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CAPILLARY PACKED COLUMNS IN GAS CHROMATOGRAPHY

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CONTENTS

1. INTRODUCTION

One method for improving the separation efficiency in gas chromatography is to use columns of small diameter. Golay[1] was the first to propose the use of capillary columns, and various useful modifications have been proposed. In recent years, the advances of capillary packed columns (CPCs) have been demonstrated, and this type of column is gaining ever-increasing recognition. However, no reviews of CPC have been published.

By the term CPCs, we generally mean sorbent-filled columns with an I.D. of 2 mm or less. This definition is subjective, of course, as there is no clear boundary between capillary and conventional packed columns. According to our observations, it is columns of I.D. 1–2 mm that begin to manifest the distinguishing features of columns of this type. The above definition actually gives the upper limit of the inner diameter. The principal investigations have been carried out on columns with I.D. < 1 mm.

Halász and Heine were the first to obtain CPCs[2] by drawing them on the machine of Desty *et al.*[3], tubes having previously been filled either with an active adsorbent[2,4–8] or with an inert support[9], with subsequent deposition of a stationary

phase by the frontal method. In columns obtained in this way, the distribution of the sorbent is non-uniform, and part of it is pressed into the capillary walls. With this method one can obtain long columns with comparatively high efficiency, but it requires a support of high mechanical strength and thermal stability. In most instances the support cannot be treated with the stationary phase beforehand.

Capillary columns with a dense and uniform sorbent packing are to be preferred, and will be considered further. This type of column was first obtained by Carter[10], who filled steel tubes of length 200 cm and I.D. 0.25 and 0.5 mm with microspherical glass (grain size 40 μm), on which a liquid stationary phase (LSP) was deposited by the frontal method. The height equivalent to a theoretical plate (H) of the columns thus obtained was 2 and 0.7 mm, respectively. More efficient columns (H = 0.36–0.39 mm) were later prepared by Virus[11], who filled metal columns of length 100 cm and I.D. 0.5 and 1 mm with Chromosorb or Kieselguhr with the aid of a vibrator, and then deposited LSP on the solid carrier in the column by the frontal method.

In 1963, capillary columns filled with a previously prepared sorbent began to be used in gas chromatography. The application of capillary columns with a previously prepared sorbent in analytical practice was described by Vidergauz and co-workers[12–17]. Simultaneously and independently, a systematic investigation into the characteristics of this type of column was carried out by Berezkin and co-workers[18–25], who for the first time systematically considered the general analytical properties of these columns in broader terms (in particular, the variation in the efficiency of these columns with the main experimental parameters), and also demonstrated promising prospects for their utilization in the measurement of physicochemical characteristics.

Two stages can be clearly identified in the development of sorbent-filled capillary columns: (1) the development of methods for the preparation and application of short columns, and (2) the development of methods for the preparation and application of long columns. Short columns (1–2 m) have a high specific efficiency (the number of theoretical plates per metre of the column is about 2000), but their overall efficiency is insignificant (usually not more than 2000–5000 theoretical plates). Short columns are best used for the rapid analysis of relatively simple mixtures. The second stage of development of CPCs began recently, the first paper by Cramers *et al.*[26] on long CPCs (over 10 m) being published as late as 1971. The high efficiency of these columns (those of efficiency up to 60,000 theoretical plates are described, but longer columns can be obtained) determines their promising prospects for investigating multi-component mixtures and mixtures that are difficult to partition and for impurity analysis.

Owing to their small inner diameters and the presence of a sorbent, CPCs effectively combine the advantages of classical capillary columns (capillaries whose inside walls are covered with LSP) and conventional packed columns. The small inner diameter determines the advantages of CPCs over the conventional packed columns: (1) high efficiency; (2) rapid operation; Shkolina[27] showed that a separation process takes half as long in CPCs as in conventional packed columns; (3) a more stable regime with temperature programming as a result of the rapid thermal response of the columns owing to their small mass and linear dimensions; (4) miniaturization of the columns, *i.e.*, the possibility of developing small equipment with a compact thermostat, in which rapid heating and cooling of the column can easily be achieved;

and (5) economy, which permits greater possibilities for the utilization of uncommon and/or expensive sorbents, as the amounts of sorbents used are small.

The disadvantages of CPCs, compared with conventional packed columns, are that a slightly more complicated and time-consuming filling technique is required, small-volume detectors, in particular a microkatharometer, are necessary because the conventional katharometer cannot be applied owing to its slow response[28], and there is a higher resistance to flow.

The use of a sorbent in capillary columns provides a number of advantages over classical capillary columns: (1) rapid operation; in separating substances that are sorbed readily or to a moderate extent, CPCs are preferred to classical capillary columns because of the shorter analysis time[27], *e.g.*, for a distribution coefficient of $K = 10$ the separation time in CPCs is almost 30 times less, and for $K = 50$ it is 2.3 times less than in classical capillary columns; (2) this type of column can be made highly reproducible by using sorbents of different polarity, for both gas–liquid chromatography (GLC) and gas–solid chromatography (GSC); (3) sufficiently high capacity which, firstly, enables one to introduce the sample without flow division, which decreases the errors in the quantitative results and reduces the requirements imposed on detector sensitivity (the use of a microkatharometer is possible), secondly, it improves the resolution of the column in separating poorly sorbed substances, and thirdly, it extends the possibilities of the use of capillary column chromatography in impurity analysis.

A comparison of the characteristics of CPCs with conventional types of column indicates that their wide application in chromatographic practice is justified and expedient.

2. SPECIFIC FEATURES OF THE CHROMATOGRAPHIC SEPARATION PROCESS IN CAPILLARY PACKED COLUMNS

When studying the chromatographic process in narrow packed columns, it is important to establish the dependence of the broadening of the chromatographic zone on the column diameter. Theoretical and experimental investigations aimed at establishing this dependence in columns of small diameter have been carried out for the gas–liquid version[27,29] and for the gas–solid version[27,30,31], where the main characteristics of efficiency taken as the broadening criteria were the minimum height equivalent to a theoretical plate ($H_{\min.}$) and the coefficient of resistance to mass transfer (C) in the Van Deemter equation, which describes the variation of H in relation to the carrier gas velocity[32]:

$$H = A + \frac{B}{u} + Cu \tag{1}$$

where A and B are coefficients that take into account the eddy and molecular longitudinal diffusion, respectively.

Comparative data on the efficiency of packed columns of different diameter (see Table 1 (ref. 27)) indicate that for GLC the $H_{\min.}$ in columns of I.D. 1.2, 0.8 and 0.5 mm changes only slightly and shows an appreciable change only for a column of I.D. 3 mm. According to other data[29], no substantial effects of the column diameter on $H_{\min.}$ were detected in columns of I.D. 0.75, 1.0 and 1.5 mm.

TABLE 1

EFFECT OF COLUMN DIAMETER ON EFFICIENCY

Type of chromatography	*Column I.D. (mm)*	*Pentane*						*Hexane*						*Octane*					
		$H_{min.}$ *(mm)*		*Optimal velocity (cm/sec)*		$C \cdot 10^2$ *(sec)*		$H_{min.}$ *(mm)*		*Optimal velocity (cm/sec)*		$C \cdot 10^2$ *(sec)*		$H_{min.}$ *(mm)*		*Optimal velocity (cm/sec)*		$C \cdot 10^2$ *(sec)*	
		N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*	N_2	*He*
GLC	3.0	0.52	0.88	0.6	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
GSC	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	0.38	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	—	—	—	—	—	—

Greater changes are observed in the coefficient of resistance to mass transfer, C. As follows from Table 1, C decreases with decreasing inner diameter of the column. Thus, in a column of I.D. 3 mm C is almost twice that in a column of I.D. 1.2 mm and approximately 3 times that in a column of I.D. 0.5 mm. This relationship has been observed for all test substances and all carrier gases.

In gas–solid chromatography (GSC), a change in column diameter results (as in GLC) in insignificant changes in $H_{min.}$; the lowest value of $H_{min.}$ has been obtained for a column of I.D. 0.8 mm (see Table 1). On decreasing the inner diameter from 3 to 0.5 mm, C decreases by almost half, while for a column of I.D. 0.8 mm, the decrease in C is 2.5–2.7-fold.

Thus, for the range of column diameters investigated, the value of $H_{min.}$ varies only slightly in GLC[27,29] and GSC[27]. The value of C in GLC decreases monotonically with decreasing column diameter (Fig. 1a), while in GSC, the graph of the dependence of C on column diameter passes through a minimum at I.D. 0.8 mm (Fig. 1b). This difference is evidently due, not to differences in separations on adsorbents and absorbents, but to the different grain sizes of the sorbent used, as in GSC use was made of a coarser sorbent (100–200 μm) than in GLC (100–160 μm), and therefore in a column of diameter 0.5 mm (GSC) the sorbent packing was evidently looser, which increased the broadening of the chromatographic zone.

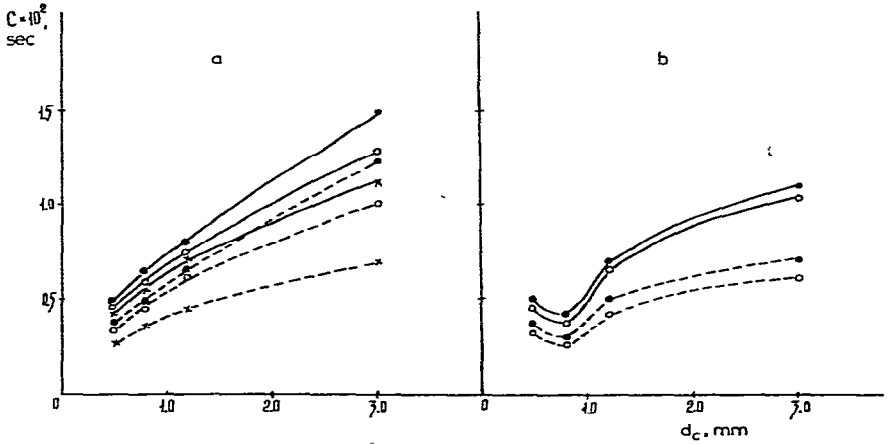


Fig. 1. Dependence of coefficient of resistance to mass transfer (C) on column diameter (d_c). Sorbent: (a) 5% squalane on Chromosorb W (100–160 μm); (b) Spherosil XOB.075 (100–200 μm). ●, Pentane; ○, hexane; ×, octane. Carrier gas: solid line, nitrogen; broken line, helium.

The investigations carried out previously on GSC[30–31] showed that, for columns of I.D. 0.6–1.6 mm, $H_{min.}$ is directly proportional to the inner diameter and increases with a further decrease in diameter (from 0.6 to 0.3 mm). An decrease in the inner diameter from 1.63 to 0.6 mm leads to a 3-fold reduction in C (see Table 2). The minimum value of C was obtained for a column of I.D. 0.6 mm.

From these results it can be concluded that the dependences of the column efficiency on the inner diameter as obtained by different workers[27,29–31] are similar.

TABLE 2

COEFFICIENT OF RESISTANCE TO MASS TRANSFER (*C*) IN COLUMNS WITH DIFFERENT INNER DIAMETERS[31]

Variable	*Value*			
I.D. (mm)	0.34	0.60	0.90	1.63
$C \cdot 10^3$ (sec)	3.8	3.5	5.0	10.4

Some divergence in optimal column diameter [0.8 mm (ref. 27) and 0.6 mm (refs. 30 and 31)] can be attributed to the different grain sizes of the sorbents used.

According to Jones' equation[33]:

$$H = A + \frac{B}{u} + C_g u + C_s u \tag{2}$$

the kinetic broadening in the chromatographic process is due to the resistance to mass transfer in the mobile (C_g) and stationary (C_s) phases. According to Giddings' theory[34], each of these factors makes an important contribution to the mechanism of broadening in the column. Therefore, in studying the broadening of a chromatographic band in CPCs, it was interesting to investigate the relative roles of mass transfer in the mobile and stationary phases in relation to the column diameter. Such investigations were first carried out for CPCs by Berezkin *et al.*[25], who proposed a graphical method for the separate determination of these resistances and estimated the contributions of the extra-diffusion and intra-diffusion resistances to mass transfer in relation to the ratio of the column diameter to the grain diameter. The coefficients of extra-diffusion resistance to mass transfer for a column of I.D. 0.58 mm with increasing grain diameter increase only slightly. For a wider column (I.D. 0.98 mm), the coefficient of extra-diffusion resistance to mass transfer (C_g) for the same ratio of column diameter to grain diameter is twice as high, and a 10-fold increase in the grain diameter results in a 10-fold increase in C_g.

The results of separate determinations of the coefficients of resistance to internal and external mass transfer carried out recently[27] for GLC and GSC by the method described by Grant[35] are given in Table 3. From Table 3, it follows that a decrease in column diameter reduces both C_g and C_s, and the value of C_s found by another two methods (those of Perrett and Purnell[36] and Novák *et al.*[37]) coincided (see Table 4), which indicates the correctness of the results obtained. The changes in C_s observed by Shkolina[27] contradict the initial classical concept of the independence of the processes that control the interphase mass transfer in a chromatographic column and agree with the conclusions of Novák and co-workers[37,38], who demonstrated theoretically and experimentally that C_s and C_g are interdependent and also depend on the average pressure in the column. In the case under consideration, the average pressure increases with increasing column diameter, which can be attributed to the increase in the permeability of narrow columns [for $d_p/d_c > 0.05$–0.1 (ref. 39)], evidently due to the stronger wall effect (d_p = particle diameter; d_c = column diameter).

From Table 3, it also follows that in GLC C_s is greater than C_g for pentane in all of the columns investigated, and the difference between them decreases on switch-

ing to substances with higher extraction coefficients. In GSC, C_g is greater than C_s only in a column of I.D. 3 mm, while in the other columns investigated their values are almost identical (with the use of nitrogen as carrier gas).

Fig. 2 illustrates the logarithmic dependence of C_g on the column diameter (d_c): $C_g \approx d_c^m$. The power index m in the dependence of C_g on d_c, as determined from the slope of the straight lines, is 0.42 for GLC and 0.8 for GSC. We attribute the different power dependences of C_g and d_c in GLC and GSC to the effects of sorbent shape and grain size on packings in columns of different diameter.

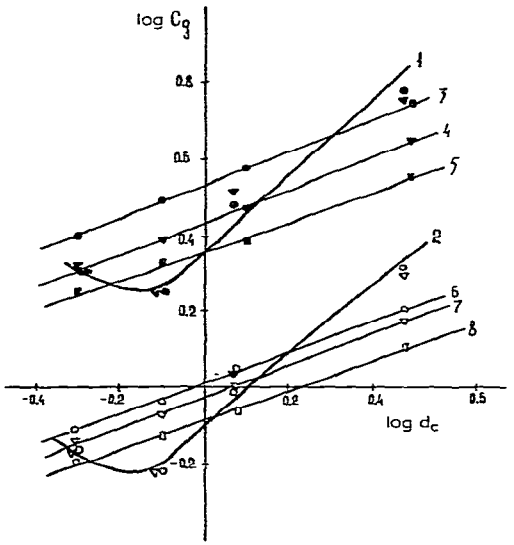


Fig. 2. Logarithmic dependence of coefficient of resistance to mass transfer in mobile phase (C_g) on column diameter (d_c). Carrier gas: closed symbols, nitrogen; open symbols, helium. ●, ○, Pentane; ▼, ▽, hexane; ■, □, octane. 1 and 2, GSC; 3–8, GLC.

