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Packed Capillary Columns in Gas Chromatography

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Data on the preparation, properties, and applications of packed capillary columns are surveyed and analysed. The characteristics of chromatographic separation in columns of this type are discussed, the principal ways of improving the efficiency of packed capillary columns are considered, and the regions where they can be employed in practice are indicated.
The bibliography includes 85 references.

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I. INTRODUCTION

One of the methods for improving the efficiency of separation in gas chromatography involves the use of small-diameter columns. The first capillary column was proposed by Golay[1] and many different useful modifications of small diameter columns, whose advantages have been demonstrated quite clearly in recent years, are now known. However, there are no reviews in the literature on packed capillary columns, which inhibits somewhat their wide-scale application.

Packed capillary columns (PCC) should be understood as columns having an internal diameter ≤ 2 mm and filled with a sorbent. This definition is arbitrary and somewhat subjective, owing to the absence of a clear-cut boundary between packed capillary columns and ordinary packed columns. According to our observations, characteristic features begin to be manifested precisely in columns whose diameter is 1–2 mm. The above definition indicates the upper limit of the diameter. Most studies have been carried out on columns having diameters less than 1 mm.

Halasz and Heine[2] obtained the first PCC by drawing on a Desty machine[3] tubes which had been filled either with an active adsorbent[2,4-8] or with an inert carrier[9], the stationary phase being deposited subsequently on the latter by the frontal method. The distribution of the sorbent is non-uniform in columns obtained by this procedure; it is partly forced into the walls of the capillary. This method can be used to obtain long columns with a comparatively high efficiency, but a carrier with an adequate mechanical strength and thermal stability is required; in most cases the carrier cannot be treated with the stationary phase beforehand. Capillary columns with regular close packing of the sorbent, obtained[10] by filling 200 cm steel tubes having internal diameters of 0.25 and 0.5 mm with glass microbeads (grain size 40 μm) and depositing on the latter the stationary liquid phase (SLP) by the frontal method, proved to be preferable. The height H of columns obtained in this way equivalent to the theoretical plate was 2 and 0.7 mm. More efficient columns ($H = 0.3$–0.39 mm) were obtained subsequently in a study[11] where metallic columns 0.5 and 1 mm in diameter and 100 cm long were filled with Chromosorb or Kieselguhr by means of a vibrator, and then the SLP was again deposited on the solid carrier in the column by the frontal method.

Capillary columns filled with the sorbent prepared beforehand have been used in gas-chromatography since 1963.[12-17] Systematic study of the characteristics of columns of this type have also been carried out in other investigations[18-25] dealing with broader aspects of their general analytical properties (in particular, a study was made for the first time of the changes in the efficiencies of columns of this type as a function of the principal experimental parameters) and their usefulness for the measurement of physicochemical characteristics was demonstrated.

In the development of sorbent-filled capillary columns, it is possible to distinguish two stages: (1) the development of methods for the preparation and application of short columns; (2) the development of methods for the preparation and application of long columns. Short columns (mainly 1–2 m long) are characterised by a high specific efficiency (the number of theoretical plates per metre of column length is approximately 2000), but their overall efficiency is small (usually not more than 2000–5000 theoretical plates). Short columns can be usefully employed for rapid analysis of relatively simple mixtures. The second stage, involving the development of long packed capillary columns (more than 10 m long) did not begin until 1971.[26] The high efficiency of these columns (columns with an efficiency equivalent to 60 000 theoretical plates have been described, but even longer columns can be prepared) makes them useful for the investigation of multicomponent mixtures and mixtures which are difficult to resolve and for the analysis of impurities.

Owing to their low diameter and the presence of the sorbent, PCC combine the advantages of classical capillary columns (capillaries whose internal walls are coated by the SLP) and ordinary packed columns. The small diameter is responsible for the significant advantages of PCC compared with columns of the usual type; these are (1) high efficiency, (2) high speed of the analysis (calculations[27] have shown that the time required for the attainment of the same degree of separation in PCC is shorter by a factor of two than in ordinary columns), (3) more stable conditions when the temperature is programmed owing to the low thermal inertia of the columns, (4) miniaturisation of the columns, i.e. the possibility of devising apparatus of small size, with a compact thermostat, in which rapid heating and cooling of the column may be

achieved, and (5) low cost, i.e. there are extensive possibilities for employing scarce and expensive sorbents, since the amounts required are small. The following disadvantages of PCC compared with ordinary packed columns may be mentioned: (1) the filling technique is somewhat more difficult and prolonged and (2) it is necessary to employ detectors with a "dead" volume less than 30 μl, particularly a microkatharometer, since an ordinary katharometer cannot be used owing to its high inertia[28].

Because of the use of a sorbent in PCC, the latter have many advantages compared with classical capillary columns: (1) a high rate of separation of readily and moderately sorbed substances[27]; thus the time for separation in PCC is shorter by a factor of approximately 30 for a partition coefficient $K = 10$ and by a factor of 2.3 for $K = 50$; (2) by employing sorbents of different polarity, one can prepare columns of this type with a high selectivity for both gas–liquid and gas–solid chromatography; (3) a fairly high capacity, which makes it possible to introduce the sample without dividing the stream and thus reduces the error in the qualitative results and makes the requirements for the sensitivity of the detector less stringent (experiments with a microkatharometer are possible). Furthermore, it leads to an increase of the separating capacity of the column in the separation of weakly sorbed substances and extends the scope of capillary chromatography in the analysis of admixtures. A deficiency of PCC compared with classical capillary columns is a fairly high resistance to flow.

Comparison of PCC characteristics with those of columns of the type usually employed shows that their wide-scale application in chromatographic practice is entirely justified.

II. CHARACTERISTICS OF THE CHROMATOGRAPHIC SEPARATION PROCESS IN PACKED CAPILLARY COLUMNS

Theoretical and experimental studies designed to elucidate the dependence on column diameter of the spreading of the chromatographic band in narrow columns have been carried out for gas–liquid chromatography[27,29] and gas–adsorption chromatography[27,30,31], where the fundamental efficiency characteristics were adopted as the spreading criteria, namely the minimum height equivalent to the theoretical plate (H_{min}) and the coefficient of resistance to mass transfer (C) in the Van Deemter equation[32]:

$$H = A + \frac{B}{u} + Cu,$$

where A and B are coefficients taking into account the turbulent and molecular longitudinal diffusion respectively and u is the carrier gas flow rate.

Comparative results for the efficiency of packed columns of different diameters (Table 1)[27] show that in gas–liquid chromatography (GLC), H_{min} changes insignificantly in columns 1.2, 0.8, and 0.5 mm in diameter and increases appreciably only in a column with a diameter of 3 mm. According to other workers[29], an appreciable influence of column diameter (d_c) on H_{min} was not observed either in columns having diameters of 0.75, 1.0, and 1.5 mm. The coefficient of resistance to mass transfer C, which decreases with decrease of d_c (Table 1), changes more significantly. This type of behaviour has been observed for all the substances tested and for all carrier gases.

In gas–adsorption chromatography (GAC) a change in d_c has been found to entail, as in GLC, only slight changes in H_{min}, the minimum value of H_{min} being obtained for the column 0.8 mm in diameter (Table 1). With decrease of the column diameter from 3 to 0.5 mm, the coefficient C diminishes almost by a factor of 2, and, compared with the column 0.8 mm in diameter, by a factor of approximately 2.5.

Fig. 1 presents the dependence of C on the column diameter d_c.

In GLC C decreases monotonically with decrease of d_c. In GAC the curve relating C to d_c passes through a minimum. This difference can apparently be accounted for by the different grain sizes of the sorbent employed: a coarser sorbent (100–200 μm) is used in GAC than in GLC (100–160 μm), so that in a 0.5 mm diameter column (GAC) the sorbent was probably more loosely packed, which led to an increase in the degree of spreading.

Earlier studies[30,31] on GAC showed a somewhat different variation of H_{min} with d_c: in the range $d_c = 1.6$–0.6 mm the quantity H_{min} is directly proportional to d_c, increasing as d_c is diminished further (on passing from 0.6 to 0.3 mm).

Table 1. The influence of the diameter of the column on its efficiency.

Method	d_c, mm	H_{min}, mm		u^*_{opt}, cm s^{-1}		10^2C, s		H_{min}, mm		u^*_{opt}, cm s^{-1}		10^2C, s		H_{min}, mm		u^*_{opt}, cm s^{-1}		10^2C, s	
		nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium	nitrogen	helium
		Pentane						Hexane						Octane					
GLC	3.0	0.52	0.88	6.0	7.0	1.5	1.25	0.54	0.78	5.0	7.5	1.3	1.00	0.60	0.72	5.0	8.5	1.10	0.70
	1.2	0.46	0.60	8.0	9.5	0.8	0.64	0.46	0.62	6.0	11.0	0.76	0.50	0.52	0.60	6.5	11.0	0.70	0.44
	0.8	0.42	0.60	8.0	9.5	0.66	0.48	0.45	0.58	8.0	11.0	0.60	0.44	0.48	0.55	6.0	11.0	0.56	0.34
	0.5	0.41	0.60	8.0	9.5	0.48	0.36	0.44	0.58	8.0	11.0	0.46	0.32	0.48	0.55	6.0	11.0	0.44	0.26
GAC	3.0	0.40	0.42	4.5	7.0	1.10	0.70	0.45	0.46	4.0	7.0	1.05	0.60	—	—	—	—	—	—
	1.2	0.40	0.40	5.0	8.0	0.70	0.50	0.42	0.52	5.0	8.0	0.65	0.42	—	—	—	—	—	—
	0.8	0.28	0.32	5.0	8.0	0.40	0.28	0.32	0.35	5.0	9.0	0.33	0.25	—	—	—	—	—	—
	0.5	0.38	0.50	6.0	9.0	0.50	0.36	0.40	0.55	5.0	9.0	0.48	0.34	—	—	—	—	—	—

*The optimum rates u_{opt} are quoted.

