CAPILLARY GAS CHROMATOGRAPHY OF ALKYLBENZENES

I. SOME PROBLEMS ENCOUNTERED WITH THE PRECISION OF THE RETENTION INDICES OF ALKYLBENZENES

L. SOJÁK

Chemical Institute of Comenius University, Bratislava (Czechoslovakia)

and

J. A. RIJKS

Department of Instrumental Analysis, Eindhoven University of Technology, Eindhoven (The Netherlands)

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SUMMARY

A high-precision gas chromatographic system, in combination with high-resolution stainless-steel capillary columns and three stationary phases of different polarity, was used to study the separation and retention behaviour of 47 alkylbenzenes up to C_{15}, including all possible isomers between C_6 and C_{10}.

The precision of the relative retention data is discussed in relation to the method of time measurement, non-ideality of the carrier gas, column temperature and ageing of the column. Taking into account these factors, the inter-laboratory agreement of the retention indices for aromatic hydrocarbons determined within and between laboratories can be improved considerably. Kováts retention indices and their temperature dependence were obtained with a precision corresponding to a standard deviation of about 0.1 index unit.

INTRODUCTION

Although a large volume of retention data for hydrocarbons on different stationary phases is available, their usefulness is limited seriously in many instances because of a lack of agreement. This problem is most serious for aromatic compounds, among which benzene and alkylbenzenes up to C_{10} are the most interesting because of their importance in research, technology and environmental problems.

In order to increase the reliability of the published retention data for this class of compounds, repetition of the measurements under the conditions nowadays applied in high-precision gas chromatography is required. This would simplify their identification on the basis of published retention data, and would also permit the identification of compounds of higher molecular weight by means of fine-structure retention correlations.

Aromatic hydrocarbons have been the subject of many gas chromatographic

studies, but only two of the most recent publications will be mentioned here. Döring *et al.*[1] measured the retention data of 120 alkylbenzenes up to C_{12} on two stationary phases of different polarity (Ucon and PEG 20000) and at different temperatures. Švob and Deur-Šiftar[2] obtained retention indices for aromatic hydrocarbons on four stationary phases (squalane, acetyltributylcitrate, SE-30 and PEG 6000).

The gas chromatographic separation, measurement of retention data and structure retention correlations have been discussed for this class of compounds in many previous papers. In this work, a high-resolution gas chromatographic system, ensuring high-precision retention data[3], was used. With this system, the influence of various factors (method of retention time measurement, nature of the carrier gas, inlet pressure, column temperature and ageing of the column) on the precision and accuracy of relative retention data for alkylbenzenes was investigated.

For the separation, three stationary phases of different polarity were used: squalane, acetyltributyl citrate and 1,2,3-triscyanoethoxypropane. In order to facilitate inter-laboratory exchange of retention data and standardization, the Kováts retention index[4], advocated by many workers[5-10], was chosen as the retention parameter in this work.

EXPERIMENTAL

The measurements were performed on a home-made gas chromatographic system described previously[3]. A liquid thermostat was used for temperature control and the temperature the column was maintained within $\pm$ 0.02°. The inlet pressure was controlled to within $\pm$ 0.002 atm during each analysis.

Samples of model mixtures ($<$ 0.1 μl) were introduced into the sampling system (splitting ratio 1:300) by means of a 10-μl Hamilton syringe together with methane, required for the determination of the gas hold-up time. The model samples were constituted such that the components were completely separated at the operating temperature. For the preparation of the mixtures, Phillips (London, Great Britain) and American Petroleum Institute (API, Pittsburgh, Pa., U.S.A.) standard substances were used. *n*-Alkanes required for the determination of Kováts retention indices were included in the model mixtures. In those instances when an aromatic hydrocarbon was not separated or was separated incompletely from an *n*-alkane, this standard was omitted from the mixture and its retention time was calculated from its relative retention time in another mixture. The measurements of retention times were effected with a digitizer–computer unit (sampling rate 1 per sec) with subsequent off-line data processing by paper-tape[11,12] and by stop-watch.

For the separation of the alkylbenzenes the same columns were used as in previous work[3] (columns 1 and 3). In addition, two other columns were prepared according to the preparation method described before[3]. The columns used are specified in Table I.

RESULTS AND DISCUSSION

Squalane as stationary phase
    Retention indices of aromatic hydrocarbons on squalane capillary columns. Squalane is the most frequently used stationary phase in the gas chromatographic analysis of complex hydrocarbons mixtures.