The high efficiency of CPCs compared with packed columns of normal diameter is due, in our opinion, to the special role of radial diffusion in band broadening in CPCs[30] and also to the nature of the sorbent packing in them[27]. To check the assumption of the strong smoothing effect of radial diffusion in narrow columns, Berezkin *et al.*[40] compared the efficiencies of a capillary and a conventional packed column filled with an inhomogeneous (mixed) sorbent, which was a mixture of a sorbent for GLC (*i.e.*, particles of a solid support impregnated with LSP) and a solid support without LSP. Comparative measurements of the efficiencies of columns with a mixed sorbent were carried out on two spiral columns: a glass column of length 3 m and I.D. 0.8 mm and a metal column of length 2.9 m and I.D. 3 mm. The two columns were filled with the same sorbent, which was a mixture of Chromaton N AW without LSP and Chromaton N AW with 5% squalane in the ratios listed in Table 5.

The results obtained with a mixed sorbent in terms of the dependence of the coefficient of resistance to mass transfer, $H_{min.}$ and the ratio of these values on the sorbent composition for columns of I.D. 3.0 and 0.8 mm are given in Table 6 and in Fig. 3. It follows that for all of the substances investigated, which are characterized

TABLE 3

COEFFICIENTS OF RESISTANCE TO MASS TRANSFER IN MOBILE ($C_g \cdot 10^2$ sec) AND STATIONARY ($C_s \cdot 10^2$ sec) PHASES

Type of chromatography	*Column I.D. (mm)*	*Pentane*					*Hexane*					*Octane*				
		$C(N_2)$	$C(He)$	$C_g(N_2)$	$C_g(He)$	C_s	$C(N_2)$	$C(He)$	$C_g(N_2)$	$C_g(He)$	C_s	$C(N_2)$	$C(He)$	$C_g(N_2)$	$C_g(He)$	C_s
GLC	3.0	1.5	1.25	0.38	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	0.084	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	0.08	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
GSC	3.0	1.10	0.70	0.61	0.21	0.49	1.05	0.60	0.67	0.23	0.38	—	—	—	—	—
	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	0.38	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	—	—	—	—	—

TABLE 4

COEFFICIENTS OF RESISTANCE TO MASS TRANSFER IN STATIONARY PHASE ($C_s \cdot 10^2$ sec) CALCULATED BY THREE METHODS

Type of chromatography	*Column I.D. (mm)*	*Method I*[35]			*Method II*[36]			*Method III*[37]		
		Pentane	*Hexane*	*Octane*	*Pentane*	*Hexane*	*Octane*	*Pentane*	*Hexane*	*Octane*
GLC	3.0	1.20	0.85	0.53	1.25	0.90	0.60	1.23	0.90	0.61
	1.2	0.56	0.46	0.33	0.6	0.41	0.30	0.67	0.46	0.28
	0.8	0.45	0.36	0.25	0.4	0.40	0.20	—	—	—
	0.5	0.30	0.25	0.19	0.3	0.30	0.15	—	—	—
GSC	3.0	0.49	0.38	—	0.45	0.36	—	0.48	0.36	—
	1.2	0.40	0.30	—	0.40	0.30	—	0.42	0.32	—
	0.8	0.22	0.19	—	0.20	0.16	—	0.18	0.16	—
	0.5	0.29	0.27	—	0.30	0.27	—	0.30	0.22	—

TABLE 5

CHARACTERISTICS OF MIXED SORBENT USED FOR FILLING CHROMATOGRAPHIC COLUMNS

Column No.	*Sorbent composition (%, w/w)*	
	Chromaton N AW with LSP	*Chromaton N AW without LSP*
1	5	95
2	50	50
3	100	0

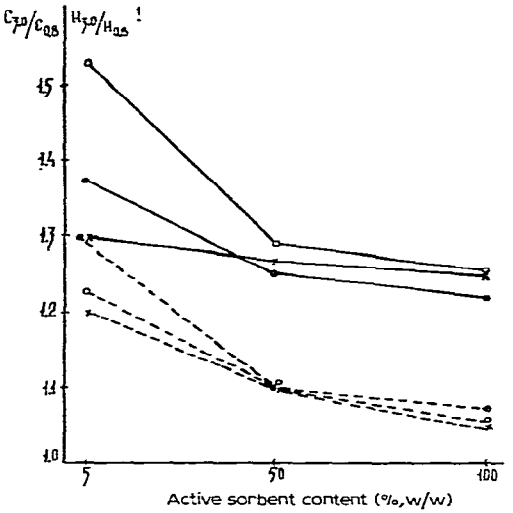


Fig. 3. Relative variation in coefficients of resistance to mass transfer and minimal values of H in columns of I.D. 0.8 and 3.0 mm in relation to sorbent composition (percentage content of sorbent). ●, Heptane; ×, toluene; ○, octane. Solid lines, $C_{3.0}/C_{0.8}$; broken lines, $H_{3.0}/H_{0.8}$.

by different values of the extraction coefficient, $H_{min.}$ and C are lower for the capillary column. These values decrease (*i.e.*, the efficiency characteristics improve) with a decrease in the inhomogeneity of the sorbent, *i.e.*, on switching from a column filled with a packing with 5% sorbent to one filled with a packing with 50% sorbent and, further, to a column filled with a pure (100%) sorbent. Note that the most pronounced decrease in $H_{min.}$ and C is observed on changing from a packing containing 5% sorbent to one containing 50% sorbent, *i.e.*, in the range of the greatest increase in adsorbent homogeneity. The experimental results are in agreement with the concept of an important smoothing role of radial diffusion in CPCs. Indeed, the time necessary for the diffusion of the molecules of the substance being analysed in the gas phase from one column wall to the other can be estimated by means of the equation

$$\tau = \frac{d_c^2}{2D} \tag{3}$$

TABLE 6

EFFICIENCY OF COLUMNS OF DIFFERENT DIAMETER FILLED WITH MIXED SORBENT

Column No.	*Sorbent*	*Column I.D. (mm)*	$C \cdot 10^2$ *(sec)*			$H_{min.}$ *(mm)*		
			Heptane	*Toluene*	*Octane*	*Heptane*	*Toluene*	*Octane*
1	5% Chromaton with 5% squalane + 95% Chromaton without LSP	3.0	2.2	2.2	4.6	1.3	1.7	1.6
2	As column 1	0.8	1.6	1.7	3.0	1.1	1.4	1.3
3	50% Chromaton with 5% squalane + 50% Chromaton without LSP	3.0	2.0	1.9	1.8	1.1	1.0	1.0
4	As column 3	0.8	1.5	1.5	1.4	1.0	0.9	0.9
5	100% Chromaton with 5% squalane	3.0	1.1	1.0	1.0	0.9	0.7	0.8
6	As column 5	0.8	0.9	0.8	0.8	0.8	0.7	0.7

where D is the diffusion coefficient of the test substance in the gas phase and d_c is the column diameter. If we assume $D = 0.5\ cm^2/sec$ then, for a capillary column of diameter 0.8 mm, $\tau = 6.4 \cdot 10^{-3}$ sec, while for a conventional packed column of diameter 3 mm, $\tau = 9 \cdot 10^{-2}$ sec, *i.e.*, 15 times as great (the effect of the sinuous path was neglected in this calculation).

Hence, with the use of a mixed sorbent the efficiency of CPCs is always higher than that of columns of large diameter. The improvement in efficiency of CPCs over conventional columns when using a mixed sorbent is not constant, as would be expected, in the case of a general reduction in the absolute values that characterize the efficiency; the relative improvement in the indicated characteristics for CPCs is enhanced with increasing inhomogeneity.

Shkolina[27] investigated qualitatively the flattening of the front of the chromatographic zone across the section of a CPC and that of a conventional analytical column. Conclusions were drawn from the shape of the boundary of the spent sorbent layer with the volatile component, which reacted chemically with the sorbent to form a coloured compound. The spent layer was formed as a result of the reaction of hydrogen sulphide with the sorbent (Chromaton N, 125–160 μm), the surface of which was coated with 3% lead acetate. The reaction yielded black lead sulphide.

The investigation was carried out with the aid of glass tubes of I.D. 3 and 0.8 m filled with sorbent. Hydrogen sulphide was injected into the carrier gas flow directly at the column wall, perpendicular to the flow of carrier gas, into the column of I.D. 3 mm with a syringe by piercing the rubber tube supplying the carrier gas near the beginning of the column, and into the column of I.D. 0.8 mm with a medical syringe needle glued into the capillary wall. On introduction of the hydrogen sulphide, the sorbent turned black.

Investigations of the spent sorbent layer after reaction with hydrogen sulphide showed that the boundary of the front of the spent sorbent forms an acute angle γ with the wall near which the hydrogen sulphide was introduced. The dependence of the slope of this angle on the reciprocal carrier gas velocity is shown in Fig. 4, which

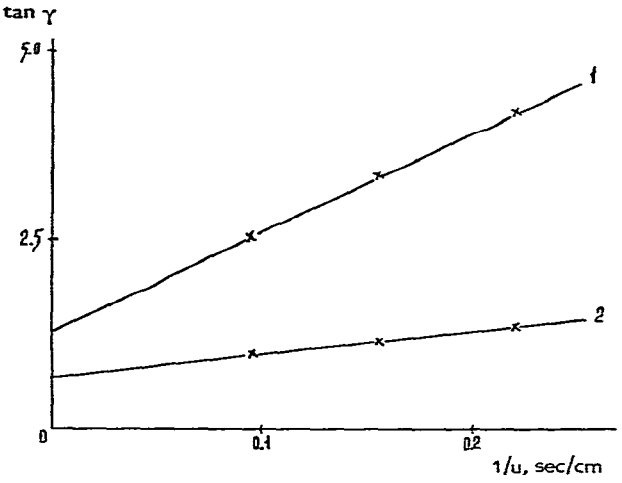


Fig. 4. Dependence of slope of boundary of spent sorbent layer (tan γ) on reciprocal linear velocity of carrier gas ($1/u$) for columns of I.D. 0.8 mm (1) and 3 mm (2).

indicates that in a column of I.D. 0.8 mm the slope of the front, at all of the carrier gas velocities investigated, is steeper than that in the conventional column of I.D. 3 mm, *i.e.*, the front of the bands in CPCs is steeper.

The larger front angle in the CPCs, which is closer to a right-angle, can evidently be attributed to the more uniform packing of the sorbent in this type of column. Using the data obtained, we can estimate the time necessary for poorly sorbed molecules in CPCs to diffuse the distance of the column diameter ($\tau = d_c/u \tan \gamma$). The values obtained (average $4.5 \cdot 10^{-3}$ sec) are in agreement with those calculated by means of eqn. 3 ($6.4 \cdot 10^{-3}$ sec).

It should be noted that in referring to packed columns, one can speak of the formation of "domains", *i.e.*, an agglomeration of some particles forming poorly cleared aived voids. It is possible that in CPC the probability of their formation in each cross-section is much lower, and the "domains" are much smaller, which must reduce the broadening in CPC. In addition, the contribution of the effect of the "remote" ducts, which was noted by Giddings[34] as the principal effect resulting in the non-uniformity of the velocity distribution across the section of packed columns, must decrease substantially in columns of small diameter, because it acts over a large distance (equal to *ca.* $7.5\, d_p$), which is less than the diameter of the columns under discussion. Thus, in CPCs the role of the non-uniform velocity distribution across the column section in reducing the efficiency is less than in the conventional columns.

The specific features of separations in CPCs, compared with classical capillary columns, are due mainly to the presence of a sorbent, which leads to a decrease in the phase ratio, β (the ratio of the volume of the gas phase to that of the liquid phase in the column). The value of β exerts a considerable effect on separation. According to the equation[41]

$$R = \frac{\alpha - 1}{4\alpha} \cdot \frac{K}{\beta + K} \sqrt{N} \tag{4}$$

where R is the degree of separation, K is the distribution coefficient, N is the number of theoretical plates and α is the relative retention volume, an increase in β must affect the separation, which is particularly disadvantageous when separating poorly sorbed compounds.

Table 7 lists the tentative amounts of LSP in columns of different types as calculated by Berezkin *et al.*[40]. It can be seen that the amount of liquid phase in

TABLE 7

AMOUNTS OF LSP IN COLUMNS OF DIFFERENT TYPES

Column		*Amount of liquid phase*
Type	*Length (m)*	*(g)*
Classical capillary column	50	0.01
CPC*	15	1
Conventional packed column*	2	3

* When estimating it was assumed that the sorbent in packed columns contains 15% squalane on Chesasorb with a grain size of 100–160 μm.

CPCs is two orders of magnitude greater than in the classical capillary columns, and hence the value of β is much lower.

The presence of a sorbent in CPCs also results in a different mechanism of broadening to that in the classical capillary columns. The main difference is the absence of eddy diffusion in the classical capillary columns and the fact that the coefficient of resistance to mass transfer in the gas phase of these columns is largely determined by dynamic diffusion. In the classical capillary columns, C_s is usually higher than that in CPCs, as the LSP film on a porous sorbent is usually thinner than that on the capillary walls. However, no investigation into the comparative characteristics of broadening in CPCs and classical capillary columns has been conducted.

3. EFFECTS OF THE MAIN EXPERIMENTAL PARAMETERS ON THE EFFICIENCY OF CAPILLARY PACKED COLUMNS

In order to use CPCs under optimal conditions, it is advisable to consider the effects of the main experimental parameters (pressure, particle size of the packing, carrier gas) on the efficiency of these columns.

A. Pressure

One means of increasing the efficiency of chromatographic columns is to increase their length and small CPCs are promising in this respect. However, an increase in length is associated with an increase in column resistance, which necessitates the use of increased inlet pressures, and it is therefore expedient to consider the question of the dependence of the efficiency of CPCs on pressure.

