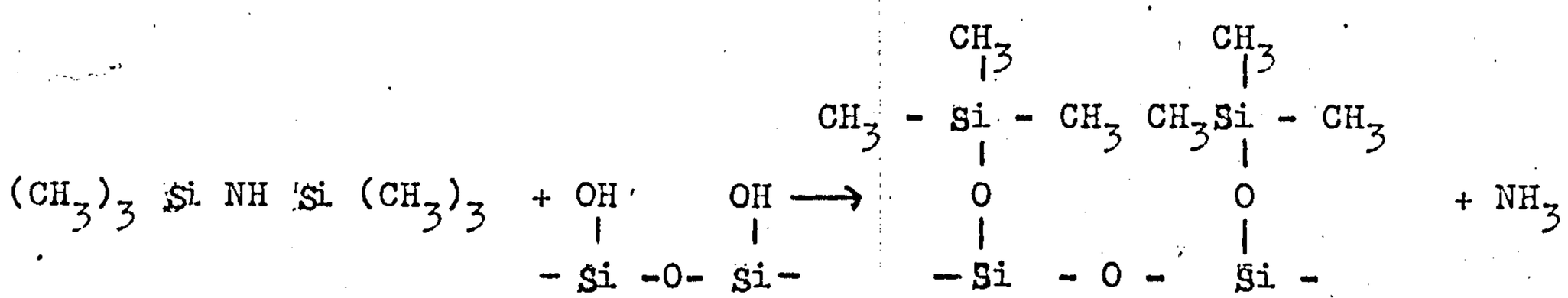
cylinder of liquified gases poses a particular problem. By repeatedly taking samples in the gaseous phase, and injecting into the chromatograph via a gas sampling valve, the percentage composition of the mixture will be seen to change. Consider a cylinder containing equal proportions of a number of gases. For early samples the gas with the greatest vapour pressure will predominate, but this gas will be used up preferentially, so that as sampling proceeds, its proportion of the total will progressively decrease.

1.2c Adsorption Effects.

Adsorption of a sample within the column can occur on the walls of the column itself[6], on the stationary phase[7] and on the inert support[8]. Preferential adsorption of one of the constituents of a mixture will render a quantitative analysis invalid. Irreversible adsorption on the column walls is not readily detected by inspection of the resulting chromatogram and is usually observed indirectly by analysing synthetic mixtures. Adsorption on column walls can be kept to a minimum by using glass columns, in which the active sites have been rendered inactive by treatment with trimethylchlorosilane or a similar material. For column inlet pressures over about 30 lb/sq.in. it is usual to use metal columns, and stainless steel is preferable to copper. If a copper column is used it is essential to pretreat it by heating strongly (800°C), and at the same time passing nitrogen through it for at least 24 hours, before packing. Even after such treatment the copper will still contain a substantial number of active sites, and in addition, when operated at high temperatures may promote dimerisation or rearrangement of the materials under analysis. In particular, the use of copper columns should be avoided for the analysis of compounds containing multiple bonds. Adsorption on a metal column can be reduced by coating the inside surface with the stationary phase

to be used on the inert support. Unfortunately only polar stationary phases will satisfactorily coat the walls and even then the coating will only last for a month or so, depending on the operating conditions.

In general, it is on the inert support that adsorption of components predominently occurs[9]. A number of methods of support pre-treatment have been proposed, to eliminate adsorption sites. Acid and alkali washing of the support to remove iron and aluminium is often employed[10], but thorough washing after treatment is essential, and even then activity is still significant. The addition of small quantities of highly polar and involatile liquids to give preferential adsorption on the support has been tried[11, 12], but is not particularly successful. Deposition of silver or gold[13] on the support has been used but although surface activity is reduced, there is a danger of chemical reaction occuring between the deposited material and the components passing through the column. Deactivation by heating the support to about 1300°C is very effective[14], but the most satisfactory method of minimising support activity is to treat the support with trimethylchlorosilane or hexamethyl disilazane[12, 15]. The latter compound is to be preferred in that it has a much lower volatility and toxicity. The surface reaction is represented by the equation:



A description of the procedure has been published[16].

Adsorption losses within the column as a whole can represent a considerable amount of the total quantity of component present. But the amount of adsorption is not proportional to the charge. The same amount of adsorption will occur, irrespective of the sample size.

Reversible adsorption affects the shape of the resulting peak, in that it displays a tail. In extreme cases the tail is very long and only just above the baseline. Peak area measurement is thus very difficult, and the results obtained geometrically and by digital integration will not include the tail and therefore will cause a significant error (see Chapter 7). The smaller the sample size injected on to the column, the greater will be the proportion in the tail of the peak. It is possible to estimate the amount of material lost by irreversible adsorption by plotting a graph of peak area as ordinate against size of sample as abscissa[1]. Assuming a detector response linear with concentration, a straight line graph will be obtained, which does not pass through the origin. The point on the abscissa cut by the line, represents the amount of change lost by adsorption. Hence it is advisable to use as large a sample size as possible, consistent with the capacity of the column and of the detector.

A somewhat different approach to minimising adsorption effects, which is used in cases of extreme adsorption, is to inject large quantities of the material which is itself adsorbed, until all the active sites are filled. Only then is a quantitative analysis of this material attempted.

1.2d Detectors.

For most quantitative work there will be a reasonable amount of sample available so that detectors of high sensitivity and low limit of detection are not essential. It is preferable to use a detector which has a predictable response factor, although its sensitivity may be low. In the analysis of trace components, and in the interests of high column efficiency and high resolution, it may be essential to use a highly sensitive detector even if extensive calibration is necessary.

The analysis of materials retained for excessive periods on a

column poses a problem. As retention time increases, the peaks will become progressively more spread, which in turn often results in peaks of small height. Area measurement becomes imprecise, and open to gross errors. A procedure has been proposed[17] to overcome this problem, in which amplification of the detector output is increased in proportion to retention time, so that all peaks are approximately the same height (assuming equal response). This makes the later peak areas rather large, but by making the recorder chart speed inversely proportional to retention time, reasonable sized areas are obtained. It is quite probable however that by adopting this method, rather than the conventional method, other errors would be introduced, thus invalidating the advantages claimed. It is preferable to avoid, whenever possible, extremely long retention times, by using higher column temperatures, and carrier gas flow rates. The analysis of a mixture containing materials of a widely different physical or chemical nature, giving retentions from a few minutes to several hours, is often carried out by increasing the column temperature as the analysis proceeds[18], thus maintaining reasonable retention times for all the materials. More recently the technique of flow programming has been introduced[19]. From the quantitative aspect, both of these procedures must be used with caution. Many detectors give a response which is either temperature dependent or flow dependent: calibration becomes difficult and even more time consuming than normal. It is often easier and more satisfactory to incorporate a column in front of the main column to remove preferentially some of the components of a mixture[20], and to analyse this fraction subsequently. By choosing suitable stationary phases the two runs can each be carried out in a reasonable time without resorting to temperature or flow programming.

There are a number of different methods of carrying out the quantitative analysis of mixtures, which to some extent depend on the nature of the detector. Several methods are described below. Absolute determinations are carried out by measuring peak areas for known amounts of each component, and calculating the calibration factors. Graphs are plotted of amount against response for each material. This method must be adopted for detectors of unpredictable response. Internal normalisation is used when the variation of the calibration factor with molecular species is predictable, e.g. the gas density balance[21]:

$$C_x = \frac{A_x/M_x}{\Sigma_1^j A/M} \qquad 1.1$$

where C_x is the fraction of component x of molecular weight M_x and giving a peak area A_x in a mixture containing j components.

Calibration may also be carried out by preparing mixtures of known composition, and measuring all response factors relative to one of the components of the mixture. For a detector which does not have a response linear with concentration, the addition of known amounts of the component to a fixed concentration of an internal standard is made, and a graph plotted of:

$$\frac{\text{peak area of component}}{\text{peak area of standard}} \quad \text{against} \quad \frac{\text{amount of component}}{\text{amount of standard}}$$

To analyse a mixture containing the component, a known amount of the standard is added, and using the calibration graph, the amount of component is estimated.

A method eliminating extensive calibration but which in itself is time consuming, can sometimes be used to advantage. A chromatogram of a number of components of unknown concentration is compared with that obtained from a known synthetic mixture, run under identical conditions. The approximate composition of the mixture is estimated,

and on identical synthetic mixture prepared. The chromatograms are compared, and a new mixture made up if necessary. This procedure is limited to about six component mixtures.

1.2e Interpretation of Chromatograms.

The accuracy of a quantitative analysis will depend a great deal on the correct interpretation of the chromatogram. The majority of detectors have a differential response, and the composition of a mixture can be estimated either by measuring peak heights or peak areas. It is more fundamental to measure peak areas in that the total area is proportional to the total amount of material present: this is the method used where the detector response is a simple function of a stoicheometric property of the components. However, in cases where the detector response is not predictable it is often easier to use peak height measurements. The measurement of peak heights has, however, no logical basis: a peak height simply represents the concentration of the component at a given time, and is not therefore a measure of the total amount of the component in a mixture. The use of peak height measurements demands constant column operating conditions. For example changes in the operating temperature during an analysis will affect retention times, and hence peak heights are affected. The corresponding peak areas remain constant. On the other hand, (in the case of the katharometer), peak areas are affected by changes in flow rate, so that flow rate variations cannot be tolerated: but by using peak height measurements, small flow rate variations do not affect the quantitative analysis. Peak height measurements are limited to symmetrical peaks: in cases where distorted peaks are obtained, peak area measurements must be employed. In general peak height measurements are acceptable for the quantitative analysis of large charges of non-polar materials. The analysis of small amounts

of polar materials often give rise to distorted peaks, caused for example, by adsorption effects. Peak height measurements are inaccurate and area measurements must be made.

Several methods of obtaining the area under a peak are used[22]. To some extent, the method adopted will depend on the geometry of the peak to be measured. For a Gaussian curve, the peak area is proportional to the product of the peak height and the peak width. The peak width is measured at a constant fraction of the peak height, usually at the half height position (which will give 84% of the true area) or at the baseline. This method demands a stable baseline and is not satisfactory for distorted peaks. For diffuse (but symmetrical peaks), peak widths at the base are difficult to measure, and the half height position is preferred.

The area of a peak can be reduced to the measurement of the area of a triangle by the following means. The area is proportional to the product of the peak height, and the distance between the intersection of the tangents to the points of inflection of the curve ~~width~~ with the baseline. The peak height, in this instance, is either the height of the chromatographic peak, or the height of the constructed triangle. Triangulation is only satisfactory for symmetrical peaks.

The product of peak height and retention distance has been used for quantitative estimation. The method assumes that column performance is independent of the substances under analysis, and that the calibration constants for the detector are proportional to retention volumes. The method is theoretically incorrect, and should not be used for serious work.

The areas of distorted peaks can be measured either by using a planimeter, or by cutting out the peaks, and weighing the paper. Planimetry requires skilled operation, and several determinations must

be carried out on each peak. The cutting out of peaks also demands care, and the result will be affected by changes in moisture content, variations in the thickness of the paper: moreover the chromatogram is destroyed.

Integrators are used for peak area measurement[23], but although producing a result rapidly, they are very expensive. Integrators may demand a stable baseline and virtually complete resolution of components. Digital integrators[24] require a finite deflection from the baseline before counting begins: they are not therefore reliable for measuring the areas of peaks with long tails (but see Chapter 7). Analogue integrators[25] produce an integral chromatogram, and hence measurements must still be performed, although step heights can be measured with more precision than peak areas. Distorted peaks, and those with long tails can be satisfactorily measured.

The most widely used methods of determining peak areas are; peak height and width measurements, triangulation, and planimetry. The repeatability and reproducibility of these three methods have been investigated[22, 26]. Repeatability is defined as the measure of precision of the results obtained by one operator using one set of apparatus. Reproducibility is defined as the measure of precision of the results obtained by different operators using different sets of apparatus. The first method is easily the most precise, and planimetry the least satisfactory. Errors arising in the first method were separately investigated and it was found that peak height errors were greater than peak width errors, caused primarily by difficulty in locating the baseline. However since widths are usually much smaller than heights, the two error sources contribute roughly in equal proportions. For wide peaks the measurement of widths depends more and more on an accurate measure of the peak heights, and hence there is a decrease in the precision of the resulting area, as retention time increases.

The Author has carried out similar experiments using peak height and width measurements, peak weights, and integrators, to determine peak areas. These results are presented in Chapter 7 and compared with those obtained by Scott[22].

The quantitative analysis of compound peaks poses an added problem. To what extent do the peaks overlap and what proportion of the compound peak is to be allocated to each component[27]? For a resolution of greater than 50%, the peak heights of the individual components are not affected, so that analysis based on peak height measurements may be used. For analysis based on peak areas, internal normalisation is carried out on the total area, and the ratios of the peak heights used to determine the proportion of the two components. This assumes equal detector response factors. In cases where the valley between the peaks is too shallow to obtain accurate peak widths for area measurement, the width can be estimated by plotting a graph of the peak widths of all the components in the mixture, against retention time; the widths of the unresolved peaks are obtained by interpolation. When resolution is less than 50%, peak heights are affected, and relative peak positions may also be affected. Results are generally unreliable. Whenever possible quantitative estimation of unresolved components should not be attempted, rather the operating conditions should be changed to obtain complete resolution.

The detector output is usually fed to a potentiometric recorder, often via an amplifier. It is therefore essential that both the amplifier and recorder respond in a linear manner. Non-linearity in the recorder-amplifier system is usually caused by incorrect setting up, or poor equipment, since equipment with linearity deviations of less than 1% are readily available. In general this part of thh chromatographic apparatus is the only one which does not introduce errors into a quantitative analysis.

1.3 Conculsions.

Loss of the more volatile components of a mixture can occur if the sample to be analysed is not properly stored. It is advisable to store samples in full bottles, and to remove aliquots with a syringe through a septum fitted to the bottle. It is preferable to inject samples directly on to the column, and to use a syringe rather than a micropipette. Adsorption effects can be minimised by use of either a stainless steel or preferably a glass column, and by deactivating the inert support with hexamethyl disilazane prior to coating with stationary phase. A detector for quantitative analysis must either be calibrated for each material at all concentrations employed, or have a predictable response. Quantitative analysis is preferably based on peak area measurements, rather than peak height measurements. The most satisfactory way of determining peak areas is from the product of the peak height and width. The quantitative analysis of unresolved peaks is not recommended.

The accuracy of quantitative gas chromatography depends on so many factors, that reliable results can only be expected when the greatest care is exercised.

1.4 References.

1. Evans, R.S., Scott, R.P.W., Chimia 17 137 1963.

2. Martin, A.J.P., James, A.T., Biochem. J. 63 138 1956.

3. Scott, R.P.W., Gas Chromatography 189 1958.

4. Amos, R., Hurrell, R.A., Gas Chromatography 1962.

5. Dimbat, M., et.al. Anal.Chem. 28 290 1956.

6. Kelso, A.G., Lacey, A.B., J. Chromatog. 18 156 1965.

7. Pecsok, R.L., et.al., Anal.Chem. 36 452 1964.
   Kusy, V., Anal.Chem. 37 1748 1965.
   Martin, R.L., Anal.Chem. 33 347 1961.

8. Bens, E.M., Anal.Chem. 33 178 1961.
   Sawyer, D.T., Barr, J.K., Anal.Chem. 34 1518 1962.
   Urone, P., Parcher, J.F., Anal.Chem. 38 270 1966.

9. Howells, K.A., Dissertation for the Degree of B.Tech, 1966, Brunel University. Studies of Surface Activity of G.L.C. Inert Supports.

10. Orr, C.H., Collen, J.E., Ann. N.Y. Acad. Sci. 72 649 1959.
    Liberti, A., Gas Chromatography 214 1958.
    James, A.T., Research 8 8 1955.
    James, A.T., Martin, A.J.P., Biochem. J. 50 679 1952.
    Cuthbertson, F., Musgrave, W., J. App. Chem., 7 99 1957.

11. Eggertsen, F.T., Greonnings, S., Anal. Chem. 30 20 1958.
    Johns, T., Gas Chromatograph 31 1958 Acad. Press.

12. Bohemen, J., et. al. J. Chem. Soc. 2444 1960.

13. Ormerod, E.C., Scott, R.P.W., J. Chromatog. 2 65 1959.

14. Blandenet, G., Robin, J.P., J. Gas Chrom. 4 288 1966.

15. Pennett, R.H., Purnell, J.H., J. Chromatog. 7 455 1962.

16. Purnell, J.H., Gas Chromatography236 published by John Wiley, 1962.

17. Palm, E., Gas Chromatography 189 1962.

18. Drew, C.M., McNesby, J.R., Vapour Phase Chromatography 213 1956.
    dal Nogare, S., Harden, J.C., Anal. Chem. 31 1829 1959.

19. Purnell, J.H., Gas Chromatography 387 published by John Wiley 1962.
    Scott, R.P.W., Nature 198 782 1963.
    Scott, R.P.W., Gas Chromatography 1964.
    Zlatkis, A., et. al., J. Gas Chromatog. 75 1965.

20. Martin, R.L., Anal. Chem. 32 336 1960.
    Kerr, J.A., et. al., Trans. Faraday Soc., 55 572 1959.
    Whitham, B.T., Nature 182 391 1958.

21. Martin, A.J.P., James, A.T., Biochem. J. 63 138 1956.

22. Scott, R.P.W., Grant, D.W., Analyst 89 179 1964.

23. Kelker, H., Gas Chromatography 125 and 187 1962.
Scott, R.P.W., Gas Chromatography 3 1960.

24. e.g. Chromalog (Fisons Ltd.).
Precision Integrator (Honeywell Controls Ltd.).

25. W.G. Pye Ltd., Cambridge.

26. Krejci, M., Janak, J., Chemie (Prague), 10 264 1958.

27. Grant, D.W., Vaughan, G.A., J. App. Chem., 10 181 1960.
Brace, R.O., Principles and Practice of Gas Chromatography (ed. Pecsok, R.L.) 145 published by John Wiley 1959.
Kalmanovski, V.I., Zhukhovitskii, A.A., J. Chromatog. 18 243 1965.

CHAPTER 2.

The Characteristics of a Detector for Gas Chromatography.

2.1 Summary.

The characteristics of a detector suitable for gas chromatography are discussed, with particular reference to the quantitative aspect. Methods are given by which the behaviour of practical detectors can be measured. The performance of detectors can be assessed by a set of numerical values, and in addition by qualitative description.

2.2. Discussion.

The properties of an ideal detector are so numerous, and in some instances conflicting,, that no single detector can satisfy all the requirements. A most important property of a detector is that it must have a predictable response. Ideally a detector should respond equally to all materials, either on a weight basis, or on some other stoichiometric property. Using such a detector, negligible calculation is involved, to find the weight percent of a mixture. In addition, absolute quantitative analysis is possible if the total amount of sample injected is known. In practice no detector is found to satisfy this requirement over anything more than a small concentration range, or for more than a limited number of materials. In general therefore it is necessary to measure experimentally the response of a detector to the materials under analysis. Qualitative analysis should therefore precede quantitative analysis. Detector calibration for the constituents of even a relatively simple mixture is a time consuming process.

For a detector, whose response factors have been measured, the amount C of any component x in a mixture will be given by the expression:

$$C_x = \frac{a_x A_x}{\sum_1^j aA} \qquad 2.1$$

where A_x is the peak area representing component x, and A is the total area of j components. 'a' values are calibration constants relating peak area to the amount of component. For an ideal detector the values

of 'a' for the 'j' components would be identical.

Allied to the requirement of predictable responses for all molecules, is that of a linear response for each material, over the whole range of concentration encountered in gas chromatography. It is found in practice that few detectors even approach such behaviour[1-3], and in general calibration is required for each material at all concentrations. The response of a detector, and hence the calibration thus falls into two parts: the response with respect to concentration, of a particular species, and the response for different species at each concentration. Both responses can normally be obtained from a single series of experiments.

2.2a Detector Calibration.

Various methods have been proposed for the calibration of detector response against concentration. For a relatively insensitive detector, the obvious method is to inject, using a syringe, known amounts of the material in question, on to the column; a graph is plotted of sample size against the peak area of the resulting chromatogram. To minimise losses due for example to adsorption within the column, the unknown mixture must be run under identical conditions. For sensitive detectors such as the flame ionisation detector[1], this method is unreliable, in view of the very small charges required (<1 µl). The diffusion of a solute from a glass capillary into the carrier gas stream has been proposed[4]: by varying the amount of solute, different concentrations of solute vapour are obtained. The procedure is time consuming in that only one substance may be used at a time. In the method used by Swoboda[5], the carrier gas is saturated with the vapour of a solution containing the components of interest (as solutes). The amount of solute in the carrier gas, is calculated from Henry's Law, and the detector response obtained. A whole range of concentration is

covered by repeating the experiment with solutions containing different proportions of solutes.

The continuous dilution of a solute by a gas stream has been used for detector calibration[6]. The concentration of the solute will decay exponentially with time, and hence for a linear response a plot of log peak area against time will be a straight line. Deviations from linearity are thus immediately obvious. Unfortunately at low concentrations, where the method would be most valuable, the rate of change of solute concentration may also depend on the rate of desorption of the solute from the walls of the dilution vessel, although this can be minimised with careful design[7]. Adsorption errors are eliminated by placing the solute in a high boiling solvent[8]. In addition, any number of solutes may be examined at one time, thus decreasing the calibration time significantly. Other methods of detector calibration by vapour dilution have been discussed by Gregory[9] and Krugers[10].

The vapour dilution technique in the form described by Fowlis and Scott[8], is ideally suited for detectors of low limits of detection and high sensitivity. For the more insensitive detectors, the Author has used the mass detector[3], whose response is predictable, to calibrate other detectors, by incorporating the two detecting systems in series or in parallel. Indeed this method is not restricted to the calibration of relatively insensitive detectors, but may also be used for the calibration of high sensitivity detectors, provided a suitable stream splitting device is incorporated in the system. A detailed description of this work, together with some calibration curves for a number of detectors is given in Chapter 6.

A detector which responds solely to a particular chemical species or which has a widely differing response for different species, can sometimes be used to advantage. For example a detector which responds

predominently to sulphur containing or halogenated compounds[11], will select these materials from a mixture, and ignore all other materials, thus simplifying analysis of the sample. Such a detector can for certain applications be as valuable as a detector giving an equal response for all the components of the sample. There still remains however, the problem of analysing the remainder of the mixture, so that even in cases such as described above, the ideal detector will be required[11].

2.2b Detector Requirements.

It is evident that a detector which does not require calibration is of great value, even if it does not satisfy all the remaining requirements of an ideal detector.

A detector should be insensitive to random changes in carrier gas flow rate and to pressure fluctuations. Similarly, a detector should be insensitive to random temperature changes, particularly if it is measuring a property which itself is temperature dependent[2]. A detector sensitive to such fluctuations, can yield erroneous quantitative data, even if it has previously been calibrated. Baseline changes are often the result of such fluctuations[12]: exact location of the baseline is made difficult, and peak area determinations become imprecise.

Detection systems which attempt to measure small changes in large values are in general unsatisfactory, although several systems have been proposed[13]: for example the measurement of the gas flow rate change accompanying the elution of a solute.

A detector must have a high signal to noise ratio in order that the two effects may be unequivocally distinguished. Noise is defined as the random fluctuations of the output of the detector occurring at any instant. The signal is the output change which occurs when a sample enters the detector.

2.2c Detector Sensitivity.

The relative merits of detectors are often described in terms of sensitivity. However there is no single definition of the term sensitivity, so that comparisions on such a basis can be very misleading. The first quantitative definition of sensitivity was made by Dimbat and co-workers[14], in a paper on quantitative analysis in general:

$$S_w = \frac{AS_rF}{TW} \qquad 2.2$$

where S_w = sensitivity ml mv mg^{-1}

A = peak area cm^2

W = weight of sample mg

S_r = recorder sensitivity mv cm^{-1}

T = chart speed cm min^{-1}

F = flow rate at exit ml min^{-1}

(The symbols have been changed to conform with those used in the remainder of this discussion).

McWilliam[15] proposed that for a differential detector the minimum detectable signal represents the minimum detectable gas concentration, but for an integral detector the minimum detectable weight is quoted. He defined sensitivity as the change in gas concentration which gives a signal equivalent to the background noise, i.e. sensitivity is expressed in terms of micrograms per millilitre S_2. It is necessary to quote the noise level R_n (μV) and in addition the baseline drift ($\mu V\ hr^{-1}$). In some cases the drift may be the limiting factor, rather than the noise level of the system. McWilliam also points out that since the sensitivity of a detector will vary for different chemical species, any relationship between detector response and some molecular parameter should be quoted with sensitivity values. Therefore quoting sensitivities in terms of the minimum detectable sample size for a differential detector is misleading, since by changing column conditions, the width of a given peak can be reduced, and hence the minimum

detectable sample size is reduced. However, such figures are readily converted to a concentration basis by dividing the minimum detectable weight by the volume V of the carrier gas in which the component is eluted (ml).

$$S_2 = \frac{S_1}{V} \qquad 2.3$$

where S_1 = sensitivity, µg and S_2 = sensitivity, µg ml^{-1}. V is obtained from the peak width.

The term detector output D introduced by McWilliam[15] is identical to the definition of 'sensitivity' given by Dimbat (equation 2.2).

In short, the Dimbat and McWilliam definitions of detector sensitivity are related by the expression:

$$S_w = \frac{R_n}{S_2} \qquad 2.4$$

The most satisfactory set of definitions to describe detector sensitivities is to be found in a paper by Young[16]. Young defined the sensitivity S, of a detector, as the ratio of the change in response R, to the corresponding change in the quantity measured, Q.

i.e., $$S = \frac{\Delta R}{\Delta Q} \qquad 2.5$$

where R is measuredin mV, Q is measured in mM ml^{-1}, therefore S is in ml mV mM^{-1}.

For a detector whose response is not linear with concentration, sensitivity will vary with the amount measured. A new term was introduced which is self descriptive. The term is the limit of detection Q_o, and can be regarded as a quantitative measure of the vague term "sensitivity" referred to in many early papers on detectors[17]. The limit of detection is the smallest amount of the quantity measured which can be detected with a specified degree of certainty. The

uncertainty is regarded as the noise level, R_n (peak to peak). The signal to noise ratio (minimum) is two, thus:

$$S = \frac{2R_n}{Q_o} \qquad 2.6$$

i.e. the limit of detection:

$$Q_o = \frac{2R_n}{S} \qquad 2.7$$

A graph of Q against R, has a slope S. If S is known, then Q_o can be calculated if R_n is estimated. The noise level may be measured directly from the chromatogram, ~~and is expressed in millivolts~~. Although the relationship only holds when R is a linear function of Q, a reasonable estimate of the limit of detection can be obtained for most detectors, provided that S is measured near the limit of detection. In addition there is an uncertainty in estimating R_n, and hence Q_o. Details of estimating the noise level by a statistical method have been published[18], but the simple graphical method mentioned above is quite satisfactory to give reasonable values for Q_o. Q_o values describe an actual situation, and take into account noise levels, whereas S is an unrealistic term and may lead to erroneous conclusions. For example a comparison of the sensitivities of a thermal conductivity cell[14] and a cross-section detector[13] gives values of S of 4×10^4 and 5.5×10^4 respectively, but identical values for Q_o, since the noise level of the cross-section detector is higher than that of the katharometer. Expression 2.5 is very similar to the definition of sensitivity given by Dimbat (expression 2.2), and can be rearranged so that values of S can be obtained directly from chromatograms. The Dimbat expression 2.2 can be written:

$$S_w = \frac{PF}{W} \quad \text{ml mV mg}^{-1} \qquad 2.8$$

The concentration units are not particularly convenient, although values of S_w are within an order of magnitude of sensitivities quoted in

volume/volume units.

The Young expressions 2.5 and 2.7 can be written:

$$S = \frac{PF}{M} \text{ ml mV mM}^{-1} \qquad 2.9$$

and

$$Q_o = \frac{2R_n\ M}{PF} \text{ mM ml}^{-1} \qquad 2.10$$

where P = peak area mV min

F = flow rate ml min^{-1}

W = weight of component mg

M = amount of component mM.

Concentration measured in millimoles per millilitre is more useful, and is about twenty times the V/V ratio under normal working conditions. It follows from equations 2.8 and 2.9 that the limit of detection can be expressed in terms of milligrams per millilitre (Q_o^W) or millimole per millilitre (Q_o).

The pQ_o value was introduced, the definition of which is analogous to the definition of pH:

$$pQ_o = \log_{10} \frac{1}{Q_o} \qquad 2.11$$

The recommendations of Young go a long way toward standardising the methods of detector comparisons. It is however necessary to standardise the conditions under which the measurements are made. This can be achieved by operating with a chromatographic column under standard conditions, or preferably using an empty column, and specifying the following variables:

flow rate, temperature and nature of the carrier gas,

the type and quantity of sample, and the manner of injection,

the dimensions of the empty column.

For the purposes of the calculation of Q_o values, the detector should be taken to include the associated amplifier, where appropriate.

It was recognised that there are two extreme types of differential detector[19]:

(i) a detector in which the response is proportional to a change in the concentration of the material eluted in the carrier gas.

(ii) a detector whose response is proportional to the rate of entry of the sample into the detector.

The former type is represented by an ideal katharometer, and the latter by a flame ionisation detector. Purnell proposes that the definition of sensitivity given by Young (equation 219) is to be used for concentration sensitive detectors. This represents a recorder response (peak height) per unit concentration of sample in the carrier gas at the detector. This is most suitable, since for an ideal katharometer, for a fixed sample size of material eluted from a column, at various different flow rates, the peak height would remain constant. Purnell extended the proposals of Young, and expresses sensitivity solely in terms of moles:

$$S_m = \frac{P\ F_m}{M} \qquad 2.12 \qquad \text{and hence} \qquad Q_o^{\ m} = \frac{2R_n M}{F_m P} \qquad 2.13$$

where P = peak area mV min (quoted as mV mM by Purnell[19])

F_m = flow rate mM min^{-1}

S_m = sensitivity mV

i.e. S_m is the sensitivity in terms of moles/mole, (i.e. V/V).

It is however simpler to calculate S_m using the equation:

$$S_m = \frac{PF}{M_1} \qquad 2.14$$

where M_1 is the gaseous volume of the sample at the temperature and pressure at which the flow rate is measured.

For detectors sensitive to the rate of entry of sample, Onkiehong[20] proposed the expression:

$$S_q = \frac{P_q}{W} \qquad 2.15$$

where P_q = peak area μA sec.

Again, after Young it is preferable to write:

$$S_q = \frac{P_q}{M} \qquad \text{and} \qquad Q_o{}^q = \frac{2R_n^q M}{P_q} \qquad 2.16$$

S_c is thus the electrical response of the detector in microcoulombs per millimole of eluted material. This definition has the added attraction that for an ionisation device $S_q/96.5$ gives the apparent ionisation efficiency of the process occuring in the detector[21]. However Q_o^q, the minimum detectable rate of entry of a component into the detector is not easy to envisage in practical terms and Condon[22] proposed that Q_o (equation 2.10) should be used, even though it may seem to be inappropriate.

It is not essential, indeed it is not always possible to quote precise figures for the limits of detection. Usually all that is required is the order of the detection limit of one detector, compared to that for another detector, under specified operating conditions.

It is particularly useful to know the smallest amount of a component which can be detected, in the analysis of trace impurities in a mixture. It can often arise that the limit of detection of a particular detector is above that of the highest acceptable concentration of an impurity. A knowledge of detection limits is thus required. It is also useful to know detection limit values when analysing materials which are difficult to separate. Since column performance approaches ideality at an infinitely small sample size, the greatest chance of successfully separating materials is when very small charges are used. It is worth noting that, irrespective of the method used to describe sensitivity, it is the peak height which limits measurement. It is of no value to obtain a large peak area, with a negligible peak height. The limits of detection for a number of detectors are given in Chapter 3.

The upper limit of detection is a value not found in the literature, but which under some circumstances it would be helpful to know. It is proposed that the upper limit of detection Q_∞, be defined as the largest quantity of sample which can be detected before detector overload (not column overload) occurs. Detector overload is readily observable in the form of distorted peaks (to be distinguished from distortions caused by adsorption within the column, too low an operating temperature etc.). For example an overloaded β-ray Argon ionisation detector will give a split peak for a single component (figure 21). The sensitivity at which overload just occurs is:

$$S = \frac{R_{max}}{Q_\infty} \qquad 2.17$$

i.e.
$$Q_\infty = \frac{R_{max}}{S} \qquad 2.18$$

with units as in equations 2.10, 2.13 or 2.16 as appropriate. R_{max} is measured in millivolts and is the point at which anomalous response begins. It could arise, through lack of recognition of the symptoms, that an operator could attempt to resolve a split peak, which was the result of detector overloading.

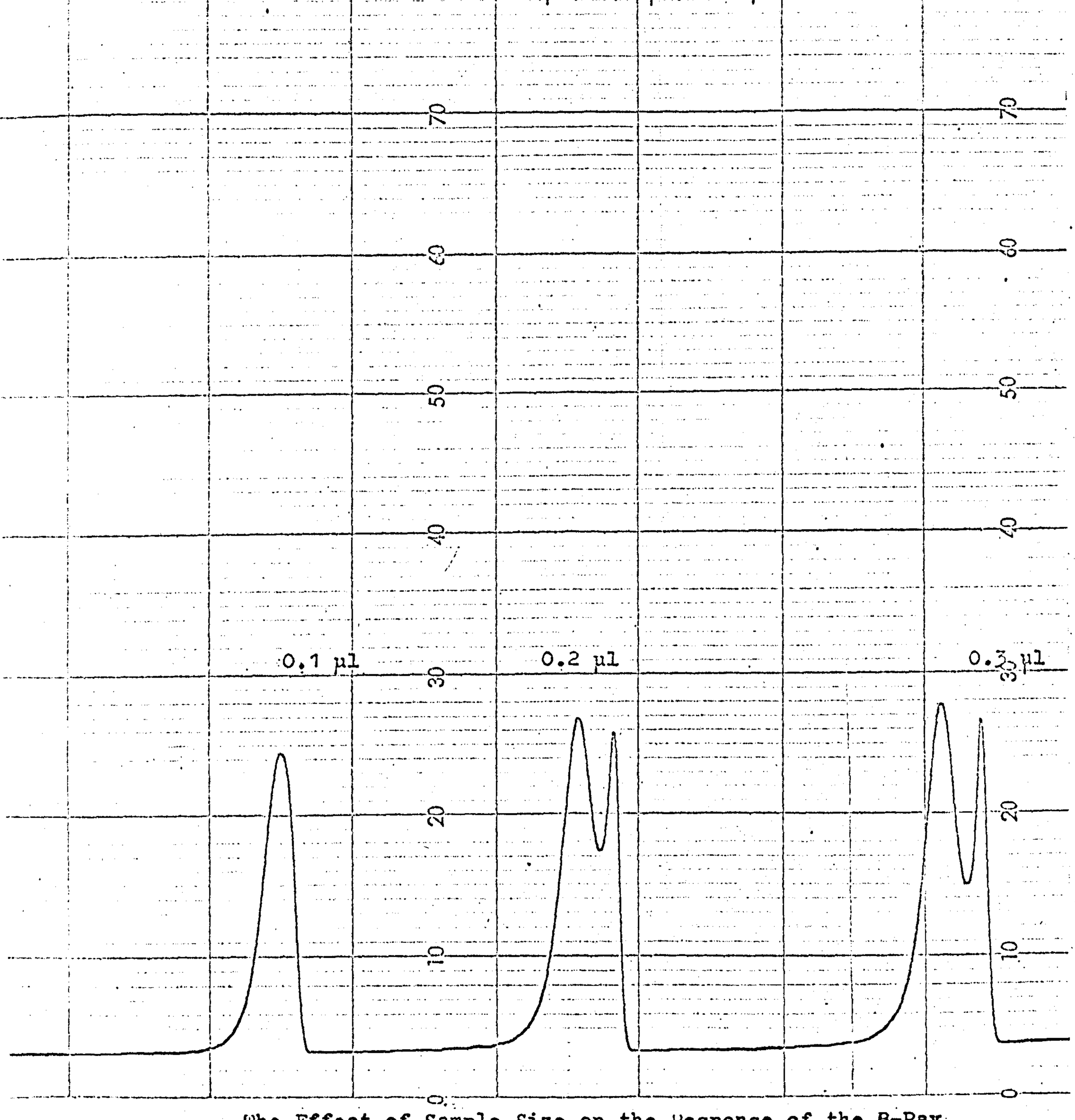
An alternative definition of overloading has been proposed[23], in which the detector is said to be overloaded at the point where the response ceases to be linear with respect to concentration. The definition is misleading in that it implies that a detector has no useful working range beyond its linear dynamic range. In many instances the useful working range of a detector is several orders of magnitude greater than the linear dynamic range.

The analysis of trace components and major components in the same mixture will frequently require a knowledge, both of the lower limit of detection and the upper limit of detection. The dynamic range of a detector may be defined as:

$$Q_\infty - Q_o \qquad 2.19$$

Figure 2.1

Apparatus	Pye Argon
Column	4' x 4 mm 60-80 Celite 20% Car. 6000
Flow rate	21 ml/min.
Carrier gas	Argon.
Chart Speed	12"/h.
Temp.	96°C.
Voltage	1 KV
Attn.	x 10.
Sample	0.1 µl, 0.2 µl, 0.3 µl acetone.



The Effect of Sample Size on the Response of the β-Ray Ionisation Detector (see page 28).

This must be distinguished from the linear dynamic range, which is the range over which the detector will give a linear response (for a given species). The linear dynamic range is usually very much smaller than the dynamic range, except in the case of an ideal detector, when the two values are equal.

Experimental determination of the limits of detection, and the dynamic ranges are carried out using the various techniques described under detector calibration.

On the basis of the above discussion, it is proposed that the following numerical description be given for each detector:

(i) the upper and lower limits of detection,

(ii) the dynamic and linear dynamic ranges,

(iii) the baseline drift,

(iv) the conditions under which (i) - (iii) were measured.

2.2d Response Time.

There are a number of other factors which must be considered. A detector should have a rapid response time[15]. Three factors contribute to the overall response time of a detector:

(i) the speed of response of the sensing element, or the process involved.

For example the changes in temperature of a katharometer filament are relatively slow compared with ionisation processes.

(ii) The detector volume.

(iii) The time constants of the associated equipment (e.g. recorder).

The speed of response of a detector can limit the resolution observed. A detector of response time 5 seconds, will not be able to distinguish between two adjacent components which have relative retention times of less than 5 seconds, even though the column itself may be capable of resolving the components. For excessively long speeds of

response, peak distortion occurs, and although the total area under the peak is not affected, it is difficult to obtain an accurate assessment of the peak area.

In the case of a detector of instantaneous response, it is possible to increase the limit of detection by suppressing the noise electrically. This will increase the response time (iii), but providedit is still small (<1 sec.) this is of little consequence.

Loss of resolution of separated components can occur within a detector if the detector volume is excessive (several cc's)[19] and distortion of peaks will occur. In addition, if the volume of the detector is greater than the volume of the peak, the detector cannot measure accurately the true differential response (i.e. the rate of change of concentration) and serious errors in analysis may result. The effects of detector volume on peak symmetry and retention volume have been considered mathematically by Johnson and Stross[24].

With commercial gas chromatographic apparatus the time constant of the associated electrical equipment is usually negligible, except for the potentiometric recorder, whose response is in general of the order of 1 second for full scale deflection. For the majority of applications this is satisfactory, but for high speed analysis using capillary columns it may be necessary to use an oscilloscope in place of the recorder[25]. In the case of high sensitivity detectors of high impedence, particularly the flame ionisation detector, even small stray capacitances can give rise to a significant increase in the overall response time. For example the presence of a capacitance of 100pF, will result in a time constant of 1 second, for a system of resistance about 10^{10} ohms.

Experimental methods of determining the speed of response of a detector are described by several authors[12, 26, 29]. Schmauch defines

response time, r_t, as the time required to introduce the gas into the measuring region (r) and the time required by the measuring transducer to reach a new equilibrium (r_a),

i.e. $$r_t = r + r_a \qquad 2.20$$

Usually $r \gg r_a$.

Only r_a is independant of the carrier gas flow rate.

The time taken for the introduction of the gas into the measuring region will depend on the construction of the detector, and on whether the gas enters by diffusion or direct flow (cf katharometer designs described in Chapter 3). Expressions are derived to describe the two means of flow, but these only represent extreme cases since in most detectors diffusion and direct flow must both contribute. For pure diffusion the concentration of the compound (C_m) in the measuring region is given by:

$$C_m = e^{-t/r} \int \frac{e^{t/r}}{r} C_o dt \qquad 2.21$$

where C_o = concentration of the compound at the opening of the diffusion channel,

t = time between introduction and measurement,

r = response time.

r will depend on the volume of the measuring region, the diameter and length of the diffusion channel, and the diffusion constants of the gas and sample. To determine the response time, an instantaneous change in the concentration of the component is applied to the detector:

$$C_m = C_o (1-e^{-t/r}) \qquad 2.22$$

and $r = t$ when $C_m = 0.632 C_o$

Hence r is calculated from the resulting chromatogram.

For direct flow:

$$C_m = \frac{C_o F}{V_d} .t \qquad 2.23$$

where F = carrier gas flow rate - ml min^{-1}, V_d = detector volume ml.

The experimental procedure is simple, and a procedure based on that described by Schmauch[12] has been used by the Author (see Chapter 6). The paper also described the effect of response time on peak geometry and position.

The method of measuring response time adopted by King[26] is based on the assumption that for a detector of zero response time the ratio peak area/retention time, is constant. By plotting a graph of this ratio as ordinate against residence time of the sample in the detector, for a practical detector, a curve is obtained. The residence time is:

$$t_d = \frac{V_d}{F} \qquad 2.24$$

The ratio, peak area/retention time will reach a maximum. At this point the residence time is equivalent to the response time, i.e.:

$$t_d = r \qquad 2.25$$

Purnell[19] gives the expression for the response time of a direct flow detector as:

$$r = \frac{V_d}{F} \qquad 2.26$$

which is of course readily obtainable from 2.23 and 2.24. No experimental procedure is given. Note that although the expressions 2.21, 2.22 and 2.26 do not include the contribution r_a, the response time which is measured experimentally will include this contribution, if the Schmauch procedure is adopted. The terms "measuring region volume" and "detector volume" are not necessarily synonymous, i.e. there is a distinction between "effective detector volume" and "geometric detector volume"[24]. An estimate of the effective detector volume can be obtained from peak widths. By injecting a sample into a short empty

column, and assuming rapid injection of a small sample size and a negligible band broadening until the detector is reached, the width of the resulting peak is governed by the effective detector volume, and the response time r. Using this procedure the contribution r_a to the total response time, is excluded. The effective detector volume, and hence r, are calculated from a knowledge of the recorder chart speed and the carrier gas flow rate (see Chapter 4).

Purnell considers, in addition to the above contributions to response, the dead volume existing between the column and the detector. However this is not strictly related to the detector performance, and can be minimised by good design. In any case, dead volume in this region will merely introduce an equal delay to all components: only in the case of fairly large dead volumes will band diffusion produce inferior results. By operating two detectors of similar volume in series, a measure of the loss of resolution occuring between the detectors can be obtained. The Author has carried out such experiments, the results of which are given in Chapter 4. The response time of a detector should be included in any table of detector characteristics.

2.2e Other Detector Characteristics.

The remaining properties of an ideal detector do not lend themselves to numerical description.

The detecting element should not be required to operate at such a temperature that pyrolysis of the detected components may occur (except with flame detectors). A system in which components never come into contact with heated filaments is to be preferred, since oxide formation on the filaments and corrosion can result in changes in the sensitivity (Young definition) of the detector during its life, thus upsetting calibration. Such a system is found in the Martin gas density balance[2]. In general a compromise must be reached. In the case of the katharometer corrosion of filaments is minimised by using

a diffusion cell (see Chapter 3), at the expense of a rapid response time.

It should be possible to automatically record the response of a detector, rather than be limited to manual plotting. This is a condition easily fulfilled in the vast majority of detecting systems.

A detector should be a simple piece of equipment, being readily constructed and requiring the minimum of maintenance. For some applications a detector is required to be robust. Ease of operation must be borne in mind, although since after initial setting up, a detector response is automatically recorded, this should present no difficulty.

The degree of control required to maintain adequate sensitivity and stability is an important factor. A detector which works perfectly satisfactorily only at a carrier gas flow rate of 100 ml $min^{-1} \pm 0.2$ ml min^{-1} is obviously very limited in applicability. A detector must be as versatile as possible, i.e. must operate over a wide range of conditions and respond to as wide a range of materials as possible.

Of great importance, at least from the non-scientific aspect, is the cost of the detecting system: this must include not only the detecting element itself, but in addition the associated amplifier, control unit and recorder. It does not follow that cost is directly related to the "degree of ideality" of a detector.

James[27] has proposed that a detector should respond not only to the instantaneous concentration, but at the same time to the total mass eluted, since integration, either geometrically or electrically, of a differential signal lends to inaccuracies (see Chapter 1). It is difficult to envisage such a detector: the nearest approach to this ideal is to operate two detectors in series, one having a differential response, and the other an integral response. Such a system has been used by the Author, and is discussed in the following chapters. The

relative advantages of detectors giving differential and integral response are listed below.

Differential Response: the component band centre (peak maximum) is readily detected. This is particularly important for the determination of retention data[28]. Partially resolved peaks and very small peaks are more readily observable.

Integral Response: the need for integration procedures is eliminated and quantitative estimation only involves step height measurements. It is more precise, easier, and less time consuming to measure step heights (see Chapter 7). Quantitative estimation is not difficult with distorted bands. ("Band" signifies the actual component profile, whereas "peak" and "step" describe the detector output profile).

The advantages of a differential detector indicate that it is more suitable for qualitative analysis, whereas the integral detector is far superior for quantitative analysis. Two detectors in series thus give the advantages of both types of detector, and do not give rise to any additional disadvantages.

Proposals are put forward for the qualitative description of detectors, listed in order of importance. In addition to the numerical description of a detector, given in sections 2.2c and 2.2d qualitative description is necessary. The extent to which a practical detector fulfils the function of an ideal detector is described in the following terms:

(i) versatility,

(ii) insensitivity to random changes in operating conditions,

(iii) ease of construction and operation,

(iv) cost,

(v) robustness.

2.3 Conclusions.

The most important characteristic of a detector suitable for quantitative analysis is that it must have a response which is predictable for all chemical species, and which varies linearly with sample size. Detectors with responses specific to certain chemical types can be useful in specialised fields.

Detector sensitivity is most satisfactorily described in terms of the system proposed by Young[16]. It is helpful to quote both the upper and lower limits of detection, and the linear dynamic range.

A detector must have a rapid response time and a small effective volume to minimise resolution losses and peak distortion.

An integral detector is the more satisfactory for quantitative analysis.

2.4 List of Symbols.

Symbol	Significance	Units
a	response factor	
A	peak area	cm^2
C	fraction of component	-
C_m	component concentration in measuring region	-
C_o	initial component concentration	as C_m
F	flow rate of carrier gas	ml min^{-1}
F_m	" " " " "	mM min^{-1}
M	amount of component	mM
M_l	" " "	ml
P	peak area	mV min
P_q	" "	µA sec
Q	quantity measured	mM ml^{-1}
Q_{o_m}	lower limit of detection	mM ml^{-1}
Q_o	" " " "	(moles/mole)
$Q_o{}^q$	" " " "	mM sec^{-1}
$Q_o{}^w$	" " " "	mg ml^{-1}
Q_∞	upper limit of detection	as Q_o's
r	sample introduction time	sec
r_a	response time of transducer	sec
r_t	response time of detector	sec
R	response	mV
R_{max}	onset of anomalous response	mV
R_n'	noise	mV(or µV)

Symbol	Significance	Units
R_n^c	noise	μA
S	sensitivity	$ml mV mM^{-1}$
S_1	"	μg
S_2	"	$\mu g\ ml^{-1}$
S_m	"	mV
S_q	"	$\mu A\ sec\ mM^{-1}$
S_r	recorder sensitivity	$mV\ cm^{-1}$
S_w	sensitivity	$ml mV mg^{-1}$
t	time lag introduction-measurement	sec
t_d	residence time	sec
$T_.$	chart speed	$cm\ min^{-1}$
V_d	detector volume	ml
W	weight of component	mg

2.5 References.

1. McWilliam, I.G., Dewar, R.A., Gas Chromatography 142 1958.
2. Martin, A.J.P., James, A.T., Biochem. J. 63 138 1956.
3. Bevan, S.C., Thorburn, S., J. Chromatog. 11 301 1963.
4. Desty, D.H., et al., Gas Chromatography 46 1960.
5. Swoboda, P.A.T., Burnett, M.G., Anal. Chem. 34 1162 1962.
6. Lovelock, J.E., Gas Chromatography 26 1960.
   Williams, H.P., Winefordner, J.D., J. Gas Chrom. 4 271 1966.
7. Krugers, J., Philips Research Report Supplement No. 1 70 1965.
8. Fowlis, I.A., Scott, R.P.W., J. Chromatog. 11 1 1963.
9. Gregory, N.L., J. Chromatog. 13 33 1964.
10. Krugers, J., Philips Research Report Supplement No. 1 83 1965.
11. Lovelock, J.E., Lipsky, S.R., J. Amer. Chem. Soc. 82 431 1960.
    Oaks, D.M., et al., Anal. Chem. 36 1560 1964.
12. Schmauch, L.J., Anal. Chem. 31 225 1956.
13. Boer, H., Vapour Phase Chromatography 169 1956.
14. Dimbat, M., et al. Anal. Chem. 28 290 1956.
15. McWilliam, I.G., J. App. Chem. 379 1959.
16. Young, I.G., 2nd International Gas Chromatography Symposium, ISA, 75 1959.
17. e.g. Scott, R.P.W., Nature 176 793 1955.
18. Johnson, H.W., Stross, F.H., Anal. Chem. 31 1206 1959.
    Johnson, H.W., Anal. Chem. 37 1582 1965.
19. Purnell, J.H., Gas Chromatography 320, published by John Wiley 1962
    Halasz, I., Anal. Chem. 36 1428 1964.
20. Onkiehong, L., Gas Chromatography 7 1960.
21. Lovelock, J.E., Anal. Chem. 33 167 1961.
22. Condon, R.D., et al. Gas Chromatography 30 1960.
23. Krugers, J., Philips Research Report Supplement No. 1 54 1965.
24. Johnson, H.W., Stross, F.H., Anal. Chem. 31 357 1959.
25. Scott, R.P.W., Nature 185 312 1960.
26. King, W.H., Anal. Chem. 36 1735 1964.

27. James, A.T., Vapour Phase Chromatography 127 1956.

28. Ettre, L.S., Anal. Chem. 36 31A 1964.
Gas Chromatography 348 1964.

29. Kieselbach, R., Anal. Chem. 35 1342 1963.

CHAPTER 3.

Detectors for Gas Chromatography.

Introduction.

The literature contains a vast number of references to detection systems. The majority of detectors never gain widespread acceptance, usually due to a failure to satisfy even a few of the requirements discussed in Chapter 2. In some instances, however, the failure of a detector to gain popularity is less readily explained. For each detector described below the principle of operation is given and reference is made to any papers giving constructional details. The response characteristics are critically discussed, and finally the value of the detector as a quantitative instrument is assessed. The two commonly used detectors, namely the katharometer and the flame ionisation detector , are described first, and these are followed by a number of flame detectors in which different modes of detection are employed. There are a number of detectors based on radiological ionisation, and each of these is discussed. Discharge detectors are mentioned, although they are little used. Detectors based on the measurement of density and volume changes are important from the quantitative aspect, and these are discussed in detail. These are followed by a number of detectors, which although not in common use have been the subject of study by some workers. The value of auxiliary detection techniques is summarised.

3.1 Katharometer Detectors.

The katharometer is one of the most widely used of all detectors, and at the same time satisfies the least number of criteria for a good detector. It was first used in gas chromatography by Ray[1] and Griffiths[2].

The response of an ideal katharometer depends on the difference in thermal conductivity between the pure carrier gas and the eluted components in the gas stream. In the basic katharometer a heated wire

is placed along the path of the carrier gas. Under constant conditions of flow rate and temperature, the resistance of the heated wire will remain constant. In the presence of a component, there is a change in the thermal conductivity of the atmosphere surrounding the heated coil and the temperature of the coil, and hence its resistance will change. In general the thermal conductivities of organic vapours are lower than those of the permanent gases so that a temperature increase occurs, and hence the resistance of the wire decreases. The thermal conductivities of a number of organic compounds have been published[3]. If the wire forms one arm of a Wheatstone bridge, balanced when pure carrier gas flows, the amount of unbalance, in the presence of a component, can be used as a measure of the amount of component present. For an ideal gas mixture, thermal conductivities (k) should be additive[4]:

$$k_{net} = x_1 k_1 + x_2 k_2 \qquad 3.1$$

x_1 = mole fraction of solvent of thermal conductivity k_1

x_2 = mole fraction of solute of thermal conductivity k_2

The change in thermal conductivity is given by:

$$\Delta k = k_1 - k_{net} \qquad 3.2$$

i.e.:

$$\Delta k = x_2(k_1 - k_2) \qquad 3.3$$

Thus by measuring the change Δk, the amount of component present on a molar basis can be found. However, expressions derived from the kinetic theory by Hoffmann[5] do not predict simple additivity of the thermal conductivities of the components of a mixture. The different molecules in a gas mixture will have different cross-sections, and hence the mean free path lengths will be different. Equation 3.1 is rewritten:

$$k = \frac{k_1 K_1'}{K_1} + \frac{k_2 K_2'}{K_2} \qquad 3.4$$

where the ratio $\frac{K'}{K}$ represent mean free path changes of components in the pure states and in mixtures. Thermal conductivities are only additive

when the sample and carrier gas are matched with respect to mass, collision diameter, intermolecular force constants etc.[6].

Numerous attempts have been made to correlate theoretical and experimental katharometer responses. Using a carrier gas such as nitrogen, which has a low thermal conductivity (i.e. the same order as organic materials), the response for different species, even at similar molar concentrations cannot be predicted[5, 7-9]. However, by using a carrier gas of high thermal conductivity, such as helium or hydrogen, the response of many organic compounds is found to be similar at similar concentrations. Using helium the theoretical responses of the katharometer to a number of organic compounds have been calculated, using equation 3.3 and compared with experimental values[10]. The majority of theoretical values were about 11% below the experimental values. Better agreement was obtained[10, 11] by basing the responses on a weight basis rather than a mole basis. Despite the lack of general agreement, it has been shown that for a limited number of homologous series, the katharometer response per mole of solute, relative to benzene (R_B), can be represented by the equation[10, 12]:

$$R_B = X_1 + X_2M \qquad 3.5$$

where M = molecular weight of carrier gas (helium)

X_1, X_2 are empirical constants for the homologous series.

The equation was found to be satisfactory over a wide temperature range (30°C to 160°C), over a ten fold concentration change, and for a wide helium flow rate range.

Schmauch and Dinerstein[9] considered the response of a katharometer to be the product of two factors, the cell factor, which depends on the operating conditions, and the thermal conductivity factor. Using helium, response is approximately linear for many compounds, and at any given temperature only a single response factor is required for each material. However, using nitrogen, complete calibration is required. The effect of changing operating parameters on detector response is discussed in detail[9, 16]. Hoffmann[5] has developed

equations to predict molar response factors. The results are in excellent agreement with experimental values for a variety of organic compounds, when helium or hydrogen is employed. The equations do not satisfactorily predict response factors when nitrogen is used. Theoretical response factors have been published by several other workers[13,14].

For semi-quantitative work, response factors based on very simple relationships are sometimes satisfactory. For example, using helium, Eastman[15] found a direct relationship between response and (molecular weight)$^{\frac{1}{2}}$ of the sample. Even using nitrogen, the expression is satisfactory for a few homologous series. In addition, compounds with similar structure and similar composition give similar response factors. Again, using helium it has been demonstrated experimentally that semi-quantitative results are obtained by calculating the percentage weights of the components of a mixture directly from the percentage areas of the peaks. The theoretical basis of this relationship has been discussed[17]. Using simple thermal conductivity corrections for response, the quantitative analysis of water-alcohol, and other simple solvent mixtures, has been successfully carried out, with helium as carrier gas[18]. Experimentally determined response factors for hydrocarbons in helium, have been published[19].

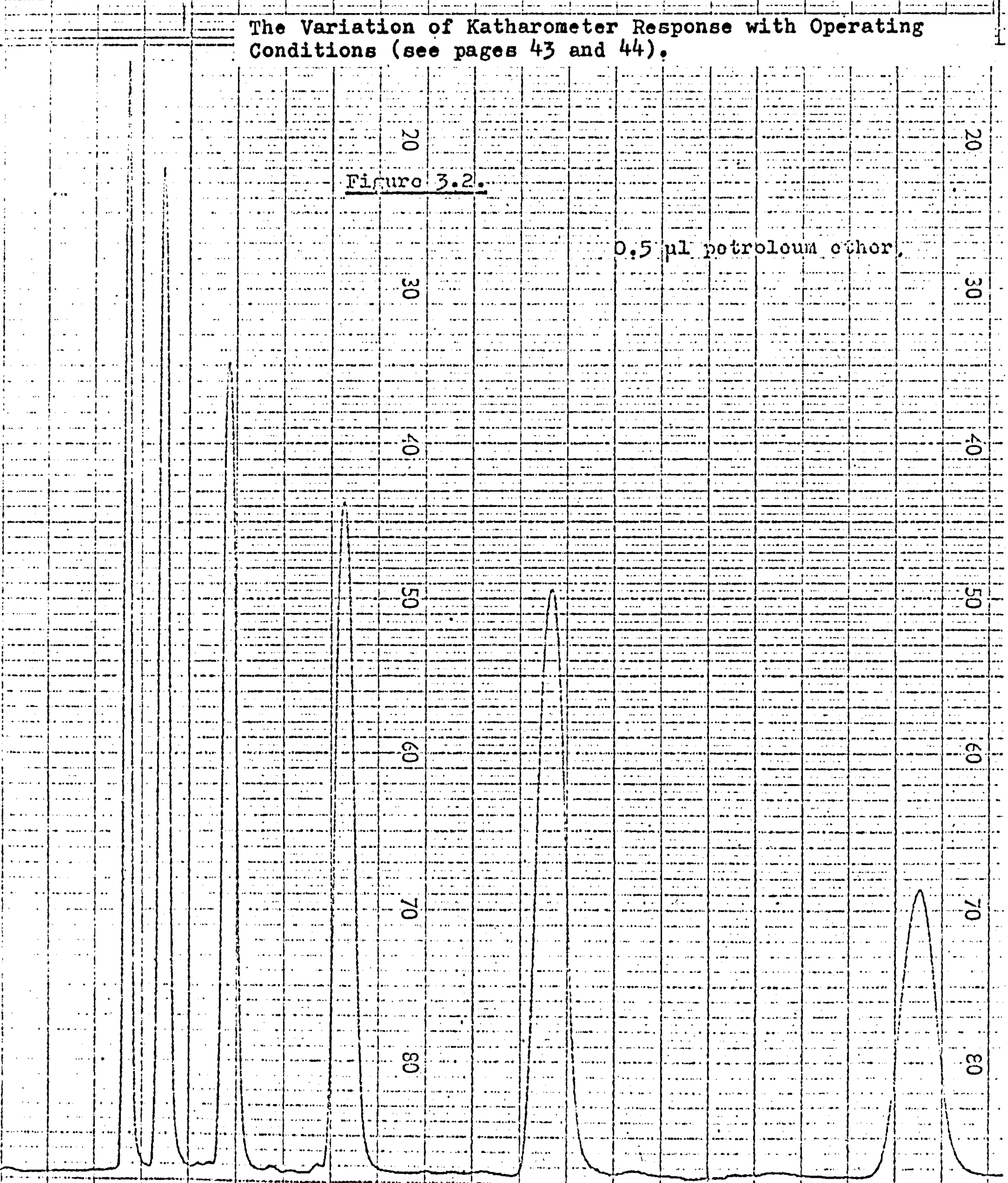
In an attempt to obtain predictable response factors on the basis of equation 3.1 Jordan et al[6] have proposed the use of mixed carrier gases such that their molecular properties match those of the components. Quantitative determinations of carbon dioxide have successfully been carried out using a mixture of helium and nitrogen as the carrier gas. Obviously such a method cannot be adopted for the analysis of complex organic mixtures.

It is clear that the response of the katharometer using nitrogen as carrier gas, is unpredictable. Under certain conditions distorted, split or negative peaks are obtained (see figure 3.1). Such effects

were first reported in 1956[20-22]. Peak inversions are most readily observed at high flow rates,[23] and are therefore probably not caused by decomposition of material on the hot wire, but by changes in the slope of thermal conductivity isotherms of the different components of a mixture[24]. This view has been substantiated by several other workers[7, 21, 25]. However this explanation is open to critisism in that peak inversions only occur in carrier gases of low thermal conductivity, whereas changes in the slope of thermal conductivity isotherms would be expected to occur with all carrier gases. In addition the detailed mechanism of peak splitting as sample size increases cannot be explained on the above basis. A comprehensive study of peak inversion effects has been carried out by Bohemen and Purnell[23], in an attempt to find a more satisfactory explanation. Inversion temperatures were found to be very dependent on flow rate, but thermal conductivity is essentially pressure and flow rate independent, thus ruling out previous explanations. The response of the katharometer depends upon the differences between the thermal conductivities and heat capacities of the solute and solvent. With nitrogen as carrier gas, these two terms are often of opposite sign, so that by changing the flow rate it is possible for either the thermal conductivity or heat capacity contribution to predominate, i.e. a positive or negative peak can be formed, and peak inversion will occur when convection and conduction are of a similar magnitude. On this basis conditions were predicted to avoid peak distortions, and these were found to be substantially correct. In general, peak distortion can be avoided by decreasing the carrier gas flow rate, and by decreasing the filament temperature. The effects of changing these parameters are illustrated in figure 3.2.

Since response factors using nitrogen as carrier gas, are so dependent on the precise experimental conditions employed, values taken from the literature must be used with caution. The only comprehensive set of response factors to be published, are those determined by Jamieson[26].

Figure 3.1.



The Variation of Katharometer Response with Operating Conditions (see pages 43 and 44).

Figure 3.2.

Katharometer design has received much attention. The simplest form of Wheatstone bridge for a katharometer consists of three external resistors, with the heated filament within the detector block. Small external temperature fluctuations will upset the bridge balance and give rise to an unstable baseline. By incorporating one other arm of the bridge in a flow of pure reference gas, adjacent to the katharometer filament proper, temperature fluctuations are minimised. The reference supply must be operated under the same conditions of temperature, pressure and flow rate, as the analytical supply. An extension of this arrangement is to incorporate all the arms of the Wheatstone bridge within the detector block, thus ensuring greater thermal stability. In addition, by incorporating opposite pairs of filaments in each gas stream, sensitivity is increased two-fold, since a change in the gas composition will upset both sides of the Wheatstone bridge, and in opposite directions. The effect of bridge current on katharometer response has been studied[9, 22]. Details of katharometer design form the subject of many papers[20,21], and a comparison between the response times of detectors of different geometry has been made by Schmauch[25]. The direct flow katharometer has a fairly rapid response time (about $\frac{1}{2}$ sec.) but is very sensitive to small flow rate fluctuations. The latter can be minimised, at the expense of a rapid response, by relying on diffusion of the components to the heated filament. When diffusion is the sole means by which components reach the filament, response times become excessively long, resulting in anomalous responses, as discussed in Chapter 2. As a compromise, the semi-diffusion pattern is generally accepted. The choice of detecting elements lies between thermistors and heated metal filaments or coils. Metal filaments are usually of platinum or tungsten. Tungsten is usually fitted to commercial katharometers. For the analysis of corrosive materials, nickel has been used[27]. Thermistors are normally operatedonly a few degrees above that of the detector cell itself, but suffer from the

disadvantage that it is difficult to obtain a pair of thermistors exactly matched for resistance, and temperature dependence of resistance. In contrast the matching of metal filaments is a simple matter. Thermistors were first used in katharometers at the National Chemical Laboratory[28], and a comprehensive study has been carried out by Cowan and Stirling[29]. The general conclusions are that thermistor katharometers should be left running permanently to minimise noise, and that in general they are no more sensitive than a good hot wire katharometer. They are however particularly useful in analyses where thermal decomposition of materials is likely to occur on a hot filament. Constructional details of a thermistor katharometer have been published[30].

The design of katharometers for operation at high temperatures (400°C) has been undertaken by several workers[31,32].

In general the detector volumes of katharometers are of the order of 2 ml., and hence for high resolution, and for use in conjunction with capillary columns, they are unsatisfactory. Micro-volume katharometers (as small as 3 μl) have been described[32-34] and are available commercially[35].

There have been several works reviewing the design and characteristics of katharometers, of which the most recent is that by Lawson and Miller[36].

A katharometer can detect all organic materials and the permanent gases. It is very sensitive to flow rate and temperature changes. The detector requires skill to construct, but its operation is simple. The detector is robust, readily commercially available, and is not expensive. The hote wire filament detector is satisfactory for qualitative analysis, provided that the materials under analysis do not corrode, or decompose on the filaments, and a rapid response time is not required. The detector may be used for quantitative work with helium as carrier gas, provided that calibration is carried out for each material under the conditions for analysis. The use of nitrogen as a carrier gas for quantitative analysis is not recommended, since

extensive calibration for each material at all concentrations is required, and anomalous response is often observed. The calculation of response factors on a theoretical basis is partially successful, provided helium or hydrogen is used as the carrier gas, but is unsatisfactory for nitrogen. The calculation of response factors demands a knowledge of the qualitative nature of the material, and frequently a knowledge of several physical constants as well.

The detector has little to recommend its adoption for quantitative work, particularly in Great Britain, where helium is extremely expensive.

3.1.1 Katharometer Performance.

Type of Katharometer	Cell Volume ml	Response Time sec.	Limit of Detection $mMml^{-1}$	Compound	Ref.
Hot wire			5×10^{-7}		11a
Hot wire - diffusion		12		Cyclohexane	25
Hot wire - semi diffusion		11		"	25
Hote wire - semi direct flow	3	2		"	25
Hot wire - semi direct flow	0.6	<1		"	25
Thermistor			8×10^{-7}		36
Hot wire - micro	0.04	0.07	5×10^{-7}	Ether	34
Hot wire - 4 filament semi-diffusion		30	8×10^{-8}	Heptane	Chapter 6
Hot wire - micro	0.003		10^{-6}	Propane	Chapter 6

3.2 Flame Ionisation Detectors.

Thermal ionisation of organic materials by a flame forms the basis of operation of the flame ionisation detector. The carrier gas from a chromatographic column is mixed with a hydrogen-oxygen supply at the column exit and is burnt at a jet. The jet forms one of an electrode pair. The other electrode is placed vertically above the flame. The electrical resistance along the length of the flame is continuously monitored. The introduction of an organic vapour into the flame greatly

increases the concentration of ions present, resulting in a decrease in the resistance of the flame. The use of such a system for gas chromatographic detection was proposed by McWilliam and Dewar in 1958[37]. Such was the simplicity and elegance of this device that it aroused considerable interest, and detailed studies were undertaken by several workers[38-41]. The mechanism of the ionisation processes occuring in the flame is not straightforward, and has been studied by several workers[42,43], most recently by Krugers[41]. The various parameters which affect the detector performance have been studied[39,45], particularly by Onkiehong[38] and McWilliam[47]. In general it is agreed that operating the electrodes at a potential difference of about 200 volts,[39] will ensure that the detector response is independent of the exact voltage, and of the electrode spacing. Electrode spacings are of the order of 1 cm. Up to about 180 volts, the linear dynamic range is a function of the applied voltage, and at any given voltage is greater if the jet is made the cathode[51], although this conflicts with earlier observations[46]. The electrode shape is not critical, but it has been demonstrated that greater sensitivity and stability are obtained if the upper electrode is the anode.

The effects of changing detector geometry on response have been studied in more detail, in an attempt to improve the overall response of the detector[41, 44, 58].

Results obtained by McWilliam[47] indicated that the response of the detector was linear with respect to concentration over a wide range, and calculable on the basis of carbon content, for many materials. It has been shown by many other workers that for a large number of substances, linearity extends over several orders of magnitude[38, 39, 48]. Indeed Purnell[49] states that the detector is linear over its whole range of operation: the detector can be calibrated with fairly large measurable quantities of material, and extropolated to zero concentration.

Details of the determination of the linear dynamic range of the detector using a logarithmic dilution technique (see Chapter 2) have been described by Scott[50]. No deviations from linearity were observed for several different species over a range of four orders of concentration A recent comprehensive study of the linear response of the detector to a variety of materials, under various operating conditions, showed that the linear dynamic range extends over at least six orders of magnitude[51]. Detector response is in many instances predictable, and empirical calibration for different materials may be avoided, provided that a response correction factor, C, is used[38]:

$$\underline{C} = \frac{M_x}{12C_x} \qquad 3.6$$

where M_x = molecular weight of component x, containing C carbon atoms, i.e. the response should be predictable on the basis of the amount of carbon present, and not on the total amount of material. This equation was found to work satisfactorily for simple hydrocarbons[52, 54, 57], and several other species[52-58] but gives less satisfactory results for oxygenated compounds[54], and in the case of halogenated materials breaks down.

The variationof calibration factors, with changes in the carrier gas, hydrogen and air flow rates has been investigated[51, 58, 59]. The lower limit of detection can be extended if great care is taken to purify the carrier gas. An improvement in sensitivity is obtained if oxygen is used for combustion in preference to air[58], and extremely pure helium or argon is used as the carrier gas[60].

The substance-specific correction factor proposed by Kaiser[61] has been used to predict detector response. The theoretical substance-specific correction factor, S_T, for a homologous series is defined as:

$$S_T = \frac{M_j \; C_s}{M_s \; C_j} \qquad 3.7$$

where M_j = molecular weight of the $_j$ th member of the series, containing C carbon atoms

M_s = molecular weight of the standard, of carbon number C_s

The experimental substance-specific correction factor S_E is:

$$S_E = \frac{1}{r_j} = \frac{M_j}{M_s R_j} \qquad 3.8$$

where r_j = relative weight response, experimentally determined,

R_j = relative molar response.

Ideally for a given compound:

$$S_T = S_E \qquad 3.9$$

This condition is found to be satisfied by many aliphatic and aromatic hydrocarbons, including some halogenated materals, but deviations are observed for other classes of compounds. However by allowing for the carbon deficiency of a compound[54], good agreement between theoretical and experimental substance-specific correction factors can be obtained. Carbon deficiency values for a number of types of compound are listed by Maggs[51]. The response factors, expressed on a weight basis, a molar basis and in terms of specific correction factors, for a number of common materials have also been published by Maggs[51].

The detector responds to all organic materials, although the sensitivity towards organo-metallic compounds is low, and decomposition of such materials in the flame leaves a metallic deposit in the detector which further suppresses sensitivity. A detector designed specifically for the detection of organosilicon materials is described below. The use of halogenated materials, will produce by pyrolysis, hydrochloric acid which results in detector corrosion. The use of solvents such as chloroform should therefore be avoided. However, Baddiel and Cullis claim that by using carbon dioxide as carrier gas, hydrochloric acid is not formed at the detector[62]. Anomalous response

effects have been reported by several workers, in particular peak splitting above a particular concentration level[47, 63].

The detector does not respond satisfactorily to water, and it has been stated by several workers, that this has no significant effect on the response of the detector to the remaining constituents of the mixture[64], unless eluted simultaneously[65]. However Foster and Murfin[66] demonstrated that the presence of moisture in a sample will suppress detector response sufficiently to invalidate response factors determined under non-aqueous conditions. The presence of moisture, derived from the carrier gas will also suppress the detector response[67], so that for reproducible results it is essential to dry the carrier gas. Water vapour is continuously produced in the detector chamber by combustion, and it is therefore essential to have sufficient ventilation and forced air to sweep out the vapour. In addition the temperature of the detector must be sufficient to prevent condensation of water vapour within the chamber. If condensed water is allowed to collect, the response is progressively suppressed and finally the flame is extinguished.

The overall performance of the flame ionisation detector is such that it approaches the performance of an ideal detector. The detector has a very low limit of detection, and is extremely stable. It has a wide linear dynamic range, and calibration at all concentrations is not necessary. Response factors, at least for simple hydrocarbons, are predictable from a knowledge of molecular weights, but for other materials it is preferable to determine experimentally the correction factors. In some instances where this is not possible, it is reasonable to calculate the detector response, on the basis of the response of a similar material. The detector has a very small dead volume, and rapid response. It is simple to construct, is robust and very cheap. The detector and associated electronic equipment can be constructed in the

laboratory[40, 68] and excellent commercial detectors are available[83]. A control unit which can give a linear, logarithmic or integral output has been described by Dewar and Maier[69]. The logarithmic output is adjusted such that no peak exceeds full scale deflection of the recorder, and at the same time, minor peaks are readily observable. The detector is "blind" to all inorganic gases. The detector totally destroys the sample under analysis, but by incorporating a stream splitting device at the column outlet, a major portion of the sample may be recovered. Sample destruction may be an advantage in the analysis of toxic materials. A disadvantage of this detector, serious in laboratories where space is limited, is that three separate gas supplies are required.

3.2a A number of modifications have been made to the basic flame ionisation detector, for the specific detection of certain elements. A detector for the qualitative and quantitative estimation of organosilicon compounds has been described by Garzo and Fritz[70]. Organic compounds are detected in the normal manner, but organosilicon compounds are detected as ~~inverted~~ split peaks (often incorrectly named inverted peaks), or negative peaks. By adding methane continuously to the carrier gas just below the jet, (i.e. by increasing the carbon content of the flame), the carbon-silicon ratio can be adjusted to give all negative peaks for silicon containing materials, and positive peaks for true organic materials. Thus a selective detector is obtained. The quantitative response of the detector can be related to the carbon-silicon ratios in the organometallic materials.

3.2b Detqils of a flame ionisation detector with an enhanced response for halogenated and phosphorus containing materials have been given by Karmen[71]. A wire gauze, treated with sodium hydroxide is placed in a hydrogen-oxygen flame. The presence of a halogen, or phosphorus increases the rate of volatilisation of sodium from the gauze, and the

metal vapour is detected by ionisation in a second flame. The detector does not respond to other materials since these are burnt in the first flame. The response of the detector is proportional to the amount of halogen present, but calibration is required. By operating the lower flame as a conventional flame ionisation detector, specific and non-specific responses are simultaneously obtained[70]. Details of the construction and performance of a combined flame ionisation detector and soidum thermionic detector have been published by Janak and Svojanovsky[72].

3.2c It was observed by Graiff[73], that, by employing a singing flame, instead of a quescent flame, in the flame ionisation detector, a two fold increase in sensitivity was obtained. Resonance was found to occur at certain gas flow rates. In a subsequent paper Graiff[74] described the operating characteristics of the detector, and proposed a mechanism to account for the enhanced response. There is probably an increase in the ion concentration orion collecting efficiency of the electrode. Since the flame is oscillating, diffusion of oxygen and components to the flame front, and removal of combustion products from the reaction zone, is encouraged. There is little quenching and heat loss, since the vibrating flame is ejected clear of the burner tip. A.C. amplification of the flame output can be used, which has the advantage over D.C. amplification that it is simpler, cheaper, and more stable. The detector is claimed to have a greater linear dynamic range and to have greater sensitivity and stability than the conventional flame ionisation detector. However subsequent workers[75] have found difficulty in producing a singing flame, and in maintaining the flame, once resonance has set in.

There are three detectors related to the flame ionisation detector, in that components emerging from the column are burnt at a jet. The mode of detection is however different.

3.3. The Flame Thermocouple Detector.

The flame thermocouple detector, introduced by Scott[76, 77] measures the change in temperature which occurs in a flame when a component is introduced at the jet. The hot junction of a thermocouple is placed slightly above the normal flame and the cold junction is placed in constant temperature surroundings. When an organic vapour enters the jet the flame lengthens and engulfs the thermocouple. The output from the thermocouple is fed directly to a suitable recorder. Although in the original work, hydrogen was used as carrier gas, improved performance is obtained if nitrogen is used, and hydrogen introduced at the column exit[38, 78, 79]. Primavesi and co-workers[80] studied the temperature contours within the flame, in order to determine the most suitable site for the thermocouple. Scott[76] showed that the response of the detector, at least for simple hydrocarbons, was directly related to the mass of material present, after a correction had been made for the heats of combustion of the components. Henderson and Knox[79] continued the investigation and obtained excellent agreement between experimentally determined relative response values, and those calculated from relative heats of combustion, for a wide range of compounds. This would suggest that provided heats of combustion are known, the detector only requires calibration with one compound, although doubt is cast on this statement by Bullock[81] and Primavesi[82]. The relationship between response factors, and heats of combustion has also been investigated by Cullis[85]. The use of oxygen for combustion is recommended[84], as this increases the linear dynamic range of the detector.

Although it is evident that the detector has many commendable features, further study of the response and linearity is necessary. The Author has measured the linearity of the detector over a limited range for a few materials, and the results are given in Chapter 6. The detector is very simple to construct, and any commercial flame

ionisation chamber may be used. No amplifying device is required and hence the detector is remarkably cheap. In common with the flame ionisation detector there is an insignificant response toward inorganic gases. The detector is not widely used, not because of any overriding disadvantage, but probably because it offers no distinct advantage over the flame ionisation detector.

3.4 Flame Photometric Detectors.

A further modification of the hydrogen flame detector was made by Grant[90]. Column effluent is combined with a stream of coal gas, and the mixture burnt at a jet. The light emitted by the flame is measured, via a reflector and condensing lens, by a photocell, and the resulting current recorded by a microammeter. The introduction of an organic vapour into the flame causes a large increase in light emission. Excellent quantitative data have been obtained with this detector, and the linear dynamic range is stated to be "good". For stable operation the device demands steady gas flow rates. A particular advantage of the detector is that although its response for the members of a particular homologous series is constant, the response between different series is in many cases quite different. Thus is offered a detector which gives characteristic responses for different chemical classes.

3.4a A simple modification, by incorporating a piece of copper wire in the flame, renders the detector specific for halogenated materials, i.e. the effluent is continuously subjected to a Beilstein test. This detector has been used successfully for qualitative work[86, 107], and the quantitative aspect has been discussed, although no experimental confirmation carried out[107].

3.4b Juvet and co-workers[91, 92] described a flame emission detector which could operate selectively or non-selectively. The detector operates selectively by examining specific emission lines, characteristic of particular functional groups or fragments. A table of response

factors relative to benzene, for two different characteristic wavelengths are given, but no attempt is made to predict response factors. Plots of molar response against carbon number for most homologous series are in general non-linear, although the linear dynamic range (for benzene) extends over three orders of magnitude. The response time is negligible, and response is virtually independent of flow rate. The detector can be made non-selective by obtaining a broad band spectrum, rather than specific emission lines. Using the non-selective mode, the lower limit of detection is increased. Constructional details of the detector are given[92]. Using a similar system Braman[93] investigated the response to various compounds at specific wavelengths and related this to the chemical structure. Using in addition a flame ionisation detector, empirical relationships between structure and the relative response ratio of the two detectors are given. The detector was found to give a non-linear response with respect to concentration for most materials although in some instances deviations from linearity were slight. Details of the design of a single detector in which both modes of detection operate, are given.

3.4c A flame photometric detector with a response specific for phosphorus and sulphur containing materials, to the exclusion of all other materials including halogens, has been developed by Brady and Chancy[94].

3.5 The Limit of Flammability Detector.

A flame detector which gives an integral response was invented by Behrendt[95]. A mixture of propane and oxygen, just below its flammability limit is fed into the column effluent and to a pilot flame. The addition of an organic material, from the column, results in a mixture above the flammability limit, an explosion occurs and a flame back flashes into the effluent gas stream. The resulting gas expansion is quantitative and by means of an electrolysis cell actuated by a relay, an exactly correct volume of oxygen is fed back into the

effluent (cf section 3.19a). Hydrogen generated is collected in a nitrometer and measured and by this means an integral response is obtained. Obvious disadvantages are the difficulties of maintaining the gas mixture just below the flammability limit and the necessity for a skilled operator.

3.5.1 Flame Detector Performance.

Type of Detector	Limit of Detection g sec^{-1}	mMml^{-1}	Linear Dynamic Range	Compound	Ref.
Flame ionisation (Section 3.2)	$3x10^{-12}$	$4x10^{-13}$	10^6	Propane	124
	$2x10^{-11}$	$2x10^{-13}$	10^6	heptane	50
	$6x10^{-11}$	$4x10^{-13}$		p-dichloro-benzene	72
	$7x10^{-11}$			di-isopropyl methyl phosphonate	72
	$1x10^{-12}$	$1x10^{-14}$	10^6	benzene	51
Flame ionisation (methane)	$1x10^{-9}$		$5x10^2$	silicon	70
Flame ionisation Na salt	$6x10^{-9}$	$4x10^{-11}$		p-dichloro-benzene	72
	$2x10^{-11}$			di-isopropyl methyl phosphomate	72
Flame thermo-couple (Section 3.3)		$4x10^{-6}$ $6x10^{-5}$	$>10^2$	benzene	152 Chapter6.
Flame emissivity (Section 3.4)	$1x10^{-5}$		10^3		41
Flame (copper wire)	$2x10^{-7}$	$6x10^{-9}$		chlorine	86
Flame photometric		$4x10^{-10}$	small	benzene	92

3.6 Radio-ionisation Detectors.

Ionisation by radiation is a process employed in several detection systems. Several different ionising reactions can be used for the measurement of concentration changes within a gas stream.

3.6a The Argon Detector.

The most popular detector of this type is the macro argon detector of Lovelock[96]. The basic detector consists of a small brass cylinder holding the ionising source (usually ^{90}Sr). The cylinder itself acts

as one electrode, and the other electrode is a length of brass rod, in the axis of the cylinder. Argon is used as the carrier gas, and on entering the ionisation chamber, the argon atoms are excited to a metastable state (of energy about 11.6 eV). On introducing any component whose ionisation potential is less than that of argon, energy transfer occurs from the metastable argon atoms, resulting in ionisation of the foreign constituents[102]. This causes an increase in the current developed across the ionisation chamber, which is amplified and recorded. The ionisation potentials of most organic compounds. **the energy of metastable argon atoms.** and several inorganic gases are lower ~~than that of argon~~. The equation relating the current increase to the concentration of the vapour in the ionisation chamber has been derived by Lovelock[96, 97]. According to this equation, at some finite concentration of organic vapour, the ionisation current will increase to infinity. This current rise is limited by placing a linearising resistor in parallel with the detector. However it has been shown that no one resistor will give more than a limited linear dynamic range, and that its presence contributes significantly to the response time of the detector[39]. To overcome these difficulties Lovelock[98, 99] modified the cell design to induce an internal positive space charge. It has been found that the detector is sensitive to some substances of ionisation potential greater than 11.6eV, contrary to expectations. This is explained by assuming that there is a small number of argon atoms or ions present in higher resonance levels.

The linearity of response of a macro argon detector has been studied by Scott and co-workers, under different conditions of applied voltage and flow rate, and for a variety of organic materials. It was concluded that the detector has a very small linear dynamic range, and that calibration for all substances at all concentration levels is necessary for accurate quantitative work[50].

Calculations of response factors for different species on the basis of collision frequencies between organic molecules and argon atoms was attempted by Lovelock[96]. From the kinetic theory the relative molar response R, is given by:

$$R = K (r_c + r_x)^2 \left[\frac{1}{M_c} + \frac{1}{M_x}\right]^{\frac{1}{2}} \qquad 3.10$$

where M_c = molecular weight of carrier gas, of radius r_c

M_x = molecular weight of organic compound, of radius r_x

K = proportionality constant.

Good agreement between calculated and experimental response factors was obtained for a number of different species of molecular weights up to about 100. Above this value there was an increasing divergence of the response factors.

The response of the detector to several classes of compounds has been published, including methyl esters[87] and steriods[88]. Complete calibration was found to be necessary, and virtually no linear response with respect to concentration was found. However, it has been shown for a variety of hydrocarbons, including aromatics and unsaturated materials, that the response for each component of a mixture, expressed as a percentage of the total, is a direct measure of the percent weight of the component, without the necessity for peak area correction factors[89].

The simple argon detector is very sensitive to most organic materials, but gives only a weak response to fluorocarbons and nitriles. It does however respond to a few inorganic gases. The detector has a rather low upper limit of detection, detector overloading resulting in peak splitting. However by using a nitrogen-argon mixture as carrier the upper limit of detection can be significantly extended[103]. The lower limit of detection is even greater than that of the flame ionisation detector, so that the detector is particularly suitable for the analysis of minor constituents, even though calibration is required. The detector does not respond to water[98], but the presence of water vapour, derived either from the carrier gas, or the sample under analysis,

seriously affects the response of detector[100]. The sensitivity is reduced, the response may become random, and recovery to normal behaviour may take several days. Sources of contamination of argon are considered by Evans and Scott[101]. It is essential to dry the carrier by passing it though a molecular sieve via metal tubing and ensure that all samples are completely free from water before analysis.

3.6b The Helium Detector.

Metastable helium atoms have a higher energy than metastable argon atoms, so that an ionisation detector using helium as carrier gas should respond to a greater variety of materials than the argon detector. Using this system detection of the permanent gases has been accomplished by several workers[104]. It is essential to use extremely pure helium, since impurities present in the helium, will themselves be ionised in the detector chamber, and give rise to a high background current. A detector in which the helium is excited by tritium has been used by Hartmann and Dimick[106]. The detector was calibrated by the logarithmic dilution technique and values for the linear dynamic range and limit of detection are quoted. The need to use extremely pure helium is stressed.

3.6c The Micro Argon Detector.

Following on from the work on the simple macro argon detector, Lovelock[105] has developed a miniature version of this device, which as the name implies has a much smaller dead volume, and hence more rapid response time. Sensitivity is significantly higher than in the macro argon detector.

3.6d The Triode Argon Detector.

A further improvement in performance is brought about by introducing a third electrode, situated near the anode tip. This forms the triode miniature argon detector[98]. The electrode is negatively charged, and its purpose is to confine the primary electrons to a narrow beam, and to collect any positive ions. Thus the background is

divorced from the signal, with a subsequent reduction in noise, and an extension of the lower limit of detection. The detector is not difficult to construct, and since its performance is superior to that of the simple argon detectors, there seems little point in employing the latter.

3.6e The Ionisation Cross-section Detector.

This was the first ionisation detector for gas chromatography and was proposed by Pompeo and Otvos[109] in 1953. Practical designs based on this proposal were introduced independently by Otvos[110] and Boer[111]. The cross-section detector consists of an ionisation chamber to which is applied a potential gradient. The gas within the detector is irradiated with a β-ray source, and the ionisation current recorded. In the presence of a carrier gas alone, the current is small, but increases significantly on the introduction of other heavier gases or vapours. The heavier gases cause an increase in the total cross-section for ionisation, and this is approximately proportional to the total number of electrons in each gas molecule. Provided that hydrogen is used as carrier gas, the introduction of any other material will cause a large increase in the number of electrons present in the chamber. The use of gases such as nitrogen of relatively high cross-section of ionisation will give an increase in the background current and hence a decrease in the lower limit of detection. Argon and helium cannot be used, since the detector would simultaneously function as an "argon" and a cross-section detector, resulting in unpredictable responses. Details of the physical basis of this detector have been published[112]. The change in current ΔI produced when a component is introduced into the gas stream is given by:

$$\Delta I = \frac{K.PV}{RT} \cdot x(Q_x - Q_c) \qquad 3.11$$

where P, R, T have the usual physico-chemical significance

V = volume of the detector chamber (cm^3)

x = mole fraction of component

Q_x = molecular ionisation cross-section of the component

Q_c = molecular ionisation cross-section of the carrier gas.

Inspection of equation 3.11 shows that the detector response is pressure and temperature dependent. The relationship assumes that the total molecular cross-section is the sum of the individual atomic cross-sections of the constituent atoms of the molecule, and is independent of the nature of the chemical combination. The relationship also assumes ideal conditions for collection and production of ions within the chamber, that a negligible amount of energy of the incident radiation is absorbed by the gas, and that no significant loss of ions, for example by recombination, takes place. The conditions can be approached in practice. Loss of energy to the gas can be minimised by using a high energy β-ray source such as ^{90}Y, although many other sources have been used[113]. If the cell volume is reduced significantly, a weak β-ray emitter such as tritium may be used[114]. Details of the construction of a micro cross section/detector have been published[108, 114]. Tritium sources are popular in view of their convenience in handling and safety, although they cannot be used above 225°C as outgassing from the foil occurs.

Consideration of equation 3.11 indicates that the detector should give a linear response, under the correct operating conditions, over its entire dynamic range, i.e. satisfy an important condition for an ideal detector. Moreover, response factors for all materials can be calculated from a knowledge of atomic cross-sections for ionisation of the atoms constituting the molecules[110, 111]. Boer gives a simple expression for the calculation of response factors, f;

$$f = \frac{Q_x - Q_c}{M_x} \qquad 3.12$$

where M_x = molecular weight of the component of ionisation cross-section Q_x.

Calculated and observed responses were in reasonable agreement for a number of hydrocarbons[111], and using several different carrier gases[117]. Matousek[118] has however observed deviations from the theoretical response when using carrier gases of high ionisation cross-section. The detector has been proposed for use as an absolute reference standard in quantitative analysis[115]. The mass m of component detected is calculated using the equation:

$$m = \frac{P\upsilon A_x M_x Q_c}{R\left[ItT(Q_x - Q_x) - A_x TPQ_c\right]} \qquad 3.13$$

where υ = volume of carrier gas in which the peak is eluted (cm^3)

I = standing current (amps)

A_x = area of peak (amp sec)

t = time taken for compound to pass through the detector i.e. peak width (sec).

The remaining symbols have the same significance as in equation 3.11 and 3.12 assuming that P and T are constant and the mole fraction of component is less than 0.01, the expression simplifies to:

$$m = \frac{P\upsilon A_x M_x Q_c}{RItT(Q_x - Q_c)} \qquad 3.14$$

M_x, Q_c Q_x and R are known, the remaining quantities can be measured, and hence the absolute mass response of the detector found. However no conclusive experimental evidence is put forward in support of equation 3.14; rather the equation is assumed to be obeyed, and quantitative analysis carried out on this basis.

Matousek[116] has used the cross-section detector to obtain both a differential and an integral response. Using two ionisation chambers, one in the analytical stream, and one in the reference stream, the sensitivity of the detector to temperature fluctuations and pressure changes is minimised, and the ionisation current produced by the pure carrier gas is automatically compensated by the second cell. To obtain an integral signal the input resistance used for a differential signal is replaced by a capacitor. In the presence of an eluted

component a current will flow and the capacitor becomes charged thus giving a time integration of the current. The potential rise E, on the capacitor, of capacity C is amplified and displayed as an integral response:

$$E = \frac{k}{C} (Q_x - Q_c) \int x dt \qquad 3.15$$

The significance of the symbols is as in equation 3.11.

In practice it is not possible to balance out completely the standing current in the two ionisation chambers, and the residual current interferes with the integral response, resulting in a drifting baseline.

The detector offers many attractive features, and the claims are such that it may represent a most satisfactory detector for quantitative analysis. The response appears to be predictable, provided that molecular weights and ionisation cross-sections are known, although confirmation of its response to a greater variety of organic species is required. Purnell[119], however states that its performance is little better than a katharometer, and that it offers no advantage over other ionisation detectors. In view of its predictable response, its ability to respond to all materials and its very high upper limit of detection, this is a surprising statement. On the other hand; the lower limit of detection does not approach that of the argon detector.

The detector has one serious practical disadvantage: the electrodes are easily contaminated, for example by stationary phase, resulting in a particularly noisy and unstable background current. The electrodes must be thoroughly cleaned, but in the case of a high energy β-ray source, they cannot be removed without the necessary safety precautions being observed. Using a tritium source contamination is even more serious since a reduction in emission, and hence in detector sensitivity occurs, although a tritium source is safe to handle without shielding.

N.B. Purnell[119] refers to the above detector as a "cross-section of capture" detector, not to be confused with the "electron capture" detector described below. Boer[111] refers to the detector as a "β-ray ionisation" detector, rather than a "cross-section" detector.

3.6f The Electron Capture Detector.

The majority of ionisation detectors are designed to minimise recombination of ions, whereas the electron capture detector depends on the process of recombination for its successful operation. The detector is thus extremely sensitive to compounds of high electron affinity. The possibility of using ion combination effects was proposed by Lovelock[120] and first employed by Goodwin[121] in 1961. An ion chamber containing an ionisable gas is maintained at a potential which is just sufficient for the collection of all free electrons produced. On introducing an electron capturing vapour a current decrease occurs, which is related to the concentration of the vapour by the expression:

$$I = I_s e^{-kcx} \qquad 3.16$$

where I_s = saturation current in pure carrier gas

I = current in the presence of a component of concentration C

k = constant depending on field strength and the electron affinity of the component

x = a factor depending on the dimensions of the ion chamber.

This simple detector was unsuitable for quantitative analysis, since anomalous responses were observed, and even small changes in operating conditions caused non-linearity of response with concentration. Several mechanisms of detection were simultaneously occurring[122]. The detector can also function as a cross-section detector, an argon detector, and an electron mobility detector. The mechanism of detection which predominates will depend on the precise conditions of operation. Lovelock[122, 123] has developed the detector so that all

mechanisms other than recombination, are virtually eliminated, thus removing the major sources of anomalous response. A simple ionisation chamber is employed: the ionising source (tritium) is attached to the cathode, and at atmosphere pressure the low energy radiation from the tritium cannot penetrate the carrier gas deeper than about 2 mm. Thus all positive ions and electrons reside in the vicinity of the cathode. The detector cannot therefore function as a cross-section detector, since the introduction of a vapour with a higher ionisation cross-section than the carrier gas will merely change the range of radiation, and not the rate of generation of ions. Argon is used as a carrier gas to which a few percent of a non ionisable gas (methane or water) has been added, to remove any argon metastable atoms as soon as they are formed. Thus the detector cannot function as an argon detector. The presence of methane or water vapour also maintains the electron energy at a constant thermal level, so that the detector cannot function as an electron mobility detector. A low pulse potential is applied between the electrodes and the free electrons present are collected. The pulses are integrated to provide a steady direct current for recording purposes. The addition of a compound of high electron affinity, results in a decrease in the number of collected electrons, and hence in the output current. Operation in the D.C. mode is sometimes used, but can produce anomalous responses since the detector can operate partially as a cross-section detector.

