The Chromatography of Gases and Vapours. Part IV. Applications of the Surface-potential Detector.*

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[Reprint Order No. 5296.]

The paper describes a device for the detection and estimation of vapours in nitrogen. Its action depends upon changes in the surface-potential difference between two metal plates, one of which is vibrating close to the other. Its application to gas chromatography is discussed and illustrated. It has also been used to determine vapour pressures.

IN previous work in this series (Phillips, *Discuss. Faraday Soc.*, 1949, **7**, 241; James and Phillips, *J.*, 1953, 1600; *J.*, 1954, 1066) the separations, achieved by the gas chromatographic columns, have been followed by means of a thermal-conductivity cell placed at the exit of the column. Although the thermal-conductivity cell is sensitive to small concentrations of vapour and readily lends itself to continuous recording, we have found that the limits of our gas-chromatographic work have largely been set by the limits of the thermal-conductivity recording system. We therefore decided to investigate a number of other methods for detecting small concentrations of vapour in nitrogen. Some of our initial results with various detectors have already been reviewed (Griffiths, James, and Phillips, *Analyst.*, 1952, **77**, 897). This paper is concerned with the surface-potential

* Part III, *J.*, 1954, 1066.

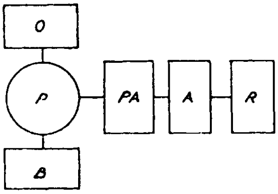
vapour detector, and in particular with its application to gas chromatography. The possibility of using changes in surface potential for detecting small vapour concentrations was first suggested to us by the work of G. Phillips (*J. Sci. Instr.*, 1951, **28**, 342), and we have followed his design in constructing much of our detector system.

Principle of Operation of the Surface-potential Detector.—If two identical metal plates are connected by a conductor, and one plate is made to vibrate close to the other, no current flows in the conductor. The potential at the surface of each plate will be the same, so that the vibrating plate is moving in zero field. If, however, the two plates are dissimilar (*e.g.*, two different metals, or a surfaced and an unsurfaced plate), the two surfaces will no longer have the same potential and an alternating E.M.F. will be set up in the conductor on vibration. The standing difference in surface potential can be measured by applying a bias E.M.F. to one of the plates until the alternating E.M.F. is reduced to zero. If the surfaces are now changed by exposure to an adsorbable vapour, the standing potential will, in most cases, also be changed. This change in potential is the signal of the surface-potential detector.

EXPERIMENTAL

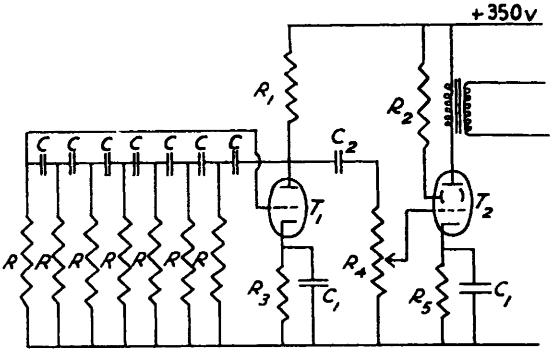
Apparatus.—Fig. 1 is a block diagram of the complete detector. The vibrating plate is attached to a microphone which is driven (200—500 cycles) by a straightforward phase-shift oscillator (Fig. 2). The plate assembly is illustrated in Fig. 3. The electrode system is made as compact as possible in order to reduce the dead volume which has to be swept out with gas. A dead volume of *ca.* 20 ml. is achieved by driving the 1″-diameter vibrating electrode with a small moving-coil headphone, the cone of which forms the "roof" of the glass electrode chamber; the stationary electrode protrudes through the bottom of the chamber to within 0·01 cm. of the vibrating plate, and is supported by an ebonite tube within a steel cylinder. The steel cylinder is ground to a standard taper and fits tightly into the ground socket which forms the bottom of the electrode chamber. The ebonite tube which supports the stationary electrode contains the first stage of amplification (Fig. 4, an E.T.3. electrometer triode, battery-driven for stability) and can be moved up and down within the steel cylinder to adjust the gap between the electrodes. The electrode region is completely screened by sheets of earthed copper foil and by silver deposited on the inside of the glass chamber.

FIG. 1. *Block diagram of apparatus.*



O, Oscillator.
P, Plate assembly.
B, Bias control.
PA, Preamplifier.
A, Amplifier.
R, Recorder.