The dependence of the efficiency of a chromatographic column on the various process parameters can be described most comprehensively by the equation[29]

$$H_i = a_d \cdot \frac{D_{im}}{\bar{u}} + \frac{a_c' d_p}{1 + a_e''(D_{im}/\bar{u}\, d_p)^{1/2}} + a_f \left(\frac{\bar{u}}{D_{im}}\right)^{1/2} d_p^{3/2} \left(\frac{k_i}{k_i + 1}\right)^2 + \\ + a_b \cdot \frac{\bar{u}}{D_{ip}} \cdot d_p^2 \cdot \frac{k_i}{(k_i + 1)^2} \qquad (5)$$

where H_i is the HETP for component i, $\bar{u}$ is the linear flow-rate, D_{im} is the diffusion coefficient of component i in the mobile phase, d_p is the diameter of the column packing particles, k_i is the coefficient of extraction of component i, D_{ip} is the total diffusion coefficient of component i in a particle; a_d, a_c', a_e'', a_f and a_b are factors reflecting the effects of the column geometry on diffusion mixing, convective mixing, dispersion due to mass exchange in a moving particle of the mobile phase and dispersion due to the mass exchange in a particle, *i.e.*, both in the "stagnant" part of the mobile phase and in the stationary phase. The diffusion coefficient in the mobile phase depends on pressure (P) according to the relationship

$$D_{im}P = \text{constant} \qquad (6)$$

From eqns. 5 and 6, it follows that H decreases with increasing pressure at low linear velocities and increases at high linear velocities. In addition, with an increase

in pressure, the minimum value of H reduces and shifts towards lower values of the linear velocity. The experimental results (see Figs. 5 and 6 (ref. 27)) indicate that this law is also inherent in CPC for both GLC and GSC. Huber *et al.*[29] showed that at high velocities the increase in H with increasing pressure tends to a minimum with a decrease in d_c and k. They gave a detailed theoretical explanation of the results obtained.

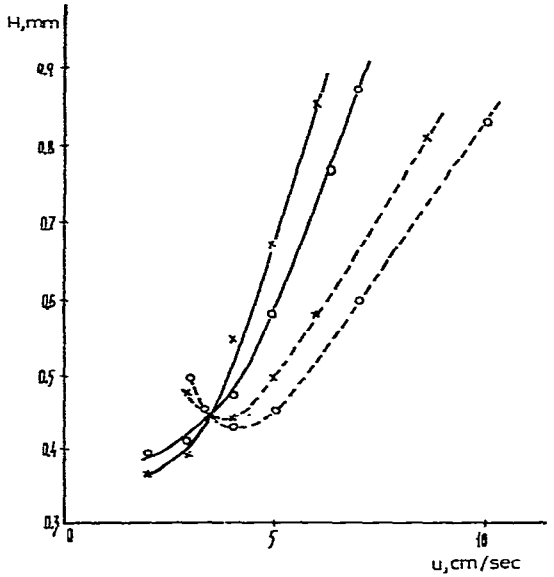


Fig. 5. Dependence of height equivalent to a theoretical plate (H) on average linear velocity of carrier gas (u) for short and long columns of I.D. 0.8 mm. Sorbent, 15% squalane on Chromosorb P (100–160 μm); temperature, 80°. ×, Hexane; ○, heptane. Column length: solid lines, 15 m; broken lines, 2 m.

In gas chromatography, the diffusion coefficients D_{im} and D_{ip} in eqn. 5 depend on pressure according to eqn. 6. With an increase in pressure, the first term in eqn. 5 decreases, the second term remains virtually unchanged in the usual range of flow-rates, while the third term increases. The effect of pressure on the first term in eqn. 5 depends on its influence on D_{ip}, which in turn depends on the filling of the particle pore space. In the simplest case, the particle pores are filled completely with a single phase; then D_{ip} is proportional to the coefficient of diffusion in this phase[42–45]. If the phase is liquid D_{ip} is independent of pressure, while if the phase is an ideal gas D_{ip} depends on pressure according to eqn. 6. In GLC, the particles are usually filled with a stationary liquid, as well as with a "stagnant" carrier gas. In this instance, the effect of pressure on D_{ip} is determined by the volume ratio of the stationary liquid and the stationary gas phase in the particle and by their mutual geometrical distributions. With an increase in pressure, D_{ip} will decrease, while the fourth term in eqn. 5 will increase, its value depending on the porosity of the particles whose accessible interior volume is filled with stationary carrier gas. According to Bruner *et al.*[46], in gas–liquid CPCs, $H_{min.}$ is independent of column length, and hence of pressure, at least up to 15 m. For gas–liquid–solid CPCs, these workers obtained, as in their first work[47], a

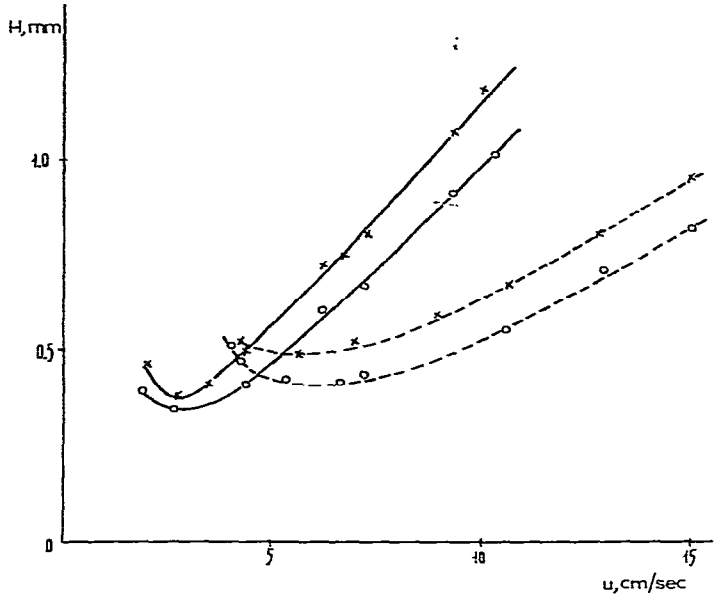


Fig. 6. Dependence of height equivalent to a theoretical plate (H) on average linear velocity of carrier gas (u) for short and long columns of I.D. 1.2 mm. Sorbent, Spherosil (100–200 μm); temperature, 62°. ○, Pentane; ×, hexane. Column length: solid lines, 8.5 m; broken lines, 1.1 m.

"deepened" minimum on the curve for the dependence of H on the linear velocity of the carrier gas for comparatively long columns, *i.e.*, at high linear velocities an increase in pressure in this type of column has virtually no effect on the efficiency. They did not give a detailed explanation of this effect, but they suggested that it might be due to the mechanism of operation of this type of column.

A chromatographic column has a pressure gradient, which causes a gradient of linear velocities of the gas phase and also of the diffusion coefficient in the mobile phase because of the high compressibility of the gas. The first three terms in eqn. 5 remain constant, as $D_{im}/\bar{u}$ remains unchanged. The effect of the pressure gradient on HETP is determined exclusively by the term representing mass exchange in the particle, *i.e.*, by the fourth term in eqn. 5. This term increases with the linear velocity, which increases along the column depending on the inlet-to-outlet pressure ratio[48]:

$$u_z = u_L\left\{\left(\frac{P_0}{P_L}\right)^2 - \left[\left(\frac{P_0}{P_L}\right)^2 - 1\right]\frac{z}{L}\right\}^{-1/2} \tag{7}$$

where L is the column length, u_L is the linear velocity at the end of the column, z is the coordinate along the length of the column, P_0 is the inlet pressure and P_L is the outlet pressure.

From eqns. 5 and 7, it follows that HETP increases from the beginning to end of the column, and this gradient can be described by an expression that is obtained by combining eqns. 5 and 7:

$$H_{iz} = \text{constant} + a_b \cdot \frac{u_L}{D_{ip}\left\{\left(\frac{P_0}{P_L}\right)^2 - \left[\left(\frac{P_0}{P_L}\right)^2 - 1\right]\frac{z}{L}\right\}^{1/2}} \cdot d_p^2 \cdot \frac{k_i}{(k_i+1)^2} \tag{8}$$

where H_{iz} is HETP in the z-position.

In GLC, eqn. 8 does not enable one to predict accurately the gradient H_i in the column, as D_{ip} is an unknown function of z.

The results of Shkolina[27] and Huber *et al.*[29] showed that the efficiency of CPCs changes only slightly, and the average pressure in the column affects the efficiency to a much greater extent.

B. Particle size of the packing

The particle size of the packing affects the permeability of the column and also (to a considerable extent) its efficiency. In an open capillary, the permeability depends theoretically only on its diameter. In practice, however, the capillary permeability is 10–30% below the theoretical value $r_0^2/8$ (ref. 49); this is evidently due to the roughness of the walls or to variations in the diameter of the tube. In packed columns, the permeability (K) depends on the particle size and on the packing density[50,51]:

$$K = \frac{\psi^2 d_p^2}{180} \cdot \frac{\varepsilon_0^3}{(1 - \varepsilon_0)^2} \tag{9}$$

where d_p is the average particle diameter, ψ is the particle non-uniformity factor and ε_0 is the column porosity, which does not include the interior volume of the particles.

The permeability of a packed column depends on the ratio of the particle and column diameters (d_p/d_c) and the roughness of the support. For conventional packed columns, where $d_p/d_c < 0.1$, the permeability is independent of the column diameter[52].

The column permeability can be determined experimentally from the slope of the straight line characterizing the dependence of the linear velocity of the carrier gas at the column outlet (u_L) on $(P^2-1)/L$, where $P = P_O/P_L$ and L is the column length, proceeding from the relationship

$$u_L = \frac{KP_L(P^2 - 1)}{2\eta L} \tag{10}$$

where η is the viscosity of the carrier gas, P_0 is the inlet pressure, P_L is the outlet pressure and K is the permeability. A graph of this dependence for different types of column is given in Fig. 7(ref.53). It can be seen that CPCs occupy an intermediate position between the classical capillary and conventional packed columns as far as permeability is concerned. A comparison of lines 2 and 4 and 3 and 5 shows that for a given particle size the permeability decreases with increasing column diameter. This relationship was confirmed by the results obtained by Cramers *et al.*[53], who showed that a decrease in column diameter, with identical grain size of the packing, necessitates the use of lower pressures at the column inlet (Fig. 8). Rijks *et al.*[54] recommend a ratio d_p/d_c of 0.2–0.25 to ensure the optimal permeability of CPCs.

The particle size of the packing also affects the efficiency of CPC. Investigations[29] indicated that a decrease in d_p results in the following changes in the efficiency of CPCs: (1) $\bar{H}_i$ decreases at low values of $\bar{u}$; (2) the limiting value of $\bar{H}_i$ attained at high values of $\bar{u}$ decreases for non-retained compounds; (3) the minimum value of $\bar{H}_i$ for retained compounds shifts towards lower values of $\bar{u}$ and diminishes

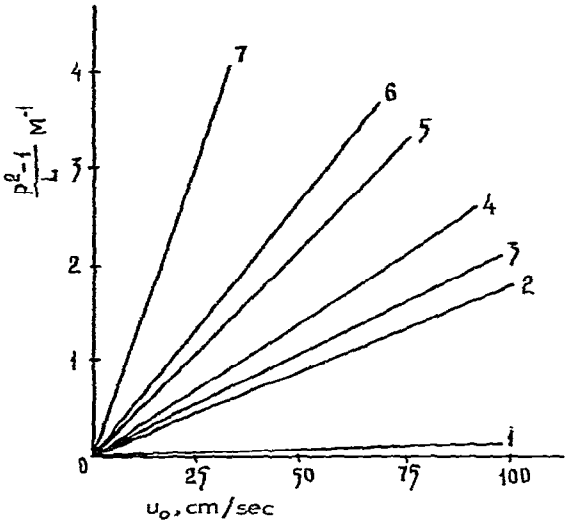


Fig. 7. Dependence of carrier gas outlet velocity, u_o, on value of $(P^2 - 1)/L \cdot M^{-1}$ for different types of column. 1, Classical capillary column (I.D. 0.25 mm); 2 and 4, packed capillary columns, d_p = 100–125 μm, d_c = 0.45 and 0.55 mm, respectively, and support, Chromosorb P; 3 and 5, filled capillary columns, d_p = 140–160 μm, d_c = 0.64 and 1.26 mm, respectively, and support, glass beads; 6 and 7, conventional packed columns, d_p = 200–250 μm, d_c = 4 mm and support, glass beads.

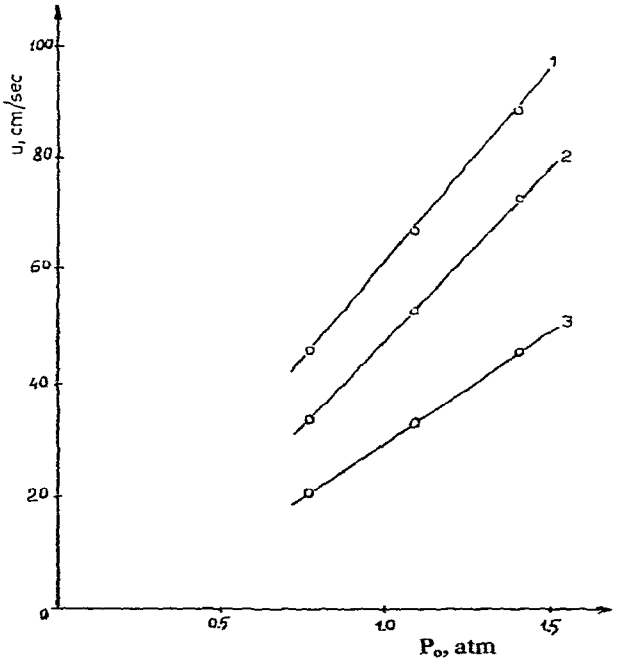


Fig. 8. Relationship between linear velocity of carrier gas (u) and inlet pressure (P_o) for columns of different inside diameter (length of each column, 1 m). Inside diameter: 1 = 1.26 mm; 2 = 0.92 mm; 3 = 0.64 mm.

considerably; and (4) the slope of the right-hand branch of the curve of the dependence of $\bar{H}$ on $\bar{u}$ for retained compounds decreases.

These results were explained[29] on the basis of eqn. 5. At atmospheric pressure at the inlet, the variations in $\bar{H}_i$ are due to the direct influence of the variations in d_p in eqn. 5, and also to the indirect effect of the dependence of the pressure drop on the particle size, according to which P increases with decreasing d_p for a given value of $\bar{u}$. With an increase in outlet pressure, P increases only slightly with a reduction in d_p for a given value of $\bar{u}$. In this instance the variations in $\bar{H}_i$ are caused mainly by the variation in d_p in eqn. 5. A decrease in the minimum value of $\bar{H}_i$ for retained compounds and the reduction in the limiting value of $\bar{H}_i$ at high $\bar{u}$ for non-retained compounds, as well as the decrease in the slope of the curves of the dependence of $\bar{H}$ on $\bar{u}$ for retained compounds at high values of $\bar{u}$, are due to the direct effect of the reduction of d_p in eqn. 5.

Thus, a reduction in the particle size of the packing improves the column efficiency.

Generalizing the results obtained so far, Huber *et al.*[29] concluded that CPCs filled with a packing of much smaller size than in conventional columns may prove to be very efficient. The columns which they prepared (I.D. 0.75–1.5 mm) with a fine-grain packing (30–35 μm) showed an efficiency of 10,000 theoretical plates per metre. In order to attain the optimal velocity (2.5 cm/sec) of the carrier gas in a column of length 1.5 m with such a sorbent, an inlet pressure of 25 bar was required. Huber *et al.*[29] inferred that it is realistic to use packed columns with an efficiency of 50,000 theoretical plates with a length of 6 m, a pressure of 50 bar and a volume output of 5 ml/min.

