The Chromatography of Gases and Vapours. Part V. Partition Analyses with Columns of Silicone 702 and of Tritolyl Phosphate.*

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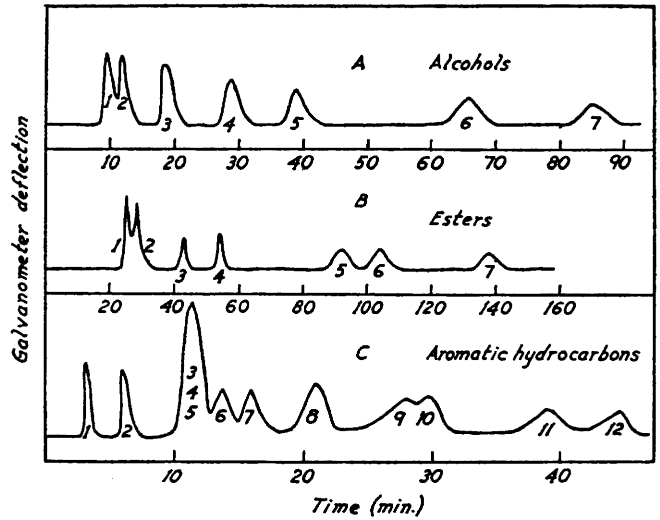
The paper describes an apparatus for partition gas chromatography. Results obtained with this apparatus for the vapours of alcohols, esters, and aromatic hydrocarbons on columns of silicone 702 fluid and of tritolyl phosphate are presented as plots of corrected retention volumes per g. of column fluid against the inverse of the column temperature.

IN Part II (*J.*, 1953, 1600) an apparatus was described for the separation and analysis of mixtures of volatile substances using the partition gas chromatographic technique, originated by Martin and James (*Biochem. J.*, 1952, **50**, 679). An improved form of this apparatus has been used to record a large number of chromatograms by means of columns of Silicone 702 fluid and of tritolyl phosphate. Typical chromatograms are illustrated in Fig. 1.

FIG. 1. *Typical chromatograms.*



(*A*) 1 µl. each of seven alcohols : ethyl (1), *iso*propyl (2), *n*-propyl (3), *iso*butyl (4), *n*-butyl (5), *iso*pentyl (6), and *n*-pentyl (7). Column : 2·82 g. of Silicone 702 on 7·05 g. of Celite 535. Temp. 76·9°. Flow rate : 11·8 ml./min. at N.T.P.

(*B*) 0·7 µl. each of seven esters : methyl propionate (1), ethyl acetate (2), *iso*butyl formate (3), *n*-propy acetate (4), ethyl *iso*butyrate (5), *iso*propyl *iso*butyrate (6), *iso*propyl *n*-butyrate (7). Column : as (*A*). Temp. 77·0°. Flow rate : 11·7 ml./min. at N.T.P.

(*C*) 5 µl. each of twelve aromatic hydrocarbons : benzene (1), toluene (2), ethylbenzene (3), *m*-xylene (4), *p*-xylene (5), *o*-xylene (6), *iso*propylbenzene (7), mesitylene (8), *sec.*-butylbenzene (9), *p*-cymene (10), indene (11), *tert.*-pentylbenzene (12). Column : 1·85 g. of Silicone 702 on 4·63 g. of Celite 535. Temp. 132°. Flow rate : 27·4 ml./min. at N.T.P. (To illustrate the effect of a large sample on a column of poor separation efficiency.)

We present a summary of some of these results in a manner which, we hope, will facilitate their use by other workers. We plot our results for a series of alcohols, esters, and aromatic hydrocarbons on these two types of column in terms of " corrected retention volumes per gram " as a function of temperature. We hope that by so doing we shall help to provide a basis for a scheme of analysis using gas chromatography as an absolute method.

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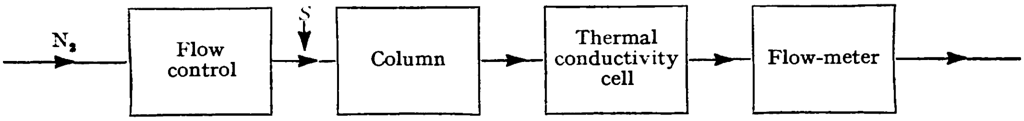
* Part IV, *J.*, 1954, 3446.

EXPERIMENTAL

Apparatus.—Fig. 2 is a block diagram of the apparatus. Nitrogen from a cylinder passes successively through the flow-control, the chromatographic column, the thermal-conductivity cell, and the flow-meter. Samples for analysis are injected at *S*.

