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Capillary gas-solid chromatography

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Abstract. The current state of gas adsorption chromatography on open tubular capillary columns is analysed. The history of the development of this method and its role in gas chromatography are considered. The preparation of open tubular adsorption capillary columns, fundamentals of the theory of retention and of broadening of chromatographic zones, and the use of columns of this type in practical analytical chemistry are discussed. The bibliography includes 148 references.

I. Introduction

Gas chromatography is among the main analytical methods; it is used successfully in various branches of industry such as the petrochemical, chemical, and gas industry, etc., in pharmaceuticals, in the control of environmental pollution, in medicine, in agriculture, and also in scientific research.[1–6]

Currently, capillary gas chromatography is used most frequently. Indeed, according to a bibliometric study,[7] 83% of the publications devoted to chromatography refer to the use of capillary columns and, according to McNair's data,[8] capillary columns account for 80% of all gas-chromatographic columns purchased. In recent years, a new type of capillary column, namely, open tubular gas adsorption (or gas-solid) capillary columns have been used advantageously in analytical practice. This makes it possible to solve numerous practically important analytical problems that cannot be solved with the use of conventional gas-liquid columns.

The aim of the present review is to analyse critically the data on capillary gas adsorption chromatography, in particular, studies by Russian scientists, who have made a substantial contribution to the development of this technique.

The vigorous development of capillary chromatography during the last 10–15 years is due to a number of advantages of capillary columns over the conventional packed columns. Firstly, open tubular capillary columns are 10–1000 times more efficient than the classical packed columns. Secondly, capillary columns permit separation of a wider range of heavy (high-boiling) compounds, since chromatography on these columns is carried out at lower temperatures than on packed columns. Thirdly, with the open tubular capillary columns, a substantially higher rate of separation can be achieved. Fourthly, the decrease in the size of columns ensures a more reproducible regime of separation. Finally, the procedures for working with capillary columns became much simpler when flexible quartz columns with polymeric coatings[9,10] or with a more thermostable metallic coating[11,12] have been introduced into the chromatographic practice. The latter columns were proposed for the first time in Russia.[11] The above advantages have stimulated the development of not only gas-liquid but also gas-solid capillary chromatography.

The separating capacity of a chromatographic column (R) is determined by three factors:

$$R = \frac{\alpha - 1}{\alpha} \frac{\sqrt{N}}{4} \frac{k}{1+k} = SEC, \quad (1)$$

where α is the relative retention of two components that form a pair, critical for separation; N is the number of theoretical plates; k is the capacity factor of the second component being separated; and S is the selectivity index of the column (of the sorbent used)

$$S = \frac{\alpha - 1}{\alpha}; \quad (2)$$

E is the efficiency index of the column

$$E = \frac{\sqrt{N}}{4}; \quad (3)$$

C is the capacity index of the column

$$C = \frac{k}{1+k}. \quad (4)$$

The capacity index C plays an important role when the capacity factors of the compounds being separated are small; for large k values, the capacity index approaches unity.

When the operation of open tubular capillary columns is analysed, their high efficiency is usually noted; however, the fact that the high selectivity of the sorbent used is also a very important factor having a considerable influence on the chromatographic separation, is often neglected.

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The selectivity index [see Eqn (1)] has the greatest influence on the degree of separation. In the case of poorly separable peaks ($\alpha \approx 1.0$), the selectivity index increases proportionally to $(\alpha - 1)$

$$S = \frac{\alpha - 1}{\alpha} \approx \alpha - 1 , \quad (5)$$

hence,

$$R = (\alpha - 1)EC . \quad (6)$$

The selectivity of a sorbent is usually the most significant criterion for its possible use. Selective sorbents used in gas chromatography include not only absorbents (stationary liquid phases) but also adsorbents. A special place among the latter belongs to geometrically ordered solids (for example, molecular sieves) or adsorbents with specific properties (for example, organic hydrophobic adsorbents) or adsorbents with extended surface, etc.

In view of this, it is natural to extend the use of solid adsorbents to capillary gas chromatography, i.e. to develop gas adsorption (gas-solid) capillary chromatography.

Gas adsorption chromatography has the following advantages.[13]

1. Enhanced selectivity and sorption capacity of adsorbents, which make it possible to separate organic or inorganic compounds having similar physicochemical properties. Examples are provided by the separation on molecular sieves, graphitised carbon black, or organic polymeric adsorbents.

2. The higher efficiency of separation compared to that in gas-liquid chromatography (GLC), which is due to the fact that mass exchange processes occur more rapidly than those in GLC.

3. The sufficiently high thermal stability of adsorbents.

4. The possibility of separating gases and volatile compounds at 40–50 °C with conventional gas chromatographs.

5. The lower 'noise' of the detector, which is due to the fact that the adsorbents are usually non-volatile.

The unique features of gas adsorption chromatography have also attracted the attention of Giddings,[14] who has written: 'One immediate advantage of gas-solid chromatography resides in the fact that a surface coated with any reasonable degree of uniformity will exhibit a coefficient of the resistance to mass transfer substantially smaller than the corresponding coefficient for a liquid adsorption layer in gas-liquid chromatography. The second immediate advantage of gas-solid chromatography resides in the great potential selectivity of the adsorption process. Surface adsorption is potentially capable of offering the most versatile and selective characteristics of any of the known retentive mechanism. The rigidly fixed forces of a solid surface contrast sharply with the fluid forces of a liquid phase.'

Of course, the gas-solid chromatography is not free from certain drawbacks. These are the following:

1. Some non-reproducibility of sorption and chromatographic characteristics of the adsorbents used (compared to those of stationary liquid phases).

2. Asymmetry of chromatographic zones resulting from some non-linearity of adsorption isotherms.

3. A higher probability (compared to that in GLC) of irreversible adsorption and catalytic transformations of the compounds being analysed on the surface of an adsorbent.

4. The narrow range of commercially available adsorbents for gas-solid chromatography.

Juxtaposition of the advantages and drawbacks of gas adsorption chromatography shows that the advantages of this variant are much more significant than its drawbacks. This is also supported by the fact that columns with such adsorbents as alumina, silica, graphitised carbon black, molecular sieves, organic polymers, etc. are widely used in practice.

The advantages of gas adsorption chromatography can be fully realised by using its capillary variant.

II. The discovery of capillary gas chromatography and its development

The author of capillary chromatography Golay was the first to point out the theoretical possibility of preparing open tubular capillary columns with a sorbent layer arranged on the inner walls. In 1960 he wrote: 'Why not make a semipacked column with a large open passage in the centre, say, nine-tenths as large as the column inside diameter, and with a large thin layer of packing material in the remaining space on the periphery? The answer is why not indeed? I believe that such columns constitute nearly ideal columns for a wider range of analysis than present-day smooth tubular columns.'[15] Note that the researcher did not indicate what particular variant of chromatography, i.e. gas-liquid or gas-solid chromatography, it would be expedient to accomplish on a capillary column with porous walls.

Some years later, open tubular gas adsorption capillary columns with their inner walls coated by an adsorbent layer were produced independently by several researchers in Russia and Germany. For example, in 1961, Kalmanovskii *et al.*,[16] who studied the modification of glasses with chlorotrimethylsilane during the production of various glass capillary columns have noted that: 'the separation on non-modified capillaries proved poor (Fig. 1 *a*), the retention time of acetone being much longer than those for other compounds and its peak being markedly asymmetrical. This indicates that the capillary surfaces contain a large number of polar sites. When the surface of these non-modified capillaries was coated with a silicone oil film, the separation became better (Fig. 1 *b*). The modification of the capillary surface with chlorotrimethylsilane (Fig. 1 *c*) led to clear-cut separation and to a change in the order of elution (acetone emerged first!) with respect to that with the unmodified capillary made of the same glass (*cf.* Fig. 1 *a*). Modified capillaries can be used for analytical purposes directly in the gas adsorption version of the capillary chromatography.'[16]

Further, the researchers noted that the application of a silicone oil film to the surface of a modified capillary improved the separation to a greater degree (Fig. 1 *d*) than its application to a non-modified capillary (see Fig. 1 *b*). It is also noteworthy that the modification of the capillary surface with chlorotrimethylsilane was performed by an unusual procedure during the production of the capillary. The initial tube, from which the capillary was to be drawn, was filled with liquid chlorotrimethylsilane. At high temperature (~700 °C), chlorotrimethylsilane apparently decomposed, and interaction of the products thus formed with the glass surface yielded an adsorption layer on the inner walls of the capillary column. The chromatograms shown in Fig. 1 were obtained at 25 °C with glass capillaries with a length of 15–20 m and with an inner diameter of 0.3 mm.

Mohnke and Saffert[17,18] have prepared a gas adsorption capillary column with a silica layer by prolonged (30 h) etching of the inner surface of a Jena glass capillary by aqueous ammonia at 170–180 °C. This yields a 10–20 μm thick silica layer. Note that Mohnke and Saffert were the first to point to a very important application of capillary gas chromatography, namely, to the separation of isotopes and nuclear-spin isomers of gases. A good degree of separation of nuclear-spin isomers and isotopes of hydrogen was achieved even in the first studies on capillary gas adsorption chromatography (Fig. 2).[18]

A fundamentally new suspension method for the preparation of open tubular absorption columns, based on the deposition of an adsorbent layer on the inner walls of a capillary from a suspension, has been proposed by Halasz and Horvath.[19,20] The preparation of an adsorbent in columns of this type is independent of the material of the inner walls of the column and does not involve any transformations of it. Fig. 3 presents a chromatogram of a fast separation of aromatic hydrocarbons on graphitised carbon black layered onto the inner walls of a copper capillary. Kirkland[21] manufactured for the first time an open tubular capillary column (75 m × 5 mm) with boehmite (Al_2O_3) and

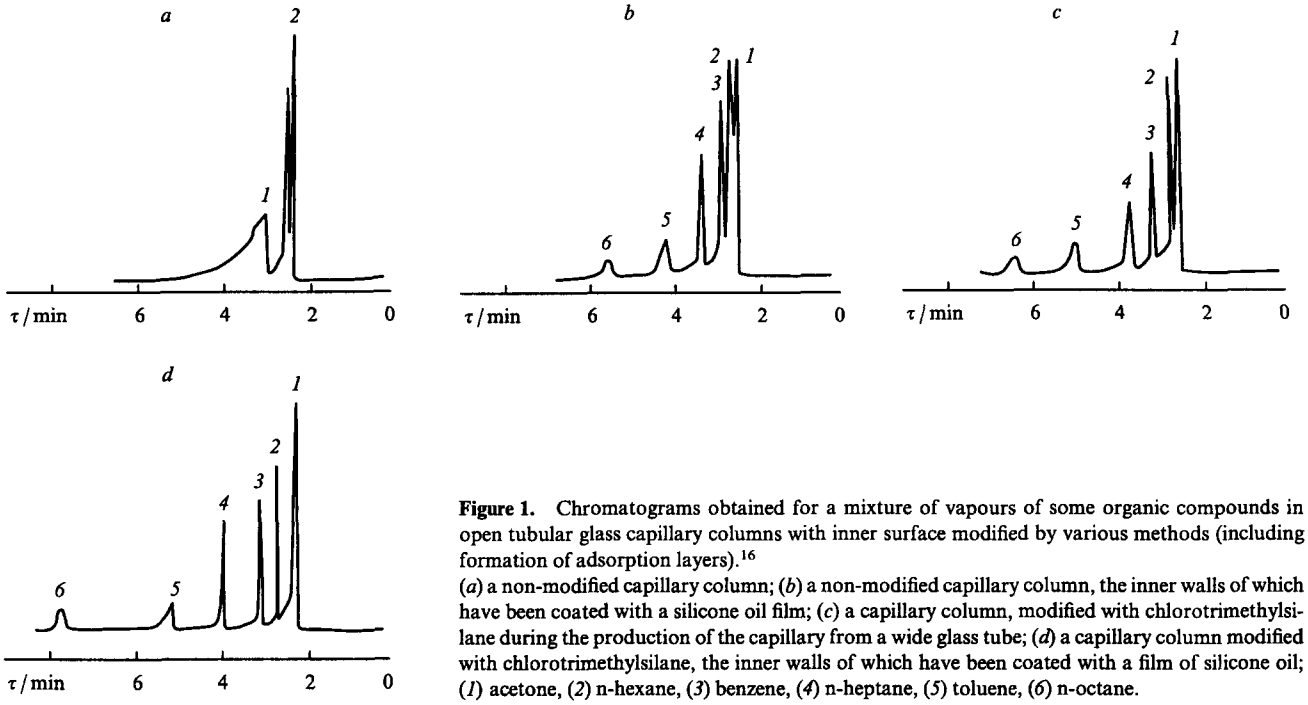


Figure 1. Chromatograms obtained for a mixture of vapours of some organic compounds in open tubular glass capillary columns with inner surface modified by various methods (including formation of adsorption layers).[16]
(*a*) a non-modified capillary column; (*b*) a non-modified capillary column, the inner walls of which have been coated with a silicone oil film; (*c*) a capillary column, modified with chlorotrimethylsilane during the production of the capillary from a wide glass tube; (*d*) a capillary column modified with chlorotrimethylsilane, the inner walls of which have been coated with a film of silicone oil; (*1*) acetone, (*2*) n-hexane, (*3*) benzene, (*4*) n-heptane, (*5*) toluene, (*6*) n-octane.

showed the possibility of using this column for the fast separation of Freons.

Among the pioneering studies dealing with the adsorption capillary chromatography, the works of Weiher,[22] Petitjean and Leftault,[23] Schwartz,[24] Liberti and coworkers,[25–29] and of Ilkova and Mistryukov[30] should be mentioned.

An important role in the development of the capillary chromatography in columns with a porous layer on the inner walls (capillary columns with adsorbent layers constitute a particular case), has been played by the studies of Ettre and coworkers[31–33] and, especially, by their review[34] devoted to the theory, methods for production, practical application, and prospects of the development of surface-layered open tubular capillary columns for gas-liquid chromatography.

