Retention in gas chromatography when there is a large pressure drop in different sections of a coupled column

A. V. Bulanova[a] *and O. N. Bezrukova*[b]*

[a]*Samara State University,*
443011 Samara, 1 ul. Akad. Pavlova, Russian Federation.
Fax: 007 (846 2) 34 5417
[b]*Institute of Physical Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: 007 (095) 952 0065. E-mail: larionov@lmm.pyche.msk.su

Methods providing control of the selectivity of a coupled column were compared. The method of vacuum barochromatography has been developed. This method allows the selectivity of a coupled column to be controlled over a broad range of the Rohrschneider scale using medium carrier-gas pressures. The possibility of identifying the components of a complex mixture based on chromatographic spectra was considered.

Key words: gas chromatography, coupled column, barochromatography, vacuum barochromatography, identification, chromatographic spectrum.

Fine control of the selectivity of a chromatographic system makes it possible to extend the capabilities of chromatography regarding both separation of complex mixtures and identification of their components.

There are several approaches to the solution of this problem. One of them involves the use of mixed stationary phases,[1,2] and another method is based on the use of coupled columns.

Attempts have been made[3] to control the selectivity using a two-section coupled column, in which the length of the second section was changed using a vernier. It was found that fine control is hard to achieve in this way, because the number of graduation lines in the vernier is limited.

Another approach involves affecting the mobile phase; in particular, the use of intermediate control of pressure,[4–6] which has been illustrated for numerous examples.[7,8]

This method is based on the use of external valves to control the pressure between the columns and the directions of the main and auxiliary flows of the gaseous eluent. This method is used mostly for reverse purging and for the transfer of the main peaks, while the carrier-gas pressure in the system is controlled either by discharging some of the eluent after the first section or by introducing an additional flow to the second section. It has been shown that the retention of substance A with respect to the retention of substance B (relative retention *r*) in a coupled column can be expressed by relation (1).[8]

$$r = \frac{\dfrac{K_{c(A)1}}{\beta_1} + \left(\dfrac{t_{m(2)}}{t_{m(1)}}\right)\cdot\left(\dfrac{K_{c(A)2}}{\beta_2}\right)}{\dfrac{K_{c(B)1}}{\beta_1} + \left(\dfrac{t_{m(2)}}{t_{m(1)}}\right)\cdot\left(\dfrac{K_{c(B)2}}{\beta_2}\right)} \tag{1}$$

Here $K_{c(A)}$ and $K_{c(B)}$ are the coefficients of the distribution of sorbates A and B, *i.e.*, the ratios between the concentrations of substances A and B, respectively, in the stationary liquids and in the gaseous eluent; β_1 and β_2 are the ratios of the volume occupied by the carrier gas to that occupied by the stationary liquid in the first and second sections of a coupled column; $t_{m(1)}$ and $t_{m(2)}$ are retention times for a non-sorbed substance in the first and second sections.

The method described above (the Deans method) has been further developed and is called multichromatography.[9–11] It includes repeated chromatography of the same sample at different selectivities of a two-section coupled column. The selectivity is changed by changing the amount of carrier gas in the second section, which is achieved by the additional introduction of gas into the joining unit.

Another method, called barochromatography, has been suggested.[12,13] In this case, the selectivity of the coupled column changes due to a pressure drop between sections containing stationary liquids with opposite polarities, while the amount of eluent in the system remains constant. The pressure drop is created using a controlled resistance, placed after the first section. It

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was shown that retention of a sorbate in a coupled column is related to the pressure in the sections through expression (2).[12]

$$V_R^0 = V_{R(1)}^0 \frac{\bar{p}_1}{\bar{p}} + V_{R(2)}^0 \frac{\bar{p}_2}{\bar{p}} \qquad (2)$$

Here $V_R{}^0$, $V_{R(1)}{}^0$, and $V_{R(2)}{}^0$ are the corrected retention volumes of the sorbate in the coupled column and in its first and second sections, respectively; $\bar{p}$, $\bar{p}_1$, and $\bar{p}_2$ are the average carrier gas pressures in the coupled column and in its first and second sections.

The features distinguishing the Deans method or barochromatography from multichromatography have been identified and the possibility of using multichromatography in high performance liquid chromatography has been considered.[14]

Thus, imparting other "active" functions,[15] in addition to the transport properties, to a gaseous eluent makes it possible to make use of a number of new possibilities for controlling the selectivity of chromatographic systems for the separation of complex mixtures.

The main goal of this study was to carry out a comparative analysis of the Deans method and barochromatography on coupled columns and to consider the effect of the average pressure in the sections on the retention of substances.