FIG. 2. *Block diagram of apparatus.*



The flow-control is illustrated in Fig. 3. This is the device described by James and Phillips (*J. Sci. Instr.*, 1952, **29**, 362), modified to work at pressures up to 2·5 atm. Nitrogen from the cylinder enters the control through *A* at a rate greater than required for the flow through the column, and passes to the column through *B via* the capillary *C*. A constant flow is maintained by keeping a constant head of mercury across *C*. In order to prevent too great a pressure drop from developing across the sintered-glass disc *D*, it is surrounded by a jacket *H* leading to *EFG*, a self-adjusting blow-off. By connecting the reservoir *G* to *A*, and placing the sintered-glass disc *E* about 10 cm. above the surface of mercury in *G*, a more or less constant pressure difference of 10 cm. is maintained across *D*. The by-pass below *C* is used when the nitrogen is first turned on and enables equilibrium pressures to be set up more rapidly. Part of *H* can be removed for repair or replacement of the sintered-disc valve *D*.

FIG. 3. *Flow control.*

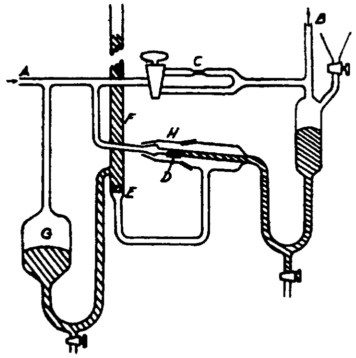


FIG. 6. *Butt-joint sample injector.*

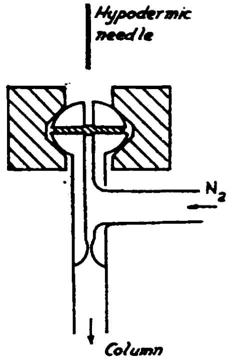


FIG. 4. *Column with vapour jacket.*

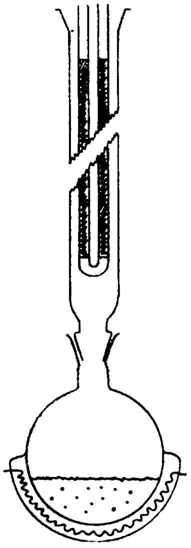


FIG. 5. *Double-cell glass thermal-conductivity unit.*

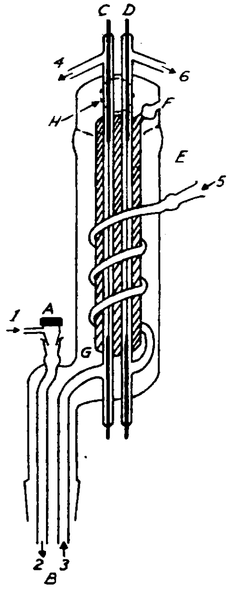


FIG. 5. Gas path indicated by arrows 1 to 6, sample injected at *A*, column sealed on at *B*, cell for measuring vapour concentration *C*, compensating cell *D*, mercury jacket *E*, mercury expansion bulb *F*, vapour jacket *G*, condenser connection *H*.

A typical column is illustrated in Fig. 4. It consists of a U-tube, of 5 mm. internal diameter and 1 m. long, enclosed in a vapour jacket maintained by an electrically heated boiler. For operation at the higher temperatures, the jacket is lagged with asbestos and can also be supplied with a small amount of auxilliary heating. The column is packed with about 10 g. of a mixture of Celite (535, Johns-Mansville) and the fixed liquid phase. This occupies about 75 cm. of each arm of the U-tube. The column mixture is prepared in the following way. The Celite is size-graded by sedimentation, washed with 4N-nitric acid, then distilled water, and dried at 120°. It is then mixed with the requisite quantity of the fixed liquid phase (about 8—20 g. of Celite) and formed into a slurry with dry ether. The ether is evaporated with continuous stirring, and finally the mixture is shaken for ½ hour. The mixture is poured into the column, 0·5 g. at a time, and is shaken down by agitating the column against the spindle of an electric motor, at the same time tamping it down with a close-fitting rod.

The thermal-conductivity unit is illustrated in Fig. 5. It contains two platinum wires (0·05 mm. diameter, 14 cm. long, resistance 8 ohms) in 5-mm. glass tubes encased in the same mercury jacket. The wires are attached to tungsten supports with silver solder. The unit is connected directly to the column, and is jacketed with the same vapour. Gas from the column passes through the left-side tube, the vapours are then condensed out from the nitrogen in a dry ice-trap (not illustrated), and the nitrogen allowed to pass on through the spiral to the second compensating tube. The two wires form adjacent arms of a direct-current Wheatstone bridge, driven by a 4-v accumulator. The output of the bridge is recorded (Ether Indicorder; Ether Ltd., Birmingham).

The flow-meter consists of a capillary across a U-tube filled with liquid paraffin.

The samples are injected on to the column by means of a hypodermic syringe through a serum cap. Fig. 6 illustrates an alternative arrangement to the serum cap, consisting of a piece of rubber compressed by a butt-joint.

The dead-volume is obtained by injecting a small sample of air or hydrogen.

