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Control of the efficiency, selectivity, and capacity in single-column capillary gas chromatography

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ABSTRACT. The present review examines published data on a key problem related to the control over wide limits of the efficiency of separation of the components of complex mixtures in single-column capillary gas chromatography and the selectivity and capacity of the capillary columns. Methods of varying these important parameters of the gas-chromatographic experiment, based on the selection of capillary columns of different types and changes in the conditions of the experiment, have been examined in relation to one another and to their influence on the operational characteristics of the capillary columns and the analysis time. The advantages, disadvantages, and ranges of application of different methods for varying the parameters of efficiency, selectivity, and capacity have been noted, and methods for their further improvement in capillary gas chromatography have been indicated.

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I. Introduction

Capillary gas chromatography (CGC) has found extensive application primarily as a method for analysing multicomponent mixtures. In recent years this method has been used to study complex mixtures containing hundreds or thousands of components belonging to different classes of chemical compound, whose boiling points sometimes differ by hundreds of degrees.[1–21] The analysis of these mixtures is often complicated by the fact that the concentration of the components to be determined varies over extremely wide limits from micro-quantities to several tens percent.[1–6,9–13,16]

In relation to these characteristics of the specimens being analysed, it is possible to distinguish three main groups of problem encountered at the present stage of development of CGC.

The first group of problems is related to the resolving power of the columns, the reliability of the results of the analysis, and the sensitivity of the method, and solutions are sought by improving the efficiency, selectivity, and capacity, and also by using highly sensitive detectors and by improving the methods used to introduce the specimens into the chromatograph.[1–8,12,14,16,20–46] The problems of the second group are associated with the identification of a wide range of components, many of which are present in extremely low concentrations.[7,8,12,15,16,35,45,47–49] The solution of the problems of these two groups is inseparable from problems associated with the improvement and the development of new methods for the treatment of chromatographic information, making it possible to increase both the reliability of the identification of the components and their quantitative determination and also the amount of detail in the data on composition obtained.[17–19,50–54] The third group of problems is related to the development and application of multi-column gas-chromatographic systems which make it possible to decrease the total time taken for determinations without decreasing the reliability and amount of detail in the information obtained.[7–13,16,18,55–66] In a number of cases the use of these systems makes it possible to increase considerably the sensitivity of the determination of micro-quantities by using large specimen volumes.[11–13,62]

The present review examines the problems of increasing the efficiency of separation in single-column CGC and the selectivity and capacity of the capillary columns (CC). In fact, the problem reduces not to the optimisation of each of these characteristics but to the optimisation of the separation factor R_s. In many cases, the requirements relating to the individual parameters may contradict one another, that is the improvement of one characteristic may lead to a simultaneous deterioration in another. To simplify the systematisation, however, it is appropriate to examine the optimisation of each of these characteristics separately.

II. The efficiency of separation in single-column capillary gas chromatography and methods for increasing it

Capillary gas chromatography originated with Golay's discovery in 1956–1957 of open CC whose internal surface was covered with a layer of a stationary liquid phase (SLP).[1,3,6,35,67–69] This discovery marked a qualitatively new giant step towards a sharp increase in the efficiency of gas-chromatographic separations in general. The very first studies, carried out using mainly metal, plastic, and glass CC with an internal diameter d_c = 0.2–0.5 mm, demonstrated the extensive possibilities provided by CGC as a result of the high permeability of the CC and their high specific efficiency.[1,3,6,35,67–71] The use of even very long CC (100 m or more) removes the need to use extremely high inlet pressures, and in practice this makes it possible to achieve a very high efficiency of separation, reaching 1 million theoretical plates (t.p.) or more.[1,3,6,35,67–71] The unique possibilities provided by CGC as a powerful method for the fine separation of complex mixtures are demonstrated particularly clearly by the chromatogram obtained for petrol, with 378 separate peaks,

obtained on a CC (300 m × 0.5 mm) containing squalane.[14,15] Only 17 of these peaks belong to unidentified components. This chromatogram is the most complete chromatogram for petrol known at present.

1. Methods for increasing the efficiency of separation based on the use of capillary columns of different types

a. Treatment of the internal surface of glass CC

In the initial stages of the development of CGC, the specific efficiency of CC was 1000–2000 t.p. m^{-1}.[1,3,6,67–71] The development of various methods for the preliminary treatment of the internal surface of glass CC (deactivation, treatment with surface-active substances, chemical modification, the production of a rough surface, the creation of an intermediate layer of polymeric materials, carbon, salts, etc.)[1–3,6,21,35,68,72–89] made it possible to increase the specific efficiency of glass CC to 3000–4000 t.p. m^{-1}. This was related to the production, by both static and dynamic deposition, of a stable and uniform film of SLP and to the decrease in the adsorption and catalytic activity of the internal surface of the CC with respect to extremely polar compounds.[1,3,6,21,35,68,69,72–86,88,90] CGC on glass CC became an extremely effective method for separating the components of tobacco smoke,[1,3,91] mixtures of various aminoacids and their enantiomers,[1,4,75,92] aliphatic acids,[1,88,91] alcohols,[75,91] esters,[6,88] amines,[75] steroids,[1,3,4,77,88] the components responsible for the odour and taste of various food products and wines,[1,3,4,49,85,88,93] mixtures of pesticides,[1,3,35,85,88] various derivatives of saccharides,[1,88] and other complex mixtures.[1,3,4,6,35,49,68,69,74–80, 85,88,90–94] The increased possibilities provided by CGC are clearly confirmed by the chromatogram for a middle fraction of cigarette smoke, containing more than 3000 components of different chemical character (hydrocarbons, acids, bases, polyalcohols, ketones, etc.), recorded as 1000 peaks; this chromatogram was obtained on a glass CC (145 m × 0.32 mm) containing Emulphor ON 870 with linear temperature programming (1 °C min^{-1} in the range 25–190 °C).[91] The reliable identification of the components of such a complex mixture obviously requires a complex approach using several columns and detectors with different selectivities.[7,8,12,13,16,35,91]

The extensive application of glass CC was facilitated by such factors as the possibility of preparing glass capillaries with a clean internal surface under laboratory conditions and by the ease of visual control of the deposition of SLP films. Other important factors in the application of glass CC at high temperatures include the possibility of observing the stability of the SLP film and the ease of determining the section in which the macromolecular compounds present in the specimens being analysed are deposited irreversibly. Nevertheless, the range of application of glass CC is restricted, because of the residual adsorption activity of the surface with respect to a whole series of chemical compounds, determined to a large extent by the type of glass and the method of treatment; moreover, the mechanical strength of glass CC is too low.[1,3,6,74,75]

b. The use of quartz CC

A new and promising direction in the development of CGC is associated with the use of flexible CC of fused quartz, having d_c = 0.05–0.32 mm and a wall thickness of 40–70 μm.[20,27,28,34,35,39,40, 68,86,95–109] These CC have a high mechanical bending strength, which together with the low adsorption and catalytic activity of their internal surface has led in recent years to the extensive replacement of glass by quartz CC.[20,27,28,34,35,86,95–110] The specific efficiency of columns of this kind with an internal diameter d_c = 0.2 mm approaches 5500 t.p. m^{-1},[109,110] and they can be used to analyse mixtures containing strongly polar and readily adsorbed compounds: polyaromatic hydrocarbons (PAH),[4,100,107–110] alcohols,[27,28,103,109] phenols,[97,109] acids,[97,98,103,109] esters,[27,28,97,98,103,109] anilines, amines, and nitro-compounds,[97,109] pyridines and quinolines,[100,103] peptides and other substances present in biological specimens,[4,111] the components of medicinal products,[28,107] the components responsible for the taste and odour of foodstuffs† and cosmetic materials,[27,28] and many other compounds.[4,105,106,111] Because of their low catalytic activity, quartz CC are used successfully to separate various labile compounds.[97,105,111]

c. The efficiency of separation on CC with a small diameter

In CGC, increasing use is being made of CC with a small internal diameter (d_c = 0.035–0.1 mm).[6,96,104,112,113] It has been shown[104] that the height equivalent to a theoretical plate (HETP), measured for n-pentadecane on a 10-metre quartz CC (d_c = 0.1 mm) containing phenylmethylsiloxane at a medium linear carrier-gas velocity corresponding to the minimum of the Van Deemter curve, is 0.105 mm, which is only 1.08 times the height 0.097 mm calculated from the equation

$$H_{\min} = \frac{d_c}{2}\sqrt{\frac{1 + 6k' + 11\,(k')^2}{3\,(1 + k')^2}} \qquad (1)$$

for the theoretical minimum value of the HETP[32,114] [the capacity (extraction) coefficient k' for an SLP film thickness d_f = 0.17 μm and a CC temperature t_{CC} = 143 °C is 6.5]. For a 70-metre CC with d_c = 0.05 mm, the HETP was 0.066 mm.[96]

