CHREV. 78

IDENTIFICATION OF GAS CHROMATOGRAPHIC ZONES IN PRACTICAL GAS-LIQUID CHROMATOGRAPHY

INFLUENCE OF ADSORPTION ON RELATIVE RETENTION

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(Received May 8th, 1974)

Gas chromatographic identification methods based on the comparison of experimentally determined retention values of chromatographed zones of unknown compounds with the corresponding values for zones of known compounds are widely used[1]. The use of this simple technique for comparing retention values is limited, however, by the inadequate inter-laboratory reproducibility of retention values. Inter-laboratory non-reproducibility of retention values can apparently be attributed to the non-uniform properties of the sorbents prepared by different workers using different procedures and solid supports of different quality. It should be noted that the differences in the properties of the sorbents in gas-liquid chromatography (GLC) have not been given sufficient acknowledgement in the literature as being the cause of inter-laboratory non-reproducibility of retention values, although the practical value of the chromatographic technique is due largely to the possibility of its wide application in many laboratories.

The advances achieved in recent years in the development of the retention theory and in investigating the properties of sorbents in GLC have helped to explain the non-reproducibility of retention values and to develop new methods for identifying chromatographic zones.

In the modern theory of GLC, the retention of compounds chromatographed is considered, taking into account the real distribution of the liquid stationary phase (LSP) on the solid support[1,2]. Investigations conducted by various methods indicate, in general, that the LSP distribution is complex. At first the LSP fills mainly the narrow pores of the solid support, then the pores of larger diameter, and the LSP film on the walls of the wide macropores grows thicker. With an LSP content on ordinary solid supports exceeding 1–3%, and with good wettability, a continuous LSP film apparently forms on the surface of the solid support; when the surface wettability of the solid support is low, the liquid phase can be observed on the surface in the form of separate insular drops. The nature of the distribution also depends greatly on the technique of applying the LSP, the conditions of the subsequent aging of the sorbent[12], etc. In practical gas-liquid chromatography, according to various workers[2,3], the model of a sorbent obtained on the basis of ordinary diatomaceous supports with an LSP content of more than 1–3% can be regarded as a porous solid (solid support) covered with a continuous LSP film of variable thickness (see Fig. 1). This model agrees well with the following different experimental data: the dependence
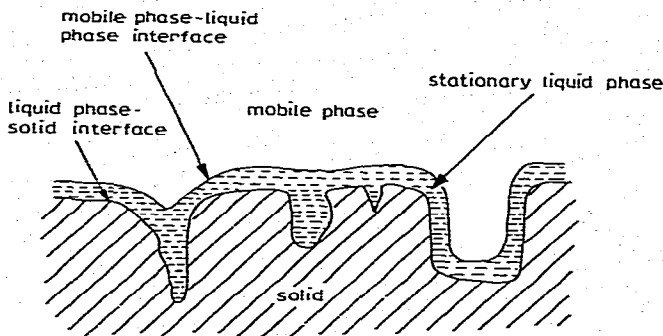
Fig. 1. Model of sorbent in gas–liquid chromatography.

of the height equivalent to a theoretical plate on the flow velocity of the carrier gas[10]; the variation in pore distribution in relation to the sorbent surface with an increase in LSP content on the solid support[5,9,11]; the dependence of retention in the vicinity of the melting point of the LSP[6]; and the results of special investigations of the support with the use of a marked surface[7].

Therefore, in considering the retention of volatile compounds, we have henceforth adopted the model of complete or quasi-complete coverage of the surface of a solid support with an LSP film.

In agreement with the above, a sorbent in GLC cannot be regarded solely as an LSP. At the LSP–gas support interface there is one surface phase (gas–liquid) and at the LSP–solid support interface another surface phase (liquid–solid). The properties of the LSP in a macrofilm on a solid support usually coincide with the properties of the bulk phase of the LSP. In the case of thin films (several molecular layers), it is necessary to take into account the effect of the field of the solid support. Thus, a sorbent in GLC is a polyphase sorbent. The development of the equilibrium theory of the retention of volatile compounds is associated with the contribution of the retentions on the separate phases of a sorbent to the total retention volume[5,13-17]. The retention value of a volatile substance is determined by its interaction with at least one bulk and two surface phases, namely the dissolution of the substance chromatographed in the LSP and its adsorption on the gas–LSP and LSP–solid support interfaces. For this case, the net retention volume (V_N) can be represented by the following equation within the framework of the theory of equilibrium chromatography under the conditions of linear isotherms of dissolution and adsorption[15]:

$$V_N = K_l v_l + K_{gl} S_l + K_l K_s S_s \tag{1}$$

where K_l is the distribution constant of the chromatographed compound in the gas–LSP system, K_{gl} is the adsorption constant of the chromatographed compound in the gas–LSP surface system, K_s is the adsorption constant of the chromatographed compound in the LSP–solid support system, v_l is the volume of LSP in the column, S_l is the total surface area of the LSP at the LSP–gas interface, and S_s is the total surface area of the LSP–solid support interface.

In the general case, when in a sorbent the number of phases capable of retain-

ing volatile substances exceeds the above three phases, the following generalized equation is valid[15]:

$$V_N = \sum_i^n \frac{\partial V_N}{\partial v_i} \cdot v_i + \sum_j^m \frac{\partial V_N}{\partial S_j} = \sum_i^n K_i \, v_i + \sum_j^m K_j \, S_j \tag{2}$$

where v_i is the volume of the i-type LSP characterized by an effective distribution coefficient $K_i = \partial V_N / \partial v_i$ (LSP types: LSP in micropores, LSP in the macrolayer, etc.), S_j is the area of a j-type surface characterized by an effective distribution coefficient K_j (surface types: the surface of an uncovered support, the surface of an LSP macro-layer, the surface of an LSP monolayer, and so on).

As a particular case, it is possible to obtain, from eqn. 1 and also from the equation for the retention volume in classical GLC[13], the equation of Martin[16], the equation for the retention volume in gas–adsorption chromatography for macroporous adsorbents[18], etc. It should be stressed that in the general case, practical utilization of Fig. 2 is complicated as it requires the use of additional quantitative data on the distribution of the LSP over the surface of the solid support, *i.e.*, on the quantitative phase characteristics of the adsorbent used. Therefore, in practice, a simplified form of eqn. 1 is usually applied, which describes the retention on a sorbent obtained with complete coverage of a solid support with an LSP macrofilm. This equation has been used successfully in analyzing adsorption phenomena and determining the distribution and adsorption constants in GLC by a number of investigators, such as Conder *et al.*[11], Urone *et al.*[19], Gritchina and Dreving[20], Liao and Mortire[21], the present author and co-workers, and by other workers. It was shown that the contribution of adsorption of the compounds chromatographed to the retention volume in GLC often has a considerable value which cannot be neglected.

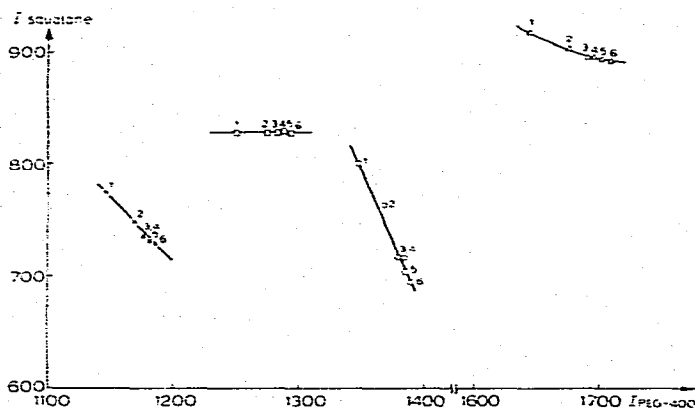The adsorption of volatile substances to be analyzed on the surface phases

Fig. 2. Dependence of retention indices for series of compounds on squalane as a function of retention indices of the same compounds on PEG–400 with the use of different solid supports (according to the data of Evans and Smith[32]). Compounds: ⊙, benzonitrile; ✕, 2-hexanone; □, chlorobenzene; ◌, 1-pentanol. Supports: 1, Chromosorb W; 2, Celite; 3, Anachrom; 4, Chromosorb G; 5, Gas-Chrom; 6, Chromosorb G, silanized.

of the sorbent must also exert an effect upon the relative retention values[5] that are used in identifying chromatographic zones.

