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EFFECT OF ADSORPTION ON THE REPRODUCIBILITY OF RETENTION INDICES OF HYDROCARBONS IN CAPILLARY GAS–LIQUID CHROMATOGRAPHY*

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SUMMARY

The relationship $I = I_0 + a_I \cdot 1/k$ was compared with experimental data for hydrocarbons separated by gas chromatography in capillary columns coated with stationary phases of varying polarity. The influence of adsorption in gas–liquid systems on the reproducibility of retention indices is discussed.

INTRODUCTION

Capillary gas chromatography (GC) has been widely adopted on account of the much higher resolution capacity of capillary columns compared with packed columns. The reproducibility of retention indices measured in various capillary columns in one laboratory and, particularly, in different laboratories has, however, remained unsatisfactory. This fact limits the practical utilization of capillary GC for peak identifications based on retention data, which is important for the characterization of unknown compounds.

There are two ways of overcoming this: either to obtain capillary columns with identical properties or to search for methods that will improve the reproducibility of retention data. Unfortunately, the preparation of capillary columns with identical properties is very complicated and almost impossible in practice.

In this work an attempt has been made to obtain reproducible retention data even under conditions involving adsorption in gas–liquid systems. The separation of hydrocarbons was selected as a model as it is assumed that the problem of reproduc-

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ibility of retention data of hydrocarbons is less serious than with other compounds.

In this paper, as in earlier papers[1–3], it is assumed that the lower reproducibility of the retention data obtained by GC is caused by adsorption interactions of the compounds being chromatographed on gas–stationary phase or stationary phase–column wall interfaces, which are difficult to control. We found a noticeable influence of the thickness of the stationary phase film on retention indices[3]. The problem of adsorption has recently been discussed by Fritz *et al.*[4] and the influence of the thickness of the stationary phase film in glass capillary columns on the retention data has also been investigated[5]. Berezkin[1] proposed the following relationship for retention indices:

$$I = I_0 + a_I \cdot \frac{1}{k} \tag{1}$$

where I_0 is the limiting value of the retention index determined only by the dissolution of the chromatographed compound in the stationary phase, a_I is a constant characterizing adsorption of this compound in the given system (carrier gas–stationary phase–column wall) and k is the capacity ratio of a standard compound, the adsorption of which can be neglected in the given system.

Now, eqn. 1 has been compared with experimental data for the separation of hydrocarbons in glass and metal capillary columns coated with stationary phases of varying polarity. The reproducibility of the I_0 values was evaluated and its dependence on the type of homologous series of the compounds used as reference standards was investigated.

EXPERIMENTAL

Gas chromatographic measurements were performed with a Carlo Erba GI 452 gas chromatograph equipped with a flame-ionization detector.

Stainless-steel capillary columns (50 m × 0.25 mm I.D.) (Laboratory Instruments, Prague, Czechoslovakia) were washed with *n*-hexane and benzene prior to the measurements. They were then coated by the dynamic method with solutions of 1,2,3-tris(cyanoethoxy)propane (TCEP) in acetone of various concentrations in order to obtain capillary columns with various thicknesses of the stationary phase film.

Glass capillary columns were prepared of soft soda-lime glass (Unihost, Glassworks, Jablonec, Czechoslovakia). The glass surface was roughened with methyl trifluoroethyl ether before the columns were coated with Carbowax 20M, and when Apiezon L was used the surface was roughened with concentrated hydrochloric acid and deactivated with trimethylchlorosilane. Stationary phases were coated on the columns by the dynamic method using a mercury piston in such a way that columns with various film thickness were obtained. In order to obtain a thicker film of Carbowax 20M, the surface of one column was covered in advance with barium carbonate. Long glass capillary columns (up to 300 m) were obtained by joining shorter coated columns by means of PTFE tubing[3].

RESULTS AND DISCUSSION

Application of equation 1

Table I gives retention indices for benzene measured at 50°C in stainless-steel capillary columns with various TCEP coatings. Table II gives analogous data for *o*-xylene obtained under the same conditions. These data are shown graphically in Figs. 1 and 2 as the dependences $I = f(k)$ and $I = f(1/k)$.

