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The influence of the carrier gas on the retention parameters and the height equivalent to the theoretical plate in gas – solid chromatography

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Abstract. The influence of the nature of the carrier gas and of its pressure on the retention and the height equivalent to the theoretical plate in gas – solid chromatography is analysed. The physicochemical processes responsible for this influence are examined. It is shown that the carrier gas is an active participant in the chromatographic process. The bibliography includes 145 references.

I. Introduction

Gas – solid chromatography is one of the principal versions of gas chromatography and its significance in the solution of important analytical and preparative problems has been increasing continuously.[1, 2]

The compounds being chromatographed, the adsorbent (solid), and the carrier gas as a rule participate in the separation process in gas – solid chromatography. The solid may also play the role of a volumetric adsorbent (for example, palladium may chemisorb hydrogen reversibly[3]), but few such absorption systems are known and we shall not consider them in the present review. It is noteworthy that inadequate attention has been paid currently to the carrier gas as a participant in the chromatographic process and as a factor capable of improving the separation significantly.

The retention of chromatographed compounds is a result of the adsorption of the analyte compounds/sorbate on a solid with a relatively high specific surface (the adsorbent).[1] In gas – solid chromatography, the retention is determined by the nature of the sorbate, the nature of the adsorbent surface and its structure, and also the nature and pressure of the carrier gas employed.

The first experimental data concerning the influence of the nature of the carrier gas and the retention of the analyte were obtained already in the initial stage of the development of gas – solid chromatography. Thus, as early as 1962, Zhukhovitskii and Turkel'taub noted that in gas – solid chromatography account must be taken primarily of the influence of the carrier gas on the sorbability of the components of the mixture being separated, because a change in the nature of the carrier gas may alter significantly the separation criteria.[4] However, in routine chromatography, this fact has not always been taken into account. This can probably be accounted for by the fact that, firstly, permanent gases, the influence of which on the retention parameters is insignificant, were usually employed as carrier gases and, secondly, the accuracy of the measurement of the retention parameters on packed columns, especially in the initial period of the development of gas – solid chromatography, was insufficiently high.

The influence of the nature of the carrier gas on the retention may be predicted by analysing the general relations describing the adsorption equilibria and the relation between these equilibria and the retention volume (see, for example, Refs 1, 2 and 6 – 9). The equilibrium is characterised by the following functional relations.

1. The equation of the adsorption isotherm for the compounds participating in the chromatographic process:

$$a_i = \mathrm{f}(c_i, c_m, a_m)\,, \tag{1a}$$

$$a_m = \psi(c_m, a_i, c_i)\,, \tag{1b}$$

where a_i is the concentration of the adsorbed compound i on the surface of the adsorbent, c_i is the concentration of compound i in the gas phase, c_m the concentration of the carrier gas in the mobile phase (proportional to its partial pressure), and a_m is the concentration of compound m (the carrier gas) on the surface of the adsorbent.

2. The equations for the effective partition coefficient $K_{im\,\mathrm{ef}}$ (see, for example, Berezkin and de Zeeuw[2]):

$$K_{im\,\mathrm{ef}} = \left(\frac{\partial a_i}{\partial c_i}\right)_{c_m} = \left[\frac{\partial f(c_i, c_m, a_m)}{\partial c_i}\right]_{c_m},$$

$$K_{im\,\mathrm{ef}} = \left(\frac{\partial a_i}{\partial c_i}\right)_{c_m} = \frac{V_{Ni}(c_i, c_m)}{S} = V_{\mathrm{s}}(c_i, c_m)\,, \tag{2}$$

where V_{Ni} is the retention volume for compound i, S the overall surface area of the adsorbent employed, and $V_{\mathrm{s}}(c_i,c_m)$ the specific

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retention volume calculated per unit surface of the adsorbent employed.

We may note that the nonideality of the gas phase and its adsorption on the surface of the adsorbent influence the retention. However, as noted in the above monograph,[2] the role of the second factor is frequently more important.

3. The equation for the retention volume:

$$V_{Ni} = \left(\frac{\partial a_i}{\partial c_i}\right)_{c_m} S = K_{im\,\mathrm{ef}} S\,. \tag{3}$$

We may note that the functions a_i and a_m [Eqns (1a) and (1b)] are functions of several variables and their derivatives are therefore expressed as partial derivatives.

Taking into account the general ideas concerning the adsorption of a mixture of gases on the surface of a solid adsorbent (see, for example, monograph by Kiselev and Yashin [1]), it follows from Eqn (3) that in the general case V_{Ni} also depends on the nature of the carrier gas, its partial pressure, and its adsorption in the chromatographic system.

If it is assumed that the adsorption of the carrier gas may be neglected, Kiselev's equation follows from Eqn (3) as a special case:[1,6]

$$V_{Ni} = K_i S. \tag{4}$$

In it, Henry's constant K_i may be expressed by the following equations:

$$K_{im\,\mathrm{ef}} = K_i\,,$$

$$K_i = \frac{\partial a_i}{\partial c_i} = \frac{a_i}{c_i}\,. \tag{5}$$

It follows from the relations quoted above that the partition coefficient depends in the general case on the partial pressure (concentration) of the carrier gas and its nature. Analysis of this relation is of theoretical and practical interest.

We believe that studies on the influence of the nature of the carrier gas on the retention are important because they make it possible, firstly, to refine the real picture of the chromatographic process, secondly, to establish the corresponding general relations, and, thirdly, to assess the carrier gas as a factor actively influencing the principal parameters of the chromatographic separation. Certain examples of the practical use of gas–solid chromatography, reflecting the role of the carrier gas, are presented in Table 1. Evidently, many carrier gases have found an application in gas–solid chromatography — ranging from the inert helium to the vapours of water and organic compounds, but helium, nitrogen, and hydrogen are mainly employed in chromatographic practice.[20]

Table 1. Examples of the chromatographic systems used in gas-solid chromatography.

Carrier	Sorbent	Sorbate	Temperature /°C	Detector	Ref.
Helium	activated charcoal	methane	20–170	TCD	10
	graphitised carbon black	argon, cyclohexane, benzene	100–400	–	11
	ditto	benzene, n-pentane	20	FID	12
	Porapak S	methane	0	"	13
	Chromosorb 101, Chromosorb 104	alkanes, aromatic hydrocarbons, n-alcohols, acids	100	"	14
	Al_2O_3	C_1-C_{10} hydrocarbons	10–250	"	15
	Al_2O_3	n-butane	100	–	16
	13X molecular sieve	H_2, HD, and D_2	−195, −183	TCD	17
	NaY molecular sieve	C_1-C_4 hydrocarbons	20–200	"	18
	Al_2O_3/KCl [a]	buta-1,3-diene	130	FID	19
	Al_2O_3/KCl [a]	propane, isobutane, n-butane	100	"	20
Nitrogen	activated charcoal	benzene, cyclohexane, volatile organic compounds	20, 30, 77, 100	TCD	21–23
	ditto	methane	20–170	"	10
	"	H_2, CO, CH_4, C_2H_4, C_2H_6, C_2H_2	20–40	TCD	15
	graphitised carbon black	argon, cyclohexane, benzene	100–400	"	11
	Al_2O_3	C_1-C_{10} hydrocarbons	100–250	FID	16
	Al_2O_3	n-butane	100	–	19
	NaY molecular sieve	C_1-C_4 hydrocarbons	20–200	TCD	18
	silica gel, activated charcoal, Al_2O_3	mixture of hydrocarbon gases	60–180	"	25
	Al_2O_3/KCl [a]	buta-1,3-diene	130	FID	19
	Al_2O_3/KCl [a]	propane, isobutane, n-butane	100	"	20
Hydrogen	graphitised carbon black	argon, benzene, cyclohexane	100–400	–	11
	Porapak Q	Kr, CO_2, H_2O, C_2H_6,C_2H_4, C_2H_2, C_3H_8, C_3H_6	70	TCD	25
	Al_2O_3	C_1-C_{10} hydrocarbons	100–250	FID	15
	Al_2O_3	n-butane	100	–	16
	13X molecular sieve	H_2, HD, D_2	−195, −183	TCD	17
	NaA molecular sieve	hydrogen isotopes	(−221)–(−161)	"	27
	silica gel, activated charcoal, Al_2O_3	mixture of hydrocarbon gases	60–180	"	25
	Al_2O_3/KCl [a]	buta-1,3-diene	130	FID	19
	5A molecular sieve [a]	CO, N_2, CH_4, C_2H_2, He, Ne, Ar, Kr, Xe	60, 100, 120	TCD	28

Table 1 (continued).

Carrier	Sorbent	Sorbate	Temperature /°C	Detector	Ref.
Hydrogen	5A molecular sieve [a]	He, O_2, N_2, CH_4, CO	25	TCD	29
	13X molecular sieve [a]	naphthene and paraffin factions of petroleum	150	FID	30
	Al_2O_3	C_1-C_{10} hydrocarbons	100 – 250	FID	15
D_2	5A molecular sieve	hydrogen isotopes	(−221) – (−161)	TCD	27
HD	ditto	ditto	(−221) – (−161)	"	27
Argon	activated charcoal	methane	20 – 170	"	10
	graphitised carbon black	cyclohexane, benzene	(−263) – 127	–	11
	Porapak S	methane	0	FID	13
	Porapak Q	Kr, CO_2, N_2O, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6	70	TCD	26
	Al_2O_3	C_1-C_{10} hydrocarbons	100 – 250	FID	15
	Al_2O_3	n-butane	100	–	16
	molecular sieves	air	–	TCD	31
Neon	acitvated charcoal	He + N_2 + Ar + H_2 + CO mixture	45 – 63	"	32
	Al_2O_3	C_1-C_{10} hydrocarbons	100 – 250	FID	15
Krypton	Al_2O_3	C_1-C_{10} hydrocarbons	100 – 250	"	15
Carbon dioxide	Porapak S	methane	0	"	13
	Porapak Q	Cr, CO_2, N_2O, C_2H_6, C_2H_4, C_2H_2, C_3H_8, C_3H_6	70	TCD	26
	Chromosorb 101, Chromosorb 104	alkanes, aromatic hydrocarbons, n-alcohols, organic acids	–	FID	14
	Al_2O_3	C_1-C_{10} hydrocarbons	100 – 250	FID	15
	NaY molecular sieve	C_1-C_{10} hydrocarbons	20 – 200	TCD	18
	molecular sieves	air	–	"	31
	activated charcoal, silica gel, Al_2O_3	mixture of hydrocarbon gases	60 – 180	"	25
	Al_2O_3/KCl [a]	propane, isobutane, butane	100	FID	20
	Al_2O_3 [a]	light organic compounds	50 – 150	"	33
Steam	Chromosorb	butane-2,3-diol, propane-1,2-diol, ethane-1,2-diol	85	FID	34
	Al_2O_3	alcohols, ethers, ketones	–	–	35
	Polysorb	C_5-C_{10} alcohols and acids	230	FID	36
	type Y potassium – barium zeolite	*m*- and *p*-xylenes	–	"	37
	Chromosorb P, AW, Al_2O_3	hydrocarbons	125 – 260	"	38
Nitrogen + steam	silica gel	C_1-C_4 hydrocarbons	–	TCD	39
	graphitised carbon black	methane, propane, isobutane, n-butane	60	FID	40
Helium + steam	teflon	ethene, ethylene glycol, propylene glycol, diethylene glycol	110 – 150	"	41
	KY zeolite	organic oxygen- and nitrogen-containing gases	40 – 300	TCD	42
Steam + ammonia	Al_2O_3	C_8-C_{12} n-paraffins, aromatic hydrocarbons	170	FID	43
Steam + formic acid, hydrazine hydrate	porous glass beads, diatomaceous brick	organic acids and amines	125 – 200	"	44
Ethyne	activated charcoal	methane	20 – 170	TCD	10
Ethyne, propene	Porapak Q	Kr, CO_2, N_2O, C_2H_6, C_2H_4	70	"	27
Methane	silica gel	nitrogen, ethene, propane	75	"	45
Propene, *trans*-but-2-ene	Polysorb 1	silicon tetrachloride	130, 150, 170	"	46

Table 1 (continued).

Carrier	Sorbent	Sorbate	Temperature /°C	Detector	Ref.
Freon 116	silica gel	nitrogen, argon, carbon dioxide, sulfur dioxide	–	FID	47
Tetrachloro-methane, chloro-form, dichloro-methane, ethanol	Porapak Q, Porapak S	ethane, n-butane	90 – 130	TCD	48
Dichloromethane	Polysorb 1	silicon tetrachloride	130, 150, 170	TCD	46
n-Hexane, n-butyl chloride, ethyl acetate, ethanol	silica gel	α- and β-naphthols, phenols, and ethers	190	UVD	49
Ethanol, methanol, propanol	Al_2O_3	anthracene, phenanthrene, *o*-, *m*-, and *p*-dinitrobenzene	140, 160, 210	–	50
Ethanol with added ethylene-cyclohexane	silica gel, Al_2O_3, Spherosil	*o*-, *m*-, and *p*-phenylenediamines, *N*-alkylanilines, isomeric *N*-phenylnaphthylamines	150, 180, 190	UVD	49
n-Hexane, ethanol	chromaton	alkanes, aromatic hydrocarbons, n-alcohols, ketones	75 – 250	TCD	51
Nitrogen + iso-pentane vapour	5A molecular sieve	oxygen, argon, neon, helium	–	FID	52

Note. The following designations have been adopted: TCD = thermal conductivity detector; FID = flame-ionisation detector; UVD = ultraviolet detector. [a] On capillary columns.

In this review, the authors attempted to survey and analyse the experimental data concerning the dependence of the retention of the compounds chromatographed on the nature and pressure of the carrier gas employed and to assess the possibility of using the carrier gas to increase the selectivity of the separation of the analyte. The physicochemical foundations of the influence of the nature of the carrier gas on the principal characteristics of the chromatographic process are examined for this purpose.

II. The role of the carrier gas in gas – solid chromatography

In the initial period of the development of gas – solid chromatography, nitrogen and air were used as the mobile phase.[21 – 23, 53 – 56] Subsequently, hydrogen [25] and helium [57, 58] also began to be used, which made it possible to improve the characteristics of the chromatographic process by increasing the sensitivity of the thermal conductivity detector. During this period, the principal chromatographic detector was the thermal conductivity detector (TCD). Subsequently individual communications appeared concerning the application of neon,[32, 59] xenon, and krypton [60] as carrier gases, but in the main this was associated not so much with the study of the influence of the nature of the carrier gas on the chromatographic process as with the need to employ highly sensitive ionisation detectors.