Various relative retention values are used for identification[1]. Known relative retention values can be represented as particular cases of the expression[22]

$$R = P\left(k + \frac{r_i - r_m}{r_n - r_m}\right) = P\left(k + \frac{\Delta r_{im}}{\Delta r_{nm}}\right) \tag{3}$$

where R is the relative retention value in a given coordinate system, P and k are constants for a given coordinate system, r_i, r_m and r_n are the corrected (net) retention values of the ith compound and the mth and nth standard substances (or their functions) and Δr_{im} and Δr_{nm} are the differences of the corrected retention values (or of their functions).

In gas chromatography, for determinations under isothermal conditions, it has been recommended that one should use the relative retention value[23,24], the retention factor[25-27] and the arithmetic factor[28], which is also used for measurements in temperature programming[29]. A characteristic similar to the arithmetic factor was proposed by Vigdergauz and co-workers[30,31]. The indicated values can be obtained as particular cases of eqn. 3 (Table 1).

TABLE I

RELATIVE RETENTION VALUES

Retention value	Parameters of eqn. 3					Equation
	P	k	r_i	r_m	r_n	
Relative retention volume	1	0	V_x	0	V_{xst}	$V_z = \dfrac{V_x}{V_{xst}}$
Retention factor (Kováts' index)	100	z	$\log V_x$	$\log V_{xz}$	$\log V_{x(z+1)}$	$I = 100z + \dfrac{\log V_x - \log V_{xz}}{\log V_{x(z+1)} - \log V_{xz}}$
Arithmetical factor	100	z	V_x	V_{xz}	$\log V_{x(z+1)}$	$A = 100z + \dfrac{V_x - V_{xz}}{V_{x(z+1)} - V_{xz}}$
Relative factor*	1	$100z$	V_x	0	V_{xz}	$RI = 100z \cdot \dfrac{V_x}{V_{xz}}$
Relative retention index*	100	1	V_x	V_{xA}	V_{xB}	$P_{AB} = 100 - 100 \cdot \dfrac{V_x - V_{xA}}{V_{xB} - V_{xA}}$

* Proposed by V. G. Berezkin and J. J. Walraven.

As mainly the relative retention volume and the retention factor are used in practical chromatography, let us consider the effect of adsorption specifically for these two relative quantities. Fig. 2 shows the dependence of the retention factor for a number of compounds on squalane as a function of the retention factor of the same compounds on polyethylene glycol 400 with the use of different solid supports (in plotting the graph, use was made of experimental results obtained by Evans and

Smith[32]. It follows from Fig. 2 that the effect of the solid support on the retention factor is considerable. The change in the retention factor exceeds 100 for some compounds, depending on the solid support.

It was generally believed in chromatography until recently that the relative retention value is determined solely by the ratio of the distribution constants of the given and the standard compounds between the gas and liquid phases and hence it is the chromatographic constant of a chemical compound. Therefore, the values of the relative retention volume were used as a basis for identification of chromatographic zones, *i.e.*, qualitative chromatographic analysis of the mixtures to be separated.
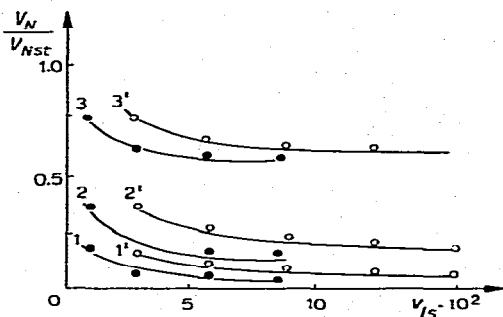

Fig. 3. Dependence of relative retention volume (standard — methyl ethyl ketone) on LSP volume (per gram of solid support) (according to data of Pecsok *et al.*[33]). Experimental conditions: LSP β,β'-thiodipropionitrile, 25 : solid support — Chromosorb W (1–3) and refractory (1'–3'). 1,1' — *n*-heptane: 2,2' — *n*-butyl ethyl ether: 3,3' — ethyl acetate.