Hence, there are evidently two means of attaining a high efficiency of CPCs: by increasing the column length or by using a short column with a very fine-grained packing.

In our opinion, the former method is to be preferred, because the application of high-efficiency long CPCs involves the use of relatively low inlet pressures. Short columns with very fine-grained packings, with the same efficiency as the long CPCs, require an inlet pressure one order of magnitude higher, which entails problems with the equipment. In addition, the resistance of long CPCs can be reduced appreciably by using surface-layer sorbents with large-diameter particles, as the efficiency of columns packed with such a sorbent is independent of the particle size[55].

C. Carrier gas

According to the Darcy law, the pressure gradient is proportional to the viscosity of the flowing medium, and therefore the inlet pressure in CPCs can be reduced by using low-viscosity carrier gases. Berezkin and Shkolina[84] demonstrated the expediency of using ammonia as the carrier gas.

The viscosity of ammonia is 1.8 times lower than that of nitrogen and half that of helium, while its density is intermediate between those of nitrogen and helium. Hence, the diffusion coefficient of the components in ammonia must be higher than in nitrogen, which must result in a higher efficiency if the band broadening is determined by the mass transfer in the mobile phase. In order to confirm these assumptions, the dependence of the column efficiency on the carrier gas was investigated. Such studies were carried out by Berezkin and Shkolina[84] with the use of a glass spiral column

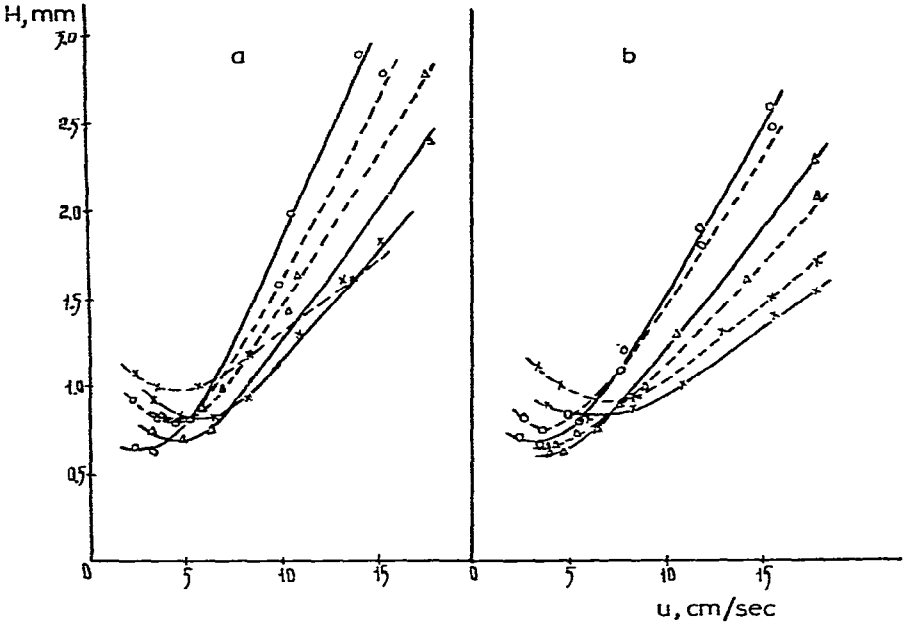


Fig. 9. Dependence of H on average linear velocity (u) of different carrier gases: ○, nitrogen; ×, helium; △, ammonia. (a) Solid lines, octane; broken lines, heptane. (b) Solid lines, *p*-xylene; broken lines, toluene.

of length 5.5 m and I.D. 0.8 mm filled with 160–200-μm Chromaton N treated with 3% potassium hydroxide and impregnated with 10% Apiezon L, using nitrogen, helium and ammonia as the carrier gases. The dependences of H on the average linear velocity for these carrier gases at 97° for aliphatic and aromatic hydrocarbons are shown in Fig. 9. It follows from Fig. 9 and Table 8 that $H_{min.}$ for aliphatic hydrocarbons when ammonia is used is slightly (1.05 times) higher than that when nitrogen is used and 1.2 times lower than that when helium is used as the carrier gas. For aromatic hydrocarbons, with the use of ammonia $H_{min.}$ is about 1.07 times lower than that obtained with nitrogen and 1.3 times lower than that with helium.

The value of C when ammonia is used as the carrier gas is intermediate between those obtained when nitrogen and helium were used for all substances chro-

TABLE 8

VALUES OF $H_{min.}$ AND C IN CAPILLARY PACKED COLUMNS FOR DIFFERENT CARRIER GASES

Component	$H_{min.}$ *(mm)*			$C \cdot 10^2$ *(sec)*		
	N_2	NH_3	*He*	N_2	NH_3	*He*
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

matographed; when hydrogen was replaced with ammonia, C decreased about 1.3-fold.

The results indicate that the use of ammonia reduces the coefficient of resistance to mass transfer compared with the use of nitrogen, without affecting the efficiency ($H_{min.}$). Compared with helium, ammonia considerably increases the efficiency in the region of $H_{min.}$. Hence, the use of ammonia as the carrier gas in capillary packed columns is justified because of the low pressure gradient which is its main advantage. Thus, for the column on which the above investigations were carried out, at an average linear velocity of 10 cm/sec the inlet pressure, when using ammonia (3.8 kgf/cm^2), is 1.5 times lower than that for nitrogen (5.9 kgf/cm^2) and 1.6 times lower than that for helium (6.2 kgf/cm^2).

The advantage of using ammonia as the carrier gas for speeding up prolonged analyses can be demonstrated with the separation of alkylcyclohexanols as an example. The analysis was conducted on a column of length 14.8 m and I.D. 0.8 mm filled with Chromosorb W + 5% Carbowax 20M at 160°. Peaks of 32 compounds were recorded on the chromatogram. The results in Table 9 show that the use of ammonia in place of nitrogen reduced the analysis time by a factor of 1.6 without impairing the separation. For equal analysis times, a better separation is achieved, and the column inlet pressure is 1.7 times lower.

TABLE 9

RESULTS FOR THE SEPARATION OF ALKYLCYCLOHEXANOLS WITH THE USE OF DIFFERENT CARRIER GASES

Carrier gas	*Pressure at column inlet (kgf/cm^2)*	*Carrier gas velocity (cm/sec)*	*Analysis time (min)*
Nitrogen	8.5	4.0	130
Ammonia	5.0	4.0	125
Ammonia	7.5	0.2	82

Consequently, the use of ammonia as the carrier gas has the following advantages over the more widely used carrier gases nitrogen and helium: (1) the pressure drop decreases because of the lower viscosity, which is important in long CPCs; (2) the value of $H_{min.}$ with the use of ammonia is about the same as that with nitrogen and is considerably lower than that with helium; (3) the capacity of ammonia cylinders is higher than that of constant gases, which increases the life of the cylinders and makes it possible to use small cylinders for portable chromatographs; and (4) the symmetry of the chromatographic zones is improved in some instances owing to the adsorption of ammonia on the active centres of the solid support.

4. METHODS FOR THE PREPARATION OF CAPILLARY PACKED COLUMNS

A. Methods of preparation

Short capillary columns (less than 5 m) can be filled with a previously prepared sorbent manually, either by tapping the column in the usual way or by moving a mechanical vibrator along the column. Sayegh and Vestergaard[56] described the

following method for filling PTFE columns. The column is plugged at the bottom end with cotton-wool and fixed rigidly; and the upper part is connected to a funnel clamped in the vibrator stage at a height equal to the column length (up to 2 m). The necessary amount of sorbent is placed in the funnel and the vibrator is switched on. After 5–20 min the column is filled with the sorbent.

These methods permit columns to be obtained that are reproducible both as regards the filling density and the retention characteristics. A disadvantage is that only short columns can be filled with the sorbent and only in a stretched form. Although short columns have a high specific efficiency, their total efficiency is low. It is advisable to increase the column length to 10 m and above, retaining the high specific efficiency. A second disadvantage of the methods is the limitation imposed on the column material; for instance, glass capillaries cannot be used.

Glass columns have a number of substantial advantages over metal columns. Thus, some substances, when coming in contact with a metal surface, are irreversibly sorbed or disintegrate[57–61]. The glass surface has a slow chemical response (glass is more chemically inert than diatomite brick). The possibility of direct observation of the filling of glass columns and the visible changes that occur in them greatly facilitates work with capillary columns. Another important advantage of glass capillary columns is the availability of equipment[3] for the preparation of capillaries of the required length and diameter. The brittleness of glass columns should not be regarded as a serious hindrance to their application.

Methods for preparation of capillary packed columns developed recently extend the possibilities for the application of long columns, including glass columns, in gas chromatography. The method proposed by Cramers *et al.*[53] consists in the following. A spiral tube (made of glass or metal) placed horizontally is joined to a cylindrical container. The packing is charged into the container, which is then joined to a pressure supply line. The lower part of the container and almost the entire spiral is placed in an ultrasonic bath, the other end of the column being located above the level of the bath. Vibration and pressure promote continuous feeding of the packing into the column. Special care is taken to maintain the pressure drop across the filled part of the column approximately constant, which ensures a uniform density of the packing throughout the column. The final pressure depends on the packing material used, but it must be of the order of 0.4–2.0 kgf/cm^2 per meter (the first figure refers to Chromosorb and the second to glass beads). The filling time is 1–2 min per meter of the column. Cramers *et al.*[53] emphasized the importance of uniformity of the packing; the range of particle diameters must not exceed 20 μm. Dust particles were removed by sifting under a vacuum, and flotation or sedimentation can also be used, depending on the density of the support. The method described was used for the preparation of columns up to 15 m long and I.D. 1.0–0.6 mm, whose efficiency was 3500 theoretical plates per meter for glass beads and 3000 theoretical plates per meter for Chromosorb, with good reproducibility.

A simpler device, which does not require the use of an ultrasonic bath, was developed in the Chromatography Laboratory at the Institute of Petrochemical Synthesis of the U.S.S.R. Academy of Sciences, jointly with the Design Office of the same Institute[62]. This device is also based on the operation of two parameters: vibration of the column and the flow of an inert gas. However, the vibration is produced by low-frequency (50–100 Hz) electromechanical vibrators, which are located

at several points along the length of the column. To improve the efficiency of the flow, the pressure at the column outlet is fed in pulses in accordance with a definite law*. The device (Fig. 10) consists of a cylinder (1) of compressed gas to which, through a reducer (2), is joined a valve (3) with an electromechanical drive for a periodic pressure supply and an upright holding several vibrators (PE-20 electromagnetic relays) (4) with an oscillation frequency of 100 Hz. A separate vibrator carriers a reservoir (5) for the sorbent, while the others are clamped to the column (6). The relays are set up along a circle on a common base in such a way that the column being filled is fastened with clamps after each 5–10 turns (depending on the column length).

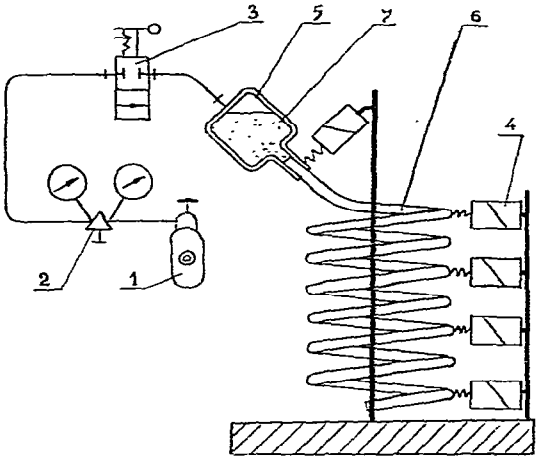


Fig. 10. Device for filling glass capillary columns with sorbent. 1 = Compressed gas cylinder; 2 = reducer; 3 = valve with mechanical drive; 4 = upright with vibrators; 5 = sorbent reservoir; 6 = column; 7 = sorbent.

The columns are filled as follows. A batch of sorbent (1–2 ml) is charged into the reservoir (5), then the gas flow and the automatic pressure programmer (3) are switched on and the vibrators (4) are started. Under the effect of the gas flow and vibration, the sorbent is fed continuously to the column. In order to ensure rapid and efficient filling of the columns, the sorbent must previously be sieved out, the fractions of the sorbent used being 100–160 and 160–200 μm.

This device can be used for filling spiral glass columns with different sorbents, including readily ionizable ones. Rapid filling with ionizable sorbents is achieved by saturating the inert gas with the vapour of a polar liquid (*e.g.*, ethanol); for this purpose, a porous material soaked in the liquid and having no contact with the sorbent is placed in the reservoir with the sorbent.

The device enables one to charge sorbents into glass columns of length up to 20 m and more and I.D. 0.6–1.2 mm with good reproducibility as regards both the packing density and the efficiency. The column efficiency was 3000 (sometimes up

* High-quality and comparatively rapid filling can also be accomplished with continuous pressure feeding.

to 4000) theoretical plates per metre[63]. Thus, the method permits columns to be obtained with efficiencies at least as good as those of columns obtained with the aid of ultrasonic treatment.

Bruner and co-workers[46,47] filled metal columns of length up to 15 m and I.D. 0.7–0.8 mm with a sorbent without the use of a vibrator. The tube was stretched in the vertical position, its lower end being fixed so that the tube was subjected to some extension and the upper end being connected to a small reservoir containing the packing. The packing was compacted by tapping with a rubber stick. The efficiency of the columns obtained was 2000–2500 theoretical plates per metre.

Less efficient columns (1250 theoretical plates per metre) were obtained[64] by joining separate filled sections of length 3 m with the aid of special fittings. Columns of length up to 12 m and I.D. 1 mm were obtained.

B. Chromatographic equipment for capillary packed columns

The use of CPCs imposes a number of requirements on the equipment because of the low carrier gas flow-rates, the high efficiency and the rapid action. To reduce the extra-column broadening, the volumes of the sampler, the connecting lines and the detector must be minimized. Fig. 11 shows the connection of a capillary packed column to a sampler and a detector, which permits the introduction of the sample without the use of a stream splitter[53]. The sample was introduced into the column through a glass tube insert of length 11 cm and I.D. 0.8 mm. One end of the insert, which was used for connection with the column, was wider and had a conical shape. The column was moved into the cone for a distance of 2 mm, and a silicone rubber seal was used. The column outlet was placed in the hydrogen and nitrogen flow in a flame-ionization detector (FID). To reduce the volume of the sampler, one can use a metal insert of I.D. 0.8–1.0 mm. Another means of reducing the broadening in the sampler is to use a stream splitter, in which case the splitting ratio may be small

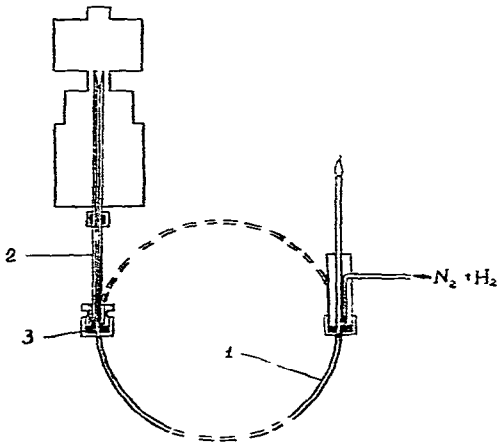


Fig. 11. Connection of capillary packed columns to gas chromatographic system. 1 = Capillary column; 2 = glass tube of I.D. 0.8 mm; 3 = silicone rubber.