DISCUSSION

(i) *Mode of expressing Results.—Corrected retention volumes per g.*, V_g. The chromatograms are recorded as plots of vapour concentration (proportional to off-balance of Wheatstone bridge) against time. Under constant experimental conditions, and for a linear absorption isotherm, the peak maximum for a particular vapour will appear at a characteristic time, the retention time. This retention time is a function of: (1) the nature of the vapour, (2) the nature of the fixed phase, and (3) the temperature of the column. It also depends upon various experimental parameters, such as the gas-flow rate, the dead volume between the point of injection and the thermal conductivity detector, and the weight of the fixed phase. Values for retention times are therefore only of relative importance [see p.1486, Results (i)(b)], and must be corrected to eliminate the effects of these experimental parameters if they are to provide results which can be used directly by other workers for the prediction of column behaviour and as a basis for a scheme of absolute identification, and which may be compared among themselves to give results of theoretical interest, such as values for the heats of solution of the vapours in the column fixed phase.

Our retention times have therefore been corrected so as to make them independent of the dead volume of the apparatus, the flow rate, and the weight of fixed phase. We call the fully corrected values " corrected retention volumes per gram," for which we use the symbol V_g. Values of V_g (on a logarithmic scale) are then plotted against $1/T$, where T is the column temperature. Such plots approximate to straight lines.

(ii) *Correction Procedure.*—The procedure is outlined in this section, and the next section gives an example worked out in detail.

(a) *Correction for dead volume.* The retention time represents the average time taken for a molecule of the vapour to pass from the injection point to the thermal conductivity cell. This time consists of two parts, the time spent in the gas phase, and that spent in the fixed phase. We are only interested in the second part; the first part depends upon the dead volume of the apparatus [which includes the volumes of the tubes leading from the injection point to the column and from the column to the thermal-conductivity cell (about 7 ml.), and the volume of the gas phase in the column (about 20 ml.)] and the flow rate. It is most simply determined by measuring the time taken for a small sample of air or hydrogen (whose absorptions in the fixed phase are sufficiently small to be neglected) to pass to the thermal conductivity cell after injection. This time is usually relatively small.

(b) *Correction for flow rate.* For a given column, the time which a vapour spends in the fixed phase will be inversely proportional to the flow rate of gas by which it is being removed. The time spent in the fixed phase is therefore multiplied by the flow rate to give the retention volume. The flow-rate correction is complicated, however, by the fact that the gas flowing through the column is a fluid whose volume changes with both pressure and temperature.

(1) Effect of pressure changes. The flow-meter is calibrated in terms of volumes of gas delivered at atmospheric pressure. The pressure at the outlet of the column will be slightly higher, by virtue of the pressure drop across the flow-meter, and at the inlet of the column considerably higher, because of the pressure drop across the column. Two corrections are therefore required. The effect of the pressure drop across the column has been treated by Martin and James (*loc. cit.*), who derived the correcting factor $2[(p_1/p_0)^3-1]/3[(p_1/p_0)^2-1]$, where p_1 is the pressure at the inlet and p_0 the pressure at the outlet of the column.

(2) Effect of temperature changes. The flow-meter is normally calibrated in terms of the volume of gas delivered at a temperature near room temperature. For convenience we have calibrated our flow-meter in terms of gas at 0°. The gas, however, passes through the column at the temperature of the column T, and the flow-meter value must be multiplied by $T/273$ to give the real volume of gas passing through the column. But as the temperature is to be one of the variables it is not essential to apply a temperature correction, and we have therefore omitted it.

(c) *Correction for weight of fixed phase.* The retention volume obtained as above is divided by the weight of fixed phase to give V_g.

(iii) *Example of Correction Procedure.*—To illustrate the application of the various correction terms we take the case of methyl propionate vapour passed through a column of Silicone 702 at a temperature of 56·2°. Measurement of the recorder chart gave a time of 58·2 min. from the time of injection to the peak maximum. Injection of a small sample of hydrogen under the same conditions gave a time of 2·7 min. The corrected retention time is thus 55·5 min.

The flow rate as determined by the flow-meter was 11·0 ml. of nitrogen per min. at N.T.P. This gives an uncorrected retention volume of 610 ml. The pressure at the inlet of the column was 123·0 cm. (of Hg), at the outlet 78·1 cm., and the atmospheric pressure was 76·0 cm. The correction factor for the pressure drop across the column is therefore

$$\frac{2}{3}\cdot\frac{(123{\cdot}0/78{\cdot}1)^3-1}{(123{\cdot}0/78{\cdot}1)^2-1}=0{\cdot}765$$

and for the pressure drop across the flow meter 76·0/78·1. The weight of Silicone 702 in the particular column was 2·82 g. The value for V_g is thus

$$610\times0{\cdot}765\times\frac{76{\cdot}0}{78{\cdot}1}\times\frac{1}{2{\cdot}82}=161\text{ ml.}$$