Detector design and electrode geometry have been discussed by several workers[124-126], and the construction of a detector has been described in detail[131].

The detector is so sensitive to compounds of high electron affinity that calibration near the lower limit of detection, even by logarithmic dilution techniques[50] cannot be used reliably. A method of calibrating the detector, using a stream splitter, and feeding the majority of the effluent to a cross-section detector as a standard, has been used by

Lovelock[122], and the response of the detector toward a number of electron capturing materials determined. The linear dynamic range of the detector is very small, and response factors based on simple additivity of the electron capturing fragments of the molecules are unsatisfactory. Response characteristics under various operating conditions, and with different carrier gases have also been studied by Maggs and Swann[127]. The sensitivity of the detector toward a halogenated hydrocarbon compared with a simple hydrocarbon can be of the order of 10^4 as large. Response factors for halogenated materials have been published by several workers[130].

In view of the selective characteristics of the detector, and its very high sensitivity it is not particularly suited to quantitative analysis. If quantitative analysis is contemplated the detector should be operated at minimum sensitivity, so that a reasonable sample size may be injected, to minimise loss by adsorption and other effects (see Chapter 1). The detector should preferably be used in conjunction with a non-selective detector for reliable quantitative work. It has been used in conjunction with the cross-section detector[122], the flame ionisation detector[128], and the gas density balance[129]. It has also been used in combination with other halogen detectors, to distinguish between similar materials, by making use of differences in response ratios[141]. Dimick and Hartmann have published an account of the operating characteristics and applications of a commercial electron capture detector[140]. The detector has the advantage that the presence of water is desirable for successful operation, so that there is no difficulty in analysing moist samples, and those contained in water as solvent.

Calibration for all materials is necessary and the linear dynamic range is small. The detector is easily disturbed by impurities, resulting in a system which is unstable and difficult to maintain.

3.6g The Electron Mobility Detector.

A detector which functions by measuring changes in electron mobility in the presence of foreign material has been described by Lovelock[132]. Collisions between electrons and noble gas atoms are elastic at low field strengths. But on introducing another gas, collisions between electrons and the molecules of this gas are non-elastic, the electrons lose energy, and their velocity decreases. This decreases the ability of the electrons to excite the noble gas, and also increases their bulk drift velocity in the direction of the applied field. Using a conventional "argon" detector several workers[133] have made use of this effect, by using as carrier gas, argon contaminated with an ionisable gas, at a high potential to ensure ionisation (referred to as indirect ionisation). The introduction of a permanent gas into the detector causes a fall in the electron energy, resulting in a decrease in metastable argon atoms and hence a decrease in the number of ionised molecules. Lovelock[132] used pure argon which was ionised by α or weak β.radiation, (i.e. direct ionisation). The use of argon is limited to those gases which are not themselves ionised by metastable argon atoms, i.e. a detector selective for the permanent gases is obtained. However by using helium (and an ionisible gas) almost all gases and vapours can be detected. The detector also forms the subject of a paper by Smith and Fidian[134].

The response to different gases is not predictable and both forms of the detector require calibration. As with other ionisation detectors, it is very readily upset by impurities. The main value of this detector lies in its ability to detect the permanent gases, and for the determination of very small quantities of water vapour.

3.6.1 Radio-ionisation Detector Performance.

Type of Detector	Cell Volume ml	Limit of Detection $g sec^{-1}$	$mM ml^{-1}$	Linear Dynamic Range	Compound	Ref.
Argon - macro (Section 3.6a)	8	$5x10^{-11}$ $1x10^{-13}$	$6x10^{-12}$ $1x10^{-15}$	10^2	heptane	41 50
Argon-micro (Section 3.6c)		$1x10^{-12}$	$1x10^{-14}$			153
Argon-triode (Section 3.6d)		$4x10^{-13}$	$4x10^{-14}$	$3x10^5$	propane	124
Helium (Section 3.6b)		$4x10^{-14}$	$1x10^{-15}$	$2x10^5$	propane	104
Cross-section (Section 3.6e)	5	$2x10^{-7}$	$5x10^{-7}$ $4x10^{-6}$	10^4 10^4		111 114
	0.08	10^{-9}		$3x10^5$		114
Electron capture (Section 3.6f)		$3x10^{-14}$	$5x10^{-15}$	10^3	carbon Tetrachloride	124
	pulse 0.8	$3x10^{-13}$		$4x10^3$	chloroform	122
	pulse	$2x10^{-9}$		10^3	oxygen	127
	d.c	$2x10^{-8}$		10^3	oxygen	
Electron mobility - indirect (Section 3.6g)		10^{-9}	$5x10^{-8}$	$3x10^2$	carbon dioxide	124
Electron mobility - direct		10^{-11}	$5x10^{-10}$	$3x10^3$	carbon dioxide	124

3.7a Glow Discharge Detector.

The electrical properties of a glow discharge at low pressures depend upon the composition of the gases present. Thus this phenomenon can be used as a basis for a gas chromatographic detector[135]. Although the response of the detector cannot be predicted, it will respond to all gases and vapours, and has been found to have a reasonable linear dynamic range[136]. The detector has been satisfactorily used to determine impurities in argon[137]. Decomposition of the components of a mixture in the discharge chamber produce carbon deposits on the cathode, which have been found to permanently affect the emission of the electrodes. A major disadvantage is that the device must be operated at reduced pressures.

3.7b Radiofrequency Discharge Detector.

A radiofrequency discharge can be maintained at atmospheric pressure, so that a detector operating on this principle would overcome one of the disadvantages of the glow discharge detector. In addition deposition on the electrodes does not appear to affect the detector response. Using

helium as carrier gas Bowman and Karmen found that on introducing a sample into the detector, there was a measurable reduction in voltage[138]. The detector is claimed to have a wide linear dynamic range and to be extremely sensitive. Its major disadvantages are that for the best results helium must be used, the response is unpredictable, and expensive ancilliary equipment is required. Hampton[143] described a similar detector in which the response, although unpredictable is linear for sample sizes of less than about 1 µl. The detector is sensitive to all materials, and has a particularly high sensitivity toward hydrogen.

3.7c Sternberg and Paulson[144] have used a Tesla discharge as a detecting device, which has the advantage that it is cheap and requires no ancilliary equipment.

Discharge detectors have also been used by several other workers, [145, 146], mainly for the analysis of permanent gas mixtures.

3.7d A discharge device in which the intensity of the emission spectra of excited components is measured photo-electrically can be used as a selective and as a non-selective detector[149]. The mode of detection is identical to that used for the flame photometric detector described previously. The detector readily distinguishes between normal hydrocarbons, and those containing halogens, phosphorus or sulphur, by a suitable choice of wavelength. It is also satisfactory for the permanent gases. Interference between different groups at a specific wavelength is measured quantitatively in terms of the selectivity ratio: this is defined as the amount of an unknown compared to the amount of hexane required to give an identical detector response. Details of selectivity ratios, characteristic wavelengths and limits of detection for a number of materials are given[149]. The detector has a linear response for nonane at least over three orders of concentration, which is the same order quoted for the flame photometric detector using benzene[92].

3.7e Photo-ionisation Detectors.

The detector[139] consists of a chamber containing a glow discharge which is supplied with a pure gas. The ultra violet irradiation from the discharge illuminates an ionisation chamber, through which column effluent passes. The discharge can either be operated at reduced pressure using a water pump, or, using a radiofrequency discharge and helium, at atmosphere pressure. The detector has a wide linear dynamic range and can respond to nearly all gases and vapours. It is not subject to contamination and does not give anomalous results with halogenated materials.

Yamane[142] has used a photo-ionisation detection in which helium is used both as the discharge gas and the carrier gas. The effect of various operating parameters on the response has been studied: the use of very pure helium is essential. The main use of photo-ionisation detectors is for the analysis of permanent gases.

3.7.1 Discharge Detector Performance.

Type of Detector	Limit of Detection g sec^{-1}	mMml^{-1}	Linear Dynamic Range	Compound	Ref.
Glow discharge (Section 3.7a)		$4x10^{-9}$	10^3		136
R/F discharge (Section 3.7b)		$1x10^{-8}$	small		138
Emission spectra (Section 3.7d)	$2x10^{-16}$			hydrocarbons	149
" "	$1x10^{-9}$			inorganic gases	149

3.8 Ultra-violet Absorbtion Detector[199].

The detector cell is irradiated with ultra-violet light at a specific wavelength and the intensity measured by a photomultiplier tube. Organic materials, on entering the cell will absorb radiation, resulting in a loss of intensity. The detector has a rapid response, is simple to construct, and has a linear dynamic range to saturation level. It is insensitive to changes in carrier gas flow rate, pressure and temperature. The response is partially selective, but is not predictable. The limit of detection is about 2×10^{-11} mMml^{-1} for benzene.

3.9 Ionisation Gauges.

The ionisation gauge is basically a conventional triode valve, the potential difference between the filament and grid, accellerating electrons which can ionise any gas present. If helium is used as carrier gas, and the potential difference is just not sufficient to ionise helium, but all materials of lower ionisation potential, then the device can be used as a gas chromatographic detector[147]. The detector is operated at a low pressure and the grid voltage must be rigorously controlled (to 0.01%) to ensure reasonable stability[148]. Although the detector has a reasonable linear dynamic range, response cannot be predicted. The response is impaired by electrode oxidation, and deposition of decomposed materials on the electrode. Oxidation can be minimised by a suitable choice of electrode metal (e.g. rhenium or tungsten[148]).

Varadi and Ettre[150] have combined an ionisation gauge and mass spectrometer as a single unit for simultaneous quantitative and qualitative analysis: however this in no way overcomes the problem of detector calibration.

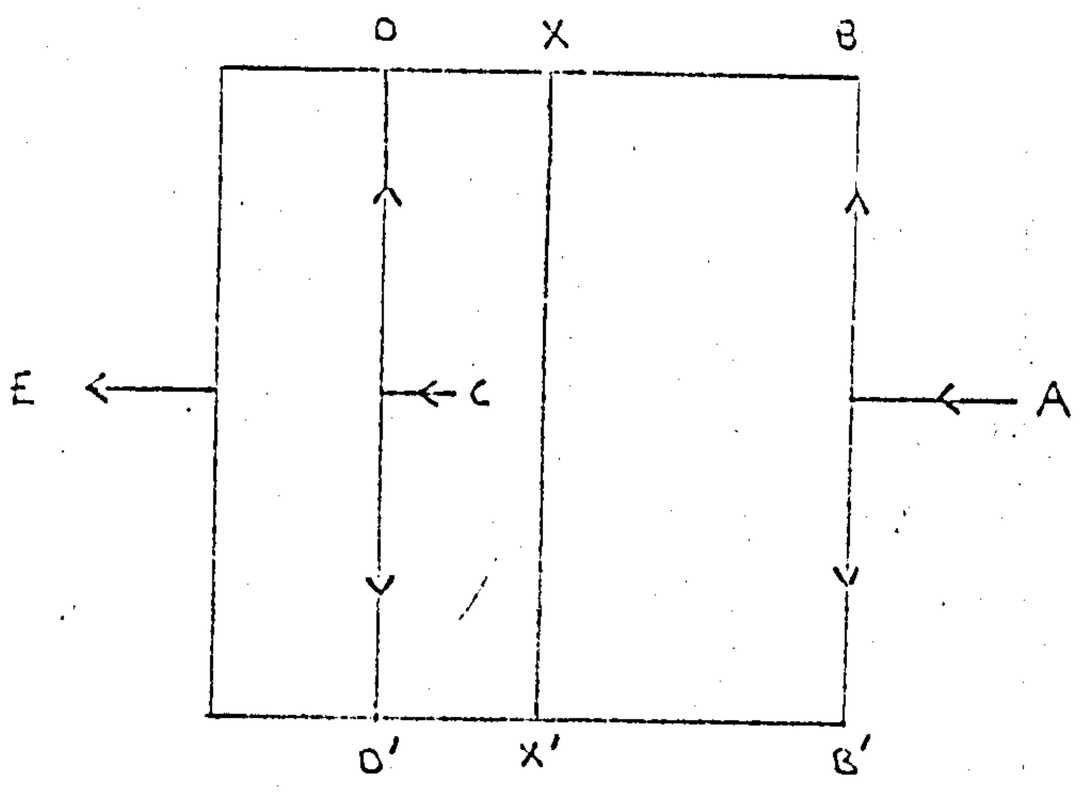
The limit of detection of the ionisation gauge is about 1×10^{-8} $mMml^{-1}$.

3.10 Gas Density Detectors.

3.10a The Martin Gas Density Balance.

The measurement of the density changes of a gas stream emerging from a chromatograph offers the basis for a detection system, since the response of the detector depends on the molecular weight differences between the carrier gas and the components. An apparatus based on this principle was first constructed by Claesson in 1946[154], but the first gas density balance designed as a chromatographic detector was made by Martin and James eight years later[155]. Figure 3.3 is a diagram of the flow system within the gas density balance. A reference gas enters the detector at A and is split equally so that one part flows upward, and

Figure 3.3



The Gas Density Balance.

the other downward. The analytical carrier gas stream enters at C, and is similarly split. The divided analytical streams combine with the divided reference streams at D and D', and these two streams themselves combine at the detector outlet E. When a component which is heavier or lighter than the carrier gas enters conduit DD', there is a pressure change at point D' which is sensed as a flow rate change in a conduit XX' parallel to DD', and hence a flow of pure gas will occur along XX'. If the component detected is heavier than the carrier gas, the gas flow in XX' will occur in an upward direction, but if the density is less than that of the carrier, flow will be in a downward direction. The detecting element, placed along XX', consists of a heated wire, at each end of which is a thermocouple. When there is no gas flow through XX' the thermocouple outputs are equal, but when a flow through XX' occurs, resulting from a component in conduit DD', there is a temperature gradient between the thermocouples, which can be related directly to the density differences between the carrier and the component. Since only reference gas passes along XX', no component ever comes into contact with the heated filament, so that contamination of the filament and pyrolysis of components cannot occur. In practice it is found that even when there is only pure carrier gas in both reference and analytical conduits, there are pressure differences within the system, caused by flow restrictions in the conduits. However, since the analytical and reference conduits each form a pneumatic Wheatstone bridge, the incorporation of variable restrictions in the bridge arms, enables the detector to be balanced. (Reference to a pneumatic bridge detector has appeared in a Russian journal[170], but design details are not known).

The original gas density balance was constructed from a solid copper block. The construction is time-consuming and demands considerable skill. Munday and Primavesi[156] have constructed a skeletal type of gas density balance from copper tubing, and have compared some of the

characteristics of the two models. The overall conclusions were that the original block detector gives less noise, but has a smaller linear dynamic range than the skeletal model. However both detectors have a linear dynamic range greatly in excess of that required for gas chromatography. The skeletal gas density balance is far easier to construct. Other minor modifications to the original Martin and James design have been proposed by several workers[157-160], but these concern mainly the construction of the detector and do not substantially alter the performance characteristics. A gas density balance for use at high temperatures has also been described[161].

The sensitivity of the detector will depend on the volume of the main conduits, the power dissipated by the heater, and the nature of the carrier gas. A gas of low thermal conductivity will increase the temperature gradient along the wire, and for this reason nitrogen is generally used as carrier gas. However for the analysis of materials of similar molecular weight to nitrogen other carrier gases should be used, to maintain a reasonable sensitivity.

The detector is temperature sensitive, and for maximum stability the temperature must be controlled to $\pm$ 0.001°C. For a correctly balanced detector, the response is completely **flow insensitiye**but flow rate is limited by the onset of turbulence within the conduits: however this is not a serious limitation of the detector.

The response of the detector is predictable from a knowledge of molecular weights. By correcting the peak areas corresponding to each of the constituents of a mixture using the expression:

$$f = \frac{M_x}{M_x - M_c} \qquad 3.17$$

where M_x and M_c are the molecular weights of the constituent x, and of the carrier gas, respectively,

the percentage composition of the mixture by weight, is obtained directly:

$$\% \text{ weight of component } x = \frac{A_x f_x}{\sum_1^j Af} \cdot 100 \qquad 3.18$$

where A = peak area.

Thus no experimental calibration of the detector is required, and the response should be linear for all materials. Although the linearity of response has been confirmed for a limited number of compounds[162], the majority of workers who have published data obtained from the gas density balance, make the assumption that response is always calculable from equation 3.17, and give no experimental support[129, 163, 164]. In the course of the present work the response of the detector to a number of different materials has been studied and no anomalous responses have been found under normal operating conditions. Experimental details and results are given in Chapter 6.

On the assumption that equation 3.17 is obeyed for all materials, and provided that the mass of x is known, the gas density balance may be used for the determination of the molecular weights of unknown materials. A number of workers[163-5], including the present Author, have used the gas density balance, as the basis for a technique to determine molecular weights. This is discussed in detail in Chapter 7.

The Martin gas density balance has many of the properties of an ideal detector. It is robust and reliable. It does not require expensive ancillary equipment. Its response is predictable for all gases and vapours, and it has a wide linear dynamic range. The detector is non destructive, and components never come into contact with the heated detector filament. However the detector is not easy to construct, its limit of detection is not very low compared with ionisation detectors, and it requires excellent temperature control.

3.10b The Gow-Mac Gas Density Balance.

A study of the gas density balance was undertaken by Nerheim[166], and as a result of his work a simplified version of the detector was designed[167]. The basic difference lies in the fact that the conduit XX' (figure 3.3) containing the detecting element, is completely removed,

and is replaced by two heated filaments, one in each of the horizontal reference gas conduits, i.e. between BD and B'D'. These filaments form two arms of a Wheatstone bridge. Adjustable flow restrictors are not incorporated in the detector. The detector appears to perform satisfactorily in that response factors for some simple organic compounds calculated from equation 3.17 agree with experimental values. Anomalous response is observed for hydrogen and ethane. No value is given for the linear dynamic range of the detector. The detector forms the basis of an instrument available commercially[168], which will be referred to as the Gow-Mac gas density balance, to distinguish it from the original Martin pattern. Little data have been published on the performance of the Gow-Mac detector, the only papers being a series by Guillemin and Auricourt[169]. [215] These authors set out to define the optimium operating conditions for quantitative analysis. The sensitivity of the detector using nitrogen is greatest for an analytical gas flow rate of 33 ml min^{-1} and a reference flow rate of 100 ml min^{-1}. The performance of the detector was examined using several different carrier gases, both permanent gases, and those of high molecular weight such as the halogenated alkanes. The effect of temperature on detector sensitivity was studied. The linearity of the detector was briefly examined, but no serious study was undertaken. Results of quantitative analysis of a number of mixtures of low boiling halogenated hydrocarbons are in good agreement with the true mixture compositions. Each mixture was analysed three times, at one sample size only.

In the present work the linear dynamic range and response of the Gow-Mac gas density balance has been determined for several different materials; it is concluded that although the detector is in most instances satisfactory for relative percentage compositionanalysis, the absolute response does not always agree with calculated values, and deviations from linearity occur. Details of this work are to be found in Chapter 6.

3.10c The Jet Stream Detector.

A very simple detector whose response is a function of density, is the jet stream detector[213]. This consists of a moving coil microammeter, to the needle of which is attached a vane, held in equilibrium position by a current passing through the coil. Reference gas impinges on one side of the vane, and the analytical gas stream on the other side. Elution of components causes a deflection of the needle, and the current required to restore the needle to its equilibrium position is measured. Since the response of the detector depends on the density difference between the two gas supplies, it is calculable, and can be used for quantitative analysis and molecular weight determinations. The main drawback of the device is that precise control of gas flow is required for stability.

3.10.1 Gas Density Detector Performance.

Type of Detector	Cell Volume ml	Response Time sec.	Limit of Detection g sec^{-1}	Detection mMml^{-1}	Linear Dynamic Range	Compound
Martin (Ref. 25)	3	3	4×10^{-7}	4×10^{-6}		Pentanol
(Ref. Chapter 6)				6×10^{-6}	$>10^3$	octane
Nerheim - filament (Ref. 166)	8		6×10^{-8}	1×10^{-6}		butane
Nerheim - thermistor (Ref. 166)	8		1×10^{-8}	2×10^{-7}		butane
Gow-Mac - filament (Ref. 35a)	8		10^{-7}	4×10^{-6} 3×10^{-8}	10^3	CCl_4
(Ref. Chapter 6)	11			6×10^{-7}	small	octane
Pneumatic bridge (Ref. 170)				5×10^{-6}		

3.11 Gas Volume Detector.

Direct measurement of the volume of components eluted from a column is the basis of a detection system devised by Janak[171]. By using carbon dioxide as carrier gas, complete absorption of the gas at the column exit, into a vessel containing potassium hydroxide, is accomplished. Other constituents of the gas, which are not absorbed by potassium hydroxide, pass into a gas micro-burette. Thus the

response of the detector is measured as a volume change, and is integral. The detector can be used for all materials which are not absorbed by, or react with caustic alkali solution and are not soluble in water: it is not very satisfactory for partially resolved components. It does not have a very low limit of detection, since volume changes smaller than 10 µl cannot readily be measured. The detector must be operated at a temperature sufficiently high to prevent condensation of constituents in the burette. In practice the detector is normally operated at room temperature, thus severely restricting materials for analysis. The system is very temperature dependent, and it is essential to use extremely pure carbon dioxide. The detector is cheap to construct, and simple to operate, and has the great advantage that response is predictable for all materials. Examples of the determination of small amounts of alkanes in gaseous olefin mixtures, using an automatic gas volume detector have been published by Janak[172]. Experimental procedure for the analysis of gaseous hydrocarbons, and permanent gases, have also been published[173].

The accuracy and precision of the method are better than 2%, and the limit of detection for any component in a mixture is given as 0.3% by volume. It is meaningless to quote the limit of detection with respect to the concentration in the carrier gas, since this never reaches the detector: in any case, the detector gives an integral response. The absolute limit of detection is of the order of 4×10^{-4} mM.

Several other papers have been published on the Janak detection system, the majority of which have appeared in the less common journals[174].

3.12 Gas Flow Impedence Detector.

The pressure developed across a choke through which a gas flows at a constant rate is a function of the gas composition. This effect has been used as the basis for a detector[175], but sensitivity is low and rigorous control of flow rate is essential. The limit of detection is about 4×10^{-5} mMml^{-1}.

3.13 Surface Potential Detector.

The measurement of surface potential changes for use as a detection system was proposed by Phillips[176], and examined for its applicability to gas chromatographic analysis by Griffiths and Phillips[175,177]. An alternating e.m.f. is set up by two dissimilar metals when one is vibrated close to the other. The e.m.f. depends on the nature of the gas passing between the plates. The device is partially selective, and sensitivity is greatest for polar materials. It suffers from the disadvantages of irreversible adsorption on the plates, non linearity of response, and long response time. The limit of detection is about 4×10^{-8} mMml^{-1}.

3.14 Dielectric Constant Detector.

Measurement of the dielectric constant changes of a gas stream have been used as a basis for a gas chromatographic detector by Phillips[175], Turner[178], and more recently by Winefordner[179]. The detector comprises a cell containing a variable capacitor between the plates of which the carrier gas is passed. In Winefordner's system this capacitor forms part of a resonant circuit, such that there is no frequency difference between a reference oscillator and an oscillator connected to the detector cell. The presence of an impurity in the cell produces a frequency difference which is a function of the amount of component. At high concentration the response, measured from peak heights (i.e. maximum frequency change), is non linear, but tends to linearity with decreasing sample size. Theoretically a linear response is expected, since the frequency change ΔF, in the presence of an impurity is given by the equation:

$$\Delta F = f_o \frac{\rho_x}{2} (K_1 + \frac{K_2}{T}) \qquad 3.19$$

where f_o = reference frequency

ρ_x = density of component x

K_1 K_2 = constants in Debye equation.

The response of the detector is claimed to be very rapid, and

virtually insensitive to gas flow fluctuations. The cell volume (10 ml.) is rather large compared to that used by Turner[178].

3.15 Ultrasonic Detector.

A detector based on the measurement of the velocity of sound was suggested by James[211] in 1956. A practical detector has been devised by Noble[180]. The detector cell is operated at a fixed frequency, and on changing the gas composition in the cell, a change in velocity, and hence a change in wavelength occurs, which is detected as a phase change. This phase change, resulting from the presence of a component in the carrier gas, can be derived from a knowledge of the molecular weights and specific heats of the constituent gases or vapours. Provided that hydrogen is used as carrier gas, the response to many materials up to a molecular weight of about 300, is in excellent agreement with the theoretical response calculated from the equation:

$$\Delta\varphi = K \frac{(M_c)^{\frac{1}{2}}}{\gamma_c} n \frac{(M_x - M_c)}{M_c} \qquad 3.20$$

where K = constant depending on cell path length, fixed frequency, temperature and the universal gas constant

γ_c = specific heat ratio for the carrier gas, of molecular weight M_c

M_x = molecular weight of component x

n = mole fraction of component x.

The response of the detector is dependent upon, temperature, pressure and flow rate. The response is linear up to about 5% by volume of the carrier gas, and the linear dynamic range extends over five orders of magnitude. Response factors, using nitrogen as carrier cannot be predicted satisfactorily. The detector may be used for molecular weight determinations, provided that the weight of the unknown material (W_x) is known:

$$M_x = \frac{W_x M_c}{W_x - K' A_x} \qquad 3.21$$

where M_x = molecular weight of component x

A_x = peak area corresponding to component x

K' = constant for given experimental conditions.

3.16 Sorptiothermal Detectors.

One junction of a thermocouple is buried in a plug of activated charcoal, in the end of a chromatographic column. The other thermocouple junction is placed in a column through which only pure carrier gas passes, and the heat liberated on adsorption of vapours is detected as a change in thermocouple output[181]. Priestley[182] described a method in which the two gas streams are switched every few seconds from one detector to the other, so that an oscillating signal is received by the recorder. He claims that the response is proportional to the weight of component present, but no experimental evidence is given. Blumer[183] has used a detector based on the same principle using thermistor probes. A sorptiothermal detector has been patented by Bevan and Thorburn[214], and a detailed study of the device was recently undertaken by Lowes[184]. The response of the detector is not linear with respect to sample size. Response factors calculated from heats of adsorption were only in fair agreement with observed responses. The response of the detector is flow rate and temperature dependent: the limit of detection is about 4×10^{-5} mM ml^{-1} (for benzene). The detector in its present form is not satisfactory for quantitative analysis without extensive calibration, but in view of its simplicity and cheapness it is useful as a qualitative device.

3.17 Semiconductor Detectors.

3.17a The Semiconductor Adsorption Detector.

Certain properties of semiconductors change in the presence of a gas or vapour. The use of thermistors in katharometer and sorptiothermal detectors has already been described. In addition the measurement of changes in the electrical properties of semiconductors can be used directly as a means of detection. It has been shown that at temperatures in the region of 400°C, the adsorption, and subsequent desorption, of a gas on a semiconductor, will change significantly the electrical conductivity of the semiconductor, and this effect can form the basis of a gas chromatographic detector[185]. Details of the construction of such

a detector have been published[186]. Using a zinc oxide film, the response to a number of organic compounds has been measured. The response of the detector depends on the electron donating or accepting power of the compound, but is non-linear, and unpredictable.

3.17b The Piezoelectric Detector.

Piezoelectric quartz crystals have been used as detectors by King[187].

A relationship between the weight of a metal film deposited on a crystal, and the resulting change in frequency ΔF has been derived[188], a simplified version of which is given below:

$$\Delta F = KF^2 \frac{\Delta W}{A} \qquad 3.22$$

where F = frequency of the quartz plate

ΔW = weight of deposited film

A = area of quartz plate.

If a liquid stationary phase is coated on to such a crystal, there is a permanent frequency decrease. When the gas emerging from the chromatograph is absorbed into the liquid there is a further decrease in frequency and amplitude of vibration, and by measuring these changes, the crystal can be used as a detector for gas chromatography. Using the frequency change ΔF as a basis for quantitative measurement, from equation 3.22, it follows that:

$$\Delta F = \Delta F_o \frac{\Delta W}{\Delta W_o} \qquad 3.23$$

where ΔF_o = frequency change due to coating of stationary phase on the crystal

ΔW_o = weight of coating

ΔW = weight increase due to sorbate.

The difference in frequency between a reference crystal, and the analytical crystal is measured. The reference crystal is identical to the analytical crystal, except that it is not coated with stationary phase. Many organic vapours show a linear relationship between the vapour concentration and the value $\Delta W/\Delta W_o$, so that provided equation

3.23 is obeyed, the response with respect to concentration will be linear over a wide range.

Since the detector is itself acting as a chromatographic column, the residence time of a given material in the detector, will depend on the nature of the crystal coating, and the material sorbed (i.e. the partition coefficient) as well as the carrier gas flow rate.

The detector may be made partially selective by a suitable choice of stationary phase. The detector requires calibration for all materials, since the response is a function of the weight of each component partitioned within the detector stationary phase, and not of the weight of material injected. Irreversible adsorption on to the crystal coating must be negligible, otherwise erroneous calibration will result, and there will be a permanent change in the basic frequency emitted by the crystal. For the same reasons the detector is presumably very susceptable to contamination by impurities in the carrier gas, and stationary phase bleed from the chromatographic column. Loss of stationary phase from the crystal itself will also give rise to instability.

3.17.1 Semiconductor Detector Performance.

Type of Detector	Cell Volume ml	Response Time sec.	Limit of Detection $mMml^{-1}$	Linear Dynamic Range	Compound	Ref.
Adsorption (Section 3.17a)			4×10^{-9}		Ethanol	179
Piezoelectric (Section 3.17b)	0.02	0.04	$\bar{c}\ 10^{-8}$	2×10^{2}		187

3.18 Electrolytic Conductivity Detectors.

Decomposition products of organic compounds burnt in oxygen are dissolved in water, and the resultant change in conductivity is measured. In general, carbon dioxide, sulphur dioxide and trioxide and hydrogen halides will be formed. Several devices based on this principle have been tried[189, 190]. The end of a chromatographic column is fitted with a combustion chamber into which oxygen is passed. The effluent from the column is thus decomposed, and is passed into a chamber through which

water is flowing at a constant rate. Dissolution occurs, and the solution flows into a conductivity cell. The response of the detector is calculable and linear over a wide range. The detector can be made specific for the detection of halogens and sulphur if the contact time of the gases is sufficiently short to prevent carbon dioxide absorption. The detector can be made specific for the detection of nitrogen alone, by hydrogenating the components over a nickel catalyst, and passing the ammonia produced into the cell[191].

Quantitative analysis relies on a knowledge of the qualitative nature of the compounds, and the method is of course destructive.

3.19 Coulometric Detectors.

Coulometry can be used for quantitative detection, the amount of material present being calculable from Faradays Laws. A non-selective detector requires the pyrolysis of all materials to carbon dioxide, which is then passed into a coulometer[192]. Several selective detectors have been described; for example the detection of sulphur is accomplished by oxidising column effluent to sulphur dioxide or reducing to hydrogen sulphide[193]. Coulson has given a detailed description of a micro-coulometer which he has used for the detection of chlorine[194].

3.19a The Reaction Coulometer[195].

In this device the coulometric cell output is maintained at a constant level by the following system. The carrier gas, emerging from the column, is passed into a combustion furnace, and then into a coulometric cell. The furnace is continuously supplied with oxygen by passing a separate pure carrier gas stream through an oxygen generator. In the absence of any eluted material, the oxygen supply to the cell remains constant, but when a component reaches the furnace it is quantitatively converted into carbon dioxide and water, which results in a decrease in the amount of oxygen reaching the cell. The cell output is thus decreased, and by means of a feedback loop, an equivalent amount of oxygen is produced in the oxygen generator,

returning the oxygen concentration in the cell to its former value. The increase in oxygen output by the generator is thus a measure of the amount of combusted material. Response is therefore calculable and linear with respect to concentration. Absolute, in addition to relative quantitative analysis, may be carried out provided that the molecular weights of the components under analysis are known. Examples are given of the quantitative analysis of simple alkane, ketone and alcohol mixtures. The results are excellent. However the detector suffers from a number of drawbacks. The response is only predictable for those materials containing carbon, hydrogen and oxygen. It is not suitable for the quantitative analysis of halogenated materials, or indeed any organic compound which contains elements other than carbon hydrogen and oxygen. The detector does not respond to water. It is necessary to have a full qualitative knowledge of a sample before quantitative results can be calculated. The method is destructive. The response time, contrary to expectation, is in general less than $\frac{1}{2}$ sec. Within the above limitations the detector offers a means of obtaining quantitative analysis without the necessity for calibration.

3.20 Titration Detector.

The titration of materials eluted from a column was used by Martin and James for quantitative estimations of fatty acid mixtures[196], amines[197] and pyridine homologues[198]. The column effluent is passed directly into a titration cell, and burette readings are taken either at fixed time intervals or by adding a fixed volume of acid (or base) and noting the time for neutralisation. Obviously the method is limited to the detection of titratable materials, but it has the great advantage that response is calculable, and the apparatus is extremely simple and cheap. It can be made to record automatically if the colour changes in the region of the equivalence point are monitored by a photocell[196,212].

3.20.1 Coulometric and Titration Detector Performance.

Section	Detector Type	Limit of Detection	Compound	Ref.
3.19	Simple coulometer	4×10^{-2} mMml^{-1}	sulphur	188
3.19a	Reaction coulometer	1×10^{-8} mMml^{-1}	hydrocarbons	190
3.20	Titration	0.3 µg equiv	acids or bases	196

3.21 Auxiliary Detection Techniques.

There are a number of methods of detection used in conjunction with gas chromatography, which form the basis of an analytical technique in themselves. Several of these have already been mentioned in connection with a particular detector (e.g. photometry and coulometry). However it is desirable to discuss some of the more important techniques, such as infra-red spectroscopy, on a more general basis. It is not proposed to give a detailed account of these methods for a number of reasons: they are not strictly gas chromatographic detectors; they are normally employed in conjunction with a conventional gas chromatographic detector; their successful operation requires workers skilled not only in chromatographic analysis, but, for example, in spectroscopic analysis in addition.

3.21a Infra-red Spectroscopy[200].

Infra-red spectroscopy can of course be applied to mixtures before chromatographic analysis, but because of the complex nature of the spectra obtained, this method is of limited value. It is far more informative to examine the spectrum of each separate component obtained by gas chromatography. There are two means of performing the analysis: each component emerging from the column, observed by a conventional detector, is passed into a trap cooled with liquid nitrogen, and subsequently transferred to the infra-red cell: alternatively the infra-red analysis is carried out on the vapour as it emerges from the column. The first method is more time consuming and there is the danger of losing altogether any minor components in the mixture caused by ineffective trapping or the formation of fogs. This can be minimised

by filling the trap with stationary phase or active charcoal. The use of an apparatus[201] in which column effluent passes directly into an infra-red cell cooled in liquid nitrogen is more efficient with respect to the length of time for analysis, and recovery of material. It is in general preferable to examine samples in the liquid phase, since more information about the liquid phase is available in the literature. However in view of the small sample sizes available from gas chromatography, this is not always possible, and analysis in the vapour phase must sometimes be carried out.

Examination of infra-red spectra has the added advantage that it may reveal the presence of a second component in a given elution band, which has not been resolved by chromatography.

3.21b Mass Spectrometry[150, 202].

Mass spectrometry offers several advantages over infra-red spectroscopy. It is extremely sensitive and may be used for almost any type of material. Interpretation of results requires calibration spectra and a knowledge of the general relationships between structure and mass spectra for a complete qualitative analysis. The mass spectrometer may be coupled to the exit of a gas chromatographic column, via a stream splitting device and the eluent continuously monitored: the complete mass spectrum is rapidly and continuously scanned throughout the run, or the spectrometer is fixed at one particular mass for each chromatographic run. Fortunately it is not essential to have a complete mass spectrum of a mixture to obtain a complete identification of all the components: all that is required is the relative intensities of several characteristic masses, e.g. for the identification of alkyl benzenes, the apparatus is set to a mass number characteristic of the molecules (e.g. 91) and an analysis carried out. Comparison of the peaks obtained by a chromatographic detector with the mass spectrum on the same time scale enables the alkyl benzenes to be readily identified.

3.21c Radioactive Detection.

For the detection of radioactive materials injected into a chromatographic column, the conventional radioactive detection systems are used[203]. A method for the analysis of ^{14}C and ^{3}H labelled compounds has been developed by James and Piper[204]. After passing through a chromatographic column, the effluent is split, a proportion passing to a chromatographic detector, and the remainder to a furnace containing copper and iron filings at 900°C. All components entering the furnace are converted into $^{14}CO_2$ or $^{3}H_2$ and these gases are passed into a proportional counter. The final result is obtained via a ratemeter, in the form of a differential or integral display. The chromatogram and corresponding radiochromatograms are compared, on the same time scale. This method is particularly valuable for the detection of materials of very small mass but high activity, which may be missed by chromatographic analysis alone. Since the column effluent is split, only a proportion of the sample is destroyed, and the remainder may be collected if necessary.

Of more general applicability, is the method described by Behrendt[205], in which non-radioactive substances can be detected after conversion to labelled materials by an exchange process.

3.21d Polarographic Detection.

By employing a polarograph in addition to a conventional detector it is possible to distinguish between various chemical species in a mixture[207]. Janak and coworkers[206] detected halogens by passing column effluent into a solution containing Ti^{III} ions, and measuring the current increase in the cell, caused by the halogens. This arrangement is particularly limited in its application, and a more useful procedure may be as follows. The use of an aprotic solvent, such as acetonitrile would anable the qualitative and quantitative analysis of many organic compounds, separated by chromatography, to be effected. Polarography is not restricted to the analysis of reducible materials

at a dropping mercury electrode, but can equally well be carried out with oxidisable materials using a rotating platinum electrode[208]. The problems associated with polarographic analysis coupled with gas chromatography are similar to those of infra-red spectroscopy. Either each component must be trapped independently and then analysed in a polarographic cell, or the electrode potential must be rapidly varied between predetermined limits during the chromatographic run. The rate of potential change must be far greater than the rate of emergence of a chromatographic peak, and it would be essential to employ a cathode ray tube for the display of results.

Purnell states that polarography is of no great value in gas chromatographic detection[209]. Its particular values would be that it acts as a specific detector for electron donating and accepting species and distinguishes between the two. In addition, by using published half wave potential data it is possible to obtain qualitative information, and at least to classify components into particular chemical classes[210]. For simple oxidation and reduction mechanisms, a quantitative result is readily obtained from the Ilkovic equation:

$$i = k\,nc \qquad 3.24$$

where k = constant depending on the experimental conditions

n = number of electrons of component x involved in the oxidation or reduction

c = concentration of component x in the cell.

The disadvantages envisaged stem from the use of a large cell volume, and the difficulty of quantitatively trapping materials in the cell. The response time can be minimised by using a rapid scan rate.

3.22 Conclusions.

The suitability of existing detectors for quantitative analysis can be assessed on the basis of the foregoing discussion. Important properties are summarised in the table below. No detector is completely satisfactory for quantitative analysis but outstanding among the detectors is the Martin gas density balance, whose response

is wholly predictable and calculable, and which has a wide linear dynamic range (3.10a). The detector responds to all materials of molecular weight different from that of the carrier gas. However, a detector must not only be suitable for quantitative analysis, but must be available commercially or be readily constructable in the laboratory. It is a matter of regret that neither of these conditions are met by the Martin gas density balance. The detailed performances of the Gow-Mac versions of the gas density balance (3.10b) have been to some extent unknown, and certainly unpublished. The Author's own observations show that small deviations from expected response do occur with some materials, but nevertheless, the detector is a good second best. For quantitative results with either form of gas density balance, it is essential to know the molecular weights of all the components of interest. The flame ionisation detector (3.2) can be used reliably for much quantitative work, and has a very wide linear dynamic range. However response is not always calculable, and the detector must be calibrated for all chemical species. Although it will not detect water, the presence of water interferes with the response of the detector toward other constituents. It does not respond significantly to the inorganic gases. For routine quantitative work, the flame ionisation detector is excellent, but for the analysis of unknown materials, it cannot be used with complete confidence.

The response of the flame thermocouple detector (3.3) is calculable from a knowledge of heats of combustion for a number of materials, but a detailed study of its value as a quantitative device has not been published.

The cross-section detector (3.6c) is claimed to give a predictable response for all materials, for hydrogen as carrier gas, based on a knowledge of atomic cross sections and molecular weights. Although it is capable of giving excellent quantitative results, insufficient evidence has been published for it to be assumed that the detector is

free from anomalous behaviour: indeed it is known to be readily disturbed by contaminants.

The gas volume detector (3.11) is capable of giving excellent quantitative results, and weight response is calculable directly from molecular weights. It is extremely temperature dependent, and is restricted to the analysis of fairly low-boiling materials, which must neither react with potassium hydroxide nor be soluble in water. High purity carbon dioxide must be used as carrier gas.

The ultrasonic detector (3.15) has a wide linear dynamic range, and response is calculable from a knowledge of molecular weights, provided that hydrogen is used as carrier gas. A more detailed study of its response characteristics is required for a true assessment of its value as a quantitative detector. Obvious disadvantages are the high cost of the associated equipment, and the use of hydrogen as carrier gas.

Conductometric detection (3.18) offers no advantage over the other detection systems discussed herein. The sample is totally destroyed, and a qualitative knowledge is necessary for quantitative estimation.

The reaction coulometer response is predictable (3.19a) again on a molecular weight basis, and should give excellent quantitative results provided that the only elements present are carbon, hydrogen and oxygen.

The above detectors are all suitable, in varying degrees and within certain limitations, for quantitative analysis, but they all require a knowledge of the molecular weights of the constituents of the sample before quantitative results can be calculated, i.e. qualitative analysis must precede quantitative analysis. Of these detectors the only ones which have found widespread adoption are the flame ionisation detector, and to a lesser extent the Gow-Mac gas density balance and the cross-section detector.

The present situation with regard to a detector suitable for quantitative analysis is thus unsatisfactory: it was with this fact in

mind that the development of the Brunel mass detector was carried out.

3.22.1 Summary Table of Detector Performance of Non-Specific Detectors.

Detector	Limit of Detection g sec^{-1}	Limit of Detection $mMml^{-1}$	Linear Dynamic Range	Response
Katharometer		10^{-6}	small	Not predictable
Flame ionisation	10^{-11}	10^{-13}	10^{6}	Predictable for many materials
Flame thermocouple		10^{-6}		Calculable for some compounds
Flame emissivity	10^{-5}		10^{3}	Predictable within a homologous series
Flame photometric		10^{-10}	small	Not predictable
Argon-macro	10^{-13}	10^{-15}	small	Not predictable
Argon-micro	10^{-12}	10^{-14}	small	Not predictable
Argon-triode	10^{-13}		10^{5}	Not predictable
Helium	10^{-14}	10^{-15}	10^{5}	Not predictable
Cross-section	10^{-8}		10^{4}	Calculable
Electron mobility	10^{-11}		10^{3}	Not predictable
Glow discharge		10^{-9}	10^{3}	Not predictable
R/F discharge		10^{-8}		Not predictable
Discharge spectra	10^{-16}		10^{3}	Not predictable
Ionisation gauge		10^{-8}	10^{4}	Not predictable
Ultra-violet absorption		10^{-11}	wide	Not predictable
Gas density balance - Martin		10^{-6}	wide	Calculable
Gas density balance - Gow-Mac	10^{-7}	10^{-6}	10^{3}	Calculable
Gas volume		10^{-4} mM	wide	Calculable
Gas flow impedence		10^{-5}		-
Surface potential		10^{-8}	non linear	Not predictable
Dielectric constant			small	No data available
Ultrasonic		10^{-11} mM	10^{5}	Calculable
Sorptiothermal		10^{-5}	non linear	Not predictable
Semiconductor - ZnO		10^{-9}	non linear	Not predictable
Piezoelectric		10^{-8}	10^{2}	Not predictable
Conductometric			wide	Calculable
Coulometric (Wiseman)		10^{-8}	wide	Calculable

3.23 References.

1. Ray, N.H., J. Appl. Chem. 4 21 1954.

2. Griffiths, J.H. et al. Analyst 77 897 1952.

3. Vines, R.G., Bennett, L.A., J. Chem. Phys. 22 360 1954.

4. Hausdorff, H.H., Vapour Phase Chromatography 377 1956.
   Lichenfels, D.H., et al. Anal. Chem. 27 1510 1955.
   " " " " " " 28 1376 1956.

5. Hoffmann, E.G. Anal. Chem. 34 1216 1962.

6. Jordan, J. et al. Anal. Chem. 37 1572 1962.
   " " " " J. Amer. Chem. Soc. 88 2398 1966.

7. Littlewood, A.B. Gas Chromatography 186 1958.

8. Van de Craats, F. Gas Chromatography 248 1958.

9. Schmauch, L.J., Dinerstein, R.A., Anal. Chem. 32 343 1960.

10. Rosie, D.M., Grob, R.L. Anal. Chem. 29 1263 1957.

11. Dimbat, M. et al. Anal. Chem. 28 290 1956.
    Eggertsen, F.T. et al. Anal. Chem. 28 303 1956.
    Fredericks, E.M., Brooks, F.R. Anal. Chem. 28 297 1956.

12. Messner, A.E. et al. Anal. Chem. 31 230 1959.

13. Luy, H. Gas Chromatography 186 1962.
    Mason, E.A., Saxena, S.C. Physics of Fluids 1 361 1958.
    Guiochon, G. J. Chromatog. 14 378 1964.

14. Smith, B.D., Bowden, W.W. Anal. Chem. 36 82 1964.

15. Eastman, R.H. J. Amer. Chem. Soc. 79 4243 1957.
    " " Anal. Chem. 29 1263 1957.

16. Neto, C.C. et al. J. Chromatog. 15 301 1964.

17. Mecke, R., Zinker, K. J. Chromatog. 7 1 1962.

18. Browning, L.C., Watts, J.O. Anal. Chem. 29 24 1957.

19. Gas Chromatography Abstracts No. 391 1965.

20. Brooks, I. et al. Vapour Phase Chromatography 281 1956.
    Keppler, J.G. et al. " " " 222 1956.
    Ryce, S.A., Bryce, W.A. Anal. Chem. 29 1386 1957.
    " " " " Nature 179 541 1957.

21. Keulemans, A.I.M., et al. Anal. Chim. Acta 16 29 1957.

22. Mellor, N. Vapour Phase Chromatography 63 1956.

23. Bohemen, J., Purnell, J.H. J. Appl. Chem. 8 433 1958.

24. Harvey, D., Morgan, G.O. Vapour Phase Chromatography 74 1956.

25. Schmauch, L.J. Anal. Chem. 31 225 1959.

26. Jamieson, G.R. J. Chrom. 3 464 494 1960.
" " " " 4 420 1960.
" " " " 8 544 1962.
" " " " 15 260 1964.

27. Ellis, J.F., Ireson, G. Gas Chromatography 300 1958.

28. Ambrose, D., Collerson, R.R. J. Sci. Inst. 22 323 1955.

29. Cowan, C.B., Stirling, P.H. Gas Chromatography (ed. Coates V.J.) 165 1958 (Academic Press).

30. Davis, A.D., Howard, G.A. J. Appl. Chem. 8 183 1958.

31. Davies, A.T., Johnson, J.K. Vapour Phase Chromatography 185 1956.

32. Blyumberg, E.A. et al., Neftekhimiya (Pergoman Press translation) 2 569 1963.

33. Camin., D.L. et al. Anal. Chem. 36 1175 1964.
Petrocelli, J.A. Anal. Chem. 35 2220 1963.

34. Preau, G., Guiochon, G. J. Gas Chromatog. 4 343 1966.

35. Gow-Mac Instrument Company, New Jersey.
Servomex Controls Ltd., Crowborough, Sussex.
Chem. Brit. 2 228.

36. Lawson, A.E., Miller, J.M., J. Gas Chromatog. 4 273 1966.

37. McWilliam, I.G., Dewar, R.A., Gas Chromatography 142 1958.
" " " " Nature 181 760 1958.
" " " " Nature 182 1664 1958.

38. Onkichong, L., Ph.D. Thesis, University of Eindhoven 1960.
" " Gas Chromatography 7 1960.

39. Condon, R.D., et al. Gas Chromatography 30 1960.

40. Thompson, A.E., J. Chromatog. 2 148 1959.

41. Krugers, J. Philips Research Report Supplement 1965.

42. Lewis, B., Van Elbe, G. Combustion, Flames and Explosions P.206 published by Acedemic Press 1951.

43. Knewstubb, P.F., Sugden, T.M., Nature 181 474 1261 1958.
" " " " Proc. Roy. Soc. A255 520 1960.

44. Speakman, P.F. Column 1 (2) 9 1966.
Dewar, R.A. J. Chromatog. 6 312 1961.
Karmen, A. J. Gas Chromatog. 3 180 1965.

45. Desty, D.H., et al. Gas Chromatography 46 1960.

46. McWilliam, I.G. Gas Chromatography 150 1958.

47. McWilliam, I.G. Gas Chromatography 147 1958.
" " J. Chromatog. 6 110 1961.

48. Kieselbach, R. Ann. Meeting ACS, September, 1959, Atlantic City, N.J

49. Purnell, J.H. Gas Chromatography 302 published by Wiley 1962.

50. Scott, R.P.W. et al. J. Chromatog. 15 471 1964.

51. Maggs, R.J. Column 1 (2) 2 1966.

52. Ettre, L.S., Kabot, F.J., J. Gas Chromatog. 1 (10) 7 1963.
" " " " J. Chromatog. 11 114 1963.

53. Ackman, R.G., Sipos, J. J. Chromatog. 16 298 1964.

54. Perkins, G. et al. Anal. Chem. 35 360 1963.

55. Ettre, L.S. J. Chromatog. 8 525 1962.

56. Moore, J.L. J. Gas Chromatog. 2 (10) 318 1964.
Paraskevopoulos, G., Cvetanovic, R.T., J. Chromatog. 25 479 1966.

57. Ardreatch, J.A., Feinland, R. Anal. Chem. 32 1021 1960.

58. Halasz, I., Schneider, W. Anal. Chem. 33 978 1961.
" " Anal. Chem. 36 461 1964.

59. Bath, L., Cruickshank, F.R. J. Chromatog. 21 296 1966.

60. Green, R., Jones, K. Nature 205 67 1965.
" " " " " 210 1355 1966.

61. Kaiser, R. Gas Phase Chromatography 3 86 106 published by Butterworths.

62. Baddiel, C.B., Cullis, C.E. Chem. Ind. 1154 1960.

63. Novak, J., Janak, J. J. Chromatog. 4 249 1960.

64. Emery, E.M., Koenar, W.E. Anal. Chem. 33 146 1961.
Murray, W.J., Williams, A.F. Analyst 86 849 1961.

65. Cincotti, J.J., Feinland, R. Anal. Chem. 36 488 1964.

66. Foster, J.S., Murfin, J.W. Analyst 90 118 1965.

67. Hill, D.W., Newell, H.A. Nature 206 708 1965.

68. Smith, J.F. Gas Chromatography 114 1960.
Purnell, J.H. Gas Chromatography 298 published by Wiley 1962.

69. Dewar, R.A., Maier, V.E. J. Chromatog. 15 461 1964.

70. Garzo, G., Fritz, D. Gas Chromatography 150 1966.

71. Karmen, A. Anal. Chem. 36 1416 1964.
" " Nature 201 1204 1964.
" " J. Gas Chromatog. 3 336 1965.

72. Janak, J., Svojanovsky, V. Gas Chromatography 166 1966.

73. Graiff, L.B. Nature 203 856 1964.

74. Graiff, L.B. J. Gas Chromatog. 3 155 1965.

75. Tuey, G.A.P. Gas Chromatography 190 1966.
Miller, W. Gas Chromatography 191 1966.

76. Scott, R.P.W. Nature 176 793 1955.

77. Scott, R.P.W. Vapour Phase Chromatography 131 1956.

78. Wirth, M.M. Vapour Phase Chromatography 154 1956.

79. Henderson, J.I., Knox, J.H. J. Chem. Soc. 2299 1956.

80. Primavesi, G.R., et al. Gas Chromatography 165 1958.

81. Bullock, P. Gas Chromatography 175 1958.

82. Primavesi, G.R. Gas Chromatography 176 1958.

83. For example, W.G. Pye Ltd., Cambridge.
Philips Chromatography Ltd., Crawley, Sussex.

84. Scott, R.P.W. Gas Chromatography 176 1958.

85. Cullis, C.F., et al. Chem. Ind. 1158 1961.

86. Gunther, F.A. et al. Anal. Chem. 34 302 1962.

87. Upham, F.T. Anal. Chem. 33 845 1961.

88. Sweeley, C.C. et al. Anal. Chem. 33 1860 1961.

89. Rouayheb, G.M., et al. Anal. Chim. Acta. 26 378 1962.

90. Grant, D.W. Gas Chromatography 153 1958.

91. Juvet, R.S., Durbin, R.P. Anal. Chem. 38 565 1966.

92. Zado, F.M., Juvet, R.S. Anal. Chem. 38 569 1966.

93. Braman, R.S. Anal. Chem. 38 734 1966.

94. Brody, S.S., Chaney, J.E. J. Gas Chromatog. 4 42 1966.

95. Behrendt, S. Z. Phys. Chem. 21 240 1959.

96. Lovelock, J.E. J. Chromatog. 1 35 1958.

97. Lovelock, J.E. Nature 181 1460 1958.

98. Lovelock, J.E. Gas Chromatography 16 1960.

99. Lovelock, J.E. Anal. Chem. 33 170 1961.

100. Hill, D.W., Newell, H.A. Nature 205 593 1965.

101. Evans, R.S., Scott, R.P.W. Nature 190 710 1961.

102. Shakin, M.M., Lipsky, S.R. Anal. Chem. 35 1562 1963.

103. Welti, D., Wilkins, T. J. Chromatog. 3 589 1960.

104. Berry, R. Nature 188 578 1960.
Parish, R.V., Parsons, W.H. Chem. Ind. 1951 1961.
Wiseman, W.A. Nature 190 1187 1961.

105. Lovelock, J.E. Nature 182 1663 1958.

106. Hartmann, C.H., Dimick, K.P. J. Gas Chromatog. 4 163 1966.
Hartmann, C.H., Thompson, K. Aerograph Research Notes, Spring 1967

107. Gas Chromatography 237 333 ed. Noebels et al. published by Academic Press 1961.

108. Abel, K. Anal. Chem. 36 954 1964.

109. Pompeo, D.J., Otvos, J.W. U.S. Pat: 2, 641, 710 (1953).

110. Deal, C.H., Otvos, J.W. Anal. Chem. 28 1958 1956.

111. Boer, H. Vapour Phase Chromatography 169 1956.

112. Otvos, J.W., Stevenson, D.P. J. Amer. Chem. Soc. 78 546 1956.

113. Graven, W.M. Anal. Chem. 31 1197 1959.

114. Lovelock, J.E., et al. Anal. Chem. 35 460 1963.
Lovelock, J.E. Anal. Chem. 36 1410 1964.

115. Simmonds, P.G., Lovelock, J.E. Anal. Chem. 35 1345 1963.

116. Matousek, S. Gas Chromatography 65 1960.

117. Boer, H. Gas Chromatography 79 1960.

118. Matousek, S. Gas Chromatography 80 1960.

119. Purnell, J.H. Gas Chromatography 311-313 published by Wiley 1962.

120. Lovelock, J.E., Lipsky, S.R. J. Amer. Chem. Soc. 82 431 1960.

121. Goodwin, E.S. et al. Analyst 86 697 1961.

122. Lovelock, J.E. Anal. Chem. 35 474 1963.

123. Lovelock, J.E., Gregory, N.L. Gas Chromatography 219 ed. N. Brenner, published by Academic Press 1962.

124. Lovelock, J.E. Anal. Chem. 33 162 1961.

125. Lipsky, S.R., Landowne, R.A. Anal. Chem. 34 726 1962.

126. Kabot, F.J., Ettre, L.S. J. Gas Chromatog. 2 (1) 21 1964.
Hartmann, C.H., Oaks, D.M. Aerograph Research Notes, Winter 1965.

127. Maggs, R.J., Swann, D.F.K. Column 1 (3) 2 1966.

128. Albert, D.K. Anal. Chem. 36 2034 1964.
Dawson, H.J. " " 36 1852 1964.
Oaks, D.M. " " 36 1560 1964.

129. Gregory, N.L. J. Chromatog. 13 33 1964.

130. Landowne, R.A., Kipsky, S.R. Anal. Chem. 35 532 1963.
Clarke, D.D. et al. J. Gas Chromatog. 4 310 1966.
Clemons, C.A., Altshuller, A.P. Anal. Chem. 38 133 1966.

131. Abbott, D.C., Maunder, M.J. Chem. Ind. 82 1965.

132. Lovelock, J.E. Nature 185 49 1960.

133. Willis, V. Nature 185 1.
Johnson, R.E. Symposium of I.S.A. Montreal 1960.
Ellis, J.F., Forrest, C.W. Anal. Chim, Acta. 24 329 1961.

134. Smith, J.W., Fidian, J.F. Anal. Chem. 36 1739 1964.

135. Harley, J., Pretorious, V. Nature 178 1244 1956.

136. Pitkethly, R.C. Anal. Chem. 30 1309 1958.

137. Riley, B. Gas Chromatography 81 1960.

138. Bowman, R.L., Karmen, A. Nature 182 1233 1958.
" " " " Anal. N.Y. Acad. Sci. 72 714 1959.
" " " " 2nd I.S.A. Symp. Lansing June 1959.
" " " " Nature 196 62 1962.

139. Lovelock, J.E. Nature 188 401 1960.

140. Dimick, K.P., Hartmann, H. Wilkens Instrument and Research Inc., Walnut Creek, Calif.

141. Goulden, R. et al. Analyst 88 951 1963.

142. Yamane, M. J. Chromatog. 14 355 1964.

143. Hampton, W.C. J. Gas Chromatog. 3 217 1965.

144. Stemberg, J.C., Paulson, R.E. J. Chromatog. 3 406 1960.

145. Evrard, E. et al. Nature 193 59 1962.
Arnikar, HJ. et al. J. Chromatog. 26 30 1967.

146. Yamane, M. J. Gas Chromatog. 9 162 1963.

147. Ryce, S.A., Bryce, W.A. Nature 179 541 1957.
" " " " Can. J. Chem. 35 1293 1957.

148. Hinkle, E.A. et al. 2nd International Symp. I.S.A. Lansing 1959.
Guild, L.V. et al. " " " " " "

149. McCormack, A.J. et al. Anal. Chem. 37 1470 1965.

150. Varadi, P.F., Ettre, K. Anal. Chem. 34 1417 1962.

151. Desty, D.H. Nature 179 241 1957.
" " " 180 22 1957.

152. McWilliam, I.G. J. Appl. Chem. 379 1959.

153. Purnell, J.H. Gas Chromatography 319 published by Wiley 1962.

154. Claesson, S. Ark. Kemi. Min. Geol. 23A 1 1946.

155. Martin, A.J.P., James, A.T. Biochem. J. 63 138 1956.
" " " " Brit. Med. Bull. 10 170 1954.
" " " " U.S. Pat. 2,728,219.

156. Munday, C.W., Primavesi, G.R. Vapour Phase Chromatography 146 1956.

157. Ellis, J.F., Iveson, G. Gas Chromatography 300 1958.

158. Ponjak, G.J., Cornforth, R.H. J. Chromatog. 4 214 1960.

159. Johnson, E.A. et al. J. Chromatog. 4 429 1960.

160. Murray, K.E. Aust. J. Appl. Sci. 10 156 1959.

161. Hawkes, J.C. Vapour Phase Chromatography 266 1956.

162. Martin, R.L., Winters, J.C. Anal. Chem. 31 1954 1959.
" " Anal. Chem. 32 336 1960.

163. Liberti, A. et al. Nature 178 1067 1956.

164. Phillips, C.S.G., Timms, P.L. J. Chromatog. 5 131 1961.

165. Revel'skii, I.A. et al., Neftekhimiya (Pergaman Press translation) 4 296 1965.

166. Nerheim, A.G. Anal. Chem. 35 1640 1963.
" " 137th Nat. A.C.S. Meeting April 1960.

167. Nerheim, A.G. U.S. Pat. 3090112 (1963), 3082616 (1963).
Rushton, J.H. U.S. Pat. 3082619 (1963).
Tucker, E.B. U.S. Pat. 3050984 (1962).

168. Gow-Mac Instrument Company, New Jersey.

169. Guillemin, C.L., Audcourt, F. J. Gas Chromatog. 1 (10) 24 1963.
" " " " " " " 2 156 1964.
" " " " " " " 4 338 1966.

170. Kulakov, V., Shkatov, E.F. Chem. Ab. 62 2513c 1965.

171. Janak, J. Collection 19 684, 700 917 1954.

172. Janak, J. Vapour Phase Chromatography 247 1956.

173. Rouit, C. Vapour Phase Chromatography 291 1956.

174. Chem. Ab. 51 4877 1957 (Leibnitz E. et al. Brennstoff. Chem. 38 14 1957).
Chem. Ab. 52 17822 1958 (Sevenster, P.G. S. African Ind. Chem. 10 75 1958).
Van der Craats, F. Anal. Chim. Acta. 14 136 1956.
" " " " Z. Anal. Chem. 164 62 1958.

175. Griffiths, J.H. et al. Analyst 77 901 1952.

176. Phillips, G. J. Sci. Inst. 28 342 1951.

177. Griffiths, J.H., Phillips, C.S.G. J. Chem. Soc. 3446 1954.

178. Turner, D.W. Nature 181 1265 1958.

179. Winfordner, J.D. et al. Anal. Chem. 33 515 1961.

180. Noble, F.W. et al. Anal. Chem. 36 1421 1964.

181. Dudenhostel, B.F., Priestley, W. Ind. Eng. Chem. 49 99A 1957.
Claxton, G. J. Chromatog. 2 136 1959.

182. Priestley, W. Vapour Phase Chromatography 165 1956.

183. Blumer, M. Anal. Chem. 32 772 1960.

184. Lowes, H. Dissertation for B.Tech., Brunel University 1966.

185. Seiyama, T. et al. Anal. Chem. 34 1502 1962.

186. Seiyama, T. et al. Anal. Chem. 38 1069 1966.

187. King, W.H. Anal. Chem. 36 1735 1964.

188. Sauerbrey, G. Z Physik 155 206 1959.

189. Boer, H. Vapour Phase Chromatography 314 1956.

190. Piringer, O. et al. J. Gas Chromatog. 2 104 1964.
Coulson, D.M. " " " 3 134 1965.

191. Coulson, D.M. J. Gas Chromatog. 4 285 1966.

192. Liberti, A., Cartoni, G.P. Gas Chromatography 321 1958.

193. Adams, D.F. et al. Anal. Chem. 38 1094 1965.

194. Coulson, D.M. Anal. Chem. 32 1245 1960.

195. Wiseman, W.A. et al. Gas Chromatography 193 1966.

196. James, A.T., Martin, A.J.P. Biochem. J. 50 679 1952.

197. James, A.T., Martin, A.J.P. Biochem. J. 52 238 1953.

198. James, A.T. Biochem. J. 52 242 1953.

199. Johnson, R.A.N., Douglas, A.G. Chem. Ind. 154 1959.

200. Martin, A.E., Smart, J. Nature 175 422 1955.
Liberti, A. et al. Chim. e. Ind. 38 674 1956.
Anderson, D.M.W. Analyst 84 50 1959.
Haslam, J. et al. Analyst 86 44 1961.
Flett, M., Hughes, J. J. Chromatog. 11 434 1963.
Bartz, A.M., Ruhl, H.D. Anal. Chem. 36 1892 1964.
Wilks, P.A., Brown, R.A. Anal. Chem. 36 1896 1964.

201. Research and Industrial Instruments Ltd., London.

202. Drew, G.M. Anal. Chem. 28 979 1956.
Holmes, J.C., Morrell, F.A. Appl. Spec. 11 86 1957.
Danner, W. et al. Anal. Chem. 29 1378 1957.
Gohlke, R.S. Anal. Chem. 31 535 1959.
Lindeman, L.P. Anal. Chem. 32 1742 1960.
Ebert, A.A. Anal. Chem. 33 1865 1961.
Varadi, P.F. I.S.A. Intern. Symp. on G.C. pp 133-140 1961.
Henneberg, D. Z. Anal. Chem.
Henneberg, D. Gas Chromatography 191 1962.

203. Kokes, R.J. et al. J. Amer. Chem. Soc. 77 5860 1955.
Piesz, P., Welrbach, K.E. J. Phys. Chem. 62 6 1958.
Wolfgang, R., Rowland, F.S. Anal. Chem. 30 903 1958.
Moussebois, C., Dajckaerts, G. J. Chromatog. 1 200 1958.
Mason, L.H. et al. J. Chromatog. 2 322 1959.

204. James, A.T., Piper, E.A. J. Chromatog. 5 265 1961.

205. Behrendt, S. Z. Phys. Chem. 20 367 1959.

206. Janak, J. et al. Chem. Listy. 52 896 1957.
Nedorost, M. Chem. Listy. 50 317 1956.

207. Reynolds, G.F. Analyst 88 493 1963.

208. Gough, T.A., Peaver, M.E. Polarography 1964 1017.

209. Purnell, J.H. Gas Chromatography 270 published by Wiley 1962.

210. Peaver, M.E. J. Chem. Soc. 4540 1962.

211. James, A.T. Vapour Phase Chromatography 129 1956.

212. James, A.T., Martin, A.J.P. Analyst 77 915 1952.
McInnes, A.G. Vapour Phase Chromatography p.304 ed Desty, D.H. Academic Press 1957.

213. Smith, V.N. Gas Chromatography 316 1962.

214. Bevan, S.C., Thornburn, S,B.P.

215. Walsh, J.T., Rosie, D.M. J. Gas Chromatog. 5 232 1967.
(published subsequent to completion of this chapter.)

CHAPTER 4.

Evaluation of the Mass Detector.

4.1 Discussion - General.

"An ideal detector for quantitative analysis might consist of a minute balance carrying a cylinder loaded with adsorbent, so that all components are totally adsorbed as they leave the chromatographic column"[1]. This summarises a statement made by Martin at the International Gas Chromatography Symposium in 1962. At the same symposium Thorburn[2] described an experimental set-up which was in effect identical with Martin's description of an ideal detector. The possibility of continuously weighing the components of a mixture emerging from a column was thus shown to be experimentally possible. Lovelock, whilst acknowledging that weighing would offer a means of detection, regarded the procedure as too laborious to be of any practical value[3].

The preliminary experiments on mass detection carried out by Bevan and Thorburn[4], were conducted on an ordinary direct reading laboratory analytical balance. On one pan of the balance was placed a vessel containing an involatile solvent. Effluent from the chromatographic column was passed into the solvent, and the presence of a component in the carrier gas was detected by an increase in weight of the vessel, due to dissolution of the component in the solvent. By plotting a graph of the weight increase of the vessel against the time from injection of the sample, an integral chromatogram was obtained. Each step height was related to the weight of component present in the mixture. This simple, and very successful experiment was the first step in the development of a quantitative detector for gas-chromatography, in which the qualitative nature of the sample does not have to be known. A detector whose response is based solely on weighing the components as they emerge from the chromatograph will have a predictable response, a linear dynamic range equal to its dynamic

range, and since an integral response is recorded, functions at its own integrator, thus eliminating errors arising from the measurement of peak areas. In addition it is not necessary to know the amount of sample injected.

The experiment described above, did however, give rise to two errors. Due to the volatile nature of the solute, there was a continuous slow loss in weight of the vessel, resulting in a drifting baseline. More serious was the buoyancy effect between the absorbent liquid and the gas inlet tube, the depth of which varied during a run. The first error was eliminated by using a chemically reactive absorbent in place of the solvent. For example the analysis of acidic materials requires a vessel containing potassium hydroxide solution. This severely limits the type of sample which can be analysed, and to extend these limits, concentrated sulphuric acid was used, which will absorb amines, alcohols, ethers etc. The second error was eliminated by causing the column effluent to flow over the surface of the absorbent liquid in the vessel, rather than into the bulk of the liquid.

4.2.1 Microbalances - Discussion.

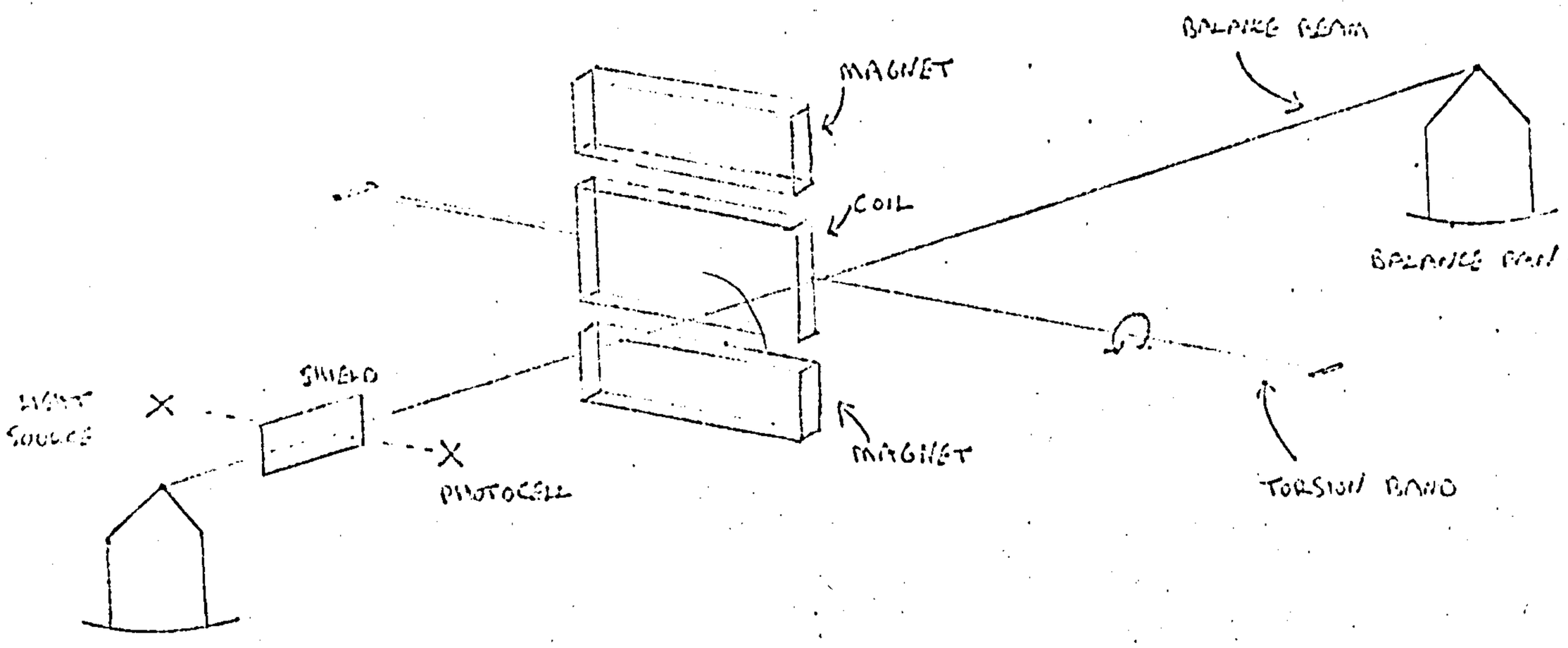
In the form described above the detector is not particularly convenient for use in gas chromatographic analysis for a number of reasons. The use of an ordinary laboratory balance limits the minimum sample size which must be injected into the column to obtain a reasonable response. With a good four-place balance, the limit of detection is about $\frac{1}{2}$ mg, so that sample sizes of at least 10 µl are required. Chromatograms must be plotted by hand, although automatic recording of the chromatograms was achieved using a Stanton recording thermobalance. With a view to overcoming the restrictions imposed by the balance system, a number of other balances have been considered. A balance was required which could weigh differences at least the order of 10µg (about 1 µl charges can then be used). Microbalances have been used for many years, particularly as an aid in the study of surface

phenomena, notably by McBain[5] who used a silica helical spring balance, and Gregg[6] who used a beam type balance. Helical spring balances have in general, only a small weight capacity, and are very fragile. The use of metal springs has enabled more robust balances to be constructed, but they are more temperature dependent than silica balances[7]. Spring balances are generally used in vacuo: they are not readily adaptable to automatic recording of weight changes. The beam balance has a greater capacity than the spring balance, and is far more robust. In the balance designed by Gregg[6], the adsorbent is held in a small container suspended from one end of the balance arm, and from the other end of the arm is suspended a small solenoid, placed between a free standing outer solenoid. By adjusting the current in the outer solenoid the balance arm can be maintained in its null position as the adsorbent weight increases; weight changes are proportional to the solenoid current changes. The balance can be adapted for the automatic recording of weight changes[8].

Surveys of microbalance design and technique have been published[9], with particular reference to operation in vacuo, and developments in microbalance technique are published annually[10]. Automatic recording electromicrobalances have been described in the literature[11, 12], and some are available commercially[11, 13]. These balances all operate on the same principle: the balance beam is attached at right angles to a coil placed between the poles of a permanent magnet. The coil is held in position by a torsion band. At one end of the balance beam is suspended the sample, and the other end is used to attach tare weights. To one side of the end of the beam containing the sample is placed a small lamp, and on the other side of the beam, a photocell. When the beam is balanced, a shield attached to the beam between the light source and the photocell, prevents illumination of the photocell. When a weight change occurs, the balance beam moves, and light reaches the photocell. The output from the photocell is fed via a servo-amplifier to the coil, and restores the beam to its equilibrium position.

Figure 4.1

The Electromicrobalance:



The light falling on the photocell is proportional to the beam deflection, and hence to the weight change. The arrangement is illustrated in figure 4.1.

The piezoelectric effect has been used to detect weight changes. The frequency of a piezoelectric crystal depends on the mass of the crystal, and hence changes in frequency can be used as a measure of the weight changes of the crystal caused by sorption or desorption of material. Quartz crystal microbalances have been developed by several workers[14], and a gas chromatographic detector using the principle has been described[15] (see section 3.17).

The electrolevel[16] detects movement from the horizontal plane in the same manner as a conventional spirit level. A glass envelope is almost filled with a solution of lithium chloride in alcohol. The envelope contains three electrodes and the solution between the electrodes forms two arms of a Wheatstone bridge. A quantitative measure of the movement out of the horizontal plane (and hence a weight change) is obtained by measuring the change in conductance of the solution resulting from a change in position of the air bubble.

An electromicrobalance model RG, manufactured by the Cahn Instrument Co., was considered. The balance has mass ranges from 1 mg fsd to 1 g fsd. The lower ranges are suitable for the detection of samples usually encountered in gas chromatography. The capacity of the balance is 1 g for a precision of $\pm$ 0.2 µg and 2½ g for a precision of $\pm$ 1 µg. Weight changes are recorded automatically, and provision for a recorder scale expansion to 20 µg fsd (1 g load) and 100 µg fsd (2½ g load) is made. The Cahn balance has been used successfully by Bevan and Thorburn, and has been incorporated into a Pye Panchromatograph. The main object of this work was to show that weighing of components on the microgram scale could be achieved as readily as weighing on the milligram scale, described at the Gas Chromatography Symposium in 1962. In addition to this the mass detector was used in conjunction with a Gow-Mac gas density balance to demonstrate the

possibility of obtaining molecular weights of unknown materials[17]. The adoption of a balance, such as the Cahn or Sartorius electromicrobalances for mass detection, suffers from one overriding disadvantage: it is very expensive compared with all existing commercially available detectors. It was necessary therefore to consider cheaper electromicrobalances which subsequently became available, even though the performance of the Cahn balance was satisfactory.

The work undertaken by the Author has been carried out with the following objects:

(i) to test suitable (i.e. cheap and reliable) apparatus for detecting weight changes,

(ii) to confirm the suitability of the principle of mass detection as a means of detecting vapours and gases,

(iii) to carry out a systematic investigation into the properties and behaviour of the mass detector,

(iv) to investigate the performance of the mass detector for quantitative analysis,

(v) to study applications of the principle of mass detection, e.g. the determination of molecular weights, and the calibration of conventional detectors.

Two electromicrobalances were investigated with a view to their use in mass detection:

(i) The balance made by Research and Industrial Instrument Company[18]. The operating principle is similar to that described above (figure 4.1). A mirror is attached to the torsion band, which reflects light from a small bulb to a pair of photocells, between which is placed a splitting device. In the null position, an equal light intensity reaches the two photocells, but when a weight change occurs, the balance beam is deflected, the torsion band, and hence the mirror is twisted, and one photocell receives a greater intensity of illumination than the other.

The resulting current is fed to a servomechanism, and the balance beam is restored to its null position. There are eight different mass ranges, the most sensitive of which is 1 mg fsd. The mass difference between the two balance pans is read from a helical potentiometer, calibrated in milligrams. The value is obtained by rotating the potentiometer dial until zero deflection is observed on a moving coil galvonometer. The potentiometer can be read to about 0.2 of a division, i.e. to 0.2 µg on the 1 mg range. The balance output can be fed to a potentiometric recorder; weight changes are observed as a recorder deflection instead of being obtained from the potentiometer dial. The maximum capacity of either balance pan is 2½ g and the maximum difference in weight between the pans is 200 mg, which is adequate for chromatographic purposes. A recorder scale expansion to 100 µg and 10 µg fsd is incorporated. There is no temperature compensating device built into the balance, and the temperature coefficient is about 1 µg per ^{o}C.

(2) The balance made by Combustion Instruments[19].

In the C.I. balance, two photocells, which form part of a Wheatstone bridge network, are placed to one side of the balance arm, and are illuminated directly by a small bulb, placed on the other side of the arm. A shield is attached to the arm, which when in the null position, allows equal illumination of the two photocells. Balance arm movement caused by weight changes, will result in unequal illumination of the photocells, and unbalance of the Wheatstone bridge. The bridge is restored to balance by a servomechanism. The balance is available with a minimum range of 250 µg fsd and a maximum of 100 mg fsd. Weight changes can be read directly from a moving coil micro-ammeter, or by means of a potentiometric recorder. A backing off control (i.e. a means of electrically taring the balance) is provided. Calibration of the balance must be performed on each range individually. The maximum load per balance pan is 1 g.

A balance for incorporation into a mass detection system, must itself satisfy all, or at least most of the conditions required for an ideal detector. The conditions have been discussed in detail in Chapter 2 and in view of their importance, some of these conditions are summarised below. The balance must respond linearly to weight changes, and be able to detect weight changes in the microgram region. The balance must be robust, reliable, not excessively expensive, and readily available commercially. The response time must be less than about 2 sec.

An experimental study of the performances of the R.I.I.C. and C.I. balances was undertaken, with a view to confirming their suitability for use in gas chromatographic detection.

4.2.2. Microbalances - Experimental.

4.2.2a. The R.I.I.C. Balance.

Experiments were designed to check the performance of the apparatus used simply as a balance, in the absence of any gas chromatographic equipment. Primary calibration of the balance was performed on the 10 mg range with a standard weight of 9.837 mg. Using a number of different weights and weighing each of these on each range of the balance, consistent results were obtained; i.e. calibration of the 10 mg range satisfactorily calibrates all the remaining ranges at the same time. An example is given in table 4.1.

Table 4.1

Range (mg)	Observed Weight (mg) (helipot readings)	
200	5.6	
100	5.5	
50	5.45	
20	5.40	
10	5.54	
5	5.515	0.710
2	5.554	0.718
1	5.593	0.719

The helical potentiometer can be read to $\pm$ 1 µg on the 10 mg range.

The linearity of the potentiometric recorder used in conjunction with the microbalance was checked. The recorder was a Honeywell twin channel (1 mV and 10 mV fsd) instrument. A decade potential divider to which was attached to $1\frac{1}{2}$ V battery, was used to inject accurately known voltages into the recorder. Each voltage was calculated, checked on a valve voltmeter, and compared with the percentage full scale deflection of the recorder. The results are given in table 4.2.

Table 4.2
Linearity of Honeywell Recorder - 10 mV Channel.

Recorder % fsd	Deflection mV	Resistance ohms	Calculated Deflection mV	Valve Voltmeter Reading mV
5.0	zero	zero	zero	zero
21.0	1.60	10.00	1.60	1.59
37.0	3.20	20.00	3.20	3.20
53.0	4.80	30.00	4.80	4.83
69.0	6.40	40.00	6.40	6.43
85.0	8.00	50.00	8.00	8.05
98.0	9.30	58.00	9.28	9.34
5.0	zero	zero	zero	zero

Voltage of battery = 1.60 V.

Total resistance of the potential divider = 10 KΩ ∴ the calculated potential is:

$$\frac{1.60 \times 10^{3}R}{10^{4}} \quad \text{i.e.} \quad 0.16R$$

where R = potential divider setting (ohms).

The precision of the resistors in the decade box = $\pm$ 0.1%.

The maximum observed error on the recorder = 0.2% fsd.

A similar experiment was carried out on the other channel of the recorder. This was a 1 mV fsd range, and was used to measure the output of detectors placed in series or in parallel with the mass detector.

Table 4.3
Linearity of Honeywell Recorder - 1 mV Channel.

Recorder % fsd	Deflection mV	Resistance ohms	Calculated Deflection mV	Valve Voltmeter Reading mV
5.3	zero	zero	zero	zero
21.0	0.157	1.00	0.160	0.158.
37.0	0.318	2.00	0.320	0.325
53.1	0.478	3.00	0.480	0.485
69.1	0.638	4.00	0.640	0.645
85.2	0.799	5.00	0.800	0.809
5.4	zero	zero		

The precision of the resistors = $\pm$0.5%. The maximum observed error in the recorder is 2%.

The linearity of the potentiometric recorder is satisfactory on both the 10 mV and the 1 mV channels.

The 10 mV channel of the recorder was used to determine the linearity of the balance response on any given range. The 1 mg balance range is the most useful for chromatographic work, and the results on this range for a number of different weights, are given in table 4.4.

Table 4.4
Linearity of Electromicrobalance - 1 mg range.

Recorder Reading (µg)	Balance Reading (µg)
370	374
397	397
401	405
470	470
663	665
739	740

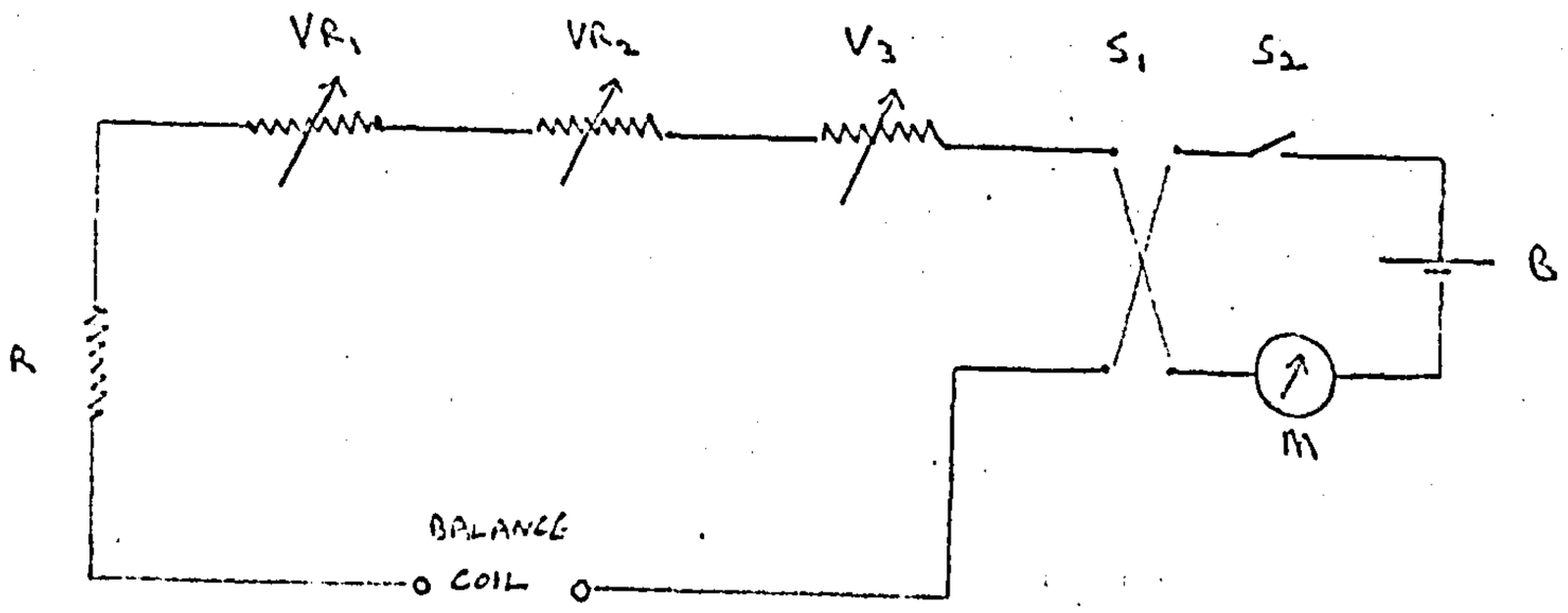
On the 1 mg range, 1 µg is represented by 0.1% fsd of the recorder (0.3 mm), i.e. the recorder readings are $\pm \frac{1}{2}$ µg. The maximum observed error is 1%. Comparison of recorder readings and balance potentiometer readings on higher blanace ranges, over a wide weight range gave

negligible discrepancies. Deviations are random, and do not depend on the percentage deflection of the recorder. This simple system cannot be used conveniently in conjunction with the mass detector as there is no means of backing off the weight increase electrically after completion of a run. The operation must be performed mechanically by adding counterweights to the balance. This is clearly inconvenient, and in view of the smallness of the weight changes involved is rather difficult. The balance is fitted with a means of zero suppression, such that by using the helical potentiometer in conjunction with the potentiometric recorder, the total weight of a sample is represented by the sum of the potentiometer reading and the recorder deflection (after calibration). Since the potentiometer setting and the recorder deflection operate in opposition, it was proposed that the potentiometer be used to back off excess weight after each chromatographic analysis. Calibration using this method was satisfactorily carried out for a number of different potentiometer settings. However, it was found that the maximum weight which could be backed off using this procedure was of the order of 2 mg on the 1 mg range. Thus the method can only be applied to a small number of runs before mechanical re-balancing becomes necessary. An attempt was made to overcome this limitation by using the balance on the 10 mg range with the ten fold scale expansion provided, i.e. the recorder deflection remains at 1 mg fsd, but the potentiometer can now be used to back off up to 20 mg. Two disadvantages arise from this procedure: balance sensitivity is decreased tenfold, and the recorder amplifier gain must be decreased considerably to minimise noise, thus increasing the deadband. The recorder also appeared overdamped, even at optimum damping control adjustment. This difficulty could be overcome to some degree either by using a recorder of lower impedence (e.g. Kent type 2M - 5KΩ) or by introducing a greater input impedence with a resistor network. The maximum impedence of the Honeywell amplifier is 25KΩ. Since all difficulties stem from the limited use of the backing off system, a

new means of backing off was devised in which a small current was applied through the coil of the balance mechanism, from a stable supply. The current was proportional to the weight backed off. The backing off device was designed such that the backed off weight was continuously variable from 3 μg to 5 mg. The current was supplied by a mercury cell, via a number of potentiometers, acting as coarse, medium, and fine adjustments, to the balance coil. A circuit diagram is shown in figure 4.2. A mercury cell was used since it offers a cheap and simple means of obtaining a small stable current. The backing off circuit does not contribute significantly to the overall instability of the balance. It is still possible to back off to a limited extent with the balance potentiometer and no interdependence between this and the new backing off unit was detected. Whereas the degree of backing off using the balance potentiometer depends directly on the mass range setting on the balance, this new unit is independent of the range setting. The backing off unit incorporates a milliammeter calibrated in micrograms. The linearity of the unit was checked, and found to be perfectly satisfactory. There is no falling off of performance of the balance up to a current of $\frac{3}{4}$mA (5 mg), but above this value slight drift was observed. The backing off unit was calibrated by the following means. A small piece of wire was weighed on the microbalance, using the potentiometric recorder. The current necessary to return the recorder to zero was measured on the backing off meter. This experiment was repeated for a number of different weights, and a graph plotted of weight backed off against current applied to the coil (figure 4.3). A straight line was obtained of slope 0.70 mg mA^{-1}. The backing off unit has proved of great value, not only in performing its intended purpose, but also in the calibration of very sensitive mass ranges which have subsequently been built into the electromicrobalance. In later work, the backing off unit was simplified by replacing the meter (M) and current control resistors (VR_1- VR_3) by a ten turn helical potentiometer fitted with a dial

Figure 4.2

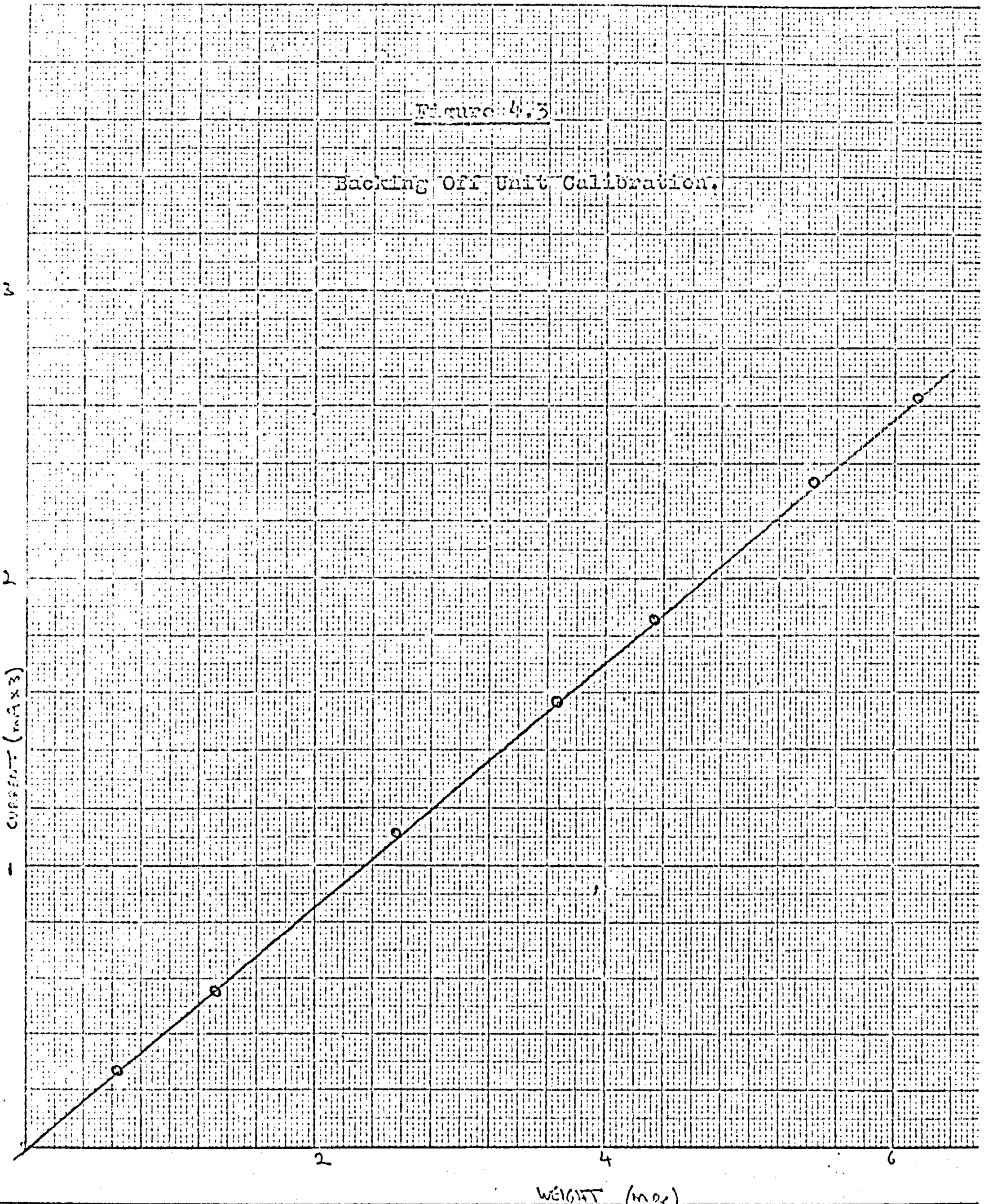
Backing Off Unit.



B	MALLORY CELL	1.3½ VOLTS
M	MOVING COIL METER	FSD 1mA
R	CURRENT LIMITING RESISTOR	1.2kΩ
S_1	DPDT SWITCH	
S_2	ON/OFF SWITCH	
VR_1	CURRENT CONTROL - COARSE	500kΩ
VR_2	" " MEDIUM	5kΩ
VR_3	" " FINE	500Ω

Figure 4.3

Backing Off Unit Calibration.



calibrated in micrograms.

Neither the recorder itself, nor the balance unit was fitted with a means of marking on the chromatograph, injection points or other relevant data. Accordingly an event marker was fitted to the recorder. This comprised a potential divider circuit driven by a 1½ volt pen battery and was designed to give 10% of full scale deflection on the recorder chart. The marker was actuated with a push-to-make switch mounted on the front panel of the recorder.

In general the 1 mg range is satisfactory for gas chromatographic analysis, where samples of the order of 1 µl are under analysis. However in cases, either where trace components are present, or analysis of samples much less than 1 µl is desired (e.g. to obtain better column performance, or due to scarcity of sample), it is useful to be able to use more sensitive ranges. Several methods of obtaining more sensitive (i.e. lower) ranges have been tried. The only method available on the original balance unit is to use the tenfold and hundredfold scale expansion device. The X10 multiplier was found to give a satisfactory and linear response on all ranges, but the effects noted previously (page 111) were observed. Noise was eliminated by introducing a 100 µF capacitor across the recorder input, but response time was increased. The X100 multiplier was not found satisfactory since noise was excessive. An alternative method of obtaining a lower series of ranges is to place a shunt across the balance coil. For example, with a coil of resistance 5Ω, if the total resistance is changed to 0.5Ω (i.e. a 0.56Ω shunt), then a tenfold increase in the sensitivity of all ranges will occur: the lowest range becomes 100 µg. This method was found to give satisfactory results on the basic ranges from 200 mg to 10 mg, but for the more sensitive basic ranges, the method was unreliable and had to be rejected. The most successful means of lowering the ranges was by changing the values of the resistors in the existing ranges. The original 2 mg range has been modified to give either 250 µg or 100 µg fsd, the required range

being selected by a dpdt switch. Calibration of such sensitive ranges cannot be carried out successfully using small lengths of wire as secondary standards. The method adopted was to use the backing off unit as a standard, since it has been calibrated and its linear response shown (figure 4.3). In addition each weight was checked using the 1 mg range. The 250 µg range performed entirely satisfactorily (see figure 4.4) but it was not possible to obtain reliable readings on the 100 µg range, since the calibrated settings continuously drifted.

