Carrier gas as a new factor influencing the selectivity of the gas–stationary liquid phase chromatographic system

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Abstract

   This paper generalizes studies on the influence of carrier gas on relative and absolute retention values. This line of research is also of importance due to the fact that, in the opinion of many chromatographers, the role of the carrier gas is limited only to transporting analyzed compounds along the column. However, even under conditions of the conventional capillary gas–liquid chromatography (i.e. at column pressures under 5 atm) carrier gas (its nature and pressure) significantly influences retention and separation of the analyzed compounds. First, carrier gas (N_2 and CO_2, for example) dramatically affects relative retention values. For this reason, one should use limit values of $\alpha_{ij}(0) = \lim \alpha_{ij}(P_{av})$ and $I_i(0) = \lim I_i(P_{av})$ $I_i(0) = \lim I_i(P_{av})$ with $P_{av} \rightarrow 0$ as chromatographic constants, rather than traditional relative retention values $\alpha_{ij}(P_{av})$ and $I_i(P_{av})$. Second, the average pressure P_{av} of the carrier gas in a column and the nature of the carrier gas influence the selectivity of the gas–stationary liquid phase chromatographic system. Third, wishing to maximize the role of the carrier gas as a factor that improves separation of analyzed compounds, we should design a special gas chromatograph that would allow work with pressures in the column up to 30–50 atm.
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1. Introduction

   The main goal of analytical chromatography is separation of multi-component mixtures [1,2]. Capillary columns has proved their high efficiency in this field. But to achieve satisfactory results, one usually has to optimize the separation process by varying the following important parameters: stationary liquid phase (SLP), carrier gas flow, column temperature, etc. (see [3,4] for examples). The polarity difference of SLP is generally used as a primary factor influenc-

ing the separation results most of all. Substitution of a liquid phase for a more selective one is a well known and commonly used method for optimizing the separation process.

   In our studies, we supposed at the start that the gas phase (carrier gas) could influence the selectivity of a chromatographic system (although not as strongly as the mobile phase in liquid chromatography). However, this assumption contradicts the opinion of many qualified researches who believed that the carrier gas did not influence the separation selectivity (see Ref. [5], for example). The above statements are surely valid in traditional gas–liquid chromatography where the average pressure of the carrier gas does not exceed 5 atm (1 atm = 101 325 Pa). Obviously,

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they are based on results obtained at initial evolution stages of gas chromatography when the accuracy of determination of the retention values was rather low. Based on this and on the fact that the contemporary capillary gas chromatography (modern gas chromatographs and capillary columns) has by far higher efficiency and the accuracy of the retention values, we supposed that carrier gas should stronger affect retention and separation than in the case of the old traditional gas–liquid chromatography.

The main purpose of this paper is, first, to generalize published data on the influence of the nature and of the average pressure of the carrier gas on relative retention values, second, to discuss the significance of the results obtained for analytical chromatography, and third, to study experimental conditions and give recommendations to the analyst allowing for the more full use of the patterns of influence of carrier gas on the selectivity of a chromatographic system that we established in recent years.

At the beginning it seems expedient to consider the influence of carrier gas on the relative retention values (and therefore, on the selectivity of a chromatographic system).

2. Influence of carrier gas on relative retention values

Relative retention values are of great importance in the estimation of particular separation [2,3,6]. Based on experimental results obtained, mainly, by English researchers (see Refs. [7–12], for example) who studied, theoretically and experimentally, the dependence of the relative retention volume (absolute retention) on the nature and pressure of carrier gas (commonly, 10 atm and higher), we obtained the following linear equations for the relationships between relative retention values and the nature and pressure of the carrier gas in a column [13–17]:

$$\alpha_{ij}(P_{av}) = \alpha_{ij}(0) + \alpha_{ij}(0)[\beta_i' - \beta_j']\, P_{av}$$
$$= \alpha_{ij}(0) + b_{\alpha ij} P_{av} \tag{1}$$

$$b_{\alpha ij} = \alpha_{ij}(0)[\beta_i' - \beta_j'] \tag{2}$$

$$I_i(P_{av}) = I_i(0) + b_{Ii} P_{av} \tag{3}$$

$$b_{Ii} = 100 \frac{0.4343}{\log \alpha_{(z+1)\,z}} \left[\frac{\Delta\beta_{(z+1)\,z} \log \alpha_{iz}(0)}{\log \alpha_{(z+1)\,z}(0)} - \Delta\beta_{iz} \right] \tag{4}$$

