322. *The Chromatography of Gases and Vapours. Part II.**

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An apparatus is described for the analysis and separation of mixtures of volatile substances by the use of chromatographic methods in which the moving phase is a gas. Results are quoted to illustrate the application of adsorption and partition techniques. Particular attention has been given to displacement (adsorption) analyses from charcoal columns at 100°, where an accuracy of better than 1% can be obtained.

Despite the wide interest in chromatographic methods, surprisingly little has been published in which the traditional moving-liquid phase has been replaced by a moving-gas phase. In part this may be ascribed to historical accident. Chromatography was first used for the more complex and therefore more feebly volatile molecules, and has since been largely employed only for those problems where other methods have failed. In many ways it would have been more logical had conventional chromatographic methods developed from gas chromatography rather than the reverse, for the behaviour of gases is simpler and better understood than that of liquids.

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* Part I is considered to be the paper by Phillips in *Discuss. Faraday Soc.*, 1949, **7**, 241.

Most of the published work on gas chromatography has been concerned with the use of adsorption columns of charcoal or silica gel. Turner (*Oil Gas J.*, April 29th, 1943; *Petrol. Refiner*, May, **1943**) described the fractional desorption of vapours from a charcoal column by means of a heater. Glueckauf (*Discuss. Faraday Soc.*, 1947, **7**, 199) obtained an enrichment of the neon isotopes on passing neon through charcoal at −196°. Turkel'taub (*J. Anal. Chem. U.R.S.S.*, 1950, **5**, 200) devised a technique in which hydrocarbons removed from a charcoal column were estimated by combustion. Cremer and Muller (*Mikrochem. Microchim. Acta*, 1951, **36**/**37**, 533) separated various acetylenes and olefins on columns of charcoal and silica gel. The curved isotherms typical of adsorption equilibria make the method particularly suitable for the application of the *displacement* technique, as was first demonstrated by the work of Claesson (*Arkiv Kemi, Min., Geol.*, 1946, *A*, **23**, No. 1), and later by Phillips (Part I, *loc. cit.*), and by Hammar (*Svensk Kem. Tidskr.*, 1951, **63**, 125). The potentialities of gas chromatography with partition columns, in which the static phase is a high-boiling liquid, has been well demonstrated by Martin and James's recent work (*Biochem. J.*, 1952, **50**, 679). The linear isotherms obtained in partition equilibria make partition columns suitable for the *elution* technique.

We believe that gas chromatographic methods deserve a much fuller investigation, because the more nearly ideal behaviour of gases should make it possible to effect separations with even greater efficiency in gas chromatography than has already been obtained in liquid chromatography. In particular, equilibria involving gases, especially between gases and surfaces, are set up much more rapidly than equilibria involving liquids, where " solvent cage " effects are present. An investigation of the use of gas-chromatographic methods has therefore been instituted, in which both the adsorption (displacement) and the partition (elution) technique are being employed side by side. Some of the general results obtained have already been reviewed (Griffiths, James, and Phillips, *Analyst*, 1952, **77**, 897). The present paper is largely concerned with the analyses and separations obtained with the displacement technique, and in particular with the use of charcoal columns operated at 100°. Some results obtained with the partition technique are also included. A later paper will describe the use of the chromatographic apparatus for the determination of adsorption isotherms.

EXPERIMENTAL

Apparatus.—The complete apparatus is represented by the block diagram (Fig. 1). The mixture to be separated is placed in one of the introductory tubes I_A or I_P, and carried on to the adsorption column C_A or the partition column C_P in a stream of nitrogen from the cylinder. For application of the elution technique a constant flow of nitrogen (solvent) is then passed through the column by operation of the flow-control *F*. For use of the displacement technique (with the adsorption column) the nitrogen stream is switched through the saturator *S*, by means of which a constant concentration of displacer vapour is introduced into the nitrogen. After leaving either column, the gas stream passes through the thermal conductivity cell (*TC*) and the fraction collector (*C*).

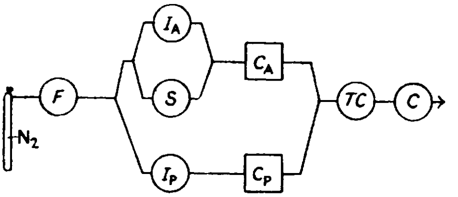


FIG. 1. *Block diagram of apparatus.*

The flow-control *F* has been specially designed for gas chromatography and is described by us elsewhere (*J. Sci. Instr.*, 1952, **29**, 362).

The adsorption column C_A is illustrated in Fig. 2. It consists of three sections (see Part I), each 10 cm. long, the first of diameter 16 mm., the second 8 mm., and the final "sharpening" section 2 mm. The column is surrounded by a jacket, kept at a fixed temperature by vapour from a smooth-boiling electrically heated flask. The charcoal used for most of the work (Sutcliffe and Speakman, 208C) was of particle size B.S.S. 30—40 (0·014—0·020″ diameter). It is dried at 140° before use.