The first publications about the systematic investigation of organic and water vapours as carrier gases appeared at the end of the 1950s.[61, 62] However, the saturation of the inert carrier gas with steam had also been used earlier. Thus Turkel'taub *et al.*[39] described the chromatographic analysis of a $C_1 - C_4$ hydrocarbon mixture and other gases on silica gel with addition of steam (1 vol.% – 8 vol.%) to the usual carrier gas. As the content of steam in the mobile phase increased, a decrease in the retention volumes of the components of the mixture analysed and a change in the shape of the peaks were observed. Similar results were obtained by Booker [63] in a study of the chromatographic separation of gaseous hydrocarbons on alumina; he confirmed that the symmetry of the chromatographic zones was significantly improved after the addition of steam to the carrier gas.

Wiseman [58] drew attention to the fact that the width of the elution curves for ethyl acetate and isobutyl alcohol was greater when nitrogen was used as the carrier gas. However, a theoretical justification of this phenomenon was not achieved.

Green and Roy [10] are the authors of the first communication in which a significant change in the retention time of the chromatographed compound was noted after the replacement of one carrier gas by another. The investigators presented the following data concerning the separation of a low-boiling gas mixture (H_2, O_2, N_2, CO, CH_4, CO_2, C_2H_4, and C_2H_6) on activated charcoal at 25 °C for five carrier gases: He, Ar, N_2, air, and ethyne. For example, the retention time of methane assumed the following values (min) other conditions being equal: 34 in helium, 22 in argon, 16 in nitrogen, 15 in air, and 5 in ethyne. Thus the retention increased by a factor of ~ 7 when ethyne was replaced by helium. Satisfactory results in the separation of a complex mixture have been obtained [10] using programmed temperatures (Fig. 1).

A change in the retention volumes when different carrier gases were employed (H_2, He, Ne, and Ar) was noted also in a study of the separation of mixtures of permanent gases on columns with activated charcoals and molecular sieves.[59]

It is known that the sorption of light gases (including carrier gases) in gas – solid chromatography on solid adsorbents may be significant. Thus, carbon dioxide is strongly adsorbed by molecular sieves. Karmen *et al.*[31] pointed out the possibility of using it as the carrier gas, which made it possible to separate nitrogen and oxygen on molecular sieves. When carbon dioxide was replaced by the inert helium, there was virtually no separation.

Further investigations demonstrated that the nature of the carrier gas influences the retention of the chromatographed compounds and this is characteristic of adsorbents of different types. Thus it has been shown that [26] the retention times (retention volumes) of various gases on porous organic polymeric adsorbents of the Porapak Q type diminish appreciably when the heavy

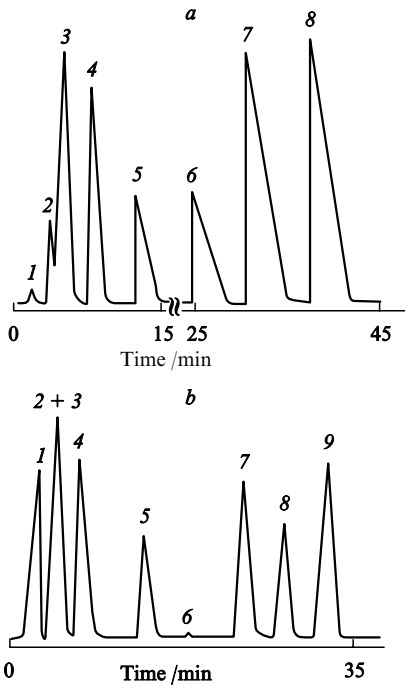


Figure 1. Chromatogram of a gas mixture of organic and inorganic compounds with helium (*a*) and argon (*b*) as the carrier gases;[10]
(*1*) hydrogen; (*2*) oxygen; (*3*) nitrogen; (*4*) carbon monoxide; (*5*) methane; (*6*) carbon dioxide; (*7*) ethyne; (*8*) ethene; (*9*) ethane.
Experimental conditions: column length 3 m, sorbent — activated charcoal (40–60 mesh), temperature programming from 25 °C to 170 °C at 3 K min^{-1} (*a*) and to 160 °C (*b*).

carbon dioxide or gaseous hydrocarbons (ethene and propene) are used as the carrier gas (Table 2).

Vyakhirev and Bruk [64] investigated the influence of the nature of the carrier gas on the chromatographic separation of mixtures of gaseous hydrocarbons on a silica gel column using hydrogen, nitrogen, and carbon dioxide as the carrier gases. The adsorption isotherms and the Henry adsorption coefficients for various carrier gases calculated from them indicate that the degree of

Table 2. Retention volumes (V_R/ml) of certain gases on a packed column with Porapak Q as the adsorbent and different carrier gases.[26]

Sorbate	Carrier gas					
	H_2	N_2	Ar	CO_2	C_2H_4	C_3H_6
Temperature 20 °C						
Kr	24	20	18	17	13	8
CO_2	70	61	53	–	41	23
N_2O	67	88	78	69	57	32
C_2H_6	265	–	–	154	–	–
Temperature 52 °C						
Kr	12	12	11	10	10	7
CO_2	28	27	25	–	23	16
N_2O	38	38	35	32	32	21
C_2H_6	88	84	86	65	61	–
C_3H_8	435	430	425	305	260	–
Temperature 70 °C						
Kr	8	8	8	8	7	5
CO_2	20	19	17	–	16	13
N_2O	24	23	23	22	18	
C_2H_6	50	50	50	46	42	–
C_3H_8	220	220	220	180	155	–

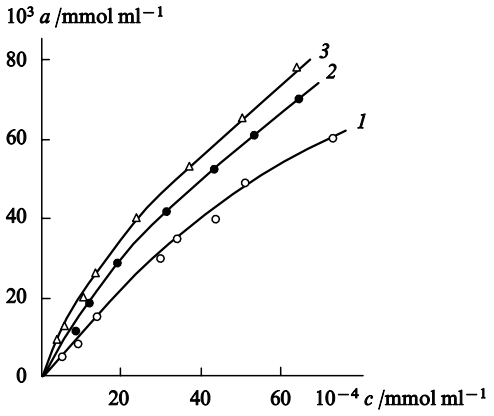


Figure 2. Adsorption isotherms of n-butane on silica gel at 40 °C.[64] Carrier gases: (*1*) carbon dioxide; (*2*) nitrogen; (*3*) hydrogen.

adsorption of n-butane in a flow of CO_2 is lower (Fig. 2) than in N_2 and H_2, which can be explained by the stronger adsorption of CO_2 on silica gel. Accordingly the retention of the components in the separation of a mixture of hydrocarbons is smaller in a flow of carbon dioxide than in a flow of nitrogen and hydrogen. The nature of the carrier gas also influences the shape of the adsorption isotherm (Fig. 2). The isotherms for n-butane in N_2 and H_2 have a more convex form (relative to the abscissa axis), while those in CO_2 are less convex. A certain degree of linearisation of the n-butane isotherm in a flow of CO_2 can undoubtedly be accounted for by the stronger adsorption of carbon dioxide on silica gel compared with the adsorption of nitrogen and hydrogen, *i.e.* by the dynamic modification of the silica gel surface by the adsorbed carbon dioxide molecules.

Turkel'taub and Zhukhovitskii [65] were some of the first investigators to note that the nature of the carrier gas plays a significant role in gas–solid chromatography. This is manifested by a change in the shape of the recorded peaks and in retention when one carrier gas is replaced by another. The adsorption coefficient of the component decreases sharply if its adsorption characteristics are close to those of the carrier gas, and at the same time the carrier gas exerts a significantly smaller influence on the effectively adsorbed component. Modification of the adsorbent surface by molecules of a heavy carrier gas improves the symmetry of the zones of the chromatographed compounds.

The characteristics of the influence of the carrier gas can be explained qualitatively (and in a number of instances also quantitatively) by competitive adsorption and by the employment of the Langmuir equation for binary mixtures in order to interpret the observed phenomena (see, for example, Kel'tsev's monograph [66]).

Thus the first investigations already showed that the mobile phase plays a more important role in gas–solid chromatography than in gas–liquid chromatography.

Subsequent studies were devoted mainly to the establishment of the general quantitative and semiquantitative characteristics of the influence of the nature of the carrier gas and of its pressure on the retention of the chromatographed compounds and also to the theoretical justification of such influence.

III. Gas–solid chromatography on packed columns

1. Gases as the mobile phase

Hoffman and Evans [15] established a linear relation between the retention times of normal hydrocarbons and the reciprocal of the square of the radius of the atom of an inert monatomic carrier gas. However, this relation is doubtful for the following reasons: firstly, the characteristic quantity (chromatographic constant) for the chromatographed substance is not the retention time but

the retention volume [67–69] and, secondly, according to the results obtained by Hoffman and Evans,[15] helium exerts a stronger modifying effect than argon, which conflicts with known data from other investigations.

Brokman *et al.*[16] investigated the influence of the nature of the carrier gas on the interphase equilibrium distribution of the volatile sorbate. The specific retention volume (V_g^T) was selected as the parameter sensitive to the alteration of the nature of the distribution for the given sorbate–sorbent pair at the given temperature. The results obtained, presented in Table 3, enabled the authors to conclude that the distribution constants hardly change on passing from one carrier gas to another. This should imply that the nature of the carrier gas hardly affects the distribution process and that the change in the retention time of n-butane can be explained solely by the different inlet pressures of the carrier gases (two parameters are actually altered — the viscosity and pressure of the carrier gas). It is noteworthy that this is the only study in which it was concluded that the nature of the carrier gas does not influence the retention of the analyte.

Table 3. The specific retention volume of n-butane on a column with activated alumina at a temperature of 100 °C with various carrier gases.[16]

Carrier gas	t /min	P_0 /Torr	James–Martin correction	V_g^T /ml g^{-1}
H_2	4.29	1025	0.830	16.8 ± 0.1
N_2	4.96	1290	0.710	16.6 ± 0.1
He	5.14	1320	0.695	16.9 ± 0.1
Ar	5.24	1420	0.660	16.3 ± 0.1

However, in our view the authors of the above study [16] treated their results incorrectly. The carrier gases arranged in order of decreasing retention volumes (ml g^{-1}) of the chromatographed compounds (*i.e.* in order of increasing influence on the retention volume) form the following series: He (16.9) > H_2 (16.8) > N_2 (16.6) > Ar (16.3). We may note that the accuracy of measurement of the retention volumes in the study under discussion was not less than to within 0.1 ml g^{-1}, so that the sequence presented above ('the influence series') may be regarded as experimentally rigorously established; it confirms the dependence of the equilibrium retention volume on the nature of the carrier gas employed. This sequence is consistent with the adopted idea that the adsorbability of the carrier gas increases in the same series. Thus the conclusion reached by the authors [16] that the retention is independent of the nature of the carrier gas conflicts with their own experimental data.

Gvozdovich *et al.*[14] confirmed the influence of the nature of the carrier gas on the retention of the chromatographed compounds on porous organic polymers (adsorbents). The retention volumes of a series of volatile compounds were measured and compared on Chromosorbs 101, 104, and 106 using strongly adsorbed carrier gases — helium, argon, carbon dioxide, sulfur hexafluoride, and water. The nonpolar Chromosorb 101 is [67] a copolymer of styrene and divinylbenzene, the polar Chromosorb 104 is a copolymer of acrylonitrile and divinylbenzene, while the nonpolar Chromosorb 106 is a polystyrene with a network structure. Table 4 presents the retention volumes of the sorbates when argon and steam are used as carrier gases. Analysis of the tabulated data shows that the replacement of argon by steam influences significantly the retention of the chromatographed compounds, especially polar ones.

It has been established experimentally [14] that the use of heavy carrier gases induces a decrease in the retention volumes when both the weakly specific adsorbent Chromosorb 101 and the highly specific adsorbent Chromosorb 104 are employed. The influence of the nature of the carrier gas intensifies with increase in its adsorbability on the surface of the porous polymer: the energies of the interaction of the carrier gases investigated diminish in the

Table 4. The retention volumes (V_R /ml) of compounds of different classes on polymeric adsorbents at 150 °C using argon and steam as the carrier gases.[14]

Adsorbate	Adsorbent — Chromosorb 110			Adsorbent — Chromosorb 104		
	V_R(Ar)	V_R(H$_2$O)	$\frac{V_R(\text{Ar})}{V_R(\text{H}_2\text{O})}$	V_R(Ar)	V_R(H$_2$O)	$\frac{V_R(\text{Ar})}{V_R(\text{H}_2\text{O})}$
n-Alkanes						
pentane	10.05	6.75	1.55	6.9	2.95	2.34
hexane	22.0	15.10	1.46	14.1	6.75	2.09
heptane	50.4	31.50	1.60	28.7	13.60	2.11
octane	108.0	64.5	1.67	55.9	24.5	2.28
n-Alcohols						
methanol	4.81	3.55	1.35	14.7	8.70	1.69
ethanol	10.5	6.60	1.59	27.4	12.85	2.13
propanol	21.5	15.1	1.42	52.2	24.5	2.13
butanol	48.1	28.2	1.71	109.0	51.0	2.14
n-Acids						
acetic	33.3	37.0	0.90	122.0	114.5	1.07
propionic	72.8	51.0	1.43	223.0	165.0	1.35
butyric	159.0	95.0	1.67	338.0	287.0	1.18
pentanoic	318.0	174.0	1.83	868.0	500.0	1.74

sequence $H_2O > CO_2 > SF_6 >$ He. According to Gvozdovich *et al.*,[14] the dependence of the retention volume on the nature of the carrier gas is a result of the influence of two main processes: the adsorption of the carrier gas on the most active surface centres of the porous polymers (and the partial displacement of the sorbate by the carrier gas) and the interaction of the sorbate and carrier gas molecules.

