A VAPOUR DILUTION SYSTEM FOR DETECTOR CALIBRATION

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INTRODUCTION

The present emphasis in gas chromatography is being placed on accurate quantitative analysis and the need for a relatively simple but reliable method for detector calibration is becoming acute. A method is described in this paper for producing accurate relative concentrations of solute vapours in a gas that can be used for the assessment of detector linearity and the determination of the relative response factors of a detector to different substances. The system can also be applied to the determination of trace compounds in the presence of a bulk component of widely different volatility. Numerous methods for producing known relative concentrations of solute vapour in a gas have been described previously in the literature. The two methods most applicable to detector calibrations are those decribed by DESTY *et al.*[1] and LOVELOCK[2]. The method described by DESTY utilises the diffusion of a solute through a narrow glass capillary into a gas stream, to produce the required solute concentration. If employed correctly this method gives absolute instead of relative concentrations, but the apparatus is somewhat complex and can only be used for a single component in the gas stream. The method described by LOVELOCK depends on the continuous dilution of a known quantity of vapour contained in a suitable vessel by means of a gas stream, which results in the concentration of the solute vapour in the exit gas decreasing exponentially with time. If the stream of gas from the dilution vessel is passed through a detector, then, providing the response of the detector is linear, the logarithm of the signal produced will be linearly related to time. The LOVELOCK system suffers from two disadvantages. At low concentrations a considerable proportion of the solute vapour is adsorbed on the walls of the dilution vessel and the dilution rate no longer varies exponentially with time. Secondly, since different substances are adsorbed to different extents on the walls of the vessel, the system is only applicable to single substances. A modified dilution system based on that described by LOVELOCK is described in this paper in which the effect of adsorption is greatly reduced and which also simultaneously produces a mixture of different solute vapours in a gas at known relative concentrations. The theory of the method is given in detail and preliminary experimental results from the assessment of the macro-argon detector using this system are shown, together with results obtained from the analysis of a mixture containing traces of toluene and chlorobenzene in benzene.

METHOD

The apparatus used is shown in Fig. 1. The dilution vessel is made of glass and consists of a small gas wash-bottle of the form shown in Fig. 2. Dry argon passes through the sintered filter into a suitable non-volatile liquid and thence to the automatic gas sampling system. The dilution vessel is charged by a hypodermic syringe through a