(1:2–1:5), just enough to increase the velocity of the sample when passing through the sampler.

When using capillary packed columns in industrial chromatographs, where samples are fed automatically, one must pay special attention to the sampling system. Specially conducted investigations[28] on gas samplers of the membrane and plunger types in series chromatographs showed that during the transportation from the sampler to the column the sample volume increases considerably, and the smaller the sample volume the greater is the increase in volume. Thus, for a dose of 0.15 ml at a flow-rate of 5 ml/min, the sample volume increases 8.7-fold. To reduce the broadening in the sampler, a membrane sampler has been built and tested[28]; contrary to the existing sampler, the dead volumes in the switching valves were eliminated. During the test, the column was replaced with a detection system, which recorded the sample profile at the column inlet. The test results showed that with a sample volume of 0.15 ml and a carrier gas flow-rate of 5 ml/min the sample volume increased 5.3-fold, *i.e.*, 1.5 times less than in the series sampler. A sampler of this design can be recommended for work with CPCs in industrial chromatographs.

Table 10 (ref. 65) lists the conditions used for the sampling system with switching valves. Using the expression of Klinkenberg[66]:

$$V_n \leqslant \frac{0.5}{\sqrt{N}} \cdot V_R \tag{11}$$

where V_n is the sample volume at the column inlet, V_R is the retention volume of the component and N is the number of theoretical plates, and the data in Table 10, one

TABLE 10

CONDITIONS USED FOR SAMPLING SYSTEMS WITH SWITCHING VALVES WITHOUT DEAD VOLUMES

Parameter	*Carrier gas flow-rate (l/h)*	*Volume of initial sample, V_g (ml)*			
		0.1	*0.15*	*0.5*	*1.0*
Sample volume at column inlet (ml)	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 sample volume to volume of initial sample	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 concentrations at sample maximum and in 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

can calculate the maximal volume of the initial sample. For instance, if according to eqn. 11 the maximal sample volume under given conditions is 0.8 ml and the carrier gas flow-rate must be equal to 0.5 l/h in accordance with the established procedure, the volume of the initial sample, as listed in Table 10, must not be more than 0.1 ml.

The columns can be connected to the sampler and detector directly or via a metal capillary. The direct connection of columns is shown in Fig. 11. It should be noted that the arrangement depicted was used in a chromatograph of our own design. In commercial chromatographs, however, this arrangement of the column is impossible, and the ends of the column have to be unbent before it is filled. This method of fastening is the most efficient from the point of view of reducing extra-column broadening and the possibility of using columns at high temperatures (up to 260°), but it is laborious. A simpler method consists in making the connection via a metal capillary. In this instance, small lengths of a metal capillary with an outside diameter less than inside diameter of the column are joined to the detector and the sampler, through a silicone rubber seal. The ends of the capillary are inserted in the column inlet and outlet and glued with epoxy resin. With this method of connection the column ends do not have to be unbent and the metal capillary, not the column itself, is tightened with a nut, which is a much more reliable technique. A drawback of this method is that high-temperature analysis is not possible. To make it possible, one has to use either a temperature-resistant adhesive or transition capillaries made of alloys (for instance, Kovar) which provide a glass–metal seal. It should be noted that other versions of including the columm in the chromatographic system are possible and expedient.

When working with capillary packed columns, FIDs are usually used. Owing to their slow response, katharometers reduce the quality of separation and column efficiency. The results of analyses of heptane hydrocracking products carried out by Anisimov *et al.*[28] on a capillary packed column with a series katharometer of the semi-diffusion type and with an FID showed that with the use of an FID the specific efficiency of the column was 1200 theoretical plates, while with a heat conductivity detector the efficiency was only 400 theoretical plates. However, the katharometer has considerable advantages such as universality, simplicity of design, ease of operation and reliability.

Workers at the Design Bureau of Automatisation of Petrochemical and Refiner Processes (ANN) investigated the possibility of using a katharometer with CPCs. The response of the heat conductivity detector depends on the volume of the detector chamber and on the response of the sensitive elements. It was established[28] that the main factor affecting the response of the katharometer is the volume of the detector chamber. Taking this into account, a microkatharometer was developed with a chamber volume of 40 μl, which can be used with CPCs. The katharometer has the same sensitive elements as the conventional device.

Certain requirements are also imposed on the system for recording the analytical results if short columns are used for rapid analysis. The limited speed of the recording device causes distortions in the shape and amplitude of the chromatographic peaks if their width is less than the minimum permissible for the instrument used.

If the speed of the recording instrument is T, the minimum width (σ_φ) of a chromatographic peak of height h_0 which is recorded without any shape distortion can be determined from the relationship

$$\sigma_\varphi \geqslant \frac{h_0}{z} \cdot \frac{T}{1.65} \qquad (12)$$

where z is the length of the scale and h_0 is the amplitude of the signal. For the peak amplitude we accordingly have[67]

$$T_a \leqslant 2.22 \cdot \frac{z}{h_0} \cdot \sigma \tag{13}$$

$$\sigma_a \geqslant \frac{h_0}{z} \cdot \frac{T}{2.22} \tag{14}$$

From eqns. 12 and 14 it is also possible to determine the minimum permissible peak width at any given height at which the peak, at a given recorder speed, is recorded without any distortion in shape or height. Proceeding from the minimum permissible peak width, because of the limited speed of the recorder one can determine the minimum possible analysis time when working with a column of given efficiency[28]. According to the equation for determining the column efficiency

$$t_R = \sqrt{\frac{N}{5.54}} \cdot \tau_{0.5} \tag{15}$$

where t_R is the time from the moment the sample is introduced into the column until the emergence of the peak maximum, N is the number of theoretical plates and $\tau_{0.5}$ is the peak width at half-height. Expressing the peak width in terms of the standard deviation (peak half-width at the height $h = h_{max.} e^{1/2}$), we obtain

$$t_R = \sqrt{\frac{N}{5.54}} \cdot \sigma \cdot 2\sqrt{2 \ln 2} \approx \sigma\sqrt{N} \tag{16}$$

Hence, the minimum permissible time of emergence of a component for there to be no distortion in the shape and amplitude of its peak will be determined by the expressions

$$t_{R_\varphi} = \frac{h_0}{z} \cdot \frac{T}{1.65} \sqrt{N} \tag{17}$$

and

$$t_{R_a} = \frac{h_0}{z} \cdot \frac{T}{2.2} \sqrt{N} \tag{18}$$

5. APPLICATION OF CAPILLARY PACKED COLUMNS

A. Partition of complex mixtures

The resolution of chromatographic columns can be improved by increasing either the sorbent selectivity or the efficiency of the columns. The first method, *i.e.*, the use of selective sorbents, is efficient only for separating pairs of substances with different properties; multi-component mixtures of narrow fractions containing substances that differ only slightly in the properties on which chromatographic separation is based require the use of highly efficient columns. At present, the only method for separating multi-component mixtures is classical capillary column chromatography, which is used mainly for separating non-polar compounds, because the preparation of high-efficiency capillary columns with a polar phase requires special and difficult treatment of the surface of the column wall. CPCs can be filled with any sorbent,

which increases the possibility of detailed investigations of multi-component mixtures of different composition. It is particularly advisable to use CPCs for separating substances with a low partition coefficient.

High-efficiency CPCs have been used successfully for determining the composition of a complex hydrocarbon mixture, *viz.*, a fraction of liquid products of high-temperature pyrolysis[68]. Shkolina *et al.*[68] investigated a pyrocondensate fraction boiling below 100° (comprising 42.4% of the whole pyrocondensate), which was obtained from the pyrolysis of benzene raffinate. The chromatogram of the fraction is shown in Fig. 12.

CPCs can be used for investigating the composition of petroleum fractions. Fig. 13 shows a chromatogram obtained in the separation of a petroleum fraction (150–180°) from the Surgut oil field (West Siberia)[27]. Bruner *et al.*[46] used CPCs in the gas–liquid–solid version for analyzing the C_4–C_{13} fraction obtained from petroleum cracking, and found that the number of peaks in this chromatogram is similar that obtained on a classical capillary column.

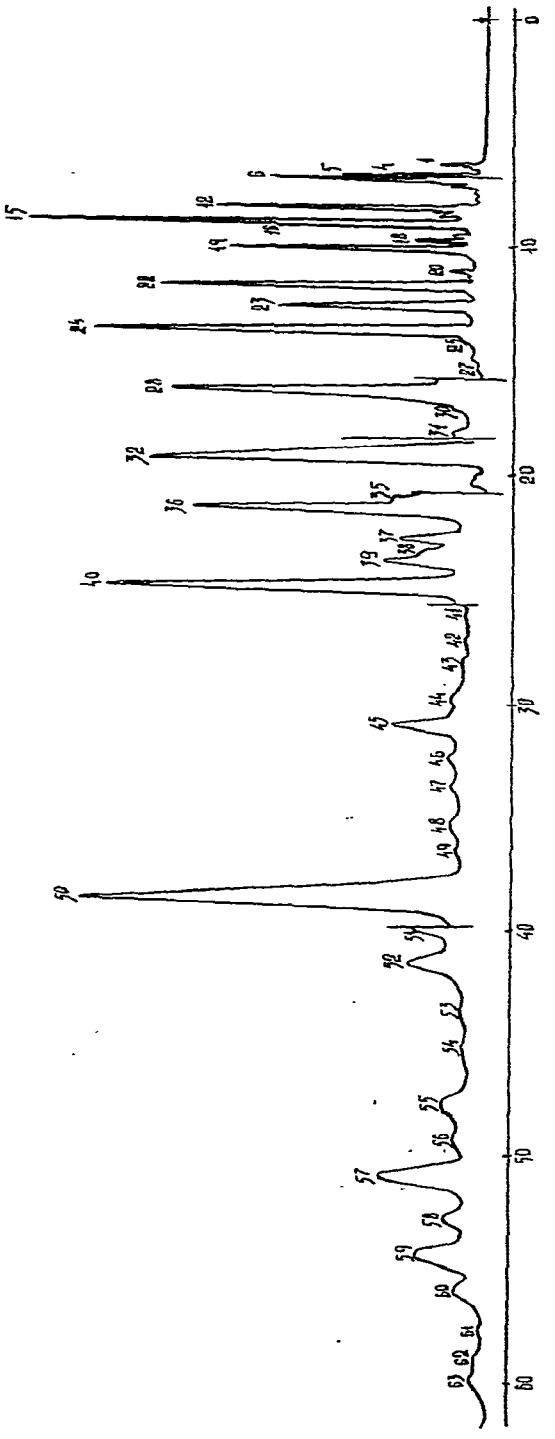
The separation of light hydrocarbons on a conventional packed column is difficult. Using the main advantages of CPCs, *i.e.*, the high efficiency and the possibility of filling them with any sorbent, one can achieve clear separations of light hydrocarbons. Examples of the separation of mixtures of low-boiling saturated and unsaturated hydrocarbons are illustrated in Figs. 14 and 15 (ref. 53).

Of particular interest is the separation on CPCs of multi-component mixtures that contain polar components. This type of column was used[27] for investigating specimens of industrial mixtures of oxygen-containing compounds obtained at different stages of oxo synthesis, and typical results are given in Table 11. For comparison, Table 11 also gives data on the separation of some samples on conventional packed columns. It can be seen that high-efficiency packed columns permit the detection of two to four times as many peaks on the chromatogram than with conventional packed columns. Fig. 16 shows one of the chromatograms of the separation of a mixture of oxygen-containing compounds (the ether overhead fraction, Table 11, No. 5).

A multi-component mixture of C_8–C_{12} hydrocarbons and alcohols, obtained by synthesis from carbon monoxide and hydrogen, has been partitioned on CPCs in the isothermal regime in combination with a linear programming regime[27]. The duration of the entire analysis was 210 min, including 30 min of separation at 120°, 30 min of linear programming at the rate of 2°/min up to 160°, and finally the isothermal regime. As can be seen from the chromatogram in Fig. 17, a sufficiently clear separation of 60 components is achieved under these conditions; in the linear programming range the zero line remains virtually unchanged.

The advantages of applying CPCs for separating polar compounds were also demonstrated by Bruner *et al.*[69] for the separation of C_1–C_6 alcohols, fatty acids and primary amines.

High-efficiency CPCs have also been used for analysing complex mixtures of steroids[53], barbiturates[54], organic mixtures in water[47] and impurities in air[46,47] and for separating stereoisomers of acyclic hydrocarbons[70] and structural isomers of aromatic hydrocarbons[71].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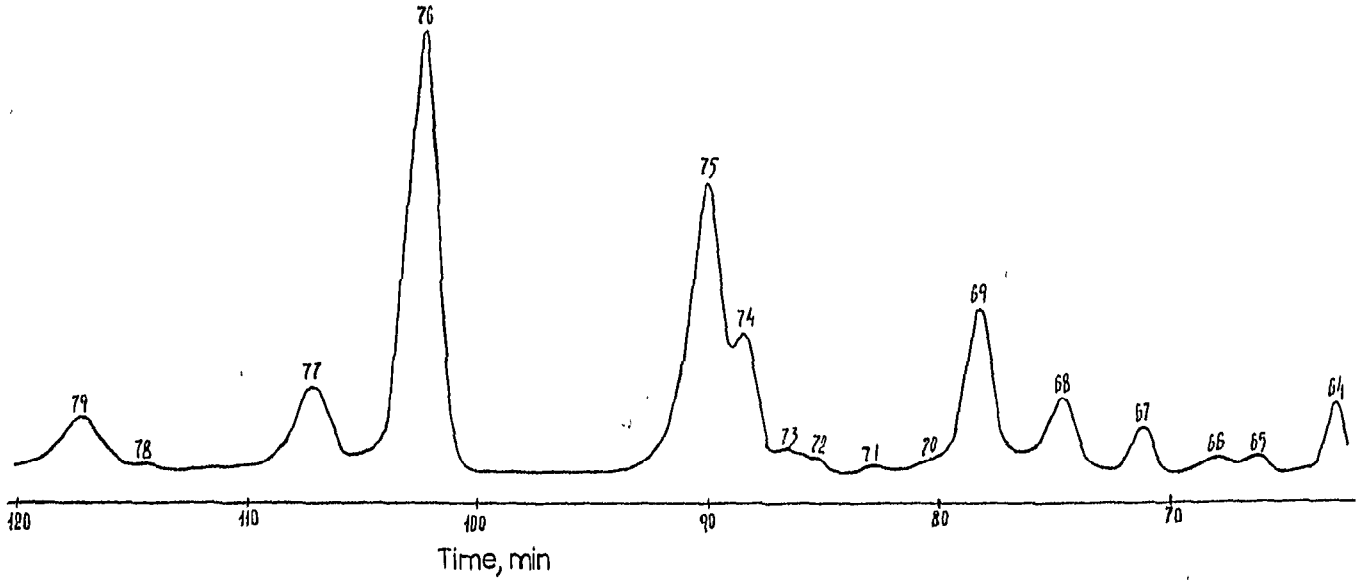