Short CC of small diameter with a high specific efficiency are characterised by a displacement of the minimum of the Van Deemter curve to high linear carrier-gas velocities (50–70 cm s^{-1}), which, together with the small quantity of SLP in these columns creates a realistic basis for increasing considerably the speed of analysis and the sensitivity of determinations.[6,96,104,112,115] For rapid separation it is appropriate to use hydrogen as the carrier gas.[116] In high-speed CGC using open tubular CC, the record time is 2 s, achieved in the separation of 15 components on a CC (1.2 m × 0.035 mm) with an efficiency of 7000 t.p.[115] It has been suggested that it should be possible to develop a high-speed analyser using a CC with a length of several centimetres and a diameter of 1 μm.[117] In addition to the high speed of analysis, specific efficiency, and sensitivity of the determinations, an undoubted advantage of CC with a small diameter is the low loss of SLP, ensuring stability of operation over a long time.[96,113] The low noise level makes it possible to use CC of small diameter for high-temperature analyses and the determination of traces of substances.[113] Nevertheless, the use of CC of small diameter involves difficulties associated with their low sorptive capacity, so that the size of the specimen calculated for one component is only 0.02–1 ng for a CC with d_c = 0.05 mm,[112] and ~8 ng for CC with d_c = 0.1 mm,[104] and also with the severe requirements to be satisfied by the inertia of the recording apparatus. The limitations associated with the need for a high inlet pressure can be overcome by creating a vacuum at the outlet from the CC, and this in turn favours the use of a mass spectrometer as detector.[104]

† T Aishima, Y Ozawa *Chromatographia*, 1989, **28** 405

The extensive application of CC of small diameter is also prevented at present by difficulties associated with the deposition of viscous high-temperature SLP. This also applies to some extent to CC with a diameter d_c = 0.1–0.25 mm. Static methods for preparing CC using traditional solvents with the boiling points of n-pentane (b.p. = 36.07 °C) and above do not always give CC with high specific efficiency and reproducible values of other gas-chromatographic parameters. This is largely due to the need to use relatively high pressures to fill the CC with the solution of the SLP in the appropriate solvent and special methods for subsequently making the ends of the CC air-tight, which do not always eliminate completely the formation of bubbles of gas and solvent vapour.[1,3,88] Of particular interest is a recently described‡ new method for the static deposition of non-polar and weakly polar SLP on the walls of CC whose internal diameter, according to the authors cited, may be smaller than 0.1 mm. Characteristic features of this method are the use of n-butane (b.p. = –0.5 °C) as solvent for the SLP, and the method used to make one of the ends of the CC air-tight by freezing the solution of the SLP in n-butane with liquid nitrogen in a closed vessel, into which gas nitrogen can be passed at a pressure of 2 atm. This method eliminates completely the formation of gas bubbles at the boundary between the liquid and solid solutions. The solvent (n-butane) is removed from the CC at room temperature and atmospheric pressure. The method developed makes it possible in practically 100% of cases to obtain CC with specified properties with a simultaneous decrease in the time taken for their preparation compared with traditional static methods. In particular, the time taken to prepare a quartz CC (25 m × 0.25 mm) at 30 °C is not more than 5 h, and this is reduced considerably (to tens of minutes) on going to CC with a smaller diameter. Other advantages of the new method for preparing CC can be seen from Table 1, which gives the gas-chromatographic parameters of quartz CC with different geometric characteristics (length L and internal diameter d_c) and different SLP. Table 1 shows, in particular, that the specific efficiency of quartz CC of small diameter (d_c = 0.10 mm), measured from the peak of n-tridecane, is close to 10000 t.p. m^{-1}. The new static method for preparing CC of any diameter should lead to their wider application in gas chromatography.

d. The influence of the SLP film thickness on the efficiency of separation

Decrease in the thickness d_f of the SLP film in CC makes it possible not only to decrease the analysis time and lower the analysis temperature but also to increase the efficiency of separation by decreasing the contribution of the intra-diffusion resistance and the resistance to mass exchange at the interphase boundaries. This follows directly from the Kahn equation for the HETP in open CC, which, unlike the familiar Golay equation, takes account of the resistance to mass transfer at the interphase boundaries:[3,6,118,119]

$$H = \frac{2D_g}{\bar{u}} + \frac{1 + 6k' + 11(k')^2}{24(1 + k')^2}\frac{\bar{u}d_c^2}{4D_g} + \frac{2k'}{3(1 + k')^2}\frac{d_f^2\bar{u}}{D_l} + \frac{2k'd_f}{(1 + k')^2 k_d} \quad (2)$$

Here, $\bar{u}$ is the average linear velocity of the carrier gas, D_g and D_l the coefficients of molecular diffusion of the sorbate molecules in the gas and liquid phases respectively; and k_d the rate constant of the desorption of the substance from the surface. The first term of this equation describes the contribution to the flattening of the chromatographic band made by the longitudinal diffusion of the sorbate molecules in the gas phase, the second term characterises the contribution of dynamic diffusion, and the third and fourth terms, which contain the quantity d_f, give respectively the resistance to mass transfer in the SLP film and the resistance to mass exchange at the interphase boundaries, which is equivalent to a slight deviation from the equilibrium state.

‡H F Yin, A J Huang, Y L Sun *Chromatographia*, 1989, **28**(5/6) 313

Table 1. Characteristics of various quartz capillary columns prepared by a new static method.

L, m	d_c, mm	SLP	t, °C	k' (measured from n-C_{13})	n, t.p. m^{-1} (measured from n-C_{13})	Efficiency of deposition, %
14	0.25	SE-54	130	14.4	3900	89
10	0.25	SE-54	130	11.1	3860	87
30	0 25	SE-54	120	9.0	4200	92
25	0.22	SE-30	120	11.5	4270	92
14	0.22	SE-30	120	9.6	4500	89
25	0.22	SE-30	120	3.9	4650	84
12	0.10	SE-54	140	5.2	9310	79
12	0.10	SE-54	120	5.8	8600	73
12	0.10	OV-1	120	5.3	9100	77

The existence of the third and fourth terms in Eqn. (2) indicates the strong dependence of the efficiency of separation on the thickness of the SLP film. The role of the film thickness increases for values of $\bar{u}$ greater than the optimum velocity u_{opt}, which corresponds to the minimum of the Van Deemter curve. Overall, however, the influence of d_f on the quality of separation of the components is much more complex, and depends on the capacity coefficient k'.[1,3,6,118,120] It should also be noted that a decrease in d_f carries the danger of overloading the CC.[104,112]

e. The efficiency of micropacked CC

Considerable advantages over open tubular CC in relation to the specific efficiency of separation, capacity, and speed of determination are shown by micropacked quartz capillary columns (MPQCC) having d_c = 0.15–0.5 mm and sorbent particle diameters of 5–100 μm.[121–127] The use of quartz CC with smooth walls simplifies considerably the filling of the column with the sorbent,[121–124,126] making it possible to achieve uniform packing of the latter. Together with the small particle size of the packing, the small internal diameter of the MPQCC, and the inertness of their internal surface, this feature ensures a high specific efficiency for the MPQCC, which for a sorbent particle diameter of 7.5 μm may reach 30000 t.p.[121–125] The high specific efficiency of MPQCC makes it possible to use short columns with typical lengths of tens of centimetres, and hence to reduce the expenditure on scarce and expensive sorbents. An important positive feature of MPQCC is the extremely weak dependence of the HETP on $\bar{u}$ at $\bar{u} > u_{opt}$,[121–123,125] particularly for a sorbent particle size less than 1 mm. This makes it possible to increase considerably the speed of the determination. The use of MPQCC, which makes it possible to miniaturise the equipment, retains all the advantages of open tubular

quartz CC, namely their flexibility, mechanical strength, and adsorption and chemical inertness.[121–126]

f. The influence of the length of the CC on the overall efficiency of separation

A radical method for increasing the overall efficiency of CC is by increasing their length. Short CC always have smaller HETP than long columns with identical properties.[116,128] This is related to the large change in the carrier-gas velocity along the length of the CC. Thus the increase in the number of theoretical plates is not directly proportional to the increase in the length of the CC. In practice, the CC used most frequently have lengths not exceeding 50 – 100 mm.[1,6,15,17–21,27–46,52–89,92–109,111–120,128,129] Further increase in the length of the CC is not appropriate, because of the increase in the total analysis time and the decrease in the sensitivity of the determinations as a result of the diffusion flattening of the chromatographic bands. Increase in the length of CC is particularly unjustified when carrying out analyses using CC with a small internal diameter (0.035 – 0.1 mm) or MPQCC, since it leads to a multiplication of the inlet pressure, makes more severe demands on the apparatus used, and also leads to a large pressure drop along the length of the CC, which in the final analysis lowers the overall specific efficiency of separation.[96,104,112,115,116,121–124,128] Moreover, the long analysis time on long CC and the need to increase the column temperature create difficulties in the study of mixtures of substances with a wide range of boiling points, non-volatile substances, and mixtures containing thermally labile and reactive compounds.[1,3,6,116,118]

g. The efficiency of CC with non-circular cross-section

In recent years there has been an increase in interest in open tubular CC with rectangular cross-section,[3,88,90,130–138] whose walls are covered with a thin film of SLP. Under certain conditions, the use of these columns leads to a marked increase in the efficiency of separation compared with CC having circular and elliptical cross-sections. This is related primarily to the significant decrease in the contribution to the HETP made by the dynamic dispersion due to the non-uniform distribution of the carrier-gas velocities over the cross-section of an open CC in a laminary stream. These theoretical postulates[132–138] were confirmed experimentally by comparing the efficiencies of CC having cross-sections with different shapes but identical areas.[133,135,137] In particular, it was shown[136,137] that the efficiency of CC having cross-sections with different shapes depends on the capacity coefficient k' and on the ratio of the sides a and b of the rectangular cross-section. Thus the efficiency of a rectangular CC increases rapidly with increase in a/b and becomes greater than the efficiency of a cylindrical CC at $a/b > 3.5$ (if $k' = 0$) and $a/b > 2$ (if $k' = 2$). The study of the influence on the efficiency of separation of a change in the cross-sectional area of a CC along its length is also of considerable and theoretical and practical interest.[132]