In fact, the chromatographic process in a coupled column can be accomplished by varying the amount of carrier gas in the sections. This results in a violation of the integrity of the system; the sample under analysis either decreases (if a part of the flow is discharged after the first section) or is diluted (if an additional amount of the carrier gas is introduced in the second section). This decreases the sensitivity of the detector with respect to the components of the sample under analysis, which is especially undesirable when the substance analyzed is present in a low concentration. Therefore, a version in which the difference between the pressures in the sections is created without changing the amount of the eluent would be preferable.

It is useful to analyze Eq. (1) and to consider the effect of the average pressure in the sections and in the whole coupled column on the retention of substances.

The retention time of a non-sorbed component in each section can be calculated from Eq. (3):[16]

$$t_m = \frac{LS}{F_c j} \cdot V_0, \qquad (3)$$

where L is the length of the section; S is the area of the cross-section; F_c is the volume velocity of the carrier gas; j is a correction factor taking into account the compressibility of the carrier gas; V_0 is the part of the column (section) filled by the gaseous eluent. Later, we shall assume that L, S, and V_0 are identical for each column.

The following expressions can be written for the volume velocities and pressures of the carrier gas at the outlets of the first and the second sections

$$\frac{F_{c0(1)}}{F_{c0(2)}} = \frac{p_{0(2)}}{p_{0(1)}}, \qquad (4)$$

and for the corresponding average values:

$$\frac{\bar{F}_{c(1)}}{\bar{F}_{c(2)}} = \frac{\bar{p}_2}{\bar{p}_1}. \qquad (5)$$

Thus, the ratio between the retention times of a non-sorbed substance in the first and second sections of a coupled column can be expressed in the following way:

$$\frac{t_{m(2)}}{t_{m(1)}} = \frac{L_2 S_2}{F_{c0(2)} j_2} \cdot \frac{F_{c0(1)} j_1}{L_1 S_1}. \qquad (6)$$

At $S_1 = S_2$:

$$\frac{t_{m(2)}}{t_{m(1)}} = \frac{L_2}{L_1} \cdot \frac{F_{c0(1)} j_1}{F_{c0(2)} j_2} = \frac{L_2}{L_1} \cdot \frac{\bar{F}_{c(1)}}{\bar{F}_{c(2)}}. \qquad (7)$$

If the amounts of the carrier gas in the first and second sections are constant, this can be written:

$$\frac{t_{m(2)}}{t_{m(1)}} = \frac{L_2}{L_1} \cdot \frac{\bar{p}_2}{\bar{p}_1}. \qquad (8)$$

By substituting expression (8) in Eq. (1), we obtain

$$r = \frac{\dfrac{K_{c(A)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{K_{c(A)2}}{\beta_2}}{\dfrac{K_{c(B)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{K_{c(B)2}}{\beta_2}}. \qquad (9)$$

In the general case, when the volume velocity is a crucial parameter, expression (9) assumes the following form

$$r = \frac{\dfrac{K_{c(A)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{F}_{c(1)}}{\bar{F}_{c(2)}} \cdot \dfrac{K_{c(A)2}}{\beta_2}}{\dfrac{K_{c(B)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{F}_{c(1)}}{\bar{F}_{c(2)}} \cdot \dfrac{K_{c(B)2}}{\beta_2}}. \qquad (10)$$

The retention of sorbate A with respect to sorbate B in the first (r_1) and second (r_2) sections can be expressed either as the ratio of the distribution coefficients or as the ratio of some other retention characteristics, for example, absolute specific retained volumes (V_g)

$$r_1 = \frac{V_{g(A)1}}{V_{g(B)1}} = \frac{\dfrac{K_{c(A)1}}{\beta_1}}{\dfrac{K_{c(B)1}}{\beta_1}} \quad \text{and} \quad r_2 = \frac{V_{g(A)2}}{V_{g(B)2}} = \frac{\dfrac{K_{c(A)2}}{\beta_2}}{\dfrac{K_{c(B)2}}{\beta_2}}, \qquad (11)$$

where $V_{g(A)1}$, $V_{g(B)1}$, and $V_{g(A)2}$, and $V_{g(B)2}$ are absolute specific retained volumes of sorbates A and B in the first and second sections, respectively. If we solve Eq. (11) for $K_{c(A)1}/\beta_1$ and $K_{c(A)2}/\beta_2$ and substitute the resulting expressions in Eq. (9), which relates the relative retention to the carrier gas pressures in the sections, we obtain:

$$r = \frac{r_1 \dfrac{K_{c(B)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot r_2 \dfrac{K_{c(B)2}}{\beta_2}}{\dfrac{K_{c(B)1}}{\beta_1} + \dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{K_{c(B)2}}{\beta_2}} . \qquad (12)$$

