# RÔLE OF DISPLACEMENT EFFECTS IN TRAPPING TRACE COMPONENTS FROM GASES IN SORBENT-PACKED COLUMNS

JIŘÍ VEJROSTA*, MILENA MIKEŠOVÁ and JOSEF NOVÁK

*Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Leninova 82, 611 42 Brno (Czechoslovakia)*

(Received January 25th, 1985)

SUMMARY

   A theoretical model is described for estimating the influence of displacement effects on the migration velocities of the frontal zones of analytes trapped from gases in sorbent-packed columns. The model is based on the concept of ideal non-linear frontal chromatography. A relationship was derived for calculating the change in the gas-phase concentrations of the analytes in the individual frontal zones within the trapping column relative to the respective concentrations in the gas analyzed. The calculation is carried out by iteration, employing the partition coefficients read from the sorption isotherms of the analytes. The model enables the estimation of the safe sampling volume when trapping mixtures of analytes from gases by the conservation method. The rôle of displacement effects in trapping substances by the equilibration and conservation methods is discussed.

INTRODUCTION

   When a multicomponent mixture of organic vapours in a non-sorbed gas passes through a sorbent-packed trapping column, frontal chromatography of the mixture takes place in the column. The fronts of the individual zones migrate down the column at velocities given by the expression $u/(1 + k)$, where $u$ is the forward velocity of the percolating gaseous mixture and $k$ is the capacity ratio of a given component (analyte) of the mixture in the sorbent–non-sorbed gas–analyte system. The capacity ratio of the analyte depends on the temperature and, within the non-linear region of the sorption isotherm, also on the analyte concentration in the gas analyzed. In systems with several frontal zones, the mutual overlap of the zones and the concomitant competitive sorption effects have to be taken into account. In trace analysis techniques involving the preconcentration of analytes on solid sorbents, these so-called interference effects complicate the quantification of the data obtained. With the method of conservation (*i.e.*, total) trapping[1] it is necessary to assess the effect of the interferences on the migration velocity of the zone of the least strongly retained analyte, whereas with the method of equilibration trapping[2] it is necessary to determine the actual partition coefficients of the analytes at equilibrium under the conditions of competitive sorption in the trapping column.

Generally, the partition coefficient of the most mobile analyte is different in each composite frontal zone. In frontal chromatography on solid polymeric organic sorbents, the partition coefficient of the least sorbed analyte gradually decreases as the competitive sorption due to more strongly sorbed analytes increases in the successive fontal zones. This partial displacement leads to an increased concentration of the most mobile analyte in its zone. The combined effects of all the interfering frontal zones may result in the concentration of the most mobile analyte in the gaseous phase becoming high enough to shift the equilibrium far beyond the Henry-law region. These effects have already been studied and described in the classical papers on frontal chromatography[3-5].

In this paper, relationships for calculating the changes in the gas-phase concentration of the least sorbed component due to the competitive sorption of interfering components are derived. The derivation involves the assumption of ideal (no longitudinal diffusion, instant equilibration, plug flow) chromatography. The significance of these interferences is demonstrated by using previous experimental data[6].