Fig. 12. Chromatogram of fraction boiling below 100° (product of high-temperature pyrolysis). Column length, 15 m; I.D., 0.8 mm; sorbent, 5% squalane on Chromosorb W; temperature, 67°. Peaks: 3 = propene; 5 = isobutane + isobutene; 6 = butadiene-1,3 + butene-1; 7 = *n*-butane; 8 = 2,2-dimethylpropane; 9 = butadiene-1,2; 10 = 3-methylbutene-1; 12 = 2-methylbutane; 13 = pentene-1; 14 = 2-methylbutene-1; 15 = *n*-pentane + isoprene; 16 = pentene-2 (*trans*); 17 = 2-methylbutene; 18 = cyclopentadiene-1,3; 19 = pentadiene-2,3 + 2,3-dimethylpentadiene-1,4; 20 = 3-methylpentene-1 + 4-methylpentene-1 + cyclopentene; 21 = 2,3-dimethylbutene-1 + 4-methylpentene-2 (*trans*); 22 = cyclopentane + 2,3-dimethylbutane + 2-methylpentane; 23 = hexene-1 + hexadiene-1,4 (*trans*); 24 = *n*-hexane + 2-ethylbutadiene-1,3 + 2-methylpentene-2; 26 = 4,4-dimethylpentene-2 (*trans*); 27 = ethylcyclobutane; 28 = 2,3,3-trimethylbutene-1; 29 = methylcyclopentane; 30 = 4,4-dimethylpentene-2 (*cis*); 31 = 1-methylcyclopentene + 3-ethylpentene-1; 32 = benzene; 34 = cyclohexane + 2-methylhexane; 35 = 2,3-dimethylpentane-3,4-dimethylpentene-2 (*cis*); 36 = 2-methylhexane + 3-methylhexane + cyclohexene; 37 = 1,3-dimethylcyclopentane (*cis*) + 3-methylhexene-3 (*trans*); 38 = 1,3-dimethylcyclopentane (*trans*); 39 = 1,2-dimethylcyclopentane (*trans*) + 2,2,4-trimethylpentane + heptene-3 (*cis*) + 2-methylhexene-2; 40 = *n*-heptane + 2-methylhexene-2 (*cis*); 42 = 3-ethylcyclopentane; 43 = 2,2-dimethylhexane; 44 = 1,2-dimethylcyclopentane (*cis*); 45 = methylcyclohexane; 46 = ethylcyclopentane + 1-ethylcyclopentene + 3-methylcyclohexene + 4-methylcyclohexene; 47 = 1-*trans*-2-*cis*-4-trimethylcyclopentane + 3,3-dimethylhexane; 48 = 1-*trans*-2-*cis*-3-trimethylcyclopentane; 50 = toluene; 52 = 3,4-dimethylhexane; 53 = 3-methyl-3-ethylpentane; 54 = 1-*cis*,*trans*-3-trimethylcyclopentane; 55 = 1-methylcyclohexadiene-1,4; 57 = octane; 64 = 4-methyl-2-propylpentene-1; 65 = 2,4-dimethylheptene-1; 67 = ethylcyclohexane; 69 = ethylbenzene; 75 = *p*-xylene; 76 = styrene; 77 = *o*-xylene; 79 = nonane; 1, 2, 4, 11, 25, 33, 41, 49, 51, 58–63, 66–68, 70–74, 78 = not identified.

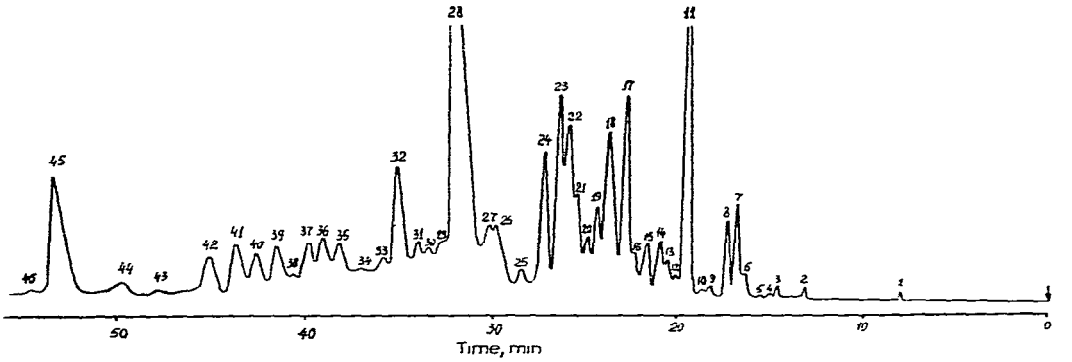

Fig. 13. Chromatogram of separation of saturated hydrocarbons of a fraction of petroleum (b.p. 150–180°) from the Surgut field (West Siberia). Column length, 15 m; I.D., 0.8 mm; sorbent, 5% squalane on Chromosorb W; temperature, 110°. Peaks: 1 = 2-methylhexane; 2 = 2,6-dimethylpentane; 3 = ethylcyclohexane; 4 = 1,1,3-trimethylcyclohexane + 1,4-dimethyl-2-ethylcyclopentane = *trans,trans* + 1,3-dimethyl-1-ethylcyclopentane; 5 = 2,3-dimethylheptane; 6 = 4-methyloctane; 7 = 2-methyloctane; 8 = 3-methyloctane; 9 = 1-methyl-2-propylcyclopentane = *trans* + 1,2,3-trimethylcyclohexane = *trans, trans* + 1-methyl-3-propylcyclopentane = *cis*; 10 = 1,2-diethylcyclopentane = *trans* + 1,1,3,5-tetramethylcyclohexane = *cis*; 11 = nonane + 1-methyl-4-ethylcyclohexane = *trans*; 12 = 1-methyl-2-ethylcyclohexane = *trans*; 13 = 2,4-dimethyloctane; 14 = 2,5-dimethyloctane + 1,1,3,4-tetramethylcyclohexane = *trans*; 15 = isopropylcyclohexane; 17 = 2,6-dimethyloctane; 18 = butylcyclopentane + propylcyclohexane; 19 = 2-methyl-3-ethylheptane; 20 = 1,1-dimethyl-3-ethylcyclohexane; 21 = 6-methylnonane; 22 = 4-methylnonane; 23 = 2-methylnonane; 24 = 3-methylnonane; 25 = 1,4-dimethyl-2-ethylcyclohexane = *trans,cis*; 26 = 1-methyl-2-butylcyclopentane = *trans*; 27 = 1-methyl-3-isopropylcyclohexane = *cis*; 28 = *n*-decane; 32 = 2,6-dimethylnonane; 35 = 3,7-dimethylnonane; 36 = amylcyclopentane; 37 = butylcyclohexane; 39 = 5-methyldecane; 40 = 4-methyldecane; 41 = 2-methyldecane; 42 = 3-methyldecane; 45 = *n*-undecane; 16, 29–31, 33, 34, 38, 43, 44, 46 = not identified.

B. Impurity analysis

When determining impurities, the efficiency becomes particularly important. In this instance the investigator faces two main problems: (1) separating the impurities from the main component and their partitioning; and (2) carrying out the determination under optimal sensitivity conditions, *i.e.*, under conditions of maximal concentration at the centre of the zone.

For separating the impurities from the main component, the efficiency of the column must be much higher than for the separation of zones of equal concentration. Thus, according to Zhukhovitsky and Turkeltaub[72], for separating substances with a concentration ratio of 1000 the column must have an efficiency 2.8 times higher than that for a similar separation of the same substances in equal concentrations.

In accordance with the theoretical plates theory[73,74], the maximal concentration in a zone increases with the efficiency (N) and the sample size (q):

$$C_{max.} = \frac{N^{1/2}}{V_R} \cdot \frac{q}{(2\pi)^{1/2}} \tag{19}$$

where V_R is the retention volume. Thus, with an increase in these parameters the sensitivity of the procedure for the determination of an impurity increases. Obviously a simpler method for improving the sensitivity is to increase the amount of sample

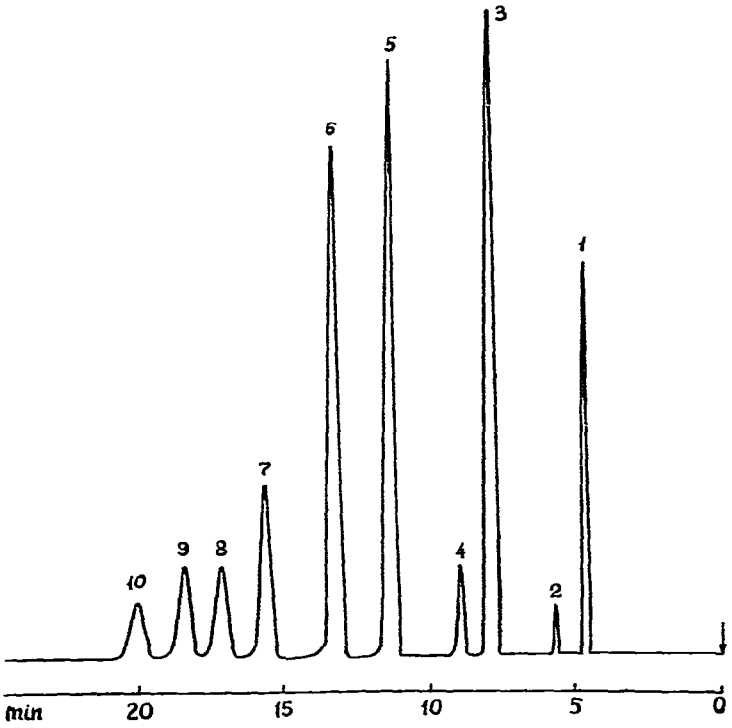

Fig. 14. Analysis of hydrocarbon mixture using a 5 m × 0.8 mm I.D. column packed with 10% squalane on Spherosil (66 m^2/g) (100–200 μm). Temperature, 70°; pressure, 3.2 kgf/cm^2; efficiency, 10,200 theoretical plates for *n*-butane. Peaks: 1 = methane; 2 = ethane; 3 = propane; 4 = propene; 5 = isobutane; 6 = *n*-butane; 7 = butene-1; 8 = *trans*-butene-2; 9 = isobutene; 10 = *cis*-butene-2.

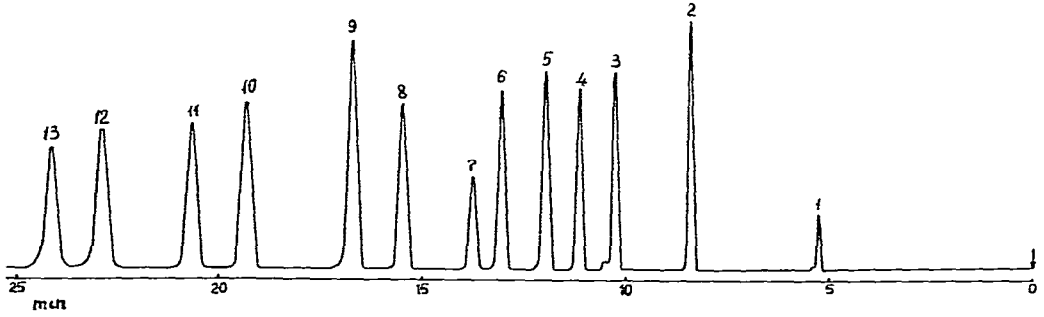

Fig. 15. Analysis of hydrocarbon mixture using a 15 m × 0.8 mm I.D. column packed with 5% squalane on Chromosorb W (180–200 μm). Temperature, 70°; pressure, 3.5 kgf/cm^2; efficiency, 33,500 theoretical plates for *n*-heptane. Peaks: 1 = methane; 2 = *n*-pentane; 3 = 4-methylpentene-1; 4 = 2,3-dimethylbutane; 5 = hexene-1; 6 = *n*-hexane; 7 = 4-methylcyclopentene-1; 8 = methylcyclopentane; 9 = benzene; 10 = cyclohexane; 11 = 3-methylhexane; 12 = 2,2,3-trimethylpentane; 13 = *n*-heptane.

TABLE 11

RESULTS FOR THE SEPARATION OF HYDROFORMYLATION PRODUCTS ON CAPILLARY AND CONVENTIONAL PACKED COLUMNS

No.	*Test mixture*	*Capillary packed columns*						*Conventional packed columns*					
		Separation conditions			*Efficiency (No. of theoretical plates)*		*Number of components separated*	*Separation conditions*			*Efficiency (No. of theoretical plates)*		*Number of components separated*
		Column	*Sorbent*	*T (°C)*	*Total*	*Specific (per metre)*		*Column*	*Sorbent*	*T (°C)*	*Total*	*Specific (per metre)*	
1	Hydroformylation product	13.8 m × 0.8 mm I.D.	15% PEG-4000 on Chromosorb P	140	42,000	3000	61	4 m × 3 mm I.D.	10% PEG-2000 on INZ-600	80	1773	440	14
2	As 1	17.6 m × 0.8 mm I.D.	22.2% DOP + 0.5% OP-10 on Celite-545	120	30,000	1700	38	4 m × 3 mm I.D.	22.2% DOP + 0.5% OP-10 on Celite-545	120	1800	450	19
3	Oxo synthesis product	13.8 m × 0.8 mm I.D.	15% PEG-400 on Chromosorb P	120	42,000	3000	40	–	–	–	–	–	–
4	Crude alcohol	13.8 m × 0.8 mm I.D.	15% PEG-400 on Chromosorb P	120	42,000	3000	46	–	–	–	–	–	–
5	Ether overhead fraction	13.8 m × 0.8 mm I.D.	15% PEG-400 on Chromosorb P	120	42,000	3000	50	–	–	–	–	–	–
6	As 5	13.8 m × 0.8 mm I.D.	15% PEG-400 on Chromosorb P	100	42,000	3000	55	–	–	–	–	–	–