The partition column C_P is illustrated in Fig. 3. It consists of a length of 3-mm. bore tubing about 75 cm. long. This column can also be jacketed when required. Silicone fluid (702), nitrobenzene, " tricresyl " phosphate, and dibutyl phthalate have been employed as column liquids. They are supported on a non-adsorbent material (Celite, Johns-Mansville). The Celite is freed from dust by sedimentation in water, dried at 100°, thoroughly mixed with about 30% by weight of the column liquid, and packed into the tube with vigorous agitation from an electric motor.

The saturator *S*, illustrated in Fig. 4, consists of a jacketed tube containing a sintered-glass disc (grade 2), through which the nitrogen passes as small bubbles into the liquid displacer. Despite its simple design, a close investigation has shown it to be extremely efficient.

FIG. 2. *Adsorption column.*

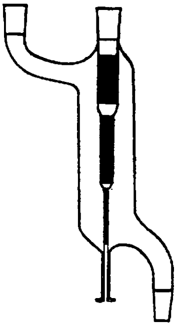


FIG. 3. *Partition column.*

FIG. 4. *Saturator.*

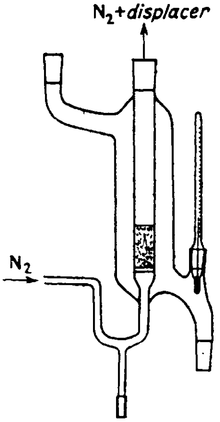


FIG. 5.

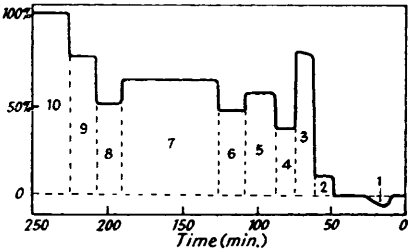


FIG. 5. *A typical displacement analysis (Analysis* O, *Table* 2).

Components of mixture : Water (1), *diethyl ether* (2), *chloroform* (3), *ethyl acetate* (4), *thiophen* (5), *dioxan* (6), *pyridine* (7), *butyl acetate* (8), *chlorobenzene* (9), *and bromobenzene* (10) *displacer.*

FIG. 6.

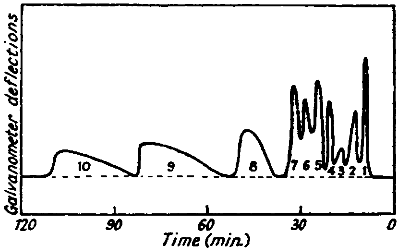


FIG. 6. *A typical partition analysis.*

Column : 1·5 *ml. of dibutyl phthalate supported on " Celite." Temperature,* 56°. *Flow rate,* 45 *ml. per min. Analysis of mixture consisting of* 0·03 *ml. each of* n-*pentane* (1), n-*hexane* (2), *siloxane* (DC 200/0·65 *cs.*) (3), cyclo*hexane* (4), *carbon tetrachloride* (5), *benzene* (6), *thiophen* (7), *toluene* (8), *pyridine* (9), *and* m-*xylene* (10).

The thermal-conductivity cell *TC* follows the design given in Part I (*loc. cit.*) and is also jacketed to prevent condensation. The cell wire forms one arm of a Wheatstone bridge, the other three arms consisting of manganin coils immersed in thermostat oil, at room temperature. The bridge is driven by a high-capacity 2-volt battery, and the out-of-balance voltage applied to a recording galvanometer (Ether Indicorder; Ether Ltd., Birmingham). The cell wire is of platinium, 14 cm. long and 0·05 mm. in diameter. It has a cold resistance of approx. 7 ohms. Under operating conditions, *i.e.*, with the jacket at 100°, and with nitrogen flowing through the cell, the resistance rises to 10·10 ohms, and the wire temperature is 127·7°. The temperature rises as vapours leave the column in the nitrogen stream, and is, for example, 128·7°

for the benzene step, and 130·0° for the bromobenzene (displacer) step. Various cell designs have been tried. All are somewhat sensitive to vibration, which leads to fluctuations on the recorder. These fluctuations are reduced to the order 0·0—0·5% of displacer step height by mounting the cell support on thick rubber. Typical results obtained on the recorder are illustrated in Fig. 5 (displacement), and Fig. 6 (elution from a partition column).

Tubes connecting saturator, column, and thermal-conductivity cell are kept at a high enough temperature to prevent condensation, by means of wire-wound heaters.

RESULTS AND DISCUSSION.