The conclusions reached are that the balance is satisfactory on the 1 mg and 250 µg ranges. The X10 scale expansion facility may be used on both of these settings to obtain the new ranges of 100 µg and 25 µg respectively. Some results are given in table 4.5.

Table 4.5.

Weight of sample (µg) 1 mg range	1 mgX10 range	Weight of sample (µg) 250 µg range	250µgX10 range
52	51.5	13	12.6
75	75.0	15	15.4
90	90.0	18	17.3
92	93.0	23	22.6

The repeatability of the response of the balance-recorder system to a given weight has been investigated. A known weight was placed on one of the balance pans, and its weight recorded 14 times, over a period of eight hours, on the 1 mg range. The step heights on the recorder chart were measured both when the recorder was switched in and out of the balance circuit, i.e. step heights were measured for increasing and decreasing pen excursions. The results are summarised in table 4.6, and in the form of a histogram (figure 4.5) of interval 0.2 mm (0.7 µg). The results show a distribution approaching a normal distribution.

Figure 4.4

250 µg Range Calibration.

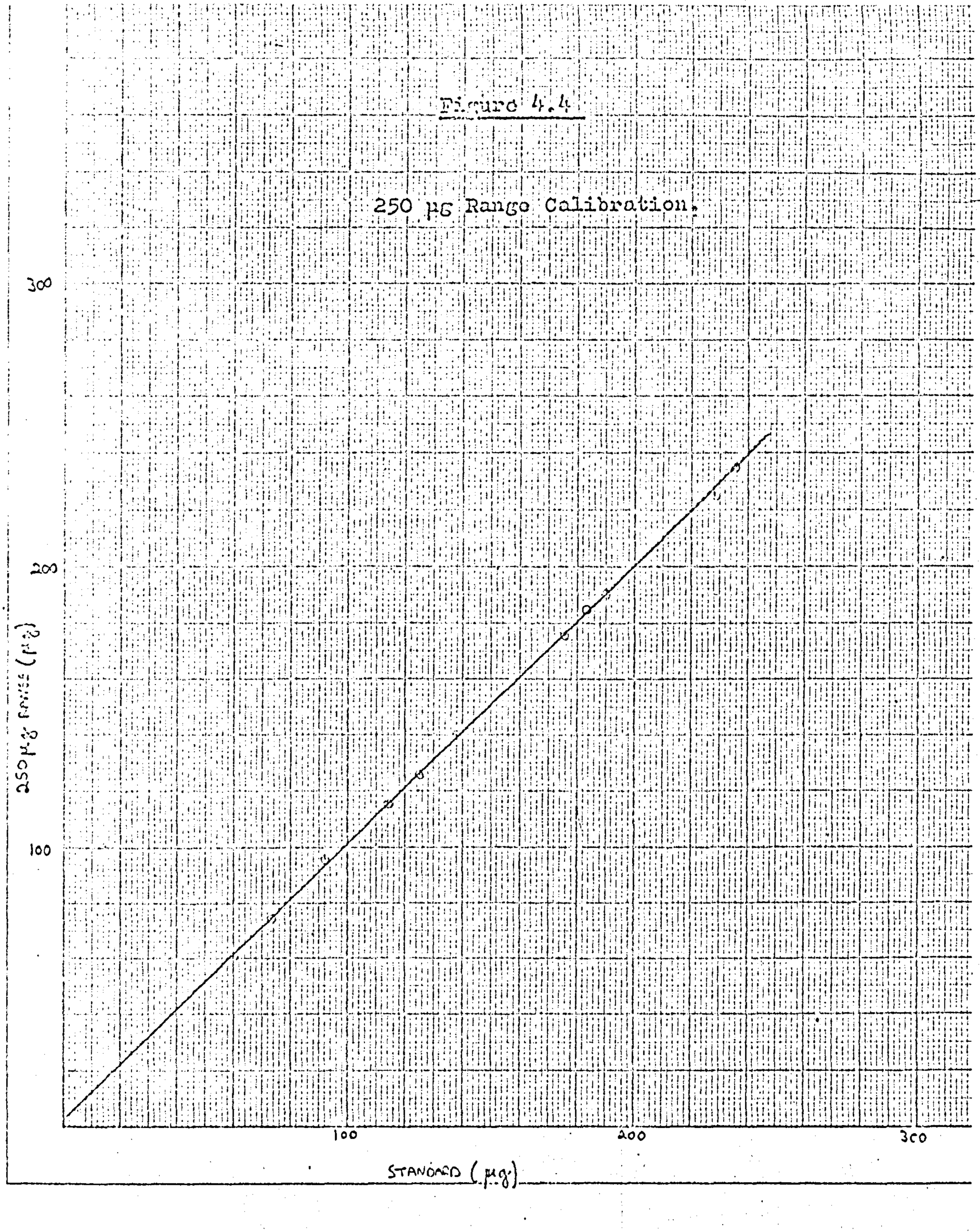


Figure 4.5

Recorder Deflection Repeatability.

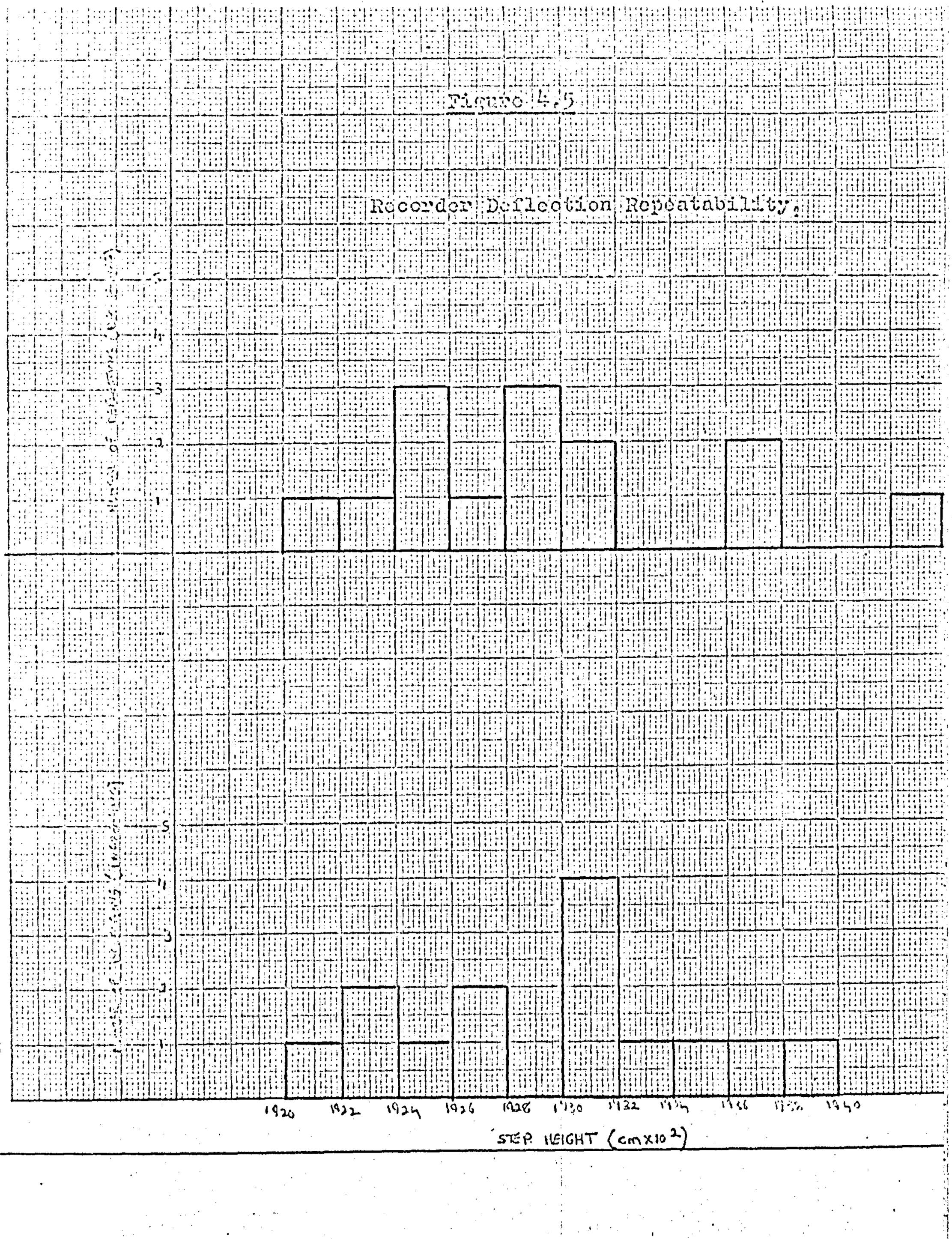


Table 4.6

	Standard Deviation	Coeff of Variation
True mass (measured by balance potentiometer) 685.0 µg	-	-
Recorder deflection (increasing) mean value 688.85 µg	2.66 µg	0.39%
Recorder deflection (decreasing) mean value 688.80 µg	1.41 µg	0.20%

There was a positive bias of about 4 µg (0.6%) of the recorder readings compared with the balance potentiometer readings. The step heights tended to show a very slight increase with time, which can be attributed to a temperature increase during the period of the experiment. Consider the first three sets of readings, and the last three sets of readings (i.e. a total of 12 readings):

Table 4.7

	Mean detected weight (µg)
First set of readings	687.12
Last set of readings	693.01
Difference	5.89
% Difference	0.86

The temperature coefficient of the balance is about 1 µg per ^{o}C. Assuming a (maximum) temperature change of 4^{o}C during any given day, **(in the laboratory in which the experiment was carried out)** the maximum error that can arise is 4 µg, i.e. 0.4% of the recorder fsd, and a 0.6% weight change in this particular experiment. Further error can arise in the actual measurement of the step heights. A steel ruler was used, calibrated at 20^{o}C. Temperature variations of $\pm$5^{o}C will have no detectable effect on the accuracy of the ruler and will not therefore contribute to any deviations observed. Assuming that the ruler can be read to the nearest 0.2mm, this represents a possible error of 0.075% fsd and 0.11% (0.75 µg) in this particular experiment. Apparent step heights will change with changes in the water content of the chart paper, i.e. with relative humidity, but this will be virtually constant

for the duration of the experiment.

The maximum source of error is due to temperature changes between calibration checks, but this is only likely to amount to about $\frac{1}{2}$% fsd, even with a $4^{\circ}C$ temperature change.

Balance Stability.

On the 1 mg range and higher (i.e. less sensitive ranges) noise was indetectable; drift, measured on the 1 mg range, over 16 hours, was 0.02% per hour. The maximum temperature variation over the duration of the experiment was $1^{\circ}C$.

The noise levels of the balance on various ranges were measured and are listed in table 4.8.

Table 4.8

Range (fsd)	Noise Level (% fsd)	Limit of Detection (µg)
1 mg	not detectable	4
250 µg	" "	1
100 µg	0.2	0.4
25 µg	0.5	0.25
10 µg	1.8	0.4

The limit of detection is greater on the 25 µg range than the 10 µg range, as a result of the lower noise level, and is about $\frac{1}{4}$ µg. (Calibration on the 10 µg range was unsatisfactory, and this range was not used for any subsequent work).

The performance of the balance is completely satisfactory when there is a negligible load (i.e. a few milligrams) on the balance pans. Experiments were conducted to see the effect of progressively increasing the total beam load, up to its maximum of 5 g ($2\frac{1}{2}$ g per pan) using the 1 mg range. The weight on each pan was increased by 50 mg increments, and a small standard weight (430 µg) added after each increment. Graphs of the observed weight of the standard weight against the total weight on one balance pan showed that the balance response decreased as the load increased. Up to a load of about $\frac{1}{2}$ g the response was constant.

The Effect of Total Load on Balance Response (see page 116).

Figure 4.6

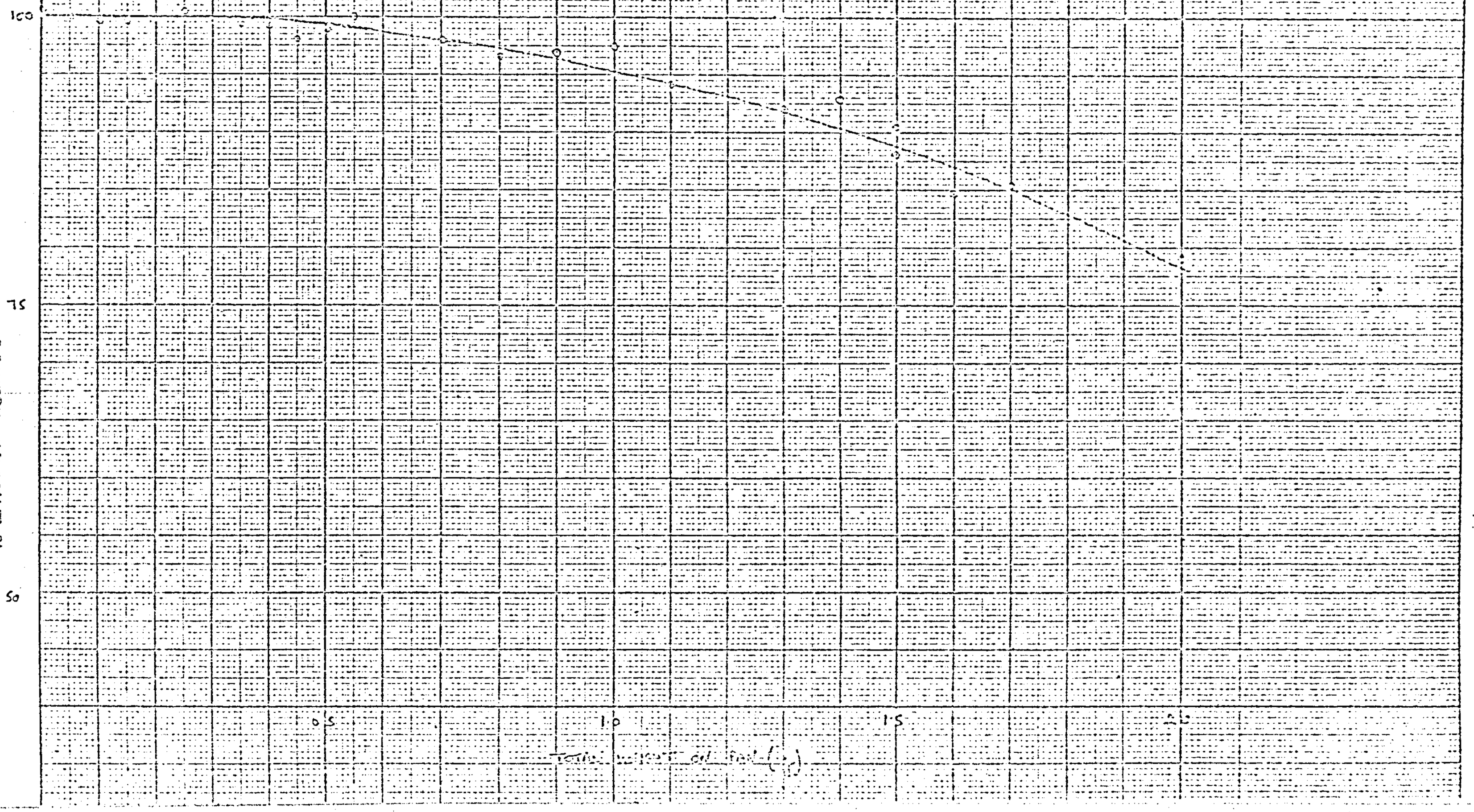
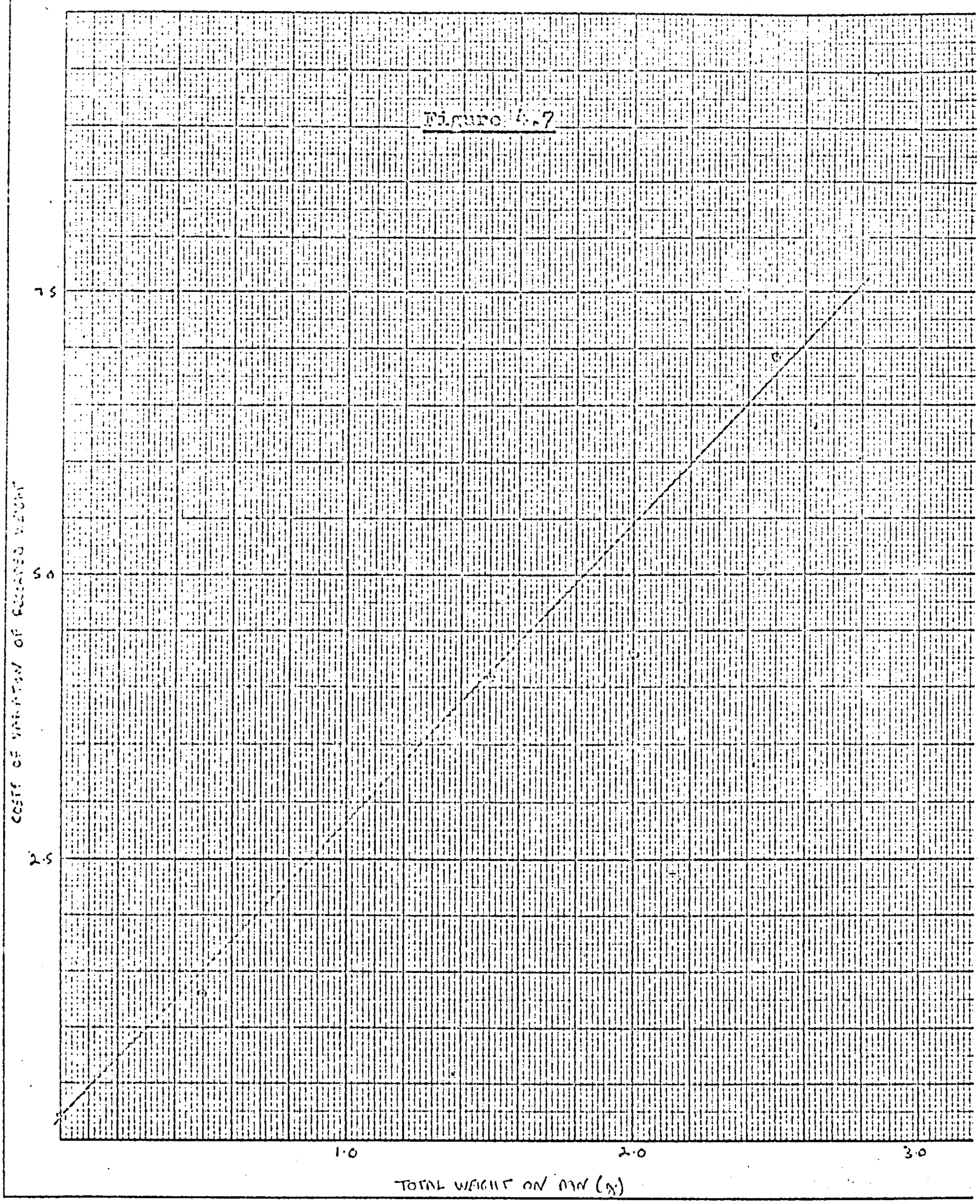


Figure 4.7



The Effect of Total Load on Repeatability of Balance Response (see page 117).

For loads over $\frac{1}{4}$ g the response of the balance progressively decreased. The results are exhibited in more general terms by figure 4.6: at zero load it is assumed that 100% response is observed. In general the effect of changing the load by as much as $\frac{1}{4}$ g has no serious effect on calibration, and any effect can be entirely eliminated by calibrating the balance with the load in place, rather than before the load is added. The repeatability of readings at various total loads for a standard weight, was measured, and the coefficients of variation calculated. Figure 4.7 shows how the coefficient of variation of the recorded weight increases, as the total load is increased, when the balance is calibrated with zero load.

4.2.2b The C.I. Balance.

A similar series of experiments was carried out on this balance to determine its reliability. It was necessary to calibrate each range in turn, and this was done using ASA class M weights. The balance takes about 4 hours to stabilise (the R.I.I.C. balance takes 15 minutes). Excessive noise was reduced by incorporating at 5000 μF capacitor across the balance input. The balance was particularly unstable on the 250 μg range. Operation of the balance on AC mains gave on all ranges far greater noise (1% fsd $2\frac{1}{2}$ mg range), than the R.I.I.C. balance, but battery operation was satisfactory (0.2% fsd). Drift on the $2\frac{1}{2}$ mg range was measured overnight and was of the order of 1 μg per hour (0.04% fsd).

The relative merits of the two balances, in the form supplied by the manufacturers, was listed in table 4.9.

Table 4.9

Comparison of R.I.I.C. and C.I. Electromicrobalances.

	Advantages	Disadvantages
R.I.I.C. Balance.		
	Negligible drift and noise	No electrical backing off over 2 mg.
	Calibration only required on any one range.	Temperature dependent.
	Maximum load per pan 2½ g.	No direct weight readout.
		Minimum range 1 mg.
		Balance is fairly bulky.
C.I. Balance.		
	Direct weight readout.	Drift and noise appreciable.
	Minimum range 250 µg.	Temperature dependent.
	Balance is compact.	Maximum weight per pan 1 g.
	Backing off device incorporated.	Calibration required for each range.

Subsequent to this work both R.I.I.C. and C.I. have introduced balances of improved specification.

4.2.3 Microbalances - Conclusions.

The cost of the balances is of the same order. The R.I.I.C. balance is more suitable for incorporation into a gas chromatograph, since it is far more stable than the C.I. balance used in this comparison. A backing off unit can be readily added to the R.I.I.C. balance at negligible cost, and more sensitive ranges can be added, with minor modifications to the balance. The overall performance is excellent and this balance was selected for the remainder of this investigation on the Brunel mass detector.

4.3.1 Detecting Elements - Discussion.

For a completely non-selective detector, a material is required which will adsorb, to the same extent, and preferably completely, all materials in the vapour phase, irrespective of their physical and chemical nature. In addition conditions must be chosen such that the carrier gas does not interfere with the process, and that desorption

of sample does not follow adsorption to any appreciable extent. The capacity of the adsorbent must be such that continual adsorption of materials is possible for a reasonable time, without deterioration of the efficiency of adsorption. If these conditions can be fulfilled, a detector will be obtained which responds directly on a weight basis and requires no calibration against standard adsorbates, or with respect to concentration for any given adsorbate.

The only material which is likely to satisfy these conditions is activated charcoal. Provided that adsorption is carried out at a suitable temperature and pressure, physical adsorption on the charcoal will predominate, and hence the detector will be completely non-selective. Chemisorption is favoured by high temperatures and pressures, so that it is to be expected that by operating a detector at atmospheric pressure and at room temperature or below, non-specific adsorption will occur. Equilibrium is rapidly reached and is readily reversible, so that the continuous passage of carrier gas into a charcoal detector, will at first give rise to a weight change, which becomes progressibely less as equilibrium is approached, until finally a constant weight is obtained, (i.e. a straight baseline is observed). The maximum amount of any given material which active charcoal can adsorb depends on the critical temperature (and hence the boiling point) of the adsorbate. By using a permanent gas such as nitrogen or hydrogen as carrier, the extent to which this is adsorbed by the charcoal is negligible compared with the amount of an organic compound (boiling above say $0^{\circ}C$) that can be adsorbed. In effect therefore no interference in the adsorption of organic materials, should be caused by the carrier gas.

It is essential that the uptake of adsorbate by charcoal increases linearly with concentration in the carrier gas, for a linear detector response. This condition can only be fulfilled up to a given weight of adsorbate, determined from the adsorption isotherm. The majority of organic vapours obey Type I isotherms when adsorbed on active charcoal so that provided the adsorbate weight does not exceed that required for

monolayer formation, complete uptake of adsorbate can occur; however it is likely that quantitative uptake of material will be affected by subsequent desorption before the monolayer capacity is reached. The capacity of the adsorbent toward a given adsorbate, under fixed conditions, is directly proportional to the weight of adsorbent present. The upper limit of detection of a gas chromatographic detector can therefore be extended simply by increasing the weight of charcoal in the detecting element.

Specific adsorbents could be used for the detection of certain materials. For example the use of a 4Å molecular sieve would enable the specific detection of straight-chain hydrocarbons to be accomplished.

4.3.1a The Design of Detecting Elements.

A practical detecting element must satisfy the following conditions. It must be light (less than 1½ g), such that it is within the capacity of the microbalance. It must be simple to construct. A granular adsorbent must be contained within an impervious material, to act both as an adsorbent support, and to promote effective trapping of all effluent prior to adsorption. The geometry of the adsorbent support must be such that there is a maximum amount of adsorbent per unit area of support. A suitable support is aluminium foil, and the majority of detecting elements have been made using this material. The adsorbent is attached to the aluminium foil with an adhesive. Since this must result in loss of active sites, an alternative support of polystyrene into which the particles of charcoal are imbedded by prior softening of the polystyrene is suggested as a possibility. No experiments were carried out to examine the suitability of this support. Loss of active sites would still occur, but to a lesser extent than with adhesives. The possibility of using fine wire mesh into which the charcoal is embedded has also be considered, but metal mesh is too heavy, and fibres lack rigidity.

The detecting elements must have a small effective dead volume to minimise resolution losses and step distortions. This requirement is

at variance with the requirement of a large surface area of adsorbent, so that a compromise must be reached. The following detector geometries have been considered, and some have been experimentally investigated (see section 4.6.1).

(i) Spherical support, with access for carrier gas. This satisfies the condition of minimum volume and maximum surface area, but was rejected for practical reasons.

(ii) Cylindrical support, open either at the top or bottom end: simple to construct.

(iii) Various modifications of the basic cylindrical design to encourage efficient trapping, and to minimise the total element weight.

(iv) Tray design, to decrease the dead volume of the element. Such detectors contain insufficient charcoal to give a detector of reasonable capacity.

4.3.2. The Construction of Detecting Elements.

Mass detecting elements are constructed from aluminium foil, the inside of which is lined with charcoal. The majority of the elements are in the form of cylinders, closed at one end.

A sheet of $1\frac{1}{2}$ thou aluminium is cut to the appropriate size for the cylinder side. It is lightly coated with Araldite epoxy resin adhesive, which is mixed with n-butyl alcohol to promote even spreading This is weighed, coated with an even layer of charcoal of a known particle size range, and reweighed. It is then wrapped round a cylindrical former and placed in an oven at about 200°C to evaporate the alcohol and cure the adhesive. The closed end of the cylinder is made in an analogous manner, and attached to the cylinder itself when dried. A suspension wire of 42 SWG is attached to the top of the cylinder. Typical detecting elements, drawn approximately full size are shown in figure 4.8. Table 4.9 gives the details of all detectors used in this work.

Figure 4.8

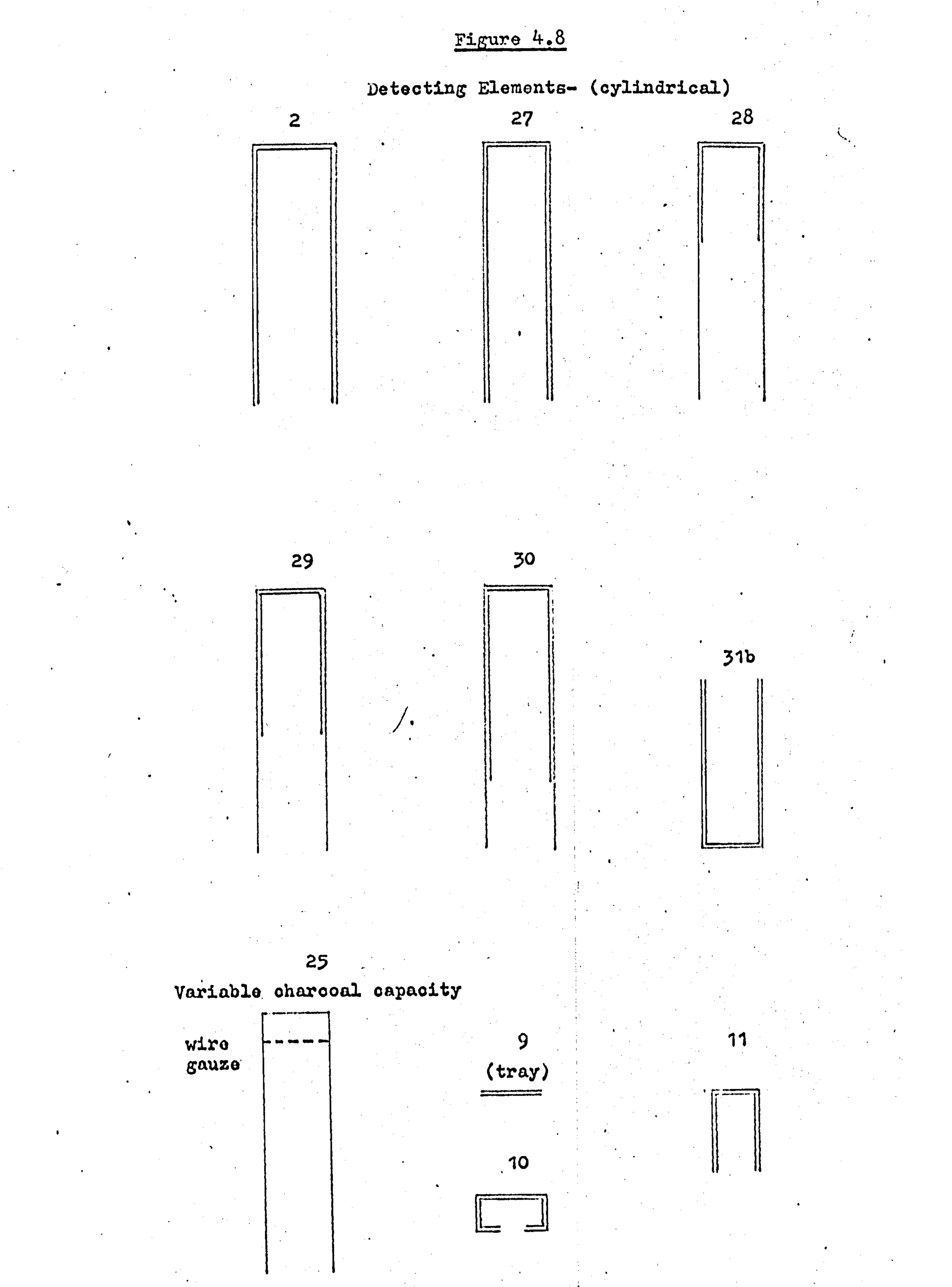

Detecting Elements- (cylindrical)
2
27
28
29
30
31b
25
Variable charcoal capacity
wire gauze
9
(tray)
10
11
Indicates element surface covered by charcoal.

Table 4.9

Detecting Elements

No.	Dimensions (cm) Lgth	Dia.	Area	Vol.	Charcoal Particle Size	Weight (g)	Total Weight (g)
1							
2	5.5	1.7	30.7	12.5	60-80	-	1.216
3	5.5	2.4	46.0	25.0	20-40	0.914	1.892
4	5.5	1.9	35.7	15.3	20-40	0.615	1.358
5	5.5	1.6	29.7	11.0	20-40	0.523	1.230
6	5.5	1.5	26.7	9.7	20-40	0.533	1.020
7	5.5	1.1	20.0	5.2	20-40	0.412	0.841
8	5.5	0.8	14.0	2.7	20-40	0.334	-
9	-	1.2	1.1	-	20-40	0.057	0.100
10	0.8	1.5	5.5	1.4	20-40	0.125	0.395
11	1.7	1.0	6.1	5.4	20-40	0.152	1.746
12	5.5	1.6	29.7	11.0	100-120	0.152	0.938
13	5.5	1.6	29.7	11.0	80-100	0.195	0.898
14	5.5	1.6	29.7	11.0	60-80	0.246	0.917
15	5.5	1.6	29.7	11.0	40-60	0.417	1.066
16	5.5	1.6	29.7	11.0	20-40	1.410	1.480
17	5.5	1.6	29.7	11.0	6-12	2.119	2.466
18	5.5	1.6	29.7	11.0	unsieved	1.902	2.452
19	5.5	1.6	29.7	11.0	12-18	1.381	1.835
20	4.1	1.6	22.7	8.2	4A sieve	-	2.733
21	5.5	1.6	29.7	11.0	40-52	0.396	1.150
22	5.5	1.6	29.7	11.0	52-60	0.343	1.034
23	5.5	1.6	29.7	11.0	60-72	0.275	1.010
24	5.5	1.6	29.7	11.0	72-80	0.244	0.943
25	5.5	1.6	29.7	11.0	-	variable	variable
26	3.7	0.8	9.8	1.9	60-80	0.106	0.353
27	5.5	1.4	24.7	8.5	60-80	0.333	0.754
28	5.5	1.4	9.9	8.5	60-80	0.156	0.592

No.	Dimensions (cm) Lgth	Dia.	Area	Vol.	Charcoal Particle Size	Weight (g)	Total Weight (g)
29	5.5	1.4	14.2	8.5	60-80	0.181	0.573
30	5.5	1.4	18.4	8.5	60-80	0.242	0.640
31a	5.0	1.3	21.8	6.6	60-72	0.238	0.584
31b	3.5	1.3	15.6	4.5	60-72	-	0.420
32	2.4	1.4	12.2	3.7	-	-	0.160

Charcoal particle size ranges are in BS mesh.

The charcoal employed in all experiments was from a single batch of "charcoal activated for Gas Analysis" supplied by Hopkin and Williams. It was crushed, and sieved into a number of different particle size ranges. The removal of the last traces of solvent in a detecting element and activation of the charcoal was carried out by heating overnight at 130°C and 0.005 mm Hg pressure. This method completely outgassed the charcoal, as no further weight loss was observed when the detector was placed for several days on a high vacuum rig. Detectors, after activation were stored (at atmospheric pressure) in an oven at 150°C.

4.3.1b Charcoal Characteristics.

The surface area of the charcoal was determined by nitrogen adsorption at -195°C on a high vacuum rig. BET plots for two different particle size ranges are shown in figure 4.9. The monolayer capacity of the charcoal V_m is given by:

$$V_m = \frac{1}{\text{Intercept} + \text{slope}} \qquad 4.1$$

from which the surface area A, per gram of charcoal is:

$$A = \frac{V_m \rho N A_m}{M_w} \qquad 4.2$$

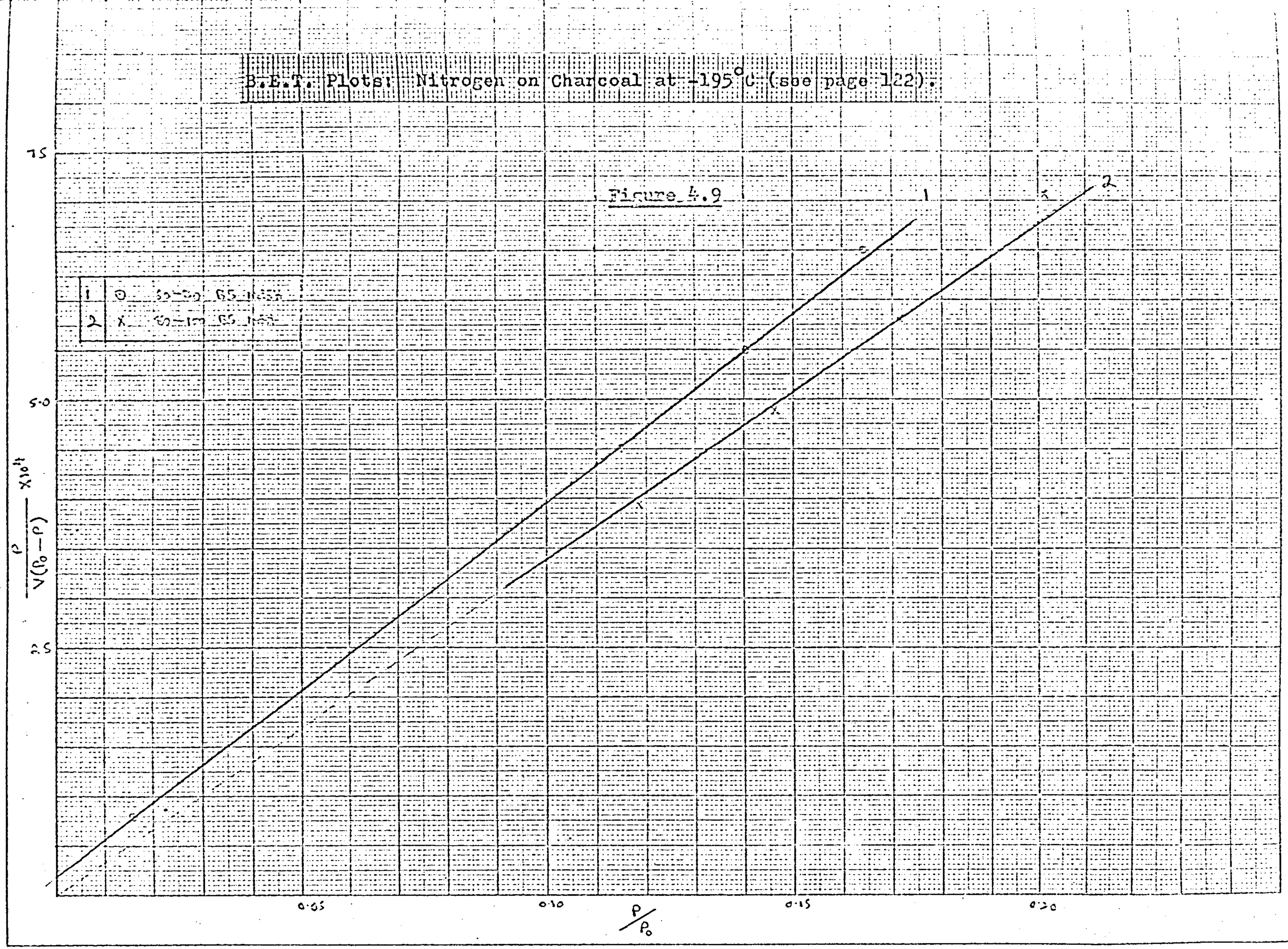
ρ = density of adsorbate M = molecular weight of adsorbate

N = Avagodros number W = weight of adsorbent.

A_m = area per molecule of adsorbate

B.E.T. Plots: Nitrogen on Charcoal at -195°C (see page 122).

Figure 4.9



For nitrogen adsorption the surface area in metre^2 per gram of adsorbent is 4.36 V_m. Values of V_m obtained from figure 4.9, and the surface areas, are given in table 4.10.

Table 4.10

Particle Size Range BS mesh	BET Plot intercept	slope	V_m	Surface Area $m^2 g^{-1}$
60-80	2×10^{-5}	3.79×10^{-3}	2.63×10^2	1144
80-100	zero	3.35×10^{-3}	2.98×10^2	1300

The precision of the surface area determinations is better than 10 $m^2 g^{-1}$, so the difference in surface area between the two particle size ranges is real. This is surprising, since it is generally accepted that the effect of different particle sizes on surface area is negligibly small[20]. The charcoal used in the mass detector can be classified as a highly active charcoal, in view of the high surface area available for nitrogen adsorption[26].

The surface area determined by nitrogen adsorption will not be a reasonable assessment of the surface area available for adsorption on a mass detecting element. The mass detector is operated in general, at about room temperature; the result of attaching the charcoal to an aluminium support with an adhesive will cut down appreciably the surface area available for adsorption of organic vapours. It was therefore necessary to measure the surface areas of several detecting elements in situ. As a typical adsorbate, benzene was selected since it has a fairly high vapour pressure at room temperature, and its molecular surface area is known[27]. Nitrogen was bubbled through benzene, diluted with a pure nitrogen stream, and passed continuously into a mass detecting element. The arrangement is shown in figure 4.10a. The element increased in weight until the rates of adsorption and desorption were identical, i.e. equilibrium was reached, and a stable baseline obtained. The partial pressure of the benzene was changed by changing the degree of dilution of the benzene/nitrogen stream with the pure nitrogen stream. By repeating this procedure several times, a reasonable relative pressure range (0.005 to 0.2) was covered, and an

Continuous Injection Systems.

Figure 4.10a

Flow System for Surface Area Determinations.

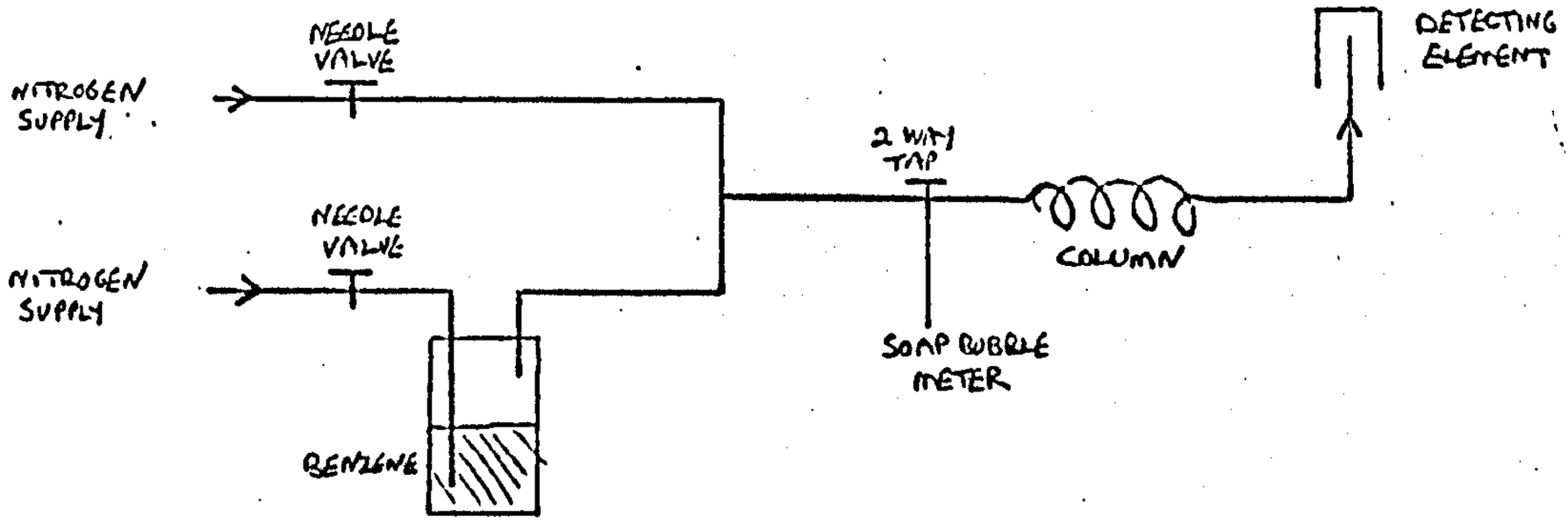
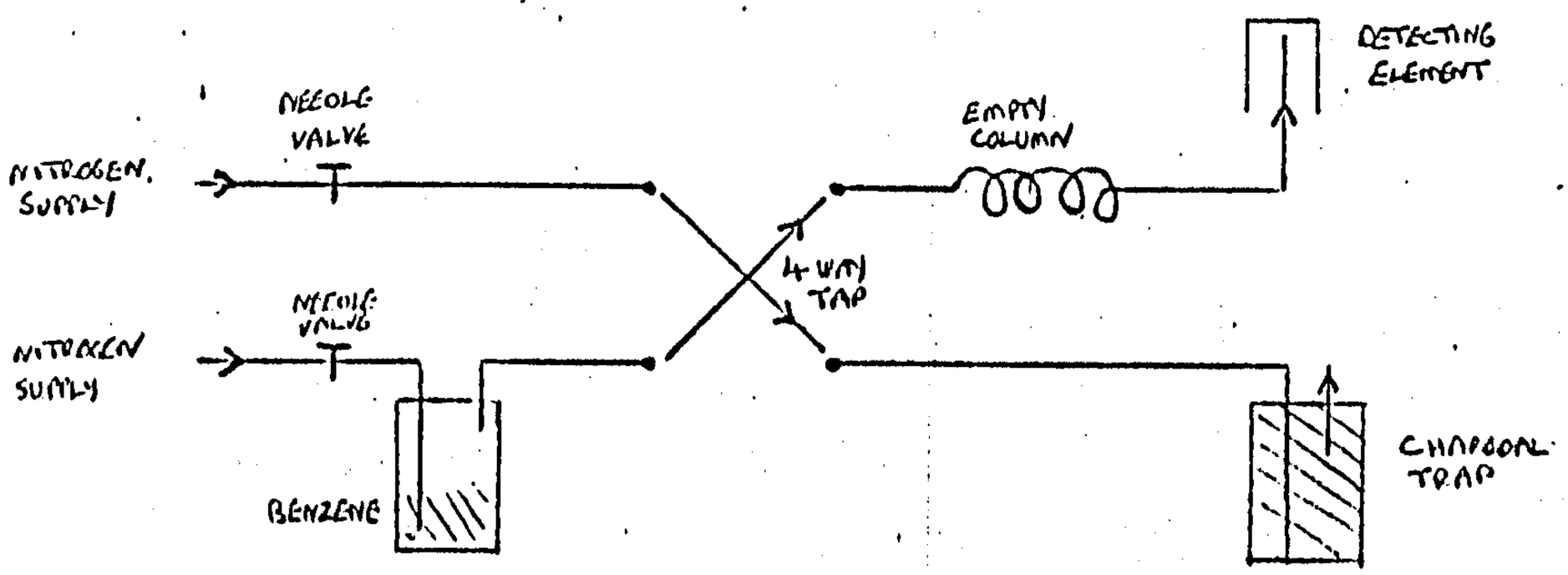


Figure 4.10b

Flow System for Linearity Determinations.



adsorption isotherm and BET plot obtained. The concentration of benzene in the benzene/nitrogen mixture was calculated from the rate of uptake of benzene by the detector and the flow rate of the mixture. From a knowledge of the flow rate of the pure nitrogen supply, the concentration of benzene reaching the detector, at any total flow rate, was calculated and hence the mole fraction of benzene in the nitrogen obtained. Assuming Henry's Law was obeyed, the partial pressure of benzene at each flow rate was obtained. The s.v.p. of benzene at the appropriate temperatures was obtained from the literature[28], and the relative pressure of benzene calculated. At each relative pressure, the uptake of benzene of the charcoal was measured directly by the microbalance. The results of a typical run are shown in table 4.11, and the isotherms and BET plots are shown in figures 4.11 and 4.12.

Table 4.11

Injection	Total Weight of benzene adsorbed		Benzene Concentration		
	mg	mg g^{-1} (charcoal)	A	B	C
1	34.46	191	4.43	0.0119	0.308
2	40.35	224	8.04	0.0216	0.481
3	43.56	242	14.5	0.0389	0.816
4	46.95	262	68.7	0.1844	4.23

Detecting element 27 at $21^{o}C$.

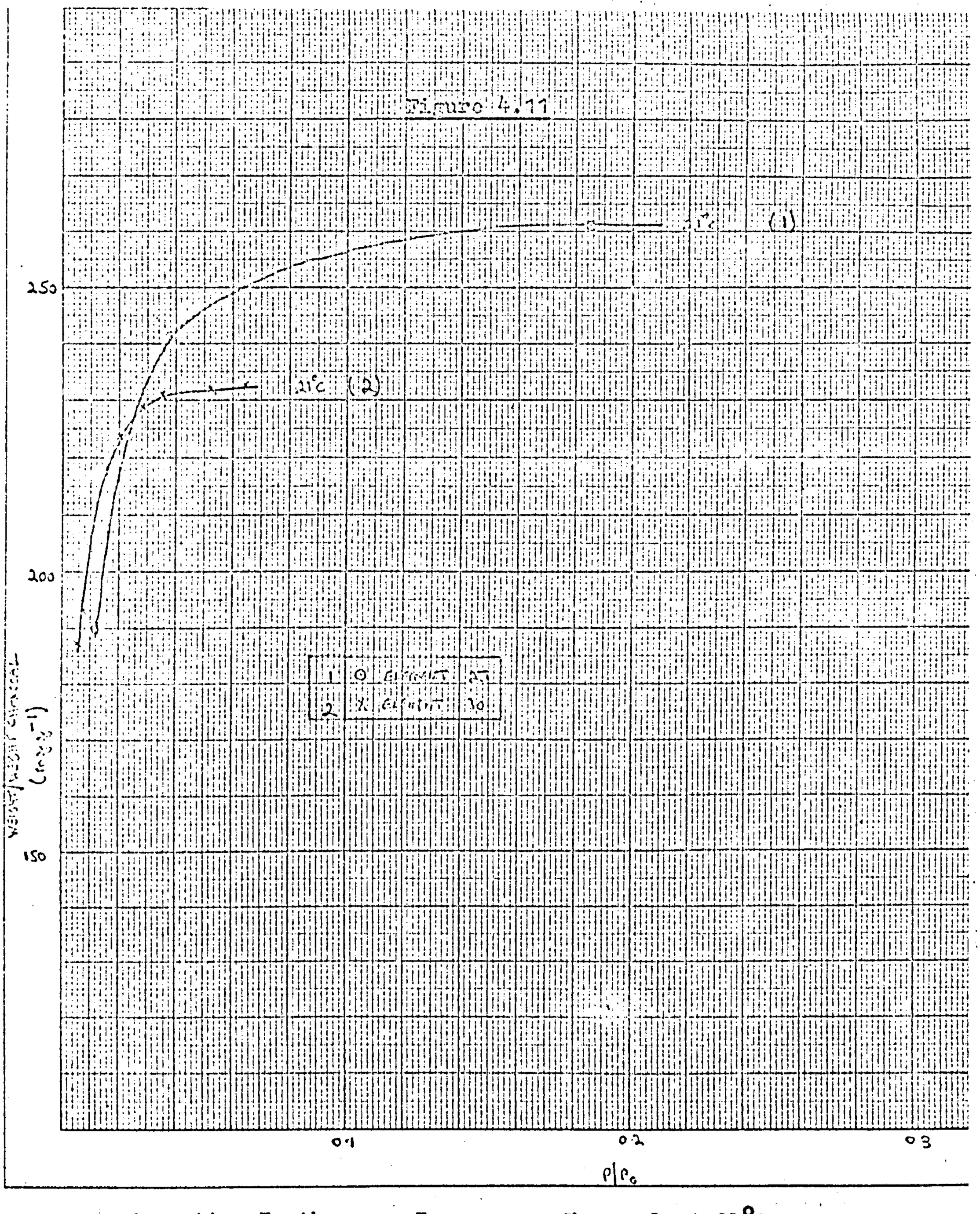
$A = mgml^{-1} \times 10^{4}$, $B = p/P_o$, $C = P/V(P_o-P)$.

The surface areas were calculated from the isotherms (by point B estimation) and from the BET plots. The results are given in table 4.12.

Table 4.12

Detecting Element	Weight of Charcoal (mg)	Surface Area (m^2) Point B	BET	Specific Surface Area ($m^2 g^{-1}$) Point B	BET
28	156	-	125	-	802
30	244	-	128	-	533
30	244	144	139	596	579
27	333	121	99	670	550
25	362	-	291	-	802

Figure 4.11



Adsorption Isotherms: Benzene on Charcoal at 21°C
(see page 124).

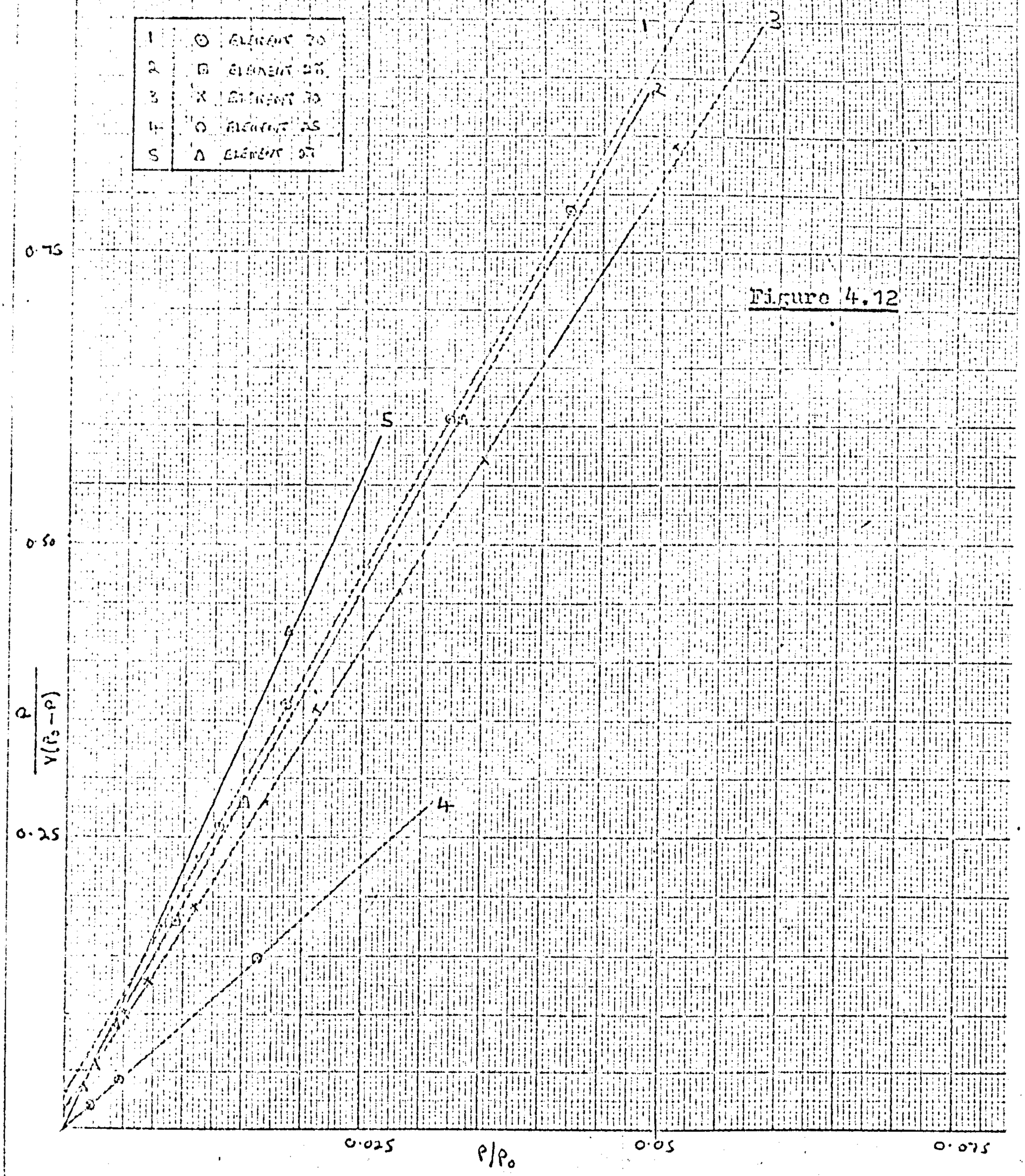


Figure 4.12

B.E.T. Plots: Benzene on Charcoal (see page 124).

Surface area does not increase regularly with weight of charcoal, but this is not a function of the reliability of the method (two determinations on the same element were within 10%), but a result of minor differences in the preparation of the elements. Indeed the surface area of element 27 is less than element 30, although it contains more adsorbent. The surface area per gram of adsorbent, in a detecting element is about $600m^2$. For a typical detecting element containing 250 mg of charcoal, the area available for adsorption is $150m^2$.

4.4 The Chromatograph.

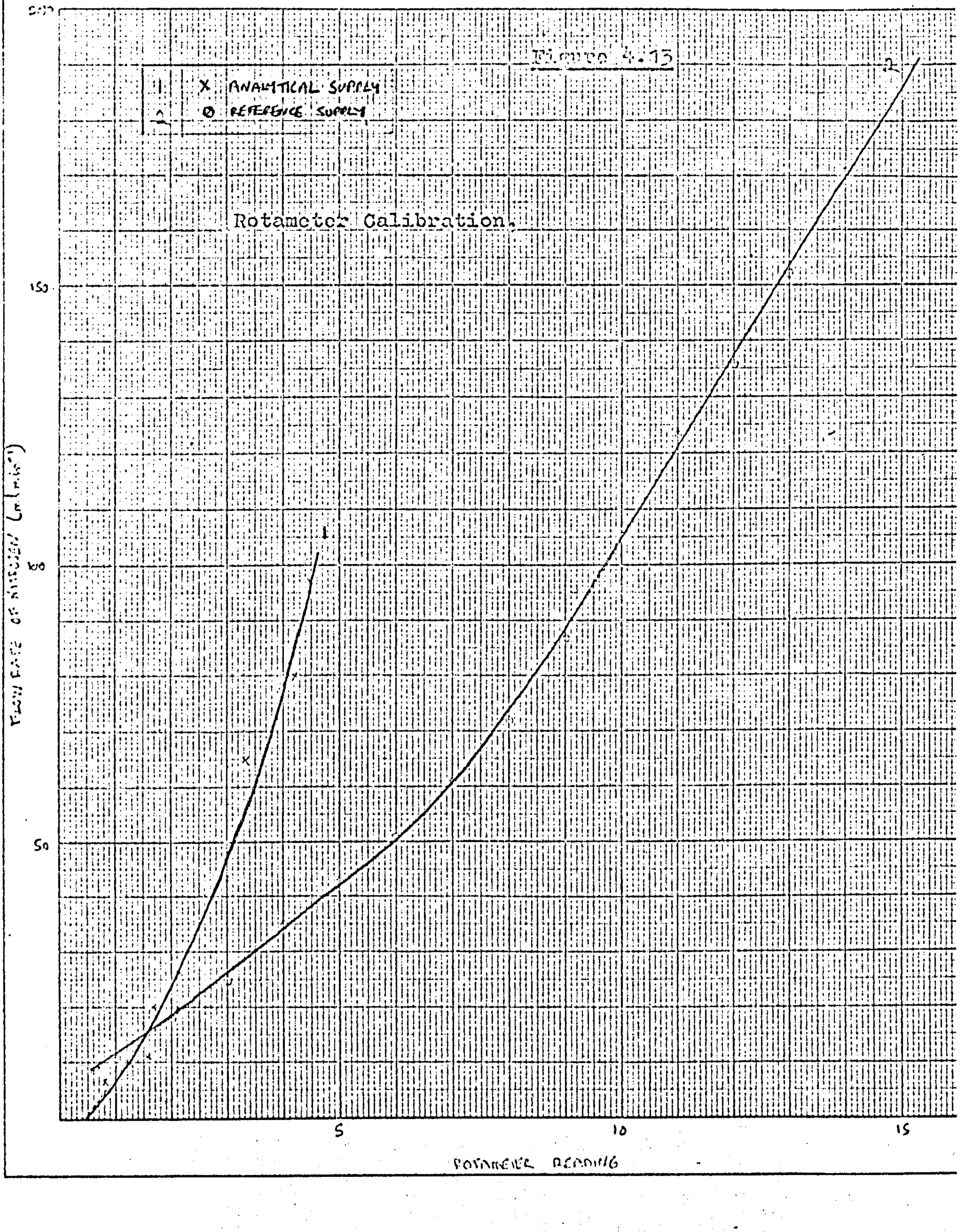
An apparatus was assembled for the analysis of materials by mass detection. The chromatograph proper comprised a Shandon KG2 oven with a temperature control of $\pm 0.1^{\circ}C$ between $50^{\circ}C$ and $300^{\circ}C$, containing a 4 metre PEGA column, the details of which are given below (section 4.4.1). Samples were injected with a microsyringe, via a silicone rubber septum. The chromatograph has two independent carrier gas supplies, controlled by needle valves, fitted to rotameters. One supply was connected to the analytical column, and the other was for use with a reference column. Carrier gas was dried by passing through a cylinder containing 5Å molecular sieve. Column effluent was fed into a mass detecting element, via a length of stainless steel tubing, contained in a small chamber, attached to the underside of the electro-microbalance. The detector was suspended from one side of the micro-balance beam by means of a length of fine wire, which passed through a small hole in the balance cabinet floor, to the detector chamber. The balance output was fed to one channel of a dual channel potentio-metric recorder. To prevent condensation of materials in the delivery tube to the mass detector, provision was made to heat the tube. A heating coil was wrapped round the tube, and the whole covered with asbestos tape. The lagging made the system rather cumbersome, and unless the heating coil was carefully wound, uneven heating of the tube resulted. For later work (see section 5.3) direct resistive heating was used.

For the purposes of comparison, the chromatograph was fitted with a Gow-Mac gas density balance for much of the work. This detector was placed before, and in series with the mass detector. With this detector in the system, the carrier gas flow rate reaching the mass detector was the sum of the flow rates through the analytical and reference columns. The gas density balance output was connected, via an amplifier to the 1 mV channel of the dual pen recorder.

A number of preliminary experiments were carried out on the chromatograph before embarking on a systematic study of mass detector behaviour. These experiments are listed below.

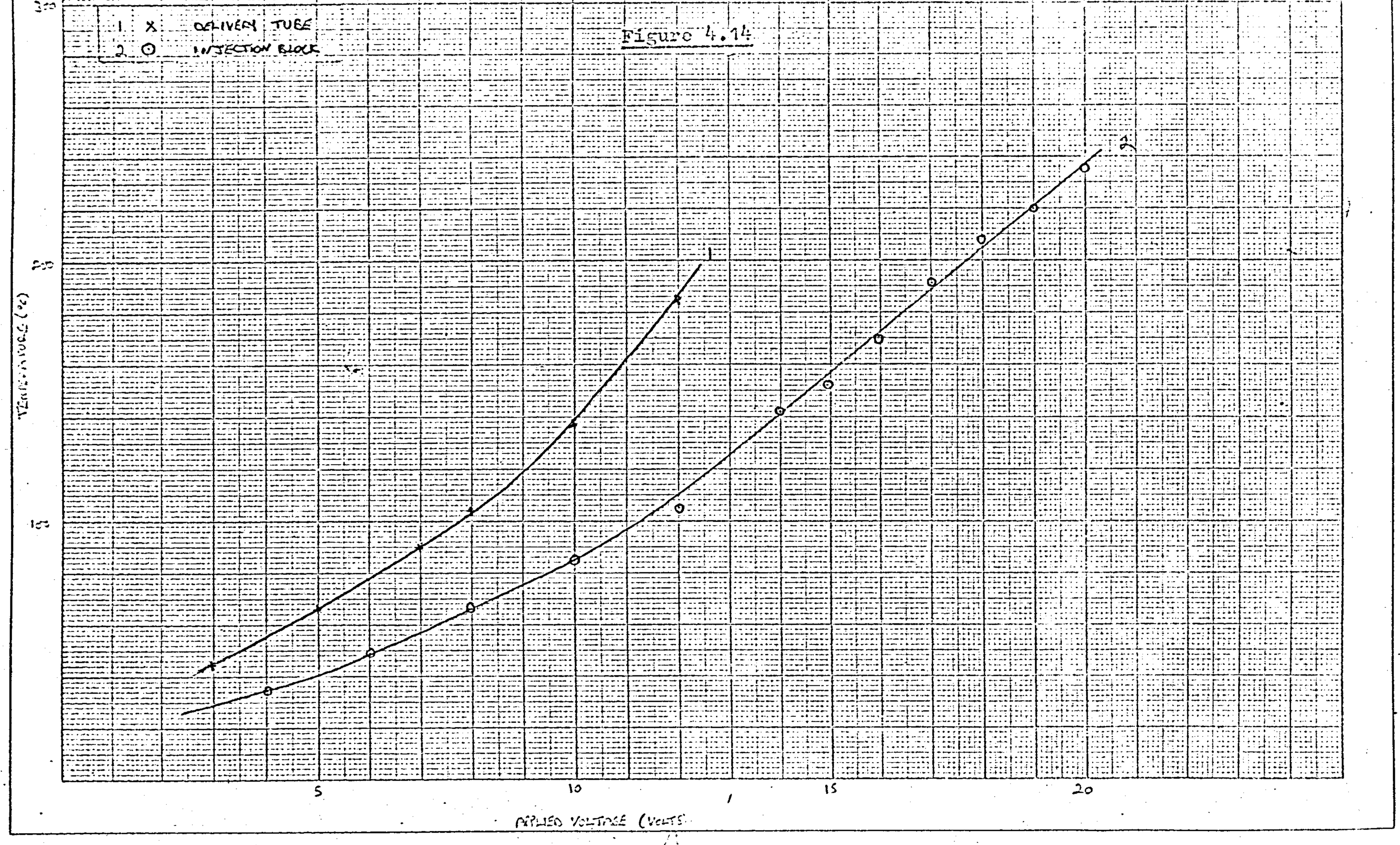
The two rotameters measure respectively the flow rate through the reference column and the analytical column of the chromatograph. The two streams can be combined at a common outlet. Calibration was carried out with a carrier gas of nitrogen at an inlet pressure of 30 lb in^{-2}, using a soap bubble meter attached to the gas outlet. The calibration was carried out at 22°C, and a correction applied for the s.v.p. of water in the bubble meter. The reference arm was calibrated from 10 to 185 ml min^{-1}, with the analytical flow turned off. The analytical arm was calibrated from 5 to 95 ml min^{-1} with the other arm off. The calibration curves are shown in figure 4.13. To determine the total combined flow rate of carrier gas, i.e. that reaching the mass detector, one rotameter was set for a given flow rate, and the other varied over a wide range. This was repeated for a number of fixed readings on each of the rotameters. The total flow rate was again measured using a soap bubble meter. A graph was plotted of total flow rate calculated from the two rotameter readings, against the total flow measured directly by the soap bubble meter. A straight line was obtained of slope 0.99, so that the total flow rate reaching the mass detector could be obtained directly from the sum of the rotameter readings using figure 4.13. The temperature of the injection block was controlled by varying the potential applied to a heating coil surrounding the block. The heater was calibrated using a thermocouple.

Figure 4.13


1 X ANALYTICAL SUPPLY
2 ⊙ REFERENCE SUPPLY
Rotameter Calibration.
150
100
50
5
10
15
1
2

Calibration of Chromatograph Heaters (see page 127).

Figure 4.14



The delivery tube heater was similarly calibrated. The calibration curves are shown in figure 4.14.

4.4.1 Column Performance.

For the majority of work, the apparatus was fitted with a 4 meter x 4 mm stainless steel column packed with 72-85 mesh chromosorb, coated with a stationary phase of (20%) polyethylene glycol adipate (PEGA). The characteristics of this column were therefore investigated more fully than any of the other columns used. To determine the flow rate range over which the efficiency of the column was in the region of its maximum, an HETP/ linear gas velocity curve was constructed. The determination was carried out over the range 15 to 250 ml min^{-1} using n-butyl acetate, and a column temperature of 100°C. Values of n, the number of theoretical plates, were calculated using the equation:

$$n = 5.545 \left[\frac{\text{retention distance}}{\text{peak width at } \frac{1}{2} \text{ height}} \right]^2 \qquad 4.3$$

For each value of n, the height equivalent to a theoretical plate, HETP, was found using the relationship:

$$\text{HETP} = \frac{l}{n} \qquad 4.4$$

where l = length of column.

The linear gas velocity, u, was calculated from flow rates, using the equation:

$$u = \frac{F_A}{60A} \quad \text{cm sec}^{-1} \qquad 4.5$$

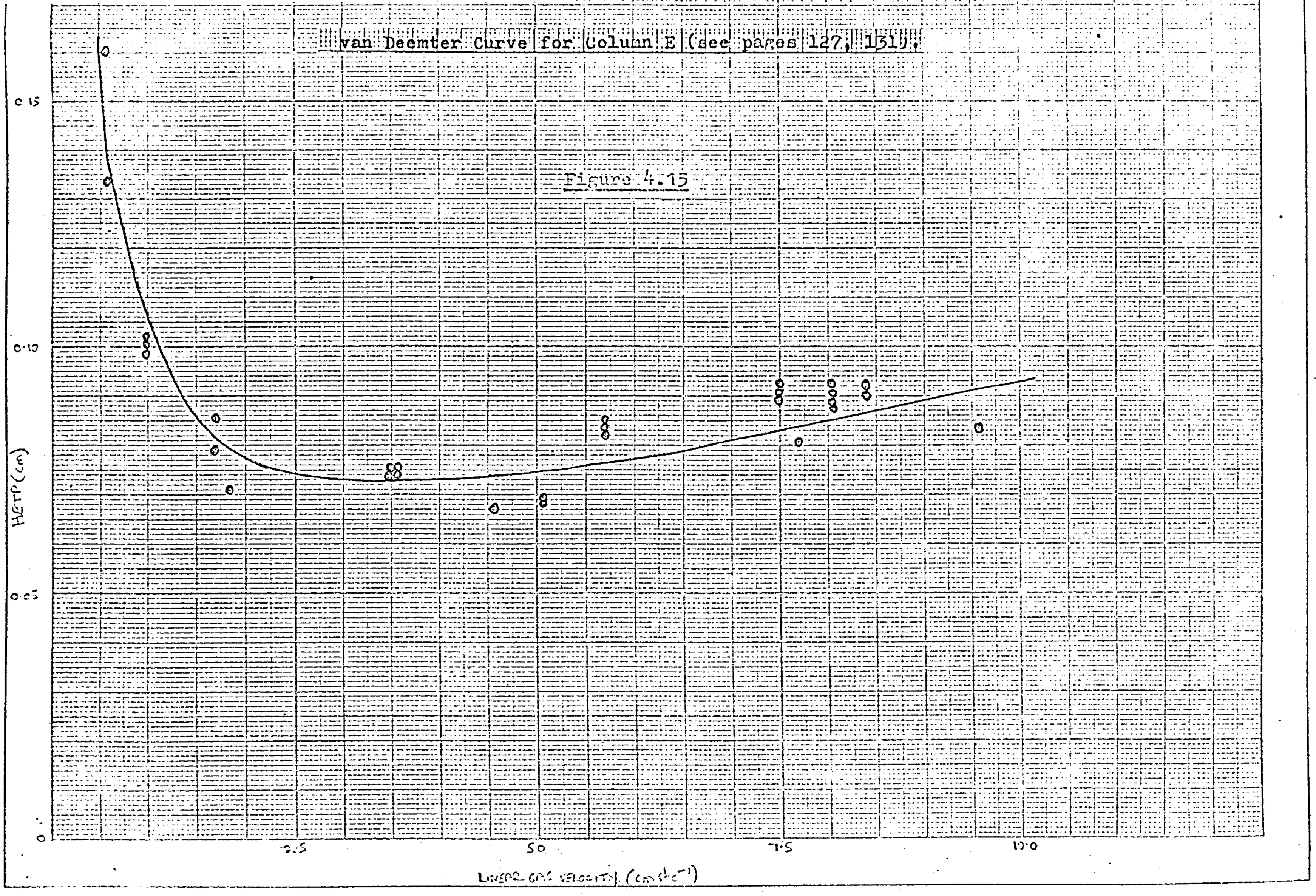
where F_A = flow rate of carrier gas through the analytical column, ml min^{-1}.

A = cross-sectional area of the column: cm^2.

Results are displayed on figure 4.15. Column performance is excellent in the range 3 to 10 cm sec^{-1}, i.e. about 20 to 75 ml min^{-1}. The number of theoretical plates per metre in this region is of the order of 1,300.

van Deemter Curve for Column E (see pages 127, 131).

Figure 4.15



4.4.2 Sample Injection.

Sample injection was by means of Hamilton syringes. The repeatability of delivery of known amounts by the syringes was determined using the electromicrobalance. In a typical experiment a 10 µl syringe was filled to the 1 µl mark and the contents injected, through a rubber septum, into a small polythene vessel containing an absorbent paper. The increase in weight of the vessel was measured on the microbalance. The determination was repeated 15 times, and the mean, and standard deviation of the delivery calculated. The percentage of the marked volume delivered was calculated from a knowledge of the density of the sample used. The same 10 µl syringe (ref. No. 1) was used in all experiments in which a syringe was used as a basis from which to calculate the adsorption efficiency of the mass detector. Its performance was measured both at the beginning of the experiments, and at the end: no deterioration was observed. About 500 injections were carried out between these two syringe performance checks. The results for several different 10 µl syringes are given in table 4.13.

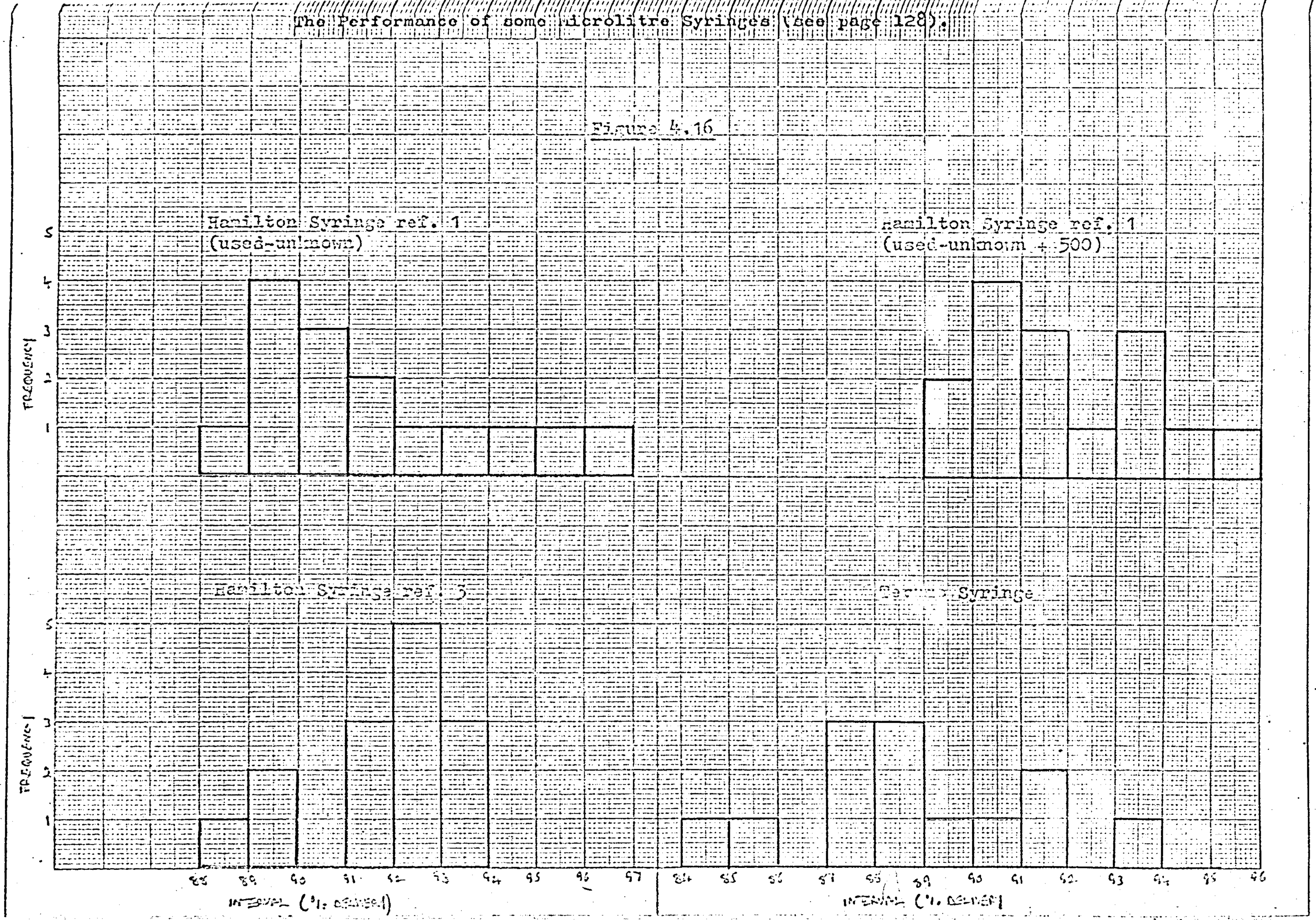
Table 4.13

Syringe Performance

Syringe	No. of times used	Mean % delivery	Standard deviation (%)	Charge (µl.)
Hamilton Ref. 1	unknown	91.6	2.2	1
Hamilton Ref. 1	+ 500	92.0	1.9	1
Hamilton Ref. 3	unused	91.4	2.1	1
Terumo	unused	87.6	3.7	1
Hamilton Ref. 4	unknown	97.5	1.9	1 to 6
Hamilton Ref. 1	+ 900	98.3	1.8	5

The material used for all injections was n-butyl acetate, which had been purified chromatographically (section 4.4.4). The performances are expressed in the form of histograms: figure 4.16. The values quoted in table 4.13 for syringe Ref. 4 were calculated from figures published by Lovelock[21], who filled the syringe with mercury to various markings

Figure 4.16


Hamilton Syringe ref. 1
(used-unknown)
Hamilton Syringe ref. 1
(used-unknown + 500)
Hamilton Syringe ref. 3
Gerber Syringe
FREQUENCY
INTERVAL (% DELIVERY)

between 1 µl and 6 µl, and injected the contents directly on to a balance. The similarity of the standard deviations for the four Hamilton syringes is striking. The 10 µl Hamilton syringes give reproducible sample deliveries, but not 100% of the quoted volume. The Terumo syringe performance is significantly poorer, and cannot be regarded as suitable for quantitative work. No other 10 µl Terumo syringes were tested, and it may be that the performance was atypical.

The conditions under which the experiments were carried out are not identical to those of an injection into the chromatograph, in that injection was at atmospheric pressure and room temperature (24°C), rather than against 30 lb in^{-2}, and at a temperature of about 200°C. If these factors have any effect on percentage delivery, it would be expected to decrease the values. A back pressure exerted on the syringe may tend to force liquid, or vaporised material, up the sides of the syringe piston.

Similar experiments were performed using 1 µl Hamilton and Terumo syringes. The repeatability of results was so excessively poor for both makes of syringe, that the quantitative use of these syringes cannot be contemplated. Many attempts to inject varying quantities into the polythene vessel (and into a column), resulted in zero delivery. No injection was more than 80% of the marked value.

For quantitative work, in which an accurate assessment of the amount injected is required, a 10 µl syringe is satisfactory, ~~could be employed~~. The smallest sample which can be reliably injected is about 1 µl. Indeed Evans and Scott[22] have suggested that for quantitative work, the maximum possible sample be injected, consistent with the capacity of the column and the detector.

4.4.3 Preparation of Columns.

In addition to the columns supplied with the Shandon chromatograph, several columns were prepared in the laboratory. In a typical preparation 20 g of Chromosorb G was sieved to give a particle size

range of 80-100 mesh; it was thoroughly dried by heating in an oven at 110°C, and then placing under an infra-red lamp for a few hours. The dried support was placed in a dry round bottom flask, and covered with 60-80 petroleum ether. 2 ml of hexamethyldisilazane was added to the flask, which was fitted with a reflux condenser and calcium chloride drying tube. The contents of the flask were refluxed for about 12 hours, when the bulk of the solvent was decanted. The support was washed successively with n-propyl alcohol and petroleum ether, and the residual solvent removed on a rotary evaporator, and finally under high vacuum.

0.8 g of Apiezon L grease was dissolved in an excess of 40-60 petroleum ether, in a round bottom flask, and 20 g of Chromosorb G added. The flask was attached to a rotary evaporator, care being taken to prevent damage to the inert support particles, and to obtain a slow rate of evaporation, thus ensuring a uniform coating of stationary phase on the support. The final traces of petroleum ether were removed by placing the material on a vacuum pump (at room temperature and 0.05 mm Hg pressure) overnight. Finally the column packing was resieved, and stored in a sealed vessel until required.

Preparation of the column. All columns prepared in the laboratory were wound to a helical shape before packing. They were cleaned by filling with chromic acid and left for several hours, after which time they were thoroughly washed with water. Each column was filled several times with hot toluene, and hot acetone. The columns were then placed in an oven and heated to 150°C overnight, nitrogen flowing through the columns during this time. Copper columns, in addition to the above treatment were deactivated by heating to about 800°C overnight in the presence of nitrogen.

Column packing. The packing densities of the materials used for column packing were determined by placing the material in a graduated measuring cylinder, tapping the material down, and weighing the measured volume. For each column, the internal volume was calculated, and hence the

amount of packing required to fill the column estimated. Examples are given in table 4.14. The columns were packed by the following means: one end was plugged with glass yarn, and to the other end was attached a steel cylindrical reservoir (of internal volume about 75 cc.), containing the column packing, a little in excess of the calculated quantity. The other end of the reservoir was attached to a nitrogen supply, and the nitrogen pressure was slowly and uniformly increased to a maximum of 30 lb in^{-2} thus forcing the packing into the column. The column was frequently tapped to ensure free movement of the packing, but was not subjected to any vigorous vibration which could damage the particles. After packing the remaining end of the column was plugged with glass yarn, and conditioned overnight at 175°C, with a slow nitrogen flow.

A complete list of columns used in this work is given in table 4.15.

Table 4.14

Column Ref. No.	Internal Volume (cc)	Packing Density g cc^{-1}	Weight required.	Weight used
A	7.9	0.58	4.58	4.68
D	3.9	0.34	1.32	1.36

Table 4.15

Manufacturer	Ref.	Stationary Phase Type	%	Inert Support Type	BS mesh size	Length (metre)	i.d. (mm)	Materia
T.G.	A	ApL	7½	chromo-sorb G	80-100	1.1	3	S/S
TG	B	Carbowax 20m	15	celite	60-80	1.1	3	S/S
T.G.	C	ApL	4	chrome-sorb G	70-80	0.3	4	Cu
T.G.	D	Porapak Q	-	-	100-120	0.56	3	S/S
Shandon	E	PEGA	20	chromo-sorb	72-85	4	4	S/S
Shandon	F	ApL	20	"	72-85	4	4	Cu
T.G.	G	ApL	7½	chromo-sorb G	80-100	1.5	4	Cu
Shandon	H	ApL	20	chromo-sorb	72-85	2	4	Cu
T.G.	I	charcoal	-	-	52-60	0.21	4	Cu
T.G.	J	-		empty column	-	1	1½	Cu
Wilkens	K	ApL	10	chromo-sorb	80-100	6	1½	S/S

4.4.4 The Preparation of Samples.

Prior to use in the experiments described in this and the following chapters, all compounds were checked for impurities by conventional gas chromatographic techniques. Starting with the purest readily available sample of each compound, the purity was checked using two different stationary phase types, in general an ApL and a PEGA column, operating under suitable conditions, using a flame ionisation or a katharometer detector. The majority of hydrocarbons were found to be of high purity, and needed no further purification. However, branched alkanes observed in some of the n-alkane samples, were removed by shaking with molecular sieve, and recovering the n-alkanes by heating the sieve. Repeating the process several times almost completely removed the impurities. The acetates, ketones and aldehydes, which were in general better than 98% pure, were all distilled before use. In addition, impurities in several of these compounds were removed by preparative scale chromatography, using a Wilkens Autoprep Chromatograph. A typical result is illustrated in figure 4.17. The lower alcohols and ketones were dried by standing over molecular sieve for several weeks before use, and the water content checked using a Martin gas density balance.

4.5.1 The Performance of the Mass Detector - Discussion.

Adsorption Efficiency.

The most important single characteristic of the mass detector is the ability to totally adsorb all vapours emerging from the column, or at least to adsorb constant proportions of all vapours. The parameters which effect adsorption efficiency can be divided into two main sections:

(i) extra detector parameters, such as carrier gas flow rate,

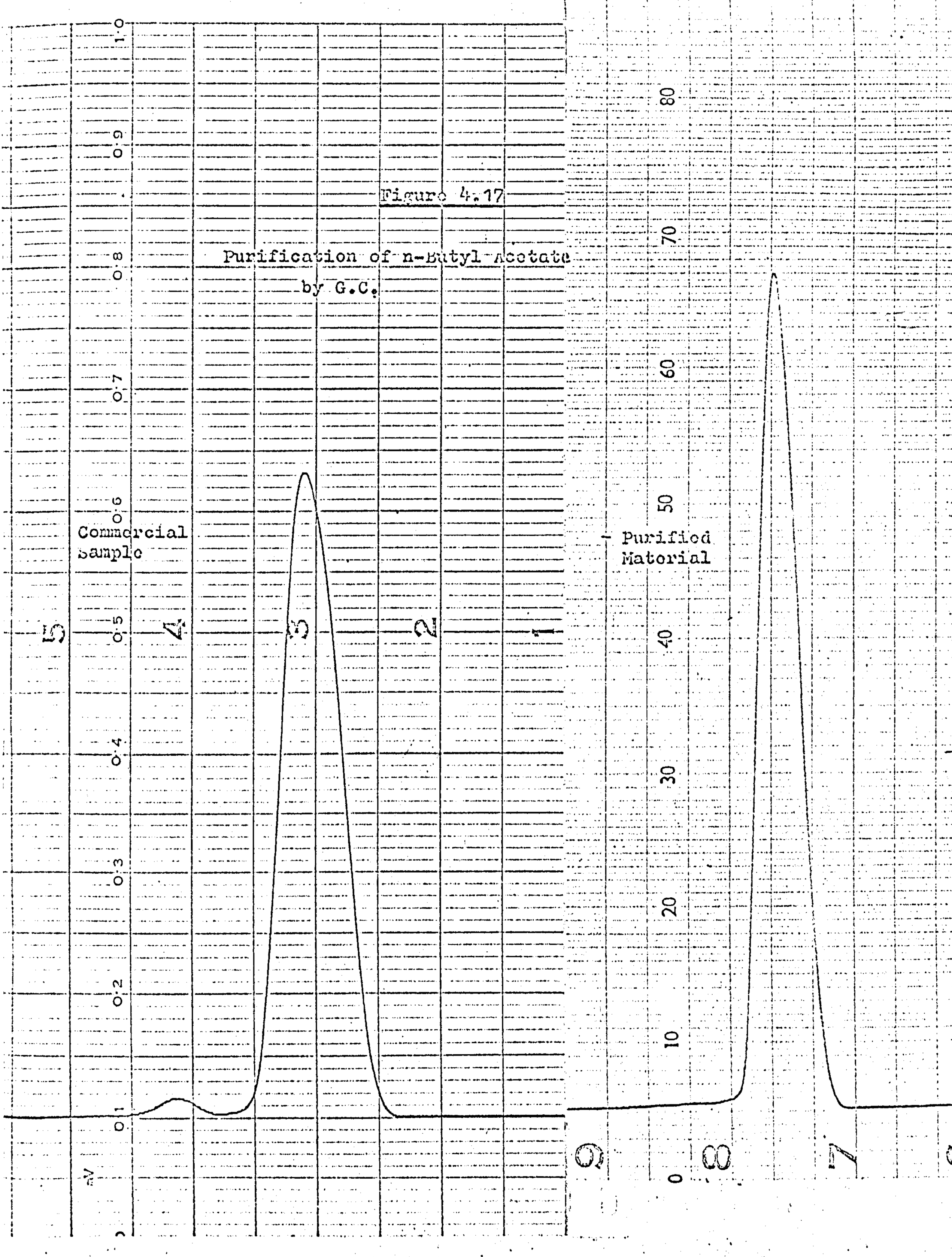
(ii) intra detector parameters, such as detector geometry.

Extra detector properties are discussed first, since to some degree these must be within certain limits, determined by the conditions required by the remainder of the chromatographic apparatus.

The relative adsorption efficiency of the mass detector is defined as the ratio of the amount of a material adsorbed, and the amount

Figure 4.17

Purification of n-Butyl Acetate by G.C.



adsorbed of a reference material (i.e. a relative response factor).

The absolute adsorption efficiency is defined as the ratio of the amount of a given material adsorbed by the detector, and the amount introduced into the detector.

To obtain relative quantitative results, the relative adsorption efficiencies of the materials in a given sample should be equal, but not necessarily known. For absolute quantitative results, the absolute adsorption efficiency must be 100% for all materials, or at least known for all materials.

4.5.2 The Performance of The Mass Detector - Experimental.

Extra Detector Parameters - Carrier gas flow rate.

The effect of flow rate into the mass detector, on the adsorption efficiency was studied using a three component/of known relative composition. The mixture was prepared by weighing directly into a 10 ml sample bottle, using a 4-place analytical balance. Precautions were taken to ensure the minimum of loss of materials by evaporation, by completely filling the bottle, and storing at -20°C when not in use. The composition of the mixture is given in table 4.18 (x_o values). Methyl acetate was not used, since its high volatility would enhance any changes in composition of the mixture with time. The operating conditions are given in table 4.16.

Table 4.16

Apparatus	Shandon KG2
Column	PEGA ref. E
Inlet pressure of nitrogen	30 lb in^{-2}
Outlet " " "	at.
Injection temperature	154°C
Column temperature	104 ± 0.1°C
Delivery tube temperature	34± 1°C
Nominal sample size	1.2 µl
Gas density balance current	150 mA
" " " sensitivity	X 200
Mass detector range	1 mg fsd

Experiments were carried out at a variety of different flow rates from 15 to 250 ml min^{-1}; a total of 87 runs were performed. To

eliminate as far as possible any changes in detector response, not caused by changes in flow rate (e.g. incorrect amount of sample injected, random temperature and flow rate fluctuations) three runs were carried out at each flow rate, and mean response values calculated. In addition the variations in flow rate were not carried out in a completely regular manner. The object of this was to eliminate the possibility of the inevitable slow change in composition of the solution, giving a false relationship between detector response and flow rate.

4.5.3. Results - The response of The Mass Detector.

An example of a chromatogram of a three component acetate mixture is given in figure 4.18. From the step heights of the chromatograms, the mass of each component adsorbed is found directly. Hence the percentage by weight of each component in the mixture is calculated. The step height results will show up any variation in absolute response with changes in flow rate, and any differences in adsorption efficiency for the different components of the mixture. The percentage composition results are not dependent on complete adsorption, and by comparison with the actual percentage composition can be used to define the flow rate range over which the mass detector gives a satisfactory relative response.

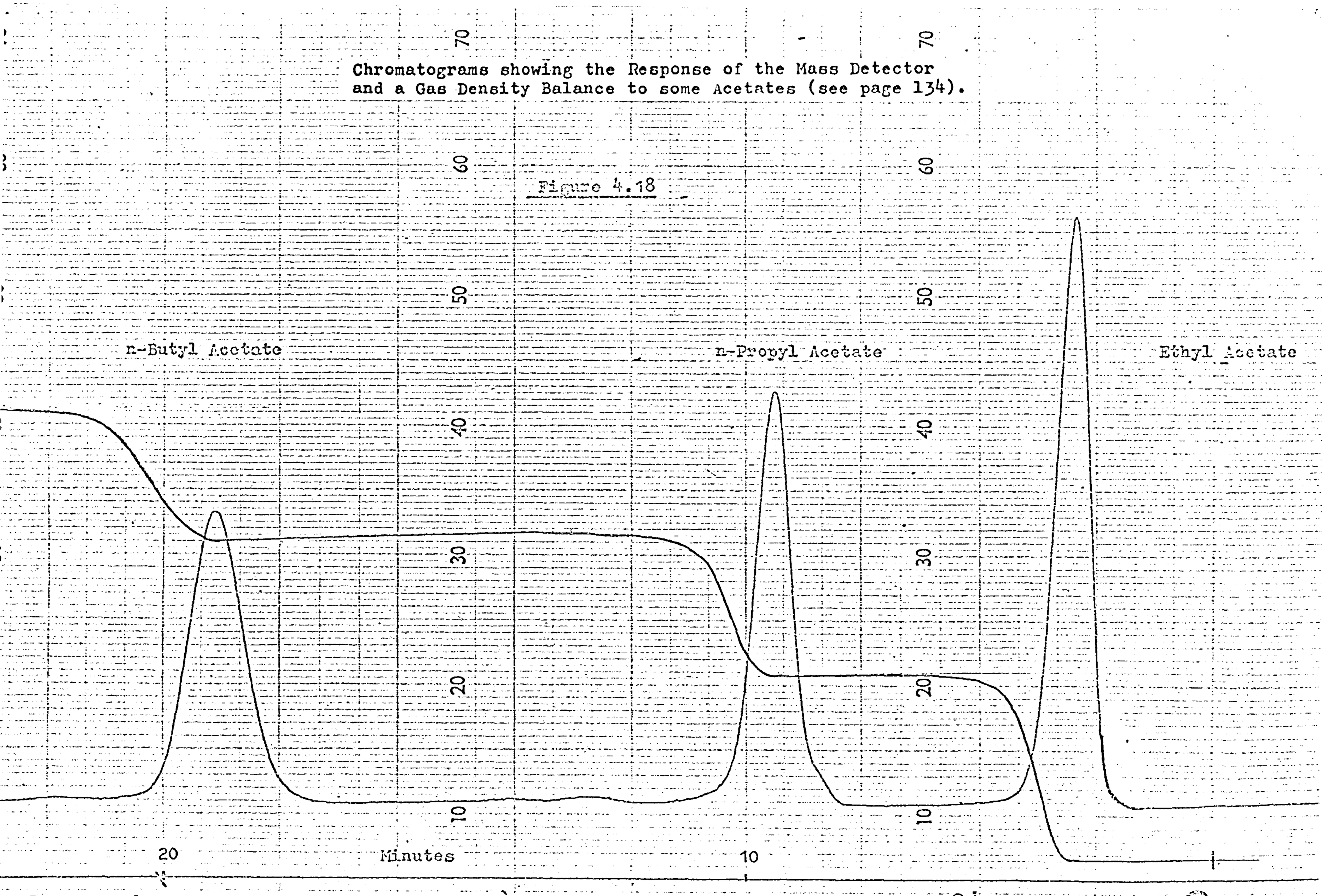
4.5.3a Relative Response.

The simplest way to express these results is by graphs of relative composition against flow rate for each material (figure 4.19). However this does not take into account any differences between the observed and true percentage composition of the mixture, i.e. the bias of the results. In addition the results only apply to one specific mixture. By expressing the results in terms of percentage bias, they are of more general applicability. Bias values are calculated as follows:

The true % weight of the component = x_o, and the measured % weight (the mean of 3 values) at a given flow rate = $\bar{x}$.

Chromatograms showing the Response of the Mass Detector and a Gas Density Balance to some Acetates (see page 134).

