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INFLUENCE OF STATIC AND DYNAMIC EFFECTS ON THE REPRODUCIBILITY OF RETENTION DATA IN GAS–LIQUID CHROMATOGRAPHY

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SUMMARY

The influence of static and dynamic effects on the reproducibility of retention data in gas–liquid chromatography was investigated.

The static effects considered are the effects due to adsorption, non-ideality of the gas–liquid partition equilibrium and the temperature. Equations are given for estimating the error caused by the non-ideality and the temperature. Adsorption is found to occur in practice mainly at the solid surface and to a smaller extent at the gas–liquid interface.

The dynamic effects considered are the effects of the plate number, the resolution, the mole fraction, the retardation of the inert tracer and the time constant of the detector. Equations are given for the quantitative estimation of the errors caused by these effects.

INTRODUCTION

Chromatographic retention data can be used as identification parameters, and are derived from the residence time distribution functions of the components in the chromatographic system. For a symmetrical gaussian residence time distribution function and a single stationary phase, the residence time of the maximum is a linear function of the distribution coefficient of a component between the stationary and mobile phases. The assumption of a gaussian residence time distribution function and a single stationary phase is an approximation. The retention data are not only determined by the nature of the solute, the nature of the phase system and the temperature but also by secondary parameters that cause a deviation from the approximation.

The statistical error in the determination of retention data may be expected to be greater for absolute than for relative values. Also, the precision of the measure-

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ments within one laboratory will be higher when only one instrument is used for obtaining identification parameters than when different instruments are used. The lowest reproducibility may be expected when the results from different instruments in different laboratories are compared. This interlaboratory precision is crucial to the usefulness of a collection of data compiled from different data sources.

All secondary effects that influence the precision of the retention data must be standardized or reduced in order to achieve highly reproducible measurements. Standardization of all secondary parameters is in part not possible and in part not practical, and it is therefore important to establish all the parameters that cannot be standardized and to reduce their influence as much as possible.

The interlaboratory reproducibility of retention data has been tested several times[1-5] and the results were unsatisfactory. Some effects that lower the precision of retention data in gas chromatography have already been discussed[6-45]. In this paper, the significant sources of errors in the measurement of retention data in gas–liquid chromatography (GLC) are identified, the conditions for the reduction of the dominating statistical errors are discussed and the limit of interlaboratory precision is estimated.

THEORY

The residence time of the maximum of the residence time distribution function of a component in a chromatographic system depends on static and dynamic effects. It differs from the retention time, which is defined as the average residence time of the component, given by the first moment of the residence time function. In practice, the difference between the retention time and the residence time of the concentration maximum is negligible when the concentration of the component in the stationary bed is a linear function of its concentration in the fluid stream (linear distribution isotherm). The residence time of the maximum, being easy to determine, can then be used as an approximation for the retention time.

Static effects

In elution chromatography, an expression for the residence time distribution in the chromatographic system can be derived assuming:

distribution equilibrium;
no mixing phenomena;
constant fluid velocity;
constant temperature;
negligibly small sample input time;
negligibly small mole fraction; and
uniform geometry along the system.

The following equation is obtained[32]:

$$t_c = \frac{L}{v}\left(1 + \frac{\mathrm{d}c^s{}_i}{\mathrm{d}c^m{}_i} \cdot \frac{1 - \varepsilon_m}{\varepsilon_m}\right) \qquad (1)$$

where

t_c = residence time of the concentration $c^m{}_i$;
$c^m{}_i$ = equilibrium concentration of component i in the moving fluid phase m;

c^s_i = equilibrium concentration of component i in the stationary bed s;
L = length of the chromatographic column;
v = fluid velocity of the moving fluid phase.

According to eqn. 1, the residence time of a concentration c^m_i in the column is determined by the first derivative of the distribution isotherm of that concentration.

The chromatographic system is, in general, a porous system with a bimodal pore size distribution consisting of wide and narrow pores. The fluid phase in the wide pores flows, whereas the fluid phase in the narrow pores is stagnant. In GLC, the flowing fluid phase in the wide pores is a gas and the stagnant fluid phase in the narrow pores consists of both carrier gas and a stationary liquid. The sample distributes itself between the flowing part of the gas on the one hand and the total of bulk phases, except the solid phase, and interfaces that form the stationary bed on the other. Taking into account all of the stationary phases that can participate in the distribution process, the following more detailed equation can be derived from eqn. 1:

$$t_c = t_{R0}\left(1 + \frac{\varepsilon_\beta}{\varepsilon_\alpha}\cdot\frac{dc^\beta_i}{dc^\alpha_i} + \frac{a_\sigma}{\varepsilon_\alpha}\cdot\frac{dc^\sigma_i}{dc^\alpha_i} + \frac{a_\lambda}{\varepsilon_\alpha}\cdot\frac{dc^\lambda_i}{dc^\alpha_i}\right) \quad (2)$$

where

t_{R0} = retention time of the mobile phase α;
c^α_i = volume concentration in the mobile phase α;
ε_α = volume fraction of the mobile phase α;
c^β_i = volume concentration in the stationary liquid phase β;
ε_β = volume fraction of the stationary liquid phase β;
c^σ_i = surface concentration at the liquid–solid interface;
a_σ = ratio between the area of the solid surface σ and the total volume of the column;
c^λ_i = surface concentration at the gas–liquid interface;
a_λ = ratio between the area of the liquid–gas interface λ and the total volume of the column.

At very low liquid loading and bad wettability of the solid support, gas–solid adsorption can occur in addition.

From eqn. 2, it follows that the residence time of the maximum of the residence time distribution depends on the first derivatives of all three distribution isotherms involved. In general, the distribution isotherms are not linear. The distribution coefficient is the average value of the first derivative in the corresponding concentration range. The different distribution isotherms with respect to the different stationary phases approach a linear function at decreasing concentration, which means that the value of the first derivative approaches the value of the corresponding distribution coefficients at infinite dilution. The residence time of the maximum of the residence time distribution then approaches the retention time t_{Ri}:

$$t_{Ri} \simeq t_{c(max.)} = t_{R0}\left(1 + \frac{\varepsilon_\beta}{\varepsilon_\alpha}K^\beta_{i0} + \frac{a_\sigma}{\varepsilon_\alpha}K^\sigma_{i0} + \frac{a_\lambda}{\varepsilon_\alpha}K^\lambda_{i0}\right) \quad (3)$$

where K^k_{i0} is the limiting value of the distribution coefficient between the stationary phase k (*e.g.*, stationary liquid β, gas–liquid interface λ or gas–solid interface σ) and the mobile fluid phase α.