The active role of the carrier gas in gas–solid chromatography and its influence on the retention have been noted also in the monograph Guiochon and Guillemin.[71] Thus, when n-alkanes were eluted on silica gel of the type of Porasil C (with a specific surface of 50–100 m^2 g^{-1}) using carbon dioxide as the carrier gas at a column temperature of 80 °C, an appreciable decrease (30%–40%) in the retention factor (capacity factor) of the column following an increase in pressure from 1.3 to 5.1 atm was noted.[71] Under these conditions, ~15% of the silica gel surface was covered by adsorbed carbon dioxide molecules.[71]

'Heavy' carrier gases may decrease significantly the adsorbability of the chromatographed compounds and hence influence the separation of gases and volatile compounds, especially when molecular sieves are employed. In gas chromatography on zeolites, the actively adsorbed carrier gases (such as steam and carbon dioxide) are hardly employed because they are selectively and strongly adsorbed by zeolites. For example, Kiselev and Yashin [72] noted that the presence of water and carbon dioxide strongly influences the retention volumes on zeolites. For the stable operation of a column with zeolites, it is therefore necessary to remove thoroughly moisture and carbon dioxide from the carrier gas being analysed.

However, the use of strongly adsorbed carrier gases is in a number of instances justified by the separation of strongly adsorbable sorbates. Thus it has been shown [73] that the use of carbon dioxide as the carrier gas appreciably improves the separation of hydrocarbon gases on zeolites at a low column temperature and reduces the duration of analysis compared with the carrier gases employed traditionally (for example, helium or nitrogen). The nature of the carrier gas strongly influences the separation of hydrocarbon mixtures. For example, a six-component mixture of hydrocarbon gases may be fully separated on the NaY zeolite at 20 °C using carbon dioxide as the carrier gas (Fig. 3), whereas traditional carrier gases (hydrogen or helium) do not ensure the separation of this mixture even at elevated temperatures as a consequence of the strong retention of its components.

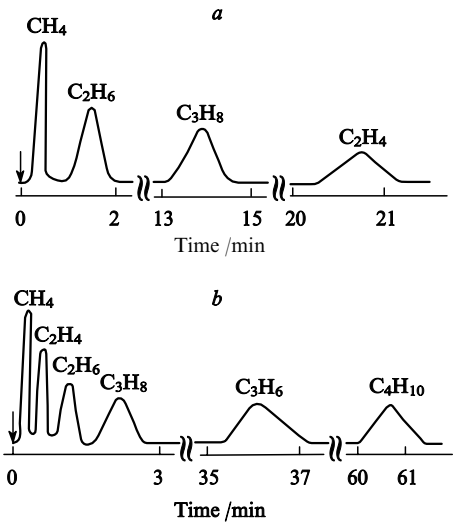


Figure 3. Chromatogram of C_1-C_4 hydrocarbon gases.[73] Experimental conditions: 0.5 m × 4 mm column, adsorbent — NaY, temperature 20 °C. Carrier gases: (*a*) helium; (*b*) carbon dioxide.

It is essential to note that the use of He or N_2 as carrier gases on this form of molecular sieve does not lead to the temperature inversion of the elution sequence of the components for the following pairs of hydrocarbon gases: propane–ethene, butane–propene. However, if the carrier gas is CO_2, then at certain temperatures the elution sequence of the above pairs of organic compounds is inverted. An appreciable decrease in the specific retention volumes of hydrocarbon gases has been noted[73] when carbon dioxide was used as the carrier gas on packed columns with the NaY and CdY zeolites. This effect is manifested most clearly at low column temperatures when CO_2 is appreciably adsorbed on zeolites. A consequence of this is the deactivation of the adsorbent surface.

The absolute retention of the chromatographed compounds on a given packed column is determined not only by the nature of the adsorbent but also by its form — bulk or surface-layer adsorbent. The amount of the adsorbent per unit volume is significantly greater for the traditional (bulk) adsorbent than for the surface-layer adsorbent, so that the use of the latter makes it possible to reduce significantly the retention of the chromatographed compounds, *i.e.* to accelerate the analysis.

Andronikashvili, Berezkin, and coworkers investigated the joint influence of the carrier gas, the type of the adsorbent (bulk or surface-layer),[18,74] and the nature of the cation in the zeolite[74] on the chromatographic separation process. The retention times of the individual hydrocarbons in the NaY zeolites in the traditional and surface-layer forms are presented in Table 5. For all the hydrocarbons investigated and for all the carrier gases, a significant decrease in the retention time is observed on passing from the bulky to the surface-layer sorbents. The nature of the carrier gas also influences to an appreciable degree the retention times of the sorbates: the longest retention time is in helium, a shorter one is in nitrogen, and a still shorter retention time occurs in carbon dioxide. If the carrier gas is CO_2, its displacement effect can be made use of in many instances, *i.e.* carbon dioxide may serve simultaneously as a carrier gas and as a displacing gas.[18,74]

Using a mixture containing n-alkanes, Andronikashvili *et al.*[74] showed that the employment of carbon dioxide as the carrier gas and of surface-layer zeolite adsorbents improves significantly the effectiveness of chromatographic columns, reduces the duration of the analysis, and makes it possible to obtain a more symmetrical peak and also to expand appreciably the range of compounds which may be analysed on zeolites. The chromatograms for the separation of a mixture of hydrocarbons are presented in Fig. 4.

Thus, when account is taken of the foregoing, it is justifiable to recommend a wider application of CO_2 as the carrier gas in gas–solid chromatography on zeolites in the form of surface-layer adsorbents.

Parbuzin and Guliants[27] proposed a version of gas–solid chromatography using adsorbable carrier gases (hydrogen deuteride and deuterium) as well as protium for the separation of a five-component mixture (hydrogen deuteride and the *o*- and *p*-isomers of hydrogen and deuterium) on a column with the NaA molecular sieve at a temperature in the range between −321 and −161 °C. The employment of the traditional version of gas–solid chromatography using inert carrier gases for the physicochemical investigation of the adsorption of hydrogen isotopes and isomers is restricted by the 'zero' degree of surface coverage of the adsorbent and by the temperature (−173 °C). The appearance of 'negative' peaks can be explained by the greater thermal conductivity of certain sorbates compared with that of the carrier gas. The application of deuterium-containing carrier gases which are adsorbed at low temperatures made it possible to obtain extensive

Table 5. The retention time of C_1-C_4 hydrocarbon gases (t_R /s) on a packed column with the NaY zeolite using helium, nitrogen, and carbon dioxide as the carrier gases.[18]

Sorbate	Helium			Nitrogen			Carbon dioxide		
	t_R(TAD)	t_R(SLAD)	$\frac{t_R(\text{TAD})}{t_R(\text{SLAD})}$	t_R(TAD)	t_R(SLAD)	$\frac{t_R(\text{TAD})}{t_R(\text{SLAD})}$	t_R(TAD)	t_R(SLAD)	$\frac{t_R(\text{TAD})}{t_R(\text{SLAD})}$
Temperature 20 °C									
CH_4	17.0	5.0	3.4	36.0	5.0	7.2	9.0	5.0	1.8
C_2H_6	115.0	10.0	11.5	108.0	10.0	10.8	50.0	8.0	6.3
C_3H_8	848.0	48.0	17.7	–	47.0	–	353.0	20.0	17.7
C_4H_{10}	–	329.0	–	–	–	–	4228.0	93.0	45.5
C_2H_4	1308.0	70.0	18.7	–	80.0	–	208.0	14.0	14.9
C_3H_6	–	–	–	–	–	–	2248.0	85.0	26.5
Temperature 100 °C									
CH_4	12.0	5.0	2.4	10.0	4.0	2.5	7.0	4.0	1.8
C_2H_6	46.0	7.0	6.6	41.0	7.0	5.9	25.0	5.0	5.0
C_3H_8	241.0	15.0	16.1	210.0	14.0	15.0	102.0	11.0	9.3
C_4H_{10}	1350.0	65.0	20.8	1005.0	62.0	16.2	555.0	40.0	13.9
C_2H_4	225.0	14.0	16.1	181.0	10.0	18.1	71.0	9.0	7.9
C_3H_6	2008.0	73.0	27.5	1315.0	68.0	19.3	450.0	36.0	12.0

Note. The following designations have been adopted: TAD = traditional (volumetric) adsorbent; SLAD = surface-layer adsorbent.

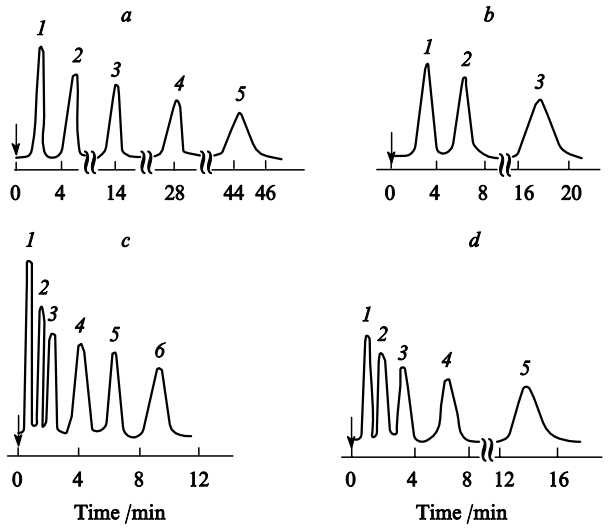


Figure 4. Chromatogram of a mixture of C_5-C_{10} hydrocarbons on a packed column (0.5 m × 4 mm) with the HY zeolite;[74]
(*a*) and (*b*) volumetric adsorbent, temperature 300 °C; (*c*) and (*d*) surface-layer adsorbent, temperature 225 °C. Carrier gases: (*a*) and (*c*) carbon dioxide; (*b*) and (*d*) helium. Sorbates: (*1*) pentane; (*2*) hexane; (*3*) heptane; (*4*) octane; (*5*) nonane; (*6*) decane.

information about the adsorption of such compounds on solid absorbents over a wide temperature range and for different degrees of surface coverage of the adsorbent and also to separate the spin isomers and isotopes of hydrogen and to improve the symmetry of the peaks due to the components being separated (Fig. 5).[27]

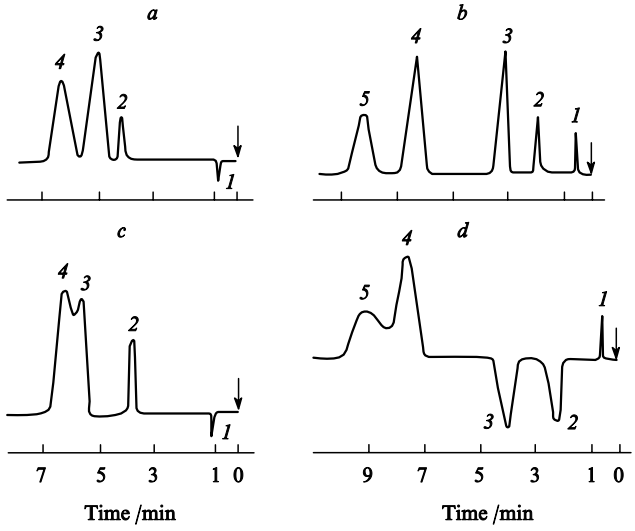


Figure 5. Chromatograms of a five-component mixture of isotopic and spin modifications of molecular hydrogen obtained on packed columns with the NaA zeolite using various carrier gases;[27]
(*a*) carrier gas helium, 2 mm × 3 mm column, temperature −140 °C; (*1*) ^3He; (*2*) H_2; (*3*) HD; (*4*) D_2; (*b*) carrier gas — protium, 0.8 m × 2 mm column, temperature −209.5 °C; (*1*) He; (*2*) H_2; (*3*) HD; (*4*) *o*-D_2, *p*-D_2; (*c*) carrier gas — deuterium, 0.6 m × 2 mm column, temperature −195.7 °C; (*1*) He; (*2*) *p*-H_2; (*3*) *o*-H_2; (*4*) HD; (*d*) carrier gas — hydrogen deuteride 0.45 m × 3 mm column, temperature −209.8 °C; (*1*) He; (*2*) *p*-H_2; (*3*) *o*-H_2; (*4*) *o*-D_2; (*5*) *p*-D_2.

2. The use of pure vapours of polar compounds or their mixtures in an inert carrier gas as the mobile phase for the dynamic modification of adsorbents

The vapours of highly polar organic and inorganic compounds, which are used as the mobile phase in a pure form or as an admixture in a fairly inert carrier gas, exert a strong and frequently nontraditional influence on the retention and the shape of the recorded peaks for the analytes. In this version of gas–solid chromatography, the mobile phase is, firstly, a transporting agent which moves the zones of the compounds separated along the column and, secondly, an agent modifying the adsorbent surface. The adsorbability of the sorbate in the mobile phase–sorbing medium system and hence the retention are altered as a result of the modification (the retention is usually reduced); the phase equilibrium of the sorbate in the mobile phase–adsorbent system is disturbed as a consequence of the nonideality of the mobile phase, which is usually manifested to an appreciable degree at an elevated pressure; the 'sensitivity of the detector' to the analytes is changed (in some cases, its increase is observed).

In the first studies employing organic eluents,[61] steam,[34,35,64] and of these substances as additives to the conventional carrier gases,[39,52] it was shown that transition to organic and mixed eluents significantly alters in many instances the picture in the gas-chromatographic separation of substances. The nature of the mobile phase influences appreciably both the retention of the chromatographed compound and the shape of the recorded peaks. For example, the vapours of the following substances may be used as the eluent (or its component): water,[38,39,42–25,62] ethanol,[41,48–50] carbon tetrachloride,[48] n-hexane, n-butyl chloride, ethyl acetate,[49] *etc*. Steam is most often employed[38,39,42–45,62,75] and in this instance one speaks of a special vapour-phase version of chromatography.

The vapours of organic compounds as the mobile phase in gas–solid chromatography. The characteristic features of the application of gases and organic vapours as carrier gases and also as additives to the usual carrier gases have been examined in detail.[76,77] The authors note that in a traditional variant of gas chromatography at low pressures, the mobile phase performed as a rule the function only of the agent transporting the substances being separated along the column, which unjustifiably narrows the role of the carrier gas.

In the literature, it is possible to find numerous examples illustrating the influence of vapour-like mobile phases (VMP) on the results of the chromatographic process. For example, Tsuda *et al*.[49] present data demonstrating clearly the significant influence of the nature of the carrier gas on the retention volumes and the chromatographic separation of the analytes. Thus, when ethanol is used as the carrier gas and alumina as the adsorbent, the retention volume of benzene constitutes one hundredth of its retention volume when the carrier gas is nitrogen while the adsorbent is the same. The retention of benzene on a column with Porapak Q changes by 60% when the N_2 carrier gas is replaced by CCl_4 vapour. Similar results have been obtained also for other chromatographic systems.