Figure 4.18



Hence $$\text{bias} = \bar{x} - x_o \qquad 4.6$$

and $$\text{(absolute) \% bias} = \frac{\bar{x} - x_o}{x_o} \times 100 \qquad 4.7.$$

$$\text{Response factor } \bar{R} = \frac{\bar{x}}{x_o} \qquad 4.8$$

The change in bias with flow rate was about 5×10^{-3}% per ml min^{-1}, for each material. This represents such insignificant changes in relative detector response with flow rate, that it is reasonable to assume that the relative response of the detector is independent of flow rate at least over the range 15 to 250 ml min^{-1}. Bias values, embracing the whole flow rate range are given in table 4.17. A statistical analysis was carried out on the results, and a measure of the repeatability obtained. The results are summarised in table 4.17, and expressed in the form of histograms (of interval 0.25%) in figure 4.20. All histograms show approximately normal distributions of the relative response variations.

Table 4.17

Mass Detector Results

Component	n	$\bar{x}$	σ	V	x_o	Bias	% Bias	$\bar{R}$
Ethyl acetate	51	33.04	0.634	1.93	33.49	-0.45	-1.37	0.99
n-Propyl "	51	31.38	0.282	0.90	31.64	-0.26	-0.85	0.99
n-Butyl "	51	35.50	0.671	1.89	34.87	+0.70	+1.99	1.02
				1.57		|0.48|	|1.40|	

$\bar{x}$ = mean % weight of n determinations.

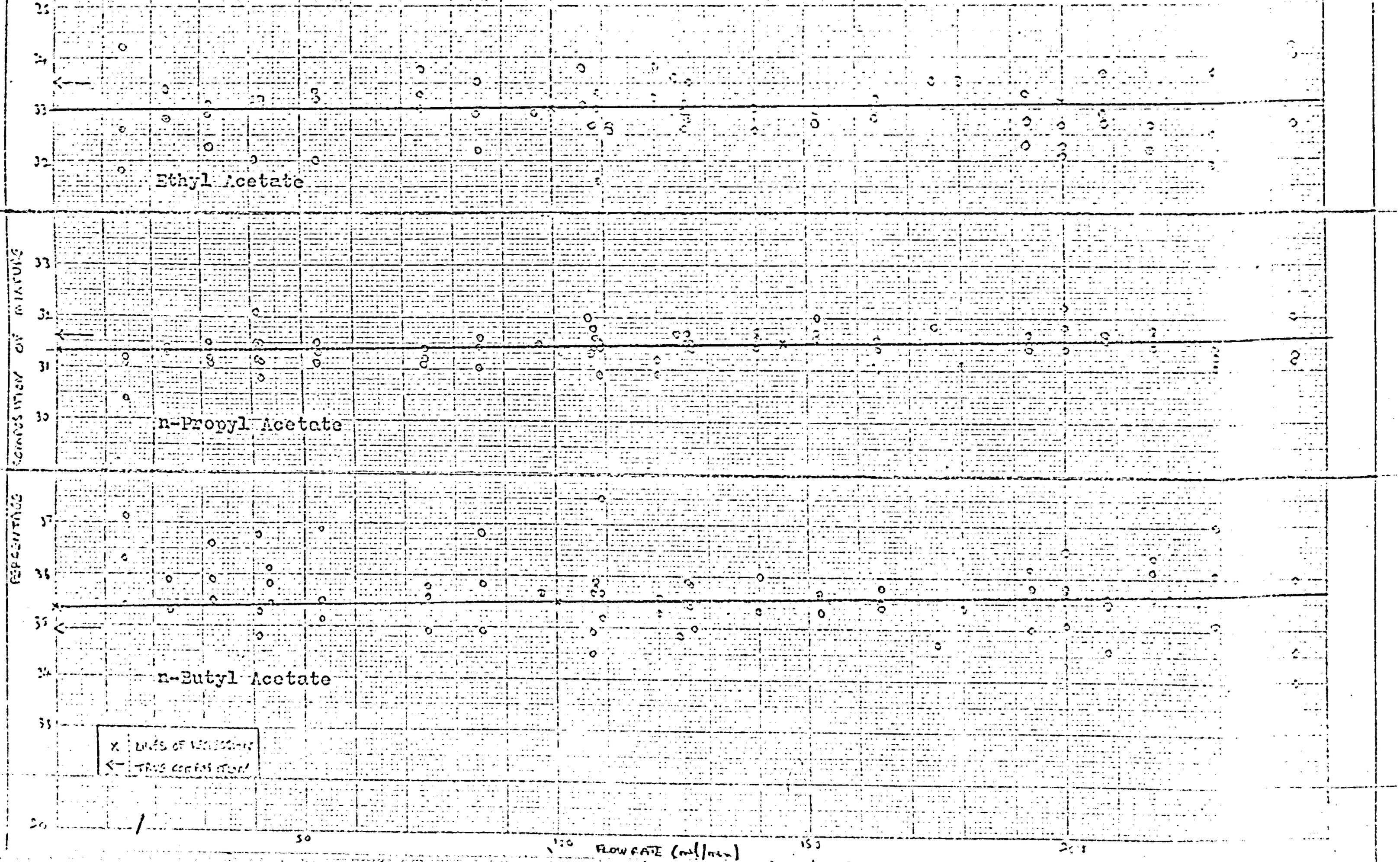
σ = standard deviation.

V = coefficient of variation (%).

Results for n-propyl acetate are in better agreement with the true value (x_o), than the other two acetates. The standard deviation is also considerably less. From the experiments performed on the balance - recorder system (see section 4.2.2a), it was concluded that errors of up to ½% may arise. The introduction of the mass detector into the system has increased the maximum error to 2%. This increase may arise from any of the following causes:

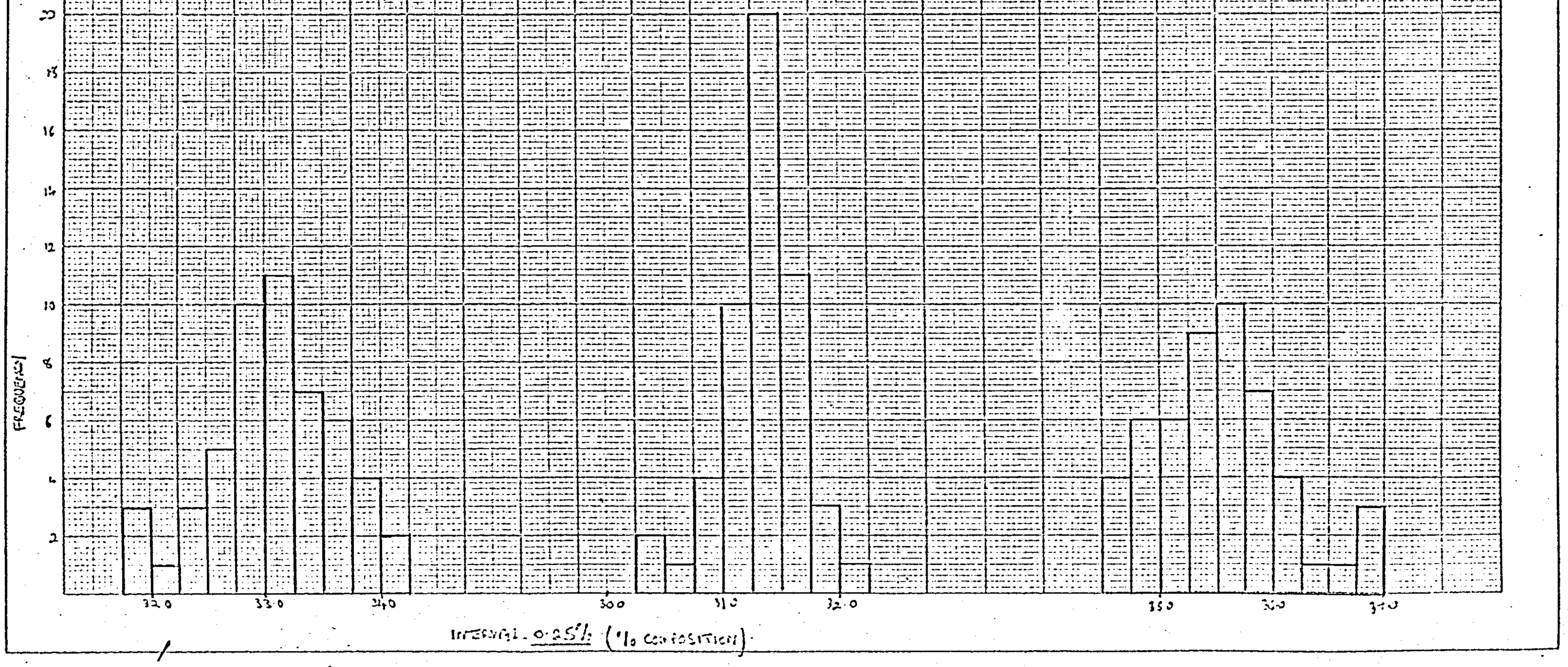
The Effect of Flow Rate on the Relative Response of the Hans Detector (see page 134).

Figure 4.19



Repeatability of the mass detector response over a wide flow Rate Range (see page 135).

Figure 4.20



(i) changes in the composition of the solution. Evaporation will cause a decrease in the amount of ethyl acetate present, and affect to a lesser extent the amount of propyl acetate. The overall effect will be an apparent increase in the amount of butyl acetate, very little change in the percentage weight of propyl acetate, and a decrease in the percentage weight of ethyl acetate. This is in line with the bias values quoted in table 4.17. An indication that changes in solution composition with age, is a contributing factor can be obtained by comparing the bias values soon after the mixture was prepared, and after a period of about a week. The complete experiment was carried out over 15 days. Bias values calculated over a period of 2 days (table 4.18 column A) were compared with a similar set of values 10 days later (column B).

Table 4.18

	A			B			
Component	n_A	$\bar{x}_A$	$Bias_A$	n_B	$\bar{x}_B$	$Bias_B$	Expected trend in bias
Ethyl acetate	10	33.31	-0.18	10	32.90	-0.59	increase
n-Propyl acetate	10	31.34	-0.30	10	31.43	-0.21	little change
n-Butyl acetate	10	35.36	+0.49	10	35.68	+0.81	increase

(ii) preferential loss of the lower boiling components at the injection point, and preferential irreversible adsorption of the more highly polar components, on the column.

(iii) Errors may have arisen during the preparation of the sample. Assuming a maximum error of $\pm$0.1 mg, the total possible error is 0.4 mg. Calculation of the % weights of each component, allowing for such errors, made no difference to the values, taken to 2 decimal places.

(iv) less complete adsorption of the lower boiling acetates by the mass detector. Any such effect would be evident by calculating the adsorption efficiency for each component of a mixture, at a given flow rate: subsequent work (e.g. section 5.2) has shown that effects of this nature are negligible.

(v) condensation of higher boiling acetates in the detector delivery

tube. This will have the opposite effect on bias values to that observed experimentally, and hence if condensation occurs, it is to a negligible extent. Condensation will also result in distorted steps, which are not observed.

(vi) rapid desorption from the mass detector. Desorption effects will be greater the lower the boiling point of the component, and will be evident by the presence of a falling baseline on the chromatogram. Although in many runs there was a baseline drift, the drift was small, regular and of the same order for all components.

(vii) the presence of impurities in the acetates: this will not affect the repeatability of response, but could enhance bias values.

The use of the Gow-Mac gas density balance in series with the mass detector, has made it possible to determine with more certainty whether the bias values quoted in table 4.17 are a function of the mass detector, or are a result of some other effect. The response of the gas density balance is predictable on a molecular weight basis (see section 3.10b).

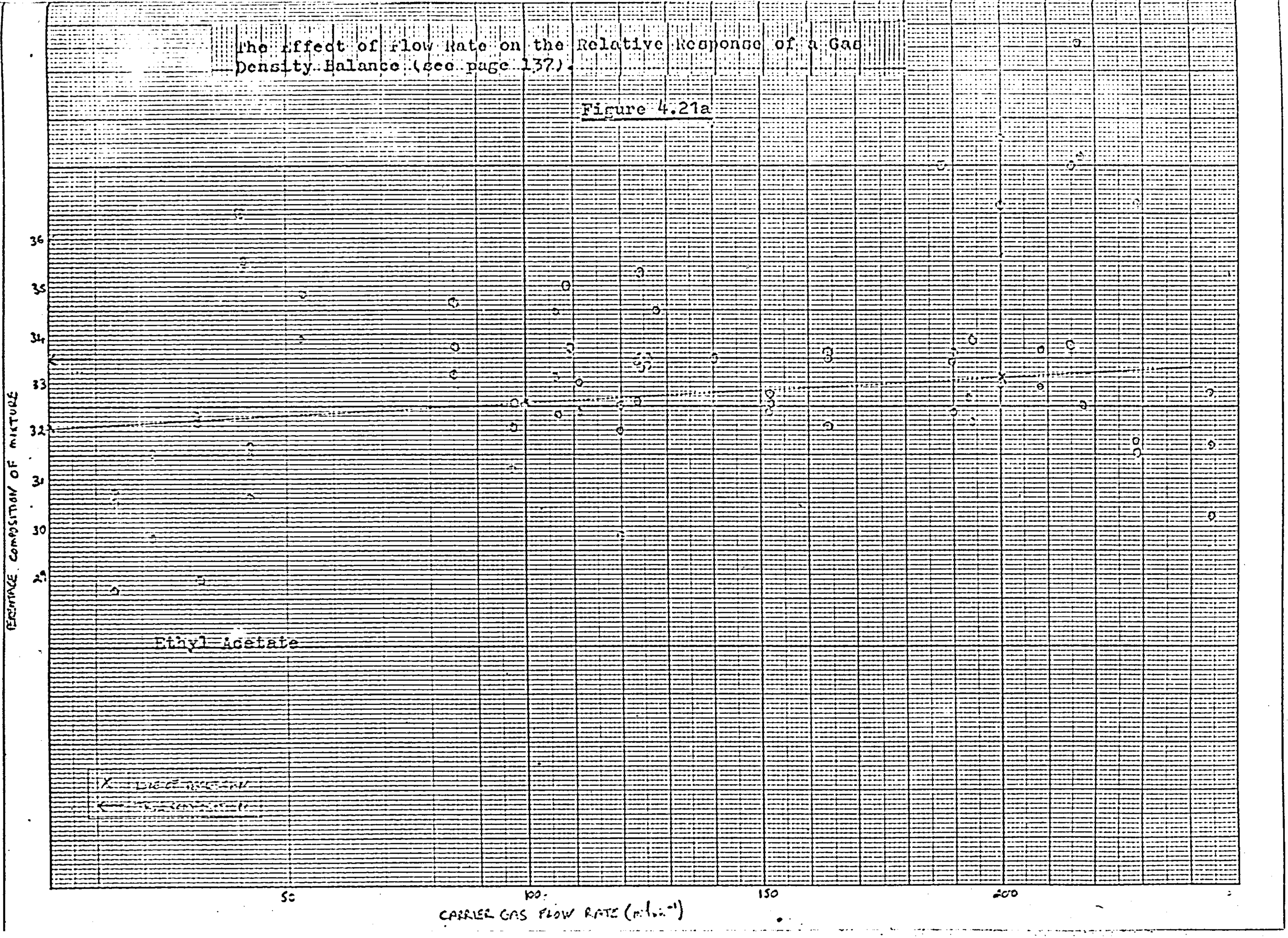
The percentage weight of any completely resolved component in a mixture is given by equation 3.18. Peak areas were measured using the equation:

$$\text{peak area} = \text{peak width at half peak height} \times \text{peak height} \qquad 4.9$$

Graphs of the percentage weight detected against flow rate are shown in figure 4.21. Scatter of points is very much greater than for the mass detector results (figure 4.19). The percentage deviation was calculated in an analogous manner to that described for the mass detector results. Variations of the values with flow rate were about 1×10^{-2}% per ml min^{-1} for each component, and although this value is greater than for the mass detector, for practical purposes the relative detector response is flow independent. The condition that there must be a substantially greater flow rate through the reference arm of the detector (> 10 ml min^{-1}) was maintained.

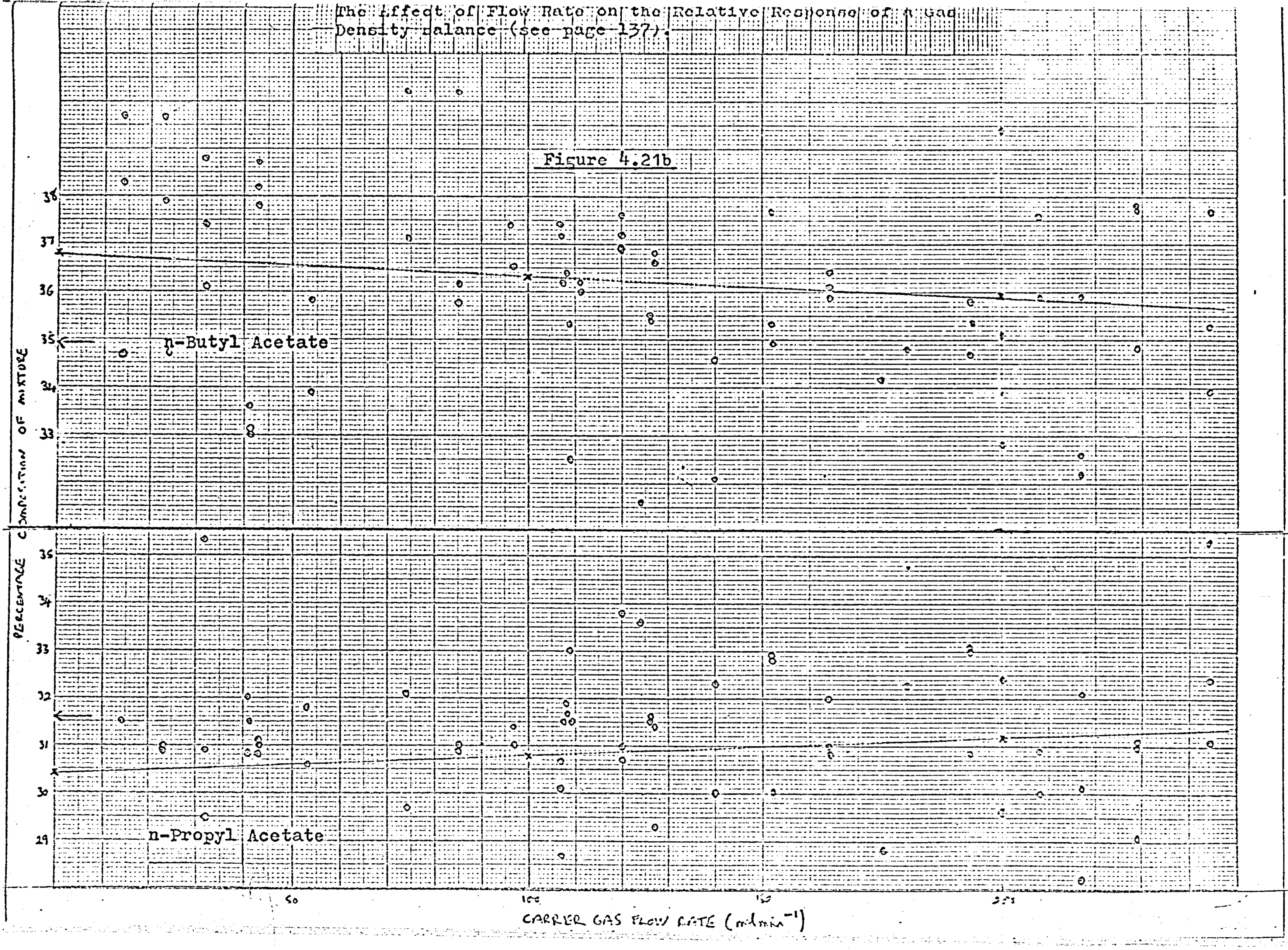
The effect of flow Rate on the Relative Response of a Gas Density Balance (see page 137).

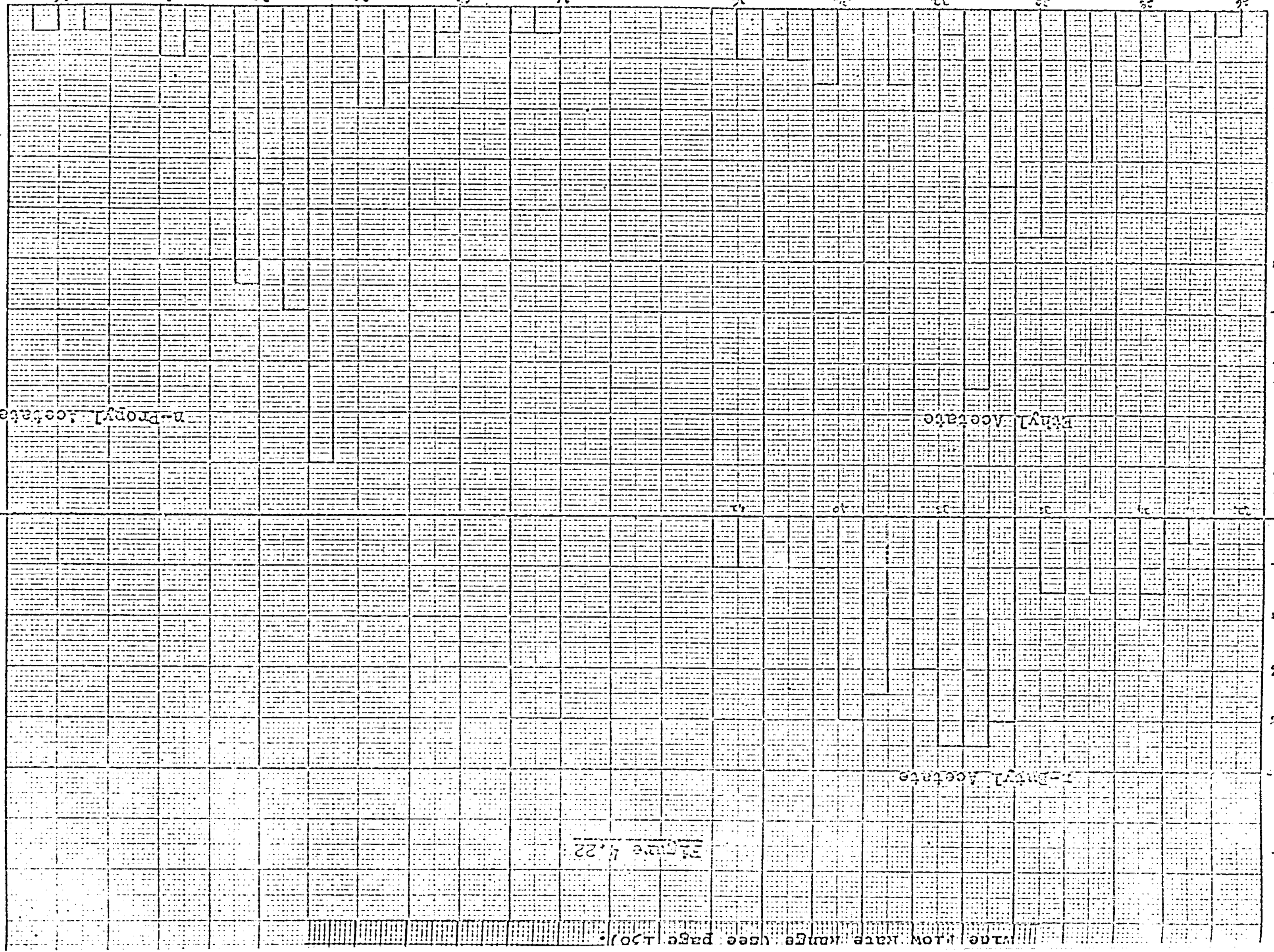
Figure 4.21a



The Effect of Flow Rate on the Relative Response of a Gas Density Balance (see page 137).

Figure 4.21b




Ethyl Acetate
n-Propyl Acetate
FREQUENCY
Figure 4.22
n-Butyl Acetate
FREQUENCY
Note: Low Rate Range (See page 430).

A statistical analysis was carried out on the results, and is expressed in the form of histograms (figure 4.22) and summarised in table 4.19 (cf figure 4.20 and table 4.17).

Table 4.19

Gas Density Balance Results

Component	n	$\bar{x}$	σ	V	x_o	Bias	Bias %	$\hat{R}$
Ethyl acetate	74	32.68	2.4	7.34	33.49	-0.81	-2.42	0.98
n-Propyl acetate	74	31.05	1.8	5.80	31.64	-0.59	-1.86	0.98
n-Butyl acetate	74	36.26	2.0	5.52 6.62	34.87	+1.39	+3.84 |2.34|	1.03

There is a similar trend in bias values to those obtained using the mass detector. It is therefore a reasonable assumption that the bias values do not depend to any appreciable extent on the performance of the mass detector. Indeed the bias values of the mass detector results are about half those of the gas density balance results. The standard deviations of the gas density balance results are all of the same order, and are much greater (3X) than those obtained using the mass detector. Repeatability can be defined numerically in terms of the coefficient of variation. If the coefficient of variation is n%, then the repeatability of 19 out of 20 results is $\pm$n%. The repeatability of the mass detector response is $\pm$2% and the Gow-Mac gas density balance $\pm$6%. The very much higher value obtained with the latter detector, may result from the difficulty of precisely assessing peak areas by graphical methods. Peak areas have also been measured using a digital integrator, and the results compared with the most satisfactory of the graphical methods. This work is discussed in detail in Chapter 7. Coefficients of variation were of the same order (3%) for both methods.

The fairly high values for the standard deviations of the results obtained from both detectors may be a result of carrying out the experiments over a wide flow rate range. A similar mixture to that used above, was analysed under the same conditions as given in table 4.16, but at a single flow rate. The flow rate range for the most satisfactory operation of the gas density balance, recommended by the

manufacturers is:

analytical flow rate 30 to 70 ml min^{-1}

reference flow rate 50 to 90 ml min^{-1}

with a difference of at least 10 ml min^{-1} between the two arms. This represents a total flow rate range of 80 to 160 ml min^{-1}. The experiment was carried out with a total flow rate of 126 ml min^{-1}, with 77 ml min^{-1} flowing through the gas density balance reference arm, and 49 ml min^{-1} through the analytical arm. The experiment was carried out over 2 days, so that changes in composition of the mixture were negligible compared to those which may have arisen in the previous work. The results for the mass detector are summarised in table 4.20 and figure 4.23.

Table 4.20

Mass Detector Results

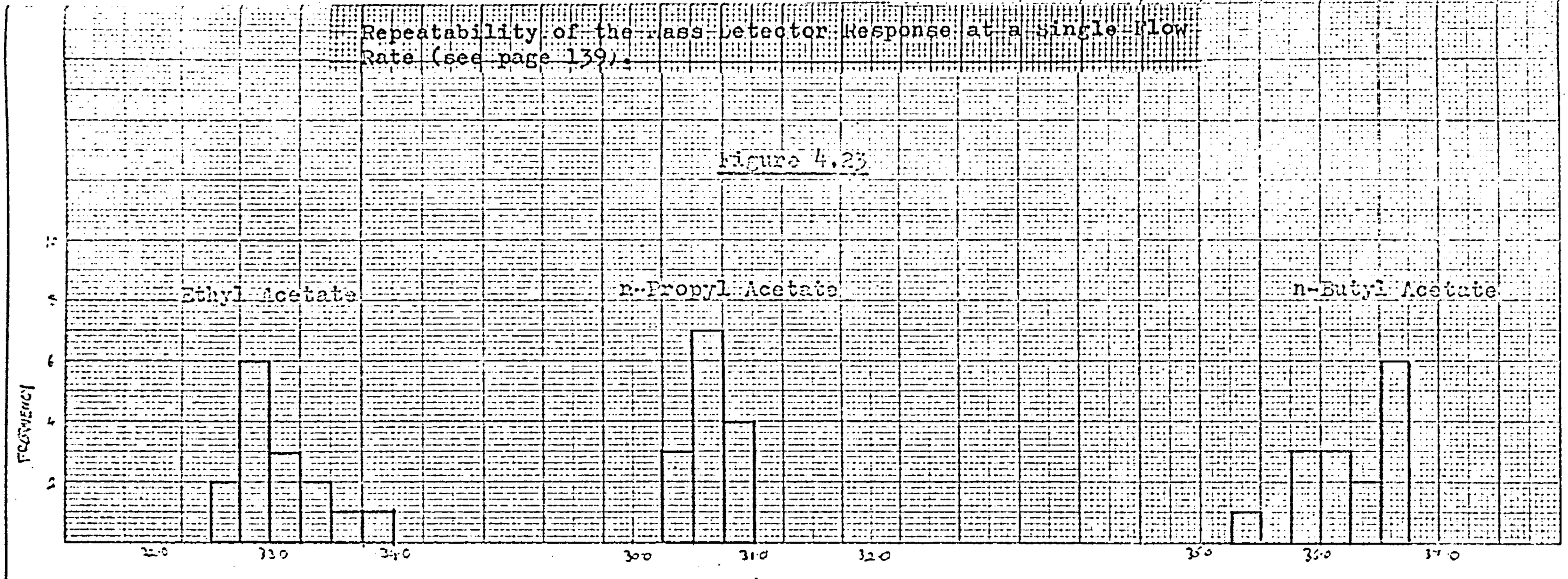
Component	n	$\bar{x}$	σ	V	x_o	Bias	% Bias	$\bar{R}$
Ethyl acetate	15	33.07	0.414	1.25	33.29	-0.22	-0.66	0.99
n-Propyl acetate	15	30.66	0.158	0.52	30.93	-0.27	-0.87	0.99
n-Butyl acetate	15	36.26	0.404	1.11	35.78	+0.48	+1.34	1.01
				0.96		|0.32|	|0.96|	

Comparison with table 4.17 shows that both the percent bias and the coefficient of variation values are lower when the experiment is conducted at a single flow rate.

Peak area measurements on the chromatograms obtained from the gas density balance were carried out firstly with a steel ruler, and repeated with a travelling microscope, in an attempt to improve on the precision of the measurements. These results are given in table 4.21, column A and B respectively, and histograms (results A) are shown in figure 4.24.

Repeatability of the Mass Detector Response at a single Flow Rate (see page 139).

Figure 4.23



Repeatability of the Gas Density Balance Response at a Single Flow Rate (see page 139).

Figure 4.24

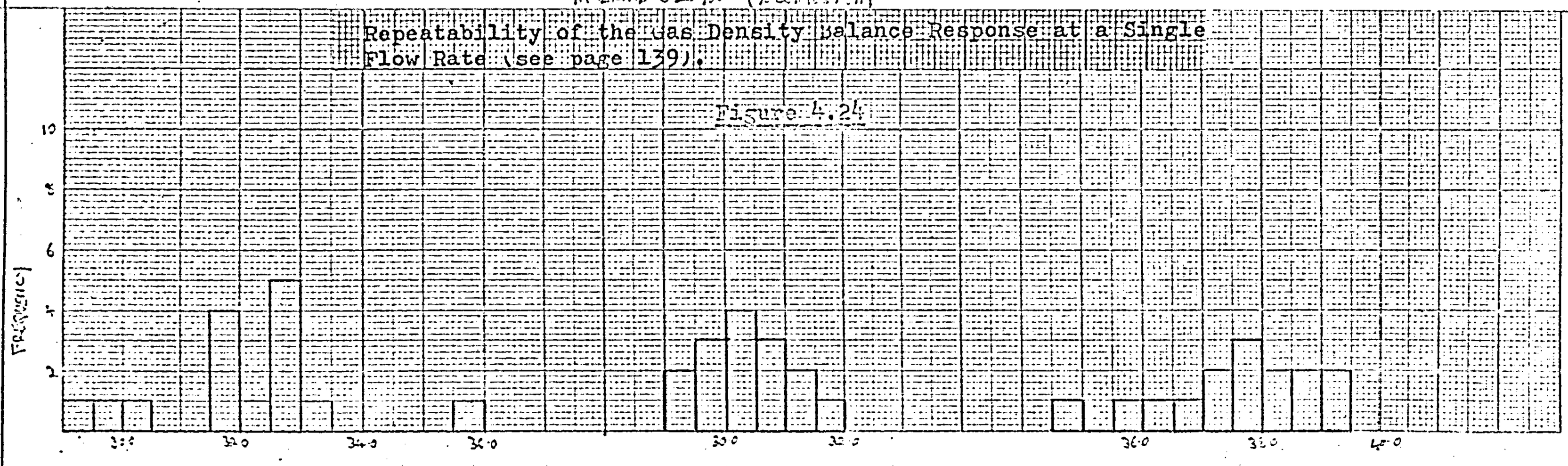


Table 4.21

Gas Density Balance Results

A

Component	n	$\bar{x}$	σ	V	Bias	% Bias
Ethyl acetate	15	34.04	1.42	4.43	+0.75	+2.25
n-Propyl acetate	15	30.21	0.76	2.52	-0.72	-2.33
n-Butyl acetate	15	35.75	1.44	3.85	-0.03	-0.08
				3.60		|1.55|

B

Ethyl acetate	33.87	1.20	3.74	+0.58	+1.74
n-Propyl acetate	30.05	0.69	2.28	-0.88	-2.85
n-Butyl acetate	36.08	1.18	3.12	+0.30	+0.84
			3.05		|1.81|

These results should be compared with table 4.19; it is evident that the performance of the detector is much improved when the analysis is carried out at one particular flow rate. Coefficients of variation have been halved, and the bias of the results considerably decreased. The use of a travelling microscope to determine peak widths and hence areas gave only marginally more repeatable results: in view of the additional length of time required to perform measurements with a travelling microscope, it is concluded that the use of a steel ruler is the preferable method.

4.5.3b Relative Response - Conclusions.

Excellent relative quantitative results were obtained with the mass detector over a wide flow rate range. Repeatability is $\pm$ 2% over this range (6% for the gas density balance). When analysis is carried out at a fixed flow rate the repeatability of the mass detector response is $\pm$ 1%, and the gas density balance $\pm$ 3%.

4.5.4 Absolute Adsorption Efficiencies.

The absolute responses of the mass detector, i.e. the adsorption efficiency, toward the components of the acetate mixture (see table 4.17) were measured. For each component a graph was plotted of the mass of material adsorbed against flow rate of carrier gas. A similar pattern emerged for all components, the amount of material adsorbed

increasing with decreasing flow rate. Considerable scatter of points was observed, and the results were not considered entirely satisfactory. It is preferable to measure adsorption efficiencies for single substances rather than mixtures, since the results cannot be affected by changes in sample composition. A new series of experiments was designed, for the measurement of absolute adsorption efficiencies.

For general chromatographic analysis flow rates of the order of 50 ml min^{-1} are commonly employed. The absolute adsorption efficiency of the detector (No. 27) has been measured at this flow rate. The conditions of operation are given in table 4.16. A total of 104 runs were performed, using n-butyl acetate, and the mean and standard deviation of the absolute adsorption efficiency was calculated. A 10 µl syringe (ref. No. 1) was used to inject 1 µl samples. The syringe had been previously calibrated using the electromicrobalance and found to deliver 92% of the quoted volume at the 1 µl level (see table 4.13). Calculations of adsorption efficiency take into account this error. Similar experiments were undertaken using 5 µl samples, of several different compounds. These results are summarised in table 4.22, but are discussed in more detail in section 4.6.2 since they form part of the programme to assess adsorption capacity.

Table 4.22

No. of runs	Sample size(µl)	Sample	Mean % Adsorption	Standard Deviation
104	1	n butyl acetate	99.2	0.7
7	5	" " "	95.9	
7	5	" " "	95.3	
4	5	n octane	95.8	
6	5	" "	93.8	
5	5	n butanol	96.5	
7	5	" "	96.3	

The absolute adsorption efficiency appears to be appreciably less for the 5 µl charges, compared with the 1 µl charges. The significance of this is discussed below.

The method of determining absolute adsorption efficiencies described above is open to a number of possible errors, all of which stem from the fact that it is not possible to guarantee that all the material with which the syringe is charged, reaches the mass detector. An experiment was designed to eliminate the need to know the quantity of sample injected, and to remove the possibility of loss of sample between the injection point and the detector. The Pye Panchromatograph was used in this experiment. The column effluent was led to a small cylindrical chamber outside the chromatograph oven, and then back into the oven to a Gow-Mac gas density balance. The chamber could contain a mass detecting element or an empty cylinder of the same dimensions. To determine the absolute adsorption efficiency of the mass detector at any flow rate, a sample was injected in the normal manner, a proportion of which was adsorbed by the mass detecting element. The remainder of the sample was detected by the gas density balance. By repeating the experiment in the absence of the detecting element, the proportion of material adsorbed, and hence the adsorption efficiency, was found. In both experiments, all conditions were identical (see table 4.23), so that any losses of material due to leakage or irreversible adsorption on the column were equal, and did not affect the results.

Table 4.23

Apparatus	Pye Panchromatograph
Column	ApL ref. A
Inlet pressure	30 lb in^{-2} N_2
Injection temperature	100°C on column
Column temperature	100°C
Mass detector temperature	25°C
Gas density balance temperature	100°C
Detecting element ref.	22

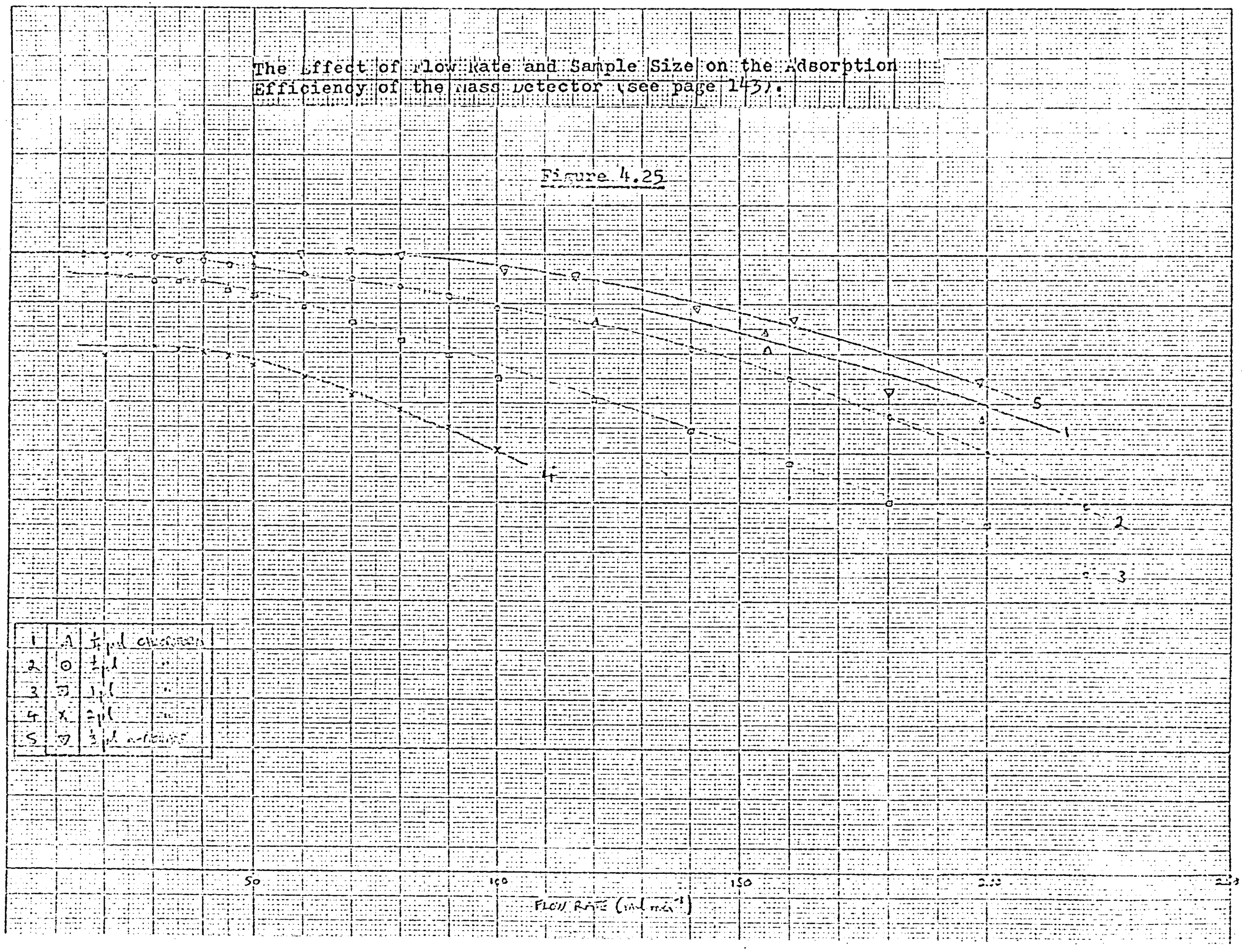
$\frac{1}{2}$ µl samples of chloroform were injected, at a number of flow rates covering the range 15 to 250 ml min^{-1}, in the absence of the mass detecting element, and the resulting peak areas were measured. The

experiment was repeated, again using $\frac{1}{2}$ µl samples, in the presence of a mass detecting element. The relative amount of material reaching the gas density balance at each flow rate, with and without the detecting element, was found, and hence the absolute adsorption efficiency of the mass detector was calculated. The results are displayed graphically on figure 4.25. The whole experiment was repeated for nominal sample sizes of $\frac{1}{4}$ µl, 1 µl and 2 µl of chloroform, and $\frac{1}{2}$ µl of n-nonane. The results were calculated in an anologous manner.

The results confirm that adsorption efficiency decreases with flow rate, which is of no consequence in the determination of the proportions of components in a mixture, assuming that the determination is carried out at a fixed flow rate. The absolute weight of materials present is obtained from the quotient of the observed step heights (in milligrams) and the adsorption efficiency at the flow rate employed. An effect of more serious consequence, illustrated in figure 4.25 is that adsorption efficiency decreases as sample size increases. For mixtures containing a number of materials in widely differing proportions, the observed composition will not agree with the true composition. This at first sight appears to be at variance with the linear response of the detector illustrated in figure 4.47. The upper end of the linearity plot was obtained by injecting varying amounts of benzene, all at the same concentration, but for different lengths of time. Injection using a syringe is normally for about the same period of time, irrespective of the sample size, i.e. although in both cases sample size is varied, in the former it is maintained at constant concentration, and in the latter the concentration is increased. Calculations show that the concentration of benzene injected in the linearity experiment was about 110 µg ml^{-1} for all quantities. The concentration of a 5 µl sample just after injection into a gas stream flowing at 30 ml min^{-1} is about 8 mg ml^{-1}, so that for a very short retention time the concentration will not be significantly less than

The Effect of Flow Rate and Sample Size on the Adsorption Efficiency of the Mass Detector (see page 143).

Figure 4.25



this value. Under the conditions given in table 4.23 the retention time of chloroform was about 1 minute, so that a high concentration was reaching the detecting element, indicating that adsorption efficiency is a function of the concentration of the adsorbate. To confirm this, adsorption efficiencies were measured at a fixed flow rate, for a number of different sample sizes of n-octane, introduced into the detecting element at varying concentrations. This was achieved by using two columns of different retention characteristics and by inserting dilution chambers between the column exit and the detecting element. The operating conditions are given in table 4.24.

Table 4.24

Apparatus	Pye Panchromatograph
Columns	ApL A,G
Dilution chamber volumes	4 ml, 74 ml
Injection temperature	100°C on column
Column temperature	100°C
Detecting element temp.	25°C
Detecting elements ref.	24, 27
Gas density balance temp.	100°C
Analytical gas flow rate	31 ml min^{-1}
Reference gas flow rate	52 ml min^{-1}

Adsorption efficiencies were calculated for each sample and at each concentration, and are shown on figure 4.26. The more dilute the sample the smaller was the effect of sample size on adsorption efficiency. The most dilute sample (column G + large dilution chamber) gave an efficiency of over 99½% for all sample sizes injected: the largest sample size was 8 µl, and the maximum concentration of the sample reaching the detecting element under these conditions was about 120 µg ml^{-1}. The most concentrated sample (using column A) never attained 100% adsorption, even for a 1 µl injection: the minimum concentration in this case was 1 mg ml^{-1}. The remaining samples were all totally adsorbed, up to a sample concentration of about 130 µg ml^{-1}.

Figure 4.26

The effect of Sample Size on the adsorption efficiency of the Mass Detector (see page 144).

4.5.4a Absolute Response - Conclusions.

It is concluded that although absolute adsorption efficiency decreases as flow rate increases, under normal operating conditions it is not affected by sample size. However for high speed analysis (with retention times the order of 1 minute) in which there is a high concentration of sample reaching the detecting element adsorption efficiency falls as sample size is increased. It is still sensibly complete for samples of less than about $\frac{3}{4}$ mg per component, and for flow rates below 30 ml min^{-1}. The effect on the analysis of samples of short retention time, carried out at more rapid flow rates is shown in the following examples:

(i) A 1 µl sample consisting of approximately equal proportions of two or more components, at any flow rate will produce negligible errors in a relative percentage composition determination.

(ii) A 2 µl sample containing a minor constituent. A sample contains say 1.424 mg of n-heptane and 0.176 mg of hexane, i.e. 89.00% and 11.00% by weight respectively. At a flow rate of about 50 ml min^{-1} the mass detector will adsorb only 98.4% of the heptane, but 99.6% of the hexane, i.e. 1.401 mg and 0.175 mg. The detected percentage composition is $\frac{1.401}{1.576} \times 100$ i.e. 88.90% heptane in the mixture, and

$\frac{0.175}{1.576} \times 100$ i.e. 11.10% hexane in the mixture. It has been established that the percentage composition values are precise to ± 1% (section 4.5.3). The above results are within these limits and negligible error has arisen through changes in absolute adsorption efficiency with sample size.

(iii) Consider an extreme case in which the total volume of the sample is 5 µl, the mixture contains about 60%, 39% and 1% of three materials of similar density, and which is analysed at 150 ml min^{-1}. Analysis details are given in table 4.25.

Table 4.25

Component	True % weight	Weight per 5 µl (mg)	Adsorption Efficiency	Weight Adsorbed (mg)	% Detected weight
A	59.12	2.365	90.7%	2.145	58.69
B	39.83	1.593	12.2	1.469	40.18
C	1.05	0.042	98.0	0.041	1.13

Again, the results are perfectly acceptable. Satisfactory results will be obtained even for components of very short retention time, and which are present in widely differing proportions.

4.5.5. Delivery Tube Dimensions.

Changing the diameter of the mass detector delivery tube will not affect the flow rate of carrier gas into the detector, but it will affect the linear gas velocity, as shown in table 4.26.

The use of a narrow bore stainless steel tubing offers several advantages over a wide bore tube: it is easier to accommodate in a detecting element; its higher electrical resistance enables direct heating of the tube to a high temperature, without requiring a high current; loss of resolution of components after leaving the column is minimised. The absolute adsorption efficiency of the detector was measured with several delivery tubes, using the same sample size of n-butyl acetate. A capillary delivery tube (0.2 mm) was used at temperatures up to 80°C, both with a standard size detecting element (ref. 2) and a miniature element (ref. 26), and flow rates between 20 and 50 ml min^{-1}. In no instance did adsorption efficiency exceed 60%. The introduction of a diffuser at the delivery tube outlet had a negligible effect on adsorption efficiency. Similar results were obtained using a 0.7 mm bore tube, but the use of a $1\frac{1}{2}$ mm bore tube under similar conditions gave an adsorption efficiency of 95%. Typical results are given in table 4.26; the results refer to a flow rate of 48 ml min^{-1} (at 23°C).

Table 4.26

Delivery Tube Outside Dia. ins.	Delivery Tube Dia. mm	Delivery Tube Bore mm	Temperature °C	Adsorption Efficiency %	Linear Gas Velocity $cm\ sec^{-1}$
-	0.42	0.22	23	22.2	2110
-	0.42	0.22	50	39.2	-
1/16	1.46	0.70	23	45.3	207
1/16	1.46	0.70	50	45.5	-
1/8	3.02	1.48	50	95.0	47

The use of a 1/8" delivery tube is recommended for reasonable (i.e. over 90%) adsorption efficiency. To minimise losses of resolution which may occur in the delivery tube (section 4.6.1.), the tube was packed with the same stationary phase as used in the main column. It was necessary to maintain the delivery tube at a higher temperature, than an empty tube, since the increase in residence time of components in the packed tube led to condensation within the tubing. In general a packed delivery tube should be maintained at column temperature. A packed delivery tube cannot be used in experiments in which another detector is placed in series with the mass detector. The back pressure exerted by the packing on the first detector chamber may cause erroneous response. In addition the time delay introduced between the responses of the two detectors is excessive, and the analysis of a complex mixture would be made difficult by the non-coincidence of the chromatograms obtained from the two detecting systems. Indeed even using an empty delivery tube, a detectable time lag occurs (see figure 4.18). At a flow rate of 50 ml min^{-1}, with a 50 cm x 1½ mm empty delivery tube, the delay is about 1 second, assuming equal detector response times.

4.5.5a Delivery Tube Dimensions - Conclusions.

The use of a narrow bore delivery tube does not give a reasonable adsorption efficiency at the flow rates demanded by the column for maximum performance. It is concluded that the most satisfactory delivery tube for quantitative adsorption by the mass detector, is a tube of the widest possible diameter, consistent with a minimal loss

of resolution. Loss of resolution and condensation of components is minimised by using the shortest possible delivery tube. An 1/8" ($1\frac{1}{2}$ mm bore) tube is recommended.

4.5.6. Delivery Tube Temperature and Position.

The adsorption efficiency of the detector will be affected if the delivery tube is operated at extremes of temperature. If the temperature of the tube is too low to give significant vapour pressures of the compounds passing through the tube, condensation within the tube will occur, resulting in a decrease in adsorption efficiency: distortion of the chromatogram also occurs, and this is illustrated in figure 4.27. By operating the delivery tube at too high a temperature, the detecting element temperature is raised, and rapid desorption of adsorbed materials will occur, resulting in peaks rather than steps for the detector response. An extreme case is illustrated in figure 4.28. Between these limits the adsorption efficiency will depend on temperature to a lesser extent and it is this dependence which is examined here. Conditions suitable for the analysis of solids and permanent gases are considered in sections 5.3 and 5.5. It is evident that it is the temperature difference between the boiling point of the adsorbate, and the detector which must be considered, rather than absolute temperatures. Experiments were carried out at a fixed detector temperature ($24^{o}C$) whilst the delivery tube temperature was varied over the range 24 to $100^{o}C$. Operating conditions are as in table 4.16 where appropriate, with a flow rate of 110 ml min^{-1}. The changes in efficiency were measured, using 1 µl samples of n-butyl acetate (bp $116^{o}C$). It was concluded (section 4.5.5) that maximum adsorption efficiency is favoured by slow flow rates. However condensation of material within the delivery tube is minimised if the residence time of the sample within the delivery tube is as short as possible, i.e. the flow rate is a maximum. Although these two conditions are incompatible, the latter may be met indirectly by operating the delivery tube at a sufficiently high temperature to prevent condensation,

Chromatogram showing the Response of the Mass Detector and a Gas Density Balance to some High Boiling Alkanes (see page 148).

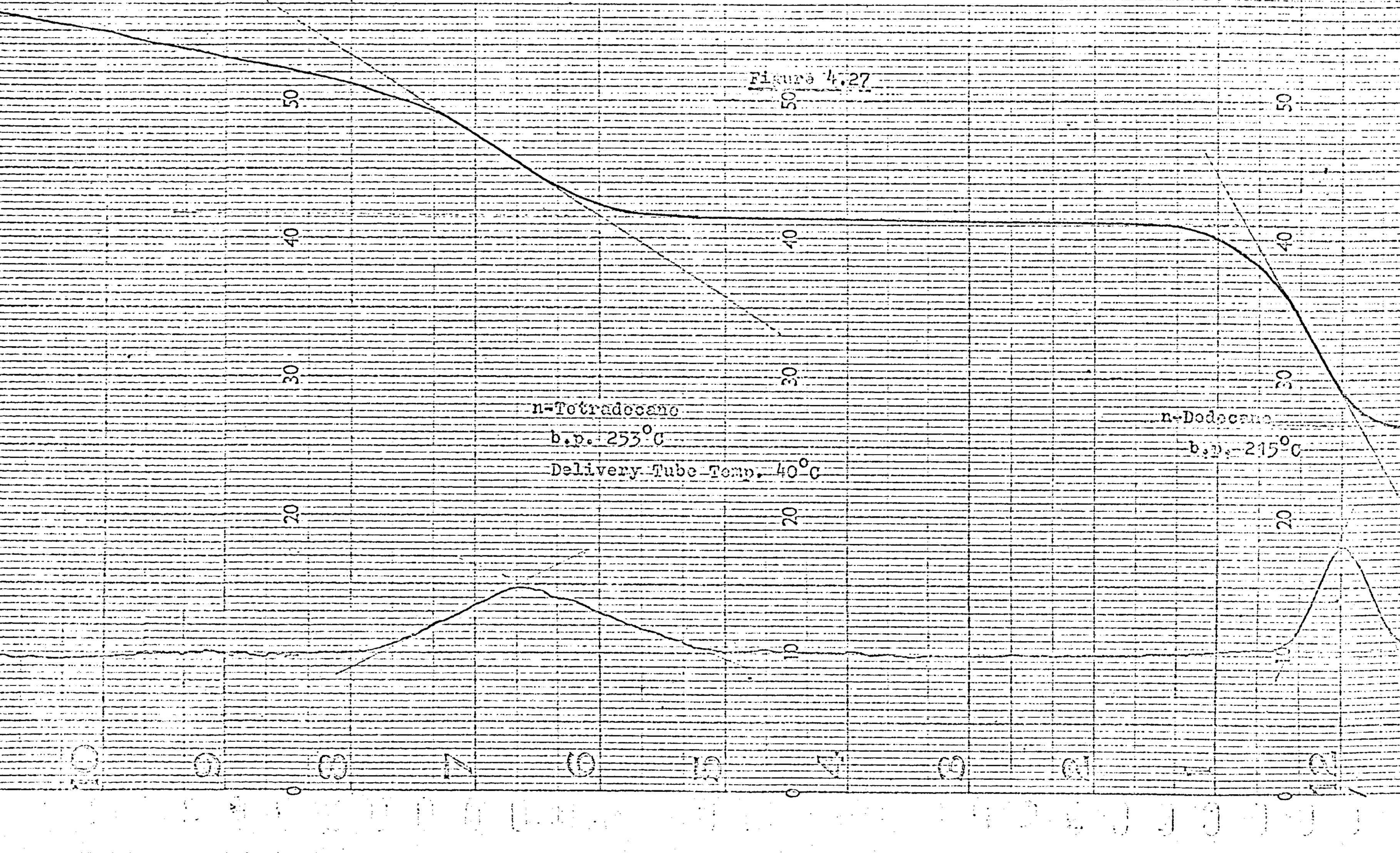
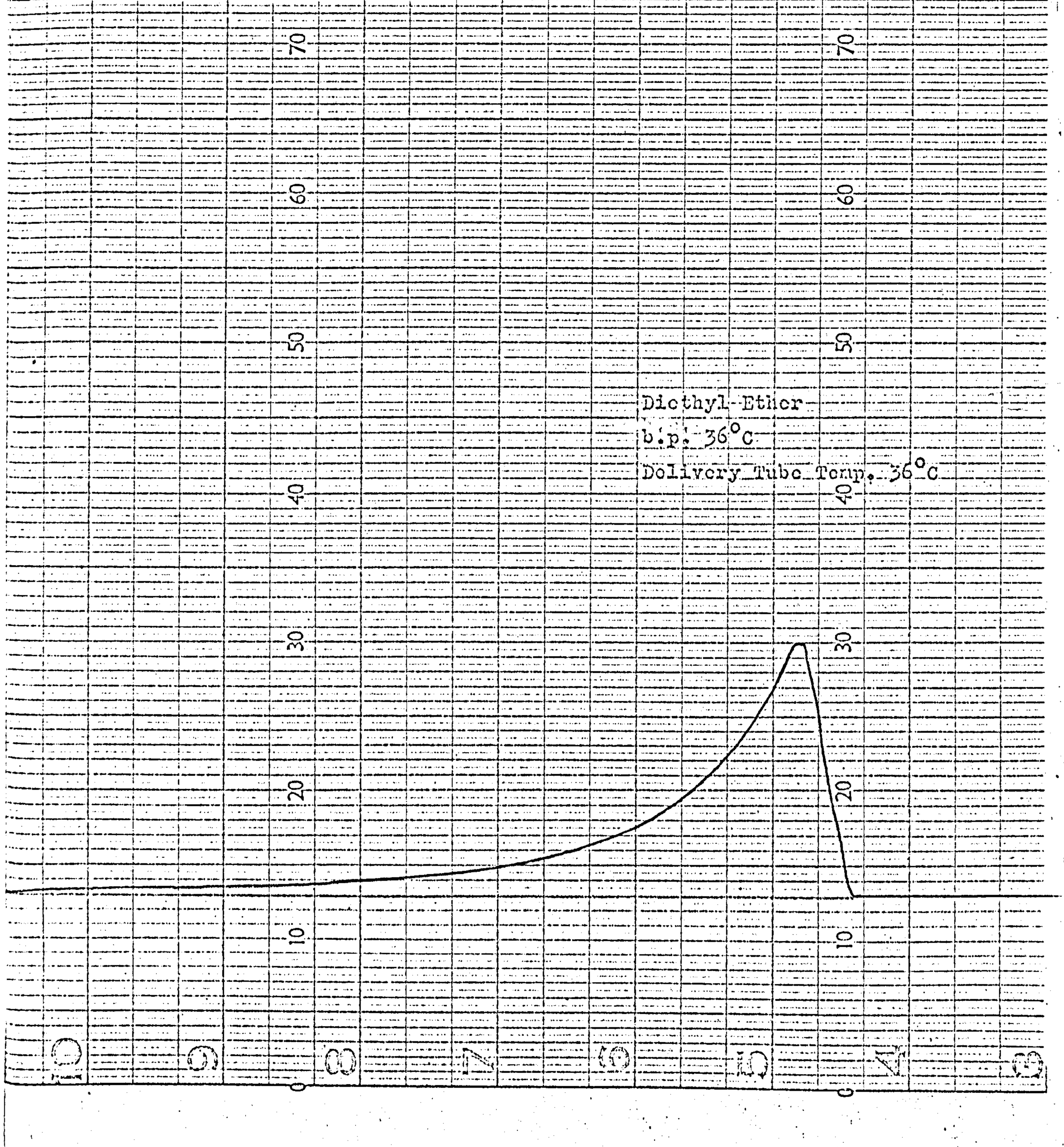


Figure 4.27

Chromatogram showing the response of the Mass Detector to Ether (see page 148).

Figure 4.28



even at slow flow rates.

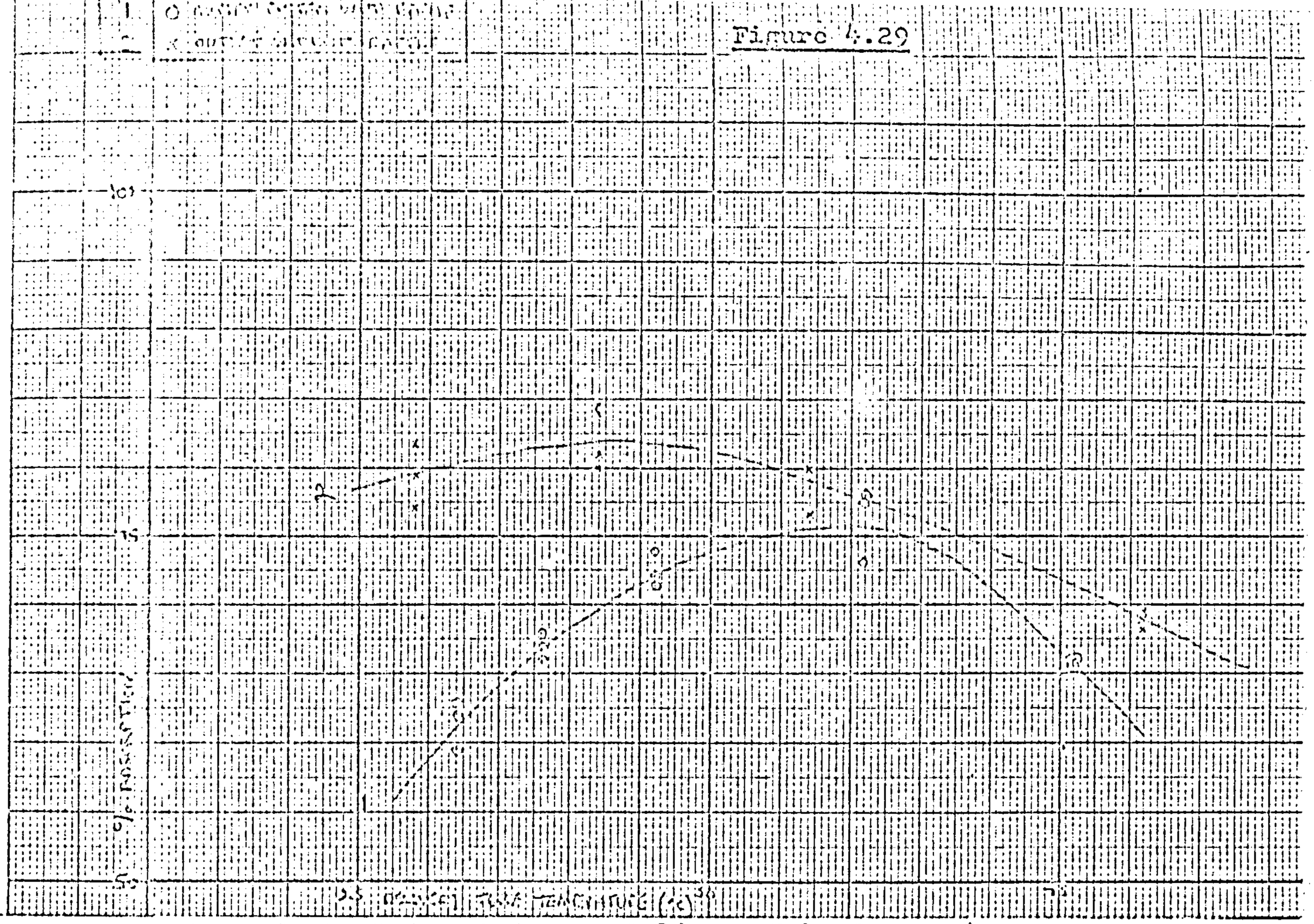
The temperature of an 1/8" o.d. delivery tube was monitored, at a point just outside the chromatograph oven, midway along the tube, and within the detecting element. The adsorption efficiency of the detector for several delivery tube temperatures was measured, in some instances with the delivery tube exit fitted with a baffle. The baffle had a marked effect on the dependence of adsorption efficiency with tube temperature, which is illustrated graphically on figure 4.29. The presence of a baffle caused the temperature range of maximum efficiency to decrease, and the actual value for the maximum efficiency was lower. A baffle could thus give erroneous results for the analysis of a wide boiling range mixture. No increase in detector noise caused by direct impingement of hot carrier gas on the walls of the detecting element was observed in the absence of the baffle: the use of a baffle was in no was advantageous, and it was discarded.

A number of experiments were carried out at several different temperatures in which the effect of changing the length of the tube within the detecting element was investigated. The results are shown in figure 4.30. The length of delivery tube within the detector is expressed as a percentage of the detector length. All curves exhibit a maximum; there was a maximum difference in adsorption efficiency between the different delivery tube positions, of about 10%. Operating over a temperature range of about 50°C, the adsorption efficiency only changed by 3%.

4.5.6a Delivery Tube Temperature and Position - Conclusions.

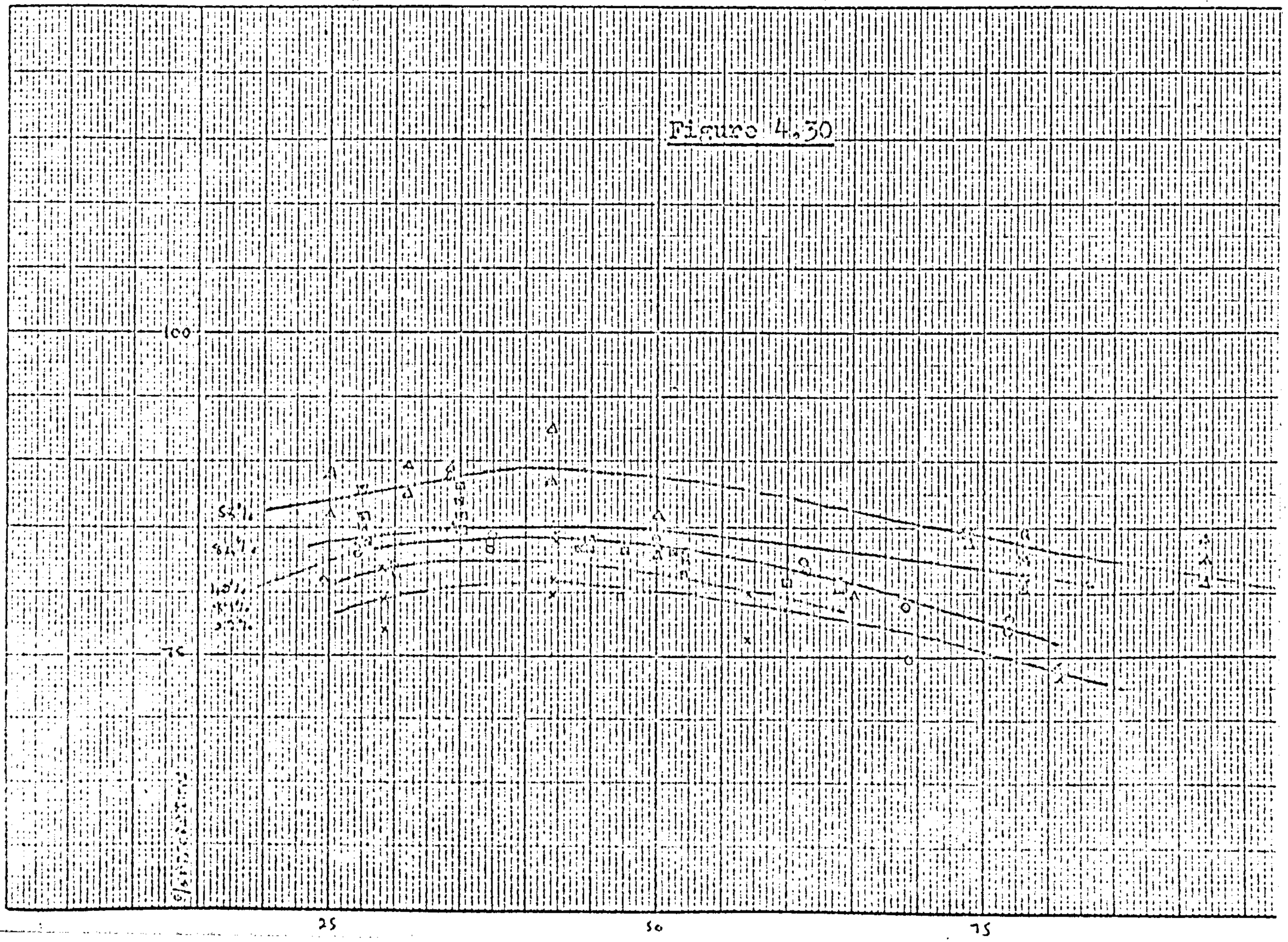
Although variations in adsorption efficiency were observed, neither the position of the delivery tube within the detecting element, nor its temperature are critical for good adsorption efficiency, even at a fairly rapid flow rate. It is recommended that, for a cylindrical detector, the delivery tube occupies about 60% of the detector length. For materials boiling in the region of 100°C, the delivery tube should be operated at about 40°C. In general the delivery tube temperature is

Figure 4.29



The Effect of Mass Detector Delivery Tube Temperature on Adsorption Efficiency (see page 149).

Figure 4.30



chosen between limits, such that condensation in the tube, and desorption from the mass detector are minimised.

4.6.1 The Performance of the Mass Detector - Intra Detector Parameters. Detector Geometry and Adsorption Efficiency.

Detecting elements used in all experimental work so far discussed have been cylindrically shaped, and closed at one end (figure 4.8). A number of other geometries have been considered (see section 4.3.1a) and several elements constructed, in an attempt to increase adsorption efficiency, and to decrease their volume and weight. The efficiencies of these elements, relative to cylindrical element ref. 2, have been measured, under identical conditions, and are listed in table 4.27. They are drawn approximately full size in figure 4.8.

Table 4.27

Element No.	Adsorption Efficiency (%)
2	100
9	68
10	75
11	86

The details of detecting element weights and dimensions are given in table 4.9. Element 9 was very light, and was mounted directly on to the balance stirrup. The stability of the balance was better than with any other detecting element, but adsorption efficiency was poor. Element 10 was difficult to construct, and to align inside the detector chamber. Element 2 was the most efficient design: although this element contained more charcoal than the other designs, it is established (see figure 4.34) that adsorption efficiency is not affected by the amount of adsorbent. Since a cylindrical detector was the most efficient investigated, and was also the simplest to construct, it was adopted for the majority of work on mass detection. The effect of changing the dimensions of a cylindrical detector was considered. A number of detectors of identical length, but different diameters, all containing the same particle size range of charcoal, were constructed, and adsorption efficiencies measured. Experimental conditions are given

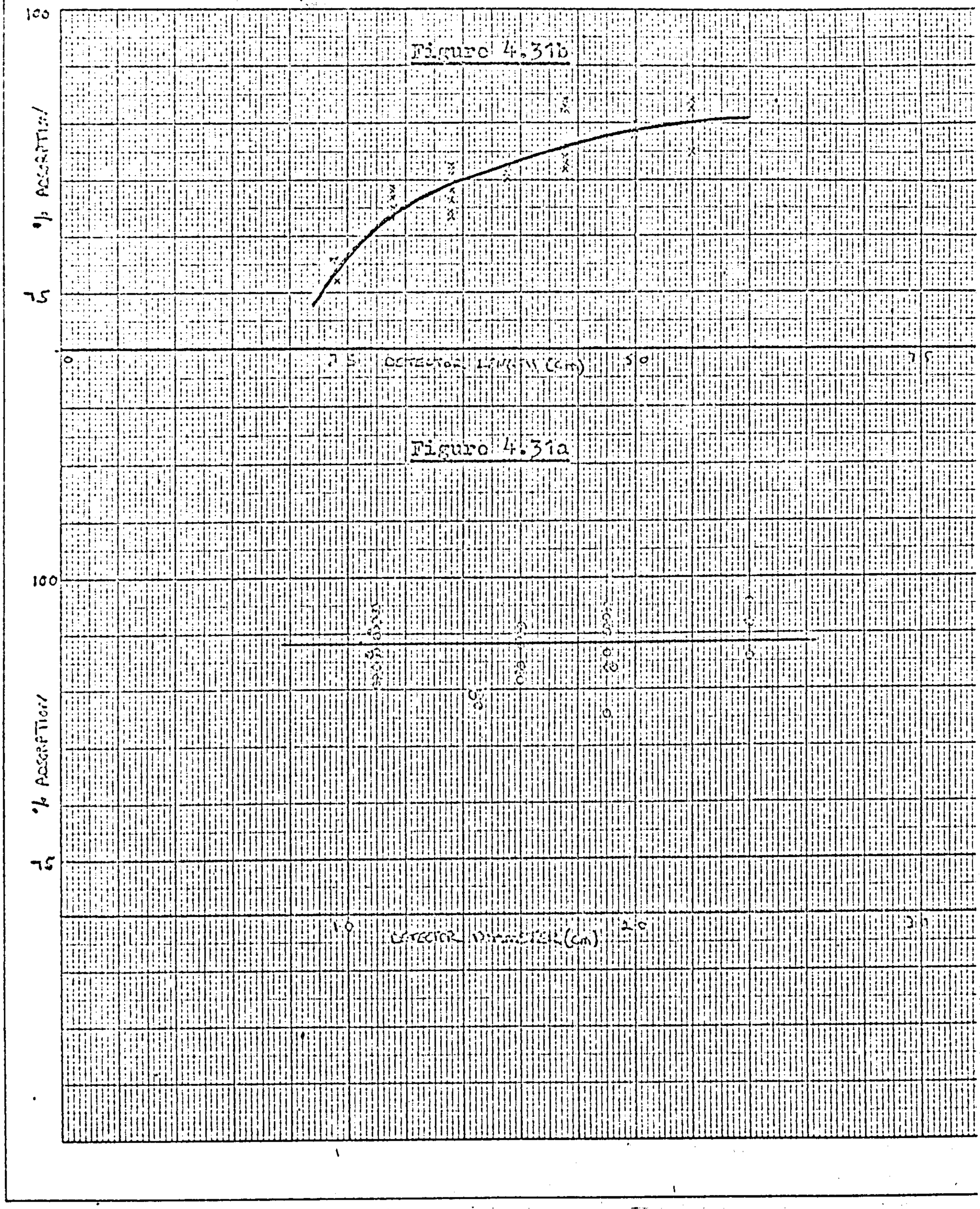
in table 4.16. 1 µl samples of n-butyl acetate were used. The delivery tube temperature was 53°C, and the carrier gas flow rate 141 ml min^{-1}. Elements 3-7 were used in the experiment, the characteristics of which are listed in table 4.9. The results are shown on figure 4.31a. No variation in adsorption efficiency was observed when the detector diameter was varied from 1 to $2\frac{1}{2}$ cm. Since the larger diameter detectors contained more charcoal, it is evident that the amount of charcoal present (i.e. the surface area of the charcoal in this particular case) has no effect on adsorption efficiency (unless effects of detector diameter and charcoal area act in opposition). A 1 cm diameter detector is the smallest which can be constructed without encountering difficulties in preparation, and alignment in the detector chamber. Detectors of diameter greater than $2\frac{1}{2}$ cm may lead to excessive loss of resolution of components entering the detecting element, although the actual dead volume of the detector is far smaller than the geometric volume of the detector (see section 4.6.4).

Resolution losses within the mass detecting element can be measured by comparing the resolution of two components observed by a detector of negligible dead volume placed in parallel with the mass detector, with that observed by the mass detector. Resolution losses along the detector delivery tube can be estimated by measuring resolution at the column exit, and at the mass detector. The detector at the column exit must have a dead volume similar to that of the mass detector. Two component mixtures were prepared and analysed under conditions which just gave complete separation: the components were in approximately equal proportions. The resolution R of the components was calculated from the equation[25]:

$$R = \frac{2\,\Delta V_R}{y_a + y_b} \qquad 4.10$$

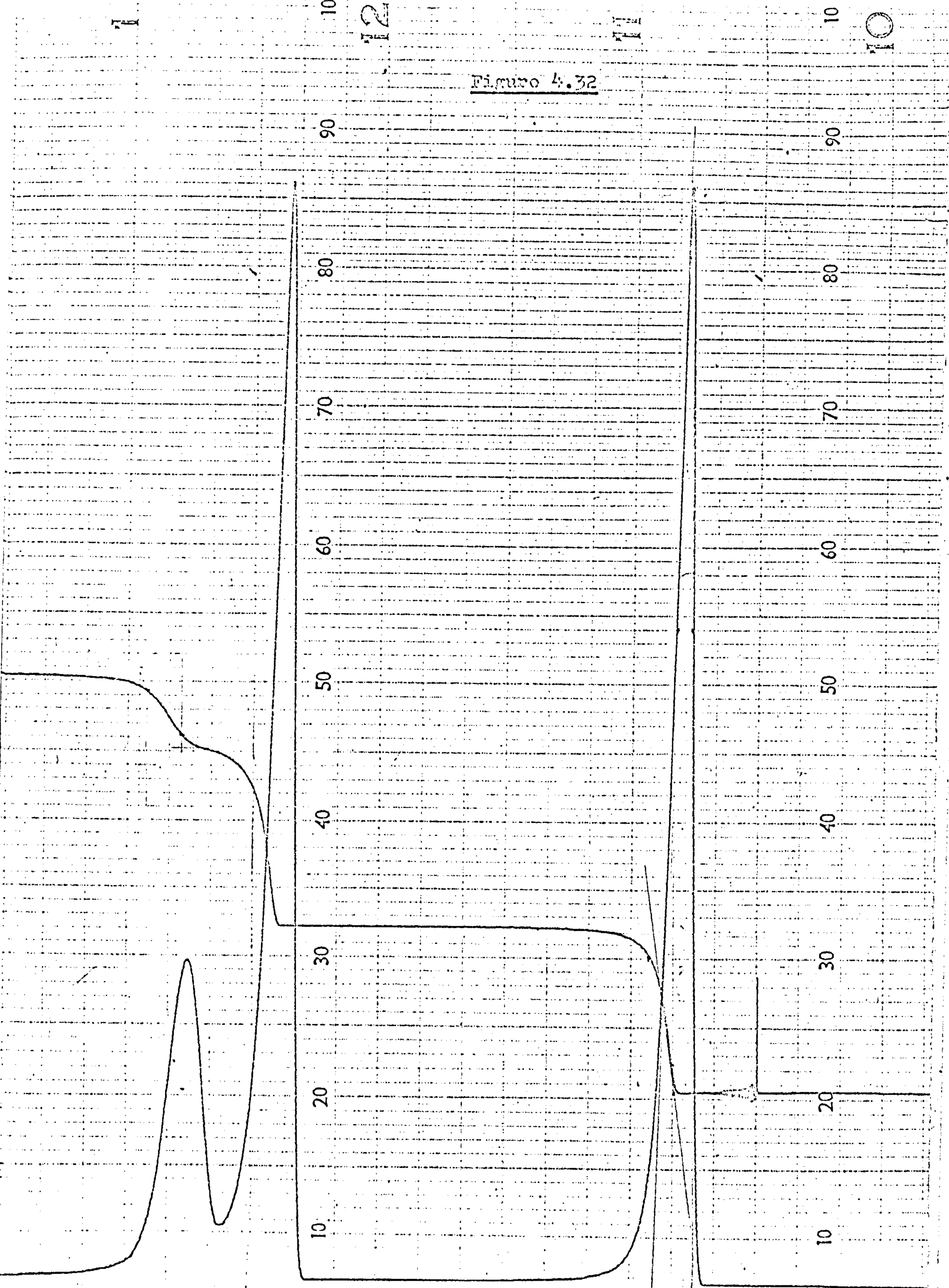
where ΔV_R = difference in retention volumes of components a and b

y_a, y_b = peak widths for components a and b, measured as the distance between the tangents to the curve, at the baseline.



The Effect of Detecting Element Geometry on Adsorption Efficiency (see pages 151 and 154).

Figure 4.32



Chromatogram comparing the Resolution of Materials observed by the Mass Detector and a Gas Density Balance (see page 152).

Experiments were carried out with the following detector combinations:

(i) A flame ionisation detector placed in parallel with the mass detector, ensuring that the narrow bore connecting tubes from the end of the column to each detector were of similar volume. If resolution losses within the stream splitter are equal, then any differences in resolution of the components between the flame ionisation detector and the mass detector must result from the effective dead volume of the latter, since the volume of the flame ionisation detector is only a few microlitres (see page 30). The contribution of the splitter was estimated by measuring resolution with first the major and then the minor stream to the mass detector, in parallel with a flame thermocouple detector.

(ii) A Gow-Mac gas density balance in series with the mass detector. The gas density balance has a dead volume of about 8 ml: the effective volume of the mass detecting element used in this experiment was not greater than $1\frac{1}{2}$ ml. The volume of the tubing, of internal diameter $1\frac{1}{2}$ mm, between the two detectors was $\frac{1}{2}$ ml.

(iii) A katharometer of dead volume about 3 ml in series with the mass detector.

Values of the Resolution R (equation 4.10) were obtained from 12 chromatograms. In no case did the mass detector impair the degree of resolution to an extent greater than the flame detectors or the hot wire detectors. An example of a chromatogram of partially resolved materials is shown in figure 4.32. Comparison of the differential and integral response curves, obtained from a gas density balance and the mass detector shows that the observed resolution is similar for both detectors.

The effect of changing the length of a cylindrical detector, at a fixed diameter was investigated. The conditions were identical to those of the diameter variation experiment. The delivery tube was a fixed distance into the detector chamber throughout the experiment,

PAGE NUMBERING AS ORIGINAL

i.e. the proportion of detector length occupied by the delivery tube varied with detector length. The overall effect of shortening the detector length is shown in figure 4.31b. Detector details are given in table 4.29.

Table 4.29

Element No.	Length (cm)	Geometric Surface Area (cm^2)	Charcoal Weight (g)	% Detector occupied by delivery tube	Mean % Adsorption
6a	5.5	26.7	0.53	49	90.2
6b	5.0	24.4	0.49	44	89.2
6c	4.4	21.7	0.44	36	89.1
6d	3.9	21.1	0.39	28	85.6
6e	3.4	17.2	0.35	18	83.8
6f	2.9	14.9	0.30	$3\frac{1}{2}$	83.1
6g	2.4	12.6	0.26	-2	77.4
6g	2.4	12.6	0.26	75	87.3

Detector diameters 1.45 cm: charcoal particle size 20-40 BS mesh.

The fall off in adsorption efficiency may be due to two factors:

(i) decrease in the weight and surface area of the adsorbent, i.e. dependent on the length of cylinder.

(ii) decrease in trapping efficiency, i.e. dependent on the fraction of delivery tube within the detecting element.

The adsorption efficiency of element 6g (the shortest element) was determined with the delivery tube below the base of the element, and also occupying 75% of its length. The increase in adsorption efficiency was marked, and approached that of the largest elements (6a, b). Thus the major contribution to the changes in adsorption efficiency is the position of the delivery tube with respect to the detecting element, and not the overall element length.

The effect of maintaining a constant element length, but changing the proportion of its surface area covered with charcoal, as illustrated in figure 4.8, yielded the results given in table 4.30.

Table 4.30

Element No.	Charcoal geometric Surface area (cm^2)	% Detector Area covered by charcoal	Adsorption Efficiency (%)
28	9.9	40	83.6
29	14.2	57	89.6
30	18.4	74	95.2
27	24.8	100	95.2

All elements were of identical dimensions (table 4.9) and lined with 60-80 BS mesh charcoal.

Reasonable adsorption efficiency is observed for percentage coverages over about 70%.

Adsorbent Particle Size Range.

Several elements of identical dimensions were constructed and lined with different particle size ranges, obtained from a single batch of charcoal. The adsorption efficiency of each element was measured under the conditions given in table 4.16. The carrier gas flow rate was 115 ml min^{-1}, and 1 µl samples of n-butyl acetate were used.

It was not possible to construct the elements such that each carried the same weight of charcoal. The adsorption efficiency of each element was measured five times, and the mean values are quoted in table 4.31.

Table 4.31

Element No.	Particle Size Range BS mesh	Mean Particle Size (µ)	Weight of charcoal (g)	Mean % Adsorption
12	100-120	138	0.152	69.6
13	80-100	165	0.195	85.5
14	60-80	213	0.246	92.6
15	40-60	310	0.417	91.5
16	20-40	500	1.410	90.8
19	12-18	1129	1.381	92.9
17	6-12	2109	2.119	90.8

The percentage element length occupied by the delivery tube was 51% in all cases. The reliability of the values obtained for elements 17 and 19 are open to question since the weights of these elements were in the region of the capacity limit of the electromicrobalance (see figure 4.6 and 4.7). Notwithstanding this, high adsorption efficiency

is obtained on elements using a mean particle size of 70 BS mesh or smaller (i.e. larger diameter). The experiment was extended to cover a narrower series of particle size ranges in the region of maximum efficiency. The results are given in table 4.32.

Table 4.32

Element No.	Particle Size Range BS mesh	Mean Particle Size (μ)	Weight of charcoal (g)	Mean % Adsorption
24	72-80	198	0.244	91.8
23	60-72	231	0.275	91.4
22	52-60	273	0.343	91.5
21	40-52	342	0.396	92.9

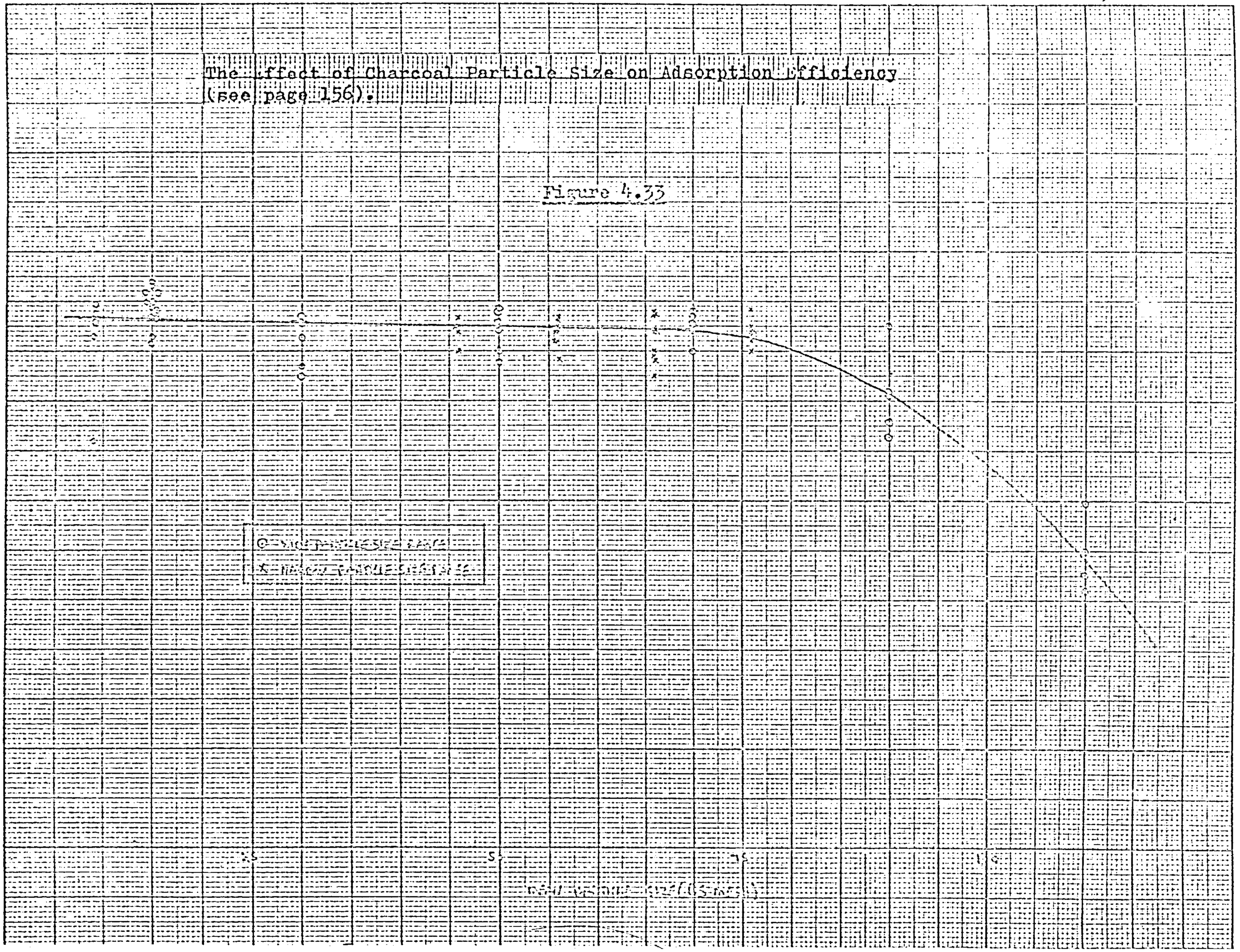
Comparison of the adsorption efficiencies in tables 4.31 and 4.32 indicate that particle size range has a negligible effect on adsorption efficiency, and that particle size has no effect over about 200 μ. The overall effect of particle size on efficiency is illustrated in figure 4.33.

On the basis of these experiments, it is recommended that the particle size range 60-80 BS mesh be used. Larger diameter particles increase the element weight to the limit of the electromicrobalance, but do not increase adsorption efficiency. Smaller diameter particles result in loss of efficiency.

To confirm that the above results, and indeed any previous results are not appreciably dependent on the differences in weight of charcoal, in different elements, an element of identical dimensions to those used above, was constructed. This element (ref. 25) was designed to hold variable weights of charcoal, and is shown in figure 4.8. Adsorption efficiency was determined under conditions identical to those above. Efficiency was measured six times for each charge of charcoal, which was increased in 50 mg increments up to 1 g. All charcoal was from the same batch as above, and had identical regeneration treatment. The range was 20-40 BS mesh, chosen, since smaller sizes would fall through the element mesh. The results are shown graphically on figure 4.34. The mean percentage adsorption remains sensibly constant for charcoal

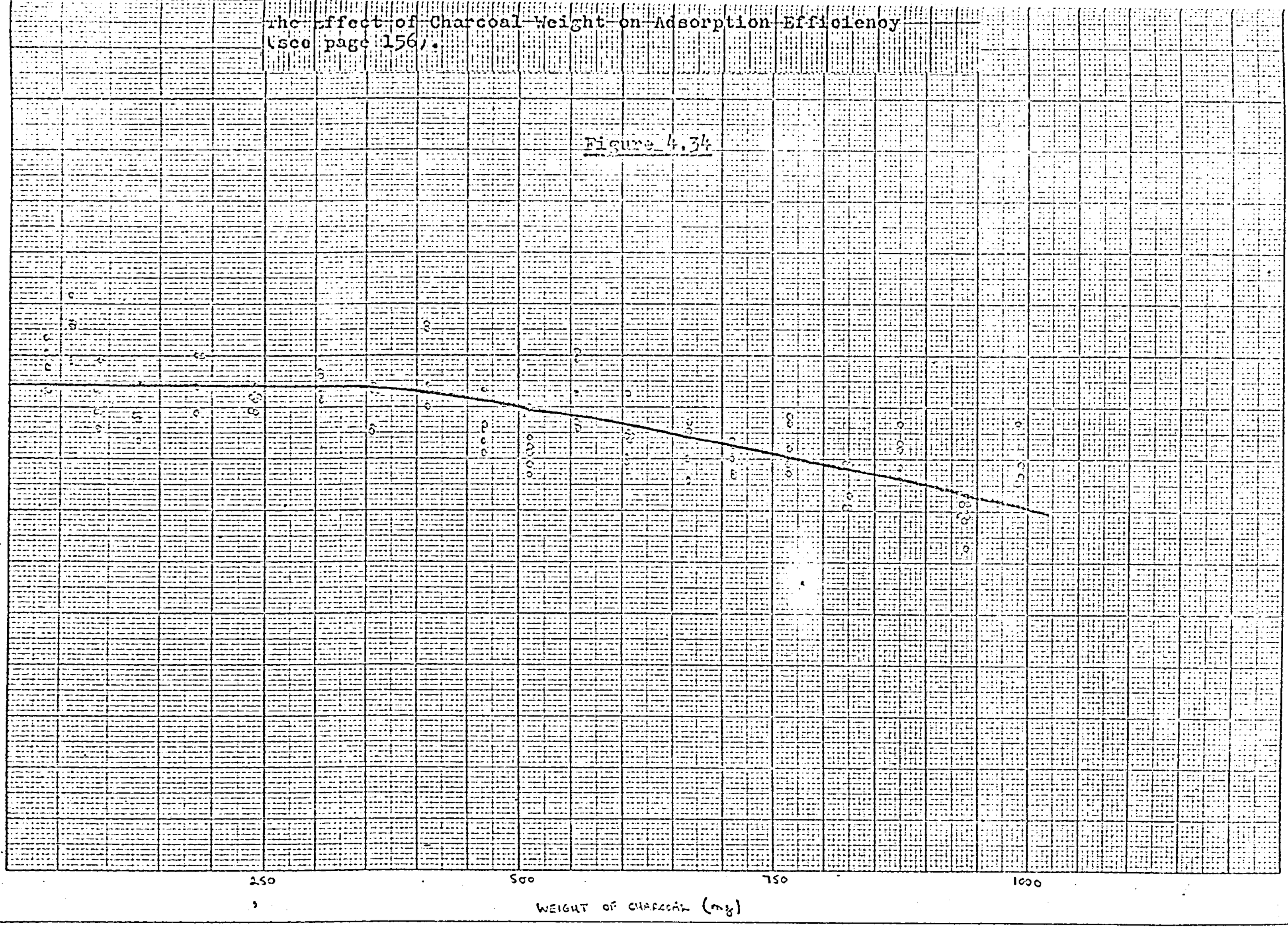
The effect of Charcoal Particle Size on Adsorption Efficiency (see page 156).

Figure 4.33



The effect of Charcoal Weight on Adsorption Efficiency
(see page 156).

Figure 4.34



charges up to about 350 mg. Even with a charge as small as 35 mg, the adsorption efficiency is relatively high: a charge of this size is represented by only about 300 particles of charcoal, which occupy a very small fraction of the element surface area. It is surprising that for charcoal charges over about 350 mg there is a gradual decrease in adsorption efficiency, when the reverse effect may be expected. This is due to a fall off in the balance performance, since the total weight of the element exceeded 1 gm. The observed deflections have been corrected for balance response fall off using figure 4.6, but conditions of operation were not directly comparable, since figure 4.6 was obtained using the standard balance stirrups and pans, and not a detecting element attached to a suspension wire.

The overall low absolute adsorption efficiency is a result of the element design. In order to charge the element with fresh charcoal, it was necessary to incorporate a removable cap on the top of the element, which it was not possible to make leak tight. In addition only the top of the element contained adsorbent, the walls of the cylinder being uncoated.

4.6.1a Adsorption Efficiency - Conclusions.

On the basis of the above work an element of high adsorption efficiency can be constructed. The most satisfactory form of detecting element is a cylinder closed at one end, and lined with charcoal. An element which will give a high adsorption efficiency, and is simple to construct, consists of a cylinder of length $5\frac{1}{2}$ cm and diameter $1\frac{1}{2}$ cm, of 60-80 BS mesh charcoal. Adsorption efficiency is not affected by the amount of adsorbent; a reasonable quantity of charcoal is 300 mg.