Following eqn. 3, the retention time is composed of a number of increments

corresponding to the different distribution processes involved:

$$t_{Ri} = t_{R0} + \Delta t_{R\beta} + \Delta t_{R\sigma} + \Delta t_{R\lambda} \tag{3a}$$

where

$\Delta t_{R\beta} = t_{R0}\varepsilon_\beta K^\beta_{i0}/\varepsilon_\alpha$ = retention time increment caused by the solution in the stationary liquid;

$\Delta t_{R\sigma} = t_{R0}a_\sigma K^\sigma_{i0}/\varepsilon_\alpha$ = retention time increment caused by the adsorption at the liquid–solid interface;

$\Delta t_{R\lambda} = t_{R0}a_\lambda K^\lambda_{i0}/\varepsilon_\alpha$ = retention time increment caused by the adsorption at the gas–liquid interface

The limiting value of the mass distribution ratio (capacity ratio), κ_{i0}, of a component i between the stationary phases and the mobile phase can be derived from eqn. 3:

$$\frac{t_{Ri} - t_{R0}}{t_{R0}} = \kappa_{i0} = \frac{\varepsilon_\beta}{\varepsilon_\alpha} K^\beta_{i0} + \frac{a_\sigma}{\varepsilon_\alpha} K^\sigma_{i0} + \frac{a_\lambda}{\varepsilon_\alpha} K^\lambda_{i0} \tag{4}$$

In GLC, the interfacial effects are small in most instances and eqn. 4 can be simplified by using the approximation

$$\kappa_{i0} \simeq \frac{\varepsilon_\beta}{\varepsilon_\alpha} K^\beta_{i0} \tag{5}$$

The magnitude of the non-linearity of the gas–liquid distribution isotherm can be estimated from the theory of regular solutions[46]. According to this theory and the theory of gas chromatographic retention, an expression for the relative difference between the actual partition coefficient K_i and the limiting value K_{i0} can be derived for dilute solutions ($x_i \ll x_s$).

$$\frac{\Delta K_i}{K_{i0}} = \frac{K_i - K_{i0}}{K_{i0}} = \frac{f_{i0} - f_i}{f_i}$$

$$\ln\left(\frac{f_{i0}}{f_i}\right) = \ln\left(\frac{V_i}{V_s} x_i + x_s\right) + \left(1 - \frac{V_i}{V_s}\right)\left[1 - \frac{1}{1 + \frac{V_i}{V_s}\cdot\frac{x_i}{x_s}}\right] + \tag{6}$$

$$+ \frac{V_i(\Delta\delta_{is})^2}{RT}\left[1 - \left(\frac{1}{1 + \frac{V_i}{V_s}\cdot\frac{x_i}{x_s}}\right)^2\right]$$

where

f_i and f_{i0} = actual and limiting values of the activity coefficient;

V_i and V_s = molar volumes of the solute i and the solvent s, respectively;

$\Delta\delta_{is} = \delta_i - \delta_s$ = difference of the solubility parameters[46] of the solute and solvent, respectively;

x_i and x_s = mole fractions of the solute and solvent, respectively.

As an example, the relative deviation of the partition coefficient from the limiting value was calculated for solutions of heptane and toluene in squalane at 100°. The results are given in Table I, from which it can be seen that the relative deviation can be positive or negative. Its value can approach the order of 0.1 % at a mole fraction of 0.1 %.

TABLE I

ESTIMATION OF THE NON-LINEARITY OF GAS–LIQUID SOLUTION ISOTHERMS FOR REGULAR SOLUTIONS

V_i = molar volume; δ_i = solubility parameter; x_i = mole fraction; $\Delta K_i/K_{i0}$ = relative deviation from the limiting value of the partition coefficient.

T(°C)	Solvent	V_i (cm^3)	δ_i ($cal\,cm^{-3}$)	Solute	V_i (cm^3)	δ_i ($cal\,cm^3$)$^{\frac{1}{2}}$	x_i	$\Delta K_i/K_{i0}$
100	Squalane	560	9.3	Heptane	163	6.5	10^{-4}	$+4.8\,10^{-5}$
							10^{-3}	$+4.8\,10^{-4}$
							10^{-2}	$+4.8\,10^{-3}$
100	Squalane	560	9.3	Toluene	117	8.0	10^{-4}	$-5.2\,10^{-5}$
							10^{-3}	$-5.2\,10^{-4}$
							10^{-2}	$-5.2\,10^{-3}$

The relative change of the liquid–gas partition coefficient due to a temperature change is related approximately to the boiling point of the solute:

$$\frac{\Delta K^{\beta}_{i0}}{K^{\beta}_{i0}} = -\frac{\Delta H_i}{RT^2}\cdot\Delta T \simeq 23\,\frac{T_{bi}}{RT^2}\cdot\Delta T \tag{7}$$

where

ΔH_i = molar enthalpy of mixing;
T = thermodynamic temperature;
T_{bi} = boiling point;
R = gas constant;
23 = Trouton constant.

The influence of the non-ideality of the gas phase on the liquid–gas partition coefficient is described by the expression[44]

$$\ln\left(\frac{K^1_{i0}}{K^2_{i0}}\right) = 2\,\frac{\bar{p}}{RT}\,(B_{i1} - B_{i2}) \tag{8}$$

Since K^1_i/K^2_i in practice is near to unity, eqn. 8 can be simplified to give

$$\ln\left(\frac{K^1_{i0}}{K^2_{i0}}\right) \simeq \frac{K^1_{i0} - K^2_{i0}}{K^2_{i0}} = \frac{\Delta K_{i0}}{K_{i0}} = \frac{2\bar{p}}{RT}\,(B_{i1} - B_{i2}) \tag{9}$$

where

K^k_{i0} = limiting value of the partition coefficient for gas phase k (1 or 2);
B_{ik} = second virial coefficient of component i in gas phase k;
$\bar{p}$ = average pressure.