(iv) *Significance of* V$_g$ *Values.*—If a particular vapour is equilibrated between gas and 1 g. of the fixed phase so that it is 50% in the gas phase and 50% in the fixed phase, then V_g will be the volume of gas (corrected to 0° at constant pressure); V_g is thus related to α, the partition coefficient defined by the equilibrium relation

$$\alpha=\frac{\text{Weight of vapour per unit volume of fixed phase}}{\text{Weight of vapour per unit volume of gas}}$$

by the equation $V_g = 273\rho\alpha/T$, where ρ is the density of the fixed phase. Alternatively we may express V_g as the volume of gas (measured at 0°) which has passed through a hypothetical ideal column, containing 1 g. of fixed phase. when the peak maximum emerges. This ideal column has a constant pressure (equal to the pressure at which the volume of gas is measured) throughout, and zero dead-volume.

We express our results in terms of V_g rather than in terms of α, in order to simplify the correction procedure. If we had divided our retention volumes by the volume of the fixed phase, instead of by the weight, then we should have eliminated the density from the relation between V_g and α. However, such a procedure would require a new factor for a particular column for each temperature. Moreover, we should need to know the temperature coefficient of expansion of the fixed phase. The variation of density with temperature enters into the calculation of heats of solution [Results (iv), p. 1488] but it gives rise to a relatively small correction, which can be inserted directly as a small constant heat value for a particular column fluid.

The factor $273/T$ in the relation between V_g and α would disappear if we measured our retention volumes at the column temperature instead of at 0°. This, however, would complicate the correction procedure. Furthermore, omission of this factor enables heats of solutions to be calculated more directly [see Results (iv), p. 1488], as it is equivalent to expressing our results in terms of Bunsen's coefficient instead of Ostwald's coefficient (α).

RESULTS

The corrected retention volumes per g. for series of esters, alcohols, and aromatic hydrocarbons have been determined over a range of temperatures for columns of silicone 702 fluid, and of tritolyl phosphate. These values are presented in Figs. 7, 8, 9, and 10 as plots of $\log_{10} V_g$ against $1/T$. The slopes of these plots are related to the heats of solution of the vapours [see Results (iv), p. 1488]. The plots prove to be straighter than might have been supposed, in view of the normal variation of heats of solution with temperature. From the plots, values of V_g may be read off for any temperature in the range. The plots can be used both analytically, to interpret and predict column behaviour, and theoretically, to deduce values for heats of solution.

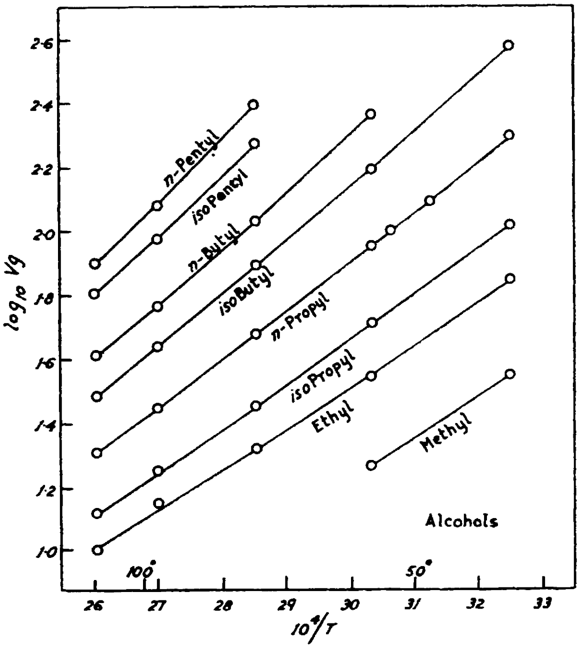


FIG. 7. $\log_{10} V_g$ *values* (*corrected retention volumes per g.*) *for alcohols on Silicone* 702 (Midland Silicones Ltd.).

(i) *Use of* V_g *values for Vapour Identification*.—When a chromatogram has been recorded, each peak is assigned its appropriate V_g value, by using the correction procedure given above. For one chromatogram this will mean multiplying each retention time by one constant. The vapours corresponding to each peak can then be identified by reference to a complete set of plots, as with a set of melting or boiling points. The identification can be checked by running the same sample at a different temperature or on a different column.

The validity of such a procedure clearly depends upon the reproducibility of the V_g values. In order to gain some idea of this, we have repeated many of our results on different columns composed of the same fixed phase. Examples are given in the next section. In general, we feel that the results which we have plotted are reliable to ±4%, which corresponds to 0·02 log unit. This accuracy is quite sufficient for most purposes, but it can be increased to ±1% by use of the method of internal standards [see (b), p. 1485].