TABLE I

COLUMNS USED IN THIS WORK

No.	Stationary phase	Length (m)	I.D. (mm)	Plate number (approx.)
1	Squalane	100	0.25	$3 \cdot 10^5$
2	Squalane	100	0.25	$3 \cdot 10^5$
3	Acetyltributyl citrate	50	0.25	$1 \cdot 10^5$
4	1,2,3-Triscyanoethoxypropane	50	0.25	$6 \cdot 10^4$

In Table II, retention indices of some aromatic compounds determined in eight different laboratories[2,3,13-18] are presented in order of increasing values. The measurements were made on stainless-steel and glass capillary columns using squalane as the stationary phase. Most of these laboratories claim a precision of less than 0.2 index units (i.u.). In order to permit a comparison of these data, they have been corrected to a temperature of 70° by means of published dI/dT values[3,16]. The maximum difference appears to be 4 i.u.

TABLE II

PUBLISHED RETENTION INDICES FOR AROMATIC HYDROCARBONS UP TO C_8 ON SQUALANE CAPILLARY COLUMNS (70°)

Column material	Carrier gas	Inlet pressure (atm)	Hydrocarbon						Reference
			Benzene	Toluene	Ethyl-benzene	p-Xylene	m-Xylene	o-Xylene	
Glass	He		641.6	748.9	838.7	853.0		874.1	13
Steel	N_2	3	641.9	750.2	839.8	854.0		875.3	3
Steel	H_2	1.9	642.1	749.3	840.0	856.3*	854.1*	875.5	14
Glass	Ar	2.0		750.4	839.8	854.2	855.9	975.3	15
Steel	N_2	4.0	642.9	750.2	840.1	854.1	856.6	875.5	16
Steel	He		643.4	750.8	839.8	854.4	856.0	875.1	2
				751.2	840.7	854.5	856.7	876.9	17
Steel	Ar	2.8	645.3	751.9	842.0	856.2	858.3	877.8	18

* Reversed retention.

In this paper, we shall discuss how far these differences can be explained by evaluating the influence of factors such as column temperature, inlet pressure, nature of the carrier gas, method of time measurement, composition of the stationary phase and ageing of the column. Obviously, highly precise measurements are required in such a study.

Repeatibility of retention indices of alkylbenzenes within the laboratory. The measurements were made on column 1 at 70.0°, 80.8° and 95.4° with nitrogen and hydrogen as the carrier gases at inlet pressures between 1 and 4 atm. Retention times were measured with a digitizer–computer system on the basis of peak maxima and the centre of gravity[11,12] and by stop-watch. A chromatogram of one of the model mixtures is shown in Fig. 1.
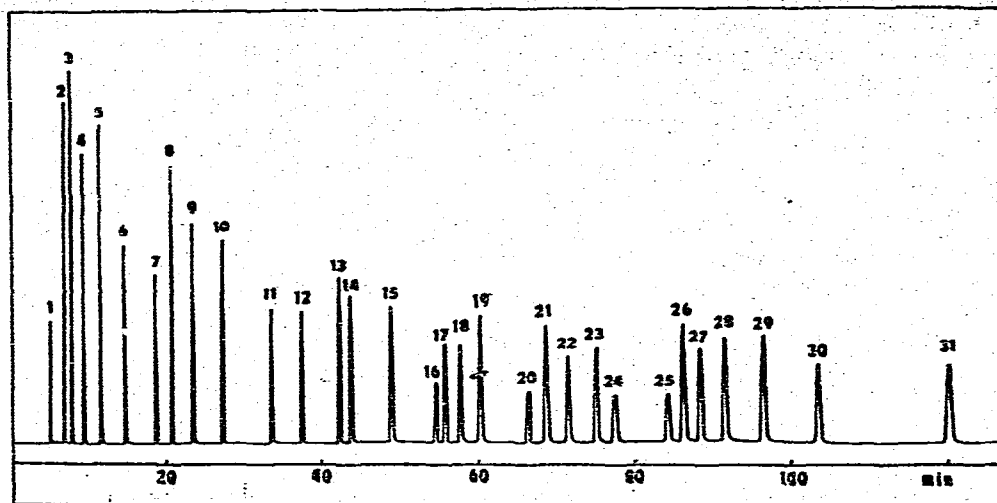
Fig. 1. Chromatogram of a model mixture of alkylbenzenes and n-alkanes. Column: length, 100 m; I.D., 0.25 mm; stationary phase, squalane; temperature, 80.7°. Carrier gas, hydrogen. Inlet pressure, 2.5 atm. Peaks: 1 = methane; 2 = n-hexane; 3 = benzene; 4 = n-heptane; 5 = toluene; 6 = n-octane; 7 = ethylbenzene; 8 = 1,3-dimethylbenzene; 9 = 1,2-dimethylbenzene; 10 = n-nonane; 11 = n-propylbenzene; 12 = 1-methyl-4-ethylbenzene; 13 = 1,3,5-trimethylbenzene; 14 = tert.-butylbenzene; 15 = isobutylbenzene; 16 = 1-methyl-3-isopropylbenzene; 17 = n-decane; 18 = 1-methyl-4-isopropylbenzene; 19 = 1-methyl-2-isopropylbenzene; 20 = 1,3-diethylbenzene; 21 = 1-methyl-3-propylbenzene; 22 = 1-methyl-4-propylbenzene; 23 = 1-methyl-2-propylbenzene; 24 = 1,3-dimethyl-5-ethylbenzene; 25 = 1,4-dimethyl-2-ethylbenzene; 26 = 1-methyl-3-tert.-butylbenzene; 27 = 1,3-dimethyl-4-ethylbenzene; 28 = 1,3-dimethyl-2-ethylbenzene; 29 = sec.-pentylbenzene; 30 = 1,2-dimethyl-3-ethylbenzene; 31 = n-undecane.