The results obtained by the adsorption (displacement) technique are discussed below [Sections (i)—(viii)]. Some typical displacement analyses are given in Tables 1, 2, and 3. The results obtained with the partition (elution) technique are discussed in Section (ix).

(i) *Range of Technique.*—The type of substance, suitable for a particular displacement analysis, is largely governed by the sensitivity of the thermal-conductivity recorder, and by the character of the displacing vapour. As a general rule the separations follow the order of boiling points fairly closely, a given vapour displacing the vapours of all other substances of lower b. p. [Exceptions on the charcoal employed include *n*-butyl alcohol (b. p. 117°) before pyridine (115°), thiophen (84°) before benzene (80°), pyridine (115°) before toluene (111°), *cyclo*hexane (81°) before benzene (80°), and siloxane (DC 200/1·5 cs.) (192°) before bromobenzene (156°).] The saturator temperature (and hence the concentration of displacer vapour in the nitrogen stream) is chosen so that the various substances leave the column at concentrations sufficient for the thermal-conductivity recorder to differentiate one step from the next. With our apparatus, a displacer concentration of about 7% (molar) in nitrogen is found to be convenient, and this has led, in most of our work, to the use of nitrogen saturated with ethyl acetate at 0° for columns at room temperature, and nitrogen saturated with bromobenzene at 77° for columns operated at 100°. This results in step concentrations of between 6 and 7 molar %. Low displacer concentrations give rise to longer steps and increased quantitative accuracy, but lowered qualitative distinction. The latter factor can, of course, be improved by altering the recording device, and by this means (see Griffiths, James, and Phillips, *loc. cit.*) we have even succeeded in using as displacer a stream of nitrogen saturated with ethyl benzoate (b. p. 213°) at 0°.

TABLE 1. *Estimation of benzene and toluene in various mixtures.*

Found	Correct	Other components of mixture	Found	Correct	Other components of mixture
	Benzene, % (by wt.)			Toluene, % (by wt.)	
99·5	100	—	100·5	100	—
100	100	—	100	100	—
50·7	51·4	PhMe	49·3	48·6	C_6H_6
49·0	49·7	PhMe	51·0	50·3	C_6H_6
41·6	41·8	PhCl	46·2	46·2	PhCl
46·6	46·8	C_5H_5N	45·7	46·2	*o*-$C_6H_4Me_2$
24·3	24·3	PhMe + PhCl	24·6	24·2	C_6H_6 + PhCl
20·3	20·2	PhMe + *o*-$C_6H_4Me_2$	38·2	38·0	C_6H_6 + *o*-$C_6H_4Me_2$
35·7	35·7	Et_2O + PhMe	35·4	35·2	Et_2O + C_6H_6

An individual step height on the recorder depends not only upon the position of the step in the displacement sequence (*i.e.*, upon b. p.), but also upon the sensitivity of the thermal-conductivity cell to the particular substance. This is illustrated in Fig. 7, where a number of typical step heights obtained with bromobenzene displacer are plotted against the corresponding b. p.s. It will be observed, for example, that chlorinated substances produce particularly large step heights.

Substances whose b. p.s lie considerably (*i.e.*, about 120—150°) below the b. p. of the displacer will not give satisfactory steps and tend to appear as elution peaks.

(ii) *Quantity required for an Analysis.*—The apparatus described will produce a clearly defined step for as little as 0·02 g. of a normal component such as benzene. Change of displacer will alter this value. Thus if the saturator is kept at 77°, *iso*amyl acetate (b. p. 139°) displacer will only give a well-defined step for 0·04 g. of benzene, while with *o*-dichlorobenzene (b. p. 179°) as displacer only 0·01 g. is required. Smaller quantities only give

Table 2. *Typical displacement analyses.*

Adsorbent: activated charcoal. Displacer: bromobenzene.
Flow-rate: 46·5 ml./min. Column temp.: 100°.

