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Gradient barochromatography

M S Vigdergauz

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Abstract. We describe the gradient barochromatography method, in which the eluent plays an active as well as a transport role, and thus offers an increased resolving power. The effect of the nonideality of the mobile gas phase, determined by its nature and pressure, on the retention and spreading of the chromatographic bands is examined, together with the prospects of controlling the selectivity of the column and the degree of separation of the sorbates. Special attention is paid to the role of the pressure gradients and of the velocity of the gas, including discontinuous changes in work with composite columns. The prospects of the practical application of gradient barochromatography to the identification of the components of complex mixtures and to the control of the chemical composition of various types of sample are examined. The bibliography includes 81 references.

I. Introduction

The nature and the working conditions of the mobile phase play only a secondary role among the many variables which control the selectivity, the effectiveness, and the sorption capacity in gas chromatography. This is because many workers treat the carrier gas merely as a transporting agent, whose influence on the completeness of the separation of sorbates is confined to a relationship between the flow rate of the carrier and the spreading of the bands. However, by assigning active functions as well as transport functions to the gaseous eluent we can obtain some quite unexpected advantages. Furthermore this is a way of building a kind of bridge between gas and liquid chromatography. Supercritical fluid chromatography is one of the best examples of an intermediate variant of chromatography.[1–3]

The active functions of the eluent are determined by the following properties: the dissolving power of the eluent with respect to the sorbates, which depends on its nature and on its pressure; the solubility of the stationary liquid phase in the eluent, which determines the nonideality of the latter; the solubility of the eluent in the stationary liquid (or its condensation, in cases of low mutual solubility) and the formation of a binary stationary phase; the adsorption of the eluent on the gas–liquid and liquid–solid interfaces of the carrier, and the consequent change in the overall sorption characteristics for the sorbates to be analysed (in the partition chromatography regime); the adsorption of the eluent on the gas–liquid interface (in the adsorption chromatography regime) and in the gas–solid carrier interface (in the partition chromatography regime for incomplete coverage of the carrier surface with a layer of stationary liquid phase); the disequilibrium of the sorption process, which increases at high flow rates of the eluent (especially when the viscosity of the stationary liquid is high) with a corresponding change in the retention of the sorbates to be analysed.

When working with nonideal eluents in highly efficient columns we can exploit various factors which have little effect on the separation in the case of ordinary packed columns (i.e. which do not significantly alter the shape of the chromatogram).

At present the range of pressure used in gas chromatography extends from tens of millimetre mercury to thousands of atmospheres, in regimes varying from almost isobaric (in the case of low pressure drops) to gradient regimes, in which the pressure is programmed both over the length of the column and in time. In this respect the active (or pseudoactive) function of the gaseous eluent can also take the form of a change in the selectivity of the composite column, which is controlled by the ratio of the pressures in the sections packed with different sorbents.

The theoretical and the applied aspects of chromatography with nonideal eluents have been examined in various monographs and review articles.[2–5] The present review is aimed at recent work on the specific features of barochromatography.

II. Classification of gas-chromatographic methods

The following classification of gas-chromatographic methods[2] can be proposed in order to allow for the effect of the nature and pressure of the carrier gas on the chromatographic process.

1. Vacuum chromatography using conventional carrier gases or the vapours of low-boiling liquids under reduced pressure.[6–9]

2. The traditional gas chromatography, using carrier gases at ordinary pressures (near-atmospheric at the column outlet, and

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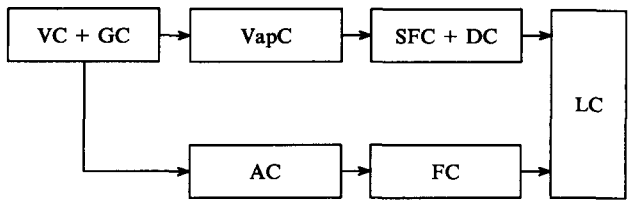


Figure 1. Variants of column molecular chromatography, classified according to the phase states of the mobile phase.
GC, traditional gas chromatography; VC, vacuum chromatography; VapC, vapour chromatography; DC, density chromatography; SFC, supercritical fluid chromatography; AC, aerosol chromatography; FC, foam chromatography; LC, liquid chromatography.

under an overpressure sufficient to give the required flow rate at the inlet).

3. Barochromatography, in which permanent-gas carriers at high pressures are used to embody some of the active functions listed above: of course, a pressure gradient along the column axis is unavoidable (unlike a temperature gradient) except in diffusion chromatography.[10]

3.1. Gradient barochromatography.

3.1.1. Gradient barochromatography with pressure and flow rate of the carrier gas programmed in time.

3.1.2. Gradient barochromatography with strong pressure gradients (pressure programmed along the column).

3.1.3. Gradient barochromatography with pressure programmed in time and strong pressure gradients.

3.2. Barochromatography with weak pressure gradients..

4. Vapour chromatography, in a flow of the vapour of low-boiling liquids (pure, or mixed with a gas) at ordinary or elevated (up to critical) pressures[11,12] including the addition of a ligand to the carrier gas in order to analyse chelates.[13] Vacancy chromatography, differential chromatography, and other forms of carrier-free chromatography can also be classified with this variant.[23,25,26]

5. Supercritical fluid chromatography, carried out in a flow of substances at a temperature and pressure just above their critical values.[3,4]

6. High-density chromatography, carried out in a flow of gases under pressures much higher than their critical values (up to thousands of atmospheres). Under these conditions the density and the solvent power can approach values typical of liquid solvents.[14]

Of course, this classification cannot claim to be complete, because it omits a number of possible methods, some of which have already been realised. The latter include, in particular, the programming of the parameters[15,16] and the establishment of conditions which favour turbulent flow,[17,18] whereas methods not yet realised include the use of heterogeneous eluents such as aerosols and foams†, and also the use of high vacua.

In the scheme shown in Fig. 1 the intermediate chromatographic methods are listed sequentially in the order of a change of the phase state of the eluent from gas to liquid. The upper branch of the diagram refers to homogeneous mobile phases, the lower branch to heterogeneous.

In order to establish a clear picture of the effect of the nature and of the operating conditions of the mobile phase on the chromatographic process it is useful to compare the above classification with the classification of the methods in which a temperature distribution is postulated. The same system of numbering is used for the variants (except variant 4).