Thus, the results of the very first studies on the adsorption capillary columns demonstrate, firstly, the high resolving power of the method, which is manifested most clearly in the separation of isotopes, and, secondly, the fact that separation takes little time.

During the last 10–15 years, interesting studies and important practical applications of open tubular gas-adsorption columns have been accomplished by de Nijs, de Zeeuw, Mohnke, and coworkers;[35–40] the 'Chrompack' company (the Netherlands) has begun the commercial manufacture of some types of these columns based on alumina, molecular sieves, and polymeric adsorbents (see for example Ref. 41).

In our opinion, classification of capillary columns is important in gas chromatography. It has been noted (see for example Ref. 42) that some researchers confuse the term 'open tubular capillary columns with a porous layer on the inner walls' (PLOT) with the term 'open tubular capillary columns with inner walls coated with a layer of a solid material' (WCOT). It is expedient to distinguish various types of columns according to the following features: first, the presence (or absence) of a porous layer on the inner walls of a capillary column and second, the presence (or absence) of a layer of a stationary liquid phase on the inner walls of a column (Fig. 4).

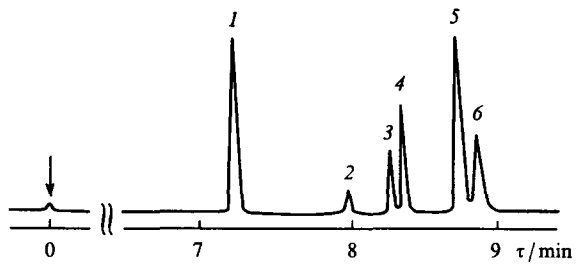


Figure 2. Chromatogram for the separation of nuclear spin isomers and isotopes of hydrogen in an open tubular adsorption glass capillary column.[18]
The 80 m long open tubular capillary column contained a 20 μm thick silica layer as an adsorbent; $T = 77.4$ K; neon was used as the carrier gas; (*1*) helium, (*2*) *p*-protium, (*3*) *o*-protium, (*4*) DH, (*5*) *o*-deuterium, (*6*) *p*-deuterium.

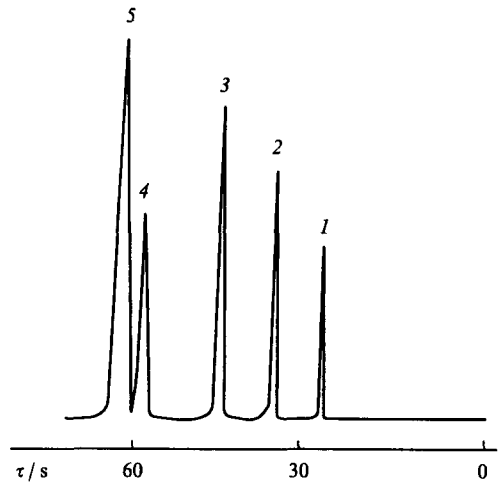


Figure 3. Chromatogram obtained for the separation of aromatic hydrocarbons in an open tubular capillary column containing graphitised carbon black.[19]
A 15 m × 0.25 mm silver-plated copper column was used, the concentration of graphitised carbon black was 5.4 mg m^{-1}; $T = 245$ °C; hydrogen was used as the carrier gas;
(*1*) benzene, (*2*) toluene, (*3*) ethylbenzene, (*4*) *m*-xylene, (*5*) *o*- and *p*-xylenes.

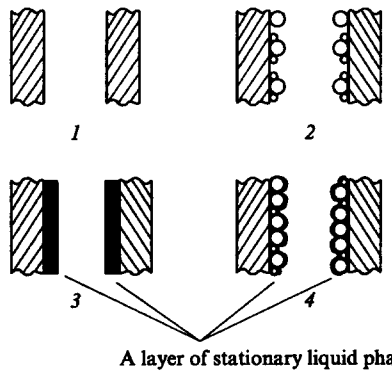


Figure 4. Various types of open tubular capillary columns.
(*1*) Open gas adsorption (gas-solid) column with smooth walls (an adsorbent); (*2*) open gas adsorption (gas-solid) column with inner walls coated with an adsorbent layer; (*3*) open gas-liquid-solid column with smooth walls (a solid support); (*4*) open gas-liquid-solid column with inner walls coated with an adsorbent layer (a solid support).

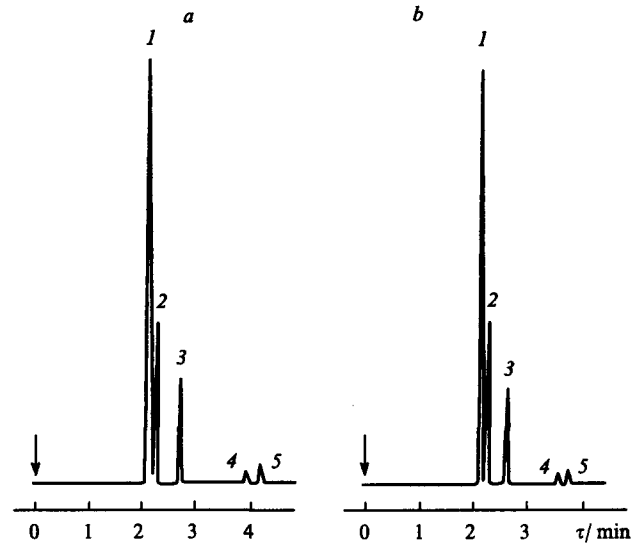


Figure 5. Chromatograms for a mixture of hydrocarbons separated in an open tubular capillary column with alumina using helium (*a*) and carbon dioxide (*b*) as carrier gases.
(*1*) Methane, (*2*) ethane, (*3*) propane, (*4*) isobutane, (*5*) n-butane. A 50 m × 0.32 mm column with Al_2O_3/KCl was used; T = 100 °C, flame ionization detector, flow splitting 1/50.

In the case of open tubular capillary columns with smooth walls (i.e. containing no porous layer), in which non-porous inner walls of the capillary are used as the adsorbent, an equilibrium in the system 'gas–planar adsorbent' under consideration is established quite rapidly; however, unfortunately, the capacity of these columns is relatively low. The theoretical possibility of using these columns was noted for the first time by Berezkin and Volkov.[43]

Columns, the inner walls of which are coated with a layer of a solid adsorbent, are most widely used in the analytical practice. Columns containing a solid adsorbent layer modified with small amounts of non-volatile liquid phases should also be classified as adsorption columns. Characteristics of open tubular capillary columns modified with non-volatile liquid phases can be found, for example, in the following studies.[44–46]

The contribution of an adsorption mechanism to the retention can also be significant in the classical columns with a layer of a stationary liquid phase on smooth walls. For example, this is the case with the chromatography of n-alkanes in open tubular capillary columns with a poly(ethylene glycol) layer.[47,48]

This review is mostly devoted to open tubular capillary columns, the inner walls of which are coated with a layer of a solid adsorbent (gas-solid chromatography).

III. Retention of compounds subjected to capillary gas-solid chromatography

Retention in gas adsorption chromatography is determined both by the nature of the surface of the adsorbent and by its structure. The mechanism of retention is discussed in detail in a number of monographs.[49–54] Kiselev[13,51] has shown that the retention volume V_N is directly proportional to the surface area (S_{ad}) of the adsorbent in the column (it has been assumed that at relatively low coverages, the accessibility of the adsorbent surface does not change):

$$V_N = K_s S_{ad}, \qquad (7)$$

where K_s is the coefficient of distribution of the substance subjected to chromatography between the adsorbent surface and the gas phase.

Note an important specific feature of the gas-solid chromatography, namely, the fact that the retention of compounds depends on the nature of the mobile phase. The replacement of light carrier gases by heavy gases leads to dynamic modification of the adsorbent surface, to a decrease in the coefficients of distribution of compounds being analysed in the 'solid adsorbent–gas' system, and, hence, to a decrease in retention times.

The chromatograms of gaseous hydrocarbons obtained on a column with alumina using two carrier gases (helium and carbon dioxide) are presented in Fig. 5. It is seen that the retention times, especially those of heavy compounds, decrease in the case where the heavy carrier gas (carbon dioxide) is used. An influence of water vapour on the modification of the adsorbent (Al_2O_3) and on the retention in the capillary adsorption chromatography has been noted by de Nijs.[35]

A further important specific feature of the capillary adsorption chromatography is the dependence of retention on the pressure of the carrier gas. The influence of the average carrier gas pressure in a column on retention values (for example, on the capacity factors) of compounds subjected to high-performance gas-solid capillary chromatography was studied systematically for the first time by Berezkin et al.[55] for various carrier gases and for the pressure range used in the conventional capillary gas chromatography (1–5 atm at the inlet of the capillary column). It is noteworthy that owing to the high resolving power of open tubular capillary columns, the experimental conditions that can have an influence on the retention are especially significant in capillary chromatography.[56] For example, in order to decrease the time required for separation by increasing the velocity of the carrier gas in the column, it is necessary to change the pressure at the inlet of the column (and, consequently, the average pressure in the column within the pressure range specified above).

The results of a study of the dependence of the capacity factor on the average pressure of the carrier gas in the column are presented in Table 1. It follows from these data that retention depends both on the nature of the carrier gas and on its pressure in the column.

To explain this, we shall use the known regularities of the adsorption of mixtures. If we assume that the adsorption of molecules of volatile compounds A and C occurs upon their collision with an unoccupied adsorption site on the surface of a solid adsorbent and that the rate of desorption of these molecules is proportional to the surface area occupied by the adsorbed molecules, the adsorption isotherm can be described by the following equations:[57]

$$a_A = \frac{K_A c_A}{1 + K_C c_C + K_A c_A}, \qquad (8a)$$

Table 1. Dependence of the capacity factors of gaseous hydrocarbons on the average pressure of the carrier gas in a capillary column.[55]

$\bar{P}$/ atm	Propene	Butane	But-1-ene	$\bar{P}$/ atm	Propene	Butane	But-1-ene
H_2 as the carrier gas				He as the carrier gas			
1.0	0.80	1.51	3.27	1.0	0.88	1.68	3.66
1.6	0.81	1.52	3.29	1.6	0.89	1.71	3.73
2.8	0.80	1.54	3.24	2.8	0.89	1.72	3.75
3.4	0.81	1.53	3.22	3.4	0.89	1.71	3.71
4.1	0.84	1.56	3.24	4.1	0.88	1.69	3.63
N_2 as the carrier gas				CO_2 as the carrier gas			
1.0	0.87	1.65	3.61	1.0	0.64	1.17	2.46
1.6	0.88	1.68	3.64	1.6	0.59	1.08	2.24
2.8	0.87	1.65	3.58	2.8	0.54	0.95	1.91
3.4	0.86	1.62	3.52	3.4	0.49	0.88	0.80
4.1	0.85	1.59	3.45	4.1	0.44	0.80	1.58

$$a_C = \frac{K_C c_C}{1 + K_C c_C + K_A c_A}, \tag{8b}$$

where a_A and a_C are concentrations (g g^{-1}) of the adsorbed compounds A and C, respectively; K_A and K_C are adsorption coefficients of the compounds A and C; and c_A and c_C are the concentrations (g l^{-1}) of A and C in the gas phase. Subsequently, A stands for the compound being chromatographed and C stands for the carrier gas.

From Eqns (8), the following equation has been derived,[55] which relates the capacity factor (k) to the average pressure of the carrier gas in the column ($\bar{P}$):

$$\frac{1}{k} = a + b\bar{P}, \tag{9}$$

where

$$a = \frac{\beta}{K_A}, \tag{10a}$$

$$b = aK_C, \tag{10b}$$

β is the ratio (v/v) of the phases occurring in the column, a_p and b_p are coefficients from Eqn (9). By using the above equations, one can determine the parameters of Eqn (8) for adsorption of a gas mixture.

The experimental data obtained are adequately described by Eqn (9) (Fig. 6). Such a processing of experimental results makes it possible to find the parameters of Eqn (9); i.e. in this case, gas chromatography can be used as a physicochemical method for determining parameters of the equation describing the adsorption of mixtures. Note that a variation of the pressure of a carrier gas at the inlet of the column is associated with a variation of its linear velocity; therefore, in this case, a dependence of the capacity factor (i.e. of the retention of a substance) on the linear velocity of the carrier gas can be manifested.

The nature of the carrier gas exerts a substantial influence on the retention of compounds in the capillary gas adsorption chromatography. It is clear that the rules that make it possible to pass from the retention values observed with one carrier gas (G_1) to the values characterising retention of the same compounds when another carrier gas is used (G_2) are of practical interest. Recently† the following correlation has been established:

$$k(G_2) = Ak(G_1) + B, \tag{11}$$

where k(G) is the capacity factor of a compound with carrier gas G, and A and B are constants. It was shown in the same study that the efficiency of separation is substantially improved by using carbon dioxide, passed at the optimal velocity, as the carrier gas.

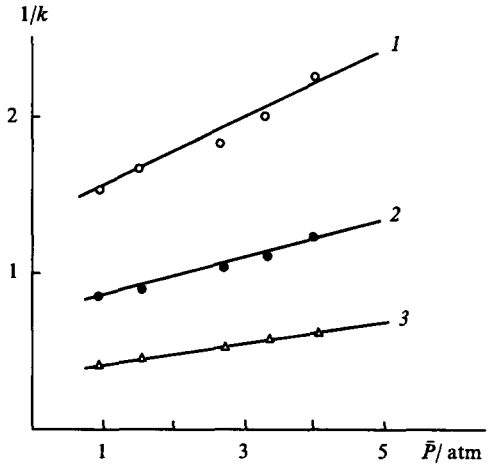


Figure 6. Dependence of $1/k$ on the average pressure of a carrier gas (carbon dioxide) in the column.
(*1*) Propylene, (*2*) butane, (*3*) but-1-ene. Experimental conditions: a 50 m × 0.32 mm column; Al_2O_3/KCl as the adsorbent; T = 90 °C.