The relations obtained[27,29-31] between the efficiency of the columns and their diameters are in the main analogous. Certain discrepancies in the optimum column diameters (0.8 mm[27] and 0.6 mm[30,31]) can probably be explained by the different grain sizes of the sorbents used.

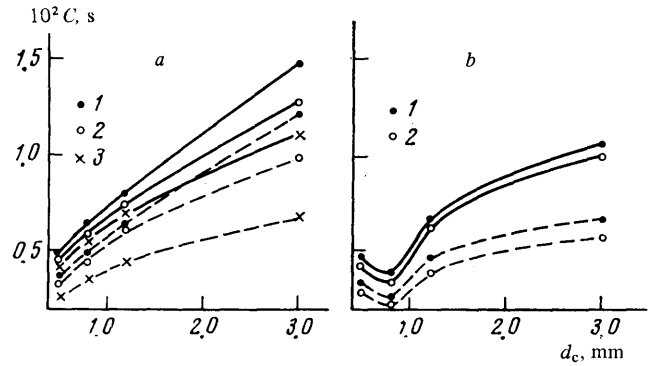


Figure 1. Dependence of the coefficient of resistance to mass transfer C on the column diameter d_c: *a*) sorbent—5% of squalane on Chromosorb W (100–160 μm); *b*) sorbent–XOB.075 Spherosil (100 – 200 μm); 1) pentane; 2) hexane; 3) octane. Continuous lines—nitrogen as carrier gas; dashed lines—helium as carrier gas.

According to the Jones equation[33]

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

kinetic spreading in the chromatographic process is due to the resistance to mass transfer in the mobile (C_g) and stationary (C_s) phases. According to the Giddings theory[34], each of these factors plays a significant role in the assessment of the spreading mechanism in the column. In the study of the spreading of a chromatographic band in PCC it is therefore of interest to investigate the question of the relative role of mass transfer in the mobile and stationary phases as a function of d_c. Such studies were made for the first time for GLC[25] and their authors proposed a graphical method for the separate determination of the coefficients of external diffusion and internal diffusion resistance to mass exchange, and estimated their contributions as a function of the ratio of d_c to the grain diameter d_p. The coefficients of the external diffusion resistance to mass transfer C_g for a column 0.58 mm in diameter increase only slightly with increase of d_p. For a column with a larger diameter (0.98 mm) and for the same ratios d_c/d_p, the quantity C_g is greater by a factor of two and an increase of d_p by a factor of ten leads to an increase of C_g also by a factor of ten.

The results of a recent separate determination of C_g and C_s in GLC and GAC[27] by the method described in Grant's book[35] are presented in Table 2. Evidently both C_g and C_s diminish with decrease of d_c, the values of C_s found by two other methods (described by Perrett and Purnell[36] and Novak et al.[37]) being in good agreement. The changes observed[27] in C_s conflict with the classical concept of the independence of processes controlling the interphase mass transfer in a chromatographic column and agree with the conclusions of Novak and coworkers[37,38], who showed theoretically and experimentally that the coefficients C_s and C_g depend on each other and on the average pressure in the column. In the case considered the average pressure increases with increasing column diameter, which may be accounted for by the increase of permeability in narrow columns (for $d_p/d_c > 0.05–0.1$)[39], apparently owing to the greater influence of the wall effect.

Table 2 also shows that in gas–liquid chromatography $C_s > C_g$ for pentane in all the columns investigated, the difference diminishing on passing to substances with larger extraction coefficients. In gas–adsorption chromatography $C_g > C_s$ for a column 3 mm in diameter; for the other columns investigated the values of these quantities are comparable (when nitrogen is used as the carrier gas).

The dependence of C_g on d_c is illustrated in Fig. 2. The power exponent m in the relation $C_g \propto d_c^m$, found from the slopes of the straight lines, is 0.42 for GLC and 0.8 for GAC; this difference has been explained[27] as the influence of the form of the sorbent and the grain size on its packing in columns of different diameters.

The greater efficiency of PCC compared with packed columns having the usual diameters is apparently due to the special role of radial diffusion in the spreading of the band in PCC[30] and the nature of the packing of the sorbent in them[27]. In order to test the hypothesis of the greater smoothing role of radial diffusion in narrow columns, a comparative study has been made[40] of the efficiencies of capillary and the usual packed columns filled with a sorbent known to be inhomogeneous (mixed), which consisted of a mixture of a sorbent for GLC (i.e. of particles of the solid

Table 2. The coefficients of resistance to mass transfer in the mobile (C_g) and stationary (C_s) phases.

Method	d_c, mm	10^2C, s		10^2C_g, s		C_s	10^2C, s		10^2C_g, s		C_s	10^2C, s		10^2C_g, s		C_s
		nitrogen	helium	nitrogen	helium		nitrogen	helium	nitrogen	helium		nitrogen	helium	nitrogen	helium	
		Pentane					Hexane					Octane				
GLC	3.0	1.5	1.25	0.33	0.130	1.12	1.30	1.00	0.45	0.15	0.85	1.10	0.70	0.57	0.16	0.53
	1.2	0.8	0.64	0.24	0.034	0.56	0.76	0.60	0.30	0.10	0.46	0.70	0.56	0.37	0.11	0.33
	0.8	0.66	0.48	0.21	0.073	0.45	0.60	0.44	0.24	0.03	0.36	0.56	0.34	0.31	0.09	0.25
	0.5	0.48	0.36	0.18	0.063	0.30	0.46	0.32	0.21	0.07	0.25	0.44	0.26	0.25	0.075	0.19
GAC	3.0	1.10	0.70	0.61	0.21	0.49	1.05	0.60	0.67	0.23	0.33	—	—	—	—	—
	1.2	0.70	0.50	0.30	0.10	0.40	0.65	0.42	0.36	0.12	0.30	—	—	—	—	—
	0.8	0.40	0.28	0.18	0.06	0.22	0.33	0.25	0.18	0.06	0.19	—	—	—	—	—
	0.5	0.50	0.36	0.21	0.07	0.29	0.48	0.34	0.21	0.07	0.27	—	—	—	—	—

carrier impregnated with the SLP) and the solid carrier without SLP. The measurements were performed on two spiral columns: a glass column 3 m long and with an internal diameter of 0.8 mm, and a metallic column 2.9 m long and with an internal diameter of 3 mm. The two columns were filled with the same sorbent, which consisted of a mixture of Chromaton N-AW without an SLP, and Chromatone N-AW with 5% of squalane in different proportions: 95 and 5, 50 and 50, and 0 and 100 wt.% respectively.

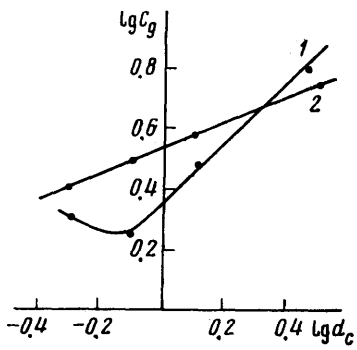


Figure 2. Dependence of the coefficient of resistance to mass transfer in the mobile phase C_g on column diameter d_c: 1) GAC; 2) GLC.

Table 3. The efficiency of columns having different diameters and filled with a mixed sorbent[40].

Sorbent, %		d_c, mm	10^2C, s			H_{min}, mm		
Chromaton + 5% of squalane	Chromaton N-AW		heptane	toluene	octane	heptane	toluene	octane
5	95	3.0	2.2	2.2	4.6	1.3	1.7	1.6
5	95	0.8	1.6	1.7	3.0	1.1	1.4	1.3
50	50	3.0	2.0	1.9	1.8	1.1	1.0	1.0
50	50	0.8	1.5	1.5	1.4	1.0	0.9	0.9
100	0	3.0	1.1	1.0	1.0	0.9	0.7	0.8
100	0	0.8	0.9	0.8	0.8	0.8	0.7	0.7

It follows from the results presented in Table 3 that, for all the substances investigated which are characterised by different partition coefficients, the values of H_{min} and C are smaller for the capillary column. They diminish (i.e. the efficiency improves) with decrease of the inhomogeneity of the sorbent. We may note that the greatest decrease of H_{min} and C is observed on passing from the packing containing 5% of the sorbent to the packing containing 50% of the sorbent, i.e. in the region of the greatest increase of the inhomogeneity of the sorbent. The experimental results are fully consistent with the idea that radial diffusion plays an important smoothing role in PCC. Indeed the time required for the diffusion of the molecules of the substance analysed in the gas phase from one wall of the column to the other may be estimated from the equation:

$$\tau = d_t^2/2D, \quad (1)$$

where D is the diffusion coefficient of the test substance in the gas phase. If it is assumed that $D = 0.5$ cm^2 s^{-1}, then we have $\tau = 6.4 \times 10^{-3}$ s for a capillary column 0.8 mm in diameter and $\tau = 9 \times 10^{-2}$ s for an ordinary packed column 3 mm in diameter, i.e. τ is 15 times longer (the influence of the tortuosity of the path was disregarded in this calculation).

Thus, when a mixed sorbent is used, the efficiency of PCC is in all cases greater than that of large-diameter columns; the relative improvement of the efficiency characteristics of PCC increases with increasing inhomogeneity of the sorbent.

The equalisation of the chromatographic band front over the cross-section of PCC and an ordinary analytical column has been studied qualitatively[27]. The shape of the boundary of the layer of sorbent saturated by the volatile component, which reacts chemically with the sorbent to form a coloured compound, was observed. The saturated (spent) layer was obtained as a result of the reaction of hydrogen sulphide with the sorbent—Chromaton N (125–160 μm), on the surface of which 3% of lead acetate has been deposited. The reaction results in the formation of black lead sulphide. Glass tubes 3 and 0.8 mm in diameter, filled with the above sorbent, were used in the investigation. Hydrogen sulphide was injected into the carrier gas directly at the column wall and at right angles to the stream. When hydrogen sulphide was introduced, the sorbent turned black. It was observed that the boundary of the front of the saturated sorbent forms an acute angle γ with the wall at which hydrogen sulphide has been injected.