FIG. 2. *Phase-shift oscillator.*

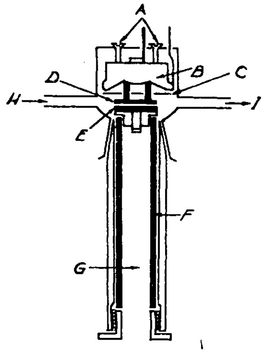


T_1, 6J5.	T_2, 6V6.	
C, 1,500 p F.	C_1, 50 μF.	C_2, 0·1 μF.
R, 470 K.	R_1, 200 K.	R_2, 1K.
R_3, 4·7 K.	R_4, 1 M.	R_5, 220 Ω.

The output from the plates is applied to the grid of the electrometer triode (preamplifier), and the output of the preamplifier is fed to an R–C coupled three-stage amplifier (Fig. 5), the first stage of which is an EF 37A low-noise pentode. The output of the amplifier is rectified, and fed to a D.C. milliammeter pen-recorder. Bias E.M.F. is applied to the plates by means of a calibrated potentiometer.

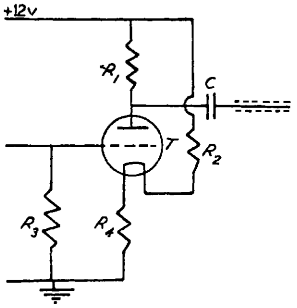
Plate Surfacing.—Although we have carried out experiments with a number of different plate surfaces, we have, in most of our work, used a detector containing two steel plates, one of which is surfaced with stearic acid or with octadecanol. The stearic acid or octadecanol is applied by the rubbing method recommended by Menter and Tabor (*Proc. Roy. Soc.*, 1951, **204**, *A*, 514). Both sets of plates prove to be highly reproducible, and are very easily prepared.

FIG. 3. *Plate assembly.*



A, Levelling screws.
B, Headphone.
C, Copper screening.
D, Vibrating plate.
E, Stationary plate.
F, Ebonite cylinder.
G, Electrometer and pre-amplifier assembly.
H, Gas inlet.
I, Gas outlet.

FIG. 4. *Preamplifier.*



T, ET3.
C, 0·1 μF.
R_1, 47 K.
R_2, 300 Ω.
R_3, 10^{10}Ω.
R_4, 80 Ω.

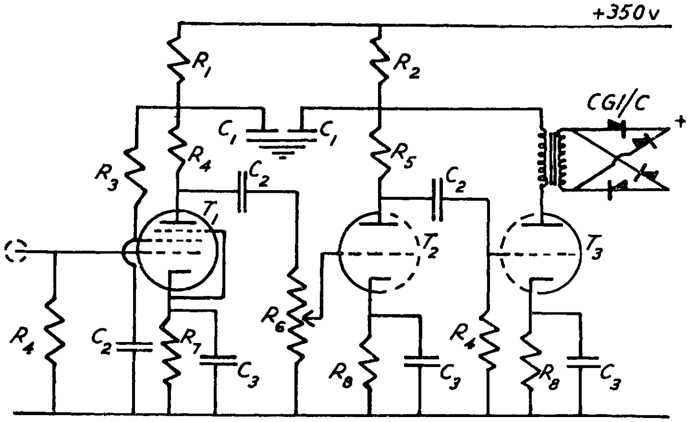


FIG. 5. *Amplifier.*

T_1, EF 37A.
T_2, T_3, two halves of 6SN7.
C_1, 8 μF.
C_2, 0·1 μF.
C_3, 50 μF.
R_1, 47 K.
R_2, 22 K.
R_3, 2·2 M.
R_4, 470 K.
R_5, 100 K.
R_6, 330 K.
R_7, 4·7 K.
R_8, 3·3 K.

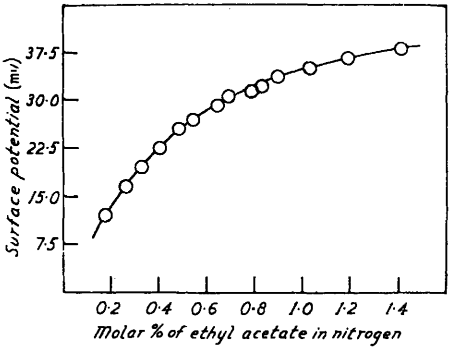
RESULTS AND DISCUSSION

Some typical results are given in Table 1. These have been obtained by passing, between the plates, nitrogen which has been saturated at 0° with the vapours of the various substances. (These have largely been selected because of their suitability for later chromatographic work). The signals obtained are, for the most part, very well above the drift noise-level of the present instrument (1 mv). The figures quoted are for the potentials which must be applied to the unsurfaced steel plate to restore the output to zero.