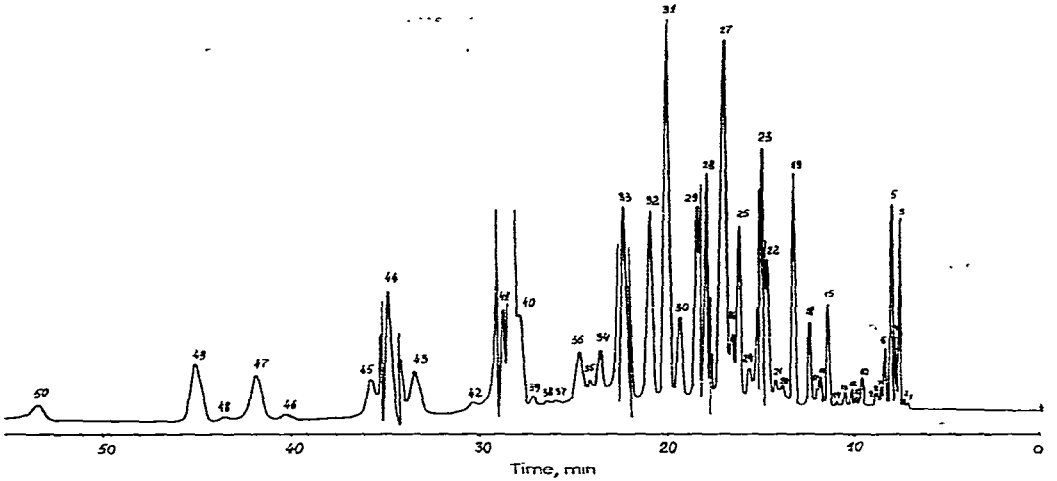

Fig. 16. Chromatogram of separation of ether overhead fraction from hydroformulation process. Column, 13.8 m × 0.8 mm I.D.; sorbent, 15% Carbowax 400 on Chromosorb P; temperature, 120°. Peaks: 9 = *n*-pentane; 12 = diethyl ether; 13 = *n*-propyl ether; 15 = diisopropyl ether; 16 = di-*tert*.-butyl ether; 17 = acetaldehyde; 18 = *tert*.-butyl isopropyl ether; 23 = di-*n*-propyl ether; 24 = diisobutyl ether; 25 = methyl ethyl acetal formaldehyde; 27 = isobutyraldehyde; 28 = methyl isopropyl acetal formaldehyde; 29 = isopropyl formate; 30 = diethyl acetal formaldehyde; 31 = *n*-butyraldehyde; 32 = ethyl acetate; 33 = methyl propionate; 34 = dimethyl isobutyrate; 35 = *n*-propyl formate; 36 = 2-methylbutyraldehyde; 37 = 3-methyl-2-butanone; 38 = ethyl *n*-propyl acetal formaldehyde; 39 = *sec*.-butyl formate; 41 = *sec*.-butanol; 43 = *n*-propanol; 44 = 2,3-butylene glycol acetal formaldehyde; 45 = *n*-butyl formate; 47 = isobutanol; 49 = *n*-butyl acetate; 50 = *n*-butanol; 1–8, 10, 11, 14, 19–22, 26, 40, 42, 46, 48 = not identified.

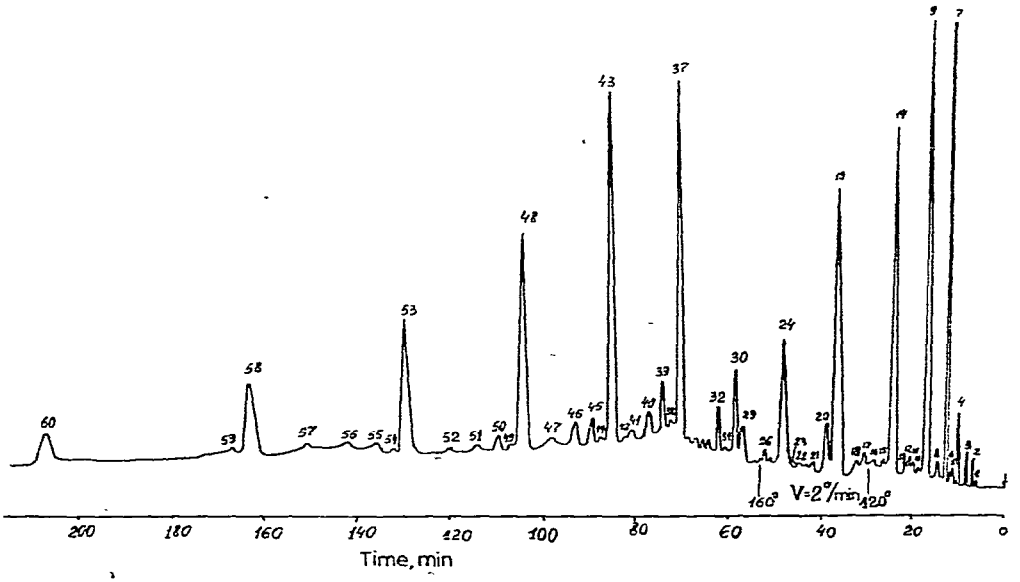

Fig. 17. Chromatogram of separation of oxo synthesis product. Column length, 15.5 m; I.D., 0.8 mm; sorbent, 15% 1,2,3-tris(2-cyanoethoxy)propane on Chromosorb P; temperature, first 30 min at 120° then linear programming up to 160° at the rate of 2°/min, and subsequently isothermal.

being analyzed. An increase in sample size, however, reduces the column efficiency and hence hinders the separation. Consequently, it is expedient to use high-efficiency columns in many instances.

The capillary columns proposed by Golay[1] still remain the most effective chromatographic columns. However, because of some disadvantages they have not found such wide use as packed columns. One of the shortcomings of the classical capillary column is that it is difficult, and often impossible, to analyse impurities, particularly at trace levels, because only small samples can be injected owing to the extremely low loading capacity of these columns, and therefore the determination of impurities requires extremely sensitive detection systems. In addition, the high phase ratio (β) adversely affects the separation, particularly when separating poorly sorbed compounds.

These drawbacks can be largely eliminated by using very long CPCs. The small diameter of these columns determines their high efficiency, and the presence of the sorbent results in a sufficiently high capacity. Long CPCs are more suitable than short CPCs for the analysis of impurities, as the latter have a lower efficiency and capacity.

If H increases by 10% compared with the limiting value of H_c for an infinitely small sample, then the limiting value of the sample, V_n, can be estimated by the equation[75]

$$V_n \approx 0.2 \cdot \frac{V_R}{\sqrt{N}} \tag{20}$$

or, assuming $V_R \approx KV_l$, where K is the gas–liquid distribution coefficient and V_l is the volume of LSP in the column,

$$V_n \approx 0.2 \cdot \frac{K \cdot V_l}{\sqrt{N}} \tag{21}$$

When comparing the limiting sample values for a capillary column (V_{nc}) and a CPC (V_{ncp}), it is advisable to use the relationship

$$\frac{V_{ncp}}{V_{nc}} = \frac{v_{lcp}}{v_{lc}} \tag{22}$$

where v_{lcp} and v_{lc} are the volumes of LSP in a CPC and a classical capillary column, respectively. Eqn. 22 was obtained under the assumption that the number of theoretical plates of the columns being compared and their distribution coefficients are similar. Considering that the volume of LSP in a CPC is about 100 times greater that that in a classical capillary column (see Table 7), we find that the sample size in a CPC is 100 times larger than that in a classical capillary column. Thus, when using a high-sensitivity detector of the same type, the minimal concentration of impurity with the use of a CPC is about 100 times greater than that for a classical capillary column.

An additional advantage of CPC over classical capillary columns is their wider field of application. Thus, in some instances it is impossible to separate the impurities from the main component on a single sorbent even when using high-efficiency columns,

but it can be achieved on a column with a binary sorbent. The possibility of using binary sorbents, as well as employing the GSC version in capillary columns, is another advantage of this type of column over the classical capillary column.

A comparison of the characteristics of the three types of column (classical capillary, capillary packed and conventional packed columns) which are necessary in determinations of impurities is given in Table 12, from which it follows that the use of CPCs is promising.

CPCs of great length have been used for impurity determination in 1,1,1-trifluoro-2-chloro-2-bromoethane (fluorothane)[76]. The most difficult part of this analysis is the separation of the impurity 1,1,2-trifluoro-2-chloro-1-bromoethane from the main substance. Figs. 18 and 19 show chromatograms of the separation of fluorothane

TABLE 12

CHARACTERISTICS OF THREE TYPES OF COLUMNS

Characteristic	*Classical capillary*	*Packed capillary*	*Conventional capillary*
Efficiency (separation of main substance from impurity depends on efficiency)	High	High	Insufficient
Sample volume	Insignificant	Sufficient	Large
Application in GSC	Limited	Extensive	Extensive
Apllication in GLC	Extensive	Extensive	Extensive
Preparation time	Medium	Medium	Short

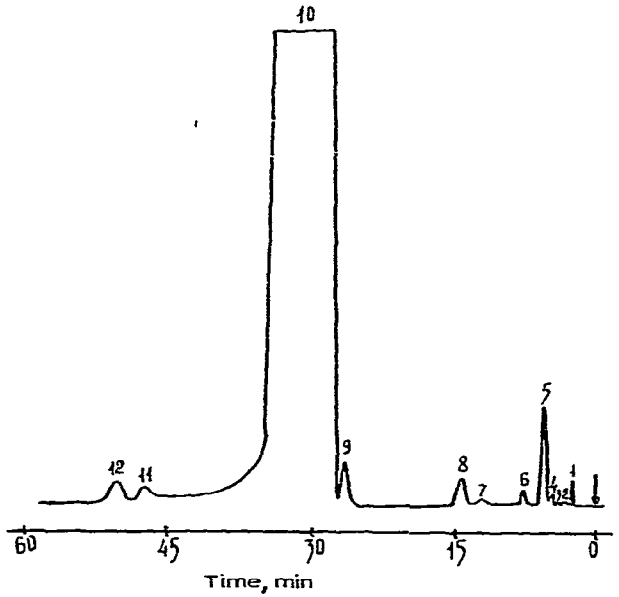

Fig. 18. Chromatogram of fluorothane on convention analytical column. Column length, 5 m; I.D., 3 mm; 2 m of column is filled with 10% dinonyl phthalate on Chromaton N and 3 m with 10% Chalcomide M18 on Chromaton N; temperature, 45°; sample size, 5 μl. Peaks: 5 = 1,2,2-trichloro-1,2,2-trifluoroethane; 9 = 1,1,2-trifluoro-2-chloro-1-bromoethane; 10 = fluoroethane; 1–4, 6–8, 11, 12 = unidentified impurities.

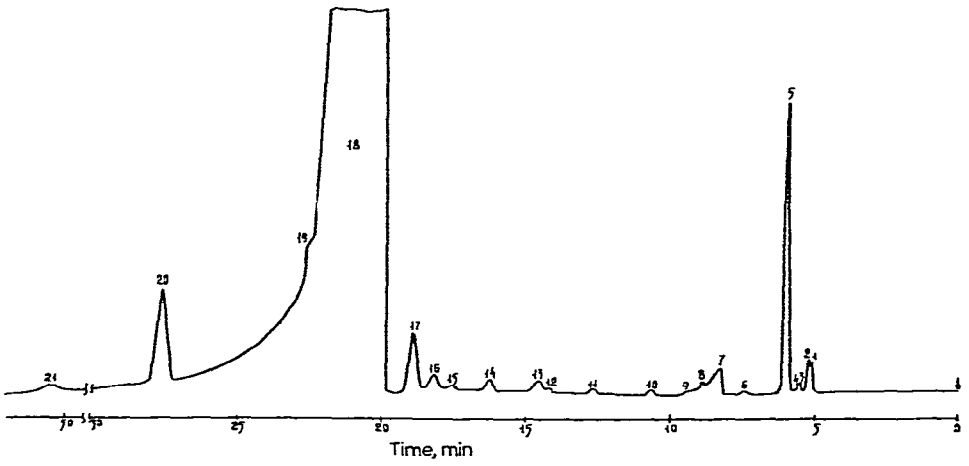

Fig. 19. Chromatogram of fluorothane on CPC. Column length, 15 m; I.D., 0.8 mm; 6 m filled with 5% DOP and 9 m with 5% Chalcomide on Chromosorb W; temperature, 63°; sample size, 1 μl.

on a conventional packed column[77] and on a CPC, respectively[76]. The use of CPCs in analyzing fluorothane opens up the possibility of determining a greater number of trace impurities (about twice as many) and, in addition, it ensures a higher separation criterion ($R \gg 1$) of the main component and the bromoisomer.

The use of short CPCs enabled Berezkin and co-workers to determine trace impurities by the micro-method[18] and the rapid method[19]. They determined trace impurities in isoprene on a 246 × 0.11 cm column filled with modified (2% squalane) aluminium oxide at 70° in 70 min; the HETP for 2-methylbutene-1 was 0.04 cm. A rapid analysis of the same isoprene sample was conducted on a 50 × 0.06 cm column with the same adsorbent at 30° in 7 min. In this instance the HETP for 2-methylbutene-1 was 0.06 cm. The chromatograms are shown in Fig. 20. It can be seen that the 10-fold reduction in analysis time is justified, despite the slight deterioration in efficiency. It should also be noted that a rapid analysis was carried out at a much lower temperature, which is important when working with readily polymerized substances. The content of the trace impurities to be determined was $2 \cdot 10^{-4}$ vol.-% in both instances.

CPCs have been used[31] for determining the impurities in a propane–propylene fraction used for the production of polypropylene. The determination of trace impurities by the rapid method was carried out in the GSC version on aluminium oxide modified with 3% squalane, using temperature programming up to 70°. The analysis time for an artificial mixture of the propane–propylene fraction, consisting of 13 components, was 8–10 min, compared with 40 min on a conventional column; the size of the sample introduced was 2 ml. The efficiency of the column (HETP) for butene-1 was 0.028 cm, *i.e.*, close to the HETP for classical capillary columns. The minimal impurity content in the sample was $8 \cdot 10^{-4}$%.

C. Rapid analysis

When using gas chromatography as a pulse transducer for regulating chemical processes, it is required to reduce the analysis cycle, *i.e.*, to carry out a rapid analysis.

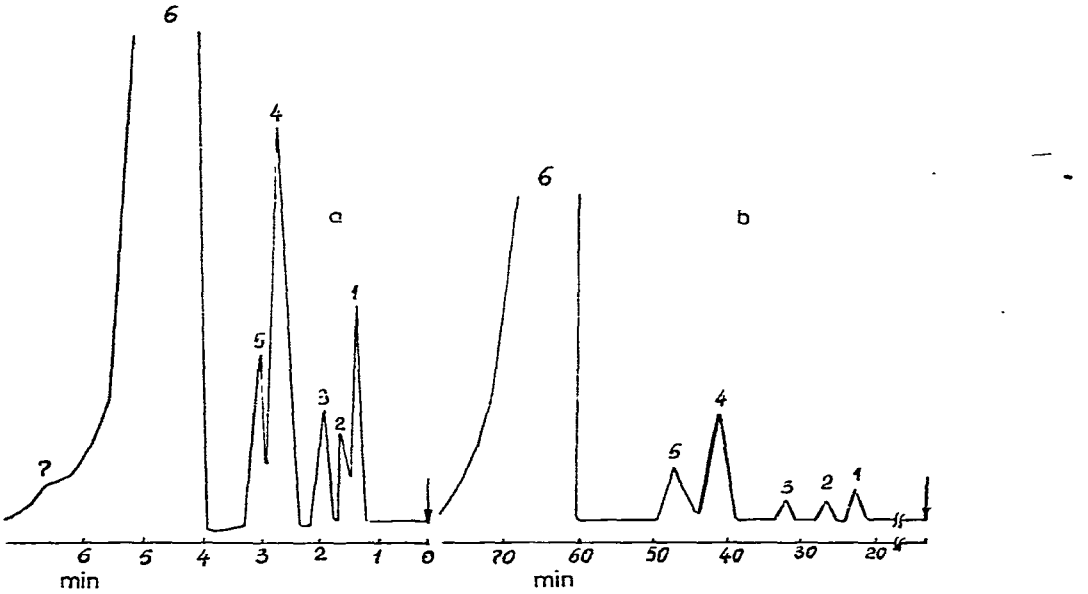

Fig. 20. Chromatograms of separation of impurities in isoprene. (a) Rapid method; carrier gas (hydrogen) flow-rate, 50 ml/sec; temperature, 30°. (b) Conventional analysis; carrier gas (nitrogen) flow-rate, 8.1 ml/sec; temperature, 70°. Peaks: 1 = 3-methylbutene-1; 2 = pentene-1; 3 = pentene-2; 4 = 2-methylbutene-1; 5 = 2-methylbutene-2; 6 = isoprene; 7 = divinyl.