The above features characterising the dependence of the retention of compounds being analysed on the properties of the mobile phase should also be taken into account in the practical use of capillary adsorption columns.

IV. Broadening of chromatographic zones in open tubular gas adsorption capillary columns

Broadening of chromatographic zones during their migration along the column is influenced by the character of movement of the carrier gas in the column, by the diffusion of the substances being separated in mobile and stationary phases, by the rate of interfacial mass transfer, and by characteristics of the adsorption layer used.[13, 34, 51–53, 58–64]

Already in first studies on capillary chromatography, Golay[58–60] proposed that, in order to increase the capacity index of the column, one should apply a layer of stationary liquid phase onto a porous layer of a solid support located on the inner walls of

† See V G Berezkin, I V Malyukova, V R Alishoev, J de Zeeuw *J. High Resol. Chromatogr.* **19** 272 (1996).

a capillary column rather than directly onto the smooth walls of the column. If the thickness of the film formed by the stationary liquid phase on separate particles of the solid support is the same as that formed on the smooth walls of the capillary, then the amount of the stationary liquid phase per unit length of the column becomes much higher, since the interior surface of the solid support is much greater in this case. This results in a decrease in the ratio of the phase volumes

$$\beta = \frac{V_g}{V_l}$$

(where V_g is the volume of the gas phase in the column and V_l is volume of the stationary liquid phase in the column), in an increase in the capacity factor k, and, hence, enhances the separation.

To describe broadening of chromatographic zones in open tubular capillary columns with walls coated by a porous layer, Golay has obtained the following equation:[14,15]

$$H = \frac{2D_g}{u} + \left[\frac{1+6k+11k^2}{(1+k)^2} + \frac{(8+32k)a_2}{(1+k)^2} + \right.$$

$$\left. + \frac{8k^2}{(1+k)^2 a_2}\frac{a_1^2}{a_2}\right]\frac{r^2 u}{24D_g} + \left[\frac{k^3}{6(1+k)^2}\frac{1+2a_2}{F}\right]\frac{r^2 u}{K_D^2 D_l}, \quad (12)$$

where H is the height equivalent to a theoretical plate (HETP); D_g is the coefficient of diffusion of the compound under analysis in the gas phase; u is the linear velocity of the carrier gas; k is the capacity factor of the compound under analysis; $a_1 = d_t/r$ (d_t is the average length of the tortuous channels in the porous layer covering the inner walls of the column); $a_2 = d_g/r$ (d_g is the effective thickness of the gas layer in the porous layer covering the inner walls of the column); r is the internal radius of the column; F is the ratio of the surface area of the liquid phase to the surface area of the capillary walls; K_D is the coefficient of distribution of the substance under analysis between the mobile and stationary phases; and D_l is the diffusion coefficient in the liquid phase.

The last term in Eqn (12) reflects the resistance to the mass transfer in the liquid phase and it is inversely proportional to F. This implies that the efficiency of a capillary column should increase with an increase in the degree of porosity of the near-surface layer (H decreases with an increase in F). Thus, the idea of a capillary column with a porous layer of a solid support has already been included in the derivation of this equation. However, it should be noted that this equation, like other Golay equations, was obtained first of all for gas-liquid-solid (or gas-liquid) chromatography.[48]

An equation relating HETP to the linear velocity of the carrier gas for gas adsorption chromatography has been proposed by Giddings.[65,66] The first terms in the Giddings equation virtually coincide with those in the Golay equation. These equations differ, firstly, in the term that reflects the resistance to the 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 differential along the column on the broadening of chromatographic zones. The Giddings equation can be represented in the following way:

$$H = \frac{2D_g}{u_0} + \left[\frac{1+6k+11k^2}{24(1+k)^2}\right]\frac{r^2 u}{D_g} f_1 +$$

$$+ \frac{8}{a_k u_m}\left(\frac{k}{k+1}\right)^2 \frac{V_g}{S} f_n u_0 f_0, \quad (13)$$

where u_0 is the linear velocity of the carrier gas at the outlet of the column.

$$u_0 = \frac{L}{t_m f_2}, \quad (14)$$

where L is the length of the column; and t_m is the 'dead time' of the column;

$$f_1 = \frac{9}{8}\frac{(P^4-1)(P^2-1)}{(P^3-1)}, \quad (15)$$

$$f_2 = \frac{3}{2}\frac{(P^2-1)}{(P^3-1)} \quad (16)$$

($P = P_i/P_0$, P_i and P_0 are carrier-gas pressures at the inlet and outlet of the column, respectively), a_k is the accommodation coefficient; u_m is the average velocity of the molecules of the substance under analysis in the gas phase, S is the overall surface area of the adsorbent layer in the column, and f_n is a factor reflecting the heterogeneity of the adsorbent.

If we neglect the influence of the pressure differential on the broadening of chromatographic zones (i.e. $f_2 \approx 1, f_1/f_2 \approx 1$), the Giddings equation for an adsorption capillary column assumes the form:

$$H = \frac{2D_g}{u} + \left(\frac{C_{gp}}{D_g} + C_{ad}\right)u \quad (17)$$

or

$$H = \frac{2D_g}{u} + Cu, \quad (18)$$

where

$$C = \frac{C_{gp}}{D_g} + C_{ad} = C_g + C_{ad}, \quad (19)$$

$$C_{gp} = \frac{1+6k+11k^2}{24(1+k)^2} r^2, \quad (20)$$

$$C_{ad} = \frac{8}{a_k u_m}\frac{V_g}{S} f_n \frac{k}{(1+k)^2}, \quad (21)$$

$$C_g = \frac{C_{gp}}{D_g}. \quad (22)$$

To verify whether Eqn (18) is in agreement with experimental results, it is convenient to write it in the following form:

$$Hu = 2D_g + Cu^2. \quad (23)$$

The D_g values can be calculated from the equation proposed by Fuller et al.[67] or by another theoretical method (see, for example, a published study[68]). If we find the values for the resistance to mass transfer C for compounds subjected to chromatography with two carrier gases in an open tubular adsorption capillary column, then we can determine the real coefficients of resistance to the mass transfer in the gas phase (C_g) and in the adsorption layer (C_{ad}). The theoretical methods have been developed earlier by Perrett and Purnell for gas-liquid chromatography.[69]

The first estimate of the coefficients of resistance to mass transfer from the Golay–Giddings equation was carried out by the Dutch researchers de Nijs and de Zeeuw.[36] They considered the chromatography of buta-1,3-diene in an open tubular adsorption capillary column (with alumina as the adsorbent) with helium and nitrogen as carrier gases and obtained the following values for $C \times 10^4$: C_g (butadiene in helium) = 1.3; C_g (butadiene in nitrogen) = 4.6; C_{ad} = 1.8. Thus, C_g and C_{ad} are of the same order of magnitude.

For comparison, we present the coefficients of resistance to mass transfer C_g and C_l reported by Cramers et al.[70] for the chromatography of tridecane in an open tubular capillary column with the inner walls coated with a stationary liquid phase layer. For a 24.7 m × 0.55 mm column (with the CP-Sil 5-CB silicone as the stationary liquid phase, T = 150 °C), the following values have been reported, $C \times 10^4$: the coefficients of resistance to mass transfer in the gas phase C_g (tridecane in helium) = 2.8; C_g (tridecane in nitrogen) = 10.6; the coefficient of resistance to mass transfer in the liquid phase C_l = 4.1. It follows from these data that the coefficients of resistance to mass transfer for the gas-solid and gas-liquid variants of capillary chromatography are of the same order of magnitude.

A similar study has been carried out for a capillary gas adsorption column of the 'Chrompack' company (the Netherlands), the inner walls of which have been coated with a layer of the adsorbent Al_2O_3/KCl.[43] The results of this study are presented in Table 2. The values listed were determined from the linear Eqn (18). The results obtained are in good agreement with the experimental data.

Table 2. Coefficients of the Golay–Giddings equation for the separation of gaseous hydrocarbons in a capillary column with alumina.

Carrier gas	Calculation		Experiment	
	D_g [a]/ cm^2 s^{-1}	B [b]/ cm^2 s^{-1}	B/ cm^2 s^{-1}	C/ s
For the analysis of ethane				
He	0.68	1.4	1.2	2.4
N_2	0.22	0.44	0.45	6.8
CO_2	0.175	0.35	0.36	8.0
For the analysis of propane				
He	0.56	1.11	0.96	3.0
N_2	0.17	0.34	0.36	8.6
CO_2	0.14	0.27	0.29	11.0
For the analysis of n-butane				
He	0.43	0.86	0.80	7.2
CO_2	0.11	0.22	0.22	24.0

[a] Calculated by the Fuller–Schettler–Giddings method.[67] [b] $B = 2D_g$.

The coefficients of diffusion of compounds subjected to chromatography in a carrier gas can be found from the coefficient B and calculated from the Fuller–Schettler–Giddings equation.[67]

Thus, the values found using the Golay–Giddings equation are in satisfactory agreement with the experimental results for open tubular capillary columns both in the type of functional dependence and in the magnitudes of the diffusion coefficients for substances in the gas phase, which are determined from the experimental chromatographic data. For example, the coefficient of diffusion for butane in helium, found from the Golay equation, is 0.40 cm^2 s^{-1}, while the corresponding diffusion coefficient calculated from the Fuller–Schettler–Giddings equation is 0.44 cm^2 s^{-1}.

It is noteworthy that the experimental data obtained by Goretti et al.[71] have also been in good agreement with Eqn (18). These investigators used open tubular glass capillary columns, the inner walls of which were coated with a graphitised carbon black layer. The parameters B and C determined from their experimental results are listed in Table 3. It follows from these data that when the velocity of a carrier gas is more than 30 cm s^{-1}, the major contribution to the broadening of the zones corresponding to the compounds under analysis is made by the term reflecting the resistance to mass transfer.

To describe the dependence of HETP on the linear velocity of the carrier gas for open tubular gas adsorption columns, the following equation has been proposed[72] (which is valid provided that the thickness of the porous adsorbent layer σ is much smaller than the radius of the column r (i.e. $\sigma/r \ll 1$):

$$H = \frac{2D_g}{u} + \frac{11k^2 + 6k + 1}{24(k+1)^2}\frac{r^2}{D_g}u + \frac{1}{3}\left(\frac{k}{k+1}\right)^2\frac{\sigma r}{D_p\chi}u, \quad (24)$$

where D_p is the diffusion coefficient of the substance being analysed in the porous layer of the adsorbent (note that normally $D_p < D_g$), and $\chi = V_{pg}/V_p$, where V_{pg} is the pore volume in the adsorbent and V_p is the volume of the whole porous layer.

This equation implies that the H value decreases (the efficiency of the column increases), firstly, as the radius of the capillary column decreases and, secondly, as the degree of porosity of the adsorption layer increases. These dependences agree qualitatively with the experimental results.

In conclusion, it should be mentioned that the authors of some recent studies (see for example Ref. 73) have noted that the dependences of HETP on the linear velocity of the carrier gas observed experimentally for adsorption capillary columns do not agree with the Golay–Giddings equation.

V. Methods for the preparation of open tubular gas adsorption capillary columns

Methods for the preparation of open tubular adsorption capillary columns have some specific features which distinguish them from the known techniques used for the production of capillary columns with a stationary liquid layer.

Only methods for the production of adsorption capillary columns with a porous adsorbent layer have been reported. Columns of this type are characterised by high capacities and stable performance.

A method for the preparation of open tubular columns has to meet fairly stringent requirements.

(1) A method should ensure uniform distribution of the layer of an adsorbent over the whole inner surface of a capillary;

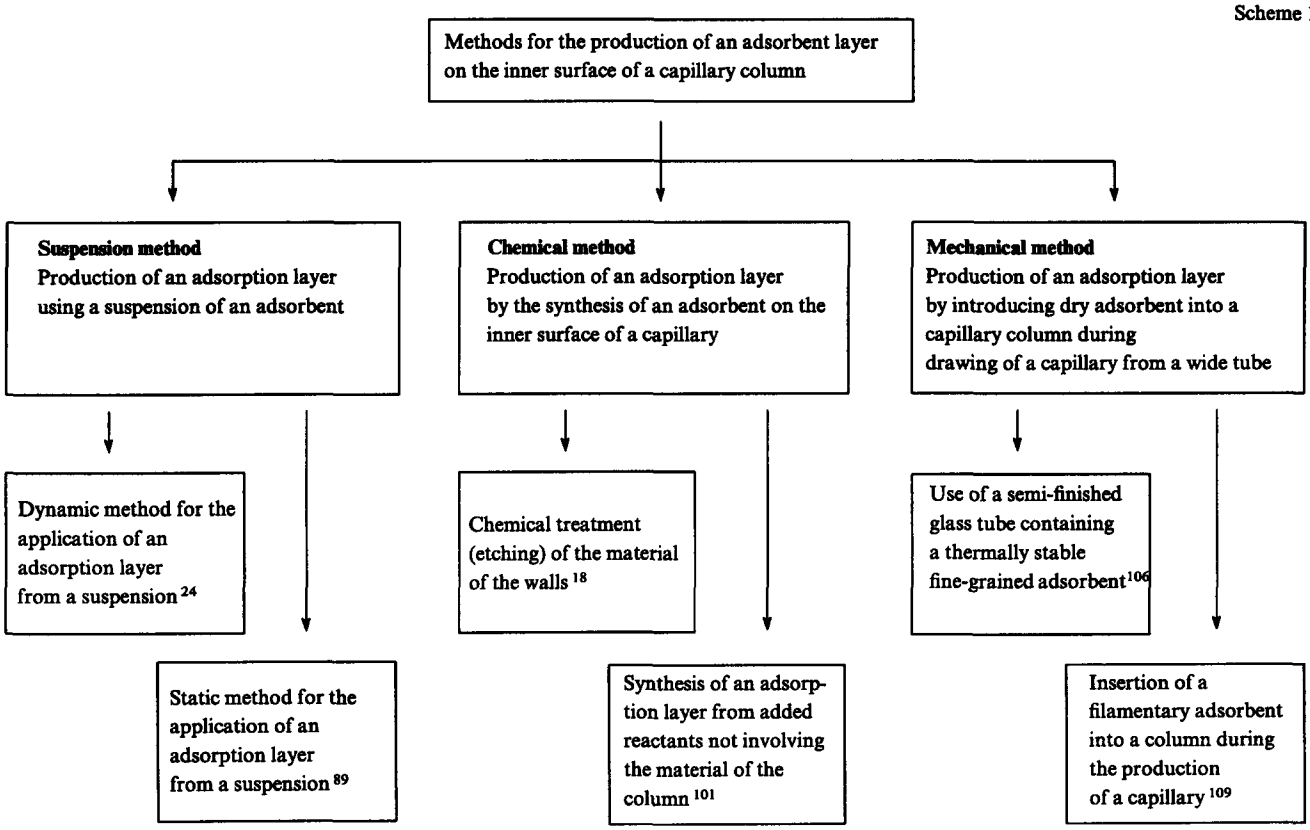
(2) the particles of the adsorption layer should be fixed fairly rigidly on the surface of the capillary;

Table 3. Characteristics of the processes of chromatography of isobutane (I) and n-butane (II) on gas adsorption capillary columns with graphitised carbon black of the MT type (7 m^2 g^{-1}).