Now we divide the numerator and denominator of Eq. (12) by $K_{c(B)1}/\beta_1$:

$$r = \frac{r_1 + r_2 \cdot \left(\dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{K_{c(B)2}}{\beta_2} \cdot \dfrac{\beta_1}{K_{c(B)1}} \right)}{1 + \left(\dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{K_{c(B)2}}{\beta_2} \cdot \dfrac{\beta_1}{K_{c(B)1}} \right)} . \qquad (13)$$

Taking into account that $K_c \sim V_g\rho$, where ρ is the density of the stationary liquid, Eq. (13) can be represented in the following form:

$$r = \frac{r_1 + r_2 \cdot \left(\dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{\beta_1}{\beta_2} \cdot \dfrac{V_{g(B)2}}{V_{g(B)1}} \cdot \dfrac{\rho_2}{\rho_1} \right)}{1 + \left(\dfrac{L_2}{L_1} \cdot \dfrac{\bar{p}_2}{\bar{p}_1} \cdot \dfrac{\beta_1}{\beta_2} \cdot \dfrac{V_{g(B)2}}{V_{g(B)1}} \cdot \dfrac{\rho_2}{\rho_1} \right)} . \qquad (14)$$

If we denote the expression in parentheses of Eq. (14) by the symbol f, we obtain the general relation

$$r = \frac{r_1 + r_2 f}{1 + f} . \qquad (15)$$

Thus, by varying the ratio between the average pressures in the sections of a coupled column ($\bar{p}_2/\bar{p}_1$), one can control the relative retention of components. It has been noted[13] that to control the selectivity of a coupled column over a wide range, the difference between the average pressures in the sections must be quite large. The theoretical derivation presented above also supports this inference.

It is clear that the theoretical representations for the methods mentioned above[8,12,13] are formally identical; however, as has already been noted, barochromatography, in which the amount of carrier gas in the system does not vary, has a number of advantages. The fact that this version is accomplished with simple equipment and requires no nonstandard instruments is among its advantages.

The foregoing is valid in the case where nonideality of the gas phase can be neglected. At high pressures, when the relationship between the retention in a coupled column and in its sections begins to deviate from linearity, it is necessary to take into account the dependence of the coefficient of the distribution of a sorbate K_c on the second virial coefficient B_{12} in the equation of state for a mixture of sorbate with a carrier gas:[17]

$$K_c = K_{c(p\to 0)} \cdot e^{\beta p} , \qquad (16)$$

where $K_{c(p\to 0)}$ corresponds to the distribution coefficient at $p = 0$; β is here a coefficient characterizing the nonideal behavior of a gaseous eluent: $\beta = (2B_{12} - V_1^{\infty})/RT$, where V_1^{∞} is the partial molar volume of the sorbate at its infinite dilution in the stationary liquid, and B_{12} is the mixed virial coefficient.

Thus, in the work with coupled columns under the conditions of gradient barochromatography, *i.e.*, with a large pressure drop between the sections, the relative retention of a sorbate should be described by Eq. (14) with allowance for the nonideal behavior of the gas phase.

A study of the broadening of chromatographic zones of sorbates in coupled columns has shown that at small pressure gradients for peak width ω (expressed in units of carrier gas volume), the following relation holds (indices 1 and 2 refer to the numbers of the sections)[16]

$$\omega^2 = \omega^2{}_1 + \omega^2{}_2, \qquad (17)$$

whereas at large pressure gradients for the corrected peak width $\omega^0 = \omega \cdot j$ (see Ref. 16),

$$\left(\omega^0\right)^2 = \left(\omega_1^0\right)^2 \cdot \left(\frac{p_{01}}{p_0}\right)^2 \left(\frac{j}{j_1}\right)^2 + \left(\omega_2^0\right)^2 \cdot \left(\frac{j}{j_2}\right)^2 , \qquad (18)$$

where p_{01} and p_0 are the pressures at the outlet of the first section and in the coupled column, respectively.

In the development of barochromatography, several approaches to the extension of the capabilities of gradient barochromatography on coupled columns have been considered.[18–21] Relations describing retention in chromatographic systems of this type have been obtained,[18] and a modification of the equation for the retention with mixed stationary phases has been reported;[22] this modification was suitable for coupled columns whose sections operate at different pressures. The equation has the following form

$$y = y_1 + \frac{x_{\mathrm{eff}_2}}{1 - b(1 - x_{\mathrm{eff}_2})} \cdot (y_2 - y_1) , \qquad (19)$$

where y, y_1, and y_2 are the values of retention of a sorbate by a barochromatographic system and by individual stationary phases in the first and second sections, respectively; x_{eff_i} is the effective mass fraction of stationary phase i in a binary sorbent: $x_{\mathrm{eff}_i} = x_i \dfrac{\bar{p}_i}{\bar{p}}$ (x_i is the mass fraction of stationary phase i, $x_i = g_i/(g_1 + g_i)$, g_1 and g_2 are the weights of the stationary liquids in the first and second sections); b is a coefficient characterizing possible deviations of the dependence of y on x_{eff} from linearity, which are due to the effect of additional factors such as nonuniformity of the bulk weight of the sorbent along the column, adsorption on the surface of a solid support, nonideal behavior of the gas phase, *etc.*