2. Methods for increasing the efficiency of separation based on a change in the parameters of the gas-chromatographic experiment

The main disadvantage of all the above methods for increasing the efficiency in single-column gas-chromatographic systems is the need to replace the CC, which is inconvenient.

a. The influence of the nature of the carrier gas, its average linear velocity, and the average pressure on the efficiency of separation

Among the methods for increasing the efficiency of separation without replacing the CC, mention must be made of readily accessible methods involving a change in the nature of carrier gas, its average linear velocity, and the average pressure.[1,3,6,115,118,119] The first two methods make it possible to change the efficiency of separation only over a narrow range, particularly at $\bar{u} > u_{opt}$.[118,119] An increase in the average pressure of the carrier gas from 1 atom to 10 atm, however, decreases H_{min} by 55% with a simultaneous displacement of the minimum of the Van Deemter curve to low linear velocities,[115] leading to an increase in the analysis time. The use of high pressure also creates experimental difficulties, and all these features make this method inefficient.

b. The use of gaseous mobile phases

An interesting method for increasing the efficiency of separation involves the use in the CC of gaseous mobile phases containing volatile polar substances.[3,6,16,122,139–144] A high efficiency of separation by this method was first achieved using water vapour.[3,140] Water vapour as a modifying additive was subsequently used successfully in a number of other studies.[141,144] Suppression of the adsorption activity of the walls of the CC, leading to the production of symmetrical peaks and an increase in the efficiency of separation of the components, can also be achieved by the constant supply of the vapours of other polar substances such as ammonia,[139] formamide,[143] formic acid,[143] and other compounds which, like water, give practically no signal when the most widely encountered flame-ionisation detector (FID) is used. The addition of these compounds to the carrier gas, which leads to a decrease in the part played by both the reversible and the irreversible adsorption of the compounds, also makes it possible to increase considerably the reliability of the quantitative analysis of the mixtures studied and the reproducibility of the retention parameters of their components.[122]

c. The influence of the method of introducing the specimen, and extra-column effects, on the efficiency of separation

The efficiency of separation in CGC depends to a marked extent on the method of introducing the specimen into the chromatograph.[1–3,6,22–24,27–32,35,36,38,88,93,144,146] To achieve the maximum efficiency of the CC it is necessary to eliminate or reduce to a minimum the unfavourable consequences of various extra-column effects leading to additional spreading of the specimen in the volatiliser of the chromatograph and its connections in front of the CC.[1,3,6,22,29,36,38,88,145,146] It is also important to eliminate overloading of the CC with the components of the specimen, which unavoidably leads to a decrease in the efficiency of separation.[1,3,6,22,23,29,88,104,112,118,119] These requirements are satisfied to a significant extent by the following methods of introducing the specimen: 1, a method based on splitting the stream of carrier gas at a volatiliser temperature equal to or greater than the boiling point of the least volatile component of the specimen;[1,3,6,23,88,104,112] 2, a method based on the so-called "solvent effect";[1,93,145,146] and 3, various modifications of a method involving the cryogenic focussing of the components in the initial section of the CC.[3,25,26,28,35–38,147–152] A high efficiency of separation is also obtained using various versions of the method of cold introduction of the specimen into the CC.[31,32,153] Promising possibilities are

provided by the recently employed method of introducing a liquid specimen with temperature programming of the injector,[29–33] which combines the advantages of the methods involving splitting of the stream of carrier gas and cold introduction.

The use of low-inertia ionisation detectors and mass spectrometers,[3,12,17,21,68,69,118,119,153] and the improvements of methods for combining them with CC[3,21,36] eliminate practically completely the loss of efficiency of separation at the outlet from the CC.[3,12,36,68,118,119,153]

Methods for introducing the specimen also have to satisfy high requirements in relation to the reliability of quantitative analysis,[1,3,23,29,31–34,37,38,113,129,149,150,153,154] the high sensitivity of determinations,[1,3,6,23,28,30,33,35,37,129,145–148,151,152,155] and the high stability of operation of the CC over a long period.[23,32]

III. The influence of various factors on the selectivity and capacity of capillary columns

High efficiency is a necessary but not a sufficient condition for the qualitative separation of components with similar physicochemical properties. This can be seen from the fundamental equation of Purnell.[1,120,122]

$$R_s = \frac{\sqrt{n}}{4}\,\frac{\alpha-1}{\alpha}\,\frac{k'}{k'+1}, \qquad (3)$$

which establishes the relationship between the separation criterion§ R_s,[1,6,119,122] characterising the completeness of the separation of two components, and not only the kinetic parameter (the number of t.p. n, measured from the second component) but also the equilibrium parameters of the chromatographic process—the selectivity coefficient α[1,16,122,] and the capacity coefficient k',[1,88,122] calculated from the second component.

The selectivity coefficient $\alpha \geqslant 1$, which is the ratio of the reduced¶ retention times (volumes) of two components being separated,[1,3,16,88,122] is determined by the partial pressures p_1^0 and p_2^0 of the vapours of these components and their activity coefficients γ_1 and γ_2 in solution in the SLP used:[16,35,156]

$$\alpha = \frac{p_1^0}{p_2^0}\,\frac{\gamma_1}{\gamma_2}, \qquad (4)$$

The quantity α is also called the "separation coefficient"[3,88] or the "separation factor".[1]

The capacity coefficient k' depends on the distribution constant K_L of the component between the liquid and gas phases and the ratio of their volumes $\beta = V_G/V_L$:[1,3,6,118]

$$k' = K_L/\beta. \qquad (5)$$

The quantity k' is sometimes called the "extraction coefficient"[1,3,88,118,122] or the "distribution ratio".[3] This is related to the fact that the capacity coefficient k' is a measure of the time for which the molecule of a given component is in the stationary phase relative to the time t_0 for which it is in the gas phase [$k' = (t_R - t_0)/t_0 = t'_R/t_0$]. In other words, k' is the ratio of the capacities of the stationary and mobile phases.

Analysis of the simple relationships (4) and (5) indicates several possible ways of controlling the selectivity and capacity in gas-chromatographic systems with one CC in the analysis of complex mixtures containing pairs and groups of components which are difficult to separate.

All known methods for controlling the selectivity and capacity in these systems can be divided into two main groups. The first is not associated with replacement of the CC,[1,3,16,35,118,119,122] while the second provides for replacement of the CC.[1,3,7,8,16] The factors influencing the selectivity of the separation of the components also influence the capacity coefficient k'. The converse does not always apply, since with change in the geometric parameters of the CC (L, d_c, d_f), the separation factor α may remain unchanged if the part played by adsorption effects at the phase interfaces in the system is negligible.[122]

1. Methods for controlling the selectivity and capacity parameters without replacing the capillary column

a. Changing the temperature conditions of the analyses

The simplest and most readily available method of varying the selectivity and capacity over wide limits is by changing the temperature conditions of the gas-chromatographic process.[1,3,15–19,21–35,87,118,119] In the analysis of complex mixtures consisting of chemical compounds of different classes, characterised by different temperature dependences of the retention parameters, however, this method is not always effective, since an improvement in the degree of separation of some pairs of compounds may be accompanied by a deterioration in the degree of separation of other pairs.[1,17–19,158] In a number of cases, a change in the temperature of the CC also changes the order of elution of compounds differing in the type and number of functional groups and the molecular framework.[1,17–19,158]

Changing the working temperature of the CC not only influences the selectivity and capacity but also opens up additional possibilities for the group identification of the components of complex mixtures, since the temperature coefficient of the retention index dI/dt depends on the structure of the molecule and the class of compound to which the component being identified belongs.[1,15,16,17–19,47,48,157–169]

Decrease in the temperature of the CC ensures a definite gain in selectivity in the separation of compounds with similar values of dI/dt. With decrease in temperature, in accordance with Eqn. (5), there is a simultaneous increase in the extraction coefficient k' according to a law close to exponential, and this unavoidably leads to a sharp increase in the analysis time.[1,118,119] For this reason, the analysis of mixtures of compounds belonging to the same homologous series and having appreciably different boiling points is carried out with temperature programming of the CC, which makes it possible not only to decrease sharply the separation time but also to increase considerably the sensitivity of the determinations.[1,3–6,15,21,44,53,87,98,108,118,119,157,168,170,171] Temperature programming also has some unfavourable consequences, associated primarily with the unsatisfactory reproducibility of the retention parameters used to identify the components,[6,15,47,48,116,172] possible decomposition of the substances being analysed, deterioration in the stability of the operation of the CC under the influence of the brief

§The quantity R_s is sometimes called the "resolution"[88] or the "degree of separation".[3,35,157]

¶As in the works cited,[6,16,157] the reduced quantities are the equilibrium characteristics of the gas-chromatographic process, calculated using the quantities obtained by subtracting from the gas-chromatographic retention time t_R the retention time t_0 of a non-sorbed component.

application of high temperatures,[1,6,8,118] and the incomplete utilisation of the potential efficiency of the CC.[1]

b. The influence of the composition and pressure of the carrier gas

In some cases the selectivity and capacity of CC can be controlled effectively by varying the composition of the carrier gas by adding to it various volatile readily adsorbed polar substances.[3,16,122,141] These substances dissolve selectively in the SLP and are adsorbed on various active centres of the CC, changing its capacity and selectivity with respect to both polar and non-polar compounds.[3,16,122,141]

The range of change in the selectivity and capacity of CC with change in the composition of the mobile phase can be increased considerably by altering the pressure of the mobile phase. Increase in pressure leads to an increased influence of the non-ideality of the gas phase on the solubility of the components in the SLP and on the retention characteristics.[16,142,173,174] Thus this method makes it possible to vary the selectivity and capacity of CC over wide limits, by controlling the pressure in the CC and the composition of both the mobile and the stationary phase. This is achieved by using vapour–gas mixtures under conditions in which the stationary phase is capable of sorbing the vapour strongly.