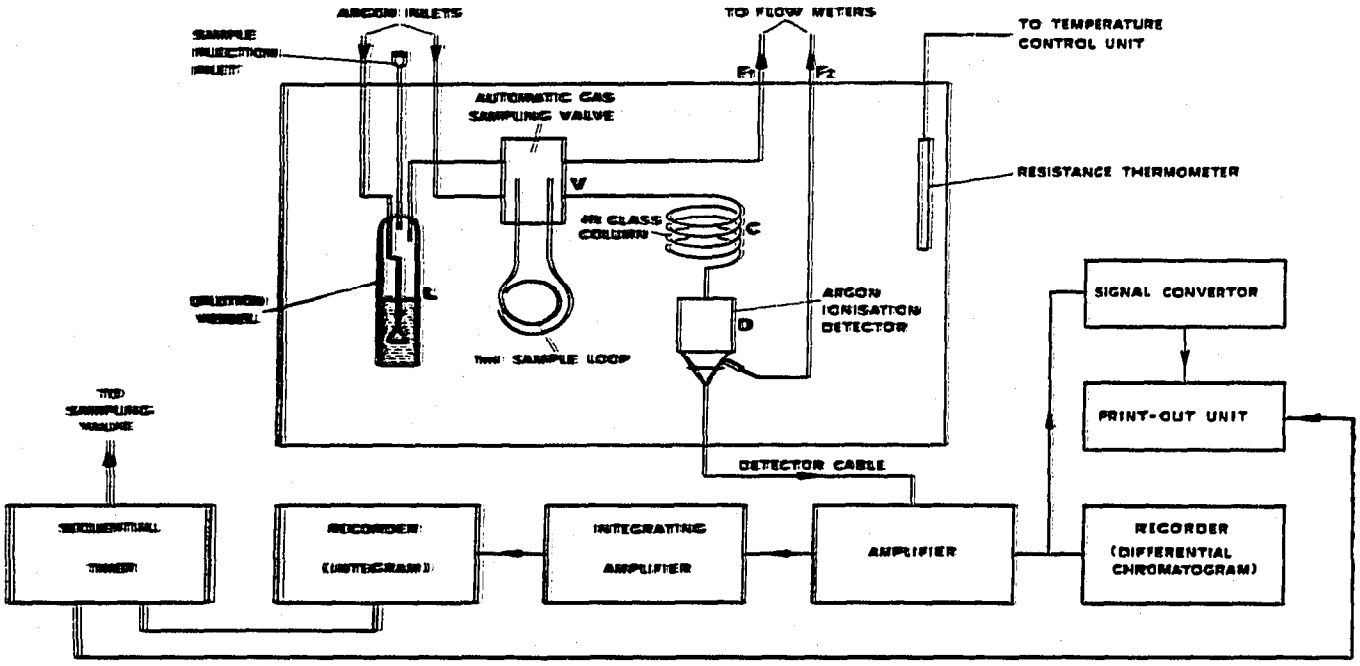

Fig. 1. Detector calibration apparatus.

serum cap. At given intervals of time a sample of the exit gas from the dilution vessel is placed in line with the argon supply to the chromatographic column and detector. The whole unit, dilution vessel, sampling system, column and detector are contained in the same thermostatically controlled oven.

Two methods of estimating peak area were employed, a digital and an electronic integrator, which were automatically reset after each peak by the timer that operated the sampling system.

THEORY

Let the volume of liquid and gas in the dilution vessel (Fig. 3) be V_l and V_g respectively and let a mass m_A of the substance A, whose partition coefficient with respect to the non-volatile liquid is K_A, be placed in the vessel. Let a volume δV of gas flow through the vessel and let the mass of solute removed change the concentrations of the solute in the gas and liquid phases from X_g^A and X_l^A by δX_g^A and δX_l^A respectively.

Then:

$$-X_g^A \delta V = V_g \delta X_g^A + V_l \delta X_l^A = -\delta m \text{ (mass removed from dilution vessel)}$$