For example, in the case of heptane at 25°, $B_{i1}-B_{i2}$ is about 200 cm^3 $mole^{-1}$ for the usual carrier gases helium and nitrogen[44], corresponding to a variation of about 2% in K_{i0} at a column pressure of about 1 bar. The influence of the column pressure for a given solute is obtained by replacing $2\bar{p}\,(B_{i1}-B_{i2})/RT$ in eqn. 8 by $\Delta\bar{p}\,(2B_{i1}-v_{i0})/RT$, v_{i0} being the molar volume of the solute at temperature T (ref. 44). For the case of heptane at 25° and a column pressure of about 1 bar the quantity $2B_{i1}-v_{i0}$ is about 100 cm^3 $mole^{-1}$ when helium is used as carrier gas and 500 cm^3 $mole^{-1}$ when nitrogen is used. This corresponds to a variation of 0.5–2% in K_{i0} when the average column pressure $\bar{p}$ changes by 1 bar.

The liquid–gas partition coefficient therefore depends not only on the nature

of the solute and solvent and on the temperature, but also, to a lesser extent, on the nature and pressure of the carrier gas.

Adsorption can be described in a general manner by means of the so-called Gibbs equation[47], which gives the excess surface concentration as a function of the surface tension and the bulk composition. For the case of a dilute solution:

$$\Gamma_i = -\frac{x^k_i}{RT} \cdot \frac{\partial \gamma}{\partial x^k_i} \tag{10}$$

where

Γ_i = excess surface concentration;
x^k_i = mole fraction of component i in bulk phase k;
γ = surface tension.

At present, no satisfactory theory exists to describe the dependence of the surface tension on the composition of the bulk phase, and eqn. 10 can therefore be solved only empirically. The retention time increments corresponding to adsorption can be derived by combining eqns. 3a and 10:

$$\Delta t_{Rk} = -t_{R0} \frac{a_k}{\varepsilon_a} \cdot \frac{K^\beta_i}{RT} \cdot \frac{\partial \gamma}{\partial c^\beta_i} \tag{11}$$

where $k = \lambda$ or σ.

The excess surface concentration and the corresponding retention time increment can be positive or negative, depending on whether the surface tension decreases or increases with increasing mole fraction. At low concentrations of component i in the bulk liquid phase, $\partial\gamma/\partial c^\beta_i$ approaches a constant value, in which case the retention time increments due to adsorption are proportional to the increment due to solution.

For identification purposes, relative retention data or standardized logarithmic relative retention data (retention indices) are used. An expression for the relative retention of a compound j with respect to a standard compound i can be derived from eqn. 4:

$$r_{ji} = \frac{\kappa_{j0}}{\kappa_{i0}} = \frac{\varepsilon_\beta K^\beta_{j0} + a_\sigma K^\sigma_{j0} + a_\lambda K^\lambda_{j0}}{\varepsilon_\beta K^\beta_{i0} + a_\sigma K^\sigma_{i0} + a_\lambda K^\lambda_{i0}} \tag{12}$$

In GLC, the following simplified expression obtained by neglecting the contribution of adsorption effects in eqn. 12, is generally used:

$$r_{ji} \simeq \frac{K^\beta_{j0}}{K^\beta_{i0}} \tag{13}$$

This means that the relative retention is considered to depend on the ratio of the liquid–gas partition coefficients of the sample and the standard compound only.

The retention index[48] is derived from the relative retention according to the definition

$$I = 100\left(n + \frac{\log r_{i,n}}{\log r_{n,n+1}}\right) \tag{14}$$

where n is the number of carbon atoms in the n-alkanes used as standards.

Dynamic effects

According to eqn. 3, the retention time in GLC at low concentration approaches a linear function of the liquid–gas partition coefficient. In the theoretical derivation of the retention time, resulting in eqn. 3, the local changes in the fluid velocity and the temperature due to the distribution process of the sample have been neglected. The local change in the fluid velocity arises from the subtraction or addition of mass from or to the fluid stream because of sorption and desorption processes, respectively. The relative error in the determination of the true capacity ratio due to the fluid velocity changes depends on the mole fraction and the capacity ratio itself. Assuming a linear distribution isotherm[32]:

$$\frac{\Delta\kappa}{\kappa_{i0}} = \frac{\kappa_i - \kappa_{i0}}{\kappa_{i0}} = \frac{t_{Ri} - t_{R0}}{t_{R0}\,\kappa_i} - 1 = \frac{\kappa_{i0}}{1 + \kappa_{i0}}(x^m{}_i)^2 - 2\,x^m{}_i \qquad (15)$$

where $x^m{}_i$ is the mole fraction of the component i in the mobile phase m. In order not to exceed a relative error of 0.1 % of the measured value of the capacity ratio with respect to its limiting value at infinite dilution, the mole fraction should not be greater than 0.05 %.

The local change in temperature[43] in GLC is due to the heat of solution produced or consumed when the sample is adsorbed or desorbed in the stationary liquid. The effect of this temperature change on the retention time increases with increasing capacity ratio and mole fraction. It is smaller, however, than the corresponding effect of the change in fluid velocity.

The cause of another error is the difference between the residence time of the concentration peak maximum and the residence time of the centre of mass, which represents the true retention time. The relative error in the determination of the retention time due to this effect depends on the theoretical plate number, N_i (ref. 49):

$$\frac{\Delta t}{t_{Ri}} = \frac{t_{max.} - t_{Ri}}{t_{Ri}} = \left(1 - \frac{1}{N_i}\right)^{+} - 1 \simeq -\frac{1}{2N_i} \qquad (16)$$

The relative error in the retention time exceeds 0.1 % if the theoretical plate number is less than 500.

An error in the determination of the capacity ratio can also be introduced by the determination of the retention time t_{R0} of the mobile phase. In GLC, this retention time is determined by means of a tracer which is assumed not to dissolve in the stationary liquid. In practice, no compound exists that is completely insoluble. The relative error in the capacity ratio created by the solubility of the tracer depends on the capacity ratio κ_i of the sample compound as well as on the capacity ratio κ_0 of the "inert tracer":

$$\frac{\Delta\kappa_i}{\kappa_i} = \frac{\kappa_i - (t_{Ri} - t'_{R0})/t'_{R0}}{\kappa_i} = \frac{\kappa_0(1 + \kappa_i)}{(1 + \kappa_0)\kappa_i} \qquad (17)$$

where t'_{R0} is the retention time of the tracer compound.

