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EVALUATION OF DYNAMIC GAS CHROMATOGRAPHIC METHODS FOR THE DETERMINATION OF ADSORPTION AND SOLUTION ISOTHERMS

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SUMMARY

Various dynamic gas chromatographic methods for the determination of distribution isotherms in gas–solid and gas–liquid–solid systems are compared. The influence of the column length, the carrier gas velocity and the nature of the carrier gas is discussed. Isotherms of different shapes are studied. An equation for the calculation of distribution isotherms from gas chromatographic data is derived which applies not only at low mole fractions but also at higher mole fractions.

(1) INTRODUCTION

Various chromatographic methods for the determination of distribution isotherms have been described in the literature[1–16]. Sometimes gas chromatographic (GC) methods are the only means of obtaining these data under the given experimental circumstances. A common feature of these methods is speed. The accuracy can be high but it will depend on the method used as well as on the operating conditions due to the systematic error, which is introduced by the kinetic nature of the chromatographic process. No comparison of the various dynamic methods has been made on the basis of accuracy so far, mainly owing to the lack of suitable reference methods. In this paper non-equilibrium GC methods for the determination of distribution isotherms are compared with an equilibrium GC method. Although in principle the classical static volumetric and gravimetric methods for determining distribution isotherms can be used as references[8,9,13,18,20,41,42,45], these methods, when compared with the equilibrium GC method, have the disadvantages of being time consuming, having smaller temperature range and being less precise.

(2) THEORY

(2.1) The transport function in non-linear chromatography

Distribution equilibrium data can be obtained from the transport function, which describes the concentration as a function of place and time. The transport function can be derived from the mass balance in a column segment of length dz by

combining the resulting mass balance equation with an equation relating the concentration in the fixed bed and fluid stream:

$$\frac{\partial \langle c_i^m \rangle}{\partial t} + \frac{(1-\varepsilon_m)}{\varepsilon_m} \cdot \frac{\partial \langle c_i^s \rangle}{\partial t} = -\frac{\partial \langle v \cdot c_i^m \rangle}{\partial z} + D_{im}^* \cdot \frac{\partial^2 \langle c_i^m \rangle}{\partial z^2} \tag{1a}$$

$$\langle c_i^s \rangle = F(\langle c_i^m \rangle) \tag{1b}$$

where:

z = length coordinate
t = time
c_i^s = concentration of component i in the stationary bed s which is considered to be homogeneous
c_i^m = concentration of component i in the fluid stream m
v = fluid velocity
$\langle\ \rangle$ = average over the corresponding cross-sectional area
ε_m = fraction of cross-sectional area occupied by the fluid stream
$1-\varepsilon_m$ = fraction of cross-sectional area occupied by the stationary bed
D_{im}^* = dispersion coefficient of component i in the mobile phase due to diffusion and convection.

An expression for the mass transfer between the fluid stream and the fixed bed can be used for eqn. 1b. In this case the transport function can be derived[47–50] if the mass transfer equation is linear which implies a linear distribution isotherm (linear chromatography).

For a non-linear distribution isotherm (non-linear chromatography) a rigorous simplification is necessary in order to achieve a solution of eqn. 1. It is assumed that:

$D_{im}^* = 0$;
$\langle c_i^s \rangle = f^*(\langle c_i^m \rangle)$ = distribution isotherm for the fixed bed and the fluid stream;
$\langle v \rangle$ is constant;

so that eqn. 1 reduces to:

$$\left(1 + \frac{1-\varepsilon_m}{\varepsilon_m} \cdot \frac{\mathrm{d}\langle c_i^s \rangle}{\mathrm{d}\langle c_i^m \rangle}\right) \cdot \frac{\partial \langle c_i^m \rangle}{\partial t} = -\langle v \rangle \cdot \frac{\partial \langle c_i^m \rangle}{\partial z} \tag{2}$$

in which $\mathrm{d}\langle c_i^s \rangle / \mathrm{d}\langle c_i^m \rangle$ is the first derivative of the distribution isotherm. Eqn. 2 can be solved[51–53] for the case when the sample enters the column in a very short time, resulting in an equation for the migration velocity u_c of a concentration $\langle c_i^m \rangle$:

$$\left(\frac{\mathrm{d}z}{\mathrm{d}t}\right)_c = u_c = \frac{\langle v \rangle}{1 + \frac{(1-\varepsilon_m)}{\varepsilon_m} \cdot \frac{\mathrm{d}\langle c_i^s \rangle}{\mathrm{d}\langle c_i^m \rangle}} \tag{3}$$

From eqn. 3 an expression which describes the residence time t_c of the concentration $\langle c_i^m \rangle$ in the column can be derived:

$$\int_0^{t_c} \mathrm{d}t = t_c = \int_0^{L} \frac{\mathrm{d}z}{u_c} = \frac{L}{u_c} = \frac{L}{\langle v \rangle} \cdot \left(1 + \frac{(1 - \varepsilon_m)}{\varepsilon_m} \cdot \frac{\mathrm{d}\langle c_i^s \rangle}{\mathrm{d}\langle c_i^m \rangle}\right) \tag{4}$$

in which L = length of the column.

The output function (elution function) describes the concentration in the column effluent as a function of time. The output function is determined by eqn. 4 and the condition[18]:

$$\int_0^{\langle c_i^m \rangle_L^{\max}} \langle c_i^m \rangle_L \cdot \mathrm{d}t = Q_i/w. \tag{5}$$

in which $\langle c_i^m \rangle_L^{\max}$ = maximum concentration of component i in the fluid stream at the column exit ($z = L$)

Q_i = amount of component i injected into the column

w = flow rate.

Eqns. 4 and 5 predict an elution peak with a sharp top, a vertical flank and a flank following eqn. 4.

(2.2) The transport function in linear chromatography with higher mole fractions

In the case of higher mole fractions the fluid velocity is influenced by the mass exchange between fluid stream and stationary bed[4,54–63]. This case can be treated if eqn. 1 is simplified by assuming:

$D_{im}^* = 0$ and $\langle c_i^s \rangle = K_i^* \cdot \langle c_i^m \rangle$ = a linear distribution isotherm, resulting in:

$$(1 + \kappa_i^*) \cdot \frac{\partial \langle c_i^m \rangle}{\partial t} = -\left(\langle v \rangle \cdot \frac{\partial \langle c_i^m \rangle}{\partial z} + \langle c_i^m \rangle \cdot \frac{\partial \langle v \rangle}{\partial z}\right) \tag{6}$$

with $\kappa_i^* = K_i^* (1 - \varepsilon_m)/\varepsilon_m$ = capacity ratio and where $K_i^* = \langle c_i^s \rangle / \langle c_i^m \rangle$ = distribution coefficient of component i between the stationary bed (s) and the fluid stream (m).

Substituting the mole fraction $\langle x_i^m \rangle$ for the concentration an expression for the migration velocity u_x of a mole fraction $\langle x_i^m \rangle$ can be derived for the case when the sample enters the column in a very short time:

$$u_x = \frac{\langle v \rangle + \langle x_i^m \rangle \cdot \dfrac{\mathrm{d}\langle v \rangle}{\mathrm{d}\langle x_i^m \rangle}}{1 + \kappa_i^*} \tag{7}$$

If eqn. 7 is used for the sample as well as for the eluent, a solution can be found which describes the dependence of the fluid velocity on the mole fraction and the capacity ratio of the component:

$$\langle v \rangle = \frac{\langle v \rangle_0}{1 - \dfrac{\kappa_i^*}{1 + \kappa_i^*} \cdot \langle x_i^m \rangle} \tag{8}$$

where $\langle v \rangle_0$ = fluid velocity in absence of component i.