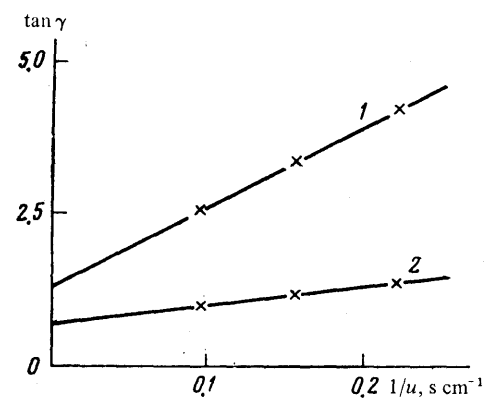


Figure 3. Dependence of the slope of the boundary of the saturated (spent) sorbent layer on the reciprocal of the linear carrier gas flow rate for columns having diameters of 0.8 mm (line *1*) and 3 mm (line *2*).

It follows from the data in Fig. 3 that, in a column 0.8 mm in diameter, the slope of the front for all the carrier gas flow rates investigated is greater than in an ordinary column 3 mm in diameter, i.e. the front of the band in PCC is steeper. This can probably be accounted for by the more regular packing of the sorbent in PCC. The time required for the diffusion in PCC of weakly sorbed molecules over a distance equal to the column diameter is $d_c/\tan\gamma \times u \simeq 4.5 \times 10^{-3}$ s, which agrees fully with the value calculated by Eqn. (1): $\tau = 6.4 \times 10^{-3}$ s.

One can apparently postulate the formation in packed columns of "domains"—regions of close-packed particles forming poorly ventilated cavities. It may be that the probability of their formation in PCC as well as their dimensions are much smaller, which should lead to a decrease of the spreading of the front. Furthermore, the effect of "remote" channels, noted by Giddings[34] as the main factor influencing the non-uniformity of the distribution of velocities with respect to the cross-sections of packed columns, should be significantly reduced in columns with small diameters, since it operates over fairly long distances, amounting to approximately $7.5d_p$, which is less than the diameters of the columns considered. Thus the non-uniform distribution of velocities with respect to the column cross-section plays a smaller role in PCC in the impairment of the efficiency characteristics than in columns having the usual diameters.

The characteristics of the separation in PCC, distinguishing them from classical capillary columns, are determined mainly by the presence of the sorbent in the former, which leads to a decrease of the phase ratio β (the ratio of the volume of the gas phase to that of the liquid phase in the column). β has a significant influence on separation. According to the equation[41]

$$R = \frac{\alpha - 1}{4\alpha} \frac{K}{\beta + K} N^{1/2}$$

(R is the degree of separation, K the partition coefficient, N the number of theoretical plates, and α the relative retention volume), an increase of β should lead to an impairment of separation, which has a particularly marked effect in the separation of poorly sorbed compounds. Calculations have shown[40] that the amount of liquid phase in PCC is greater by two orders of magnitude than in classical capillary columns, and β is therefore much smaller.

The presence of the sorbent in PCC is also responsible for a different spreading mechanism than in classical capillary columns. The main characteristics of classical capillary columns are the absence of turbulent diffusion and a dependence of the coefficient of resistance to mass transfer in the gas phase mainly on dynamic diffusion. The coefficient C_S in classical capillary columns is usually greater than in PCC, since the film of the SLP on the porous sorbent is usually thinner than on the walls of capillaries. However, there have been no experimental studies of the comparative characteristics of spreading in PCC and classical capillary columns.

III. THE INFLUENCE OF THE PRINCIPAL EXPERIMENTAL PARAMETERS ON COLUMN EFFICIENCY

1. The influence of Pressure

One of the ways of increasing the overall efficiency of chromatographic columns involves increasing their length. Small PCC are promising in this respect. However, the increase in length entails an increase in the resistance of the columns, which leads to the necessity of employing increased pressures at the inlet to the column. For this reason, it is useful to examine the problem of the dependence of the efficiency of PCC on pressure.

The variation of the efficiency of the chromatographic column on various process parameters can be most fully described by the equation[29]

$$H_i = a_d \frac{D_{im}}{\bar{u}} + \frac{a'_c d_p}{1 + a''_e (D_{im}/\bar{u}d_p)^{1/2}} + a_f \left(\frac{\bar{u}}{D_{im}}\right)^{1/2} d_p^{3/2} \left(\frac{k_i}{k_i + 1}\right)^2 + a_b \frac{\bar{u}}{D_{ip}} d_p^2 \frac{k_i}{(k_i + 1)^2}, \quad (2)$$

where H_i is the value of H for the ith component, $\bar{u}$ the average linear flow rate, D_{im} the diffusion coefficient for the ith component in the mobile phase, k_i the partition coefficient of the ith component, D_{ip} the overall diffusion coefficient of the ith component in a particle, and a_d, a'_c, a''_e, a_f, and a_b are factors reflecting the influence of the geometry of the column on the diffusional and convective mixing, the dispersion caused by the mass exchange in the moving part of the mobile phase, and the dispersion caused by mass exchange in the particle, both in the "stagnant" component of the mobile phase and in the SLP. The diffusion coefficient in the mobile phase is related to pressure by the following equation:

$$D_{im} p = \text{const}, \quad (3)$$

where p is the pressure.

It follows from Eqns. (2) and (3) that H decreases with increase of pressure for low linear flow rates and increases for high linear flow rates, the latter effect diminishing with decrease of d_p and k. In addition, as the pressure increases, the minimum value of H falls and shifts towards lower linear flow rates. The experimental results (Fig. 4)[27] show that this relation is characteristic of PCC in both gas–liquid and gas–adsorption chromatography. Huber et al.[29] obtained a detailed theoretical explanation of the results on the basis of Eqns. (2) and (3). With increase of pressure, the first term of Eqn. (2) diminishes, the second hardly changes in the usual range of flow rates, and the third increases. The influence of pressure on the fourth term of Eqn. (2) depends for its effect on D_{ip}, which in its turn depends on the degree of saturation of the pore space of the particles. In the simplest case the pores are completely filled by one phase, whereupon D_{ip} is proportional to the diffusion coefficient in this phase[42–45]. In gas–liquid chromatography the particles are usually saturated by the stationary liquid and the "stagnant" carrier gas. In this case the influence of pressure on D_{ip} is determined by the ratio of the volumes of the stationary liquid and gas phases in the particle and their relative geometrical distribution. With increase of pressure, the fourth term of Eqn. (2) increases and its value depends on the porosity of the particles, the accessible internal volume of which is filled by the stationary carrier gas.

According to the data of Bruner et al.,[46] H_{min} in gas–liquid PCC is independent of column length and hence of pressure (at least up to 15 m). For PCC of the gas–liquid–solid type, these workers observed, as in their first study[47], a "deepened" minimum on the curve relating H to u for comparatively long columns, i.e. with increase of the rate above u_{opt}, H initially increases, and then remains virtually unchanged. The authors suggest this effect may be caused by the mechanism of the operation of columns of this type.

The pressure gradient in the chromatographic column determines the presence of gradients of linear flow rates of the gas phase and of the diffusion coefficient in the mobile phase (owing to the high compressibility of the gas). The first three terms of Eqn. (2) remain constant,

since the ratio D_{im}/u does not change. The influence of the pressure gradient on H is determined exclusively by the fourth term, describing the mass exchange in the particle. This term increases with increasing linear flow rate, which increases along the column as a function of the ratio of the inlet and outlet pressures[48]:

$$u_x = u_L \left\{ \left(\frac{p_i}{p_0}\right)^2 - \left[\left(\frac{p_i}{p_0}\right)^2 - 1\right]\frac{x}{L} \right\}^{-\frac{1}{2}}, \quad (4)$$

where L is the column length, u_L the linear flow rate at the end of the column, x the coordinate along the length of the column, and p_i and p_0 are the pressures at the inlet and outlet.

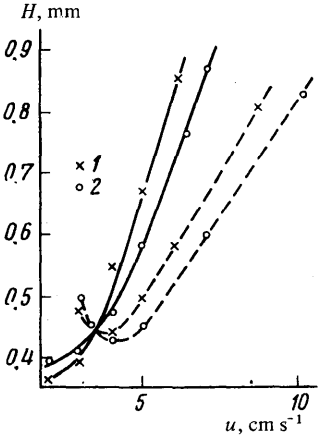


Figure 4. Dependence of H on the average linear carrier gas flow rate for short and long columns with an internal diameter of 0.8 mm, using 15% of squalane on Chromosorb P as the sorbent (100–160 μm) at 80°C: 1) hexane; 2) heptane. Continuous lines—15 m column; dashed lines—2 m column.

It follows from Eqns. (2) and (4) that H increases from the beginning to the end of the column in accordance with the expression

$$H_{ix} = \text{const} + a_b \frac{u_L}{D_{ip}\left\{\left(\frac{p_i}{p_0}\right)^2 - \left[\left(\frac{p_i}{p_0}\right)^2 - 1\right]\frac{x}{L}\right\}^{1/2}} \cdot d_p^2 \frac{k_i}{(k_i+1)^2}, \quad (5)$$

where $H_{ix} = H$ at the position defined by x. Eqn. (5) does not allow an exact prediction of the H_i gradient in the column, since D_{ip} is an unknown function of x.

Experimental results[27,29] have shown that the efficiency of PCC depends only slightly on the pressure gradient; the average pressure in the column has a much greater influence on the efficiency.