Because of adsorption phenomena in partition chromatography, the problem of identification of chromatographic zones should be considered from another viewpoint. As a result of adsorption during chromatographic separations, the relative retention value is determined, in general, not only by the ratio of the distribution constants of the given and the standard compounds (see, for instance, ref. 1), but also by the adsorption properties of the solid support, the content of the liquid stationary phase on the solid support, the phase characteristics of the sorbent, which depend, in particular, on the conditions of its preparation, etc.[7,15]. As an example, Fig. 3 depicts the dependence of the relative retention volume on the content of the LSP on the solid support calculated by us from the data of Pecsok *et al.*[33]. It follows from the data listed that the relative retention value during adsorption in the chromatographic process is not a chromatographic constant of a compound. Indeed, in general, on the strength of eqn. 2, the relative retention can be expressed by the equation

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} \cdot \frac{1 + \left(\sum\limits_{i=2}^{m} K_{li}\, v_{li} + \sum\limits_{j=1}^{n} K_{sj}\, S_{sj} \right) \cdot \frac{1}{K_l\, v_l}}{1 + \left(\sum\limits_{i=2}^{m} K_{list}\, v_{li} + \sum\limits_{j=1}^{n} K_{sjst}\, S_{sj} \right) \cdot \frac{1}{K_{lst}\, v_l}} \tag{4}$$

where V_N is the net retention volume of the substance on a polyphase sorbent, V_{Nst}

is the net retention volume of the substance adopted as the standard. K_l is the equilibrium constant of the substance between the gaseous and stationary liquid phases, K_{lst} is the equilibrium constant of the standard substance between the gas phase and the LSP, K_{li} is the equilibrium constant between the mobile phase and the i-type LSP, v_{li} is the volume of the i-type LSP in the chromatographic column, K_{sj} is the equilibrium constant between the LSP and the j-type interface, and S_{sj} is the area of the j-type surface in the column. Thus, the relative retention value in the general case cannot be used for the identification of compounds on the basis of data published in the literature, as the production of sorbents having identical phase characteristics, with the same LSP distribution on the solid support in different laboratories using different batches of commercial materials, is virtually impossible in most instances.

It should be noted that the known methods for the modification of solid diatomaceous supports (for instance, silanization) or the use of polymer (PTFE) supports decrease the role of adsorption phenomena, but the contribution of adsorption to the relative retention value often remains considerable (see, for instance, refs. 34 and 35). The use of capillary columns does not solve the problem of interlaboratory reproducibility, as the contribution of adsorption still remains appreciable[36]. Therefore, for chromatography to be used extensively as a method of qualitative analysis, it is necessary to devise methods for determining the distribution constant ratio on the basis of experimentally determined relative retention values. Some of the versions of these methods, based on the use of the dependences of the relative retention values on the reciprocal of the LSP content on a solid support, are considered below.

If the retention volume is determined exclusively by the dissolution of the chromatographed substance in the LSP and the adsorption at interfaces with a mobile phase and a solid support (this is rather often the case[7,11,14,15]), eqn. 4 simplifies, and the relative retention volume can be expressed by the equation

$$\frac{V_X}{V_{Xst}} = \frac{K_l}{K_{lst}} \cdot \frac{1 + (K_{al} S_{ls} + K_l K_s S_s)/K_l v_{ls}}{1 + (K_{alst} S_{ls} + K_{lst} K_{sst} S_s)/K_{lst} v_{ls}} \tag{5}$$

Expanding this equation in a Maclaurin series with respect to the variable $1/v_{ls}$, we can write

$$\frac{V_X}{V_{Xst}} = \frac{K_l}{K_{lst}} - \lambda \cdot \frac{1}{v_{ls}} = V^0 - \lambda \cdot \frac{1}{v_{ls}} \tag{6}$$

where

$$\lambda = \frac{(K_{al} K_{lst} - K_{alst} K_l) S_l + (K_s - K_{sst}) K_l K_{lst} S_s}{K_{lst}^2} \tag{7}$$