In Table III, retention indices are compared for some representative compounds of a mixture of 16 alkylbenzenes (C_8–C_{12}), obtained with hydrogen as carrier gas at an inlet pressure of 4.0 atm with different methods of time measurement.

With the digitizer–computer system, a repeatability corresponding to a standard deviation of 0.02 i.u. was obtained on the basis of peak maxima (I_m^c). On the basis of the centre of gravity ($I_{c.g.}^c$), the standard deviation was only slightly higher (0.05 i.u.), which indicates that the precision is not significantly influenced by the symmetry of the

TABLE III

RETENTION INDICES OF SOME ALKYLBENZENES, REPRESENTING A MODEL MIXTURE OF 16 COMPOUNDS (C_8–C_{12}), ON A SQUALANE CAPILLARY COLUMN AT 80.8°

Carrier gas: hydrogen. Inlet pressure: 4.0 atm. Number of measurements: between 4 and 8.

Compound	I_m^c	$I_{c.g.}^c$	I_m^t	$\Delta I_{m-c.g.}^c$	ΔI_m^{c-t}
o-Xylene	877.48	877.53	877.49	−0.05	−0.01
1,2,4-Trimethylbenzene	979.93	979.96	979.93	−0.03	0.00
1,4-Dimethyl-2-ethylbenzene	1054.52	1054.49	1054.50	0.03	0.02
tert.-Pentylbenzene	1062.48	1062.46	1062.50	0.02	−0.02
1,3,5-Triethylbenzene	1188.46	1148.47	1188.47	−0.01	−0.01
Mean standard deviation for the whole mixture	0.02	0.05	0.03		

TABLE IV

INFLUENCE OF PRESSURE DROP ON THE RETENTION INDICES OF SOME ALKYL-BENZENES

Carrier gas: hydrogen.

Compound	$I^{54}_{80.8°}$ $(P_t = 2.5\ atm)$	$I^{54}_{80.8°}$ $(P_t = 4.0\ atm)$	ΔI
o-Xylene	877.40	877.48	0.08
tert.-Butylbenzene	967.23	967.32	0.09
1,3-Dimethyl-5-ethylbenzene	1043.55	1043.64	0.09
1,4-Dimethyl-2-ethylbenzene	1054.43	1054.52	0.09
1,2-Dimethyl-3-ethylbenzene	1080.92	1081.05	0.13

peaks. The repeatibility obtained by stop-watch measurements (I^c_m) is of the same order (standard deviation 0.03 i.u.). These standard deviations for alkylbenzenes are very close to the values measured with the same system for other types of hydrocarbons[3].

In this work, the influence of the method of time measurement on the absolute values of the retention indices can be neglected. According to these results, a study of the effect of systematic error sources (e.g., nature and inlet pressure of the carrier gas, column temperature and ageing of the column) on relative retention data appears to be possible.

Influence of the nature of the carrier gas and the inlet pressure. The influence of variations in the inlet pressure on the retention index of some alkylbenzenes using hydrogen and nitrogen as the carrier gas is shown in Tables IV and V respectively. For hydrogen, an increase in the inlet pressure from 2.5 to 4.0 atm results in an increase in the retention index of about 0.1 i.u. for aromatic hydrocarbons. For nitrogen, on increasing the inlet pressure from 1.0 to 4.0 atm, an increase of about 0.3 i.u. is observed. As a result of earlier work[10], it can be said that for helium, variation of the inlet pressure up to 4.0 atm does not influence the retention index of any type of hydrocarbon at a precision corresponding to a standard deviation of about 0.05 i.u. The same applies for alkanes and alkenes when helium and hydrogen are compared.