## THEORETICAL

*Mixture of two analytes in a non-sorbed gas*

This simple model is well suited for demonstrating the principle of the interference effects. Fig. 1 shows schematically a part of a trapping column through which the above mixture is drawn. The frontal zone of the more mobile analyte 1 moves down the sorbent bed at a velocity determined by the partition coefficient $K_1$, and the velocity of the frontal zone of the interfering analyte 2 is determined by the partition coefficient $K_2$. The meaning of the other symbols is as follows: $c_{g_1}$ = concentration of analyte 1 in the gas entering the trapping column (in the gaseous phase of the mixed zone with analytes 1 and 2 inside the column); $c_{g_1}^i$ = concentration of analyte 1 in the gaseous phase of the zone of analyte 1 alone inside the column; $c_s^2$ and $c_{s_1}$ = concentrations of analyte 1 in the sorbent, corresponding to equilibrium with concentrations $c_{g_1}$ and $c_{g_1}^i$, respectively; $K_1^2$ = partition coefficient of analyte 1 in the mixed zone with analytes 1 and 2. The following relationships apply: $K_1 = c_{g_1}/c_{g_1}^i$; $K_1^2 = c_{s_1}^2/c_{g_1}$; $K_1 > K_1^2$ and $K_2 > K_1$. The change in the gas-phase
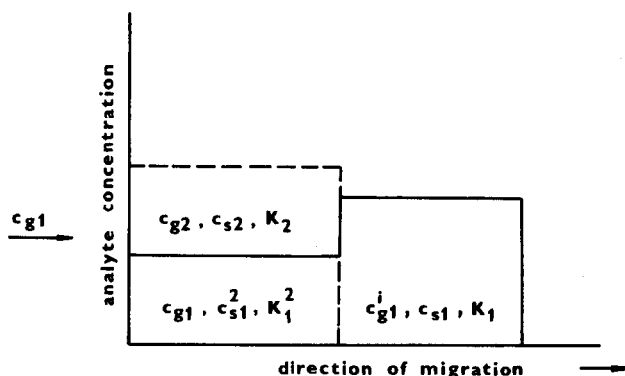


Fig. 1. Schematic representation of displacement effects with a binary mixture of analytes in a non-sorbed gas.

concentration of analyte 1, *i.e.*, from $c_{g_1}$ to $c_{g_1}^i$, is brought about by the competitive sorption of analyte 2. In the frontal zone of analyte 2, analyte 1 is partially displaced, its partition coefficient being decreased to a value of $K_1^2$ relative to $K_1$. The problem proper consists in the determination of the resultant gas-phase concentration of analyte 1 in the zone of this analyte alone, $c_{g_1}^i$, as it is this concentration that actually determines the value of the partition coefficient $K_1$ and the velocity at which the zone migrates down the column. The concentration $c_{g_1}^i$ can be calculated from the mass balance of analyte 1 after the volume $V$ of the gas to be analyzed has been drawn through the trapping column

$$V c_{g_1} = \frac{V c_{g_1}^2}{K_2} + \left( \frac{V}{K_1} - \frac{V}{K_2} \right) c_{g_1} + \frac{V V_M c_{g_1}}{K_2} + \left( \frac{V}{K_1} - \frac{V}{K_2} \right) V_M c_{g_1}^i \tag{1}$$

where $V_M$ is the gas hold-up volume per unit mass of sorbent. Neglecting the terms with $V_M$ ($V_M/K_2 \ll 1$, $K_1 \gg V_M$), we obtain:

$$c_{g_1}^i = c_{g_1} \cdot \frac{K_2 - K_1^2}{K_2 - K_1} \tag{2}$$

*Mixture of n analytes in a non-sorbed gas*

Eqn. 2 will now be used to derive the relationship for calculating the concentration $c_{g_1}^i$ in a system with $n$ analytes. In this case it is not possible to proceed simply from the mass balance of the most mobile analyte. The meanings of the symbols used follows from Fig. 2: $K_s$ ($s = 1, \ldots, n$) are the partition coefficients of the individual analytes within those regions of their frontal zones that are not overlapped by the subsequent zone; $K_1^s$ ($s = 2, \ldots, n$) are the partition coefficients of analyte 1 in the same regions of the frontal zones and $c_{g_1}^s$ ($s = 2, \ldots, n-1$) are the corresponding gas-phase concentrations of analyte 1.
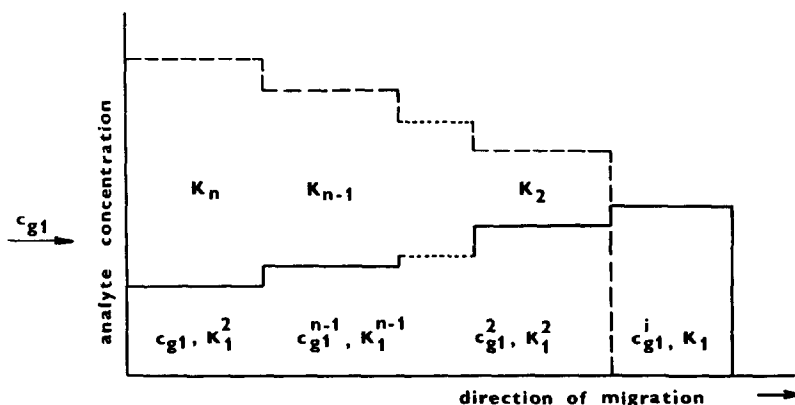