Analysis	Component	Step height (% of PhBr)	Wt., g. Found	Wt., g. Correct	Wt., % Found	Wt., % Correct
A	*cyclo*Hexane	36·0	0·0750	0·0740	48·2	47·9
	Pyridine	60·0	0·0805	0·0805	51·9	52·1
B	Ethyl acetate	36·5	0·1445	0·1460	50·0	50·4
	Butyl acetate	50·0	0·1445	0·1435	50·0	49·6
C	Methyl acetate	26·0	0·1410	0·1400	45·0	44·7
	Siloxane (D.C. 200/0·65 cs.)	34·0	0·1720	0·1725	55·0	55·3
D	Propyl acetate	46·0	0·1610	0·1595	52·6	52·3
	Butyl acetate	50·0	0·1445	0·1455	47·4	47·7
E	Pyridine	60·0	0·3940	0·3920	69·2	69·0
	Butyl acetate	50·0	0·1755	0·1760	30·8	31·0
F	*n*-Hexane	30·0	0·0405	0·0396	26·4	26·2
	n-Heptane	41·5	0·1130	0·1120	73·6	73·8
G	*cyclo*Hexane	36·0	0·0775	0·0775	18·2	18·3
	Pyridine	60·0	0·1690	0·1698	39·6	39·9
	Chlorobenzene	76·0	0·1810	0·1775	42·2	41·8
H	Benzene	44·5	0·0797	0·0793	20·3	20·2
	Toluene	55·0	0·1482	0·1492	38·2	38·0
	o-Xylene	61·5	0·1625	0·1640	41·5	41·8
I	Ethyl acetate	36·5	0·0882	0·0875	28·3	28·3
	Propyl acetate	46·0	0·0875	0·0865	28·2	27·9
	Butyl acetate	50·0	0·1360	0·1360	43·6	43·8
J	*n*-Pentane	16·0	0·1240	0·1250	31·7	31·9
	n-Hexane	30·0	0·1320	0·1320	33·5	33·5
	n-Heptane	41·5	0·1370	0·1360	34·8	34·6
K	*n*-Propyl chloride	24·0	0·1780	0·1780	17·9	18·3
	n-Pentane	16·0	0·1190	0·1210	11·9	12·4
	Ethyl acetate	36·5	0·1260	0·1800	12·6	18·4
	Carbon tetrachloride	75·0	0·3960	0·3200	39·6	32·8
	Propyl acetate	46·0	0·1800	0·1760	18·0	18·1
L	*cyclo*Hexane	36·0	0·0920	0·0935	9·1	9·0
	Benzene	44·5	0·1800	0·1760	17·7	17·0
	Toluene	55·0	0·1630	0·1730	16·2	16·7
	Pyridine	60·0	0·1880	0·1960	18·5	18·9
	Chlorobenzene	76·0	0·2200	0·2220	21·7	21·5
	o-Xylene	61·5	0·1700	0·1730	16·8	16·9
M	*n*-Pentane	16·0	0·1270	0·1260	11·5	11·4
	*cyclo*Hexane	36·0	0·1560	0·1560	14·1	14·0
	n-Hexane	30·0	0·0920	0·1320	8·4	11·8
	Benzene	44·5	0·2130	0·1760	19·3	15·9
	Pyridine	60·0	0·1760	0·1760	15·8	15·9
	o-Xylene	61·5	0·3420	0·3340	30·9	31·0
N	Water	no step	0·0820	0·0800	10·6	10·4
	*iso*Pentane	10·0	0·0160	0·0160	2·1	2·1
	n-Pentane	16·0	0·0838	0·0838	10·9	11·0
	n-Hexane	30·0	0·0746	0·0725	9·6	9·4
	Benzene	44·5	0·1330	0·1340	17·2	17·5
	n-Heptane	41·5	0·0980	0·0950	12·7	12·4
	Toluene	55·0	0·1313	0·1313	17·0	17·0
	Chlorobenzene	76·0	0·1540	0·1550	19·9	20·2
O	Water	no step	0·0430	0·0400	1·9	1·8
	Diethyl ether	12·0	0·0775	0·0785	3·4	3·5
	Chloroform	77·0	0·1920	0·1950	8·5	8·7
	Ethyl acetate	36·5	0·1155	0·1170	5·1	5·2
	Thiophen	55·0	0·2025	0·2070	9·1	9·3
	Dioxan	45·0	0·1650	0·1660	7·4	7·4
	Pyridine	61·0	1·0855	1·0800	48·5	48·3
	Butyl acetate	50·0	0·1830	0·1765	8·2	7·9
	Chlorobenzene	76·0	0·1755	0·1770	7·9	7·9

Table 3. *Displacement analyses with one component present as a small percentage.*

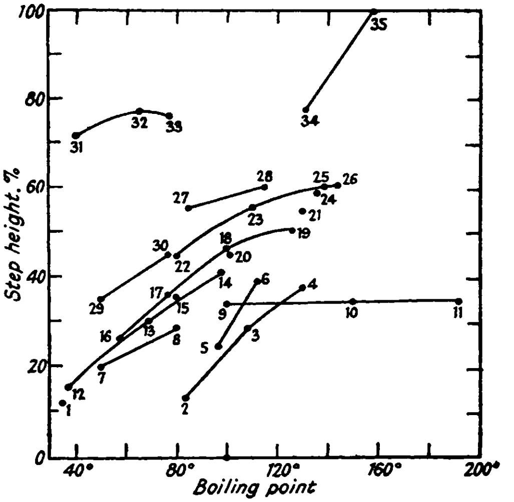
Conditions as in Table 2.