The results for any one set of plates tend to fall into three groups : positive signals (esters and ethers), zero signals (non-polar substances), and negative signals (chlorinated compounds). Within the series of esters, it is to be noted that there is no marked falling off of signal with increase of molecular weight (and hence decreasing vapour pressure at 0°). This must mean that the reduced vapour pressure is to some extent counterbalanced by increased adsorption on the plates. Thus ethyl oxalate, whose vapour pressure is 4×10^{-2} mm., produces a signal of the same order of magnitude as ethyl acetate, which has a vapour pressure of 24 mm. Although both sets of plates give somewhat similar results, the stearic acid/steel set being slightly more sensitive, there are a number of differences between the two sets, the most marked of which is the reversal of sign observed with aniline.

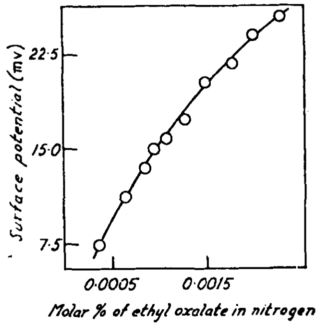
Relation between Surface Pontential and Concentration.—The relation between the surface-potential change and the concentration of vapour has been determined for a number of substances. Figs. 6, 7, and 8 illustrate the relations, or surface-potential isotherms, obtained for ethyl acetate, ethyl oxalate, and chloroform on the stearic acid/steel set of plates. All the isotherms prove to be of the same type, suggesting an

FIG. 6. *Surface-potential isotherm for ethyl acetate.*



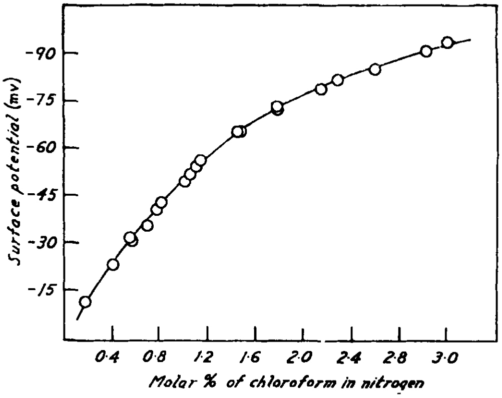
Detector plates : stearic acid/steel.

FIG. 7. *Surface-potential isotherm for ethyl oxalate.*



Detector plates : stearic acid/steel.

FIG. 8. *Surface-potential isotherm for chloroform.*



Detector plates : stearic acid/steel.

FIG. 9. *" Langmuir " plot for ethyl acetate.*

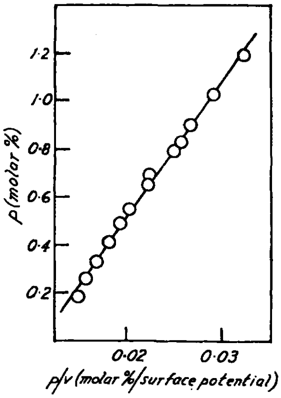


TABLE 1. *Response of detector to various vapours.*

(Values quoted are for saturated vapour pressures at 0°, and represent the potentials which must be applied to the unsurfaced plate to return the output signal to zero.)

Vapour	Surface potential (mv) * (A)	(B)	Vapour	Surface potential (mv) * (A)	(B)
Ethyl acetate	70	43	Decalin	0	0
*cyclo*Hexyl acetate	96	160	Benzene	0	0
" Cellosolve " acetate ...	30	80	Carbon tetrachloride.........	0	0
*iso*Amyl *n*-butyrate	62	110	Chloroform	−84	−140
n-Amyl *n*-butyrate	52	96	*m*-Dichlorbenzene	−12	− 60
Methyl benzoate	26	20	*o*-Dichlorbenzene	− 6	− 30
Ethyl oxalate	40	34	2 : 2′-Dichlorodiethyl ether	−10	− 34
Ethyl malonate	66	68	3 : 3′-Dichlorodipropyl ether	−18	− 76
Amyl ether	8	0	Aniline	20	− 50
Phenetole	8	20			