In order to obtain a relative error less than 0.1 %, the capacity ratio κ_0 must be smaller than $0.001\ \kappa_i/(1 + 0.999\ \kappa_i)$, which means that, as expected, the error can become significant at low values of the capacity ratio κ_i.

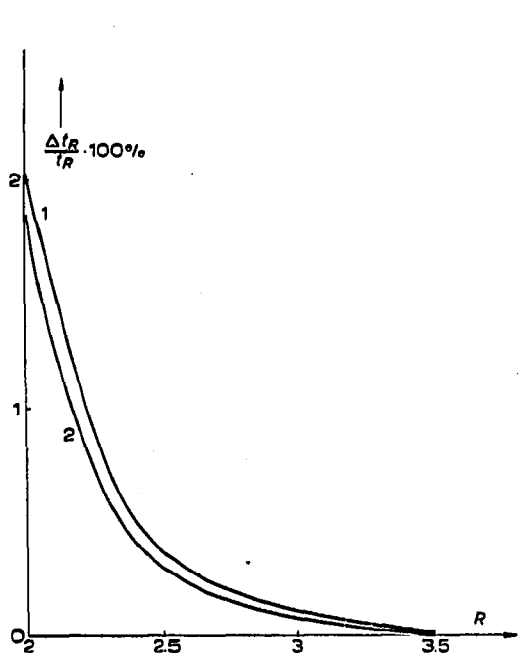
In principle, the migration velocity of a component can be influenced by other components from which it is incompletely separated. This is due to non-ideality of the solute–solvent system and, if relevant, competition for adsorption sites[50]. The

magnitude of this effect is difficult to estimate but, certainly at higher concentrations of the interfering components, cannot be neglected.

Further errors arise from the retention time measurement itself, where a starting point and an end-point have to be determined. The error in the determination of the starting point is caused mainly by the use of the time of injection instead of the time of entry into the column, which cannot be determined. This error depends on the design of the sampling device. The error of the end-point is due to a difference between elution time of the peak maximum indicated by the detector and the true value. Such a difference can be caused by insufficient resolution of successive peaks and by a too slow response of the detector.

The shift in the peak maximum in the case of incomplete resolution due to superposition of the single peaks in the detector depends on the resolution and the peak size ratio. Assuming peaks of a given shape, the relative shift can be calculated by the use of an analogue computer[51]. Results for gaussian peaks are shown in Figs. 1 and 2, where a theoretical plate number of 2500 is assumed and the peaks are considered within $\pm 3.5\,\sigma$ (σ = standard deviation). The corresponding shift in the capacity ratio is calculated from

$$\frac{\Delta\kappa_i}{\kappa_i} = \frac{1+\kappa_i}{\kappa_i} \cdot \frac{\Delta t_{Ri}}{t_{Ri}} \qquad (18)$$



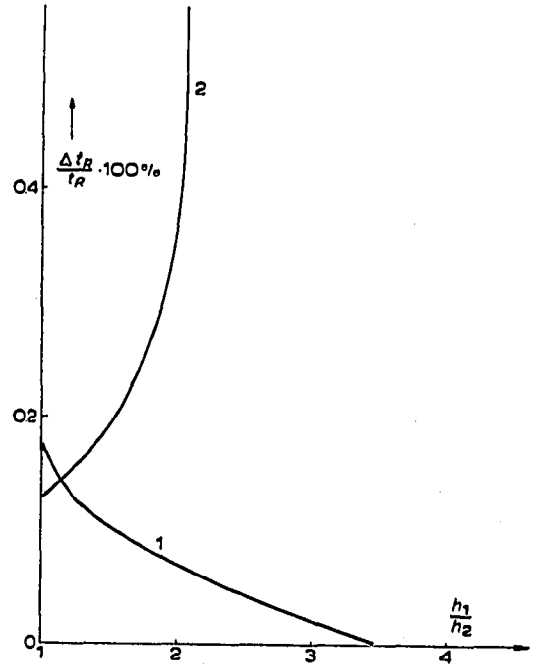


Fig. 1. Relative shifts in retention times of two gaussian peaks (1, 2) at constant peak height ratio ($h_1/h_2 = 1$) as a function of their resolution (R). The shift is positive for peak 1 and negative for peak 2. Results are given corresponding to a plate number of 2500 and a standard deviation (σ) of the first peak (1) of 2 sec. Both peaks are considered within $\pm 3.5\,\sigma$.

Fig. 2. Relative shifts in retention times of two gaussian peaks at constant resolution ($R = 2.8$) as a function of the ratio of the height of the first peak and the height of the second peak (h_1/h_2). Other conditions as in Fig. 1.

From Fig. 1, it can be concluded that a resolution of at least 3 is needed in order to achieve a relative error of 0.1 % in the retention time for a peak size ratio of unity.

The dynamic signal transfer characteristics of the detector can be described, to a first approximation, by a first-order differential equation, characterized by a time constant τ. The resulting relative error in the retention time is then found to be[52,53]

$$\frac{\Delta t_{Ri}}{t_{Ri}} = \frac{\tau}{t_{Ri}} = \frac{\tau}{\sigma_{ti}\sqrt{N_i}} \tag{19}$$

where σ_{ti} is the standard deviation of the peak.

Fig. 3 shows that eqn. 13 holds up to $\tau/\sigma_{ti} \simeq 0.2$. The corresponding relative error in the capacity ratio, as determined from the retention time t_{Ri}, is found by applying eqn. 18:

$$\frac{\Delta\kappa_i}{\kappa_i} = \frac{1+\kappa_i}{\kappa_i}\,\frac{\tau}{\sigma_{ti}\sqrt{N_i}} \tag{20}$$

As in the case of incomplete resolution, the error will increase with decreasing capacity ratio. With a retention time of 100 sec, a time constant of 0.1 sec is needed in order to achieve a relative error of 0.1 % in the retention time (plate number = 2500).