2. The Influence of the Particle Size of the Packing

The permeability of the column and to a large extent its efficiency depend on the particle size of the packing. Theoretically the permeability of an open capillary depends only on its diameter, but in practice the permeability of a capillary is smaller by 10–13% than the theoretical values r_0^2,[49] which can probably be accounted for by the roughness of the walls or fluctuations in the tube diameter. The permeability P of packed columns depends on the particle size and on the packing density[50,51]:

$$P = \frac{\psi^2 d_p^2}{180} \cdot \frac{\varepsilon_0^3}{(1-\varepsilon_0)^2},$$

where ψ is the particle inhomogeneity factor and ϵ_0 the column porosity, which does not include the internal volume of the particles. In practice the permeability of packed columns depends on the ratio of the particle diameter to the column diameter (d_p/d_c) and on the degree of roughness of the carrier. The permeability of the usual packed columns, where $d_p/d_c < 0.1$, is independent of the column diameter[52].

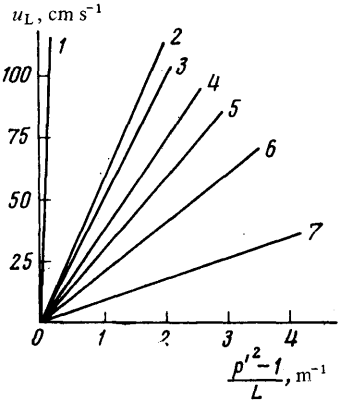


Figure 5. Dependence of the carrier gas flow rate at the outlet u_L on $(p^2 - 1)/L$ for columns of different types: 1) classical capillary column (internal diameter 0.25 mm); 2) and 4) PCC, d_p = 100 – 125 μm, d_c = 0.45 and 0.55 mm respectively with Chromosorb P as the carrier; 3) and 5) PCC, d_p = 140 – 160 μm, d_c = 0.64 and 1.26 mm respectively with glass beads as the carrier; 6) and 7) usual packed columns, d_p = 200–250 μm and d_c = 4 mm with glass beads as the carrier.

The column permeability may be determined experimentally from the slope of the plot of the linear carrier gas flow rate at the outlet of the column u_L against $(p'^2 - 1)/L$:

$$u_L = \frac{P p_0 (p'^2 - 1)}{2\eta L},$$

where η is the viscosity of the carrier gas, p_0 the pressure at the outlet from the column, $p' = p_i/p_0$, and p_i the pressure at the inlet. Plots of this relation for different types of column are illustrated in Fig. 5.[52] Evidently the permeabilities of PCC occupy an intermediate position between those of classical capillary columns and ordinary packed columns; for a given particle size, the permeability diminishes with increase in column diameter. Cramers et al.[53] showed that a decrease of the column diameter with

the same grain size of the packing requires the application of lower pressures at the inlet to the column (Fig. 6). Rijks et al.[54] recommend the ratio $d_p/d_c = 0.2-0.25$ for the optimum permeability of PCC.

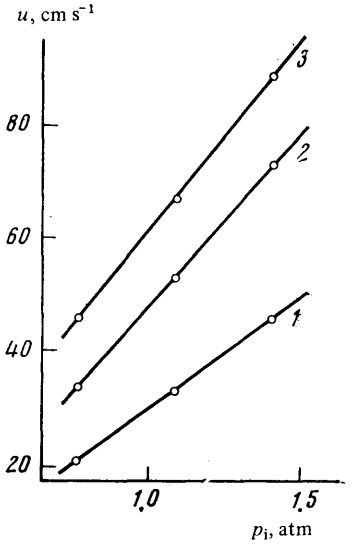


Figure 6. Dependence of u on the inlet pressure p_i for 1 m columns with different diameters (mm): 1) 1.26; 2) 0.92; 3) 0.64.

It has been shown[29] that a decrease of d_p leads to the following changes in the efficiency of PCC: (1) $\bar{H}_i$ diminishes for low values of $\bar{u}$; (2) the limiting value of $\bar{H}_i$, obtainable at high values of $\bar{u}$, diminishes for non-retained compounds; (3) the minimum value of $\bar{H}_i$ for retained compounds shifts towards lower values and its magnitude is greatly diminished; (4) the slope of the right-hand branch of the plot of $\bar{H}$ against $\bar{u}$ decreases for retained compounds. These experimental results have been explained[29] on the basis of Eqn. (2). With atmospheric pressure at the inlet the changes in $\bar{H}_i$ are induced directly by the change in d_p in Eqn. (2) and by the indirect influence of size owing to the dependence of the pressure drop on d_p (p' increases with decrease of d_p for a given value of $\bar{u}$). When the pressure at the outlet is increased, p' increases only slightly with decrease of d_p for a given value of u. In this case the changes in $\bar{H}_i$ are caused mainly by the change in d_p in Eqn. (2). The decrease in the minimum value of $\bar{H}_i$ for retained compounds and the decrease of the limiting value of $\bar{H}_i$ for high values of $\bar{u}$ for non-retained compounds, as well as the decrease of the slope of the curves relating $\bar{H}$ to $\bar{u}$ for retained compounds at high values of $\bar{u}$ are caused directly by the decrease of d_p in Eqn. (2). Thus the decrease of the particle size of the packing has a favourable influence on the column efficiency.

Generalising the results obtained, Huber et al.[29] concluded that PCC filled with a packing having particles much smaller than usual may prove to be extremely effective. The columns which they prepared (internal diameter 0.75–1.5 mm) with fine-grained packing (30–35 μm) had an efficiency equivalent to 10 000 theoretical plates per metre. In order to attain the optimum carrier gas flow rate (2.5 cm s^{-1}) in a column 1.5 m long and containing this type of sorbent, a pressure of 25 atm is necessary. It was concluded[29] that packed columns with an efficiency equivalent to 50 000 theoretical plates, which requires a length of 6 m, a pressure of 50 atm, and a volume flow rate at the outlet from the column of 5 ml min^{-1}, are realistically attainable.

Consequently there are two ways of attaining a high-efficiency of PCC: (1) by increasing the column length; (2) by employing short columns with a very fine-grained packing. We believe that the first procedure is preferable, because the use of highly efficient long PCC involves the employment of relatively low pressures at the inlet to the column. Short columns with a very fine-grained packing require an inlet pressure higher by an order of magnitude in order to achieve the same efficiency as for long PCC, which entails difficulties as regards apparatus. Furthermore, the resistance of long PCC may be appreciably reduced by employing surface-layer sorbents with large-diameter particles, since the efficiency of columns with such a sorbent is independent of particle size[55].

3. The Influence of the Nature of the Carrier Gas

According to the D'Arcy law, the pressure gradient is proportional to the viscosity of the flowing medium, so that the inlet pressure in PCC may be reduced by employing carrier gases with low viscosities. The usefulness of ammonia as the carrier gas has been demonstrated[56]. The viscosity of ammonia is a factor of 1.8 smaller than that of nitrogen and a factor of 2 less than that of helium. The density of ammonia is intermediate between those of nitrogen and helium, so that the diffusion coefficients of the components in ammonia should be higher than in nitrogen and this should lead to a higher efficiency if the spreading of the band is determined by the slow mass transfer in the mobile phase. In order to confirm these hypotheses, a study was made[56] of the dependence of column efficiency on the nature of the carrier gas. A spiral glass column 5.5 m long and with an internal diameter of 0.8 mm, filled with Chromaton N treated with 3% potassium hydroxide (160–200 μm) and impregnated with 10% Apiezon L, was used. Nitrogen, helium, and ammonia were compared as carrier gases.

Table 4. The values of H_{min} and C in packed capillary columns for different carrier gases.

Component	H_{min}, mm			10^2C, s		
	nitrogen	ammonia	helium	nitrogen	ammonia	helium
Heptane	0.82	0.85	1.0	2.0	1.5	0.8
Octane	0.65	0.70	0.84	2.4	1.7	1.2
Toluene	0.74	0.68	0.92	1.6	1.2	0.8
m-Xylene	0.66	0.63	0.82	1.7	1.4	0.9

The experimental results (Fig. 7 and Table 4) show that the employment of ammonia reduces the coefficients of resistance to mass transfer compared with chromatography in a stream of nitrogen, virtually without impairing the

efficiency H_{min}. Compared with helium, ammonia leads to a considerable increase of efficiency in the region of H_{min}. The use of ammonia as the carrier gas in packed capillary columns is justified also because of its main advantage—a low pressure gradient. Thus, for the column used in the above investigations, with $u = 10$ cm s^{-1}, the pressure at the inlet was smaller by a factor of 1.5 compared with nitrogen (5.9 atm) when ammonia was used (3.8 atm) and smaller by a factor of 1.6 compared with helium (6.2 atm).

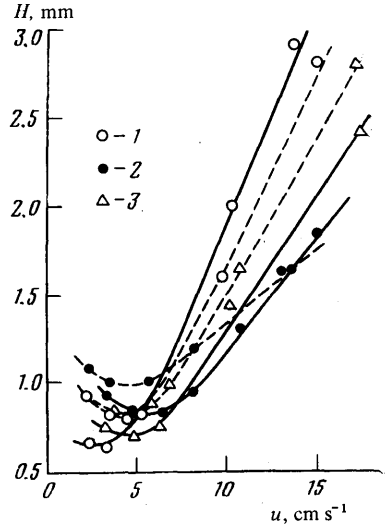


Figure 7. Dependence of H on u for different carrier gases: 1) nitrogen; 2) helium; 3) ammonia; continuous lines—octane; dashed lines—heptane.

The use of ammonia as the carrier gas to accelerate prolonged analyses has been demonstrated[56] in the separation of alkylcyclohexanols. The analysis was performed on a column 14.8 m long with an internal diameter of 0.8 mm filled with Chromosorb W containing 5% of Carbowax 20M at 160°C. Peaks of 32 compounds were detected on the chromatograms. Table 5 shows that the use of ammonia instead of nitrogen made it possible to reduce the analysis time by a factor of 1.6 without impairing the separation. For the same analysis time, a more clear-cut separation is attained and the pressure at the inlet to the column is smaller by a factor of 1.7.