Generally:

$$\mathrm{Re}l_i(P_{av}) = \mathrm{Re}l_i(0) + b_{\mathrm{Re}li} P_{av} \tag{5}$$

$$\mathrm{Re}l_i(0) = \lim_{P_{av}\to 0} \mathrm{Re}l_i(P_{av}) \tag{6}$$

We note that:

$$\beta_i' = \frac{2B_{i2} - V_i^\infty}{RT} + \lambda \left[1 - \left(\frac{\partial \ln \gamma_i^\infty}{\partial X_2} \right)_{X_2=0} \right] \tag{7}$$

$$\beta_j' = \frac{2B_{j2} - V_j^\infty}{RT} + \lambda \left[1 - \left(\frac{\partial \ln \gamma_j^\infty}{\partial X_2} \right)_{X_2=0} \right] \tag{8}$$

$$P_{av} = P_0 J_4^3 \tag{9}$$

$$J_4^3 = \frac{3}{4} \frac{\left[(P_i/P_0)^4 - 1 \right]}{\left[(P_i/P_0)^3 - 1 \right]} \tag{10}$$

where $\alpha_{ij}(P_{av})$ and $\alpha_{ij}(0)$ are relative values of the sorbate retention in stationary liquid phase (SLP)–gas system at the average carrier gas pressure P_{av} and ''zero'' pressure, respectively; P_i and P_0 are pressures of carrier gas at the column inlet and outlet, respectively; β_i' and β_j' are coefficients characterizing the influence of the carrier gas on retention of sorbates i and j; J_4^3 is the correction factor taking account of the pressure drop in the column; B_{12} is the second virial coefficient characterizing the carrier gas–sorbate interaction in the gas phase; V_i^∞ and V_j^∞ are molar fractional volumes of dissolving substances i and j at the infinite dilution (usually, in calculations in place of V_i^∞ and V_j^∞ one uses the mole volume of the liquid sorbate at the absolute temperature T [12]; X_2 is the mole part of the carrier gas in the SLP (usually, $X_2 \approx \lambda P$, moreover, λ is the mole solubility of the carrier gas in the SLP); γ_i^∞, γ_j^∞ are the activity coefficients of the sorbate in the SLP at the infinite dilution; R is the gas constant.

As follows from the above equations, the value of relative retention is determined not only by prop-

erties of the sorbate and the SLP, as was established earlier, but also by properties of the carrier gas. The relative retention values vary linearly with the average pressure of the carrier gas in the column.

In all our works, the experimental technique did not differ from the established technique for studying the dependence of the retention time on some experimental parameters. We studied the dependence of retention upon the nature of the carrier gas and its average pressure in the column (see Eq. (9)). A detailed description of the technique can be found in Ref. [13–15]. Thorough verification of the above basic equations showed good agreement with the experimental results [13–18]. Helium, hydrogen, nitrogen and carbon dioxide gases commonly used in gas chromatography were studied. In verification of the above linear relationships, particular attention was paid to helium recognizing its wide use in chromatography and also its behavior similar to the ideal gas. Parameters of the linear relationship between the retention index and helium average pressure in a column are shown in Table 1 [18]. As has been noted earlier in this paper, the linear Eq. (3) agrees quite well with the experimental data.

As one would expect, the value of $dI_i/dP_{av} = b_{Ii}$ in Eq. (3) for hydrogen and nitrogen is higher than for helium (see Table 2) [5].

Based on our studies and on the above equations, we can draw the following conclusions useful for the analytical practice:

The relative retention value (relative retention α_{ij} or retention index I_i) is not a chromatographic constant for the sorbate, as can be found in the literature. These values depend on the nature of the carrier gas and its average pressure in the column (see Eqs. (1) and (3) above). The chromatographic constants for the sorbate are the corresponding limit values:

Table 2
Retention index I_i changes with increase of the average pressure of carrier gas by 2 atm [column 75 m×0.14 mm, SLP SE-30 ($d_f = 0.13$ μm), temperature is 120 °C] [5]

