

CHROM. 11,585

Note

Detection of adsorption in gas-liquid chromatography

G. DAHLMANN, H. J. K. KÖSER and H. H. OELERT

Institut für Chemische Technologie und Brennstofftechnik der TU, Erzstrasse 18, D-3392 Clausthal-Zellerfeld (G.F.R.)

(Received September 18th, 1978)

Bulk liquid partition (absorption), adsorption on the solid support interface and adsorption on the liquid stationary phase interface contribute to the solute retention in gas-liquid chromatography (GLC). Although the usual assumption is that the absorption dominates, it is increasingly believed¹ that for most packed columns with liquid loadings below 5% (w/w) the separation is caused by a mixed retention mechanism. The relative importance of the three basic mechanisms depends on the surface-to-volume ratio, *i.e.*, on the liquid phase loading. Mixed retention often affords better separation than pure liquid partition. All isomeric hydrocarbons from C₁ to C₆ can only be separated on a column capable of adsorbing the light hydrocarbons, whereas the higher members are retained by partitioning. For analytical purposes, one therefore often deliberately employs columns showing mixed retention. When attempting to reproduce work from other laboratories, one has to consider that separation on these columns depends not only on the nature of the liquid phase but also on the solid support employed. Retention times are also likely to be dependent on the sample size².

On the other hand, GLC finds increasing use for the determination of thermodynamic properties such as the enthalpy and entropy of solution or the heat of vaporization³. It is obvious that for these applications one has to make sure that only liquid partitioning contributes to the measured retention volume.

The relative contributions of adsorption and partitioning are also dependent on the nature of the solute. Relative retention data, like Kováts' retention index⁴, are therefore affected by the mixed retention mechanism. This has to be taken into account when characterizing the polarity of stationary phases via the retention indices of certain solute probes⁵. Consequently, there is a need for a test which confirms that adsorption is negligible. When determining absolute data, such as specific retention volumes, such methods have been proposed^{1,6,7}. Even today the accurate determination of retention volumes is still a laborious procedure.

One therefore usually injects small samples and determines whether the retention time is dependent on the sample size, the idea being that small sample sizes ensure that one is in the domain of infinite dilution, where bulk partition is concentration-independent. Adsorption, being concentration dependent, should show a decreasing retention time with increasing sample size. However, at small sample sizes, adsorption is sometimes only moderately concentration-dependent. Only when the

active sites are appreciably covered does the adsorption-based retention become sensitive towards solute concentration. At high concentrations the surface is completely covered and the adsorption is again concentration-independent. It was felt that, besides sample size, some other test should be considered.

The present communication describes, based on readily accessible index measurements, a method of ensuring that adsorption effects have a negligible influence on retention.

EXPERIMENTAL

Reagents

The *n*-alkanes and alcohols were of analytical quality. The supports were purchased from Johns-Manville, Denver, Colo., U.S.A. (G) and E. Merck, Darmstadt, G.F.R. (W). The stationary phase was obtained from Imhausen Werke (Witten/Ruhr, G.F.R.). Fig. 1 shows that the dioctyl phthalate was impure.

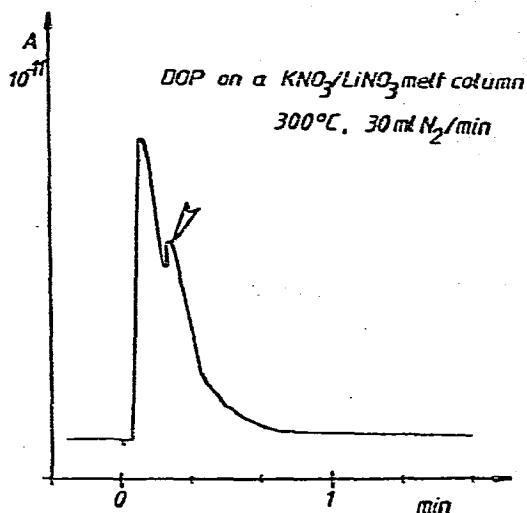


Fig. 1. Chromatogram of the impurities in dioctyl phthalate.