The employment of ammonia as the carrier gas has the following advantages over the carrier gases usually employed (nitrogen and helium): (1) the pressure drop diminishes owing to the lower viscosity, which is important for long PCC; (2) when ammonia is used, H_{min} is smaller than in the case of helium; (3) the capacity of ammonia cylinders is larger than that of nitrogen and helium cylinders, which makes it possible to change cylinders less frequently and to employ small cylinders for mobile chromatographs; (4) the symmetry of the chromatographic bands is sometimes improved owing to the adsorption of ammonia on the active centres of the solid carrier[57].

Table 5. Results of the separation of alkylcyclohexanols using different carrier gases.

Carrier gas	P_i, atm	u, cm s^{-1}	Duration of analysis, min
Nitrogen	8.5	4.0	130
Ammonia	5.0	4.0	125
Ammonia	7.5	6.2	82

IV. THE PREPARATION AND USE OF PACKED CAPILLARY COLUMNS IN GAS CHROMATOGRAPHS

1. The Preparation of Packed Capillary Columns

Short capillary columns, (with a length up to 5 m) can be filled by hand with a sorbent prepared beforehand, either by tapping the column or by moving a mechanical vibrator down its length[58]. These procedures make it possible to obtain columns reproducible with respect to both packing density and retention characteristics. A common disadvantage is the possibility of filling with the sorbent only disassembled and short columns. The overall efficiency of short columns is low; in order to obtain highly efficient columns, it is desirable to increase their length to 10 m and more while retaining their high specific efficiency. Furthermore, the employment of these sorbents imposes a limitation on the material of the columns; for example, one cannot use glass capillaries, which have many significant advantages compared with metallic capillaries. Thus, on contact with a metallic surface, certain substances are sorbed irreversibly or decomposed[59-63]. A glass surface is chemically highly inert (the chemical inertness of glass is superior to that of diatomaceous brick). The possibility of direct observation of the filling of glass columns and of the visual changes occurring in them greatly facilitates the experiment. An important advantage of glass capillary columns is also the relatively ready availability of the apparatus[3] for the preparation of capillaries of the required length and diameter.

The methods developed recently for the preparation of long PCC, including glass ones, have extended the scope of their application in gas-chromatographic analysis. The procedure proposed by Cramers et al.[53] is as follows. A spiral tube (glass or metallic), arranged horizontally, is connected to a cylindrical container, the packing is poured into the container, and the latter is connected to the pressure supply line. The lower part of the container and almost the entire spiral tube are placed in an ultrasonic bath, the second end of the column being placed above the level of the bath. Vibration and pressure promote a continuous transfer of the packing into the column. By maintaining an approximately constant pressure drop across the filled part of the column, a homogeneous packing density throughout the column is ensured. The final pressure depends on the material of the packing

employed, but it should be approximately 0.4–0.2 atm per metre of column length (the first figure refers to Chromosorb and the second to glass beads). The time required for filling is 1–2 min per metre of the column. The homogeneity of the packing particles, the scatter of which should be not more than 20 μm, is important. Dust particles are removed by vacuum screening. Depending on the density of the carrier, flotation or sedimentation may be used instead of screening to obtain a homogeneous fraction. Columns with lengths up to 15 m and internal diameters of 1.0–0.6 mm, the efficiency of which was equivalent to 3500 and 3000 theoretical plates per meter (with satisfactory reproducibility) for glass beads and Chromosorb respectively, were obtained by this method described above.

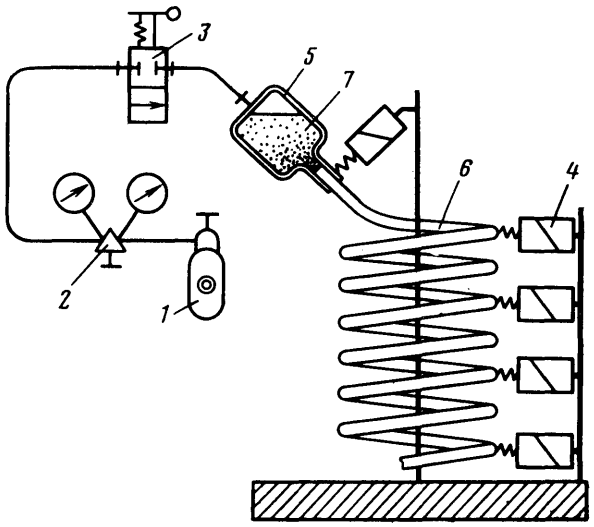


Figure 8. Schematic illustration of the device for filling capillary glass columns with the sorbent[64].

A simpler device, which does not require the use of an ultrasonic bath and is also based on the action of two factors—the vibration of the column and the pressure of an inert gas—has been developed[64]. The vibration is achieved by means of electromechanical low-frequency (50–100 Hz) vibrators placed at certain points along the length of the column. To improve the effectiveness of the stream, the pressure at the outlet from the column is applied in pulses in accordance with a specified programme†. The device (Fig. 8) consists of a compressed gas cylinder *1*, to which a valve *3*, with an electromechanical actuating device for the periodic application of pressure, is connected via a reduction valve *2*, and stands with several vibrators consisting of PE-20 electromagnetic relays *4*, with a vibration frequency of 100 Hz. A reservoir *5*, for the sorbent *7*, is attached to one of the stands, and clamps used to hold the column *6* are attached to the remaining stands. The relays are mounted along the circumference of the common base in such a way that the filled column is held by the clamps at intervals corresponding to 5–10 turns (depending on the column length).

The columns are filled as follows: a portion of the sorbent (1–2 cm^3) is poured into the reservoir *5*, the supply of gas is turned on, the automatic pressure programmer *3* is started simultaneously, and the vibrators *4* are switched on. Under the influence of the gas stream and the vibration, the sorbent is continuously transferred to the column. To ensure rapid and effective filling of the columns, the sorbent must be subjected to preliminary screening and the 100–160 and 160–200 μm fractions are used. The above device can be employed to fill spiral gas columns with various sorbents, including those which are readily charged electrically. Rapid filling by the latter is achieved by saturating an inert gas with the vapour of a polar liquid (for example ethanol); for this purpose, a porous material moistened with the liquid is placed in the reservoir with the sorbent, but does not come into contact with the latter. The device makes it possible to fill with the sorbent glass columns having lengths up to 20 m and more and with an internal diameter in the range 0.6–1.2 mm, a satisfactory reproducibility being achieved as regards both packing density and efficiency. The efficiency of the columns was equivalent to 3000 and sometimes up to 4000 theoretical plates per metre[65], which is not less than the efficiency of the columns obtained with the aid of ultrasound.

Bruner and coworkers[46,47] filled with the sorbent metallic columns having lengths up to 15 m and internal diameters in the range 0.7–0.8 mm without using a vibrator. The tube was extended in a vertical position, the lower end being fixed in such a way that the tube was subjected to a certain amount of tension. The upper end was connected to a small reservoir containing the packing, which was compacted by tapping with a rubber rod. The efficiency of the resulting columns was equivalent to 2000–2500 theoretical plates per metre of column length.

Less effective columns (1250 theoretical plates per metre) were prepared[66] by connecting individual filled sections, having lengths up to 3 m, by means of special junctions. Columns having lengths up to 12 m and an internal diameter of 1 mm were prepared.

2. Chromatographic Apparatus for Packed Capillary Columns

The use of PCC imposes a number of requirements on the apparatus owing to the following characteristic features of the analysis on such columns: low flow rates of the carrier gas, high efficiency, and high speed of analysis. In order to reduce the spreading outside the column, the volumes of the metering device, the connecting tubes, and the detector must be reduced to a minimum. Fig. 9 illustrates schematically the connection of a packed capillary column to the metering device and the detector, which makes it possible to inject the sample without dividing the stream[53]. The sample is introduced into the column via a tubular glass insert 11 cm long and with an internal diameter of 0.8 mm. One end of the insert, used to make a junction with the column, is broader and conical in shape. The column is fitted onto the cone to a depth of 2 mm. A seal is achieved with the aid of a silicone rubber washer. The exit end of the column is inserted in a stream of hydrogen and nitrogen in a flame-ionisation detector[53].

† An effective and comparatively rapid filling can be achieved also with a continuous application of pressure.

The volume of the metering device may be reduced by employing a metallic insert with an internal diameter of 0.8–1.0 mm. Another way of reducing spreading in the metering device involves the employment of a stream divider. The stream can be divided in proportions corresponding to a small ratio (1 : 2–1 : 5), which is required merely to increase the rate of passage of the sample through the metering device.

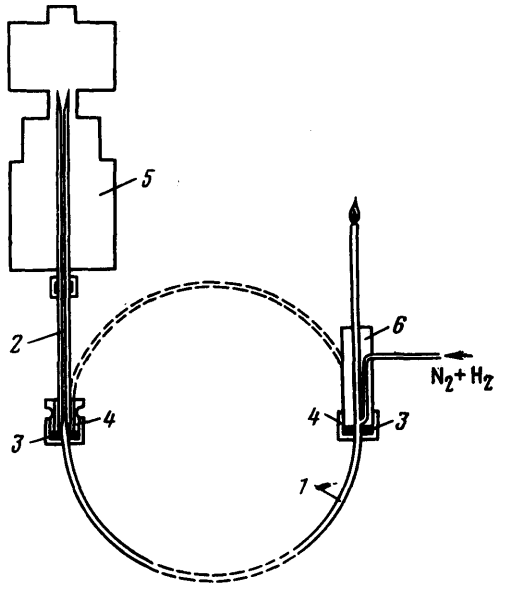


Figure 9. The connection of PCC to the gas–chromatographic system: 1) capillary column; 2) glass tube 0.8 mm in diameter; 3) silicone rubber; 4) lock-nut; 5) evaporator; 6) detector.