TABLE I

RETENTION INDICES, CAPACITY RATIOS AND RECIPROCAL CAPACITY RATIOS OF BENZENE ON TCEP COLUMNS AT 50°C

Column	I_{50}^{TCEP}	k	$1/k$
1	770.0	0.03	35.7
2	1014.5	0.25	4.00
3	1049.7	0.69	1.45
4	1060.2	0.42	2.39
5	1109.0	1.01	0.99
6	1111.9	1.04	0.96
7	1124.0	0.97	1.03
8	1146.6	1.87	0.53
9	1169.0	2.50	0.40
10	1180.6	5.12	0.19

TABLE II

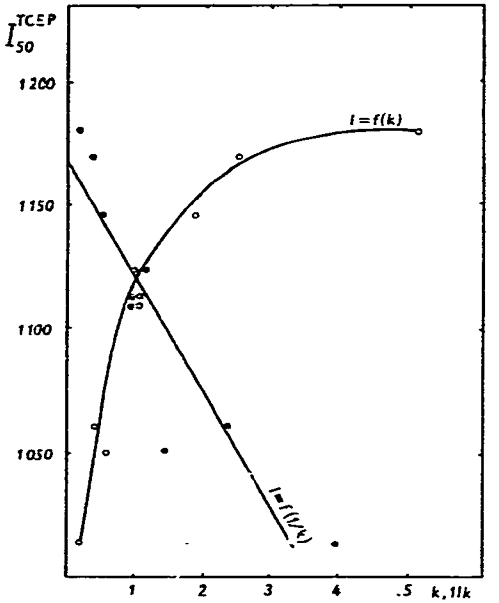
RETENTION INDICES, CAPACITY RATIOS AND RECIPROCAL CAPACITY RATIOS OF *o*-XYLENE ON TCEP COLUMNS AT 50°C

Column	I_{50}^{TCEP}	$I_{50}^{TCEP\star}$	k	$1/k$
1	988.0	–	0.18	5.55
2	1231.5	–	1.22	0.82
3	1249.0	905.5	3.45	0.29
4	1332.2	906.5	5.26	0.19
5	1340.8	905.5	4.30	0.23
6	1364.0	907.0	4.60	0.22
7	1375.4	907.1	9.20	0.11
8	1395.7	908.0	12.10	0.08
9	1398.1	906.6	8.21	0.12
10	1398.8	905.1	8.20	0.12
11	1421.2	908.9	26.70	0.04

⋆ *n*-Alkylbenzene standards.

The experimental results do not disagree substantially with eqn. 1; one experimental point obtained at a small thickness of the stationary phase film (low value of k) is the only exception. Despite this, the limiting values of I_0 were determined with an accuracy that is not sufficiently high. Thus, for benzene $I_0 = 1163 \pm 30$ and $a_I = -42.4 \pm 7.6$ with a regression coefficient $r = 0.90 \pm 0.25$, and for *o*-xylene $I_0 = 1405 \pm 38$ and $a_I = -245 \pm 54$ with $r = 0.84 \pm 0.36$.

Hence the determination of I for *n*-alkanes as standard compounds for the



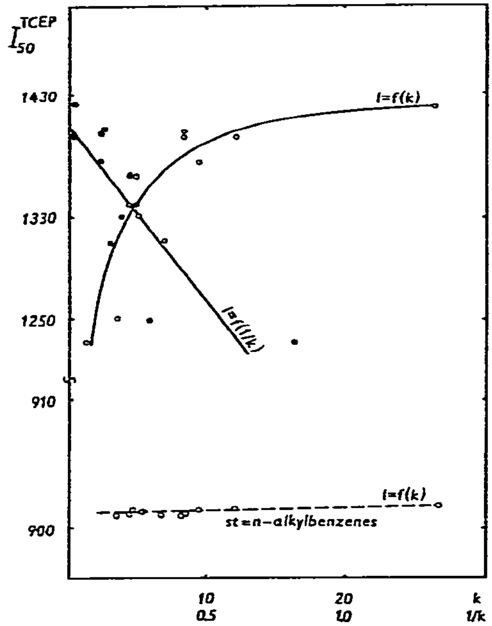


Fig. 1. Dependence of retention index of benzene (n-alkanes as standards) on capacity ratio or its reciprocal ($1/k$), obtained by measurement at 50°C in nine metal capillary columns coated with TCEP.