Now if X_l^A is small

$$X_l^A = K_A X_g^A$$

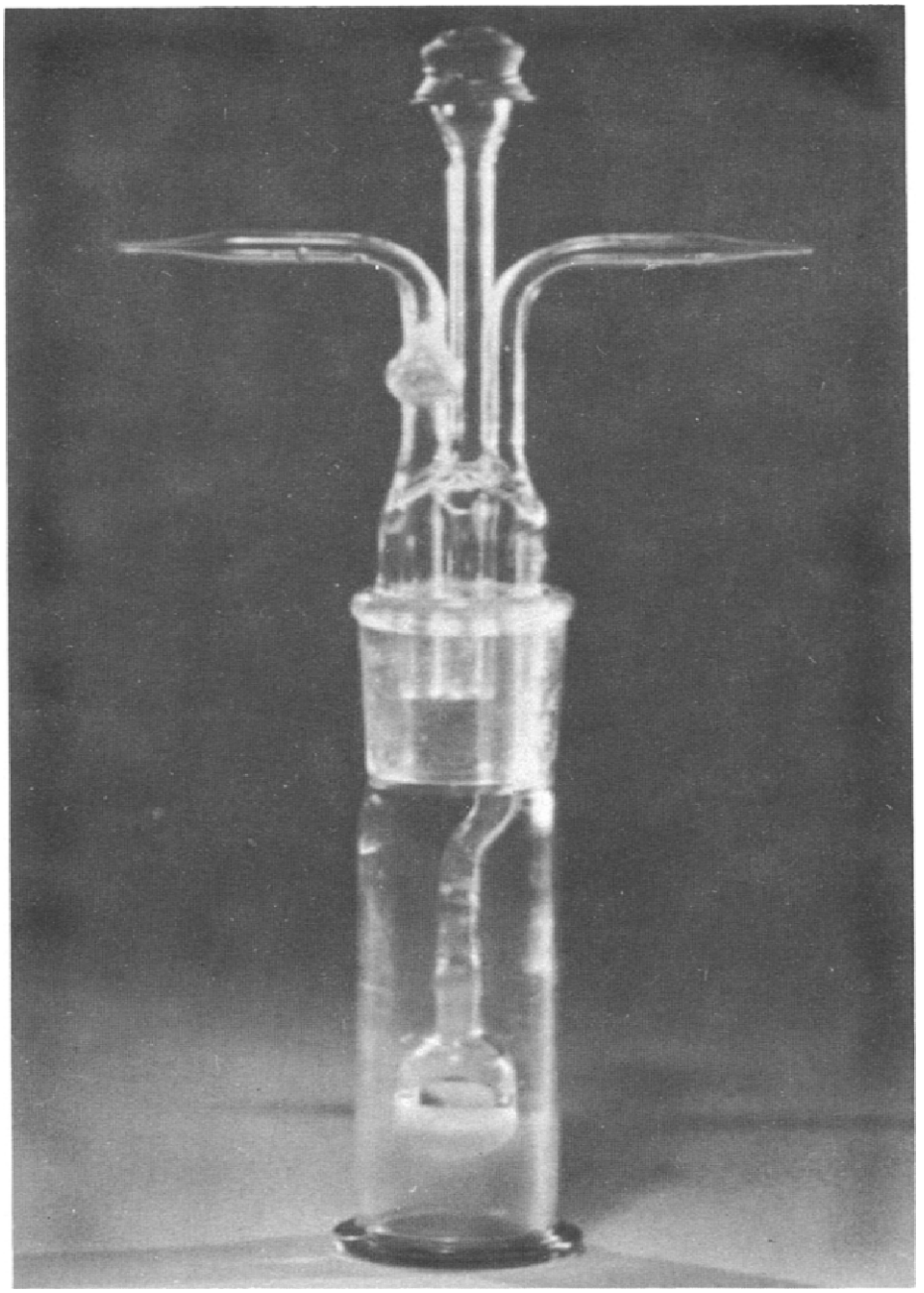

Fig. 2. Dilution vessel.

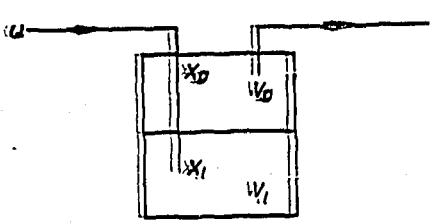

Fig. 3. Diagram of the dilution vessel.

Then:

$$X_g^A \delta V = -(V_g + K_A V_l)\, \delta X_g^A$$

Thus:

$$\frac{\delta X_g^A}{X_g^A} = \frac{-\delta V}{(V_g + K_A V_l)}$$

Integrating:

$$X_g^A = Y e^{-\frac{V}{V_g + K_A V_l}}$$

where Y is a constant.

Now $V = Qt$ where Q is the flow of gas through the vessel in volume/unit time and t is the time. Thus when:

$$t = 0,\ X_g^A = X_{g_0}^A \text{ and } \therefore\ Y = X_{g_0}^A$$

Thus:

$$X_g^A = X_{g_0}^A e^{-\frac{Qt}{V_g + K_A V_l}} \qquad (1)$$

Consider the peak produced on the chromatogram resulting from a single operation of the injection device. The concentration in the detector at any point on the curve is given by the equation of the elution curve:

$$X_{g_n} = \frac{X_{g_0} e^{-\frac{w^2}{2n}}}{\sqrt{2\pi n}}$$

where X_{g0} is the initial concentration placed on the first plate, and $w = v - n$ where v is the "plate volumes" of gas passed through the column, and n is the efficiency of the column. Now let the signal given by the recorder $D\delta w = \sigma(X_{g_n})^\phi\, dw$ where σ and ϕ are constant *i.e.* the response of the detector is a function of a power of the concentration of solute contained in it.

