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Fundamentals of the Theory of Capillary Gas-Liquid-Solid Chromatography

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It is shown that the known instances of the separation of volatile compounds actually refer to gas-liquid-solid chromatography and not gas-liquid chromatography, the walls of the capillary column fulfilling the function of the solid. The theories of the retention and spreading of the chromatographic bands in elution gas-liquid-solid chromatography are examined. The results of theoretical and experimental studies indicate the need to take into account the role of adsorption in capillary gas-liquid chromatography.
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I. INTRODUCTION

Gas–liquid chromatography is the commonest version of capillary chromatography. The retention of the chromatographed compounds in capillary gas–liquid chromatography is characterised by the same fundamental features as in gas–liquid chromatography on packed columns. It is therefore useful to examine the general theory of the retention of chromatographed compounds together with the main results of the application of this theory to capillary chromatography.

The discovery by Martin and Synge in 1941 of partition chromatography, based on the different partitions (adsorptions) of the substances to be separated between two phases, namely the mobile (gas, liquid) and stationary (liquid) phases, was an important stage in the development of chromatography.[1] In the conclusion of their communication, Martin and Synge noted that they proposed a new type of chromatography based on the partition of the solutes between two liquid phases and not on adsorption on a solid phase.[1] We may note that they also proposed[1] a new type of partition chromatography, namely gas–liquid chromatography (GLC). The first experimental study on GLC was published by James and Martin in 1952,[2] who found that the separation of the lower aliphatic acids (formic and acetic) exhibited asymmetric peaks (diffuse tails and steep fronts). This phenomenon was explained by the adsorption of the acids being separated on the surface of kieselguhr. It was shown that the adsorption can be weakened by introducing phosphoric acid into the stationary liquid phase (SLP) or by depositing it on the surface of kieselguhr (a solid carrier). Thus in the first study on GLC James and Martin should already have taken into account the phenomenon of the adsorption of the substance being separated on the solid carrier and should have taken special measures to reduce it.

Subsequently, as a result of the efforts of many investigators,[3-20] the qualitative idea concerning the role of adsorption in GLC was formulated perhaps most clearly by Dal Nogare and Juvet in a monograph.[18] In their view, adsorption on the active surface of the solid carrier is the factor responsible for the formation of tails behind the peaks. Although diatomaceous carriers are weak adsorbents compared with alumina, silica get, etc., their activity is usually sufficient for the above adsorption effect to be fully evident in the case of polar substances, for example, alcohols, water, ketones, and ethers. Adsorption on refractory brick is stronger than on celite. It is less evident in the case of non-polar substances and large relative amounts of the liquid phase and in cases where polar liquid phases, saturating the active sections of the adsorbent surface, are used.[18] An analogous view has also been expressed in the monographs of Zhukhovitskii and Turkel'taub[20] and Moshier and Sievers.[19]

We may note that capillary gas chromatography is a version of gas–liquid chromatography in which the internal walls of the capillary tube play the role of the solid carrier.

The experimental data for the adsorption of the substances separated in GLC conflicted with the view, current at the time, that GLC is a purely partition version of chromatography, and also with the theory adopted for the retention of the compounds separated in GLC, which related the retention of such compounds solely to their dissolution in the stationary liquid phase (SLP). This contradiction stimulated studies of the role of adsorption in GLC. Theoretical and experimental investigation of adsorption phenomena in GLC led to significant progress in understanding the processes occurring in chromatographic columns.

II. FUNDAMENTALS OF RETENTION THEORY

In analysing the chromatographic process in GLC, it is useful to examine primarily the model of the sorbent which can be regarded solely as an SLP. The real sorbent is a multiphase material and its simplest model is illustrated in Fig.1. The surface of the solid carrier (internal walls of the capillary column) is coated by a continuous film of the SLP of non-uniform thickness. This model of the sorbent is consistent with porometric data, mass transfer kinetic data (see, for example, Berezkin and co-workers[21,22]), data for the filling

of the pores of the solid carrier with SLP,[23] and the results of special studies based on the use of a version of the "labelled" surface method.[24] It also agrees with the results obtained in the investigation of the partition of the stationary liquid phase on the surface of the solid carrier by scanning electron microscopy.[25]

Despite its simplicity, systematic analysis of this model makes it possible to elucidate the main features of the retention of volatile compounds on a real sorbent. Indeed, it is necessary to isolate in the sorbent not one (SLP) but three phases which absorb and adsorb the substances to be separated, namely the SLP, the gas–SLP interface, and the SLP–solid carrier interface.

The equilibrium retention theory, taking into account the adsorption of the compounds to be separated, is based on a logical allowance for the contribution of the retention on individual bulk and surface phases of the real sorbent to the overall retention volume and also on the experimental test of the equations obtained (including their test by independent methods).

If the SLP layer covers fully the surface of the solid carrier, then the retention volume is determined by the equilibrium characteristics of three processes: (1) dissolution of the compound chromatographed in SLP, (2) its adsorption at the gas–SLP interface, and (3) the adsorption at the SLP–solid carrier interface. The equilibrium theory of the retention of the compounds chromatographed must take into account the contributions of all three processes indicated to the overall retention.

The need to take into account, in addition to dissolution, the adsorption of chromatographic compounds at the gas–SLP interface when an allowance is made for the contributions of these processes to retention in GLC was first pointed out by Martin,[26,27] who confirmed experimentally his postulate. An equation has been proposed[28,29] for the retention volume, which took into account both the dissolution and also the adsorption of the substance chromatographed on the surface of the solid carrier.

For the model of the sorbent with a thick SLP layer which we are considering and which usually obtains on sorbents containing more than 3% of SLP on the solid carrier, the system of equations relating to the development chromatography of one component subject to the operation of longitudinal spreading factors with allowance for absorption in the SLP and adsorption at the interfaces differs from the equation adopted previously in chromatography (see, for example, the relevant monograph[30]) by the presence of terms which take into account the adsorption at the interfaces between the SLP and the carrier gas and the solid carrier.

We shall consider the equations for the retention volume relating to the model in which the SLP covers in a continuous film the surface of the solid carrier under conditions of ideal non-linear chromatography. The system of equations for the ideal (non-equilibrium) non-linear development chromatography of one substance taking into account the adsorption of the latter on the SLP and at the interfaces can be described as follows:

$$u\frac{\partial c_g}{\partial x}+\chi_g\frac{\partial c_g}{\partial t}+\chi_{gl}\frac{\partial a_{gl}}{\partial t}+\chi_l\frac{\partial a_l}{\partial t}+\chi_{ls}\frac{\partial a_{ls}}{\partial t}=0, \qquad (1)$$

$$a_{gl}=f_{gl}(c_g), \qquad (2)$$

$$a_l=f_l(c_g), \qquad (3)$$

$$a_{ls}=f_{ls}(a), \qquad (4)$$

where u is the linear flow rate of the carrier gas, x the coordinate, t the time, c_g the volume concentration of the chromatographed substance in the gas phase, a_l the volume concentration of the substance in the SLP, a_{ls} the surface concentration of the substance at the SLP–solid carrier interface, χ_g the fraction of the gas phase along the column cross-section, χ_l the fraction of the liquid phase along the column cross-section, χ_{gl} the ratio of the area of the SLP–solid carrier interface to the volume of the sorbent, and a_{gl} the surface concentration of the test substance at the gas–SLP interface.

Eqns.(2) and (4) are the equations of the adsorption isotherms of the chromatographed compound at the SLP–solid carrier and gas–SLP interfaces and Eqn.(3) is that of the isotherm of absorption (dissolution) in the SLP. Eqn.(1) differs from that usually considered (see, for example, Rachinskii[30]) by the presence of two additional terms – the third and the fifth. The introduction of these terms made it possible to take into account the adsorption at the interface between the SLP and the carrier gas and the solid carrier.

The solution of the above system of equations on the assumption of the carrier gas pressure drop along the length of the chromatographic column is small so that the correction for the compressibility of the carrier gas can be disregarded, yields the following equation for the pure retention volume:

$$V_N=V_R^0-V_M=f'_{gl}S_l+f'_lH_l+f'_lf'_{ls}S_s, \qquad (5)$$

where $f'_{gl}=da_{gl}/dc_g$, $f'_l=da_l/dc_g$, $f'_{ls}=da_{ls}/da_l$, S_l is the area of the gas–SLP interface for the sorbent in the column, H_l the volume of the SLP in the column, S_{ls} the area of the SLP–solid carrier interface, V_N the pure retention volume,

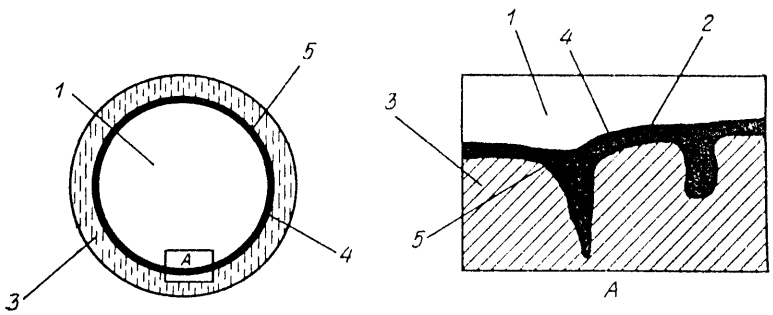


Figure 1. A simplified model of the real sorbent in capillary GLC: 1) gas phase; 2) SLP; 3) solid carrier (wall of capillary column); 4) gas–SLP interface; 5) SLP–solid carrier interface.

V_R the retention volume, and V_M the dead volume of the column. If the adsorption and absorption isotherms are linear, the derivatives f'_{gl}, f'_l, and f'_{ls} are constant.

Eqn.(5) establishes the relation between the retention volume and the characteristics of the sorbent employed taking into account the dissolution in the SLP and the adsorption at its interfaces. It follows from this equation that the retention volume in equilibrium chromatography is an additive function of the retention volumes in the separate phases of the real sorbent. We may note that previously Giddings[31] proposed an additive equation for the second quantity (the lag factor) characterising the relative retention (R_f), which is used widely in thin-layer chromatography.

There is also a possibility of another derivation of the additivity equation for the ideal non-linear chromatography based on Wicke's Law using the adsorption isotherms for a real complex sorbent in its equation. In this case the sorption also consists of the adsorption at the SLP interfaces and the dissolution in the SLP film.

Since in the general case the real sorbent may contain not three but a significantly greater number of phases, each of which is capable of retaining the chromatographed compounds, the relations obtained above can be usefully extended to the case of a large number of phases. Within the framework of ideal non-linear chromatography (i.e. on the assumption of the instantaneous establishment of equilibrium and of the absence of diffusional spreading effects), it has been shown[32,33] that the pure retention volume V_N in a real multiphase sorbent consists of the sum of the partial retention volumes V_{li} and V_{sj} due respectively to the adsorption and absorption of the chromatographed substance on the individual phases of the sorbent:

$$V_N = \sum_{i=1}^{m} V_{li} + \sum_{j=1}^{n} V_{sj} \qquad (6)$$

or

$$V_N = \sum_{i=1}^{m} K_{li} H_{li} + \sum_{j=1}^{n} K_{sj} S_{sj}, \qquad (7)$$

where K_{li} is the constant for equilibrium of the test substance between the mobile phase and the SLP of the ith type, H_{li} the volume of the SLP of the ith type in the chromatographic column (for example, the volume of the macrolayer or microlayer in the liquid phase on the surface of the solid carrier, the volume of the liquid phase in the micropores, etc), K_{sj} the constant for equilibrium of the test substance between the stationary phase and the jth type interface, and S_{sj} the area of the jth type interface in the column (for example, the gas–solid carrier, SLP–solid carrier, gas–SLP, etc. interfaces).

Eqns.(6) and (7) are fairly general. It can be shown that the known equations for the retention volume are special cases of these equations. For specific values of the parameters i and j, it is possible to obtain directly from Eqn.(7) the familiar equations for the retention volume: the equation of the traditional GLC (see, for example Dal Nogare and Juvet[18]); the equation taking into account the dissolution and the adsorption at the gas–SLP interface,[26] the equation taking into account the dissolution and adsorption at the SLP–solid carrier interface;[28] the equation taking into account the dissolution and adsorption of the sorbate on the SLP–solid carrier and SLP–carrier gas interfaces;[32] the equation reflecting the interaction between the sorbate and the solid alone;[34] the equation taking into account only the adsorption at the gas–SLP interface;[35] the equation for the retention volume on complex sorbents (for example, a solid carrier combined with an adsorbent modified by the SLP).[36]

If the adsorption isotherm is described by a non-linear equation, then in this case Eqns. (6) and (7) are valid only within the framework of ideal non-linear chromatography, which naturally limits their applicability. However, one should note that development gas-chromatographic methods for the determination of non-linear adsorption isotherms, developed on the basis of ideal non-linear chromatography, have been used successfully in chromatographic practice and the results obtained are independent of the carrier gas flow rate, the sample size, etc. In gas–solid chromatography the adsorption isotherms measured by the gas-chromatographic and static methods mentioned above are in good agreement with one another (see, for example, Kiselev and Yashin[34] and Roginskii et al.[37]). The region of the applicability of Eqns. (6) and (7) is therefore fairly broad also for non-linear isotherms.