†This method should not be confused with the well-known variant of foam chromatography in which the retention is determined by the formation of a foam between the sorbent and the stationary phase.[19]

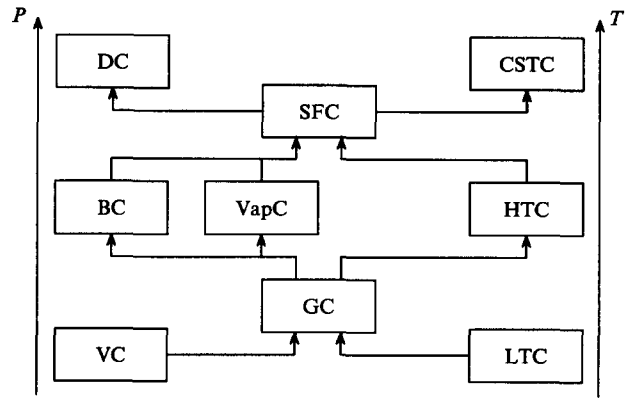


Figure 2. Chromatography methods and their intermediate variants, classified according to pressure and temperature levels (symbols as in Fig. 1); LTC, low-temperature chromatography; HTC, high-temperature chromatography; STC, super-high temperature chromatography; BC, barochromatography.

1. Low-temperature chromatography, including cryogenic.[20-22]

2. Gas chromatography at ordinary temperatures (up to 200–250 °C).

3. Isothermal and gradient chromatography at elevated temperatures (up to 500–600 °C).

3.1. Programmed temperature chromatography.

3.1.1. Chromatography with time-programmed temperature.

3.1.2. Chromatography with time-programmed temperature and a constant temperature gradient along the column axis.

3.1.3. Chromathermography[23] and other variants of temperature programming in time and space. A variant[24] which stipulates the programmed transfer of the column from one part of the thermostat to another part (set for a different temperature) can also be classified in this section.

3.2. Isothermal chromatography.

5. Supercritical fluid chromatography.

6. 'Ultra-high temperature' chromatography (up to 1200–1350 °C).[27] Pyrolytic gas chromatography can be arbitrarily included in this section, since it features a large (though formal) increase in the mobility of the sorbate.[28]

The change from one methodology to another in terms of temperature and pressure is shown schematically in Fig. 2. In both cases an increase in the stated parameter tends to lower the sorption capacity of the stationary phase and hence to increase the mobility of the sorbates‡.

III. Effect of the nature of the mobile phase on the retention of sorbates under the conditions of barochromatography

Barochromatography covers the range from ordinary pressures to several tens of atmospheres when traditional carrier gases are used. Therefore in order to calculate the retention values we can use virial equations of state including the second and the third virial coefficients.[2] Obviously in most cases the solvent power of the eluent towards the sorbate and its dissolution in the stationary liquid are relatively small. However, they are usable for analytical purposes and for physicochemical measurements.

The first unambiguous example of the influence of the nature of the carrier gas on the retention was provided by the

‡Departures from this tendency in the right-hand loop of the scheme are due to phase transitions in the stationary phase (e.g., melting in the LC–GC stage). Little is known about the special problems of working with high vacua.

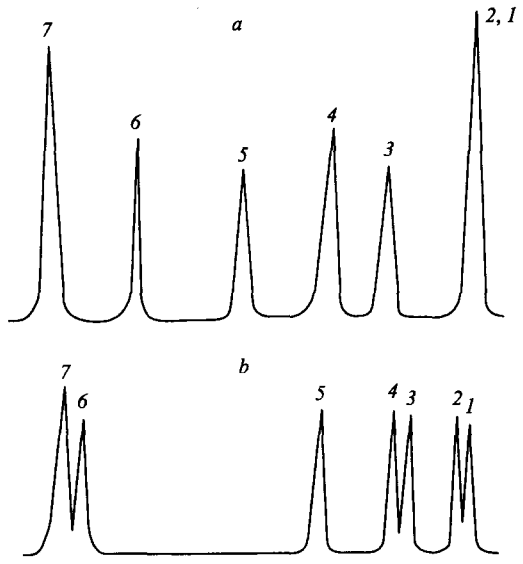


Figure 3. Chromatograms of a mixture of hydrocarbons obtained on a capillary column (270 m × 0.15 mm) with squalane and nitrogen (*a*) or hydrogen (*b*) as the carrier gas:[29] *1*, methylcyclopentane; *2*, 2,2-dimethylpentane; *3*, 2,4-dimethylpentane; *4*, benzene; *5*, 2,2,3-trimethylbutane; *6*, 3,3-dimethylpentane; *7*, cyclohexane.

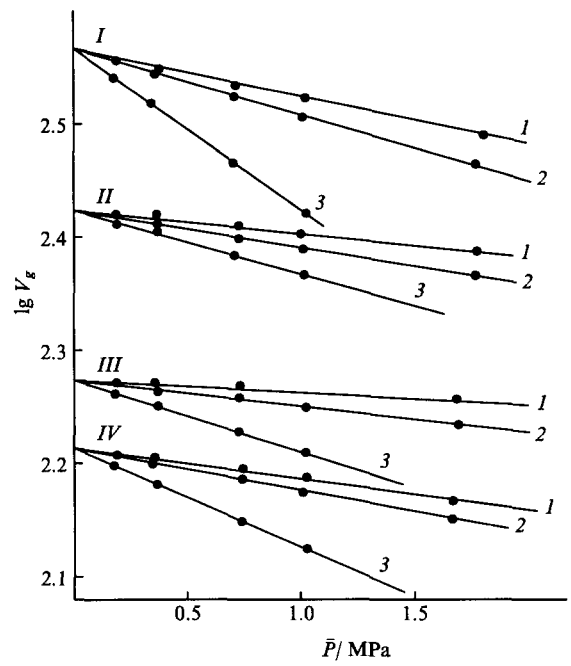


Figure 4. Plots of the logarithm of the absolute specific retention volume against the average pressure in the column at 80 °C in a nitrogen (*I*), argon (*2*), or carbon dioxide medium (*3*) for butyl acetate (*I*), toluene (*II*), n-octane (*III*), and dioxan (*IV*).[34]

chromatograms for hydrocarbons obtained on a capillary column 270 m long with a squalane stationary phase and using nitrogen and hydrogen as the carrier gases at an inlet pressure of 10.7 atm.[29] As can be seen from Fig. 3, replacing one carrier gas by the other affects both the retention and the selectivity of the separation of these sorbates. This effect is due to the well known relationship between the separation coefficient of the sorbate Γ and the second virial coefficient B_{12} in the gas-state equation for the mixture of sorbate and carrier gas:[30]

$$\Gamma = \Gamma_{(P\to 0)}\exp(\beta P)\,, \qquad (1)$$

where $\Gamma_{(P\to 0)}$ corresponds to zero pressure, $\beta = (2B_{12} - V_1^{\infty})/RT$ [V_1^{∞} is the partial molar volume of the sorbate at infinite dilution in the stationary liquid], and P is the pressure in the column.