The effect of the nature of the carrier gas on the retention indices of hydrocarbons increases in the order alkanes < alkenes < cycloparaffins < aromatics. For instance, comparing helium with nitrogen at an inlet pressure of 4 atm, for alkanes the effect can be neglected, for alkenes the effect is about 0.1 i.u., for cycloparaffins it is

TABLE V

INFLUENCE OF PRESSURE DROP ON THE RETENTION INDICES OF SOME AROMATIC HYDROCARBONS

Carrier gas: nitrogen.

Compound	$I^{44}_{70°}$ $(P_t = 1.0\ atm)$	$I^{44}_{70°}$ $(P_t = 4.0\ atm)$	ΔI
Benzene	642.86	643.18	0.32
Toluene	750.05	750.35	0.30
Ethylbenzene	839.65	839.93	0.28
p-Xylene	853.80	854.07	0.27
o-Xylene	875.04	875.37	0.33

between 0.4 and 0.7 i.u., depending on the number of carbon atoms in the ring, while for aromatic hydrocarbons the difference is about 1 i.u. (Table VI).

To summarize, it can be concluded that the nature of the carrier gas and the inlet pressure of the column should be carefully considered in inter-laboratory comparisons of retention data and standardization, especially for aromatic hydrocarbons.

TABLE VI

INFLUENCE OF THE NATURE OF THE CARRIER GAS ON THE RETENTION INDICES OF SOME AROMATIC HYDROCARBONS

Inlet pressure: 4.0 atm.

Compound	$I_{70^\circ}^{54}$		$\Delta I_{N_2-H_2}$
	H_2	N_2	
Benzene	642.07	643.34	1.27
Toluene	749.30	750.49	1.19
Ethylbenzene	838.94	840.12	1.18
p-Xylene	853.26	854.27	1.01
o-Xylene	874.41	875.56	1.15

Influence of the column temperature. In Table XIII are given the temperature increments of the retention indices of 47 alkylbenzenes up to C_{15}. They were calculated from measurements of retention indices on a capillary squalane column at 80.8 and 95.4°. The variations of the temperature increments of the retention indices, covering a relatively large interval from 0.01 to 0.45 i.u./°C, reflect the fine-structure differences of alkylbenzene isomers. This effect will be discussed in a later paper. With a few exceptions the dI/dT values of alkylbenzenes are about 0.3 i.u./°C. This demonstrates the importance of precise measurement and control of the column temperature.

Effect of ageing of the column. Column 1 had been prepared 3 years ago and used irregularly at temperatures between 50 and 70° for hydrocarbon analysis. The increase in retention index during this period for aromatic hydrocarbons was about 0.1 i.u. at 70°. In this work, the column was used during 6 weeks at 80.8° and during a further 4 weeks at 95.4°. The increase in retention index was about 0.2 i.u. at 70° for the same compounds.

At an inlet pressure of 4.0 atm, using hydrogen as carrier gas, a decrease in capacity ratio of 1.3% was observed for alkylbenzenes during a period of 8 days at 95.4°. The same decrease was observed for n-alkanes. Obviously the relative retention times (the standard was isopropylbenzene) did not change significantly, as was confirmed by measurements.

The effect of ageing of squalane columns can be illustrated with another example. A squalane capillary column of length 200 m was used in the laboratory of the first author[16,19] during 6 years at temperatures between 86° and 130°. During this period, the retention index increased by about 10 i.u. for aromatic hydrocarbons, about 5 i.u. for dienes and 2 i.u. for alkenes, while for alkanes no change was observed.

The results show that it is possible to obtain constant retention indices even for aromatic compounds during a period of 1 year at a precision of 0.1 i.u. at column temperatures below 70°. At higher temperatures, the change in retention indices for

these compounds becomes more significant as the temperature increases. However, for the application of tabulated retention data for identification purposes, a correction for this systematic effect is possible.

Reproducibility of retention indices within and between laboratories. Comparing retention indices for aromatic hydrocarbons obtained with a freshly prepared squalane column (No. 2) with those obtained on squalane column No. 1, a difference of about 0.1 i.u. was observed at 70°. Both of the columns were prepared according to the same procedure[3]. Comparing our results with those given by Švob and Deur-Šiftar[2], differences of between 0.3 and 2.8 i.u. were found (less than 1 i.u. for 80% of the compounds considered). In order to permit this comparison, the last data were corrected to 80.0° by means of dI/dT values given in Table XIII. Our results were systematically lower, and this discrepancy cannot be explained by differences in carrier gas and/or inlet pressure.