In particular, it was found[18] that irrespective of the intermediate resistance, the average pressure in a coupled column is expressed as

$$\bar{p} = \frac{L_1}{L}\frac{p_{01}}{j_1} + \frac{L_2}{L}\frac{p_0}{j_2}, \tag{20}$$

where L is the length of the coupled column. Since $\bar{p} = p_0/j_{\text{eff}}$ (j_{eff} is the effective value of the correction factor for compressibility of the carrier gas), we obtain[18]

$$\frac{1}{j_{\text{eff}}} = \frac{L_1}{L}\cdot\frac{p_{01}}{p_0}\cdot\frac{1}{j_1} + \frac{L_2}{L}\cdot\frac{1}{j_2}. \tag{21}$$

It has been shown[16] that the absolute specific retained volume (V_g) for coupled columns, with allowance for a pressure gradient, can be calculated from the following equation

$$V_g = \frac{g_1}{g}V_{g_1}\frac{j\,p_{01}}{j_1 p_0} + \frac{g_2}{g}V_{g_2}\frac{j}{j_2}, \tag{22}$$

where V_{g_1}, V_{g_2}, g_1, and g_2 are the absolute specific retained volumes of the sorbates and the weights of the stationary liquid phases in the first and second sections, respectively; j_1 and j_2 are factors taking into account pressure gradients in the first and second sections of a coupled column, respectively; p_{01} and p_0 are the pressures at the outlets of the first and second sections; $g = g_1 + g_2$; $g_i/g = x_i$.

Since the average pressures in the column are $\bar{p} = p_0/j$; and $\bar{p}_i = p_0/j_i$, respectively, it is expedient to present Eq. (22) in the following form:[18]

$$V_g = \left[x_1\frac{\bar{p}_1}{\bar{p}}\right]V_{g1} + \left[x_2\frac{\bar{p}_2}{\bar{p}}\right]V_{g2}, \tag{23}$$

where $x_1\frac{\bar{p}_1}{\bar{p}}$ and $x_2\frac{\bar{p}_2}{\bar{p}}$ are the effective mass fractions (x_{eff_1} and x_{eff_2}) of the stationary phases in the first and second sections. Thus, it is assumed that a variation of the pressure distribution in the sections of the column is equivalent to a variation of the ratios between the amounts of individual stationary phases in these sections.

A version of gradient barochromatography on coupled columns that makes it possible to extend the possibilities of this method has been suggested.[19,20] According to this approach, a vacuum is developed in the second section. This permits the necessary pressure gradient in a coupled column to be established without using high carrier-gas pressures at the outlet.

Vacuum barochromatography on coupled columns has not been described in detail in the literature; however, the possibility of using it for qualitative analysis of complex mixtures has been considered.[21] Therefore, it was expedient to continue studies dealing with this approach. It is this version that we used in the experimental part of our work.

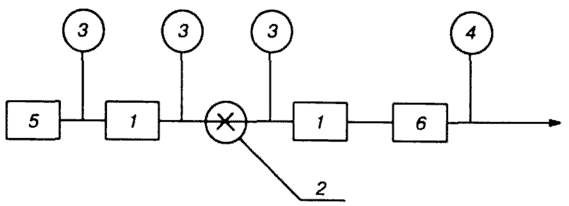

Fig. 1. Scheme of a barochromatographic system involving coupled columns: sections of a coupled column (*1*), controlling valve (*2*), manometers (*3*), vacuum gage (*4*); evaporation chamber (*5*); detector (*6*).

Experimental

The work was carried out using an LKhM-80 M6 chromatograph with a thermo-conductivity detector. Steel tubes (2 m×3 mm) served as the sections of a coupled column. The pressure at the inlet of the coupled column did not exceed $4.5 \cdot 10^5$ Pa. The vacuum in the second section was created using a water-jet pump. Figure 1 shows a scheme of the barochromatographic system; the second section of the coupled column operated at reduced pressure. The controlling valve located between the sections was placed outside the thermostat containing the columns and was connected to the sections through capillaries.