Note that a similar relationship is obtained when considering a more general equation (eqn. 4) if an increased LSP content on a solid support increases only the thickness of the LSP film. In Fig. 4, the experimental data of Pecsok et al.[33] are presented in accordance with eqn. 6. From this, it follows that the use of eqn. 6 enables the distribution constant ratio, which is independent of the experimental con-
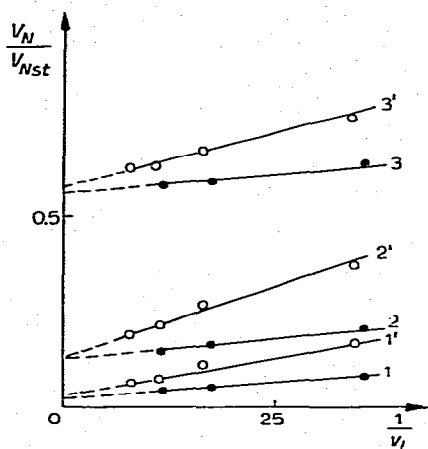
Fig. 4. Dependence of relative retention volume (standard = methyl ethyl ketone) on reciprocal of LSP volume in terms of 1 g of solid support (according to data of Pecsok et al.[35]). Experimental conditions and notation as in Fig. 3.

ditions, to be determined. It is advisable to choose for the standard a substance for which the retention is determined only by dissolution. In this case

$$V_{Nst} = K_{lst} \, v_l \tag{8}$$

$$\lambda_1 = \frac{K_{al} \, S_l + K_l \, K_s \, S_s}{K_{lst}} \tag{9}$$

$$\frac{1}{v_l} = K_{lst} \cdot \frac{1}{V_{Nst}} = \frac{100 \, d_l}{P_s} \cdot \frac{1}{P_l} \tag{10}$$

where v_l is the volume of the LSP in the column, d_l is the LSP density, and P_l is the percentage LSP content in the column (weight of the solid support = 100%).

Using eqns. 8–10, we can represent eqn. 6 by

$$\frac{V_N}{V_{Nst}} = \frac{K_l}{K_{lst}} + \lambda_2 \frac{1}{V_{Nst}} = \frac{K_l}{K_{lst}} + \lambda_3 \cdot \frac{1}{P_l} = \nu^0 + \lambda_3 \cdot \frac{1}{P_l} \tag{11}$$

Eqn. 11 can be used in those cases where the determination of v_{ls} is difficult.

In Figs. 4–6 are shown the dependences of the relative retention volume on the reciprocal of the LSP content on the solid support or on a value proportional to it (see eqn. 11, derived on the basis of the data of refs. 33 and 35). It follows from Figs. 4–6 that the proposed methods can be applied successfully to determine the distribution constant ratio, the thermodynamic characteristic of a substance from which one can identify it. The values of K_l/K_{lst} obtained are independent of the LSP content and the type of solid support.

In gas chromatography, together with the relative retention values, extensive use is made of Kováts' index system[37]:

$$I = 100z + 100 \log \left(\frac{V_N}{V_{Nz}}\right) \Big/ \log \left(\frac{V_{N(z+1)}}{V_{Nz}}\right) \tag{12}$$
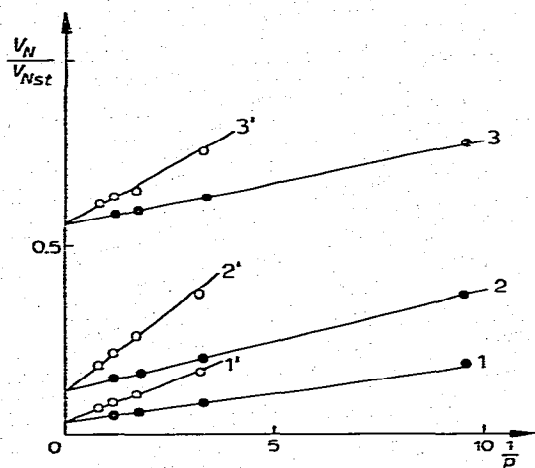
Fig. 5. Dependence of relative retention volume (standard = methyl ethyl ketone) on reciprocal of LSP content, % (according to data of Pecsok *et al.*[33]). Experimental conditions and notation as in Fig. 3.