Substitution of eqn. 8 in eqn. 7 gives the final expression for the migration velocity of a mole fraction $\langle x_i^m \rangle$:

$$u_x = \frac{\langle v \rangle_0}{(1 + \kappa_i^*)\left(1 - \frac{\kappa_i^*}{1 + \kappa_i^*} \cdot \langle x_i^m \rangle\right)^2} \tag{9}$$

From eqn. 9 an expression for the residence time t_x of a mole fraction $\langle x_i^m \rangle$ in the column can be derived:

$$t_x = \frac{L}{u_x} = \frac{L}{\langle v \rangle} \cdot (1 + \kappa_i^*)\left(1 - \frac{\kappa_i^*}{1 + \kappa_i^*} \cdot \langle x_i^m \rangle\right)^2 \tag{10}$$

Eqn. 10 determines the output function at higher mole fractions of component i in the fluid stream. At low mole fractions eqn. 10 approaches eqn. 4 taking into consideration that for a linear distribution isotherm $d\langle c_i^s \rangle / d\langle c_i^m \rangle = K_i^*$. Equations[4,59] slightly different from eqn. 10 can be obtained as a result of a more simplified treatment of the problem.

(2.3) Influence of the heterogeneity of the stationary bed

In the theoretical model the stationary bed is assumed to be homogeneous. In practice however the stationary bed is far from homogeneous. A chromatographic column in general consists of a stationary bed of porous particles and a fluid flowing through the space between the particles. The porous particles which together with the column wall form the stationary bed consist of a solid matrix and pores filled with either mobile phase (gas or liquid) or stationary liquid or both. A packed column contains pores of two sizes: wide inter-particle pores in which flow occurs and narrow intra-particle pores in which no flow occurs. In the theoretical model the distribution of the sample between the fluid stream on the one hand and all of the stationary phases on the other hand is considered. Leaving out the bulk of solid matrix, which does not absorb the sample, the following stationary phases can take part in the distribution process:

(a) the stagnant part of the mobile fluid phase in the intra-particle pores
(b) the stationary liquid in the intra-particle pores;
(c) the surface of the solid matrix; and
(d) the interphase of the mobile fluid and stationary liquid.

Accordingly the total differential change $(1 - \varepsilon_m) \cdot d\langle c_i^s \rangle$ of the amount of a component in the stationary bed per unit of volume of the column equals the sum of the partial differential changes in the various stationary phases. By substituting the corresponding sum: $(\varepsilon_\alpha - \varepsilon_m) \cdot dc_i^\alpha + \varepsilon_\beta \cdot dc_i^\beta + a_\sigma \cdot dc_i^\sigma + a_\tau \cdot dc_i^\tau$ for $(1 - \varepsilon_m) \cdot d\langle c_i^s \rangle$ in eqns. 3 and 4 the migration velocity and residence time of a concentration c_i^α are described as functions of the equilibrium distribution isotherms for the various stationary phases and the mobile phase:

$$u_c = u_0 \Big/ \left(1 + \frac{\varepsilon_\beta}{\varepsilon_\alpha} \cdot \frac{dc_i^\beta}{dc_i^\alpha} + \frac{a_\sigma}{\varepsilon_\alpha} \cdot \frac{dc_i^\sigma}{dc_i^\alpha} + \frac{a_\tau}{\varepsilon_\alpha} \cdot \frac{dc_i^\tau}{dc_i^\alpha}\right) \tag{11}$$

$$t_c = t_{R_0} \cdot \left(1 + \frac{\varepsilon_\beta}{\varepsilon_\alpha} \cdot \frac{\mathrm{d}c_i^\beta}{\mathrm{d}c_i^\alpha} + \frac{a_\sigma}{\varepsilon_\alpha} \cdot \frac{\mathrm{d}c_i^\sigma}{\mathrm{d}c_i^\alpha} + \frac{a_\tau}{\varepsilon_\alpha} \cdot \frac{\mathrm{d}c_i^\tau}{\mathrm{d}c_i^\alpha} \right) \tag{12}$$

where:

$u_0 = \langle v \rangle \cdot \varepsilon_m / \varepsilon_\alpha$ = migration velocity of the mobile phase
ε_α = fraction of the column volume occupied by the mobile phase
ε_β = fraction of the column volume occupied by the stationary liquid
$c_i^\alpha = c_i^m$ = concentration of component i in the mobile phase α, which consists of the fluid stream and possibly a stagnant film
c_i^β = concentration of component i in the stationary liquid β
a_σ = ratio between the surface area of the solid matrix and the total volume of the column
c_i^σ = surface concentration of component i on the surface σ of the solid matrix
a_τ = ratio between the interphase area of the fluid phases and the total column volume
c_i^τ = surface concentration of component i in the interphase τ of the fluid phases
$t_{R_0} = L/u_0$ = retention time of the mobile phase.

Since the equilibrium concentrations in the different phases are considered the symbol $\langle\ \rangle$ for the average value may be omitted.

Often only one of the stationary phases takes up a significant part of the distributed sample. Therefore the complex distribution may be considered as a simple two phase distribution, which can be the distribution between either a stationary liquid phase or the solid surface of the matrix and the mobile phase. In this case only the corresponding terms of eqns. 11 and 12 are significant and the others may be neglected.

(3) CHARACTERIZATION OF THE GAS CHROMATOGRAPHIC METHODS FOR THE DETERMINATION OF DISTRIBUTION ISOTHERMS

The distribution isotherm is determined point by point. It is assumed that the sample compound is distributed between a single stationary phase and the mobile phase. The concentration in the stationary phase is calculated[9,11,18] from an area on the recorder chart:

$$\overline{c_i^s} = \frac{A}{S \cdot V_s} \tag{13}$$

in which:

$\overline{c_i^s}$ = average equilibrium concentration in the stationary phase; an average value for the whole column is obtained because of the gas compressibility (see 5.2).
A = area on recorder chart according to Figs. 1 and 2.
S = sensitivity, defined as the area on the recorder chart divided by the corresponding amount of component i.
V_s = volume of the stationary phase.

The concentration in the mobile phase can be calculated from the recorder deflection:

$$\overline{c_i^m} = \frac{y \cdot \omega}{\overline{w} \cdot S} \qquad (14)$$

in which:

$\overline{c_i^m}$ = average equilibrium concentration in the mobile phase; the average value for the whole column has to be calculated since the average concentration in the stationary phase has been obtained by eqn. 13

y = recorder deflexion

ω = recorder chart speed

$\overline{w}$ = average flow rate of carrier gas in the column.

The sensitivity S can be determined from the area of a chromatographic peak when the corresponding amount of component i is known, as well as from the recorder deflection obtained with a known mass flow of the component.

(3.1) *Nonequilibrium methods*

(3.1.1) *Peak maxima method*[26,33,45] (Fig. 1). A series of chromatograms, obtained by injecting various amounts of a component i, is produced in order to determine c_i^s as a function of c_i^m at constant temperature. If it is assumed that eqn. 4 can be applied to the locus of the peak maxima, c_i^s and c_i^m can be calculated from eqns. 13 and 14.

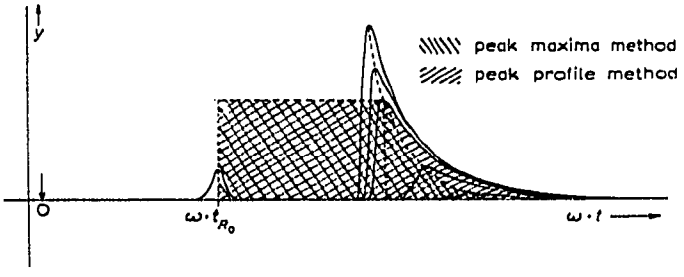


Fig. 1. Types of chromatograms used in the peak maxima and peak profile methods for the GC determination of distribution isotherms.

(3.1.2) *Peak profile method*[4,10,11–14,18,19,21,27–29,32,33,41–43,45,46] (Fig. 1). This method is similar to the peak maxima method, however the distribution isotherm is now determined from a single chromatogram. Either the peak flank at the front or at the rear, depending on which of the two is flatter, is assumed to be described by eqn. 4. The isotherm can then be calculated by means of eqns. 13 and 14 from points on the appropriate boundary.