Analysis	Component	Step height (% of PhBr)	Wt., g. Found	Wt., g. Correct	Wt., % Found	Wt., % Correct
P	Benzene	44·5	0·0592	0·0588	1·68	1·66
	Toluene	55·0	3·47	3·47	98·3	98·3
Q	Benzene	44·5	3·54	3·52	98·1	98·2
	Toluene	55·0	0·0690	0·0695	1·94	1·75
R	Pentane	16·0	0·0207	0·0205	0·60	0·60
	Benzene	44·5	3·72	3·72	99·4	99·4

rise to points of inflexion, which, however, may still be used for quantitative and rough qualitative analysis. It is to be noted that the limit is an absolute one, and is independent of the amount of other components present in a mixture. This feature of the method makes it very suitable for the analysis of traces of one substance in relatively large amounts of another, as is shown by Analyses P, Q, and R in Table 3. Furthermore, small traces of a component will be concentrated in the column, so that the method is also very suitable for its isolation.

(iii) *Accuracy of Analyses.*—The accuracy of an analysis depends upon the accuracy with which a step length can be measured, and the accuracy with which various experimental parameters (such as flow-rate, saturator, and column temperatures) can be kept constant. The latter tend to vary more from one run to another than they do during one run itself, so the relative values for the components of one mixture are often more accurate than the absolute accuracy with which each is measured. The step length measurement is essentially one of time and can be made with more precision than the measurement of step height, which depends upon the response of the thermal-conductivity cell. The method is therefore particularly suited for quantitative work. An accuracy of better than 1% is readily obtained as will be seen from the tables.

FIG. 7. *Plot of step height (measured as % of displacer-bromobenzene-step height) against boiling point, for a number of compounds displaced from a charcoal column at* 100°.



1. Diethyl ether.
2. *iso*Propyl alcohol.
3. *iso*Butyl alcohol.
4. *iso*Amyl alcohol.
5. *n*-Propyl alcohol.
6. *n*-Butyl alcohol.
7. Acetone.
8. Ethyl methyl ketone.
9. Siloxane DC 200 0·65 cs.
10. ,, ,, 1·0 cs.
11. ,, ,, 1·5 cs.
12. *n*-Pentane.
13. *n*-Hexane.
14. *n*-Heptane.
15. *cyclo*Hexane.
16. Methyl acetate.
17. Ethyl acetate.
18. Propyl acetate.
19. Butyl acetate.
20. Dioxan.
21. *cyclo*Pentanone.
22. Benzene.
23. Toluene.
24. Ethylbenzene.
25. *m*- and *p*-Xylene.
26. *o*-Xylene.
27. Thiophen.
28. Pyridine.
29. *n*-Propyl chloride.
30. *n*-Butyl chloride.
31. Methylene dichloride.
32. Chloroform.
33. Carbon tetrachloride.
34. Chlorobenzene.
35. Bromobenzene.

(iv) *Time required for an Analysis.*—The time taken for an analysis will depend upon the nitrogen flow-rate employed and the amount of material to be analysed. Throughout our work we have employed a constant flow-rate of 46·5 ml. of nitrogen per minute. A faster flow-rate reduces the accuracy somewhat, but there has been little improvement on reducing the flow-rate below this figure. An analysis of 0·1 g. takes about 20 min.' running time, and correspondingly with 1 g., 200 min. The actual manipulation time required is, of course, considerably less, for the recording equipment runs automatically.

The various operations required to change from one analysis to the next (change of charcoal, introduction of mixture to be analysed, and connection to the saturator) can be effected in under 10 min., and will be very nearly independent of the amount of sample.

(v) *Efficiency of Separations.*—It has been found in liquid chromatography that it is possible, as a result of complex adsorption isotherms, for sharp displacement steps to be produced, which nevertheless do not consist of pure components. The high accuracy of the gas-chromatographic analyses over wide variations of mixture composition suggests that this cannot be so in the case of gas chromatography. It seemed, however, essential to confirm this, and a number of separate checks have been made on samples isolated from individual steps by the fraction collector. Mixed steps were only found when it was attempted to separate benzene and *cyclo*hexane on the normal coarse charcoal, or in other instances when the column had been seriously overloaded. The separation of benzene and *cyclo*hexane proved to be quite satisfactory with finer charcoal [see (vii) below]. For an example of overloading, compare results M and N in Table 2. Analysis M was carried out with only 15 ml. of charcoal, and results in a poor separation of *n*-hexane and benzene. Analysis N, carried out with 25 ml. of charcoal, gave a good separation.

The checks on the purity of individual fractions have been made by measurements of liquid density and of b. p.s, and by running samples on partition columns. Liquid densities were determined by a micropyknometer capable of handling 0·02 ml. with an accuracy of 0·2%.

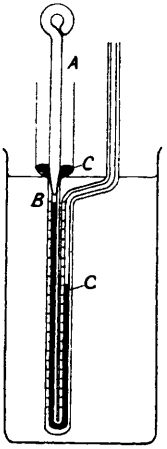


FIG. 8. *Micro-apparatus for determination of boiling points.*

A, Ground glass stopper. B, Sample. C, Mercury.