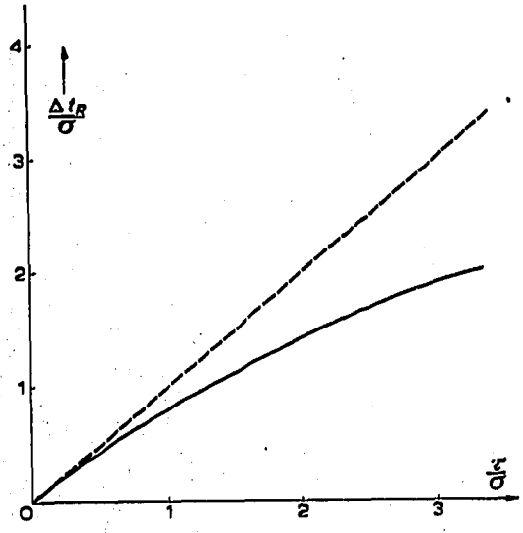


Fig. 3. Plot of the shift in retention time as a function of the ratio of the time constant of the detector ($= \tau$) and the standard deviation (σ) of the (gaussian) input peak.

Systematic and statistical errors

The influence of static and dynamic effects on the error in the capacity ratio was discussed theoretically in the preceding sections. The errors were considered to be systematic, having definite positive or negative values. The corresponding errors in the relative retention and retention index can be derived by determining the propa-

gation of the errors in the capacity ratio as given by eqns. 12 and 14. The relative systematic error in the retention ratio, $r_{jl} = \kappa_j/\kappa_l$, is the sum of the relative systematic errors of the two capacity ratios:

$$\frac{\Delta r_{jl}}{r_{jl}} = \frac{\Delta \kappa_j}{\kappa_j} - \frac{\Delta \kappa_l}{\kappa_l} \tag{21}$$

The systematic error in the retention index can be found in a similar way by determining the propagation of the systematic errors in the retention ratio in eqn. 14.

When the errors in the variables describing the retention data functions are not constant but fluctuate irregularly, the propagation of statistical errors must be determined. Accordingly, the coefficient of variation of the retention ratio is calculated from the coefficients of variation of the capacity ratios:

$$\frac{S_r}{r_{jl}} = \left[\left(\frac{S\kappa_j}{\kappa_j}\right)^2 + \left(\frac{S\kappa_l}{\kappa_l}\right)^2\right]^{\frac{1}{2}} \tag{22}$$

where

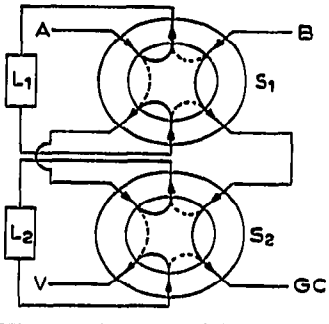
S_k = estimated standard deviation of parameter k ($k = r_{jl}$, κ_j or κ_l);
S_k/k = coefficient of variation.

Similarly, the coefficient of variation of the retention index can be found by determining the propagation of the statistical errors in the retention ratios in eqn. 14.

EXPERIMENTAL

Apparatus

The distribution coefficients were determined with the apparatus described in a previous paper[50]. The main part of the system consists of two thermostatted switching valves, S_1 and S_2 (Valco VSV 6HT in Becker air-bath 1452 P) connected as shown in Fig. 4. Carrier gas A consists of helium and an inert tracer (nitrogen) and contains the compound of which the distribution coefficient is to be determined. Carrier gas B consists of pure helium. The phase system in which the distribution of the test com-



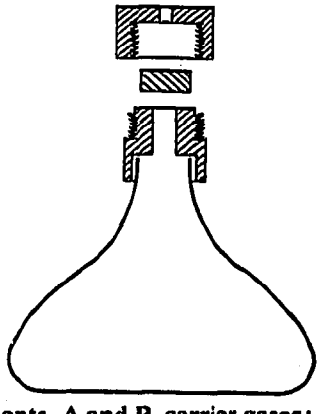


Fig. 4. Diagram of the apparatus for the determination of partition coefficients. A and B, carrier gases; S_1 and S_2, switching valves; L_1 and L_2, sample tubes; V, vent; GC, gas chromatograph.

Fig. 5. Flask used to determine the solubility of nitrogen in squalane.

pound takes place is contained in the tube L_1. Another tube L_2, of exactly known volume, is filled with the gas phase only and is used as the reference. The contents of the tubes can be analyzed by means of the gas chromatograph, GC, equipped with a thermal conductivity detector. In such a way, all of the parameters necessary to calculate the distribution coefficient are obtained.

The determination of the solution of a gas in a liquid was carried out in a glass flask (see Fig. 5), about 30 ml in volume and with a narrow neck, fitted with a sampling device containing a PTFE-coated septum (Hamilton).

Reagents

Refined diatomaceous earth, 0.1–0.2 mm, 1.1 m^2/g (Chromosorb W NAW, Johns-Manville) and silanized diatomaceous earth, 0.1–0.2 mm, 0.3 m^2/g (Chromosorb G DMCS, Johns-Manville) were used as chromatographic supports. The solvents used as stationary liquids were specified for gas chromatography (Merck). Pure carrier gases (Air Liquide) were used and were further purified on-line with an activated molecular sieve (Linde 4A) column. All of the sample compounds were of analytical grade (Merck).

RESULTS AND DISCUSSION

From the theoretical considerations, it can be concluded that the most significant errors in the determination of retention data in GLC are caused by adsorption effects and the solubility of the inert tracer.

Errors due to adsorption

The samples and chromatographic systems investigated for adsorption effects are given in Table II. The distribution coefficients were determined as a function of the amount of the liquid phase on the solid support, assuming only liquid–gas distribution. The concentration in the liquid phase is given in moles per gram, the concentration in the gas phase in moles per milliliter. Consequently, the liquid–gas partition coefficient is given in milliliters per gram. The concentration of the sample in the mobile phase was kept constant. The measurements were carried out following the method described in a previous paper[50]. The component of which the distribution is to be measured is mixed with inert carrier gas and led through a tube containing the chromatographic system. After attainment of equilibrium, the contents of the tube are analyzed with a gas chromatograph. In addition to the tube containing the chromatographic packing, a tube of known volume, filled with the gas mixture only, is used as reference in exactly the same way. In this manner, all of the parameters necessary for the calculation of distribution data can be obtained.