Fig. 2. Schematic representation of displacement effects with a multicomponent mixture of analytes in a non-sorbed gas.

The interference of any analyte, bringing about a change in the gas-phase concentration of any more mobile analyte, can be expressed by means of eqn. 2. When expressing the changes in the gas-phase concentrations of analyte 1 in the individual frontal zones by eqn. 2, the following set of equations is obtained:

$$c_{g_1}^i = c_{g_1}^2 (K_2 - K_1^2)/(K_2 - K_1)$$

$$c_{g_1}^2 = c_{g_1}^3 (K_3 - K_1^3)/(K_3 - K_1^2) \tag{3}$$

.
.
.

$$c_{g_1}^{n-1} = c_{g_1}(K_n - K_1^n)/(K_n - K_1^{n-1})$$

The gas-phase concentrations of analyte 1 in the individual composite frontal zones, occurring in the right-hand sides of these equations, are expressed explicitly by each subsequent equation. Upon substituting for this concentration in each equation from the subsequent one, the following relationship is obtained

$$c_{g_1}^i = c_{g_1} \prod_{s=2}^{n} (K_s - K_1^s)/(K_s - K_1^{s-1}) \tag{4}$$

where $K_1^1 \equiv K_1$.

DISCUSSION

The interference effect in a system of only two analytes in a non-sorbed gas, as described by eqn. 2, depends on the absolute values of the partition coefficients of the analytes. The mutual relationship between these partition coefficients and the consequences that follow from it for the extent of the interference effect become more evident when eqn. 2 is transformed into a dimensionless form

$$F = \frac{y_2 - y_1}{y_2 - 1} \tag{5}$$

where the factor $F = c_{g_1}^i/c_{g_1}$ is a direct measure of interference. The constants $y_1 = K_1^2/K_1$ and $y_2 = K_2/K_1$ characterize, respectively, the degree of displacement and the ratio of the migration velocities of the frontal zones of the interferent and the more mobile analyte. A graphical representation of eqn. 5 is shown by the plot of $F$ against log $y_2$ for three constant values of $y_1$ (0.2, 0.5, and 0.8) in Fig. 3.