In order to facilitate the exchange of retention data for aromatic hydrocarbons between laboratories, the factors discussed above should be considered very carefully. Of these factors, the nature of the carrier gas and, to a lesser extent, the inlet pressure of the column play a more important role than had previously been expected. The differences in the retention indices for aromatic compounds between some of the laboratories[3,13,16] as given in Table II can be explained mainly only by the non-ideality of the carrier gas.

A difference in the retention index of benzene on squalene and squalane of 152 i.u. at 120° was reported by Ettre[20]. Assuming a random distribution of squalene molecules in a squalane stationary phase, a concentration of 0.1% of squalene will result an increase of 0.15 i.u. The importance of the purity and/or the composition of the stationary phase can also be demonstrated by the following example. On "freshly" prepared columns (stationary phase Apiezon L), obtained from the same manufacturer, systematic differences up to 8 i.u. were observed for aromatic hydrocarbons[19].

The study of the influence of factors such as composition or purity of the stationary phase, "polarity" of the column and column material by means of standardized experiments will be possible when the factors discussed in this paper are carefully considered.

Separation of alkylbenzenes. As the retention indices on squalane have been measured for all possible isomers of the C_6-C_{10} alkylbenzenes at two temperatures, their mutual separation can be discussed. The differences in retention behaviour of some pairs of alkylbenzenes are so small that capillary columns are required for their separation.

The separation of 1,2,3-trimethylbenzene and 1-methyl-4-isopropylbenzene, which are not sufficiently separated at 80.8°, can be achieved by an optimization of the column temperature and column length. For 1,2-diethylbenzene, 1-methyl-4-propylbenzene and 1,4-diethylbenzene, or 1,2-dimethyl-4-ethylbenzene and 1,3-dimethyl-2-ethylbenzene, a change in column temperature and/or an increase in column length cannot be expected to give an acceptable separation and capillary columns with a more polar stationary phase are required.

Acetyltributyl citrate as stationary phase

Retention indices of aromatic hydrocarbons on acetyltributyl citrate capillary columns. For the separation of those aromatic hydrocarbons which can hardly or not

be separated on squalane capillary columns, a well defined polar stationary phase should be selected. Acetyltributyl citrate was chosen for this purpose on account of its stability below 70° [3] and because literature data are available for comparison.

The difference in the retention index of benzene on this phase compared with that on squalane, giving an indication of its polarity, is about 138 i.u. at 70° [3]. Highly precise measurements for about 170 hydrocarbons on this phase at 50° and 70° were published recently[3], benzene and toluene being the only two aromatic hydrocarbons. Švob and Deur-Šiftar[2] gave retention indices for 46 aromatic hydrocarbons. For aromatic hydrocarbons with retention indices up to 1200 i.u., the data were given at 70°, while values between 1200 and 1400 i.u. were measured at 90°.

The reliability of retention indices on this phase is discussed below, considering the same factors as for the squalane column.

During this study, a special problem arose concerning the ageing of the column.

Repeatibility of retention indices of alkylbenzenes within the laboratory. The measurements were made on columns at 81.5° and 95.4°, with nitrogen as the carrier gas at an inlet pressure of 1.0 atm. Retention times were measured with a digitizer–computer system on the basis of peak maxima (I_m^c) and the centre of gravity ($I_{c.g.}^c$) and by stop-watch (I_m^s). A chromatogram of a model mixture is given as an example in Fig. 2.

In Table VII, retention indices and standard deviations are compared for different methods of time measurement. Only a few of the results for all of the possible
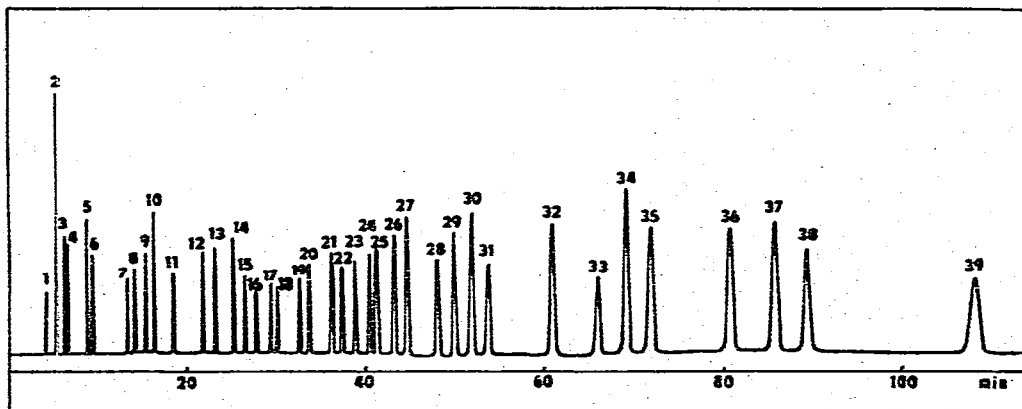