When PCC are used in industrial chromatographs, where samples are introduced automatically, particular attention must be devoted to the metering system. Special studies[28] on gas metering devices of membrane and plunger types in commercial chromatographs showed that, during the period of transport from the metering device to the column, the volume of the sample greatly increases and, with decrease of the initial volume of the sample, the relative increase in volume becomes more pronounced. Thus an initial sample volume of 0.15 cm^3 at a flow rate of 5 cm^3 min^{-1} increases by a factor of 8.7. To reduce the spreading, a membrane metering device, where "dead" volumes had been eliminated from the switching valves, was prepared and tested[28]. In the tests the column was replaced by a detection system, which determined the profile of the sample at the inlet to the column. The results of the test showed that, for a sample volume of 0.15 cm^3 and a carrier gas flow rate of 5 cm^3 min^{-1}, the volume of the sample increases by a factor of 5.3, i.e. is smaller by a factor of 1.5 than in a commercial metering device. A metering device of this design can be recommended for use with PCC in commercial chromatographs.

Table 6[67] presents the parameters of the sample for a metering system with switching valves. Using Klinkenberg's expression[68]

$$V_S \leqslant \frac{0.5}{N^{1/2}} V_R,$$

(where V_S is the volume of the sample at the inlet to the column, V_R the retention volume of the component, and N the number of theoretical plates) and the data in Table 6, it is possible to calculate the permissible initial volume of the sample. Thus, for a permissible sample volume of 0.8 cm^3 and a carrier gas flow rate of 0.5 litre h^{-1}, the volume of the initial sample must be not more than 0.1 cm^3.

Table 6. Parameters of the sample for a metering system incorporating switching valves without "dead" volumes.

Parameter	Carrier gas flow rate, litre h^{-1}	Volume of initial sample V_g, ml			
		0.1	0.15	0.5	1.0
Volume of sample at inlet to column, cm^3	0.1	0.55	0.6	0.75	—
	0.15	0.62	0.7	0.85	—
	0.3	0.72	0.8	1.0	1.5
	0.5	0.82	1.0	1.2	1.7
	0.8	0.92	1.15	1.4	2.0
	1.0	1.1	1.4	1.8	2.45
Ratio of given sample volume to initial volume	0.10	5.5	4.0	1.5	—
	0.15	6.2	4.7	1.7	—
	0.3	7.2	5.3	2.0	1.5
	0.5	8.2	6.7	2.4	1.7
	0.8	9.2	7.7	2.8	2.0
	1.0	11.0	9.3	3.6	2.45
Ratio of the concentrations in the sample at the maximum and in the initial sample	0.1	0.6	0.7	1.0	—
	0.15	0.55	0.65	1.0	—
	0.3	0.5	0.6	1.0	1.0
	0.5	0.42	0.45	0.9	0.95
	0.8	0.36	0.4	0.8	0.85
	1.0	0.32	0.35	0.7	0.8

The columns may be connected to the metering device in the detector either directly (Fig. 9) or via a metallic capillary. One should note that the scheme illustrated in Fig. 9 has been used in a chromatograph prepared in the laboratory. On the other hand, in commercial chromatographs such arrangement of the column is not possible and the ends of the column must be straightened before filling. This method of attachment is most effective from the standpoint of reducing the spreading outside the column and the possibility of employing columns at high temperatures (up to 260°C), but it is fairly laborious. A simpler procedure[27] involves making a connection via a metallic capillary: small sections of a metal capillary, the external diameter of which is smaller than the internal diameter of the column, are joined to the detector of the metering device (also via a silicone rubber washer). The ends of the capillaries are inserted into the inlet and outlet of the column and are glued on by means of an epoxy-resin. In this method of connection there is no need to straighten the ends of the column and the metal capillary and not the column itself is clamped by a nut, which is a much more reliable arrangement. For high-temperature analysis, it is necessary to use heat-resistant adhesives, or intermediate capillaries made of alloys (for example Kovar), forming a junction with glass, must be employed.

Flame-ionisation detectors are mainly used in conjunction with PCC. Owing to their considerable inertia, katharometers impair the quality of the separation and

reduce the column efficiency. Comparative results of analyses of the products of the hydrocracking of heptane on PCC in conjunction with commercial katharometers of a polydiffusion type and with a flame-ionisation detector showed[28] that, when the latter was used, the specific efficiency of the column was equivalent to 1200 theoretical plates, while in the experiment with a katharometer the efficiency was equivalent to only 400 theoretical plates. However, the katharometer has significant advantages owing to its universality, simplicity of the apparatus involved, ease of operation, and reliability.

Studies have been made[28] on the possibility of employing a katharometer in work with PCC. The inertia of the katharometer is determined by the volume of the chamber and the inertia of the sensor elements. It has been established that the main factor determining the inertia of the katharometer is the volume of the detector chamber. A microkatharometer with a volume of the chamber of 40 μl, in which the same sensor elements as in an ordinary katharometer are employed, was therefore developed for experiments with PCC[28].

Certain requirements must also be met by the system for the recording of the results of analysis when short columns are used in rapid analysis. The limited speed of the response of the recording device is the cause of the distortion of the shape and amplitude of the chromatographic peaks, if the width of the latter is smaller than the permitted value. If the speed of the response of the recording device is T, then the minimum width σ_f of a chromatographic peak with a height h_0, which can be measured without distortion of its shape, may be determined from the relation

$$\sigma_f \geqslant \frac{h_0}{l}\frac{T}{1.65}, \qquad (6)$$

where l is the length of the scale and h_0 the amplitude value of the signal. For the peak amplitude, we have correspondingly[69]

$$\sigma_a \geqslant \frac{h_0}{l}\frac{T_a}{2.22}. \qquad (7)$$

The minimum permissible width of the peak at any specified height, for which the peak is measured with the specified response time of the recording device without distortion of the shape or height respectively, can also be determined from Eqns. (6) and (7). The minimum possible duration of analysis on a column with a specified efficiency can be determined from the minimum permissible peak width. The period from the instant of the injection of the sample into the column to the instant when the peak maximum emerges (t_R) is defined by the equation[28]

$$t_R = (N/5.54)^{1/2}\tau_{0.5}.$$

Having expressed the peak width in terms of the standard deviation σ (the peak half width at a height $h = h_{max}e^{1/2}$), we can obtain

$$t_R = (N/5.54)^{1/2}\cdot\sigma\cdot 2\sqrt{2\ln 2} \simeq \sigma N^{1/2}.$$

Hence the minimum permissible elution time of the component for recording without distortion of the shape and amplitude of its peak is determined respectively by the expressions

$$t_{R_f} = \frac{h_0}{l}\frac{T}{1.65}N^{1/2}; \qquad t_{R_a} = \frac{h_0}{l}\frac{T}{2.2}N^{1/2}.$$

V. THE APPLICATIONS OF PACKED CAPILLARY COLUMNS IN GAS CHROMATOGRAPHY

1. The Separation of Complex Mixtures

The separating capacity of chromatographic columns can be increased by increasing either the sorbent selectivity or the efficiency of the columns employed. The use of selective sorbents is effective only for the separation of pairs of substances which differ in their properties; for the separation of multicomponent mixtures consisting of narrow fractions of substances whose properties differ little, highly efficient columns are necessary. The only method for the separation of multicomponent mixtures available at present is classical capillary chromatography, employed mainly for the analysis of non-polar compounds. The preparation of highly efficient capillary columns with a polar phase requires special treatment of the surface of the columns and still constitutes an art [rather than a science]. Packed columns can be filled with any sorbent and the scope of detailed studies of multicomponent mixtures of different compositions is thus extended. It is particularly useful to employ PCC for the separation of substances with small partition coefficients.

Table 7. Results of the separation of industrial mixtures of oxygen-containing compounds on capillary and ordinary packed columns.

Type of column	Sorbent	t, °C	Mixture analysed	Efficiency, N		No. of separated components
				overall	specific, per metre	
13.8 m × 0.8 mm PCC	15% PEG-400 on Chromosorb P	120	Product of oxo synthesis in Salavat [Combine]	42 000	3000	40
Ditto	ditto	120	crude alcohol	42 000	3000	46
"	"	120	ether head	42 000	3000	50
"	"	100	ditto	42 000	3000	55
"	"	140	hydroformylation product	42 000	3000	61
"	22.2% DOP + 0.5% OP-10 on celite 545	120	ditto	30 000	1700	38
4 m × 3 mm ordinary backed column	ditto	120	"	1 800	450	19
Ditto	10% PEG-2000 on INZ-600	80	"	1 773	440	14

Highly efficient PCC have been applied successfully to the determination of the compositions of complex hydrocarbon mixtures—fractions of liquid high-temperature pyrolysis products[70] and fractions (150–180°C) of the petroleums of the Surgut deposit (Western Siberia)[27]. Analysis of the C_4–C_{13} petroleum cracking fraction on PCC by gas–liquid–solid chromatography established[47] that, in terms of the number of peaks, the resulting chromatogram is analogous to that obtained on a classical capillary column.

The separation of light hydrocarbons on a usual packed column is fairly difficult. Using the main advantage of PCC—high efficiency and the possibility of filling with any sorbent—it is possible to achieve a clear-cut separation of light hydrocarbons[53].

The separation on PCC of multicomponent mixtures incorporating polar components is of particular interest. Specimens of industrial mixtures of oxygen-containing compounds—products obtained at different stages of oxo synthesis—has been studied[27] with the aid of PCC. The results of the separation are presented in Table 7, which includes for comparison also data for the separation of certain specimens on ordinary packed columns. Table 7 shows that PCC make it possible to detect on the chromatogram a number of peaks greater by a factor of 2–4 than on ordinary packed columns.

A multicomponent mixture of hydrocarbons and C_8–C_{12} alcohols, obtained as a result of synthesis from carbon monoxide and hydrogen, was separated by PCC under isothermal conditions in combination with linear programming conditions[27]. The duration of the entire analysis was 210 min; during the first 30 min, the separation was carried out at 120°C and during the next 30 min linearly programmed heating at a rate of 2 K min^{-1} was employed up to 160°C, this being followed by isothermal conditions. The chromatogram presented in Fig. 10 shows that under these conditions a fairly clear-cut separation of 60 components is achieved, and that during linearly programmed heating there is almost no displacement of the base line.