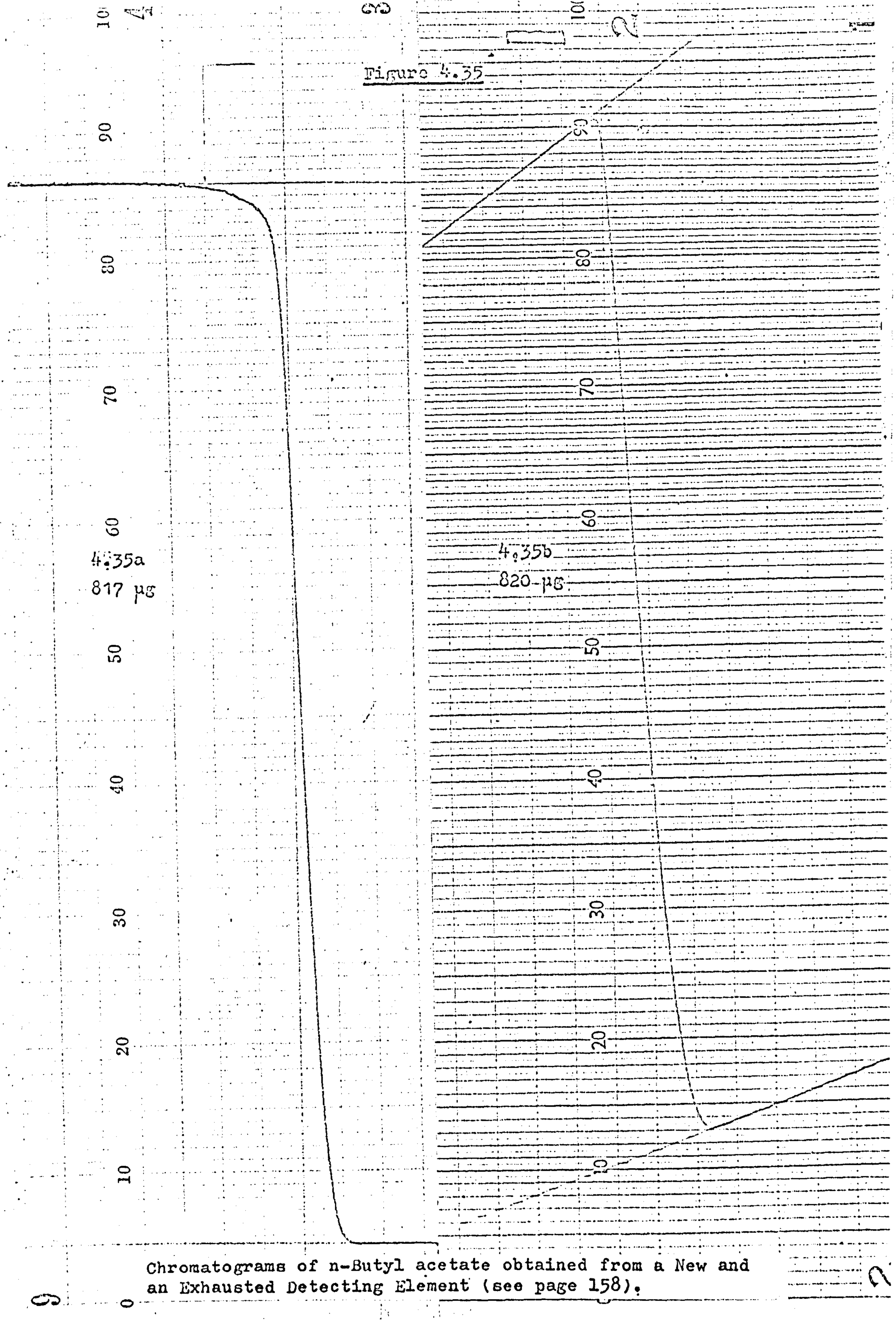
4.6.2 Adsorption Capacity.

The adsorption capacity of a detecting element is defined as the weight of a given material which the element can hold under given conditions before desorption of that material takes place. It is necessary to have a knowledge of adsorption capacity to predict the frequency with which the element must be regenerated. It is of little

use to have an element giving high adsorption efficiency if regeneration is required after each run. An experimental study of the adsorption capacity of mass detecting elements toward several compounds covering a wide boiling range was undertaken. An element (No. 27) of high adsorption efficiency was constructed, and its capacity determined. 1 µl charges of n-butyl acetate were injected into the chromatograph, at fixed intervals of time, and the total amount of the sample which could be held by the element before desorption occurred, was measured. The experiment was carried out over 80 hours of continuous running. The overnight periods were used to measure the detector noise and drift (see section 4.6.5). Experimental conditions are given in table 4.16. Carrier gas flow rate was 48 ml min^{-1}. Rates of desorption of the n-butyl acetate were calculated from the chromatograms, and the total weight of sample on the element found, taking into account the rates of loss of sample. The value was checked by weighing the element both at the beginning of the experiment, and after completion of the run. To determine the adsorption capacity of the detecting element a graph (of the type shown in figure 4.36) was plotted of the rate of desorption against the total sample weight on the element. The element adsorbed 25 mg of material before there was any perceptable desorption. This is equivalent to 33 1 µl injections. The experiment was repeated using 5 µl sample injections to determine whether adsorption was affected by the size of the charge. Desorption was not observed until the element had adsorbed 25 mg of material. Charges greater than 5 µl were not introduced, since this would be outside the capacity of a normal analytical chromatographic column. Charges significantly smaller than 1 µl would increase the time of the experiment to at least 15 days continuous running, and in any case, quantitative analysis of very small charges is not recommended. Figure 4.35 shows examples of chromatograms obtained at the beginning of the run, and on an exhausted detecting element.

The effect of adsorbing compounds of different polarity (but

Figure 4.35



Chromatograms of n-Butyl acetate obtained from a New and an Exhausted Detecting Element (see page 158).

similar boiling point) on adsorption capacity was investigated. The compounds chosen were n-octane (bp 125°C), n-butyl acetate (bp 124°C) and n-butyl alcohol (bp 118°C). Thus, major differences in adsorption characteristics are not a result of boiling point differences. For each compound, 5 µl injections were made at fixed time intervals, until rapid desorption was observed: the element was regenerated under identical conditions before its capacity toward each of the materials was measured. The weight of the detecting element was checked before each set of runs, to ensure a clean adsorbent surface, and no experiment was started until a stable baseline was obtained. This was usually about one hour after placing the detecting element in the detector chamber. It was found more satisfactory to measure the adsorption capacity at a finite rate of desorption, rather than at the point at which desorption just occurred, since this point was difficult to locate graphically (see figure 4.36). Capacities for a desorption rate of 100 µg min^{-1} are given in table 4.33. Estimates of the point at which desorption just occurs is more readily made by inspection of the chromatograms, and it is these values which are quoted in the table below. The adsorption capacity per gram of charcoal was calculated from these values.

Table 4.33

Compound	Charge (µl)	Adsorption zero desorption	Capacity $(mg)_{-1}$ 100 µg min^{-1}	Capacity per gram of charcoal (mg g^{-1})
n-Octane	5	26	53	780
n-Butyl acetate	1	25	-	750
n-Butyl acetate	5	25	70	750
n-Butyl alcohol	5	27	56	810

Adsorption capacity values are similar for all the materials, and for both sample sizes.

Adsorption capacity will depend upon the physical surface area of the charcoal exposed to the adsorbates. Using the same particle size range of charcoal, the adsorption capacities of three detecting elements of identical dimensions, containing different amounts of charcoal, were

measured. Detector details are given in table 4.34.

Table 4.34

Element No.	Weight of Charcoal (g)	Area of Element containing adsorbent (cm^2)	Adsorbent Weight Ratio
28	0.156	9.9	1.0
29	0.181	14.2	1.2
30	0.244	18.4	1.6

The adsorption capacities are given in table 4.35, and a representative graph (capacities toward n-butyl acetate) is shown in figure 4.36.

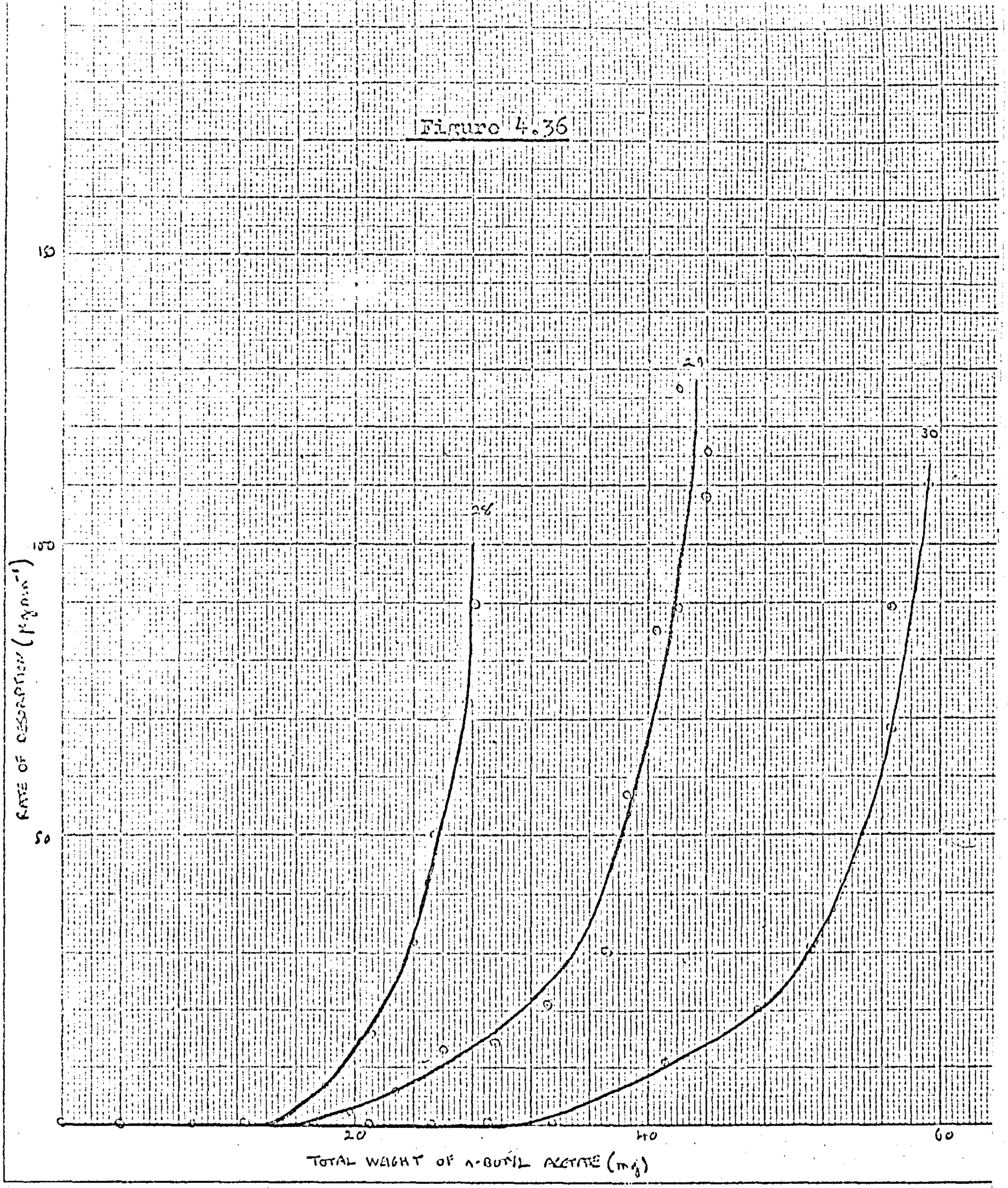
Table 4.35

Compound	Element No.	Adsorption Capacity (mg) zero desorption	100 µg min^{-1}	Capacity per gram of charcoal (mg g^{-1})
n-Octane	28	11	26	70
	29	21	36	116
	30	30	48	123
n-Butyl acetate	28	16	28	103
	29	19	42	105
	30	28	59	115
n-Butyl alcohol	28	12	27	77
	29	23	39	134
	30	37	57	152

Adsorption capacity increases as the weight of adsorbent is increased, and on each element is similar for all the adsorbates.

The adsorption efficiency of an element may depend on the degree of saturation of the charcoal. To determine whether adsorption efficiency decreases with the total sample load on the element, efficiencies were calculated from the above runs, and graphs plotted of efficiency against the total sample load. Figure 4.37 shows the results for 1 µl charges of n-butyl acetate on element 27. No decrease in the adsorption efficiency was observed, even at high total sample loadings, although scatter of points is greater. The mean adsorption efficiency was 99.2% with a standard deviation of 0.7% for 104 runs. Using 5 µl charges fall off in adsorption efficiency was observed, as

Figure 4.36

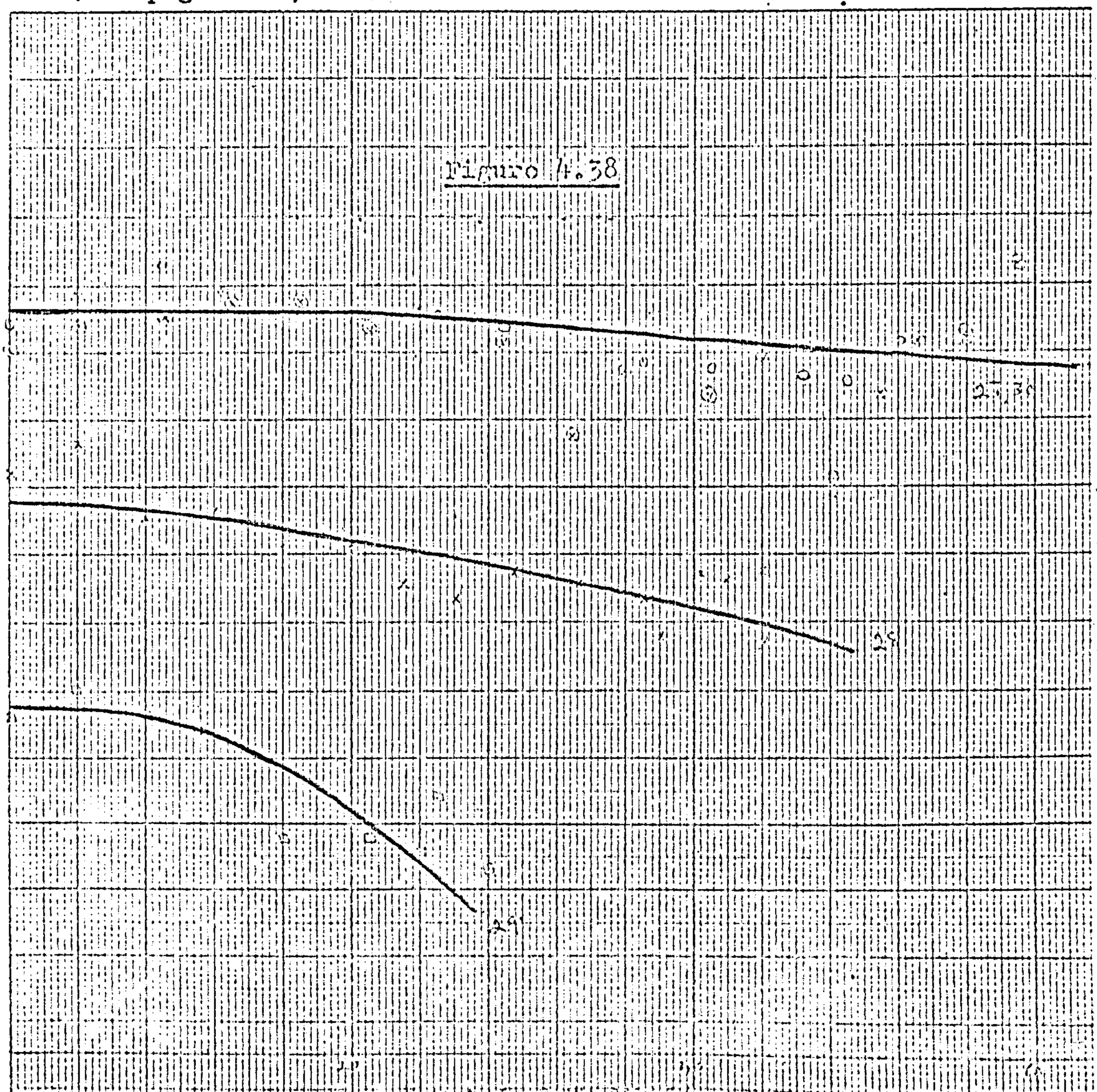


The Effect of Charcoal Weight on Adsorption Capacity (see page 160).

Figure 4.37

The Effect of Total Sample Loading on Adsorption Efficiency
(see pages 160, 161).

Figure 4.38



shown on figure 4.38, which gives the results for n-butyl acetate on elements 27-30. The rates of fall off in adsorption efficiency for n-ortane and n-butyl alcohol gave identical patterns, so that the effect on determining the relative composition of a mixture using a partially exhausted element is negligible. The total sample weight at which efficiency begins to fall off, for each compound, and on three different detectors is given in table 4.36.

Table 4.36

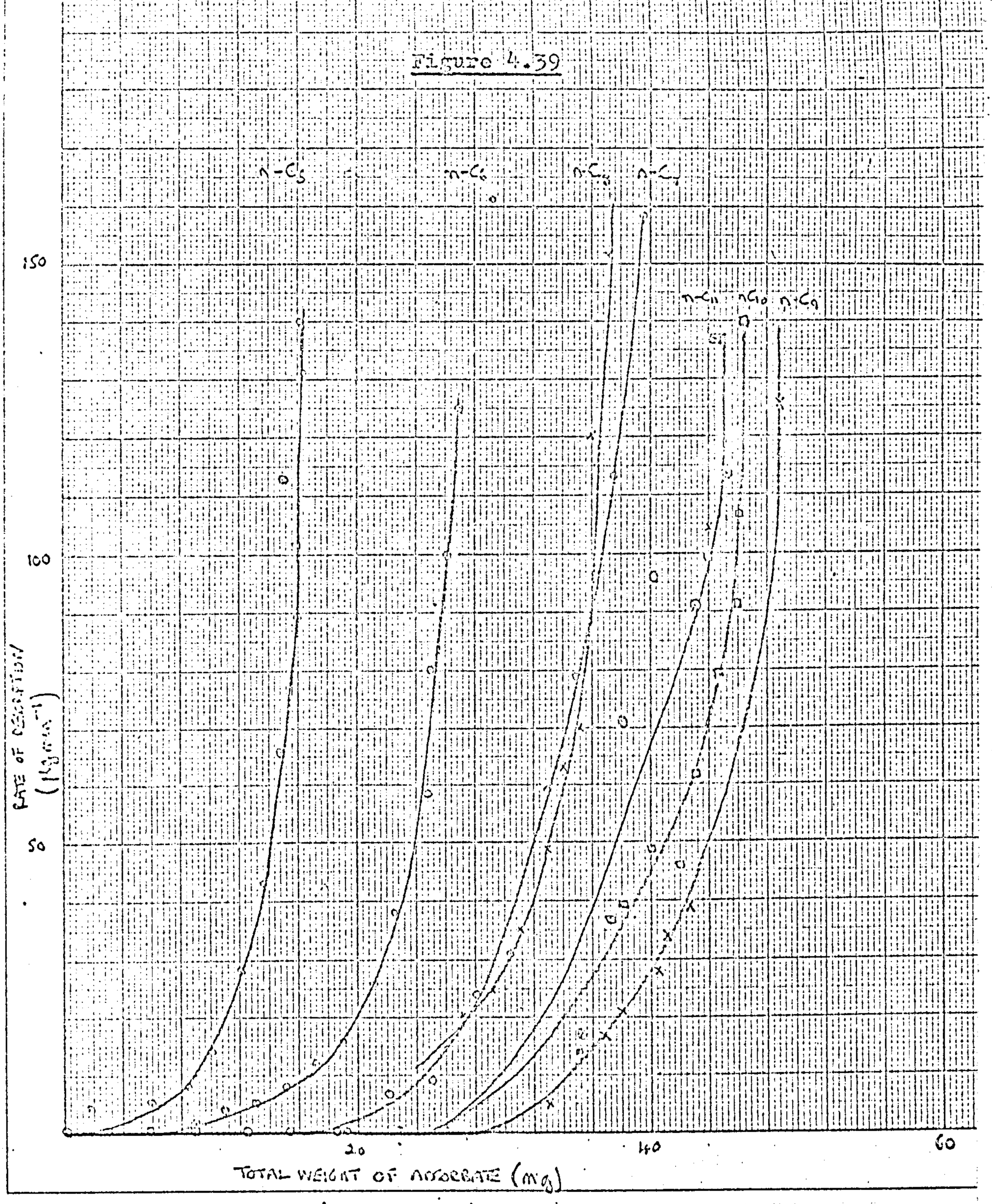
Element	n-octane		n-butyl acetate		n-butyl alcohol	
	a	b	a	b	a	b
28	7	4½	7	4½	7	4½
29	10	5½	10	5½	15	8
30	20	8	25	10	22	9

a = total sample weight on the element when adsorption efficiency begins to fall off (mg)

b = percentage of the charcoal weight on which adsorption has occurred when efficiency begins to fall off.

The variation of adsorption capacity with temperature was determined indirectly by keeping the detector temperature constant and adsorbing materials of different boiling points. A homologous series covering the boiling range 36°C (n-pentane) to 193°C (n-undecane) was analysed under conditions similar to those used for the determination of the adsorption capacities of materials of different polarity. Difficulty was encountered with materials boiling higher than 150°C, since condensation in the detector delivery tube gave rise to distorted steps. To change the conditions of the runs for high boiling materials would invalidate the comparison of the results with the lower boiling materials. Element 27 was used for the experiments, and the results are given in figure 4.39 and summarised in table 4.37.

Figure 4.39



Adsorption Capacity of the Detector toward some n-alkanes (see page 161).

Table 4.37

Compound	Boiling Point (°C)	Temperature Difference bp -detector (°C)	Adsorption (mg) zero desorption	Capacity 100µg min^{-1}
n-Pentane	36	12	4	16
n-Hexane	68	44	9	26
n-Heptane	98	74	19	36
n-Octane	125	101	21	36
n-Nonane	150	126	23	48
n-Decane	173	149	-	46
n-Undecane	193	169	-	44

In order that the results may be of more general applicability, a graph (figure 4.40) was plotted of the difference in temperature between the boiling point of each compound and the detector, against capacity. For a temperature difference of up to about 100°C capacity increases fairly regularly; for temperatures greater than 100°C there is little change in capacity.

The change in capacity with boiling point may arise solely from adsorption effects or from condensation of materials on the walls of the detecting element. It is evident that adsorption plays the major role for the following reasons: simple condensation of materials on the detecting element would result in continuous evaporation from the detecting element, irrespective of the total sample load, which would be detected by a drifting baseline. This is not observed until a definite sample loading is exceeded. In addition the amount of condensed material would increase as the homologous series was ascended, and would not reach the maximum, which is observed experimentally. Hence it is reasonable to assume that adsorption effects predominate.

The increase in adsorption capacity with temperature difference is expected, and will continue until all available sites on the charcoal are occupied. At this point adsorption capacity can no longer increase with temperature difference, and a stable value for capacity is reached. It is difficult to be certain whether the slight decrease in capacity at high temperature differences is a real effect, or caused by

difficulties in measuring the chromatograms, which were less well defined. The capacity decrease can be explained by considering the changes in molecular dimensions of the adsorbates. As the homologous series is ascended the size of the molecule adsorbed increases, so that fewer and fewer sites become available within the pore structure of the charcoal. However, the effect of increasing the boiling point of the adsorbates is to increase the amount which can be adsorbed. For the lower members of the series boiling point effects predominate, but for the high members, molecular dimensions are more important.

The effect of adsorbing a branch chain hydrocarbon on the adsorption capacity (below the capacity limit) was investigated. The capacity of element 27 toward 2,2,4,-trimethyl pentane was measured, and compared with that obtained for a straight chain hydrocarbon of similar boiling point, under identical conditions. The results are shown in figure 4.41: no difference in adsorption capacity was observed Both the straight chain and branch chain hydrocarbons were sufficiently small to be accommodated in the majority of adsorption sites, thus giving similar adsorption capacity values.

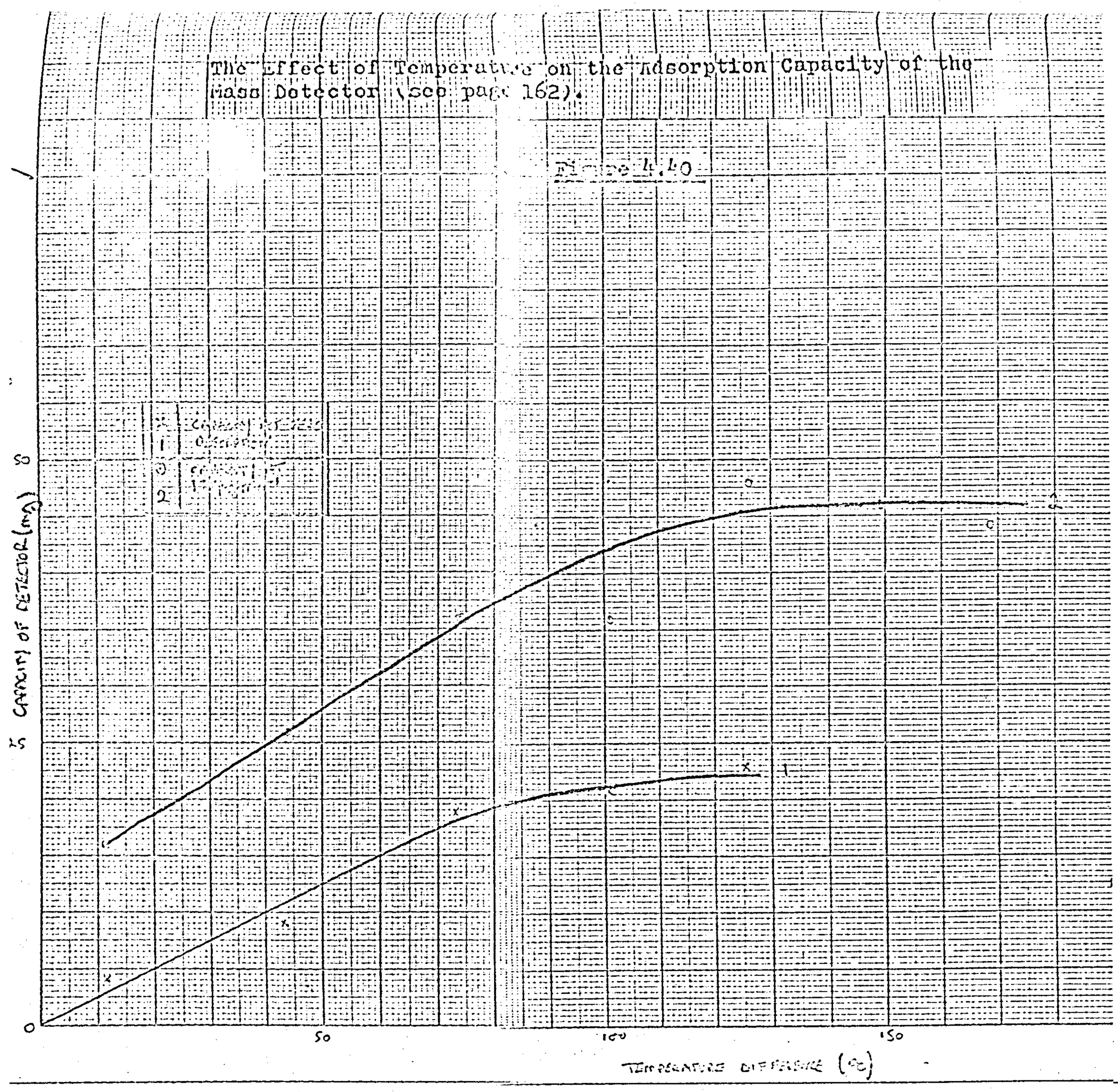
Experiments were performed to determine the effect of flow rate into the detecting element, on its adsorption capacity. The chromatographic column E was replaced by an empty column J (see table 4.15) and flow rates controlled by a needle valve. The capacity of element 30 at 25°C was measured with 5 µl samples of n-heptane, at several flow rates covering the range 17 to 220 ml min^{-1}. Figure 4.42 shows the relationship between rate of desorption and sample loading on the element for each flow rate. Using this graph, the relationship between adsorption capacity and flow rate was found, and the results are shown on figure 4.43 for various different rates of desorption.

4.6.2a Adsorption Capacity - Conclusions.

Adsorption capacity is independent of chemical species, but is increased by increasing the temperature difference between the boiling point of the adsorbate and the detecting element. Capacity decreases

The Effect of Temperature on the Adsorption Capacity of the Mass Detector (see page 162).

Figure 4.40



Adsorption capacity of the Mass Detector toward Straight and Branched Chain Alkanes

Figure 4.41

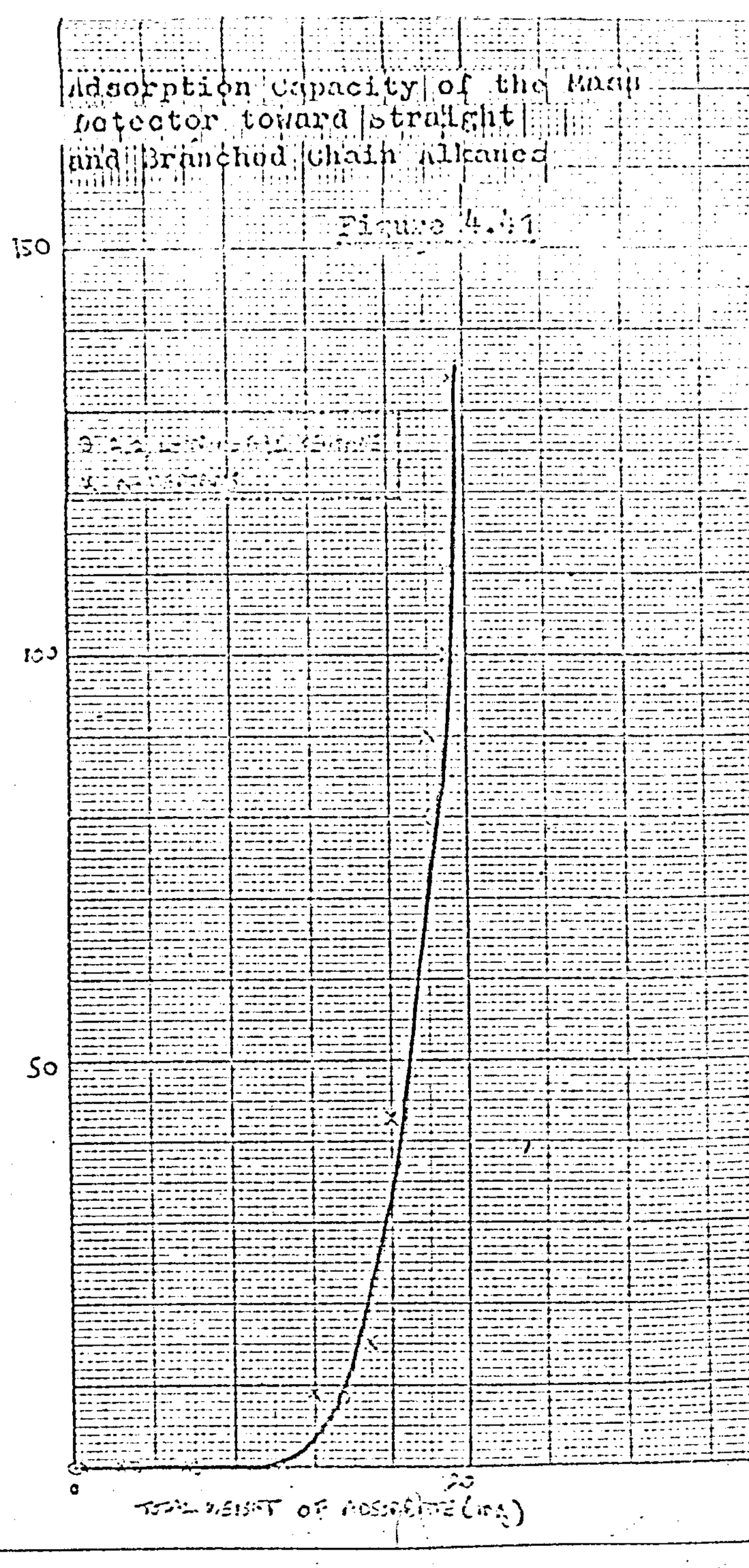
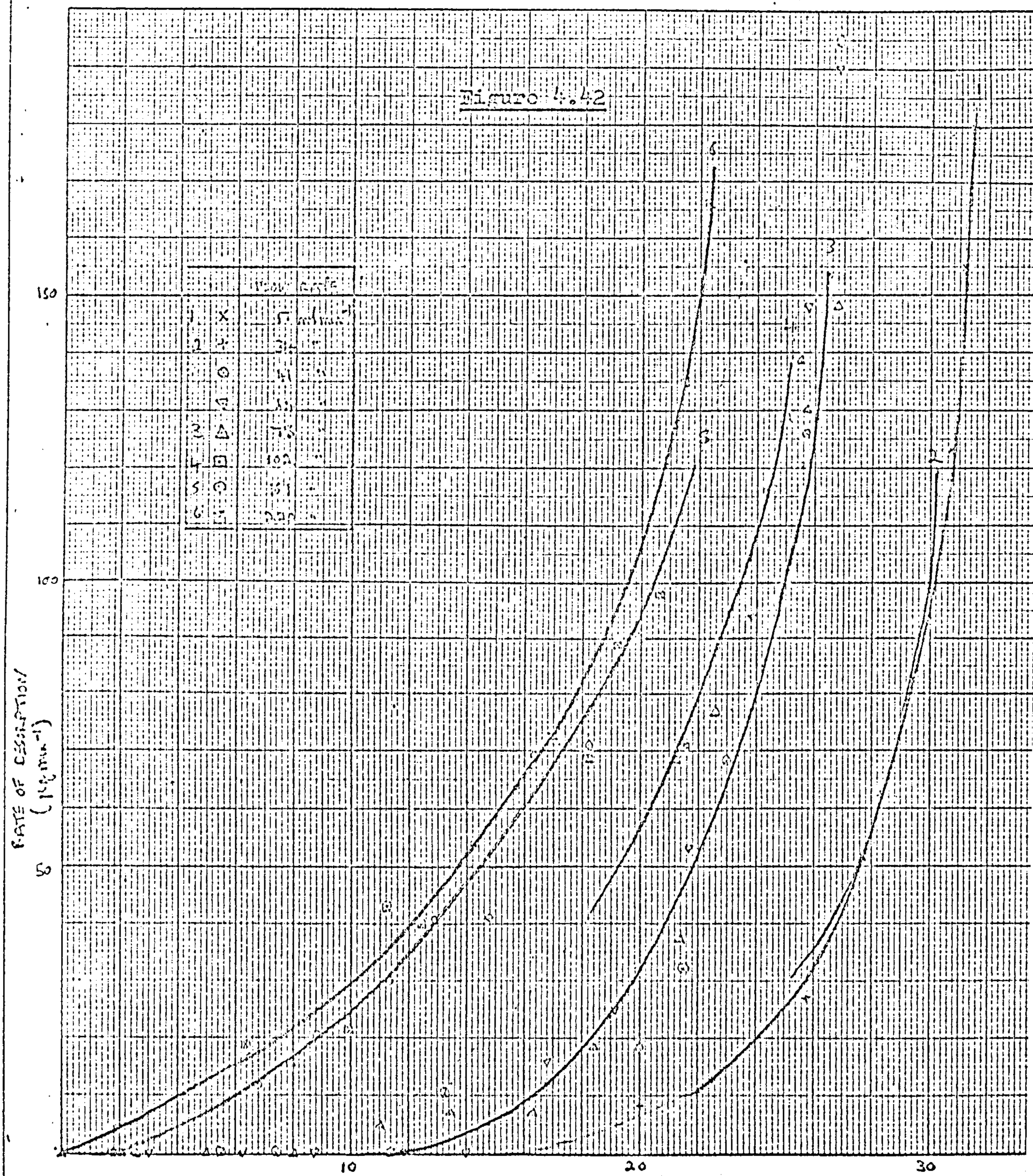


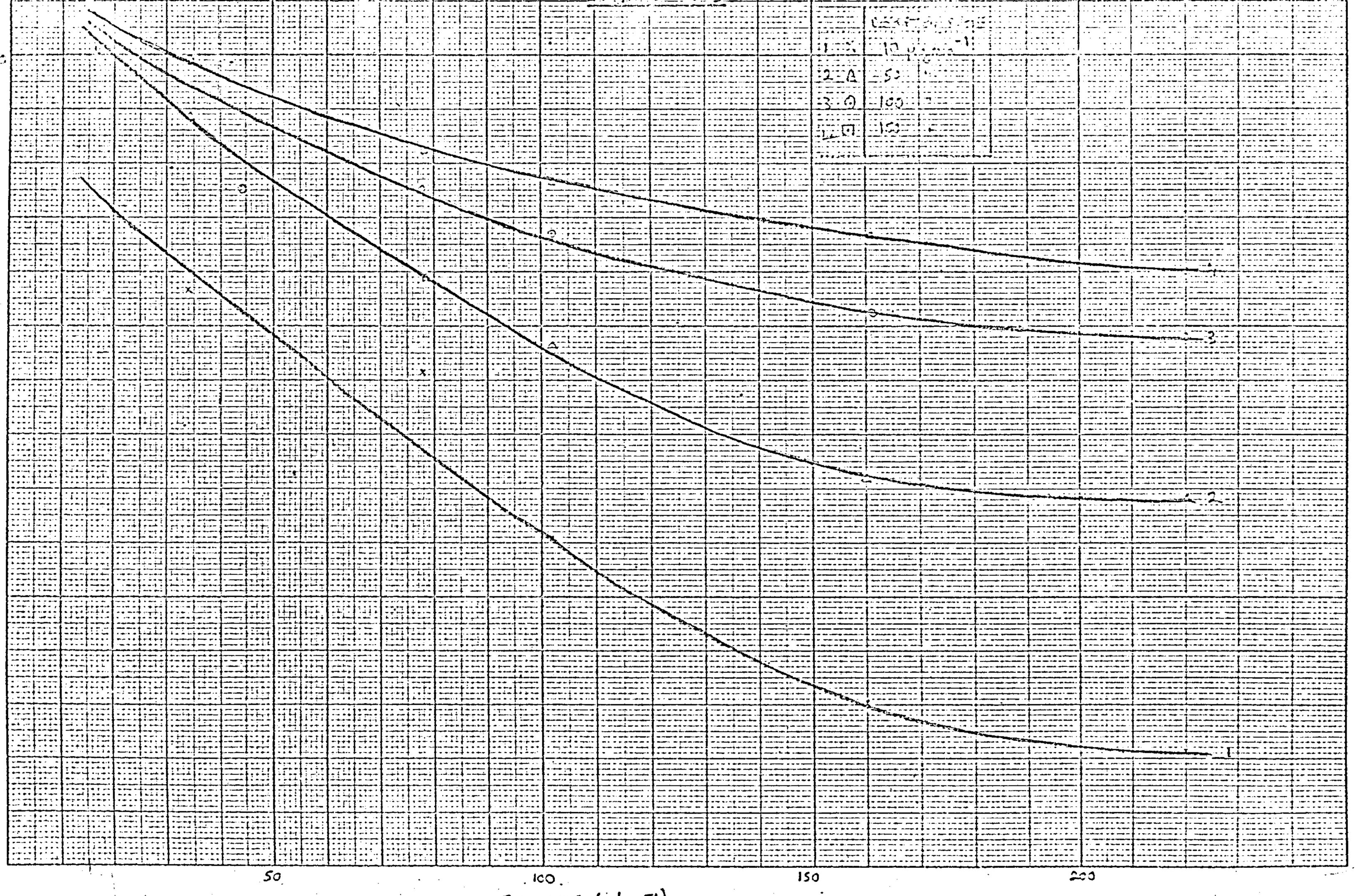
Figure 4.42



Adsorption Capacities of the Mass Detector at various Flow Rates (see page 163).

The effect of flow Rate on the Adsorption Capacity of the MAGB Detector (see page 163).

Figure 4.43



as flow rate of carrier gas into the detecting element is increased. In general the adsorption capacity of an element containing a few hundred milligrams of adsorbent is sufficient for many analyses, and regeneration may be conveniently carried out during overnight periods, when the detector is not in use.

4.6.3 Detector Linearity.

The linear responses of the electromicrobalance and the potentiometric recorder have been demonstrated in section 4.2.2. Experimental evidence to confirm the linear response of the mass detector to weight changes is given in this section.

The vapour dilution technique of Scott[23] was tried, but this was found to be too time consuming and not ideally suited to a detector of only moderate sensitivity. Direct injection of known volumes of samples is not reliable, since a syringe does not necessarily deliver the same fraction of its charge for each different volume injected (see table 4.13). In addition it would be necessary to use a 10 µl and a 1 µl syringe to cover the weight range as fully as possible, thus introducing further errors. Calibration of the mass detector was carried out using two methods which overcame the difficulties noted above. One method was suitable for small samples, less than 1 mg, and the other method for large samples.

(i) Method of calibration for small samples.

A 10 µl syringe which had previously been calibrated for the 1 µl setting using n-heptane, was used to deliver 1 µl charges of a mixture of n-hexane as solvent and pure (99.9%) n-heptane as solute. These two compounds form virtually ideal solutions over the whole mole fraction range[24]. By varying the amount of heptane in hexane it was possible to cover a wide mass range (15 to 700 µg). This method rules out any errors due to the syringe, and overcomes the difficulty of using very small amounts of material. All solutions were weighed out on a 4-place analytical balance using a total of about ½g of material.

No solution was kept for more than two hours after preparation, and samples were removed via a septum fitted to the containing vessel. The response of the detector to n-heptane in each solution was measured at least three times (on each mass range). The experiments were carried out under the conditions quoted in table 4.16 with a carrier gas flow rate of 36 ml min^{-1}. The results were calculated directly from the weights of heptane adsorbed and not relative to the total sample injected, i.e. absolute weight response and not percentage composition was measured. The results are shown on figure 4.44 covering the mass range up to 200 µg, and figure 4.45 covering the range up to 1 mg. A straight line, of slope unity passing through the origin is obtained in both instances, i.e. adsorption is sensibly complete over this range and at a flow rate of 36 ml min^{-1}. The detector thus gives an ideal response at least up to a sample size of 1 mg. The results are summarised in table 4.38 which quotes the mean response values for each sample size, and expresses detector response as the ratio of the detected and injected quantities. The mean and standard deviation of the response on each mass range have been calculated, and these values are shown in table 4.39 (line a). These low values have been included for completeness.

Table 4.38

% heptane in solution	Injected Quantity (µg)	Mean Detected Quantity (µg)	Response
	100 µg range		
2.3	13.0	15.1	1.16
3.6	20.8	19.8	0.95
7.2	38.7	37.9	0.98
9.9	56.8	58.8	1.03
10.0	57.9	56.5	0.98
	250 µg range		
8.2	47.0	43.9	0.94
9.9	56.8	51.3	0.91
10.0	57.9	53.1	0.92
11.1	64.2	65.7	1.02
15.6	90.2	87.9	0.97
18.0	104.3	99.4	0.96
21.9	126.6	125.7	0.99
24.0	139.2	135.7	0.98

1 mg range

% heptane in solution	Injected Quantity (µg)	Mean Detected Quantity (µg)	Response
8.2	47.0	42.9	0.92
9.9	57.2	51.2	0.90
11.1	64.2	64.7	1.01
21.9	126.6	127.9	1.01
24.0	139.2	134.1	0.97
25.9	149.8	152.4	1.02
26.3	152.6	146.8	0.97
48.3	282.1	288.1	1.02
76.3	450.4	442.2	0.98
100.0	595.6	590.1	0.99
100.0	714.7	727.9	1.02
100.0	833.8	839.8	1.01

On all ranges the detector gave a response close to unity except where only a small fraction of the recorder full scale deflection was employed. Since these discrepancies occurred on all ranges they can be attributed to the difficulty in measuring precisely the small step heights which were involved (< 3 cm). In addition, in all instances the amount of heptane in the mixture was less than 10%, so that minor errors in sample weighing during preparation, and evaporation will be magnified considerably. The coefficient of variation was recalculated, ignoring results of less than 10% of the recorder full scale deflection on each range, and a marked improvement was observed (see table 4.39 line b).

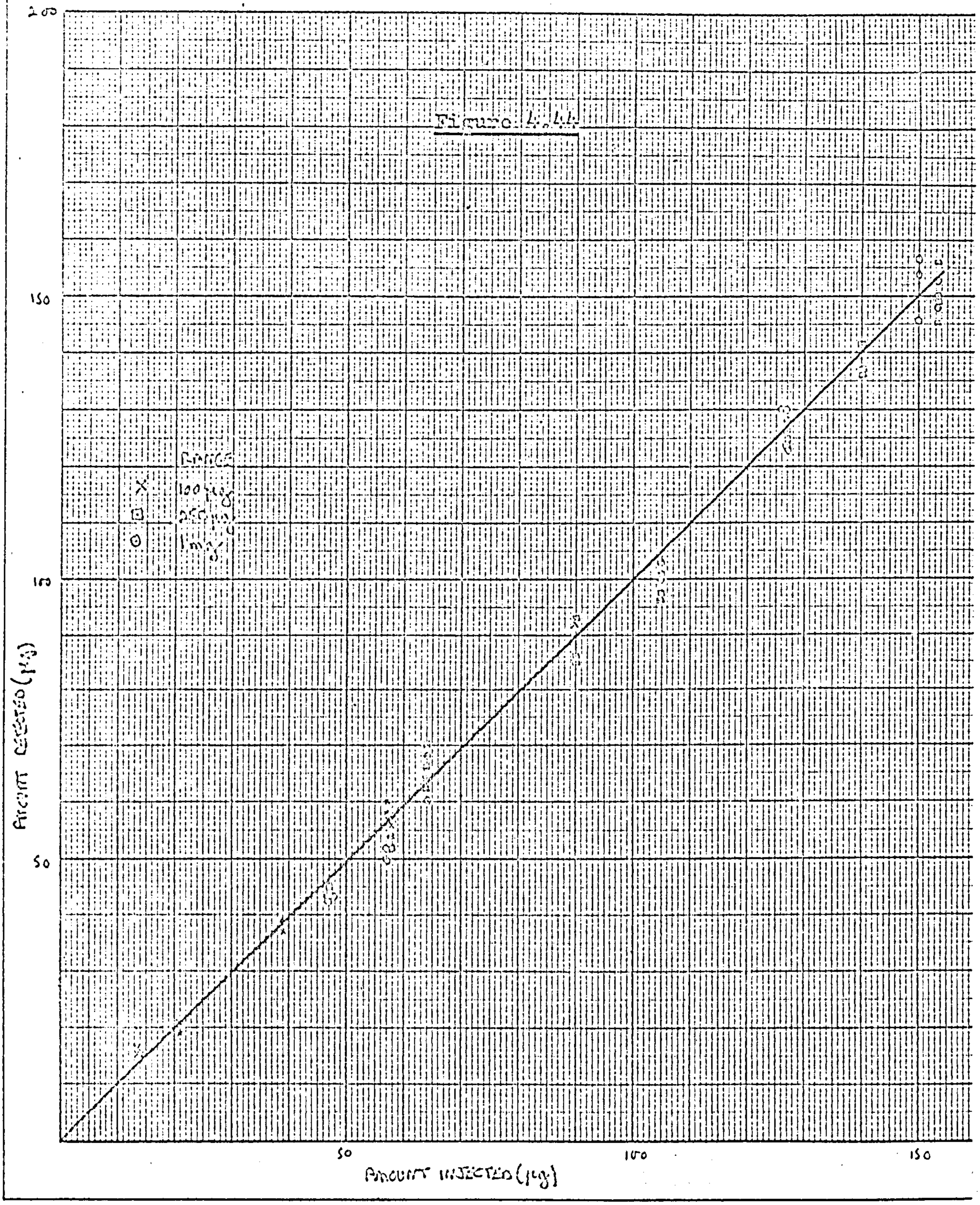
Table 4.39

	n	Mean Response	Std Deviation	Coeff of Variation (%)
a	25	0.98	5.2×10^{-2}	5.2
b	19	0.99	2.8×10^{-2}	2.8
c	9	0.99	2.1×10^{-2}	2.1

(ii) Method for large sample sizes.

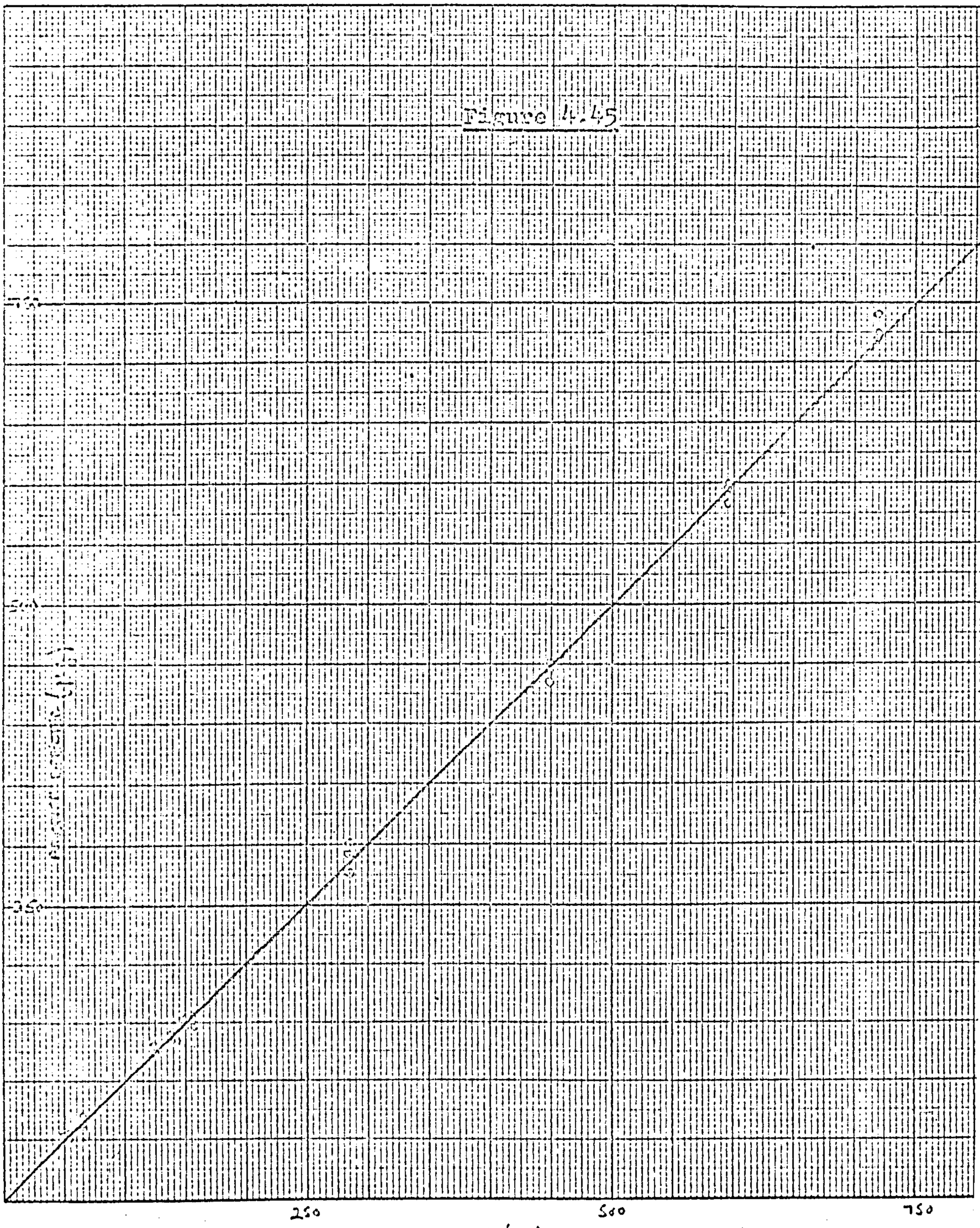
It is difficult to inject, using a syringe, large quantities of material on to the column, due to the possibility of column overloading, and back pressure effects causing blow back of the sample via the syringe

Figure 4.44



Linearity of Response of the Mass Detector (see page 165).

Figure 4.45



Linearity of Response of the Mass Detector (see page 165).

piston. A reliable method of quantitative sample introduction must overcome these difficulties, and the following method was adopted. The column E was removed, and replaced by empty column J, operated at room temperature. Pure carrier gas at a known flow rate was passed continuously through the column and into the detector. A separate carrier gas supply, at the same flow rate, was bubbled continuously through benzene, also at room temperature. This stream was introduced into the column, in place of the pure nitrogen flow, for fixed interval of time, by means of a 4-way tap. A diagram of the system is given in figure 4.10b. The amount of benzene introduced per unit time was measured by covering the upper part of the calibration curve obtained using a syringe (figure 4.45), using this new injection system. Hence by comparing the amount of benzene detected during various known intervals of time, with the calculated injected values, the mass range was greatly extended. The partial pressure of benzene was constant throughout the experiment, since only the length of injection time, and not the flow rate or temperature, was varied. The amount of benzen injected was 66 μg sec^{-1}.

The response curve is shown in figure 4.46, and response values for each injection are given in table 4.40.

Table 4.40

Injection Time (sec)	Injected Quantity (mg)	Detected Quantity (mg)	Response
20.6	1.357	1.357	1.00
40.7	2.686	2.660	0.99
60.7	4.000	4.000	1.00
80.6	5.320	5.285	0.99
100.2	6.613	6.374	0.96
120.7	7.966	8.160	1.02
139.8	9.227	9.285	1.00
160.8	10.613	10.177	0.96
180.2	11.893	11.963	1.01
200.4	13.226	12.677	0.96
200.9	13.259	11.963	0.90
240.7	15.886	14.067	0.88
300.5	19.833	17.319	0.87
420.5	27.753	20.710	0.74

The mean and standard deviation of the response over the linear portion of the curve are given in table 4.39 (line C).

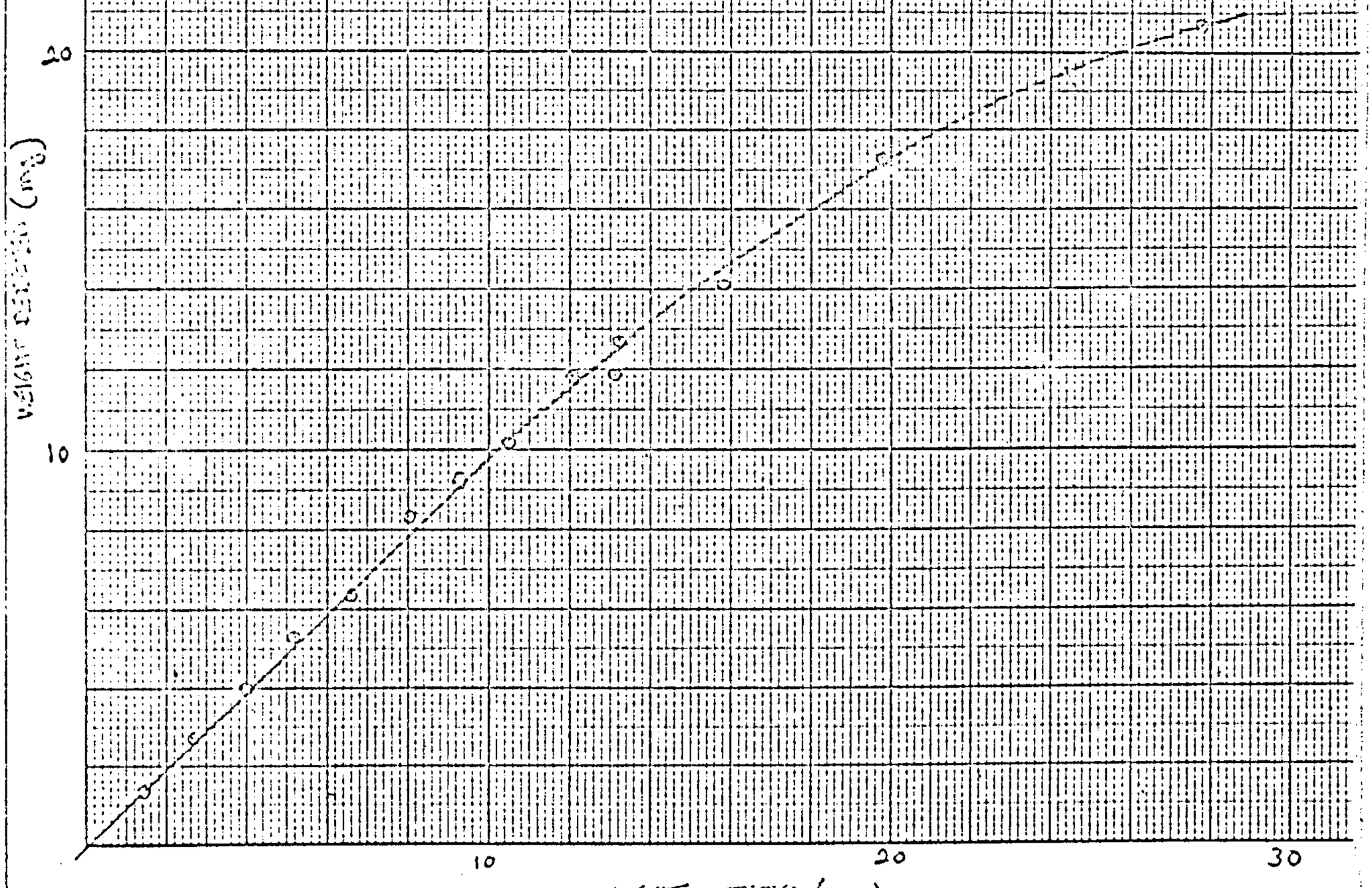
The mass detector gives a linear response and quantitative adsorption up to a sample size of about 12 mg. This represents about 5% by weight of the total amount of adsorbent in the detector. Above this weight the response of the detector slowly falls, and much desorption occurs. The adsorption capacity of this particular system is estimated at 10 mg, using the adsorption capacity results previously quoted (section 4.6.2). The value obtained from the chromatograms is between 8 and 11 mg. Thus linearity of response does not break down until the adsorption capacity of the detector is reached, and can readily be extended by increasing the quantity of adsorbent available. However this is by no means essential, since the upper limit of the linear dynamic range well exceeds the upper limit of sample sizes normally employed in analytical gas chromatography. The non linearity of response at high sample sizes may also result from the difficulty in the interpretation of chromatograms with rapidly falling baselines.

The lower limit of detection is more difficult to extend, and will depend, as with other detectors, on being able to maintain a high signal to noise ratio. The microbalance is capable of detecting quantities as small as $\frac{1}{4}$ µg but the incorporation of the mass detecting element, and the continuous flow of nitrogen into the system gives rise to significant noise at such low masses.

The overall linear response of the detector, embracing all the balance ranges, is shown on figure 4.47, which is drawn to a log/log scale. The line of regression has a slope of 1.02 and an intercept of -0.05. The linear dynamic range of the particular detecting elements investigated (27 and 30) is 10^3, with a lower limit of detection of 10^{-5}g (see also table 4.43). The detector gives a linear response over a wide range of sample sizes, and in addition at the particular flow rate employed the mean absolute response factor is unity. This will only be the case if the absolute adsorption efficiency of the detector

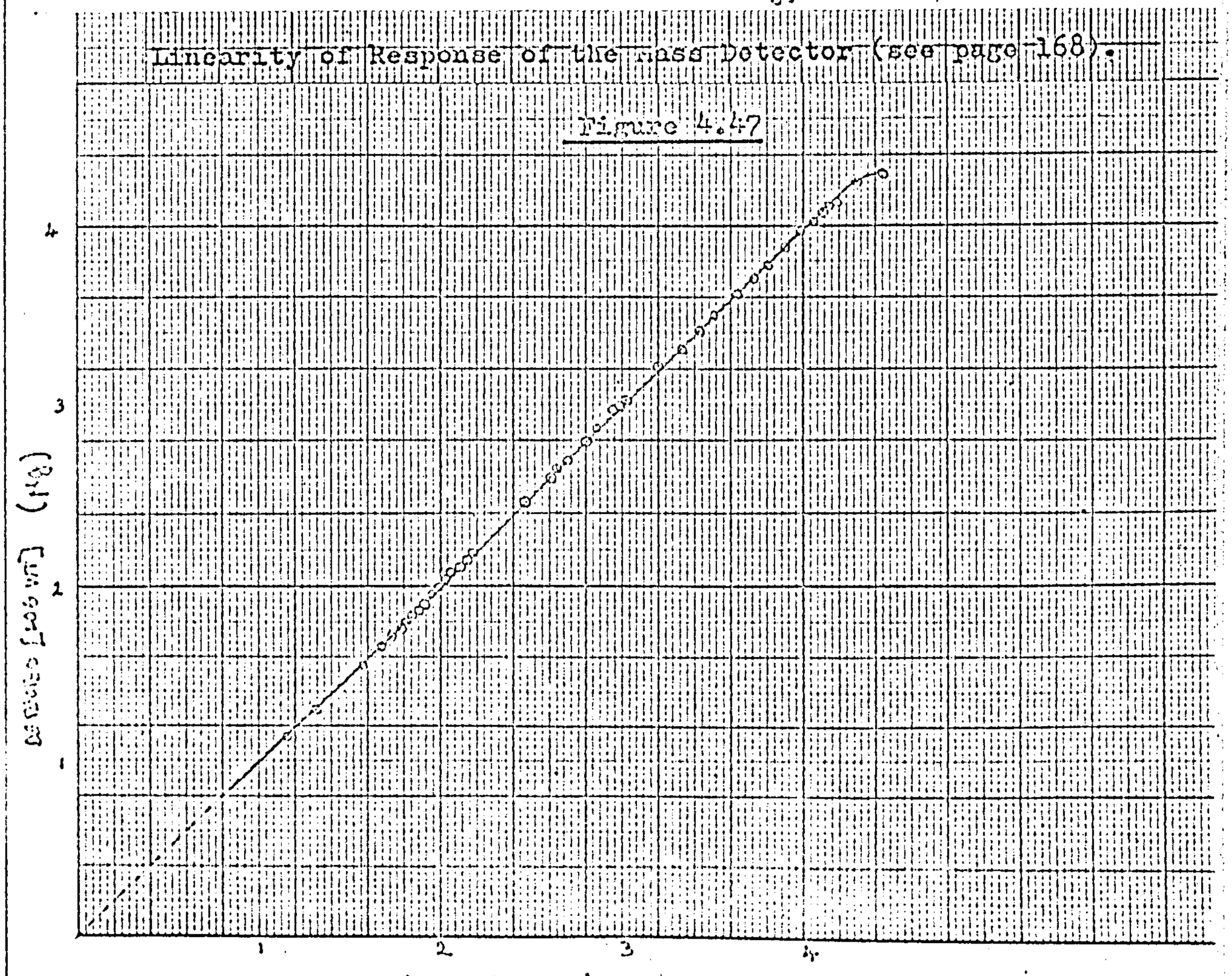
Linearity of Response of the mass Detector (see page 167).

Figure 4.46



Linearity of Response of the mass Detector (see page 168).

Figure 4.47



is 100%, since the results are expressed, not in terms of the percentage of heptane detected in the mixture, but in terms of absolute weights of heptane.

It has previously been established that absolute adsorption efficiency decreases with increasing flow rate. It may arise that the use of a rapid flow rate is necessary for a particular analysis. Experiments were carried out to determine whether a linear response is still observed, even though absolute adsorption efficiency is decreased. A flow rate of 105 ml min^{-1} was used: all other conditions were identical to those used for the determination of linearity described above. The results (table 4.41) are expressed in the same manner as above and are to be compared with table 4.38.

Table 4.41

% heptane	Injected Quantity (µg)	Mean Detected Quantity (µg)	Response
8.7	50.6	47.6	0.94
24.1	139.5	135.1	0.97
54.8	320.9	305.9	0.96
68.7	403.6	383.3	0.95
100.0	595.5	580.9	0.97

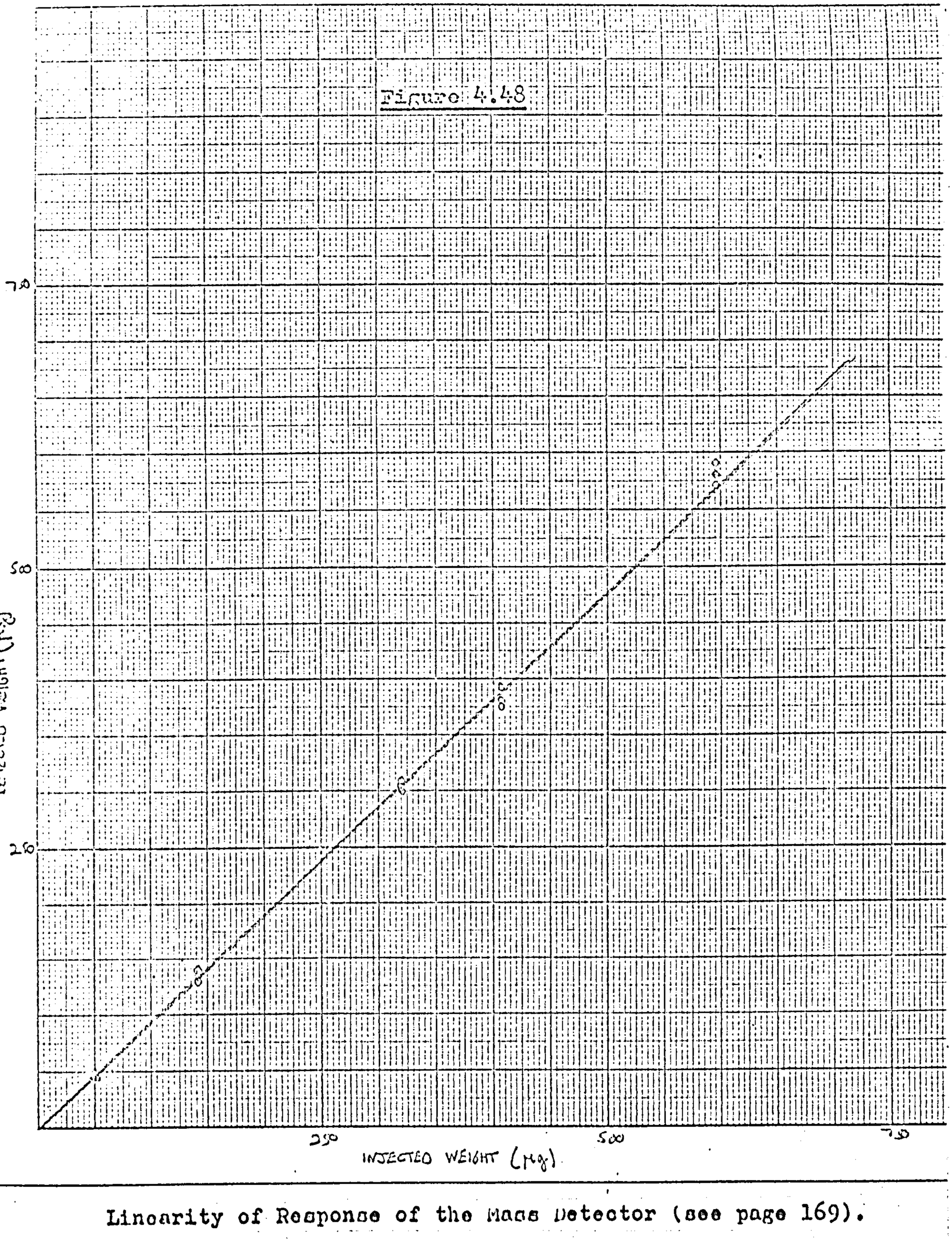
The overall mean response is 0.96 with a standard deviation of 2×10^{-2} for 15 runs. The results are shown graphically on figure 4.48. The response is less than unity, since, as expected adsorption efficiency is decreased: nevertheless, the response is linear over the whole range investigated. It is reasonable to assume therefore that the detector will give a linear response with respect to mass, over a wide flow rate range, embracing at least flow rates between 30 and 100 ml min^{-1}.

4.6.4. Detector Response Time.

In general, provided the response time of a detector, including the associated equipment is less than about 2 seconds, negligible peak or step distortions will occur.

The response time of the mass detector (see equation 2.20) i.e. the time lag between a sample entering the detecting element, and a movement

Figure 4.48



Linearity of Response of the Mass Detector (see page 169).

occurring on the recorder, was measured by the means described below. The technique was very simple and cannot be expected to give a precise value for the response time. However, since response time will depend on the effective detector volume and the carrier gas flow rate, both of which are variable, an order of response time is all that is required.

The response time was estimated using detector No. 29, by comparing the observed and calculated retention times of a n-alkane. 1 µl samples of n-heptane were injected into an empty column about 30 metre long, and the time taken for a response to be observed on the recorder was noted. The expected retention time of the same compound under identical conditions was calculated from the volume of the column, and the flow rate of the carrier gas. The volume of the column was found by filling it completely with a known weight of water: a correction was made for the depth of insertion of the syringe needle at the injection point. The results are summarised in table 4.42.

Table 4.42

Retention Times (mins) Calculated	Observed	Difference	Response Time (secs)
2.68	2.70	0.02	1.2
1.68	1.68	zero	zero
1.41	1.40	0.01	0.6

The order of the response time of the detector is the same as that of the recorder. It can therefore be regarded as satisfactory for normal packed column chromatographic analysis.

Alternative methods of determining response times were described in Chapter 2. The method proposed by the Author in which an estimate of the effective detector volume is obtained from peak or step widths was used. An empty column about 10 cm long was attached to the mass detector. The column injection port was maintained 134°C and 1 µl samples of n-octane were injected. For a ½ second injection time, the volume of the carrier gas containing the octane at the column exit can be calculated, assuming no diffusion within the column. The volume of carrier gas containing the sample can be measured from the step width

of the chromatogram, and the difference between the two values is the effective detector volume. This method will give a maximum value, since some band spreading must occur, however short the column. For flow rates of the order of 30 ml min^{-1} the effective detector volume of element 31b was no greater than $1\frac{1}{2}$ ml. The geometric detector volume was $4\frac{1}{2}$ ml. The detector can therefore distinguish all peaks of retention time difference greater than 3 seconds (a retention distance difference of $1\frac{1}{2}$ mm at 30"/hr). The dead volumes of katharometers and gas density balances are normally about 3 ml, and are sometimes greater.

The procedure used by King[15] to measure response time, assumes that the absolute response of a detector is independent of flow rate: the method is not therefore widely applicable.

4.6.5. Mass Detector Stability.

The noise of the mass detector has been measured on all the ranges employed for gas chromatographic analysis.

From the noise values, the limits of detection on each range have been estimated: since the detector gives an integral response the values are quoted in terms of absolute weight. However in order to be able to compare the limit of detection of the mass detector with conventional differential detectors, the concentration limit of detection has been estimated from step widths and carrier gas flow rates. The values quoted in table 4.43 are for a carrier gas flow rate of 30 ml min^{-1} and elution time of 2 minutes, for a compound of molecular weight 100 (n-heptane).

Table 4.43

Range	Noise level (% fsd)	Limits of Detection µg	mMml^{-1}
1 mg	not detectable	4	6.6×10^{-7}
250 µg	negligible	2	3.3×10^{-7}
100 µg	0.25	0.5	8×10^{-8}
25 µg	2	1	1.7×10^{-7}

The lower limit of detection of the mass detector is 0.5 µg. The linear dynamic range can be estimated from the limit of detection, and

by using figure 4.47, and is 2×10^4. The smallest amount of material which has been directly measured using the mass detector is 0.8 µg: the chromatogram is shown in figure 4.49. The limit of detection of the microbalance in the absence of the detecting element is 0.25 µg (table 4.8): the incorporation of a detecting element and the continuous flow of carrier gas into the element, do not result in a significant decrease in balance stability.

The limits of detection of conventional detectors are given in table 3.22.1. Although the limit of detection of the mass detector does not approach that of ionisation detectors, it is of the same order as the katharometer and the gas density balances.

Detector drift was measured on the 1 mg range over a period of 15 hours. The major contribution to drift is desorption of materials from the detecting element. It is of little value to measure the drift of an unused and regenerated detector since this represents an ideal condition: the experiment was carried out using a partially exhausted detector which contained a total sample load of 17 mg of n-butyl acetate. The total loss of sample was 32 µg, which represents a rate of loss of 2 µg per hour (0.2% fsd per hour). The drift of the microbalance in the absence of a detecting element is 0.02% fsd per hour, (section 4.2.2a).

4.7 Conclusions.

The continuous weighing of materials as they emerge from a chromatographic column is a satisfactory basis for a quantitative detector. The characteristics of the mass detector show that it is a most satisfactory device for quantitative analysis and offers outstanding advantages over conventional detectors. The characteristics are given on the lines proposed in Chapter 2:

Lower limit of detection	0.5 µg
Upper limit of detection	25 mg
Dynamic Range	5×10^4

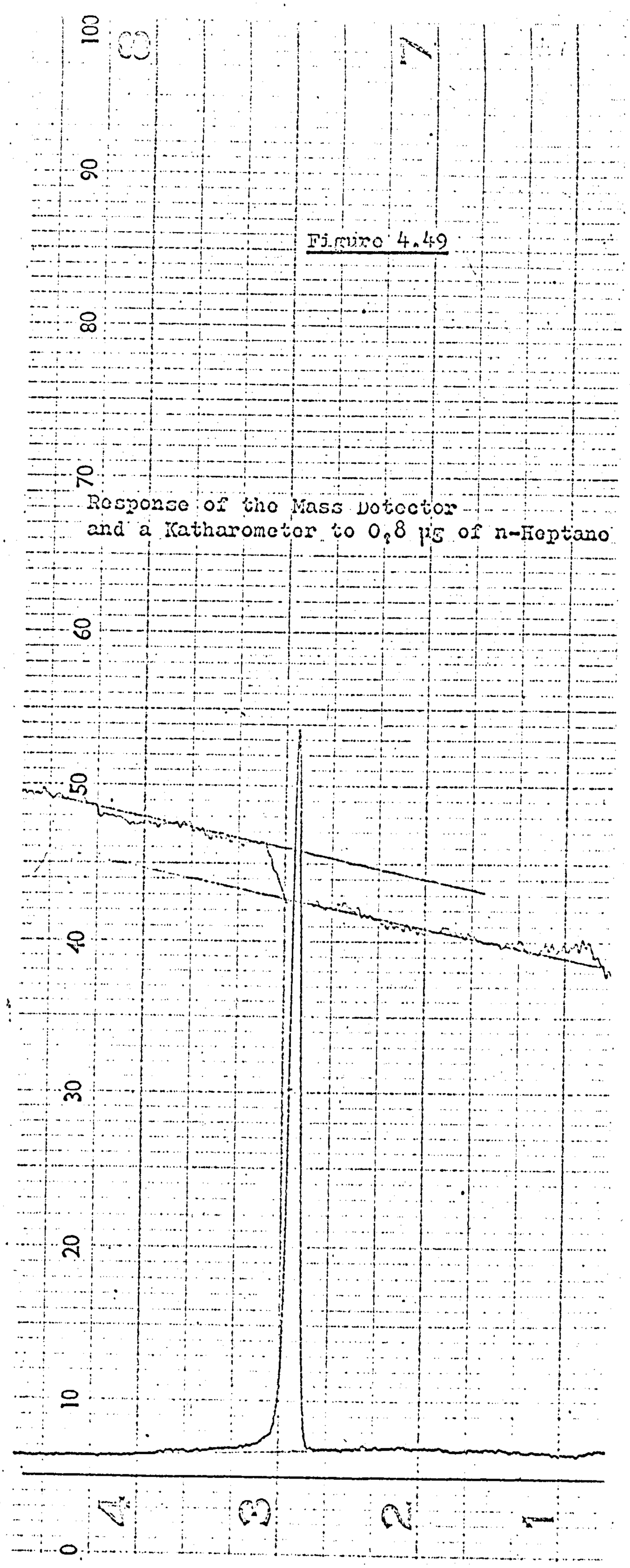


Figure 4.49

Response of the Mass Detector and a Katharometer to 0,8 µg of n-Heptane

Linear Dynamic Range	2×10^4
Baseline drift	2 $\mu g\ hr^{-1}$ (1 mg range)
Response time	$\bar{c}$ 1 sec.
Effective detector volume	$< 1\frac{1}{2}$ ml

The lower limit of detection is similar to that for hot wire detectors, and the upper limit of detection exceeds that required for normal gas chromatographic analysis. The detector has a wide linear dynamic range, which approaches the dynamic range. Baseline drift is negligible, and response time and dead volume are sufficiently small for normal packed column analysis.

The response of the mass detector is predictable on a weight basis. The relative response of the detector is independent of carrier gas flow rate, and repeatability of the response at a fixed flow rate is $\pm 1\%$. The absolute response of the detector decreases as flow rate is increased, but is independent of chemical species. The detector has sufficient capacity to adsorb material from many runs before regeneration is required: the capacity is a function of the amount of adsorbent and the temperature difference between the adsorbate and adsorbent. Changes in operating temperature and flow rate result in a baseline shift, but random fluctuations do not affect the stability of the detector.

Detecting elements are simple to construct, and the operating procedure is straightforward. The cost of the detecting element is negligible, and the cost of the complete detector, including the micro-balance and associated equipment is of the same order as a katharometer complete with amplifier and control unit. In addition the mass detector functions as its own integrator. The detecting element and micro-balance are sufficiently robust to withstand normal careful handling: the detector operates perfectly satisfactorily on an ordinary wooden laboratory bench.

The advantages of the mass detector for quantitative analysis, over all other detectors are:

(i) the response is predictable and no calibration with respect to sample size or chemical species is required.

(ii) since response is a function of mass, no qualitative information is required for a complete quantitative analysis.

(iii) peak area measurements are eliminated since quantitative data are obtained directly from step height measurements.

4.8 References.

1. Martin, A.J.P. Gas Chromatography XXIX 1962.

2. Thorburn, S. Gas Chromatography 187 1962.

3. Lovelock, J.E. Anal. Chem. 35 1345 1963.

4. Bevan, S.C., Thorburn, S. J. Chromatog. 11 301 1963.

5. McBain, J., Bakr, A. J. Amer. Chem. Soc. 48 690 1926.

6. Gregg, S.J. J. Chem. Soc. 561 564 1946.

7. Anderson, P.J., Horlock, R.F. Trans. Farad. Soc. 58 1993 1962.

8. Gregg, S.J., Wintle, M.F. J. Sci. Inst. 23 259 1946.

9. Rhodin, T.N. Adv. Catalysis 5 39 1953.
   Gulbransen, E.A. Adv. Catalysis 5 119 1953.

10. Vacuum Microbalance Techniques, published by Plenum Press, 1960etsec.

11. Gorbach, G. Anal. Chim. Acta 29 453 1963.
    Cahn, L., Schultz, H.R. Vacuum Microbalance Tech. 2 7 1962.
    " " " 2 19 1962.

12. Pope, M.I. J. Sic. Inst. 34 229 1957.
    Cochran, C.N. Vacuum Microbalance Tech. 1 23 1960.
    Honig, J.M. " " " 1 55 1963.

13. Cahn Instrument Co., Paramount, Calif.
    Sartorius-Werke, A.G., Germany.

14. Sauerbrey, C. Z. Physik. 155 206 1959.
    Warner, A.W., Stockbridge, C.D. Vacuum Microbalance Tech. 2 71 93 1962.
    Haller, I., White, P. Rev. Sci. Inst. 34 677 1963.

15. King, W.H. Anal. Chem. 36 1735 1964.

16.

17. Bevan, S.C., Thorburn, S. Chem. Brit. 206 1966.

18. Research and Industrial Instruments Co., London: Electromicrobalance model EMB1.

19. C.I. Electronics Ltd., Wimborne, Dorset. Electromicrobalance Mark I

20. Gregg, S.J. The Surface Chemistry of Solids, Chapman and Hall 1951 p 64.

21. Lovelock, J.E. Anal. Chem. 35 1346 1963.

22. Evans, R.S., Scott, R.P.W. Chimia 17 137 1963.

23. Fowlis, I.A., Scott, R.P.W. J. Chromatog. 11 1 1963.

24. Calingaert, G., Hitchcock, L.B. J. Amer. Chem. Soc. 49 750 1927.

25. Gas Chromatography 429 1960.

26. Kipling, J.J. Quart. Rev. 10 1 1956.

27. Gregg, S.J. The Surface Chemistry of Solids, Chapman and Hall, 1951 p 97.

28. Young, S. J. Chem. Soc. 55 486 1889.
Jolly, V.G., Briscoe, H. J. Chem. Soc. 129 2154 1926.

CHAPTER 5.

Quantitative Analysis by Mass Detection.

5.1 Discussion.

The absolute and linear response of the mass detector has been demonstrated over a variety of operating conditions and a number of simple acetate mixtures have been quantitatively analysed. The purpose of the present chapter is to cover a wider range of materials, and thereby demonstrate the value of the mass detector for the quantitative analysis of mixtures. A wide variety of species was analysed, and it is convenient to divide the results into several sections, relating to the boiling ranges of the materials under analysis. This is not a consequence of any peculiarity of the mass detector, but arises from the conditions under which the chromatograph itself must be operated to give a satisfactory performance. In general, it is convenient to place materials for chromatographic analysis into the following categories:

(i) normal boiling materials covering approximately the range 50 to 150°C,

(ii) high boiling materials: liquids boiling over 150°C (including solids at room temperature),

(iii) low boiling materials (0 to 50°C),

(iv) gases.

The mass detector was used to analyse materials in all these categories, and the results are presented below. Any problems associated with a particular boiling range are described in the appropriate section.

5.2 Normal Boiling Range Materials.

The precautions necessary to prevent deterioration of samples have been discussed in Chapter 1. Mixtures were prepared by weighing directly into sample bottles which were filled almost to the limit. Samples were removed with a syringe via a rubber septum. No mixture was kept for more than a few hours. A number of different sample sizes of each mixture were analysed covering the mass range 10 µg to 1 mg per component

of a mixture. Usually this amounted to a total of about 10 determinations

The choice of constituents for mixtures. Several mixtures comprised homologous series, or materials of similar chemical nature, embracing both aliphatic and aromatic compounds. Mixtures containing different chemical species were prepared, covering aromatic and aliphatic hydrocarbons, including halogenated materials, oxygen containing compounds, saturated and unsaturated compounds, polar and non-polar materials, and aqueous solutions. The conditions of analysis are given below, and this is followed by a summary of the results. For each mixture the mean observed percentage weight of the components ($\bar{x}$) was calculated, and the standard deviations (σ) and coefficients of variation (v) of these values were found. The mean detector response ($\bar{R}$) defined as the ratio of the mean observed percentage weight and the true percentage weight $\left(\frac{\bar{x}}{x_o}\right)$ is given. Bias values represent the discrepancy between the mean observed composition and the true composition and are calculated using expressions 4.6 and 4.7. For each mixture, the components are listed in order of increasing retention time.

Table 5.1

Conditions of Operation.

Chromatograph	Shandon KG2
Column	PEGA E
Column Temperature	101°C
Carrier gas	Nitrogen
Inlet pressure	30 lb in^{-2}
Carrier gas flow rate	51 ml min^{-1}
Sample sizes	0.1 to 5 µl.
Mass detector ranges	100 µg to 5 mg fsd
Detecting elements	27, 30
Detector temperature	22 to 24°C

Table 5.2

Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias
Benzene	39.71	1.32	3.32	39.20	1.01	+0.51
Toluene	29.97	0.91	3.04	30.25	0.99	-0.28
Ethyl benzene	30.32	1.03	3.32	30.55	0.99	-0.23
Methyl ethyl ketone	38.75	1.84	4.75	37.56	1.03	+1.19
Methyl n-propyl "	29.84	1.73	5.70	29.77	1.00	+0.07
Methyl n-butyl "	31.41	0.54	1.72	32.67	0.96	-1.26
Ethyl acetate	41.45	0.73	1.74	40.36	1.03	+1.09
n-Propyl acetate	31.63	0.66	2.08	31.58	1.00	+0.05
n-Butyl acetate	26.92	1.06	3.95	28.06	0.96	-1.14
n-Heptane	17.72	0.40	2.26	17.82	1.00	-0.10
n-Octane	17.30	0.56	3.24	17.50	0.99	-0.20
Ethyl acetate	21.38	0.79	3.70	21.73	0.98	-0.35
Methyl ethyl ketone	16.39	0.55	3.36	16.09	1.02	+0.30
Benzene	27.22	0.33	1.21	26.86	1.01	+0.36
Cyclohexane	22.63	0.67	2.96	22.86	0.99	-0.23
n-Octane	15.52	0.97	6.27	15.46	1.00	+0.06
Carbon tetrachloride	35.95	0.50	1.39	35.02	1.03	+0.93
Dichloromethylene	25.90	0.72	2.78	26.65	0.97	-0.75
2,2,4-Trimethyl pentane	44.27	0.61	1.37	43.97	1.01	+0.30
n-Octane	28.47	1.34	4.70	27.86	1.02	+0.61
1-Octene	27.26	0.84	3.07	28.16	0.96	-0.90
n-Octane	35.79	0.74	2.06	34.28	1.04	+1.51
Butylene oxide	32.91	0.55	1.67	32.03	1.03	+0.88
Dioxan	31.30	0.91	2.90	33.69	0.93	-2.39

The results shown in table 5.3 were obtained using a Pye Panchromatograph fitted with column A, and using detector 31. All other conditions are as given in table 5.1. Figure 5.1 shows two chromatograms, representing different sample sizes of the three component mixture given in table 5.3.

Table 5.3

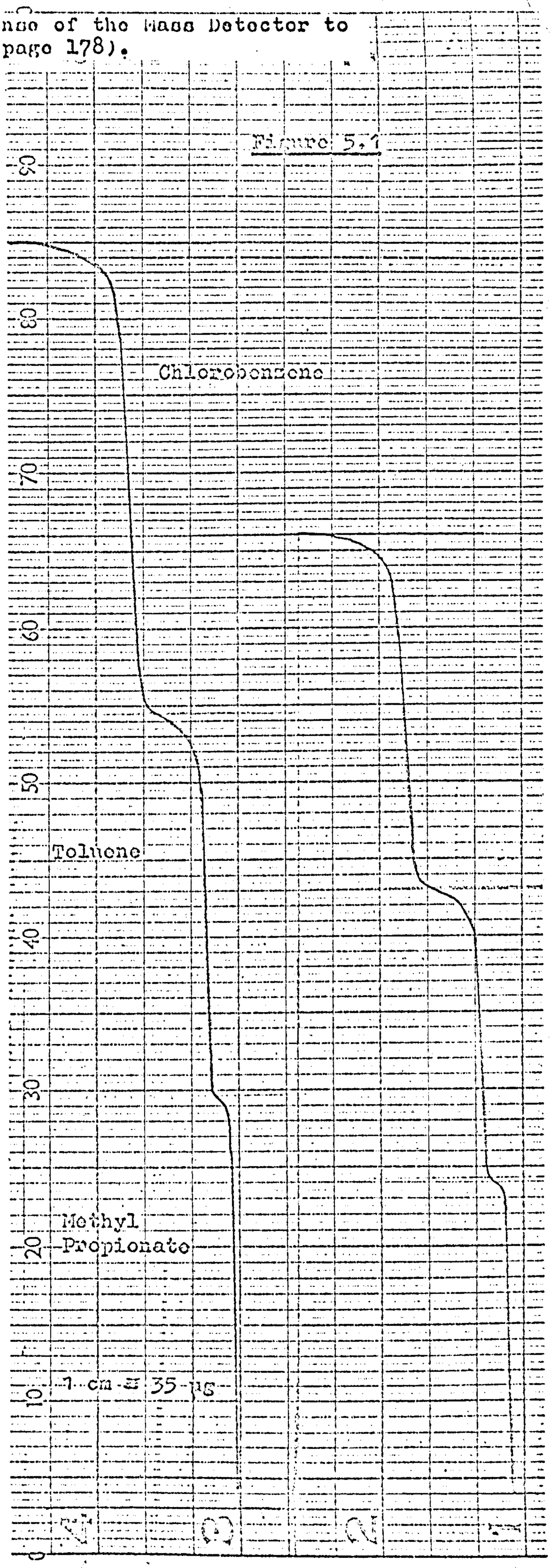
Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias
Methyl propionate	33.05	0.60	1.81	33.51	0.99	-0.46
Toluene	30.35	0.41	1.35	30.41	1.00	-0.06
Chlorobenzene	36.59	0.44	1.20	36.08	1.01	+0.51
Ethyl alcohol	54.25	0.55	1.01	53.63	1.01	+0.62
n-Propyl alcohol	45.75	0.57	1.24	46.37	0.99	-0.62

Many analyses of similar mixtures were carried out at a flow rate of 105 ml min^{-1}, on the Shandon KG2 chromatograph, under the conditions given in table 5.1 where appropriate. Variations in conditions are noted at the foot of table 5.4, which summarises these results.

Table 5.4

Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias
n-Pentane[a]	22.30	0.66	2.95	22.50	0.99	-0.20
n-Hexane	18.40	0.71	3.86	17.57	1.05	+0.83
n-Heptane	15.16	0.59	3.85	14.67	1.03	+0.49
n-Octane	16.46	0.64	3.87	16.45	1.00	+0.01
n-Nonane	27.69	0.89	3.23	28.82	0.96	-1.13
Benzene	41.35	0.70	1.70	41.33	1.00	+0.02
Toluene	30.94	0.69	2.23	31.00	1.00	-0.06
Ethyl benzene	27.72	0.60	2.16	27.67	1.00	+0.05
Methyl ethyl ketone	43.05	0.57	1.32	42.20	1.02	+0.85
Methyl n-propyl "	25.75	0.84	3.28	25.69	1.00	+0.06
Methyl n-butyl "	31.20	1.32	5.58	32.10	0.97	-0.90
Methyl acetate	21.46	0.83	3.85	23.72	0.90	-1.26
Ethyl acetate	25.50	0.81	3.17	23.47	1.09	+2.03
n-Propyl acetate	23.03	1.01	4.38	22.82	1.01	+0.21
n-Butyl acetate	30.02	0.46	1.53	29.99	1.00	+0.03
n-Heptane	18.61	0.20	1.08	18.44	1.01	+0.17
n-Octane	13.81	0.34	2.46	13.77	1.00	+0.04
Ethyl acetate	23.92	0.31	1.30	23.68	1.01	+0.22
Methyl ethyl ketone	16.28	0.36	2.21	16.49	0.99	-0.21
Benzene	27.37	0.31	1.13	27.63	0.99	-0.26

Chromatograms showing the Response of the Mass Detector to a Three Component Mixture (see page 178).



Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias
Cyclohexane	19.39	0.59	3.04	19.30	1.00	+0.09
n-Octane	16.14	0.43	2.68	15.87	1.02	+0.27
Carbon tetrachloride	34.79	0.63	1.81	34.92	1.00	-0.13
Dichloroethylene	29.68	-	-	29.92	0.98	-0.24
2,2,4-Trimethyl pentane	38.25	0.72	1.88	38.03	1.01	+0.22
n-Octane	35.52	0.71	2.00	35.59	1.00	-0.07
1-Octene	26.23	2.00	7.65	26.38	0.99	-0.15
n-Octane	27.63	0.47	1.71	26.74	1.03	+0.89
Butylene oxide	28.56	0.59	2.06	28.80	0.99	-0.24
Dioxan	43.81	0.82	1.87	44.45	0.99	-0.64
n-Butyraldehyde[a]	39.24	1.03	2.62	39.80	1.00	-0.56
Methyl ethyl ketone	60.76	1.06	1.74	60.20	1.00	+0.56
n-Butyl alcohol[b]	53.42	1.05	1.97	52.95	1.01	+0.47
n-Amyl alcohol	46.58	1.05	2.26	47.05	0.99	-0.47
n-Propyl alcohol[b]	45.36	0.28	0.62	44.94	1.01	+0.42
Methyl n-propyl ketone	54.64	0.52	0.96	55.06	0.99	-0.42

a Column temperature 66°C.

b Porapak column D at 140°C.

There is a negligible difference between the precision and accuracy of the results at 51 and 105 ml min^{-1}. The overall standard deviation (σ) was 0.75%, and the coefficient of variation (V) 2.5%, for 180 analyses. The corresponding values for runs carried out at a single sample size on a single mixture were 0.4% and 1.0% respectively (table 4.20). Values for a single mixture over a wide flow rate range were 0.6% and 1.6% (table 4.17). The accuracy of the results is expressed in terms of bias, and the mean value of the runs in tables 5.2 to 5.4 is 0.54% (absolute bias 1.8%); cf tables 4.17 and 4.20 for a single three component mixture. Response factors are very similar for all materials, and for practical purposes can be taken as unity.

The detector gives satisfactory quantitative analyses for a wide

variety of materials, in proportions ranging from 15% to 60% in a mixture, and covering the mass range 10 µg to 1 mg per component.

5.2.1 The Quantitative Analysis of Minor Constituents.

In tables 5.2 to 5.4 details of the analyses of mixtures in which the percentage weight per constituent varied between 15 and 60% of the total quantity, have been given. In order to assess the reliability of the mass detector for the analysis of minor constituents and to detect any trends in bias and precision with respect to percentage composition, a number of mixtures of heptane and hexane were prepared, in which the proportion of one compound was progressively increased from 2% to 100%. This experiment was combined with the determination of detector linearity given in Chapter 4 (see table 4.38). Experimental conditions are given in table 5.5. Results are calculated solely on the basis of the weight of heptane present and not on the proportion of heptane in the mixture. The results, given in table 5.6, were only used to determine the bias of the measurements, and not the precision of the measurements for each mixture.

Table 5.5

Experimental Conditions

Chromatograph	Shandon KG2
Column	PEGA E
Column Temperature	64°C
Carrier gas	Nitrogen
Inlet pressure	30 lb in^{-2}
Carrier gas flow rate	32-36 ml min^{-1}
Sample size	1 µl
Mass detector range	100 µg to 1 mg
Detecting elements	27, 31
Detector temperature	24°C

Table 5.6

% Heptane	Bias µg	Bias %	% Heptane	Bias µg	Bias %
2.3	+2.1	+15.8	18.0	-4.9	-4.7
3.6	-0.8	-4.0	21.9	-0.9	-0.7
7.2	-0.9	-2.2	21.9	+1.3	+1.0
8.2	-4.1	-8.7	24.0	-5.1	-3.6
8.2	-3.1	-6.4	24.0	-3.5	-2.5
9.9	-6.0	-10.5	25.9	+2.6	+1.7
9.9	-5.5	-9.6	26.3	-7.8	-5.2
9.9	+2.1	+3.5	26.3	-2.6	-1.7
10.0	-1.4	-2.5	48.3	+6.0	+2.1
11.1	-0.5	+0.8	67.5	+5.6	+1.4
11.1	+1.5	+2.4	76.3	-8.2	-1.8
15.6	-2.3	-2.6	100.0	-5.5	-0.9

The percentage bias values show a slight improvement when the proportion of heptane exceeds about 10%. The mean value of the (absolute) bias is 4%.