Then:

$$\text{Peak area} = \int_{-\infty}^{+\infty} D\delta w = \int_{-\infty}^{+\infty} \sigma(X_{g_n})^\phi\, \delta w = \int_{-\infty}^{+\infty} \sigma\left(\frac{X_{g_0}}{\sqrt{2\pi n}} e^{-\frac{w^2}{2n}}\right)^\phi \delta w$$

Thus:

$$\text{Peak area} = \int_{-\infty}^{+\infty} \sigma\left(\frac{X_{g_0}}{\sqrt{2\pi n}}\right)^\phi e^{-\frac{\phi w^2}{2n}}\, \delta w = \sigma\left(\frac{X_{g_0}}{\sqrt{2\pi n}}\right)^\phi \frac{\sqrt{2\pi n}}{\phi} = A X_{g_0}^\phi \qquad (2)$$

when:

$$A = \sigma\left(\frac{1}{\sqrt{2\pi n}}\right)^\phi \frac{\sqrt{2\pi n}}{\phi}$$

Now X_{g0} will be proportional to the charge placed on the column *i.e.* $X_{g0} = \gamma X_g^A$, where γ is a constant, thus combining eqns. (1) and (2):

$$\text{Peak area} = A\left(\gamma X_{g_0}^A \cdot e^{-\frac{Qt}{V_g + K_A V_l}}\right)^\phi$$

Thus:

$$\log(\text{Peak area}) = \log A + \log(\gamma X_{g_0}^A)^\phi - \frac{Qt\phi}{V_g + K_A V_l} = C - \frac{Qt\phi}{V_g + K_A V_l} \qquad (3)$$

Thus if the detector has a linear response a plot of log peak area against time will give a straight line and:

$$\phi = \alpha \frac{((V_g + K_A V_l))}{Q} = 1$$

where α is the slope of the line.

Having ascertained that the detector is linear and $\phi = 1$ then $X_g^A \propto S^A$, where S^A is the area of the respective peak on the chromatogram, and the linearity of the detector can be assessed from the correlation coefficient[3] of the line obtained by plotting $\log S^A/t$. By extrapolation of this linear curve to $t = 0$, a value of S_0^A can be obtained which will be proportional to X_{g0}^A.

Now:

$$X_{g_0}^A = \frac{m_A}{V_g + K_A V_l}$$

and if $V_g \ll K_A V_l$, which can be easily arranged experimentally, then:

$$X_{g_0}^A = \frac{m_A}{K_A V_l}$$

Now if m_A and m_B grams of two substances A and B are injected into the dilution vessel then:

$$\frac{X_{g_0}^A}{X_{g_0}^B} = \frac{m_A}{K_A} \cdot \frac{K_B}{m_B} = \frac{D_A S_0^A}{D_B S_0^B}$$

Where D_A and D_B are the detector response factors to the two substances A and B. If the nonvolatile liquid used in the dilution vessel is the same as the liquid phase on the column then $K_B/K_A = R_{B-A}$ where R_{B-A} is the retention ratio of B to A obtained from the chromatogram:

$$\frac{D_A}{D_B} = \frac{m_A}{m_B} \cdot \frac{S_0^B}{S_0^A} \cdot R_{B-A} \qquad (4)$$

If circumstances arise such that V_g is not small compared with KV_l, then:

$$\frac{X_{g_0}^A}{X_{g_0}^B} = \frac{m_A}{m_B} \cdot \frac{V_g + K_B V_l}{V_g + K_A V_l}$$

However, if α and β are the slopes of the log S^A/t curves, then:

$$\frac{\alpha}{\beta} = \frac{Q}{V_g + K_A V_l} \cdot \frac{V_g + K_B V_l}{Q} = \frac{V_g + K_B V_l}{V_g + K_A V_l}$$

Thus eqn. (4) becomes:

$$\frac{D_A}{D_B} = \frac{m_A}{m_B} \cdot \frac{S_0^B}{S_0^A} \cdot \frac{\alpha}{\beta}$$

Thus if a known mixture of substances A and B is placed in the dilution vessel, the linearity and relative response factors of the detector to the substances concerned can be accurately assessed. The relevant data required are the correlation coefficient

of the line obtained by plotting log S/t (the verification that $\phi = 1$), the values of S_0^A and S_0^B by extrapolation of these lines to $t = 0$, and the relative retention ratio R_{B-A}. It should be noted that a knowledge of the absolute masses of A and B placed in the dilution vessel is not necessary. The effect of adsorption of the solute vapour on the walls of the column is insignificant at low concentration levels, as the concentration of the solute in the gas phase is dependent on the concentration of the solute in the bulk of the liquid.