Size of the column [a] /m × mm	Thickness of the sorbent layer/ μm	K		B/ cm^2 s^{-1}		$10^3 C$/s		H_{min}/ mm	
		I	II	I	II	I	II	I	II
9.6 × 0.2	100	1.00	1.54	0.17	0.13	5.7	6.0	–	1.41
11.0 × 0.25	65	1.97	3.02	0.17	0.14	8.3	10.0	–	1.26
11.0 × 0.3	45	1.57	2.42	0.17	0.15	6.4	7.1	–	1.64
11.0 × 0.2 [b]	100	2.05	3.14	0.17	0.13	4.3	4.5	–	0.91

[a] The length (m) and the diameter (mm) of columns are given. [b] In this column, graphitised carbon black of the FT type was used (15 m^2 g^{-1}).

Scheme 1



(3) a method should ensure the possibility of preparing capillary columns with reproducible characteristics;

(4) a method should be suitable for producing adsorption layers based on various adsorbents;

(5) the procedure involved should take little time.

Development of a procedure satisfying all these requirements is a fairly complicated task involving various aspects.

The characteristics of the known methods for the preparation of open tubular adsorption capillary columns are shown in Scheme 1. It can be seen that three main techniques have been described to date, namely, suspension, chemical, and mechanical (construction) technique in which dry sorbent is introduced into a glass tube during the production of a capillary.

1. Suspension technique

The suspension method is similar to that used to apply a stationary liquid phase onto the inner walls of a capillary column. An adsorbent is dispersed in an appropriate liquid medium and introduced into a column as a suspension, and the volatile liquid is then removed. As in the 'classical' procedure for the deposition of a stationary liquid phase, dynamic and static versions of the suspension method have been developed. The main specific feature of the latter is heterogeneity (or microheterogeneity) of the system introduced into a capillary in order to prepare an open tubular adsorption column. In this case, the suspension which migrates along the capillary is a non-newtonian liquid, which often exhibits clear-cut thixotropic properties. During the flow of this liquid, the particles are segregated according to their sizes, in conformity with the regularities of flow chromatography in a force field.[74-78] As a result, the rheological properties of the suspension vary during the application or during the filling of the column and hence, it is difficult to obtain an adsorbent layer which is uniform over the whole length of the capillary.

Nevertheless, the suspension method has been used even in the earliest works on the capillary adsorption chromatography. For example, silica has been applied onto the inner surface of polymeric, copper, or steel capillaries with lengths ranging from 4 m to 400 m and with an internal diameter of ~0.5 mm.[24,75,79] It was noted that the use of suspensions containing micron-size particles is associated with some difficulties and that colloidal solutions of silica are preferred. Schwartz et al.[24] used a 22% sol of silica in a water–isopropyl alcohol system. After removal (evaporation) of the dispersion medium, a thin layer of solid silica remained on the inner walls of the capillary. The workers[24] did not mention whether a suspension stabiliser, which is usually present in systems of this sort, has remained on the silica particles after drying. Apparently, surfactants, which are used as stabilisers of suspensions, modify the surface and, consequently, have an influence on the retention.

The particle size in these sols does not exceed 0.02 μm; therefore, the adsorption layer has a large specific surface area. A column produced by the suspension method was used to separate pentane and hexane isomers. However, the specific efficiency of the column, calculated from the chromatograms, did not exceed 100 theoretical plates per metre. In all probability, this low efficiency is due to the fact that the solid sorbent particles are nonuniformly distributed over the inner surface of the column. This is a result of the disadvantages peculiar to the dynamic method (fluctuations of the velocity at which the suspension meniscus moves and instability of the film formed), as well as of some specific features of the suspension.

Schwarz et al.[79-81] have prepared adsorption columns using larger silica particles (~4 μm) with the surface modified with an organic surfactant, because the use of adsorbent particles with a size not exceeding that of colloidal particles can lead to the formation of a dense adsorption layer, which substantially hampers mass transfer.

The modified silica was applied by the dynamic method as a 7.5% suspension in n-hexane. The glass capillary column thus formed with a length of 120 m and with an inner diameter of 0.5 mm permitted separation of 13 isomeric C_5-C_7 hydrocarbons over a period of 18 min. The specific efficiency of the column determined in relation to 2,4-dimethylpentene was 550 theoretical plates per metre.[79-81]

In the early 60s, the dynamic method for the application of a solid support was used by the Perkin-Elmer company for the commercial production of copper gas-liquid capillary columns with a length of 15–30 m and 0.5 mm in diameter, meant for quick analysis of light gaseous hydrocarbons.[82]

Capillary adsorption columns with graphite have been obtained by application of graphitised carbon black by the dynamic method.[19,20] 15 m long copper columns with an internal diameter of 0.25 mm, the inner surface of which was coated with silver, were treated with a suspension of carbon black preliminarily graphitised at 3000 °C. The suspension was prepared by intense stirring (8000 rpm) of a mixture consisting of 15 g of carbon black, 220 ml of trichlorotrifluoroethane, and 30 ml of tetrachloromethane. Thus, the dispersion medium of this suspension had a density of ~ 1.5 g cm^{-3}. The high density of the dispersion medium made it possible to obtain a fairly stable suspension, which passed through a column without aggregation of particles. The surface area of the capillary column thus obtained was 0.2–0.8 m^2, which made it possible to separate all the isomers of heptane at 245 °C.[19]

Ultrasonic treatment of graphite suspensions has been proposed in order to increase their stability.[71,83,84] A suspension consisting of 0.25 g of Carbopack A, 5 ml of dichloromethane, and 20 ml of tetrachloromethane was sonicated (frequency 20 to 24 kHz and amplitude 2 μm). The optimal time of irradiation was 40 min. The suspension thus prepared was passed through a column at a velocity of 0.6 ml min^{-1} in both directions. The glass capillary column used was 10–15 m long and 0.4–0.5 mm in diameter.

A suspension of graphitised carbon black 'Sterling MT' prepared in a similar way has also been used for the production of an adsorption capillary column. The suspension was passed through a column with a reduced pressure at the outlet. This was possible, because the suspension had a low viscosity, due to the fact that its concentration did not exceed 1%.[84] However, the amount of the sorbent applied in this way proved insufficient to be used efficiently in the adsorption variant of chromatography. Therefore, the layer thus formed was used as a solid support for a stationary liquid phase, i.e. in the absorption–adsorption variant of chromatography.

Purcell[85] has used the dynamic method to prepare a column coated from the inside by a layer of 5 Å molecular sieves with a particle size of up to 20 μm. Later, the 'Chrompack' company has started the production of columns with molecular sieves applied by the dynamic method.[41] The most interesting results on the application of an adsorbent layer by the dynamic method have been obtained with alumina suspensions.

The first attempt along this line was undertaken by Kirkland,[21] who used Al_2O_3 as the fibrous mineral boehmite. Microscopic studies have shown that an elementary fibre of this mineral has a length of ~ 1000 Å and a diameter of 50 Å; the fibres are joined in aggregates ~ 2 μm in diameter. The specific surface area of this sorbent is 275 m^2 g^{-1}. To prepare an adsorption column, a 7% aqueous sol of boehmite was injected into a glass (or stainless-steel) capillary of length 10 m and with an inner diameter of 0.25 mm (or 0.5 mm). When the suspension was passed and the adsorption layer was dried, the capillary column was ready for use. This column made it possible to separate a number of Freons; however, its efficiency was not very high.

The dynamic method for the application of Al_2O_3 has been developed further by Schneider et al.[86] They noted the following advantages of glass capillary columns, the walls of which are coated by an alumina layer, over metallic capillaries: (1) the adsorption activity of the walls of the columns is low; (2) finely powdered alumina is readily applied onto a glass surface without any fixing agents and forms thin layers, which do not fall off the walls even when the capillary is deformed within its elasticity limits; (3) the process of application and the quality of the column can be monitored visually; (4) glass capillaries of any size can be easily produced in a laboratory.

The following procedure can serve as an example of filling a capillary column. The suspension is prepared by mixing 20 g of alumina (obtained by calcination of aluminium hydroxide with particles no larger than 2 μm) with 70 ml of a 5% colloidal solution of Al_2O_3 and with 0.3 ml of glacial acetic acid. The resulting suspension is exposed to ultrasound, filtered through 300 mesh sieves, and allowed to stand for 24 h for maturing. The suspension thus obtained possessed thixotropic properties.

The use of a colloidal solution of alumina provides a dispersion medium with high density and viscosity, which increases the stability of the suspension. In addition, colloidal particles of alumina cement large particles of the sorbent and thus fix them additionally on the capillary surface.

Prior to the application of Al_2O_3, the capillary column is washed with 1% acetic acid. For the deposition of an alumina layer onto the inner walls of the column, the suspension is pressed through a capillary at a velocity of 4 ml min^{-1}. At this rate, 0.6 ml of the suspension is sufficient to coat 15 m of the column. As the final stage of the process, the column is stored for 10 h and is subsequently dried at room temperature in a flow of nitrogen. A 65 m long column of diameter 0.4 mm is dried for a week at a nitrogen pressure of 0.3 MPa at the inlet.

After drying, the column is activated for 3 h at 300 °C. The column thus obtained has been reported[87] to contain ~ 6 mg of Al_2O_3 per metre. The quantity of the sorbent can be varied over a relatively wide range by varying the viscosity of the suspension, the velocity at which it is pressed through the column, or the volume of the suspension introduced in one portion.

To decrease the adsorption activity, the column is washed twice with a 2% solution of potassium chloride. After repeated drying and heating, the column is ready for use. The columns obtained in this way are sufficiently efficient for the separation of various substances. For example, their efficiency with respect to the peak for 3-methylbut-1-yne (the capacity factor is 7.1) is 700 tp m^{-1}. Altogether more than 50 light hydrocarbons present in a gas mixture in concentrations of about 1 part per billion each, were separated under isothermal conditions at 130 °C. A similar procedure for the application of an adsorbent onto inner walls of the column has been employed by de Nijs[35] to prepare quartz capillaries, which have been widely used for capillary columns in recent years. The application by virtue of the dynamic method requires using concentrated suspensions, since the amount of an adsorbent remaining in the column is only that contained in the thin film formed after passing the suspension. It is of interest that when a suspension prepared from spherical silica gel particles with a diameter of ~ 5 μm, meant for high performance liquid chromatography (HPLC), is passed through a column, only a loose monolayer of silica gel particles covering only 50% of the whole inner surface of the capillary is formed.

Preparation of capillary columns containing a barium sulfate layer (a solid adsorbent) on the surface has been reported.[87] Barium sulfate (which is an ionic adsorbent) is known to exhibit high selectivity in the separation of polar organic compounds.[88]

The barium sulfate used as the adsorbent in open tubular capillary columns was prepared separately by the reaction between 1.5 M solutions of barium chloride and sodium sulfate. The precipitate was filtered off and washed, until chloride ions were no longer detected ($S = 10.2$ m^2 g^{-1}). Barium sulfate was applied onto the inner walls of a capillary column (Pyrex) by the dynamic method. The solvent was removed and then the columns were conditioned at a temperature programmed to increase to 250 °C. Since the asymmetry A_s of the columns obtained amounted to 4.5 with respect to benzene, they were modified by a dynamic method using small amounts of poly(ethylene glycol) (Carbowax 3000) and polydimethylsiloxane (E-301). After modification, the efficiency of the columns sharply increased (from 900 to 2500 tp m^{-1}) and the chromatographic zones became more symmetrical. The retention of compounds in this column is caused by both adsorption and absorption processes.

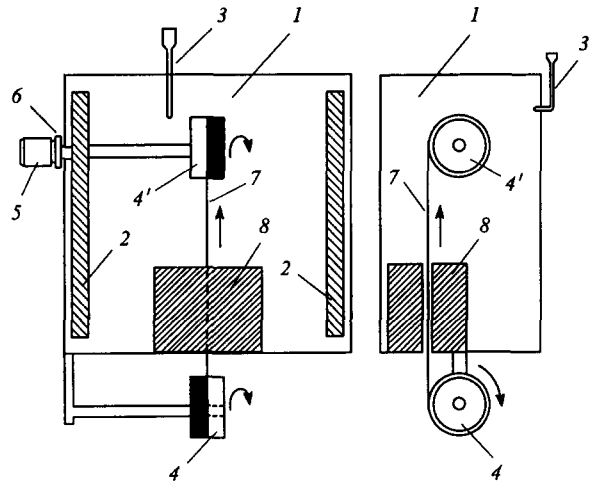


Figure 7. Arrangement for the production of open tubular adsorption capillary columns by applying an adsorbent to their inner walls using a high-pressure static method.[89]
(*1*) Air thermostat, (*2*) heater, (*3*) thermometer, (*4*, *4'*) reels, (*5*) electric motor, (*6*) connection, (*7*) capillary tube, (*8*) heated metallic unit.