A dependence of the retention volumes of the sorbates on the eluting power of the mobile phase, which is 0.00 for n-hexane, 0.30 for n-butyl chloride, 0.58 for ethyl acetate, and 0.88 for ethanol, is observed in gas–solid chromatography employing VMP (in both liquid and thin-layer chromatography).[49] With decrease in the eluting power, the retention volumes increase appreciably (Fig. 6), but the general characteristics of the retention, known for the carrier gases employed traditionally, are retained. Thus the linear dependence of the logarithms of the retention volumes of the sorbates on their boiling points is observed for all the vapour systems investigated. Tsuda and Ishii[48] also noted a change in the elution order for a mixture of n-hexane, cyclohexane, and benzene (Fig. 6). When helium is used as the carrier gas, the compounds are eluted in order of increasing boiling point [n-hexane (69 °C),

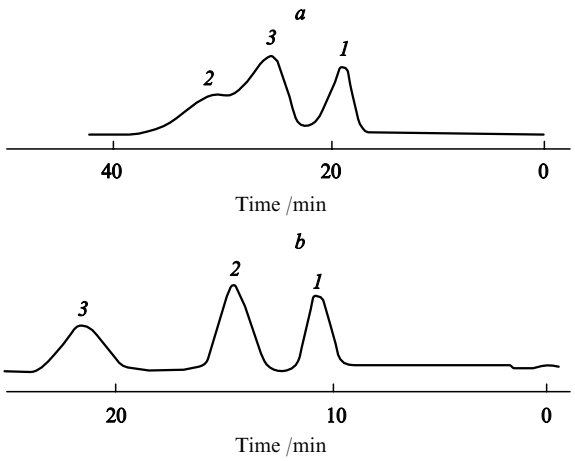


Figure 6. The change in the retention of C_6 hydrocarbons after the replacement of helium (*a*) by carbon tetrachloride vapour (*b*).[48]
Experimental conditions: 1 m × 3 mm column, adsorbent — Porapak S (80–100 mesh). Sorbates: (*1*) n-hexane; (*2*) cyclohexane; (*3*) benzene.

benzene (80 °C), cyclohexane (81 °C)], while in the case where organic eluents are employed the elution order is determined by the polarisabilities of the chromatographed compounds and the retention time increases in the sequence n-hexane < cyclohexane < benzene.

Kyazimov and Agaeva[51] investigated the retention of compounds of different classes (n-paraffins and aromatic hydrocarbons, n-alcohols, and ketones) on packed Chromaton-filled columns at different temperatures (75–250 °C) in a stream of hexane and ethanol vapours.

Multicomponent vapour-phase eluents are used in gas–solid chromatography and the components of such mixtures may be not only organic vapours but also permanent gases, steam, ammonia, *etc*. Such an approach makes it possible to regulate the selectivity

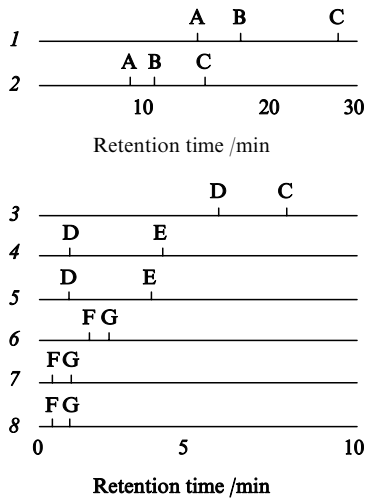


Figure 7. Chromatographic spectra indicating the influence of the nature of the mobile phase on the retention of sorbates.[49]
Carrier vapour: (*1*) benzene; (*2*) ethanol containing 10% of benzene; (*3*) and (*6*) ethanol containing 1% of isooctane; (*4*) and (*7*) ethanol; (*5*) and (*8*) ethanol containing 1% of methanol; flow rate 200 μl min^{-1}. Sorbates: A = phenol; B = *o*-cresol; C = *m*-cresol; D = *p*-diisopropylbenzene; E = admixture in component D; G = cumene; F = admixture in component G. Adsorbent: (*1*) and (*2*) silica gel K-923, 50 cm × 3 mm column, temperature 140 °C; (*3*)–(*8*) aluminium oxide, 1 m × 2 mm column, temperature 150 °C.

of the chromatographic system within very wide limits by varying the composition of the eluent and the concentration of the polar component. For example, in the analysis of a mixture of α- and β-naphthols on a silica gel column, the retention time of the naphthols increased by 5–8 min if a mixture of ethanol and water vapours[49] and not pure ethanol served as the eluent.[49] Similar effects were observed also when the vapours of mixtures of ethanol with methanol, isooctane, benzene,[49] and hexanes were employed.

The influence of the nature and composition of the eluent on the retention of the sorbate is illustrated in Fig. 7. Tsuda *et al*.[49] suggested that, when the carrier gas is adsorbed on the adsorbent surface, a thin layer of a modifying film is probably formed, which weakens the interaction of the analysed components and the adsorbent and hence accelerates their elution from the column. According to their data,[49] the thickness of the film is 2–10 molecules when ethanol is used as the carrier gas and alumina as the adsorbent at temperatures of 100–150 °C.

Steam as the mobile phase in gas–solid chromatography. Many investigators have paid particular attention to water as the mobile phase in gas–solid chromatography. Steam is capable of modifying the surfaces of solid adsorbents. As the mobile phase in gas–solid chromatography, water has the following advantages over other compounds: (1) it is a polar compound actively interacting (usually with formation of hydrogen bonds) with the polar groups, for example, the silanol groups, on the surfaces of solids; (2) the adsorbed water may interact with the polar components of the mixtures analysed, actively altering their retention; (3) water is a relatively stable compound and it can therefore be used for modification at high temperatures; (4) pure water is a comparatively cheap product; (5) water hardly gives rise to a signal when a flame-ionisation detector is used.

In the first communications concerning the employment of steam as the mobile phase[62] and also in subsequent studies,[35, 44, 54, 79] an advantage of the steam eluent, such as the blocking of the active centres on solid carriers and adsorbents promoting the appearance of symmetrical peaks in the separation of polar substances and the acceleration of analysis, was pointed out.

Sultanovich *et al*.[80] showed that, in the separation of high-boiling and polar compounds on Silochrom 80, the replacement of nitrogen as the carrier gas by steam lowers the retention times of the test components and leads to the formation of symmetrical peaks. The authors explained the influence of steam on chromatographic separation, firstly, by the blocking of individual active centres on the adsorbent surface by water molecules and, secondly, by the fact that the surface of Silochrom is covered by a thin water film, formed as a consequence of the multilayer adsorption of water and playing the role of a quasi-stationary phase. Since the usual vapour pressure of water under the conditions of the chromatographic experiment is many times greater than the partial pressure of water in the mobile phase, the thickness of the water film is extremely small and its properties differ from those of ordinary water at the temperature of the analysis. The nonideality of the gas phase can apparently also exert a small influence on the retention.

Thus steam improves the chromatographic properties of adsorbents (and in particular Silochrom) as well as the special (usually irreversible) methods for the modification of silica gels.

When any phenomenon is investigated, it is important to discover definite functional relations. It has been established[81] that an increase in the steam content in the carrier gas leads to more complete deactivation of the active centres (Fig. 8). The logarithms of the retention factor decrease linearly under these conditions, which is naturally most notable in the separation of polar compounds (for example, acetone and ethyl methyl ketone). This feature is of definite interest for the development of analytical methods and their optimisation.

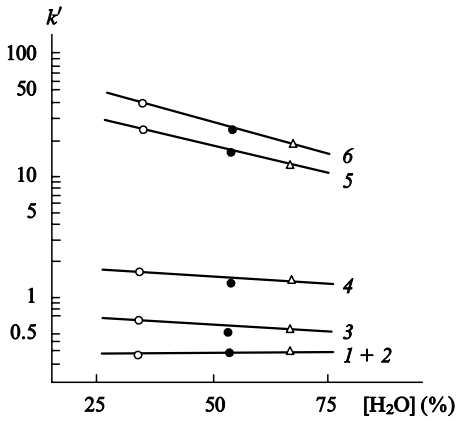


Figure 8. Dependence of the retention factors of sorbates on the content of water vapour in the carrier gas.[81]
Experimental conditions: 2 m × 4 mm column, adsorbent — Spherosil, 150–200 μm, column temperature 115 °C, carrier gas — nitrogen + water vapour, flow rate 50 cm^3 min^{-1}. Sorbates: (*1*) 3-methylpentane; (*2*) cyclohexane; (*3*) n-heptane; (*4*) 1,2-dichloroethane; (*5*) acetone; (*6*) ethyl methyl ketone.

Rakhmankulov and Vigdergauz[43] investigated the possibility of modifying adsorbents by employing steam as the eluent in the pressure range from 1.6 to 7.2 atm in a chromatographic column filled with alumina (Table 6). In the case of nonpolar sorbates, a sharp decrease in the specific retention volume with increase in pressure was noted (by a factor of several tens for high-boiling paraffins). The authors explain this effect by the formation of an adsorbed water layer on the Al_2O_3 surface, although they do not rule out also the influence of the nonideality of the mobile phase. Unfortunately, no direct experiments permitting the characterisation of the state of water on the alumina surface were performed.

Table 6. The specific retention volumes (V_g^T/ml g^{-1}) of sorbates at different pressures of the eluent (steam).[43]

Sorbate	Eluent pressure /atm			
	1.6	4.1	5.6	7.2
n-Octane	3.52	1.22	1.02	–
n-Nonane	6.3	2.28	1.54	–
n-Decane	11.48	3.82	2.31	1.54
n-Undecane	20.94	6.34	3.41	2.17
n-Dodecane	38.0	10.45	5.11	2.98
n-Tridecane	109.7	17.7	11.48	5.96
n-Pentadecane	187.7	45.06	16.86	8.43
n-Hexadecane	320.2	–	–	12.6
n-Heptadecane	545.0	–	–	17.6
n-Octadecane	926.8	–	–	24.4
n-Nonadecane	1575.0	–	–	32.8
n-Eicosane	2676.0	–	–	45.8
Isopropylbenzene	7.78	3.78	2.91	2.09
Acetone	3.72	3.78	3.76	3.02
Butyl acetate	35.76	20.56	11.86	7.78
Ethanol	10.6	6.91	6.3	–
Pyridine	14.26	10.82	10.19	8.00

It is of interest that the retention of polar sorbates soluble in water decreased less than that of nonpolar sorbates with increase in the water vapour pressure. A sharp decrease in the retention of n-alkanes leads to a significant increase in the Kovats indices (with n-alkanes as the standard) for polar compounds. For example, the retention index of pyridine at 7.2 atm is higher by 454 units than at 1.6 atm.[43] Such results indicate the possibility, in principle, of the group separation of nonpolar and polar compounds at an elevated vapour pressure.

In the separation of polar amines and organic acids, chromatographers encountered certain difficulties due to the reversible, semireversible, and irreversible adsorption of the compounds on the surface of the solid support (see, for example, Berezkin[82,83]). Modification of the surface of the solid support by acid compounds (for the elution of acids) or basic compounds (for the elution of amines) usually permits a satisfactory solution of this problem.

We may note a non standard, in our view, solution of certain analytical problems in steam chromatography. Nonaka[44] suggested that an acid or basic modified surface be created by adding an acid (formic acid) or basic (hydrazine hydrate) reagent to the steam, which makes it possible to separate organic acids (with formic acid as the modifying agent) or amines (with hydrazine hydrate as the modifying agent).

Unusual results have been obtained on KY zeolites using a moist carrier gas.[42] As noted above, the employment of a moist carrier gas is not recommended in gas chromatography. However, interesting results were obtained when the latter was employed. The water absorbed by the zeolite exerts a significant influence on its chromatographic properties (Fig. 9). At low temperatures, where much water is still adsorbed in the zeolite cavities, the specific retention volumes (V_d^T), for example, of ethane, decrease sharply and almost linearly with increase in the partial pressure of steam in the adsorbent–sorbate system. With increase in temperature against the background of an overall decrease in the retention volumes of the sorbates, a tendency towards a retardation of the decrease in V_d^T is manifested appreciably. At the minimum water vapour pressure (0.35 atm) and $T > 100$ °C, the opposite tendency towards an increase in the retention volumes of the chromatographed compounds is observed. An increase in the partial pressure of steam in the zeolite–sorbate system leads to a mutual approach, in terms of time, of the chromatographic zones of the eluted components owing to the intensifying shielding of the adsorption centres (in the first place cations) by water molecules and the duration of the chromatographic separation is also diminished. It is necessary to note that, when a moistened carrier gas is employed, the effectiveness of the separation of volatile compounds on zeolites increases appreciably. Thus the use of steam as the modifying agent for molecular sieves is, in our view, of interest and this version of chromatography can be easily realised in practice.

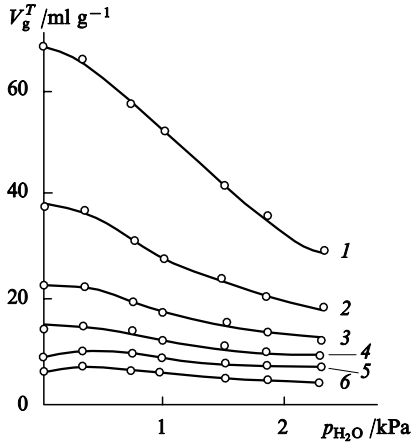


Figure 9. Dependence of the specific retention volume of ethane on the partial pressure of water vapour.[42]
Experimental conditions: 1 m × 3 mm column, adsorbent — KY zeolite. Temperature (°C): (*1*) 60; (*2*) 80; (*3*) 100; (*4*) 120; (*5*) 140; (*6*) 160.

Modification of the adsorbent surfaces by water-soluble hydrophilic inorganic salts constitutes a possible new solution of the problem of creating selective polar sorbents for steam chromatography. Only the steam version gas–liquid chromatography has been realised at the present time.[84–86] A new class of stationary liquid phases (aqueous salt solutions), which we have proposed, is autostable under the conditions of steam chromatography. On contact with steam over a wide range of temperatures, many salts form aqueous solutions which are characterised by a very high selectivity.[84–86] This principle can undoubtedly serve as the basis of the modification of the surface of the adsorbent: if a salt is deposited on its surface at very low concentrations (~0.1%–0.01%), then aqueous salt phases are formed under the conditions of steam chromatography.