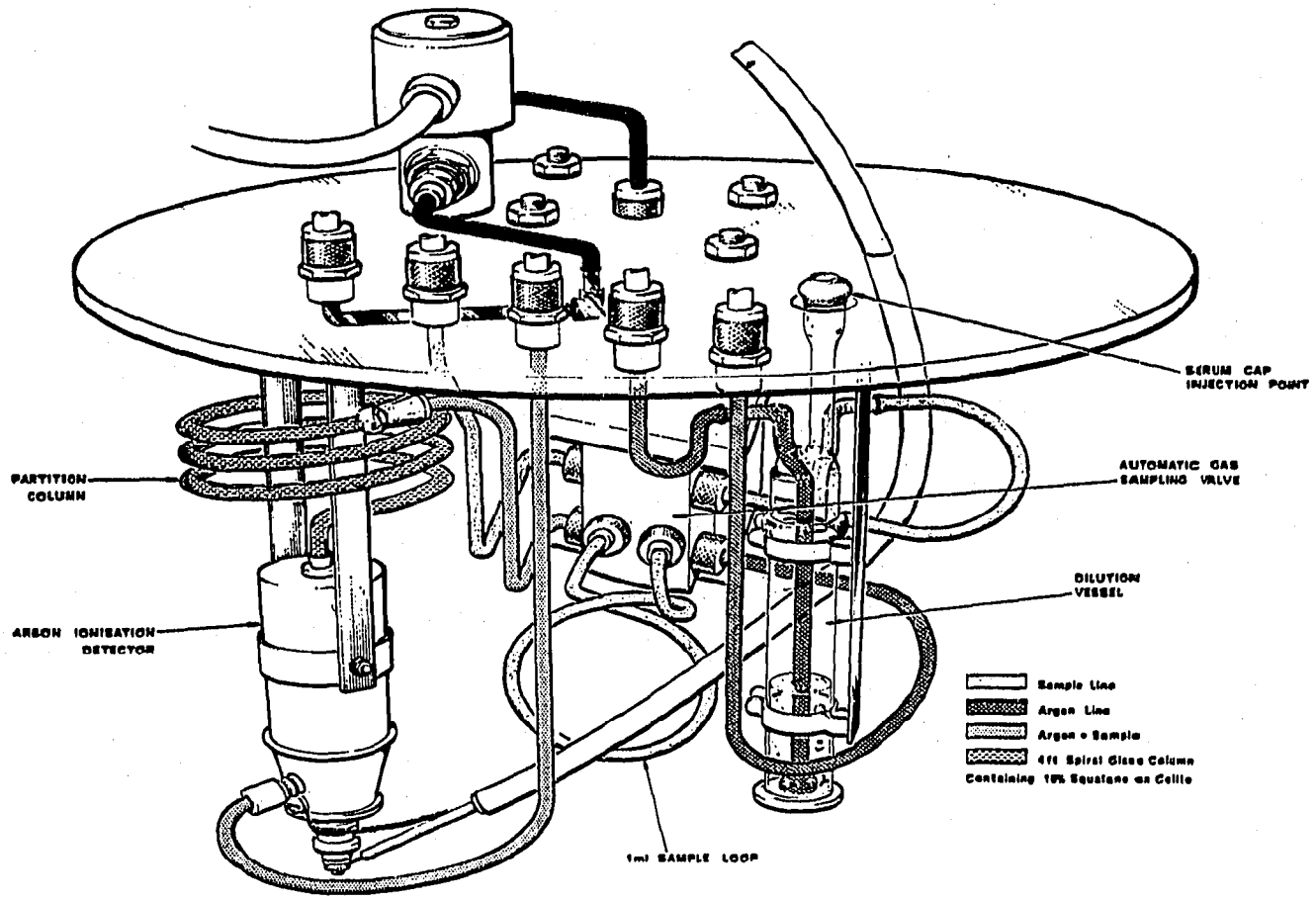

Fig. 4. Detail of dilution vessel and column system.