(a) *Reproducibility of* V_g *values*. (1) Effect of repacking the column. A column containing Silicone 702 as fixed phase was packed to give a total length of 142·4 cm. A mixture of methyl acetate, ethyl acetate, methyl propionate, and benzene was chromatographed. The column was then shaken out, and repacked in the same tube to approximately the same density as before. Its length was now 141·6 cm. The same mixture was chromatographed on this column. Finally, the column was again shaken out and repacked very tightly, so that its length was 107·0 cm. A third chromatogram of the mixture was recorded. In each case the column was jacketed at 77°. The V_g values obtained in these three experiments are given in Table 1.

TABLE 1. *Effect of repacking column on reproducibility of* V_g *values.*

Column length (cm.)	142·4	141·6	107·0
		V_g Values	
Methyl acetate	33·9	32·8	33·3
Ethyl acetate	68·5	67·1	68·0
Methyl propionate	78·7	76·3	78·0
Benzene	102·0	99·5	100·7

FIG. 8. V_g *Values for aromatic hydrocarbons and esters on Silicone* 702.

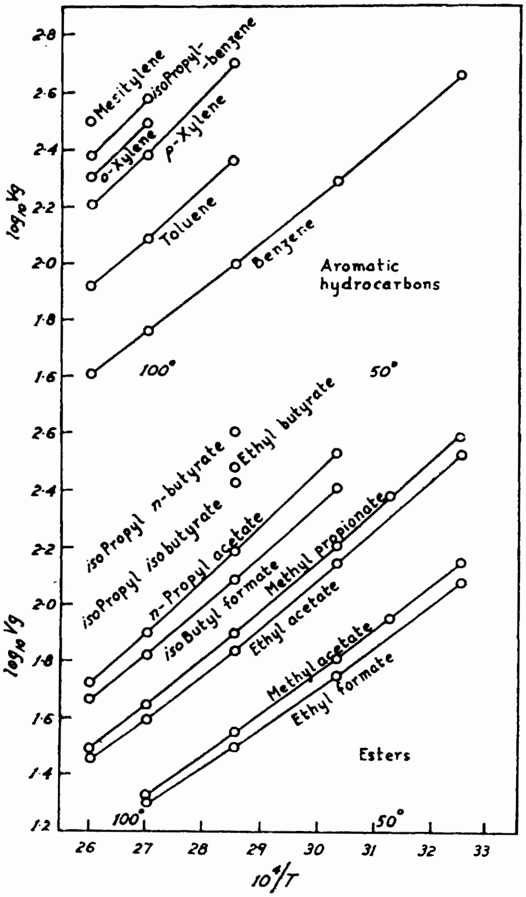
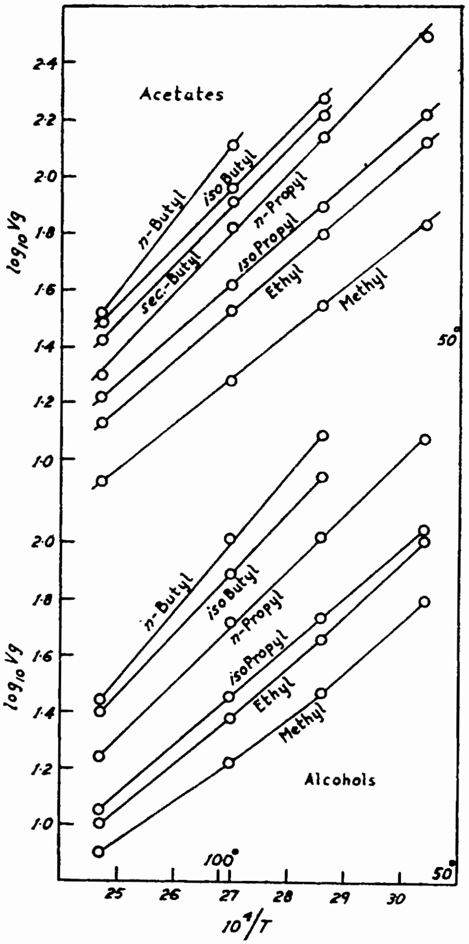


FIG. 9. V_g *Values for acetates and alcohols on tritolyl phosphate.*



(2) Use of different samples of fixed phase. Two columns were constructed with different samples of Silicone 702 fluid (Batch Nos. EE 44 and EE 67, supplied by W. Edwards and Co.). Values of V_g obtained with these two columns are given in Table 2.

(b) *Use of an internal standard.* While a reproducibility of about ±4% can be expected in experiments performed with different columns, the results obtained on one column are more reproducible. The variation in these results will arise from slight variations of column temperature, flow rate, and injection procedure. The effect of these can be very much reduced by using a substance as an internal standard. Table 3 gives, for example, the retention times for a series of esters on a column of tritolyl phosphate, the retention time of *n*-propyl acetate being used as the standard. The first two columns contain values given by mixtures containing all seven esters (Fig. 11), while the third column contains values obtained separately for each of the esters in company with *n*-propyl acetate.