(3.1.3) *Step profile method* [1–3,5,9,15,17,22,23,32,34,35,37–40,43] (Fig. 2). In this method carrier gas, containing the vapour of the component for which the distribution isotherm is to be determined, and pure carrier gas are alternately led into the column by means of a switching device. Switching results in the formation of positive or negative steplike concentration changes. Points on either the boundary resulting from the positive steplike concentration change or the boundary resulting from the negative steplike concentration change, depending on which of the two is flatter, are used to calculate the distribution isotherm, using eqns. 13 and 14 and assuming eqn. 4 to hold.

(3.1.4) The minor disturbance method[24,25,30,36,43,44] (Fig. 2). Into the vapour stream of a component, as is used in (3.1.3) and (3.2), a very small amount of the component is injected. The resulting peak maxima at various levels of vapour content of the carrier gas are processed as in the peak maxima method (3.1.1). At high relative vapour pressures precautions must be taken to overcome the effect of condensation on the needle of the syringe.

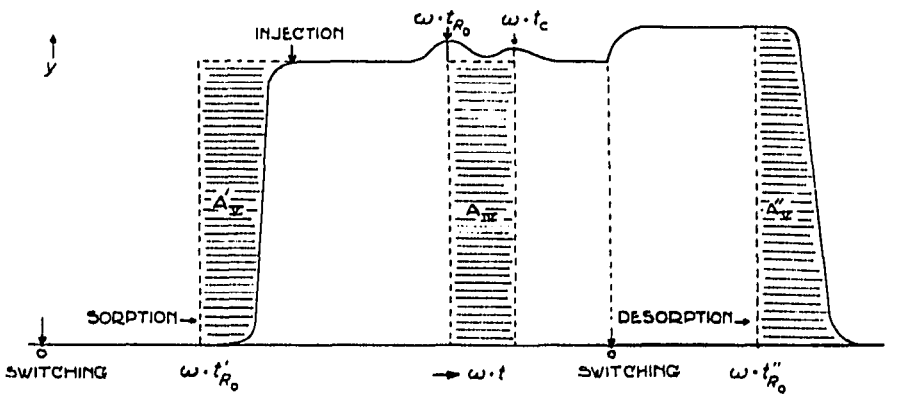


Fig. 2. Types of chromatograms used in the step profile, minor disturbance and equilibrium methods for the GC determination of distribution isotherms.

(3.2) Equilibrium method[6-9,16,20,31,43] (Fig. 2)

Just as in the step profile method carrier gas, containing vapour and pure carrier gas, are alternately led into the column until equilibrium is achieved, resulting in chromatograms of the type shown in Fig. 2. The areas A′ and A″ correspond to the amount which is sorbed and desorbed respectively. The area between the point of switching and $\omega \cdot t_{R_0}$ on the recorder corresponds to the amount of the vapour present in the mobile phase in the column. The retention times t_{R_0}' and t_{R_0}'' are determined with a non-retarded component. At the switching point for desorption a step is observed if a change in the flow rate occurs. By varying the vapour content of the carrier gas a series of chromatograms of the type shown in Fig. 2 is obtained. This can then be processed according to eqns. 13 and 14 to give the distribution isotherm.

(4) APPARATUS

(4.1) Construction

In order to perform the various dynamic GC methods on one and the same column under exactly the same experimental conditions the set-up as shown in Fig. 3 was devised.

The carrier gas flow is regulated by a pressure control valve (Fairchild Hiller Kendall 30) and a mass flow controller (Brooks, model 8743).

R_1 and R_2 are two matched restrictions consisting of stainless steel capillary tubing, 0.1 mm internal diameter and 5 m length.

The column C_1 contains the liquid, the vapour of which is led to the column C_x in which the adsorption or solution of the vapour will be measured. The column C_1 consists of a copper tube, 1 m length and 4 mm I.D., packed with a solid support (Chromosorb W, 120–130 μm) coated with the liquid to 30–40% w/w.

Either a thermostat (Becker 1452 P), when working at temperatures above 40°, or a cryostat (Haake T 21), when working at temperatures below 40°, is used to control the temperature of C_1, depending on the volatility of the vapour and the sensitivity of the detector. Temperature control is within 0.2°.

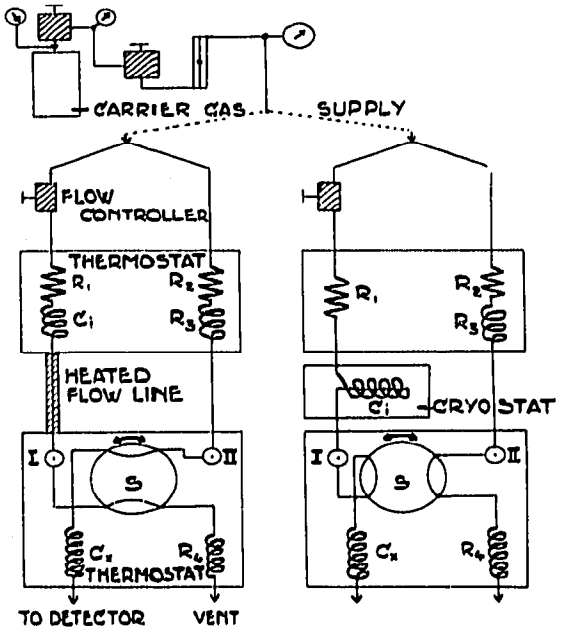


Fig. 3. Schematic diagram of the apparatus for measuring distribution isotherms by the various GC methods. When C_1 is to be thermostatted the set-up on the left is used, when C_1 is to be cryostatted the set-up on the right is used. R_1, R_2, R_3, R_4 = flow restrictors; C_1 = evaporation column; I and II = injection ports; S = switch valve; C_x = sorption column.

R_3 is a restriction matching C_1. It consists of a packed column, like C_1 but without the liquid coating.

The injection ports I and II can be heated up to 200°. It was found necessary to use special Teflon®-coated injection septa (Hamilton) as other materials invariably caused deactivation of adsorbents at the injection temperatures used (100–200°). A precision syringe (Hamilton) is used for the injection of the sample into the injection port.

The volume of the tubing from injection port I to C_x was estimated to be 0.15 ml and from injection port II to C_x 0.06 ml.

The switching valve is a high temperature sampling valve (Valco VSV-6-HT). Depending on which of the two possible positions it is in, either pure carrier gas or carrier gas loaded with vapour can be fed to column C_x.

C_x is the column containing either the adsorbent or the solvent, the latter coated on a granular (ideally inert) support, upon which or in which the distribution isotherm of the vapour, generated in C_1, is determined. The column is thermostatted by an air bath (Becker 1452 P) to within 0.2°.

R_4 is a restriction matching C_x and consists of a column, like C_x, packed with an inert granular material with the same particle diameter as that used in C_x.

A flame ionization detector (FID) of our own construction was used as sensor.

The signal is processed by an electrometer amplifier (Becker 2032-E) and recorded by a potentiometric recorder (Philips PR-2210).

Time measurements are done with a stopwatch with a precision of 0.1 sec.

(4.2) Operation

The following procedure is followed for the equilibrium method (3.2).

(1) The switching valve is set in the position where only carrier gas is admitted to C_x. The recorder deflection is adjusted to zero for this position.

(2) The switching valve is now set in the position where carrier gas loaded with vapour is fed to column C_x, in which the vapour is sorbed.

(3) After a constant recorder deflection is attained the valve is switched back to the first position and the vapour is desorbed from column C_x.

(4) The equilibrium concentrations of the vapour in the mobile phase (gas) and stationary phase (solvent or adsorbent surface) in column C_x are calculated from the recorded chromatograms (Fig. 2).