* (A) = Octadecanol/steel surface; (B) = stearic acid/steel surface.

approach to a limiting value for the surface-potential change at high vapour concentrations. The isotherms resemble single adsorption isotherms, though we are concerned with two surfaces. Moreover, if p is plotted against p/v as is customary for Langmuir-type adsorption, reasonable straight lines are obtained as is shown for example in Fig. 9 for the case of ethyl acetate. (The corresponding B.E.T. plots are more curved). From such plots we have estimated values for the saturation surface potentials (for plates at room temperature, 17°). These values are (in mv) : chloroform 187, water 60, ethyl acetate 55, ethyl oxalate 47, ethyl methyl ketone 38, *iso*amyl acetate 47.

Application to Chromatography.—Because of the sensitivity of the detector to low vapour concentrations, the scale of gas chromatography may be considerably reduced. We have, therefore, largely concentrated on its use for following the chromatography of high-boiling substances on low (room)-temperature columns. Such columns have to be packed with weak adsorbents, and we have used either sand (graded by sedimentation in a stream of water, B.S.S. 60—80) or small glass beads (Ballotini, No. 15 grade, less than 0·1 mm. diam., The English Glass Co., Ltd., Leicester) in most of the work. The various substances have been displaced from these columns by nitrogen saturated with diethyl malonate at 0°. The columns of sand have proved quite satisfactory for esters, as is shown by the results plotted in Fig. 10, but 3 : 3′-dichlorodipropyl ether, *cyclo*hexanone (Fig. 11), methyl*cyclo*hexanone, and aniline appear to be somewhat irreversibly adsorbed. This irreversible adsorption would appear to be confirmed by the following observations :

TABLE 2. *Displacement analyses on Ballotini.*

[Column temp. 15°; displacer, diethyl malonate (saturation at 0°); flow rate of nitrogen, 68 ml. min.; detector plates, stearic acid/steel.]

Substance and step height (mv)	Quantity, µl.	Step length, min.	Specific length, min./µl.
Methyl benzoate	0·060	2·4	40
(+ 20)	0·072	3·0	42
	0·114	5·6	49
	0·168	8·0	48
	0·240	11·0	46
n-Amyl butyrate	0·072	6·0	83
(+ 30)	0·108	9·0	84
	0·144	11·6	81
	0·180	14·4	80
*iso*Amyl butyrate	0·060	5·2	87
(+ 36)	0·084	7·0	83
	0·096	8·4	87
	0·144	11·8	82
	0·150	11·6	78
*cyclo*Hexyl acetate	0·048	4·6	96
(+ 24)	0·084	8·2	98
	0·120	11·0	92
	0·144	14·0	97
" Cellosolve "	0·072	7·2	100
acetate (+ 26)	0·096	9·8	102
	0·120	12·8	107
	0·138	14·1	102
	0·186	19·2	103
	0·192	19·6	102
Amyl ether (0)	0·036	3·4	95
	0·072	7·0	97
	0·120	11·2	94
	0·168	18·0	107
3 : 3′-Dichlorodi-	0·108	5·2	48
propyl ether	0·156	7·0	45
(— 30)	0·234	9·2	39
	0·270	11·0	41
	0·354	13·2	37
Aniline (— 28)	0·060	6·4	107
	0·072	7·8	108
	0·090	9·8	109
	0·120	12·8	107
	0·144	16·2	112
	0·168	17·0	101
*cyclo*Hexanone	0·048	12·8	270
(+ 10)	0·084	20·0	240
	0·108	26·0	240
	0·132	31·0	235

(i) The displacer moves more rapidly through a column containing one of these substances; for instance, for a 0·5-g. column of sand, the displacer normally (clean column or only reversibly adsorbed substances on the column) takes 46 min. to break through. If aniline is present this value is reduced to 37 min., or if *cyclo*hexanone is present to 42 min.

(ii) Only poor separations are achieved with mixtures involving one of these substances, when chromatographed on sand.

(iii) On a 0·5-g. column the calculated amounts of methyl*cyclo*hexanone and of 3 : 3′-

dichlorodipropyl ether irreversibly adsorbed are 100 and 92 μg. respectively. On a 1·0-g. column these values become 200 and 188 μg.