ANALYSIS OF MIXTURES CONTAINING COMPONENTS AT WIDELY DIFFERING CONCENTRATION LEVELS

Examination of eqn. (1) shows that, providing a sufficiently large charge is placed in the dilution vessel and a constant volume of the exit gas is placed on to the chromatographic column, there will be a period of time, during the dilution, in which each component will be shown on the chromatogram as a series of peaks over a given concentration range. If the logarithm of the peak area for each substance is plotted against time, for the period in which they are "on scale" on the chromatogram, then the initial concentration of each component present at $t = 0$ can be determined by extrapolation. Providing that the relevant response factors for each substance are known, the mass ratios of the components can be determined from the peak area

intercepts at $t = 0$ and the retention ratios of the substances concerned. Further, by this method, all components present are determined with similar accuracy independent of their original concentration level.

EXPERIMENTAL

The determination of detector linearity

Details of the construction of the dilution system are shown in Fig. 4. The argon supplies to the column and dilution vessel were carefully dried by passage through cylinders containing activated Linde molecular sieve 5A. The drying agent was reactivated every time the argon cylinder was renewed. Normally, a column flow rate of 40 ml/min was found to be quite adequate and a flow of about 60 ml/min through the dilution vessel ensured that a complete "run" could be carried out in about 8 h. In order to determine the value of ϕ accurately precise measurements of Q, K_A, V_g and V_l were required. Q was measured by means of a carefully calibrated soap film meter at room temperature and this value was corrected for the pressure and temperature existing in the dilution vessel. The temperature of the liquid in the dilution vessel was continuously measured by means of a thermocouple immersed in the liquid and the gas pressure in the vessel determined by means of a static mercury manometer. V_l was taken as the volume of liquid added to the vessel and V_g taken as the difference between the total volume of the vessel and the volume of liquid added. Values for K were taken from the results of DESTY AND GOLDUP[4] and EVERED AND POLLARD[5]. Squalane was used in the dilution vessel and samples were injected through a serum cap by means of a hypodermic syringe fitted with a 10 in. needle. The column consisted of a coiled glass tube 4 ft. in length and 4 mm in diameter, packed with 10% w/w of squalane on 100–120 mesh celite. The detector employed was the macro-argon detector containing a strontium-90 radioactive source. The whole apparatus

TABLE I

CHARACTERISTICS OF THE MACRO ARGON DETECTOR

Compound	*Correlation coefficient*	*No. of observations*	*Detector response index ϕ*	*Concentration range*
Chloroform	> 0.999	4	0.931	10^3
	< 1.0	4	0.975	
Di-isopropyl ether	> 0.999	4	0.889	10^3
	< 1.0	4	0.808	
Toluene	> 0.999	8	0.950	10^1
		8	0.906	
	< 1.0	8	0.951	
Chlorobenzene	> 0.999	8	0.945	10^1
		8	0.994	
	< 1.0	8	1.042	
Heptane	> 0.999	8	1.095	10^1
		8	1.061	
	< 1.0	8	1.056	

was situated in an oven controlled at 45° ± 0.2°C. The automatic gas sampling valve was actuated by a sequential timer and sampled the exit gas from the dilution vessel every 40 min. The detector was operated at 770 V and the output fed to a Pye Argon Chromatograph amplifier and Integrating amplifier. Differential and integral curves were obtained on two Honeywell Brown recorders and the integrating amplifier was automatically reset after each peak, by use of additional channels on the timer. Graphs of log peak area/time for a mixture containing chloroform, di-isopropyl ether, toluene and chlorobenzene are shown in Fig. 5. The lines shown on this figure are the regression lines for the points obtained. The correlation coefficients and the respective values of ϕ for a series of substances are shown in Table I.

Analysis of mixtures of widely varying composition

The vapour dilution apparatus was used to provide representative vapour sample of a mixture containing 98.9 % benzene, 1.0 % toluene and 0.1 % chlorobenzene. Approxi-