At moderately high pressures, which satisfy the condition $\beta P \ll 1$, we can use the expression[31]

$$\Gamma = \Gamma_{(P\to 0)}(1 + \beta P)\,. \qquad (2)$$

Over a wider range of pressure we must include the third (mixed) virial coefficient C_{122} (See Ref. 32):

$$\ln\Gamma = \ln\Gamma_{(P\to 0)} + \beta P + \xi P^2\,, \qquad (3)$$

where

$$\xi = \frac{3C_{122} - 4B_{12}B_{22}}{2(RT)^2}\,. \qquad (4)$$

(B_{22} is the second virial coefficient in the equation of state of the carrier gas). A more complex equation was obtained when allowing for the solubility of the carrier gas in the stationary liquid.[33]

The effect of the nature of the carrier gas and of the pressure in the column on the retention of the sorbates is clearly shown by the plots in Fig. 4. Clearly, the commonly used carrier gases can be conveniently classified into three groups. The first includes hydrogen and helium, which are characterised by relatively small values of the second virial coefficient in the equation of state for the gas, and therefore in these gases the change in retention of the sorbates at higher pressures is very slight. In the case of nitrogen and argon (the second group) these changes become significant, and lastly to the third group we must assign carbon dioxide and some Freons, which produce an even larger shift in the phase equilibria of the sorbates. Furthermore the critical state of these eluents is reached at pressures as low as 30 atm.

A study of the dependence of the retention indices of the hydrocarbons in gasoline on the mean pressure of helium, argon, and carbon dioxide at pressures between atmospheric and 18 atm (using a capillary column 120 m long with octadec-1-ene) has been reported.[35] The results are consistent with the above argument (Fig. 5, see over). It was also established that the analysis time decreases when argon is replaced by carbon dioxide and the pressure is increased. The changes in the retention indices of aromatic hydrocarbons with increasing pressure in nitrogen and carbon dioxide have been discussed[36,37] by analogy with the corresponding changes in the retention index caused by an increase in temperature.

It has been pointed out[35] that carbon dioxide is sorbed by the wall of a copper capillary and blocks the active centres on the liquid – solid interface. This effect produces narrower and more symmetrical peaks for the aromatic hydrocarbons on the chromatograms: in a stream of CO_2 the height of the benzene peak is almost double that of the same peak in a stream of argon.

Of course, in gas adsorption chromatography the nature of the eluent produces even more marked effects, as shown by the possibility of separating gases by adsorption methods.[38,39]

Data on the role of the solubility of the eluent in the stationary phase and of the stationary phase in the eluent have been reviewed.[2] The most striking effects are seen in vapour chromatography. However, the effects can be substantial also when traditional carrier gases are used. For example, increasing the pressure of carbon dioxide in a column with a liquid-crystalline stationary phase suppresses the characteristic meta-para selectivity of the mesophase because of the disordering of the structure caused by the dissolution of the carbon dioxide.[40]

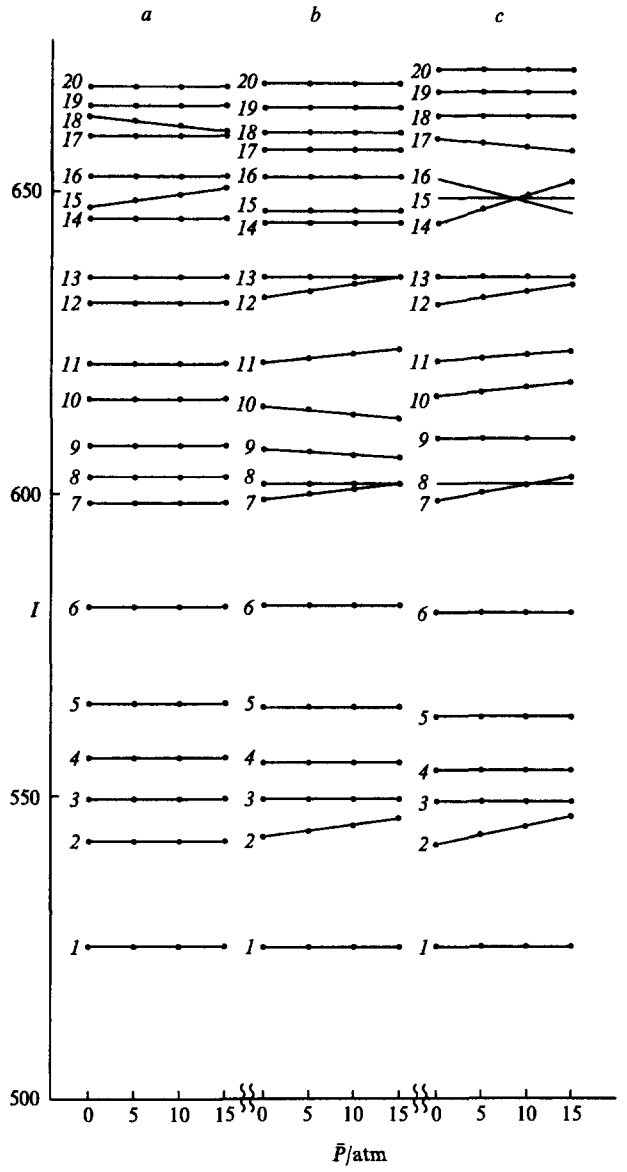


Figure 5. Dependence of the retention index of hydrocarbons at 25 °C on the average pressure in a column with octadec-1-ene with helium (*a*), argon (*b*), or carbon dioxide (*c*) as the carrier gas.[35] *1*, 2,2-dimethylbutane; *2*, cyclopentane; *3*, 2,3-dimethylbutane; *4*, 2-methylpentane; *5*, 3-methylpentane; *6*, n-hexane; *7*, methylcyclopentane; *8*, 2,2-dimethylpentane; *9*, 2,4-dimethylpentane; *10*, 2,2,3-trimethylbutane; *11*, benzene; *12*, cyclohexane; *13*, 3,3-dimethylpentane; *14*, 1,1-dimethylcyclopentane; *15*, 2-methylhexane; *16*, 2,3-dimethylpentane; *17*, 3-methylhexane; *18*, *cis*-1,3-dimethylcyclopentane; *19*, *trans*-1,3-dimethylcyclopentane; *20*, *trans*-1,2-dimethylcyclopentane.