When the general Eqns.(6) and (7) are used, it is necessary in the general case to resort to data for the phase characteristics of the sorbent employed and for the distribution of the SLP on the surface of the solid carrier. In the case occurring commonly in chromatographic practice, where the surface of the solid carrier is fully coated by a macrofilm of the liquid, Eqn.(8), which is a corollary of Eqn.(5), is therefore used most frequently:

$$V_{Ns} = K_l H_{ls} + K_{gl} S_{ls} + K_{ls} S_{ss}, \qquad (8)$$

where V_{Ns} is the retention volume referred to 1 g of the solid carrier, K_l, K_{gl}, and K_{ls} are the constants for equilibrium of the chromatographed substance between the SLP and the gas phase, between the SLP–gas interfacial phase and the gas phase, and between the SLP–solid carrier interfacial phase and the SLP respectively, H_{ls} is the volume of the SLP in the column referred to 1 g of the solid carrier, S_{ls} and S_{ss} are the areas of the SLP–gas and solid carrier SLP interfaces referred to 1 g of the solid carrier respectively, $K_l = a_l/c_g$, $K_{gl} = a_{gl}/c_g$, and $K_{ls} = a_{ls}/a_l$.

Eqn.(8) establishes the relation between the retention volume and the characteristics of the sorbent used. The retention volume in equilibrium linear chromatography with operation of longitudinal spreading factors is an additive function of the retention in the individual phases of the real sorbent. The first term of this equation reflects the contribution of the adsorption of the chromatographed substance on the SLP, the second term the contribution of the adsorption on the gas–SLP interface, and the third term the contribution of the absorption of the SLP–solid carrier interface.

Table 1 presents the main stages in the development of ideas about adsorption in GLC along three main pathways: theory, chromatographic experiment undertaken to test the theory, and independent experimental tests of the theory by non-chromatographic methods. Naturally, the isolation of specific stages in the development of ideas about the role of adsorption in GLC is fairly subjective. Like any important trend in science, it arose and developed by virtue of the investigations of many workers from different countries. The work of Nikolov,[52,53] Suprinowicz, Waksmundski, Rudzinski, and co-workers,[54–56] Hüber and Gerritse,[57] Eon and Guiochon, [58,59] Kovats and co-workers,[60] and many other investigators[61–86] has also made an important contribution to the study of the role of adsorption in GLC. Thus, revolutionary changes involving the study of adsorption phenomena have occurred in the last two decades in the ideas concerning the mechanism of the retention of chromatographed compounds in GLC as a result of the work of many investigators from different countries.

The view that adsorption on the surface of the solid carrier (walls) in capillary chromatography is negligible and can be neglected has been expressed fairly frequently. Investigators sharing this view usually adduce the following arguments in its defence. Firstly, the surface of the capillary column (glass, quartz, stainless steel) is more inert than the surfaces of solid carriers used in packed columns and the chromatographic bands in capillary chromatography are as a consequence usually more symmetrical than in packed columns.

Table 1. The principal stages in the development of ideas concerning the role of adsorption in GLC.

Stage	Characteristic	Refs.
Adsorption at gas–SLP interface	Theory	[26]
	Experiment	[26]
	Independent test	[27]
Adsorption at SLP–solid carrier interface	Theory: linear isotherm	[28, 31]
	Theory: non-linear isotherm	[32, 39]
	Experiment: determination of isotherm	[40, 41]
	Experiment: determination of heat of adsorption	[42]
	Independent test	[43, 45]
Joint determination of the contribution of adsorption at gas–SLP and SLP–solid carrier interfaces	Theory and experiment	[32]
The influence of adsorption on the relative retention parameters (relative retention time and Kovats retention index)	Theory and experiment	[33, 46]
Retention on sorbents with thin SLP films (less than 3% on solid carrier)	Theory and experiment	[47, 48]
Adsorption in open capillary columns	Theory and experiment	[49, 51]

Secondly, the ratio of the volume of the SLP to the surface area of the solid carrier is usually greater in capillary chromatography than in packed columns, which should decrease the contribution of adsorption to the overall retention volume. As regards the first argument, glass and quartz surfaces cannot be regarded as inert with respect to adsorption. Experimental data have shown that even the most inert quartz columns exhibit distinct adsorption properties in relation to polar compounds (see, for example, Jennings[87]). One should also note that the symmetry of the chromatographic band is only a necessary but not a sufficient condition for the adsorption inertness of the given surface in relation to a given compound under the given conditions. Furthermore, glass (and other) surfaces are frequently subjected to a preliminary treatment whose purpose is to roughen the surface, which increases its adsorption capacity. The second argument does not appear to be convincing for the following reason. On average, the separation temperature in capillary chromatography is lower by ~50–100 °C than the separation temperature in packed columns. Since the heat of adsorption of polar chromatographed compounds when non-polar SLP are used is several times higher than the heat of solution, a significant decrease of the separation temperature causes a relative increase of the contribution of adsorption to the retention compensating at least partially the increase of the thickness of the SLP layer. We may note that the retention volume varies exponentially with the heat of the decisive chromatographic processes and linearly with the thickness of the SLP film, i.e. the heat of the process has a more significant influence on the retention.

Yet another factor enhancing the degree of adsorption in capillary chromatography is noteworthy: the resolving capacity of the capillary column is ~5–10 times higher than that of a packed column. Indeed it is known (seen, for example, Dal Nogare and Juvet[18]) that the separation factor for two compounds R is a function of the following characteristics of the chromatographic column employed:

$$R = \frac{N^{1/2}}{4}\left(\frac{\alpha-1}{\alpha}\right)\frac{k}{k+1}\ , \qquad (9)$$

where N is the number of theoretical plates of the column, α the column selectivity (the relative retention of the compounds separated), and k the capacity coefficient. The ratio of the separation factors in capillary (R_{cc}) and packed (R_{pc}) columns can be represented by the following relation:

$$\frac{R_{cc}}{R_{pc}} = \frac{(\alpha_{cc}-1)}{(\alpha_{pc}-1)}\cdot\frac{\alpha_{cc}}{\alpha_{pc}}\cdot\frac{k_{cc}}{k_{pc}}\cdot\frac{k_{pc}+1}{k_{cc}+1}\cdot\left(\frac{N_{cc}}{N_{pc}}\right)^{1/2}\ , \qquad (10)$$

where the subscripts cc and pc refer respectively to quantities characterising the capillary and packed columns.

Since the first terms of Eqn.(10) are close to unity and $N_{cc} \cong 60 \times 10^3$ and $N_{pc} \cong 10^3$, we obtain in accordance with Eqn.(10).

$$\frac{R_{cc}}{R_{pc}} \simeq \left(\frac{60\cdot 10^3}{10^3}\right)^{1/2} \simeq 8\ . \qquad (11)$$

Thus, under the conditions examined above, the width of the chromatographic band in a capillary column is 10 times smaller than in a packed column. This means that the real accuracy of the measurements of the retention using capillary columns is 10 times greater than for packed columns; even small contributions of adsorption to the retention have a greater importance in capillary chromatography owing to the greater resolving capacity of the latter.

We shall consider certain most important consequences arising from allowance for adsorption phenomena in GLC.

III. THE INTERACTION OF THE SOLUTE WITH THE STATIONARY LIQUID PHASE UNDER THE CONDITIONS OF THE ADSORPTION OF THE CHROMATOGRAPHED SUBSTANCES AT THE STATIONARY LIQUID PHASE INTERFACES

In his Nobel Lecture in 1952 Martin noted that the application of the chromatographic method and apparatus makes it possible to measure fairly simply the free energies of solution of volatile compounds in the SLP and thus to investigate successfully the molecular forces in solutions.[88] The development of GLC fully confirmed the validity of this prediction, but the correct employment of the methods for the investigation of the interaction of the solute and the involatile SLP, which have been thoroughly developed in gas chromatography is possible only when the contribution determined solely by the dissolution of the chromatographed substance in the SLP is isolated from the overall retention volume. For example, in order to determine V_{gtl}, which is the initial quantity needed to determine the specific retention volume due solely to the dissolution of the test substance in the SLP, it is useful to employ Eqn.(12):

$$V_{gt} = \frac{V_N}{W_l}\ , \qquad (12a)$$

$$V_{gt} = \frac{V_{NL}}{W_l} + \frac{1}{W_l}\sum_{i=2}^{n} V_{Ni}\ , \qquad (12b)$$

$$V_{gtl} = \frac{V_{Nl}}{W_l}\ , \qquad (12c)$$

where $V_{gtl} = V_{gl}\ (273/T)$, V_{gl} is the specific retention volume due solely to the dissolution of the volatile substance in the SLP, V_{Nl} the part of the pure retention volume due solely to the dissolution of the chromatographed substance in the SLP macrolayer, W_l the mass of the SLP in the column, and V_{Ni} the part of the pure retention volume due to the retention of the volatile substance by the ith phase of the sorbent (with exclusion of the SLP macrolayer).

Fig. 2 presents the ratios $\psi = V_g$ (refractory brick)$/V_{gt}$ (Chromosorb W) and $\psi_l = V_{gil}$ (refractory brick)$/V_{gt}$ (Chromosorb W) which we calculated[21] from the experimental data of Pecsok et al.;[14] the type of the solid carrier used to prepare the sorbent is indicated in brackets. The calculation was performed by Eqn. (12c) and also by the traditional method, i.e. by Eqn. (12a). The data presented in Fig. 2 were obtained for sorbents containing 8.8% of the SLP.

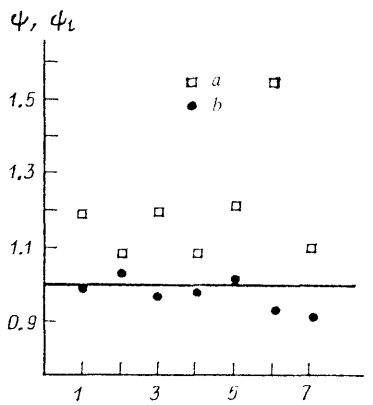


Figure 2. Dependence of ψ (points a) and ψ_l (points b) on the nature of the chromatographed compounds; the numerals along the abscissa axis denote the chromatographed compounds: 1) propionaldehyde; 2) benzene; 3) ethyl acetate; 4) acetone; 5) ethyl methyl ketone; 6) hex-1-ene; 7) cyclohexene. The $\psi_l = 1.0$ straight line, corresponding to the complete compensation of adsorption and other effects, is shown.

It follows from the results presented that the extrapolation method, taking into account adsorption, yields stable constant values of ψ_l, which are independent of the type of solid carrier, while the values of ψ obtained by the traditional method do depend on the type of solid carrier and higher values for the sorbent are obtained using refractory brick, which has a higher adsorption activity, as the solid carrier.

We may note that the contribution of adsorption to the overall retention volume is appreciable for the series of systems (solid carrier–SLP–sorbate) usually employed in GLC (Table 2).[21,22,24,36] Thus, in a quantitative study of the interaction of the solute with the SLP, it is essential either to take into account adsorption or to show that it can be neglected compared with dissolution.

We shall consider the main results obtained using the additive theory of retention in capillary chromatography. In the first quantitative study[49] of the contribution of adsorption to retention in capillary chromatography, the experimental data of Brunner and Cartoni[79] were used to test the applicability of the theory.[32] It was shown that the retention theory developed previously can be applied successfully also to capillary chromatography. Fig. 3 illustrates the dependence of V_N^0/W_l on $1/W_l$, which is described satisfactorily by the equation:

$$\frac{V_N^0}{W_l} = V_g + A\frac{1}{W_l}, \qquad (13)$$

where A is a coefficient characterising the contribution of adsorption to retention and V_N^0 the pure retention volume adjusted to 0 °C and a pressure of 1 atm. Eqn. (13) is a corollary of the general Eqn. (8) when the contribution of adsorption can be regarded as constant. Eqn. (13) can be usefully employed to determine the specific retention volume V_g, which is normally used in various physicochemical calculations (see, for example, Dal Nogare and Juvet[18] and Conder and Young[89]).

Table 2. Estimation of various contributions to the overall retention volume.

Chromatographic system	*a*	*b*	*c*	*d*	*e*
Refractory brick (INZ-600)–Apiezon K–benzene	60	150	57	—	43
Chromosorb P–stearic acid–n-hexane	72	63	75	5.0	20
Chromosorb W–stearic acid–n-hexane	72	65	81	—	19
Polychrom-1–diethylene glycol succinate–diethylene glycol	138	3500	80	20	—
Graphitised black–squalane–cyclohexa-1,4-diene	28	980	72	—	28
Bentone-245–di-iso-octyl sebacate–benzene	50	380	15	—	85
Refractory brick–ββ-thiodipropionitrile–heptane	25	18	25	67	8.0
Chromosorb W–ββ-thiodipropionitrile–heptane	25	19.9	54	42	4

Notation: *a*) temperature (degrees C); *b*) distribution constant of the sorbate in the gas–SLP system; *c*) contribution of dissolution to the retention volume (%); *d*) contribution of adsorption at the gas–SLP interface (%); *e*) contribution of adsorption at the SLP–solid carrier interface.