The advantages of PCC in the separation of polar compounds have been demonstrated[71] in the analysis of C_1–C_6 alcohols, aliphatic acids, and primary amines. Highly efficient PCC have also been used to analyse complex mixtures of steroids[53], barbiturates[54], organic mixtures in water[47], and impurities contaminating air[46,47] and for the separation of the stereo-isomers of acyclic hydrocarbons[72] and structural isomers of aromatic hydrocarbons[72].

2. Analysis of Impurities

In the determination of impurities it is necessary (1) to separate them from the main component and then from one another, and (2) to carry out the determination under optimum conditions as regards sensitivity, i.e. under the conditions of maximum concentration in the centre of the zone. In order to separate the impurities from the main component, a much higher column efficiency is necessary than in the separation of zones with identical concentrations. Thus, in the separation of substances with a concentration ratio of 1000, it is necessary to employ a column with an efficiency higher by a factor of 2.8 than that of the column used to separate substances with identical concentrations[74].

In conformity with the theoretical plate theory[75,76], the maximum concentration in the zone increases with efficiency and with the weight of the sample:

$$C_{max} = \frac{N^{1/2}}{V_R} \frac{q}{(2\pi)^{1/2}},$$

where q is the weight of the sample.

The simplest method of increasing the sensitivity is to increase q. However, an increase of q entails a decrease of column efficiency and an impairment of separation. For this reason, it is in many cases more useful to employ highly efficient columns.

The capillary columns proposed by Golay[1] have been and still are the most efficient chromatographic columns. However, owing to their disadvantages they have not found applications on quite such a wide scale as packed columns. In particular, one of the disadvantages of classical capillary columns is the difficulty and in many instances the

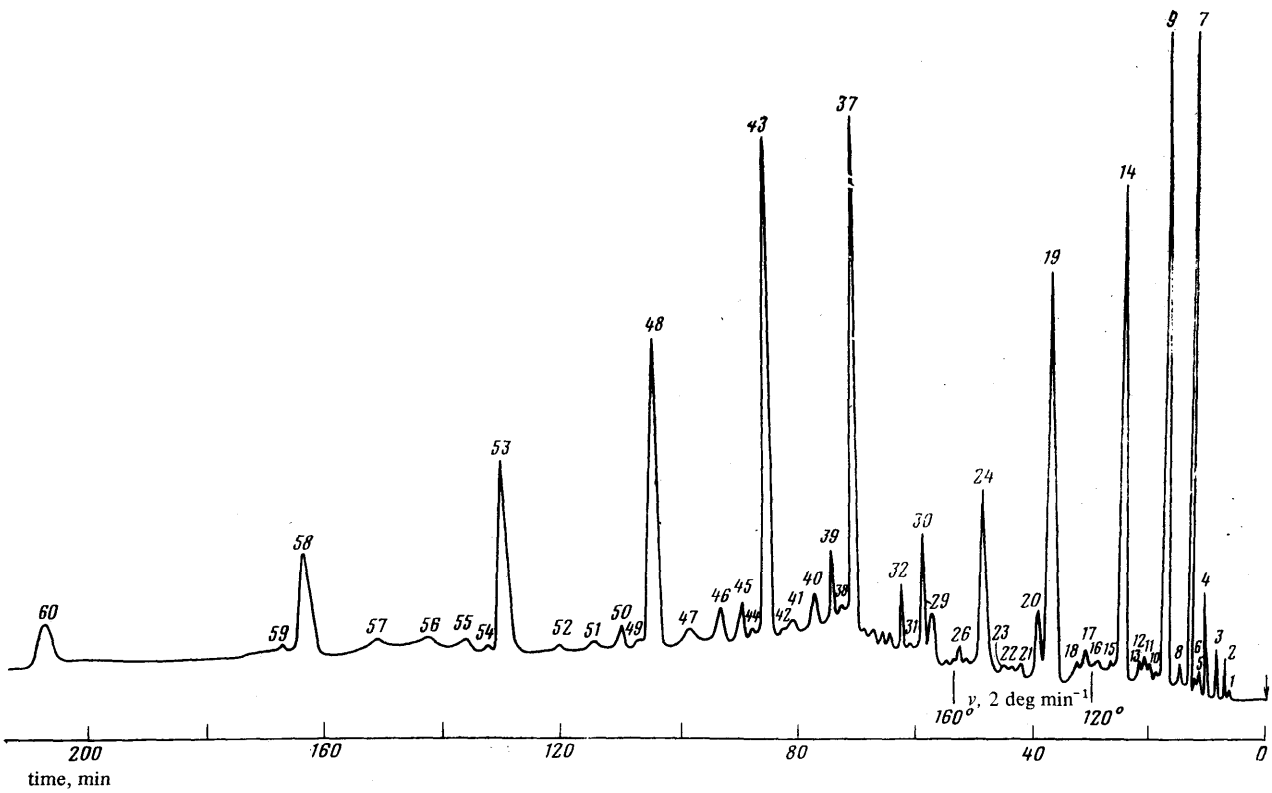


Figure 10. Chromatogram of the separation of the oxo synthesis products. 15.5 m × 0.8 mm column; sorbent—15% of 1,2,3-tris-(2-cyanoethoxy)propane on Chromosorb P.

impossibility of analysing admixtures and especially micro-impurities, since, owing to the extremely small amount of charge which the columns can handle, the determination of impurities requires unduly sensitive detecting systems. Furthermore, the high phase ratio β impairs the separation, which has a particularly marked effect in the separation of weakly sorbed compounds. These disadvantages may be to a large extent eliminated by employing long PCC, the small diameter of which ensures their high efficiency, and the presence of a sorbent ensures a high capacity.

If H is increased by 10% compared with the limiting value H_C for an infinitesimally small sample, then the limiting sample size V_{lim} can be estimated from the equation[77]

$$V_{lim} \simeq 0.2 V_R / N^{1/2},$$

or, assuming that $V_R \simeq K v_l$ (K is the gas–liquid partition coefficient and v_l the volume of the SLP in the column), from the expression

$$V_{lim} \simeq 0.2 K v_l / N^{1/2}.$$

In comparing the limiting sample sizes for capillary (V^c_{lim}) and packed capillary (V^{cp}_{lim}) columns, it is useful to employ the relation

$$V^{cp}_{lim} / V^c_{lim} = v^{ce}_l / v^c_l, \quad (8)$$

where v^{cp}_l and v^c_l are the volumes of SLP in packed capillary and classical capillary columns respectively. Eqn. (8) was obtained on the assumption that the number of theoretical plates in the columns compared and the partition coefficients in the latter are similar. Since the volume of the SLP in PCC is approximately 100 times greater (see Section II) than in classical capillary columns, the sample size in PCC is one hundred times greater than in classical capillary columns. Consequently, when detectors of the same sensitivity are used, the minimum concentration of the impurity which can be determined with the aid of PCC is approximately 100 times smaller than that which can be determined by means of classical capillary columns.

Additional advantages of PCC compared with classical capillary columns are the possibility of employing mixed sorbents and the possibility of gas–adsorption chromatography in packed capillary columns.

Long PCC have been used[78] to determine impurities in 2-bromo-2-chloro-1,1,1-trifluoroethane (fluorothane). The separation of the isomeric 1-bromo-2-chloro-1,1,2-trifluoroethane impurity from the main substance constitutes a particular difficulty in this analysis. The application of PCC in the analysis of fluorothane made it possible to determine a larger number of microimpurities (almost by a factor of two). Furthermore, this ensures a higher separation factor ($R \gg 1$) for the main component and the isomer[78,79].

The use of short PCC permits the determination of microimpurities by a micromethod[18] and a high-speed method[19]. The authors of these investigations carried out an analysis (at 70°C over a period of 70 min) of microimpurities in isoprene on a 2.5 m × 1.1 mm column filled with modified (with 2% of squalane) alumina; H for 2-methylbut-1-ene amounted to 0.04 cm. Rapid analysis of the same isoprene specimen (at 30°C over a period of 7 min) was carried out on a 0.5 m × 0.6 mm column with the same adsorbent; in this case H for the same component was 0.06 cm. Fig. 11 shows that the reduction of the analysis time by a factor of 10 is entirely worthwhile, despite the slight impairment of efficiency. One should also note that rapid analysis has been achieved for a much lower temperature, which is very important in experiments with readily polymerisable substances. The content of the impurities determined in the two instances was 2×10^{-4} vol.%.

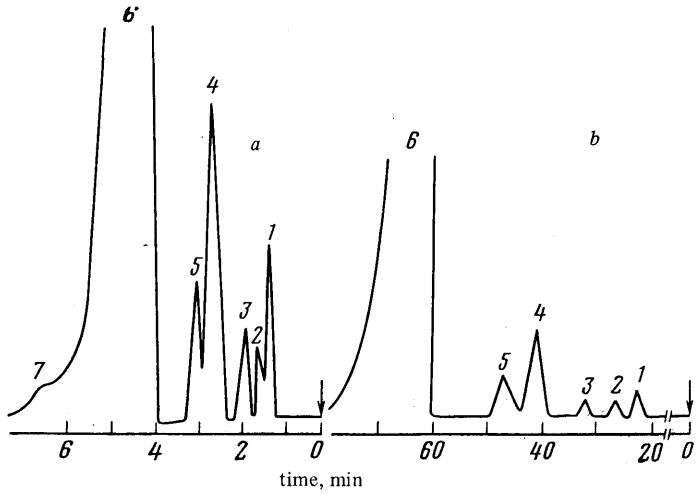


Figure 11. Chromatograms of the separation of impurities in isoprene: *a*) high-speed method; carrier gas (hydrogen) flow rate 50 cm s^{-1}; 30°C; *b*) usual analysis; carrier gas (nitrogen) flow rate 8.1 cm s^{-1}; 70°C; 1) 3-methylbut-1-ene; 2) pent-1-ene; 3) pent-2-ene; 4) 2-methylbut-1-ene; 5) 2-methylbut-2-ene; 6) isoprene; 7) butadiene.