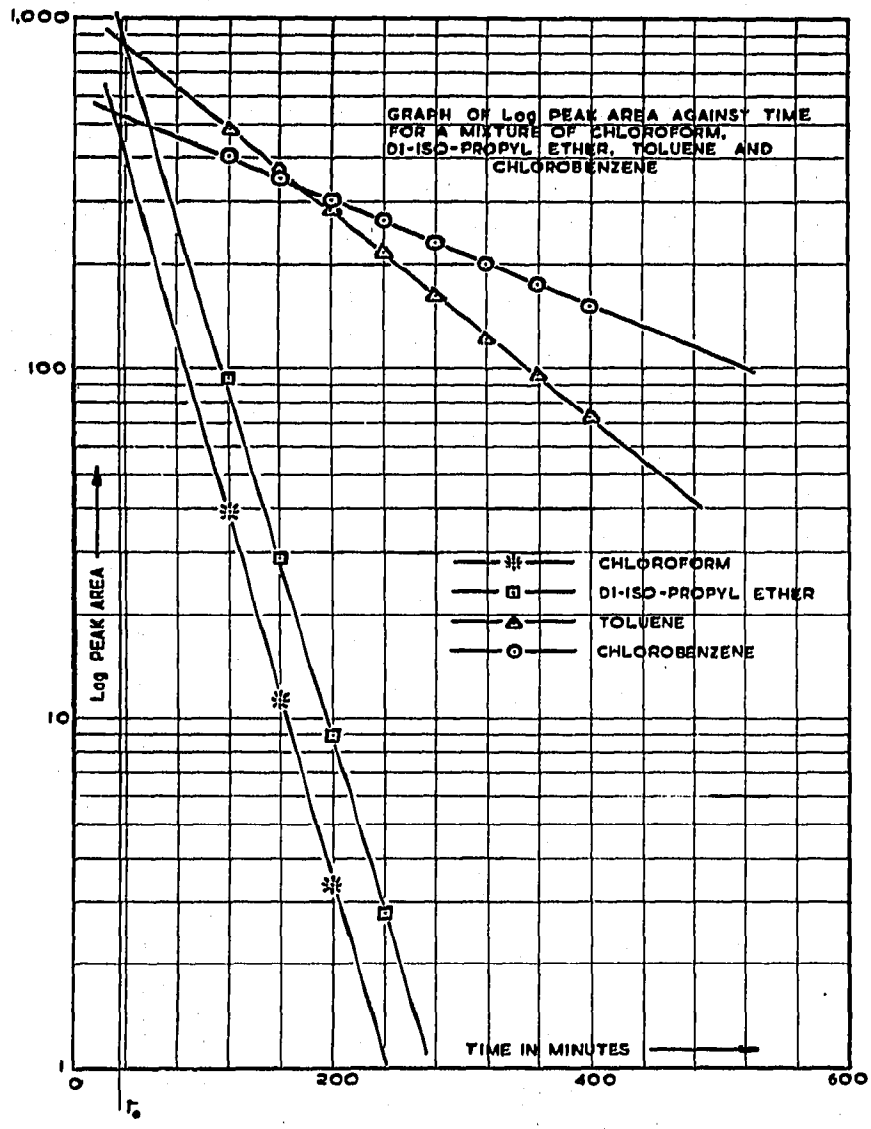

Fig. 5. Graph of log peak area against time for a mixture of chloroform, diisopropyl ether, toluene and chlorobenzene.

mately 250 μl of the mixture was injected into the dilution vessel and samples of the vapour were automatically taken every 40 min for 10 h.

A graph of the peak height against time for each component is shown in Fig. 6, and it may be seen from the intercepts at $t = 0$, that the concentration of each component can be calculated with similar precision although the range of concentrations between the components was as great as 1,000. It should be noted that the values shown in Fig. 6 are based on peak heights and do not take into account relative response factors. It may also be seen that by variation of the flows through the column