Two series of experiments were performed. In the first series, the coupled column contained Apieson L and 1,2,3-tris(2-cyanoethoxy)propane as stationary phases. The stationary phases (20% (w/w)) were applied on Chromaton N-AW. Rohrshneider standards served as sorbates.[23]

In the second series, the sections contained 15% Apieson L and poly(ethylene glycol) 20M (PEG-20M) applied on Chromaton N-AW as the stationary phases. *n*-Alkanes, *n*- and *iso*-alcohols, aromatic hydrocarbons, ketones, aldehydes, esters, and cyclic hydrocarbons served as sorbates.

To characterize the chromatographic properties of the coupled column, polarity factors were calculated from the equation[16]

$$\Phi = \frac{I - I_{\text{Ap}}}{100}, \tag{24}$$

where I and I_{Ap} are the retention indices for a coupled column and for Apieson, which are found from the equation[24]

$$I = 100\frac{\log t'_{\text{R}(x)} - \log t'_{\text{R}(z)}}{\log t'_{\text{R}(z+1)} - \log t'_{\text{R}(z)}} + 100z, \tag{25}$$

where $t'_{\text{R}(x)}$, $t'_{\text{R}(z)}$, and $t'_{\text{R}(z+1)}$ are the adjusted retention times for the sorbate and for *n*-alkanes with z and $z+1$ carbon atoms in the molecules.

The effective mass fraction of 1,2,3-tris(2-cyanoethoxy)propane was calculated from Eq. (19).

Qualitative analysis was based on chromatographic spectra, which consisted of sets of the differences between the retention indices of a component on a phase of an intermediate polarity and on Apieson L.

Figure 2 shows chromatograms for mixtures of organic compounds of various classes at various x_{eff_2}.

Table 1 presents the capacity factors of the coupled column calculated for various sorbates from the following equation[25]

Table 1. Capacity factors (k) of a coupled column operating under conditions of gradient barochromatography (Apieson-L and 1,2,3-tris(2-cyanoethoxy)propane (TCEP) as stationary phases, T = 383 K)

Sorbate	Effective mass fraction of TCEP, x_{eff_2}								
	0	0.113	0.174	0.251	0.745	0.789	0.847	0.923	1
Butan-2-one	2.425	2.347	2.265	2.225	2.097	2.087	2.071	2.029	1.977
Nitromethane	3.345	3.789	4.058	4.156	5.578	5.825	5.973	6.190	6.459
Benzene	4.378	3.789	3.534	3.400	2.035	2.087	2.071	2.069	1.977
Isobutyl acetate	5.170	4.298	4.058	3.779	3.034	2.895	2.847	2.736	2.707
Toluene	7.797	7.125	6.879	6.545	4.252	3.989	3.759	3.327	3.155
Pyridine	7.797	7.695	7.802	7.877	7.955	8.019	8.127	8.199	8.296