where V_{x_z} is the net (or corrected) retention volume of an *n*-alkane whose molecule contains z carbon atoms. $V_{x_{(z+1)}}$ is the net (or corrected) retention volume of an *n*-alkane whose molecule contains $z + 1$ carbon atoms, V_x is the net (or corrected) retention volume of the compound to be analyzed. and

$$V_{x_z} \leqslant V_x \leqslant V_{x_{(z+1)}}$$

For the set of standard substances, it is advisable to select compounds for which the retention is determined exclusively by dissolution in the LSP. In this case,
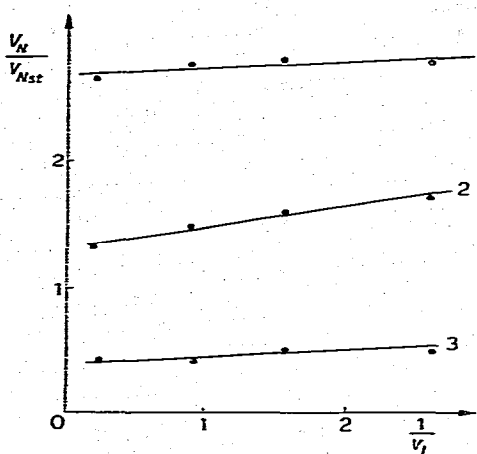

Fig. 6. Dependence of relative retention volume (standard = ethanol) on reciprocal of LSP volume (in terms of 1 g of solid support) (according to data of ref. 35). 1 = *n*-Butylamine; 2 = *n*-hexane; 3 = water. Experimental conditions: LSP = dinonyl phthalate, 86°, solid support = Teflon.

expanding the numerator of the second term of eqn. 12 in a Maclaurin series with respect to $1/v_{ls}$ and taking only the first two terms, we obtain

$$\log \frac{V_N}{V_{N_z}} = \log \left(\frac{K_I}{K_{Iz}} + \lambda \cdot \frac{1}{v_{ls}} \right) = \log \left(\frac{K_I}{K_{Iz}} \right) + 0.43 \, \lambda_1 \cdot \frac{1}{v_{ls}} \tag{13}$$

where $\lambda_1 = \lambda \cdot K_{Iz}/K_I$. Taking into account eqn. 13, we can transform eqn. 12 to give

$$I = 100z + 100 \log \left(\frac{K_I}{K_{Iz}} \right) \Big/ \log \left(\frac{K_{I(z+1)}}{K_{Iz}} \right) + \frac{43 \, \lambda_1}{\log \left(\frac{K_{I(z+1)}}{K_{Iz}} \right)} \cdot \frac{1}{v_{Iz}} \tag{14}$$

or

$$I = I^0 + \lambda_1 \cdot \frac{1}{v_{ls}} \tag{15}$$

where

$$I^0 = 100z + 100 \log \left(\frac{K_I}{K_{Iz}} \right) \Big/ \log \left(\frac{K_{I(z+1)}}{K_{Iz}} \right) \tag{16}$$

and

$$\lambda_1 = 43 \, \lambda \, K_{Iz}/K_I \log \left(\frac{K_{I(z+1)}}{K_{Iz}} \right) \tag{17}$$

For non-polar phases and medium-polarity phases, the requirements for standard compounds are usually met by n-alkanes, but in the case of polar LSP it is advisable to choose polar compounds (for instance, n-alcohols) as standards. As an example, Fig. 7 shows the dependence of the Kováts' indices on the reciprocal of the LSP content: in this case, the standards used were n-alkanes, and in another case n-alcohols (re-calculated by us from the data of ref. 38). From the above information, it follows that the use as standards of n-alcohols, whose retention, in contrast to n-alkanes, is largely determined by dissolution in the LSP, enabled stable Kováts' indices to be obtained for oxygen-containing compounds, but not for n-alkanes.

In Fig. 8, the corresponding graphs for the determination of I^0 are given for n-alkanes. The use of eqn. 15 enables the constant value I^0 to be determined in this case also. Similar results have been obtained upon treatment of the experimental data[39].