Using a similar series of hexane/heptane mixtures, and carrying out 10 determinations per mixture, a measure of the precision of the detector at each heptane composition was obtained. All values were calculated on a percentage weight rather than an absolute basis, and the results are given in table 5.8 in the same manner as table 5.2, with which they may be compared. Experimental conditions are given in table 5.7.

Table 5.7

Experimental Conditions

Chromatograph	Pye Panchromatograph
Column	ApL G
Column temperature	100°C
Carrier gas flow rate	40 ml min^{-1}
Sample size	1 µl, 3½ µl
Mass detector range	1 mg to 5 mg
Detecting element	31
Detector temperature	24°C

Table 5.8

$\bar{x}$(%)	σ	V	x_o(%)	Bias	% Bias
0.34	0.05	14.7	0.29	+0.05	17.2
1.51	0.04	2.65	1.38	+0.13	9.4
4.17	0.20	4.80	4.39	-0.12	2.7
12.16	0.32	2.63	12.65	-0.49	3.9
22.19	0.51	2.29	22.45	-0.26	1.2
35.87	0.18	0.50	35.94	-0.07	0.19
44.68	0.29	0.65	44.79	-0.11	0.24
55.33	0.29	0.52	55.21	+0.12	0.22
64.13	0.18	0.28	64.06	+0.07	0.11
77.82	0.17	0.22	77.55	+0.27	0.35
87.85	0.33	0.38	87.36	+0.49	0.56
95.80	0.21	0.22	95.61	+0.19	0.20
98.49	0.00	-	98.62	-0.11	0.11
99.66	0.05	0.05	99.71	-0.04	0.04

All runs were carried out using 1 µl samples on the 2 mg range, except those samples of percentage composition less than 2% and greater than 98%. For these runs $3\frac{1}{2}$ µl samples were used, with the 5 mg range for the major constituent and the 1 mg range for the minor constituent.

The changes in standard deviation and coefficient of variation with sample composition are shown on figure 5.2. The coefficient of variation is less than 1% for all sample compositions over 30%, and evan at 5% composition has only increased to about 4%. The standard deviation remains sensibly constant throughout the whole range of sample compositions, at about 0.25%. The overall mean bias is 0.2% (absolute bias 2.6%).

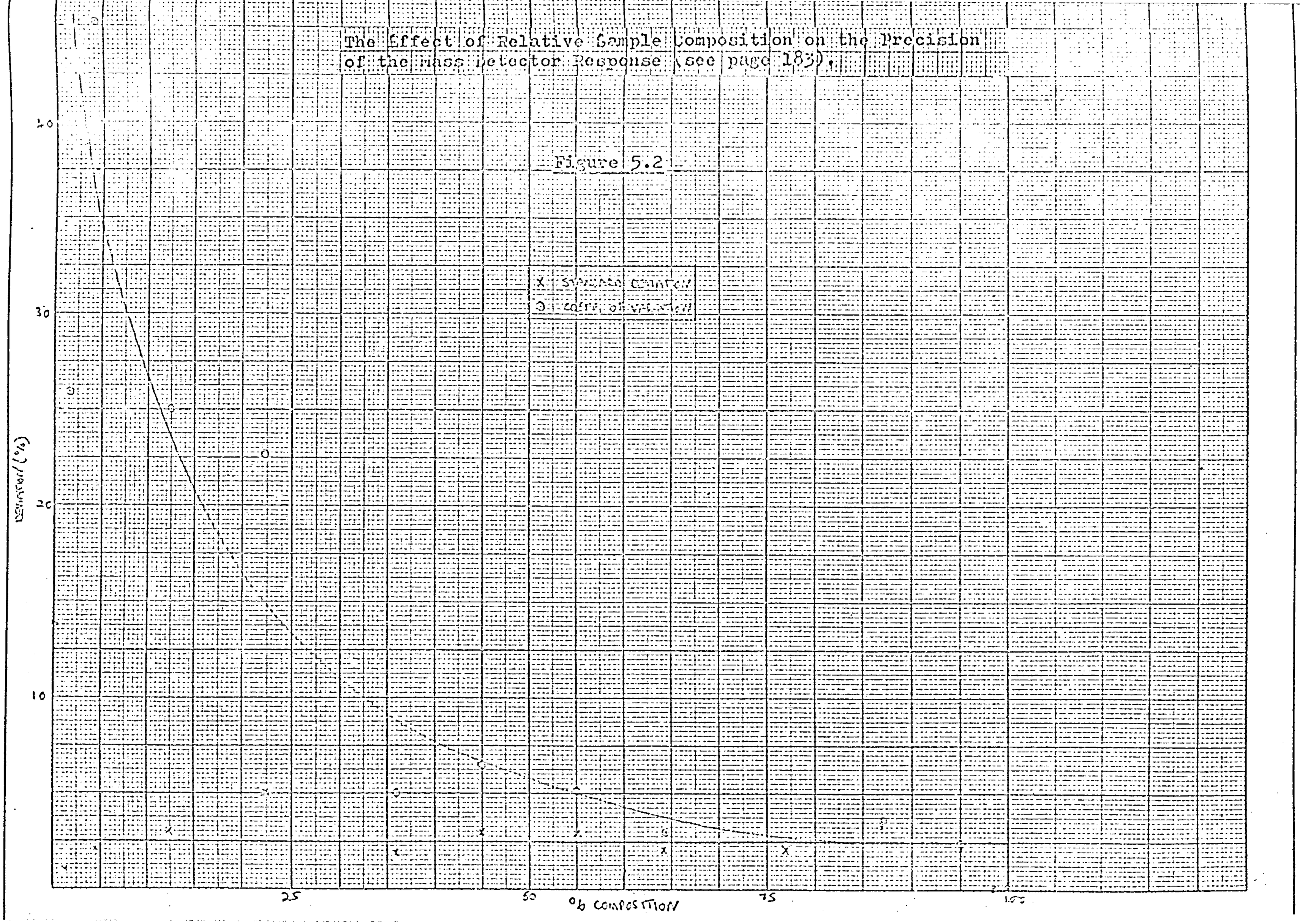
Satisfactory quantitative analysés may be obtained for minor constituents in mixtures.

5.2.2 The Determination of Water by the Mass Detector.

The adsorption of water on activated charcoal follows the type V isotherm, but this should not give rise to any difficulty in a quantitative estimation, using the mass detector. The analysis of aqueous samples by chromatography is however particularly difficult in that the excessively polar nature of water invariably produces grossly

The Effect of Relative Sample Composition on the Precision of the Mass Detector Response (see page 183).

Figure 5.2

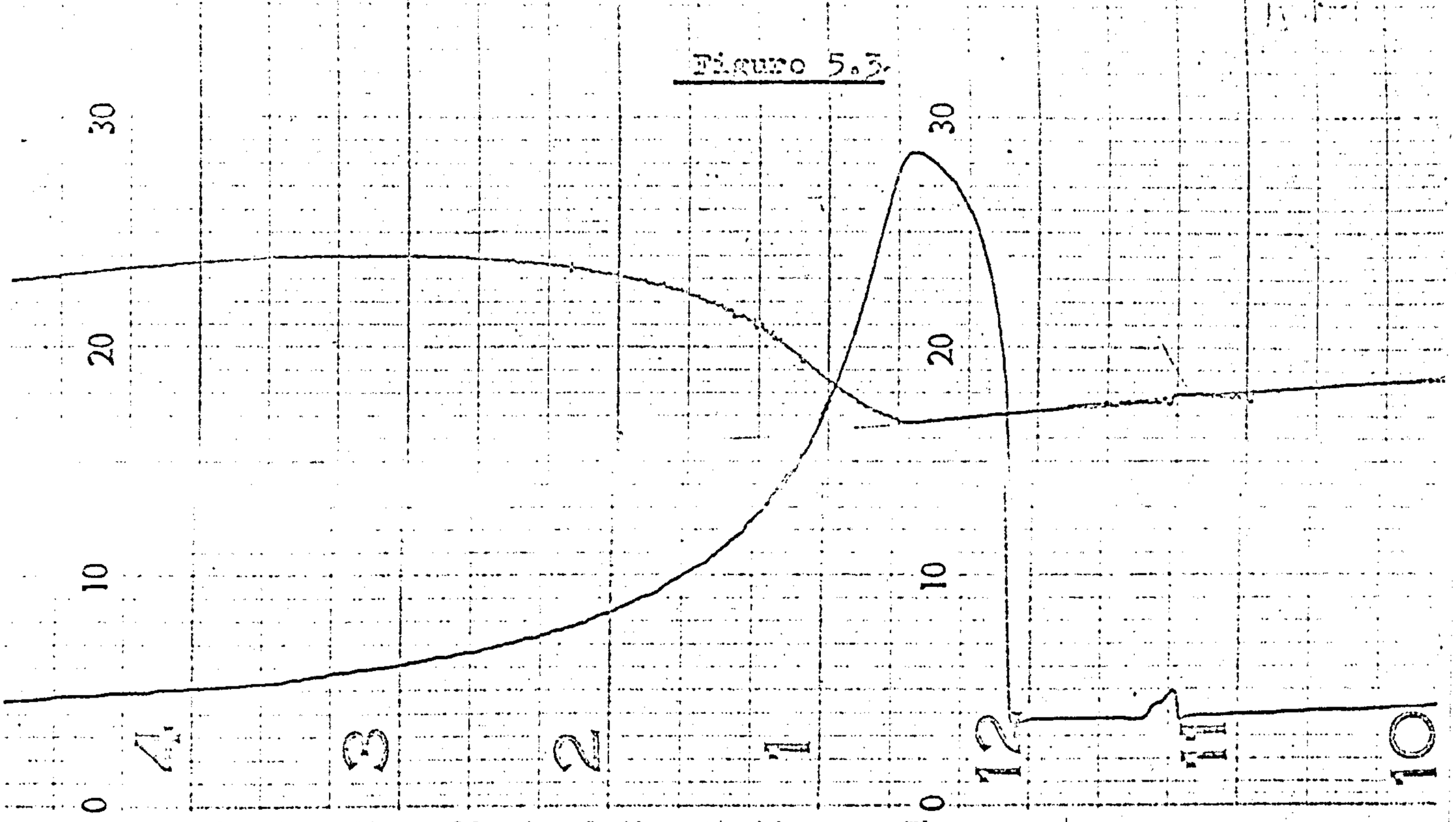


distorted peaks, with all conventional stationary phases: a high proportion of water is irreversibly adsorbed on the stationary phase. Similar effects are observed with the lower members of the alcohol series. As a consequence, even assuming that a detector will respond quantitatively to water, the results bear little resemblance to the composition of the sample injected. Moreover, several of the commonly employed detectors give spurious responses toward water vapour. The Bray ionisation detector (section 3.6a) will not respond to water, but the response factors for the other constituents of an aqueous sample are different from those of the same constituents in a non-aqueous medium. The flame-ionisation detector (section 3.2) will scarcely respond to even a large proportion of water in a sample, which after affects the response of the detector to the remaining constituents. The effect is by no means as marked as in the Bray ionisation detector, and does not inferfere with subsequent analyses. The katharometer (section 3.1) will detect the presence of water in a sample, but requires extensive calibration. The gas density balance (section 3.10) should give a normal response to water vapour, which will be negative if for example nitrogen or argon is used as carrier gas.

The problem associated with the analysis of aqueous samples is thus two-fold; a chromatographic column is required which will give a symmetrical and quantitative pass of the water band, and a detector is required which will give a quantitative estimate of the water present, without affecting the response factors toward the remaining constituents.

An example of a chromatogram of water, obtained from a conventional column[1] (ApL ref C, table 4.15) using a katharometer in series with the mass detector is shown in figure 5.3. Clearly an estimate of the peak area by any means would be difficult in view of the gross distortion of the peak: step height measurement, on the other hand would be relatively simple.

Recently a new type of column packing has been introduced[1], which it is claimed gives symmetrical elution peaks for highly polar materials,



Chromatograms showing the Effect of the Stationary Phase on the Peak Symmetry of Polar Materials: (see page 184).

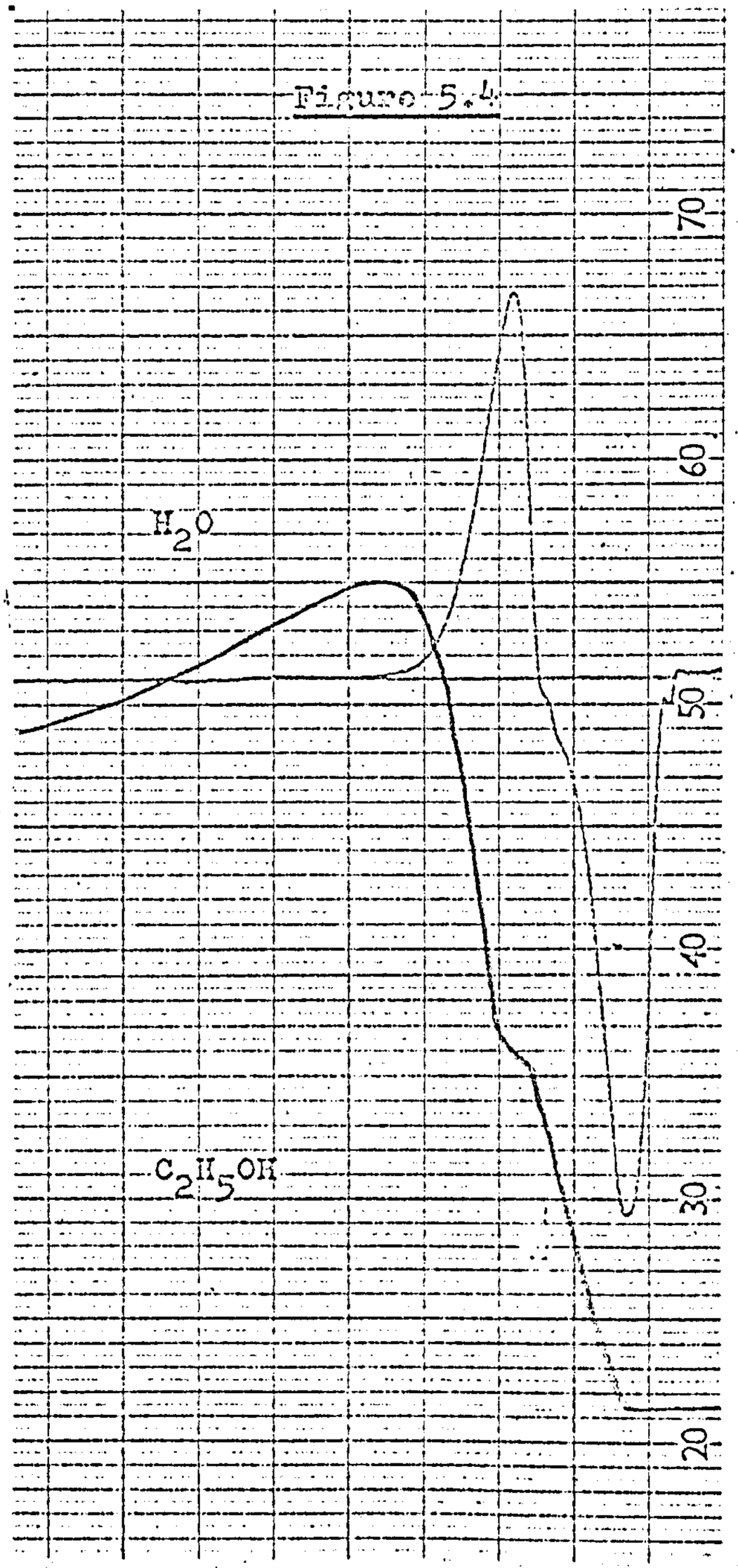


Fig. 5.3 ApL stationary phase
Fig. 5.4 Parapak column.

and that all materials including water are not irreversibly adsorbed. This material appears to be ideal for the quantitative analysis of aqueous samples. The material is basically a cross linked polystyrene, but details of the modifications to the standard polystyrene preparation, which make the material suitable for use in chromatography have not been published. A column, D, (see table 4.15) was prepared using a packing such as that described above, which is commercially available under the name Porapak[2]. A number of samples of known composition were prepared, and quantitatively analysed using column D fitted to the KG 2 chromatograph, with a Martin gas density balance in series with the mass detector. The conditions under which the analyses were carried out are given in table 5.9.

Table 5.9

Carrier gas	Nitrogen
Flow rate (analytical)	56 ml min^{-1}
" " (reference)	55 ml min^{-1}
Column temperature	70°C
Gas density balance sensitivity	10^3 (maximum)
Mass detector range	5 mg
Detecting element	27

An example of a chromatogram obtained for a mixture of ethyl alcohol and water is given in figure 5.4. Excellent peak shapes are obtained, comparable with those expected for a typical analysis of non-polar materials on a non-polar stationary phase. The results are summarised in table 5.10a.

Table 5.10a

Compound	n	Composition by Mass Detector $\bar{x}$	σ	V	% Bias	x_o
Water	7	47.30	0.98	2.0	-12.4	
Ethyl alcohol		52.70	1.00	2.0	+12.4	
		Composition by Gas Density				
Water		47.29	1.45	3.1	-12.5	54.02
Ethyl Alcohol		52.71	1.63	3.1	+12.5	45.98

Table 5.10b

Compound	n	Composition by Mass Detector $\bar{x}$	σ	V	% Bias	x_o
Water	3	43.41	-	-	-16.8	52.53
Ethyl alcohol		56.59	-	-	+16.8	47.47

The percentage compositions determined by the two detectors are in excellent agreement with each other, but are completely different from the prepared composition. To ensure that no error in sample preparation had occurred, a fresh sample was prepared and analysed under identical conditions (table 5.10b). A similar discrepancy was observed. A major change in the composition of the mixtures was therefore occurring after injection, but before either of the detectors. There was a substantial loss of water resulting in a marked decrease in the percentage of water reaching the column outlet. There may in addition have been a loss of alcohol, but this was small compared with the amount of water which was lost. An estimate of the amount of water and ethyl alcohol lost between injection and detection can be obtained by comparing the expected and observed adsorption efficiencies at the mass detector. For a 3 µl sample of the water/alcohol mixture, the expected amounts of constituents detected by the mass detector are 1.134 mg of water and 1.329 mg of alcohol. The mean observed weights were 0.873 mg and 0.959 mg, i.e. a loss of 0.459 mg of water, and 0.175 mg of alcohol.

The analysis of one of the mixtures was repeated for sample sizes between 0.2 µl and 4 µl. The results are given in table 5.11.

Table 5.11

Nominal Sample Size (µl)	% Water Detected in mixture
0.2	36.22
0.5	38.23
1.0	39.29
2.0	43.48
4.0	44.68
(∞)	(52.53)

It is clear that as the sample load is increased, so the percentage of water reaching the detector increases.

Preferential loss of water may also arise from condensation in the injection block, or in the mass detector delivery tube. The boiling point of ethyl alcohol is only 22°C below water, and injection temperature was maintained at 235°C, so that no condensation at the injection block is likely. Condensation in the mass detector delivery tube, would result in significantly lower values of water content in the mixture between the gas density balance and the mass detector. The mass detector results for water are identical with the gas density balance results. In addition condensation in the delivery tube results in excessively broad and distorted steps, which were not observed.

It is concluded that the loss of water between injection and detection was predominately due to adsorption on the column, even though symmetrical elution bands were observed. Adsorption effects may be minimised by more vigorous column pretreatment, and by conditioning with large volumes of water (several milligrams) before undertaking quantitative analysis.

Molecular weight determinations, using the above samples have been carried out, and gave entirely satisfactory values, again indicating that all water losses occur before either detector, and that both detectors give normal responses. These results are presented in Chapter 7.

The mass detector gives satisfactory quantitative results for the analysis of aqueous samples.

5.3 High Boiling Materials.

It is to be expected that a number of experimental difficulties, not present to any significant extent at normal temperature operation, will become apparent when analysing high boiling materials. For example, the temperature of the carrier gas emerging from the chromatographic column may be sufficiently high to create disturbances by convection within the mass detector chamber. Condensation of materials in the delivery tube prior to reaching the mass detector is more likely, and

could lead to erroneous results, in particular with samples containing materials covering a wide boiling range. Experiments were designed to measure any decrease in stability of the detector as the carrier gas temperature was increased, and to determine the extent to which condensation within the delivery tube occurred. On the basis of these experiments the mass detection system was modified to be suitable for high temperature analysis. The aim was to have a detecting system capable of detecting the highest boiling material which the column could accept, i.e. the highest boiling material which could be analysed, must be a result of column limitations and not detector limitations.

5.3a Experimental.

The column outlet tube, and the detector delivery tube which was heated resistively, were electrically insulated with a short length (2") of PTFE 1/16" o.d. tubing. The detector chamber was used in the same form as that for normal temperature operation for the initial experiments, in which a mixture of n-nonane and n-dodecane was analysed. The experimental conditions are given in table 5.12.

Table 5.12

Apparatus	Shandon KG2
Column	ApL H
Column temperature	176°C
Carrier gas flow rate through column	43 ml min^{-1}
Sample size	1 µl
Mass detector range	1 mg
Detecting element	27

The flow rate of carrier gas through the column was kept constant, and by introducing an additional nitrogen supply at the column exit, the flow rate along the delivery tube could be varied over a wide range (43 to 250 ml min^{-1}). With this secondary gas supply off, the step corresponding to dodecane was very broad, more so than expected from the normal band spreading within the column. On increasing the overall flow rate to the detector, the step became more well defined, demonstrating that partial condensation in the delivery tube was

contributing significantly to the spreading of the band. The temperature inside the detector delivery tube, i.e. the carrier gas temperature, was monitored at several points: a temperature drop from 134°C to 28°C occurred over the last few centimetres of the delivery tube. Delivery tube temperature was not affected by the flow rate of the carrier gas through the tube. The improved chromatograms at rapid flow rates were a result solely of decreasing the residence time of materials in the tube.

Typical analyses of the nonane-dodecane mixture are given in table 5.13a for a delivery tube temperature of 134°C, and in table 5.13b for an overall delivery tube temperature of 26°C. The total gas flow rate into the detector was 43 ml min^{-1} for both runs.

Table 5.13a

Compound	x	x_o	Bias	% Bias	Uptake$_{-1}$ ($\mu g\ sec^{-1}$)
n-Nonane	56.49	54.86	-		9.6
n-Dodecane	43.51	45.14	-1.63	3.6	0.8

Table 5.13b

n-Nonane	56.77	54.86	-		7.5
n-Dodecane	43.23	45.14	-1.91	4.2	0.4

The percentage composition results (x values) are similar for both a cold and a heated delivery tube, and show a small permanent loss of the higher boiling alkane (a table of boiling points is given at the end of this section). The rate of uptake of each material by the detector, which is a measure of the band spreading, is similar at both temperatures, but is vastly lower for the dodecane. Since no appreciable improvement in results occurred when a heated delivery tube was used, it is clear that the majority of the loss of material was occurring in the last few centimetres of the tube, which was heated only by conduction. Indeed the tube was designed so that this part, all of which was within the detector chamber, did not exceed room temperature, to avoid convection currents.

The temperature of the delivery tube within the detector chamber was increased to 40°C, the main length of the tube remaining at 134°C, and the analysis was repeated. The results are given in table 5.14a for a flow rate of 43 ml min^{-1} and table 5.14b for 100 ml min^{-1}.

Table 5.14a

Compound	x	x_o	Bias	% Bias	Uptake ($\mu g\ sec^{-1}$)
n-Nonane	55.91	54.86	-		11.4
n-Dodecane	44.09	45.14	-1.05	2.3	1.3

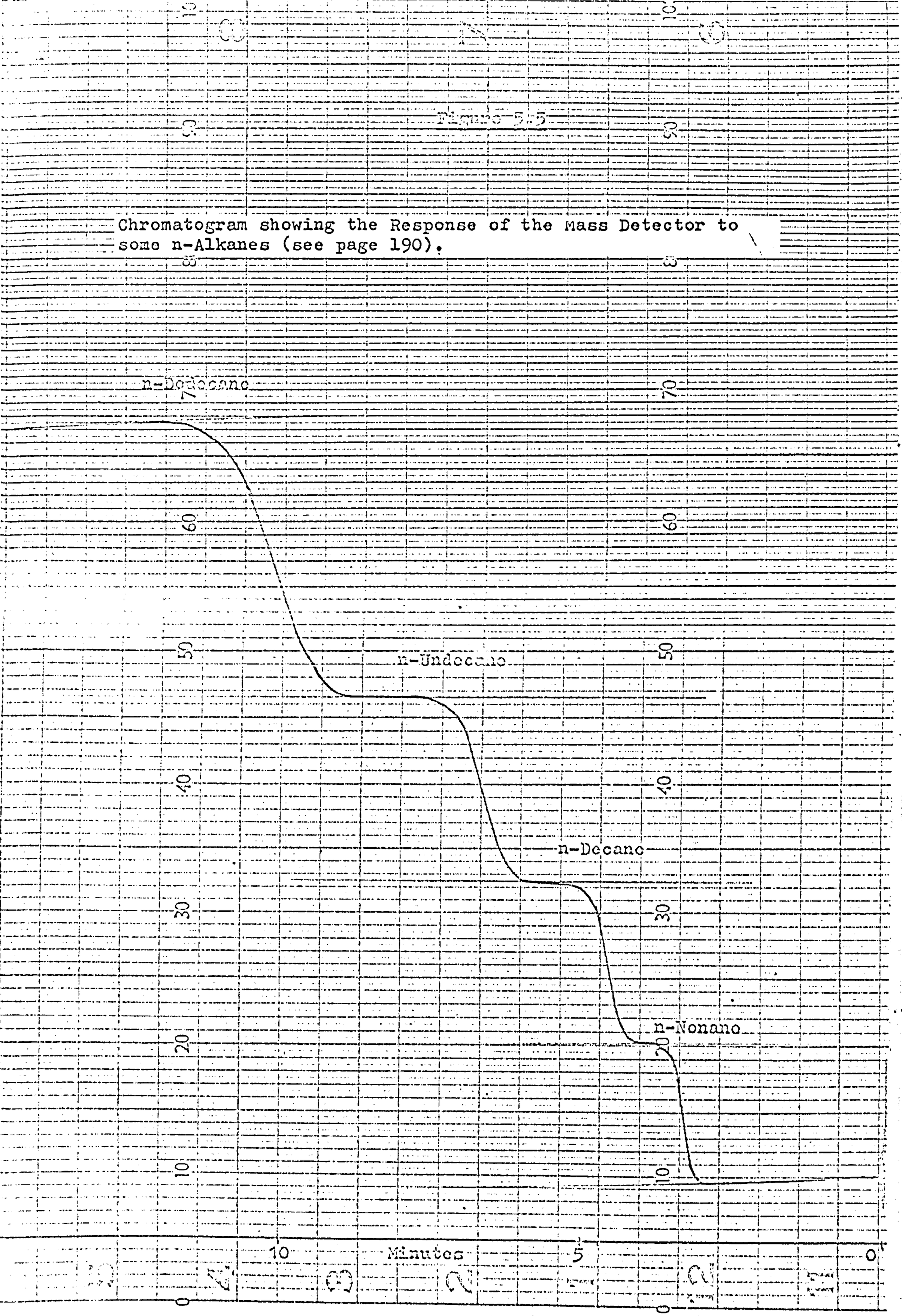
Table 5.14b

n-Nonane	56.14	54.86			11.8
n-Dodecane	43.86	45.14	-1.28	2.8	2.1

Comparison with table 5.13 shows an increase in the recovery of dodecane, and an overall increase in the rates of uptake. Although the results for dodecane are only about 1% low (2½% absolute), improvement is essential, if the analysis of higher boiling materials is to be successful. The main temperature of the delivery tube was increased to 162°C, and the run repeated. Rates of uptake were not increased significantly, again indicating that condensation is occurring mainly in the last few centimetres of the tube, which was still at 40°C. A mixture containing all the normal alkanes from nonane to dodecane was analysed under the conditions given in table 5.12, with a total flow rate into the detector of 100 ml min^{-1}, and a mean delivery tube temperature of 159°C. The temperature of the section heated by conduction was 38°C. The results appear in table 5.15. The analysis was carried out eight times, and the mean percentage weight and standard deviations calculated. A chromatogram is shown in figure 5.5.

Table 5.15

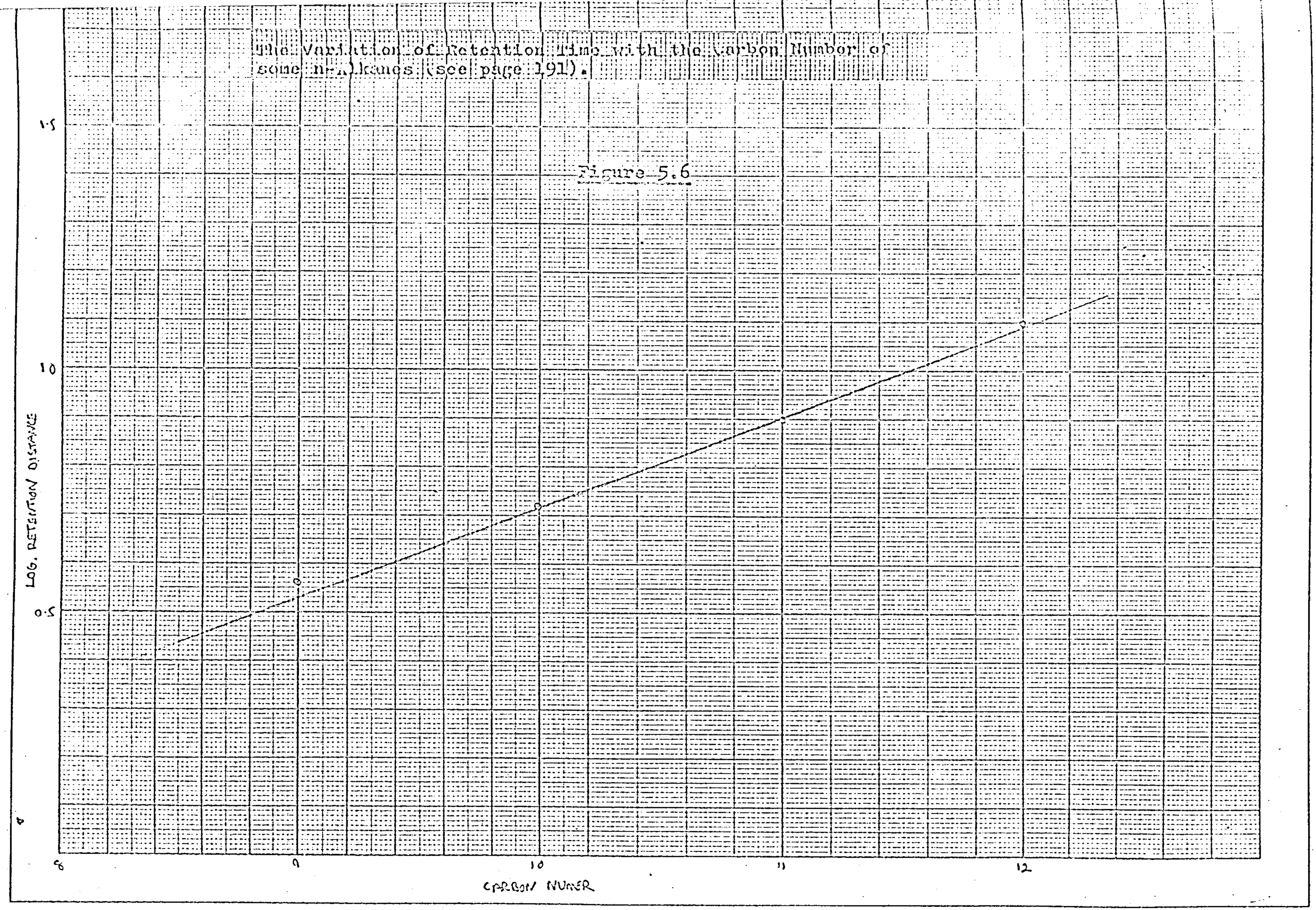
Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias	% Bias
n-Nonane	18.42	0.63	3.4	18.19	1.01	+0.21	1.2
n-Decane	20.60	0.27	1.3	20.26	1.01	+0.34	1.7
n-Undecane	24.52	0.55	2.2	24.38	1.00	+0.14	0.6
n-Dodecane	36.46	0.39	1.1	37.17	0.98	-0.71	1.9



Chromatogram showing the Response of the Mass Detector to some n-Alkanes (see page 190).

The Variation of Retention Time with the Carbon Number of some n-Alkanes (see page 191).

Figure 5.6



The observed % composition for each component is satisfactory.

At a given temperature there is an increasing tendency toward condensation, the lower the vapour pressure of the solute. As a result there is an increase in distortion of the steps as the homologous series is ascended, and the points of inflection on the chromatogram become progressively more difficult to locate (see for example figure 4.27). A graph of log. retention distance against carbon number for a homologous series will in general give a straight line. However, as a result of step distortion, a straight line may no longer be obtained. Using the chromatograms from which table 5.15 was compiled such a graph was plotted, and is shown in figure 5.6: a straight line plot was obtained. The analysis of hydrocarbons, certainly up to undecane is satisfactory. In general, the quantitative analysis of materials boiling up to about 200°C can be carried out satisfactorily, but for higher boiling materials it is evident that further improvements in the delivery system are essential. The delivery tube exit temperature was raised to 65°C (the bulk was maintained at 159°C): chromatograms obtained under these conditions were more well defined than those previously obtained, and the analyses of hydrocarbons up to tetradecane (bp 253°C) were satisfactorily accomplished. Experimental details are given in table 5.16, and the results in table 5.17.

Table 5.16

Experimental Conditions

Column	ApL H
Column temperature	203°C
Flow rate through column	86 ml min^{-1}
Flow rate to mass detector	141 ml min^{-1}
Delivery tube temperature	159°C
Exit temperature	65°C
Detector temperature	32°C

Table 5.17

Compound	$\bar{x}$	σ	V	x_o	Bias	% Bias
n-Decane	31.56	0.85	2.7	31.48	+0.08	0.35
n-Dodecane	26.64	0.82	3.1	26.31	+0.33	1.3
n-Tetradecane	41.80	0.68	1.6	42.21	-0.41	1.0

Both standard deviations and bias values are less than 1%, which is acceptable.

The analysis of hexadecane and octadecane under the same conditions gave slightly distorted chromatograms, but the effect of raising the temperature of the end section of tube without significantly changing the overall temperature had so improved the chromatograms that further increase in the exit temperature should overcome condensation problems entirely. It was to be expected that since heating was well within the detecting element itself, a significant increase in noise would occur. Noise measurements were made, with the tube exit at 110°C and a flow rate of 120 ml min^{-1}. The noise level was unacceptably high on the 1 mg balance range (table 5.18), but was decreased by a factor of ten, by lagging the inside of the detector chamber with expanded polystyrene, making operation on the 1 mg range satisfactory. The effect of delivery tube exit temperature on detector stability is shown in table 5.18.

Table 5.18

Delivery Tube Temp. Main	Exit(°C)	Flow Rate ml min^{-1}	Mass range mg	Noise % fsd	Limit of Detection µg
26	26	43	1	0.7	14
106	26	43	1	0.5	10
134	38	43	1	0.5	10
138	39	100	1	0.4	8
180	78	168	1	4.3	90
180	78	121	1	0.7	14
180	110	121	1	5.0	100
180	110	121	5	0.4	40
180[a]	110	121	5	zero	-
180[a]	110	121	1	0.5	10
196[a]	140	151	5	0.3	30

a = lagged detector chamber.

Detector noise levels at normal operating temperatures are shown in table 4.43. Operating the delivery tube in the region of 200°C has decreased the limit of detection by a factor of ten.

To confirm that the delivery tube system was satisfactory at least for materials which could be analysed up to the maximum operating temperature of the column, replicate analyses of high boiling mixtures, including materials solid at room temperature were carried out (see table 5.20): the results are tabulated below, (table 5.19). The n-alkanes were analysed on an ApL column H, at a flow rate of 108 ml min^{-1}. The column temperature was 232°C, the delivery tube temperature 196°C, and the detecting element temperature 51°C. The mixtures containing aromatic hydrocarbons were analysed on the same column at 155°C with a delivery tube temperature of 112°C, and a flow rate of 35 ml min^{-1}.

No runs were carried out above 232°C, which was regarded as the limit above which very rapid deterioration of the column would occur. Evan at this temperature measurable bleeding of the stationary phase occurred, resulting in a steady increase in detector baseline. At this temperature the retention times of the high alkanes were excessive; for example the retention time of n-tetracosane was 8 hours, at a flow rate of 108 ml min^{-1}.

Some samples of the high alkanes contained one member much lower in the series. The object of this was twofold:

(i) to act as a solvent,

(ii) to eliminate the possibility that all materials within a small boiling range were condensing to the same extent, and thus giving a false impression of satisfactory performance.

Before injection, samples were warmed to ensure complete mixing and liquifaction, and the syringe needle was warmed before use.

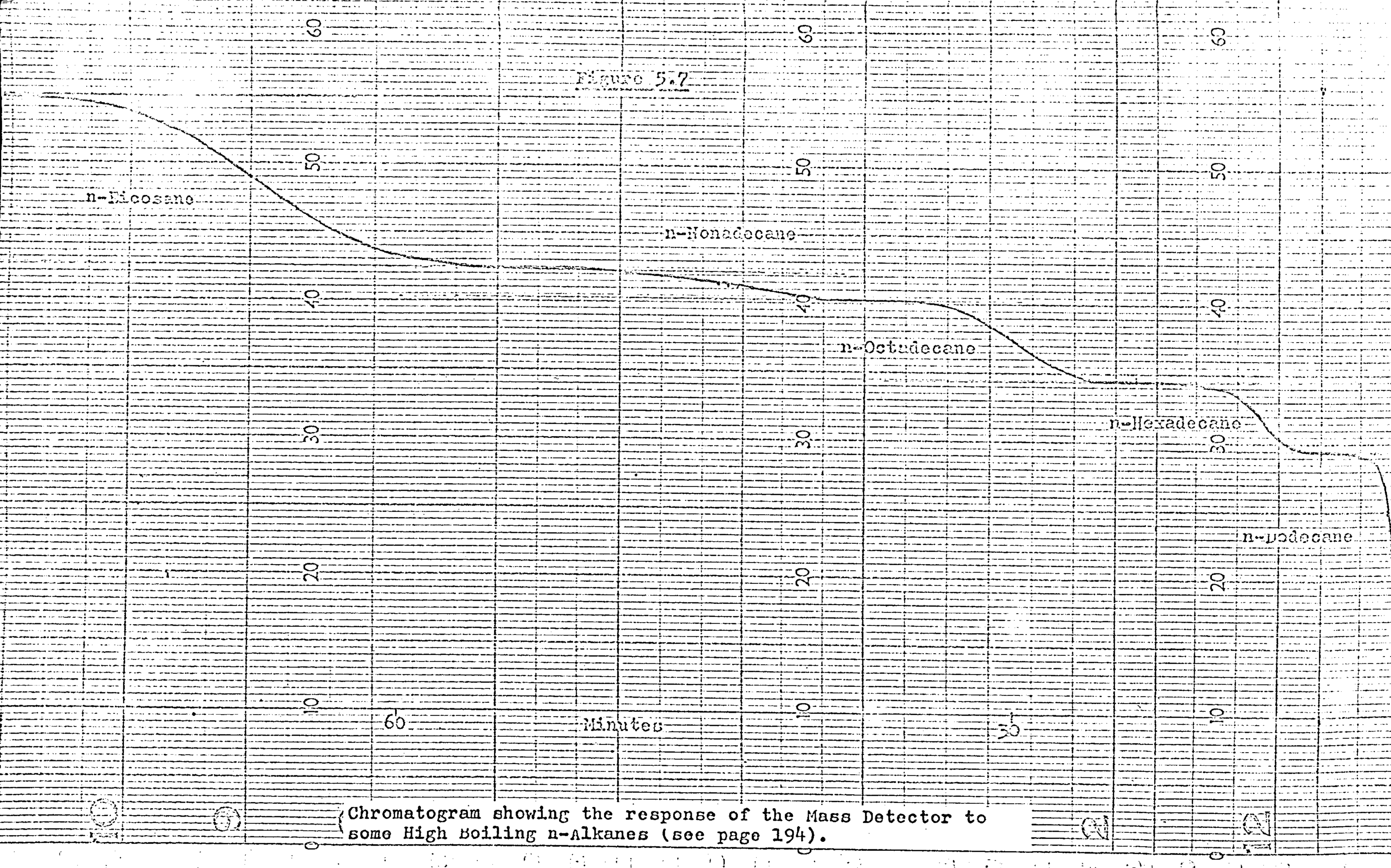
Table 5.19

Compound	$\bar{x}$	σ	V	x_o	$\bar{R}$	Bias
n-Dodecane	24.44	0.82	3.4	24.92	0.99	-0.48
n-Tetradecane	14.90	0.47	3.1	15.61	0.96	-0.71
n-Hexadecane	32.98	0.63	1.9	32.44	1.02	+0.54
n-Octadecane	27.68	1.26	4.5	27.03	1.02	+0.65
n-Dodecane	26.12	0.57	2.2	27.11	0.96	-0.99
n-Hexadecane	14.96	1.00	6.7	14.86	1.01	+0.10
n-Octadecane	17.72	0.85	4.8	18.32	0.97	-0.60
n-Nonadecane	4.28	0.41	9.6	3.84	1.12	+0.44
n-Eicosane	36.92	0.96	3.1	35.88	1.02	+1.04
n-Dodecane	35.33	0.64	1.8	33.92	1.04	+1.41
n-Eicosane	27.47	0.60	2.2	28.18	0.98	-0.71
n-Docosane	27.80	1.07	3.9	28.57	0.97	-0.77
n-Tetracosane	9.40	1.30	13.8	9.33	1.01	+0.10
n-Eicasane	42.45	2.09	4.9	42.65	1.00	-0.20
n-Docosane	42.99	1.48	3.4	43.24	1.00	-0.25
n-Tetracosane	14.57	1.71	11.7	14.12	1.03	+0.45
n-Hexadecane	40.16	2.91	7.2	40.05	1.00	+0.11
n-Eicosane	41.85	2.78	6.6	41.57	1.00	+0.28
n-Docosane	18.00	2.19	12.2	18.38	0.98	-0.38
Cumene	15.01	0.29	1.9	15.26	0.98	-0.25
Mesitylene	20.98	0.74	3.5	21.68	0.97	+0.30
p-Cymene	12.81	0.47	3.7	13.06	0.98	-0.25
Iodobenzene	51.20	2.13	4.2	49.99	1.02	+0.21
n-Nonane[a]	27.71	0.74	2.7	27.56	1.00	+0.15
p-Cymene	53.53	0.36	0.7	53.44	1.00	+0.09
Iodobenzene	18.76	0.79	4.2	19.00	0.99	-0.24

a This mixture was prepared outside the laboratory, and its true composition unknown to the Author until after analysis by mass detection.

A chromatogram, showing the analysis of some hydrocarbons between n-C_{16} and n-C_{20} is shown in figure 5.7. Retention distances, obtained from the alkane mixtures listed in table 5.19 were plotted against carbon number, and a straight line relationship was obtained embracing the normal alkanes dodecane and tetracosane, (figure 5.8).

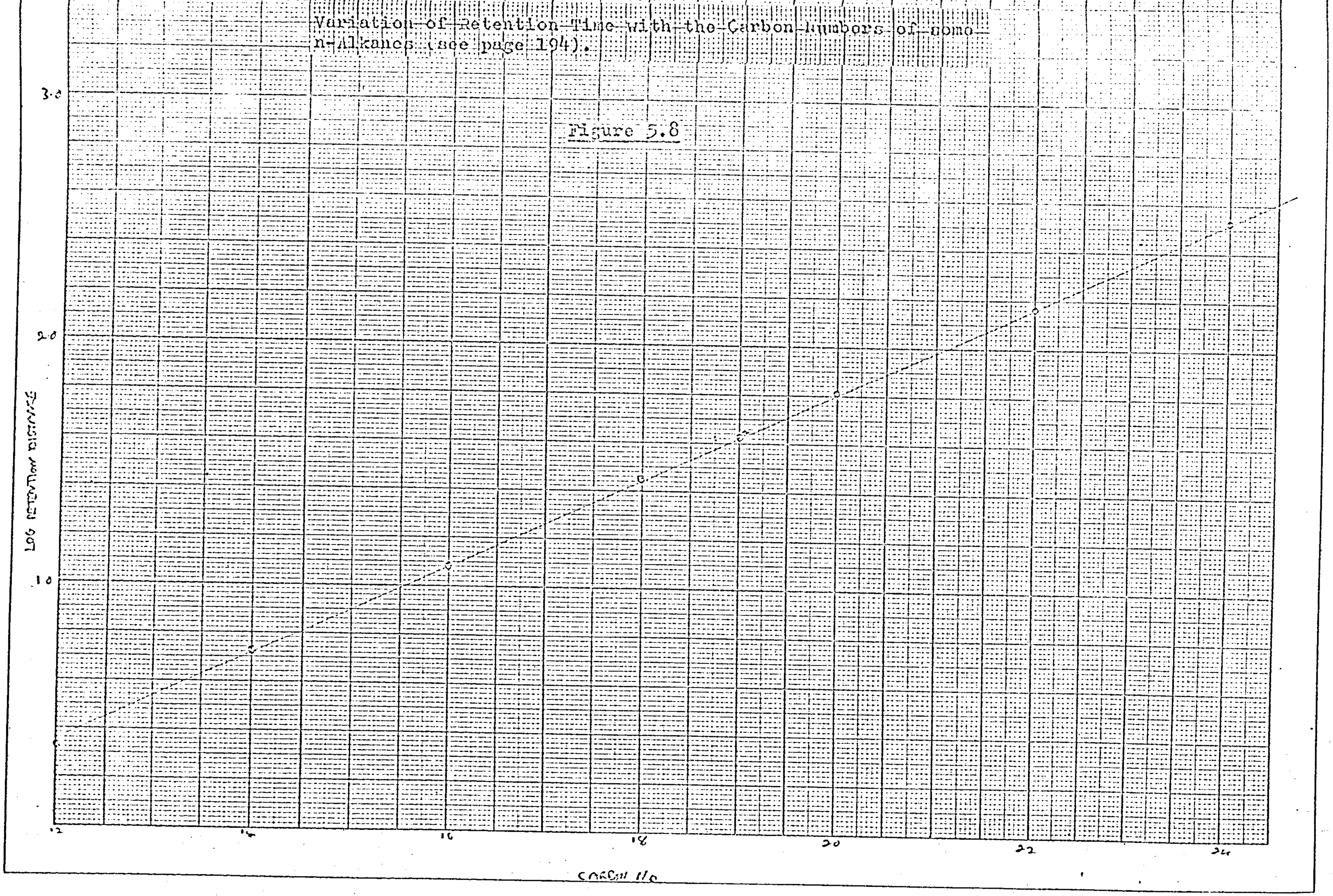
Figure 5.7



Chromatogram showing the response of the Mass Detector to some High Boiling n-Alkanes (see page 194).

Variation of Retention Time with the Carbon Numbers of homo-n-Alkanes (see page 194).

Figure 5.8



From table 5.19, the mean value for the standard deviation of the results was 1.2%, and the coefficient of variation 5.2%. The bias of the results was 0.6% (about 2% absolute). The precision of the results is poorer than obtained under normal operating temperatures (tables 5.2 to 5.4), but nevertheless is still acceptable: bias values, on the other hand are identical with those obtained for normal boiling materials.

A list of the melting points and boiling points of the n-alkanes used in the above experiments is given below.

Table 5.20

Compound	Carbon No.	Melting Point (°C)	Boiling Point (°C)
n-Nonane	9		150
n-Decane	10		174
n-Undecane	11	-27	196
n-Dodecane	12	-12	215
n-Tetradecane	14	+6	253
n-Hexadecane	16	20	288
n-Octadecane	18	28	317
n-Nonadecane	19	32	330
n-Eicosane	20	38	205 (15 mm)
n-Docosane	22	44	224 (15 mm)
n-Tetracosane	24	52	243 (15 mm)

5.4 Low Boiling Materials.

The work on adsorption capacity (section 4.6.2) shows that the capacity of the detector decreases as the boiling point of the adsorbate approaches that of the detecting element temperature. From table 4.37, the adsorption capacity of a typical detector is only about 4 mg when there is a 12°C temperature difference. It is therefore advisable to operate the mass detector below room temperature to obtain a reasonable adsorption capacity, and to decrease the frequency with which the detector must be regenerated.

An electrical cooling unit, manufactured by Frigistor Ltd.[3] was used. The unit comprised a block of aluminium, the centre of which was drilled, such that a detecting element fitted snugly, without touching

the sides. The block, which was faced with cooling modules, was designed to operate at any temperature between +10°C and -30°C. Water cooling of the modules was essential. The cooling unit was lagged with expanded polystyrene and placed in a 3" cube perspex chamber, in place of the metal detector chamber used in previous work. The new detector chamber, and the balance cabinet were sealed to prevent moisture entering the system, and condensing on the cooler parts. The temperature of the cooling unit was monitored in the centre of the block, this being the temperature of the atmosphere within the detecting element. Noise measurements at various detecting element temperatures were taken and these are listed in table 5.21. Readings were taken both in the absence of carrier gas, and with a gas flow rate of 55 ml min^{-1}.

Table 5.21

Detector Noise Levels below Room Temperature

Detector Temperature °C	Flow Rate ml min^{-1}	Noise % fsd	Noise µg	Weight Increase µg
25	-			-
10	-	0.25	12	500
$2\frac{1}{2}$	-	0.36	18	205
$2\frac{1}{2}$	55	0.25	12	-
$-5\frac{1}{2}$	-	0.25	12	98
-15	-	0.25	12	continuous

No increase in noise with decreasing temperature was observed, and the introduction of carrier gas had no measurable effect. During each temperature decrease the mass detector gained weight due to adsorption of air, but reached a new equilibrium after several minutes. However, on cooling to -15°C the uptake became continuous and was caused predominently by moisture condensing on the outside of the detecting element. After several hours the ice thickness on the detecting element was such that there was no clearance between it and the cooling block sides. The temperature of the apparatus was raised and the apparatus dried. The experiment was repeated, at -15°C with carrier gas flowing, but condensation again occurred and the system

was clearly inadequate in its present form. No ice was observed on the inside of the detecting element, as a result of contiguous purging by dry nitrogen. No further experiments significantly below zero (^{o}C) were carried out, but it is proposed that in the first instance condensation on the detecting element could be eliminated if a colder surface was placed in the vicinity of the element. A more elaborate system is to place the complete detecting unit, including the balance, in a sealed glass envelope of the type used for weighing in vacuo.

All runs on low boiling materials were carried out with a detecting element temperature of $+2.5^{o}C$, thus avoiding ice formation. This limited quantitative analysis to materials boiling in the region of $35^{o}C$, to obtain reasonable adsorption capacity. However, the detection of some amines boiling at much lower temperatures was also accomplished. The following materials (boiling points in parenthesis) were detected by the mass detector, under the conditions given in table 5.22:

n-pentane ($36^{o}C$), methylene dichloride ($40^{o}C$), ethyl bromide ($38^{o}C$), methyl iodide ($43^{o}C$), ethylamine, in ethanol ($17^{o}C$), methylamine, in water ($-7^{o}C$).

Table 5.22

Apparatus	KG2
Column	ApL H
Column temperature	$25^{o}C$
Flow rate	55 ml min^{-1}
Delivery tube temperature	$25^{o}C$
Detecting element "	$2\frac{1}{2}^{o}C$

The quantitative preparation of mixtures of low boiling materials is particularly difficult in view of their high volatility. The preparation of n-pentane and methylene dichloride mixtures was attempted, but weight loss during preparation was observed. Three analyses of such a mixture, under the conditions quoted in table 5.22, yielded the results given below (table 5.23).

Table 5.23

Compound	$\bar{x}$	x_o	Bias	% Bias
n-Pentane	17.53	16.95	+0.58	3.4
Methylene dichloride	82.47	83.05	-0.58	0.7

The limited number of experiments carried out on low boiling materials indicate that the mass detector will give satisfactory quantitative results. The conventional method for the preparation of mixtures of known composition is not satisfactory for low boiling materials. A system in which materials are vaporised prior to injection, and the percentage composition calculated from a knowledge of vapour pressures may be suitable. Considerable improvement in detector chamber design is essential for the successful operation of the mass detector below $0^{\circ}C$.

5.5. The Analysis of Gases.

The analysis of gases by the mass detector can be approached in two ways:

(i) an extension of the principle described in section 5.4, in which the detecting element is operated at say $-100^{\circ}C$ for the quantitative adsorption of propane and higher boiling materials (using nitrogen as carrier), and at $-200^{\circ}C$ for the detection of methane, ethane and the inorganic gases, using helium as carrier.

(ii) operation of the detecting element at room temperature, and observing a combination of buoyancy and adsorption effects.

The first alternative clearly offers a more satisfactory basis from which to obtain quantitative results, but the technical difficulties are such that the system represents a research project in its own right. The effects of condensation have already been observed, and at very low temperatures the contribution of the carrier gas to the adsorption process may become significant. Detection at room temperature on the other hand, is now an established procedure, and extension to the detection of gases presents little difficulty. This system was therefore adopted with a view to examining its value, at least for the

qualitative detection of gases.

Detection will occur as a result of buoyancy changes and adsorption on to the charcoal when a component enters the detecting element. If the adsorption effect predominates, then quantitative estimation based on step heights may be satisfactory, even though the adsorption efficiency of the detector is low, since it may be of a similar order for all the components of a mixture. In practice it was observed that desorption was so rapid that peaks rather than steps were observed: the peak height is a measure of the amount of material adsorbed. It may be possible to apply a correction to the peak height, for the rate of desorption, to obtain a true step height. Partial displacement of carrier gas by sample gas may interfere with the quantitative assessment.

If buoyancy effects predominate then detector response is calculable from a knowledge of molecular weights. The peak height at any instant will represent the weight change due to the difference in density between the carrier and sample gas, and hence the peak area will be a measure of the total amount of sample passing through the detector.

A combination of adsorption and buoyancy will result in an unpredictable response, but either effect on its own will enable quantitative estimations to be made. Measurements based on buoyancy will require a knowledge of the qualitative nature of the sample, but adsorption measurements will not.

Experiments were designed to estimate the contribution of the two effects, by using a standard detecting element, and a cylinder of similar dimensions containing no adsorbent (see table 4.9). Experimental conditions are given in table 5.24.

Table 5.24

Apparatus	Wilkens 1520
Column	ApL K
Column temperature	80°C
Carrier gas	Nitrogen
Flow rate	33 ml min^{-1}
Detector range	1 mg, 10 mg
Detecting elements	31b 32
Detector temperature	20°C

The detecting elements were closed at the bottom end. Gas samples were injected via a stainless steel gas sample valve fitted with sample loops prepared from copper tubing. The volumes of the loops were measured by filling with known weights of water, and checked by calculating the volume from the internal diameter. Loops of capacities between 0.2 cm^3 and 1.2 cm^3 were made. The volumes do not include the contribution of the gas sampling valve itself, which was estimated from the results obtained (table 5.28). For each sample size in turn 5 injections of each gas were made, and the mean response values calculated. The gases used together with relevant physical data are listed in table 5.25.

Table 5.25

Gas	bp (°C)	Molecular Weight
Hydrogen	-253	2
Methane	-162	16
Argon	-186	40
Carbon Dioxide	-79	44
Dichlorodifluoromethane	-30	121

For each gas the weight injected was calculated from a knowledge of the sample loop volume, assuming ideal behaviour and injection at atmospheric pressure. This weight excludes any gas trapped in the sample valve itself which will add a constant amount to all sample injections. Care was taken to ensure that sample gases were supplied to the sample loop at the minimum pressure necessary to maintain a flow rate, to avoid errors due to compression. Using a detecting element containing adsorbent (31) all samples gave peaks rather than steps

indicating that if adsorption plays any part, it is accompanied by very rapid desorption. The introduction of hydrogen into the detecting element resulted in a weight loss, indicating a predominance of buoyancy effects. The whole series of experiments was repeated using an unlined detecting element (32), and the same effects were observed. Examples of chromatograms are given in figure 5.9.

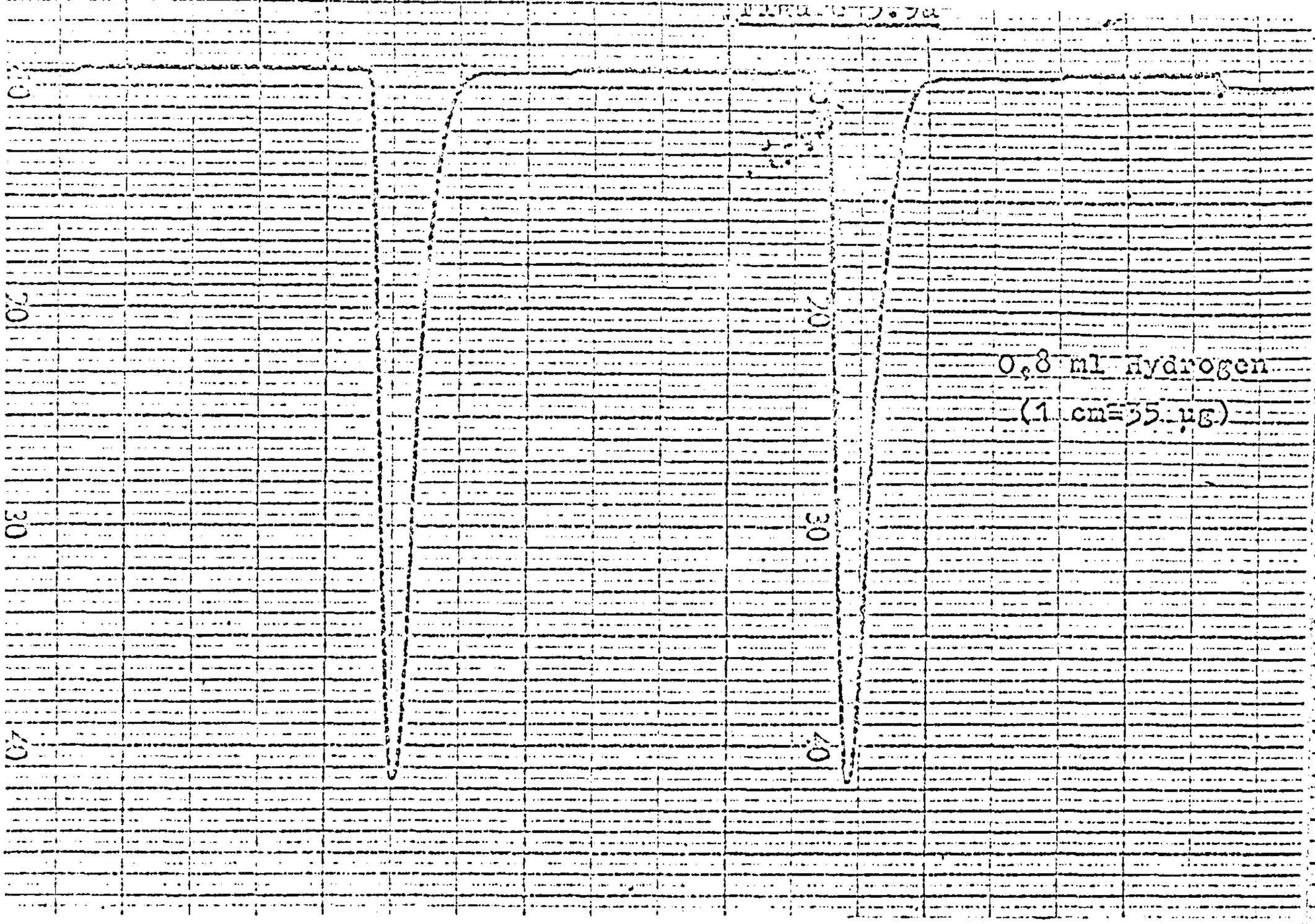
For each series of runs, graphs were plotted of the weight of gas injected against the weight detected, obtained from the peak heights. These are shown on figure 5.10 for hydrogen and methane, and 5.11 for argon and carbon dioxide. Straight line plots were obtained both with a lined and an unlined detecting element, except for methane which gave curves, and distorted peaks for high sample sizes.

Response factors, defined as the ratio of the detected weight change and the injected weight are given in table 5.26.

Table 5.26

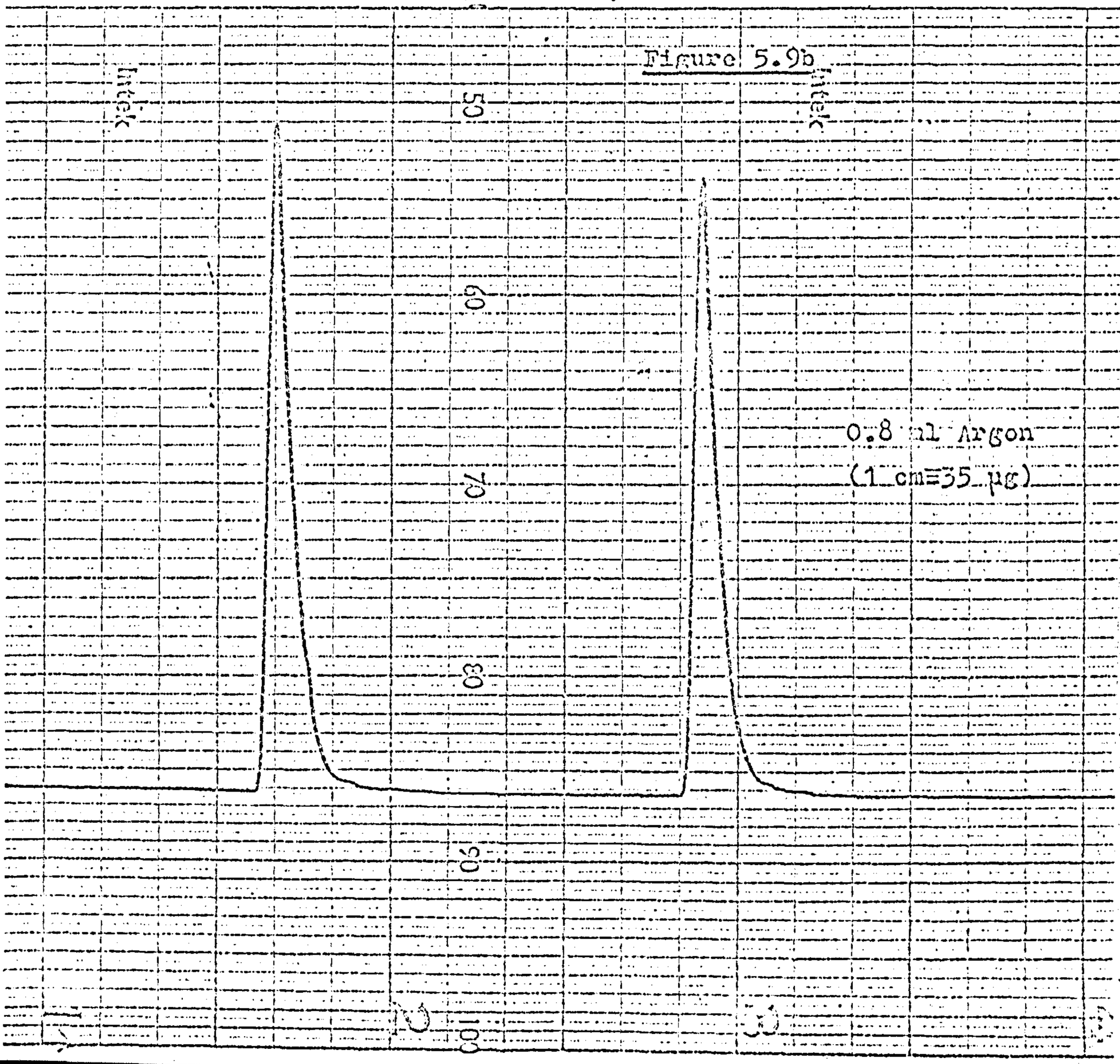
Gas	Mean Response Factor	
	Lined detector	Unlined detector
Hydrogen	-4.5	-3.5
Methane	(0.22)	(0.15)
Argon	2.19	1.68
Carbon Dioxide	2.87	2.45
Dichlorodifluoromethane	0.47	0.29

In all cases the slopes of the graphs for each material converge and give finite responses for zero injected weight, indicating that the sample value volume is significant. For simple adsorption, a response factor cannot exceed unity and certainly cannot be negative. Response factors, both for lined and unlined detectors were of the same order so that buoyancy must contribute predominantly to the detector response (but least for dichlorodifluoromethane). Although detector response in terms of peak height cannot be predicted, the response is linear at least over the range investigated for all gases except methane, and could therefore be used as a basis for quantitative measurement with



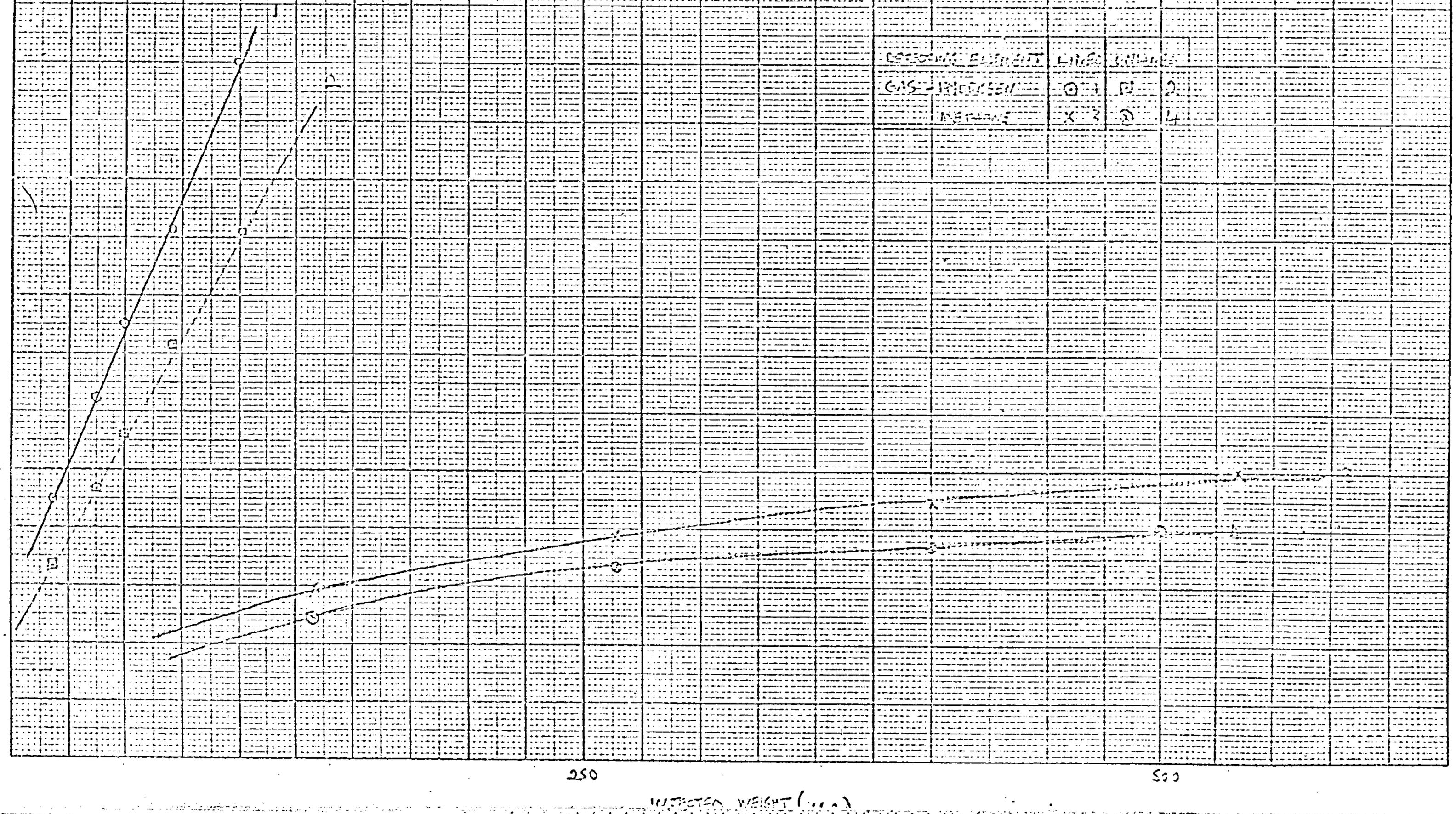
Chromatograms showing the Response of the Mass Detector to some Permanent Gases (see page 201).

Figure 5.9b



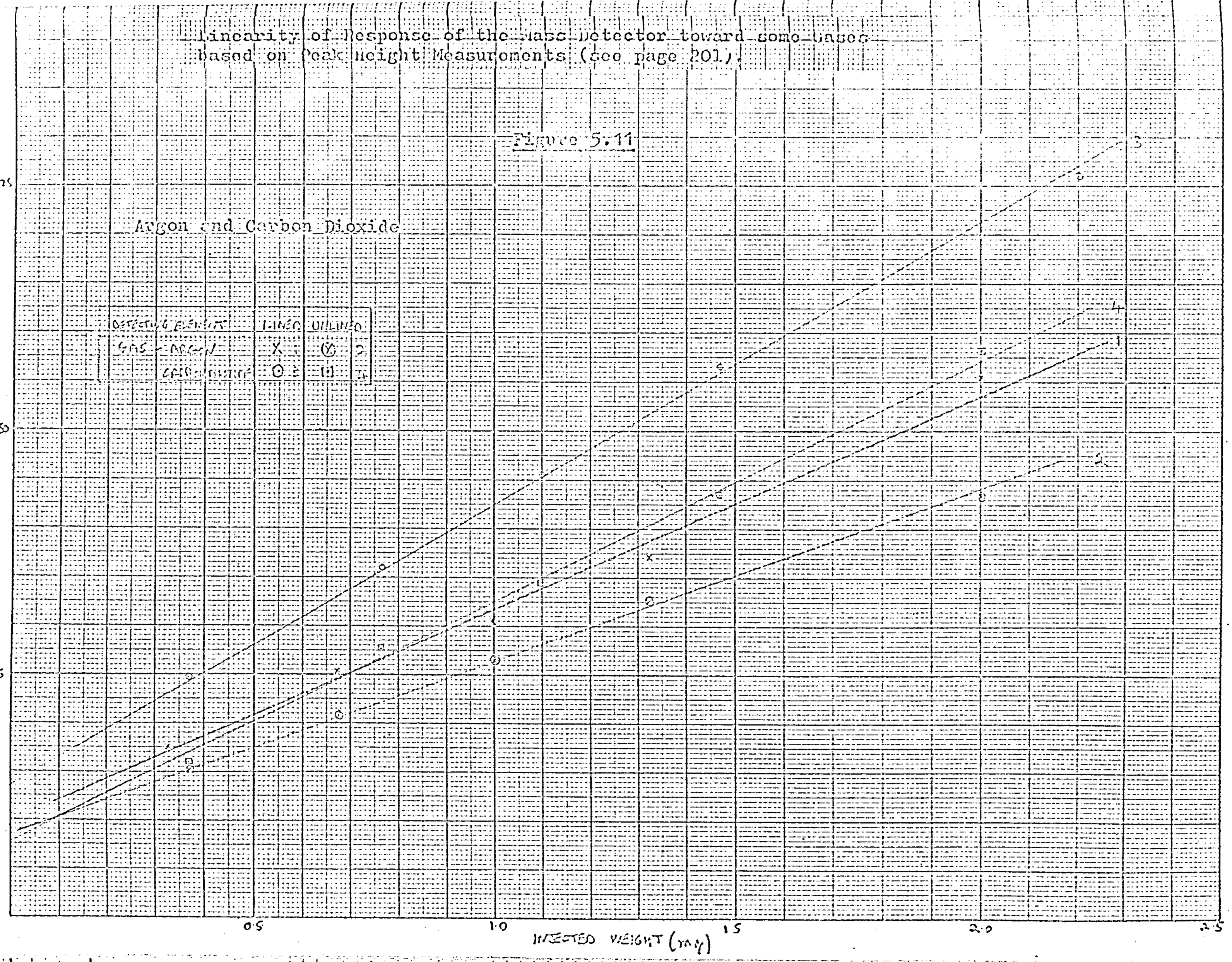
Linearity of Response of the Mass Detector toward some Gases
based on Peak Height Measurements (see page 201).

Figure 5.10



Linearity of Response of the Mass Detector toward some Gases
based on Peak Height Measurements (see page 201).

Figure 5.11



calibration.

The response of the unlined detector, based on peak area measurements is shown in figures 5.12 to 5.14. A straight line was obtained in all cases. Scatter of points was greater than for the step height plots, but this is to be expected, in view of the inherent difficulties in measuring peak areas. The sensitivities of the detector, i.e. the slopes of the graphs, have been measured, and assuming a response based solely on buoyancy have been corrected for the density differences of the different gases. The results are given in table 5.27.

Table 5.27

Gas	Figure	Sensitivity $cm^2 mg^{-1}$	Correction factor	Corrected Response $cm^2 mg^{-1}$
Hydrogen	5.12	-34.7	-0.077	2.67
Methane	5.13	-3.15	-1.33	4.21
Argon	5.13	2.50	3.33	8.35
Carbon Dioxide	5.13	3.18	2.75	8.74
Dichlorodifluoro-methane	5.14	7.12	1.30	9.27

The corrected response values are not identical for all gases, but increase with increasing molecular weight. For those materials of molecular weight greater than the carrier gas, the values are very similar, and much greater than those for materials of lower molecular weight than the carrier gas. This is to be expected, since the detecting element was closed at the base, rather than the top, thus ensuring more efficient trapping of the heavier materials. Materials lighter than the carrier gas (and lighter than air) are not effectively trapped and therefore the detector cannot give a calculable response.

An estimate of the sample valve dead volume was obtained from figures 5.12 to 5.14. The weight of material detected at zero sample loop volume was calculated from the intercept of the curves with the ordinates, and assuming ideal behaviour, the corresponding gas volumes found. The results are given below (table 5.28).

Linearity of Response of the Mass Detector toward some Gases based on Peak Area Measurements (see page 202).

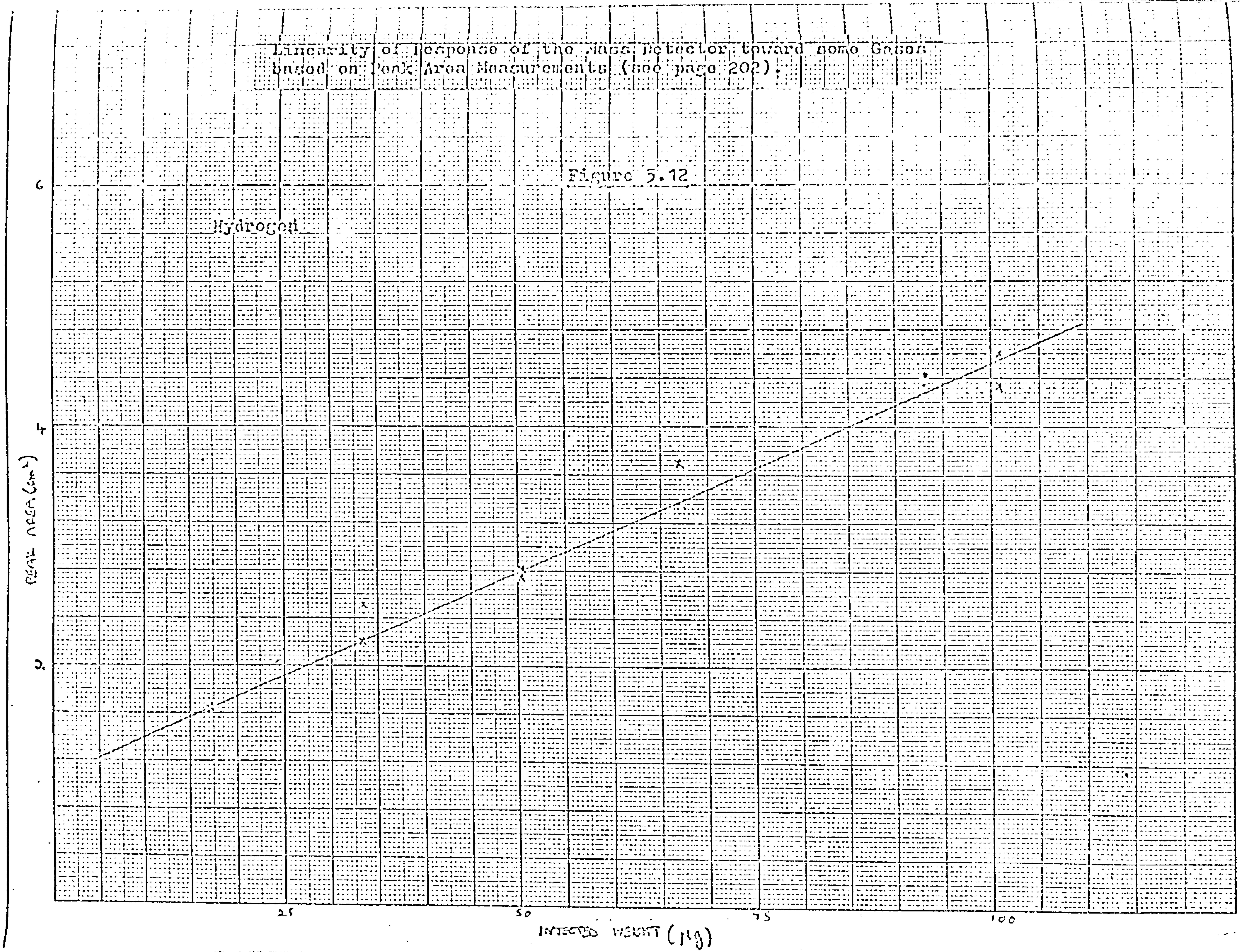


Figure 5.12

Linearity of Response of the Mass Detector toward some Gases
based on Peak Area measurements (see page 202).

Figure 5.13

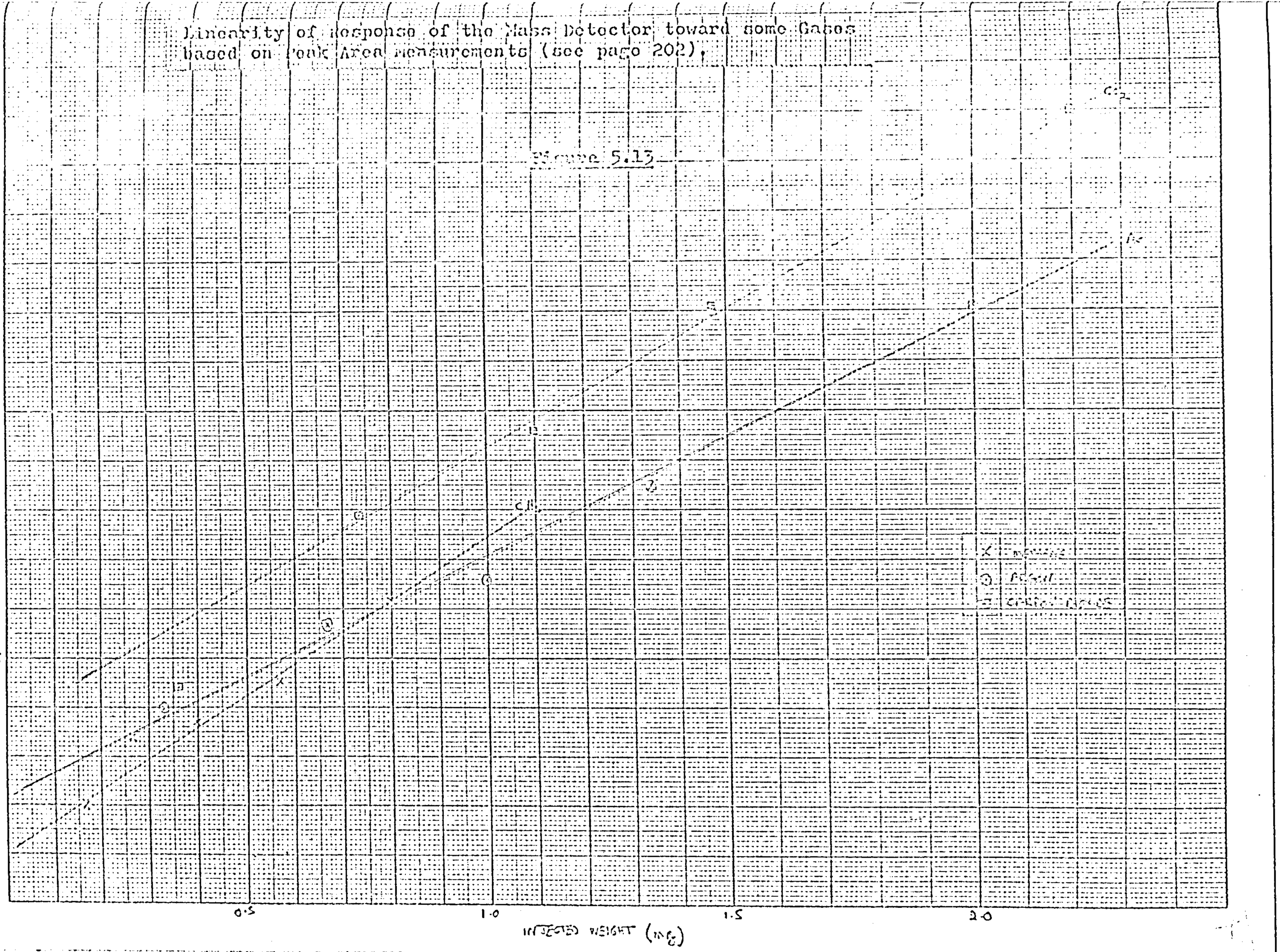
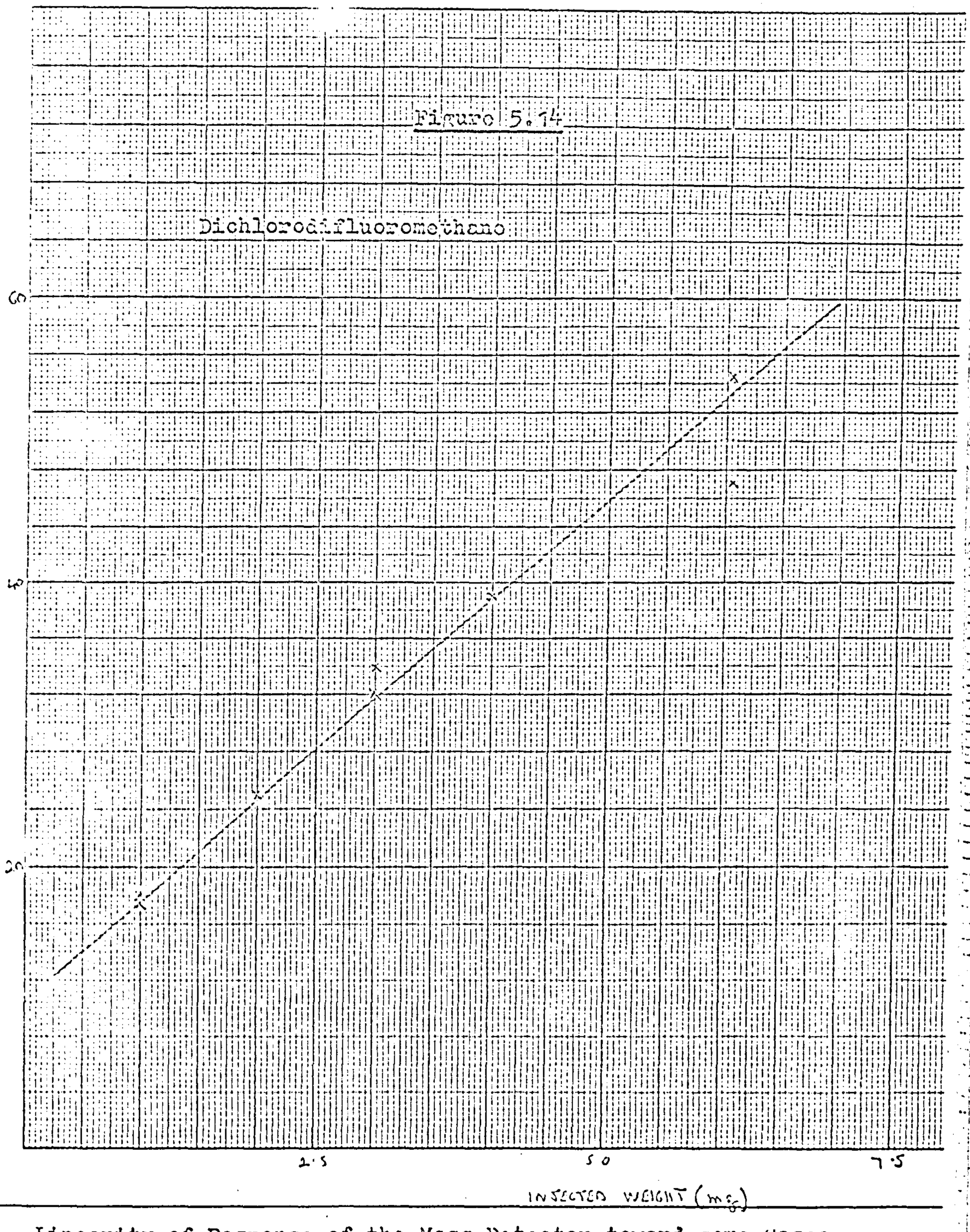


Figure 5.14



Linearity of Response of the Mass Detector toward some Gases. based on Peak Area Measurements (see page 202).

Table 5.28

Gas	Intercept (cm^2)	Amount of gas mg	ml
Hydrogen	-1.04	0.030	0.36
Methane	-0.58	1.85	0.28
Argon	0.98	0.393	0.23
Carbon Dioxide	1.22	0.384	0.21
Dichlorodifluoromethane	10.4	1.46	0.29

The dead volume of the sample valve is about 0.3 ml, which is larger than the smallest sample loop used. An estimate of the sample valve volume, calculated from the dimensions of the valve, the associated tubing and unions, is 0.22 ml.

A conventional lined detecting element can be used for the qualitative analysis of all gases of molecular weight different to that of the carrier gas. The response of the mass detector, at room temperature, to gases is predominantly a function of molecular weight, and adsorption effects are negligible. Using an unlined detecting element, the detector response based on peak area measurements was linear for all gases analysed, covering the mass range 15 µg to 6 mg, although the sensitivity of the detector was species dependent. For quantitative work, using the present system a simple calibration procedure is necessary, although sensitivity values were very similar for all materials denser than the carrier gas. Improvements in the detector design to ensure complete transient trapping of all materials may enable the quantitative analysis of gas mixtures to be carried out, without prior calibration. The detector would then function solely as a gas density detector with a response calculable from a knowledge of molecular weights.

5.6 Conclusions.

The mass detector will respond to all materials, except the carrier gas. It will respond on a weight basis to materials boiling up to at least 350°C, and will give quantitative analyses without calibration. The detector will quantitatively adsorb low boiling

materials (bp $< 40^{\circ}C$) provided the detecting element is cooled sufficiently to prevent desorption. The apparatus can be used at room temperature for the analysis of gases, including the permanent inorganic gases, provided the detector is calibrated: a linear response, based on buoyancy changes is normally observed. The detector will respond quantitatively to water, and gives satisfactory results for aqueous solutions.

No commercially available detector combines all these properties, which are the minimum requirements for a satisfactory quantitative device.

5.7 References.

1. Hollis, O.L. Anal. Chem. 38 309 1966.
Hollis, O.L., Hayes, W.V. J. Gas Chromatog. 4 235 1966.
Hollis, O.L., Hayes, W.V. Gas Chromatography 1966.

2. Porapak, manufactured by Waters Associates Inc. Mass.

3. De La Rue Frigistor Ltd., Langley, Bucks.

CHAPTER 6.

Applications of The Mass Detector I

The Calibration of Detectors

6.1 Discussion.

Based on the information presented in Chapters 4 and 5, it is established that the response of the mass detector is species independent, and that its response is linear over a wide operating range. The detector thus offers an excellent, rapid and reliable means of calibrating other detectors. It is not necessary to prepare carefully weighed out mixtures, and the amount of material injected into the chromatograph need not be accurately known. Calibration errors arising from effects such as irreversible adsorption on the column are eliminated, the only precaution necessary is to ensure that there is no leakage or condensation of material between the detector undergoing calibration, and the mass detector. A detector may be calibrated using either a single substance, or a number of components simultaneously. A detector may be calibrated absolutely, since the absolute adsorption efficiency of the mass detector at any flow rate is readily determined, or it may be calibrated relative to a pure standard material.

Several detectors have been calibrated with the aid of the mass detector: the Gow-Mac and Martin gas density balances were calibrated to confirm that response is a function of molecular weight. A katharometer was calibrated to demonstrate the value of the technique for use with a detector of completely unpredictable response. Destructive detectors must be operated in parallel with the mass detector: the flame thermocouple detector was calibrated by this means. Detectors, such as the flame ionisation detector, whose sensitivities differ significantly from that of the mass detector must also be calibrated in parallel, the major portion of the split eluent stream being fed to the less sensitive detector.

The mass detector is of value in the determination of limits of detection, since the amount of material present in the region of the detection limits is readily obtained from the mass detector response.

6.2 Calibration of the Gow-Mac Gas Density Balance (type 091).

The response of a gas density balance to different chemical species is calculable provided that the molecular weight of the species is known (section 3.10). The Gow-Mac gas density balance should therefore have a predictable and linear response over a wide concentration range. The gas density balance was operated under the conditions for optimium behaviour given by the manufacturers[1], and the mass detector was operated within the range known to give a linear response (section 4.6.3).

The mass detector was placed in series with, and following the gas density balance. The operating conditions are given in table 6.1.

Table 6.1

Apparatus	Shandon KG2
Column	PEGA E
Column Temperature	101°C
Carrier gas	Nitrogen
Analytical gas flow rate	45 ml min^{-1}
Reference gas flow rate	60 ml min^{-1}
Sample sizes	0.1 µl to 5 µl
Gas density balance - filament current	125 mA
sensitivity	X500 to X50
temperature	101°C
Mass detector - ranges	100 µg to 5 mg
elements	27, 30
temperature	24°C.

The response of the gas density balance to a wide variety of materials covering the mass range 10 µg to 1 mg was measured. The samples used were identical with those listed in table 5.4 and the two sets of experiments were carried out simultaneously.

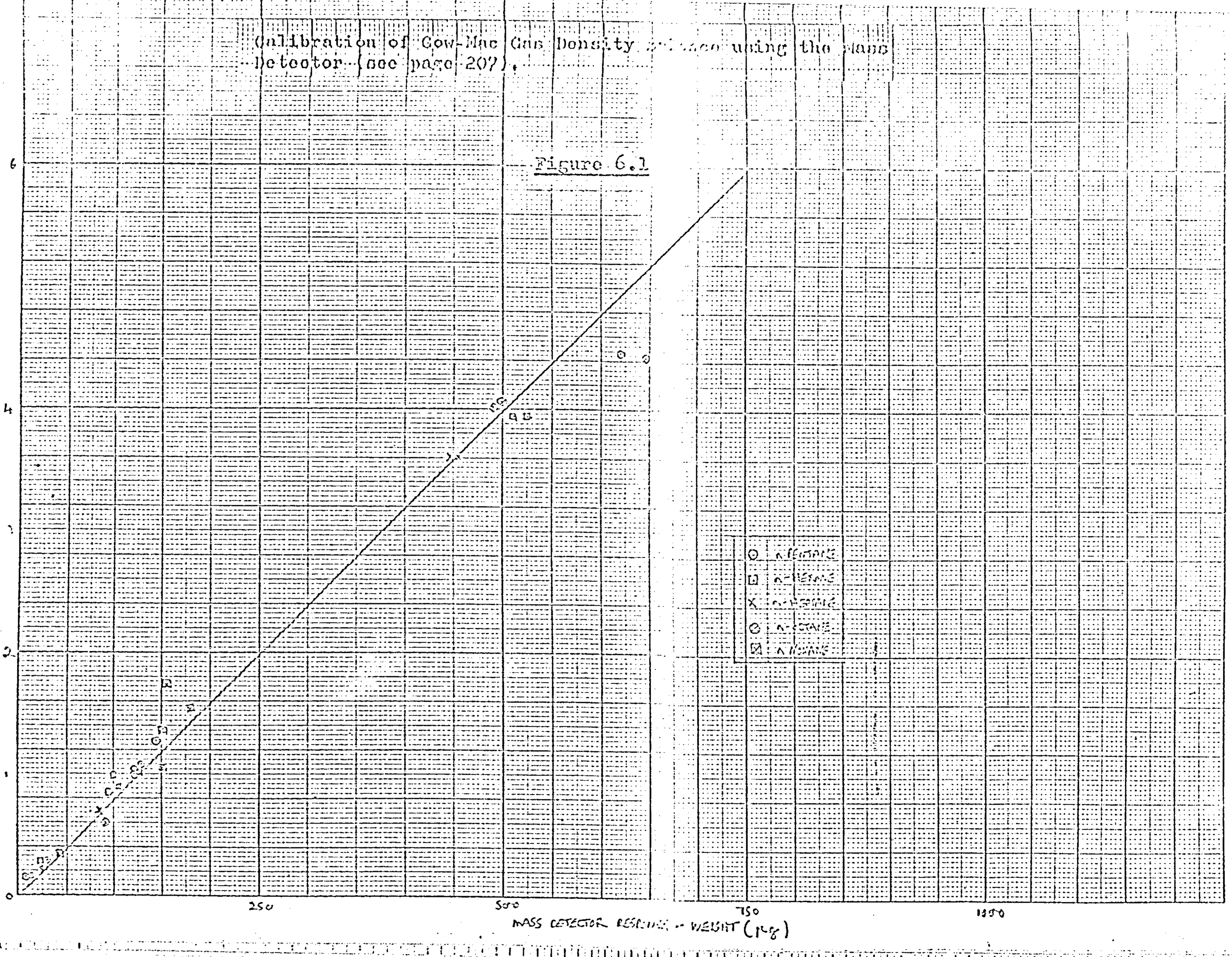
6.2a The Linearity of the Gas Density Balance.