In conclusion, we may note that the use of steam significantly expands the possibilities of the traditional gas chromatography and in many instances permits an appreciable improvement of the separation process. It is noteworthy that the characteristics of steam chromatography (with steam or the vapours of other organic compounds) and liquid chromatography are similar. The introduction to the gas-chromatographic practice of its steam version will undoubtedly make it possible to simplify the solution of many practical problems.

IV. Capillary gas–solid chromatography

Capillary gas chromatography is nowadays most actively employed. Thus, according to Berezkin's data,[87,88] more than 83% of the publications devoted to chromatographic problems relate to capillary gas chromatography; according to McNair's data,[89] 80% of the gas-chromatographic columns sold are capillary columns. A new type of capillary column — open (tubular) capillary gas–solid columns — has been successfully introduced into analytical practice. The characteristics influencing the changes in the retention of chromatographed compounds, for example characteristics such as the nature and pressure of the carrier gas, assume a particular importance in capillary chromatography. (The influence of these characteristics on the resolution had been established earlier for packed columns.)

A series of publications have been devoted to the theoretical and experimental study of the role of the carrier gas in capillary gas–liquid chromatography.[90–94] The influence of the average column pressure of the carrier gas in the column on the retention volumes and indices at an inlet pressure > 5 atm at the inlet to the capillary column has been demonstrated experimentally.[90–92] This is significantly greater than the pressure of the carrier gas in the traditional analytical experiment. The importance and value of the results obtained for the usual routine chromatographic analysis therefore remained obscure.

Berezkin and Korolev[93,94] were the first to show that the relative retention data (retention factor, relative retention, and retention index) in capillary gas–liquid chromatography depend on the nature of the carrier gas and its average column pressure under the conditions of the traditional analytical experiment, *i.e.* at inlet pressures less than 3–5 atm.

Bearing in mind the common nature of the processes in gas–liquid and gas–solid chromatography, one may expect a dependence of the retention on the pressure and nature of the carrier gas for both types of chromatography.

Berezkin and Volkov[20] confirmed a previously established feature of chromatography in a gas–solid system, namely the relation between the retention and the nature of the carrier gas. It was shown that transition from light carrier gases to heavy ones leads to a dynamic modification of the adsorbent surface by the carrier gas molecules and hence to a decrease in the partition coefficients of the chromatographed compounds in the solid adsorbent–carrier gas system and therefore to a decrease in the retention time. The experimental data obtained on a Chrompack capillary gas–solid column (50 m × 0.32 mm) with alumina at 100 °C may serve as an example illustrating the dependence of the retention factors of hydrocarbon gases on the nature of the carrier gas:[20] the retention for C_3–C_4 hydrocarbon gases are virtually the same when helium and nitrogen are used as carrier gases but decrease significantly when they are replaced by carbon dioxide. For example, the retention factors diminished by ~30% following the replacement of nitrogen by carbon dioxide.[17] Thus, by selecting the carrier gas, it is possible to reduce significantly the duration of the chromatographic experiment.

Two studies by Berezkin and coworkers[95,96] were devoted to the systematic investigation of the influence of the average column pressure of the carrier gas in the column on the relative retention of the chromatographed compounds in high-performance capillary chromatography in a gas–solid system. Different carrier gases and pressure ranges traditionally employed in analytical capillary gas chromatography (1–5 atm at the inlet to the capillary column) were used. The results of the study of the dependence of the retention factors of hydrocarbon gases on a capillary column with alumina modified by potassium chloride on the average column carrier gas pressure in the column are presented in Table 7.[96] It is seen that the retention depends both on the nature of the carrier gas and on its column pressure.

Table 7. The retention factors of hydrocarbon gases at different carrier gas pressures in a capillary column with Al_2O_3/KCl (temperature 90 °C).[96]

P /atm	Propene	Butane	But-1-ene
Carrier gas — helium			
1.0	0.88	1.68	3.66
4.1	0.88	1.69	3.63
Carrier gas — hydrogen			
1.0	0.80	1.51	3.27
3.4	0.81	1.53	3.22
Carrier gas — nitrogen			
1.0	0.87	1.65	3.61
4.1	0.85	1.59	3.45
Carrier gas — carbon dioxide			
1.0	0.64	1.17	2.46
4.1	0.44	0.80	1.58

The influence of steam as the modifier of the Al_2O_3 adsorbent surface on the change in retention in capillary gas–solid chromatography has been noted by de Nijs.[97] Water is strongly adsorbed on the hydrophilic surface of the polar alumina, which lowers its sorption activity. With increase in the concentration of water in the carrier gas (and hence on the adsorbent surface), the retention factors of the sorbates are therefore reduced.

Not only the nature of the carrier gas but also the characteristics of the chromatographic system as a whole exert a significant influence on the retention of the sorbate. In this connection, one should note the study of Armstrong *et al.*,[98] who investigated the influence of steam and carbon dioxide on the characteristics of two capillary adsorption columns, in one of which alumina and in the other GasPro™ were employed as the adsorbents. Water and carbon dioxide are known to influence strongly the retention and selectivity in the separation of sorbates and also the effectiveness of the operation of the chromatographic column, for example, an alumina column.[30,99–101] In contrast to columns based on alumina, neither water, nor carbon dioxide nor sulfur-containing gases are adsorbed appreciably on the surface of capillary columns with GasPro™ and they do not therefore influence the separation of the analytes and the column characteristics.[98] Figure 10 presents the results of the study of the influence of the repeated introduction of water samples and aqueous acetone samples on the retention of the analytes. Evidently even repeated introduction of water samples does not affect the column characteristics, the retention, and the separation of the analytes. The retention of the chromatographed compounds hardly depends on the water vapour pressure on the nonpolar adsorbent GasPro™ and this

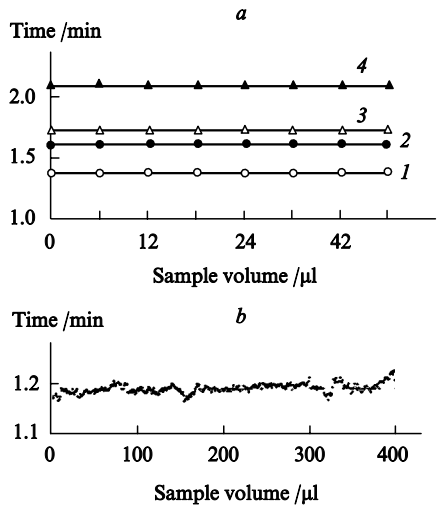


Figure 10. The influence of repeated introduction of samples of water (*a*) and an aqueous sample of acetone (*b*) on the retention times of the compounds analysed on a GasPro^{TM} capillary column.[98]
Experimental conditions: (*a*) 30 m × 0.32 mm column, carrier gas — nitrogen (40 cm s^{-1}), temperature 85 °C; (*b*) 5 m × 0.32 mm column, carrier gas — helium. Sorbates: (*1*) methane; (*2*) ethane; (*3*) ethene; (*4*) ethyne.

enabled the authors of the present review to express the view that the principal processes in the carrier gas–chromatographed compound interaction occur on the surface of the solid adsorbent and that the influence of these interactions in the gas phase is slight for the systems investigated.

Many gases and volatile compounds are retained fairly strongly on GasPro^{TM} columns, but in relation to organic compounds of various classes these columns are more inert than those with alumina. Consequently, the compounds analysed, which undergo catalytic degradation on Al_2O_3 at elevated temperatures, may be readily separated and determined quantitatively on GasPro^{TM} columns.

Thus the nature of the carrier gas and its pressure are important characteristics of the chromatographic experiment. The study of the characteristic features of the variation of the retention factors (capacity factors) of the chromatographed compounds on passing from one carrier gas (G_1) to another (G_2) on the same chromatographic column is of practical interest in this connection. The following correlation has been established recently (Fig. 11):[101]

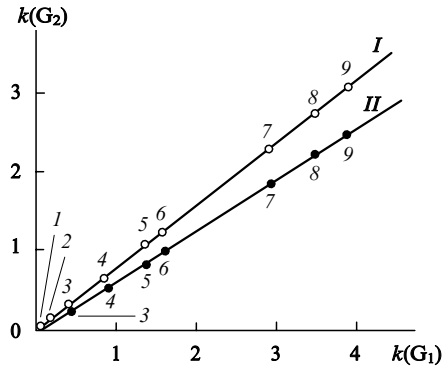


Figure 11. Correlation between the retention factors using the carrier gases $G_1 = H_2$. $G_2 = N_2$ (*I*) or CO_2 (*II*).[101]
Experimental conditions: 50 m × 0.32 mm column, adsorbent — Al_2O_3/KCl, T = 90 °C. Chromatographed compounds: (*1*) ethane; (*2*) ethene; (*3*) propane; (*4*) propene; (*5*) isobutane; (*6*) n-butane; (*7*) *trans*-but-2-ene; (*8*) isobutene; (*9*) *cis*-but-2-ene.

$$k(G_2) = Ak(G_1) + B\,, \tag{6}$$

where $k(G_1)$ and $k(G_2)$ are the retention factors (capacity coefficients) of the compound when the carrier gases G_1 and G_2 respectively are employed and A and B are constants.

Experimental studies performed using various chromatographic systems revealed the following features of the influence of different carrier gases on the retention.

1. Permanent carrier gases (helium, hydrogen, argon, nitrogen, *etc.*), as well as carbon dioxide exert an appreciable influence on the retention of the chromatographed compounds. The influence of such carrier gases on the retention usually increases in the sequence helium < hydrogen < nitrogen < carbon dioxide. The relations established may be used to reduce (by 20% – 30%) the retention, *i.e.* to reduce the duration of the chromatographic process, and for the deliberate alteration of the selectivity of the separation.

2. Steam as well as the vapours of organic compounds (carbon tetrachloride, ethanol, *etc.*) influence to a greater extent the retention process than gaseous eluents. The change in retention is especially significant when 'strong' adsorbents are employed (for example, adsorbents of the type of molecular sieves, organic polymeric adsorbents, *etc.*). A change in the elution sequence of the analytes after the replacement of the mobile phase has been noted for a series of chromatographic systems investigated.

3. On passing from one carrier gas to another, it is possible to determine the retention of the chromatographed compounds for 'another' carrier gas using the linear correlation equation.

The studies of the influence of the carrier gas on retention cannot be regarded as complete. By no means all the new analytical possibilities of gas–solid chromatography, determined by the rational selection of the active mobile phase, have been discussed and examined in the literature. Thus the influence of superheavy carrier gases (for example, SF_6) using specific adsorbents such as molecular sieves, *etc.* has not been investigated systematically.

The expansion of steam chromatography is held back, in our view, by the lack of simple and effective apparatus permitting the performance of the steam chromatographic process on any gas chromatograph.

V. Theoretical aspects of the influence of the nature of the carrier gas and of its pressure on the retention in gas–solid chromatography

1. The retention of a strongly adsorbed sorbate in a poorly adsorbed carrier gas

The mechanism of retention has been discussed in detail in monographs.[1, 2, 6, 71, 102, 103] Kiselev *et al.*[6, 103] proposed the concept of the net retention volume for gas–solid chromatography and showed that the net retention volume V_N is directly proportional, firstly, to the surface area of the adsorbent (S) in the column (it is postulated that the accessibility of the adsorbent surface does not change for low degrees of coverage of the latter) and, secondly, to the partition coefficient [see Eqn (3)].

The net retention volume can be determined from the equation

$$V_{Ni} = V_{Ri} - V_M\,, \tag{7}$$

where

$$V_{Ri} = t_R F j\,,$$

$$V_M = t_M F j\,, \tag{8}$$

t_R is the retention time of the sorbate, F the flow rate of the carrier gas at the column outlet, j the James–Martin correction taking into account the pressure drop along the column, V_M is the dead retention volume, and t_M is the dead time.

Naturally Eqn (7) should be modified in relation to specific cases (for example, when it is necessary to take into account the

nonideality of the carrier gas, the nonlinearity of the adsorption isotherm for the chromatographed compound, *etc.*).

In the monograph by Zhukhovitskii and Turkel'taub,[4] attention is drawn to the fact that in gas–solid chromatography account should be taken primarily of the influence of the carrier gas on the sorbability of the components of the mixture being separated (Table 8). In discussing the results of a study of the retention of the components of four mixtures (propane–butane, helium–methane, carbon monoxide–methane, helium–carbon monoxide) on the AG-2 charcoal using three carrier gases (hydrogen, air, and carbon dioxide) at 25 °C, the authors note that the retention volume of a poorly sorbable substance diminishes sharply when hydrogen is replaced by carbon dioxide.

Table 8. The influence of the nature of the carrier gas on the separation of mixtures using the AG-2 charcoal as the adsorbent (temperature 25 °C).[4]

Carrier gas	Mixture	V_N/ml
Carbon dioxide	propane + butane	25 + 247
Air	ditto	99 + 305
Hydrogen	"	255 + 630
Carbon dioxide	helium + methane	10 + 1739
Air	ditto	151 + 3744
Hydrogen	"	237 + 464
Carbon dioxide	helium + carbon monoxide	10 + 682
Air	ditto	151 + 1235
Hydrogen	"	237 + 1540

At the time of the publication by the monograph of Zhukhovitskii and Turkel'taub,[4] there was no unambiguous answer in the literature to the question of the dependence of the retention volume on the carrier gas pressure. This is associated, in particular, with the low accuracy of the chromatographic measurements in the initial period of the development of gas–solid chromatography and the limited choice of carrier gases. The introduction into chromatographic practice of capillary columns, characterised by an increased resolution compared with packed columns, made it possible to establish a clear dependence of the relative retention on the carrier gas pressure even in the region of low pressures.

In conclusion, we may note that the development of the theory of retention in gas–liquid chromatography has had a positive influence on the development of gas–solid chromatography. The influence of the interaction of the sorbate with the carrier gas in the gas phase on the retention was demonstrated within the framework of this theory (see the relevant monographs [77, 104, 105]). The study of the interactions of the chromatographed compound in both gas and stationary (adsorbent) phases became a logical extension of the development of the theory of retention in gas chromatography.

2. The retention of the sorbate taking into account the interactions in the gas and solid phases

The theoretical aspects of the influence of the nature and pressure of the carrier gas on the net retention volume or the partition coefficient in gas–liquid chromatography have been examined in a series of investigations (see, for example, Refs 106–112). It has been shown that the influence of the carrier gas on the retention is determined by the interaction of the molecules of both the sorbate and the carrier gas in the gas phase, on the one hand, and of the carrier gas and sorbate dissolved in the stationary phase, on the other, as well as the change in the properties of the stationary liquid phase when the carrier gas is dissolved in it.