Sorbate	He	H_2	N_2
Octanol-1	0.01	0.18	0.40
2,6-Dimethylphenol	−0.16	0.28	0.66
2,6-Dimethylnaphthalene	−0.19	0.31	0.72
Naphthalene	−0.20	0.30	0.82

$$\alpha_{ij}(0) = \lim_{P_{av} \to 0} \alpha_{ij}(P_{av}) \tag{11}$$

$$I_i(0) = \lim_{P_{av} \to 0} I_i(P_{av}) \tag{12}$$

Therefore, strictly speaking, earlier published data dealing with retention are not correct. When publishing retention data it is useful to point out the average pressure of the carrier gas in the column and its nature. In this case, having, for example, measured values of the carrier gas retention indexes $I_i(P_{av}(1))$ and $I_i(P_{av}(2))$ at two pressures, one can determine the invariant value of the retention index $I_{ij}(0)$:

$$\frac{P_{av}(1) \cdot I_i[P_{av}(2)] - P_{av}(2) \cdot I_i[P_{av}(1)]}{P_{av}(1) - P_{av}(2)} = I_{ij}(0) \tag{13}$$

A similar method can be used for a new interpretation of the "separation factor" value. It is variable and depends on the average pressure of carrier gas in the column:

$$\alpha_{A/B} = \alpha_{A/B}(0) + \beta_{A/B}P_{av} \tag{14}$$

$$b_{\alpha AB} = \alpha_{A/B}(0)[\beta'_A - \beta'_B] \tag{15}$$

As follows from Eq. (14), we can determine the value of the separation factor by varying the pressure of the carrier gas in the column or by substituting one gas for another.

Table 1
Characteristics of retention index linear dependence on pressure (Eq. (3)) for helium carrier gas

Sorbate	I_{0i}	b_{Ii}	R	SD
Octanol-1	1054.61±0.03	0.0056±0.0022	0.87	0.022
2,6-Dimethylphenol	1090.07±0.11	−0.0825±0.0104	0.98	0.093
2,6-Dimethylnaphthalene	1148.81±0.10	−0.0939±0.0103	0.98	0.092
Naphthalene	1176.40±0.07	−0.1032±0.0069	0.99	0.061

Capillary column 75 m×0.14 mm, coated SE-30 ($d_f = 0.13$ μm) at 120 °C (R=correlation coefficient; SD=summary dispersion) [18].

Unfortunately, some chromatographers do not take account of the well known facts and use as the main chromatographic terms variable values depending on the nature of the carrier gas and on its pressure in the column. They also ignore the fact that, potentially, carrier gas is an important factor for improving separation.

3. Influence on separation of the nature of carrier gas and of its average pressure in the column: advisability of designing a special chromatograph for optimizing separation

The nature of carrier gas and its pressure influence the peak resolution R_s. As we had shown earlier [19], the relationship between XX and the average pressure in the column has the following form:

$$R_s(P_{av}) = R_s(0) + b_R P_{av} \qquad (16)$$

$$R_s(0) = \lim_{P_{av} \to 0} R_s(P_{av}) \qquad (17)$$

$$R_s(0) = EC\left[\alpha_{ij}(0) - 1\right] \qquad (18)$$

where R_s is the peak resolution; $R_s(P_{av})$ is the peak resolution at the average gas pressure P_{av}; $R_s(0)$ is the maximum peak resolution at $P_{av} = 0$; b_R is a constant factor; P_{av} is the average pressure in the column; E is the efficiency of the column ($E = \frac{1}{4}\sqrt{N}$, where N is the number of theoretical plates; $C = k/(k + 1)$; k is the retention factor.

We experimentally demonstrated that the separation and the elution order of compounds depend on the nature of the carrier gas [5] (see Fig. 1). Therefore, the theory and the experiment allow for concluding that carrier gas is a new important factor in chromatography (capillary gas chromatography, in particular) influencing the separation. Consider, for example, separation of a hardly separable pair of pesticides: dicofol (1) and methoxychlor (2) using two carrier gases: helium (a) and carbon dioxide (b) in a capillary column Carbowax 20M. As follows from the figure, substitution of one carrier gas (helium) for the other (carbon dioxide) gives the following practically important results: first, the elution order of the pesticides is reversed, second, the separation of the pesticides is improved. This
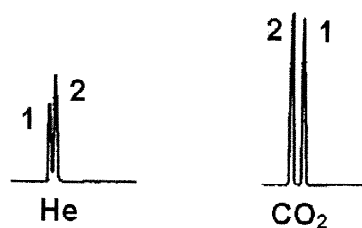