The requirement of minimizing the analysis time is also imposed in series analyses when investigating complex multi-component systems, in kinetic measurements, etc. The analysis time can be reduced by improving the resolution of the column under optimal separation conditions, using a higher mobile phase velocity, and using shorter columns, faster amplifiers and computer integrators compared with the conventional ones.

CPCs are characterized by a high resolving power per unit length, which permits the utilization of short separating systems with no serious deterioration in resolving power. The high permeability of this type of column enables one to use high carrier gas velocities with flow-rates ensured by moderate pressures. A stable regime with temperature programming and a low mechanical mass makes it possible to accelerate the separation with the aid of temperature and pressure programming without any noticeable reduction in separating power.

To optimize rapid chromatographic separations, Kaiser[78] proposed the use, as the main criteria, of the carrier gas pressure and the separation number (Tz) per unit time, Tz/t.

The separation number, Tz, is determined by the relationship

$$Tz = \frac{t_2 - t_1}{b_{0.5(2)} - b_{0.5(1)}} - 1 \qquad (23)$$

where t_1 and t_2 are the uncorrected retention times of the first and second components and $b_{0.5(2)}$ and $b_{0.5(1)}$ are the peak widths at half-height. The separation number can

be measured in the course of temperature and pressure programming, and therefore it is preferred to base measurements on the HETP concept. Kaiser[78] evaluated short CPCs on the basis of the proposed criteria with reference to the use of columns for rapid analyses.

Capillary columns filled with a sorbent were used[31] for the rapid analysis of C_1–C_4 low-boiling hydrocarbons in the GSC version on modified aluminium oxide. The separation of a mixture of 11 components was achieved in 90 sec, *i.e.*, one peak per 8 sec. An example of a rapid analysis of a mixture of light hydrocarbons in 3.5 sec is shown in Fig. 21 (a column with alumina gel modified with 5% squalane). The methane emergence time was less than 2 sec, the efficiency of the column for *n*-butane being $H = 0.1$ cm. On a 43 × 0.058 cm column Svyatoshenko[31] separated a mixture of 8 components (the mixture may be further complicated), obtaining a higher

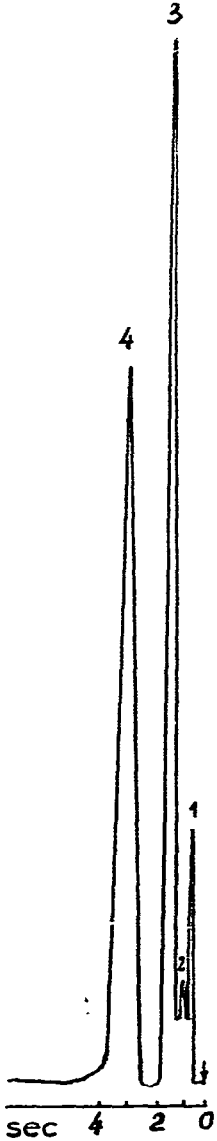

Fig. 21. Chromatogram of rapid separation of C_1–C_4 hydrocarbons. Column, 20 × 0.058 cm; carrier gas (hydrogen) flow-rate, 40 ml/sec; room temperature. Peaks: 1 = methane; 2 = ethylene; 3 = propane; 4 = *n*-butane.

efficiency ($H = 0.056$ cm), but the analysis time of 53 sec could not be reduced because of the high inlet pressure (5 kgf/cm^2).

A further reduction in analysis time involves equipment problems. Thus, for instance, the time required for the introduction of a sample is almost equal to the emergence time of the first component, which distorts the shape of the peak; it is impossible to measure accurately the emergence time of the components with a conventional stop-watch (the measurement error is 100% or more); the sharp increase in pressure due to the increased ratio of division of the flow into the column and to waste with the aim of reducing the sample size (at high velocities the amount of the substance fed to the detector per unit time increases) impedes sample injection with a syringe; and the excessive volume velocities in the flow-rate detector restrict stable combustion and adversely affect the accuracy of measurement. Thus, in order to carry out a rapid analysis (1 peak per second), it is necessary to have special automatic sampling, recording and integrating (computing) devices.

The possibility of reducing the analysis time by a factor of 2–5 was demonstrated by Cirendini *et al.*[79] on capillary columns filled with Spherosil in the gas–solid version and in the same version modified with LSP.

D. Industrial automatic chromatographs

Industrial automatic chromatographs are used as transducers of the composition in systems for the automatic control and regulation of chemical engineering processes. A specific feature of industrial chromatographs is that they are installed directly at sampling points on plant units and operate automatically. Therefore, these devices must be as compact as possible, consume moderate amounts of carrier gas and be reliable. The columns of such devices must meet the requirement of prolonged service without a change in separation characteristics. Therefore, the range of suitable sorbents and liquid phases for industrial chromatographs is much smaller than for laboratory devices. Together with such characteristics as sensitivity and error, an important feature for industrial chromatographs is the analysis time, which determines the possibility of obtaining information on the composition of a test mixture at a given time.

CPCs meet all of the above requirements to a much better extent than conventional packed columns. The high specific efficiency of CPCs and the possibility of carrying out analyses at a sufficiently high linear carrier gas velocity without impairing the efficiency of separation makes it possible to reduce the analysis time considerably. Limited consumption of carrier gas and sorbent enable one to use carrier gases and sorbents that may be expensive and/or available in limited amounts, and the small size of the columns permits the construction of a compact analyzer ensuring good thermostating and safety from explosion risks.

It should be remembered, however, that CPCs impose certain requirements on the equipment, especially on the automatic sampler and detector. Thus, if considerable sample broadening occurs in the sampling system, the column becomes overloaded and its efficiency is reduced[66]. The detector response must correspond to the peak parameters[80], otherwise the separation efficiency is reduced and a large error is introduced into the results.

The appropriate equipment, *viz.*, an automatic sampler and a fast-response heat conductivity detector, which are suitable for operation with CPCs, have been

developed at the Design Bureau of ANN and served as a basis for an industrial automatic explosion-proof chromatograph, the Microchrom. This device has been used successfully for determining the composition of a number of industrial mixtures directly on plant units. As an example, Fig. 22 shows the chromatogram from an analysis for trace impurities in the product from the rectification of ethylbenzene.

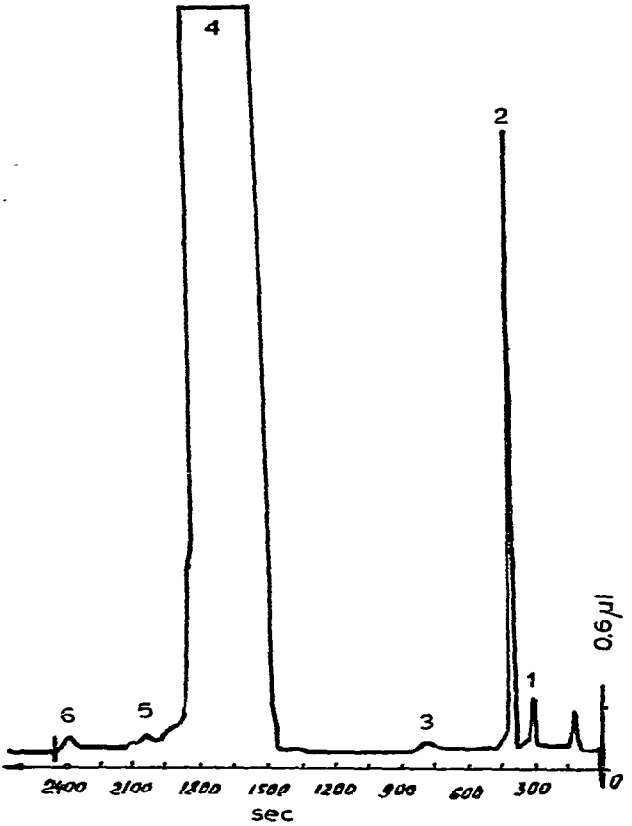

Fig. 22. Chromatogram from an analysis for trace impurities in the product from the rectification of ethylbenzene. Glass column, length, 10 m, I.D., 0.8 mm. Sorbent, Chromaton N (160–200 μm) impregnated with 5% squalane; temperature, 90°; carrier gas (helium) flow-rate, 4 ml/sec. Peaks: 1 = *n*-hexane; 2 = benzene; 3 = toluene; 4 = ethylbenzene; 5 = *o*-xylene; 6 = isopropylbenzene.

In recent years, when investigating individual stages of manufacturing processes under development, wide use has been made of automated miniaturized pilot-plant installations. One of the most important criteria in evaluating the results obtained from such installations is the composition of the products at the outlet of the micro-reactor, which are a multi-component mixture. The most suitable analyser is an automatic chromatograph; it must be compact and fast-acting, while the volume of the samples must be small. This will make it possible to analyse the products at the outlet of a series of reactors connected in parallel with the aid of a single device and to place the analyser in the immediate vicinity of the reactors. The small volume of the samples enables one to calculate the material balance without needing to take

into account the amount of the substance collected for analysis. The indicated requirements are best met by a chromatograph with CPC.

For work with a miniature pilot-plant installation in the U.S.S.R. Research Institute of the Petroleum Industry "Progress", use was made of a Microchrom non-explosion-proof chromatograph[81]. The chromatograph analysed the composition of the products in an investigation of the degree of deactivation of the catalysts used in hydrocatalytic cracking processes. The installation operated on model raw materials, *viz.*, *n*-heptane and toluene. The chromatogram of the product from the hydrocatalytic cracking of *n*-heptane is shown in Fig. 23.

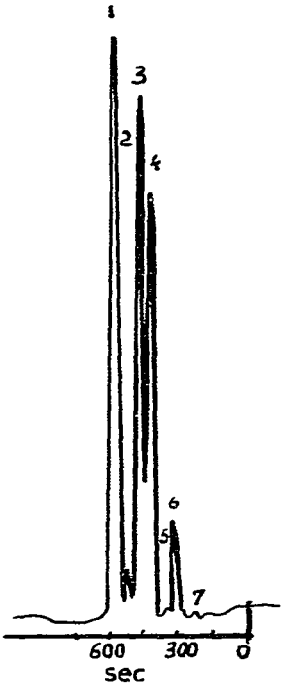

Fig. 23. Chromatogram of separation of products of hydrocatalytic cracking of *n*-heptane. Metal column, length, 1.2 m, I.D., 1.0 mm. Sorbent, Chromosorb P (120–150 μm) impregnated with 15% squalane; temperature, 60°; carrier gas (nitrogen) flow-rate, 2.4 ml/sec. Peaks: 1 = *n*-heptane; 2 = 3-ethylpentane; 3 = 3-methylhexane; 4 = 2-methylhexane; 5 = 2,4-dimethylpentane; 6 = methylcyclopentane; 7 = *n*-hexane.

E. Measurement of physico-chemical characteristics

An important application of CPCs is in the determination of the physico-chemical characteristics by the micro-method, *i.e.*, in the presence of small amounts of substances and sorbent (reagent), which was first proposed by Svyatoshenko *et al.*[24]. The method was used for determining the reaction rate constant and heats of adsorption.

The micro-method for determining the rate constants on CPCs was developed[24] for the reaction of isoprene with maleic anhydride in the liquid phase by the pulse chromatographic method. The conditions were as follows: stainless-steel columns

(50 × 0.098 and 200 × 0.098 cm); the amounts of charged sorbent were 0.25 and 1 g, respectively; the sorbent was prepared by depositing 45% liquid stationary phase (30% maleic anhydride and 15% tricresyl phosphate) on to a solid diatomite support (Spherochrom); the carrier gas was nitrogen; and the stream-splitting ratio was 1:25. The degree of conversion was determined from the changes in the areas of the chromatographic peaks of isoprene and non-reacting *n*-pentane (internal standard). The contact time of the reacting compounds was calculated from the retention time of the diene, account being taken of the dead-time of the chromatograph. The reaction rate constants were determined at 42, 48, 56 and 62°, and were in good agreement with the results obtained on a conventional column[82]. The calculated activation energy was 12.1 kcal/mole, which coincides with the literature value[82] (12.1 kcal/mole).

Hence CPCs can be used successfully for studying the kinetics of chemical transformations, thus making it possible, in principle, to reduce the amount of reagent and substance used. Another advantage of this type of column is the possibility of using it (owing to its high efficiency) for determining the rate constants of rapid reactions. Calculation showed that the kinetic coefficient of sorption and desorption (intra-diffusion mass exchange) at a maximal degree of conversion is 2000 times greater than the rate constant (for an analytical column it is one order of magnitude lower).

CPCs can also be used for determining heats of adsorption. The heats of adsorption of butene-1 on various specimens of aluminium oxide were determined[24] on a 50 × 0.058 cm capillary packed column in the temperature range −20° to +100° with a carrier gas velocity of 1.7 cm/sec and, for comparison, on a conventional column (100 × 0.4 cm) for one specimen of aluminium oxide.

The results obtained indicate that the heat of adsorption of butene-1 on a pure (initial) aluminium oxide has a maximum value and modified alumina gels have lower heats of adsorption. However, heats of adsorption on modified alumina gels are much higher than those on squalane, which indicates that adsorption on the squalane and aluminium oxide surfaces plays a considerable role.

According to the data in the literature[83], the heat of adsorption of *n*-butane is 8.2 kcal/mole, while the value obtained experimentally on CPCs was 8.1–8.5 kcal/mole. Hence, the above-described micro-method for determining heats of adsorption is reliable and accurate, which is particularly important when the amounts of sorbent and substance present are small.

In conclusion, it should be noted that CPCs extend the possibilities of gas chromatographic investigations both in analytical chemistry (especially when investigating complex multi-component mixtures that are difficult to partition) and in measuring physicochemical values, which is undoubtedly of great practical interest, and we believe that the use of this type of column in gas chromatography will continue to expand considerably.

6. SUMMARY

The preparation, properties and utilization of capillary packed columns are reviewed. The specific features of chromatographic separations on this type of column are discussed, principal methods for improving their efficiency are considered and the range of practical application is indicated.

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