TABLE 2. V_g *Values obtained with two samples of Silicone* 702 *fluid.*

	Sample EE 44	Sample EE 67		Sample EE 44	Sample EE 67
	Columns at 77°			Columns at 35°	
Benzene	101	100	Methyl acetate ...	140	141
Toluene	237	229	Methyl propionate	393	387
p-Xylene	512	503	Ethyl alcohol ...	66·2	72·0
Methyl acetate ...	33·9	35·6	*iso*Propyl alcohol	101	105
Ethyl acetate	68·5	69·0	*n*-Propyl alcohol	196	200
Methyl propionate	78·7	79·7	Ether	78·4	82·0
n-Butyl alcohol ...	104	109			

TABLE 3. *Use of an internal standard: retention times relative to* n-*propyl acetate.* (Column of tritolyl phosphate at 98°).

Methyl acetate	0·426	0·427	0·420	*sec.*-Butyl acetate	1·17	1·16	1·16
Ethyl ,, ...	0·605	0·606	0·606	*iso*Butyl ,, ...	1·32	1·31	1·31
*iso*Propyl ,, ...	0·683	0·685	0·690	*n*-Butyl ,, ...	1·82	1·80	1·81
n-Propyl ,, ...	(1·00)	(1·00)	(1·00)				

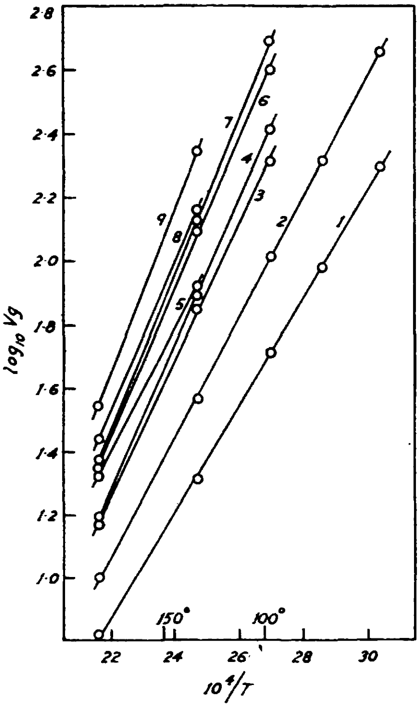
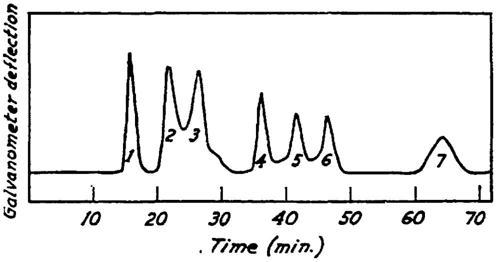


FIG. 10. $\text{Log}_{10}\ V_g$ *values for aromatic hydrocarbons on tritolyl phosphate:* (1) benzene, (2) toluene, (3) *p*-xylene, (4) *o*-xylene, (5) *iso*propylbenzene, (6) mesitylene, (7) *sec.*-butylbenzene, (8) *p*-cymene, (9) *tert.*-pentylbenzene.

FIG. 11. *Chromatogram obtained with mixture o 0·5 µl. each of seven acetates on tritolyl phosphate at* 98°: methyl (1), ethyl (2), *iso*propyl (3), *n*-propyl (4), *sec.*-butyl (5), *iso*butyl (6), *n*-butyl (7).



(c) *Correction for asymmetry of peaks.*—Reproducible values of V_g, or of retention times by reference to an internal standard, are only obtained so long as the peaks are symmetrical or nearly so. If the column is overloaded (so that the isotherms become non-linear), asymmetric peaks are produced with diffuse fronts and sharp tails, and the value for the peak maximum rises with the quantity of vapour. The beginnings of these peaks, however, prove to be reasonably reproducible, and by an empirical procedure in which the time between the peak maximum and the end of the peak is added to the time for the beginning of the peak (equivalent to turning the peak back to front), a good value for the symmetric peak retention time can be obtained. Thus even an asymmetric peak may be identified. Table 4 provides an illustration. The results obtained by using the empirical correction procedure are given in the last column.

(d) *Extrapolation of* V_g *values.* A complete scheme of identification would require a knowledge of V_g values for all possible vapours. It is to be hoped that in the course of time something approximating to such a complete set of values will become available from the results of a number of workers. It is, however, often possible to obtain a very good estimate for V_g values by appropriate extrapolation. Thus, Fig. 12 illustrates the relation between values of $\log_{10} V_g$ and the number of carbon atoms for a series of *n*-alcohols. It will be seen that, except for the lowest member (methyl alcohol), the values lie on good straight lines. Similar results are obtained for other homologous series, and good straight lines are obtained, for example, for a whole series of aromatic hydrocarbons if their $\log_{10} V_g$ values are plotted against number of carbon atoms with use of the empirical rating of 1·0 for CH_3, 0·8 for CH_2, 0·4 for CH, and 0·2 carbon atom for a quaternary carbon, and if 0·2 carbon atom is added for *ortho*-groups.