Fig. 1. Change of the elution order of pesticides from capillary column when one carrier gas (He) is substituted for another (CO_2). Chromatogram of pesticides: dicofol (1) and methoxychlor (2) using helium (He) and carbon dioxide (CO_2) as carrier gas. Experimental conditions: capillary column 12 m$\times$0.32 mm coated with Carbowax 20M (film thickness: 0.25 μm), 260 °C. Retention times (min): (He) dicofol, 8, 11; methoxyclor, 8, 26; (CO_2) methoxyclor, 16, 00; dicofol, 16,32.

shows the possibility for principal improvement of separation efficiency.

At present, basically only one method to control the column selectivity is used in gas chromatography—substitution of the stationary liquid phase. However, a simpler and softer method can be applied for the same purpose which is based on substitution of one carrier-gas for another and on changing carrier gas pressure in the column. The results obtained demonstrate that, first, by substituting one carrier gas for another, and second, by changing its pressure in the column, one can substantially influence the selectivity of the chromatographic system, or, simply speaking, the selectivity of the chromatographic column. The above example, shows the possibility of even qualitative changes in the selectivity (see Fig. 1).

However, to fully implement the established principles and to substantially amplify the effect of the carrier gas, one should have the possibility to run chromatographic columns not at traditional pressures of 3–5 atm but at significantly higher pressures up to 20–50 atm. At such pressures the role of the carrier gas for optimizing separation can be utilized to a full extent.

We should like to draw attention of chromatographers also to the fact that the development of a high pressure gas chromatograph is expedient also by the following reasons:

(1) High pressure would allow for the use of micropacked capillary columns of high efficiency; this type of columns can be used without a flow

splitter (therefore, with higher determination sensitivity);

(2) High pressures will open new potential for the use of highly efficient open capillary columns of small diameter and great length which is important for the implementation of highly efficient express chromatography.

Finally, we should remark that the approach used in this paper differs in principle from the ''solvating gas chromatography'' method. To make this difference more evident, we refer to the definition of that method as given by its author [20]:

Solvating gas chromatography (SGC) utilizes packed capillary columns together with the solvating power of carbon dioxide mobile phase. Although packed columns are inherently known for their high retention characteristics, the solvating properties of the mobile phase help promote movement along the column and allow for fast separations under SGC conditions. Instrument requirements are similar to SFC, except that the SFC restrictor at the end of the column is removed, resulting in a pressure gradient along the column. A pressure drop thus exists from supercritical conditions ($>$72 atm for carbon dioxide; 1 atm $= 101$ 325 Pa) at the column inlet to 1 atm at the outlet, which significantly increases the mobile phase linear velocity compared with SFC, while still taking advantage of the mobile phase solvating properties for rapid analyte elution.

4. Conclusion

The following conclusions can be drawn from the results of our study:

First, a new concept was introduced concerning the role of the carrier gas in conventional gas–liquid chromatography; in contrast to the widespread chromatographic opinion as published in the literature, we showed that relative retention values linearly depend on the average pressure in the column and on the nature of the carrier gas.

It was shown that the nature of the carrier gas and its pressure in the column noticeably influence relative retention and separation of analyzed compounds which, in principle, seems very similar to the role of the mobile phase in liquid chromatography.

Second, according to the theory developed and the results obtained here, the chromatographic constant of the sorbate in traditional gas chromatography (at pressures up to 5 atm) is the limit value of relative retention interpolated to zero pressure of the carrier gas, rather than the commonly used relative retention values.

Third, it was shown that the mobile phase in gas chromatography can affect the separation of mixtures and, in some cases, the elution order can change when one carrier gas is substituted for another.

Finally, carrier gas is a new factor allowing for changes in the selectivity of a chromatographic system. Using this factor for changing the selectivity is simpler than changing the nature of the stationary liquid phase. For the practical realization of this factor to control the selectivity of a chromatographic system, a gas chromatograph must be developed allowing to work with pressures at the column inlet up to 30–50 atm.

Acknowledgements

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