Fig. 2. Dependence of retention index of o-xylene (n-alkanes or n-alkylbenzenes as standards) on capacity ratio or its reciprocal ($1/k$), obtained by measurement at 50°C in ten metal capillary columns coated with TCEP.

determination of Kováts retention indices is not precise enough and reflects the obvious influence of the adsorption of n-alkanes on the polar stationary phase. In this connection it is worth noting that a_I is a much larger negative value for o-xylene than for benzene. As most of the measurements (eight out of ten) were performed in the same capillary columns, this difference is associated with the use of different n-alkane standards for the expression of the retention of o-xylene to those used for benzene (adsorption increases with molecular weight).

Influence of homologous standards on the variance of I_0 values

It was shown earlier[1] that the dependence of retention data on the amount of stationary phase in the column can be reduced significantly for polar stationary phases by replacing homologous series of n-alkanes with series of other compounds that are readily soluble in the stationary phase. This is why the measurements were performed with the use of homologous series of n-alkylbenzenes as standards (Table II). The precision of the determination of I_0 values improved significantly and the value of a_I characterizing the adsorption was reduced substantially in this case: $I_0 = 908.3 \pm 2.0$ and $a_I = -10.4 \pm 4.0$ with $r = 0.68 \pm 0.90$. The results obtained confirm the assumption that adsorption represents a significant contribution to the retention of n-alkanes in the column with TCEP.

Table III summarizes the values of I_0 and a_I for isomeric n-pentadecenes separated in three glass capillary columns coated with Carbowax 20M and for two types

TABLE III

VALUES OF I_0 AND a_I CALCULATED FOR *n*-PENTADECENE ISOMERS SEPARATED ON CARBOWAX 20M AT 110°C

n-Pentadecene isomer	*n-Alkane standards*				*1-Alkene standards*			
	I_0	s^*	a_I	s^*	I_0	s^*	a_I	s^*
cis-7-	1525.4	3.0	−11.7	1.3	1476.8	1.7	1.9	0.74
cis-6-	1528.5	2.9	−12.1	1.3	1480.4	1.6	1.2	0.72
cis-5-	1533.7	4.8	−13.5	2.2	1485.9	0.2	−0.2	0.15
cis-4-	1539.9	4.4	−14.5	2.1	1491.9	0.3	−0.4	0.12
cis-3-	1548.4	5.0	−16.0	2.4	1500.5	0.1	−1.4	0.02
cis-2-	1576.4	7.2	−23.6	4.0	1529.0	2.2	−7.4	1.21
trans-7-	1526.2	3.6	−9.6	1.6	1477.9	1.1	3.8	0.50
trans-6-	1528.2	3.5	−9.7	1.6	1479.6	1.5	3.9	0.69
trans-5-	1531.1	3.5	−10.4	1.6	1482.8	1.4	3.5	0.65
trans-4-	1533.0	3.8	−11.1	1.7	1484.5	0.6	3.0	0.26
trans-3-	1542.6	4.9	−13.6	2.4	1493.7	0.1	1.6	0.04
trans-2-	1562.2	6.4	−18.4	3.4	1514.4	1.7	−2.7	0.89
1-	1547.9	5.0	−14.7	2.5	–	–	–	–

* s = standard deviation.

of standards, *n*-alkanes and 1-alkenes[3]. The application of 1-alkenes made it possible to improve the reproducibility of I_0 values and to reduce a_I values 2–50-fold in the former instance and 3–70-fold in the latter. However, certain characteristic differences in the reproducibility for individual isomers were maintained, but they can be correlated with the structure of the compounds. Thus, not even 1-alkenes as standards for the expression of retention indices eliminated entirely the influence of adsorption on the reproducibility of the retention indices of *n*-alkene isomers on the polar stationary phase. It can be assumed that this effect will increase with increasing polarity of the stationary phase.