The effects of the carrier gas on the adsorption of the chromatographed compound, and not its interactions with the sorbate in the gas phase, apparently exert the greatest influence on the separation process in gas–solid chromatography. In this connection, one should note the study by Sato *et al.*,[17] in which the influence of the carrier gas on the absolute retention is considered (within the framework of the Langmuir adsorption theory) as a result of its adsorption. Despite the fact that the results of this approach make it possible to establish the causes of the experimentally observed decrease in the retention volume as a function of the carrier gas, a fully adequate explanation of all the principal features has not been given.

This problem was examined in adequate detail in relation to gas adsorption chromatography for the first time by Locke.[113] For certain chromatographic systems, differing in the type of adsorption isotherm and in the nature of the carrier gas, he proposed a series of equations relating the partition coefficient to pressure and taking into account the nonideality of the carrier gas. As in gas–liquid chromatography (see, for example, Desty *et al.*[107]), the partition coefficient in these equations depends on the average column pressure and diminishes with increase in the pressure of the nonideal carrier gas.

Despite the correct and prior formulation of this important problem, the expressions obtained by Locke contained a series of inaccuracies. One of them was noted by Young,[114] whilst the remaining ones were discussed by Gzubrut *et al.*[13]

The interphase partition coefficient is defined by the following expression according to Locke [113]

$$K = \frac{N_a V_m}{N_m S}, \tag{9}$$

where N_a and N_m are the numbers of moles of the sorbate adsorbed on the adsorbent surface and in the gas (mobile) phase respectively, V_m is the volume of the mobile phase in the column, and S is the surface area of the adsorbent.

According to Locke,[113] the following expression can be written for N_a:

$$N_a = kSf, \tag{10}$$

where k is the adsorption constant and f the fugacity of the sorbate.

The following relation holds for the fugacity:

$$\ln f = \ln P_s + \frac{P_m}{RT}\left[B_{22} - (1-y)^2(B_{11} - 2B_{12} + B_{22})\right], \tag{11}$$

where P_s is the partial pressure of the sorbate, P_m is the average pressure of the carrier gas, y is the mole fraction of the sorbate in the carrier gas, B_{11} and B_{22} are the second virial coefficients of the pure sorbate and the carrier gas respectively, and B_{12} is the second virial coefficient reflecting the interaction between the molecules of the sorbate and the carrier gas.

Using the same approach and the same assumptions as Locke [113] (namely that the sample size is small and that the adsorption isotherms of the sorbates are therefore linear), Gzubrut *et al.*[13] established the following expression for the partition coefficient taking into account both the influence of the nonideality of the carrier gas in the gas phase and its adsorption on the adsorbent surface:

$$\ln K = \ln K_0 + \frac{(2B_{12} - V_0)}{RT} P_m, \tag{12}$$

where

$$K_0 = \mathrm{K}(P \to 0), \tag{13}$$

V_0 is the molar volume of the pure sorbate,

$$P_m = P_0 J_3^4, \tag{14}$$

$$J_3^4 = \frac{3}{4}\,\frac{(P_i/P_0)^4 - 1}{(P_i/P_0)^3 - 1}, \tag{15}$$

and P_i and P_0 are the inlet and outlet pressures of the carrier gas, respectively.

Using the equations presented above, Gzubrut *et al.*[13] explained the experimental data on the retention of methane obtained on a packed column with Porapak S at 0 °C, using He, Ar, and CO_2 as the carrier gases. It was found that in all cases the influence of the nonideality of the carrier gas on the net retention volume is very much smaller than the influence of the adsorption of the carrier gas. The relative degree of adsorption of the carrier gas increases in the sequence He < Ar < CO_2.

The equations for the retention volume or the retention time taking into account the nonlinearity of the adsorption isotherm have been obtained by numerous investigators. The most general equations, taking into account the deviation of the adsorption isotherm of the sorbate from linearity owing to the intermolecular sorbate–sorbate and sorbate–carrier gas interactions in the gas phase, have been proposed by Valentin and Guiochon:[115]

$$n_1^{\mathrm{g}} = f\,\frac{yV_m}{RT}, \tag{16}$$

$$f = P\left(1 - \frac{BP_{\mathrm{s}}}{RT}\right), \tag{17}$$

$$B = B_{11}y^2 + 2B_{12}y(1-y) + B_{22}(1-y)^2, \tag{18}$$

where n_1^{g} is the number of moles of the adsorbate in the gas phase, y is the mole fraction of the sorbate in the gas phase, V_m is the volume of the gas phase in the column, B is the second virial coefficient of the gas mixture (the carrier gas sorbate), B_{11} and B_{12} are the second virial coefficients of the pure sorbate (1) and the carrier gas (2) respectively, B_{12} is the second virial coefficient characterising the interactions of the sorbate and the carrier gas.

The influence of the nonideality of the mobile phase and of its adsorption on the adsorbent in gas–solid chromatography was taken into account by Martire [116] in the equation relating the true specific retention volume $V_{\mathrm{g},0}^T$, which would be observed for an ideal unretained gas or for the 'zero' gas pressure, to the measured specific retention volume:

$$\log V_{\mathrm{g}}^T = \log V_{\mathrm{g},0}^T + \frac{2B_{12}P_{\mathrm{m}}}{RT}\left(1 - \frac{\phi}{y}\right), \tag{19}$$

where B_{12} is the second mixed virial coefficient of the sorbate and the carrier gas, while ϕ and y are the fractions of the sorbate in the adsorbed monolayer and in the gas phase respectively at equilibrium; the equation was obtained on the assumption that a uniform adsorbent is employed.

The ratio ϕ/y is called the retention factor for the given carrier gas. In the derivation of Eqn (19), it was assumed that this coefficient is small and Henry's law therefore still holds for the carrier gas in the range of pressures employed and that P_{m} is relatively small, the degree of adsorption of the carrier gas therefore remaining negligible.

Poshkus [11] obtained the virial equation for the retention volume taking into account the influence of the pair interactions of the sorbate and carrier gas molecules both in the gas phase ($A_g \ldots B_g$) and in the adsorbed state ($A_{ads} \ldots B_{ads}$) and also the sorbate–sorbate interactions ($A_{ads} \ldots A_{ads}$):

$$V_N(\mathring{a}_1) = K_{1,1} + 2(K_{2,11} + 2K_{1,1}B_{11})\mathring{a}_1 + K_{2,12} + \\ + 2K_{1,1}B_{12}[(\mathring{a}_2 - \mathring{a}_1) - 2(B_{12} - B_{22})\mathring{a}_1\mathring{a}_2], \tag{20}$$

where $K_{1,1}$ is Henry's constant for the sorbate, $K_{2,11}$ and $K_{2,12}$ are the second virial adsorption coefficients taking into account the pair interactions between the adsorbed adsorbate molecules ($A_{ads} \ldots A_{ads}$) and between the adsorbed sorbate and carrier gas molecules ($A_{ads} \ldots B_{ads}$) respectively B_{11} and B_{22} are the second virial coefficients for the pure sorbate and the pure carrier gas respectively, c_1 and c_2 are the concentrations of the sorbate (1) and the carrier gas (2) respectively, and B_{12} is the second virial coefficient characterising the intermolecular sorbate–carrier gas interactions.

According to Poshkus's data,[11] the relative difference between the quantities V_N and $K_{1,1}$, caused by the influence on V_N by the interactions of the adsorbate and carrier gas molecules, is expressed by the equation

$$\frac{V_N - K_{1,1}}{K_{1,1}} = \left(\frac{K_{2,12}}{K_{1,1}} + 2B_{12}\right)\frac{P_{\mathrm{m}}}{RT}. \tag{21}$$

For a series of sorbate (argon, benzene, cyclohexane)–carrier gas (He, H_2, N_2, Ar)–adsorbent (graphitised thermal black) systems, the contributions of the pair interactions to the retention volume of the sorbate have been estimated theoretically. In the range of temperatures at which the $K_{1,1}$ were determined using He as the carrier gas, the sorbate–carrier gas interactions increase V_N by tenths per cent mainly due to the intermolecular interactions in the gas phase. When other carrier gases are employed (H_2, N_2, Ar), the $A_g \ldots B_g$ as well as the $A_{ads} \ldots B_{ads}$ intermolecular interactions diminish the true retention volume, the contributions of both interactions being close as regards order of magnitude. At P = 101 kPa, the overall influence of the above interactions on V_N may reach several per cent.

Rudzinski [117] described in detail and rigorously the dependence of the retention volume on the nonideal interactions of the sorbate in the gas and solid phases.

In all the studies examined above, the specific retention volume was used as the retention parameter. However, for the calculation of this quantity, it is essential to know the amount of the adsorbent in the column, the exact determination of which involves certain difficulties, especially in capillary columns. Furthermore, the specific retention volume is an absolute quantity and in gas chromatography the determination of absolute quantities involves significantly greater errors than the determination of relative retention data. It therefore appeared useful to obtain the corresponding equations for the relative retention data (the retention factor, the relative retention time, the retention index), reflecting their dependence on the pressure (and nature) of the carrier gas.

We employed a new version of the Langmuir equation [95] based on the allowance for the substitution of the adsorbed carrier gas molecules by sorbate molecules:

$$a_i = \frac{l_i a_{\mathrm{m}i} K_i P_i}{1 + K_i l_i P_i + K_{imi} l_m P_{\mathrm{m}}}, \tag{22a}$$

$$a_i = \frac{a_{\mathrm{m}i} K_i c_i}{1 + K_i c_i + K_{imi} l_m P_{\mathrm{m}}}, \tag{22b}$$

$$a_i = \frac{a_{\mathrm{m}i} b_i P_i}{1 + b_i P_i + b_{mi} P_{\mathrm{m}}}, \tag{22c}$$

where a_i is the surface concentration of the adsorbed compound i, l_i and l_m are constant conversion coefficients for compounds i and m respectively, P_i and c_i are respectively the partial pressure and the concentration of compound i in the mixture with the carrier gas, $K_{imi} = K_i/K_{im}$, K_{im} is the equilibrium constant of the reversible process involving the substitution of the adsorbed compound m by compound i, P_{m} is the average column pressure of the carrier gas, $c_i = l_i P_i$, $c_m = l_m P_{\mathrm{m}}$, a_{ami} is the capacity of the monolayer for compound i, K_i is the equilibrium constant of the reversible adsorption process involving compound i in the gas–adsorbent system, $b_i = l_i K_i$, and $b_{mi} = l_m K_{imi}$.

The main difference in the treatment of the above equations and the classical equation of the Langmuir adsorption isotherm for a mixture of substances [118] consists in the fact that the adsorption coefficient at P_{m} is determined by the properties of both the carrier gas and the chromatographed compound, which is a consequence of the allowance for the substitution reaction.

The rate of migration of the chromatographic zone w_i for compound i in a chromatographic column filled with the adsorbent may be described by the equation [119–121]

$$w_i = u\left[1 + \frac{V_s}{V_m}\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m}\right]^{-1}, \quad (23)$$

where u is the linear velocity of the carrier gas in the column, V_s and V_m are the volumes of the solid (adsorbent) and gas phases in the column respectively, a_i is the concentration of the volatile chromatographed compound i in the adsorbent, and c_i is the concentration of the sorbate i in the gas phase.

The equation for the retention time t_i of the chromatographed compound follows from Eqn (23):

$$t_i = \frac{L}{w_i} = \frac{L}{u}\left[1 + \frac{V_s}{V_m}\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m}\right] = t_M\left[1 + \frac{V_s}{V_m}\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m}\right], \quad (24)$$

where L is the column length (the carrier gas pressure drop along the column is not taken into account) and $t_M = L/u$ is the dead time of the column (the retention time of the unretained component).

Having transformed Eqn (24), it is possible to obtain the following simple expression for the retention factor k_i for compound i:

$$k_i(C_i, P_m) = \frac{t_i - t_M}{t_M} = \frac{V_s}{V_m}\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m}. \quad (25)$$

For the special case where the adsorption isotherm is linear ($a_i = K_i c_i$), the following familiar expression for the retention factor is obtained from Eqn (25):[65]

$$k_i = K_i\left(\frac{1}{\beta}\right), \quad (26)$$

where K_i is the distribution constant of the chromatographed compound i between the stationary and mobile phases and $\beta = V_m/V_s$ is the phase ratio in the column.

In the general case, the retention factor can also be represented by the equation [65]

$$k_i = \frac{V_{Ri}(c_i, P_m) - V_M}{V_M}, \quad (27)$$

where V_{Ri} is the retention volume of compound i.

On combining Eqns (25) and (27), we obtain

$$\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m} = \frac{V_{Ri}(c_i, P_m) - V_M}{V_s} = V_V(c_i, P_m), \quad (28a)$$

where V_V is the volume of the sorbent.

If a_i is expressed in units of the surface concentration, then

$$\left(\frac{\partial a_i}{\partial c_i}\right)_{P_m} = \frac{V_{Ri}(c_i, P_m) - V_M}{S} = V_s(c_i, P_m). \quad (28b)$$

Thus the derivative of the adsorption isotherm represents the specific retention volume calculated per unit volume of the sorbent V_V or per unit surface of the adsorbent V_s. We may note that previously (see, for example, Ref. 83), the quantity $\partial a_i/\partial c_i$ was designated in our communications as the effective distribution constant, because $\partial a_i/\partial c_i = K_{i,ef}$ for a linear isotherm.

In order to obtain the analytical dependence of the retention factor on the carrier gas pressure P_m, we make use of Eqn (25), whilst Eqns (22b) and (22c) are adopted as the expressions for the adsorption isotherm. After simple transformations, we obtain

$$k_i = g_i\frac{(1 + b_{mi}P_m)}{(1 + b_iP_i + b_{mi}P_m)^2}, \quad (29)$$

where $g_i = a_{mi}b_i/\beta l_i$.

Since the adsorption of the traditionally employed carrier gases on the adsorbent is usually extremely slight (*i.e.* $b_{mi}P_m \ll 1$), Eqn (29) can be usefully expanded in Maclaurin's series in $b_{mi}P_m$. We restrict the expansion to the first two terms of this series:

$$k_i \approx k_{i0} - k_{i0}\frac{b_{mi}(1 - b_iP_i)}{(1 + b_iP_i)}P_m = k_{i0}\left[1 - \frac{b_{mi}(1 - b_iP_i)}{1 + b_iP_i}P_m\right], \quad (30)$$

$$k_{i0} = k_i(\text{at } P_m = 0) = \frac{g_i}{(1 + b_iP_i)^2}. \quad (31)$$

We may note that, according to d'Alembert's criterion,[122] the above Maclaurin's series is convergent if $b_iP_i < 1$. According to our estimate, this condition holds for the sorption of hydrocarbon gases on Al_2O_3 in the range of carrier gas pressures up to 10 atm (*i.e.* in the range of pressures traditionally employed in gas chromatography).