In practice perfect matching of the flow resistances, so that no change in flow through C_x occurs on switching, is difficult to achieve. However, matching is less critical when the detector response is proportional to the mass flow (FID) than when the response is proportional to the concentration (catharometer). A check on the effect of incomplete matching is made possible by the fact that the resulting areas of sorption and desorption should be equal. The difference between the areas of sorption and desorption was found to be less than 2 % in most experiments. In the case of methanol however the areas of sorption were significantly greater than the corresponding areas of desorption (see section 5.4). This effect is due to the higher non-linearity of the isotherm resulting in a tail which almost disappears in the base line but which represents a significant portion of the sorbed component. The standard deviations of the areas for sorption or desorption were found to be 1 % for $[(1-\varepsilon_m)/\varepsilon_m] \cdot [\mathrm{d}\langle c_i^s\rangle/\mathrm{d}\langle c_i^m\rangle] \geqslant 0.5$.

Only a small correction for the volume (0.15 or 0.06 ml) of the tubing between the injection port and the column C_x, which in practice has a volume of 5–20 ml, has to be made. Cross leakage at the switching valve connections was found to be undetectable at first, but to have increased to about 1 % after regular use over a period of six months. The switching valve showed no memory.

The step profile method (3.1.3) is carried out analogously to the equilibrium method except for the interpretation, in which eqns. 13 and 14 are applied to points on the positive or negative steplike boundary. The peak methods (3.1.1 and 3.1.2) are performed with the switch in the position where pure carrier gas is fed into column C_x. The sample is then injected through injection port II. The minor disturbance method (3.1.4) is performed with the switch in the position where vapour containing carrier gas is fed into C_x. In this case injection port I is used.

The reproducibility of the FID characteristics from day to day is hampered by the varying ionization efficiency. In accordance with the literature[64] it was found that the sensitivity varies up to 10 % depending on the magnitude of the atmospheric pressure fluctuations. The FID is adjusted to maximum sensitivity with the aid of a signal resulting from feeding vapour containing carrier gas to C_x. First the air flow to the flame is set for maximum signal and then the hydrogen flow. It was found that the sensitivity S is practically independent of the flow rate of the carrier gas provided

the FID is operated within its linear range. The linear range of the FID is determined by plotting the logarithm of the recorder deflection at constant carrier gas flow rate *vs.* the inverse of the absolute temperature at which the vapour, fed into the carrier gas, is generated. The ordinate of the resulting graph is calibrated with vapour pressure values obtained from the literature. The end of the linear range is recognized by a deviation from linearity in the experimental graph. Two extreme cases are shown in Fig. 4, *viz.* dodecane for which the FID has a high sensitivity and carbon tetrachloride for which the FID has a low sensitivity. From graphs of various other components the end of the linear range of the FID was found to be practically the same as found from Fig 4. The linear range of the FID is thus seen to be independent of the component used.

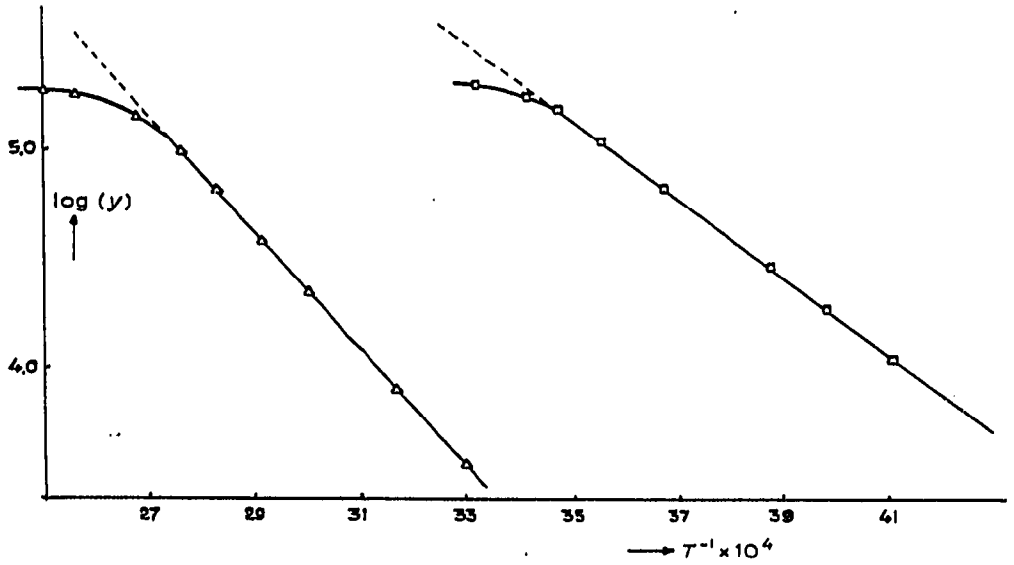


Fig. 4. Logarithmic plot of the detector signal (y in mV) *vs.* the inverse of the absolute temperature ($°K^{-1}$) of the evaporation column in Fig. 3. △, results obtained for dodecane, □, results obtained for carbon tetrachloride.

A more direct method of determining the linear range of the detector, made possible by the set-up used, is to compare the areas of sorption and desorption in the equilibrium method when matching is incomplete as shown in Fig. 2. If at a certain vapour content of the carrier gas the area for adsorption becomes significantly larger than the corresponding area for desorption the end of the linear range has been reached.

The upper limit of the range of the FID was found to be of the order of 10^{-8} A by both methods, thus giving a linear dynamic range of 10^5, the standard deviation of the noise being estimated at 4.10^{-13} A.

(5) EXPERIMENTAL RESULTS

The following notation is used to characterize the results of the different GC methods for the determination of distribution isotherms: I, peak profile method (■); II, peak maxima method (▲); III, step profile method (●); IV, minor disturbance method (×); V, equilibrium method (⊙).

Diatomaceous earth was used as adsorbent or support for the liquids (Chromosorb W® (Johns-Manville), non-acid-washed, particle diameter d_p 120–130 μm, spe-

cific surface area 2 m^2/g and Chromosorb G® (Johns-Manville), acid-washed, treated with dimethyldichlorosilane, particle diameter d_p 120–130 μm, specific surface area 0.3 m^2/g).

All the chemicals (Merck, Analar or B.D.H.) used were the purest grade available.

(5.1) *Effect of the length of the column*

The adsorption isotherms of acetone and methanol on Chromosorb W at 110° were determined by the various GC methods in columns of 50, 100 and 200 cm length and 4 mm I.D. The isotherms were determined in triplicate by each method on each column. The precision of the measurements in a given column by a given method was found to be better than 3 %. Examples of chromatograms obtained and used with the different methods are shown in Fig. 5. A systematic difference was found between the results obtained by the various GC methods. Typical examples are shown in Figs. 6a and b.

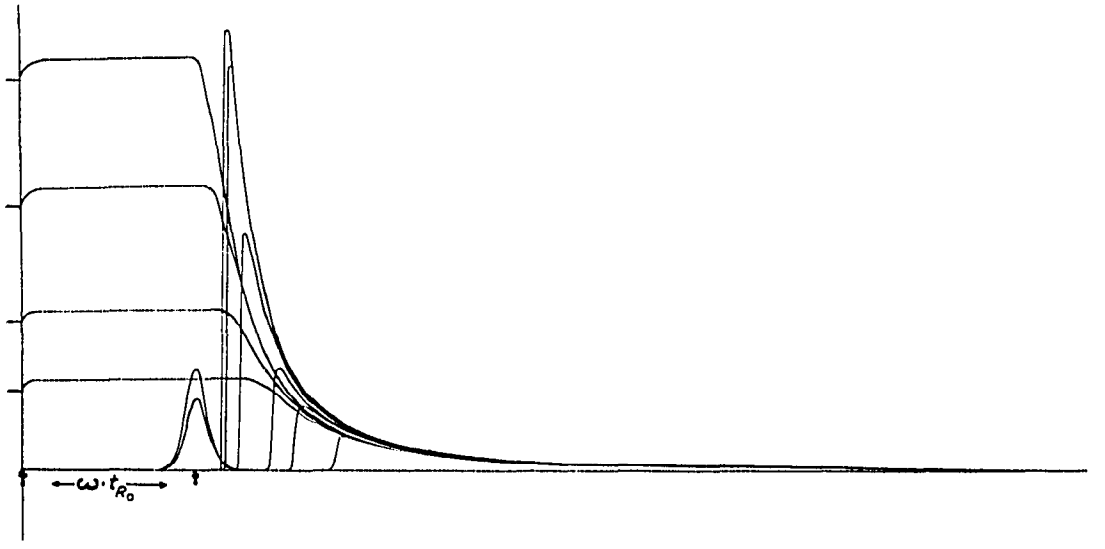


Fig. 5. Chromatograms obtained by the various GC methods for a convex distribution isotherm. Sample: methanol; column: 100 × 0.4 cm, packing 3.39 g Chromosorb W; temperature: 110°; carrier gas: nitrogen 1.25 cm sec^{-1}.