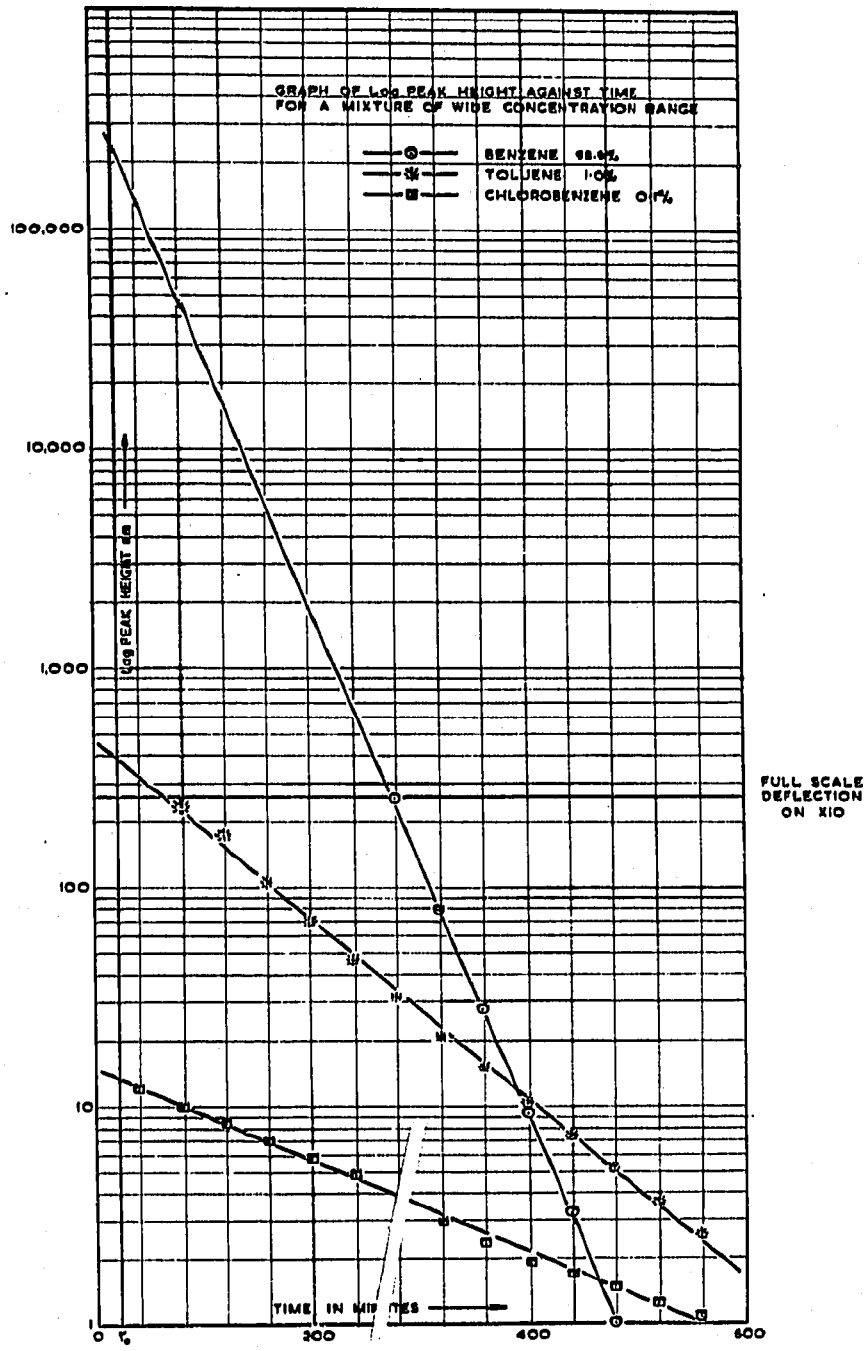

Fig. 6. Graph of log peak height against time for a mixture of wide concentration range.

or dilution vessel, or operation at different temperatures or with different liquid phases, the analysis time can be shortened and the system can be applied to the analysis of a wide range of substances present in diverse relative concentrations.

CONCLUSIONS

The vapour dilution system described in this paper provides a very precise method for determining detector linearity and relative response factors. Due to the wide limits of variation for each operating parameter the system can be made applicable to almost all substances that can be separated by a gas–liquid chromatographic technique. The apparatus can also be used to advantage for the analysis of mixtures containing substances at concentration levels that differ by several orders. By using the system described, each component of such a mixture is determined with the same precision.

The paper gives preliminary results for a macro argon detector and is the first of a series that will be concerned with the investigations of the characteristics of various ionisation detectors. The effect of the various operating parameters of each detector on the linearity and response factors will be examined.

SUMMARY

A vapour dilution apparatus, very suitable for detector calibrations, is described which provides known relative concentrations of a vapour in a gas for sampling on a partition column. The theory of the system is considered in detail, and examples given of the application of the method to the determination of detector linearity and detector response factors and to the analysis of mixtures, whose components are present at widely different concentration levels.

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