On Ballotini all the substances so far investigated seem to be reversibly adsorbed, *i.e.*, the plot of step length against quantity passes through the origin. Some typical results are collected in Table 2. On Ballotini, the following displacement sequence is observed (the figures given in parentheses are the b. p.s.): butyl acetate (126°), amyl acetate (142°), amyl ether (188°), 2 : 2′-dichlorodiethyl ether (178°) *cyclo*hexanone (156°), methyl*cyclo*hexanone (169°), *cyclo*hexyl acetate (175°), *iso*amyl butyrate (185°), *n*-amyl butyrate (185°), methyl benzoate (199°), 3 : 3′-dichlorodipropyl ether (187°), ethyl oxalate (185°), and aniline (184°), followed by diethyl malonate (199°) displacer. From mixtures, the vapours leave the column in this order, only ethyl oxalate and aniline not being clearly separated from one another.

Determination of Latent Heats and Vapour Pressures.—The surface-potential detector has also proved useful for the determination of latent heats and vapour pressures.

(a) *Latent heats.* To determine a latent heat, the signal corresponding to a nitrogen stream saturated with the vapour at $T°$ is first obtained. A stream of nitrogen saturated with the vapour at $(T + t)°$ is then diluted with a second nitrogen stream, until it produces the same signal. From the dilution required and the difference in temperature $t°$, the latent heat is readily computed; *e.g.*, for ethyl oxalate the ratio (Saturated vapour pressure at 30°)/(Saturated vapour pressure at 20°) obtained from the dilution experiments is 2·30 ± 0·02, which gives a value for the latent heat of 14·70 ± 0·15 kcal. (Stoll, *Ind. Eng. Chem.*, 1947, **39**, 517, gives a mean value of 14·65 kcal. at 45—70°). The chief merit of the detector in this connection would seem to be the ease with which latent heats can be determined at temperatures well below the b. p. Values of such latent heats are of interest because of the light they throw on problems of liquid structure (cf. Staveley and Tupman, *J.*, 1950, 3597).

FIG. 10. *Plot of step-length against quantity in displacement analysis of* iso*amyl* n*-butyrate* (○) *and methyl benzoate* (●) *from columns of sand.*

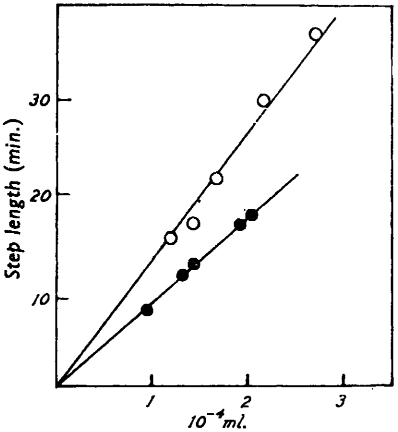
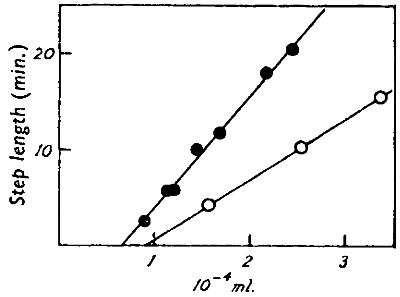


FIG. 11. *Plot of step-length against quantity in displacement analysis of* cyclo*hexanone* (●) *and 3 : 3′-dichlorodipropyl ether* (○) *from columns of sand.*



(b) *Vapour pressures.* The determination of latent heats depends upon obtaining an accurate value for the *ratio* of the vapour pressures at $T°$ and $(T + t)°$. To obtain absolute values of the vapour pressures the chromatographic column can be employed. A steady stream of nitrogen, saturated with the vapour at the required temperature, is passed on to the column for a measured number of minutes. The vapour is thus adsorbed, and is then displaced from the column, and its step length in the displacement chromatogram determined. This step length is then compared with the step length produced by a known weight of the same substance. Thus for ethyl oxalate (average values from a number of experiments) the following results were obtained: Nitrogen saturated with ethyl oxalate at 0°, and flowing at a rate of 65 ml./min. (at 0°) was passed on to the column. The step length obtained was 1·78 min./min. of original saturated flow; $1{\cdot}3 \times 10^{-4}$ g. of ethyl oxalate (*M*, 146) produces a step length of 10·50 min. Hence the vapour pressure at 0° (the gas laws being assumed to hold for such a dilute vapour) is given by the relation

$$\frac{760 \times 1{\cdot}78 \times 1{\cdot}3 \times 10^{-4} \times 22{\cdot}4 \times 10^{3}}{10{\cdot}50 \times 146 \times 65} = 3{\cdot}9 \times 10^{-2} \text{ mm.}$$