IV. Contribution from pressure gradients to the retention and spreading of the bands

When discussing the role of the nonideality of the carrier gas and of its solubility (or adsorption) in the stationary liquid in the barochromatography regime it should not be forgotten that the contribution of these factors to the retention of sorbates in the presence of substantial pressure gradients can vary along the length of the column.

Since the specific retention volume V_g^T for a column temperature T is related to the distribution coefficient Γ (in gas – liquid chromatography) by the simple expression

$$V_g^T = \frac{\Gamma}{\rho_1} \tag{5}$$

(where ρ_1 is the density of the stationary liquid at the temperature T) we can use the expressions (1) – (4) given above to calculate the retentions.

According to van Swaay[41]

$$\ln V_g^T = \ln V_{g(P\to 0)}^T + \frac{\beta P_0}{J_3^2} . \tag{6}$$

Here $V_{g(P\to 0)}^T$ is related to the coefficient $\Gamma_{(P\to 0)}$, and J_3^2 is the pressure gradient factor,[42] equal to

$$J_3^2 = \frac{3(P_1/P_0)^2 - 1}{2(P_1/P_0)^3 - 1},$$

where P_1 and P_0 are the pressure at the inlet and at the outlet of the column respectively. The mean pressure over the length of the column is $\bar{P} = P_0/J_3^2$.

According to Everett,[30]

$$V_g^T = V_{g(P\to 0)}^T \left(1 + \frac{\beta P_0}{J_4^3}\right), \tag{7}$$

where the pressure $\bar{P} = P_0/J_4^3$ is averaged over the residence time of the sorbate in the column.

In general the pressure gradient factor can be expressed as

$$J_n^m = \frac{n}{m} \frac{(P_1/P_0)^m - 1}{(P_1/P_0)^n - 1} .$$

Equations of the following type are often used in published papers:[43,44]

$$\ln V_g^T = \ln V_{g(P\to 0)}^T + \beta P_0 J_3^4 \left[1 - aP_0(J_4^5 - J_3^4)\right], \tag{8}$$

where $a = cB_{22}/RT$ (and c is a constant).

Allowing for the dissolution of carrier gas in the stationary liquid Eqn. (6) becomes[37,45]

$$\ln V_g^T = \ln V_{g(P\to 0)}^T + \left[\beta + \lambda\left(1 - \frac{\delta \ln \gamma^\infty}{\delta X}\right)\right] \frac{P_0}{J_3^2}, \tag{9}$$

where λ is the molar solubility of the carrier gas in the stationary liquid, and $(\delta \ln \gamma^\infty)/\delta X$ is the change in activity coefficient of the sorbate as a function of its mole fraction in the stationary phase.

It follows that the slope of the straight lines in Fig. 4 is determined not by the virial coefficient B_{12} (which determines the factor β) but by its effective value[37]

$$B_{ef} = B_{12} + 0.5\lambda\left(1 - \frac{\delta \ln \gamma^\infty}{\delta X}\right) RT . \tag{10}$$

The effect of pressure and of the pressure gradients on the blurring of the bands has already been discussed in depth.[46] It was shown that the effectiveness of the column increases with pressure for the optimum flow rate of the carrier gas (the flow rate corresponding to the minimum on the curve, which defines the dependence of the height equivalent to a theoretical plate on the velocity of the gas). The latter decreases as the pressure increases. Theoretically, pressure gradients cannot lower the number of plates by more than 1/9, since

$$n^0 \geqslant n \geqslant \left(\frac{\varkappa}{J_3^2}\right)^2 n^0 , \tag{11}$$

where n^0 is the number of theoretical plates for the minimum gradient and

$$\varkappa = \sqrt{\frac{2}{(P_1/P_0)^2 + 1}}.$$

These conclusions are valid for a laminar flow of the eluent, to which Darcy's law applies. Changing to a turbulent regime by choosing an appropriate Reynolds number equalises the velocities over the cross-section and lowers the mass transport between the phases, increasing the effectiveness and the operating speed of the column.[17,18,47] Turbulence is produced not only by increasing the velocity of the mobile phase (i.e. by increasing the pressure at the column inlet) but also by increasing its density, since the Reynolds number is $d\alpha\rho/\eta$, where d is the diameter of the tube and α, ρ, and η are the linear velocity, the density, and the dynamic viscosity of the eluent respectively.

However, we should note that in addition to causing turbulence (which increases the effectiveness of the column) an increase in flow rate can disturb the thermodynamic equilibrium of the sorbate in the sorbent – carrier gas system. The equilibrium is usually shifted in the direction of a decrease in the distribution coefficient, and also it induces additional spreading of the bands.

Thus, it has been shown[48] that in a column with apiezon L (30% on hexasorb) an increase in the linear velocity of the carrier gas to 19.4 cm s^{-1} produces a relative change of 5% in the retention values. The problems resulting from the failure of the sorbate molecules to diffuse through the whole layer of liquid phase at high flow rates are even more serious when the viscosity is high. In a study[49] of polymers with a high molecular weight non-equilibrium was observed even at ordinary velocities of the carrier gas: this suggested a method of determining the retentions by extrapolating the experimental data to zero flow rate.

Kirsh et al.[50] have proposed the use of the equilibrium displacement effect to control the selectivity of chromatographic columns containing multilayer stationary phases. An experiment with columns 1.2 m long and an internal diameter of 3 mm with layers of apiezon L and 1,2,3,4,5,6-hexakis(β-cyanoethoxy)-hexane successively deposited on chromaton (from different solvents) showed that an increase from 5–8 to 500–550 cm^3 min^{-1} in the volume flow rate (at 60 °C) can lower the specific retention volumes of the sorbates by tens of per cent, the magnitude of the effect depending on the order in which the layers are deposited. The Kovats retention index can decrease by 4–13 units.