Boiling points were measured in a modified micro-Schleiermacher apparatus. It was found impossible to obtain accurate results with the recommended sealing-off technique, as a result of the trapping of small air bubbles and the presence of air in the mercury. This technique was replaced by the use of a ground-glass stopper (Fig. 8), which enables such bubbles of air to be removed with ease whenever they appear. With this simple modification it was then found possible to measure b. p.s on as little as 0·02 ml. of a liquid, with an accuracy of ±0·1°. A larger version of this apparatus, with essentially the same design, has been described by Simmons (*J. Chem. Educ.*, 1947, **24**, 233).

TABLE 4. *Analysis of fractions from a displacement run.*

	B. p.		Density	
Step	Found	Correct	Found	Correct
Diethyl ether	34·5°	34·5°	0·709	0·714
Benzene	80·1	80·2	0·880	0·879
Toluene	110·9	110·8	0·864	0·866

Some typical results obtained for an ether, benzene, and toluene mixture are given in Table 4. Boiling-point data for ether–benzene and benzene–toluene systems (see I.C.T.) show that ether containing 1% of benzene would boil 0·25° higher, and benzene containing

1% of toluene would boil 0·23° higher. These results on the purity of individual steps were confirmed by partition experiments in which no small extra peaks could be discerned when each fraction was run separately.

(vi) *Recovery of Components.*—Small amounts of irreversible adsorption would lead to less than 100% recovery, although sharp steps could still be obtained, and accurate analyses performed under constant conditions. It is, however, found that the step length is independent of the amount of charcoal employed. The 100% recovery has been further confirmed by comparison with careful vapour pressure–step height measurements undertaken in connection with the isotherm determinations (James and Phillips, unpublished). The foregoing remarks do not hold good for the adsorption of aldehydes and acids on charcoal, or for the adsorption of olefins on silica gel, where irreversible adsorption appears to take place.

(vii) *Separation of Close-boiling Mixtures.*—The efficiency of the gas-chromatographic technique is well illustrated by the ease with which many close-boiling mixtures are separated. The following mixtures have been readily separated by the normal technique: (*a*) *n*-butyl alcohol (b. p. 117°) and pyridine (115°), (*b*) *iso*butyl alcohol (108°) and toluene (111°), (*c*) water (100°) and dioxan (101°) (see Fig. 5), and (*d*) ethyl acetate (77·2°) and carbon tetrachloride (77·5°). Such mixtures are naturally somewhat more difficult than those containing only substances of very different boiling points. Analysis K (Table 2) has been inserted to illustrate this point. It was carried out with only 15 ml. of charcoal, which was insufficient to separate completely the ethyl acetate and the carbon tetrachloride although all the other components are well separated. Another case is afforded by the separation of benzene (80·2°) and *cyclo*hexane (80·8°). In this case sharp steps are produced, but although the *cyclo*hexane step is pure, the benzene step contains about 10% of *cyclo*hexane. The *cyclo*hexane can be removed completely from the benzene by use of a fine charcoal, obtained by sedimentation.

In certain instances a poor separation is emphasised by an increase in the normal diffuse zone between two steps, which are themselves quite pure. Thus in the separation of thiophen (84°) and benzene (80°) the diffuse zone contains 0·10 g. instead of the normal 0·02 g. of a mixture. By use of fine charcoal the diffuse zone can be reduced again to 0·02 g. This system shows a further point of interest with a reversal of displacement order. With bromobenzene displacer and the column at 100°, the thiophen is displaced first, but with heptane displacer and the same (crude) charcoal column at 20° the benzene step precedes the thiophen step. In this case the diffuse zone contains 0·05 g. of the mixture.

In some cases it is possible to simplify the separation of close-boiling mixtures by an appropriate change of adsorbent. Thus silica gel, which has a low affinity for chloro-compounds, may be used to separate carbon tetrachloride (77·5°) and *n*-butyl chloride (78°) from other substances such as benzene (80·2°), ethyl methyl ketone (79·6°), and ethyl acetate (77·2°). The chloro-compounds appear as separate elution peaks, ahead of the steps formed by the other components.

It has also been found possible quite readily to separate other mixtures, which, though not close-boiling, are difficultly separable by normal distillation methods, *e.g.*, water and pyridine, water and toluene, and water and dioxan.