In Fig. 6, distribution data are plotted for carbon tetrachloride (solute) and dinonyl phthalate (solvent) on two different supports. This system was chosen as data for a similar system were available from the literature[28], thus allowing a comparison of results. From Fig. 6, it can be seen that for liquid loadings above 0.5% (g/g), a linear relationship exists between the amount sorbed in the entire stationary bed and the amount of liquid coated on the solid support. The type of solid support appears to have no effect on the distribution data. Both results suggest that only bulk solution is significant. The partition coefficient was found to be 62 and 65 $cm^3\ g^{-1}$ using solid

TABLE II

SOLUTION AND ADSORPTION DATA IN GAS–LIQUID–SOLID SYSTEMS AT CONSTANT TEMPERATURE (100°) AND CONSTANT PARTIAL PRESSURE (1 OR 10 mm Hg AT 0°) OF THE SOLUTE

Solute	*Gas*	*Liquid**	*Solid***	*r****	$a \pm s_a$§ ($mol\,g^{-1}$) $\times 10^8$		$b \pm s_b$§ ($mol\,g^{-1}$) $\times 10^8$		*Lower limit of linear range (%(g/g) liquid loading)*	$100.\frac{bRT}{p_l}$ *(see eqn. 25)* (ml/g)
Carbon tetrachloride	He	DNP	W	1.000	−1.3	1	27.5	0.2	0.5	63.9
			G	0.994	2.8	3	27.7	0.6	0.4	64.4
Acetone		SQ	W	0.986	167	11	5.1	0.6	4	11.8
			G	1.000	3.0	0.5	5.0	0.1	1	11.6
		PEG	W	0.999	−6	1.5	11.6	0.2	1	26.9
			G	0.996	−1	1.8	11.4	0.5	1	26.5
Ethanol		SQ	W	0.997	173	13	4.2	0.6	4	9.7
			G	0.996	2.5	0.4	3.3	0.1	1	7.7
		PEG	W	0.998	−11	3	20.1	0.4	1	46.7
			G	0.998	−3	3	22.7	0.6	1	52.8
Toluene		SQ	W	0.999	17	16	70.3	1.1	2	163
			G	1.000	−2	1.4	70.8	0.2	0.5	164
		PEG	W	0.999	−11	6	45.1	0.8	0.5	105
			G	0.995	−5	8	44.8	2.0	0.3	104
Heptane		SQ	W	0.999	−4	11	46.3	0.7	2	108
			G	1.000	1	3	46.3	0.4	0.5	108
		PEG	W	0.995	3	1.4	5.1	0.2	4	11.9
			G	0.993	1	1.1	5.2	0.3	1	12.0

* DNP = dinonyl phthalate; SQ = squalane; PEG = polyethylene glycol 20,000.
** W = Chromosorb W NAW; G = Chromosorb G DMCS.
*** r = correlation coefficient.
§ a and b = parameters of the linear regression following eqn. 24; s_a and s_b = estimated standard deviations of a and b, respectively.

supports W and G, respectively. The coefficient of variation of the measurement was 5%. Measurements at partial pressures of 1 and 10 mm Hg (at 0°) gave the same results. At liquid loadings less than 0.5% (g/g), it can be seen that the relationship becomes non-linear and different results are obtained with different supports. This is attributed to the influence of adsorption effects, most probably at the solid–liquid interface.

Data from the literature[28] suggest that liquid surface adsorption should be predominant. For instance, in the case of a loading of DNP of 5% (g/g) on a diatomite support with a specific surface area of 3.17 m^2/g (Polsorb C) at 100°, the bulk liquid phase was calculated to contribute only 26.8%, the liquid surface 72.5% and the solid surface 0.7% to the total distribution of carbon tetrachloride. These data were obtained from the residence times of the peak maxima on columns of various liquid loadings (1, 2 and 5% (g/g)). Sample sizes ranged from 0.05 to 0.3 μl. The concentration in the mobile phase corresponding to the maximum of the elution peak can

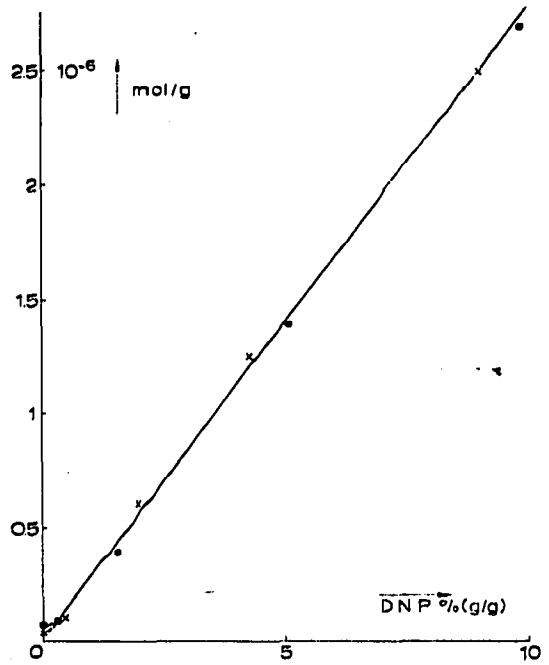


Fig. 6. Distribution data for carbon tetrachloride (solute) and dinonyl phthalate (solvent) on Chromosorbs W and G. The total amount of carbon tetrachloride sorbed is given as a function of the percentage of dinonyl phthalate related to the mass of support. ×, Data on Chromosorb G; ●, data on Chromosorb W.

be calculated assuming a gaussian peak shape:

$$C^{m}_{l(max.)} = \frac{Q_l}{\sigma_{tl}\, W(2\pi)^{\frac{1}{2}}} \tag{23}$$

where

Q_l = amount injected;
σ_{tl} = standard deviation of the gaussian elution peak;
W = flow-rate at the column exit.

From eqn. 23, it can be estimated that the concentration in the gas phase at 100° was up to 3.10^{-3} mole l^{-1}, corresponding to a mole fraction of 10%. This suggests that significant errors can be involved according to eqns. 6 and 15. The phase ratio can be estimated to range approximately from 0.005 to 0.03 at liquid loadings from 1 to 5% (g/g). Since a value of 65 ml/g was found for the partition coefficient, the corresponding capacity ratios range approximately from about 0.3 to 2. For this reason, a further significant error may arise due to eqn. 17. Summarizing, it can be said that significant adsorption of carbon tetrachloride at the gas–liquid interface of the system DNP–diatomite support is doubtful and that the data can be satisfactorily described by assuming only distribution between the gas phase, the bulk liquid and the solid surface.

