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INTERFERENCE EFFECTS IN TRAPPING TRACE COMPONENTS FROM GASES ON TENAX-GC

SORPTION OF BENZENE IN THE PRESENCE OF n-BUTANOL, o-XYLENE AND n-PENTANE

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SUMMARY

Sorption equilibria were measured in systems of Tenax-GC and benzene–n-butanol–nitrogen, benzene–o-xylene–nitrogen and benzene–n-pentane–nitrogen gaseous mixtures at 19.9, 27.1 and 35°C. With all the systems the benzene (a model analyte) concentration was kept at 0.5 ppm and the concentrations of n-butanol, o-xylene and n-pentane (interferents) were varied over a range of four orders of magnitude. The dependences of the partition coefficient of benzene on the concentrations of the interferents are discussed in terms of the conservation and equilibration modes of concentrating trace substances in sorbent-packed trapping columns.

INTRODUCTION

The concentration of trace components of gaseous mixtures on solid sorbents is mostly carried out by employing the method of conservation trapping[1]. The method of equilibration trapping was introduced[2] as an alternative to conservation trapping and applied with the use of both liquid[3] and solid[4–7] sorbents as trapping column packings. Both modes of trapping have been discussed in detail in earlier papers[8,9]. The choice of the method of trapping depends above all on the properties of the material to be analysed, namely, the nature and concentration range of the components. These criteria are also most relevant for the choice of suitable sorbent packings for the trapping column.

In order to assess the breakthrough volume with the conservation method, it is necessary to know the sorption isotherm of the most weakly sorbed (most mobile) analyte in the trapping column and the plate number of the latter. The changes in the retention of the most mobile analyte in its zone migrating down the trapping column, due to displacement by the succeeding frontal zones of more strongly (less mobile) analytes, are usually negligible[10].

Two of the reasons why the conservation method has found such wide application are its simplicity and the possibility of easily estimating experimentally the

safe sampling volume. Usually a control trapping column is connected to the outlet of the working column, and different sample volumes are drawn through the series of the columns while checking the control column for the content of the substances being trapped. The use of the method of equilibration trapping is limited to cases in which it is possible to determine reliably the partition coefficients of the analytes in the trapping sorbent–analysed mixture system under the actual conditions of analysis.

In this paper, the effect of *n*-butanol, *o*-xylene and *n*-pentane as interfering components on the partition coefficient of benzene on Tenax-GC in model systems of known compositions is demonstrated. The findings are interpreted and discussed in terms of the concentration of trace substances in sorbent-packed columns by the above two methods of trapping.

EXPERIMENTAL

Systems with three gaseous model mixtures were investigated: (i) benzene–*o*-xylene–nitrogen, (ii) benzene–*n*-butanol–nitrogen and (iii) benzene–*n*-pentane–nitrogen. With all the three systems the concentration of benzene was kept at 0.5 ppm while the concentrations of the other (interfering) components were varied over a range of about four orders of magnitude. The method of preparation of the model mixture and the measurement and calculation of the partition coefficients have been described earlier[8,11]. For each system, the partition coefficients of benzene and of the interfering component, as a function of the interferent concentration, were determined at three temperatures: 19.9, 27.1 and 35°C. The data obtained are presented graphically in Figs. 1–3.

RESULTS AND DISCUSSION

The model systems (i)–(iii) were chosen with a view to demonstrating three possible cases of the mutual relationship between the partition coefficients of benzene (K_1) and of the interferent (K_2), namely: (i) $K_2 > K_1$, (ii) $K_2 = K_1$ and (iii) $K_2 < K_1$, respectively. The partition coefficient is defined as the ratio of the sorbate concentrations in the sorbent (c_s, mol/g) and in the gaseous phase (c_g, mol/ml), and hence the dimensions of $K = c_s/c_g$ are ml/g.

With all the model systems, the partition coefficient of benzene decreases with increasing concentration of the interferent in the gaseous phase. In view of the conservation mode of trapping, the increase in the gas-phase concentration of benzene within its migrating frontal zone, caused by partial displacement of benzene from the sorbent by the more slowly advancing interferent frontal zone, is important, as it is this concentration that determines the migration velocity of the zone of benzene.