Retention indices were measured for *n*-pentadecene isomers depending on the thickness of Carbowax 20M for three groups of homologous standards: *n*-alkanes, 1-alkenes and 1-ethyl-2-alkylbenzenes (Fig. 3). The least variance of the retention indices was obtained for 1-alkenes, *i.e.*, for the compounds most closely related in chemical character to the compounds under analysis. As it is mixtures of compounds of different types that are analysed in practice, the selection of suitable reference substances for polar stationary phases will be problematical (see also ref. 4).

The effect of adsorption on the retention index of an *n*-alkene in capillary columns with a non-polar stationary phase is, as expected, substantially lower. 1-Pentadecene was analysed in four capillary columns coated with Apiezon L and the capacity ratios at 164°C were in the range 0.40–1.87[3]. When *n*-alkanes were used as standards, the value of I_0 was 1489.6 with a standard deviation of 1.0 and the value of a_I was -0.38. The influence of ageing on the retention indices of hydrocarbons, caused by the loss of part of the stationary phase from the column, is for the same reason also substantially less with a non-polar stationary phase[2].

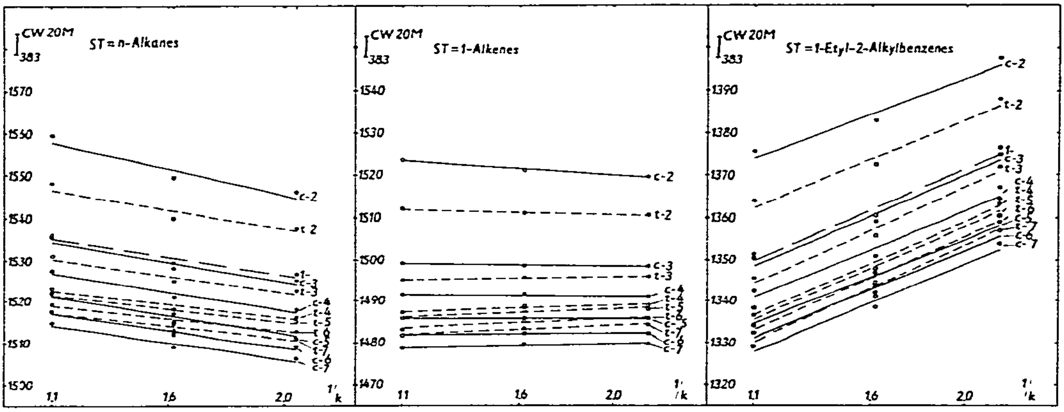


Fig. 3. Dependence of retention indices of all *n*-pentadecene isomers on reciprocal of capacity ratio of 1-ethyl-2-pentylbenzene, obtained by measurement at 110°C in three glass capillary columns coated with Carbowax 20M and with the use of *n*-alkanes, 1-alkenes and 1-ethyl-2-alkylbenzenes as standard compounds for expressing retention indices (*c* = *cis*, *t* = *trans*, 1- = 1-pentadecene).

CONCLUSION

Experimental data for hydrocarbons separated on both polar [1,2,3-tris(cyanoethoxy)propane, Carbowax 20M] and non-polar (Apiezon L) stationary phases appear to be in general agreement with relationship $I = I_0 + a_I \cdot 1/k$. With the polar stationary phases, the reproducibility of the limiting values of I_0 depends significantly on the type of homologous series of the compounds used as standard substances for the expression of retention indices, with the variance increasing as the adsorption of the standard and the compound under analysis increases. By selecting homologous compounds other than *n*-alkanes, the reproducibility of I_0 values can be improved significantly in certain cases. Retention indices can be obtained with good reproducibility only on stationary phases in which both the analysed and standard compounds dissolve well, *i.e.*, in systems in which adsorption plays a subsidiary role.

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