TABLE 4. *Correction for asymmetry of peaks.* Values (in min.) for the retention time of ethyl acetate on a column of silicone 702 (1·85 g.). Nitrogen flow rate 20·6 ml./min. Column at 56°.

Quantity, μl.	Peak maximum	Peak beginning	Corrected peak max.	Quantity, μl.	Peak maximum	Peak beginning	Corrected peak max.
2·5	19·8	18·4	19·8	10	20·7	18·2	19·6
5	19·7	18·4	19·7	20	21·5	18·0	19·7
10	20·7	18·2	19·7	40	22·8	17·9	19·3

FIG. 12. V_g *Values as a function of number of carbon atoms for* n-*alcohols on Silicone 702 column at three temperatures.*

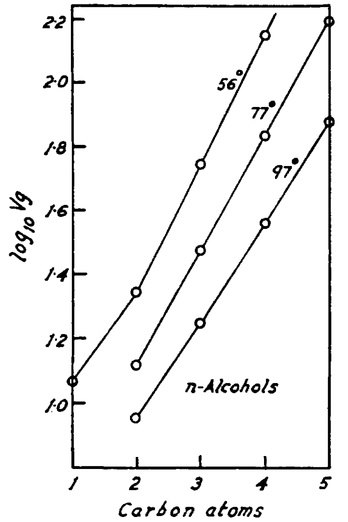
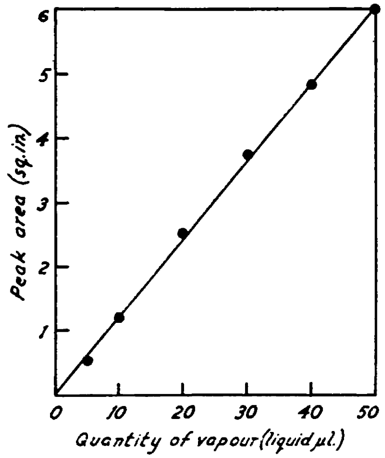


FIG. 13. *Relation between peak area and quantity of vapour for* n-*propyl acetate on a Silicone 702 column at 77°.*



(ii) *Quantitative Analyses.*—Quantitative analyses have been made by measuring the areas under peaks by means of a planimeter. Linear relations are obtained between quantity of vapour and peak area, as illustrated by Fig. 13. Our recorder did not have a fast enough response to justify the use of peak heights as Ray has done (*J. Appl. Chem.*, 1954, **4**, 21).

(iii) *Efficiency of Separations.*—The separative ability of a column may be expressed in terms of the number of theoretical plates. This can be calculated from the recorded chromatograms by measurement of the height of a peak *h*, its area *a*, and its retention distance *l*, and use of the formula

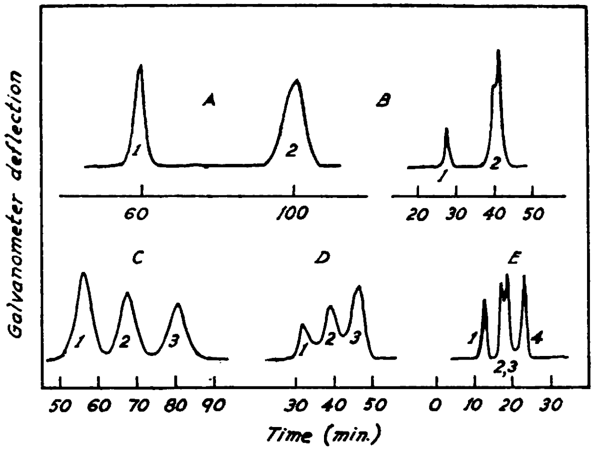
$$\text{Number of plates} = 2\pi(hl/a)^2$$

which is equivalent to Martin and Synge's method I (*Biochem. J.*, 1941, **35**, 1358). The values obtained for our columns vary considerably, but average values are 1000 for the silicone column, and 700 for the tritolyl phosphate column.

The efficiency of a column increases as the quantity of vapour is reduced. Thus on a particular column of Silicone 702 (containing 1·82 g. of silicone) at 56°, the peak for 10 μl. of ethyl acetate corresponded to 560 theoretical plates, for 5 μl. 840 theoretical plates, and for 2·5 *μl.* 1100 theoretical plates. The efficiency also increases with retention volume, though this is in part due to the rather slow response of our recording system.