As a result of the expansion in Maclaurin's series, the fraction $(1 - b_iP_i)/(1 + b_iP_i)$ can be expressed approximately as follows:

$$\frac{1 - b_iP_i}{1 + b_iP_i} \approx 1 - 2b_iP_i, \quad (32)$$

so that

$$k_i \approx k_{i0} - k_{i0}b_{mi}(1 - 2b_iP_i)P_m. \quad (33)$$

If $b_iP_i \ll 1$, then Eqn (33) can be represented also in a simpler form:

$$k_i \approx k_{i0} - k_{i0}b_{mi}P_m. \quad (34)$$

Thus the retention factor in gas–solid chromatography is a linear function of the average carrier gas pressure P_m. We may also note that, with increase in carrier gas pressure, we have, firstly, a decrease in the retention factor k_i and, secondly, the first term of Eqn (34) then represents the retention factor of the chromatographed compound at the 'zero' pressure of the carrier gas, *i.e.* precisely the quantity which could be considered as the chromatographic constant of the sorbate.

Table 9. Parameters of Eqn (34) for the following experimental conditions: 50 m × 0.32 mm quarts capillary column, Al_2O_3/KCl adsorbent, temperature 90 °C, carrier gases — N_2 and CO_2, inlet pressure at the inlet to the capillary column 1–5 atm.[95]

Sorbate	k_{i0}		$k_{i0}b_m$		Correlation coefficient		Standard deviation	
	N_2	CO_2	N_2	CO_2	N_2	CO_2	N_2	CO_2
Propane	0.887	0.699	0.008	0.062	0.937	0.993	0.005	0.011
Butane	1.703	1.278	0.025	0.117	0.937	0.998	0.014	0.008
But-1-ene	3.708	2.719	0.057	0.286	0.961	0.996	0.024	0.035

In order to check the equation obtained, we used the experimental data for the dependence of the retention factors of hydrocarbon gases on the average pressures of various carrier gases in capillary columns with alumina (Table 9). It follows from the data presented in the table that the $k_i = f_i(P_m)$ relations are linear and are characterised by a negative slope, *i.e.* the linear equation (34) agrees well with the experimental data (the correlation coefficient is > 0.9 in all the cases considered).

A similar approach has been used to obtain the dependence of the relative retention time and the retention index on the carrier gas pressure.

We shall examine the dependence of the relative retention times for two carrier compounds i and j on the average carrier gas pressure P_m:

$$a_{ij} = \frac{k_i}{k_j} = \frac{k_{i0}}{k_{j0}}\left(1 - \frac{b_{mi}(1 - b_iP_i)}{1 + b_iP_i}P_m\right)\Big/ \Big/\left(1 - \frac{b_{mj}(1 - b_jP_j)}{1 + b_jP_j}P_m\right). \quad (35)$$

Having expanded Eqn (35) in Maclaurin's series in P_m and having restricted the expansion to the first two members of the series, we obtain

$$\alpha_{ij} \approx \alpha_{ij0} + \alpha_{ij0}(b_{mj}\lambda_j - b_{mi}\lambda_i)P_m\,, \tag{36}$$

where $\alpha_{ij0} = k_{i0}k_{j0}$ is the limiting relative retention at $P_m \to 0$, $\lambda_i = (1 - b_iP_i)/(1 + b_iP_i)$, and $\lambda_j = (1 - b_jP_j)/(1 + b_jP_j)$.

Since usually $b_iP_i \ll 1$ and $b_jP_j \ll 1$, it follows that λ_i and λ_j are close to unity, so that

$$\alpha_{ij} \approx \alpha_{ij0} + \alpha_{ij0}(b_{mj} - b_{mi})P_m\,. \tag{37}$$

Thus the relative retention in the region of low carrier gas pressures also depends linearly on the carrier gas pressure. For example, for open capillary columns with the Al_2O_3 as an adsorbent (with KCl as the modifying agent), the experimental dependence of the relative retention for but-1-ene (with propene as the standard) on the average carrier gas pressure P_m is described by a linear equation of type (37). The correlation coefficient in the description of experimental data by Eqn (37) is 0.93 and the standard deviation is 0.092.

Since the retention index is also used in gas – solid chromatography,[2] we present an expression for the linear dependence of this quantity on the average column gas pressure of the carrier gas in the chromatographic column:

$$I_i = I_{0i} + b_{Ii}P_m\,, \tag{38}$$

where I_{0i} is the limiting value of the retention index i as P_m approaches to zero,

$$I_{0i} = 100n + 100\frac{\log\alpha_{in0}}{\log\alpha_{(n+1)n0}}\,, \tag{39}$$

where b_{Ii} is a coefficient:

$$b_{Ii} = \frac{43.43}{\left[\log\alpha_{(n+1)n0}\right]^2}\left[(b_{mn} - b_{mi})\log\alpha_{(n+1)n0} - \right. \tag{40}$$

$$\left. -(b_{mn} - b_{m(n+1)})\log\alpha_{in0}\right],$$

Here α_{in0} is the limiting retention of compound i relative to the standard, the molecule of which contains n carbon atoms and $a_{(n+1)n0}$ are the limiting retentions of standards (for example, n-alkanes the molecules of which contain $n + 1$ and n carbon atoms).

The approach developed by Berezkin and Malyukova [95] made it possible to develop new ideas concerning the influence of the carrier gas on the relative retentions in gas – solid chromatography. The linear dependences of the relative retention on the average column pressure of the carrier gas agree satisfactorily with experimental data. The general relations established in the above study [95] can be usefully taken into account in precise analytical and physicochemical studies.

VI. The influence of the carrier gas on band broadening in gas – solid chromatography

The broadening of chromatographic bands during their migration along the column is influenced by the nature of the movement of the carrier gas in the column, the diffusion of the compounds being separated in the mobile and stationary phases, the rate of interphase mass transfer, and the characteristics of the adsorption layer employed.[6, 71, 107, 123–150] The theory of the broadening of chromatographic bands has been examined in detail in monographs [2, 65, 71] and other communications.[20, 125–127, 131–134] For this reason, the authors of this review have written this section in a compact form.

The main contribution to the development of the theory of band broadening in chromatographic columns has been made by Van Deemter,[135] Golay,[125–127, 132] and Giddings,[133, 134] the results of the theoretical researches of which have been applied successfully in chromatography.

1. Packed columns

Van Deemter's equation is most widely used in chromatography on packed columns.[135] For gas – solid chromatography, it can be represented in the form of the dependence of the height equivalent to the theoretical plate (H) on the carrier gas flow rate (u):

$$H = A + \frac{B}{u} + C_s u\,, \tag{41}$$

$$A = 2\lambda d_p\,, \tag{42}$$

$$B = 2\gamma D_g\,, \tag{43}$$

$$C_s = C\frac{k}{(1+k)^2}\,\frac{d_p}{D_s}\,, \tag{44}$$

where λ is a dimensionless coefficient characterising the nonuniformity of the column packing, d_p the diameter of the particles of the packing, γ is the tortuosity coefficient, D_g is the diffusion coefficient of the sorbate in the gas phase, k is the retention factor, D_s is the diffusion coefficient of the sorbate in the stationary phase, and C is a constant coefficient.

We shall examine the physical meaning of the individual terms of Van Deemter's equation.

The term A takes into account eddy diffusion. Eddy diffusion as a spreading factor in packed columns is due to the multiplicity of the paths followed by the carrier gas in the packing and their nonidentity (for this reason the times of the transfer of individual molecules of the compound by the flow of carrier along the column are different). As a result of the processes indicated above, the chromatographic zones do in fact undergo broadening associated with eddy diffusion.

The term B/u takes into account the longitudinal molecular diffusion. The longitudinal diffusion is determined by the familiar Fick's laws of diffusion, which operate not only in the stationary gas phase but also in the moving flow. The diffusion of the sorbate in the direction of lower concentrations leads to the symmetrical broadening of the band.

The term C_su takes into account the resistance to mass transfer in the gas – adsorbent system. The quantity C_s is determined by the slowness of the mass transfer between the gas phase and the adsorbent.

The band broadening process is a fairly complex physical phenomenon. For this reason, Van Deemter's equation (like, incidentally, other equations) only approximately describes the principal physical spreading processes in our view. This standpoint is supported also by the fact that a whole series of equations have been proposed for the description of band broadening processes.[71]

The most general expression taking into account the principal factors influencing the band broadening in a packed column over a wide range of carrier gas flow rates is the Giddings equation:[124]

$$H = \left[\frac{1}{A} + \frac{1}{C_m u}\right]^{-1} + \frac{B}{u} + C_u\,. \tag{45}$$

The physical meaning of the quantities A and B/u was elucidated above. Here $B = 2D_g$ (D_g is the diffusion coefficient of the chromatographed compound in the gas phase), $C_m = \beta^2 d_p^2/2D_g$ is the coefficient of the resistance to mass transfer in the gas phase associated with the coupled eddy diffusion coefficient, β is a coefficient characterising the multichannel nature of the packing and the diffusion into gas cavities, and the quantity C_u is determined by internal and external diffusion mass transfer.

All the terms of this equation (with the exception of C_mu) have been used in the classical Van Deemter's equation [135] for the description of the broadening of the bands of the chromatographed compounds. The coupled theory of eddy diffusion, developed by Giddings, made it possible to eliminate a series of

contradictions observed in the interpretation of experimental data using Van Deemter's equation (for example, the dependence of the term A on the carrier gas flow rate, the negative values of A, *etc.*). However, it is fairly difficult to determine the coefficients of the Giddings equation. In certain cases, the use of graphical methods yields satisfactory results.[136]

Keller and Giddings [137] proposed a version of this equation in the following form:

$$H = \left[\frac{1}{2\lambda d_p} + \frac{1}{\omega(d_p^2/D_g)u}\right]^{-1} + \frac{2\gamma D_g}{u} + \mu\frac{d_p^2}{D_g}u + v\frac{d_p^2}{D_g}u\,, \quad (46)$$

where ω, μ, and v are constants depending on the capacity retention factor of the chromatographed compound. The penultimate term of the equation is determined by the external diffusion mass transfer, whilst the last term is determined by the internal diffusion mass transfer.

When account is taken of the pressure gradient (see, for example, the monograph by Guiochon and Guilleman [71]), the component influenced by the properties of the carrier gas (the diffusion coefficient in the gas phase, as well as the pressure drop and the carrier gas flow rate at the column outlet, which also depend on viscosity of the carrier gas) may be isolated from the preceding equation.

$$H_g = \left\{\frac{2\gamma D_g}{u_0} + \left[\frac{1}{2\lambda d_p} + \frac{1}{\omega(d_p^2/D_g)u}\right]^{-1} + \mu\frac{d_p^2}{D_g}u\right\}f, \quad (47)$$

$$f = \frac{9}{8}\,\frac{[(P_i/P_0)^4 - 1][(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]^2}\,. \quad (48)$$

The quantity f is a function of the ratio of the inlet and outlet pressures at the inlet to (P_i/P_0). The dependence of f on P_i/P_0 is presented in Fig. 12. For P_i/P_0 in the range from 1.0 to 7.0, the quantity f increases by $\sim$10%. Therefore the quantity f may be neglected in approximate calculations.

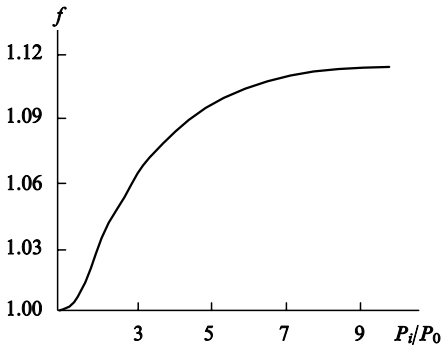


Figure 12. Dependence of the correction coefficient f on the ratio of the inlet and outlet pressures of the carrier gas.[130]

It follows from the equations presented above that the properties of the carrier gas employed have an appreciable influence on the height equivalent to the theoretical plate (HETP).

The limiting factor in band broadening is usually the slowness of the mass transfer. In the region of high carrier gas velocities, the use of hydrogen (instead of, for example, carbon dioxide) makes it possible to increase the efficiency of the chromatographic column and hence to reduce the duration of the analysis. This feature of the chromatographic process in the region of high velocities is due to the high diffusion coefficients of the chromatographed compounds in hydrogen.

The few tests of the equations reflecting the dependence of the HETP on the carrier gas flow rate have in the main confirmed them (see, for example, Refs 15, 18, 65, 138, and 139).

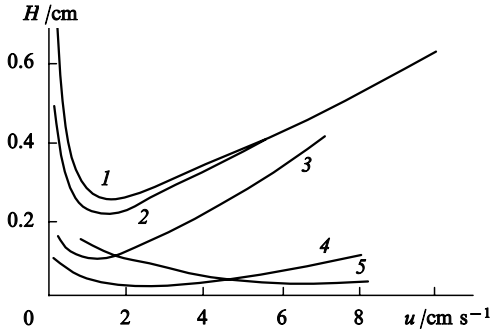


Figure 13. Dependence of the column efficiency on the carrier gas flow rate and on the nature of the carrier gas.[49] Carrier gases: (*1*) methane; (*2*) nitrogen, ethane, ethene; (*3*) carbon tetrachloride; (*4*) nitrogen; (*5*) helium.

We may note that the calculated diffusion coefficients in the carrier gas may be used for the estimation of the individual terms of the equations presented above. These methods have been described in detail.[136, 140] As an example, Fig. 13 presents the $H = f(u)$ relations for various carrier gases obtained on a packed column with Porapak S.

When carrier gases with a lower diffusion coefficient (higher molecular mass) than that of hydrogen are employed, an increase in the efficiency of the chromatographic column is observed at low gas flow rates, but for high-speed analysis it is desirable to employ gases with a high rate of mass transfer, *i.e.* with a high diffusion coefficient.