It is the magnitude of $F$ that decides the extent of the change in the gas-phase concentration of the more mobile analyte. The maximum value of this factor occurs in the limiting case when $y_1 \to 0$ and $y_2 \to 1$, i.e., when the interferent is a strongly displacing agent and the velocity of its frontal zone is only slightly lower than that of the more mobile analyte. Clearly, both these conditions would have to be met simultaneously for $F$ to be large. With an interferent having a large partition coef-
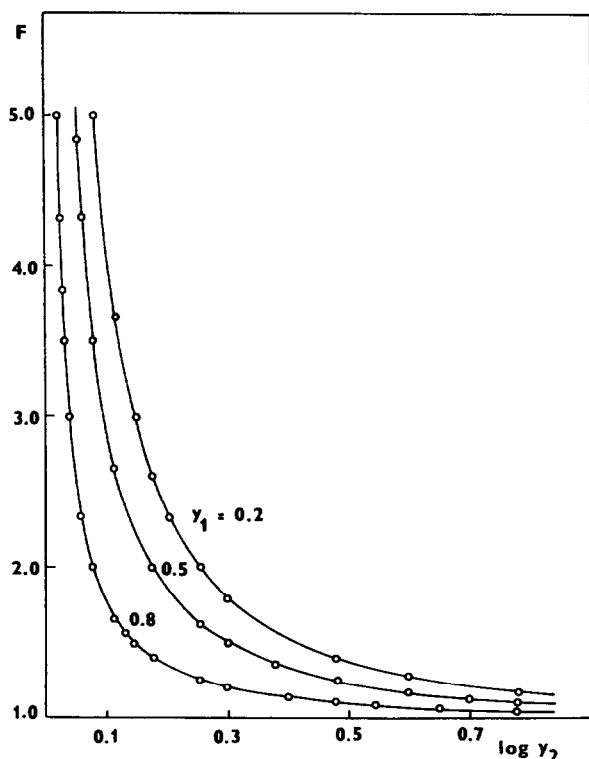
Fig. 3. Plot of the factor $F$ against log $y_2$ for different values of $y_1$.

ficient relative to that of the more mobile analyte ($y_2 \gg 1$), the factor $F$ will not differ much from unity even if the displacement effect is large, and the same applies for the case when both the partition coefficient of the interferent and the displacement effect are small ($y_2 \to 1$, $y_1 \to 1$). However, the conditions $y_1 \to 0$ and $y_2 \to 1$ apparently contradict each other, and it is very unlikely that both of them will be fulfilled at the same time.

The above considerations can be applied also to systems with $n$ analytes in a non-sorbed gas. In this case, $F$ represents a measure of the overall interference effect of all the $(n-1)$ interferents, and is the product of the $(n-1)$ partial factors due to the individual interferents;

$$F = \frac{c^i_{s_1}}{c_{s_1}} = \prod_{s=2}^{n} F_s = \prod_{s=2}^{n} \left( \frac{K_s - K^s_1}{K_s - K^{s-1}_1} \right) \tag{6}$$

The right-hand side of eqn. 6 can be transformed into a dimensionless form

$$F = \prod_{s=2}^{n} \left( \frac{y_s - y_{s-1}}{y_{s-1}} \right) \tag{7}$$

where the constants $y_s$ and $y_{s-1}$, i.e., $y_s = K_s/K_1^{s-1}$ and $y_{s-1} = K_1^s/K_1^{s-1}$, refer to the effects of the individual interferents and have the same meaning as the quantities $y_1$ and $y_2$. Hence, in this more general case, the effects of the individual interferents can be treated separately in the same way as with the mixture of two analytes.

   With mixtures containing several analytes the problem to be solved is the estimation of the effect of the dominant interferent with the largest interference factor, $F_s$. Less mobile interferents with larger $y_s$ values, relative to the dominant component, have an insignificant effect on the resultant factor, $F$. It is not only higher values of the partition coefficients, $K_s$, but also appreciably lower $K_1^{s-1}$ values, due to the displacement of analyte 1 from the sorbent by the dominant interferent, that lead to high $y_s$ values. Clearly, all the individual interfering analytes are gradually influenced in the same way as is analyte 1. The relationships for describing these effects are the same as eqn. 7, except that the number of terms decreases in the order of decreasing mobilities of the respective frontal zones. Though the interference effects of some analytes towards analyte 1 may be negligible, they can markedly enhance the gas-phase concentrations and, consequently, the interference effects of the next more mobile analytes.