The results are expressed graphically, by plotting the weight of each compound detected by the mass detector against the (corrected) peak area obtained from the gas density balance. Peak areas were in general measured with a digital integrator, but for comparison some areas were in addition calculated from peak height and width measurements. These results are discussed below, and a general discussion on peak area measurement is to be found in Chapter 7.

Although each compound formed part of a mixture the results are absolute in the sense that response is expressed in terms of detected weight and not percentage composition. The composition of the mixtures in no way affects the results, and all components ware well resolved. Each figure (6.1 to 6.8) shows the response of the detector to each of the components of a mixture. Since corrected peak areas were used, all curves on all figures should be coincident and linear, assuming an ideal detector response. In practice it is difficult to ensure complete reproducibility of operating conditions from day to day, so that it is only reasonable to expect coincidence of the curves obtained from a single mixture, i.e. the curves on any one figure should be coincident, but not necessarily have the same slope as the remaining figures. The only compounds to give a linear response over the whole range investigated were dichloroethylene, toluene, ethyl benzene, dioxan and butylene oxide. In general all compounds gave a linear response over a fairly limited range (about 10^1). All response curves were virtually coincident at low sample sizes, but became progressively divergent as the sample size increased. 1-Octene gave a significantly lower response, attributed at least in part to the presence of partially resolved impurities. All peaks in all determinations were reasonably symmetrical, so that deviations from linearity as a result of inaccurate area measurement are unlikely. Several figures were constructed from digital integrator results, which were compared with

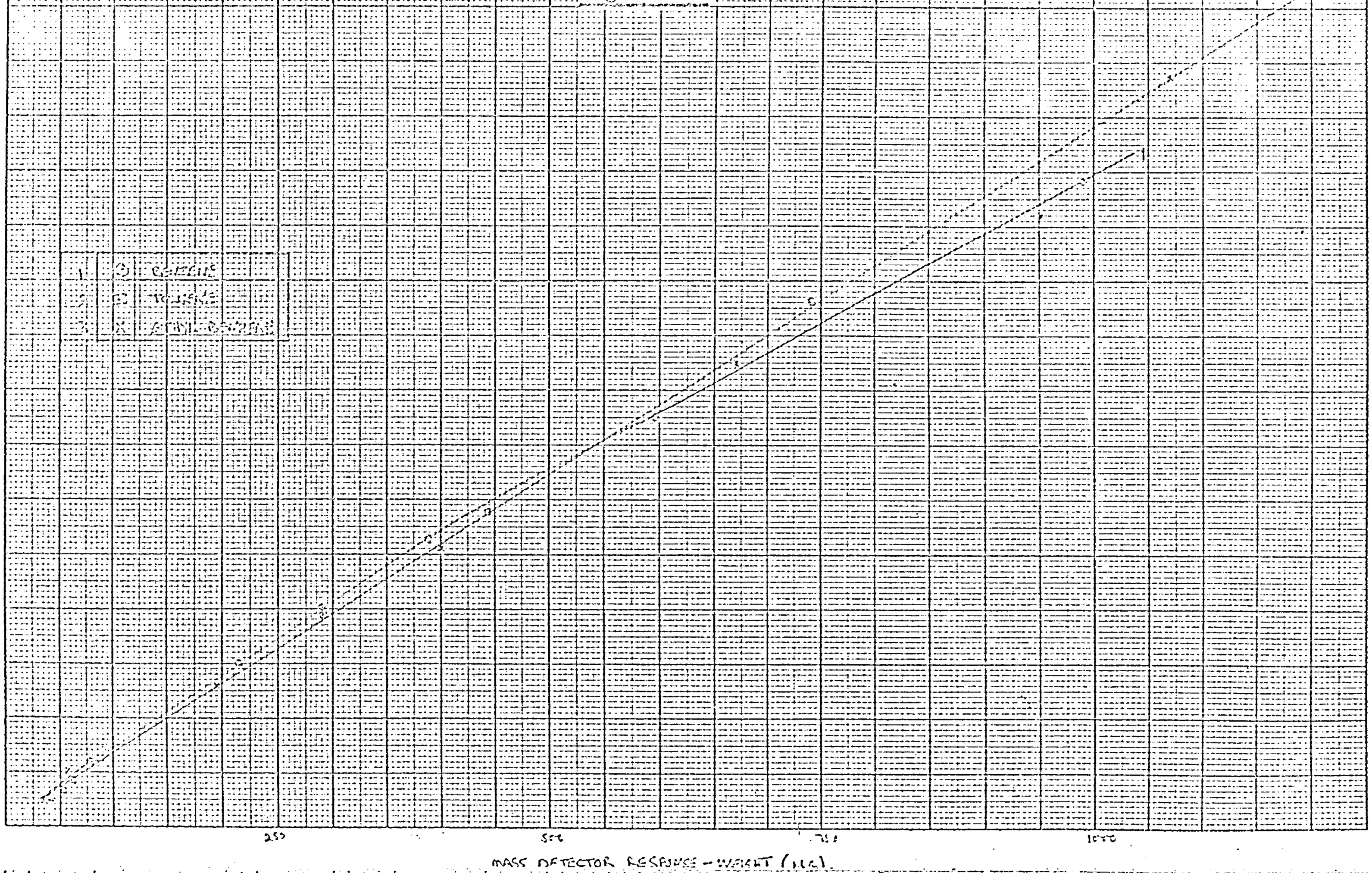
Calibration of Gow-Mac Gas Density [illegible] using the Mass Detector (see page 207).

Figure 6.1



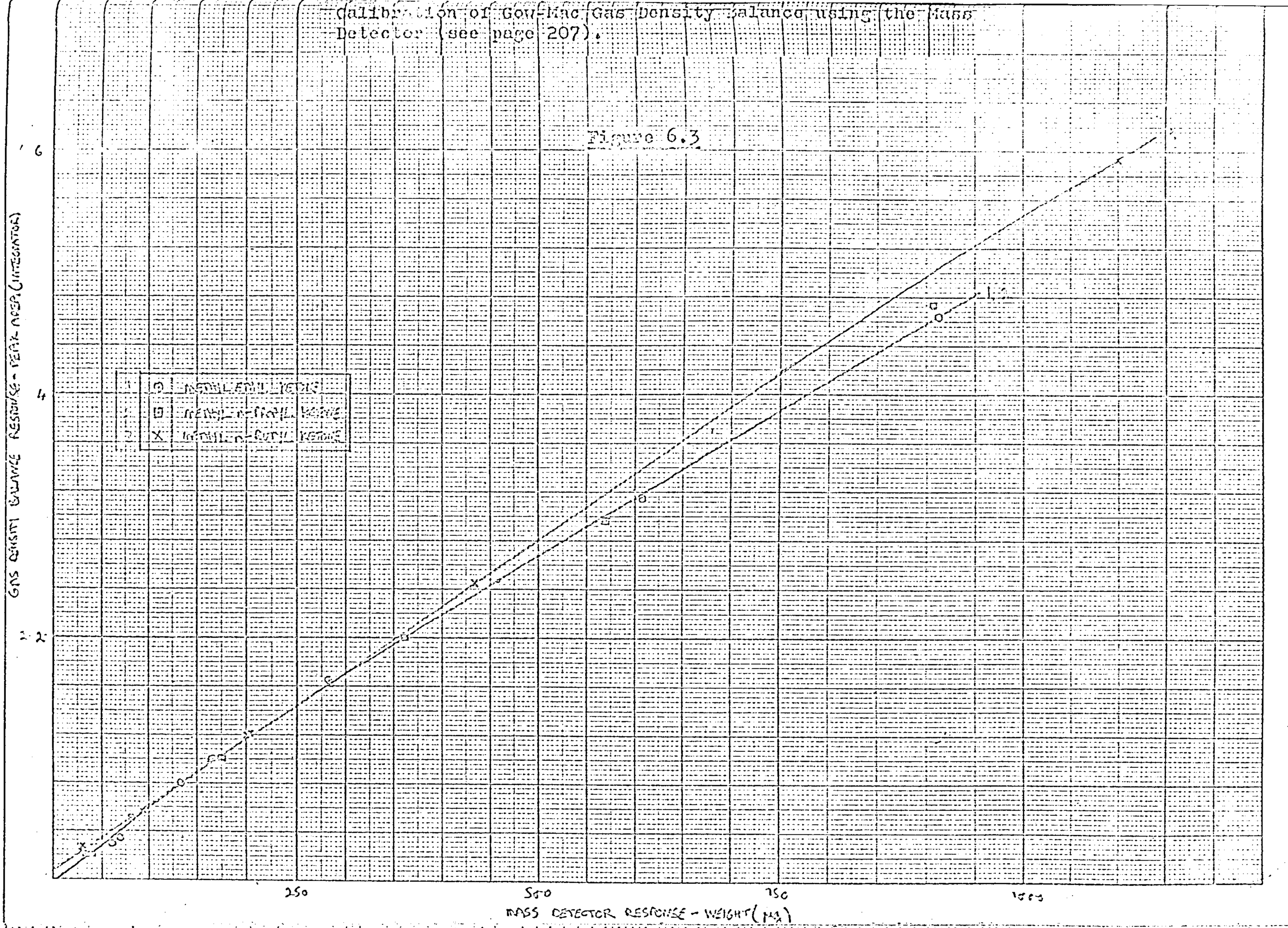
Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.2



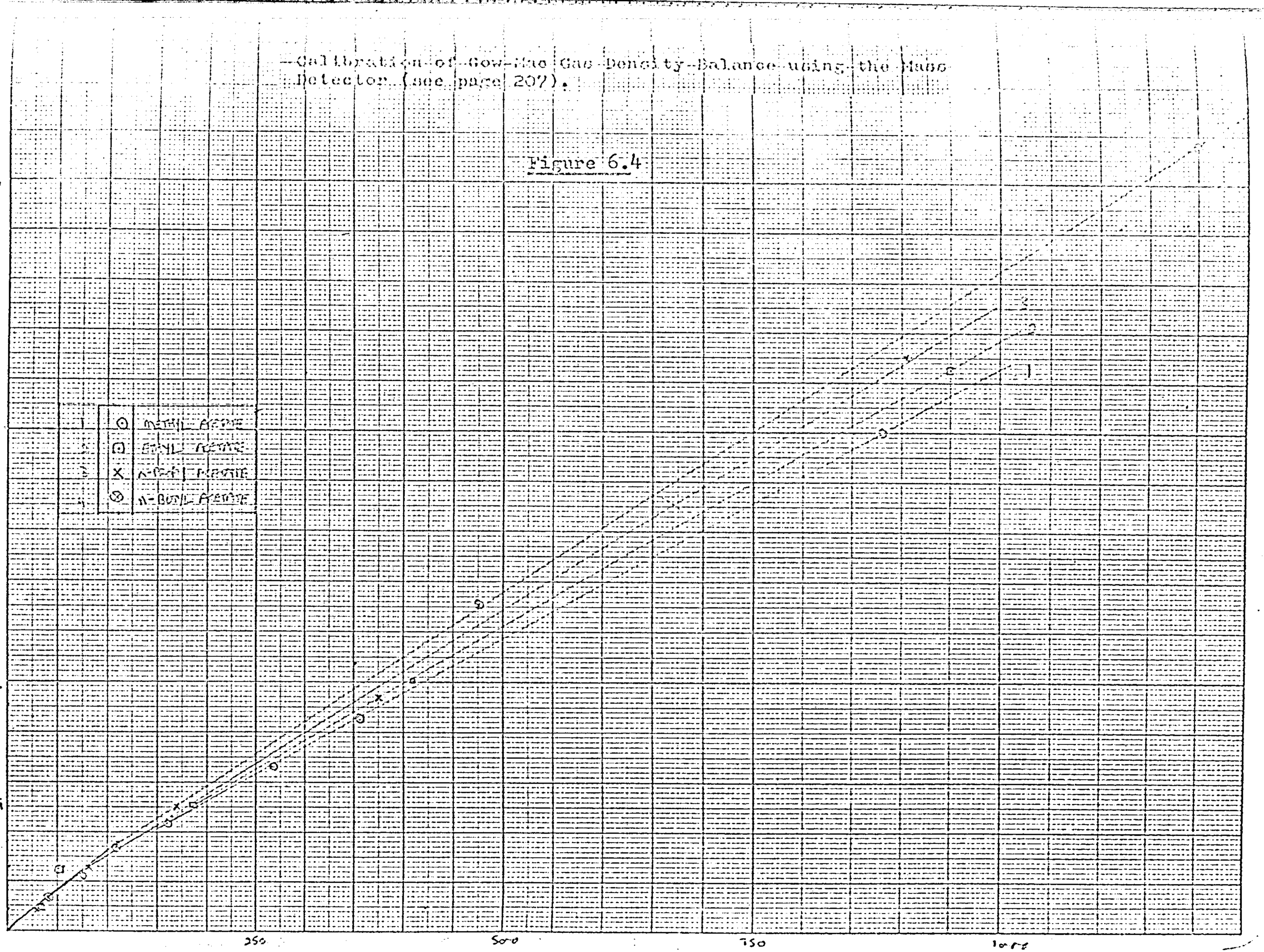
Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.3



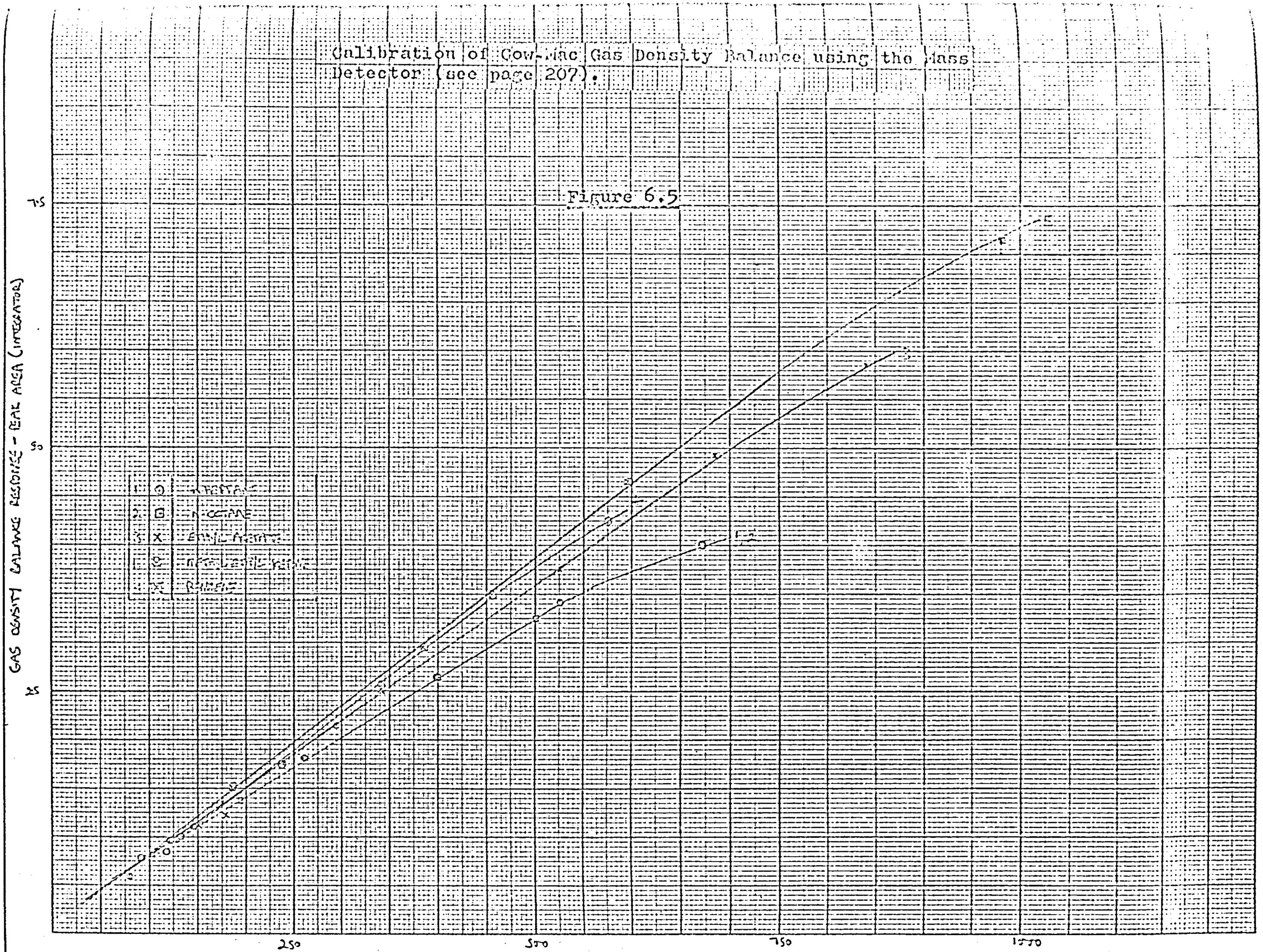
—Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.4



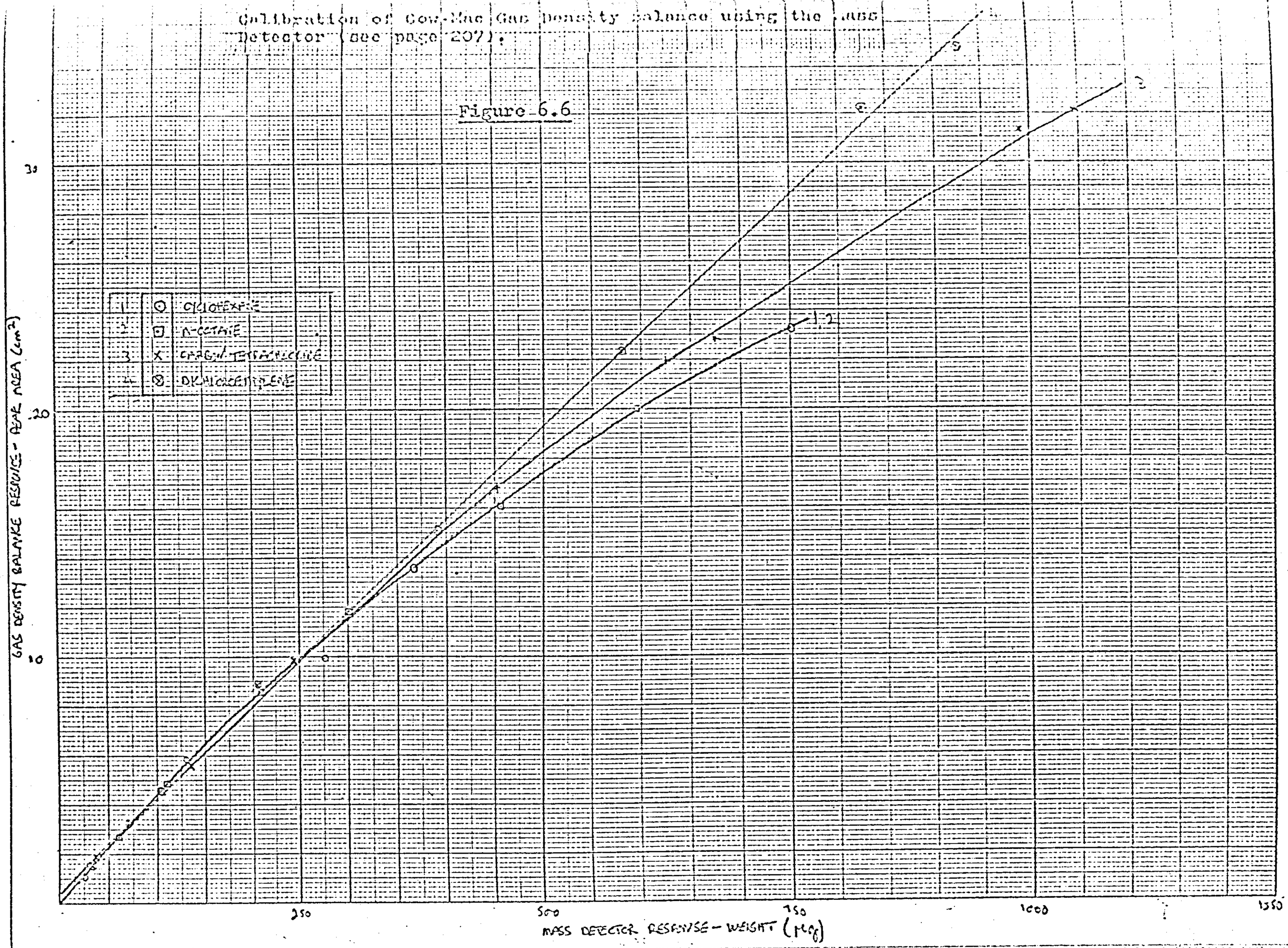
Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.5



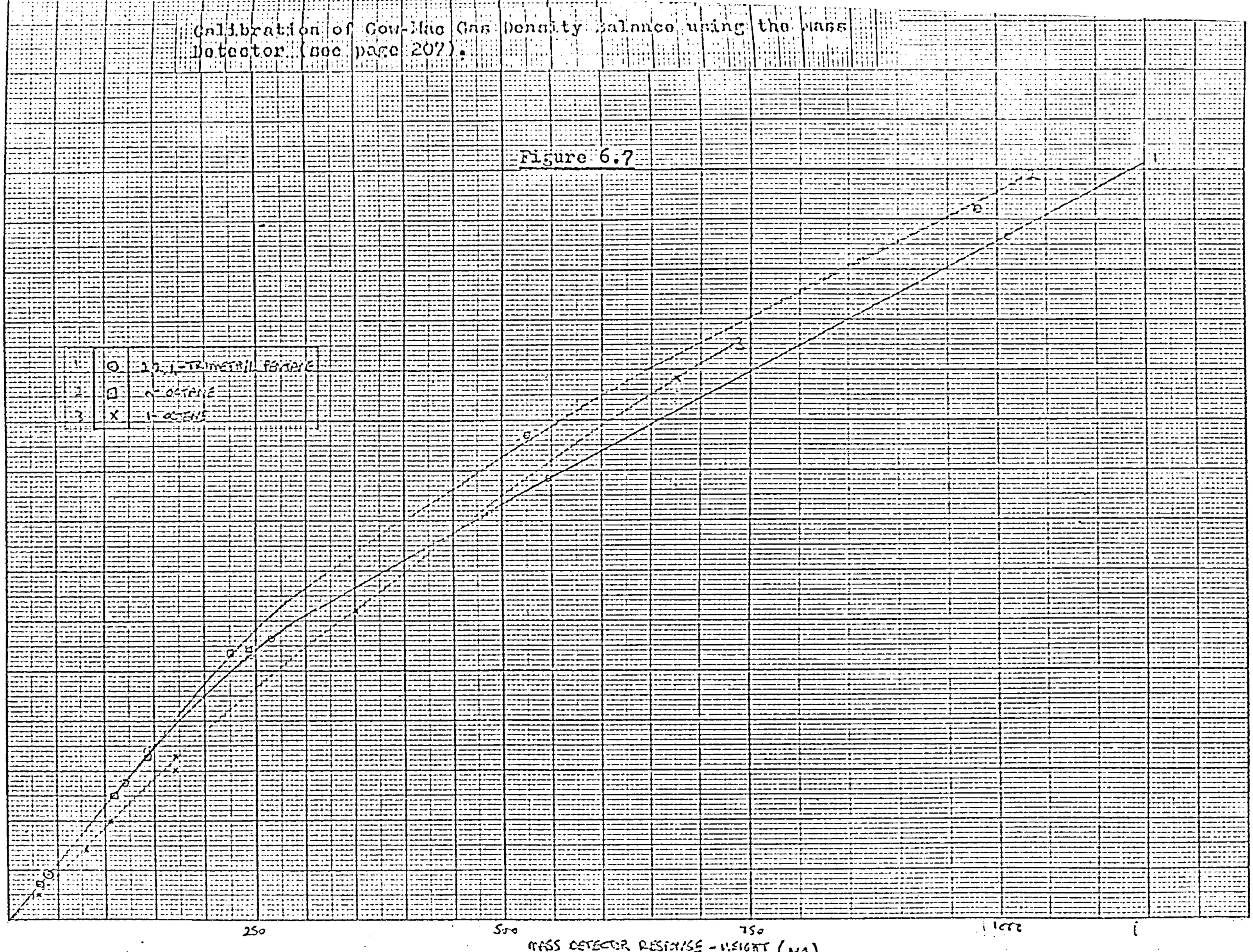
Calibration of Cow-Mac Gas Density Balance using the ABC Detector (see page 207).

Figure 6.6



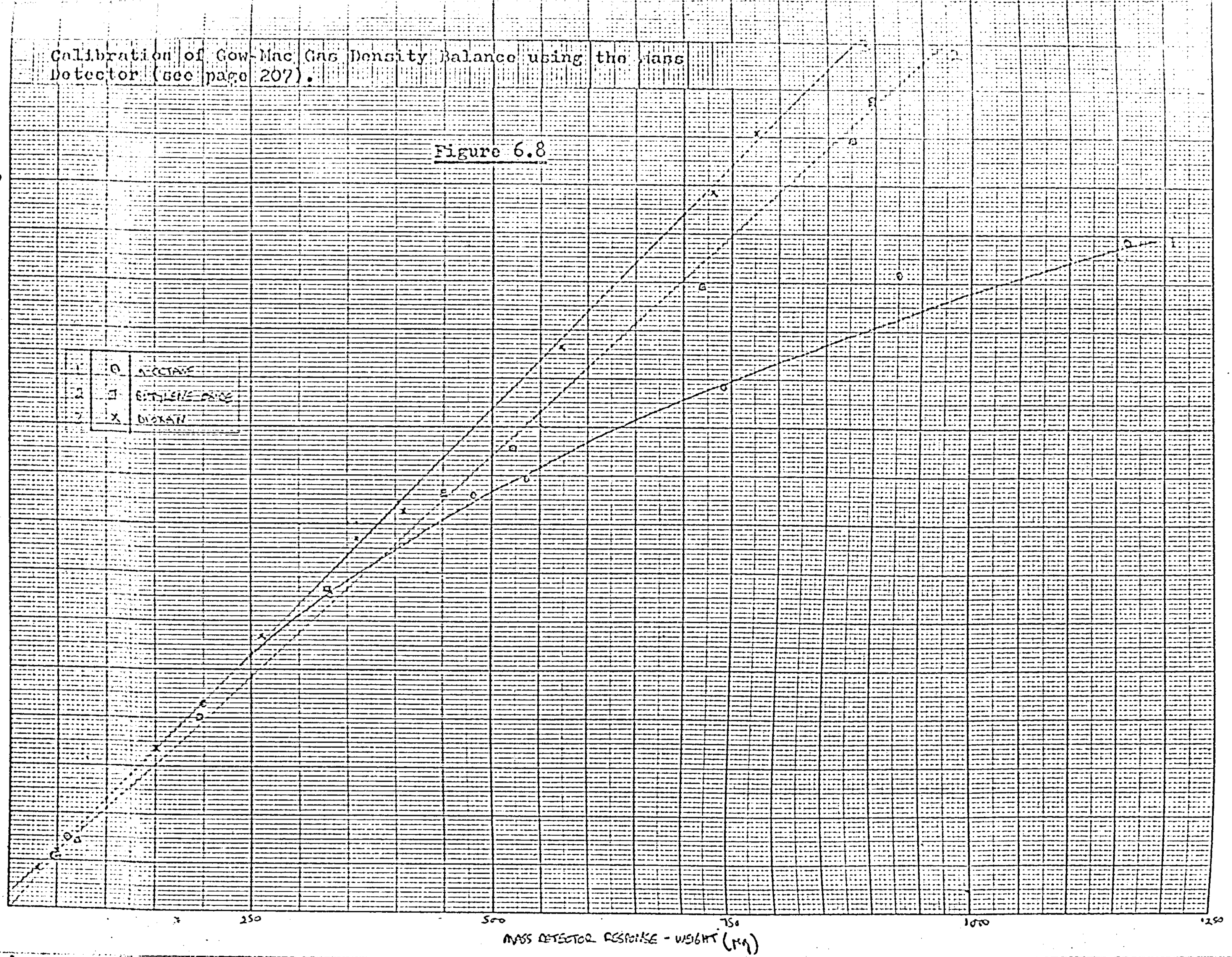
Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.7



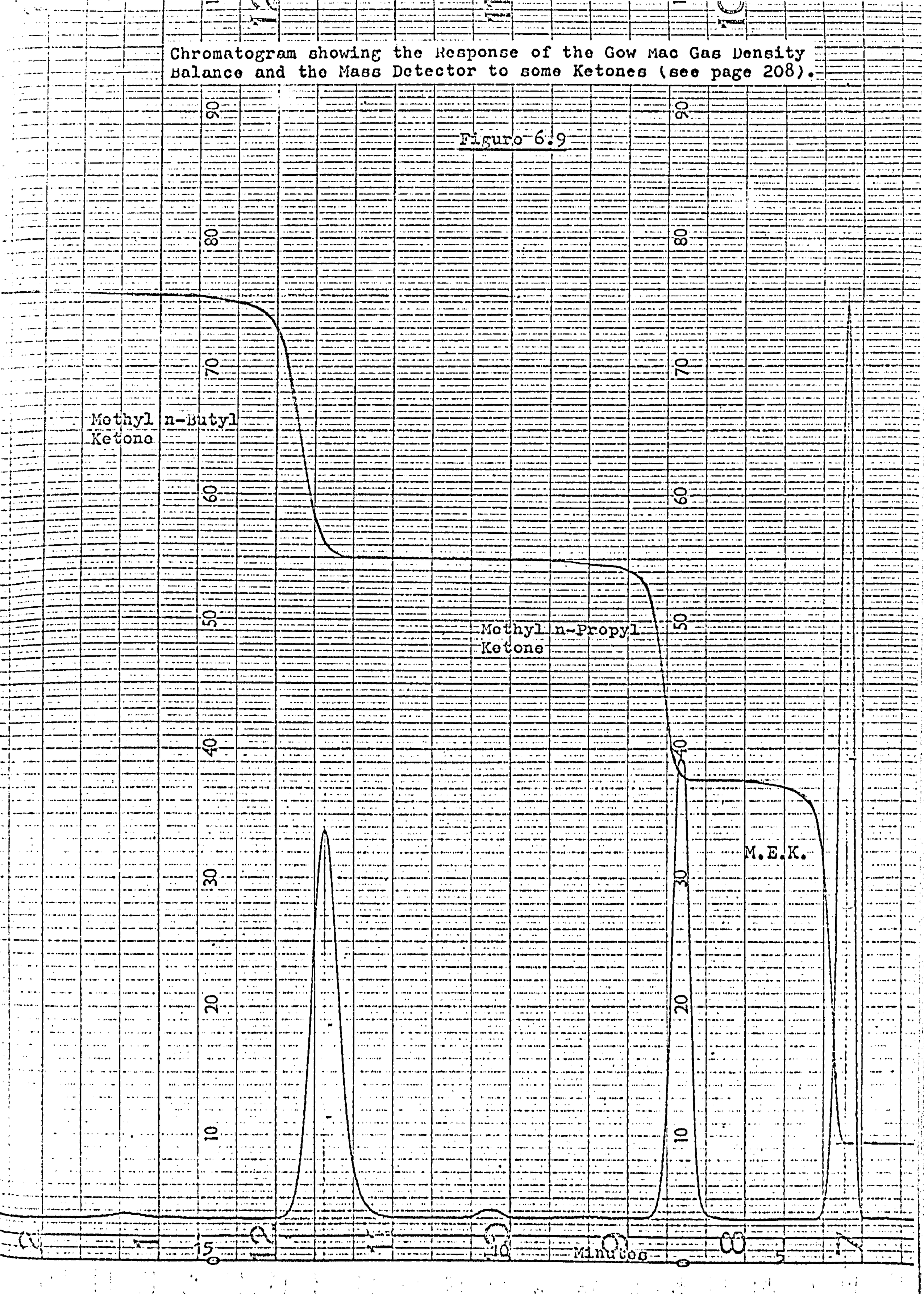
Calibration of Gow-Mac Gas Density Balance using the Mass Detector (see page 207).

Figure 6.8



Chromatogram showing the Response of the Gow Mac Gas Density Balance and the Mass Detector to some Ketones (see page 208).

Figure 6.9



manual peak area measurements: identical response patterns emerged. It is reasonable to conclude therefore that deviations from linearity are a real effect. A sample chromatogram, which shows the analysis of a 1 µl sample of a ketone mixture, is shown in figure 6.9.

A linear gas density balance response is not a sufficient criterion for satisfactory quantitative performance. On figure 6.5 for example, all components of the mixture give a linear response to about 500 µg, but only the n-heptane and n-octane curves coincided, i.e. only these two materials give identical absolute response, which differs from the remaining constituents. To obtain satisfactory quantitative results the detector must give a response linear with concentration and equal for all materials, at all sample sizes: even with heptane the absolute response decreases with sample size (see table 6.3).

6.2b Relative Composition Analysis using the Gas Density Balance.

For each mixture, using the linear and coincident portion of the response curves, the mean values of the percentage weights detected by the gas density balance were calculated from the corrected peak areas ($\bar{x}_D$ values). These results are given in table 6.2. The mean percentage weights of the components in each mixture were also calculated from the mass detector results, ($\bar{x}_M$ values) and using these as a standard, the response of the gas density balance with respect to the mass detector was found. The response factor was defined as:

$$R_{DM} = \frac{\bar{x}_D}{\bar{x}_M} \qquad 6.1$$

All mixtures were of known composition (x_0 values), so that in this particular case, a check could be made on the response factors obtained using the mass detector as standard. The response factor was defined as:

$$R_{DO} = \frac{\bar{x}_D}{x_0} \qquad 6.2$$

The factors R_{DM} should be the more reliable, since losses due to evaporation of sample before injection, and column adsorption effects, are eliminated.

Table 6.2

Compound	Composition			Response		Fig.
	x_O	$\bar{x}_M$	$\bar{x}_D$	R_{DO}	R_{DM}	
n-Pentane[a]	22.50	22.30	21.62	0.96	0.97	6.1
n-Hexane	17.57	18.40	17.55	1.00	0.96	
n-Heptane	14.67	15.16	15.69	1.07	1.03	
n-Octane	16.45	16.46	16.81	1.02	1.02	
n-Nonane	28.82	27.69	28.32	0.99	1.02	
Benzene	41.33	41.35	40.56	0.98	0.98	6.2
Toluene	31.00	30.94	31.50	1.02	1.02	
Ethyl benzene	27.67	27.72	27.94	1.01	1.01	
Methyl Ethyl ketone	42.20	43.05	42.63	1.01	0.99	6.3
Methyl n-propyl ketone	25.69	25.75	25.67	1.00	1.00	
Methyl n-butyl ketone	32.10	31.20	31.70	0.99	1.00	
Methyl acetate	23.72	21.46	20.62	0.87	0.96	6.4
Ethyl acetate	23.47	25.50	24.16	1.03	0.95	
n-Propyl acetate	22.82	23.03	23.58	1.03	1.02	
n-Butyl acetate	29.99	30.02	31.64	1.06	1.05	
n-Heptane	18.44	18.61	18.25	1.00	0.98	6.5
n-Octane	13.77	13.82	13.45	0.99	0.99	
Ethyl acetate	23.68	23.92	24.43	1.03	1.03	
Methyl ethyl ketone	16.49	16.28	16.29	0.99	1.00	
Benzene	27.63	27.37	27.59	1.00	1.00	
Cyclohexane	19.30	19.39	19.02	0.99	0.99	6.6
n-Octane	15.87	16.14	16.54	1.04	1.02	
Carbon tetrachloride	34.92	34.79	33.80	0.97	0.97	
Dichloroethylene	29.92	29.68	30.63	1.02	1.03	
2,2,4-Trimethyl pentane	38.03	38.25	40.56	1.07	1.06	6.7
n-Octane	35.59	35.52	37.09	1.04	1.04	
1-Octene	26.38	26.23	22.35	0.85	0.85	
n-Octane	35.64	36.26	37.17	1.04	1.02	6.8
Butylene oxide	35.71	36.20	33.81	0.95	0.94	
Dioxan	28.65	27.54	29.02	1.01	1.05	

a = column and gas density balance at 66°C.

Relative composition analyses given by the gas density balance operating within its linear dynamic range are satisfactory, provided absolute corrected response factors are identical. The standard deviation of both sets of response factors have been calculated and are 4.8×10^{-2} for R_{DO}, and 4.2×10^{-2} for R_{DM}.

The effect of calculating the percentage composition of a mixture when response curves are not coincident is shown in the following example (table 6.3). The absolute response of the gas density balance is the ratio of the gas density balance and mass detector responses, i.e. is area per unit weight. The table gives the response for maximum sensitivity. The true percentage weight of the component (n-heptane) was 18.44%.

Table 6.3

Weight of Material detected (µg)	GDB Response ($cm^2\ \mu g^{-1}$)	% Heptane detected Mass Detector	GDB
129	0.779	18.71	18.54
143	0.768	18.93	18.35
259	0.695	18.29	17.98
400	0.657	18.65	17.20
523	0.651	18.70	16.69
670	0.597	18.77	16.31

The absolute response of the gas density balance to n-heptane decreases as sample size is increased. Similar effects occur for the remaining constituents of the mixture, but to different extents and hence the proportion of n-heptane detected by the gas density balance changes with sample size. The repeatability of the detector response toward a fixed sample size of a material under constant operating conditions was determined in section 4.5.3a. The coefficient of variation of 45 results was 3.6%: for the same mixture the coefficient of variation of the mass detector response was 1.0% (tables 4.20 and 4.21).

6.2c Limits of Detection and Response Time.

The lower limit of detection Q_o of the gas density balance was calculated using the Young equation (Chapter 2, p 25):

$$Q_o = \frac{2R_n M}{PF} \qquad 6.3$$

The noise level of R_n of the detector was measured on the maximum sensitivity. The response to very small amounts of n-octane (in terms of peak area, P) was measured, and the absolute masses of the samples (in millimoles, M) were obtained from the mass detector. It is reasonable to assume that the response of the gas density balance is linear and predictable over a small range in the region of the limit of detection, and hence by using equation 6.3 a value for the lower limit of detection was calculated.

The lower limit of detection = 6.4×10^{-7} $mMml^{-1}$. Under the conditions of the experiment, this represents a mass limit of detection of 0.6 μg. The upper limit of detection exceeds that normally required for gas chromatography, and certainly exceeds the capacity of column E.

The response time of the gas density balance was measured by the Schmauch procedure[2], described in section 2.2d, using the apparatus shown in figure 4.10b. The value was determined at room temperature for benzene and ether, with an analytical gas flow rate of 51 ml min^{-1} and reference flow of 75 ml min^{-1}. The response time was 11 sec: a value can be obtained from the equation:

$$r = \frac{V_d}{F} \qquad 6.4$$

where V_d is the detector dead volume and F the carrier gas flow rate. For the gas density balance V_d = 8 ml and hence at 51 ml min^{-1}, the response time is 9½ sec.

Literature values for limits of detection and response times are given in table 3.10.1, and agree well with those quoted above.

6.2d The Gow-Mac Gas Density Balance - Conclusions.

For all materials examined the detector gave a response close to the calculated value, over a small concentration range. Provided that the detector is used within this range, excellent quantitative results are obtained. It is however not obvious when this limit is exceeded. The linear dynamic range of the detector does not approach the dynamic range, and is species dependent. The detector is very stable and had

a reasonable lower limit of detection, but the response time is rather long, although satisfactory for most packed column analyses.

6.3 The Martin Gas Density Balance.

The response and linear dynamic range of the Martin gas density balance toward a number of compounds were determined in a manner analogous to that described for the Gow-Mac gas density balance. Operating conditions are given in table 6.4, the remaining conditions being as quoted in table 6.1.

Table 6.4

Analytical gas flow rate	50 ml min^{-1}
Reference gas flow rate	50 ml min^{-1}
Sample sizes	0.2 µl to 5 µl
Gas density balance - filament current	1.9 A
sensitivity	X1000 to X 500
Mass detector - ranges	1 mg to 5 mg

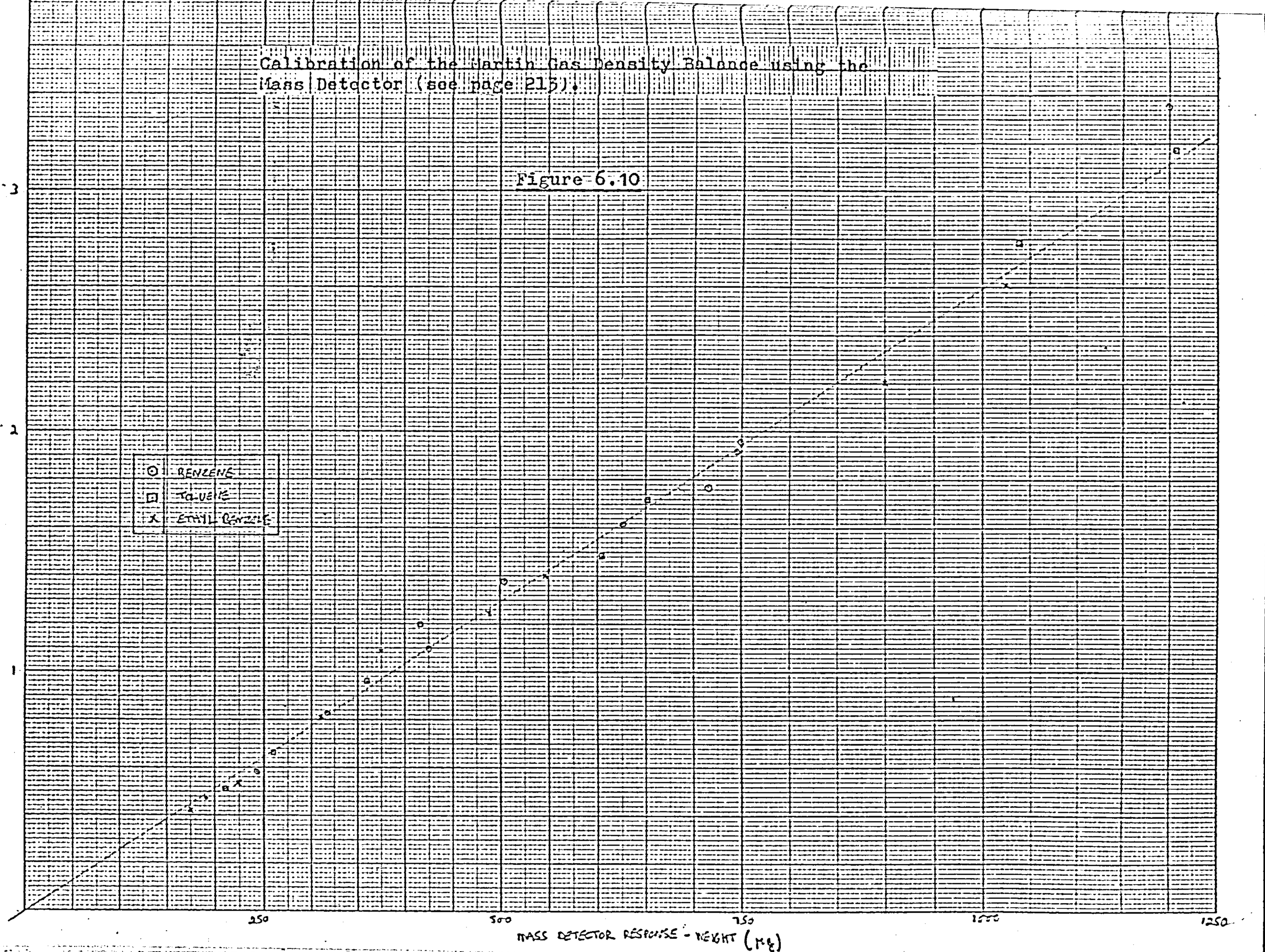
For most work the detector was operated on its maximum sensitivity ($X10^3$) to avoid the use of excessively large sample sizes which would overload the column, and give distorted peaks. A new series of mixtures, including the same compounds listed in tables 5.4 and 6.2 was prepared. The results of the analyses are expressed in the same way as the Gow-Mac gas density balance results.

6.3a The Linearity of the Gas Density Balance.

For each component of a mixture, a graph was plotted of response of the gas density balance (corrected peak area) against the mass detector response (weight adsorbed). In all cases a straight line relationship was found, i.e. the Martin gas density balance gives a linear response at least over the range investigated (about 10^2). In addition the slopes of the lines were identical for all components of a mixture, they passed through the origin and the response per unit weight (the sensitivity) was identical at all sample sizes (see for example table 6.6): the response of the detector is predictable on a molecular weight basis. There were however small variations in response per unit weight from one mixture to another, but these can be attributed

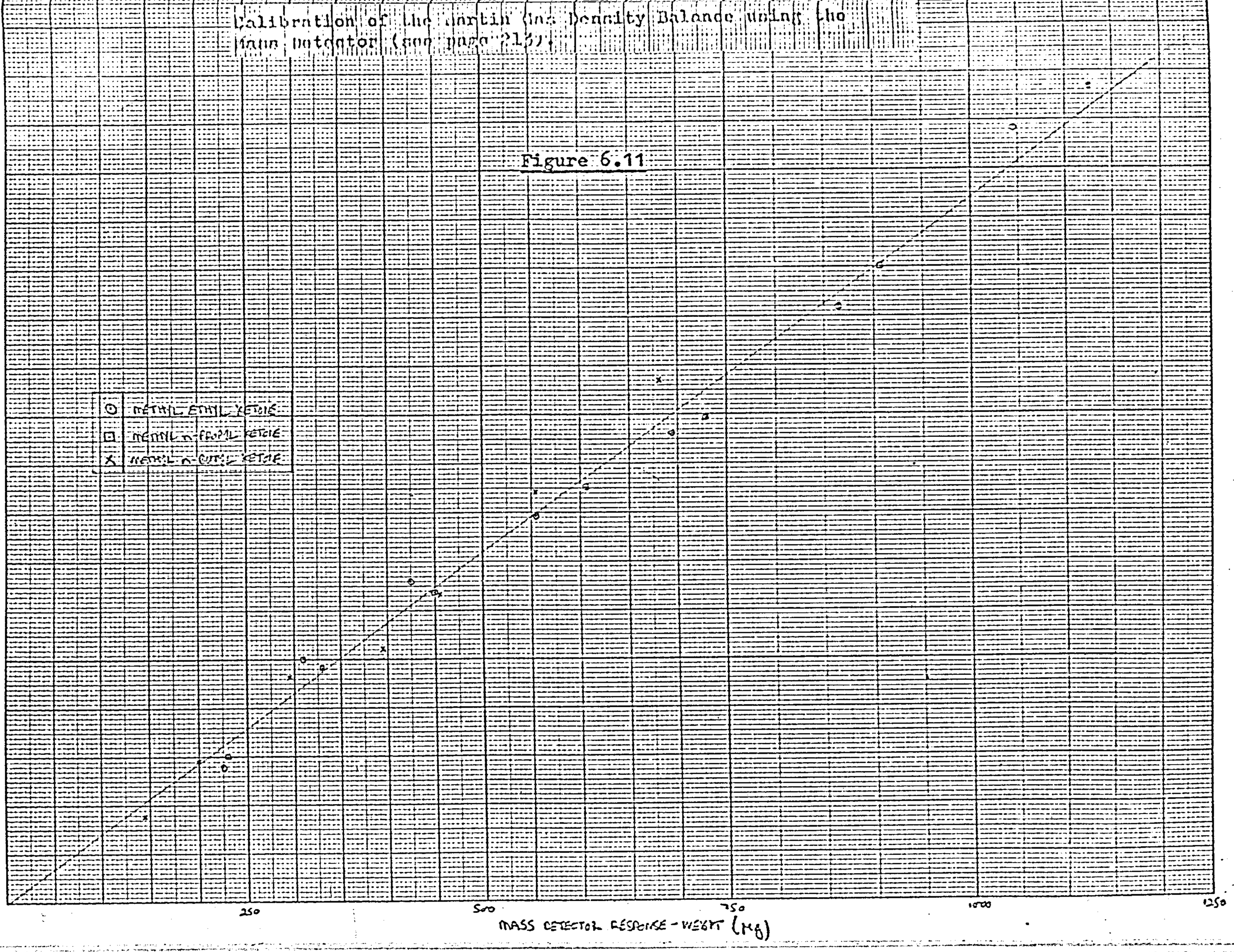
Calibration of the Martin Gas Density Balance using the Mass Detector (see page 215).

Figure 6.10



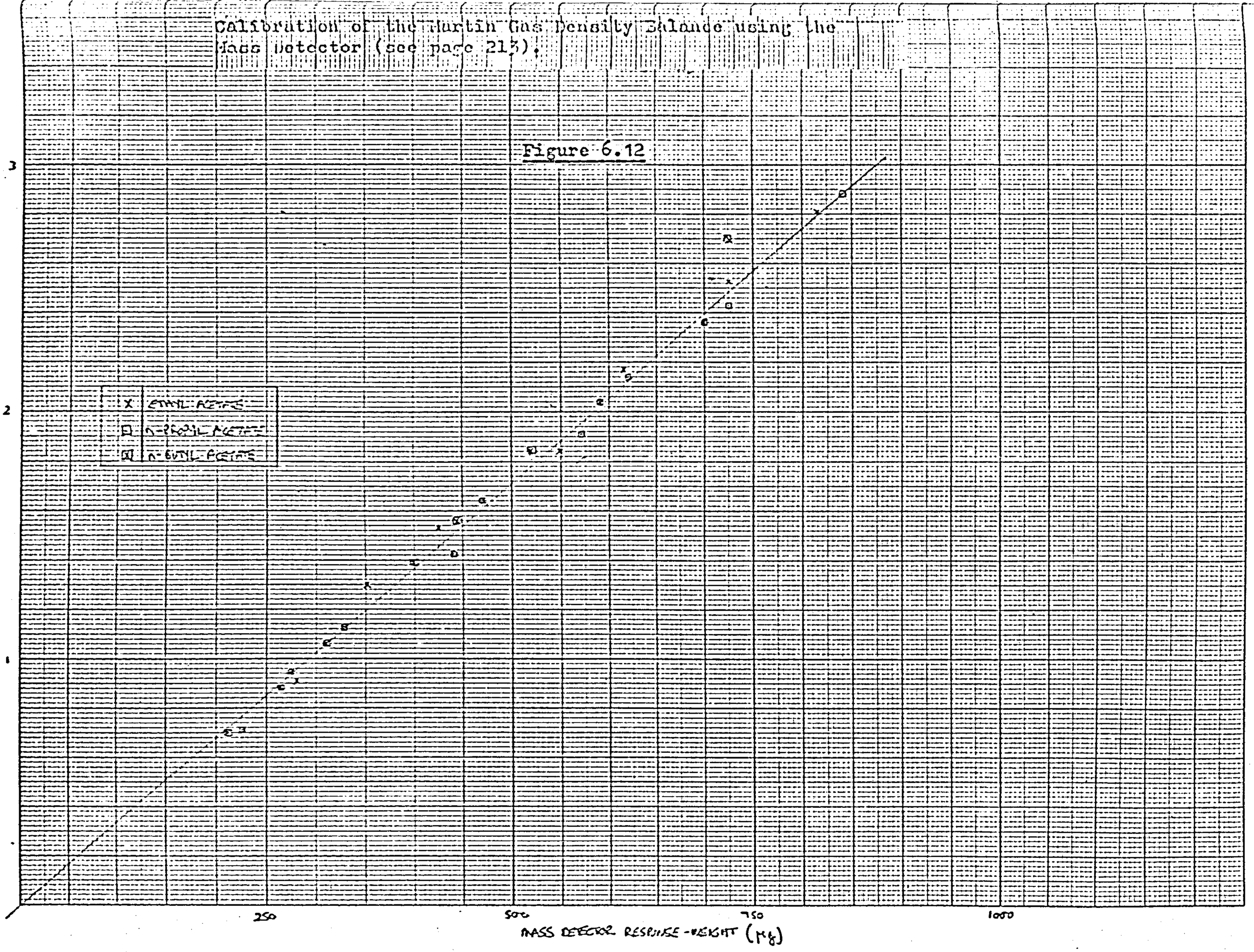
Calibration of the Martin Gas Density Balance using the Mass Detector (see page 218).

Figure 6.11



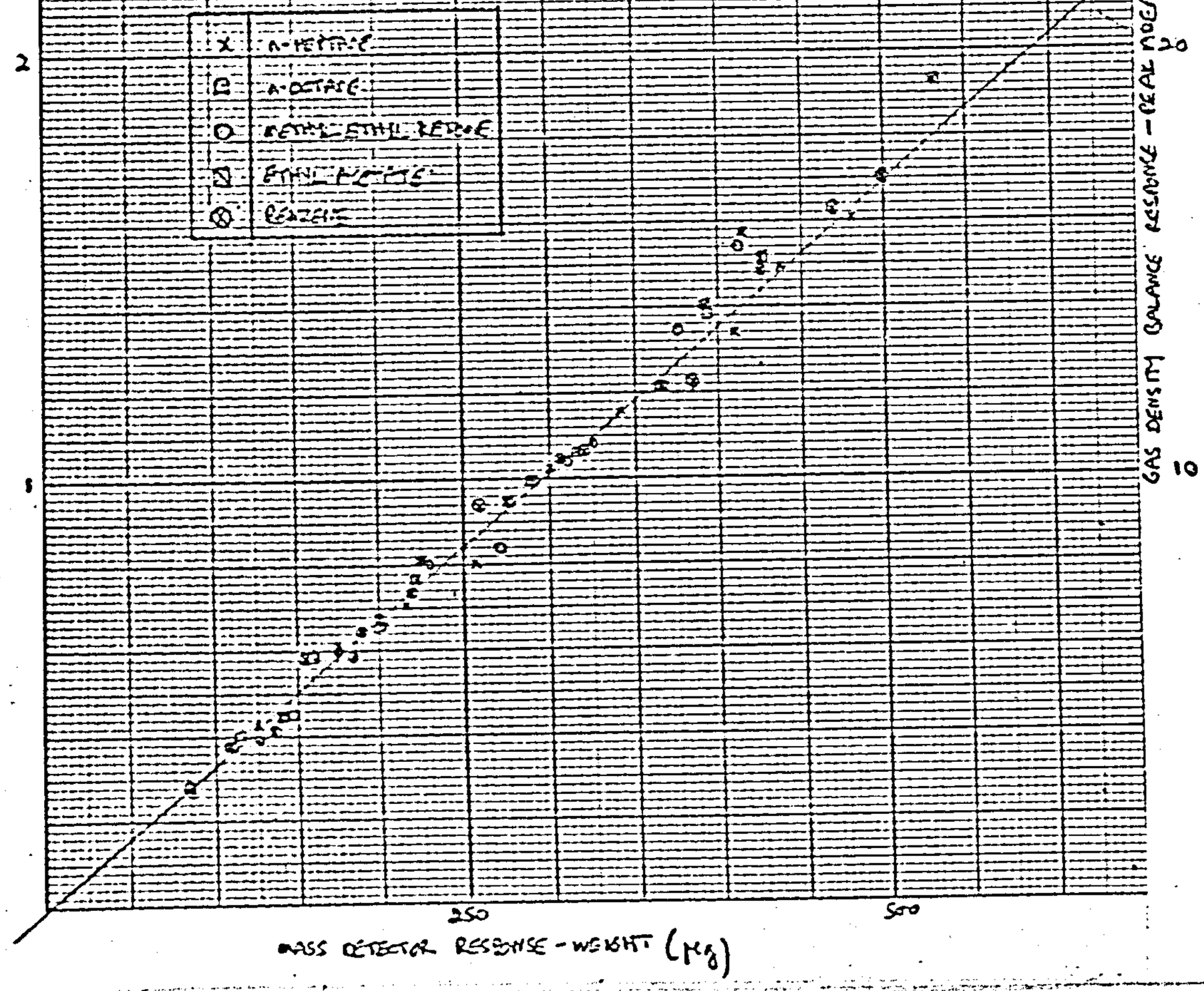
Calibration of the Martin Gas Density Balance using the Mass Detector (see page 213).

Figure 6.12



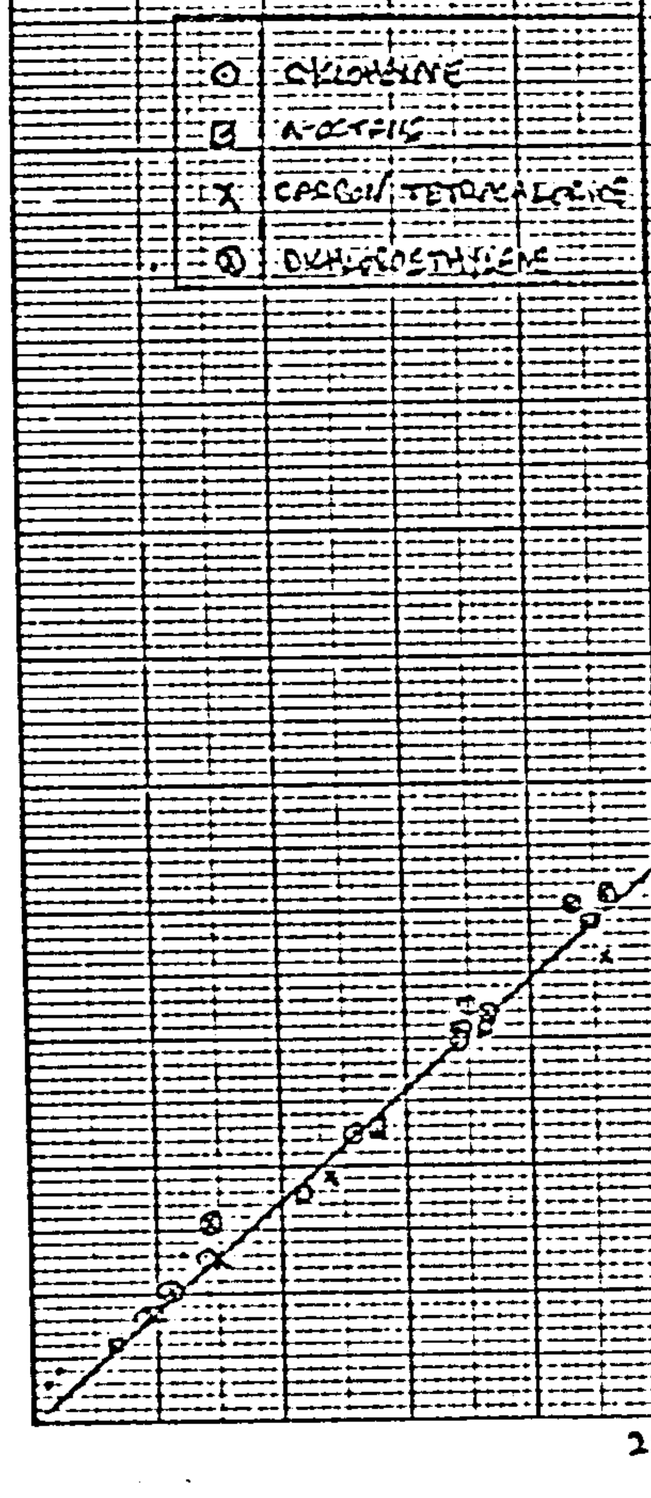
Calibration of the Martin Gas Density Balance using the Mass Detector (see page 213).

Figure 6.13



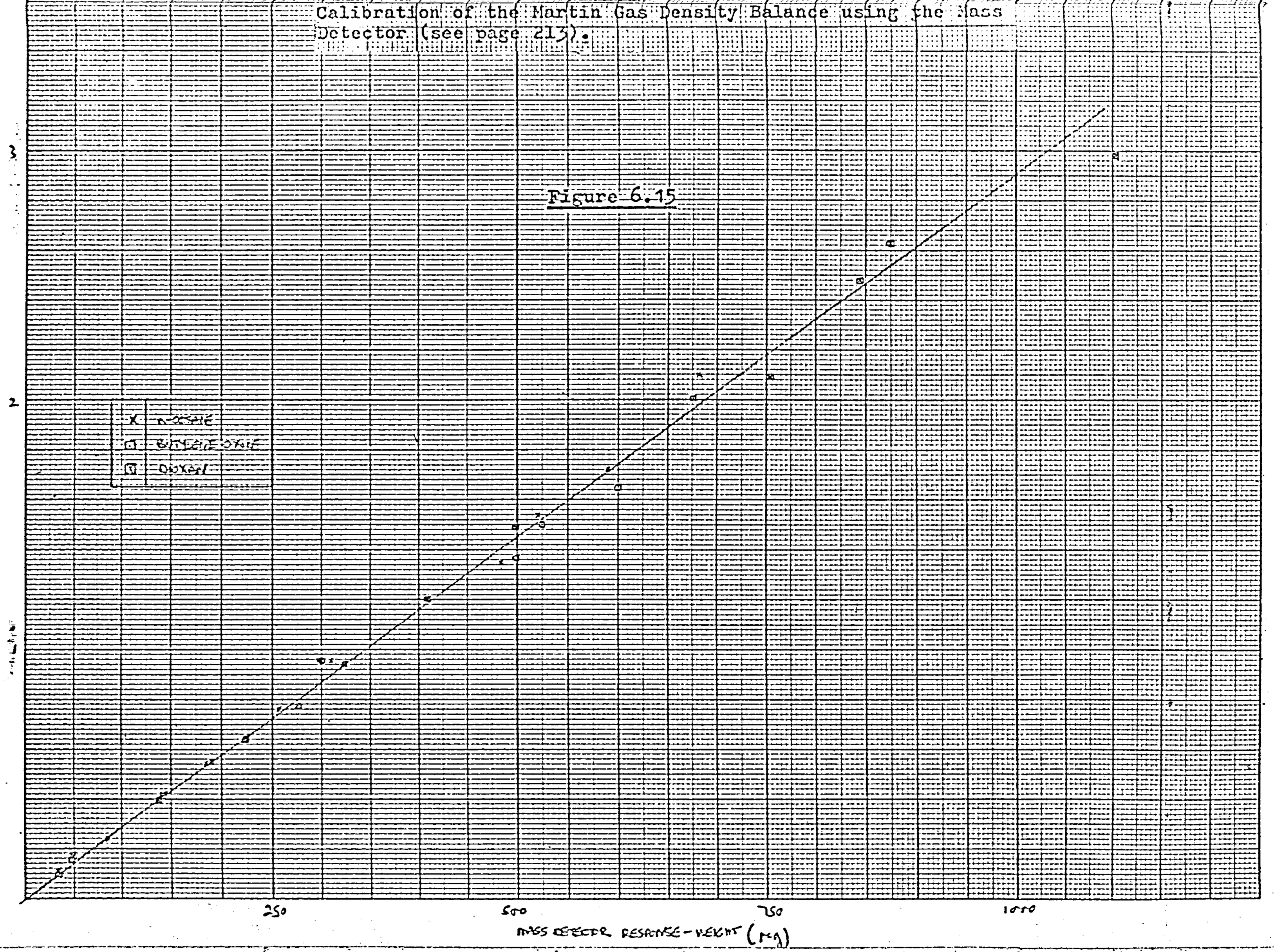
Calibration of the Martin Gas Density Balance using the Mass Detector (see page 213).

Figure 6.14



Calibration of the Martin Gas Density Balance using the Mass Detector (see page 213).

Figure 6.15



to the day to day fluction of conditions (temperature, flow rate etc). This is borne out by the observation that a given compound analysed at different times, gave a slightly different response per unit weight. The results are shown on figures 6.10 to 6.15 for all the mixtures containing more than two components. The coefficients of variation of the absolute response factors ($cm^2\ \mu g^{-1}$) have been calculated. The overall variation for 137 determinations was 5.1%.

6.3b Relative Composition Analysis.

The mean percentage weight of each component in the mixture $\bar{x}_D$, over a wide mass range, was found and compared with that obtained by the mass detector ($\bar{x}_m$). These values, together with the true percentage weight (at injection), x_o, are given in table 6.5. R_{DM} and R_{DO} have the same significance as in section 6.2b.

Table 6.5

Compound	Composition			Response		Fig.
	x_o	$\bar{x}_m$	$\bar{x}_D$	R_{DO}	R_{DM}	
Benzene	38.45	38.90	39.05	1.02	1.00	6.10
Toluene	33.22	33.14	33.11	1.00	1.00	
Ethyl benzene	28.33	27.96	27.84	0.98	1.00	
Methyl ethyl ketone	35.88	36.72	37.16	1.04	1.01	6.11
Methyl n-propyl ketone	38.21	38.93	38.30	1.00	0.98	
Methyl n-butyl ketone	25.92	24.34	24.54	0.95	1.01	
Ethyl acetate	39.33	39.71	40.34	1.03	1.02	6.12
n-Propyl acetate	31.32	31.18	30.54	0.98	0.98	
n-Butyl acetate	29.36	29.11	29.12	0.99	1.00	
n-Heptane	22.79	23.33	23.30	1.02	1.00	6.13
n-Octane	15.38	15.38	15.40	1.00	1.00	
Ethyl acetate	21.54	21.00	21.76	1.01	104	
Methyl ethyl ketone	16.10	15.74	15.47	0.96	0.98	
Benzene	24.19	24.55	24.07	1.00	0.98	
Cyclohexane	21.17	20.57	21.07	1.00	1.02	6.14
n-Octane	16.65	16.17	16.71	1.00	1.03	
Carbon tetrachloride	34.54	35.34	34.94	1.01	0.99	
Dichloroethylene	27.64	27.92	27.28	0.99	0.98	

Compound	Composition x_o	$\bar{x}_m$	$\bar{x}_D$	Response R_{DO}	R_{DM}	Fig.
n-Octane	26.74	27.63	27.44	1.02	1.01	6.15
Butylene oxide	28.80	28.56	27.01	0.94	0.95	
Dioxan	44.45	43.81	45.55	1.03	1.04	
Benzene	52.51	52.31	52.02	0.99	0.99	
Toluene	47.49	47.69	47.98	1.01	1.01	
n-Butyraldehyde[a]	39.80	39.24	38.96	0.98	0.99	
Methyl ethyl ketone	60.20	60.76	61.05	1.02	1.01	
Isopropyl alcohol	40.12	42.40	42.18	1.06	1.00	
Nitromethane	59.88	57.60	57.82	0.94	1.00	
Water[b]	54.02	47.30	47.29	0.88	1.00	
Ethyl alcohol	45.98	52.70	52.71	1.12	1.00	
Ethyl alcohol[c]	53.63	54.25	53.68	1.00	0.99	
n-Propyl alcohol	46.37	47.75	46.32	1.00	1.01	
n-Propyl alcohol[c]	52.83	54.91	54.59	1.04	1.00	
n-Butyl alcohol	47.17	45.09	45.41	0.94	1.00	
n-Butyl alcohol[c]	52.95	53.42	51.74	0.98	0.97	
n-Amyl alcohol	47.05	46.58	48.26	1.02	1.03	
n-Propyl alcohol[c]	44.94	45.36	45.57	1.02	1.00	
Methyl n-propyl ketone	55.06	54.64	54.43	0.98	1.00	

a = column temp. 66°C

b = Porapak column D at 70°C

c = Porapak column D at 140°C.

Excellent quantitative results were obtained for all samples. The standard deviations of the relative response factors are 2.2×10^{-2} for R_{DO} and 1.8×10^{-2} for R_{DM}. It has been shown that the response of the detector is linear with respect to sample size. It is interesting to compare the absolute response of the detector, with the Gow-Mac detector for the same material analysed under the same conditions. Response values for n-heptane for a variety of sample sizes are given in table 6.6. The Gow-Mac detector results are given in table 6.3.

Table 6.6

Weight of Material detected (μg)	GDB_2 Response ($cm^2 \mu g^{-1}$)	% Heptane detected Mass detector	GDB
124	0.0241	22.95	23.78
175	0.0251	23.20	23.88
213	0.0239	23.38	23.59
254	0.0251	23.51	21.43
300	0.0246	23.50	23.74
338	0.0249	22.69	23.26
411	0.0235	23.57	24.29
436	0.0246	23.02	22.72
479	0.0240	23.47	22.95

x_o = 22.79.

Comparison with table 6.3 reveals that the Martin gas density balance is less sensitive than the Gow-Mac version, by a factor of about 30: the absolute response of the Martin gas density balance is constant whereas the Gow-Mac detector response depends on sample size: the Martin detector will therefore give reliable relative composition data, over a wide sample size range, but the Gow-Mac detector will only give accurate results within a limited range.

The repeatability of the relative composition results was determined over the whole sample size range used: the coefficient of variation of 165 determinations was 2.1%. The same value was obtained for the mass detector repeatability. A similar calculation for the Gow-Mac detector is meaningless, since response is concentration dependent; even the result for single sample size was significantly greater, at 3.6%. The overall bias of the Martin gas density balance results is 0.5%, (i.e. 1.5% absolute bias). Very similar values were obtained for the mass detector bias (see tables 5.2 and 5.4). Bias values for the Gow-Mac detector increase as sample size increases (see table 6.3): bias values for a single sample size are similar to the Martin and mass detector values, quoted above.

6.3c Limits of Detection of the Martin Gas Density Balance.

The lower limit of detection was determined by the procedure outlined in section 6.2c. The lower limit of detection = 6.3×10^{-6}

$mMml^{-1}$, representing a mass limit of detection of 8 µg. The Gow-Mac detector exceeds this value by a factor of 10, although it is more sensitive by a factor of 30. The discrepancy is a result of the lower noise level on the Martin detector. The upper limit of detection exceeds that normally required for gas chromatography.

Using equation 6.4 the response time of the Martin detector, at a flow rate of 50 ml min^{-1} is 3½ seconds. The value determined by Schmauch[2] was 3 seconds (see table 3.10.1).

6.3d The Martin Gas Density Balance - conclusions.

The Martin gas density balance gives excellent quantitative results over a wide range of sample sizes. No deviations from linearity were observed, and all responses were predictable on a molecular weight basis. Its performance is entirely satisfactory and it may be used with confidence.

6.4 Calibration of a Katharometer.

A Gow-Mac katharometer type 9285D fitted with tungsten-rhenium filaments was placed in series with the mass detector. The operating conditions are given in table 6.7.

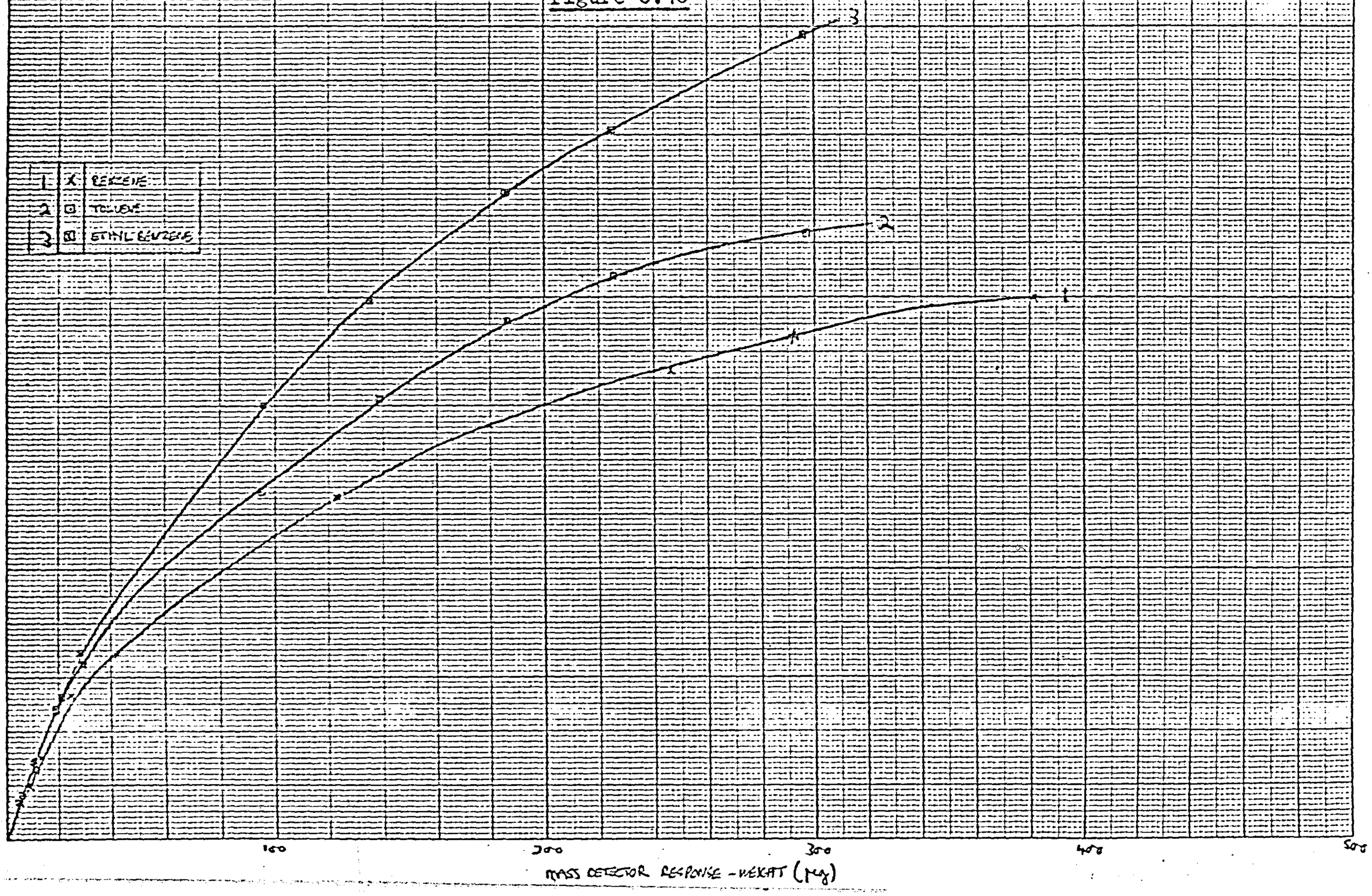
Table 6.7

Apparatus	Shandon KG2
Column	PEGA E
Column temperature	101°C
Carrier gas	Nitrogen
Analytical gas flow	51 ml min^{-1}
Reference gas flow	51 ml min^{-1}
Sample sizes	0.1 to 1 µl
Katharometer - filament current	150 mA
sensitivity	X500 to X50
temperature	101°C
Mass detector - ranges	100 µg to 1 mg
elements	27, 30
temperature	24°C

A series of mixtures containing the same compounds listed in table 6.2 were analysed covering the mass range 10 µg to 300 µg per

Calibration of a Katharometer using the Mass Detector
(see page 217)

Figure 6.16



Calibration of a Katharometer using the Mass Detector
(see page 217).

Figure 6.17

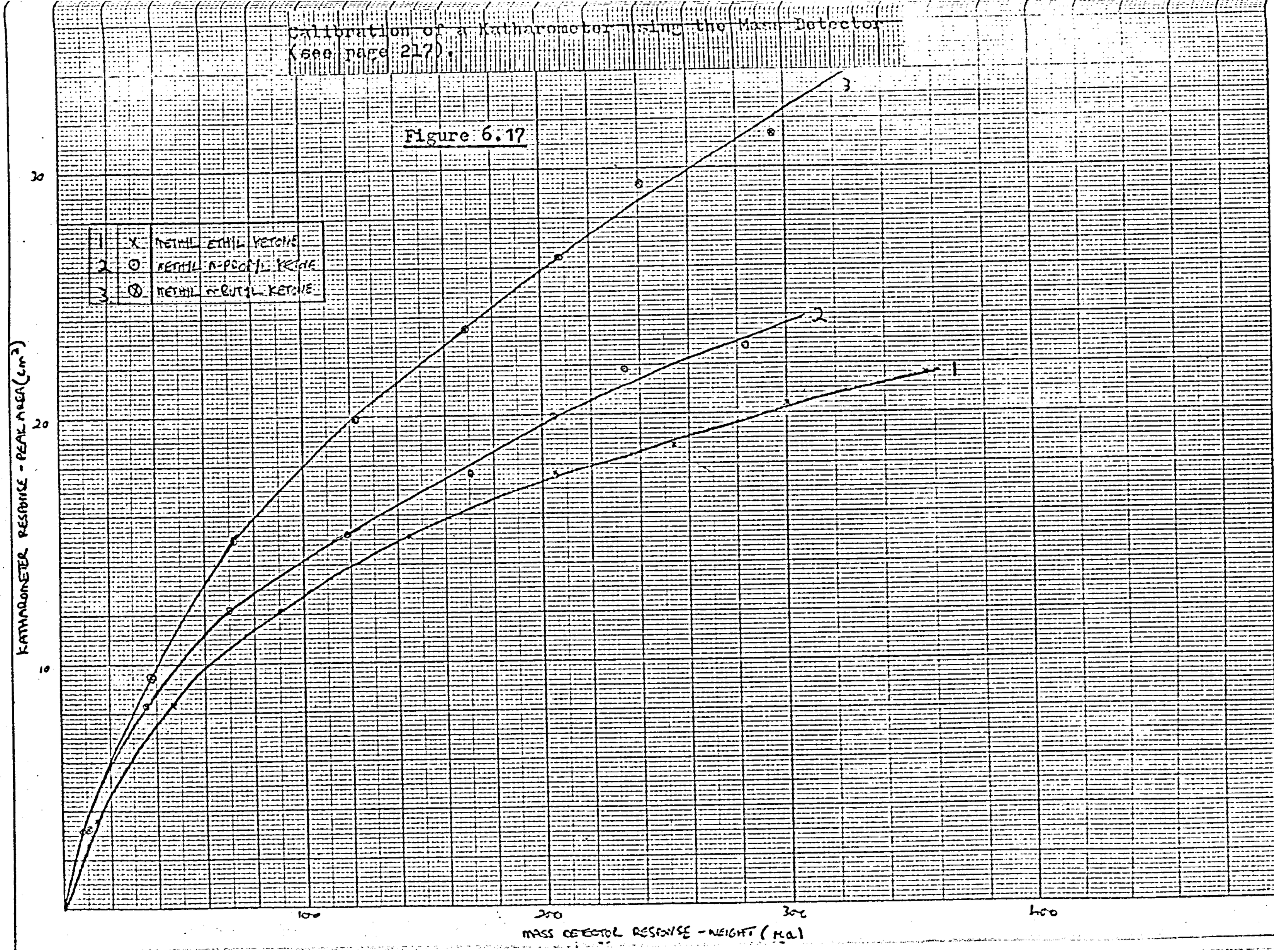
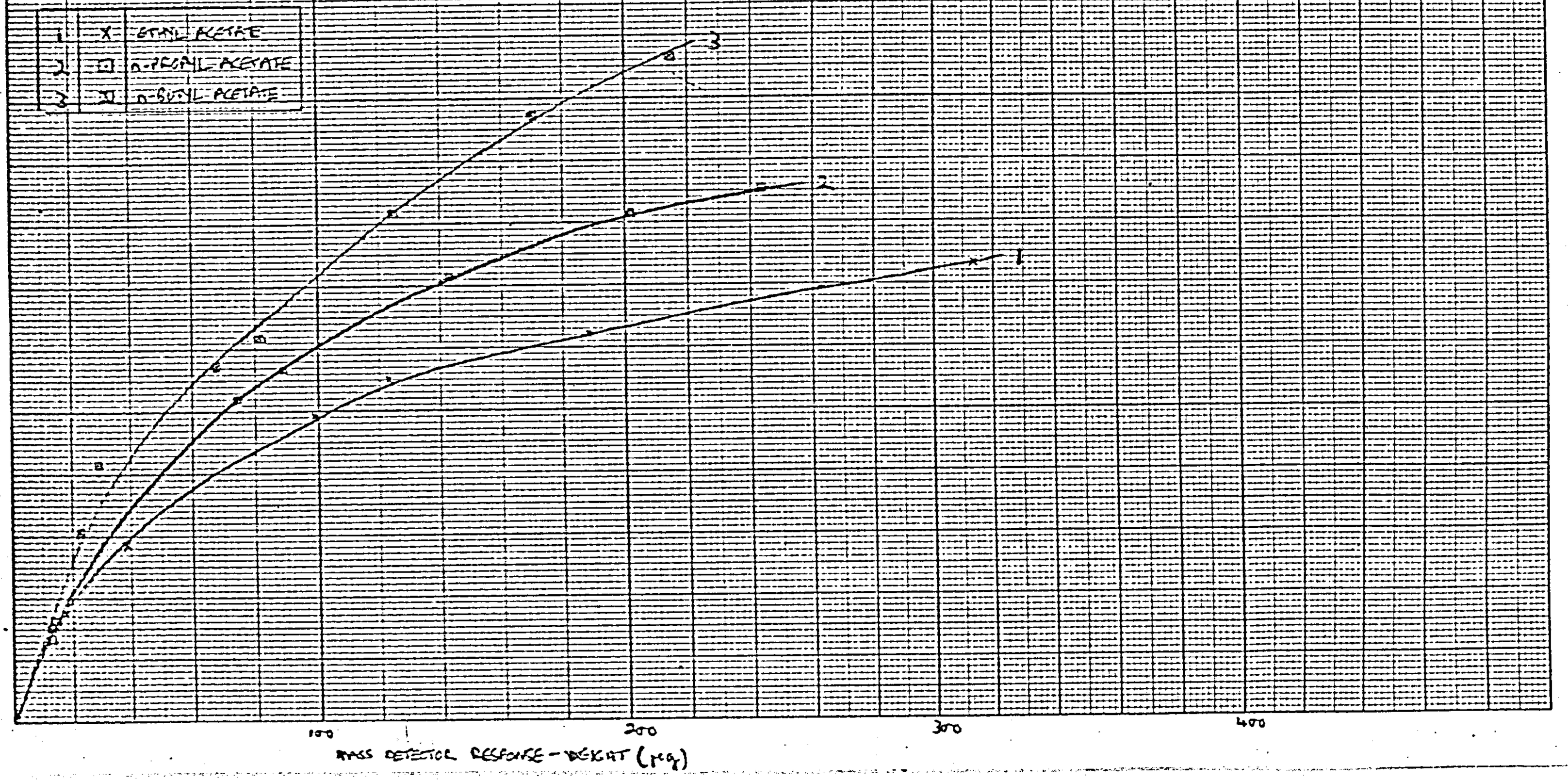
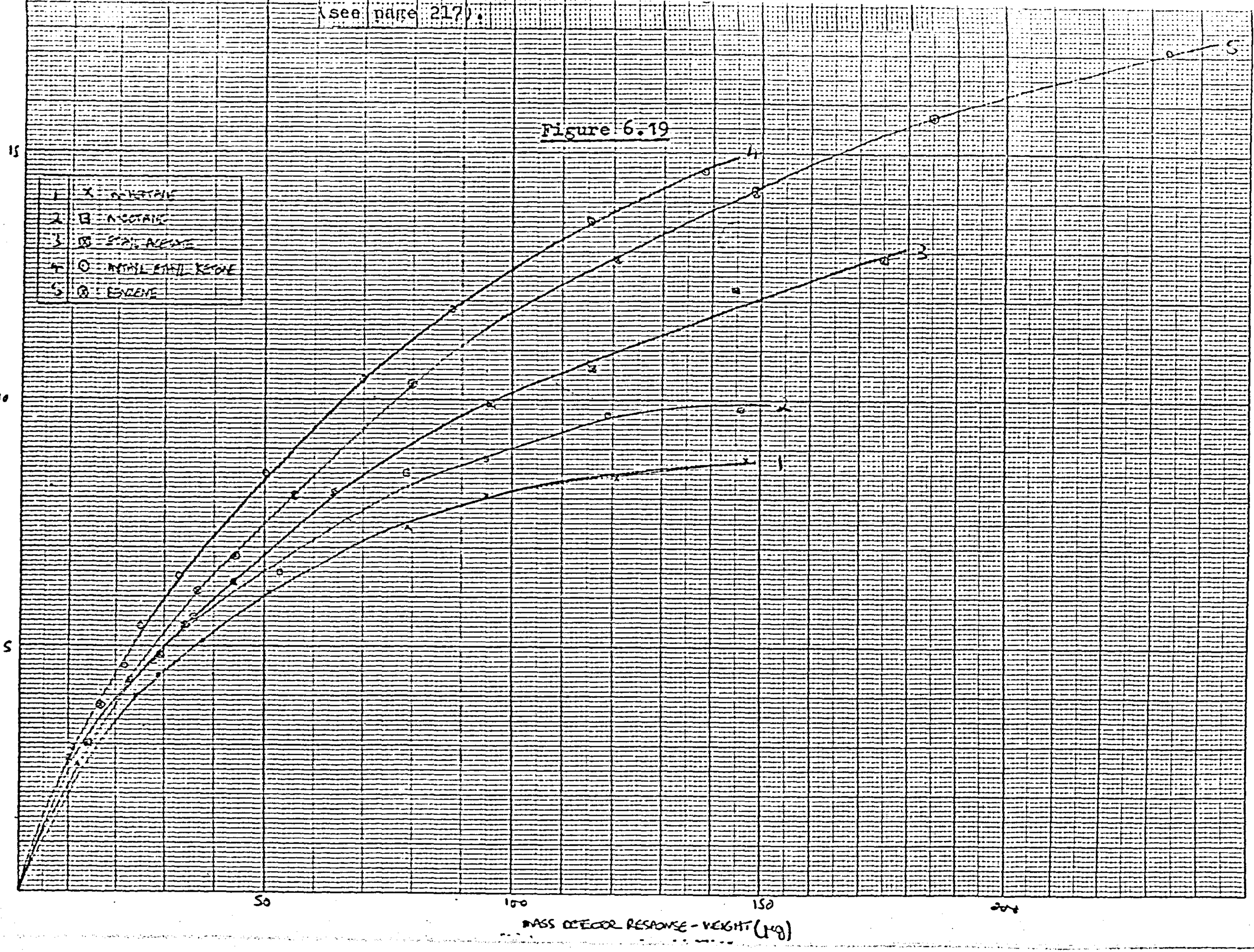


Figure 6.18


1 X ETHYL ACETATE
2 □ n-PROPYL ACETATE
3 ▽ n-BUTYL ACETATE
KATHAROMETER RESPONSE - PEAK AREA (cm²)
MASS DETECTOR RESPONSE - WEIGHT (μg)
100
200
300
400

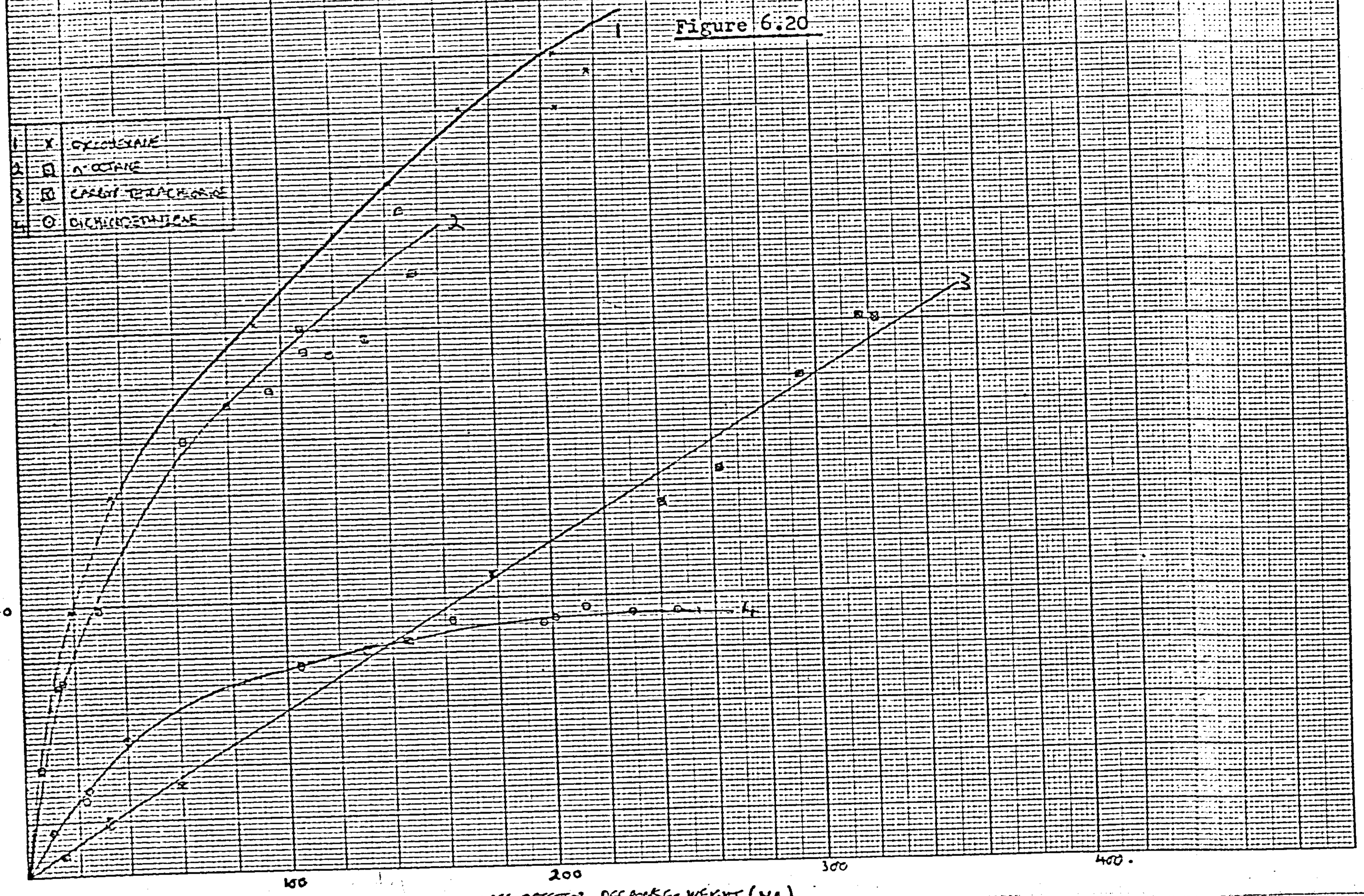
(see page 217).

Figure 6.19



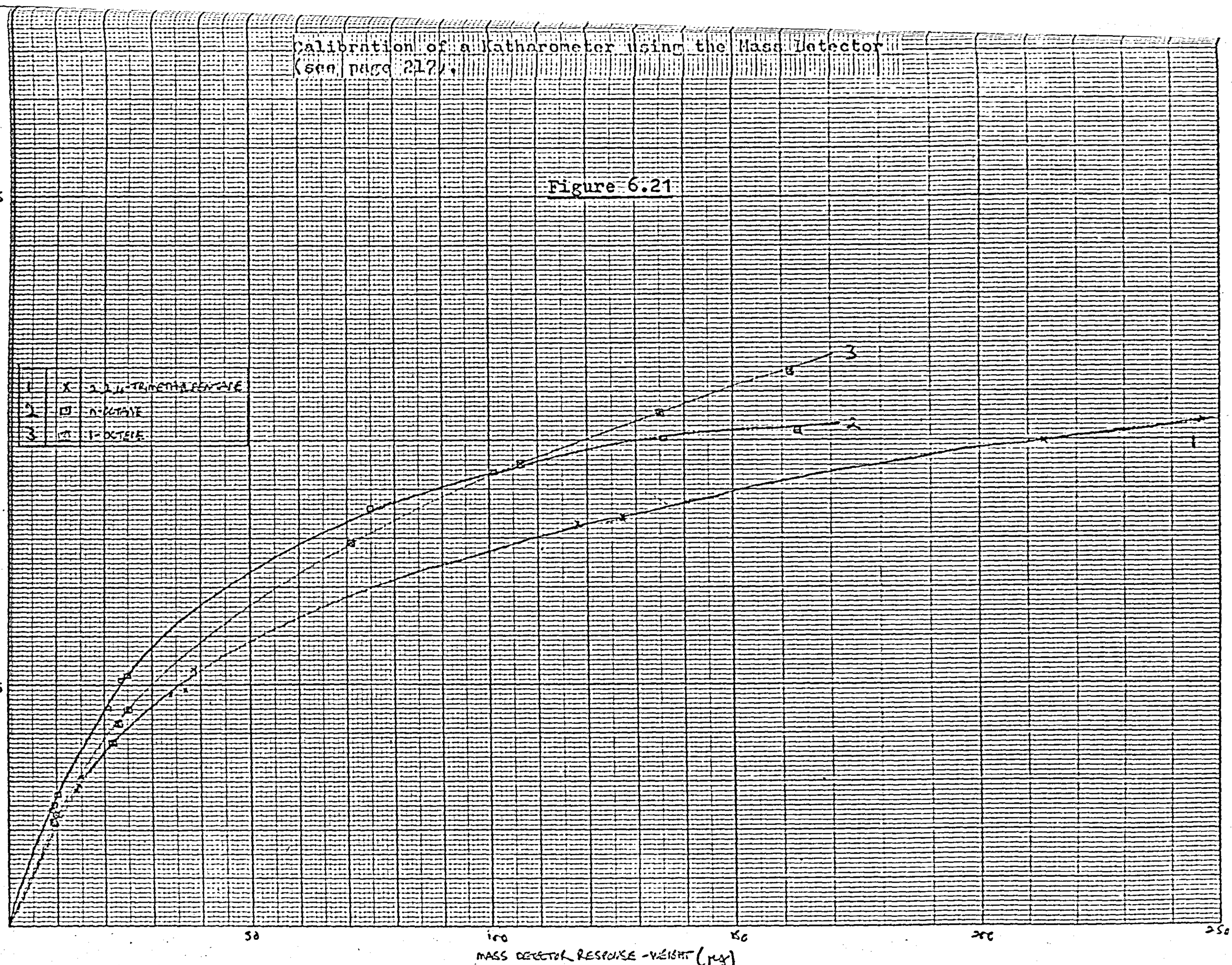
(see page 217)

Figure 6.20



Calibration of a Katharometer using the Mass Detector
(see page 272)

Figure 6.21



Calibration of a Katharometer using the Mass Detector
(see page 217).