The ratio of the gas-phase concentration of an analyte within its migrating frontal zone to that in the mixture fed into the trapping column, F, has been defined[10] as

$$F = (K_2 - K_1^2)/(K_2 - K_1) \tag{1}$$

where K_2 and K_1 are the actual partition coefficients (at the actual concentrations of the respective compounds) of the interferent and analyte alone within their frontal

TABLE I

VALUES OF THE FACTOR F FOR BENZENE (ANALYTE) AND o-XYLENE, n-BUTANOL AND n-PENTANE (INTERFERENTS) AT THE BENZENE GAS-PHASE CONCENTRATION OF 0.5 ppm AND DIFFERENT GAS-PHASE CONCENTRATIONS (c_{g1}) OF THE INTERFERENTS

Interferent	Parameter	Value				
o-Xylene	c_{g1} (ppm)	0.08	0.25	0.8	2.5	7.9
	F	1.00	1.01	1.05	1.24	2.0
n-Butanol	c_{g1} (ppm)	0.8	2.5	8.0	25.0	79.0
	F	1.86	2.60	10.7	37.0	—

zones, and K_1^2 is the actual partition coefficient of the analyte within the mixed analyte–interferent zone. The values of the factor F for the benzene gas-phase concentration of 0.5 ppm and several gas-phase concentrations of o-xylene and n-butanol at 19.9°C are presented in Table I.

As quoted earlier[10], the interrelation between K_2 and K_1 renders it necessary to employ an iterative procedure when calculating the factor F using eqn. 1, in which the Henry-law K_1 value is used as the first approximation. However, as this K_1 value is larger than K_2 with benzene–n-butanol systems, eqn. 1 cannot be used to calculate the factor F in this case. Within the mixed benzene–n-butanol zone at n-butanol concentrations lower than 50 ppm, the benzene partition coefficient, K_1^2, is smaller than the partition coefficient of n-butanol, K_2, i.e. $K_2 > K_1^2$. Within this range of n-butanol concentrations, the displacing action of n-butanol induces a gradual increase in the benzene gas-phase concentration ahead of the mixed frontal zone, thus decreasing the partition coefficient of benzene within this zone and accelerating the latter.

The decrease in the partition coefficient of n-butanol on increasing its concentration is steeper than that with benzene. Hence, at certain concentrations of these two compounds their partition coefficients have the same values, i.e., $K_2 = K_1$, and the value of F is infinity. Considering the mixed benzene–n-butanol frontal zone at n-butanol concentrations below 50 ppm from this point of view, we can imagine the following situation: as benzene is gradually being displaced by n-butanol from the migrating mixed zone, a leading zone of benzene alone is formed in wich the benzene gas-phase concentration gradually rises and the respective partition coefficient decreases until K_1 in this zone becomes equal to K_2 in the rear mixed zone. From that moment, a stationary state is established in which the benzene partition coefficient in the leading zone is only slightly smaller than that of n-butanol in the rear zone, and both zones migrate at virtually the same velocities. Clearly, this is a typical case of classical displacement chromatography[12].

The behaviour of o-xylene as an interfering component differs from that of n-butanol. Whereas with benzene–n-butanol mixtures the displaced benzene zone ahead of the mixed one develops gradually in the course of mixed zone migration, i.e., during frontal chromatography of the two components, with benzene–o-xylene mixtures this benzene zone is developed immediately after the mixture enters the column. Hence, pure displacement chromatography takes place from the very beginning of the trapping process with benzene–o-xylene mixtures on Tenax-GC. Clearly,

this is so because o-xylene is a more strongly sorbed compound and, consequently, a more efficient displacer than n-butanol. In the case of the interference by n-butanol, the gas-phase concentration of benzene ahead of the mixed benzene–n-butanol zone increases proportionately to the volume of the gas mixture having been drawn through the trapping column until the benzene gas-phase concentration in the leading benzene zone reaches a value at which the partition coefficient of benzene within this zone becomes equal to that of n-butanol. The values of the factor F in Table I were calculated under the assumption that $K_1 = K_2$, using the experimental data published earlier[8]. At an n-butanol gas-phase concentration of 79 ppm the n-butanol frontal zone moves faster than that of benzene, and the interfering effect of n-butanol becomes identical with that of n-pentane.