To increase the thickness of the layer, attempts have been made to use the static variant of the suspension technique. Horvath[89] has constructed a special device (Fig. 7) for this purpose. A metallic capillary column was completely filled with a suspension of a sorbent in a volatile solvent; then one of the ends of the column was closed, while the other end was introduced into an air thermostat heated to 90–150 °C (through a metallic unit heated to 200–250 °C). The volatile liquid was evaporated in the metallic unit, and its vapour did not condense owing to the high temperature.

A similar device modified by Mistryukov et al.[30] has been used by Guiochon et al.[90] for the preparation of an open tubular capillary column containing 'Sterling FTG' graphitised carbon black. Initially, a 5% suspension of carbon black in dichloromethane was prepared. When squalane (0.05%) was used as the stabiliser, this suspension was stable over 24 h. This procedure makes it possible to apply 10 mg m^{-1} of the sorbent. A mixture of *o*-, *m*- and *p*-xylenes was separated at 165 °C in columns (19 m × 0.5 mm). The use of a 20% suspension of carbon black and a high-pressure static method made it possible to increase the thickness of the layer to 20 μm.[91]

A simple method for the production of adsorption capillary columns has been proposed.[92] Silica particles (5 μm) and carbon particles were suspended in a solvent, together with polydimethylsiloxane. The suspension was passed through a column (25 m × 0.32 mm), then the column was dried and heated. This gave a very stable layer.

Using the device proposed by Horvath,[89] Ettre et al.[31] have manufactured a capillary column containing a layer of Johns–Manville diatomite with an average thickness of 60 μm. In view of the fact that a sorbent with a particle size of 10 μm was used, it can be inferred that it was possible to deposit ~6 layers of the sorbent in one entry. Apparently, this result could not be achieved by the dynamic method. However, the static procedure also suffers from some drawbacks. First of all, the necessity to fill capillaries with a suspension should be regarded as being a drawback, i.e. this method, too, does not make it possible to avoid movement of a suspension along the tube. Consequently, the structure of the suspension is disturbed, particles are combined into aggregates, which are nonuniformly distributed along the column, and this leads to the formation of an inhomogeneous layer and decreases the efficiency of the separating system. In addition, this method is applicable only to volatile dispersion media, which usually possess low densities.

2. Chemical synthesis of an adsorbent on the inner surface of a capillary column

Conduction of chemical reactions yielding adsorbents directly in a column has been employed already in the early papers dealing with the preparation of open tubular capillary columns. A possible advantage of this method is that the preparation of an adsorption layer does not require using suspensions and involves only homogeneous reagents, which easily fill the whole column and can be easily removed from it. In addition, this technique provides the possibility of repeating the reaction in order to increase the thickness of the adsorption layer.

a. Etching of a capillary

The first attempts to use the technique under consideration involved preparation of a sorbent by a chemical transformation of the material from which the column was produced. This approach has been used most widely in relation to glass columns; in this case, etching or leaching of the walls by various procedures affords layers of adsorption-active silica gel.

The first results obtained by this approach have been published in a number of papers.[16–18,93] Kiselev et al.[93] have separated gaseous hydrocarbons C_1-C_4 in column (10 m × 0.5 mm), which had been preliminarily treated for a short period with 0.1 M HCl and then washed with distilled water.

Mohnke and Saffert[17,18] have filled a capillary of length 80 m with a diameter of 0.27 mm with a 17% solution of ammonia, sealed both ends of the column, and kept it for 70 h at 170 °C. After that, the liquid was removed, and the column was dried at 190 °C in a flow of a carrier gas. This procedure yielded a ~20 μm thick adsorption layer on the inner surface of the capillary. The column thus produced was used for the separation of isotopes and nuclear spin isomers of hydrogen.

Alkaline etching of glass has also been used by other researchers.[28,94–96] Their procedure involved treatment of the walls of a column with a 20% solution of NaOH for 6 h followed by activation in a flow of nitrogen at 200 °C. The columns thus produced proved suitable for the separation of oxygen and nitrogen isotopes.

The production of open tubular capillary columns, containing an internal porous layer with a fixed thickness, by etching has been patented.[97,98] Initially, a two-layer column was produced from a two-layer half-finished article consisting of two coaxial tubes. The outer tube was made of a chemically stable glass, while the inner tube was made of a chemically less stable sodium borosilicate glass. The resulting two-layer capillary was treated with alkali, which led to almost complete leaching of the inner glass layer. The porous glasses thus obtained were used as adsorbents in a capillary column. Porous glasses are known to be used successfully in gas chromatography (see for example Ref. 99).

Similar procedures have been proposed for covering the inner surface of a column with alumina (keeping aluminium capillaries in a flow of oxygen[23]) or with copper(II) oxide (treatment of copper capillaries with 40% HNO_3 followed by oxidation with dry oxygen).[100]

The known methods for chemical treatment of capillary walls are facile but not versatile and are limited only to glass (or, more rarely, to metallic) columns. In addition, the composition and properties of the resulting adsorption layer are markedly dependent on the composition of the material of the column, which can vary.

b. Synthesis of an adsorbent inside the column

A variety of adsorbents (and capillary adsorption columns) can be obtained by synthesising them inside the columns. The walls of the column are not involved in these processes. An example is provided by the reported[101] synthesis of an inorganic adsorbent, crystalline barium carbonate, on the walls of a capillary, which makes it possible to obtain a markedly more extended surface. This method has been applied successfully to a quartz capillary column.[102]

Apparently, a similar method can also be used for the preparation of capillary columns containing barium sulfate (as an adsorbent). First, barium hydroxide is applied to the inner surface of a column and then gaseous sulfur trioxide is passed through it.

Recently, a method for the production of a capillary column containing an adsorption silica layer has been proposed. The method is based on hydrothermal treatment of a sol of silica directly in a capillary column.[103] A capillary is filled with a silica sol, then a part of the sol (15% – 20% in the case of glass columns) is displaced from the column by a compressed gas, in order to avoid damage of the column during its subsequent heating; then both ends are hermetically closed, and the column is kept in a thermostat at 180 – 210 °C for several hours. Under these conditions, a silica film forms on the inner surface of the column; this results from two processes occurring in parallel, namely, dissolution of small particles of the sol and polymerisation of silica gel on the surface of the column having a large radius of curvature. Washing and drying afford a stable and relatively uniform coarse-pored layer of silica, which is not washed out from the walls. The thickness of the layer depends on the concentration of the sol and on the duration of treatment. The optimum concentration of the sol is 0.1% – 1.5%. At higher concentrations, the thickening of the silica film on the surface ceases, and coagulation of the sol in the bulk occurs instead. When the sol concentration is lower than 0.1%, dissolution predominates, and the silica film does not form at all. Under the conditions specified, the treatment of the column should last for 5 – 11 h. Heating for a longer period does not lead to any substantial increase in the layer thickness, since the rate of polymerisation markedly decreases at the end of heating. Shorter heating results in the formation of a very thin layer with low adsorption activity. The columns obtained in this way can be used advantageously for quick analysis of light hydrocarbons.[103]

Volkov et al.[104] have proposed a simple method for producing an adsorption layer based on magnesian cement.

It is noteworthy that the technique involving synthesis of an adsorbent inside a capillary has also been used to produce adsorption capillary columns with organic hydrophobic adsorbents.[105]

3. Mechanical method (formation of an adsorption layer during production of a glass capillary)

When a glass capillary is manufactured, a ready-for-use sorbent can be introduced into it without being converted into a suspension. Since a capillary is drawn from a relatively wide tube, a sorbent can be easily placed into it before drawing.

Halasz and Heine[106] have produced in this way columns with alumina. In order to preserve an open passage inside the column, they inserted a steel wire 1 mm in diameter into it. As the tube was drawn, alumina particles were captured by the softened glass. The resulting 2 m long column was an intermediate version between a packed column and an open tubular capillary column and exhibited a relatively high efficiency, 3500 tp m^{-1} with respect to ethylene.

In a later modification of this technique, the diameter of the wire was diminished to the size of the inner passage in the column, and the wire itself passed through the area of softening and ended in the capillary (Fig. 8). This design permitted the diameter of the inner tube in the column and, hence, the thickness of the layer to be exactly specified. For example, Grant[107] has manufactured a column with an inner diameter of the capillary of 0.3 mm and with a 100 μm thick alumina layer by using a 0.1 mm thick tungsten wire. In this study, lithium chloride was used as a binding agent in the preparation of the adsorption column. The height equivalent to a theoretical plate for this column was ~0.5 mm.

Since this technique involves heating of adsorbents to high temperatures (700 – 800 °C), the range of adsorbents used is limited to thermally stable substances withstanding temperatures up to the temperature of glass softening. Therefore, apart from alumina, graphitised carbon black has been used. Goretti et al.[108] has produced by this method capillary columns with a length of ~10 m containing 50 – 100 μm thick layers of graphitised carbon black. The efficiency of the columns obtained was ~1500 tp m^{-1}, their permeability being relatively high.

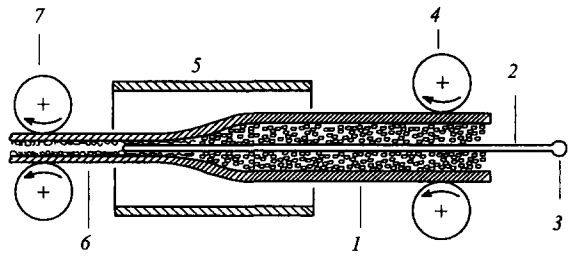


Figure 8. Arrangement for the production of open tubular adsorption columns during drawing of a capillary from a wide tube.[107]
(*1*) Pyrex tube (outer diameter 9 mm, inner diameter 5 mm) filled with particles of a solid packing material (support or adsorbent) and with particles of anhydrous lithium chloride, (*2*) tungsten wire (diameter 0.3 mm), (*3*) the point of fastening of the tungsten wire, (*4*) feeding rollers, (*5*) electric furnace, (*6*) the column with a sorbent layer on the inner walls being produced, (*7*) pulling rollers.

According to the interesting method proposed by Liberti et al.,[109] a graphitised fibre (7.5 – 10 μm in diameter) was inserted into the initial tube. When this tube was drawn into a capillary by the usual procedure, the fibre reeled out of the spool and entered the capillary; as this occurred, a gap of 0.2 – 0.3 mm remained inside the capillary. The length of the column thus obtained varied from 1.5 to 10 m, and the inner diameter varied from 0.4 to 0.5 mm.

In our opinion, application of an adsorption layer during the production of a glass capillary from a wide tube is among the most promising techniques; however, it also suffers from some drawbacks. Firstly, it is applicable only to thermally stable adsorbents (for example, polymeric adsorbents cannot be used in this method). Secondly, to obtain a tightly fixed adsorption layer, a specific binding material should be selected for each type of adsorbent and for each material of the column. Thirdly, in the case of sorbents, which are unstable in air at high temperatures, the process must be conducted under an inert atmosphere, which complicates the apparatus used.

The method for the production of open tubular adsorption capillary columns by synthesising sorbents directly in the capillary permits the simultaneous solution of two problems — preparation of the sorbent and its fixing to the walls. However, it is applicable to a limited range of adsorbents.

In our opinion, the suspension method is most universal as regards the preparation of open tubular capillary columns. However, in this method, too, the problem of fixing an adsorbent on the inner walls of a capillary column has not been solved. The way of fixing and the substance suitable for this purpose should be specially selected. What particular method is optimum in each case depends apparently on the type of sorbent used and on the material of the column.

In conclusion, it should be noted that the problem of the preparation of open tubular capillary columns with walls coated by an adsorption layer cannot be regarded as already solved. This delays somewhat the application of the adsorption capillary chromatography. Elaboration of new methods for the preparation of highly efficient open tubular capillary columns is a basic challenge in the development of capillary gas adsorption chromatography.

VI. The use of open tubular gas-solid capillary columns

At present, gas-solid capillary chromatography is widely used in analytical practice. The area of application of gas adsorption capillary columns is constantly extending. In 1995, columns of this type were presented at the Pittcon-95 workshop by four well-known companies from the USA alone (Table 4). However, the

Table 4. Some characteristics of new capillary gas adsorption columns presented at the Pittcon-95 workshop.[110]

Sorbent	Thickness of the sorption layer /μm	Dimensions of the column[a] /m × mm	Notes
Carboxen-1006 column from Supelco			
Carbon molecular sieves, $S = 750\ m^2\ g^{-1}$	–	30 × × 0.32 (0.53)	Separation of permanent gases and C_1-C_3 hydrocarbons, temperatures of up to 250°C
Gas-Pro-GSC column from Astec			
Not indicated	–	(5–60) × × 0.32	C_{10} and lighter hydrocarbons; carbon, sulfur, and nitrogen oxides; sulfur and halogen-containing organic compounds, permanent gases
HP PLOT Molsieve column from Hewlett-Packard			
5A Molecular sieves	12.50	Various	Permanent gases, separation of argon and oxygen at ambient temperatures, separation of krypton and nitrogen
RT Molsieve 13X column from Restek			
13 X Molecular sieves	1.2–4.0	(15; 30) × × (0.32; 0.53)	Permanent gases, 13X molecular sieves ensure faster and more effective separation than 5A molecular sieves
RtD PLOT column from Restek			
Divinylbenzene	2	30 × 0.53	Permanent gases and hydrocarbons, separation of air, carbon dioxide, light hydrocarbons, natural gas
Supel Q PLOT column from Supelco			
Divinylbenzene	–	30 × × (0.32; 0.53)	C_1-C_{10} hydrocarbons, chlorofluorohydrocarbons, sulfur-containing gases

[a] The length (m) and the diameter (mm) of the columns are given.

current level of practical application of open tubular capillary columns is far from their real potential. While developing new analytical procedures, one should take into account the advantages and the limitations of the gas-adsorption chromatography (see above). The adsorption capillary chromatography is a hybrid method combining the advantages of the adsorption and capillary versions of chromatography.