Fig. 2. Chromatogram of a mixture of alkylbenzenes and *n*-alkanes. Column: length, 50 m; I.D., 0.25 mm; stationary phase, acetyltributyl citrate; temperature, 81.5°. Carrier gas, nitrogen. Inlet pressure, 1.0 atm. Peaks: 1 = methane; 2 = *n*-heptane; 3 = benzene; 4 = *n*-octane; 5 = toluene; 6 = *n*-nonane; 7 = ethylbenzene; 8 = 1,3-dimethylbenzene; 9 = *n*-decane; 10 = 1,2-dimethylbenzene; 11 = isopropylbenzene; 12 = *n*-propylbenzene; 13 = 1-methyl-3-ethylbenzene; 14 = 1,3,5-trimethylbenzene; 15 = 1-methyl-2-ethylbenzene; 16 = *n*-undecane; 17 = isobutylbenzene; 18 = sec.-butylbenzene; 19 = 1-methyl-3-isopropylbenzene; 20 = 1-methyl-4-isopropylbenzene; 21 = 1,2,3-trimethylbenzene; 22 = 1-methyl-2-isopropylbenzene; 23 = 1,3-diethylbenzene; 24 = 1-methyl-4-propylbenzene; 25 = *n*-butylbenzene; 26 = 1,2-diethylbenzene; 27 = 1-methyl-2-propylbenzene; 28 = 1,4-dimethyl-2-ethylbenzene; 29 = 1,3-dimethyl-4-ethylbenzene; 30 = 1,2-dimethyl-4-ethylbenzene; 31 = *n*-dodecane; 32 = 1,2-dimethyl-3-ethylbenzene; 33 = 1,2,4,5-tetramethylbenzene; 34 = 1,2,3,5-tetramethylbenzene; 35 = 1,3-diisopropylbenzene; 36 = *n*-pentylbenzene; 37 = 1,2,3,4-tetramethylbenzene; 38 = 1,3-dimethyl-5-*tert.*-butylbenzene; 39 = *n*-tridecane.

TABLE VII

INFLUENCE OF THE METHOD OF TIME MEASUREMENT ON THE RETENTION IN-
DICES OF SOME ALKYLBENZENES, REPRESENTING A MIXTURE OF 31 COMPOUNDS
(C_6–C_{12}), ON AN ACETYLTRIBUTYL CITRATE CAPILLARY COLUMN AT 81.5°

Carrier gas: nitrogen. Inlet pressure: 1.0 atm. Number of measurements: between 4 and 8.

Compound	I_m	$I_{c.v.}^c$	I_m^s	$\Delta I_{m-c.g.}^c$	ΔI_m^{c-s}
Toluene	883.27	883.21	883.54	0.06	−0.27
o-Xylene	1011.69	1011.73	1011.98	−0.04	−0.29
1,3,5-Trimethylbenzene	1085.11	1085.15	1085.43	−0.04	−0.22
1,2-Diethylbenzene	1168.09	1168.05	1168.39	0.04	−0.30
1,2,3,4-Tetramethylbenzene	1267.01	1266.98	1267.37	0.03	−0.36
Mean standard deviation for the whole mixture	0.04	0.11	0.07		

C_6–C_{10} alkylbenzenes are given in order to illustrate the influence of different methods
of time measurements.

With the digitizer–computer system, a repeatibility corresponding to a standard
deviation of 0.04 i.u. was obtained for peak maxima measurements.

On the basis of the centre of gravity, the standard deviation was only slightly
higher (about 0.1 i.u.) The repeatability obtained by stop-watch measurements was
of the same order (standard deviation about 0.07 i.u.).

As shown below, the systematic difference between retention indices based on
time measurements by the digitizer–computer system and stop-watch can be ex-
plained in terms of the ageing of the column. The influence of the method of time
measurement on the absolute retention indices is therefore not expected to be signifi-
cant. According to the experimental evidence obtained from the measurements on
this phase, it seems that the slightly lower precision compared with squalane can also
be explained by column ageing effects.