As the column temperature is raised, the efficiency is found to remain more or less constant for a given retention volume. Thus for the Silicone column described on p. 1481, values of $\log_{10} V_g$ (see Figs. 7 and 8) near 1·9 correspond to about 800, values near 2·2 to about 1300 and near 2·6 to about 2000 theoretical plates. If follows, therefore, that for any particular vapour the effective number of theoretical plates in a given column will increase as the temperature is reduced. Thus on a tritolyl phosphate column, the following theoretical plate values (number of plates at 105°, number of plates at 56°, ratio of number at 56° to number at 105°) were calculated; methyl acetate (200, 600, 3·0), ethyl acetate (265, 960, 3·6), benzene (360, 1410, 3·9), propyl acetate (710, 1910, 2·7). There are also differences between different classes of compounds. For example, on Silicone 702 columns, values for esters are always considerably higher than values for alcohols and aromatic hydrocarbons of comparable retention volumes.

FIG. 14. *Chromatograms to illustrate dependence of separation efficiency on number of theoretical plates and on differences* (Δ) *in the values of* $\log_{10} V_g$.



Column	Substance	$\Delta \log_{10} V_g$
(*A*) Silicone 702, 35°, 1500 plates	(1) *cis*-Dichloroethylene	0·23
	(2) *trans*-Dichloroethylene	
(*B*) Silicone 702, 157°, 800 plates	(1) 1 : 2-Di-*n*-propyl*cyclo*hexane	0·17
	(2) 1 : 2-Di-*n*-propylbenzene (with impurity)	
(*C*) Silicone 702, 111·4°, 1500 plates ...	(1) *p*-Xylene	0·08
	(2) *o*-Xylene	0·08
	(3) *iso*Propylbenzene	
(*D*) Tritolyl phosphate, 157°, 650 plates	(1) Aniline	0·09
	(2) *N*-Methylaniline	0·07
	(3) Di-*N*-methylaniline	
(*E*) Silicone 702, 132°, 600 plates	(1) *iso*Butyl *iso*butyrate	
	(2) *iso*Butyl *n*-butyrate	0·05
	(3) *iso*Pentyl propionate	
	(4) *n*-Butyl *n*-butyrate	

In order to illustrate the relations between separation, difference in values of $\log_{10} V_g$, and the number of theoretical plates, some chromatograms are given in Fig. 14. The relation between separation and number of theoretical plates is shown in particular by a comparison of chromatograms *C* and *D* ($\log_{10} V_g$ differences 0·08), and of chromatogram *E* (*iso*butyl *n*-butyrate and *iso*pentyl propionate, $\log_{10} V_g$ difference 0·05, 600 plates) with the separation of *iso*propyl *iso*butyrate and ethyl *iso*butyrate in Fig. 1 ($\log_{10} V_g$ difference 0·05, 2500 plates).

(iv) *Heats of Solution.*—The heat of solution, ΔH, of a vapour in the fixed phase of the column will be given by the relation

$$(\mathrm{d} \ln c/\mathrm{d}T)_p = \Delta H/\boldsymbol{R}T^2$$

where c is the concentration of vapour in the liquid at constant vapour pressure. Now $\mathrm{d}\ln\alpha/\mathrm{d}T$ is equal to $\mathrm{d}\ln c/\mathrm{d}T$ at constant weight of vapour per gas volume. Therefore

$$\mathrm{d}\ln\alpha/\mathrm{d}T = (\mathrm{d}\ln c/\mathrm{d}T)_p + (\mathrm{d}\ln p/\mathrm{d}T)_v$$
$$(\mathrm{d}\ln c/\mathrm{d}T)_p = \mathrm{d}\ln(\alpha/T)/\mathrm{d}T$$

Since $V_g = \rho\alpha 273/T$, it follows that

$$\mathrm{d}\ln V_g\,\rho/\mathrm{d}T = \Delta H/\boldsymbol{R}T^2$$
$$\Delta H = -2{\cdot}3\boldsymbol{R}\,[\text{Gradient}] + \boldsymbol{R}T^2\,\mathrm{d}\ln\rho/\mathrm{d}T$$

where [Gradient] is gradient of plot of $\log_{10} V_g$ against $1/T$.

The last term can be calculated from the cubical expansion coefficient of the column liquid. Values for this coefficient are 0·00083 for Silicone 702 fluid, and 0·0012 for tritolyl phosphate. The corresponding terms are −0·16 and −0·23 kcal. (the negative sign indicating a numerical increase in the value of the heat of solution). Table 5 gives a series of heats of solution calculated in this way. Wherever the plots are curved the value of the gradient is taken at the boiling point of the vapour in question. In Table 5 are also quoted values for the latent heats at the boiling point, for comparison.

TABLE 5. *Heats of solution of vapours* (in kcal./mole).

Vapour	Heat of solution in tritolyl phosphate	Heat of solution in Silicone 702	Latent heat of evapn. at b. p.
Ethyl alcohol ...	8·1	5·9	9·3
Propyl alcohol...	9·4	7·0	9·9
Methyl acetate	7·7	7·1	7·3
Ethyl acetate ...	8·3	7·8	7·8
Propyl acetate	9·0	8·4	8·1
Benzene	8·2	7·4	7·4
Toluene	9·0	7·9	8·1

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