Considering the advantages of capillary columns over packed columns, only the higher efficiency of the former is often mentioned. At the same time, capillary columns are also characterised by higher rates of separation (quicker analysis), by more reproducible temperature regimes, by small sizes of the apparatus needed, and by lower consumption of carrier gases and sorbents; they also extend the field of application of gas adsorption chromatography, due to lower separation temperatures.

In order to select the optimum conditions while developing a procedure for separation, it is expedient to consider a plot that makes it possible to estimate quickly the number of theoretical plates needed (and, hence, the length of the column), if the selectivity and capacity of the adsorbent used are known.

Figure 9 shows the dependence of the number of theoretical plates needed for separation (N_r) on the selectivity of the sorbent used (α) for compounds characterised by different capacity factors (k):

$$N_r = \varphi[(\alpha-1), f^2]\,. \tag{25}$$

The influence of the capacity factor is reflected in this plot by the following function

$$f^2 = \left(\frac{k+1}{k}\right)^2 = \left(1+\frac{\beta}{K_D}\right)^2, \tag{26}$$

each f^2 value being matched by a particular curve:

$$N_r = \varphi[(\alpha-1), f^2] = \text{const}\,. \tag{27}$$

Let us consider an example of practical application of the plot shown in Fig. 9. Assume that we have to determine the number of theoretical plates needed to separate two components with $\alpha = 1.05$ and $K_D = 100$ in a column with $\beta = 40$. For this pair of compounds, $f^2 = 2$. For the characteristic curve $f^2 = 2$, the point $\alpha-1 = 0.05$ on the abscissa in Fig. 9 corresponds to the point $N_r = 16000$ theoretical plates on the ordinate. Thus, we determined the desired efficiency of the column, which is needed to separate the pair of compounds in question.

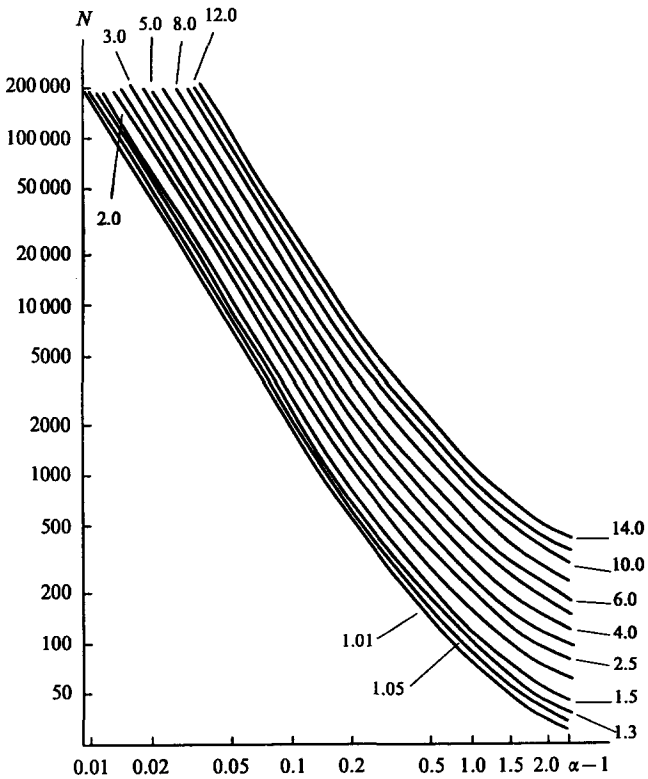


Figure 9. Graphical determination of the number of theoretical plates N_r, needed to separate a pair of compounds, depending on the selectivity of the sorbent α and the parameter f^2, which is determined by the capacity factor k.[111]
The numbers on the curves give the magnitudes of f^2.

An important field of practical application of gas chromatographic analysis is the analysis of impurities.[13,52,61,63,112] Sensitivity (detection limit) is often a crucial characteristic of a method used for this kind of analysis. As samples become larger, the sensitivity of determination increases, but the efficiency of the column simultaneously decreases. Therefore, the dependence of the efficiency (i.e. of the HETP) on the size of the sample being analysed is of practical interest regarding the optimisation of the separation conditions, since to achieve a higher sensitivity, the samples subjected to analysis should be as large as possible.

The dependence of HETP on the size of the sample in the capillary chromatography determines whether a capillary column without a flow splitter can be used, and also whether the use of a particular column in the traditional methods for the determination of impurities would be expedient. The dependence of the chromatographic zone broadening on the size of the sample under analysis has been discussed in a number of studies (see for example Refs 61,63,112).

It would be convenient to evaluate this dependence quantitatively using a linear equation relating HETP to the size of the sample. An equation of this type has been proposed.[113] It is in satisfactory agreement with the experimental results obtained for open tubular capillary columns containing a stationary liquid layer (as an adsorbent) and for packed capillary columns.[114]

The dependence of the efficiency of a column on the size of the sample under analysis has been studied in relation to an open tubular gas adsorption column with alumina-coated inner walls (produced by 'Chrompack').[43] The experimental results were processed in terms of the following equation:[113]

$$\sqrt{H} = \sqrt{H_0} + \lambda W, \qquad (28)$$

where H_0 is the limiting HETP value corresponding to the sample size approaching zero, λ is a constant determined by characteristics of the system in question; W is the size of the sample injected into the column (or a quantity proportional to it). Eqn (28) makes it possible to determine both the H_0 value and the variation of H as a function of W.

The dependences $\sqrt{H} = \Psi(W)$ corresponding to Eqn (28) and obtained in experiments with the same open tubular capillary column but using different methods for the injection of the sample (with and without a flow splitter), are shown in Fig. 10. The plots of HETP against the size of the sample in these coordinates are linear, which experimentally confirms Eqn (28). When the sample is introduced with a flow splitter, the efficiency of the column increases (the $\sqrt{H}$ value decreases). However, as regards the increase in the sensitivity, the least flow splitting (i.e. the least possible discharge) or even no splitting are desirable.

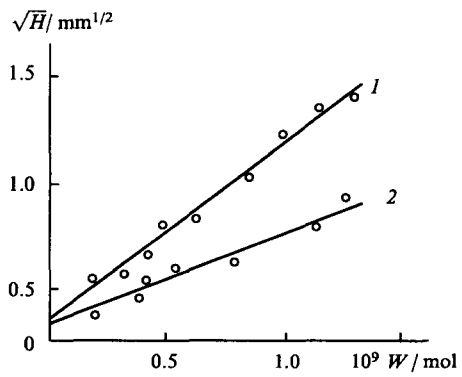


Figure 10. Dependence of $\sqrt{H}$ on the size of the sample under analysis for *n*-butane in an open tubular capillary adsorption column with inner walls coated with alumina, the sample being injected without a flow splitter (*1*) and with a flow splitter (*2*).[43]
A 50 m × 0.32 mm quartz column from Chrompack (Netherlands) with an alumina layer and a flame ionisation detector were used; T = 100 °C.

Note that irrespective of the method used for the injection of samples (with or without a flow splitter), the limiting value of the efficiency of the column H_0 is nearly the same. This specific feature of the dependence observed is additional evidence for the validity of Eqn (28).

The results obtained indicate that an open tubular packed column with inner walls coated with an adsorption layer can also be used in a gas chromatograph without a flow splitter (although in this case, the efficiency markedly decreases). However, the decrease in the efficiency is not very significant for a fairly broad range of analytical procedures.

At present, gas adsorption chromatography is used most frequently for the analysis of volatile compounds with various isotope compositions, of inorganic and organic gases, of volatile organic polar compounds, and of aqueous solutions of organic compounds.

The separation of nuclear spin isomers and isotopes of hydrogen[18] was the first prominent example of the practical application of the adsorption capillary chromatography (see Fig. 2). Later, it has been shown that the time required for the separation of the nuclear isomers of protium and deuterium could be shortened by decreasing the temperature of the column to 47 K.[115]

Oxygen isotopes ($^{16}O_2$ and $^{18}O_2$) have been separated in an adsorption capillary column[96] (Fig. 11). The adsorption layer on the inner walls of a glass column was produced by etching the walls with 20% NaOH for several hours at 100 °C. When this process was prolonged enough (more than 4 h), clear separation of the isotopes was achieved. The efficiency of the capillary columns used was ~350 000 theoretical plates. A mixture of nitrogen (65%) and helium (35%) was used as the carrier gas.

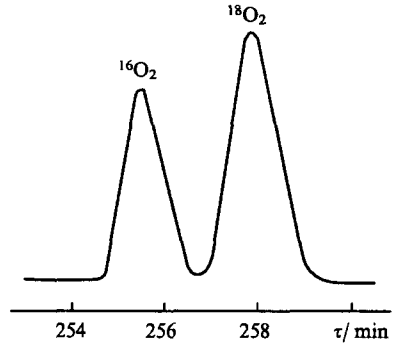


Figure 11. Chromatogram for the separation of a mixture of $^{16}O_2$ and $^{18}O_2$ isotopes in an adsorption glass capillary column (175 m × 0.3 mm) at 77 K, and with the N_2 (65%) – He (35%) binary carrier gas.[96]

Nitrogen isotopes ($^{14}N_2$ and $^{15}N_2$) have been separated by Cartoni and Possanzini[94] in an open tubular gas adsorption glass capillary column, the inner walls of which had been etched in order to produce an adsorption layer. The procedure for the preparation of this column has been reported.[95]

Figure 12 shows the chromatogram for the separation of the nitrogen isotopes. The experiment lasted for ~3 h; however, only partial separation was achieved. It is obvious that the separation can be markedly improved, for example, by optimising its conditions.[116]

It is noteworthy that the nitrogen isotopes have been separated on a sorbent with a very low selectivity (α = 1.006). A mixture of helium and carbon dioxide (45%) was used as the carrier gas, the latter also acting as a modifying agent for the adsorption layer of silica coating the walls of the column.

A sharp separation of neon isotopes (^{20}Ne and ^{22}Ne) has been achieved by Purer et al.[116] at a low temperature (19 K). The height equivalent to a theoretical plate for the glass column used (82 m × 0.28 mm) amounted to 0.8 mm at k = 0.8 and α = 1.06.

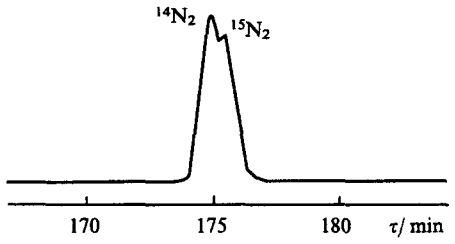


Figure 12. Chromatogram for the separation of nitrogen isotopes.[94]
An open tube glass capillary column (175 m × 0.28 mm) with walls coated by an adsorption layer obtained by etching and a mixture of helium and carbon dioxide (45%) as the carrier gas were used; $T = 77$ K.

Complete separation of neon isotopes can be achieved if a shorter column (45 m) is used.

To obtain the adsorption layer on the walls, the initial capillary was etched with 10% sodium hydroxide for 6 h at 100 °C according to the procedure proposed by Brunner and Cartoni.[28] It has been reported[116] that mixtures containing ^{21}Ne can also be separated by this procedure.

The separation of hydrogen isotopes[18] has certainly stimulated studies aimed at the separation of isotopically substituted molecules of organic compounds.

Figure 13 presents a chromatogram obtained for the separation of methanes with different isotopic compositions.[27] It is of interest that not only the methane molecules containing different hydrogen isotopes but also those with different carbon isotopes were separated in this experiment. Thus, we can agree with the opinion stated sometimes that a chromatograph is also a simple and cheap mass spectrometer.

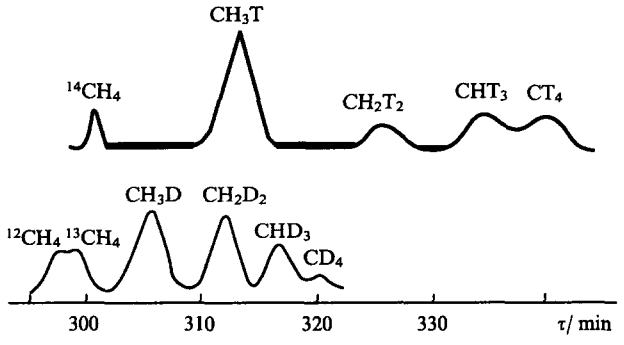


Figure 13. Chromatogram for the separation of deuterated and tritiated methanes.[27]

The separation of methanes (see Fig. 13) was carried out using an open tubular adsorption capillary column containing a silica layer, which had been etched with a sodium hydroxide solution, according to a previously described procedure.[28] The column used was fairly effective (70 000 theoretical plates), and the peaks were symmetrical even at low temperatures. A mixture of helium (30%) and nitrogen (70%) was used as the carrier gas. A clear separation of tritiated methanes in a substantially more prolonged experiment has been also reported.[117]

In our opinion, the use of adsorption capillary columns with molecular sieves as the adsorbent holds the greatest promise for the separation of isotopically substituted molecules. Separation of molecules of gaseous compounds differing in the isotope composition is a promising branch of capillary gas adsorption chromatography.

Some progress has been achieved in the separation of isotopically substituted liquid organic compounds. For example, separation of benzene and deuteriobenzene and of toluene and deuteriotoluene has been reported.[108] This was accomplished on a capillary column with a layer of graphitised carbon black.

The above examples indicate that adsorption capillary columns can be successfully used for the separation of isotopically substituted compounds. Further studies along this line will substantially simplify tracer techniques.