As an example, Fig. 9 shows the determination of the invariant value with respect to experiment for the methyl ether of myristic acid and n-decanol. It follows from Fig. 9 that the utilization as a solid support of a sufficiently inert Chromosorb, washed with an acid and treated with dimethyldichlorosilane, guarantees the absence of adsorption processes in GLC. Adsorption phenomena also manifest themselves in capillary chromatography[36]. In this case, however, owing to the fact that the determination of the values of v_l (or P) involves some difficulties, it is advisable to select, for values proportional to the amount of the LSP in the capillary column, the value
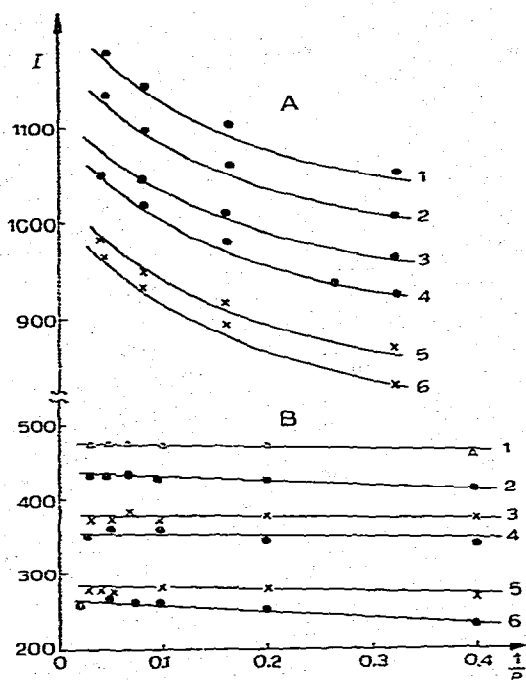
Fig. 7. Effect of choice of standard substances on dependence of retention factors upon reciprocal of LSP content (%) on solid support (according to data of refs. 38 and 39). 1 = 2-Heptanone; 2 = ethylbenzene; 3 = 2-hexanone; 4 = toluene; 5 = 2-pentanone; 6 = benzene. Standard substances: C_5–C_{12} *n*-alkanes (A) and C_2–C_4 *n*-alcohols (B). Experimental conditions: LSP = Carbowax 20M, 120°; support = Chromosorb P.
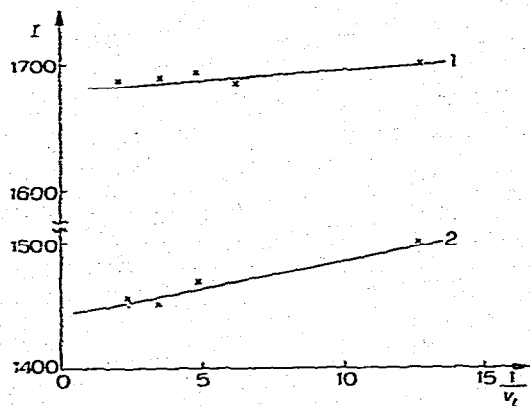

Fig. 8. Dependence of retention factors of *n*-dodecane (1) and *n*-nonane (2) (standards = C_2–C_4 *n*-alcohols) on reciprocal of LSP content on solid support (%) (according to data of refs. 38 and 39). Experimental conditions as in Fig. 7.
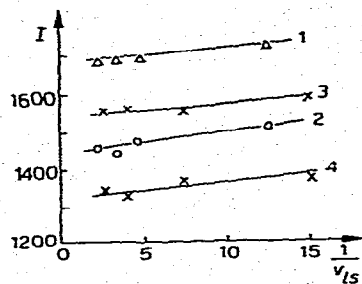
Fig. 9. Dependence of retention factors on reciprocal of LSP volume in column. 1 = Methyl ether of myristic acid; 2 = *n*-dodecanol; 3 = C_{12} alcohols; 4 = C_{10} alcohols. Experimental conditions: LSP for 1 and 2 = Apiezon L; LSP for 3 and 4 = silicone oil DC-550; 150°; solid support = Chromosorb G washed with acid and modified with dimethyldichlorosilane; column, 100 × 0.3 cm.

of the extraction coefficient of a standard substance whose adsorption can be neglected. In this case, we obtain eqn. 18 for the relative column volume:

$$V_2 = \frac{K_{li}}{K_{lst}} + \frac{K_{ali}\,S_l + K_{li}\,K_{si}\,S_s}{V_m} \cdot \frac{1}{k_{st}} = \frac{K_{li}}{K_{lst}} + \lambda_i \cdot \frac{1}{k_{st}} = V^0 + \lambda_1 \cdot \frac{1}{k_{st}} \quad (18)$$

where

$$\lambda_i = \frac{K_{ali}\,S_l + K_{li}\,K_{si}\,S_s}{V_m} \approx \text{constant}$$

V_m is the dead volume of the column and k_{st} the capacity ratio of the standard compound.