V. Chromatography with programmed pressure and flow rate of the carrier gas

Programmed flow rate of the carrier gas has been applied since 1959, usually by controlling the pressure at the column inlet.[51] It has been pointed out[16] that the use of this variant creates an alternative to temperature programming, since it makes possible the separation of mixtures of components boiling at very different temperatures as well as compressing the chromatographic bands, with a marked increase in sensitivity§. Also, since the analysis is carried out at relatively low temperatures, thermally unstable compounds can be separated, using more volatile and less thermally stable stationary phases if necessary. Both linear[52,53] and exponential[54,55] pressure programmes have been used, with or without a corresponding temperature programming. The relative advantages of packed and of capillary columns in pressure-programmed chromatography have been compared.[56,57]

There is no reference to the relationship between retention and changes in the nonideality of the eluent in papers on pressure-programmed measurements published so far, though it is evident from the above discussion that such a relationship exists.

§The height of the peak observed with a flow-type detector (for example, a flame ionisation detector) increases with the flow rate: this produces a convergence of the lower detection limits of light and of heavy sorbates.

VI. Retention of sorbates and the effectiveness of composite columns. Role of pressure gradients

Composite columns are widely used to achieve an intermediate separation of multicomponent mixtures. The selectivity is controlled by varying the ratio of the section lengths (or, more strictly speaking, the ratio of the amounts of individual sorbents). The classification of the binary sorbents and the fundamental relationships between the retention and the composition of the columns in each of the variants are discussed, in particular in our recent monograph.[46]

For low pressure gradients the retention volume on a composite column is determined by the sum of the retention volumes in the individual sections. For example, the specific retention volume in a two-section column is

$$V_g^T = \frac{g_1}{g} V_{g_1}^T + \frac{g_2}{g} V_{g_2}^T, \qquad (12)$$

where the subscripts 1 and 2 refer to the first and the second section respectively, and g is the total mass of the two stationary phases ($g = g_1 + g_2$).

However, in the presence of large pressure gradients we observe departures from this expression, which can be attributed to the difference in average pressure between the sections, and therefore to differences in the velocity of the carrier gas. The possibility of controlling the retention and the other chromatographic characteristics is determined mainly by the increased flow rate associated with the decrease in pressure along the column, so that the volume of substance entering the second section is greater than the volume corresponding to the average pressure in the first section. We can allow for this factor by using the expression

$$V_g^T = \frac{g_1}{g} V_{g_1}^T \frac{P_{0_1}}{P_0} \frac{J_3^2}{J_{3(1)}^2} + \frac{g_2}{g} V_{g_2}^T \frac{J_3^2}{J_{3(2)}^2} \cdot$$

$$= \frac{g_1}{g} V_{g_1}^T \frac{\bar{P}_1}{\bar{P}} + \frac{g_2}{g} V_{g_2}^T \frac{\bar{P}_2}{\bar{P}}, \qquad (13)$$

where $P_{0_{(1)}}$ is the pressure at the inlet of the first section; the pressure gradient factors J_3^2, $J_{3(1)}^2$ and $J_{3(2)}^2$ (and also the average pressures $\bar{P}$, $\bar{P}_1$, and $\bar{P}_2$) refer to the whole composite column and to its separate sections respectively.

Expressions for the effective values of the separation coefficients and for other quantities which characterise the retention (the coefficient Γ, associated with the volume composition, the molar retention volume, the molar composition, etc.) can be obtained in a similar way. The equation for the retention volume for unit length of the column V_L is

$$V_L = \frac{\bar{L}_1}{\bar{L}} V_{L_1} + \frac{\bar{L}_2}{\bar{L}} V_{L_2}, \qquad (14)$$

where the effective length $\bar{L}$ is equal to the product of the length of the column and of the average pressure (for each of the sections as well as for the whole column).

The linear retention index is calculated by the equation[46]

$$J = \frac{t_{R_i} - t_{R_z}}{t_{R_{(z+1)}} - t_{R_z}} + z,$$

where t_{R_i}, t_{R_z}, $t_{R_{(z+1)}}$ are the retention times of the experimental sorbate and of n-paraffins containing z and $z + 1$ carbon atoms. For a composite column

$$J = \frac{J_1 + mJ_2}{1 + m}, \qquad (15)$$

where $m = (\bar{L}_2/\bar{L}_1)(\Delta V_{L_2}/\Delta V_{L_1})$; ΔV_{L_1} and ΔV_{L_2} are the differences between the retention volumes of the standard n-paraffins (contains z and $z + 1$ carbon atoms) in the first and the second section.

From Eqn. (14) it follows, in particular, that inverting the order of the two sections in a given composite column affects the ratio of the average pressures in the sections, thus affecting also the total retention. This effect was first observed experimentally during the separation of a mixture of C_2-C_5 hydrocarbons using a composite column with mineral oil and β,β′-dicyanodiethyl ether.[23,58]

We have described[59] a method of determining propadiene and methylacetylene impurities in the propane–propene fraction in a composite column 7.1 m long consisting of two sections, one containing 20% n-heptadecane and the other 20% di-isodecyl phthalate on a diatomite carrier (2.4 and 4.7 m respectively). As can be seen from Fig. 6*a*, with the sections in the above sequence the impurities are detected as a single peak, which is convenient for operational production control. With the opposite arrangement of the sections (Fig. 6*b*) propadiene and methylacetylene give separate peaks, which allows a more detailed analysis of the chromatogram.

A 13-component mixture of naphthalene and its methyl and dimethyl derivatives was separated on a composite column with liquid-crystalline *p,p′*-azoxyphenetole and poly(ethylene glycol)-2000 on chromosorb.[60] The optimum value of $\bar{L}_2/\bar{L}$, which allows the separation of 12 peaks with a given effectiveness (broken line *A*), corresponds to the real column, consisting of a 4 m long poly(ethylene glycol)-2000 section and a 3 m long azoxyphenetole section (Fig. 7). In this case only the 2,6 and the 2,7 pair of dimethylnaphthalenes remains unresolved. Arranging the sections in the opposite order increases $\bar{L}_2/\bar{L}$ (broken line B) and allows even these isomers to be separated.