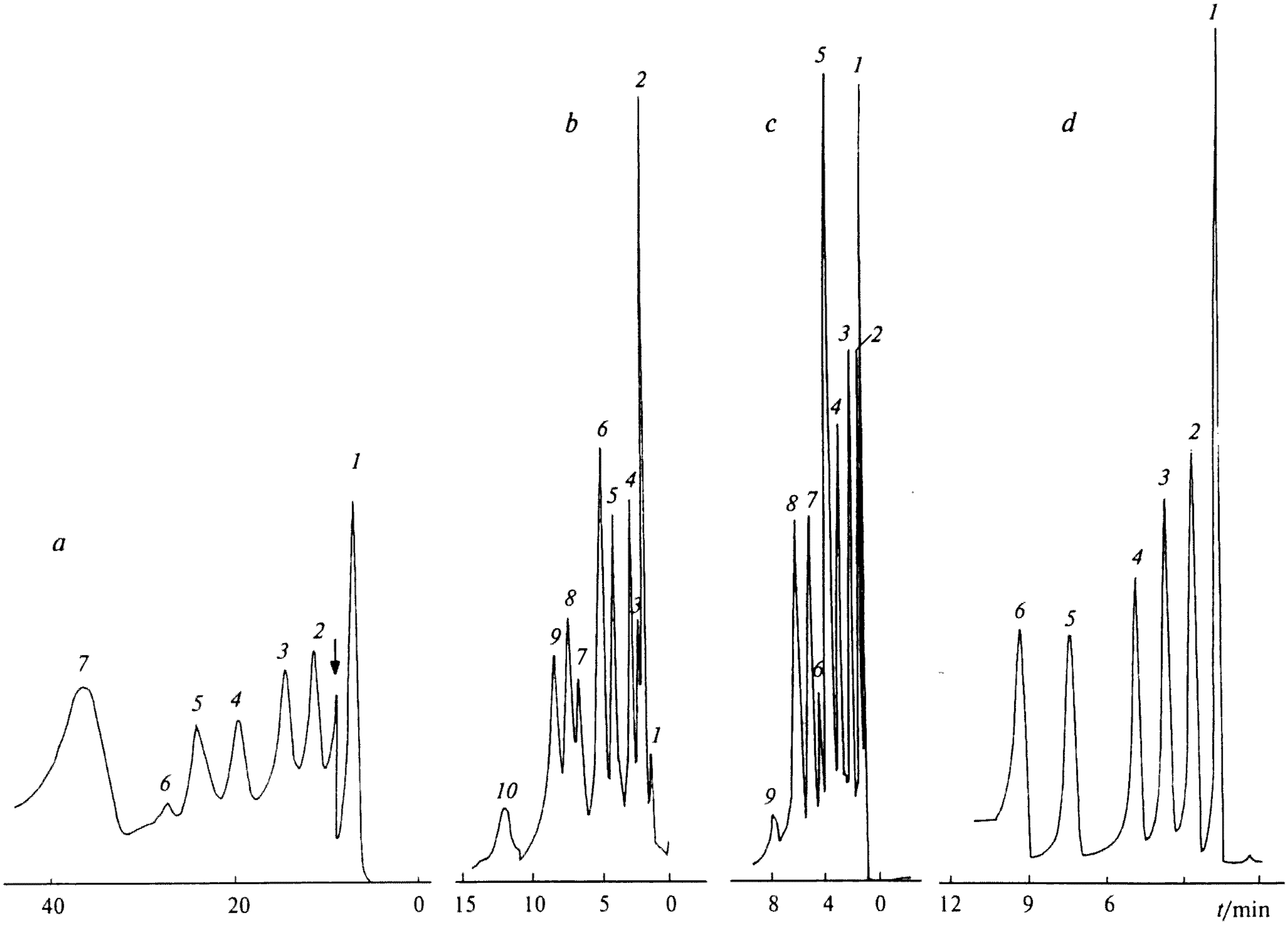

Fig. 2. Chromatograms of mixtures obtained on a coupled column operating under the conditions of gradient barochromatography (Apieson L and 1,2,3-tris(2-cyanoethoxy)propane as stationary phases in the first and second stages, respectively, T = 383 K). The arrow marks switching of the detector. *a.* x_{eff_2} = 0: ethanol (*1*), butan-2-one (*2*), nitromethane (*3*), benzene (*4*), isobutyl acetate (*5*), octane (*6*), toluene+pyridine (*7*). *b.* x_{eff_2} = 0.174: pentane (*1*), ethanol (*2*), hexane (*3*), butan-2-one (*4*), benzene (*5*), nitromethane+isobutyl acetate (*6*), octane (*7*), toluene (*8*), pyridine (*9*), nonane (*10*). *c.* x_{eff_2} = 0.213: pentane (*1*), ethanol (*2*), butan-2-one (*3*), benzene (*4*), isobutyl acetate (*5*), octane (*6*), toluene+nitromethane (*7*), pyridine (*8*), nonane (*9*). *d.* x_{eff_2} = 0.789: ethanol (*1*), butan-2-one+benzene (*2*), *iso*-butyl acetate (*3*), toluene (*4*), nitromethane (*5*), pyridine (*6*).

$$k = \frac{t'_{\mathrm{R}}}{t_{\mathrm{m}}}. \qquad (26)$$

The dependence of the capacity factor of the column on $x_{\mathrm{eff}2}$ is illustrated in Fig. 3.

The absolute specific retained volumes[16] were calculated from experimental data and from Eq. (19). The experimental and calculated values are presented in Tables 2 and 3.

Characteristics of the chromatographic spectra are listed in Table 4. The results of group identification of components of a

Table 2. Logarithmic indices (*I*) and relative retentions (*r*) of sorbates (with benzene as the standard) obtained experimentally with a coupled column operating under conditions of barochromatography and calculated from Eq. (19) (Apieson L and PEG-20M as stationary phases)

Sorbate	x_{eff_2}											
	0		0.508				0.796				1	
			Exp.		Calc.		Exp.		Calc.			
	I	*r*	*I*	*r*	*I*	*r*	*I*	*r*	*I*	*r*	*I*	*r*
Propan-2-one	441	0.65	648	0.78	648	0.78	751	0.82	751	0.82	815	0.85
Butan-2-one	552	0.81	758	0.91	754	0.91	846	0.92	848	0.92	904	0.94
Pentan-2-one	646	0.95	847	1.02	846	1.02	932	1.02	933	1.02	983	1.02
Hexan-3-one	750	1.10	941	1.13	927	1.10	1002	1.10	1009	1.10	1058	1.02
Methyl acetate	470	0.60	664	0.80	652	0.80	748	0.82	755	0.82	824	0.86
Ethyl acetate	551	0.90	741	0.89	725	0.90	810	0.89	818	0.90	879	0.91
Propyl acetate	653	0.95	842	0.99	829	0.99	908	1.00	915	1.00	967	1.01
Buthyl acetate	756	1.11	945	1.13	933	1.11	1010	1.10	1016	1.11	1066	1.11
Isobutyl acetate	712	1.04	890	1.07	884	1.04	957	1.04	960	1.04	1055	1.04