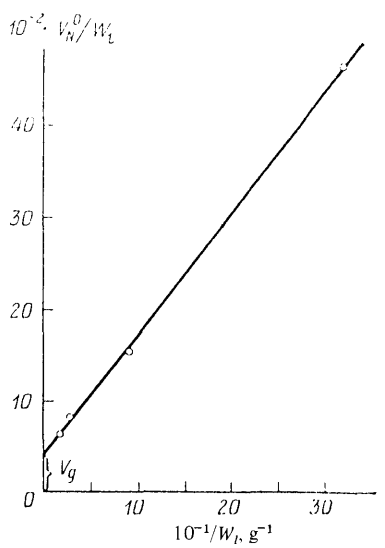


Figure 3. Dependence of V_N^0/W_l on $1/W_l$ (according to the experimental data of Brunner and Cartoni[79]).

It is noteworthy that the glass capillary columns used by Berezkin et al.[49] had a high internal surface area; the pure retention volume of heptane at 40 °C on a 38 m column (0.22 mm in diameter) was 14.7 ml. Furthermore, the absolute retention volumes are quoted by Brunner and Cartoni[79] only for one hydrocarbon (n-heptane). It therefore appeared essential, firstly, to investigate the role of adsorption in capillary columns which do not exhibit such a high adsorption activity and, secondly, it was necessary to develop rational forms of the equations of the additive theory to calculate retentions specifically in capillary chromatography. The latter task was undertaken because the use of the absolute mass or volume of the SLP in capillary chromatography presents certain difficulties.

The following study of the role of adsorption in capillary columns was therefore carried out for aromatic hydrocarbons and paraffins in the perdeuteriosqualane–stainless steel system.[50]

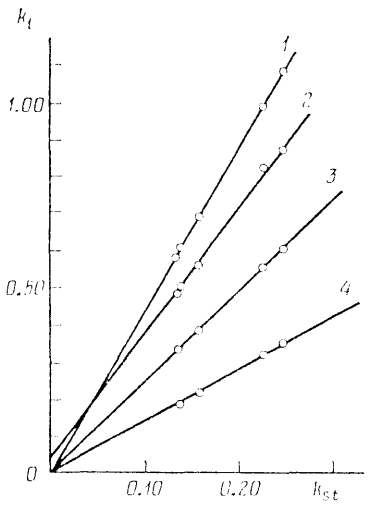


Figure 4. Dependence of k_i on k_{st} for hydrocarbons on a stainless steel column (standard–n-heptane): chromatographed substance: 1) cyclohexane; 2) benzene; 3) n-hexane; 4) 2,2-dimethylbutane.

Using the general Eqn.(8) obtained previously and assuming that the retention volume is independent of the sample size, that the properties of the thick SLP layer do not differ from those of the corresponding bulk phase, that the area of the gas–SLP interface hardly changes with increase of the thickness of the SLP film on the inner wall of the column, and that the SLP film covers the entire internal surface of the column, it is possible to obtain by means of simple transformations, the following equations, which can be usefully employed for the quantitative estimation of the role of adsorption in capillary chromatography:

$$V_{ri} = \frac{V_{Ni}}{V_{N,st}} = \frac{K_{li}}{K_{l,st}} + \frac{A_i}{V_M} \cdot \frac{1}{K_{st}} , \qquad (14)$$

where V_{ri} is the relative retention volume of the ith substance, A_i a coefficient reflecting the contribution of adsorption to the relative retention volume, and k_{st} the extraction coefficient or the capacity coefficient of the compound adopted as the standard. The standard compound is chosen in such a way that its retention is determined virtually only by the dissolution in the SLP and adsorption can be neglected, i.e. so that the relation $V_{N,st} = K_{l,st}\ H_l$ (H_l is the volume of the SLP in the column) holds. The capacity coefficient and not the relative retention volume can be usefully employed in many instances as the determining quantity. Eqn.(14) can then be expressed in the following form:

$$k_i = \frac{A_i}{V_M} + \frac{K_{li}}{K_{l,st}} \cdot k_{st} . \qquad (15)$$

The parameters of Eqns.(14) and (15) can be determined graphically, for example. The limiting retention is then of greatest interest:

$$V_{rli} = \frac{K_{li}}{K_{l,st}} . \qquad (16)$$

The limiting retention V_{rli} can be used as the initial retention for various calculations characterising the sorbate–SLP interaction and, by resorting to the absolute thermodynamic parameters for one compound (the standard), it is possible to obtain the absolute values of the physicochemical characteristics of all the compounds used in the chromatographic experiment.

Eqns.(14)–(16) have been used to interpret experimental data obtained in Keulemans' laboratory.[50] A stainless steel capillary column 100 mm long and with an internal diameter of 0.25 mm was used: the SLP was perdeuteriosqualane; the column temperature was 70 °C. Fig.4[50] presents the experimental results obtained on this column; it is seen that Eqn.(15) describes the experimental data satisfactorily. Calculation by Eqn.(15) makes it possible to determine the limiting relative retention V_{rli} and to estimate the contribution of adsorption to the retention.

Table 3[50] presents the parameters of Eqn.(15) evaluated by the method of least squares (on a computer). For the saturated hydrocarbons investigated, including cyclic hydrocarbons, adsorption can be neglected. However, adsorption exerts a significant influence on the retention of aromatic compounds, for example, benzene. For example, $V_{rli} = 3.42$ for benzene, while the limiting retention index is 636.0; the experimental retention indices of benzene determined on this column amounted to 639.8–643.8.[50]

Table 3. The ratio of the distribution constants and the adsorption characteristic of the sorbate for a stainless steel capillary column [parameters of Eqn.(15)].[50]

Compound	$K_{li}/K_{l,st}$	A_i/V_M
n-Pentane	1.000	0.000
2,2-Dimethylbutane	1.438	−0.004
2,3-Dimethylbutane	1.888	−0.004
3-Methylbutane	2.184	−0.004
n-Hexane	2.469	+0.002
Methylcyclopentane	3.250	−0.003
Benzene	3.418	−0.033
Cyclohexane	4.480	−0.008
3-Methylhexane	4.939	−0.008
n-Heptane	5.968	+0.010

Thus the additive theory of retention is fully applicable also in capillary chromatography. Exact measurements of the ratio of the partition constants of the chromatographed compounds in gas–liquid capillary chromatography are possible only when account is taken of the contribution of adsorption.

IV. THE ADSORPTION OF VOLATILE COMPOUNDS

Gas chromatography has been used traditionally as a physicochemical method for the investigation of adsorption on solid adsorbents from the gas phase.[34] Since the adsorption of chromatographed compounds at the interfaces between the SLP and the carrier gas and the solid carrier influences their retention volumes [see Eqns.(7) and (8)], the above relations can be used for the quantitative study of the adsorption of volatile compounds at the gas–SLP and SLP–solid carrier interfaces.

Many investigators have studied the influence of adsorption on the retention indices. As an example, Table 4 presents data for the relative retention of methyl oleate, methyl linoleate, and methyl linolenate on Rheoplex 400 using different solid carriers, including a stainless steel capillary column.[70] It follows from the data presented in Table 4 that the solid carrier (in the first place the area and type of its surface) exerts a significant influence on retention.

Table 4. The influence of the solid carrier (SLP–Rheoplex 400) on the retention of the methyl esters of unsaturated C_{18} acids (standard–methyl stearate).[70]

Solid carrier	Relative retention time		
	methyl oleate	methyl linoleate	methyl linolenate
Gas-chrom P, silanised	1.10	1.33	1.71
Chromaton N AW HMDS	1.10	1.32	1.70
Gas-chrom Q	1.09	1.31	1.70
Chromosorb W, silanised	1.09	1.32	1.69
Chromosorb P, silanised	1.10	1.32	1.70
Chezasorb AW HMDS	1.09	1.31	1.68
Chromosorb G AW	1.09	1.31	1.64
Celite 545	1.08	1.30	1.60
Chromosorb W	1.06	1.28	1.52
Chromosorb P	1.05	1.23	1.51
Kieselguhr	1.07	1.27	1.62
Capillary column*	1.10	1.32	1.69

*Stainless steel.

The development of methods for the quantitative assessment of adsorption phenomena in GLC has led to fundamental new possibilities in the investigation and quantitative measurement of the degrees of adsorption of volatile substances, in the first place at the gas–liquid interface and in the second place at the SLP–solid carrier (solid) interface.

After the determination of the dependence of the partial retention volumes on concentration, which is in its turn determined by the adsorption at the interfaces between the SLP and the gas and the solid, it is possible to calculate the adsorption isotherms at the gas–SLP and the SLP–solid interfaces using the following equation:[90]

$$a_{sj} = \frac{1}{S_{sj}} \int_0^c V_{sj}(c)\,\mathrm{d}c \ , \qquad (17)$$

where a_{sj} is the concentration of the test substance in the stationary surface phase of the jth type, S_{sj} the surface area of the surface phase of the jth type, and $V_{sj}(c)$ the partial retention volume of the test substance when its concentration in the mobile phase is c.

The methods for the "isolation" of the pure partial retention volumes from the overall retention volume and the methods for the determination of the isotherms have been described in detail.[24,36,43,90–92] As an example, Fig.5[43] presents the isotherm for the adsorption of *p*-xylene on the dimethyldioctadecylammonium derivative of vermiculite impregnated with di-iso-octyl sebacate, which has been obtained gas-chromatographically at 65 °C, as well as the experimental points for the same system obtained from static experiments. The results of the gas-chromatographic and static experiments agree satisfactorily. Other examples of analogous experiments for solid carriers have been published elsewhere.[44,45]

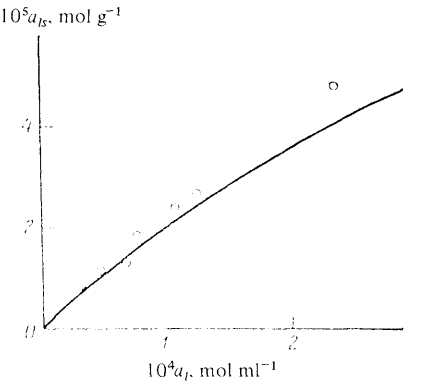


Figure 5. Isotherm for the adsorption of *p*-xylene on methyldioctadecylammonium vermiculite from solutions in di-iso-octyl sebacate; continuous line–adsorption isotherm according to gas-chromatographic data; circles–data obtained by a static method.

For linear dissolution and adsorption isotherms, the retention volume depends on the characteristics of the adsorption in accordance with Eqn.(8). Having determined experimentally the dependence of the retention volume on the content of the SLP on the solid carrier V_{Ns} on H_{ls} and the dependence of the area of the gas–SLP interface S_{ls} on H_{sl} as well as the surface area of the solid carrier S_s, it is possible to determine the adsorption coefficients K_{gl} and K_{ls}; the methods of calculation have been described.[24,32,91]

Table 5. Heats of solution (ΔH_s) in Apiezon K and adsorption (ΔH_a) at the Apiezon K–INZ-600 (solid carrier) interface measured by the gas-chromatographic method.[42]

Compound	ΔH_s, kcal mol^{-1}	ΔH_a, kcal mol^{-1}
n-Hexane	5.8	4.6
Hex-1-yne	5.2	10.9
n-Heptane	6.6	7.6
Hept-1-yne	8.6	17.8

The procedures proposed[42] for the measurement of the dissolution coefficients of volatile compounds in the SLP and of the adsorption coefficients on the SLP–solid carrier interface made it possible to determine the heats of solution and adsorption from the temperature variation of these coefficients. Table 5[42] presents the results of the determination of the

heats of solution and adsorption for a sorbate–refractory brick (INZ-600)–Apiezon K system. It follows from the results that the heats of adsorption of alkynes are much higher than the heats of solution, which can be accounted for by their specific interactions with the silanol surface groups.

In order to test the ideas developed, measurements have been made[32] by gas–liquid and liquid chromatography of the adsorption coefficients K_S at the SLP–solid interface for the hexadecane–Chromosorb P and hexadecane–Chromosorb W systems at 26 °C. The adsorption coefficients measured by these two independent methods are close to one another. For example, the K_S obtained by the GLC and liquid chromatographic methods for benzaldehyde in the hexadecane–Chromosorb P system are 0.091 and 0.090 $cm^3\ g^{-1}$; the values for ethyl methyl ketone in the hexadecane–Chromosorb W system are respectively 0.109 and 0.09 $cm^3\ g^{-1}$, and those for pyridine in the hexadecane–Chromosorb W system are respectively 0.165 and 0.164 $cm^3\ g^{-1}$. Hence an independent test of the proposed methods confirmed their validity.[45] Thus, using the methods developed, it is possible to calculate not only the partition (absorption) isotherms but also the (adsorption) isotherms at the SLP isotherms. which is a fundamentally new physicochemical application of chromatography.