A study[61] of the spreading of sorbate bands in composite columns has shown that whereas at low pressure gradients the width ω of the peak (in units of the volume of carrier gas) is given by the formula

$$\omega^2 = \omega_1^2 + \omega_2^2 , \tag{16}$$

with large gradients the following expression should be used for the corrected peak width $\omega^0 = \omega J_3^2$:

$$(\omega^0)^2 = (\omega_1^0)^2\left(\frac{P_{0_{(1)}}}{P_0}\right)^2\left(\frac{J_3^2}{J_{3_{(1)}}^2}\right)^2 + (\omega_2^0)^2\left(\frac{J_3^2}{J_{3_{(2)}}^2}\right)^2 . \tag{17}$$

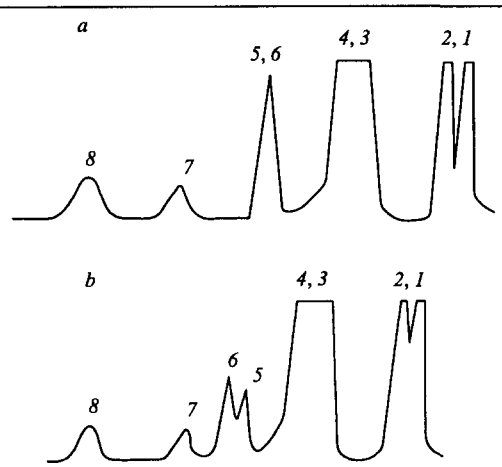


Figure 6. Chromatograms of a propane–propene fraction on a composite two-section column for different relative positions of the sections (see text).[59] *1*, ethylene; *2*, ethane; *3*, propene; *4*, propane; *5*, propadiene; *6*, methylacetylene; *7*, isobutane; *8*, n-butane.

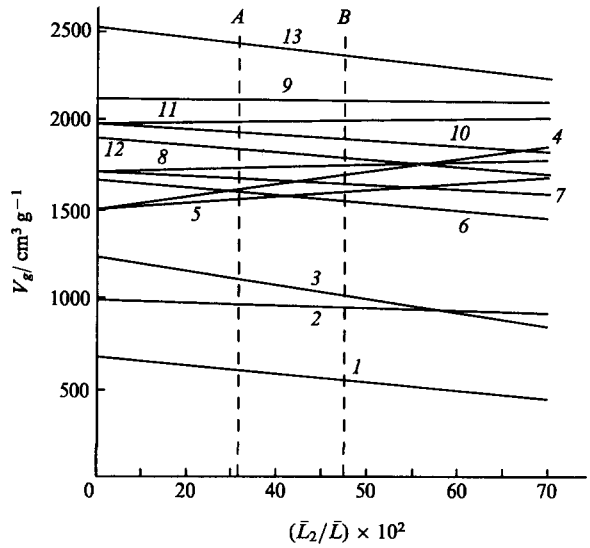


Figure 7. Plots of the retention volumes of alkylnaphthalenes against the ratio of the effective section lengths with *p,p′*-azoxyphenetole and poly(ethyleneglycol)-2000.[60] *1*, naphthalene; *2*, β-methylnaphthalene; *3*, α-methylnaphthalene; *4*, 2,6-dimethylnaphthalene; *5*, 2,7-dimethylnaphthalene; *6*, 1,7-dimethylnaphthalene; *7*, 1,3-dimethylnaphthalene; *8*, 1,6-dimethylnaphthalene; *9*, 1,2-dimethylnaphthalene; *10*, 1,5-dimethylnaphthalene; *11*, 2,3-dimethylnaphthalene; *12*, 1,4-dimethylnaphthalene; *13*, 1,8-dimethylnaphthalene.

Corresponding expressions have been obtained for the number of theoretical plates and for the degree of separation.[61]

VII. Chromatography with discontinuous changes in the pressure and/or flow rate of the carrier gas between the sections of a composite column

As was said above the retention of the sorbates (and therefore also the selectivity of the column) can be controlled by varying the ratio of the average pressures in the sections of a composite column, since this procedure varies the relative values of the volume flow rates in the sections and of the effective section lengths.

An analysis scheme[63] based on a system developed for multistage programmes includes introducing an additional flow between the sections (or extracting part of the flow emerging from the first section). By regulating the pressure of this additional flow we can control the pressure drop between the sections and thus determine the ratio of the average pressures and rates in the sections for constant inlet (P_1) and outlet pressures (P_0). A suitable assembly is shown diagrammatically in Fig. 8.

Deans and Scott[62] have shown that the relative retention of the sorbates A and B on a composite column, equal to the ratio of the reduced retention times

$$r = \frac{t'_{R(A)}}{t'_{R(B)}} \tag{18}$$

(where $t'_R = t_R - t_0 = t_0\Gamma/\beta'$, t_R is the retention time of the sorbate, t is the retention time of the non-sorbed gas, and $\beta' = \kappa/\kappa_1$ is the ratio of the volume fractions of the column occupied by the gas and the liquid phase respectively), can be expressed in terms of the ratio of the t_0 values for the two sections:

$$r = \left[\frac{\Gamma_{A_{(1)}}}{\beta'_1} + \frac{t_{0_{(2)}}}{t_{0_{(1)}}}\frac{\Gamma_{A_{(2)}}}{\beta'_2}\right] \Big/ \left[\frac{\Gamma_{B_{(1)}}}{\beta'_1} + \frac{t_{0_{(2)}}}{t_{0_{(1)}}}\frac{\Gamma_{B_{(2)}}}{\beta'_2}\right] . \tag{19}$$

The change in the pressure drop between the section produced by the insertion (or extraction) of an additional flow alters the velocities in the sections and thus affects the ratio $t_{0_{(1)}}/t_{0_{(2)}}$.

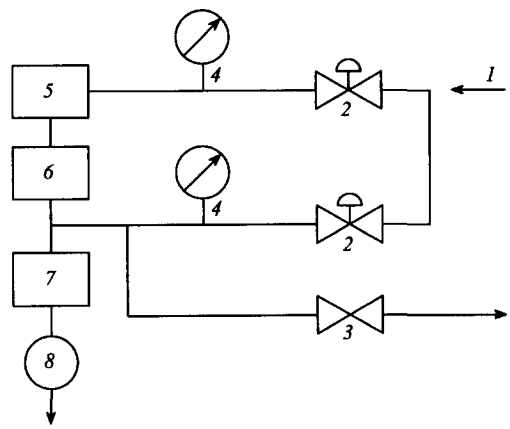


Figure 8. Two-section column with control of the flow and of the pressure drop between the sections.[68] *1*, gas flow; *2*, pressure regulator; *3*, needle valve; *4*, manometer; *5*, sample injection system; *6*, and *7*, sections of the composite column; *8*, detector.

Commercial equipment for assembling a similar scheme can be obtained from the German firms Gerstel and Siemens.