The deviations between equilibrium and non-equilibrium measurements can be explained by the kinetic nature of the chromatographic process. Diffusion, convective mixing and mass transfer will affect the results of non-equilibrium measurements to some extent.

As can be expected the results obtained by the equilibrium method are not affected by the length of the column, whereas the differences in the isotherms obtained by the different non-equilibrium methods diminishes slightly with increasing column length. The endpoint of the isotherms measured by the step profile method coincide with the equilibrium measurements since these values are determined in the same way in both methods.

The detector was calibrated according to Fig. 7 which shows a plot of the logarithm of the recorder deflection *vs.* the inverse of the absolute temperature at which the vapour was generated. The sensitivity S for the vapour in the FID can then be

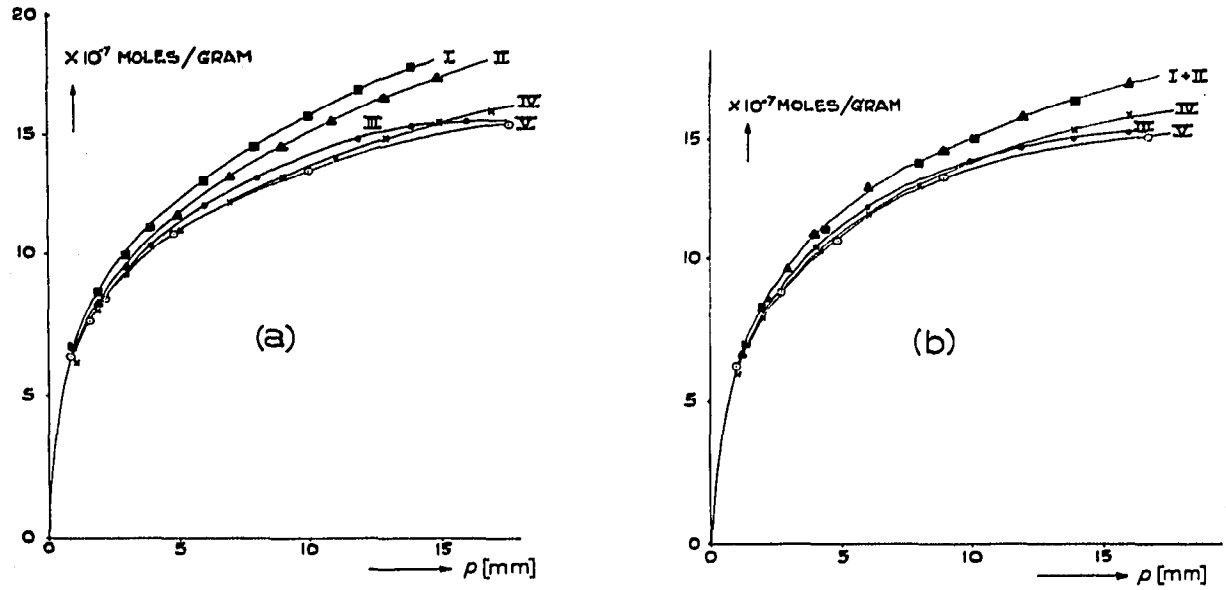


Fig. 6. Examples of convex distribution isotherms obtained by the various GC methods using different column lengths. Sample: acetone; system: Chromosorb W/nitrogen; temperature: 110°. (a) column length 50 cm; (b) column length 200 cm.

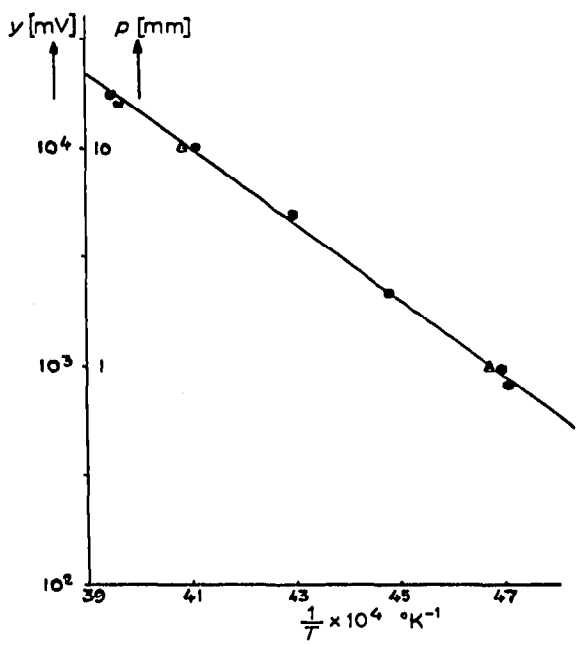


Fig. 7. Calibration of the detector: ● = detector response y (mV); △ = corresponding vapour pressures p (mm) of acetone from the literature[65].

found by calibration with vapour pressure values from the literature or by extrapolating to the boiling point at the pressure used.

(5.2) Effect of the velocity of the carrier gas and pressure drop across the column

First of all the effect of the carrier gas flow on the detector characteristics has to be considered. For the detector used (FID) it was found that the sensitivity S was independent of the flow rate providing the detector was operated within its linear

range. The linear range of the FID, when expressed in units of vapour pressure of a given component, decreases as the flow of the carrier gas increases. The latter effect limits the vapour pressure up to which the effect of the carrier gas velocity on the isotherm measurement can be investigated.

In deriving eqn. 4 the fluid velocity was assumed constant along the column. When the eluant is a gas, however, the fluid velocity increases with the length coordinate z because of the gas compressibility. The following expression can be derived for the velocity gradient in the column:

$$\langle v \rangle = \langle v \rangle_{z=0} \left[1 - \frac{z}{L} \left(1 - \frac{p_L^2}{p_0^2} \right) \right]^{-1/2} \tag{15}$$

where $\langle v \rangle_{z=0}$ is the fluid velocity at the beginning ($z = 0$) of the column and p_0 and p_L are the pressures at the beginning and end of the column, respectively. As long as the velocity gradient remains small, eqn. 4 may be applied after substituting the average linear velocity of the mobile phase over the length of the column $\overline{\langle v \rangle}$ for $\langle v \rangle$.

In the stationary state, a concentration gradient occurs along the column because of the gas compressibility. The concentrations in the mobile and stationary phase obtained by the equilibrium method are therefore average values. From the equation[66,67] describing the pressure gradient expressions for the average concentration $\overline{c_i^m}$ in the mobile phase in the column can be derived:

$$\overline{c_i^m} = \frac{2}{3} \cdot \frac{1 - (p_L/p_0)^3}{1 - (p_L/p_0)^2} \cdot c_{i0}^m = \frac{2}{3} \cdot \frac{(p_0/p_L)^3 - 1}{(p_0/p_L)^2 - 1} \cdot c_{iL}^m \tag{16}$$

where c_{i0}^m and c_{iL}^m are the concentrations at the beginning and end of the columns, respectively. The concentration c_{iL}^m can be calculated from the detector response, the concentration c_{i0}^m can be obtained by calibrating the evaporation column C_i (see Figs. 4 and 7). An analogous relation for the partial pressure p_i is obtained by replacing the concentration c_i^m in eqn. 16 by the corresponding partial pressure. The average concentration in the stationary phase in the column is calculated by means of eqn. 13 in which $A/S = Q_i^s$, *i.e.* the amount of sample contained in the stationary phase.