The use of gaseous mobile phases with modifying polar additives increases not only the selectivity and capacity of the CC but also, as noted above, the efficiency of separation and the reliability of the qualitative and quantitative analysis of complex mixtures.[3,6,16,35,122,139–144] An important factor is the increase in the sensitivity of the determination with a simultaneous decrease in the analysis time as a result of a decrease in the contribution of adsorption retention centres to the total retention of the sorbates[122] and an increase in the carrier-gas velocity.

An increase in the selectivity with change in the pressure of the carrier gas in CC is achieved even without adding polar additives to the carrier gas. This is particularly characteristic of argon and carbon dioxide, which are appreciably non-ideal at increased pressures.[16,141,142,173,175] This method of varying the selectivity of CC is also of interest for the group identification of components, since the value of $dI/d\bar{p}$, characterising the dependence of the retention index I on the average pressure $\bar{p}$ in the CC, is specific for definite groups of compound and is related to the value of the second virial coefficient in the equation of state of the vapour.[1,173,175] A study of the retention of various aromatic sorbates from benzene to 1,2,3,4-tetramethylbenzene (a total of 31 compounds) on CC with an efficiency of 150–200 thousand t.p. with polyethylene glycol 400 at 80 °C showed that in this series the value of $dI/d\bar{p}$, changes in the range 1.0–1.5 index units per atom[173] (the range of change in the pressure of Ar and CO_2 was 1.2–30 atm).

c. A method for continuously changing the selectivity and capacity

An interesting method for gradually changing the selectivity and capacity is based on the continuous removal from the CC of a volatile component of a binary SLP under isothermal conditions.[7,174] The possibilities provided by the method have been examined for the case of an analysis of petrol on a CC filled with a mixture of FS-16 fluorinated silicone and octadec-1-ene, which is gradually removed at 60 °C.[174] When both components of the binary SLP used are non-volatile at the working temperature, the CC is heated between analyses to remove a definite quantity of one of the phases. This method makes it possible, by examining the set of chromatograms, to establish the regularities of the change in the order of elution of the components of a complex mixture on going from one phase to another and on this basis to compile a binary (two-dimensional) spectrum of the signals relating to each component of the mixture. The method is restricted to a relatively narrow range of control of the selectivity and capacity of the CC, determined by the characteristics of the binary SLP used and its less volatile component, and also by the inadequate reproducibility of the retention parameters.

d. The use of an electric field

An extremely promising method of controlling the selectivity of liquid-crystalline SLP is by applying an electric field.[176] The method makes it possible, by changing the modulus and direction of the electric field intensity vector, to vary over a wide range not only the selectivity of the CC but also its capacity, and even to achieve the complete retention of some components. After the removal of the electric field, the compounds retained in the CC are rapidly eluted with a stream of carrier gas. In this way it is possible to achieve the complete separation of substances showing only extremely small differences in their molecular structures.[35,176] The method is restricted by the need to use liquid-crystalline SLP.

2. Methods for improving the selectivity and capacity by selecting capillary columns with different properties

General advantages of all the above methods for controlling the selectivity and capacity of CC are their simplicity and the possibility of achieving fairly smooth control of these important parameters.[16] Nevertheless, the impossibility in a number of cases of achieving the selectivity and capacity parameters required for the separation of all the components of complex mixtures of organic compounds, and the insufficient reproducibility of the retention characteristics, make it necessary in single-column gas-chromatographic systems to use a succession of several CC with different sorbents and SLP.[6–8,16,18,19,21,47,48,157,177] The possibilities provided by this approach have increased significantly in recent years as a result of the introduction into gas-chromatographic practice of different types of CC,[1,3,6,35,42,68,74,75,86,88,95–108,113,121–125,178–194] and also such SLP as nematic liquid crystals, showing a high selectivity with respect to many pairs of components difficult to separate,[7,35,39–41,66,89,195,196] and chemically grafted,[42,80,88,113,191,192,194,198] immobilised (transverse cross-linked),[35,42,68,102,105,107–109,171,194,197–205] mixed,[86,206,207] and colloidal[122,208,209] SLP.

The successive use of CC with different sorbents and SLP makes it possible to carry out separations using different types of intermolecular interaction, and on this basis to obtain a many-element chromatographic spectrum characterising the retention of the individual components of the complex mixture being analysed on the CC used.[7,8,16,18,19,48,177] To increase the reliability of the identification of the components and decrease the volume of excess information, it is desirable that the elements of the spectrum be as far as possible mutually independent.[7,8,16,18,19,48,177] It is therefore appropriate to reduce to a minimum the number of CC used, in which there is a predominance of definite types of interaction giving a selective separation and the required operational characteristics of the CC, the most important of which are the upper temperature limit (UTL) at which the SLP can be used, the efficiency and capacity of the CC, the stability of its operation over a long period, and the possibility of combining the CC with selective detectors.[1,3,6–8,12,35,46,68,107,113]

The change in the order of separation of components belonging to different classes of organic compound with change in the temperature of the CC and the polarity of the SLP has been successfully used[17–19,177] to identify the components and increase the amount of detail in the information obtained on the composition of complex natural mixtures of hydrocarbons. A method has been proposed[17–19,177] for the treatment of chromatographic data based on the combination of the results of the quantitative analysis of the compounds, determined at different temperatures on one CC, and also on different CC with different selectivities with respect to the same pairs of compound. The applicability of the method, which makes it possible to obtain information on the separate concentrations of components which do not give independent peaks, has been examined for the case of the analysis of specimens with markedly different quantitative compositions, namely broad petrol fractions from low-boiling to 150 °C and unfractionated petroleums and condensates, on relative short 50-metre CC containing squalane[17,18,56] and dinonyl phthalate.[18,19,177] The use of a method for the treatment of chromatograms to give detailed information on the composition of complex specimens identified approximately 200 C_1-C_9 hydrocarbons, and 17 [177] groups of hydrocarbons remained unseparated, whereas on CC with squalane and dinonyl phthalate the number of these groups was 46 and 40 respectively. From the increase in the amount of detail in the information on the composition, the combination of the results of quantitative analysis obtained under different gas-chromatographic conditions is equivalent to the use of long CC at low temperatures. This unavoidably leads, however, to a multiple increase in the analysis time and to a considerable decrease in the sensitivity of the determinations. In the works cited,[17–19,177] the results of the quantitative analysis of complex organic mixtures were used for the first time in gas chromatography to identify their components.

a. The production of a highly developed internal surface in CC

Various methods have been described for preparing CC with a high sorptive capacity. The nineteen-sixties saw the beginning of the intensive development of methods for the treatment of the internal surface of glass CC by etching it and giving it different types of roughness,[1,3,6,35,68,73,77,80,81,84,88,186,210] and also by forming on it thin layers of crystals of different substances[1,3,6,68,73,80,83,211] and whiskers.[1,6,68,73,76,81,84] The surface obtained in this way is readily wetted by a thick layer of both polar and non-polar SLP. Despite the high stability of the CC obtained,[1,83] they have a low efficiency, since the porous layer formed by etching has an extremely strong adsorbing power,[1,6,77,88] leading to the production of unsymmetrical chromatographic zones. Salt crystals formed on the internal surface of CC are also unstable to water vapour.[6,212] These features restrict considerably the application of glass CC with a highly developed surface in gas–liquid chromatography, and in a number of cases it is necessary to carry out subsequent operations to deactivate the surface.[1,3,6,88] These CC are fully applicable, however, in gas-adsorption chromatography.[6,77,88]

b. Columns with a porous layer of sorbent

The disadvantage of CC with a highly developed surface, noted above, led to the development of open capillary columns (OCC) containing a porous layer of sorbent on the internal surface. Theoretically, these columns should be free from one of the main disadvantages of OCC (WCOT) with a thin layer of SLP deposited directly on a smooth internal surface, namely the large ratio β of the volumes of the mobile and stationary phases.[3,68,213] This idea was first successfully realised by the application of a static method for depositing porous layers of carriers and active adsorbents from a suspension of these materials in various solvents.[1,3,6,35,68,88,214,215] After the deposition of the porous layer, the internal surface of a metallic capillary (d_c = 0.5 mm) was increased by a factor of 130.[214,215] This led to a decrease in the value of β from 208 to 35.5 with preservation of the HETP characteristic of the original capillary covered with a uniform SLP film with a thickness $d_f \simeq 0.6$ μm. A similar method of preparing CC has been used in other studies.[1,3,88,179] In addition to the static method, use is also made of a dynamic method, which is more suitable for glass CC.[1,3,6,88,216]

Two main types of OCC can be distinguished, depending on the nature of the porous material used: with a porous layer (OCC-PL, or SCOT) and with a solid carrier or adsorbent (OCC-SC, or PLOT).[1,6,68,73,88,113,216–222] The OCC-PL columns used in gas–liquid chromatography are prepared in two ways: a, by depositing a solid carrier previously impregnated with SLP; and b, by the preliminary deposition of a carrier and its subsequent impregnation with the SLP. The thickness of the porous layer in CC of this type is 1–5 μm.[88] In contrast to OCC-PL columns, OCC-SC columns with internal walls carrying a porous layer with a thickness of 10 μm or more, deposited or obtained by chemical methods, are most frequently used in gas-adsorption chromatography.[1,3,6,88,113,215,222] If a porous layer obtained by chemical methods is wetted with an SLP, $d_f > 1$ μm. It is often difficult to draw a line between OCC-PL columns containing an SLP and OCC columns of the WCOT type, obtained by depositing an SLP on an internal surface modified by various methods.[1,3,6,68,88]

OCC-PL columns are prepared using finely divided diatomite carriers,[1,3,6,88,179,214,216] or a mixture of celite with LiCl [223] or with glass.[224] The porous layers may occupy up to 42% of the transverse cross-section of the CC, leading to an increase in the quantity of SLP in the column and hence in the capacity coefficient k' by a factor of more than 100.[3,179] This makes it possible to increase considerably the volume of the specimen introduced, without the danger of overloading the CC.