A group of papers[64,65] published in 1985 described a systematic study, with the scheme shown in Fig. 8, of the practical application of this method of analysis, called the multi-chromatographic method. In later work the technique was combined with liquid (column) chromatography and thin-layer chromatography. The method was used for 'tuning' the selectivity of capillary columns.[66,67]

Another suggested variant of barochromatography with composite columns uses an intermediate controllable throttle (Fig. 9) which allows the contribution of each section to the total retention to be varied precisely and between wide limits. Obviously, for a large enough ratio of the pressures in the sections the second section can be effectively 'switched off' (or the first, if the sections are connected in the opposite order). Thus by filling the sections with a suitable mixture of polar and of nonpolar sorbents the control range can be made to approach Rohrschneider's range of chromatographic polarities.[70]

Fig. 10 (see over) shows a series of chromatograms of a mixture of hydrocarbons and oxygen compounds recorded in a baro-chromatographic apparatus with different pressures in the sections, using poly(ethylene glycol adipate) and 1,2,3,4,5,6-hexakis-(β-cyanoethoxy)hexane on zeolite at 85°C in a stream of carbon dioxide.[68] Obviously the system offers adequate control over the selectivity of the separation: even the order in which the peaks appear in the chromatogram can be controlled.

The total effective sorption capacity is also controllable. Table 1 shows the absolute specific retention volumes $[V_g = V_g^T(273.15/T)]$ on a composite column which included sections with 1,2,3,4,5,6-tetrakis-(β-cyanoethoxy)hexane and almost com-pletely nonpolar silicon grease on chromosorb W at

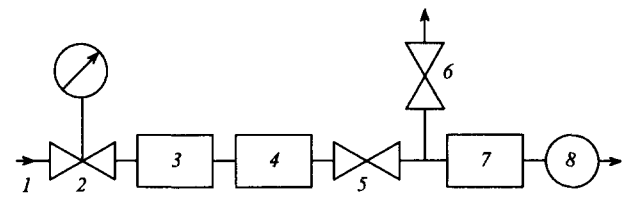


Figure 9. Barochromatography apparatus.[68,69] *1*, gas flow; *2*, pressure regulator; *3*, sample injection system; *4*, and *7*, column sections; *5*, intermediate throttle; *6*, vent to atmosphere; *8*, detector. In studies of the regime the pressure was measured also before and after the throttle *5* and after the section *7*.

353.15 K.[69] Of course in this case, since carbon dioxide was used as the eluent, the sorption capacity and the selectivity at high pressures are also affected by the nonideality of the mobile phase.

We have also examined[71] the possibility of using a universal equation for the *a priori* calculation of the retention of sorbates by binary sorbents[72] in a barochromatographic system. The equation takes the form

$$y = y_1 + \frac{X_{ef_2}}{1 - b(1 - X_{ef_2})}(y_2 - y_1)\,, \tag{20}$$

where y_1 and y_2 are the retentions of the sorbate by the binary and by the individual sorbents respectively, X_{ef_2} is the fraction of sorbent 2 in the total amount of binary sorbent (or the ratio of the length of section 2 or of its internal volume to the total length or volume of the composite column), and b is a coefficient which characterises the given system. It was shown, in particular, that whether or not the system included an intermediate throttle the average pressure in the composite column was

$$\bar{P} = \frac{L_1}{L}\frac{P_{0_{(1)}}}{J^2_{3_{(1)}}} + \frac{L_2}{L}\frac{P_{0_{(1)}}}{J^2_{3_{(2)}}}\,. \tag{21}$$

Since $\bar{P} = P_0/(J_3^2)_{ef}$, where $(J_3^2)_{ef}$ is the effective pressure gradient factor along the column, we have

$$\frac{1}{(J_3^2)_{ef}} = \frac{L_1}{L}\frac{P_{0_{(1)}}}{P_0}\frac{1}{J^2_{3_{(1)}}} + \frac{L_2}{L}\frac{1}{J^2_{3_{(2)}}}\,. \tag{22}$$

In general, if the intermediate throttle is used in conjunction with an additional gas flow (or with the partial extraction of the flow from the system) the equation for the relative retention becomes

$$r = \frac{(\Gamma_{A_{(1)}}/\beta'_1)\varkappa_{(1)} + K_V K_\alpha(\Gamma_{A_{(2)}}/\beta'_2)\varkappa_{(2)}}{(\Gamma_{B_{(1)}}/\beta'_1)\varkappa_{(1)} + K_V K_\alpha(\Gamma_{B_{(2)}}/\beta'_2)\varkappa_{(2)}} = \frac{\Gamma_{A_{(1)}}\varkappa_{l_{(1)}} + K_V K_\alpha \Gamma_{A_{(2)}}\varkappa_{l_{(2)}}}{\Gamma_{B_{(1)}}\varkappa_{l_{(1)}} + K_V K_\alpha \Gamma_{B_{(2)}}\varkappa_{l_{(2)}}}\,. \tag{23}$$

Table 1. Absolute specific retention volumes of the sorbates for different average pressures (in atm) in the sections.[69]

Sorbate	$\bar{P}_1 = 1.74$ $\bar{P}_2 = 1.36$	$\bar{P}_1 = 3.86$ $\bar{P}_2 = 1.66$	$\bar{P}_1 = 6.99$ $\bar{P}_2 = 1.65$	$\bar{P}_1 = 10.16$ $\bar{P}_2 = 1.68$	$\bar{P}_1 = 12.96$ $\bar{P}_2 = 1.68$	$\bar{P}_1 = 19.89$ $\bar{P}_2 = 2.18$
n-Hexane	13.3	11.6	6.9	5.6	5.0	4.5
Cyclohexane	24.1	19.9	12.2	10.3	9.3	8.6
Ethanol	24.7	29.8	29.0	29.7	29.2	29.6
Iso-octane	28.0	22.8	13.2	10.8	9.7	8.8
Ethyl methyl ketone	33.0	33.2	31.9	32.2	31.0	30.3
n-Heptane	29.7	23.8	14.0	11.5	10.3	9.6
Benzene	33.3	30.6	25.4	24.4	23.7	23.5
n-Octane	63.2	48.7	28.0	24.2	22.5	19.6
n-Nonane	–	–	–	51.0	47.2	42.9