      As it is actually the sorbent-phase concentration of the interferent that controls the extent of displacement, the mere gas-phase concentrations of the interferents are not unequivocal criteria of the interfering effects. There is the same decrease in the benzene partition coefficient, relative to that in the absence of any interferent, at substantially different gas-phase concentrations of the three interferents studied. On the other hand, the sorbent-phase concentrations of these interferents that bring about the same displacement of benzene do not differ much from each other. Thus, at 19.9°C the sorbent-phase concentrations of o-xylene, n-butanol and n-pentane at which the benzene partition coefficient amounts to half of that in the absence of
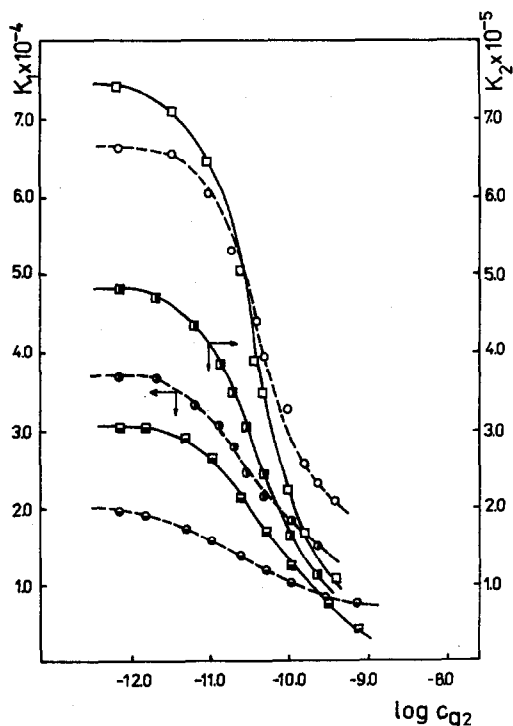

Fig. 1. Dependences of the partition coefficients of benzene (O, K_1, c_{g1} = 0.5 ppm) and o-xylene (□, K_2) on the gas-phase concentration (c_{g2}) of o-xylene. □, O, 19.9°C; ■, ◑, 27.1°C; ▨, ◓, 35°C.
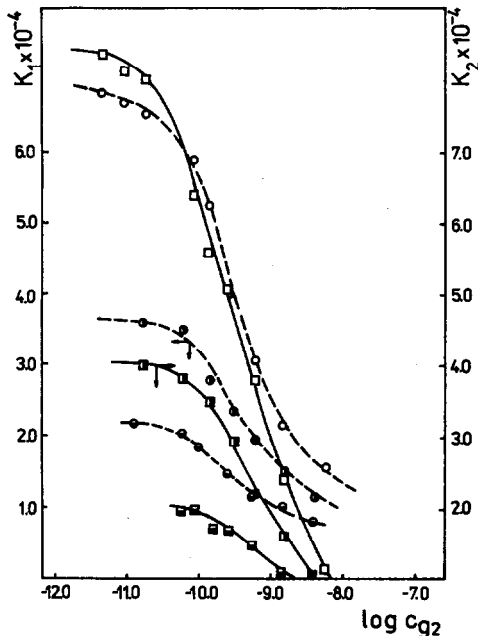
Fig. 2. Dependences of the partition coefficients of benzene (O, K_1, c_{g1} = 0.5 ppm) and n-butanol ($\square$, K_2) on the gas-phase concentration (c_{g2}) of n-butanol. $\square$, O, 19.9°C; ■, ◑, 27.1°C; ◨, ◒, 35°C.

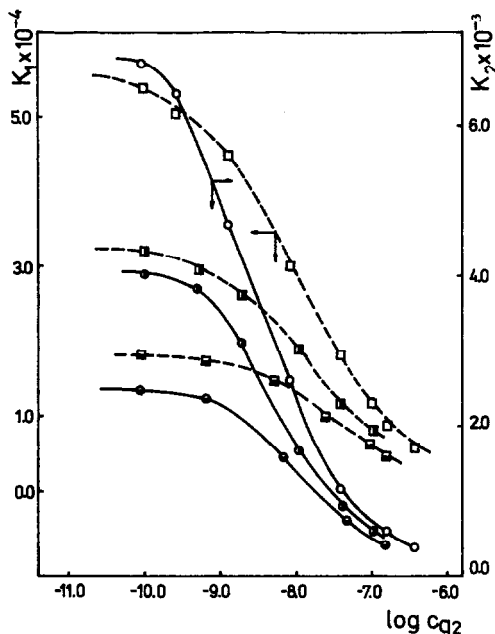Fig. 3. Dependences of the partition coefficients of benzene (O, K_1, c_{g1} = 0.5 ppm) and n-pentane ($\square$, K_2) on the gas-phase concentration (c_{g2}) of n-pentane. $\square$, O, 19.9°C; ■, ◑, 27.1°C; ◨, ◒, 35°C.