The separation of inorganic and organic gases in capillary columns is of great practical significance. In our opinion, capillary columns with molecular sieves are the most promising. Purcell[85] was the first to use columns of this type for the separation of permanent gases. An interesting example of using 13 Å molecular sieves for separation of hydrocarbons of various types in capillary columns has also been reported.[118–120]

The procedure used currently for the separation of permanent gases in an open tubular flexible quartz capillary column with molecular sieves was apparently described for the first time by de Zeeuw and de Nijs.[121] Verga,[122] who has used a similar column, has demonstrated that columns of this type are suitable for solving a number of practically important problems. He used a highly sensitive helium ionisation detector. Fig. 14 shows the results of separation of a standard mixture of permanent gases in helium and of determination of carbon monoxide present in air in a concentration of 2–3 ppm. It is noteworthy that oxygen and argon (3 ppm) are clearly separated under these conditions at 35 °C.

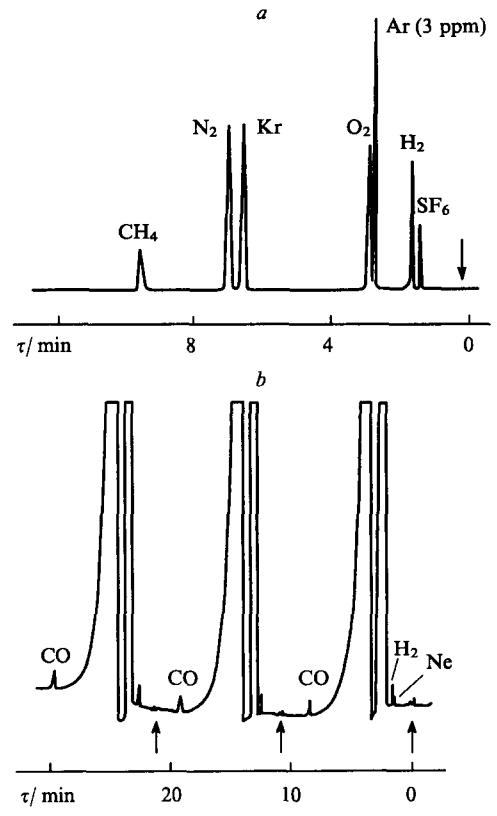


Figure 14. Chromatogram for the separation of a mixture of permanent gases in helium at 35 °C (*a*) and for determination of carbon dioxide in air at 80 °C (*b*).[122]
A 25 m × 0.32 mm column with 5 Å molecular sieves was used.

Oxygen and argon as well as samples of methane differing in the hydrogen isotope composition have been separated[123] in a capillary column with 5 Å molecular sieves at room temperature.

Among the numerous fields of application of open tubular adsorption capillary columns, space research should be mentioned. For example, for the studies dealing with the atmosphere of Titan (a satellite of Jupiter), a procedure for the analysis of a gas

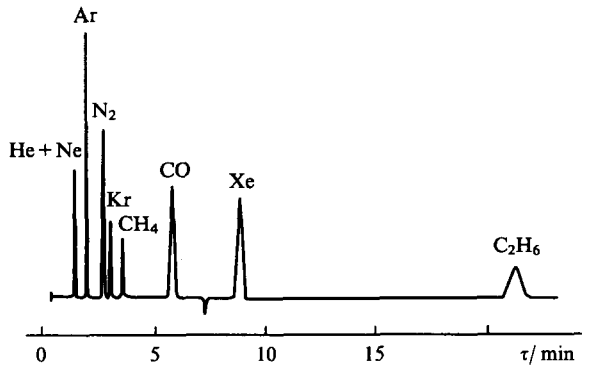


Figure 15. Chromatogram for the separation of a mixture of inorganic and hydrocarbon gases in a quartz adsorption column.[73]
A 10 m × 0.53 mm column with 5 Å molecular sieves was used (the adsorption layer was 50 μm thick); $T = 90$ °C; hydrogen with a velocity of 2 ml min^{-1} at the outlet of the column was used as the carrier gas, the flow spitting was 1 : 40, and a katharometer was used as the detector.

mixture simulating qualitatively the suggested composition of the atmosphere of this satellite has been developed by Vanssay et al.[73] (Fig. 15).

Analysis of mixtures of gaseous hydrocarbons and light hydrocarbons is a practically important problem. Alumina is widely used for the separation of these compounds. The analytical potential of columns containing alumina was demonstrated for the first time by Schneider et al.[86]

A significant contribution to the perfection of columns of this type has been made by researchers of the 'Chrompack' company.[35-37,41,124] In recent years, this company has been manufacturing open tubular capillary columns based on metallic capillaries with an inert inner surface coated with a layer of an inert material (Ultimetal column). Two modifications of these columns containing alumina are produced; they differ in the salt used for the modification.[125] The columns containing Al_2O_3/KCl are less polar than those with Al_2O_3/Na_2SO_4. Chromatograms obtained in the separation of a mixture of C_1–C_4 hydrocarbons using columns of both types are shown in Fig. 16. It is advisable to use the columns with Al_2O_3/Na_2SO_4 as the adsorbent for the separation of a mixture of butenes.

Capillary columns with alumina are also used for the separation of light halocarbons. The data on retention obtained experimentally for halo-derivatives of hydrocarbons in a capillary adsorption column with Al_2O_3 (60 m × 0.32 mm) have been supplemented by the data on the retention obtained by calculations.[126] The calculations have been mostly carried out by two methods — correlation equations[127,128] and additive schemes.[129] High resolving power of adsorption capillary columns with Al_2O_3 has been noted;[126] the researchers were able to separate such isomers as CF_2ClCF_2Cl and CF_3CFCl_2 (previous attempts to separate these isomers in gas-liquid capillary columns have failed).

Adsorption capillary columns possess relatively high capacities; therefore, they are suitable for the analysis of impurities.

While considering the range of practical application of capillary columns with alumina, one should mention the possibility of conducting fast analysis of gaseous hydrocarbons (the analysis can take no more than 100 s).[124] This is of special interest for the purposes of industry.

Adsorption capillary columns are successfully used in complex chromatographic systems for fast separation of mixtures containing components with different boiling points.

The separation of complex multicomponent mixtures can be substantially improved if sorbents, optimum for the selective separation of individual fractions of the mixture (or even of individual groups of compounds) are specially selected for each particular case. Therefore, gas chromatographic systems with adaptable structures have been used for a fairly long period in

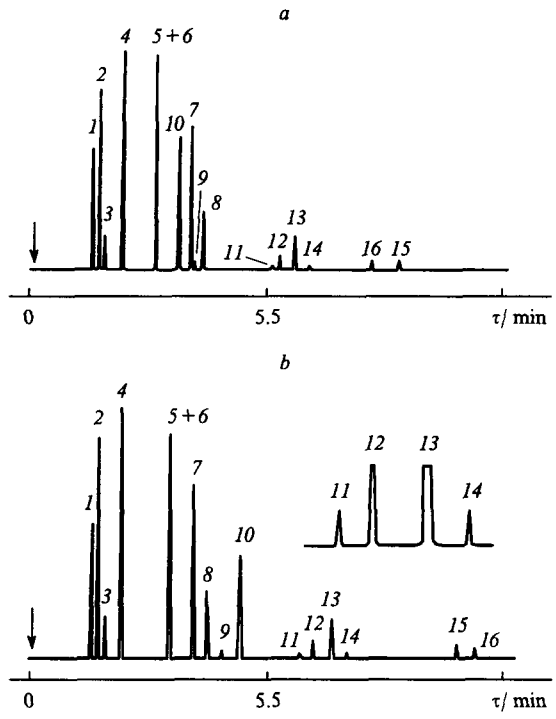


Figure 16. Chromatogram for the separation of C_1 – C_4 hydrocarbons in special metallic capillary columns with Al_2O_3/KCl (*a*) and Al_2O_3/Na_2SO_4 (*b*).[125]
Peaks: (*1*) methane, (*2*) ethane, (*3*) ethene, (*4*) propane, (*5*) cyclopropane, (*6*) propene, (*7*) isobutane, (*8*) butane, (*9*) propadiene, (*10*) acetylene, (*11*) *trans*-but-2-ene, (*12*) but-1-ene, (*13*) isobutene, (*14*) *cis*-but-2-ene, (*15*) buta-1,3-diene, (*16*) methylacetylene. A 50 m × 0.32 mm column and hydrogen as carrier gas were used, the temperature increased from 70 to 130 °C at a rate of 5 °C/min.

gas chromatography on packed columns, especially for industrial purposes. These schemes make it possible to change automatically, during the analysis, the order in which the columns are connected and the direction of the carrier-gas flow in the individual sections (or in the whole scheme) and also to include individual columns into the scheme or to exclude them from it. Thus, the conditions for the separation of individual groups of compounds can be optimised, the time required for the analysis can be shortened, and the stability of the operation of the columns used can be increased.

The use of such schemes also in the capillary chromatography would certainly be expedient and would markedly improve the separation. The first gas chromatograph 'Siechromat' based on an adaptable multicolumn scheme was developed by Siemens (Germany). Fig. 17 shows two chromatograms obtained in the separation of a mixture of C_1 – C_8 hydrocarbons in n-pentane with this instrument. The boiling points and chromatographic characteristics of the components of this mixture were essentially different. Initially, this mixture was separated at 75 °C in an open tubular capillary column (24 m × 0.27 mm), the inner walls of which were coated with a modified clay (Bentone-34) impregnated with di-*iso*-decyl phthalate. This main column ensured clear separation of benzene (*11*), toluene (*12*), ethylbenzene (*13*), *p*-xylene (*14*), *m*-xylene (*15*), and *o*-xylene (*16*). The C_1 – C_5 light hydrocarbons were rapidly eluted from the column; therefore, they were responsible for one common peak in the chromatogram.

Fast separation of light hydrocarbons was achieved by injecting them into another open tubular capillary column (80 m × 0.4 mm), the inner walls of which were coated with a layer of alumina modified with potassium chloride. The separation in this column was carried out at 15 °C. Light hydrocarbons — methane (*1*), propane (*2*), propene (*3*), isobutane (*4*),

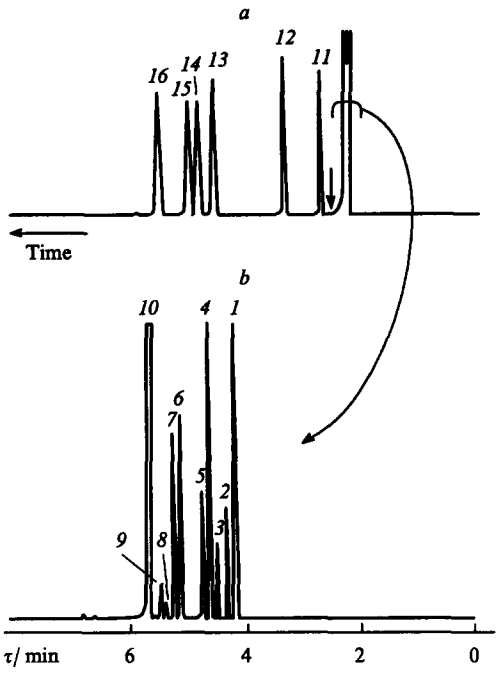


Figure 17. General chromatogram for the separation of C_1-C_8 hydrocarbons in an open tubular capillary column (*a*) and the partial chromatogram for the fraction of C_1-C_5 hydrocarbons (*b*).[130]
Experimental conditions 24 m × 0.27 mm columns with Bentone-34 impregnated with diisodecyl phthalate as adsorbent (*a*) and a 80 m × 0.4 mm column with alumina (*b*).

Table 5. Reproducibility of retention values and concentrations of components found in a mixture being analysed for an open tubular gas adsorption capillary column from Chrompack.

Compound	Retention time		Concentration	
	τ/ min	R (%)[a]	c, %	R (%)[a]
CO_2	2.11	0.5	5.3	0.8
O_2	2.58	0.3	1.1	0.7
N_2	2.58	0.3	4.4	0.6
CH_4	$\left(\frac{3.77}{5.54}\right)^b$	$\left(\frac{0.25}{0.15}\right)^b$	5.0	0.8
CO	4.33	0.25	4.9	0.7
C_2H_6	6.91	0.15	2.2	0.6
C_2H_4	8.05	0.12	0.6	0.7
C_3H_8	9.05	0.10	2.1	0.8
C_3H_6	10.28	0.12	1.9	0.6
iso-C_4H_{10}	11.73	0.10	0.4	0.8
n-C_4H_{10}	12.13	0.10	7.4	0.5
iso-C_4H_8	13.05	0.10	6.7	0.5
C_4H_8	13.95	0.10	4.83	0.5
2-*trans*-C_4H_8	14.27	0.10	10.80	0.4
2-*cis*-C_4H_8	14.66	0.10	4.7	0.7
Buta-1,3-diene	16.28	0.09	38.8	0.8
n-C_5H_{12}	22.18	0.08	1.0	0.8

[a] R — mean square deviation from the average value. [b] The numbers above the bar refer to a packed column, those below the bar refer to a capillary column. The statistical data were obtained from 10 experiments (calculations were carried out by the internal normalisation method).

n-butane (*5*), but-1-ene (*6*), *trans*-but-2-ene (*7*), butadiene (*8*), isobutene (*9*), and *cis*-but-2-ene (*10*) — were separated in this column. The separation in the two capillary columns occurred simultaneously, the time required for the process in each column not exceeding 6 min. This example clearly illustrates the advantages of using adaptable multicolumn schemes in gas chromatography and the possibility of increasing markedly the separating capacity of capillary chromatography. These schemes make it possible to gain a larger amount of chromatographic information than a traditional single analysis.

Chromatographic schemes in which adsorption capillary columns are used together with packed columns have also been reported (see for example Ref. 131). Poy and Cobelli[131] have shown experimentally that the use of a gas chromatograph with a flame-ionisation detector ensures fairly high reproducibilities of the retention values and of the proportions of the components determined for a mixture subjected to the analysis (Table 5). The results obtained by these workers can be regarded as experimental justification for using open tubular capillary columns for analytical and physicochemical purposes.