It has been found that the influence of adsorption on the separation has not only a physicochemical but also an analytical application. The influence of adsorption on the separation in capillary gas–liquid chromatography has been investigated by Sojak and Berezkin.[93] Since the resolution in capillary columns is greater than in packed columns by a factor of 5–10, even relatively small changes in the contribution of adsorption can induce an appreciable change in the separation up to an alteration of the order in which the components emerge. Therefore allowance for and employment of the adsorption factor is particularly justified, in our view, for the improvement of the separation in gas–liquid capillary chromatography. The sorbate-adsorbent adsorption interactions are of a type fundamentally different from that of the sorbate–SLP interaction and are particularly sensitive to the structure of the compounds separated (see, for example, Kiselev and Yashin[34]). The change in the separation can be a result of the ageing of the columns, a change in the content of the SLP in the capillary column, an increase in the adsorption activity of the internal surface of the column, or a change in the adsorbent present in the SLP layer.

Since the separation depends significantly on the selectivity of the sorbent employed, whose measure is the relative retention, it is useful to examine the dependence of the selectivity α on the degree of adsorption in the capillary column:

$$\alpha = \frac{V_{N1}}{V_{N2}} = \frac{K_{l1}}{K_{l2}} \cdot \frac{1 + a_1/H_l}{1 + a_2/H_l} , \qquad (18)$$

where

$$a_1 = \frac{K_{Gl1}S_l + K_{l1}K_{ls1}S_s}{K_{l1}} ;$$

$$a_2 = \frac{K_{Gl2}S_l + K_{l2}K_{ls2}S_s}{K_{l2}} .$$

The subscripts 1 and 2 in Eqn.(18) refer to the compounds separated (the first and second respectively). Having expanded this expression in a Maclaurin's series in terms of the variable $1/H_l$, we obtain

$$\alpha = \frac{K_{l1}}{K_{l2}} + \frac{K_{l1}}{K_{l2}}(a_1 - a_2) \cdot \frac{1}{H_l} . \qquad (19)$$

Depending on the relative values of the degrees of adsorption ($a_1 > a_2$ or $a_1 < a_2$), the quantity α can increase or decrease with increase of H_l. For components with similar properties, whose separation is of interest, one can assume that $K_{l1}/K_{l2} \cong 1$; we then obtain

$$\alpha - 1 \simeq \frac{K_{l1}}{K_{l2}}(a_1 - a_2) \cdot \frac{1}{H_l} \simeq (a_1 - a_2) \cdot \frac{1}{H_l} . \qquad (20)$$

On substituting this expression in Eqn.(9), we obtain

$$R \simeq \frac{1}{4} N^{1/2} \cdot \frac{k}{1+k} \cdot \frac{a_1 - a_2}{H_l} . \qquad (21)$$

Thus in the case which we have considered the separation factor depends significantly on the ratio of the difference between the adsorption terms of the retention to the amount of SLP in the capillary column.

Fig. 6[93] presents chromatograms illustrating the influence of the adsorption factor on the separation. A change in the thickness of the SLP layer alters the ratio of the adsorption and absorption factors, which alters the separation. A mixture of pentadecene isomers has been separated on two glass columns *A* and *B*. Comparison of the chromatograms shows that the order of the emergence of *trans*-pentadec-6-ene and *cis*-pentadec-5-ene separated in the two columns is different.[93] The capacity coefficient, which reflects the thickness of the SLP film is 2.1 in column *A* and 1.3 in column *B* for *cis*-pentadec-5-ene, i.e. the difference is not very great. The difference between the retention indices for these isomers is 1.2 in column *A* and 0.9 in column *B*.

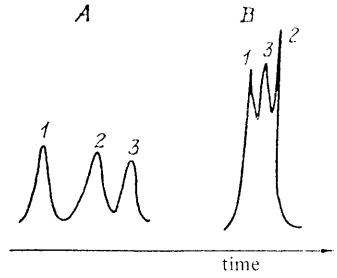


Figure 6. The influence of the thickness of the SLP layer on separation in capillary gas–liquid chromatography.[93] Separation conditions: 300 m × 0.25 mm glass columns *A* and *B*; SLP–Carbowax 20M; temperature 95 °C; the thickness of the SLP layer is greater in column *A*; compounds: 1) *trans*-pentadec-7-ene; 2) *trans*-pentadec-6-ene; 3) *cis*-pentadec-5-ene.

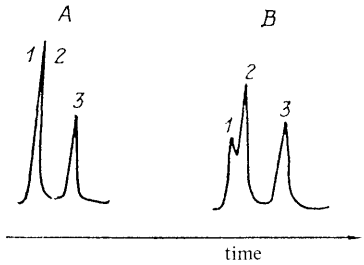


Figure 7. The influence of the adsorption activity of the column on separation.[93] Separation conditions: 100 m × 0.2 mm glass capillary columns; SLP–Apiezon L; temperature 164 °C; compounds: 1) n-heptadecane; 2) *trans*-heptadec-2-ene; 3) *cis*-heptadec-2-ene.

Fig. 7 illustrates the separation of *cis*-heptadec-2-ene and *trans*-heptadec-2-ene and n-heptadecane on two glass capillary columns *A* and *B*.[93] The adsorption activity of the internal surface of column *B* is appreciably higher than that

of column *A*, which accounts for the successful separation of *trans*-heptadec-2-ene and n-heptadecane on column *B*.

The examples presented show that adsorption can exert a significant influence (both positive and negative) on the separation of the compounds analysed, including compounds with similar properties, for example, isomers, in capillary chromatography.

V. METHODS FOR THE IDENTIFICATION OF CHROMATOGRAPHIC BANDS TAKING INTO ACCOUNT THE ADSORPTION PHENOMENA IN GAS–LIQUID–SOLID CHROMATOGRAPHY

The qualitative interpretation of the chromatograms of complex organic mixtures is an important stage in gas-chromatographic analysis. The identification methods, based on a comparison of the experimental retentions of the unknown compounds chromatographed with the available literature data, are widely used in gas-chromatographic analytical practice. However, the application of this simple and effective method is restricted owing to the inadequate reproducibility of the retention parameters in different laboratories.

The retention theory developed above makes it possible to explain a number of causes of the non-reproducibility of the retentions and suggests new effective chromatographic methods for the identification of compounds.

In the general case the relative retention can be expressed by the equation

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} \cdot \frac{1 + \left(\sum_{i=2}^{m} K_{li} H_{li} + \sum_{j=1}^{n} K_{sj} S_{sj}\right)(1/K_l H_l)}{1 + \left(\sum_{i=2}^{m} K_{li,st} H_{li} + \sum_{j=1}^{n} K_{sj,st} S_{sj}\right)(1/K_{l,st} H_l)} , \quad (22)$$

where $V_{N,st}$ is the true retention volume of the substance adopted as the standard $K_{l,st}$ the constant of the equilibrium involving the standard substance between the SLP and the gas phase, $K_{sj,st}$ the constant for the equilibrium involving the standard substance between the SLP and the *j*th type interface, and $K_{li,st}$ the constant of the equilibrium involving the standard substance between the *i*th type SLP and the mobile phase.

Apart from dissolution processes, Eqn.(22) takes into account the adsorption interactions associated with the properties of the solid carrier and the phase characteristics of the sorbent. It follows from Eqn.(22) that the relative retention is not a constant for a given chromatographed compound and cannot be used for qualitative analysis on the basis of literature data. The modification of solid diatomaceous carriers or the employment of polymeric solid carriers lead in many instances solely to a decrease of the role of adsorption phenomena, but the contribution of adsorption to the retention frequently remains appreciable.

If the retention volume is determined solely by the dissolution of the chromatographed substance in the SLP and by the adsorption at the interfaces between the SLP and the mobile phase in the solid carrier [see Eqn.(8)], then the relative retention volume can be expressed by the equation

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} + \lambda_1 \frac{1}{H_l} , \quad (23)$$

where

$$\lambda_1 = \frac{(K_{gl}K_{l,st} - K_{gl,st}K_l) S_{ls} + (K_s - K_{s,st}) K_l K_{l,st} S_s}{K_{l,st}^2} . \quad (24)$$

It is desirable to select as the standard a substance for which the retention is determined solely by dissolution, i.e. $V_{N,st} = K_{l,st} V_l$; in this case we obtain

$$\lambda_{10} = \frac{K_{gl} S_{ls} + K_l K_s S_s}{K_{l,st}} . \quad (25)$$

Eqn.(23) is linear in $1/H_l$ and makes it possible to determine the relative distribution constants. In many instances, when the determination of H_l presents certain difficulties, it is convenient to employ the percentage content *P* of the SLP in the column as a characteristic:

$$\frac{V_N}{V_{N,st}} = \frac{K_l}{K_{l,st}} + \lambda_2 \frac{1}{P} , \quad (26)$$

where λ_2 is a constant.

The proposed methods can be used to determine the ratio of the distribution constant to the thermodynamic characteristic of the substance which can be used to identify it. The relative distribution constant is independent of the content of the SLP and of the type of solid carrier.

Together with relative retentions, the system of Kovats indices[94] is used in gas chromatography for the identification of compounds:

$$I = 100z + 100 \cdot \frac{\lg (V_N/V_{Nz})}{\lg (V_{N(z+1)}/V_{Nz})} , \quad (27)$$

where V_{nz} and $V_{N(z+1)}$ are the corrected retention volumes of n-alkanes whose molecules contain *z* and *z*+1 carbon atoms. This equation can be reduced to equations of the type

$$I = I_0 + \lambda_3 \cdot \frac{1}{H_l} , \quad (28)$$

$$I = I_0 + \lambda_4 \cdot \frac{1}{P} , \quad (29)$$

where λ_3 and λ_4 are constants, which are determined by the adsorption interactions of the sorbate in the chromatographic system and by the dimensions of the argument employed; I_0 is an invariant quantity for the determination of which one employs the corresponding relative distribution constants instead of the relative retention volumes, i.e. it is a universal constant:

$$I_0 = 100z + 100 \cdot \frac{\lg (K_l/K_{lz})}{\lg (K_{l(z+1)}/K_{lz})} . \quad (30)$$

It is desirable to select as standard a substance whose retention is determined solely by dissolution. For non-polar phases and phases of medium polarity, n-alkanes meet the requirements for standard compounds, while in the case of polar SLP it is convenient to select polar compounds (for example, alcohols) as standards. Consequently, in order to identify the compounds analysed, it is essential in the general case to separate from the overall retention volume the contribution due solely to the dissolution of the chromatographed substance in the SLP.

Thus general methods have been proposed for the identification of chromatographed compounds in gas–liquid chromatography,[90] based on the use of invariant characteristics of the retention, independent of adsorption.

We used the methods[46,90] based on the employment of the relation between the relative retentions and the reciprocal of the content of the SLP on the solid carrier to interpret both literature data and our own experimental data. A completely satisfactory agreement between experiment and theory was obtained in all cases.

As an example, Fig.8 presents the relations between the relative retention volume and the reciprocal of the content of the SLP on the solid carrier; experimental data obtained by Pecsok et al.[14] were used to derive these relations. It is seen from Fig.8 that, in conformity with the theory, the graphs for all the substances chromatographed are linear and make the same intercept on the ordinate axis for different solid carriers, which corresponds to the ratio of the distribution constants of the given substance and the standard. The methods

proposed can therefore be used successfully to determine the ratio of the distribution constants – a thermodynamic characteristic of the substance on the basis of which it can in fact be identified. The ratios $K_l/K_{l,st}$ obtained are independent of the content of SLP and of the type of solid carrier. As already mentioned above, the application of the additive theory of retention in capillary chromatography has a number of specific features associated with the need to use the capacity coefficient k_{st} as the characteristic of the content of SLP in the capillary column. Since the Kovats retention indices are at present the most widely used system of retention units in gas chromatography, it appeared essential to test the validity of the following expression for the retention indices in capillary chromatography:[51]

$$I_i = I_{0i} + a_{Ii} \cdot \frac{1}{k_{st}} \quad (31)$$

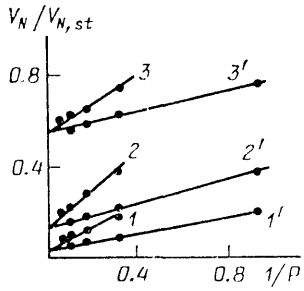


Figure 8. Dependence of the relative retention volume (standard–ethyl methyl ketone) on the reciprocal of the SLP content on the solid carrier (according to the data of Pecsok et al.[14]). Experimental conditions: SLP–ββ'-oxydipropionitrile, temperature 25 °C, solid carrier–Chromosorb W (lines 1'–3') and refractory brick (lines 1–3); compounds: 1) and 1') n-heptane; 2) and 2') butyl ethyl ether; 3) and 3') ethyl acetate.