2. Capillary gas – solid columns

The term due to eddy diffusion, associated with the multiple path nature of the movement of the gas in packed columns, is absent in the case of capillary columns. The dependence of the HETP on the carrier gas flow rate in capillary gas – solid chromatography has been discussed in greatest detail in the book of Berezkin and de Zeeuw.[2]

Golay obtained the following equation for the description of the band broadening in open capillary columns with a porous layer and containing a stationary liquid phase:[127]

$$H = \frac{2D_g}{u} + \left[\frac{1 + 6k + 11k^2}{(1+k)^2} + \frac{(8 + 32k)a_2}{(1+k)^2} + \frac{8k^2}{(1+k)^2}\,\frac{a_1^2}{a_2}\right]\frac{r^2 u}{24D_g} + \left[\frac{k^3}{6(1+k)^2}\,\frac{1 + 2a_2}{r_s}\right]\frac{r^2 u}{K^2 D_1}\,, \quad (49)$$

where k is the retention factor of the chromatographed substance, $a_1 = d/r$ (d is the average length of the twisted channels in the porous layer on the internal walls of the column), r_s is the ratio of the surface areas of the sorbent (liquid phase) and of the capillary wall, $a_2 = d_g/r$ (d_g is the effective thickness of the gas layer in the porous layer of the sorbent located on the inner walls of the column and r is the internal radius of the capillary column), K is the partition (equilibrium) coefficient of the chromatographed compound between the stationary and mobile phases, and D_1 is the diffusion coefficient of the chromatographed compound in the sorbing phase.

The last term, reflecting the resistance to mass transfer in the film of the liquid phase located on the solid carrier, is inversely proportional to r_s. Thus Eqn (49) reflects the fact that, with increase in the porosity of the wall layer, the efficiency of the capillary column should increase (the HETP should diminish with increase in r_s). Hence the idea of creating a capillary with a porous layer of solid carrier on its inner walls was introduced already in the derivation of this equation.

However, it is essential to note that this equation like, incidentally, Golay's other equations, apply directly primarily to gas – liquid – solid (or gas – liquid) chromatography, but, as noted

in the monograph of Berezkin and de Zeeuw,[2] Eqn (49) may be fully applicable also to gas – solid chromatography if it is assumed that r_s is the ratio of the surface areas of the adsorbent and the capillary wall and D_1 is replaced by D_s, *i.e.* by the diffusion coefficient of the chromatographed compound in the adsorbent layer.

An equation for the dependence of the HETP on the linear carrier gas flow rate for gas – solid chromatography has also been proposed by Giddings.[133, 134] The Giddings equation does not differ functionally from the Golay equation and the first terms of the Giddings equation are virtually identical with those of the Golay equation. The difference consists, firstly, in the term reflecting the resistance to mass transfer in the adsorption layer located on the inner walls of the capillary column and, secondly, in the allowance for the influence of the carrier gas pressure drop in the column on the band broadening. The Giddings equation can be expressed in the following form:

$$H = \frac{2D_g}{u_0} + \left[\frac{1+6k+11k^2}{24(1+k)^2}\right]\frac{r^2 u}{D_g} f_1 + \\ + \frac{8}{a_k u_m}\left(\frac{k}{k+1}\right)^2 \frac{V_m}{S} f_h u_0 f_2 , \quad (50)$$

$$u_0 = \frac{L}{t_M f_2}, \quad (51)$$

$$f_2 = \frac{3}{2}\frac{[(P_i/P_0)^2 - 1]}{[(P_i/P_0)^3 - 1]}, \quad (52)$$

where a_k is the accommodation coefficient, u_m the average velocity of the molecules of the chromatographed compound in the gas phase, V_m the volume of the gas phase in the column, S the overall surface area of the adsorbent layer in the column, and f_h the adsorbent heterogeneity factor.

If the influence of the pressure drop on the band broadening is neglected (*i.e.* it is assumed that $f_2 \approx 1$ and $f_1/f_2 \approx 1$),[20] then Eqn (50) can be expressed in the form

$$H = \frac{2D_g}{u} + \left(\frac{C_m'}{D_g} + C_A\right)u , \quad (53)$$

or

$$H = \frac{2D_g}{u} + Cu , \quad (54)$$

$$Hu = 2D_g + Cu^2 , \quad (55)$$

(we note that $2D_g = B$), where

$$C = \frac{C_m'}{D_g} + C_A = C_m + C_A , \quad (56)$$

$$C_m' = \frac{1+6k+11k^2}{24(1+k)^2} r^2 , \quad (57)$$

$$C_A = \frac{8}{a_k u_m}\frac{V_m}{S} f_h \frac{k}{(1+k)^2}, \quad (58)$$

$$C_m = \frac{C_m'}{D_g}. \quad (59)$$

The coefficients of the resistance to mass transfer were first estimated on the basis of Eqn (55) for buta-1,3-diene on an open capillary adsorption (with alumina as the adsorbent) column were first estimated by the Dutch investigators de Nijs and de Zeeuw.[141] They determined the coefficients of the resistance to mass transfer for buta-1,3-diene; in the gas phase, $G_m(He) = 1.3 \times 10^{-4}$ s and $G_m(N_2) = 4.6 \times 10^{-4}$ s, whilst in the stationary phase $C_A = 1.8 \times 10^{-4}$ s. The data presented show that the nature of the carrier gas influences the quantity G_m: the smaller the diffusion coefficient (the greater the molecular mass of the carrier gas), the greater the broadening of the chromatographic band occurring as a result of the increase in the contribution of the resistance to mass transfer in the gas phase and the greater the diminution in column efficiency in the region of high rates.

Berezkin and Volkov[20] carried out a similar investigation for the capillary adsorption column with Al_2O_3/KCl (Chrompack, Holland). The results are presented in Table 10. It follows from the tabulated data that the principal contribution to the broadening of the bands of the chromatographed compounds is made by the term C reflecting the resistance to mass transfer.

Table 10. The coefficients of Eqn (55) for hydrocarbon gases separated on a capillary column with alumina.[20]

Carrier gas	Calculated		Experimental	
	D_g /cm^2 s^{-1}	B /cm^2 s^{-1}	B /cm^2 s^{-1}	C /s
Chromatographed compound — ethane				
He	0.68	1.36	1.2	2.4
N_2	0.22	0.44	0.45	6.8
CO_2	0.175	0.35	0.36	8.0
Chromatographed compound — propane				
He	0.56	1.12	0.96	3.0
N_2	0.17	0.34	0.36	8.6
CO_2	0.14	0.28	0.29	11.0
Chromatographed compound — n-butane				
He	0.43	0.86	0.80	7.2
CO_2	0.11	0.22	0.22	24.0

The influence of the carrier gas on the coefficients of the resistance to external and internal mass transfer for a capillary adsorption column with alumina has been estimated.[142] The data obtained are presented in Table 11. Evidently, the overall coefficient of the resistance to mass transfer for n-butane (C) is smaller by a factor of 2.4 with hydrogen as the carrier gas than in nitrogen and this difference is due to the corresponding difference between the coefficients of the resistance to mass transfer in the alumina layer. In order to employ the column under the conditions of high-speed analysis, it is therefore essential to use hydrogen as the carrier gas.

Table 11. Diffusion coefficients and resistances to mass transfer for n-butane with hydrogen and nitrogen as the carrier gases.[142]

Parameter	Carrier gas	
	hydrogen	nitrogen
D_g /cm^2 s^{-1}	0.625	0.162
Coefficient of resistance to mass transfer /10^{-3} s		
C_m	1.8	6.9
C_s	1.8	1.8
C	3.6	8.7

Relatively 'heavy' carrier gases should increase significantly the efficiency of the chromatographic column in the region of low carrier gas flow rates by diminishing the broadening of the chromatographic bands due to longitudinal molecular diffusion. This has been confirmed experimentally.[101] Analysis of the experimental data presented in Table 12 and in Fig. 14 made it possible to discover[101] the following feature of the band broadening process in capillary gas – solid chromatography: the greatest efficiency of the chromatographic column may be achieved by employing the 'heavy' carbon dioxide and the greatest 'gain' in efficiency is observed for 'light' chromatographed compounds. The maximum column efficiency increases for all the sorbates investigated (H_{min} diminishes in the following series of carrier gases: hydrogen < helium < nitrogen < carbon dioxide).

Table 12. Parameters of a capillary adsorption column for different carrier gases.[101]

Parameter	Chromatographed compound		
	propene	butane	isobutene
Carrier gas — hydrogen			
k	0.81	1.54	3.45
H_{min} /mm	0.60	0.48	0.46
Carrier gas — helium			
k	0.79	1.51	3.35
H_{min} /mm	0.43	0.41	0.45
Carrier gas — nitrogen			
k	0.68	1.26	2.77
H_{min} /mm	0.29	0.31	0.33
Carrier gas — carbon dioxide			
k	0.58	1.06	2.24
H_{min} /mm	0.25	0.29	0.36

The experimental and calculated coefficients of the resistance to mass transfer in the gas phase for certain carrier gases are presented in Table 13. The values of D_g have been calculated [101] from the Fuller–Schettler–Giddings equation.[140] It follows from the data in Table 13 that the main band broadening takes place in the gas phase. However, publications have appeared in the literature in which it is noted that the observed dependences of

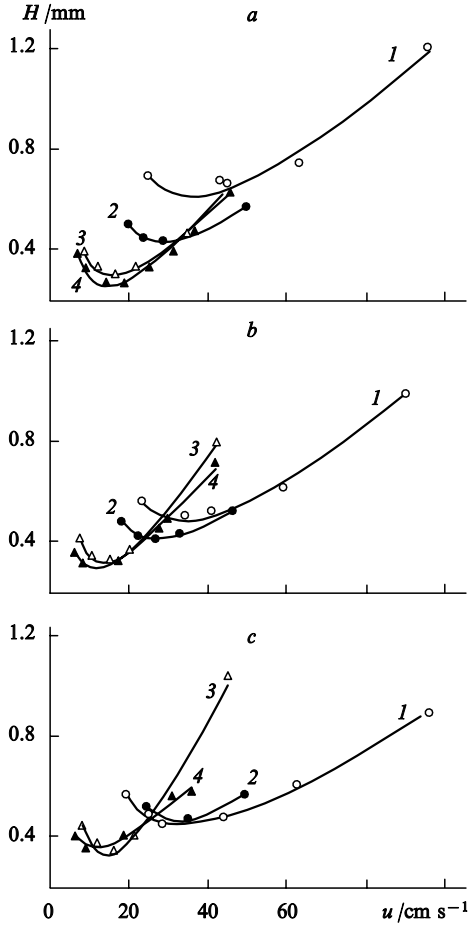


Figure 14. Dependence of the HETP on the linear carrier gas flow rate for certain hydrocarbon gases characterised by different retention factors;[101] (*a*) propene; (*b*) butane; (*c*) isobutene.
Carrier gases: (*1*) hydrogen; (*2*) helium; (*3*) nitrogen; (*4*) carbon dioxide. Experimental conditions: 50 m × 0.32 mm, stationary phase — Al_2O_3/KCl, T = 90 °C.

Table 13. Coefficients of resistance to mass transfer for the following experimental conditions: 50 m × 0.32 mm column, adsorbent — Al_2O_3/KCl, temperature 90 °C.[101]

Parameter	Chromatographed compound	
	propene	isobutene
Carrier gas — hydrogen		
k	0.81	3.45
D_g(calc.) /cm^2 s^{-1}	0.365	0.228
C_m(calc.) /10^{-3} s	0.47	1.40
C_m(exp) /10^{-3} s	1.4	0.8
Carrier gas — carbon dioxide		
k	0.58	2.24
D_g(calc.) /cm^2 s^{-1}	0.081	0.067
C_m(calc.) /10^{-3} s	1.7	4.2
C_m(exp) /10^{-3} s	1.8	2.8

the HETP on the linear carrier gas flow rate for capillary adsorption columns are inconsistent with the Golay–Giddings equation (see, for example, Refs 28, 143, and 144).

Thus the consistency of the Van Deemter [Eqn (41)], Golay–Giddings [Eqn (54)], and the extended Golay–Giddings equations with the authors' experimental data and certain literature data has been analysed [144] in order to determine the most suitable equation for the description of the dependence of the HETP on the linear carrier gas flow rate in capillary gas–solid columns with various adsorbents.

The extended Golay–Giddings equation describes satisfactorily the $H = f(u)$ relation in the region of high carrier gas flow rates:[145]

$$H = \frac{B}{u} + Cu + Du^2, \tag{60}$$

where

$$B = 2D_g \tag{61}$$

$$C = \frac{1 + 6k + 11k^2}{24(1+k)^2}\,\frac{r^2}{D_g} + \frac{2k}{3(1+k)^2}\,\frac{d_f^2}{D_l}, \tag{62}$$

$$D = \frac{\sigma^2(tEC)}{(1+k)^2 L}, \tag{63}$$

r is the internal radius of the capillary column, d_f the film thickness in the column, D_l the diffusion coefficient in the stationary liquid phase, σ^2 (tEC) the characteristic of the extra column contribution, and L the column length.

Analysis of the results obtained [144] showed that, among the 32 examples considered, Eqn (54) is the most suitable for the description of experimental data in only two cases (6%), the Van Deemter equation [Eqn (41)] is suitable in nine cases (28%), while the extended Golay–Giddings equation [Eqn (60)] is suitable in 21 cases (66%).

Thus the extended Golay–Giddings equation should be more widely employed for the description of the $H = f(u)$ relation in capillary adsorptions columns. However, it is essential to put forward a well founded theoretical interpretation of this relation, because virtually all the examples considered refer to the usual experimental conditions and not to high-speed analysis.

VII. Conclusion

As shown by numerous investigators, the nature of the carrier gas (and its pressure in the chromatographic column) employed in gas–solid chromatography exerts an appreciable influence on the principal chromatographic characteristics of sorbates, namely on the retention parameters and band broadening. Unfortunately, due attention to the role of the carrier gas employed is not always

paid in the scientific literature and particularly in chromatographic practice.

The analysis of the results of published studies carried out in the present review indicates a real possibility of a significant improvement of analytical separation with the aid of a simple and nontraditional method such as the alteration of the carrier gas and of its column pressure. It is essential to note that this factor assumes a particular importance for high-performance capillary chromatography.

In the optimisation of the analytical separation process, the dependence of the column efficiency on the carrier gas flow rate is important. The results of the latest studies have shown that the classical Golay – Giddings equation for capillary gas – solid chromatography, reflecting this dependence, is not optimal for the description of experimental data and that this must be taken into account in chromatographic practice.

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