The average values found for the concentrations in the mobile and stationary phases are equilibrium data as long as the portion of the isotherm over which the concentrations are averaged can be considered as linear.

The systematic error introduced by the compressibility of the carrier gas is negligible in dynamic GC methods for the determination of distribution isotherms as long as the pressure ratio p_L/p_0 is nearly 1. In this work the pressure drop was 0.05–0.2 atm and the outlet pressure atmospheric.

The influence of the carrier gas velocity was investigated for the adsorption of acetone on Chromosorb W at 110° in a column of 1 m length and 4 mm diameter. In the velocity range of 0.5–4 cm/sec, the effect of the carrier gas velocity on the isotherms obtained by the various methods was not found to be significant.

(5.3) Effect of the nature of the carrier gas

When using helium instead of nitrogen as carrier gas similar results are obtained with respect to the scattering of the isotherms, the only difference being that the deviation between the peak maxima and peak profile method is somewhat increased due to the larger diffusion coefficient in helium.

The effect of the carrier gas on the distribution coefficient can be calculated[68,69] by means of the following equation:

$$\ln (K_i^{He}/K_i^{N_2}) = \frac{(1 - x_i^m)^2}{RT} \cdot (\Delta B_{mm} - \Delta B_{mi}) \qquad (17)$$

in which:

K_i = the distribution constant in either helium or nitrogen,
x_i^m = the mole fraction of component i in the carrier gas,
ΔB_{mm} = the difference in second virial coefficients of the mobile phases nitrogen and helium,
ΔB_{mi} = the difference in second virial cross coefficients between the component i and the mobile phase nitrogen or helium.

In eqn. 17 it is assumed that the average pressure in the column when comparing the results in helium and nitrogen remains constant. Eqn. 17 was verified for the linear distribution of toluene and dodecane on Chromosorb W, coated with 2 % w/w squalane, at T = 100°. The following results were obtained:

$$(K^{He}/K^{N_2})_{toluene} = 1.02 \pm 0.005,$$

$$(K^{He}/K^{N_2})_{dodecane} = 1.04 \pm 0.005.$$

The sensitivity S of the FID was found to be about 10 % lower when helium was used as carrier gas instead of nitrogen under otherwise identical conditions. In contrast to the literature[70], it was found that the optimum flow settings for the hydrogen and air to the FID were practically unaffected when changing from nitrogen to helium as carrier gas, providing the FID was operated within its linear range.

(5.4) Effect of the shape of the isotherm

In Fig. 8 isotherms convex to the pressure axis, obtained by the various GC methods for acetone on Chromosorb W, coated with squalane, are shown. The total amount adsorbed on the solid surface and solved in the liquid is related to the mass of solid. From these results and Fig. 6 it can be concluded that increasing linearity of the isotherm brings an increasing relative agreement between the equilibrium and the peak maxima methods.

Chromatograms corresponding to a concave distribution isotherm are shown in Fig. 9. Convex and concave distribution isotherms as obtained for dodecane on Chromosorb W and Chromosorb W coated with squalane, respectively, by various GC methods are shown in Fig. 10.

It can be seen that the isotherms obtained by the nonequilibrium methods lie above the isotherms obtained by the equilibrium method in the case of a convex shape and below in the case of a concave shape. This can be explained by the influence of the kinetic effects.

Fig. 11 shows a chromatogram corresponding to an isotherm which is both convex and concave to the pressure axis (see also Fig. 12) for the case of adsorption of dodecanone-2 on silanized Chromosorb G. The profile methods are not practicable in this case. Comparing the sigmoid shaped isotherms obtained by the equilibrium and peak maxima methods for this case an alternating discrepancy can be seen on going from the convex to the concave part of the isotherm, resulting in a "straightening" of the isotherm obtained by the peak maxima method as compared with the isotherm obtained from the equilibrium method.

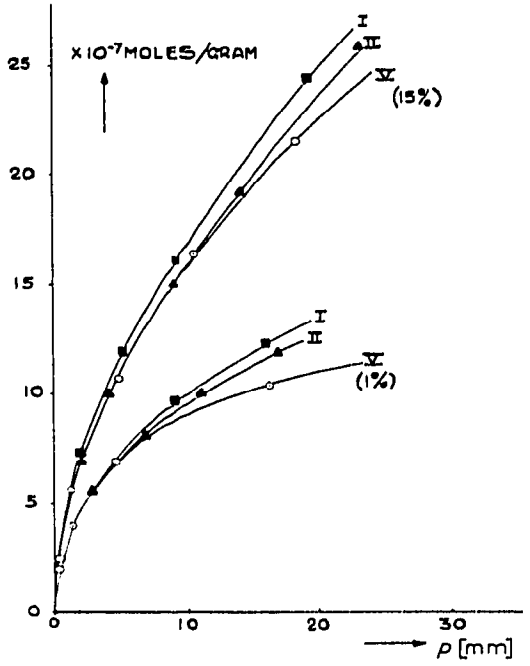


Fig. 8. Influence of the shape of convex isotherms on the results obtained by different GC methods. Sample: acetone; column: 100 × 0.4 cm, packing (1%) (= 3.54 g Chromosorb W coated with 0.039 g squalane) and (15%) (= 3.88 g Chromosorb W coated with 0.58 g squalane); carrier gas: nitrogen, 1.25 cm sec^{-1}; temperature 110°.

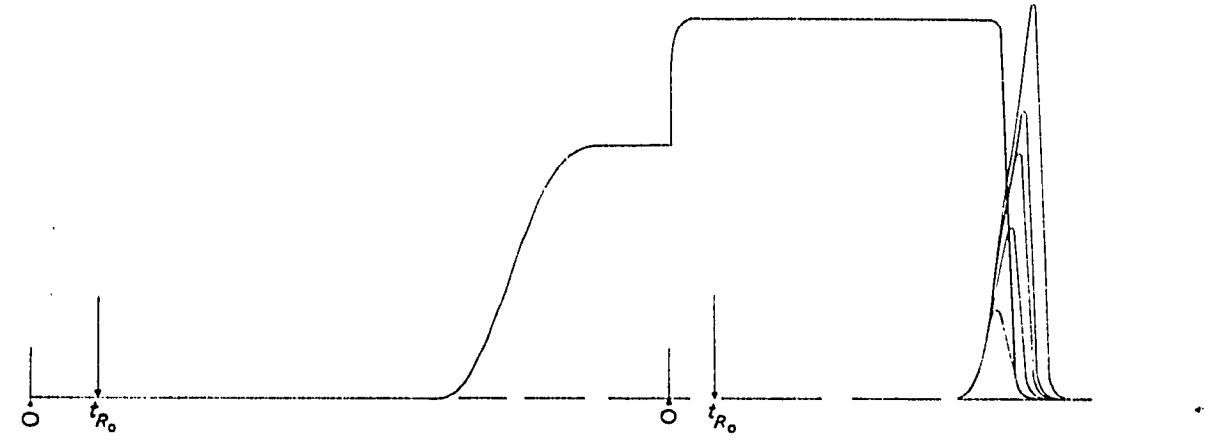


Fig. 9. Chromatograms corresponding to a concave distribution isotherm obtained by different GC methods. Conditions as in Fig. 10 (1%).