Table 3. Absolute specific retained volumes (V_g) found experimentally with a coupled column operating under conditions of gradient barochromatography and calculated from Eq. (19) (Apieson L and 1,2,3-tris(2-cyanoethoxy)propane (TCEP) as stationary phases, T = 383 K)

Sorbate	Effective mass fraction of TCEP, x_{eff_2}											b*
	0	0.277			0.336			0.447			1	
		Exp.	Calc.	Δ (%)	Exp.	Calc.	Δ (%)	Exp.	Calc.	Δ (%)		
Ethanol	3.39	6.60	6.48	1.8	7.11	7.21	1.4	8.66	8.66	0.0	17.83	−0.406
Butan-2-one	10.91	12.79	12.70	0.7	13.14	13.18	0.3	14.21	14.21	0.0	24.73	−1.577
Benzene	26.79	21.34	22.25	4.3	22.08	21.87	0.9	21.34	21.34	0.0	20.14	0.822
n-Butanol	17.25	23.36	21.75	6.9	23.90	24.22	1.3	26.97	26.97	0.0	45.96	−0.579
Nitromethane	6.99	26.97	26.68	0.4	29.80	31.11	4.4	39.72	39.72	0.0	88.19	−0.197
Pyridine	44.49	53.25	53.13	0.2	54.80	55.34	1.0	59.97	59.97	0.0	98.40	−1.007
Octane	63.37	44.39	44.33	0.1	42.01	40.78	2.9	34.52	34.52	0.0	9.54	0.300
Nonane	128.85	88.92	89.94	1.1	85.56	82.68	3.4	69.86	69.86	0.0	18.55	0.297

* See Eq. (19).

mixture based on chromatographic spectra formed using a coupled column operating under the conditions of gradient barochromatography (with Apieson L and PEG-20M as stationary phases), are presented below.

x_{eff_2}	Groups of compounds identified
0.340	*n*-Alcohols, esters, *iso*-alcohols
0.619	Aromatic hydrocarbons, aldehydes, *n*-alcohols, ketones, *iso*-alcohols
0.679	Aromatic hydrocarbons, aldehydes, *iso*-alcohols, ketones, esters, *n*-alcohols
0.766	Aromatic hydrocarbons, aldehydes, *iso*-alcohols, ketones, *n*-alcohols, esters

Results and Discussion

The chromatograms (see Fig. 2) illustrate the variation of the selectivity of a coupled column as a function of the average pressures in the sections. For example, at $x_{eff_2} = 0$ (p_1 = 4.5, p_2 = 0.5; p_{01} = 4.4, p_2 = 1.2 atm), toluene and pyridine come out as a single peak; at x_{eff_2} = 0.174 (p_1 = 4.5, p_2 = 0.7; p_{01} = 4.2, p_2 = 1.5 atm), toluene is separated from pyridine but nitromethane emerges together with isobutyl acetate; at x_{eff_2} = 0.213 (p_1 = 4.5, p_2 = 0.8; p_{01} = 4.1, p_2 = 1.6 atm), nitromethane is retained better and is thus separated from isobutyl acetate; however, in this case it forms a single peak with toluene; at x_{eff_2} = 0.789 (p_1 = 4.6, p_2 = 0.9; p_{01} = 4.2, p_2 = 0.3 atm), nitromethane comes out as an individual peak, but due to the variation of the polarity factor x, benzene forms a common peak with butan-2-one. Thus, the effect of a sharp pressure drop between the sections enhanced by the use of stationary phases of different polarities, makes it possible to control finely the selectivity of a coupled column.

Broadening of chromatographic zones is a significant problem in vacuum barochromatography on coupled columns. Calculations carried out for peaks of pyridine, isobutyl acetate, and ethanol showed that broadening of the zone amounts to $9.7 \cdot 10^{-3}$, $8.2 \cdot 10^{-3}$, and $6.4 \cdot 10^{-3}$%, respectively, per Torr of pressure drop.