TABLE 2

COMPARISON OF RELATIVE RETENTION VALUES CALCULATED VIA EQNS. 11 AND 20 FROM DATA IN REF. 33

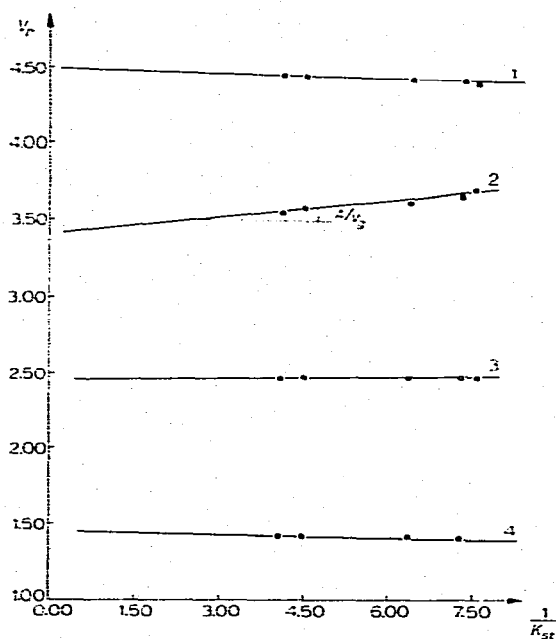| Compound	Eqn. 11	Eqn. 20		Experimental data[33]	
		Firebrick	Chromosorb	Firebrick, 8.99"., LSP	Chromosorb, 8.75"., LSP
n-Heptane	0.015	0.016	0.019	0.079	0.045
n-Butyl ethyl ether	0.105	0.112	0.113	0.129	0.151
Ethyl acetate	0.550	0.549	0.553	0.629	0.590

Fig. 10. Dependence of relative retention volume on reciprocal of extraction factor of capacity ratio. 1 = Cyclohexane; 2 = benzene; 3 = n-hexane; 4 = 2,2-dimethylbutane.

Fig. 10 shows that the relative retention volume is a linear function of the reciprocal of the capacity ratio. The intercept on the y-axis is equal to V^0.

Thus, a linear equation of the type represented by eqn. 18 can be used in capillary chromatography also.

The question naturally arises whether it is possible to reduce the experimental time by rapid measurement of I^0 and V^0. These values can be obtained by measuring I and V, with two different contents of the LSP on the solid support:

$$I^0 = \frac{I_1 P_1 - I_2 P_2}{P_1 - P_2} \tag{19}$$

$$V^0 = \frac{V_1 P_1 - V_2 P_2}{P_1 - P_2} \tag{20}$$

where I_1 and I_2 are retention factors with LSP contents P_1 and P_2, respectively, and V_1 and V_2 are the relative retention volumes with LSP contents P_1 and P_2, respectively.

Table 2 gives the values of V^0 calculated according to data of Pecsok et al.[3] by eqns. 11 and 20. It follows from the data listed that both equations lead to similar results.

CONCLUSION

Accurate and meaningful relative retention data in GLC can be obtained only by correcting retention volumes for adsorption effects. In general, it is advisable to use at least two sorbents impregnated with different amounts of stationary phase to check the magnitude of the adsorption.

When the variation of the relative retention data depends appreciably upon the loading of the support, it is necessary to use one of the methods described to take adsorption into account.

ACKNOWLEDGEMENTS

SUMMARY

Adsorption phenomena in GLC lead to a considerable inter-laboratory non-reproducibility of relative retention values on the basis of which chromatographic zones are identified. This paper considers the application, for identification purposes, of limiting relative retention values that are determined exclusively from the ratio of the distribution coefficients of the substance under study and the standard between the gas and liquid phases. and suggests methods for determining their values.

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