As shown in Fig. 6, adsorption effects can be identified[13–28] by representing the amount of solute contained in the liquid–solid system, including interfaces, as a function of the mass of liquid coated on the solid. Both the amount of solute as well as the mass of liquid are normalized with respect to the mass of solid. If, at a

given concentration, the distribution isotherm is non-linear, this function must be given for a constant concentration in the gas phase. The systems specified in Table II were investigated for partial pressures of 1 and 10 mm Hg (at 0°) in the gas phase at 100°. It was found that the data could be described by a linear function at liquid loadings above about 1 % (g/g) liquid on solid G and 3 % (g/g) on solid W, corresponding to about 0.03 g/m² in all instances:

$$\frac{n_i^{\beta,\sigma,\lambda}}{m_s} = a + b\frac{m_\beta}{m_s}\cdot 100 \tag{24}$$

where

$n_i^{\beta,\sigma,\lambda}$ = number of moles of solute i in the total liquid–solid system. The solute can be present in the liquid phase β, at the liquid–solid interface σ and at the liquid–gas interface λ;

m_s = mass of solid s;

m_β = mass of liquid phase β on the solid.

The parameters a and b were calculated from the data by determining the linear regression. The corresponding correlation coefficient characterizing the degree of linearity was also calculated and the results are given in Table II. The concentration (mole g^{-1}) of the solute in the liquid phase is given by the slope b in eqn. 24. The liquid–gas partition coefficient can therefore be calculated from this value and the partial pressure p_i:

$$K^\beta_{i0} = \frac{b\,RT}{p_i}\cdot 100 \tag{25}$$

These data are included in Table II.

The results show that the value of a is significantly different from zero in a number of instances. The magnitude of a corresponds to the amount of solute adsorbed at the gas–liquid and liquid–solid interfaces at a given concentration in the gas phase. The linear relationship at higher liquid loadings shows that the adsorption is independent of the liquid loading, which suggests that the adsorption on the liquid–solid surface dominates, since this interface area is constant whereas the liquid–gas interface area decreases with increasing liquid loading of the solid. The magnitude of a was found to be especially large for ethanol and acetone with squalane as solvent coated on solid W, which is to be expected since this support is not silanized and a non-polar solvent such as squalane does not compete effectively with the solute for the adsorption sites on the solid surface. Even with the silanized solid support G, the value of a is not zero for this case. Weak adsorption effects can also be observed for acetone and ethanol with the polar solvent PEG. It is interesting to note that in this case the values of a are negative, suggesting negative adsorption.

The gas–liquid partition coefficient is independent of the nature of the solid support and the amount of liquid coated on the solid. In agreement with this, the values of the partition coefficient calculated with eqn. 25 and given in Table II are constant for liquid loadings above 0.03 g/m², which proves that under these conditions the liquid contained in the pores has the same solvent properties as a bulk liquid.

When the liquid loading is decreased to below 0.03 g/m², the contribution of the adsorption given by the value of a in eqn. 24 is not constant, but changes with

TABLE III

GAS–SOLID ADSORPTION OF DIFFERENT COMPOUNDS AT 100° AND CONSTANT PARTIAL PRESSURE OF 10 mm Hg AT 0°

Relative standard deviation of the data ≈ 10%.

*Solid**	*Adsorbate concentration on the solid surface (mole g^{-1}) × 10^7*				
	Carbon tetrachloride	*Acetone*	*Ethanol*	*Toluene*	*Heptane*
W	0.8	19.8	22.9	8.7	1.9
G	0.3	0.2	0.1	0.15	0.2

* W = Chromosorb W NAW; G = Chromosorb G DMCS.

decreasing liquid loading from the combined value for gas–liquid and liquid–solid adsorption to the value for gas–solid adsorption in the case of uncoated solid support. The concentrations (mole g^{-1}) of the adsorbates on the uncoated solid at 100° and 10 mm Hg (at 0°) are given in Table III for the two solid supports studied. In Figs. 7 and 8, the transition from gas–liquid and liquid–solid adsorption to gas–solid adsorption is shown for low liquid loadings. The participation of gas–liquid adsorption cannot easily be recognized.

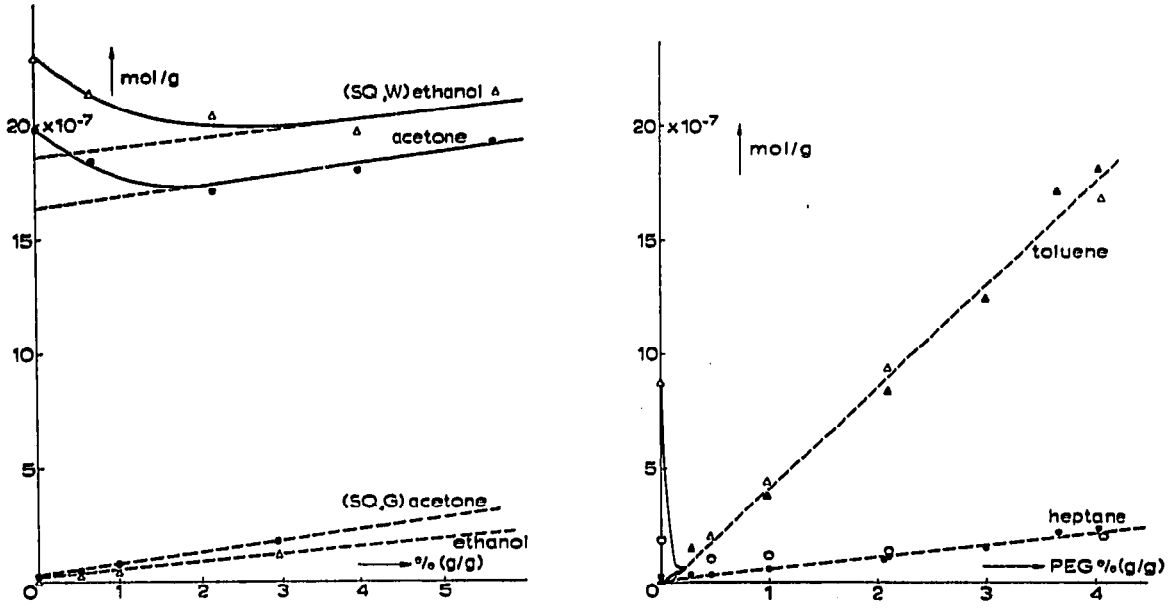


Fig. 7. Distribution data for ethanol and acetone (solutes) and squalane (solvent) on Chromosorbs W and G. Plot as in Fig. 6. △, data for ethanol; ●, data for acetone; – – – – –, regression lines according to Table II.