Effect of ageing of the column. During the first week of this investigation, re-
tention indices were measured for benzene and toluene on column No. 3 at 81.5°, and
were compared with the corresponding data measured on the same column 2 years
earlier after correction for the difference in column temperature by means of published
dI/dT values[3]. The difference (about 0.1 i.u.) is not significant. During the previous 2
years, the column had not been used frequently and the column temperature was
always below 70°.

In this study, the column was used during the first three weeks (29/10–18/11) at
81.5° and a decrease of about 0.3 i.u. was observed for aromatic hydrocarbons during
this period. This is shown in Table VIII for some compounds that represent alkyl-
benzenes isomers up to C_{10}.

The history of the column in the next 3 months (18/11–21/2) was complicated,
with many changes in temperature, the maximum being 95.4°, and therefore only the
difference in retention index for alkylbenzenes [0.7 ± 0.1 i.u. during the whole period
(29/10–21/2)] is given in Table VIII. The changes in capacity ratios and relative
retention times (standard = isopropylbenzene) of some representative aromatic
hydrocarbons and n-alkanes during this period are given in Table IX. The decreases in
capacity ratios for n-alkanes (31.6%) and aromatic hydrocarbons (32.0%) are signifi-

TABLE VIII

INFLUENCE OF AGEING OF THE COLUMN ON RETENTION INDICES OF SOME ARO-
MATIC HYDROCARBONS, REPRESENTING ALL POSSIBLE ISOMERS BETWEEN C_8–C_{10},
ON AN ACETYLTRIBUTYL CITRATE CAPILLARY COLUMN AT 81.5°

Carrier gas: nitrogen. Inlet pressure: 1.0 atm. Number of measurements: between 4 and 8.

Compound	Date				
	29/10–4/11	5/11–11/11	18/11	14/2–21/2	ΔI (29/10–21/2)
Toluene	883.54	883.49	883.27	882.91	0.63
o-Xylene	1011.98	1011.90	1011.69	1011.31	0.67
1,3,5-Trimethylbenzene	1085.43	1085.34	1085.11	1084.75	0.68
1,2-Dimethylbenzene	1168.39	1168.29	1168.09	1167.68	0.71
1,2,3,4-Tetramethylbenzene	1267.37	1267.30	1267.01	1266.68	0.69

TABLE IX

INFLUENCE OF AGEING OF THE COLUMN ON THE CAPACITY RATIOS AND RELA-
TIVE RETENTION TIMES OF SOME ALKYLBENZENES AND n-ALKANES, REPRESENT-
ING A MODEL MIXTURE OF 18 COMPOUNDS, ON AN ACETYLTRIBUTYL CITRATE
CAPILLARY COLUMN AT 81.5°

Carrier gas: nitrogen. Inlet pressure: 1.0 atm. Number of measurements: between 4 and 8.

Compound	Capacity ratio (k)				Relative retention time (r)			
	30/10	17/2	Δk	(rel.-%)	30/10	17/2	Δr	(rel.-%)
n-Octane	0.643	0.440	31.6		0.1734	0.1744	0.57	
Toluene	1.207	0.822		31.9	0.3256	0.3259		0.09
n-Nonane	1.367	0.934	31.6		0.3689	0.3702	0.35	
n-Decane	2.890	1.976	31.6		0.7795	0.7834	0.50	
o-Xylene	3.160	2.150		32.0	0.8523	0.8525		0.02
1,3,5-Trimethyl-benzene	5.461	3.716		32.0	1.4731	1.4735		0.03
n-Undecane	6.087	4.163	31.6		1.6420	1.6507	0.53	
sec.-Butylbenzene	6.708	4.568		31.9	1.8103	1.8107		0.02
n-Dodecane	12.784	8.738	31.6		3.4485	1.4644	0.46	
1,2,3,5-Tetramethyl-benzene	16.760	11.408		31.9	4.5211	4.5229		0.04
n-Tridecane	26.743	18.288	31.6		7.2143	7.2508	0.51	

cantly different; the relative retention times of n-alkanes increased by about 0.5%, while for alkylbenzenes they did not change significantly ($< 0.1\%$). It will be shown below that this effect is even more important for a more polar stationary phase.

    Influence of temperature. As shown in table X, the effect of ageing of the column can considerably influence the temperature coefficients of the retention indices of aromatic hydrocarbons. The larger the difference in the time interval between the measurements at different temperatures, the larger will be the deviations of the dI/dT values. This is a serious limitation to the application of dI/dT values for confirmation of identity and fine-structure retention correlations.