Apparatus

A F & M 810 chromatograph with flame ionization detection was used. The temperature was maintained with a liquid thermostat at $100 \pm 0.1^\circ$. The carrier gas was nitrogen. Steel columns ($2 \text{ m} \times 2.5 \text{ mm O.D.}$) and capillary columns made of steel and glass ($2 \text{ m} \times 0.35 \text{ mm O.D.}$) were employed. The phthalate was deposited on the solid support from chloroform solution. The capillary columns were prepared by the dynamic method with a 10% chloroform solution. The glass columns had been previously etched with HCl gas. The average film thickness was calculated to be $0.2 \mu\text{m}$ according to the empirical equation of Kaiser⁸. The reproducibility of the quoted retention indices was ± 1 unit.

RESULTS AND DISCUSSION

Retention indices can give only limited quantitative information on mixed retention mechanisms^{4,9}. All our knowledge in this area therefore rests on relatively few studies of the dependence of the retention volume of a limited number of solutes on selected stationary phase-support systems^{1,6,7,10}. No quantitative prediction can be made. However, the following qualitative reasoning seems to apply generally¹.

The adsorption on the solid support is strongest for polar solutes and apolar stationary phases. Treatment of the support with alkylchlorosilane reduces this effect considerably. The influence of adsorption on the surface of the support will also be marked if the surface tension of the stationary phase does not exceed the critical surface energy of the support, *i.e.*, the phase does not wet the support¹¹. Less can be done to avoid the adsorption on the surface of the liquid stationary phase. According to Gibbs, the excess concentration of the solute on the surface over that in the bulk liquid, X_2 , is proportional to $(\partial\alpha/\partial X_2)$, the change of the solution surface tension α with solute mole fraction X_2 . Not much work has been reported on the evaluation of $(\partial\alpha/\partial X_2)$ for gas chromatographic stationary phases and volatile solutes. However, it can be said that the Gibbs adsorption effect will be appreciable for non-polar solutes on polar stationary phases. In general, any system in which the solute activity coefficient is high will show marked liquid surface effects.

The retention volume can be analyzed by an additive model according to eqn. 1:

$$V_N = K_L V_L + K_A A_A + K_S A_S \quad (1)$$

where K_L is the gas-liquid partition constant, V_L the volume of the liquid phase, K_A , K_S the constants of adsorption and A_A , A_S the surfaces of the liquid phase and solid support, respectively.

The retention index is defined as

$$I = 100 [n + \log (V_{N(X)}/V_{N(n)})/\log (V_{N(n+1)}/V_{N(n)})] \quad (2)$$

where n and $(n + 1)$ indicate the carbon number of two n -paraffins, and X is the solute. Only if the first term of eqn. 1, the partition, is dominant is the retention index independent of liquid loading (V_L).

Working with large sample sizes has been suggested² for decreasing the importance of the adsorption terms in eqn. 1. Phases show high Gibbs adsorption for solutes because the interaction forces are different between like and unlike molecules. These systems are consequently likely to show nonlinear solution isotherms at moderate concentrations, where adsorption may still play a role. Thus, only in certain cases will this method give adsorption-independent infinite dilution retention indices.

Whenever possible, the importance of partitioning should be increased by augmenting the liquid loading. The amount of liquid phase a stationary phase can hold is limited. Highly loaded columns have low efficiencies. One would like to work with the minimum necessary loading giving adsorption-independent retention indices.

We finally settled on the following procedure. n -Alkanes and n -alcohols have very different adsorption and absorption properties: the former are sensitive indicators

TABLE I

RETENTION INDICES OF n -ALCOHOLS ON DIOCTYLPHTHALATE (DOP) AS A FUNCTION OF LIQUID LOADING AND SUPPORT MATERIAL

The loading is quoted in wt. % DOP per solid support (without stationary phase).