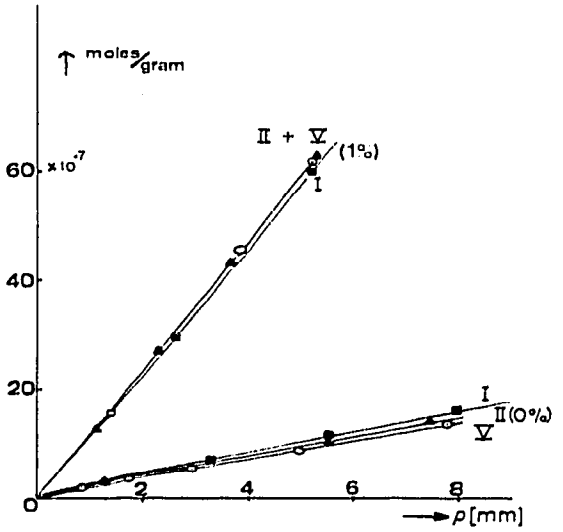
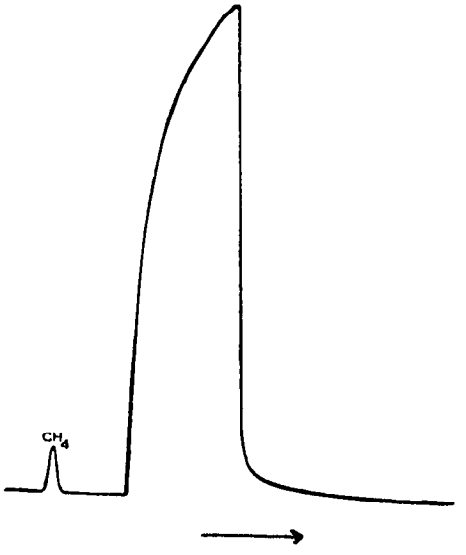


Fig. 10. Comparison of the results of different GC methods for a convex and a concave distribution isotherm. Sample: dodecane; column: 100 × 0.4 cm; packing: (0%) (= 3.55 g Chromosorb W) and (1%) (= 3.54 g Chromosorb W coated with 0.039 g squalane); carrier gas: nitrogen, 1.25 cm sec^{-1}; temperature 120°.



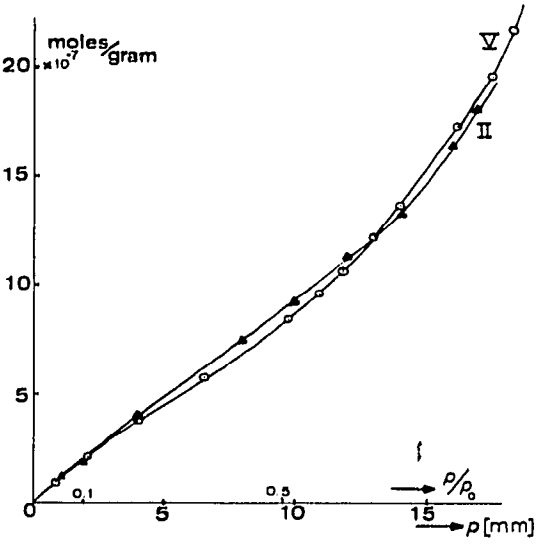


Fig. 11. Typical chromatogram corresponding to a sigmoid shaped distribution isotherm obtained by the peak maxima method. Sample: dodecanone-2; column: 100 × 0.4 cm; packing: 8.54 g Chromosorb G; carrier gas: nitrogen, 1.25 cm sec^{-1}; temperature 100°. The corresponding isotherm is shown in Fig. 12.

Fig. 12. Sigmoid shaped isotherm determined by the equilibrium and peak maxima methods. Conditions as in Fig. 11.

The determination of isotherms showing a strong convexity towards the pressure axis is systematically affected in all GC methods owing to the fact that the area under the tail cannot be accurately measured. In the equilibrium method an estimate of this error can be made by comparing the area obtained for desorption with the area of ad- or absorption. Both areas have to be equal. Only in the case of the adsorption of methanol on Chromosorb W was this systematic error found to be significant, as shown in Table I, decreasing relatively as the vapour pressure increases. All data are averages of three measurements. The standard deviation of the measurements

increased from about 1 % at low vapour pressures to about 5 % at high vapour pressures. It can be seen that the absolute difference of both areas remains constant.

TABLE I

ACCURACY OF THE MEASUREMENT OF THE AREA OF DESORPTION IN THE EQUILIBRIUM METHOD

Sample: methanol; column: 500 × 4 mm, nitrogen/Chromosorb W, 100°.

Area of adsorption (*V sec*)	*Area of desorption* (*V sec*)	p_i (*mm*)
31.5	24.0	1.55
48.5	41.1	3.9
60.1	53	8.0
70	65	18.2
79	72	33.3
90	84	66.6

(5.5) Effect of the number of theoretical plates of the inert tracer peak

When the column in which adsorption or solution is investigated does not have a sufficient number of theoretical plates for the inert component which is used to determine t_{R0}, the isotherms calculated by GC methods will be systematically affected. In this case the residence time t_{max} of the peak maximum will be smaller than the average residence time t_{R0}. A relation between t_{max} and t_{R0} can be derived mathematically[71].

$$(t_{max})^2 = t_{R0}^2 \cdot (1 - N^{-1}) \qquad (18)$$

N being the number of theoretical plates in the column.

All experiments were carried out with theoretical plate numbers greater than 300 for methane, which was used as inert tracer.

(5.6) Effect of the mole fraction in the mobile phase

The FID has a low sensitivity S for carbon tetrachloride. Due to this fact the upper linear range of the FID corresponds to a high vapour pressure of carbon tetrachloride (see Fig. 4). When used in a column containing Chromosorb W, coated with 15 % w/w squalane, the result is a linear isotherm; carbon tetrachloride is thus well suited to study the effect of the mole fraction. In Fig. 13 the isotherms shown are those obtained by the peak maxima and equilibrium methods. From the linear shape of the isotherm it can be concluded that in view of the results in preceding sections the isotherm from the peak maxima method should be identical with the isotherm obtained from the equilibrium method and that any discrepancy between the isotherms found by these two methods may be explained by eqn. 10 which after rearrangement reads:

$$\frac{t_x - t_{R0}}{t_{R0}} = \kappa_i^* \cdot \left(1 - 2\langle x_i^m \rangle + \frac{\kappa_i^*}{1 + \kappa_i^*} \cdot \langle x_i^m \rangle^2\right) \qquad (19)$$

assuming $L/\langle v \rangle = t_{R0}$, that is $\varepsilon_\alpha = \varepsilon_m$.

The peak maxima method allows the determination of $(t_x - t_{R0})/t_{R0}$ as a function of the vapour pressure, from which κ_i^* values can be calculated from eqn. 19. The capacity ratio κ_i^* can also be determined as a function of the vapour pressure with the equilibrium method. In Fig. 14 the experimental values of κ_i^* obtained by both methods are compared. As can be seen the corrected values of the peak maxima method and the experimental values of the equilibrium method are in good agreement in the range of mole fractions studied (< 0.1).

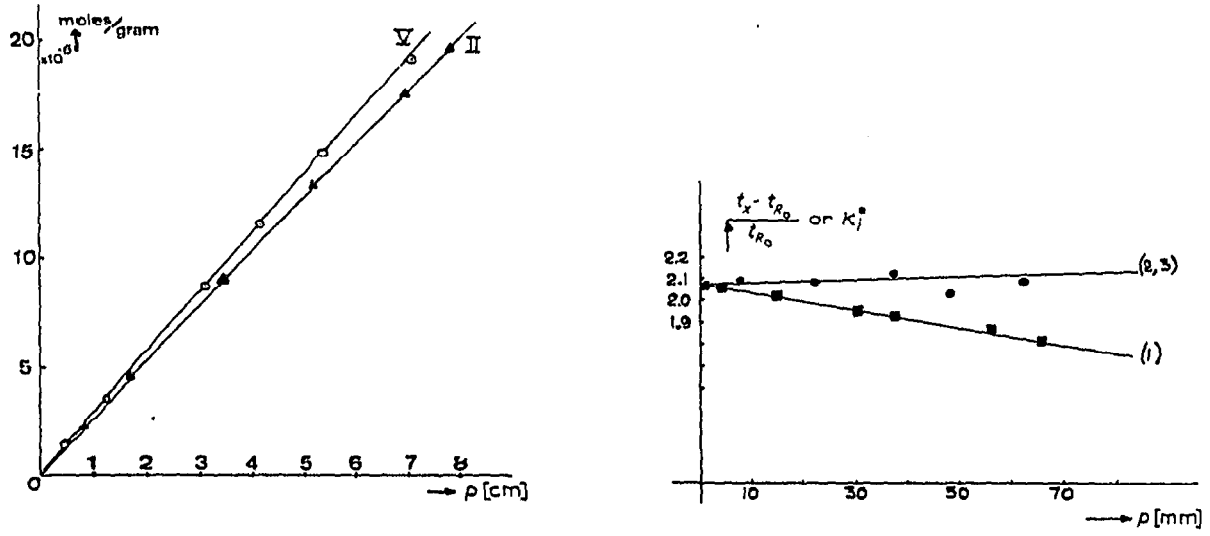


Fig. 13. Influence of the mole fraction on the isotherms obtained by the peak maxima method. Sample: carbon tetrachloride; column: 100 × 0.4 cm; packing: 3.88 g Chromosorb W coated with 0.58 g squalane; carrier gas: nitrogen, 1.25 cm sec^{-1}; temperature 100°.