Using this equation, it is possible to determine the limiting value of the retention index I_{0i}, which depends solely on the solubility of the chromatographed substance in the SLP, and the quantity a_{Ii}, which depends on the adsorption of the chromatographed substance on the interfaces between the SLP and the carrier gas and the solid carrier. Experiments on a capillary column were carried out using different chromatographic systems: gas–polar phase [1,2,3-tris(cyanoethoxy)-propane]–stainless steel, gas–polar phase (Carbowax 20M)–alkaline glass, and gas–non-polar phase (Apiezon L)–alkaline glass. For all the systems indicated and compounds investigated (benzene, *o*-xylene, and *cis*- and *trans*-isomers of pentadecene), it has been shown[95] that Eqn.(31) describes satisfactorily the experimental data (Fig.9).

An important condition for the successful employment of an equation of type (31) is the selection of a system of standards for the retention indices. For the homologous series of compounds employed as standards as well as the compound whose capacity coefficient was used in Eqn.(31), it is useful to choose substances whose properties approach ideality, i.e. whose retention is determined mainly by dissolution and the contribution of adsorption to retention is minimal. The importance of this factor had been demonstrated earlier for packed columns and it has been studied systematically for capillary columns.[95] In the case of a stainless steel column (50 m × 0.25 mm) with 1,2,3-tris(cyanoethoxy) propane as the SLP at 50 °C, $I_{0i} = 1405 \pm 38$ and $a_{Ii} = 245 \pm 54$ (with n-alkanes as standards) or $I_{0i} = 908.3 \pm 2.0$ and $a_{Ii} = -10.4 \pm 4.0$ (with n-alkenes as standards) have been obtained for *o*-xylene. Table 6[95] presents the values of I_{0i} and a_{Ii} obtained for n-pentadecene isomers on Carbowax 20M at 110° on a 50 m × 0.25 mm stainless steel column. Evidently the use of the homologous series of alk-1-enes made it possible to improve the reproducibility of the quantities I_{0i} by a factor of 2–50 and that of the quantities a_{Ii} by a factor of 3–70. 2-Alkyl-1-ethylbenzenes have also been used[95] as standards. However, a better reproducibility of I_{0i} and a_{Ii} was achieved using as standards alk-1-enes, i.e. compounds whose chemical properties are closest to those of the compounds investigated.[33]

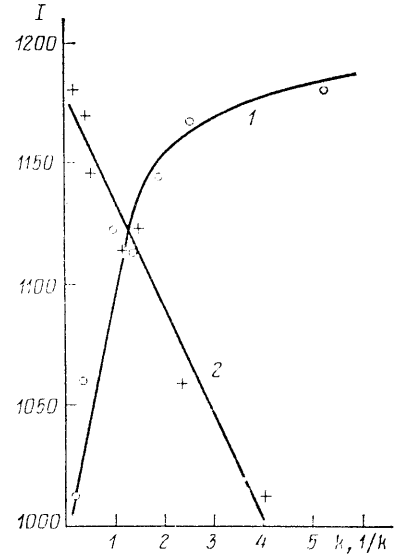


Figure 9. Dependence of the retention index of benzene (standards–n-alkanes) on the capacity coefficient (curve 1) and on its reciprocal (curve 2).[95] Experimental conditions: 50 m × 0.25 mm stainless steel columns, SLP–tris(cyanoethoxy) propane, temperature 50 °C.

The analysis of n-alkenes (for example, pentadec-1-ene) on a non-polar phase (Apiezon L) at 164 °C using compounds in the homologous series of n-alkanes as standards yielded $I_{0i} = 1489.6 \pm 1.0$ and $a_{Ii} = -0.38$.

A rational choice of the homologous series of compounds to be used as standards for the system of Kovats indices significantly improves the reproducibility of the latter for the compounds chromatographed and the reproducibility of the limiting value of I_{0i}. Thus, instead of the usually employed retention index I, the quantity I_{0i} can be usefully employed for the identification of compounds on the basis of chromatographic data; this quantity should in fact be used in tables bearing in mind its better reproducibility in experiments in different laboratories.

The differences between the retention characteristics of hydrocarbons as a function of their type (for example, the *cis*- or *trans*-isomers of alkenes) on columns with different SLP contents can be employed in gas–liquid–solid chromatography for the identification of the compounds analysed. This assumption was first made in a study[51] where it was shown that the relative retentions of n-paraffins and aromatic hydrocarbons vary unequally as the column ages, which can

be employed for the identification of these classes of compounds.

Indeed, if the retention of compounds analysed is determined by two groups of phenomena—the dissolution in the SLP and adsorption at the SLP interfaces, then, following a change in the SLP content, one in fact obtains a new column with new chromatographic properties, which is equivalent to the employment of a new phase. In analysing this phenomenon, one should note that, in conformity with the available data (see, for example, Berezkin et al.[92]), the contribution of adsorption to retention is unique as regards the chromatographic separation effects attained and can be particularly usefully employed in the separation of isomeric compounds. Therefore, using jointly dissolution and adsorption, it is possible in many instances to improve the separation and, when two and more columns are employed, it is possible to achieve the group identification of compounds.

Table 6. The invariant values of the retention index I_{0i} and the adsorption parameter a_{Ii} and the corresponding standard deviations s for n-pentadecene isomers [calculation by Eqn. (31)].[95]

n-Pentadecene isomers	Standards—n-alkanes				Standards—alk-1-enes			
	I_{0i}	s	a_{Ii}	s	I_{0i}	s	a_{Ii}	s
cis-Pentadec-7-ene	1525.4	3.0	−11.7	1.3	1476.8	1.7	1.9	0.74
cis-Pentadec-6-ene	1528.5	2.9	−12.1	1.3	1480.4	1.6	1.2	0.72
cis-Pentadec-5-ene	1533.7	4.8	−13.5	2.2	1485.9	0.2	−0.2	0.1
cis-Pentadec-4-ene	1539.9	5.4	−14.5	2.4	1491.9	0.5	−0.7	0.2
cis-Pentadec-3-ene	1548.4	5.9	−16.0	2.4	1500.5	0.1	−1.1	0.2
cis-Pentadec-2-ene	1576.4	7.2	−23.6	4.0	1529.8	2.2	−7.4	1.2
trans-Pentadec-7-ene	1526.2	3.6	−9.6	1.6	1477.9	1.1	3.8	0.5
trans-Pentadec-6-ene	1528.2	3.5	−9.7	1.6	1479.6	1.0	3.0	0.5
trans-Pentadec-5-ene	1531.1	3.5	−10.4	1.6	1482.8	1.1	3.0	0.5
trans-Pentadec-4-ene	1533.0	3.8	−11.1	1.7	1484.6	0.9	3.0	0.4
trans-Pentadec-3-ene	1542.6	4.9	−13.6	2.4	1493.7	0.1	1.8	0.1
trans-Pentadec-2-ene	1562.2	6.4	−18.4	3.4	1514.1	1.7	−2.7	0.8
Pentadec-1-ene	1547.9	5.0	−14.7	2.5	—	—	—	—

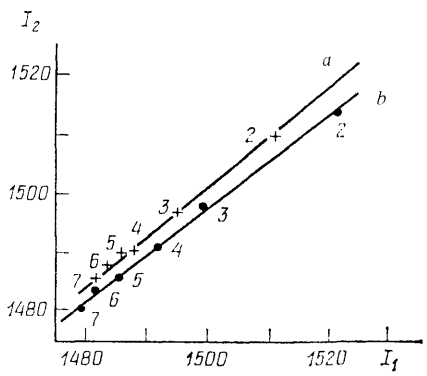


Figure 10. Relation between the retention indices for the *cis*- and *trans*-isomers of pentadecene on Carbowax 20M at 110 °C on two glass columns differing in the effective thickness of the SLP film;[51] I_1 and I_2 are the retention indices of the compound on columns *1* and *2* respectively; the thickness of the SLP layer on column *2* is twice as great as on column *1*: *a*) relation for the *trans*-isomers of pentadecene; *b*) relation for the *cis*-isomers of pentadecene; the numerals opposite the points denote the position of the double bond in the pentadecene isomer.

Fig. 10 presents data obtained on glass columns[51] differing only in the SLP content (the thickness of the SLP film on the second column was approximately twice as great as on the first). The use of data obtained on these two columns makes it possible to trace clearly two linear relations for the *cis*- and *trans*-isomers of pentadecene, which can be used for identification. We may note that relations of this type had been employed earlier solely for columns with different SLP.[96] In order to enhance the role of the adsorption factor, it may be that in the future it will prove desirable to employ one of the following procedures: (1) to increase the surface area of the walls of capillary columns and to subject them to extensive special treatment (for example, etching, deposition of a porous layer, etc); (2) to introduce specially into the SLP a small amount of a finely dispersed solid adsorbent. New possibilities for identification can be particularly usefully employed in capillary chromatography bearing in mind the selectivity and accuracy of the measurements of the retention characteristics.

VI. THE ROLE OF ADSORPTION PHENOMENA IN THE AGEING OF CAPILLARY COLUMNS

An important problem in capillary chromatography is the time variation of the properties of capillary columns (ageing), which has a negative influence on almost all the chromatographic properties of the columns (efficiency, separation, symmetry of chromatographic bands, reproducibility, retention characteristics, etc.). The ageing of packed columns was investigated long ago (see, for example, Dal Nogare and Juvet[18]): different investigators put forward the following main causes of the time variation of the properties of packed columns during their use: (1) the volatilisation of the stationary liquid phase from the columns;[18,97] (2) the redistribution of the SLP on the sorbent;[98,99] (3) the variation of the properties of the SLP as a result of its decomposition or oxidation by admixtures of oxygen in the carrier gas.[100]

The ageing of columns in capillary chromatography has not been studied in detail, although a number of hypotheses have been put forward concerning its nature.[87] Thus, according to Schomburg et al.,[101] one of the main causes of ageing is the transition from a continuous homogeneous film of SLP to a coating on the internal walls of the columns made up of isolated droplets. In a study specially devoted to the problem of ageing of capillary columns,[51] the hypothesis was put forward that the ageing process is associated mainly with the volatilisation of part of the SLP from the column. Jennings pointed out in a monograph[87] the great importance of the problem of the ageing of capillary columns in connection with the increase of their useful life.

Ageing has been studied on stainless steel columns (50 m × 0.25 mm) with 1,2,3-tris(cyanoethoxy)propane (TCEP) as the SLP. The changes in the properties of the columns were investigated at 130 °C in a stream of nitrogen (the pressure at the inlet to the column was 2.0 atm). The ageing of the columns was assessed from the change in the retention index I and the capacity coefficient k for benzene; I and k were measured at 50 °C and a nitrogen pressure at the inlet to the column of 0.6 atm. The maximum permissible working temperature for TCEP is 150–160 °C.[87,103]

In the first place it is essential to note that ageing influences not only the retention characteristics but also the separating capacity of the capillary column. Fig. 11[102] presents two chromatograms obtained on an ageing column over a period of two weeks. As a result of ageing for two weeks, two pairs of hydrocarbons, which were satisfactorily separated on a freshly prepared column, virtually ceased to

separate. The above example demonstrates the significant influence of ageing and the importance of studying its causes.

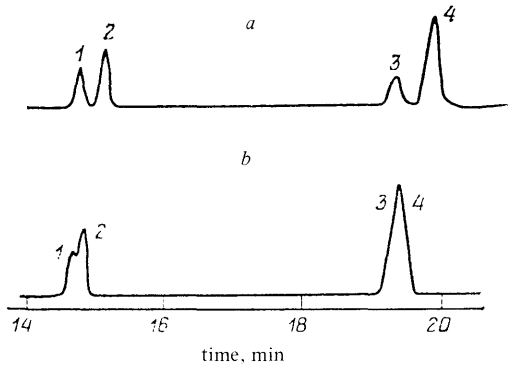


Figure 11. Variation of the separation during the ageing of the capillary column:[102] *a*) separation on a freshly prepared column; *b*) separation on the same column after ageing for 2 weeks. Experimental conditions: column length 50 m; SLP–tris(cyanoethoxy)propane; ageing temperature 130 °C; temperature of the measurement of the chromatographic characteristics 94 °C; compounds: 1) n-tetradecane (C_{14}); 2) 1-ethyl-4-methylbenzene; 3) n-pentadecane (C_{15}); 4) 1-methyl-2-propylbenzene.

The results of the variation of the quantities I and k for benzene as a function of the duration of ageing on capillary columns at 130 °C are presented in Fig. 12.[102] The retention index and the capacity coefficient were measured at 50 °C.