Chromosorb	n -C ₃ H ₇ OH to n -C ₈ H ₁₇ OH					
	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈
W AW (% w/w)						
2	770	866	923	1004	1164	1267
5	719	822	886	998	1126	1227
8	699	805	872	993	1112	1213
11	696	802	871	993	1110	1211
14	691	798	868	992	1107	1207
W AW DMCS (% w/w)						
5	681	787	860	989	1100	1202
11	673	783	859	988	1099	1201
G AW DMCS (% w/w)						
3	674	784	859	989	1098	1199
5	676	785	860	991	1099	1201
8	672	783	860	991	1100	1202
Steel apillary (50 m)	671	785	856	990	1098	1200
Glass capillary (40 m)	671	783	856	991	1095	1197

of Gibbs adsorption, the latter of adsorption on the support. The relative retention of the alcohols compared with the alkanes should be independent of the liquid loading only if adsorption plays a negligible role. The Kováts' retention index is such a measure.

It has the additional advantage of being easily determined. In Table I an example is outlined. On acid-treated Chromosorb W AW the retention indices of the alcohols change even at a liquid loading as high as 14% (w/w) dioctyl phthalate (DOP). DMCS-treated Chromosorb W AW gives smaller retention indices. The lower alcohols seem to be the most sensitive towards adsorption. The retention indices on Chromosorb G AW DMCS are above 3% (w/w) DOP, within the experimental uncertainty, and independent of the loading.

In Table II the specific surface areas for the support are listed. It can be seen that Chromosorb G coated with 5% (w/w) has about the same loading per m² square metre of surface area as Chromosorb W loaded with 10% (w/w). Hence the surface of Chromosorb W is not much more active than Chromosorb G. Chromosorb G AW DMCS coated with 5% (w/w) DOP should show only negligible adsorption.

TABLE II

SURFACE AND BULK DENSITY OF CHROMOSORB PHASES

From refs. 12 and 13.

Chromosorb	Surface		Bulk density (g/ml)
	m ² /g	m ² /ml	
W	1.0	0.30	0.3-0.4
P	4-6	1.8-2.0	0.6-0.7
G	0.5	0.29	0.58

To check this assumption one can compare this column with a capillary column. Wetted capillary columns have, generally, a ten times higher loading per square metre than packed columns. According to eqn. 2 the adsorption effect on capillary columns should be less important. Table I shows that the indices on a steel and glasscapillary are the same as those on Chromosorb G AW DMCS coated with 5% (w/w) DOP.

We feel that the latter column could be used to evaluate the characteristic polarity values of the stationary phase, and that this column is a good starting point for determining precise partition coefficients K_L (ref. 6). For each new investigated stationary phase we applied a similar checking procedure. These results will be published separately.

ACKNOWLEDGEMENT

The authors thank the Deutsche Forschungsgemeinschaft for financial support.

REFERENCES

- 1 R. L. Martin, in J. H. Purnell (Editor), *Progress in Gas Chromatography*, Vol. 6, Interscience, New York, 1968, p. 93.
- 2 L. Mathiasson, J. Å. Jönsson, A. M. Olsson and L. Haraldson, *J. Chromatogr.*, 152 (1978) 11.
- 3 E. F. Meyer, R. H. Weiss and T. H. Gens, *J. Chem. Thermodyn.*, 9 (1977) 439.
- 4 E. Grushka and T. A. Goodwin, *Chromatographia*, 10 (1977) 549.
- 5 L. Rohrschneider, *J. Chromatogr.*, 22 (1966) 6.
- 6 D. F. Cadogan, J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 708.
- 7 J. R. Conder, D. C. Locke and J. H. Purnell, *J. Phys. Chem.*, 73 (1969) 700.
- 8 L. Blomberg, *J. Chromatogr.*, 138 (1977) 7.
- 9 J. Klein and H. Widdecke, *J. Chromatogr.*, 129 (1976) 375.
- 10 T. Komaita, K. Naito and S. Takei, *J. Chromatogr.*, 114 (1975) 1.
- 11 L. Bokszányi and E. sz. Kováts, *J. Chromatogr.*, 126 (1976) 87.
- 12 R. Kaiser, *Chromatographie in der Gasphase*, Bd. III, 1. Teil, Bibliographisches Institut, Mannheim, 1969.
- 13 *Chromosorb, FF 101D, RWC 11/71*, Johns-Manville, Denver, Colo., 1971.