Fig. 14. Correction for the influence of the mole fraction: (1) ■ = results of the peak maxima method; (2) ● = results of the equilibrium method; both corresponding to Fig. 13; (3) results of the peak maxima method corrected by means of eqn. 19.

A critical point in the equilibrium method is the determination of the retention time t_{R0} of the mobile phase. The retention time t_{R0} (see Fig. 2) in the sorption mode can be measured after equilibrium is attained *i.e.* when the recorder trace becomes constant. In the desorption mode, t_{R0} (see Fig. 2) cannot be measured since the flow rate changes slightly due to the change in flow resistance when the switch is set to the desorption position. Therefore it must be calculated according to eqn. 8 from the retention time t''_{R00} which is measured after desorption taking into account that $t_{R0}/t_{R00} = \overline{\langle v \rangle}_0/\overline{\langle v \rangle}$:

$$t''_{R_0} = t''_{R00}\left(1 - \frac{\kappa_i^*}{\kappa_i^* + 1}\langle x_i^m \rangle\right) \qquad (20)$$

According to eqns. 10 and 4 the mole fraction in the fluid stream and the curvature of the distribution isotherm affect the residence time t_{max} of the peak maximum and the peak shape either analogously or oppositely depending on whether the distribution isotherm is convex or concave. In order to estimate the effect of the de-

pendence of flow on the mole fraction and of the curvature of the isotherm, eqns. 4 and 10 may be combined to give:

$$t_{max} = t_{R_0}\left(1 + \frac{1-\varepsilon_m}{\varepsilon_m}\frac{d\langle c_i^s\rangle}{d\langle c_i^m\rangle}\right)\cdot\left(1 - \frac{\kappa_i^*}{1+\kappa_i^*}\langle x_i^m\rangle\right)^2 \qquad (21)$$

where $\langle c_i^m\rangle / \sum_i \langle c_i^m\rangle = \langle x_i^m\rangle$ and assuming $\varepsilon_\alpha = \varepsilon_m$.

Eqn. 21 is not exact since eqn. 10 is derived for a linear distribution isotherm. It is, however, a useful approximation which describes the combined effect of the mole fraction and curvature.

The combined effect of both phenomena on the results of the dynamic gas chromatographic methods for the determination of distribution isotherms can be demonstrated by changing the temperature. In general the slope and the curvature of the distribution isotherms decrease with temperature. Therefore an inversion of the peak asymmetry may be expected in the case of concave isotherms when the temperature is changed. At low temperature the effect of the curvature of the isotherm dominates whereas at high temperature the influence of the mole fraction on the fluid velocity dominates. An example of this "inversion" phenomenon is shown in Fig. 15. The correct slope of the isotherm can be estimated by means of eqn. 21. In agreement with expectations a concave isotherm is found which tends to become linear at high temperatures.

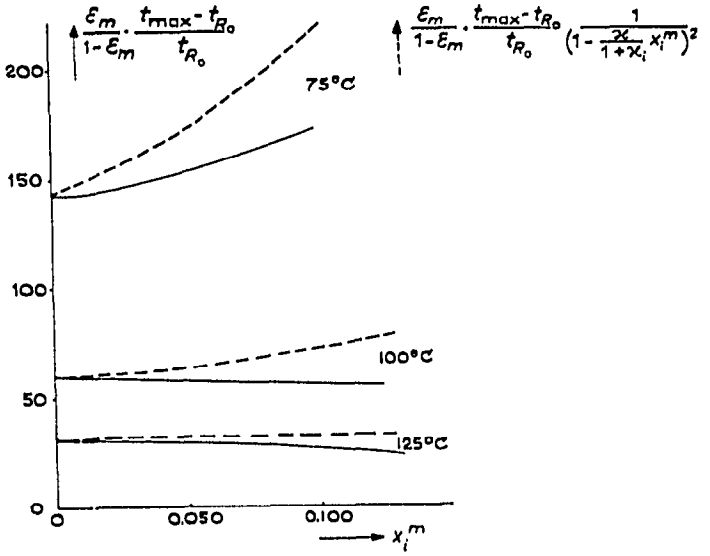


Fig. 15. Reversal of the peak asymmetry with the temperature: (———) results of the measurement; (– – – –) corrected according to eqn. 21. Sample: heptane; system: squalane/nitrogen; temperatures: 75, 100, 125°. By optimizing the flow rate of nitrogen, hydrogen and air the linear range of the FID was increased in order to make measurements with heptane up to 0.1 mole fraction possible.

(6) CONCLUSIONS

Dynamic GC methods allow a rapid determination of distribution isotherms in gas–solid and gas–solid–liquid systems over a wide temperature range.

The peak maxima and the peak profile methods can be carried out in a con-

ventional gas chromatography. The step profile, minor disturbance and equilibrium methods require a device for the preparation of a constant sample stream and a high temperature, non-absorbing, switching valve. In the case of the profile methods a certain section of the distribution isotherm is obtained in a single experiment, whereas with the other methods only a single point of the isotherm is obtained. Due to the kinetic nature of the chromatographic process the results obtained by the various dynamic GC methods differ somewhat. The highest accuracy may be expected for the equilibrium method. The greatest difference is found between the results of the peak profile method and the equilibrium method. Depending on the curvature of the isotherm the data obtained by the non-equilibrium methods are higher (convex shape) or lower (concave shape) than the data obtained by the equilibrium method. The most important phenomena influencing the accuracy in all the methods are the pressure drop across the column and the mass transfer, which affects the fluid velocity in the column and becomes significant at higher mole fractions. In the case of non-equilibrium methods the accuracy can be affected significantly by the kinetics (diffusion, convective mixing, mass transfer) of the chromatographic process and the influence of the sorption or desorption on the local temperature[72]. The relative error caused by the kinetics of the chromatographic process can be reduced by choosing conditions corresponding to a high number of theoretical plates for the linear chromatographic case. The pressure drop across the column should be kept as small as possible. For the interpretation of the elution curve an equation must be used which takes into account the change of the fluid velocity due to the mass exchange between the fluid stream and the stationary bed.

A limiting factor in improving the accuracy of the dynamic GC measurements of distribution isotherms is the accuracy of the determination of the detector sensitivity. In the case of volatile liquids it becomes especially difficult to inject an accurately known amount of sample. Therefore it is better to determine the vapour pressure, as described in 5.1, in order to determine the detector sensitivity.

Another factor which limits the accuracy of all dynamic GC methods for the determination of distribution isotherms is the measurement of the average flow rate $\bar{w} = \varepsilon_m V/t_{R0}$, V being the total volume of the column. The average flow rate in the column can be obtained by measuring the flow rate at the column exit and by converting it to the flow rate at average column pressure. Another method is to determine the volume of the mobile phase $\varepsilon_m V$ from the volumes of the column and the packing. In the equilibrium method the accuracy can be improved by making certain modifications, which also allow the determination of the simultaneous distribution isotherms of the components of a mixture. It is hoped to report on this subject in the near future.

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