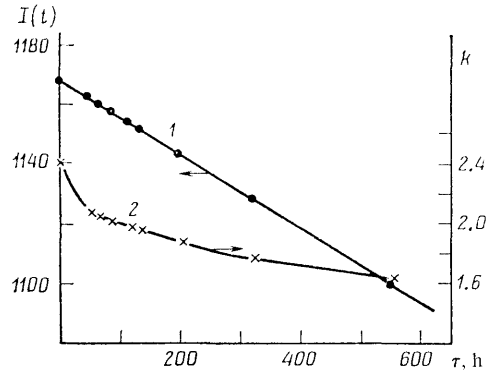


Figure 12. Variation of the retention index I (line *1*) and the capacity coefficient k (line *2*) for benzene as a function of the duration of ageing τ of a capillary column with tris(cyanoethoxy)propane at 130 °C.[102]

Independent experiments have shown that the variation of the chromatographic properties of open capillary columns for small carrier gas pressure drops in the column is associated mainly with the volatilisation of the SLP in the initial sections of the column. Thus, a small initial section consists of a column with a very thin layer of SLP. The separation in the initial (first) column is due mainly to adsorption processes. Therefore an ageing capillary column can be regarded to a first approximation as a compound column. Using the theory of retention on compound columns,[104] the following equation has been obtained:[102]

$$I(t) = I(0) - dt, \qquad (32)$$

where $I(t)$ is the retention index of the test substance at time t, t the ageing time, d a constant, and $I(0)$ the retention index in the initial instant. This equation describes experimental data satisfactorily (Fig. 12).

In order to increase stability, it is useful to employ the SLP in capillary columns at a temperature 50 °C below that recommended for packed columns. It is recommended that a carrier gas fully or partly saturated by the vapour of the SLP employed be used at elevated temperatures in order to increase the lifetime of capillary columns. A device proposed recently is useful for the realisation of this recommendation.[105]

VII. THE INFLUENCE OF ADSORPTION PHENOMENA ON THE SPREADING OF CHROMATOGRAPHIC BANDS IN GAS–LIQUID CAPILLARY CHROMATOGRAPHY

The first studies on the theory of the efficiency of capillary chromatographic columns were the familiar investigations by Golay,[107,108] which have still not lost their importance even at the present time. A straight capillary column with a circular or slit-like cross-section and smooth walls coated by a thin layer of SLP was considered in these studies. Golay obtained an expression for the HETP in the cases indicated. The influence of the finite rate of diffusion within the SLP film was taken into account approximately with the aid of an equivalent electrical circuit for the retaining layer.[109,110] In subsequent studies by Golay[111–114] the above theory was developed in several directions. Following the introduction of capillary columns with a porous layer, Golay modified his equation and extended it to such columns.[111] A detailed investigation of this equation was described subsequently.[115] Golay[112] considered a flow of the Poiseuille type in a bent column and showed that, under the conditions of the Poiseuille type in such a column, the operation of centrifugal forces creates a "secondary flow", which decreases the HETP. An expression has been obtained[113] for the dynamic diffusion coefficient, which plays a significant role in the spreading of the chromatographic band in capillary chromatography in columns (tubes) with an elliptical cross-section. Golay[114] considered the question of the magnitude of this coefficient for tubes with an extended rectangular cross-section.

In a series of communications, Giddings[116–120] considered in general terms the processes occurring in chromatographic capillary columns; using the approximate principle of additivity, the author estimated the contributions of different mechanisms leading to the spreading of the chromatographic band.

The influence of various types of mass transfer in gas–liquid capillary chromatography was estimated approximately in the book of Zhukhovitskii and Turkel'taub.[20]

A mathematically more rigorous study of the chromatographic band in a capillary column, compared with the work of Golay and Giddings, has been carried out by Khan[121] using the method of moments; it took into account the effect of the finite rate of mass transfer through the gas phase–liquid phase interface (see also another communication by the same author[122]).

The expression obtained by Golay for the height equivalent to a theoretical plate H in the case of a capillary column having a circular cross-section with a radius r_0 is

$$H = \frac{2D_g}{u} + \left[\frac{(1+6k+11k^2)}{24(1+k)^2}\frac{r_0^2}{D_g} + \frac{2}{3}\frac{k}{(1+k)^2}\cdot\frac{\delta^2}{D_l}\right]u \cdot \qquad (33)$$

For a column having a slit-like cross-section with a slit width $2h$, this expression is somewhat modified:

$$H = \frac{2D_g}{u} + \left[\frac{4}{105}\cdot\frac{(1+9k+25.5k^2)}{(1+k)^2}\frac{h^2}{D_g} + \frac{2}{3}\cdot\frac{k}{(1+k)^2}\frac{\delta^2}{D_l}\right]u \quad (34)$$

where D_g and D_l are the diffusion coefficients of the chromatographed substance in the gas and liquid phases and δ is the thickness of the SLP film.

The first (identical) terms in Eqns.(33) and (34) describe the effect of longitudinal diffusion in the gas phase, while the second terms are due to the phenomenon of dynamic diffusion arising from the fact that in the capillary column there is a distribution of the flow rate with respect to the radius. The last term, which is also identical for the columns of the forms considered, is associated with the effect of diffusion within the SLP film.

A more general expression for the HETP, obtained by Khan,[121,122] includes an additional term:

$$H_M = \frac{2k}{(1+k)^2}\cdot\frac{\delta}{k_d}, \quad (35)$$

where k_d is the rate constant for the desorption of the test substance from the gas phase–liquid phase interface. This term reflects the effect of the additional resistance to mass transfer at the gas–liquid boundary associated with the finite rate of attainment of equilibrium at this boundary. However, it has been shown[123] that the above term does not usually make an appreciable contribution to the spreading of the chromatographic peak in gas–liquid capillary chromatography.

As in gas–liquid chromatography on packed columns,[32,124,125] allowance for the influence of adsorption phenomena on such a spreading process appears much more significant in this instance. In this connection mention should be made of a study[126] in which the theory of the spreading of peaks in a capillary column proposed by Golay was tested and the occurrence of peak spreading not taken into account by Golay's theory was demonstrated. This spreading is associated with the mass transfer in the stationary phase but is independent of the thickness of the liquid film. The authors[126] believe that it is caused by the adsorption of the substances analysed from the stationary liquid phase on the walls of the nylon capillary.

It therefore appears useful to discuss briefly a theoretical model of the chromatographic process in a capillary column taking into account the adsorption at the gas–SLP and SLP–solid wall interfaces. In order to obtain the principal characteristics of the chromatographic elution curve, we shall employ the method of static moments which is nowadays widely used in the theory of chromatography [see, for example, Zolotarev's review[127]]. The approach described below has been proposed by Zolotarev et al.[128]

We shall consider initially a straight cylindrical column with a circular cross-section. Suppose that $c_g^*(x,r,t)$ is the local concentration of the chromatographed substance in the gas phase. Then, if the distribution of the local velocity $v(r)$ in the gas along the tube cross-section is parabolic, the local differential equation of mass transfer in the capillary column can be formulated as follows:

$$D_g\left(\frac{\partial^2 c_g^*}{\partial r^2} + \frac{1}{r}\frac{\partial c_g^*}{\partial r} + \frac{\partial^2 c_g^*}{\partial x^2}\right) - v(r)\frac{\partial c_g^*}{\partial x} - \frac{\partial c_g^*}{\partial t} = 0,$$
$$v(r) = 2u\left(1 - \frac{r^2}{r_0^2}\right), \quad (36)$$

where x is the coordinate along the column axis, r the radial coordinate reckoned from the centre of the column, t the time, u the carrier gas flow rate averaged with respect to the cross-section, and r_0 the radial coordinate of the boundary of the free part of the column (Fig.1). Eqn.(36) represents the mass balance of the chromatographic impurity in a small volume element at a distance r ($r<r_0$) from the column axis. The mass balance condition should hold at the gas–SLP ($r = r_0$) interface: the diffusion flux of the impurity across this interface should be equal to the sum of the rates of change of the masses of the impurity in the liquid phase and in the adsorbed states at the interfaces:

$$\gamma_l\frac{\partial a_l}{\partial t} + \gamma_{gl}\frac{\partial a_{gl}}{\partial t} + \gamma_{ls}\frac{\partial a_{ls}}{\partial t} = -\frac{2\gamma_g D_g}{r_0}\cdot\left.\frac{\partial c_g^*}{\partial r}\right|_{r=r_0}. \quad (37)$$

We shall average Eqn.(36) with respect to the free volume of the column. For this purpose, we shall apply to each term of Eqn.(36) the averaging operator with respect to the cross-section and we shall take into account Eqn.(37). We then obtain

$$\gamma_l\frac{\partial a_l}{\partial t} + \gamma_g\frac{\partial c_g}{\partial t} + \gamma_{gl}\frac{\partial a_{gl}}{\partial t} + \gamma_{ls}\frac{\partial a_{ls}}{\partial t} =$$
$$= \gamma_g D_g\frac{\partial^2 c_g}{\partial x^2} - 4\gamma_g\frac{u}{r_0^2}\int_0^{r_0}\frac{\partial c_g^*}{\partial x}\left(1 - \frac{r^2}{r_0^2}\right)r\,dr, \quad (38)$$

where $c_g(x,t)$ and $a_l(x,t)$ are the average concentrations of the chromatographed impurity in the mobile phase and in the SLP. The local concentration of the impurity in the SLP will be designated by $a_l^*(x,y,t)$.

We shall assume as usual that the SLP is thin ($\delta \ll r_0$). For such a thin film, we have

$$\gamma_l + \gamma_g = 1;\ \gamma_g = \frac{r_0^2}{(r_0+\delta)^2} \simeq 1 - \frac{2\delta}{r_0};\ \gamma_l \simeq \frac{2\delta}{r_0^2};\ \gamma_{gl} \simeq \gamma_{ls} \simeq \frac{\gamma_l}{\delta}. \quad (39)$$

We shall assume that the equilibrium at the interfaces is established at an infinitely high rate. The following equilibrium relation between the local concentrations of the impurity in the gas and liquid phases will then hold at the gas–SLP interface:

$$(a_l^*)_i = K_l(c_g^*)_i, \quad (40)$$

where K_l is the partition coefficient between the gas and liquid phases and the subscript i refers to this interface. In addition, assuming that the gas adsorption isotherm is linear with a Henry coefficient K_{gl}, we have at the above interface

$$a_{gl} = K_{gl}(c_g^*)_i. \quad (41)$$

The diffusion of the impurity in the thin SLP film ($\delta \ll r_0$) can be described by the one-dimensional equation for diffusion along the coordinate y at right angles to the film boundaries (Fig.1):

$$\frac{\partial a_l^*}{\partial t} = D_l\frac{\partial^2 a_l^*}{\partial y^2};\ a_l(x,t) = \frac{1}{\delta}\int_0^{\delta} a_l^*(x,y,t)\,dy;\ 0 \leqslant y \leqslant \delta. \quad (42)$$

At the $y = 0$ (solid wall) boundary and at $y = \delta$ we also obtain the following relations in the case under consideration:

$$a_{ls} = K_{ls}a_l^*|_{y=0};\ \frac{\partial a_{ls}}{\partial t} = D_l\left.\frac{\partial a_l^*}{\partial y}\right|_{y=0};\ a_l^*|_{y=\delta} = (a_l^*)_i. \quad (43)$$

The first of these relations takes into account the adsorption at the SLP–solid interface in terms of the linear isotherm approximation, while the second represents the local mass balance equation at this interface with allowance for adsorption. On solving Eqn.(42) with the aid of the Laplace transformation with respect to time,[129] we obtain the following expression for the representation $\tilde{a}_l = \int_0^{\infty} e^{-st}a_l^* dt$:

$$\tilde{a}_l^* = \frac{(\tilde{a}_l^*)_i[\sinh(\varkappa y) + (D_l\varkappa/K_{ls}s)\cosh(\varkappa y)]}{\sinh(\varkappa\delta) + (D_l\varkappa/K_{ls}s)\cosh(\varkappa\delta)};\ \varkappa = \left(\frac{s}{D_l}\right)^{1/2}. \quad (44)$$

Application of the Laplace transformation to Eqn.(43) and substitution of Eqn.(44) for $\tilde{a}_l^*$ yields after simple rearrangements

$$(\tilde{a}_l^*)_l = P_1(s)\,\tilde{a}_l$$

$$P_1(s) = \frac{(\varkappa\delta)\{\sinh(\varkappa\delta) + [1/(\varkappa K_{ls})]\cosh(\varkappa\delta)\}}{\{\cosh(\varkappa\delta) + [1/(\varkappa K_{ls})]\sinh(\varkappa\delta) - 1\}} \quad . \tag{45}$$

Using Eqns.(43)–(45), we find the following formula for a_{ls}:

$$\tilde{a}_{ls} = P_2(s)\cdot\tilde{a}_l$$

$$P_2(s) = \frac{\delta}{\cosh(\varkappa\delta) + [1/(\varkappa K_{ls})]\sinh(\varkappa\delta) - 1} \quad . \tag{46}$$

Taking into account the boundary conditions (40) and (41) and also Eqn.(45), we obtain

$$\tilde{a}_{gl} = (K_{gl}/K_l)\,P_1(s)\,\tilde{a}_l \quad . \tag{47}$$

For subsequent treatment, we express[107,108,121] the local concentration of the test substance in the gas phase c_g^* by the equation

$$c_g^* = c_g + \Delta c_g;\ \int_0^{r_0} \Delta c r\,\mathrm{d}\,r = 0 \quad . \tag{48}$$

In addition we assume that the relation

$$\Delta c \ll c_g \tag{49}$$

holds.