Fig. 8. Distribution data for heptane and toluene (solutes) and polyethylene glycol 20,000 on Chromosorbs W and G. Plot as in Fig. 6. ○, Data for heptane on Chromosorb W; ●, data for heptane on Chromosorb G; △, data for toluene on Chromosorb W; ▲, data for toluene on Chromosorb G; – – –, regression lines according to Table II.

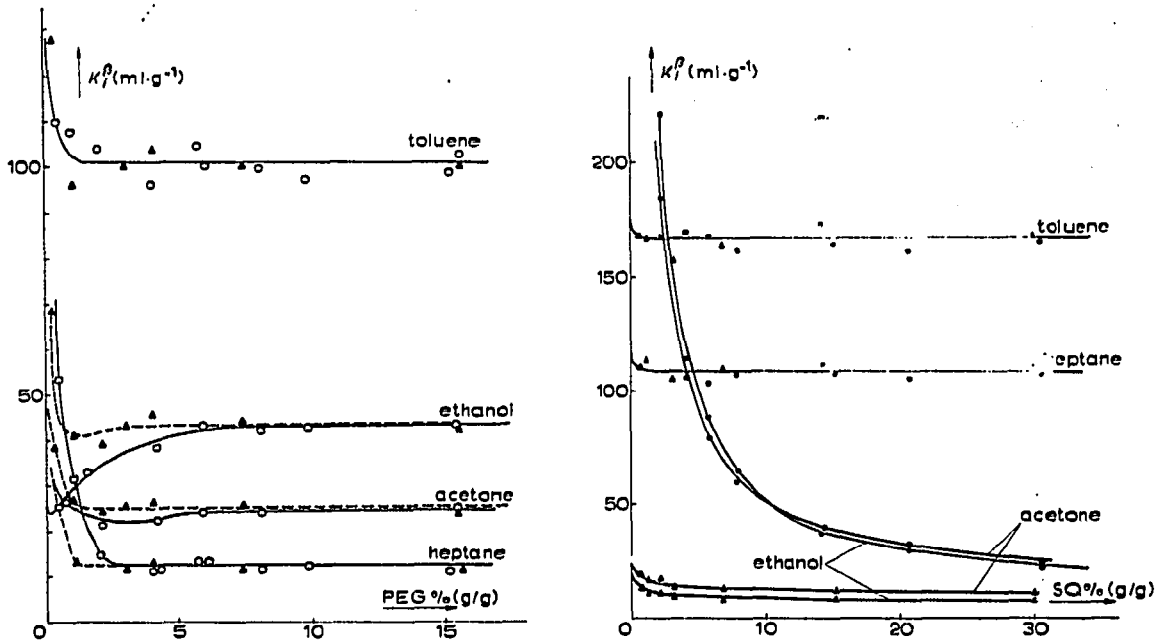


Fig. 9. Plot of the apparent gas–liquid partition coefficient as a function of polyethylene glycol liquid loading on Chromosorbs W and G. ○, Data on Chromosorb W; ▲, data on Chromosorb G.

Fig. 10. Plot of the apparent gas–liquid partition coefficient as a function of squalane liquid loading on Chromosorbs W and G. ●, Data on Chromosorb W; ▲, data on Chromosorb G.

In Figs. 9 and 10, the apparent gas–liquid partition coefficient, calculated by assuming the entire solute present in the liquid phase and the interfaces to be contained in the liquid phase only, is given as a function of liquid loading. If positive adsorption effects occur, the apparent partition coefficient should decrease with increasing liquid loading. This is generally found. In the case of ethanol and acetone in PEG coated on solid W, however, a minimum value of the partition coefficient is observed, which suggests that a negative adsorption effect is involved, which, according to eqn. 10, could be due to the gas–liquid interface. Another explanation can be given if it is assumed that the thin film of liquid (0.01 μm thick) on the solid surface has solvent properties that differ from those of the bulk liquid owing to the orienting influence of the solid surface. In particular, a thin film of a polar liquid, *e.g.*, PEG, may be structurally oriented by the solid surface[29–31] and should then be considered more as an adsorbed layer than as a liquid film.

Errors due to sorption of the inert tracer

In principle, the compound used as inert tracer for the determination of t_{R0} is also sorbed to some extent by the stationary bed. Mostly methane and nitrogen are used as the inert tracer with the flame ionization detector and the thermal conductivity detector, respectively.

The solution of nitrogen in the liquid phase squalane was investigated as an example. In order to determine the distribution coefficient, a flask designed for the

measurement of the solubility of gases was filled with 20 ml of squalane that had previously been saturated with nitrogen at a pressure of 1 bar. The flask was thermostatted in an air-bath at 100° for 24 h. Excess pressure was relieved by piercing the septum. A sample of 30 μl was taken from the solution in the flask with a syringe and injected into a chromatographic system consisting of a pre-column containing a porous material (Chromosorb W) to trap the squalane, and a column packed with molecular sieve 5A to separate oxygen and nitrogen. The amount of nitrogen dissolved in squalane was calculated from the resulting peak area. The distribution coefficient of nitrogen at 100° was found to be 0.15 ($\pm$ 4%) ml g^{-1}.

The relative systematic error in the capacity ratio caused by the dissolution of the compound used as inert tracer can be calculated following eqn. 12. Assuming a mass to volume ratio of 0.1 for the liquid and gas phases, the capacity ratio of nitrogen in squalane at 100° is 0.015. For a strongly retained compound ($\kappa_i \gg 1$), the corresponding relative systematic error in the capacity ratio approaches 1.5%, and increases when the capacity ratio of the inert tracer increases or when the capacity ratio of the sample component decreases. For example, values of 2 and 3% are obtained when nitrogen is used as inert tracer under the same conditions as before for compounds having capacity ratios of 2 and 1, respectively. The relative systematic error in the retention ratio of two compounds can be calculated from eqn. 22. When the error in the capacity ratio is 2 and 3%, respectively, as shown in the previous example, the systematic error in the retention ratio is found to be 1%.

The partition coefficient of methane in squalane was estimated[54] to be 0.16 at 70°, so that the corresponding errors in the capacity ratio and relative retention are of the same order of magnitude as for nitrogen. Summarizing, it can be said that the use of nitrogen or methane as inert tracer can cause significant errors in absolute, as well as relative, retention data.

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