At present, porous organic polymers are used fairly frequently as adsorbents in adsorption chromatography (especially for polar compounds).[132, 133] Capillary columns with porous organic adsorbents have been used[125] for the analysis of the following classes of compounds: C_1-C_5 alcohols, C_2-C_7 fatty acids, C_1-C_2 halohydrocarbons, C_1-C_5 hydrocarbons, solvents, C_1-C_5 aldehydes, gases, mixtures of gases with water, C_3-C_8 ketones, and C_1-C_9 thiols.

The use of porous organic polymers as adsorbents offers a number of advantages; the main of them are high homogeneity of the surface with controllable (within certain limits) porosity and hydrophobicity of particular types. Therefore, porous polymers can be figuratively regarded as organic polymeric phases that have come to a standstill.

Open tubular capillary columns containing a polymeric layer on the inner walls were produced for the first time by Hollis,[105] while the modern variant of these columns based on flexible quartz capillaries has been developed by Dutch researchers of the 'Chrompack' company;[39, 125, 134] the same researchers have also developed special metallic capillary columns with polymeric adsorbents.[38] Fig. 18 presents three chromatograms obtained for the separation of C_1-C_4 hydrocarbons using three different types of columns. It is seen that the retention of hydrocarbons on the organic adsorbent differs sharply from that on methylsilicone and alumina; in the case of the organic adsorbent, groups of hydrocarbons differing in the number of carbon atoms in their molecules can be clearly distinguished. Examples of successful separation of polar organic compounds in columns of this type have been reported.[38, 39, 123, 125]

Note that natural organic adsorbents can also be used in capillary columns. Fig. 19 shows the results of the separation of organic acids of natural origin on a natural polymer, *Staphylococcus aureus* cells. A quite satisfactory degree of separation was achieved. The use of natural adsorbents seems promising.

Gas capillary chromatography has been used for the separation of hydrocarbons and nitriles.[136,137] Porapak Q and Al_2O_3/KCl were used as adsorbents, a thin layer of which covered the inner walls of a capillary column. Good results were achieved with the PoraPLOT Q column (10 m × 0.32 mm); in the case of the PLOT Al_2O_3/KCl column, nitriles are held tightly, some of the peaks being asymmetrical.

Determination of buta-1,3-diene in air carried out using a PLOT capillary column containing Al_2O_3/KCl (50 m × 32 mm) has been described by Finnish researchers.[138]

Columns with traditional adsorbents, for example, with graphitised carbon black, also find practical application. 'Structural sensitivity', which is manifested in the separation of isomers, is a specific feature of graphitised carbon black used as an adsorbent. This feature, which is very attractive for an analyst, can be illustrated by the separation of hydrocarbons, the chromatogram for which is shown in Fig. 20. All the three isomers of xylene were separated in a capillary column with

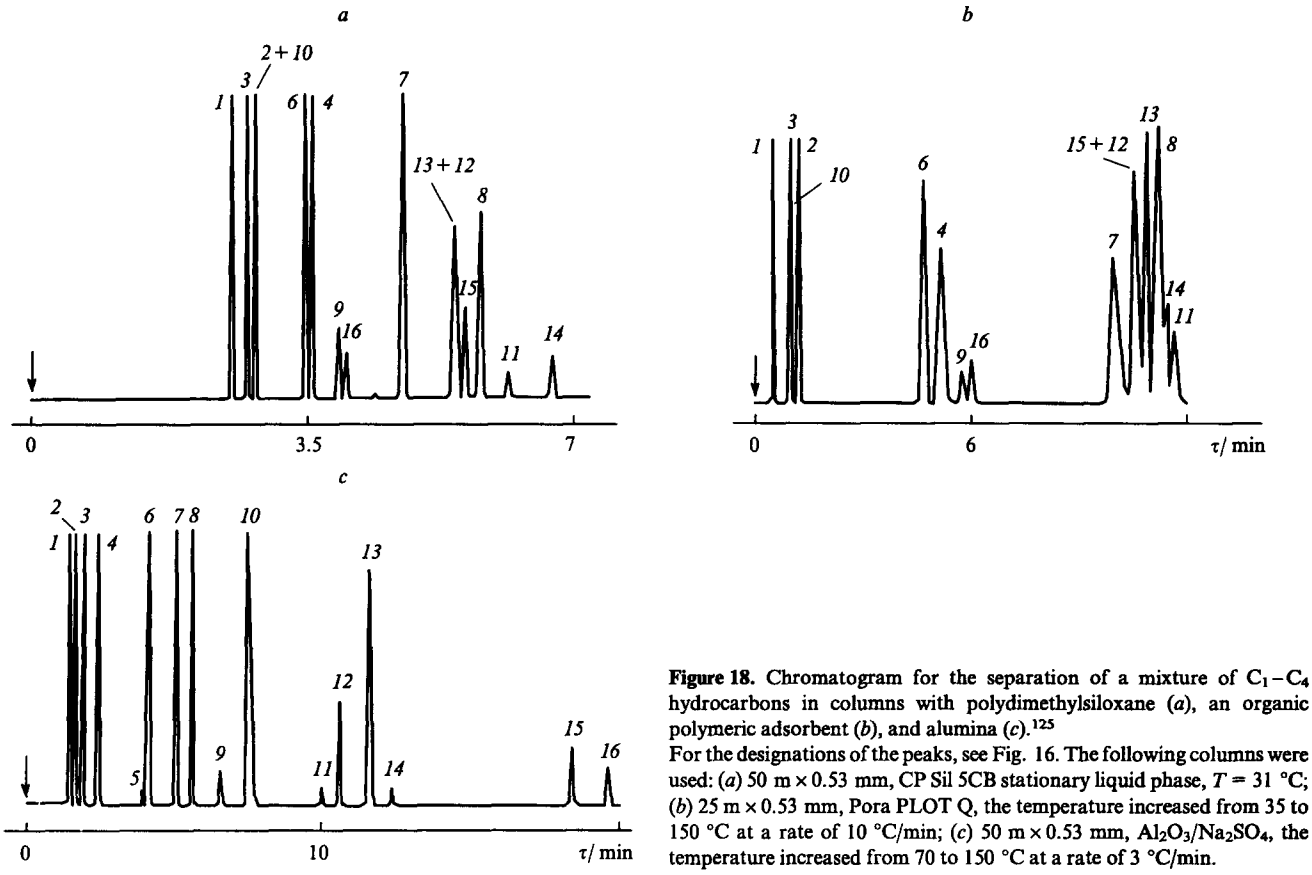


Figure 18. Chromatogram for the separation of a mixture of C_1-C_4 hydrocarbons in columns with polydimethylsiloxane (*a*), an organic polymeric adsorbent (*b*), and alumina (*c*).[125]
For the designations of the peaks, see Fig. 16. The following columns were used: (*a*) 50 m × 0.53 mm, CP Sil 5CB stationary liquid phase, T = 31 °C; (*b*) 25 m × 0.53 mm, Pora PLOT Q, the temperature increased from 35 to 150 °C at a rate of 10 °C/min; (*c*) 50 m × 0.53 mm, Al_2O_3/Na_2SO_4, the temperature increased from 70 to 150 °C at a rate of 3 °C/min.

graphitised carbon black. In another study,[136] adsorption columns with Carbopack B modified with a non-volatile liquid phase have been used; these columns are usually called Carbon Layer Open Tubular (CLOT) columns.

Graphitised carbon black can be used for the analysis of mixtures of halohydrocarbons. The results of separation of some halohydrocarbons in an adsorption capillary column (Carbopack B + 1% SP 1000) are shown in Fig. 21.

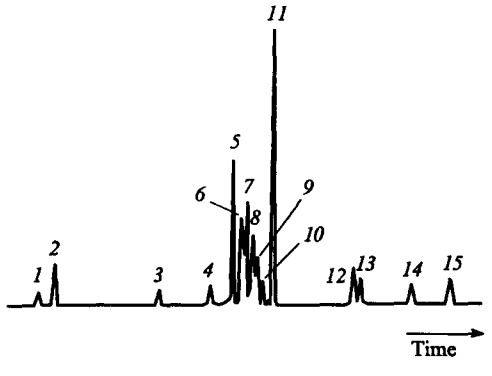


Figure 19. Chromatogram for the separation of unsaturated acids in an open tubular capillary column in which *Staphylococcus aureus* cells were used as the adsorbent.[135]
Acids: (*1*) 14 : 1 tetradecenoic; (*2*) 14 : 0 myristic; (*3*) 15 : 0 pentadecanoic; (*4*) cΔ^8 16 : 1 *cis*-hexadec-8-enoic; (*5*) cΔ^9 16 : 1 *cis*-hexadec-9-enoic (palmitic); (*6*) cΔ^{10} 16 : 1 *cis*-hexadec-10-enoic; (*7*) cΔ^{11} 16 : 1 = tΔ^9 16 : 1 *cis*-hexadec-11-enoic and *trans*-hexadec-9-enoic; (*8*) tΔ^{10} 16 : 1 *trans*-hexadec-10-enoic; (*9*) tΔ^{11} 16 : 1 *trans*-hexadec-11-enoic; (*10*) tΔ^{12} 16 : 1 *trans*-hexadec-12-enoic; (*11*) 16 : 0 palmitic; (*12*) cΔ 17 : 0 *cis*-methylenehexadecanoic; (*13*) tΔ 17 : 0 *trans*-methylenehexadecanoic; (*14*) 18 : 0 octadecenoic; (*15*) 18 : 0 stearic.

Columns with graphitised carbon black are used mostly for the separation of gaseous and relatively light hydrocarbons; however, Brunner et al.[141] have shown that they can also be used for the determination of some herbicides in water.

A practically significant separation of halo-derivatives of hydrocarbons in open tubular capillary columns containing a layer of solid adsorbents on the inner surface of the capillary has been studied by de Zeeuw et al.[142] They showed that the PLOT columns with Al_2O_3/KCl are very selective towards the separation of volatile compounds of this type; however, proportions of some of these compounds in the mixture changed during the elution.

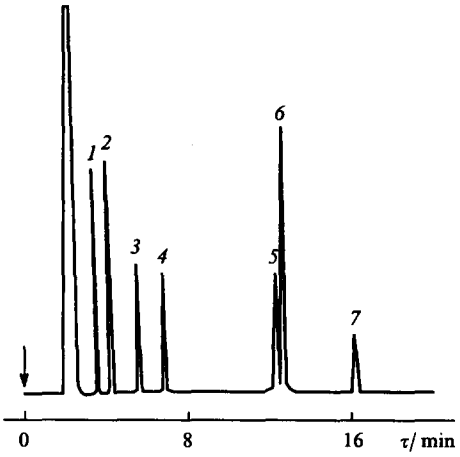


Figure 20. Chromatogram for the separation of a mixture of aromatic hydrocarbons in a capillary column with graphitised carbon black.[139]
(*1*) n-Octanol; (*2*) benzene; (*3*) n-nonane; (*4*) toluene; (*5*) *p*-xylene; (*6*) *m*-xylene; (*7*) *o*-xylene. A 30 m × 0.32 mm column with Carbopack B was used; T = 60 °C; helium was used as the carrier gas.

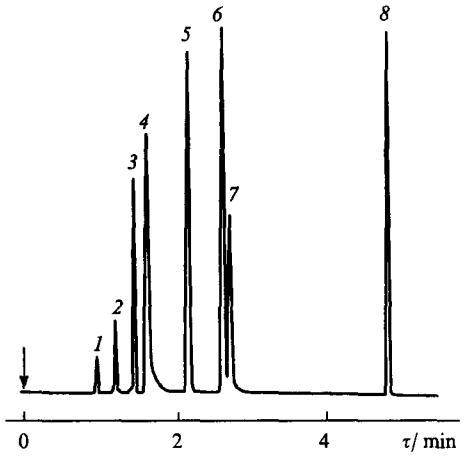


Figure 21. Chromatogram for the separation of a mixture of halohydrocarbons in a capillary column with Carbopack B modified with 1% of a stationary liquid phase.[140]
(*1*) CFC 12; (*2*) CFC 114; (*3*) CFC 11; (*4*) $C_2H_2Cl_2$; (*5*) CFC 113; (*6*) CH_3CCl_3; (*7*) CCl_4; (*8*) C_2Cl_4. A 32 m × 0.53 mm column was used; hydrogen was used as the carrier gas, $T = 30$ °C (2 min) followed by heating to 180 °C at a rate of 20 °C/min.

The use of capillary columns with the PoraPLOT Q adsorbent is promising for the analysis of chlorofluoro-derivatives of hydrocarbons.

Bruner et al.[143] have developed a procedure for the determination of hydrocarbons and amines in a capillary column with graphitised carbon black modified with various liquid phases.

Stationary liquid phases are widely used for the modification of solid adsorbents in gas adsorption chromatography. The retention in these systems can be described in terms of the additive absorption–adsorption theory.[144] In recent years, colloidal stationary liquid phases have been used in order to increase the capacity of the columns and to change their selectivity.[145,146]

The field of application of gas adsorption capillary columns is progressively extending, and the number of companies producing these columns is increasing.[147]

Unfortunately, the use of open tubular adsorption capillary columns in Russia is still limited, although these columns can be manufactured in almost any chromatographic laboratory.[148]

* * *

The use of capillary gas adsorption chromatography makes it possible to improve markedly the main characteristics of chromatographic separation of volatile compounds (selectivity, efficiency, speed, the area of application, etc.). Capillary gas-adsorption chromatography is a modern version of the adsorption chromatography, which makes it possible to take full advantage of this earliest version of gas chromatography.

The wide experience accumulated by researchers from various countries forms a strong basis for the extensive use of adsorption capillary columns for solving numerous important routine problems.

From our viewpoint, in the future, attention should be concentrated on the following branches of gas adsorption capillary chromatography: the theory and optimisation of the separation conditions, reproducible methods for the manufacture of capillary columns, and the extension of the number of various selective adsorbents used in the capillary variant of chromatography.

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