interferents are $2.05 \cdot 10^{-5}$, $1.96 \cdot 10^{-6}$ and $2.36 \cdot 10^{-5}$ mol/g, respectively. With benzene alone, the decrease in its partition coefficient to half of that at infinite dilution is achieved at $1.85 \cdot 10^{-5}$ mol/g of benzene in the sorbent.

The finding that the same displacement effect is achieved with all the sorbates investigated at about the same molar concentrations in the sorbent indicates the non-selective sorption of these compounds on Tenax-GC. Under these circumstances, it is possible to assess the change in the analyte partition coefficient from the known overall concentration of the interferents in the sorbent, which is very important in view of the equilibration mode of trapping. As can be seen in Figs. 1–3, the same relative changes in the sorbent-phase concentrations result in about the same relative changes in the partition coefficients with benzene and the interferents.

At as gas-phase concentration of 0.5 ppm, the effect of benzene on the partition coefficients of the interferents is negligible. Hence the data obtained can be used to estimate the breakthrough volumes of o-xylene, n-butanol and n-pentane on Tenax-GC. With all the model systems investigated, an increase in temperature results in widening of the concentration range over which Henry's law is valid for the sorbates involved. This behaviour is apparently due to the decrease in the partition coefficients and, consequently, the sorbent-phase concentrations of the sorbates.

CONCLUSION

When trapping trace substances from complex gaseous mixtures in columns packed with solid sorbents, significant interferences among the sorbates may occur. These interferences not only result in decreases in the partition coefficients of the analytes on the given sorbent, but they can even induce a change in the mechanism of the process taking place in the trapping column. In the absence of interferences, and/or if they are not very strong, the compounds being trapped are subjected to frontal chromatography in the trapping column and, after a state of equilibration has been attained with all the components of the gas sample mixture throughout the trapping column, the latter contains all these components in concentrations given by the products of their gas-phase concentrations and the respective actual partition coefficients on the given sorbent (provided that the contents of the components in the gas mixture occurring in the interstitial space of the trapping column are negligible). However, if there are great differences in the sorbabilities of the sample components, and some of the components are sorbed so strongly as to displace completely less strongly sorbed components, the latter will be subjected to displacement rather than frontal chromatography. In this instance, the components that form displacement zones during the sampling process are gradually pushed out of the trapping column, and only very small amounts (those present in the sampled gas mixture that occurs in the interstitial space within the trapping column) of them will be found in the trapping column in the state of final equilibration. Hence, with the conservation mode of trapping these strong displacement effects need not necessarily influence the situation drastically, but with equilibration trapping the displaced components become virtually lost for analysis.

REFERENCES

1 F. R. Cropper and S. Kaminski, *Anal. Chem.*, 35 (1963) 735.
2 J. Novák, V. Vašák and J. Janák, *Anal. Chem.*, 37 (1965) 660.
3 M. Selucký, J. Novák and J. Janák, *J. Chromatogr.*, 28 (1967) 285.
4 J. Gelbičová-Růžičková, J. Novák and J. Janák, *J. Chromatogr.*, 64 (1972) 15.
5 J. Goliáš, J. Růžicková and J. Novák, *Acta Univ. Agric., Brno*, 23, No. 1 (1975) 115.
6 A. Ševčik, *Thesis*, Institute of Geological Engineering, Brno, 1980.
7 J. Goliáš and J. Novák, *J. Chromatogr.*, 346 (1985) 43.
8 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 217 (1981) 167.
9 J. Vejrosta, M. Roth and J. Novák, *J. Chromatogr.*, 265 (1983) 215.
10 J. Vejrosta, M. Mikešová and J. Novák, *J. Chromatogr.*, 324 (1985) 269.
11 J. Vejrosta, and J. Novák, *J. Chromatogr.*, 175 (1979) 261.
12 S. Claesson, *Ark. Kemi, Mineral. Geol.*, 23A, No. 1 (1946) 133.