The properties of OCC-PL columns are intermediate between those of ordinary packed columns and CC with an SLP deposited on the internal walls.[178] Thus in the separation of the methyl stearate–methyl oleate pair (α = 1.12) the values of R_s for a packed column (2.4 m × 2.2 mm), a column with an SLP on the internal wall (WCOT) (46 m × 0.25 mm), and an OCC-PL column (15.2 m × 0.5 mm) were 1.54, 7.06, and 4.09 respectively for analysis times of 35.6, 51.7, and 23.0 min. Increase in the carrier-gas velocity in the capillary columns to values at which R_s = 1.54, as in the case of the packed column, decreased the analysis time to 3.25 min on the OCC-PL column, and to 2.46 min on the WCOT capillary column. Short OCC-PL columns have been used extremely successfully for the rapid analysis of complex organic mixtures, where the times taken for the determination are measured in seconds and tens of seconds.[70,225,226]

OCC-PL columns, while retaining all the main advantages of ordinary packed columns (high capacity, relative short analysis time, stability of operation for a long time) and WCOT capillary columns (high efficiency of separation, possibility of achieving rapid analysis using short CC), show a high stability, durability and reproducibility of the results of qualitative and quantitative analysis.[1,3,6,88] Despite the major achievements of CGC associated with the extensive use of glass and more particularly quartz CC with the most varied

diameters, and also the use of SLP of new types, the importance of OCC-PL columns has not decreased in recent years.[5,68] This is indicated by the fact that one of the leading firms, namely Perkin–Elmer (USA), is continuing up to the present (since 1964) to produce columns of this type.[88]

OCC-SC (PLOT) columns, used in gas-adsorption CGC, have a fairly high capacity and selectivity even in the analysis of low-boiling substances with extremely similar physicochemical properties.[3,5,35,113,180–190,222,227–229] They are therefore widely used to separate isotopes and spin isomers of hydrogen.[227,228] The extensive possibilities provided by capillary gas-adsorption chromatography are indicated, in particular, by the separation at 190 °C of six isotopically substituted methanes on a glass CC (47 m × 0.2 mm) treated with sodium hydroxide.[190] A mixture of gases (He, Ne, Ar, O_2, N_2, and CH_4) was completely separated in 10 min using a 25-metre CC containing as porous layer a thin film of molecular sieves (5 Å).[229] OCC-SC columns have also been used for the successful separation of multicomponent mixtures of hydrocarbons (including C_9), present in natural gases,[3,5,35,113,180,229] and also higher-boiling compounds.[35,181–186,222] In particular, an OCC-SC column (50 m × 0.32 mm) containing as sorbent a mixture of Al_2O_3 and KCl has been used for the successful separation of hydrocarbons up to n-C_{10} and some of their halogen derivatives.[222]

The undoubted advantages of high-capacity OCC-SC columns, namely their high stability, practically unlimited thermal stability, the absence of complications associated with the volatilisation and degradation of SLP, and the fairly high separating power, guarantee a promising future for columns of this type. New methods for preparing OCC-SC columns have much in common with the methods used to prepare OCC-PL columns.[88] CC with high-capacity porous layers with a thickness of 100 μm or more are most frequently prepared by drawing capillaries from tubes containing the adsorbent or carrier.[1,3,88]

c. CC containing colloidal SLP

CC containing colloidal SLP can also be regarded as a form of OCC-SC.[6,84,122,208,209,230–235] Columns of this type are obtained by depositing under static and dynamic conditions a previously stabilised suspension of micro-particles of an active adsorbent with dimensions of $10^{-5}-10^{-7}$ cm in a solution of an SLP which acts as the dispersion medium.[6] Various inorganic substances are used as dispersion phases, including silanised silicas (Silanox),[6,84,230–232,235] highly dispersed silica adsorbents (Aerosil),[208,209] carbon blacks, and zeolites.[3,6,88,122,236,237] The advantages of CC containing colloidal SLP include the possibility of varying their selectivity over a wide range (from the selectivity of the pure SLP forming the dispersion medium to the selectivity of the active adsorbent used as the dispersion phase), the much higher thermal stability of colloidal SLP compared with ordinary SLP, and the universal nature of these columns.[209] Moreover, the use of colloids ensures a higher reproducibility of the adsorption properties of the sorbent compared with SLP modified by small quantities of additives, since in the colloidal deposition, the particles of the dispersion phase are covered with a macro-layer of the SLP.[122] This achieves reproducibility of the retention parameters of the sorbates. While having the same efficiency, CC with colloidal SLP, as a result of their high sorptive capacity, show better separating power than columns on which the stationary phase is deposited from the individual liquid.[208,237]

d. CC with a thick layer of SLP

There is a simple relationship between the extraction coefficient k' and the thickness d_f of the SLP film in WCOT capillary columns; from Eqn. (5) it follows that

$$k' = 4K_L d_f/d_c. \qquad (6)$$

Eqn. (6) indicates one of the most radical methods of increasing the sorptive capacity of these CC, namely by increasing the thickness of the SLP film uniformly deposited on their internal surface. This method became possible as a result of: 1, the introduction into CGC of flexible quartz CC with an internal diameter d_c = 0.32 mm and 0.53 mm, and also glass CC with d_c = 0.75 mm[42,107,113,194,238] and d_c = 0.85 mm;[239] 2, the development of effective methods for treating the internal surface of glass and quartz CC to improve its wettability, making it possible to achieve d_f = 1–8 μm;[42,192,194,197,203,205,240] and 3, the development of varied methods for preparing CC with chemically grafted and transverse cross-linked (immobilised) SLP.[35,42,68,80,88,102,105,109,191,192,194,197,203–205,240–250]

Until early 1983, the thickness of the SLP film in quartz CC with an internal diameter of 0.25 mm and 0.32 mm did not usually exceed 1 μm (as a rule d_f amounted to 0.1–0.5 μm). This made it possible to introduce into CC about 400 ng of any component of a mixture being analysed, without the danger of appreciable overloading.[194] The use of CC with thick SLP films (d_f = 1–8 μm) made it possible to increase several fold the volume of the specimens introduced and to determine the concentration of traces without lowering the efficiency of separation of the components of complex mixtures. Thus when quartz CC (50 m × 0.32 mm) with a methylsilicone immobilised SLP (d_f = 5 μm) was used, increase in the volume of a petrol specimen from 6.5 μg to 130 μg had practically no influence on the separation of the components (the splitting ratio of the stream of carrier gas was 1 : 10, and the specimen was introduced directly into the CC[107]). In the same work, in an analysis of the middle fraction of hydrocarbons extracted from coal, it was possible to increase the size of the specimen introduced into the CC to 758 μg. Analysis of Eqn. (3) shows that it is appropriate to use CC of large diameter (d_c = 0.53 mm), characterised by high values of k', when the specimen contains pairs of light components difficult to separate.[194] Thus to achieve a degree of separation R_s = 1.5 for a pair of components with α = 1.05 on a CC having a film thickness d_f = 1 μm (k' = 1.9), it is necessary that the number of theoretical plates (n_{req}) be 37120, whereas for a five-fold increase in d_f (k' = 9.6), n_{req} = 19356 t.p. At the same time the ratio of the phase volumes changes from 132 to 26. According to Grob and Grob,[42] an increase in d_f for elastomeric silicone SLP in quartz CC (d_c = 0.32 mm) at the optimum carrier-gas (nitrogen) velocity leads to practically no decrease in the efficiency of separation.

e. The use of immobilised SLP

CC of large diameter (d_c = 0.32, 0.53, and 0.75 mm) with immobilised SLP, operating under isothermal conditions or with temperature programming, are used for the analysis of natural,[113,194,229] petroleum, and fuel gases,[42,107] petrols,[42,194,198,238] mixtures of heavier hydrocarbons,[194,198,239] mixtures of aliphatic acids,[194] pesticides,[194] alcohols,[194] phenols,[194] amines,[201] and various medicinal products.[107,194]

Of particular interest is the use of high-capacity CC with ordinary and chemically cross-linked SLP for the analysis of mixtures of low-boiling compounds having low values of the distribution constant K_L.[42,113,192–194,198,229,238,251] This follows from an analysis of the factor $f(k') = k'/(k' + 1)$ in Eqn. (3). Thus for large values of k', when $k' \simeq k' + 1$, the function $f(k')$ approaches 1 asymptotically with increase in k', and can be regarded as a constant. At low values of k', increase in k' leads to an increase in the function $f(k')$, and hence to an increase in the separation criterion R_s.