For most sorbates, the capacity factor of a coupled column decreases as x_{eff_2} increases. The increase in the capacity factor observed in the case of nitromethane and

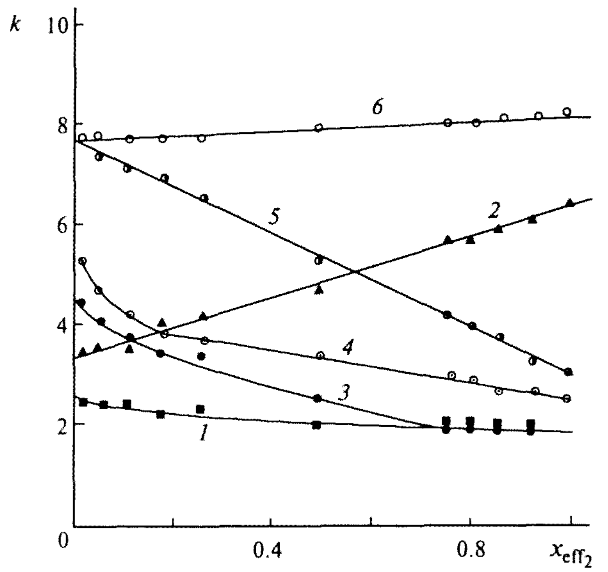

Fig. 3. Dependence of the capacity factor of a coupled column operating under conditions of gradient barochromatography on the effective composition of a binary sorbent. Stationary phases: Apieson L and 1,2,3-tris(2-cyanoethoxy)propane in the first and second stages, respectively, T = 383 K. Butan-2-one (*1*), nitromethane (*2*), benzene (*3*), isobutyl acetate (*4*), toluene (*5*), pyridine (*6*).

Table 4. Characteristics of chromatographic spectra (ΔI) obtained with a coupled column operating under conditions of gradient barochromatography ($\Delta I = I_{x_{\mathrm{eff}_2} > 0} - I_{x_{\mathrm{eff}_2} = 0}$) (Apieson L and PEG-20M as stationary phases, T = 393 K)

Sorbate	Effective mass fraction of PEG 20M (x_{eff_2})				
	0.340	0.619	0.679	0.766	1
Benzene	73	153	179	197	258
Toluene	164	275	305	344	445
Methanol	120	191	203	203	272
Ethanol	107	199	235	204	317
Propanol	146	234	274	300	403
Butanol	143	208	252	269	332
Pentanol	140	249	272	293	366
Isobutanol	105	192	246	250	344
Isopentanol	127	223	230	260	338
Acetone	83	147	163	118	266
Acetylacetone	114	190	213	201	307
Propanal	71	145	140	154	216
Butanal	109	132	159	179	293
Diethyl ether	8	13	15	16	19
Ethyl acetate	105	208	268	294	325
Isoamyl acetate	89	131	162	178	243
Nitromethane	128	225	242	283	356
Pyridine	102	205	229	262	358
Cyclohexane	15	11	12	17	19

pyridine is apparently due to adsorption at the gas—liquid interface, which is typical of polar sorbates and polar stationary phases. The dependence of the capacity factor on x_{eff_2} (see Fig. 3) makes it possible to choose the optimal conditions for the operation of a coupled column needed to achieve complete separation of a mixture.

The calculation of absolute specific retained volumes from Eq. (19) showed that the calculated values are in good agreement with the experimental results. Thus, Eq. (19) is quite suitable for predicting the retention by barochromatographic systems.

During gradient barochromatography on coupled columns, a chromatographic spectrum of the sorbate is formed.[26] This spectrum consists of the set of differences between the indices of retention of a substance by a phase of intermediate polarity (for $x_{\mathrm{eff}_2} > 0$) and by Apieson L ($x_{\mathrm{eff}_2} = 0$). A comparison of the chromatographic spectrum thus formed with the spectra contained in a database in the Samara State University allowed us to carry out group qualitative analysis of a mixture. The results or this analysis are presented in Table 5. For example, *n*-alcohols, *iso*-alcohols, and esters are identified at x_{eff_2} = 0.340, while at x_{eff_2} = 0.765, aromatic hydrocarbons, aldehydes, *n*-alcohols, *iso*-alcohols, ketones, aldehydes, and esters are identified.

Thus, the Deans method and the multichromatography and barochromatography methods are theoretically described in the same way and allow the selectivity of a chromatographic system to be controlled quite finely. Variation of the average pressures in the sections is equivalent to variation of the amounts of stationary phases in a coupled column; this allows the system to operate over the whole range of chromatographic polarities, which is determined by the properties of the individual stationary phases.

The method of barochromatography on coupled columns has the following advantages: (a) simplicity of the equipment involved, and (b) the vacuum in the second section makes it possible to carry out the process at normal carrier-gas pressures. The equations proposed for the calculation of the retention values make it possible to select the optimal ratio of the average pressures in the sections of a coupled column for the separation of a particular mixture.

Since the chromatographic properties of a system can be changed gradually, the data on the retention of a sorbate by phases of intermediate polarities is obtained over a single cycle of analysis, which makes it possible to carry out qualitative analysis of the components of a mixture.

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