   From the value of the resultant factor, $F$, alone it cannot be inferred whether a change in the migration velocity of the frontal zone of analyte 1 will occur. It is necessary to know the shape of the sorption isotherm of analyte 1 and the approximate concentration of this analyte in the mixture analyzed. Considering eqn. 2 in the form

$$F = \frac{K_2 - K_1^2}{K_2 - K_1} \tag{8}$$

it is seen that the partition coefficient $K_1$, calculated as above, determines the migration velocity of the frontal zone of analyte 1. Provided the values of $K_2$ and $K_1^2$ are known, the value of $k_1$ is given by that of $F$ and *vice versa*. The calculation proper is then carried out by iteration, substituting for $K_1$ a value corresponding to the Henry-law region and calculating the factor $F$ as a first approximation. This value of $F$ is used to calculate the gas-phase concentration of analyte 1, and the second approximation of $K_1$ is obtained according to the sorption isotherm, etc. hence, the method of calculation depends on the data available.

*Example*
   In order to illustrate the situation quantitatively, the interferecne effect of *o*-xylene on the migration velocity of the frontal zone of benzene in a Tenax GC column was calculated employing the experimental data (Fig. 3) taken from our previous paper[6]. The initial gas-phase concentration of benzene, $c_{g_1}$, is 0.5 ppm, and the partition coefficient[7] of benzene alone at this concentration is 20000 ml/g. Within the frontal zone of *o*-xylene at a concentration that renders the partition coefficient, $K_2$, of this solute equal to 114000 ml/g, the partition coefficient of benzene amounts only to half the value of $K_1$, i.e., $K_1^2 = 10000$ ml/g. Upon substituting into eqn. 8 we obtain $F = 1.1$. If the above data had not been available, then eqn. 5 and/or directly eqn. 3 could be used. A large displacement effect is assumed, e.g., $y_1 = 0.2$, because of the similar nature of the analytes, and the constant $y_2$ is approximated by the

ratio of the Henry-law partition coefficients of the solutes. These partition coefficients can either be read from the linear sections of the respective sorption isotherms or calculated from gas chromatographic retention data. In our case, we obtain $y_2 = 15.0$ and $F = 1.06$ according to eqn. 5. Hence, the increase in the gas-phase concentration of benzene is negligible, and the frontal zone of benzene still migrates at a velocity given by the Henry-law partition coefficient[7].

CONCLUSIONS

As stated in the introduction, the rôle of interference effects in trace analysis involving sample-enrichment techniques has to be considered with regard to the method of trapping the analytes. In equilibration trapping the rôle of these effects is generally very significant[6]. The determination of the actual partition coefficients meets with difficulties, and, in most applications in which solid adsorbents are employed as trapping column packings, the effort necessary to obtain the data needed can hardly be countervailed by the practical merits of the method. A special situation occurs if the dominant component has a very low retention on the sorbent employed, such as water vapour on non-polar organic polymers. In this case the effect of the ballast component on the partition coefficients of the analytes may be practically insignificant[8].

In the method of total trapping the interference effects become significant if they lead to an increase in the migration velocity of the frontal zone of the most mobile analyte. As follows from the preceding discussion, a significant change would occur only under the following conditions:

(a) a relatively small value of the ratio of the partition coefficients of the interfering and determined compounds

(b) a large displacement effect

(c) higher concentrations of the compound under determination (concentrations near the "end" of the Henry-law region of the respective sorption isotherm)

(d) marked non-linearity of the sorption isotherm of the compound to be determined.

Only the simultaneous action of all the above factors can bring about a significant interference effect, which occurs very rarely in practice.

REFERENCES

1 F. R. Cropper and S. Kaminsky, *Anal. Chem.*, 35 (1963) 735.
2 J. Novák, V. Vašák and J. Janák, *Anal. Chem.*, 37 (1965) 660.
3 S. Claesson, *Ark. Kemi, Mineral Geol.*, 23 A (1946) 1.
4 S. Claesson, *Ann. N.Y. Acad. Sci.*, 49 (1948) 183.
5 S. Claesson, *Discuss. Faraday Soc.*, 7 (1949) 34.
6 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 265 (1983) 215.
7 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 217 (1981) 167.
8 J. Janák, J. Růžičková and J. Novák, *J. Chromatogr.*, 99 (1974) 689.