The use of a quartz CC (50 m × 0.32 mm) with an immobilised OV-1 methylsilicone SLP (d_f = 1.5 μm) made it possible, with temperature programming, to achieve the practically complete separation of complex mixtures containing saturated, alkene, diene, and acetylene hydrocarbons, formed by the thermal and catalytic transformation of hydrocarbon raw materials.[238]

In addition to the main advantages of CC of large diameter (d_c = 0.53 mm and 0.75 mm) with thick films of immobilised SLP, namely the achievement of high values of the capacity coefficient k',[239,252–254] these columns have a number of other advantages, leading to their extensive application. These advantages are the following: 1, the possibility of introducing the specimen directly into the CC[107,113,194,254] and using other techniques for introducing the specimen without splitting the stream of carrier gas;[239,252,254] 2, the possibility of using CC with an immobilised SLP not only with a flame-ionisation detector but also with other detectors, including a katharometer, a mass spectrometer, and a detector based on Fourier transform infrared spectroscopy;[107,113,194,254] 3, the absence of any need for an additional supply of carrier gas to the detector;[239,254] 4, the possibility of setting up these CC in the thermostat of a chromatograph designed for ordinary packed columns;[107,113,254] 5, the high efficiency of separation (like that of CC of small diameter 0.2–0.25 mm);[107,113,254] 6, a high upper temperature limit for the use of SLP (300–325 °C) with minimum drift of the zero line;[193,239] 7, rapid determination (as when packed columns are used);[252–254] 8, good reproducibility of the specified properties and operational characteristics of the CC during their preparation;[194] 9, the possibility of removing from the CC by means of various solvents the non-volatile components and SLP particles which have not undergone chemical cross-linking, while preserving a high efficiency of separation;[113,194,240] 10, the resistance of the film of immobilised SLP to extraction and elution under the influence of solvents and large specimens of mixtures being analysed;[113,194,240] 11, high stability, which is preserved practically without limit;[113,194,240] 12, a significant decrease in the relative contribution of adsorption effects to the total retention of the sorbates;[254] 13, low catalytic activity, which makes it possible to analyse mixtures containing labile compounds;[239,254] 14, the higher (compared with packed columns) efficiency of CC with a thick SLP film under programmed-temperature conditions, due to the appreciably smaller transverse temperature gradient in the CC and hence the less extensive spreading of the chromatographic zones during the separation;[254] and 15, the low inertia of the heating (compared with packed columns) of CC of large diameter in temperature programming in the thermostat of the columns.[254]

Advantages 8–13 increase considerably the reliability of the identification of the components from the retention parameters. Moreover, the stability of the operation of quartz and glass CC with a thick layer of immobilised SLP under high-temperature conditions makes them particularly convenient for the determination of traces of components in complex mixtures of organic compounds, since a low background level is preserved, and, in particular, it is possible to introduce large specimens directly into a column of large diameter (d_c > 0.32 mm) with a small stream splitting ratio or without splitting of the stream of carrier gas.

A significant disadvantage of CC with thick immobilised SLP films is that their efficiency of separation is lower than that of classical open tubular WCOT capillary columns, because of the increased contribution of intra-diffusion spreading and dynamic diffusion to the spreading of the chromatographic bands.[253]

f. CC with a thin film of immobilised SLP

Chemical immobilisation of the SLP is used not only to increase the extraction coefficient k' of the components but also to increase the selectivity of separation of high-boiling polar and adsorption-active compounds, and also non-polar high-boiling isomers with extremely similar physicochemical properties.[105,108–110,200,203–205,242–250] For this purpose, use is generally made of CC with a diameter of 0.20–0.32 mm with a thin SLP film ($d \leqslant 0.5$ μm), which simultaneously leads to an increase in the efficiency of separation.[105,108–110,200,201,203–205,242–250] Columns of small diameter with a thin film of immobilised SLP retain many of the above-mentioned advantages (5–11, 14, and 15) characteristic of analogous CC of large diameter. On a CC of length 25 m (d_c = 0.20–0.22 mm) with immobilised silicone (SE-30 and OV-101) SLP under programmed-temperature conditions it was possible to achieve the complete separation of fifteen PAH from naphthalene to benz[*g*,*h*,*i*]perylene; C_8, C_{14}, C_{16}, C_{18}, C_{20}, C_{22}, and C_{24} n-alkanes and squalane were added to the mixture.[108,109,204] The analysis on glass CC with grafted SLP (OV-1701 methylphenylsiloxane and methylsilicone rubber) of a methylene chloride extract of the particles present in car exhaust gases detected sixteen PAH from phenanthrene to coronene.[250] The high selectivity of immobilised SLP is indicated by the fact that it has been possible, on a CC with a length of not more than 25 m, under programmed-temperature conditions, to achieve the separation of compounds difficult to separate, such as alkyl- and arylcycloalkylphenols (SLP OV-101 and SKTFT-50) and the diastereoisomers of the isoprene alkanes pristane and phytane (SE-30 SLP) in diesel fuel.[109] Capillary columns with immobilised SLP have been used successfully to separate mixtures of varied polar compounds such as amines,[201] phenols, and alkylanilines,[109,205,249] esters, pyridines, alcohols, and free aliphatic acids,[203,205,249] mixtures of high-boiling petroleum distillation products,[105] perfumery products,[249] and mixtures of chemically unstable compounds used in biology and medicine.[105,250]

Relatively short (14–15 m) glass and quartz CC with a thin film of immobilised SLP (d_f = 0.07–0.1 μm) have been used under programmed-temperature conditions[255] to obtain the distillation curve of heavy fractions of petroleum products containing hydrocarbons up to C_{60}–C_{120} (sometimes up to C_{140}) with boiling points of 615–800 °C. Depending on the SLP, the maximum working temperature of the CC was 350–450 °C, and the analysis time did not exceed 2–2.5 h.

g. The preparation of CC with an immobilised SLP

The variety of methods for the immobilisation of the most varied non-polar and polar SLP is leading to their extensive application in CGC.[88,110,194,200,201,238,240,241,256] Grafted SLP are obtained by the reaction of the functional groups of the liquid phase with the surface

hydroxyl groups of the glass.[240,241] The most widely encountered method of immobilisation is by the transverse cross-linking of polymeric liquid phases, carried out directly in the CC.[42,88,105,108–110,194,201–205,240,242–250,256] The phases immobilised include polyethylene glycols,[113,201,203,205,240] methylsilicone phases (SE-30, SE-52, OV-1, OV-101),[102,108–110,194,200,204,238,255] polysiloxane phases SE-54, SE-31, OV-1701, and OV-225 with a small concentration of vinyl and phenyl groups,[42,197,240] phenyl-containing silicone SLP of the OV-17 type,[194,257] phenyl-substituted silicones,[102] etc. Quartz CC with immobilised SLP of the SKTFT-50 silicone type, with operational characteristics equivalent to those of non-Soviet quartz CC, have been obtained in the Soviet Union.[109] The materials used to initiate the transverse cross-linking include various organic peroxides,[42,108–110,197,200,204,238,240,249,256,257] for example benzoyl, dibenzoyl, dicumyl, and t-butyl peroxides, and also cumene and ethylene oxides,[201] and ozone.[240,258] Increased temperature in the presence of a catalyst,[102,203,205] radioactive irradiation,[240,256] and other methods are also used. SLP based on Carbowax 20M have been prepared by carrying out the chemical reaction between the terminal hydroxyl groups of polyethylene glycol and the NCO groups of 1,6-di-isocyanate in glass CC [(11–14) m × 0.25 mm] in the presence of a catalyst at 110–145 °C for 1–5 h.[203] Films of immobilised SLP based on Carbowax 20M-TPA, FFAP, or OV-351 can be obtained by the thermal treatment of these phases in CC at 145 °C for 5 h in the presence of the catalysts Desmodur L-75 (0.002 M) and DABCO R-8020.[204] The immobilisation of silicones leads not only to a marked increase in the UTL at which the SLP can be used (up to 370 °C), but also to an increase in the selectivity, achieved by the preliminary introduction of phenol groups into the framework of the molecule instead of definite oxygen atoms.[102] The polymer obtained in this way, subsequently subjected to dimethyl-substitution and thermal treatment, is immobilised to the extent of 60%, whereas the cross-linking of dimethylsiloxane polymers takes place to the extent of 10%. The extensive application of CC with SLP differing in their selectivity and other important operational characteristics to solve the most varied analytical problems is to a large extent due to studies carried out in the last six years by the firm of Supelco (USA), which has begun the production of columns of this kind with different diameters (0.25, 0.32, 0.53, and 0.75 mm).[113,259,260]

The use of immobilised and other high-temperature SLP extends considerably the range of analytical problems that can be solved by CGC, and enables the latter to compete successfully with highly efficient liquid and fluid chromatography for the determination of high-boiling compounds. Of considerable interest in this connection, in particular, are the carborane–siloxane SLP, many of which (Dexyl-300GC, Dexyl-400GC, Dexyl-410GC, KBS-2, KBS-3, KBS-2F, and KBS-3F) have an UTL of 450–500 °C.[217] Thus an efficient glass CC containing Dexyl-300 (UTL 350 °C) has been used to achieve the complete separation of isomer pairs, difficult to determine, in a 36-component mixture containing a number of PAH from biphenyl to coronene and dibenz(*a*,*h*)pyrenene.[261] These pairs include phenanthrene and anthracene, benz(*a*)anthracene and chrysene, and benz(*e*)pyrene and benz(*a*)pyrene.