(viii) *The Problem of Closely Similar Step Heights.*—It may happen that adjacent steps in a displacement analysis are so similar in height that they are not easily distinguished from one another by the normal thermal-conductivity recorder. This is particularly the case with isomeric mixtures; *e.g.*, some of the different pentanes, hexanes, and heptanes give steps which are virtually indistinguishable from those of their isomers. Good separations are, however, effected, as has been shown by careful measurement of b. p.s (Fig. 9). Ethylbenzene forms a step which is just distinguishable from that of the xylenes, but the individual xylenes appear to form one step. Boiling point measurements again show that *o*- (144°) is clearly separated from *m*- (138·8°) and *p*-xylene (138·4°).

An interesting case of partial separation of two isomers differing only in the position of a double bond is afforded by an analysis of a mixture of 2 : 6-dimethylhepta-2 : 5- and -2 : 6-diene. Fractions were collected and analysed by infra-red measurement by L.

Bateman (British Rubber Producers' Research Association), giving the results quoted in Table 5.

TABLE 5. *Analysis of heptadienes.*

Displacer : bromobenzene		Displacer : *o*-dichlorobenzene	
Fraction	2 : 5-Diene, %	Fraction	2 : 5-Diene, %
1	5	1	5
2	35	2	5
3	45	3	40
		4	40

The problem of closely similar step heights may be solved in a number of ways. First, the sensitivity of the thermal conductivity cell can be increased. Secondly, it is possible to collect fractions for analysis as in the examples quoted above or, more conveniently, to make use of another continuous analysing device either as a substitute or as an auxiliary for the thermal-conductivity cell. It is quite easy for the gas leaving the column to flow through a number of different analysing devices in turn, and this possibility has led us to make a general investigation of alternative analysers to the thermal-conductivity cell. A review of some of this work has already been given (Griffiths, James, and Phillips, *loc. cit.*). A third method employs a marker substance, chosen so as to be displaced between the two difficultly distinguishable components. As more substances are investigated by the technique, the choice of suitable marker substances becomes easier. A simple illustration of the principle is, however, given by Analysis O (Table 2). There, it will be seen that the step heights of chloroform and chlorobenzene are sufficiently close to make it difficult to distinguish them with an insensitive thermal-conductivity cell. They are, however, separated from one another in Analysis O by the steps of ethyl acetate, thiophen, dioxan, pyridine, and butyl acetate, all of which would be suitable marker substances. Another illustration is afforded by Analysis L, where chlorobenzene acts as a marker between pyridine and *o*-xylene.

FIG. 9.

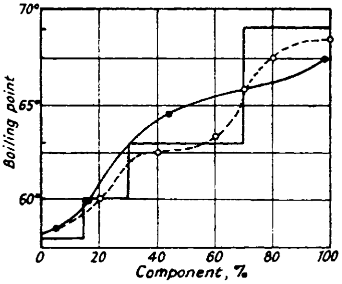


FIG. 10.

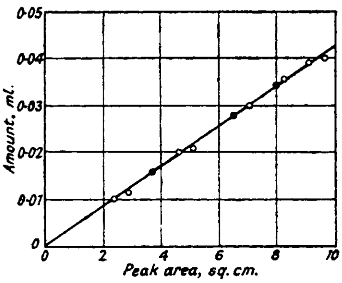


FIG. 9. *Characterisation of hexane fractions from displacement columns by means of boiling points.*

Full curve : Fractions obtained from 0·7 *ml. of hexane, using* 12 *ml. of charcoal. Broken curve : Fractions obtained from* 0·7 *ml. of hexane, using* 24 *ml. of charcoal. Sharp steps represent ideal separation of the four isomers present :* 2 : 3-*dimethylbutane* (*b. p.* 58°), 2-*methylpentane* (60°), 3-*methylpentane* (63°), *and* n-*hexane* (68°).

FIG. 10. *Quantitative analysis on partition columns.*

Plot of area under cyclo*hexane peak, against amount of* cyclo*hexane. Open circles represent elutions from silicone* (702) *column. Full circles represent elutions from nitrobenzene column.*

(ix) *Results obtained with the Partition Columns.*—Fig. 6 illustrates the result of a typical partition analysis. The qualitative analysis is effected by a measurement of " retention volumes," *i.e.*, the volumes of nitrogen which have to be passed through the column before the peak maxima occur. Provided the flow-rate is kept constant, these are more conveniently measured as the times before the various maxima appear. Some typical results are given in Table 6. The quantitative analysis is effected by measurement of the area under a peak, and is illustrated by the results shown in Fig. 10.

For linear partition isotherms the peaks will have a symmetrical structure, and this is generally found so long as only small amounts of the component are dissolved in the column liquid. If larger quantities are employed, *i.e.*, if the column approaches an overloading condition, the solutions are no longer dilute, and non-linear isotherms and skew structures for the peaks may be obtained.