Then, substituting Eqn.(48) in Eqns.(36) and (38), and taking into account formula (49), we obtain the following equation for Δc after a few steps which we omit here:

$$\frac{\partial^2\Delta c}{\partial r^2} + \frac{1}{r}\frac{\partial\Delta c}{\partial r} = \frac{u}{D_g}\left(1 - 2\frac{r^2}{r_0^2}\right)\frac{\partial c}{\partial x} - \frac{\chi_l}{D_g\chi_g}\frac{\partial a_l}{\partial t} - \frac{\chi_{gl}}{\chi_g D_g}\cdot\frac{\partial a_{gl}}{\partial t} - \frac{\chi_{ls}}{\chi_g D_g}\cdot\frac{\partial a_{ls}}{\partial t} \quad . \tag{50}$$

On solving this equation taking into account condition (45) and the requirement that Δc be finite at $r \to 0$, we find

$$c_g^* = c_g + \frac{u}{D_g}\left(\frac{r^2}{4} - \frac{r^4}{8r_0^2} - \frac{r_0^2}{12}\right)\frac{\partial c_g}{\partial x} - \frac{\chi_l}{D_g\chi_g}\left(\frac{r^2}{4} - \frac{r_0^2}{8}\right)\left(\frac{\partial a_l}{\partial t} + \frac{\chi_{gl}}{\chi_l}\frac{\partial a_{gl}}{\partial t} + \frac{\chi_{ls}}{\chi_l}\frac{\partial a_{ls}}{\partial t}\right) \quad . \tag{51}$$

Application of the Laplace transformation to Eqn.(51) at the gas–SLP interface taking into account Eqns.(40) and (41) yields

$$(\tilde{c}_g^*)_l = \frac{(\tilde{a}_l^*)_l}{K_l} = \frac{P_1(s)}{K_l}\,\tilde{a}_l = \tilde{c}_g + \frac{ur_0^2}{24D_g}\frac{\mathrm{d}\,\tilde{c}_g}{\mathrm{d}\,x} - \frac{r_0^2 s}{8D_g}\frac{\chi_l}{\chi_g}\times\left(\tilde{a}_l + \frac{\chi_{gl}}{\chi_l}a_{gl} + \frac{\chi_{ls}}{\chi_l}a_{ls}\right) \quad . \tag{52}$$

On substituting Eqns.(44)–(46) in Eqn.(52) and on solving the resulting expression for $\tilde{a}_l$, we find

$$\tilde{a}_l = K_l\left[P_1(s) + \frac{r_0^2 s}{8D_g}k\left(1 + \frac{\chi_{gl}K_{gl}}{\chi_l K_l}P_1(s) + \frac{\chi_{ls}P_2(s)}{\chi_l}\right)\right]^{-1}\times\left(\tilde{c}_g + \frac{ur_0^2}{24D_g}\cdot\frac{\mathrm{d}\,c_g}{\mathrm{d}\,x}\right), \qquad k = \chi_l K_l/\chi_g. \tag{53}$$

We now differentiate Eqn.(53) with respect to x and substitute the resulting expression in Eqn.(47). After integration and subsequent application of the Laplace transformation taking into account Eqns.(44)–(46) and (53), we obtain the following expression for $\tilde{c}_g$:

$$B\frac{\mathrm{d}^2\tilde{c}}{d\,x^2} - \frac{\mathrm{d}\tilde{c}_g}{\mathrm{d}\,x} - E\tilde{c}_g = 0 \ ,$$

$$B = \frac{1}{u\theta}\left\{\left(D_g + \frac{u^2r_0^2}{48D_g}\right)\left[P_1(s) + \frac{r_0^2 s}{8D_g}kQ(s) - ksQ(s)\left(\frac{ur_0^2}{24D_g}\right)^2\right]\right\}, \tag{54}$$

$$E = \frac{1}{u\theta}\left\{s\left[P_1(s) + \frac{r_0^2}{8D_g}skQ(s) + ksQ(s)\right]\right\} \ ,$$

$$\theta = P_1(s) + \frac{sr_0^2}{24D_g}ksQ(s) \ ,$$

$$Q(s) = 1 + \frac{\chi_{gl}K_{gl}P_1(s)}{K_l\chi_l} + \frac{\chi_{ls}P_2(s)}{\chi_l} \quad .$$

We shall assume that the impurities are introduced into the column in the form of a rectangular pulse of duration ε:

$$x = 0 \quad \begin{cases} c_g = c_0, & 0 < t \leqslant \varepsilon \\ c_g = 0, & t > \varepsilon \end{cases} \tag{55}$$

Accordingly, we have the following boundary conditions for Eqn.(54):

$$\tilde{c}_g = \frac{c_0}{s}(1 - \mathrm{e}^{-\varepsilon s}),\ x = 0 \ , \tag{56}$$

where $\tilde{c}_g$ is finite at $x \to \infty$.

The solution of Eqn.(52) subject to conditions (54) is

$$\frac{\tilde{c}_g(L, s)}{\varepsilon c_0} = \left(1 - \frac{\varepsilon s}{2!} + \frac{\varepsilon^2 s^2}{3!} - \cdots\right)\exp\left\{\frac{L}{2B}[1 - (1 + 4BE)^{1/2}]\right\}, \tag{57}$$

where $x = L$ is the distance from the beginning of the column at which the chromatographic elution curve is measured.

We apply the familiar methods for the calculation of the moments of the elution curve from its representation[129,130] and then, using Eqns.(57) and (54), we obtain

$$m_1(L) = \int_0^\infty \frac{c_g(L, t)}{\varepsilon c_0}\,t\,\mathrm{d}\,t = -\lim_{s\to 0}\frac{\mathrm{d}}{\mathrm{d}\,s}\left[\frac{\tilde{c}_g(L, s)}{\varepsilon c_0}\right] = \frac{\varepsilon}{2} + \frac{L}{u}(1 + k_*), \tag{58}$$

$$m_2(L) = \int_0^\infty \frac{c_g(L, t)}{\varepsilon c_0}\,t^2\,\mathrm{d}\,t = \lim_{s\to 0}\frac{\mathrm{d}^2}{\mathrm{d}\,s^2}\left[\frac{\tilde{c}_g(L, s)}{\varepsilon c_0}\right] = \frac{\varepsilon^2}{12} + \left[\frac{\varepsilon}{2} + \frac{L}{u}(1 + k_*)\right]^2 + \frac{L}{u^2}(1 + k_*)^2\left[\frac{2D_g}{u} + \frac{ur_0^2}{D_g}\frac{(1 + 6k_* + 11k_*^2)}{24(1 + k_*)^2} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\frac{\delta^2}{D_l}f_1(K_{gl}, K_{ls})\right], \tag{59}$$

$$f_1 = \frac{\delta^2 + 3K_{ls}\delta + 2K_{ls}^2}{\delta^2 + K_{gl}\delta/K_l + K_{ls}\delta}; \quad k_* = \frac{\chi_l}{\chi_g}K_l\left(1 + \frac{K_{gl}/K_l + K_{ls}}{\delta}\right) . \tag{60}$$

Here

$$m_k(x) = \int_0^\infty t^k c_g(x, t)\,\mathrm{d}\,t \Big/ \int_0^\infty c_g(x, t)\,\mathrm{d}\,t$$

is the initial moment of the kth order chromatographic elution curve.

In order to obtain, in particular, the HETP, we make use of the relation

$$H = L\mu_2^{(0)}/(m_1^{(0)})^2,\ \mu_2^{(0)} = m_2^{(0)} - [m_1^{(0)}]^2 \ , \tag{61}$$

where $m_1^{(0)}(x)$, $m_2^{(0)}(x)$, and $\mu_2^{(0)}(x)$ are the first and second initial moments and the second central moment of the chromatographic curve for a sample volume tending to zero ($\varepsilon \to 0$).

Taking into account Eqns.(54)–(57), we obtain the following formula for the HETP:

$$H = \frac{2D_g}{u} + \frac{1 + 6k_* + 11k_*^2}{24(1 + k_*)^2}\frac{ur_0^2}{D_g} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\frac{\delta^2}{D_l}f_1(\delta, K_{gl}, K_{ls}) . \tag{62}$$

The expression for the HETP in a column with a slit-like cross-section can be readily obtained with the aid of the method used above for the evaluation of the moments and the HETP for a cylindrical column. Here the term describing the internal diffusion for the thin SLP films considered ($\delta \ll r_0$, $\delta \ll h$) will be the same as for a cylindrical column. For a column with a rectangular cross-section, the expression for the HETP is

$$H = \frac{2D_g}{u} + \frac{4}{105}\cdot\frac{(1 + 9k_* + 25.5k_*^2)}{(1 + k_*)^2}\cdot\frac{uh^2}{D_g} + \frac{2}{3}\frac{uk_*}{(1 + k_*)^2}\cdot\frac{\delta}{D_l}f_1(\delta, K_{gl}, K_{ls}) \tag{63}$$

It is evident from the expressions obtained that adsorption at the gas–SLP and SLP–solid interfaces influences H in two ways. Firstly, the capacity coefficient k changes (increases):

$$k_* = k\left(1 + \frac{K_{gl}/K_l + K_{ls}}{\delta}\right), \quad (64)$$

as already stated in previous Sections. Secondly, an additional multiplier appears in the component of H taking into account the contribution of the internal diffusion resistance to mass transfer:

$$f_1(\delta, K_{gl}, K_{ls}) = \frac{\delta^2 + 3K_{ls}\delta + 3K_{ls}^2}{\delta^2 + (K_{gl}/K_l)\delta + K_{ls}\delta}, \quad (65)$$

whose magnitude is greater than unity and which takes into account the adsorption phenomena.

The contribution of adsorption phenomena at the interfaces to the spreading, i.e. to the HETP, can be taken into account also within the framework of the approximate approach developed by Giddings[118] (see also Garbuzov et al.[131]). However, the above approximate approach does not permit the estimation of the contribution of adsorption phenomena to the moments of the chromatographic elution curve of an order higher than the second; the higher order moments characterise the degree of asymmetry of this curve, its steepness, etc. The above treatment allows this. As an example, we shall write the formula for the asymmetry coefficient

$$\gamma = \mu_3^{(0)}/[\mu_2^{(0)}]^{3/2}$$

($\mu_3^{(0)}$ is the third central moment of the elution curve) for the chromatographic elution curve:

$$\gamma = \left[\frac{2D_g L(1+k_*)^2}{u^3} + \frac{r_0 L}{D_g u}(1 + 6k_* + 11k_*^2) + \frac{2}{3}\frac{k_*}{u}\frac{\delta^2}{D_l} f_1\right]^{-3/2} \times$$
$$\times \left[\frac{12D_g^2 L(1+k_*)^2}{u^5} + 4k_*(1+k_*)\frac{D_g L}{D_l u^3}\cdot\delta^2 f_1 + \frac{r_0^2 L}{2u^3}(1 + 6k_* + 12k_*^2 + 7k_*^3) + \right.$$
$$\left. + 2k_*\frac{\delta^2 L}{D_l^2 u} f_2 + \frac{r_0^2 L}{12 D_g u}\frac{\delta^2}{D_l} k_*(3 + 11k_*) f_1 + \frac{3}{(24)^2}\frac{r_0^4 L}{u D_g^2}(1 + 11k_* + 45k_*^2 + 65k_*^3)\right], \quad (66)$$

where

$$f_2(\delta, K_{gl}, K_{ls}) = f_1(\delta, K_{gl}, K_{ls})\left(\delta K_{ls} + \frac{\delta^3}{3}\right) + \frac{\delta^4}{15\left(\delta^2 + \frac{K_{gl}\delta}{K_l} + K_{ls}\delta\right)}. \quad (67)$$

Golay's Eqns.(33) and (34) and their extended forms taking into account adsorption phenomena [Eqns.(62) and (63)] are valid only for short sections of the column, because the absence of a pressure drop and the constancy of the carrier gas flow rate along the column length were assumed in their derivation. Furthermore, in these equations no account is taken of the additional contribution of the spreading outside the column to H, which is[132] a quadratic function of the gas flow rate:

$$H_0 = [\sigma_0^2/L(1+k)^2]u^2, \quad (68)$$

where σ_0 is the variance of the peak associated with the spreading outside the column. For real long gas–chromatographic capillary columns, it is necessary to take into account the effect of the compressibility of the gas, which leads to the appearance of corrections for the pressure drop[108,133] (see also Garbuzov et al.[131]).

The terms of Eqns.(33) and (34) and (62) and (63) referring to the gas phase which remain unchanged along the length of the column must be multiplied by the correction factor ψ_g given by

$$\psi_g = \frac{9}{8}\frac{[(p_i/p_0)^4 - 1][(p_i/p_0)^2 - 1]}{[(p_i/p_0)^3 - 1]^2}, \quad (69)$$

where p_i and p_0 are the pressures of the carrier gas at the inlet to and outlet from the column.