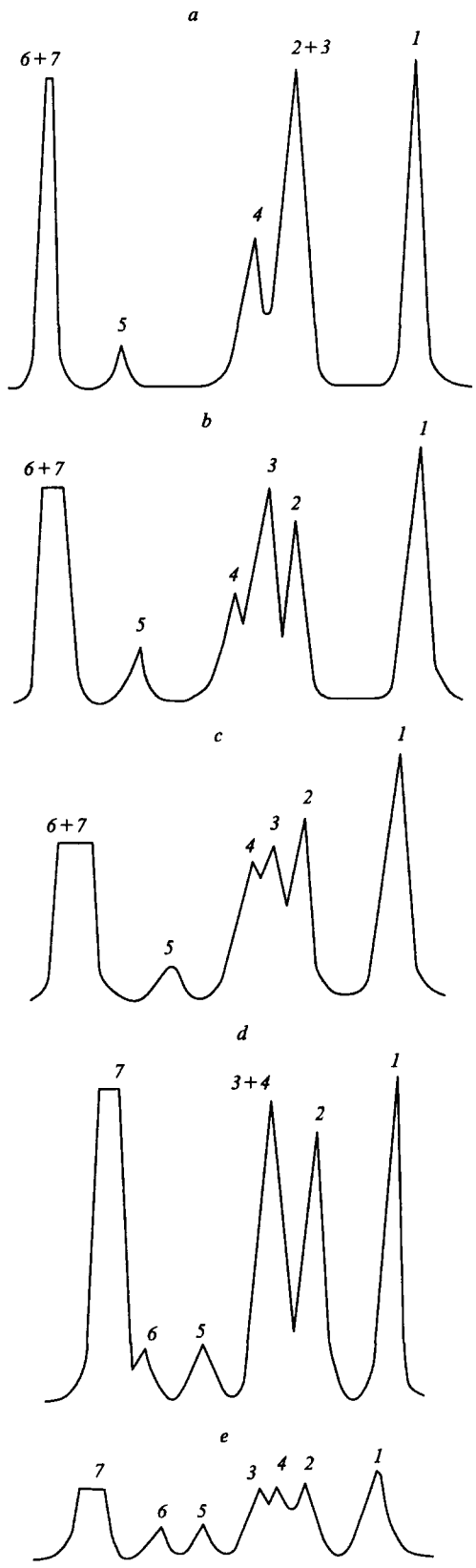


Figure 10. Chromatograms of a mixture of organic compounds obtained at different pressures in a barochromatographic column.[68] *1*, n-octane; *2*, propionaldehyde; *3*, n-nonane; *4*, acetone; *5*, butyraldehyde; *6*, ethyl methyl ketone; *7*, benzene. Average pressures in the first and the second section/atm:

	a	*b*	*c*	*d*	*e*
$\bar{P}_1$	2.24	3.79	6.67	9.69	19.72
$\bar{P}_2$	1.37	1.47	1.44	1.38	1.73

Here $K_V = [V_{\alpha_0} \pm (PV_\alpha)_{exc}]/V_{\alpha_0}$ is a coefficient which allows for the additional flow (the minus sign corresponds to the injection of an additional flow into the system, the plus sign to the extraction of part of the flow from the system). If the flow is injected (or extracted) at a point downstream from the intermediate throttle the pressure and the flow are P_2 and V_{α_2}; V_{α_0} is the flow of gas emerging from the second section (normalised to a pressure of 1 atm). If the fraction of the volume occupied by the phase $\varkappa_1$ is the same in both sections we can write

$$r = \frac{\Gamma_{A_{(1)}} + K_V K_\alpha \Gamma_{A_{(2)}}}{\Gamma_{B_{(1)}} + K_V K_\alpha G_{B_{(2)}}} . \qquad (24)$$

With sections of the same size $K_V = \bar{P}_2/\bar{P}_1$. In the absence of an additional flow (or extraction) we have $K_\alpha = 1$.

The above expressions do not allow for the nonideality of the gas or for the effect of pressure on its solvent power for the sorbate. A correction for the former effect can be inserted into K_α and K_V (by using the equation $PV = ZRT$), and a correction for the latter effect can be inserted into Γ [see Eqn. (1)].

VIII. Modifications of the gradient barochromatography method

The examples of the methods of controlling chromatographic processes discussed above can be used in practice to identify the optimum conditions of analysis of multicomponent mixtures while using the smallest possible number of stationary phases.[73] Since the use of composite columns with a controlled ratio of effective section lengths allows us to evaluate the chromatographic properties of sorbents of moderately high selectivity the presence of several sections with 6–10 sorbents undergoing different intermolecular interactions with the sorbates should enable us to solve a wide range of analytical problems by gas chromatography.

Furthermore in the chromatographic identification of substances from multiple retention spectra[74] an unambiguous correspondence between peaks obtained in columns with sorbents of different nature can be established by a series of measurements on columns with a gradually varying selectivity.[74–76] The barochromatographic method is a convenient way of obtaining the required series of chromatograms (see Fig. 10).

In a proposed variant of the design of the column, three sections are connected in a triangular arrangement. They contain sorbents of different types, and controllable flow resistances are mounted between the sections. The location of the points of insertion (or extraction) of the gas into or out of the system and the point at which the gas flow is led from the sections to the detector can be varied to produce the required sequence of sections.

Multielement spectra can be obtained in a cruciform barochromatographic column[77] (a modification of a column already described),[78] which includes sections with different sorbents, intermediate throttles, and detectors.

The range of possible applications of composite columns can be extended by the following methods: by operating both sections under vacuum conditions, which combine large values of $\bar{P}_1/\bar{P}_2$ with adequate resolution; by operating the first section under near-atmospheric pressure and the second in a vacuum,[79,80] which offers (as before) a wider range of selectivity control and a saving in eluent without introducing experimental complications or allowing nonideality to appear in the carrier gas; by assembling combined variants of chromatography,[81] in particular by operating the first section in the supercritical fluid chromatography regime and the second in the barochromatography or traditional gas chromatography regime; by programming the pressure in the course of the analysis in one or both of the sections (for example, by varying the pressure at the inlet to the first section, by varying the throttle setting, by varying the pressure of the gas flow inserted between the sections or by varying the flow of

gas vented to the atmosphere); by combining the partition and the adsorption regime; by programming the temperature in one or both sections; by using sections of different diameter, including narrow packed columns and capillary columns; by inserting samples and standards at intermediate points (between the sections); by using several parallel sections; by extracting from the system some components or fractions separated in the first section; by combining barochromatography with other multistage schemes (reverse, semireverse, parallel exhaust, etc.).

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