Figure 6.22

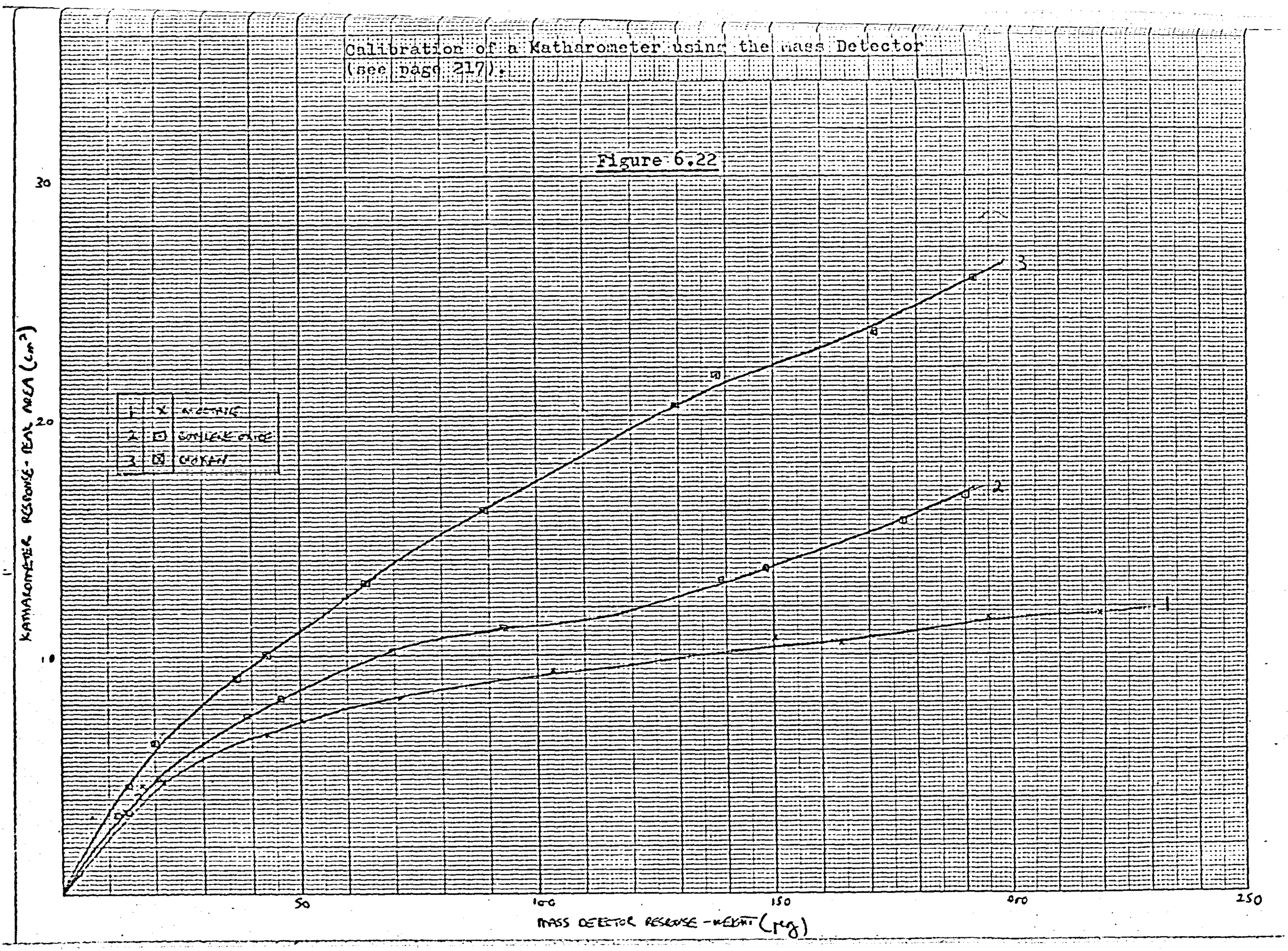
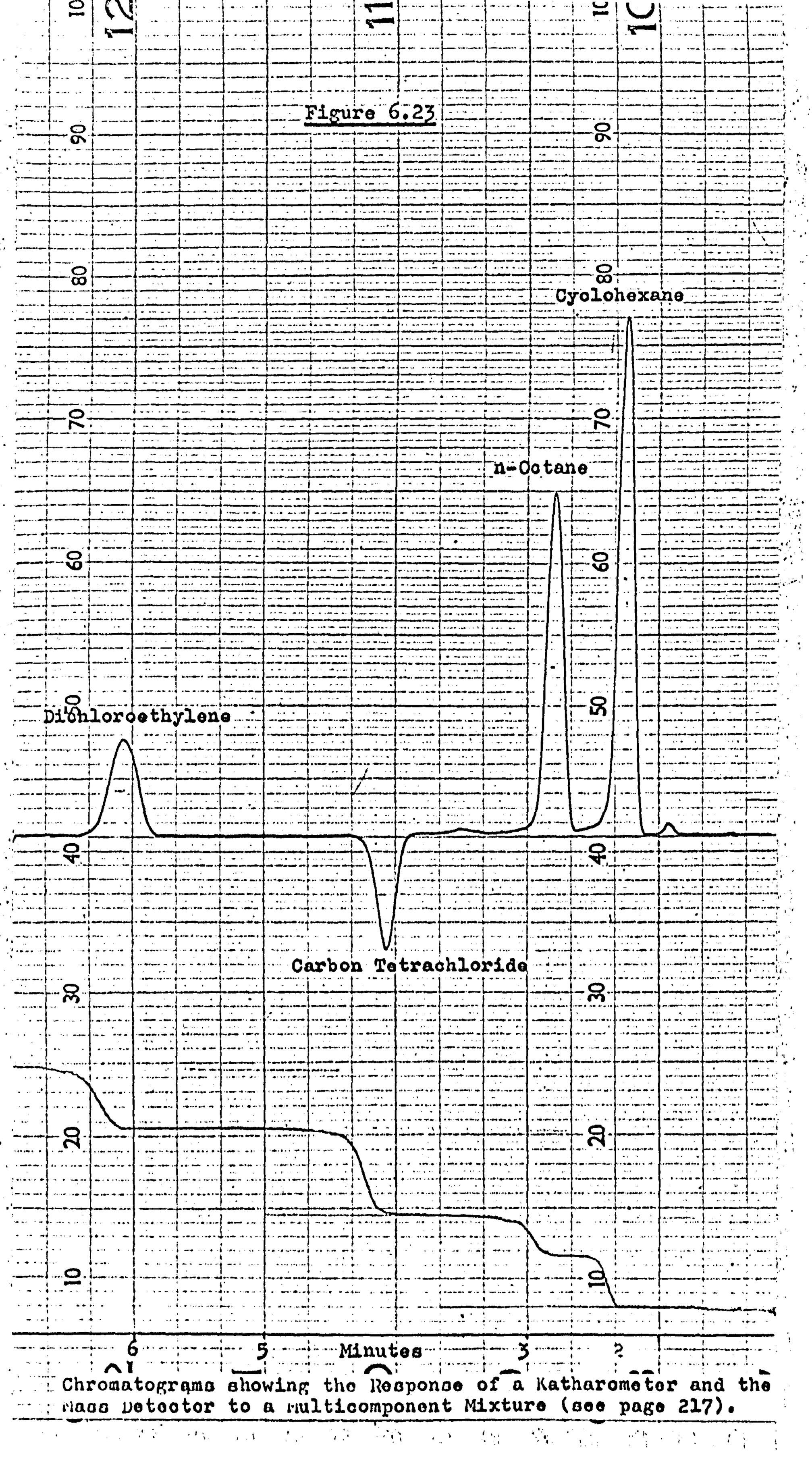


Figure 6.23



Chromatograms showing the Response of a Katharometer and the Mass Detector to a Multicomponent Mixture (see page 217).

component. Since the response of a katharometer is not predictable when nitrogen is used as carrier gas, the results are most satisfactorily expressed graphically. Response curves are shown as plots of peak area, obtained from the katharometer, against the weight of component, determined by the mass detector. Each figure shows the response of the detector to the constituents of each mixture, (figures 6.16 to 6.22). All compounds, except carbon tetrachloride gave a response of similar pattern, namely a gradual fall off in sensitivity as sample size was increased. Carbon tetrachloride was the only material to give a response linear with concentration, but for all sample sizes the response was negative. A chromatogram of the mixture containing carbon tetrachloride is shown in figure 6.23.

n-Heptane was used as a reference standard, and the response of pure n-heptane (99.99%) was measured over the mass range 50 to 170 µg: the response curve is shown on figure 6.24. The response of any other compound with respect to n-heptane can be calculated using the appropriate calibration curve. The following response factors have been calculated and are listed in table 6.8: response per unit weight of material ($cm^2 \mu g^{-1}$), and response with respect to n-heptane (by weight and in molar proportions) for 100 µg of material. The alternative way of expressing molar response is to read directly from the response curve, the response per mole and express this value relative to one mole of the standard material (R_M values).

Table 6.8

Compound	Area/unit weight ($cm^2 \mu g^{-1}$)	Weight response wrt heptane	Molar response wrt heptane R	Molar response wrt heptane R_m	Fig.
n-Heptane	0.79	1.00	1.00	1.00	6.24
Benzene	1.11	1.41	1.81	1.24	6.16
Toluene	1.33	1.69	1.84	1.62	
Ethyl Benzene	1.64	2.09	1.97	2.17	

Compound	Area/unit weight ($cm^2 \mu g^{-1}$)	Weight response wrt heptane	Molar response wrt heptane R	Molar response wrt heptane R_m	Fig.
Methyl ethyl ketone	1.28	1.63	2.27	1.38	6.17
Methyl n-propyl ketone	1.42	1.81	2.11	1.68	
Methyl n-butyl ketone	1.80	2.29	2.30	2.29	
Ethyl acetate	0.98	1.25	1.42	1.17	6.18
n-Propyl acetate	1.21	1.54	1.51	1.55	
n-Butyl acetate	1.43	1.82	1.57	1.99	
n-Heptane	0.81	1.03	1.03	1.03	6.19
n-Octane	0.90	1.15	1.01	1.21	
Ethyl acetate	1.01	1.29	1.46	1.21	
Methyl ethyl ketone	1.27	1.62	2.25	1.34	
Benzene	1.18	1.50	1.93	1.39	
Cyclohexane	1.07	1.36	1.62	1.26	6.20
n-Octane	0.96	1.22	1.07	1.30	
Carbon tetrachloride	-0.30	-0.38	-0.25	-0.62	
Dichloroethylene	0.38	0.48	0.50	0.47	
2,2,4-Trimethylpentane	0.77	0.98	0.86	1.04	6.21
n-Octane	0.93	1.18	1.04	1.24	
1-Octene	0.93	1.18	1.06	1.24	
n-Octane	0.91	1.16	1.02	1.20	6.22
Butylene oxide	1.13	1.44	2.00	1.31	
Dioxan	1.72	2.19	2.49	2.04	
Benzene	0.57	1.78	-	1.39	-
p-Cymene	1.53	3.60	-	2.04	

The weight response factors do not follow any trends. Molar response factors R, are about unity for simple paraffins; simple aromatics approach two, and halogenated compounds give very low values. The difference between benzene and p-cymene is striking.

Calibration of a katharometer by conventional techniques is very time-consuming. Calibration of the detector for a number of compounds, which can be contained in a single mixture, can be carried out quite

rapidly using the mass detector. The composition of the mixture does not have to be known, and a response curve covering a reasonable concentration range can be obtained from about twelve runs.

6.4a Limits of Detection and Response Time of the Katharometer.

Since the response of the katharometer is not predictable, a response curve in the region of the detector limits is required, in addition to determinations of noise levels and the onset of peak splitting.

The response curve from which the lower limit of detection was estimated is shown in figure 6.25. The limit of detection in terms of peak area is estimated from the point at which the extrapolated response curve cuts the noise level of the detector: the weight, and hence the concentration of material represented by this peak area is estimated from the mass detector response. The lower limit of detection for n-heptane is 8×10^{-8} mMml^{-1} (0.5 µg). The upper limit of detection was estimated from figure 6.24, and is 1×10^{-4} (150 µg).

Although the sensitivity of the detector (cm^{2}µg^{-1}) is species and concentration dependent, it is similar to, and a little greater than the Gow-Mac gas density balance, for many materials.

The response time of the detector at room temperature, determined by the Schmauch procedure[2], using benzene and ether was 30 seconds, at a flow rate of 50 ml min^{-1}. This is a particularly high value, even for use with packed columns, and is a result of the design of the detector, which is a semi-diffusion type. The internal volume of the detector is 2 ml. Response times of semi-diffusion detectors, published by Schmauch are of the order of 11 seconds, at 50 ml min^{-1}.

6.4b The Katharometer - conclusions.

The katharometer must be calibrated for all materials at all concentrations when nitrogen is used as carrier gas. A convenient and rapid method is to use the mass detector placed in series with the katharometer.

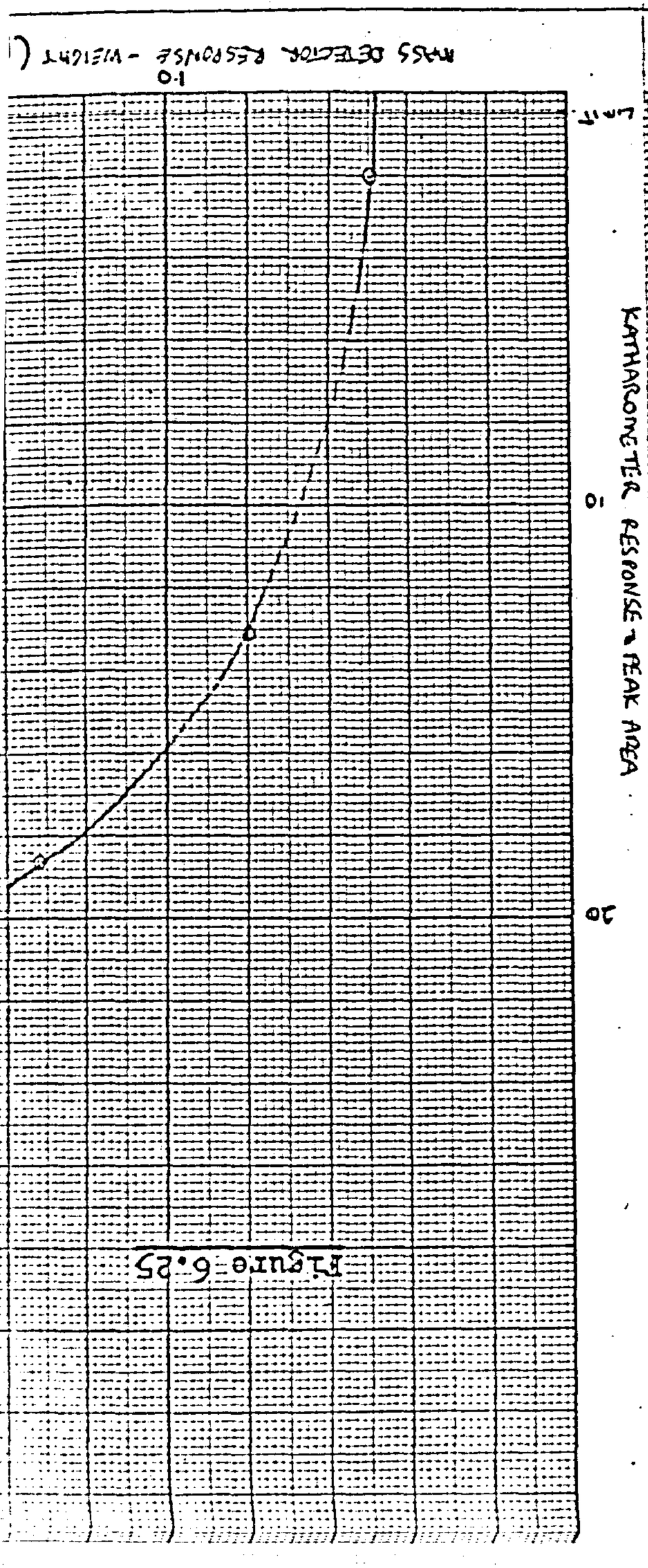


Figure 6.25

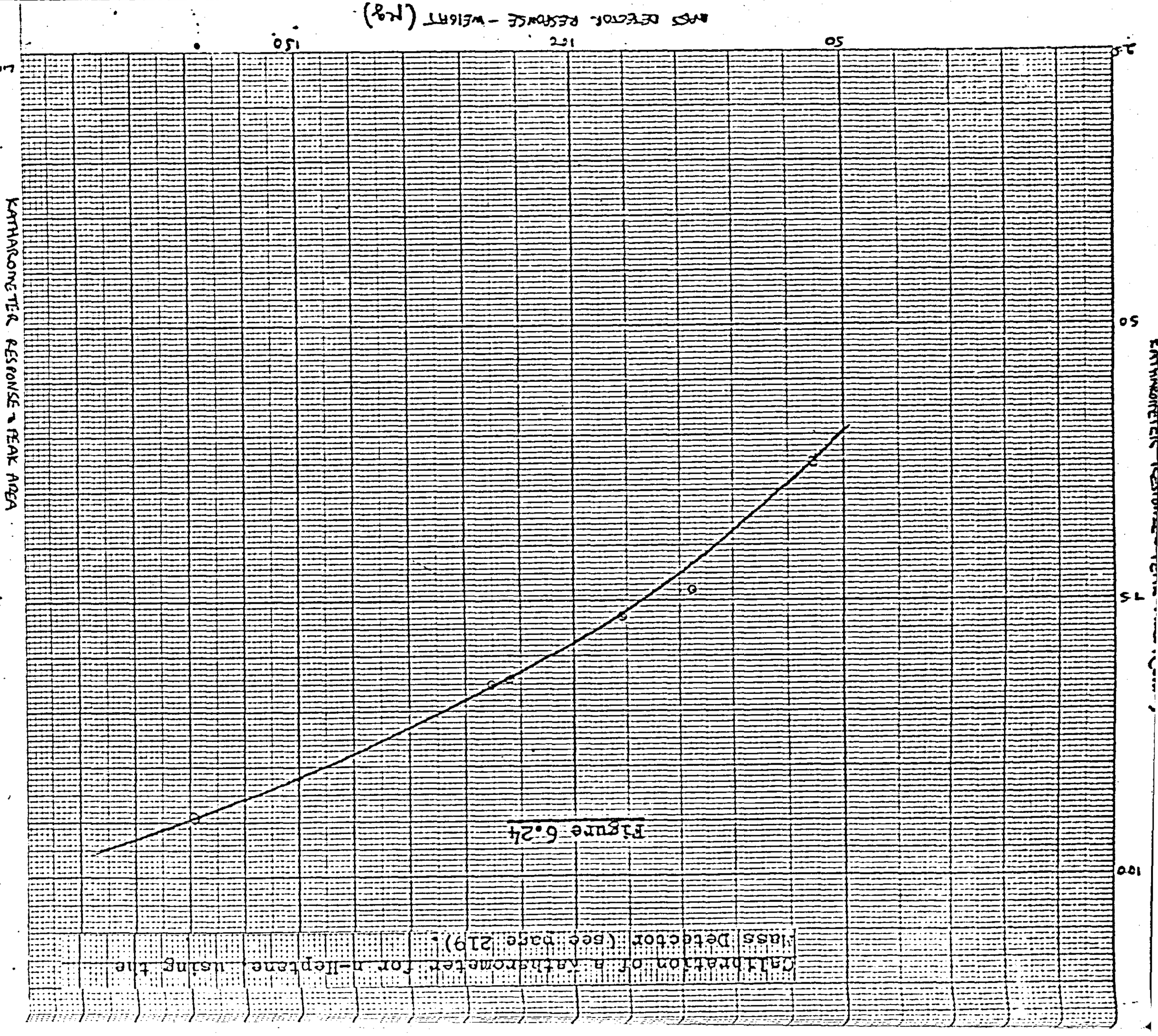


Figure 6.24

Calibration of a katharometer for n-heptane using the Mass Detector (see page 219).

6.5 Calibration of a Flame Thermocouple Detector.

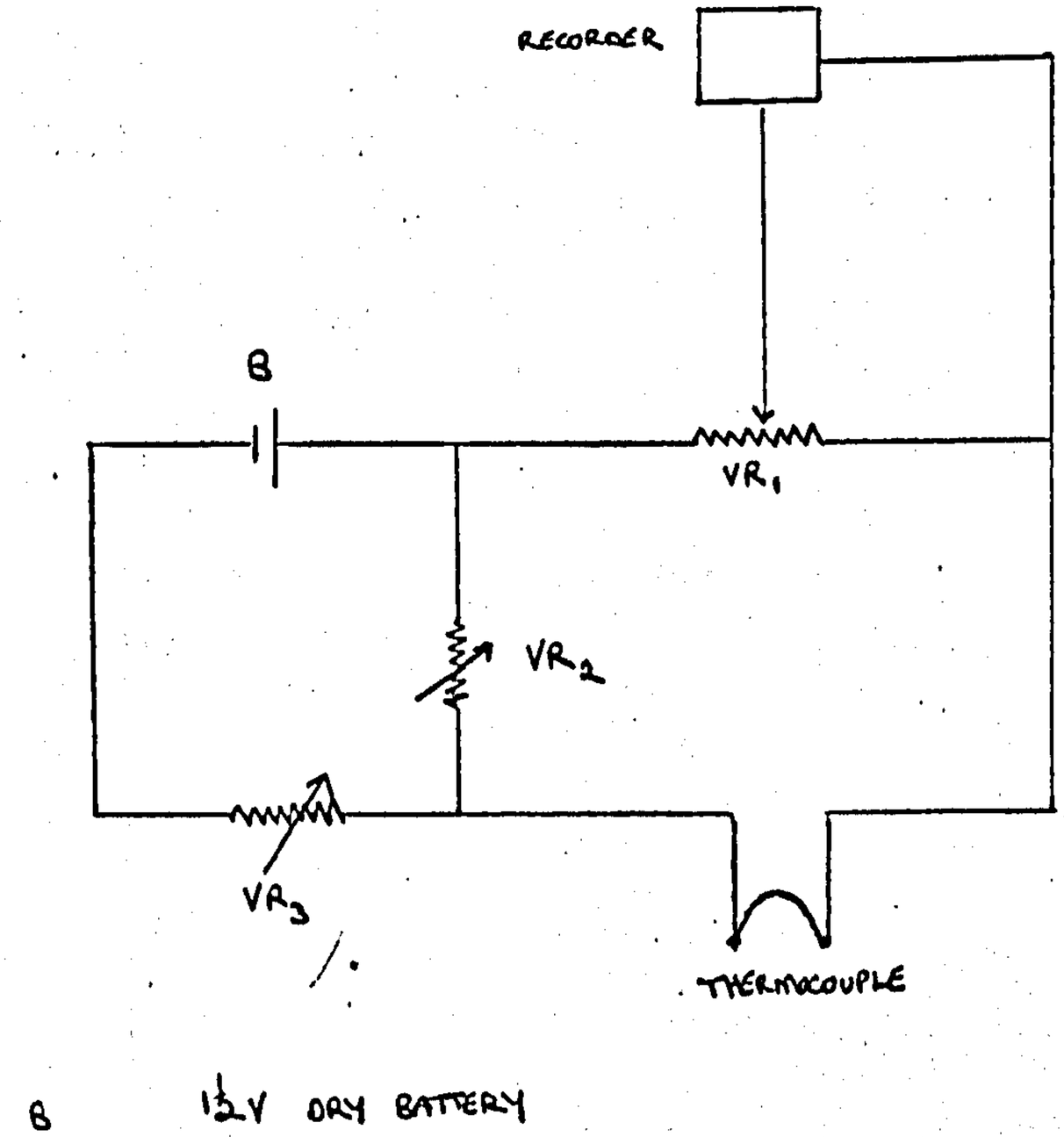
The calibration of a destructive detector can be carried out by placing the detector in parallel with the mass detector. The flame thermocouple detector has a sensitivity of similar order to the mass detector, so that by splitting the column effluent in approximately equal proportions, a reasonable response will be obtained from each detector. Ideally the ratio of the amounts of material reaching the two detectors will be in the ratio of the flow rates at the detectors. However it may arise that the split ratio is dependent on gas viscosity and hence will be different for different materials: it may also depend on the concentration of material. Such variations in split ratio will interfere with the calibration curve of the detector if it is to be subsequently used in the absence of a stream splitter. Using approximately equal split streams, and small concentrations of material in the carrier gas, and for materials of a similar nature, variations in split ratio should be negligible compared with the errors resulting from peak area measurements. The linearity of a flame thermocouple detector was determined using a 2:1 splitter, and the quantitative analysis of a two component mixture was carried out.

6.5a Experimental and Results.

The Pye Panchromatograph flame ionisation detector chamber was modified to take a flame thermocouple detector. The cold junction of the detector was maintained at room temperature, and placed in a large block of expanded polystyrene to minimise random temperature fluctuations. The output of the detector was fed directly to a 10 mV potentiometric recorder, without amplification. The standing thermocouple emf was backed off with a simple potential divider driven by a $1\frac{1}{2}$ V battery. For a temperature difference of about 800°C, the thermocouple emf is 8mV. A 1mV change in output represents a temperature change of 80°C. A circuit diagram is shown in figure 6.26. Operating conditions are given in table 6.9.

Figure 6,26

Control Unit for Flame Thermocouple Detector,



B 1½V DRY BATTERY

VR_1 . ATTENUATION - 1kΩ

VR_2 BACKING OFF - COARSE - 100Ω

VR_3 BACKING OFF - FINE - 10kΩ

Table 6.9

Apparatus	Pye Panchromatograph
Column	ApL A
Column temperature	50°C
Carrier gas	Nitrogen
Flow rate - major stream	60 ml min^{-1}
minor stream	33 ml min^{-1}
Sample sizes	0.2 µl to 3½ µl
Flame thermocouple -	
thermocouples	Pt - Pt/Rh
cold junction	23°C
Hydrogen flow rate	50 ml min^{-1}
Air flow rate	250 ml min^{-1}
Mass detector - ranges	1 mg to 5 mg
element	31b
temperature	23°C

A two component mixture was prepared (table 6.11) and analysed several times covering the mass range 200 µg to 2 mg per component, firstly with the major stream, and then with the minor stream to the flame thermocouple detector. For each set of runs a response curve of peak area against weight detected by the mass detector, was plotted (figure 6.27). In all cases the response of the flame thermocouple detector varied linearly with sample size. The response of the detector should be predictable on the basis of heats of combustion (section 3.3). For the materials analysed the heats of combustion were for practical purposes identical. The response curves for the two materials at each split ratio should therefore coincide if response is based solely on heats of combustion. Heats of combustion, and the slopes of the response curves, obtained from figure 6.27, are given in table 6.10.

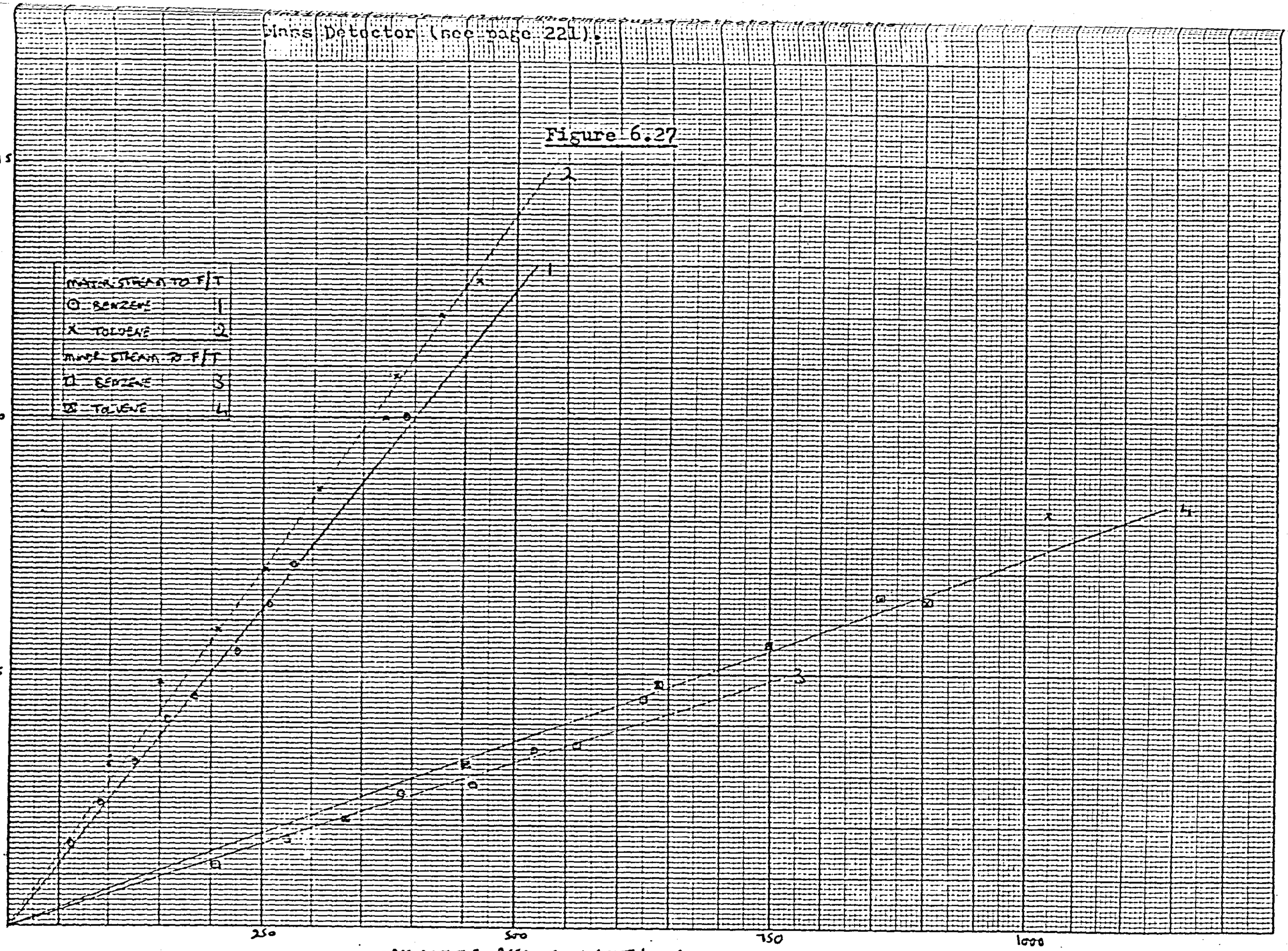
Table 6.10

Compound	Heat of Combustion (Kcal g^{-1})	Response (cm^2 μg^{-1}) Major stream	Minor stream
Benzene	10.02	0.013	0.032
Toluene	10.15	0.014	0.036

Since the streams were split, the slopes of the response curves do not represent absolute sensitivities. An estimate of the split

Linns Detector (see page 221).

Figure 6.27



ratio is given by the ratio of the flow rates at the two detectors and is 60/33, i.e. 1.82:1. The split ratio can be calculated from the ratio of the weight of injected material and the weight of material detected by the mass detector. A 1 µl sample of the mixture will contain 0.30 mg of benzene. With the major stream to the mass detector 0.20 g of benzene was detected, i.e. the split ratio is 2:1. The same value was obtained for toluene. This method relies on injection of a known amount of sample and no loss of material within the column. Since the detector gives a linear response with respect to concentration, an estimate of the split ratio for each material can be obtained from the response curves. Using figure 6.27, the response of the flame thermocouple detector for each material at the 500 µg level was found, and the split ratio calculated from the differences in response when the major and minor streams were interchanged: e.g. for 500 µg of benzene detected by the mass detector, with the major stream to the mass detector, and with a split ratio of n:1,

$$500\frac{(n+1)}{n} = 1.6\ (n+1)\ K$$

where K is a proportionality constant.

For the minor stream to the mass detector:

$$500\ (n+1) = 6.25\ \frac{(n+1)}{n}\ K$$

from which n = 1.98 i.e. the split ratio is 1.98:1.

For toluene n = 1.97 i.e. the split ratio is 1.97:1.

Thus the absolute sensitivity of the detector is 0.0065 $cm^2 \mu g^{-1}$ for benzene and 0.0070 $cm^2 \mu g^{-1}$ for toluene. The limit of detection (without amplification of the thermocouple output) is 5.9×10^{-5} mM ml^{-1} for benzene.

The percentage composition of the mixture of benzene and toluene was calculated directly from the ratios of the peak areas (corrected for heats of combustion) ($\bar{x}$ values). The composition of the mixture

was also estimated using the experimentally determined response factors ($\bar{x}_E$ values). The results are given in table 6.11.

Table 6.11

Compound	Mass Detector			Flame Thermocouple Detector		
	x_o	$\bar{x}$	V(%)	$\bar{x}$	$\bar{x}_E$	V(%)
Benzene	37.48	37.86	0.8	35.38	36.76	2.9
Toluene	62.52	62.14	-	64.62	63.24	-

More accurate results were obtained using the experimentally determined response factors rather than those based on heats of combustion. The coefficient of variation of the results was significantly greater than the mass detector results, and similar to the value obtained using the Martin gas density balance.

6.6 Calibration of A Flame Ionisation Detector.

The use of the mass detector for calibration purposes is not restricted to detectors of comparable sensitivity. It is possible, using a stream splitting device, to calibrate detectors of much greater sensitivity. To demonstrate this, a flame ionisation detector was calibrated. The conditions of operation are given in table 6.12.

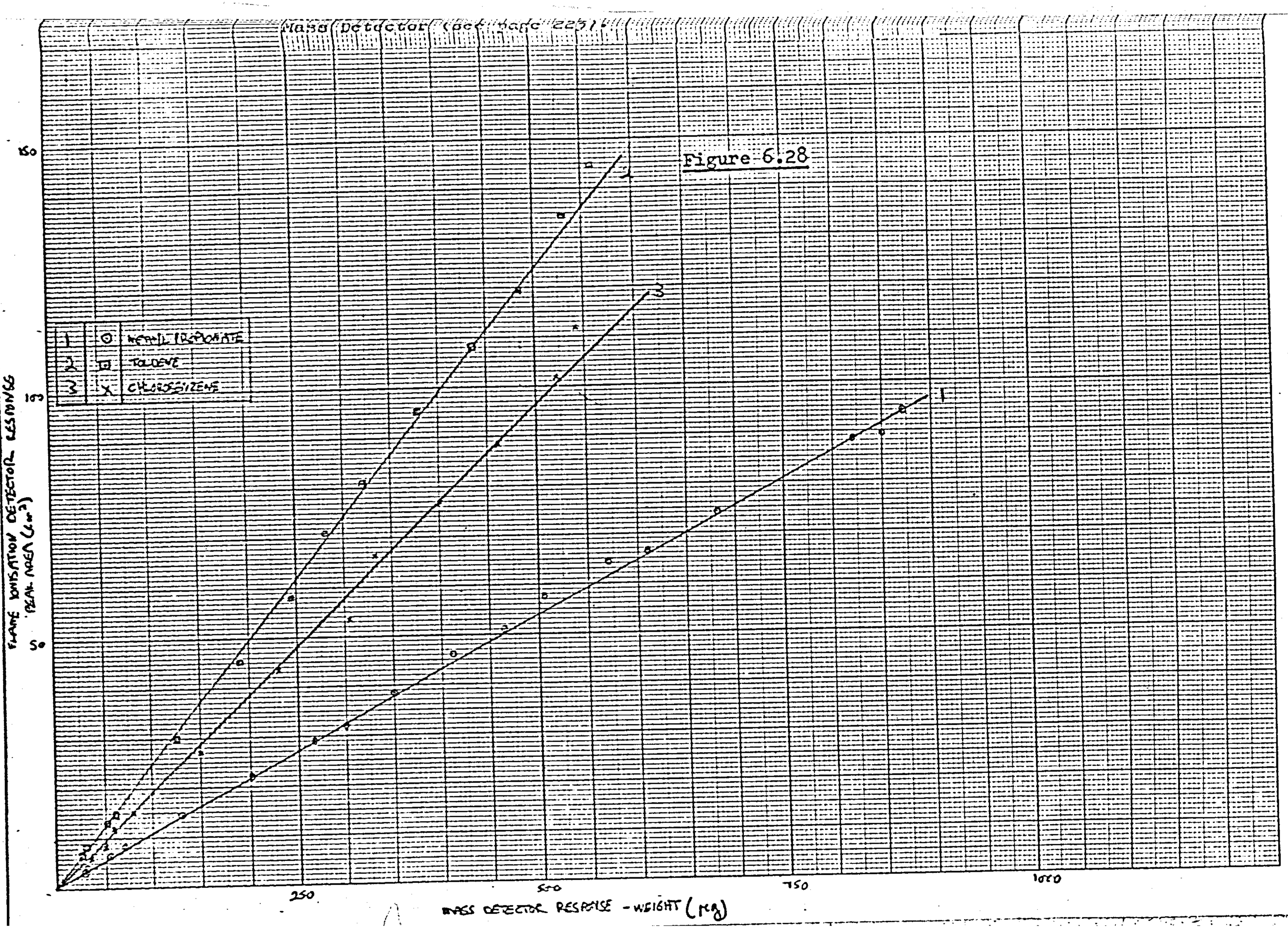
Table 6.12

Appartus	Pye Panchromatograph
Column	Car. 20M B
Column temperature	100°C
Carrier gas	Nitrogen
Column flow rate	48 ml min^{-1}
Flame ionisation detector:	
Voltage	50V
Hydrogen flow rate	50 ml min^{-1}
Air flow rate	250 ml min^{-1}
Sensitivity	10^{-9}, 10^{-8}
Mass detector:	
Element	31b
temperature	23°C.

The response of the detector toward methyl propionate toluene and chlorobenzene was determined: the results are illustrated on figure 6.28 as plots of peak area against weight detected by the mass detector. The response of the detector was linear over the whole range

Mass Detector (pack hand 2251)

Figure 6.28



investigated. From the slopes of the response curves, the response per unit weight for each material was found, and hence the response relative to one component as standard can be calculated. These values, together with the coefficients of variation (V) of the response factors are given in table 6.14.

The response factors must be corrected for the contribution of the stream splits if the detector is to be used in the absence of the splitter. Since the response for each material was linear, it follows that the splitting ratio remained constant over the concentration range covered, but was not necessarily the same for all the components in the mixture. The split ratio was determined for each compound individually, under conditions as near as possible to those used in the linearity experiment. The mass detector was connected firstly to the minor stream, and a number of injections of identical size made. The detector was then attached to the major stream and the experiment repeated. The split ratio was calculated from the mean value of the step heights in each experiment. The results are given in table 6.13.

Table 6.13

Compound	Mean detected weight (mg) Major stream	Minor stream	Ratio
Methyl propionate	6.928	0.1045	66.3:1
Toluene	6.249	0.0946	66.1:1
Chlorobenzene	8.428	0.1178	71.5:1

The response per unit weight obtained from the calibration curves (figure 6.28) can be corrected using the values given in table 6.13. The values are given below, and are compared with published response data (table 6.14).

Table 6.14

Compound	Response per unit weight ($cm^2 \mu g^{-1}$)	V(%)	Relative Response	Corrected Response	Published Response[3]
Methyl propionate	0.108	4.2	0.44	0.44	0.40
Toluene	0.247	3.8	1.00	1.00	1.00
Chlorobenzene	0.192	5.1	0.78	0.72	0.69

Comparison of the response factors with those quoted by Maggs[3] shows excellent agreement, especially since neither the detector nor the operating conditions were identical.

Using the response factors obtained from the calibration curves, the mean percentage composition of the mixture was calculated ($\bar{x}_F$ values) and compared with the results obtained from the mass detector ($\bar{x}_M$ values, see table 5.3).

Table 6.15

Compound	x_o	$\bar{x}_M$	$\bar{x}_F$	σ	V(%)	Bias
Methyl propionate	33.51	33.05	33.09	0.81	2.45	-0.42
Toluene	30.41	30.35	30.35	0.44	1.45	-0.06
Chlorobenzene	36.08	36.60	36.56	0.66	1.81	+0.48

The coefficient of variation of the absolute response (area per unit weight) for 45 determinations was 4.4%, and the coefficient of variation of the percentage composition was 1.9%. Very similar values were obtained with the Martin gas density balance (section 6.3a).

6.7 Conclusions.

The response of the Gow-Mac gas density balance, although predominantly a function of molecular weight, varies with chemical species and sample size. However the response of the Martin gas density balance is completely predictable on the basis of molecular weight changes, and has a wide linear dynamic range. The mass detector can be used as a rapid means of calibrating detectors of completely unpredictable response, and as an example a katharometer was calibrated. Although the responses of the flame thermocouple and flame ionisation detectors are linear over a wide concentration range, both detectors require calibration with respect to chemical species, and this can be conveniently carried out using the mass detector.

6.8 References.

1. Gow-Mac Bulletin No. GADE 3-63-2M.

2. Schmauch, L.J. Anal. Chem. 31 225 1959.

3. Maggs, R.J. Column 1 (2) 2 1966.

CHAPTER 7.

Applications of The Mass Detector II
The Determination of Molecular Weights.

7.1 Discussion.

An ideal procedure for the determination of the molecular weights of the constituents of a mixture would comprise the separation of the constituents by gas chromatography, and at the same time, the use of the detector response to determine the molecular weight of each component as it emerged. Present methods require pure and isolated materials: ebullioscopic and cryoscopic methods are straightforward, but give only moderate accuracy. Mass spectrometry gives very accurate results but demands expensive equipment. Using a gas chromatographic detector whose response depends solely on molecular weight, the accuracy of the method will depend on the accuracy to which peak areas can be measured (section 7.4). The response of several detectors is a function of molecular weight; namely the gas density balance, the jet stream detector (section 3.10), and the ultrasonic detector (section 3.15). The gas density balance has been used by several workers for molecular weight determinations[1-5,12] but no data have been published, using the remaining detectors.

The response of the gas density balance is given by the equation:

$$A = k\, q\, \frac{M_x - M_c}{M_x} \qquad 7.1$$

where q = amount of component x, M_x = molecular weight of x

A = peak area M_c = molecular weight of carrier gas.

The proportionality constant k, can be found by measuring the response to a known amount of a pure material of known molecular weight. By injecting under identical conditions a known amount of an unknown material, its molecular weight can be calculated, using equation 7.1. In practice this method is open to a number of serious objections. It is not possible merely to separate the constituents of a mixture in the gas chromatographic column, and to determine the molecular weight of

each component as it emerges, since values for q for each component are not known. Both the standard material and the unknowns are required in the pure isolated state. In addition it is particularly difficult to inject a known amount of material into the apparatus, and to ensure that no fraction is lost before reaching the detector. It is difficult to maintain precisely the same experimental conditions over the period of time required for calibration and subsequent analysis of unknowns. A satisfactory practical procedure for the determination of molecular weights using a gas density balance was first carried out by Liberti[2]. To an unknown material (possibly a mixture whose constituents can be resolved), is added a material of known molecular weight, M_s, and the mixture analysed in the conventional manner. For a two component mixture, two peaks of areas A_x and A_s, for the unknown and standard respectively, are obtained:

$$A_{x1} = k\, q_{x1}\, \frac{M_x - M_1}{M_x} \qquad 7.2$$

and

$$A_{s1} = k\, q_{s1}\, \frac{M_x - M_1}{M_s} \qquad 7.3$$

where M_1 = molecular weight of carrier gas 1.

The experiment is repeated using a carrier gas of different molecular weight, M_2, to give:

$$A_{x2} = kq_{x2}\, \frac{M_x - M_2}{M_x} \qquad 7.4$$

and

$$A_{s2} = kq_{s2}\, \frac{M_s - M_2}{M_s} \qquad 7.5$$

It is not essential to inject precisely the same quantity of the mixture in each series of runs since the ratio:

$$\frac{q_{x1}}{q_{s1}} = \frac{q_{x2}}{q_{s2}} \qquad 7.6$$

so that by combining equations 7.2 to 7.5:

$$\frac{A_{x1}\ (M_s - M_1)}{A_{s1}\ (M_x - M_1)} = \frac{A_{x2}\ (M_s - M_2)}{A_{s2}\ (M_x - M_2)} \qquad 7.7$$

The A values are obtained directly from the peak areas of the chromatograms, and all molecular weights are known except M_x, which can be calculated. Using nitrogen and hydrogen as the two carrier gases, molecular weights to about 4% of the true values were obtained for materials of molecular weight about 150[2]. Similar results were obtained by Revel'skii[3] using nitrogen and argon. In an attempt to improve upon the accuracy of the results, Parsons[4] used one carrier gas of molecular weight lower than the unknown, and the other carrier gas of molecular weight higher than the unknown, (e.g. nitrogen and dichlorodifluoromethane). Errors the order of 1-2% are quoted in the published data[4]. Molecular weight dterminations based on the Liberti scheme, although giving acceptable results suffer from the disadvantage that column conditions must remain constant for the duration of the two sets of runs, although it is no longer necessary to know the amount of sample injected, or to work with pure isolated materials. The need to change the carrier gas is tiresome, but is not regarded as a very serious disadvantage.

An alternative method for determining molecular weights using the gas density balance was devised by Phillips and Timms[5]. Equation 7.1 is rearranged and rewritten:

$$PV = \frac{KA}{M_x - M_c} \qquad 7.8$$

where P and V are the pressure and volume of a vapour x, and K a constant. Pressure-volume measurements are made on the vapour, which is then passed into a gas density balance. K is found using a material of known molecular weight. The method gives molecular weights, in general to within 1% of the true values, for materials of boiling point up to about 200°C. The P - V equipment requires considerable skill to operate and the determination of a single molecular weight is

fairly time consuming. Pure isolated materials are required. Preparative chromatography or other methods of purification must therefore be employed before molecular weight determinations can be carried out.

A chromatographic method for the determination of molecular weights based on the measurement of the increase in flow rate which occurs as a component emerges from a column was proposed by Scott[6]. The gas volume ΔV, occupied by m grams of solute vapour is given by the equation:

$$\Delta V = m \frac{K}{K+1} \cdot \frac{22.4 \times 10^3}{M} \cdot \frac{T}{273} \qquad 7.9$$

where K = partition coefficient

M = molecular weight of solute.

For a two component mixture, containing one material of known molecular weight, M_s:

$$\frac{\Delta V_s}{\Delta V_x} = \frac{M_x m_s}{M_s m_x} \qquad 7.10$$

provided that $K \approx K + 1$.

If the detector responds solely to flow rate changes:

$$\frac{\Delta V_s}{\Delta V_x} = \frac{A_s}{A_x} \qquad 7.11$$

where A_s and A_x are peak areas representing the standard and the unknown respectively. The molecular weight of the unknown is given by:

$$M_x = \frac{A_s m_x M_s}{A_x m_s} \qquad 7.12$$

It is essential to know the weights of the injected materials, which using syringe injection implies that the densities of the standard and unknown must be known. The assumption that $K \gg 1$ will give rise to negligible errors provided that retention times are long and similar for standard and unknown.

The flame thermocouple detector (section 3.3) is sensitive to

both flow rate changes and changes in temperature caused by the presence of an eluted material. These two effects can be isolated by preventing the material from reaching the detector. The detector will then respond only to flow rate changes. Scott used the following system to accomplish this effect. The exit of a normal partition column was attached to a length of empty tubing which itself was attached to a column containing activated charcoal. A substance on emerging from the partition column, produced a flow rate change which was detected as a positive peak by the flame thermocouple detector. On entering the adsorption column the material was totally adsorbed, resulting in a flow rate decrease, which was detected as a negative peak. By using the adsorption peak area rather than the partition peak area, the assumption that $K \gg 1$ is removed. Using the results quoted by Scott[6], the molecular weights of a number of materials determined by this method have been calculated, and are quoted in table 7.1.

Table 7.1

Compound	Detector Response (area/unit weight)	Molecular Weight Calculated	Molecular Weight True	Bias
n-Hexane (standard)	5.8	86.2	86.2	Standard
Carbon tetrachloride	3.2	156.2	153.8	+2.4
Chloroform	4.1	122.0	119.5	+2.5
Dichloroethylene	5.3	94.4	97.0	-2.6
n-Butyl chloride	5.3	94.4	92.7	+1.7
Ethyl acetate	5.6	89.3	88.1	+1.2
Ether	6.8	73.5	74.2	-0.7
Acetone	8.6	58.2	58.1	+0.1

Errors the order of 2% are encountered. On the assumption that the detector is responding only to flow rate changes, the major errors arise from the difficulty of injecting known weights of each material, and of measuring the resulting peak areas.

The requirement that the amount of injected material must be known (and hence densities known) is common to all of the detectors which can

be used for molecular weight determinations, and constitutes the major limitation and error source in the determination of molecular weights by gas chromatography.

It has been established that the mass detector will give reliable quantitative analyses over a wide range of operating conditions, and that response is proportional to mass. If the mass detector is operated in conjunction with a detector responding to molecular weight changes; then the amount of material present is obtained directly from the mass detector response. A knowledge of the amount of material injected, its density, and the percentage composition of the mixture is not required, and losses of material within the column do not affect the results. It was demonstrated by Bevan and Thorburn[1] that by using a gas density balance and the mass detector in series, the molecular weights of the constituents of an unknown mixture could be found in a single run. Two chromatograms are obtained: the mass detector will give values of q (equation 7.1) for each material, and the gas density balance the corresponding values of A: k is found by adding to the mixture a material of known molecular weight. It is not necessary to add a precisely measured amount of standard. The only requirement is the same for any conventional quantitative analysis, namely that resolution of the components should be complete. It would appear that the use of the mass detector in conjunction with the gas density balance offers an ideal method for the determination of molecular weights. There are however two factors which limit the versatility of the method:

(i) the calculation of a molecular weight depends on the accuracy with which a peak area and a step height can be measured, as with any other method involving gas chromatography detectors,

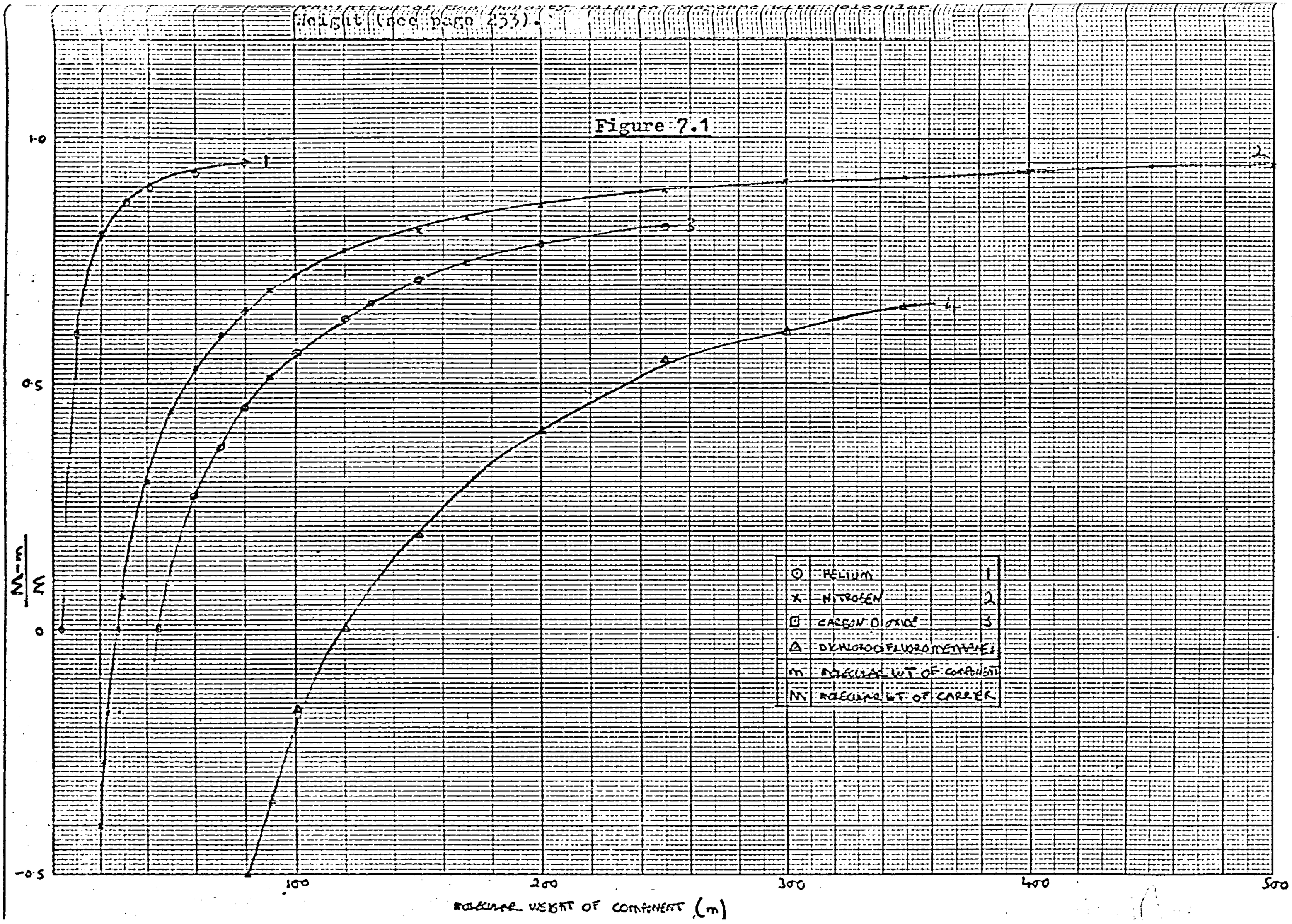
(ii) the change in response of the gas density balance for species of different molecular weight is a maximum when values of M_c and M_x (equation 7.1) are of the same order: but the absolute response of

the detector is a minimum when M_c and M_x are similar, and zero when they are equal. As the values of M_c and M_x diverge it becomes more and more difficult to distinguish between the responses of compounds of similar molecular weight; in the limiting case $(M_x - M_c)/M_x = 1$, and the molecular weight term disappears. The effect is shown graphically for a number of carrier gases covering the molecular weight range 4 to 121, on figure 7.1. It will not be possible to determine the molecular weight of a material with certainty if its molecular weight is at a point on or approaching the plateau of the curve. Consider the curve for nitrogen. It should be possible to determine the molecular weight of any material up to about 120, including values below that of nitrogen, but with decreasing certainty as the molecular weight increases. Over about 120, even a small discrepancy in the measurement of A, will result in an error in the value of $(M_x - M_c)/M_x$, and the error in M_x itself will be grossly magnified. Consider a peak area measured to within 6% of its true value. For a standard of molecular weight 80, the values obtained for an unknown of molecular weight 61, will lie between 57 and 65. Using the same standard and an unknown of molecular weight 150 the experimentally determined values will lie between 121 and 200, clearly an unacceptably wide variation. However if a carrier gas of comparable molecular weight is used (e.g. dichlorodifluoromethane, 121) the molecular weight of the unknown will lie between 149 and 154, which is a significant improvement.

For a detector to be of value for molecular weight determinations it is essential that the response depends only on molecular weight changes. It was established that the Gow-Mac gas density balance rarely gave a linear response over a wide concentration range, and even for a specific sample size, response was not wholly predictable on a molecular weight basis (section 6.2). On the other hand the Martin gas density balance was found to give a response predictable on a molecular weight basis over a wide concentration range for all

(see page 453).

Figure 7.1



materials investigated (section 6.3). The Martin gas density balance was therefore used in the present work.

The fall off in precision as molecular weight is increased, limits the value of the gas density balance - mass detector combination. Combination of the mass detector with the flame thermocouple detector operated as an anemometer overcomes this limitation, since although the response of the flame thermocouple decreases as molecular weight increases, it does so linearly and hence a marked fall off in precision does not occur. Using a combination of partition and adsorption to create flow rate changes, it would appear to be necessary to operate the two detectors in parallel. However the incorporation of a stream splitting device may interfere with the flow rate pattern as a material is eluted. Preferably, the two detectors should be operated without the need for a stream splitter. This could be accomplished by replacing the adsorption column with a second short partition column. Elution from the main partition column will give a positive detector response; the material is then partitioned on the second column, after which the gas stream is deflected to the mass detector, by means of a two-way tap. Such a procedure could only deal with widely separated components, and the condition that $K \gg 1$ must be satisfied.

An alternative method which would be satisfactory for multi-component mixtures is to trap all components on the adsorption column, and after completion of the run, place this column in front of the partition column, in a chamber sufficiently hot to quantitatively desorb all material; the run is repeated using the mass detector in place of the flame thermocouple detector.

A detector which functions solely as an anemometer would overcome these difficulties, and it is proposed that a Gow-Mac gas density balance, operated in the horizontal position would function as such a device. The mass detector could then be placed in series with the anemometer, using a single partition column to create a flow rate

change. Multicomponent mixtures could be analysed without difficulty.

7.2a Molecular Weight Determinations using the Martin Gas Density Balance.

The molecular weights of a number of materials have been determined using the Martin gas density balance in series with the mass detector. Operating conditions are given in table 7.2.

Table 7.2

Apparatus	Shandon KG2
Column	see table 7.3
Carrier gas	Nitrogen
Analytical gas flow rate	51 ml min^{-1}
Reference gas flow rate	51 ml min^{-1}
Gas density balance - filament current	1.9A
sensitivity	X10^3
Mass detector - ranges	1 mg 5 mg
elements	27, 30

The linearity of response of the gas density balance toward each sample was checked by covering a reasonable concentration range and plotting graphs of detector response (peak area) against the mass detector response (weight adsorbed). The molecular weight can be calculated from the slopes of the curves, since the slope gives A/q (equation 7.1) directly. However more precise values can be obtained by calculating the mean value of A/q.

Several two component mixtures were analysed, and the molecular weight of each component calculated assuming that the remaining component was the standard. The molecular weight values given in table 7.3 are the mean of about 10 determinations. Bias values are given in terms of molecular weight, and not as percentage error.

Table 7.3

Compound	Mean Molecular Weight	Std Deviation	True Molecular Weight	Bias
Water[a]	17.5	-	18.0	-0.5
Ethyl alcohol	43.8	-	46.1	-2.3
Water[a]	18.0	0.13	18.0	zero
Ethyl alcohol	46.1	0.63	46.1	zero
Methyl alcohol[b]	>28		32.0	$\bar{c}$ -2
Ethyl alcohol	52.9		46.1	+5.8
Ethyl alcohol[c]	45.2	0.61	46.1	-0.9
n-Propyl alchhol	62.3	1.70	60.1	+2.2
n-Propyl alcohol[c]	59.1	3.27	60.1	-1.0
n-Butyl alcohol	75.9	6.06	74.1	+1.8
Iso-propyl alcohol[d]	59.4	4.67	60.1	-0.7
Nitro-methane	61.8	5.22	61.0	+0.8
n-Propyl alcohol[c]	59.7	3.03	60.1	-0.4
Methyl n-propyl ketone	87.1	6.35	86.1	+1.0
n-Butyraldehyde[e]	70.8	7.29	72.1	-1.3
Methyl ethyl ketone	73.4	4.65	72.1	+1.3
Iso-propyl alcohol[d]	60.4		60.1	+0.3
n-Propyl alcohol	59.8		60.1	-0.3
Benzene[d]	76.5	2.41	78.1	-1.6
Toluene	94.7	4.57	92.1	+2.6
n-Heptane[f]	90.9	15.23	100.2	-9.3
n-Octane	128.4	24.25	114.2	+14.2
n-Heptane[d]	107.6		100.2	+7.4
n-Nonane	144.2		128.5	+15.7
n-Octane[f]	98.6	23.24	114.2	-15.6
n-Nonane	159.8	29.75	128.5	+31.3

a column D at 70°C
b column E at 70°C
c column D at 140°C
d column E at 101°C
e column E at 68°C
f column H at 106°C.

the variations of bias and standard deviation with molecular weight are shown on figures 7.2 and 7.3 respectively. Clearly accuracy and precision are inadequate over a molecular weight of about 100. In the region of 100, values are as good as those obtained by Liberti[2], and become progressively better as molecular weight decreases.

For a relative composition analysis using the gas density balance, the molecular weight of the components of the mixture must be known. The analysis of mixtures containing free fatty acids cannot be carried out using correction factors based on simple molecular weights, since the lower members of the series dimerise. The degree of dimerisation is dependent on temperature and pressure, so that the correction factors will depend on the conditions under which the analysis is carried out. The molecular weight of formic acid was estimated using water as a standard, and under the same conditions the percentage composition of a formic acid - acetic acid mixture was calculated. The results are given in table 7.4.

Table 7.4

Compound	Observed Molecular Weight	Monomer Mol. Weight	x_o	$\bar{x}_M$	$\bar{x}_D$
Water (standard)	18.0	18.0	-	-	-
Formic acid	54.8	46.0	-	-	-
Formic acid	54.8	46.0	62.04	60.79	56.74
Acetic acid	82.2	60.0	37.96	39.21	43.26

The mass detector gives excellent quantitative results, but the gas density balance results are only fair.

Molecular Weight Determinations of Multicomponent Mixtures.

An advantage of the determination of molecular weights by gas chromatography is that pure isolated materials are not required. The analysis of multicomponent mixtures therefore represents a more realistic situation than the analysis of a two component mixture in which one material is the added standard.

The precision of molecular weight determinations using the Gas Density Balance and Mass Detector (see page 237).

Figure 7.2

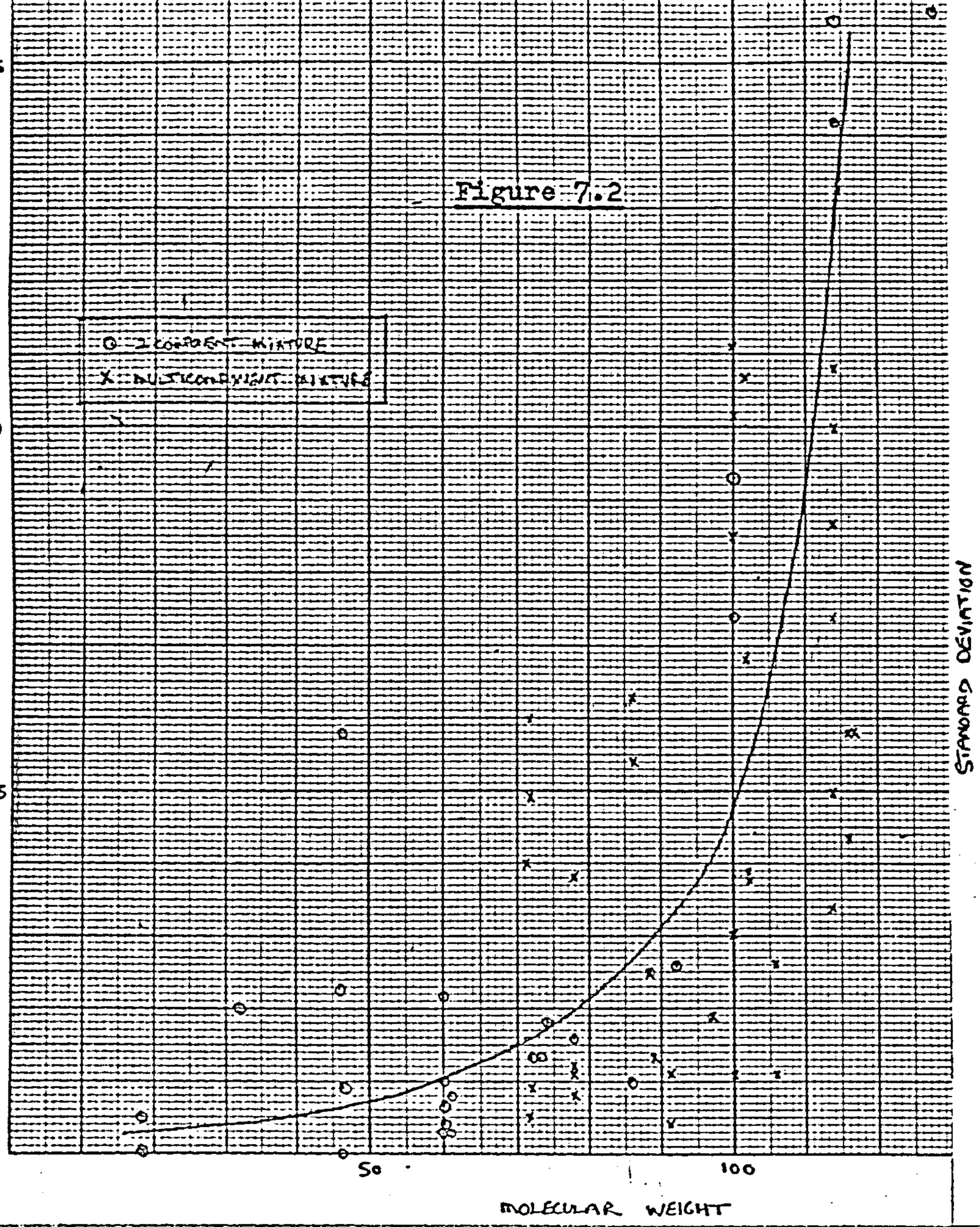
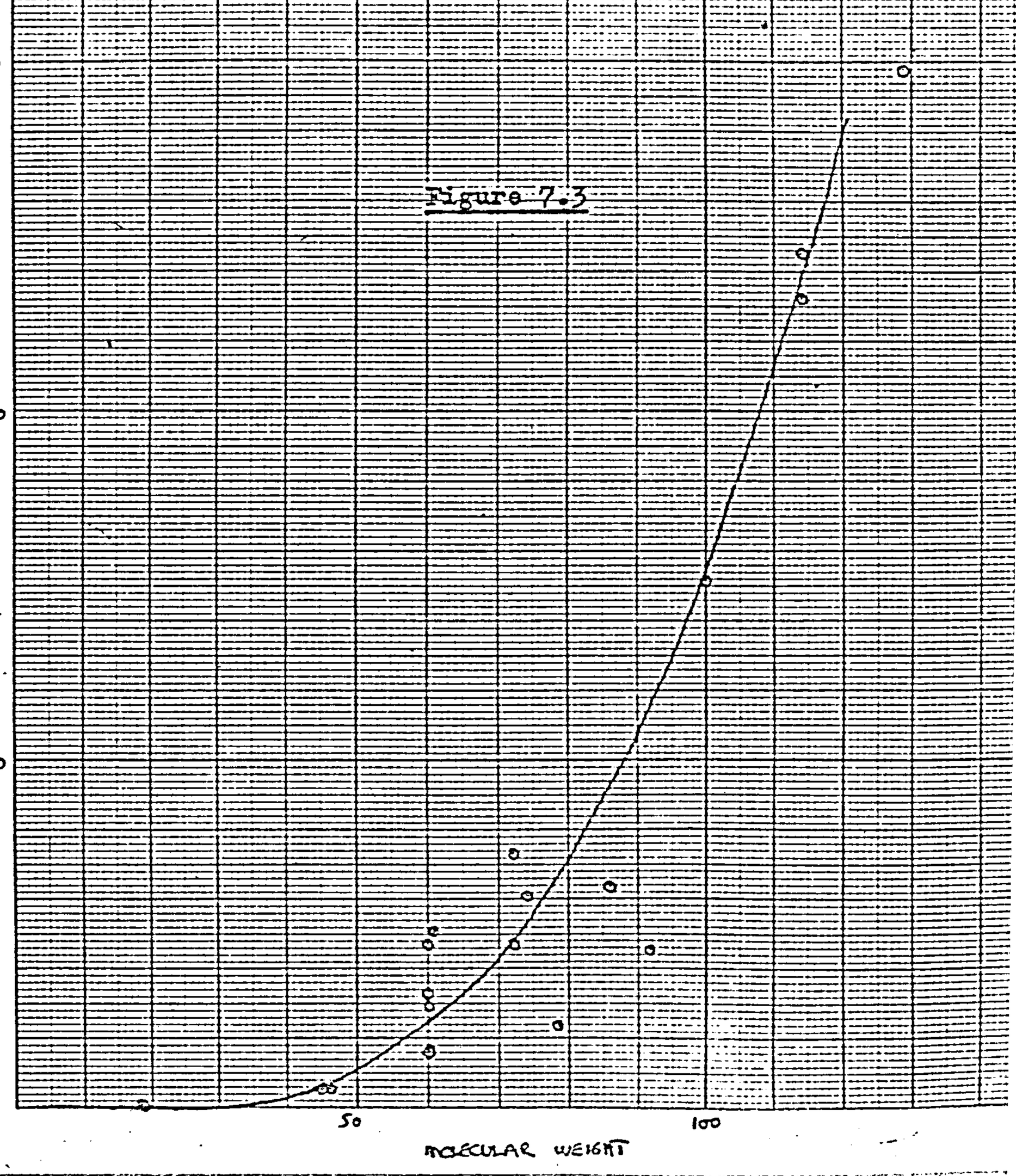


Figure 7.3



For the multicomponent mixtures, listed in table 7.5, each component in turn was taken as the standard, and the mean molecular weight of all the remaining constituents calculated. Thus for an n component mixture, there will be n standards and n - 1 values for the mean molecular weight of each component. It is not valid to calculate the mean of the (n - 1) molecular weights, to give a single value, since the different standards used to calculate the values, all have different molecular weights themselves, and hence fall on different parts of the curve shown in figure 7.1.

Table 7.5

Compound		True Molecular Weight	Mean Detected Molecular Weight 1	2	3	4	5
Cyclohexane	1	84.2	-	82.9	86.7	105.6	
Dichloroethylene	2	97.0	98.9	-	102.7	132.9	
n-Octane	3	114.2	109.3	106.9	-	154.8	
Carbon tetrachloride	4	153.8	108.9	106.5	113.6	-	
Benzene		78.1	-	78.9	79.2		
Toluene		92.1	91.0	-	92.5		
Ethyl benzene		106.2	103.7	105.1	-		
Methyl ethyl ketone		72.1	-	77.0	72.6		
Methyl n-propyl ketone		86.1	79.8	-	80.5		
Methyl n-butyl ketone		100.2	99.1	110.4	-		
Methyl ethyl ketone		72.1	-	71.2	65.7	68.1	69.1
Benzene		78.1	79.3	-	71.2	74.3	75.6
Ethyl acetate		88.1	102.7	100.5	-	93.5	75.8
n-Heptane		100.2	111.3	108.7	94.0	-	103.0
n-Octane		114.2	125.0	121.6	102.9	110.8	-
Ethyl acetate		88.1	-	93.8	90.5		
n-Propyl acetate		102.1	95.3	-	98.2		
n-Butyl acetate		116.2	111.9	122.0	-		
Ethyl acetate		88.1	-	82.1	79.8		
n-Propyl acetate		102.1	112.8	-	98.3		
n-Butyl acetate		116.2	138.6	122.0	-		

Compound	True Molecular Weight	Mean Detected Molecular Weight 1	2	3	4	5
Butylene oxide	72.1	-	63.4	66.1		
Dioxan	88.1	110.8	-	94.8		
n-Octane	114.2	140.4	104.1	-		

The variation of bias with molecular weight is shown on figure 7.2. For all materials of molecular weight below 100, the results are reasonably satisfactory. The method does not yield sufficiently accurate results over this value; e.g. the results for carbon tetrachloride, (row 4), and using carbon tetrachloride as standard (column 4) are completely unsatisfactory.

There is no significant decrease in the precision and accuracy of the molecular weights of the multicomponent mixtures compared with the two component mixtures.

7.2b High Molecular Weight Carrier Gases.

It was established in the preceding section that the use of nitrogen as a carrier gas can only yield satisfactory molecular weight values up to about 100, and above this a carrier gas of significantly higher molecular weight must be used. Any gas should be suitable provided it is chemically inert and non-toxic. It must also be readily available and not expensive. Several gases, listed in table 7.6 fulfil at least some of these conditions.

Table 7.6

Compound	bp °C	mp °C	Critical Temp. °C	Molecular Weight
Dichlorodifluoromethane	-30	-158	112	120.9
Chlorotrifluoromethane	-81	-181	29	104.5
Chlorodifluoromethane	-41	-160	96	86.5
Sulphur hexafluoride	-63	sublimes	46	146.1

For satisfactory operation in conjunction with the mass detector, additional conditions must be fulfilled.

(i) physical adsorption must predominate,

(ii) the boiling point must be very low, compared with the boiling points of the materials under analysis.

(iii) the carrier gas must not interfere with the adsorption of the eluted materials.

A satisfactory gas would appear to be dichlorodifluoromethane, which is readily available as a liquified gas[9].

The amount of dichlorodifluoromethane adsorbed by active charcoal at 15°C, was estimated, from published data[10], to be 513 mg g^{-1}. A similar estimation for nitrogen at 15 °C gave 6 mg g^{-1}. The uptake of dichlorodifluoromethane by the charcoal used for mass detecting elements was 600 mg g^{-1}. Since this is significantly greater than nitrogen, and is the same order as the materials under analysis, it is likely that the presence of dichlorodifluoromethane as a carrier, may interfere with the adsorption process.

Prior to entering the chromatograph, the dichlorodifluoromethane was dried by passing through a 4A molecular sieve. Dichlorodifluoromethane is slightly toxic and precautions were taken to prevent the gas entering the atmosphere on leaving the mass detector: the outlet from the detector chamber was fed to a cold trap at -70°C, attached to a water pump.

Experiments to establish satisfactory operating conditions using the Martin gas density balance in the absence of the mass detector, were carried out. Using a mixture of n-heptane and n-octane, peak splitting readily occured, but satisfactory response was obtained by a suitable choice of conditions. The mass detector was incorporated into the system. Air was swept from the detector chamber by a continuous flow of the gas, in addition to that reaching the chamber as carrier gas. The analysis of the two component alkane mixture produced a most unexpected result: the elution of each component was detected as a weight decrease, indicating displacement of adsorbed carrier gas by the new adsorbate. If simple displacement occurs, the use of an adsorbate of higher molecular weight than the carrier, should result in a weight increase. The analysis of n-nonane and n-decane, also resulted in a weight decrease, so that the displacement cannot be

a simple function of molecular weight. Several other compounds were analysed, and the results compared with the weight increases observed when nitrogen was used as carrier gas (table 7.7).

Table 7.7

Compound	Molecular Weight	Weight Change (µg) CCl_2F_2	Weight Change (µg) N_2
n-Pentane	72.2	-227.7	-
n-Hexane	86.2	-226.1	+420.2
n-Heptane	100.2	-201.2	+451.9
n-Octane	114.2	-197.4	+489.4
n-Nonane	128.3	-77.6	+515.4
n-Decane	142.2	-157.8	+551.6
Benzene	78.1	-130.4	+549.2
Toluene	92.1	+100.0	+59.1
o-Xylene	106.2	+64.3	-
p-Xylene	106.2	+71.4	-
Chlorobenzene	112.6	+175.7	+714.7
Iodobenzene	204.0	+398.2	+975.0
Carbon tetrachloride	153.8	+238.0	+762.0

Although the basic mechanism is that of displacement, it is a function not only of molecular weight, but of the area occupied by the adsorbate and the critical temperature of the adsorbate, in relation to these values for the carrier gas. Consider an adsorbate of lower molecular weight than the carrier, and having a similar critical temperature. A weight decrease will occur if the cross-sectional areas of the two molecules are similar, since one molecule of carrier will be replaced by one molecule of the new adsorbate. However if the area of the molecule is greater than a carrier gas molecule, then several carrier molecules will be replaced by one new adsorbate molecule, again resulting in a weight decrease. If on the other hand, the molecular cross-sectional area of the new adsorbate is smaller than the carrier, then several adsorbate molecules will replace one carrier molecule, and there may be a weight increase. To predict response on the basis of such a mechanism, requires an extensive knowledge of the nature of the adsorbates. A calculation of the expected response of the detector to carbon tetrachloride,

neglecting the critical temperature contribution, gives the value of 163 μg: the experimental value was 238 μg. The use of dichlorodifluoromethane as a carrier gas for molecular weight determinations is clearly unsatisfactory. However by using a mixture of dichlorodifluoromethane and nitrogen as carrier, response based solely on the weight of eluted material may occur if the dichlorodifluoromethane is in a sufficiently small proportion. The advantages of using a high molecular weight carrier gas for the gas density balance are maintained by introducing the nitrogen supply at the gas density balance outlet. The effects of such a combined carrier gas, on the mass detector were investigated. Buoyancy effects were separated from adsorption effects by running two series of experiments, one with a conventional lined detecting element and the other with an unlined element. The detecting element was saturated with dichlorodifluoromethane, after which nitrogen was introduced in varying proportions. The continuous passage of nitrogen resulted in a weight decrease (see table 7.8) in all cases, indicating that nitrogen was adsorbed in preference to dichlorodifluoromethane. Adsorption sites should therefore be available for adsorption of other materials without the need to displace dichlorodifluoromethane.

Table 7.8

Flow Rate (ml min^{-1}) CCl_2F_2	N_2	Ratio	Weight change mg
28	-	-	(20.9)
28	28	1:1	-2.54
28	60	1:2.1	-3.48
28	122	1:4.4	-4.73
28	288	1:10.3	-6.82
-	288	-	-8.50

A mixture of n-nonane and n-decane of known composition was analysed using the carrier gases mixed in various proportions. The results are given in table 7.9.

Table 7.9

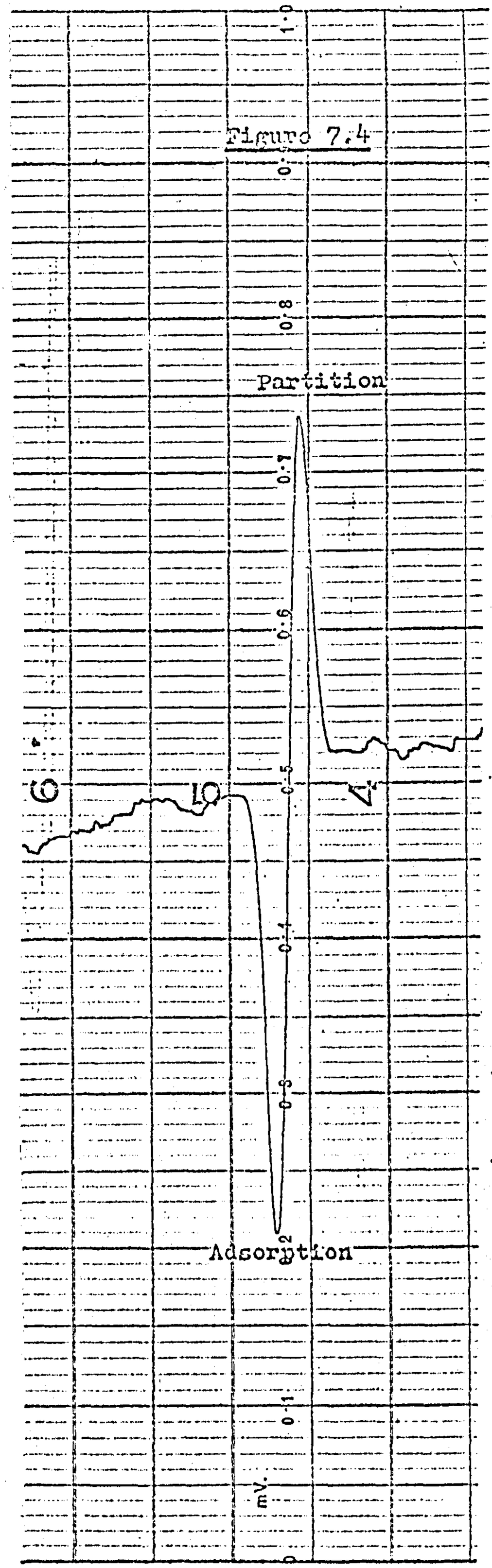
Flow Rate (ml min^{-1}) CCl_2F_2	N_2	Ratio	% Weight of n-nonane	Bias
29	54	1:1.9	23.12	-9.5
29	107	1:3.7	29.92	-2.7
29	154	1:5.3	31.92	-0.7
True value→			32.58	

A satisfactory response based predominently on the weight increase due to adsorption of the alkanes is obtained when nitrogen forms the major proportion of the gas mixture. Such a system may therefore be satisfactory for molecular weight determinations, although no experiments were carried out to confirm this.

7.3 Molecular Weight Determinations using The Flame Thermocouple Detector.

The work was limited to a number of preliminary experiments of an exploratory nature to determine suitable conditions for molecular weight determinations.

A Pye Panchromatograph was fitted with a Pt-Pt/Rh flame thermocouple detector (see section 6.5a) and the output fed directly to a 10 mV potentiometric recorder. The chromatograph was fitted with a partition column (ApL ref. G) and an adsorption column (charcoal ref. I) after the method described by Scott[6]. An empty column (8m x 1½ mm) was placed between these two columns to induce a time lag between partition and adsorption. Using 20 µl samples of n-hexane, well defined partition and adsorption peaks were observed, but they were insufficiently large for accurate peak area measurements. The sample size could not be increased without overloading the partition column. No significant improvement in sensitivity resulted by changing the thermocouple position with respect to the flame, or by changing the hydrogen and air flow rates. An amplifier with a maximum gain of about 50 was constructed and used in conjunction with the thermocouples. Noise was excessive at all amplifications, and peak area measurement could not be attempted.



Chromatogram showing the Response of the Flame Thermocouple Detector (see page 244).

The thermocouples were replaced by iron-constantan thermocouples, which will give a sensitivity increase of 5 mV per °C at about 800°C. Reasonable peak heights were observed for 5 µl charges of n-hexane and n-heptane, but the detector was noisy, and accurate peak area estimation was not possible (figure 7.4).

It was concluded that the detector will respond to flow rate changes most satisfactorily when a Pt-Pt/Rh thermocouple is used, without amplification, provided that a partition column of high capacity is used. The method offers promise, but a considerable amount of work is necessary before it can be regarded as better than the gas density balance, or gas density balance/mass detector methods for molecular weight determination.

Mention has been made previously of the possibility of operating the Gow-Mac gas density balance in the horizontal position to obtain a response dependent solely on flow rate. The Pye Panchromatograph was fitted with a gas density balance in the horizontal position and 10 µl samples of n-hexane were injected. A very small response was observed which may be attributed at least in part to inaccurate levelling of the detector. However, by changing the reference or analytical flow rate by even a few ml min^{-1}, significant response was obtained. Further amplification of the detector output, or the use of larger sample sizes may produce a measurable response.

7.4 The Measurement of Peak Areas and Step Heights.

In Chapter 1 the measurement of the peak areas obtained from a differential detector was discussed. A number of different methods of determining peak areas were described, and the limitations of the various methods noted. For quantitative analysis it is essential to measure peak areas with good accuracy and precision. In the present chapter it has been established that the value of the technique of determining molecular weights using the gas density balance and mass detector relies to a greater and greater extent on the ability to

measure peak areas accurately as molecular weight increases.

A study was undertaken to compare the reliability of measurement of peak areas by the methods commonly regarded as the most satisfactory, namely peak weight, and peak height x width at ½ height measurements. In addition the results using a digital and mechanical integrator are assessed. Since the main purpose of the experiment was to select the most satisfactory method for use in molecular weight determinations, the study was limited to completely resolved peaks, and peaks where only a small amount of distortion was observed. It is necessary to separate effects not caused by errors in area measurement. The results must be independent of errors caused by syringe delivery etc. This can be accomplished by injecting nominally the same amount of material of a two component mixture several times, and expressing peak areas as percentage composition. The true composition of the mixture is not required to calculate the standard deviation of the results (precision), but it is required to find the bias (accuracy). The accuracy and precision of step height measurements, using the mass detector were measured using the same procedure.

7.4a Experimental.

A sample was prepared of composition 44.94% by weight of n-propyl alcohol and 55.06% methyl n-propyl ketone. The Martin gas density balance was used, the output of which was connected to a potentiometric recorder in the usual manner, and in addition to a digital integrator[11]. A total of 31 runs were performed, each using a nominal sample size of 3 µl. The peak areas of all these runs were calculated from peak height and width measurements, and the results are given in table 7.12. Peak heights, and step heights were of the order of 5 cm. The areas of 14 of the runs were measured by the digital integrator used in the conventional manner. In this mode the integrator cannot begin counting until there is a finite baseline shift, which was set for this experiment at 0.5% fsd. The integrator will not take into account any fraction

of the peak area below this value. This is insignificant for symmetrical peaks, but could lead to a substantial error in the case of a peak exhibiting a long tail. This mode also relies on a completely stable baseline throughout a run, and any drift in baseline above the 0.5% level will contribute to the peak areas. 15 of the runs were carried out using the integrator in a different mode. The integrator was set above the zero count position when no signal was received from the gas density balance, and by means of a micro-switch printed out the number of counts at fixed intervals of time. It is thus possible to follow any drift in baseline by observing the change in count rate when no components are being eluted. On elution of a component the count rate of the integrator will change in the normal manner, but it will continue to print out at the same time interval. The peak area is obtained from the sum of the counts, above the zero signal count rate. The method has several advantages over the conventional operating procedure:

(i) detector baseline drift and integrator zero drift can be taken into account in peak area calculations,

(ii) there is no threshold below which the integrator does not count,

(iii) the integrator will count negative peaks without the need for a signal polarity reversal switch, provided that the zero count rate is set sufficiently high. In the conventional operating mode the integrator will not count negative peaks, and a polarity reversing switch can only be used satisfactorily if peaks are well separated.

The device used to trip the print-out mechanism of the integrator at fixed time intervals was made in the laboratory. To the shaft of a synchromous motor, geared to give a speed of rotation of 2 r.p.m. at 50 cycles sec^{-1}, was attached a Meccano wheel of $2\frac{1}{2}$" diameter. Near the circumference of the wheel was attached at equal distances apart, small protrusions made from 4BA screw heads. A wiping contact was positioned such that each screw head in turn was touched by the

wiper as the wheel rotated, thus momentarily completing an electrical circuit and causing the integrator to print. With 4 contacts spaced at intervals of 90^{o}, print out will occur every $7\frac{1}{2}$ sec. Provision was made for print out at other time intervals by changing the number of contacts, and by using a 1 r.p.m. motor. For the device to be satisfactory the following conditions must be fulfilled:

(i) mains frequency must not fluctuate significantly,

(ii) the distance between each contact must be identical,

(iii) the wiper must always make contact at the same point on each head.

The performance of the device was checked by timing 10 contacts starting at each contact point in turn. The results are given in table 7.10.

Table 7.10

Contact No.	Time for 10 contacts (sec)	Time per contact (sec)
1	74.8	7.48
2	74.9	7.49
3	75.0	7.50
4	75.0	7.50
1	75.1	7.51
2	75.1	7.51

The performance was regarded as satisfactory.

The peak areas of 15 of the runs were obtained by cutting out the peaks and weighing them on an ordinary laboratory 4-place balance. The repeatability of weighing a single peak was measured: no variation of results measured to 0.1 mg (1% of the total weight) was observed. The variation of weight of the chart paper over the length containing the runs was measured, by cutting out small squares of equal size, about the weight of a typical peak. The results are given in table 7.11.

Table 7.11

No. of Squares	Mean Weight mg	σ mg	V %
6	12.00	0.36	3.0
6	11.62	0.21	1.8

Variations in chart speed during a run will affect peak areas obtained by all methods except the digital integrator: no measurable variations in chart speed were observed, and the accuracy of the speed on each setting was excellent.

The performance of a ball and disc integrator[7] was assessed. The integrator was attached to a potentiometric recorder, and a similar mixture to that used above was analysed using a Pye 104 chromatograph fitted with a flame ionisation detector. The results are given in table 7.12.

Data published by Scott and Grant[8] have been recalculated in the form used in the present work and are given at the foot of table 7.12.

Table 7.12

Method of Area Measurement	n	$\bar{x}$	σ	V	% Bias
Peak width and height	31	43.41	1.4	2.9	3.4
Peak weight	15	44.90	2.1	4.7	0.1
Digital integrator - conventional mode	14	45.12	1.2	2.5	0.4
fixed interval print out	15	46.20	1.1	3.0	2.8
Step height (mass detector)	8	45.36	0.9	2.0	1.0
Disc integrator	18	45.54	1.0	2.2	3.0[a]
Peak width and height[8]	20	23.37	0.28	1.2	
Triangulation[8]	20	22.56	0.60	2.7	
Planimetry[8]	16	23.49	1.23	5.2	

n = No. of determinations.

$\bar{x}$ = mean % weight of n-propyl alcohol.

a = assumes equal detector response for both constituents of the mixture.

7.4b Peak Area Measurements - Conclusions.

The most satisfactory peak area measurements were obtained using the digital integrator, but contrary to expectations, better results

were obtained using the integrator in the conventional mode. The peak areas under study were "typical" rather than ideal peaks. For a very broad and low peak it would be expected that the results obtained using the integrator conventionally would become poorer, but that the performance of the integrator using the fixed interval print-out technique would be unaffected. A similar result would occur for a peak with a long tail, irrespective of its height. The precision of the results obtained using the ball and disc integrator was equally satisfactory. Peak weight determinations gave a very accurate result, but the coefficient of variation was high due in part to variations in paper weight (table 7.11). The mass detector gave results as good as the best peak area results.

7.5 Conclusions.

The mass detector can be used in conjunction with a Martin gas density balance to obtain the molecular weights of the components of a mixture in a single run, but the method is only satisfactory for molecular weights up to about 100, when nitrogen is used as carrier. To increase this limit, dichlorodifluoromethane was used as carrier, but the response of the mass detector was not a simple function of the weight of material eluted. Preliminary experiments with a flame thermocouple detector indicated that combination with the mass detector would enable molecular weights to be determined without the limitations of the gas density balance/mass detector combination, provided a sufficiently large sample could be used. The determination of molecular weights relies on accurate peak area determination. The most satisfactory results were obtained using digital and ball and disc integrators.

7.6 References.

1. Bevan, S.C., Thorburn, S. Chem. Brit. 2 206 1966.

2. Liberti, A. et al. Nature 178 1067 1956.

3. Revel'skii, I.A. et al. Neftekhimiya (Pergamon Press translation) 4 296 1965.

4. Parsons, J.S. Anal. Chem. 36 1849 1964.

5. Phillips, C.G.S., Timms, P.L. J. Chromatog. 5 131 1961.

6. Scott, R.P.W. Anal. Chem. 36 1455 1964.

7. Series 200 Disc Integrator, Disc Instruments Ltd., Hemel Hempstead.

8. Scott, R.P.W., Grant, D.W. Analyst 89 179 1964.

9. e.g. available in cylinders at c̄ 60 lb in^{-2} from I.C.I. Ltd.

10. Purnell, J.H. Gas Chromatography p 14 published by Wiley 1962.

11. Honeywell Precision Integrator, Honeywell Controls Ltd., London.

12. Walsh, J.T., Rosie, D.M. J. Gas Chromatog. 5 232 1967.

APPENDIX.

The mass detector has been used on several post graduate courses in chromatographic techniques. Quantitative analysis of synthetic mixtures using the mass detector has been compared with the results obtained from conventional detectors using the same mixtures, by the participants of these courses. The results are summarised in the tables below. Each analysis was only carried out once, and the tables are composed of the results of 12 operators.

Percentage Composition

	Detector Apparatus Method	Mass Pan[b] Step ht.	F/I 104[c] Area[a]	F/I 104 Peak wt.	F/I 104 Disc	GDB Pan Area
Compound	True comp.					
n-Nonane	33.2	33.0	33.5	34.1	32.6	32.3
n-Decane	27.3	27.9	27.5	28.2	27.9	27.6
n-Undecane	39.5	39.1	39.0	37.7	39.5	40.1

		F/I Fl1[d] Digit.	F/I 104 Area	F/I 104 Peak wt.	F/I PV4000[e] Area	F/I PV4000 Triang.
n-Nonane	33.2	30.1	32.6	30.3	34.2	33.5
n-Decane	27.3	29.6	27.2	29.3	26.9	27.3
n-Undecane	39.5	40.5	40.2	40.4	38.8	39.3

		F/I Fl1 Digit.	F/I Fl1 Area	F/I Fl1 Wt.	F/I PV4000 Area	F/I PV4000 Triag.
n-Octane	30.36	28.90	28.6	29.65	33.1	31.0
n-Nonane	31.30	31.64	31.8	31.52	30.7	29.9
n-Decane	38.34	39.44	39.6	39.13	36.2	39.1

		Mass Pan Step ht.	F/I 1520[f] Digit.	F/I 104 Disc
n-Heptane	24.46	27.8	27.55	24.3
n-Octane	70.00	68.8	60.30	70.0
n-Nonane	5.42	6.3	12.40	5.5
n-Heptane	5.06	5.30	7.69	5.03
n-Octane	37.30	37.60	34.20	37.0
n-Nonane	57.70	57.20	58.30	58.0

Percentage Composition

	Detector Apparatus Method	Mass Pan Step ht.	F/I 1520 Digit.	F/I 104 Disc	F/I PV4000 Triang.
Compound	True comp.				
n-Heptane	34.9	32.4	26.55		
n-Octane	42.0	43.2	39.75		
n-Nonane	23.1	24.4	33.70		
n-Heptane	57.2	55.2	33.85	56.5	
n-Octane	7.15	7.2	7.28	6.8	
n-Nonane	35.65	37.7	53.5	36.5	
n-Heptane	41.4	40.7			
n-Octane	28.5	29.4			
n-Nonane	30.1	30.1			
n-Heptane	24.76	24.85			
n-Octane	70.00	68.80			
n-Nonane	5.42	6.30			
n-Heptane	39.4	39.6			38.9
n-Octane	25.0	25.4			24.6
n-Nonane	35.6	35.0			36.3

		Mass Pan Step ht.	F/I 104 Triang	GDB Pan Digit.	Kath. 104 Peak wt.	Kath. 104 Triang
Benzene	24.0	23.4	26.5	23.8	23.5	23.7
Toluene	23.2	23.4	26.2	22.2	22.8	22.4
Chlorobenzene	52.8	53.3	47.3	54.0	53.7	54.0

		F/I 104 Digit.	F/I 104 Area	F/I 104 Peak wt.	F/I 104 Triang	F/I 104 Planim.
n-Pentane	22.5	18.4	16.6	20.2	16.1	17.4
n-Hexane	17.6	16.6	15.4	17.4	16.4	16.5
n-Heptane	14.6	15.6	14.1	16.2	15.4	15.4
n-Octane	16.5	17.6	18.8	16.8	18.8	17.9
n-Nonane	28.8	31.3	33.6	29.8	33.4	33.2

a peak area from peak height x width at half height

b Pye Panchromatograph

c Pye 104

d Perkin Elmer F11

e Philips PV4000

f Wilkens 1520

The mass detector gave satisfactory quantitative analysis for all mixtures. Results using the disc integrator were excellent, but the digital integrator results were rather variable. Manual peak area results were acceptable for all runs.

The mass detector is in use at the Laboratory of the Government Chemist and is discussed in the Laboratory Report for 1964 (pp 72/3).

The mass detector forms the subject of patent No. B.P.982,500, and other patents are pending.

ACKNOWLEDGEMENTS.

The Author would like to thank Philips Chromatography Ltd. for a generous award, enabling him to undertake this work.

The Author expresses his gratitude to his Supervisors, Dr. S.C. Bevan and Mr. S. Thorburn for their help and encouragement: also to Mr. D. Carruthers for carrying out the surface area determinations by nitrogen adsorption.

The Author is grateful for the part played by his Wife, not only in typing the work, but for her patience and understanding throughout the work. Thanks are also due to Miss J.R. Gough for her help in proof reading the typescript.