Open tubular glass CC with a solid carrier on the internal walls, impregnated with Dexyl-300, can be used under conditions of linear increase in temperature up to 400 °C.[217–221] These CC have been used to separate mixtures of PAH up to coronene,[218] and also microcrystalline waxes.[221]

h. The use of packing as an effective method of increasing the sorptive capacity and selectivity of CC

The most radical method of increasing the sorptive capacity of CC is by filling them with a packing consisting of either an active adsorbent[1,121–123,262–264] or a solid carrier impregnated with the SLP.[1,122,123,126,262,264] To ensure simultaneously a high efficiency of separation, capillary packed columns (CPC) with internal diameter not exceeding 1 mm are generally used.[1,121–125,262–264] Filling CC with a sorbent leads to a sharp decrease in the value of β compared with open tubular CC, with a corresponding marked increase in the capacity coefficient k'. A 23-component mixture containing air, CO_2, and saturated and unsaturated hydrocarbons up to C_6 (specimen volume 50 μl) has been separated on a steel CPC (3 m × 1 mm) filled with aluminium oxide modified with oleic acid (sorbent particle diameter 0.14–0.25 mm) in 16 min at 40 °C.[263] The range of application of these CPC with d_c = 0.6–1 mm is much wider, however.[262–264] The use of long columns, including glass columns, makes it possible to carry out the rapid gas-chromatographic analysis of complex mixtures of alcohols, steroids, barbiturates, and various impurities in air.[1,262]

As noted above in the examination of the efficiency of separation in CGC, in recent years there has been intensive development in a new direction involving the use of micropacked quartz capillary columns (MPQCC) of small diameter (d_c = 0.15–0.37 mm), filled with fine sorbent granules (5–100 μm).[121–127] Short MPQCC with lengths measured in tens of centimetres combine the advantages of open tubular CC and packed columns in relation to their efficiency, capacity, selectivity, and reproducibility of the results of qualitative and quantitative analysis. This makes it possible to use them for the rapid analysis of not only complex mixtures of hydrocarbons[121,123] but also mixtures of strongly polar compounds such as ketones[122,126] and aliphatic and aromatic alcohols.[123]

CPC in general, and MPQCC in particular, have a number of advantages over open tubular CC of the WCOT type.[1,124,126,127,262,263] These advantages, which are a consequence of the high capacity of these CC, are: 1, the possibility of adding the specimen directly to the CC and avoiding splitting of the carrier-gas stream, which decreases the uncertainty in quantitative determinations and lowers the requirements to be satisfied by the sensitivity of the detector (micro-katharometer, mass spectrometer, etc.); 2, the possibility of determining traces; 3, the possibility of separating substances which are weakly sorbed; and 4, the possibility of the micro-preparative separation of extremely narrow fractions of a complex mixture for their subsequent more detailed study by gas-chromatographic and other physicochemical methods. Other advantages of CPC are their practically unlimited thermal stability and their stability of operation when filled with adsorbents, and the much less severe requirements to be satisfied by the solid carrier and the SLP, compared with OCC-PL and columns in which a phase is deposited directly on the internal surface.

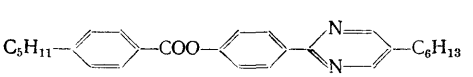
Nevertheless, the extensive use of these columns is limited by the complexity and time-consuming nature of the procedure for filling CPC (and more particularly MPQCC) and by the high pressure drops established during use, which in a number of cases reach several MPa.[122]

i. The use of liquid-crystalline SLP

The use of nematic liquid-crystalline SLP in CGC is directed mainly to increasing the selectivity of separation of isomeric

compounds with extremely similar boiling points and other physicochemical properties.[7,35,39–41,66,89,122,176,195,196,237,265–269] The high selectivity of liquid crystals in the nematic state is due to the long-range orientational order of the arrangement of the long axes of their molecules. The use of these SLP combined with highly effective CC makes it possible to solve the most complex analytical problems, including the separation of stereoisomers. The possibility of separating C_8 arenes and isopropylbenzene on a 50-metre CC containing *p,p'*-azoxyphenol (AOP) and *p,p'*-methoxyethoxyazoxybenzene (MEAB) has been studied.[268] A more detailed study of the *meta–para* selectivity of liquid-crystalline SLP and their mixtures in the temperature range 90–160 °C in copper CC (40 m × 0.35 mm) showed that the maximum selectivity is achieved with the maximum steric effect in the liquid-crystalline melt.[195] An interesting feature is that in the temperature range of existence of the nematic liquid-crystalline state, the more linear isomer *p*-xylene is retained more strongly than *m*-xylene, distinguishing these SLP from most other SLP which are not liquid crystals.[195,237,268] The influence of temperature on the efficiency of separation, the separation factor α, and the capacity coefficient k' in CC with liquid-crystalline phases is much more complex than in the case of SLP in which there is only short-range translational order. This is related both to the change in the state of aggregation of the SLP on passing through the melting point and to the change in the phase state of the liquid phase with increase in temperature (the change from the smectic to the nematic and then to the isotropic state).[89,195,237] In general, the temperature of maximum selectivity does not necessarily coincide with the temperature of the maximum capacity.[195] The optimum separation temperature may not coincide with the temperature of maximum retention in the range of the meso-phase.[195]

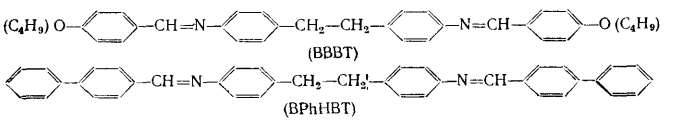
The use of sodium glass capillary columns (d_c = 0.23 mm) of different length containing the new liquid-crystalline SLP 2-[4-(4-pentylbenzoyloxy)phenyl]-5-hexylpyrimidine (PBHP)



(PBHP)

in the temperature range 80–130 °C has been used to separate a complex 32-component mixture consisting of C_8–C_{13} n-alkanes and C_8–C_{13} alkylbenzenes.[66] The specific efficiency of the CC used was 3500 t.p. m^{-1}, the capacity coefficient k' = 3.5 (at 90 °C), and d_f = 0.115 μm. A remarkable feature is that despite the fact that the SLP used by the authors cited[66] had a higher selectivity with respect to *p*- and *m*-xylenes than all known liquid-crystalline SLP ($\alpha^{100\ °C}$ = 1.09, $\alpha^{50\ °C}$ = 1.13, $\alpha^{25\ °C}$ = 1.20), it was not possible to separate all the components of the mixture studied on a single column of length 50 m. An extremely satisfactory separation in a relatively short time (~20 min) at 25 °C was achieved only using a combined CC, the first section of which, of length 35 m, contained OV-101 methylsiloxane rubber as SLP, while the second, of length 15 m, contained PBHP. The temperature range corresponding to the nematic liquid-crystalline state of PBHP is 38–159 °C.

Interesting studies have been carried out on the separation of PAH.[89,196] In particular, a CC with the liquid-crystalline SLP N,N'-bis-4-butoxybenzylidene-*a,a'*-bi-*p*-toluidine [N,N'-bis-(BaBT)] has been used for the complete separation of benz(*a*)anthracene and chrysene.[196] The complete separation of a number of tricyclic, tetracyclic, and pentacyclic PAH and two benzofluoranthenes has been carried out using glass CC containing the liquid-crystalline SLP



(BBBT)

(BPhHBT)

whose nematic phase is thermodynamically stable at relatively high temperatures (188–300 °C for BBBT).[89] To increase the UTL and the stability of operation of the CC at high temperatures, the BPhHBT and BBBT were deposited on a previously treated surface carrying $BaCO_3$ crystals. The further development of this promising field is restricted at present by the non-availability of liquid crystals having sufficient thermal stability and undergoing phase transitions in the range 300–350 °C, so that it is not possible to cover all the PAH present in the specimens in the analysis of petroleum products and environmental specimens. Difficulties arise as a result of the instability of the separating power of liquid crystals, which leads to a sharp deterioration in the efficiency of the CC during use, particularly under temperature-programming conditions at high temperatures. When combined with highly efficient liquid chromatography, however, the use of CC containing liquid-crystalline SLP provides unique analytical possibilities for determining PAH in various technical and natural materials. As noted above, the separating power of CC containing liquid-crystalline SLP can be increased considerably by the action of an electric field.[176]

Interesting results have been obtained[39] using a quartz CC with a liquid-crystalline SLP to separate isomeric polycyclic aromatic compounds whose molecules contain different heteroatoms. Quartz CC (15 m × 0.20 mm) containing a nematic polysiloxane SLP have been used to separate PAH with relative molecular masses of 276–302 at 280 °C, and quartz CC (25 m × 0.20 mm) with a smectic polysiloxane SLP have been used to separate the methyl esters of aliphatic acids at 140 °C.[40] The unique selectivity of liquid-crystalline SLP is indicated by the results of studies[41] in which a glass CC was used to separate a number of geometric isomers of various polar and non-polar compounds.