For the term taking into account the resistance to mass transfer in the SLP, the correction coefficient has the same form as the factor of James and Martin:

$$j = \frac{3}{2}\frac{(p_i/p_0)^2 - 1}{(p_i/p_0)^3 - 1} \quad (70)$$

For the term describing the spreading outside the column, the correction for the compressibility of the carrier gas can be shown to be equal to j^2. The procedure involved in the introduction of these corrections, presupposes that the diffusion coefficient in the carrier gas and its linear flow rate correspond to the conditions at the outlet from the column, i.e. that $D_g = D_0$ and $u = u_0$. Introducing the average quantities $\bar{D}_g = D_0 p_0/\bar{p}$ and $\bar{u} = u_0 p_0/\bar{p}$ and bearing in mind that $D_0 = D_g^* p_0$, $\bar{u} = j u_0$, and $\bar{p} = p_0/j$ (D_g^* is the diffusion coefficient of the substance analysed in the carrier gas at a pressure of 1.00 atm), it is possible to obtain the following general equation for the HETP of long cylindrical columns with a circular cross-section taking into account the spreading outside the column:

$$H = \frac{2D_g^* \psi_g}{\bar{p}\bar{u}} + \frac{1 + 6k_* + 11k_*^2}{24(1+k_*)^2}\frac{r_0^2 \psi_l \bar{p}\bar{u}}{D_l} + \frac{2}{3}\frac{k_* f_1(K_{gl}, K_{ls})}{(1+k_*)^2}\frac{\delta^2 \bar{u}}{D_l} + \frac{k_* \delta^2 \bar{u}^2}{D_l(1+k_*)^2}. \quad (71)$$

An expression analogous to Eqn.(71) can be obtained also for long columns with a rectangular cross-section.[81] The equation for the HETP for long columns without taking into account the contribution of adsorption phenomena to the internal diffusion resistance can be obtained from Eqn.(71) if one puts $f_1 = 1$ (the modified Golay equation):

$$H = \frac{2D_g^* \psi_g}{\bar{p}\bar{u}} + \frac{1 + 6k_* + 11k_*^2}{24(1+k_*)^2}\frac{r_0^2 \psi_l \bar{p}\bar{u}}{D_l} + \frac{2}{3}\frac{k_* \delta^2 u}{(1+k_*)^2 D_l} + \frac{k_* \delta^2 u^2}{D_l(1+k_*)^2}. \quad (72)$$

It is seen from Eqns.(71) and (72) that the $H(u)$ relation is not hyperbolic in the general case [the last term of Eqn.(71) is a quadratic function of the flow rate]. In addition, in practice the average pressure in the column frequently varies simultaneously with the average flow rate, since the flow rate is regulated by altering either the inlet or outlet pressure (this factor has been noted by Garbuzov and co-workers[131,134]). In connection with the foregoing, the test of Golay's theory undertaken by Hazeldean and Scott and Desta and Goldup[125,135,136] appears to us to be insufficiently rigorous. This test was based on the statistical analysis of the dependence of the HETP on the average carrier gas flow rate. The coefficients of Golay's equation, found on the assumption that the latter is hyperbolic, were compared[126,135,136] (see also Giddings[147]) with the calculated values.

Another method of testing the theory has been proposed by Garbuzov and co-workers.[131,134] It is based on the analysis of the dependence of the widening of the chromatographic bands (characterised by the square of the width of the peak at the half height level in units of time–b_t^2) for C_{13}–C_{24} n-alkanes on their mass-transfer (capacity) coefficients k. The capillary tubes were made from borosilicate glass. The methylsilicone OU-101 was used as the SLP.

The HETP is related (see, for example Giddings[31] and Rudenko[138]) to the quantity b_t^2 by the expression

$$\bar{H} = b_t^2 \bar{u}^2/[(1+k)^2 L \times 8 \ln 2]. \quad (73)$$

Fig.13[131] presents the dependence of the experimental (curve *1*) and calculated (curve *2*) values of b_t^2 on the coefficient k for C_{13}–C_{20} n-alkanes (column with OU-101; the average linear flow rate of the helium carrier gas was $\bar{u} = 37.14$ cm s^{-1}). The calculation was based on Eqn.(72) without taking into account the last term (the spreading outside the column) and with allowance for Eqn.(73). It is readily seen that the effect of the spreading outside the column is reflected in the graph by the section *FE*, which can be found by extrapolating the extent of the spreading on plots of b_t^2 against k, obtained experimentally and calculated, to $k = 0$. On average, the effect of the spreading outside the column for three flow rates $\bar{u}$ amounted to $b_t^2(0) \approx 0.5c^2$.

A contribution to the spreading of the peak not taken into account by the theory has been discovered[131,134] with the aid of this procedure. In order to elucidate the causes of the band spreading which had not been accounted for, Garbuzov et al.[131] investigated the influence of the nature of the carrier gas on the behaviour of the n-tetracosane chromatographic band in a glass column with the SE-30 SLP (the carrier gases were hydrogen, helium, nitrogen, and argon). The maintenance of an identical average linear flow rate would have required the establishment of different pressure drops in the column and for this reason the average pressure in the column was different for each gas. The discrepancy between the experimental [determined with the aid of Eqn.(73)] and calculated [Eqn.(72) without the last term] values of HETP increases with increase of the molecular weight of the carrier gas. The difference $\Delta H = H_{exp} - H_{calc}$ (Fig.14) is a linear function of the reciprocal of the diffusion coefficient of n-tetracosane in the gases employed at the corresponding average pressures in the column. The discrepancy between the contribution of dynamic diffusion and the observed arrest of the mass transfer in the gas phase can be estimated from the slope of the straight line; it amounts to ~24% of the calculated value [the second term of Eqn.(72)]. According to Garbuzov et al.,[131] the discrepancy is caused by the non-ideality of the geometry of the column, which exerts a fairly powerful influence on the contribution of dynamic diffusion.[109,110,112-114] When the capillary is extended and at the same time twisted into a spiral, the column may acquire an elliptical cross-section. In addition, the different curvatures of the inner surface of the tube should produce inhomogeneity of the thickness of the liquid film along the perimeter of the column cross-section.[139] The mass rate of movement of the test substance in the gas near a wall with a greater sorption capacity is lower than the corresponding rate at a wall with a lower capacity, which should lead to additional band spreading as a result of an increase of the contribution of dynamic diffusion.

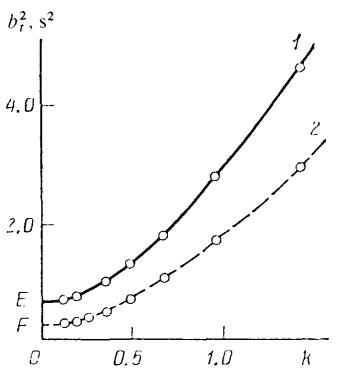


Figure 13. Dependence of the experimental (curve *1*) and calculated (curve *2*) values of b_t^2 on the mass-transfer coefficient k for C_{13}–C_{20} n-alkanes.

The intercept on the ordinate axis made by the straight line in Fig.14 characterises the band spreading which is independent of the nature of the carrier gas. It consists of the contribution to the HETP outside the column, namely $\bar{H}_0 \cong 4.3 \times 10^{-3}$ mm [this contribution is estimated from the quantity $b_t^2(0) \cong 0.5c^2$, which had been found previously by Eqn.(73)], and the contribution of the resistance to the mass transfer in the SLP.

Estimation of the internal diffusion resistance to mass transfer in the SLP film from the third term of Golay's Eqn.(72) using the experimental value $D_l(n\text{-}C_{24}H_{50}$, SE-30, 200 °C) = 2.49×10^{-6} cm²s^{-1} [139] yields a value which is smaller by a factor of 6.5 than that determined from the plot in Fig.(14).

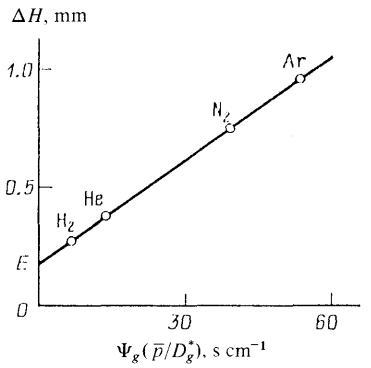


Figure 14. Dependence of the unexplained contribution to the HETP on the reciprocal of the diffusion coefficient of n-tetracosane in various carrier gases at the corresponding average pressures in a column with SE-30.

Garbuzov et al.[131] draw from this finding the entirely justified conclusion that the most probable cause of the above discrepancy is the contribution to the spreading by the adsorption phenomena at the interfaces. They attempted to estimate this contribution using an expression for H_{ads} analogous to the third term in Eqns.(62) and (71); the adsorption of n-tetracosane at the gas–SE-30 interface is then neglected. It is also assumed that the adsorption of n-tetracosane from the SE-30 liquid phase on the solid wall is 200 times less intense than the adsorption of the same substance from the gas on the same wall (the gas–solid distribution constant is known: $K_{gs} \cong 1.242 \times 10^{-4}$ m). Under these conditions, we have $f_1(\delta, K_{gl}, K_{ls}) \cong 6.6$. In other words, it has been shown that even insignificant adsorption of the substance analysed from the liquid phase on the surface of the walls of the capillary column can lead to an appreciable increase of the resistance to mass transfer in the SLP, which also follows from a qualitative model examination of the process.

We may note that we are unaware of studies in capillary chromatography in which the contributions of the adsorption at the SLP interfaces to the column efficiency have been determined rigorously and by a direct experimental method. We believe that such an estimate could be achieved by carrying out two series of experiments on the same column: (1) measurement of the efficiency of a column with adsorption-active walls on which a layer of the SLP has been deposited; (2) measurement of the efficiency of columns with suppressed adsorption activity of the walls. Suppression of adsorption at the SLP–solid interface by modifying the sorbent with small amounts of added polar substances has a positive effect on the efficiency of the preparation of the sorbent. For example, ethyl methyl ketone is eluted in the form of a diffuse band at 50 °C from unmodified Sterchamol impregnated with squalane and the HETP is 11 mm; after modification with 1% triethylene glycol, the HETP falls to 1.6 mm.[140] In the second series of experiments the substances employed to suppress adsorption may be, for example, silanising agents which modify the surface or substances which are not detected by

the flame-ionisation detector and which suppress the adsorption on the active surface centres (for example, ammonia, formamide, formic acid, etc.).

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The development of ideas concerning the role of adsorption has led to the necessity for the refinement of the classification of the types of chromatography based on the state of aggregation of the phases involved in the chromatographic process. The traditional classification considers four main types of chromatography: gas–solid, liquid–solid, gas–liquid, and liquid–liquid.[18] However, the last two types of chromatography are strictly speaking unknown in a pure form, since they cannot be realised without the involvement of a third phase – the solid phase (solid carrier). It is therefore correct to refer to these versions as follows: gas–[liquid–solid] chromatography and liquid–[liquid–solid] chromatography.[32,106]

A rational classification of the types of chromatography which we propose is presented in Table 7. In connection with this classification, it must be emphasised that the gas–liquid chromatography which we have been considering has not so far been realised in the strict sense of its definition and that only gas–[liquid–solid] chromatography has been described. The theoretical ideas concerning the role of adsorption described systematically in this review agree also with the experimental facts obtained in the study of adsorption in capillary columns.

Table 7. Classification of certain common types of chromatography in terms of the state of aggregation of the mobile and stationary phases.

Mobile phase	Stationary phase: solid	Stationary phase: liquid–solid	
		proposed terminology	traditional terminology
Gas	gas–[solid]–phase chromatography	gas–[liquid–solid]–phase chromatography	gas–liquid chromatography
Liquid	liquid–[solid]–phase chromatography	liquid–[liquid–solid]–phase chromatography	liquid–liquid chromatography

In conclusion we may note that the new ideas about the role of adsorption in GLC have led to a significant development of the familiar trends in chromatography and the appearance of new ones. A considerable expansion of the applications and an increase of the accuracy of the chromatographic methods for the investigation of the interactions of dissolved compounds with the SLP have been achieved as a result of allowance for the adsorption of the chromatographic substances at the interfaces. The gas-chromatographic study of the adsorption of volatile compounds at the interfaces between the SLP and the solid carrier and the carrier gas has begun to develop (a new physicochemical application of gas chromatography). New ideas and new universal methods for the identification of the chromatographic bands, taking into account the adsorption phenomena in GLC, have been developed. A new classification of the types of chromatography, taking into account the role of the solid carrier (the solid) is proposed.

We may note that the development of capillary gas–[liquid–solid] chromatography is being vigorously continued also at the present time. There is no doubt that in the immediate future the efforts of many investigators will lead to a more complete understanding of the role of adsorption processes in capillary chromatography and to the development of new effective methods for chromatographic separation and physicochemical measurements.

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