Packed capillary columns have been used[31] to determine gaseous hydrocarbon impurities in the propane–propene fraction used to make polypropylene. The high-speed method for the determination of microimpurities has been applied in gas-adsorption chromatography on alumina modified with 3% of squalane using a programmed temperature up to 70°C. The analysis time of an artificial propane–propene fraction consisting of 13 components was 8–10 min (on a column of the usual type, it is 40 min); the volume of the sample injected was 2 cm^3. The column efficiency H for α-butene was 0.028 cm, i.e. was close to H for classical capillary columns. The minimum impurity content in the sample was 8×10^{-4} vol.%.

3. High Speed Analysis

When a gas chromatograph is used as a pulse generator for the regulation of chemical processes, the duration of the analytical cycle must be reduced, i.e. high speed analysis is necessary. It is also required in routine analyses, in the study of complex multicomponent systems, in kinetic measurements, etc. The duration of analysis may be reduced by means of a higher separating capacity of the column under optimum separation conditions, by increasing the flow rate at the mobile phase, and by employing shorter columns, high-speed amplifiers, and computer integrators.

Since PCC are characterised by high resolving capacity per unit length, this makes it possible to employ short separating systems. The high permeability of columns of this type permits the use of higher carrier gas flow rates, which can be ensured by moderate pressures. The stable conditions which obtain when the temperature is programmed permit an increased rate of separation by programming the temperature and pressure without an appreciable decrease of separating capacity.

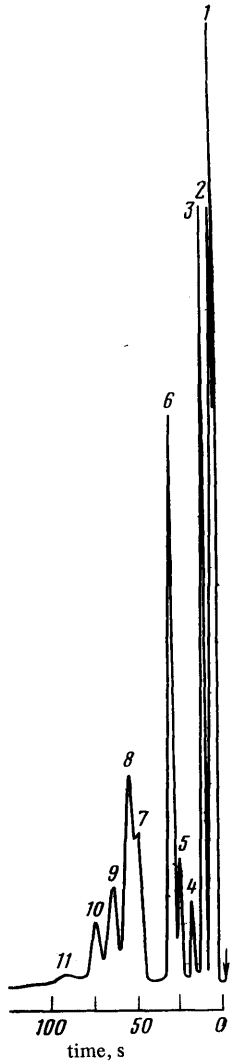


Figure 12. Chromatogram of the high-speed separation of C_1-C_4 hydrocarbons. 0.2 m × 0.58 mm column; carrier gas (hydrogen) flow rate 40 cm min^{-1}; room temperature: 1) methane; 2) ethylene; 3) propane; 4) n-butane.

Kaiser[80] suggested that the carrier gas pressure and the separation number per unit time Tz/t be used as the principal characteristics of high-speed chromatographic separation. The separation number Tz is defined by the relation

$$Tz = \frac{t_2 - t_1}{\tau_{0.5}^{(2)} + \tau_{0.5}^{(1)}} - 1,$$

where t_1 and t_2 are the uncorrected retention times of the first and second components and $\tau_{0.5}^{(2)}$ and $\tau_{0.5}^{(1)}$ are the widths of peaks at the level of half their height. The separation number can be measured with programmed temperature and pressure, so that it is preferable as a criterion to measurements based on the theoretical plate theory. Short PCC have been assessed[80] in terms of the proposed criteria when the columns were used for high-speed analyses.

Capillary columns filled with a sorbent have been employed[31] for the high-speed analysis of low-boiling C_1-C_4 hydrocarbons by gas–adsorption chromatography on modified alumina. A mixture of eleven components was separated in 90 s. An example of high-speed analysis of a mixture of light hydrocarbons over a period of 3.5 s is illustrated in Fig. 12 (column with alumina gel modified with the aid of 5% of squalane). The methane elution time was less than 1 s and the column efficiency for n-butane was $H \simeq 0.1$ cm.[31]

A further decrease of the duration of analysis is hindered by difficulties associated with the apparatus. Thus the sample injection time is almost equal to the elution time of the first component, which distorts the shape of the peak; it is impossible to measure accurately the elution times of the components with the aid of the usual stop watch (the error of the measurement is 100% and more); the unduly high volume flow rates in a flow-type detector limit stable combustion and accuracy of the measurement. High-speed analysis (1 peak in 1 s) therefore requires special automatic metering, recording, and integrating (counting) devices.

The possibility of reducing the duration of analysis by a factor of 2–5 has been demonstrated[81] in a study where capillary columns filled with Spherosil were used in gas–solid chromatography and gas–solid chromatography with a modified SLP.

4. The Use of Packed Capillary Columns in Industrial Automatic Chromatographs

Industrial automatic chromatographs are used as sensors of composition in automatic monitoring and control systems for technological processes. A specific feature of industrial chromatographs is that they are mounted directly at the sampling points in technological apparatus and operate under automatic conditions. These devices must therefore be more compact, must require a fairly small amount of carrier gas, and must be reliable. The columns in such apparatus must meet another requirement: long operating time without alteration of the characteristics of the separation process. For this reason, the number of sorbents and liquid phases suitable for industrial chromatographs is much smaller than for laboratory chromatographs. Apart from characteristics such as sensitivity and error, an important parameter of industrial chromatographs is the analysis time, which determines the possibility of obtaining information about the composition of the mixture analysed in a specified time.

Packed capillary columns satisfy all the requirements enumerated above to a much greater extent than the usual packed columns. The high specific efficiency of PCC and

the possibility of carrying out analyses at a fairly high linear flow rate of the carrier gas without reducing the efficiency of the separation make it possible to reduce greatly the duration of the analysis. The small amounts of carrier gas and sorbent required permit the use of scarce and expensive carrier gases and sorbents and the small size of the columns permits the construction of a compact analyser ensuring effective temperature control and the possibility of ensuring any category of protection from explosion.

However, one should bear in mind that PCC impose definite requirements, primarily as regards the automatic metering device and the detector. Thus, when appreciable spreading of the sample occurs in the metering system, the column is overloaded, and its efficiency falls[66]. The inertia of the detector should correspond to the parameters of the peak[82], otherwise the apparent efficiency of the separation falls, and an appreciable error is introduced into the results of the measurements.

The following apparatus has been developed[81]: an automatic metering device and a low-inertia thermal conductivity detector, suitable for PCC, and on their basis, an industrial automatic "Mikrokhrom" chromatograph with an explosion-resistant device was constructed. The apparatus has been used successfully for the determination of the compositions of many industrial mixtures directly in industrial plants.

In the study of individual stages of the technological processes under development automated pilot microapparatus has been used recently. One of the most important parameters in the assessment of the results is the composition of the multicomponent mixture at the outlet from the microreactor. The most suitable analyser is a compact high-speed automatic chromatograph with a small volume of samples removed (this makes it possible to calculate the material balance without taking into account the amount of substance taken for analysis). The chromatograph with PCC meets the above requirements to the greatest extent.

The Mikrokhrom chromatograph of normal design (not the explosion-resistant design) has been used in experiments with a pilot microapparatus for catalytic hydrocracking[83]. The chromatogram of a mixture of catalytic n-heptane hydrocracking products is illustrated in Fig. 13.

5. Measurement of Physicochemical Characteristics

One of the most important applications of PCC involves the determination of physicochemical characteristics by a micromethod, i.e. using small amounts of the test substances and the sorbent (reagent). The determination of rate constants on PCC was first developed[24] for the reaction of isoprene with maleic anhydride in the liquid phase by a chromatographic pulse micromethod. The degree of conversion was determined from the change in the area under the chromatographic isoprene peaks (n-pentane was used as the internal standard). The contact times of the reactants were calculated from the retention times of the diene taking into account the "dead" time of the chromatograph. The reaction rate constants, determined at 42°, 48°, 56°, and 62°C, and the activation energy of 12.1 kcal mole^{-1} agree satisfactorily with the values obtained on a column of the usual type[84].

An advantage of PCC is the possibility of employing them (by virtue of their high efficiency) for the determination of the rate constants for rapid reactions. A special calculation showed[24] that the kinetic coefficient of sorption and desorption (internal-diffusion mass exchange) corresponding to the maximum degree of conversion is a factor of 2×10^3 greater than the rate constant (for an analytical column, the ratio is smaller by an order of magnitude). PCC can also be used to determine heats of adsorption. The heats of adsorption of α-butene on various alumina specimens have been determined[24] using a 0.5 m × 0.58 mm PCC in the temperature range from −20° to +100°C. According to literature data[85], the heat of adsorption of n-butane is 8.2 kcal mole^{-1}; values in the range 8.5–8.1 kcal mole^{-1} have been obtained on PCC. Consequently the micromethod described above for the determination of heats of adsorption is entirely reliable and accurate.

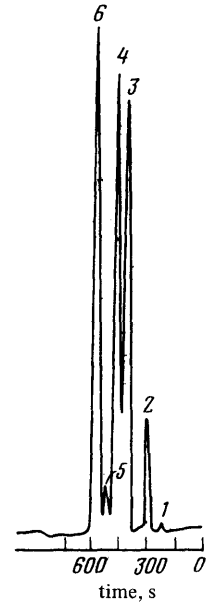


Figure 13. Chromatogram of the separation of the products of the catalytic hydrocracking of heptane. 1.2 m × 1.0 mm metallic column; sorbent—Chromosorb P (120–150 μm) impregnated with 15% of squalane; 60°C; carrier gas (nitrogen) flow rate 2.4 cm^3 min^{-1}: 1) n-hexane; 2) methylcyclopentane; 3) 2-methylhexane; 4) 3-methylhexane; 5) 3-ethylpentane; 6) n-heptane.

In conclusion we may note that PCC extend the scope of gas-chromatographic studies both in the field of analysis, particularly of multicomponent mixtures and mixtures difficult to separate, and in the measurement of physicochemical quantities. Also promising is the application of PCC in microchemistry, particularly for microseparations on a preparative scale.

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