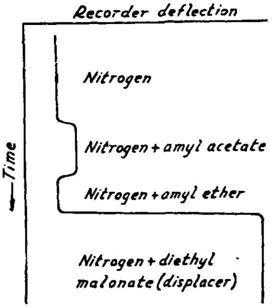
Some typical values obtained in this way are given in Table 3. So far as we have been able to discover, these vapour pressures have not been measured before, but we also give in the Table some values extrapolated from values given in the literature. Since these extrapolations have been made over a temperature range of between 25° and 40°, they are, of course, only very rough approximations.

TABLE 3. *Vapour pressures determined by displacement chromatography.*

Substance	Satd. v. p. at 0° (mm.)	Extr'd. values
Ethyl oxalate	0·039	0·020
Methyl benzoate	0·049	0·047
n-Amyl butyrate	0·11	—
*iso*Amyl butyrate	0·11	0·20
*cyclo*Hexyl acetate	0·29	—
*cyclo*Hexanone	0·73	0·91
2 : 2′-Dichlorodiethyl ether	0·12	0·17
3 : 3′-Dichlorodipropyl ether	0·091	—
Aniline	0·079	0·053
" Cellosolve " acetate	0·331	—
*iso*Amyl ether	0·195	0·26

Conclusion.—The most important feature of the surface-potential detector would seem to be its *high sensitivity.* Thus 4 p.p.m. of ethyl oxalate in nitrogen will give a signal of 7·5 mv. This represents a signal to noise ratio of 7·5/1 in our present experimental detector, but we believe that the noise level can be considerably improved, and we are at present working on an improved detector which we hope will have a noise level of the order of one microvolt. The high sensitivity is of value in gas chromatography for the following reasons: (1) Columns can be operated with the vapours at very low concentrations, with a corresponding increase in efficiency. (2) They can be operated at temperatures considerably below the b. p.s of the substances to be separated. This means that thermolabile substances (such as must be distilled under very reduced pressure) can be conveniently handled. (3) The gas chromatographic method need require only very small samples for an analysis.

FIG. 12. *Displacement analysis of substance with zero signal.*



As has been shown above, the detector is also often highly *selective*, so that its use has a certain diagnostic value (for example, distinguishing chloro-compounds from esters). This selectivity can be most important in displacement analysis, where successive steps frequently have similar concentrations. In particular, it makes it an easy matter to employ a " marker " technique, in which, say, a chloro-compound is chosen so as to place a trough between similar steps produced by two esters otherwise adjacent in the displacement sequence. It is to be noted that substances which give zero signal on the detector can still be handled by the method if in suitable admixture with " active " components, as shown in Fig. 12.

In comparison with thermal conductivity, its main disadvantages are sluggishness, non-linearity of response, and, in a few instances, irreversibility.

Sluggishness. A certain time always elapses before the detector comes into equilibrium with the gas stream passing between the plates. This is to some extent due to the fact that it takes some time to fill the plate assembly. The lag is particularly marked in the desorption of high-boiling substances from the plates. Thus the removal of the acetone signal has a time constant (time to fall to 1/e of maximum) of 30 sec., while for ethyl oxalate the value is 4·5 min. (In both cases flow-rate of 68 ml./min.).

Irreversibility. Aldehydes have been found to produce an irreversible signal, so that the plates have to be resurfaced after use. This is presumably due to irreversible adsorption, such as we have already experienced on chromatographic columns (Phillips, *Discuss. Faraday Soc.*, 1949, **7**, 241).

Non-linearity. As will be seen from Figs. 6, 7, and 8, the response curve is not linear (as it is with thermal conductivity). This factor, combined with the sluggishness, militates against its use for accurate partition work, where rapid concentration changes (peaks) have to be followed. Most of our work has therefore been done by using adsorbent columns and the displacement technique.

Throughout all our work we have had very great assistance from Mr. G. Phillips (S.R.D.E., Christchurch, Hants). One of us (J. H. G.) is indebted to the Department of Scientific and Industrial Research for a maintenance grant. We thank Imperial Chemical Industries Limited for the loan of a recorder.

INORGANIC CHEMISTRY LABORATORY, OXFORD. [*Received, April* 12*th*, 1954.]