Additional possibilities for the rapid determination of various hydrocarbons, aliphatic acids, esters, and nitriles are provided by the use of short CC (up to 10 m) containing colloidal liquid-crystalline SLP.[237]

j. The influence of adsorption effects

An important factor controlling the selectivity and capacity in CGC is the adsorption of the sorbates at the inter-phase surfaces in CC in which their internal surface plays the part of the solid carrier.[75,122,269,270] It has been shown convincingly[122,270–273] that the additive theory of retention is equally applicable to capillary and packed columns. The important part played by adsorption phenomena in CGC is indicated primarily by the dependence of the retention indices of a number of compounds, including even low-boiling C_6–C_7 hydrocarbons, on the nature of the surface of the walls of the capillary and the thickness of the SLP film.[122,169,269–274] The factors indicated have a significant influence on the retention of compounds in chromatography using both polar and non-polar SLP. A change in selectivity has been observed with increase in the effective thickness of the film of a liquid-crystalline SLP.[269] The influence of the thickness of the layer of SLP on retention has been observed for CC of practically all types.[122,169,270] An extremely important practical feature is that in some cases a change in the

concentration of the SLP in the CC even changes the order of elution of the compounds being determined. For example, in a glass CC containing Carbowax 20 M (k' = 2.1 for *cis*-pentadec-5-ene), *trans*-pentadec-6-ene is eluted first, followed by *cis*-pentadec-5-ene, whereas in a CC with a thin layer of the same SLP (k' = 1.3), the opposite order of elution is observed.[270,271]

k. The use of mixed SLP

Despite the high specific efficiency of CC, in particular quartz CC, the use of mixed SLP to carry out complex separations in single-column CGC is still of considerable interest, since it makes it possible to control the capacity and selectivity factors over wide limits and to some extent to avoid the successive use of several individual SLP.[86,174,206,207,275] The smooth control of the polarity of the stationary phase by the simultaneous deposition of two readily available individual SLP in definite proportions is appropriate for separating extremely complex organic mixtures consisting of substances of different classes which differ in the polarity of the molecules to be separated.[206] Here, the polarity of molecules is understood to mean not the empirical value of their dipole moment but a quantity determined by the concentration of polar functional groups or by the ratio of the polar and non-polar atomic groups in the sorbate molecule.

Glass (d_c = 0.45 mm) and quartz (d_c = 0.22 mm and 0.33 mm) CC with binary SLP containing Superox 20M† (polar component) and OV-1 (non-polar component) in different proportions (1 : 3, 1 : 1, and 3 : 1) have been used to separate synthetic mixtures containing alcohols, aliphatic acids, diols, phenols, anilines, primary and secondary amines, and the components of vegetable oil from hops with the addition of various aromatic substances.[68] It has been shown that by varying the composition of this mixed SLP over a wide range it is possible to cover a wide range of McReynolds constants, characteristic of five individual SLP of the Yukon type. An important result of the work cited[86] is that it proved that it is possible to deposit, on the untreated internal surface of a CC, films of mixed SLP capable of stable functioning up to 250 °C, in spite of the fact that one of its components (Superox 20M) tends to form droplets, and the UTL of each of the individual SLP does not exceed 170–180 °C. The formation of stable films of mixed SLP on a smooth fused quartz surface which has not been treated to give it roughness has made it possible to make full use of the advantages of quartz CC, which have low adsorption and catalytic activity, and at the same time to achieve a high efficiency of separation.

A number of mixtures of PAH have been analysed in CC with liquid-crystalline SLP of the N,N′-bis-(BaBT) type, mixed with OV-101 polysiloxane, and the optimum ratio of the polysiloxane and the liquid-crystalline components of the SLP has been determined.[207]

The use of CC with mixed SLP previously made possible the detailed determination of the light hydrocarbons present in petrol fractions.[158,170,276–278] In particular, a CC with a mixed SLP was used under programmed-temperature conditions to obtain detailed information on the composition of a broad C_4–C_{12} petrol fraction.[170] CC with a mixed SLP have been used to separate aromatic C_6–C_{10} hydrocarbons.[277,278]

The use of mixed SLP often makes it possible to pass smoothly through the entire range of polarity. The optimum composition of the binary SLP and the length of the CC are usually calculated from the required degree of separation of the components of the mixture being analysed and the minimum analysis time. The most convenient for this purpose is the method of "window" diagrams,[279] subsequently extended to the selection of the optimum experimental conditions for the use of combined columns (connected in series).[66,275,280–282] In this method, the linear dependence of the coefficient k' on the composition of the mixed SLP is constructed for each component of the mixture being analysed. From these relationships, for any specified composition of the SLP, it is possible to calculate the selectivity coefficient α for pairs of components most difficult to separate. The plot of α against the SLP composition, called the "windows" diagram, makes it possible to select the optimum composition of the binary SLP corresponding to the maximum value of α. The length of the CC required for the separation is selected from the number of theoretical plates (n_{req}) required for the complete separation of the components.

Despite their obvious advantages, the extensive use of mixed SLP in CGC is associated with a number of difficulties, including the following: 1, the limited mutual solubility of the polar and non-polar components of the SLP, which in a number of cases leads to the adsorption of the sorbates on a new inter-phase boundary which is difficult to take into acocunt, and the possibility of varying the capacity and selectivity factors only in a relatively narrow range;[275] 2, the deterioration in the efficiency of separation and the poor reproducibility of the properties of the CC as a consequence of the insufficient wettability of their internal surface by the mixed SLP;[275] and 3, the need in a number of cases for the successive application of CC containing mixed SLP with different compositions to obtain the required volume of information.

IV. Summary

The examination of a large number of methods for controlling efficiency, selectivity, and capacity in single-column CGC indicates the significant achievements and the promising possibilities of this most widely encountered and flexible method for the analysis of multicomponent mixtures of organic and inorganic compounds. At the same time there are obvious limitations and difficulties associated with use of CGC to solve various complex analytical problems, which cannot always be overcome using gas-chromatographic systems with one CC. This applies primarily to the analysis of natural and other mixtures boiling over a wide temperature range and consisting of representatives of varied classes of chemical compound. The separation of these mixtures often becomes possible only after the preliminary isolation of the fractions to be analysed, which unavoidably leads to distortion of the initial composition of the specimens being studied and is also time-consuming. In a number of cases, to obtain detailed data on the concentration of the individual components in specimens characterised by a wide variation in composition, it is necessary to carry out parallel or successive analyses using several instruments, sometimes under different temperature conditions and using CC with SLP having different polarity. The frequent replacement and alternation of CC having different efficiencies, selectivities, and capacities, and analyses using different chromatographs, are also time-consuming and inconvenient, and lead to an increase in the number of sources of error in the determination of the composition of complex mixtures.

Difficulties frequently arise, associated with the need to carry out analyses at a low temperature or, on the other hand, a temperature

†Superox 20 M is a linear polyethylene glycol with a relative molecular mass of 20000–40000, readily soluble in dichloromethane.

which is too high, with large pressure drops, when using long CC and CC of other types characterised by a high specific resistance to the flow of carrier gas (CC with a diameter reaching 0.1 mm, MPQCC, etc.). Change in the temperature of the CC and the use of temperature programming in the analyses are not always effective in the study of complex mixtures, since improvement in the separation of some pairs of compound may be accompanied by a deterioration in the separation of other pairs. Moreover, the use of high temperatures, even for a short time interval, leads to the danger of decomposition of the substances being analysed, to a decrease in the lifetime of the CC, and to the incomplete realisation of their potential efficiency.

Although glass and more particularly quartz CC with ordinary and immobilised SLP have good operational characteristics, their use in large-scale analyses requires highly qualified workers. Many types of CC and SLP are difficult to obtain, in short supply, and expensive. Certain difficulties are associated with the procedures preceding the deposition of SLP on the internal surfaces of CC and carried out to eliminate or decrease its adsorption and catalytic activity and to improve the wettability of this surface by the liquid phase.

Despite the fact that the chromatographic characteristics of OCC-PL, OCC-SC, and micropacked glass and quartz CC are highly stable for a long time, and their UTL fairly high, they have not yet been widely applied, because of the difficulty of their preparation.

The extensive use of liquid-crystalline, mixed, and colloidal SLP in CGC is prevented by the changeability of their separating power, particularly at relatively high temperatures, and by the difficulty of achieving reproducibility of the efficiency and selectivity of columns containing these phases.

Extensive possibilities for varying the efficiency of separation over a wide range are provided by two-stage systems with capillary columns functioning under circulation gas-chromatographic conditions.[283–286] Programming the length of the layer of sorbent in the gas-chromatographic process makes it possible, at low carrier-gas inlet pressures, and by the repeated use of each of two CC with the same SLP, to achieve values of the efficiency of separation measured in tens of millions of t.p., which makes it possible to achieve values of the separation factor α extremely close to 1 (1.002 – 1.01) in the separation of isotopically substituted organic compounds with extremely similar properties (cyclohexane, benzene, naphthalene, acetone) and their partly or completely deuteriated analogues.[283–286]

Promising possibilities for the extension of the use of CGC for the analysis of complex mixtures and the reliable determination of micro-quantities are provided by the use of gas-chromatographic systems with several columns, of which at least one is a capillary column.[9–13,16,18,55–64,66,177,275,280–282,287–291] These systems make it possible to obtain extremely detailed information on the composition of the mixture being analysed, since it is possible to vary the capacity and selectivity parameters over an extremely wide range and to carry out the analyses at relatively low temperatures. The last feature guarantees the high stability of the CC for a long time, and extends the range of compounds that can be determined, by including thermally labile and reactive substances. This makes it possible, even with an extremely limited number of CC and SLP and small quantities of the substance being analysed, to decrease the total time taken for the determination and to increase the reliability of the analysis by eliminating undesirable operations of specimen preparation, using relatively short CC, and decreasing the total number of experiments. The use of high-capacity packed columns combined with highly efficient CC provides extensive possibilities for increasing the sensitivity of determinations. By carrying out analyses in multi-stage gas-chromatographic systems containing two or more CC with different SLP and detectors, it is also possible in a number of cases to increase the reliability of the identification of the components of complex mixtures of organic compounds.

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