TABLE 6. *Partition analyses on three columns.**

Dibutyl phthalate column at 56°					Tritolyl (" tricresyl ") phosphate column at 56°				Nitrobenzene column at 15°			
Substance	Appearance of maxima (min.)				Substance	Appearance of maxima (min.)			Substance	Appearance of maxima (min.)		
	1	2	3	4		1	2	3		1	2	3
*cyclo*Hexane	6·5	6·5	6·5	6·5	*iso*Propyl chloride	3·5	3·5	3·5	Pentane ...	3·5	3·5	3·5
Benzene ...	14	14	14	14	*n*-Propyl chloride	5	5	5	Hexane	11·5	11·5	11·5
Thiophen ...	19	18·5	19	19	*n*-Butyl chloride	11·5	11·5	11·5	Heptane	37	37	37

* Run numbers are recorded above the times.

In contradistinction to the adsorption columns, the partition columns have no self-sharpening properties, so there is no tendency for small traces to concentrate, and a diffuseness once obtained is only increased along the length of the column. In consequence, some little care must be exercised in placing materials on the partition column, for if one component arrives in two bursts it will remain as two separate peaks during the column development. The fact that a band spreads out along the column is particularly a defect when a wide range of substances is to be separated. The later components then appear as long bands of low concentration (*e.g.*, Fig. 6). This defect may, however, be overcome by use of a column the temperature of which is rising continuously throughout the run (*idem, ibid.*). In general, retention volumes are very sensitive to column temperature, a change of approximately 10% in retention volume resulting from a 1° change in column temperature, which has therefore to be controlled carefully. Displacement columns, however, are relatively insensitive, a 1% change of column temperature producing about 0·5% change in a typical step height (Part I, *loc. cit.*).

FIG. 11.

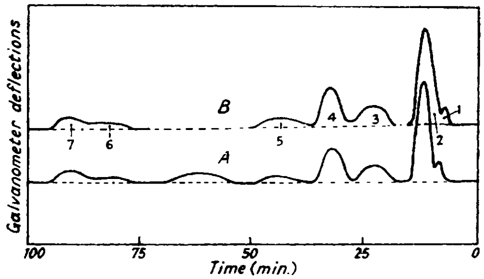


FIG. 12.

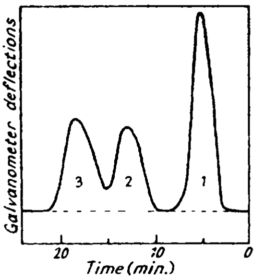


FIG. 11.

A. *Partition analysis of light petroleum fraction (b. p. 40—100°) from column of silicone* (702). B. *Composite picture constructed from separate analyses of pure hydrocarbons from same column*: (1) i*sopentane*, (2) n-*pentane*, (3) 3-*methylpentane*, (4) n-*hexane*, (5) 2-*methylpentane*, (6) 3-*methylhexane and* 2 : 3-*dimethylpentane, and* (7) n-*heptane*.

FIG. 12. *Partition analysis of* cyclo*hexane* (1), *benzene* (2), *and thiophen* (3) *from* 1·5 *ml. of dibutyl phthalate at* 56°.

On the other hand, because of the peak structure obtained, the partition method has decided advantages for the analysis of mixtures of isomers, or mixtures of certain close-boiling substances where the similarities of the step heights produced in the displacement method make differentiation and estimation difficult. Such an example is provided by the pentane and hexane isomers, which are readily separated on a column of silicone fluid (702) as is illustrated by Fig. 11, which represents an analysis of a light petroleum fraction (b. p. 40—100°), with the separate elution analyses of various pentanes, hexanes, and heptanes also displayed for comparison. The separation of the close-boiling *cyclo*hexane, benzene, and thiophen is illustrated in Fig. 12. Another useful feature of the partition column is the manner in which it may sometimes be possible to alter the separations in a more or less predictable way by an appropriate change of column fluid. Thus with column lengths so chosen as to give a constant retention time of 10 min. for the *cyclo*hexane peak, the following values (min.) were obtained for benzene : 15 (silicone fluid 702), 23 (dibutyl phthalate, or tritolyl phosphate), and 37 (nitrobenzene).

Conclusion.—The results described above show that the gas-chromatographic methods are capable of effecting remarkably sharp separations of mixtures of volatile organic compounds, and that they are convenient for the analysis of small quantities of material. Quantitative analyses can be made with an accuracy of better than 1%. The two basic techniques, adsorption (displacement) and partition (elution), tend to be complementary to one another. The displacement technique produces concentrated zones, ideally suited for quantitative analysis and general preparative work. The partition method produces zones of low concentration, which are ideal for the differentiation of closely similar substances and for the sharpest separations. The adsorption columns possess self-sharpening properties, which make them useful for the isolation of trace materials, and allow good results to be obtained with only the crudest type of column packing.

Gas-chromatographic techniques should have many applications in both analytical and preparative work. We propose to employ them for the more detailed analysis of the products obtained in certain organic reactions, and also in a general investigation of volatile inorganic compounds.

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