    According to Table X, the agreement between dI/dT values of measurements carried out within 1 week (temperature range 81.5–95.4°) and literature data[3] in the range 50–70° is within experimental error. This indicates that the temperature co-

TABLE X

INFLUENCE OF AGEING OF THE COLUMN ON THE DETERMINATION OF TEMPER-
ATURE COEFFICIENTS OF RETENTION INDICES ON ACETYLTRIBUTYL CITRATE

Compound	dI/dT		
	Ref. 3 (50–70°)	This work, $\Delta t < 1$ week (81.5–95.4°)	This work, $\Delta t = 4$ months (81.5–95.4°)
Benzene	0.192	0.190	0.153
Toluene	0.215	0.213	0.168

efficients of aromatic hydrocarbons are constant between 50° and 100° at this preci-
sion. The dI/dT values, listed in Table XIII, were measured in time intervals that were
as short as possible. These values, with a relatively large range from −0.074 up to
0.432 i.u./°C, can be applied to studies of fine structure–retention correlations, as
will be discussed in a later paper.

Reproducibility of retention indices. As shown above, ageing of the column can
influence the reproducibility of retention indices of aromatic hydrocarbons on acetyl-
tributyl citrate. In order to prevent this problem, the column temperature should be
as low as possible.

Comparing retention indices for 46 hydrocarbons measured in our laboratory
with literature data[2], differences ranging from −1.4 to 8.5 i.u. were found after
correction by means of the dI/dT values given in Table XIII. Some systematic correc-
tions, *e.g.* for differences in carrier gas and inlet pressure, can be made, although this
will hardly influence the large discrepancies in this case. The literature data involved
in this comparison are not very precise. At 90°, a standard deviation of 0.7% was re-
ported, while at 70° the value was 0.2%.

Separation of alkylbenzenes. Some pairs of aromatic hydrocarbon isomers up
to C_{10} could hardly or not be separated on squalane capillary columns, but all of them
can be separated on acetyltributyl citrate capillary columns. Some pairs of aromatics
that are difficult to separate on this phase are *n*-butylbenzene and 1,4-diethylbenzene,
1-methyl-3-ethylbenzene and 1-methyl-4-ethylbenzene and 1,2,4-trimethylbenzene
and isobutylbenzene.

1,2,3-Triscyanoethoxypropane as stationary phase

*Retention indices of alkylbenzenes on 1,2,3-triscyanoethoxypropane (TCEP)
capillary columns.* TCEP is one of the most polar stationary phases available and its
selectivity for aromatic hydrocarbons is excellent. Stuckey[21] reported on the separa-
tion of 29 aromatic hydrocarbons by temperature programming between 50° and 90°
on TCEP capillary columns. The retention data were expressed as relative retention
times. In disagreement with our results, which will be discussed below, this phase was
reported to be stable up to 170°.

In our work, retention indices were measured on column No. 4 for 47 aromatic
hydrocarbons (C_6–C_{15}) using nitrogen and hydrogen as carrier gases at inlet pressures
between 1 and 2 atm. The repeatibility was determined using a stop-watch for the
measurement of retention times.

A study was made of the influence of the nature of the carrier gas, the inlet

pressure and the ageing of the column on the relative retention data and the temperature dependence of the retention indices.

Repeatibility of retention indices. The influence of ageing of acetyltributyl citrate capillary columns in comparative studies and on dI/dT measurements was discussed above. In order to prevent these problems, all measurements required for these studies were made as rapidly as possible and always within 1 day.

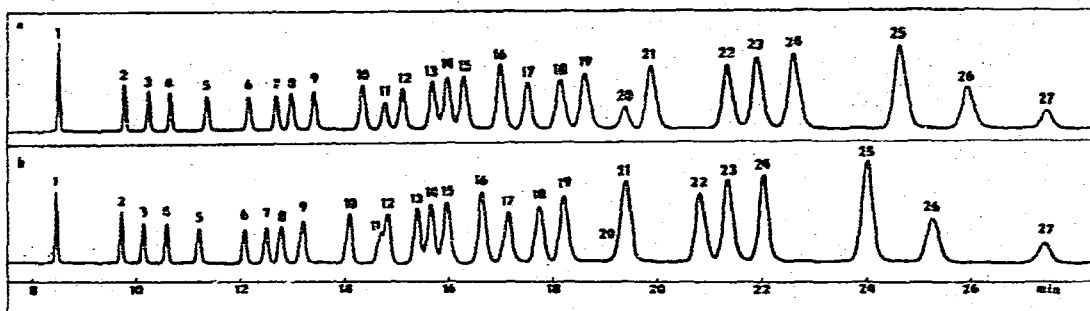Chromatograms of one of the model mixtures are shown in Fig. 3.

Fig. 3. Chromatogram of a model mixture of alkylbenzenes and n-alkanes. Column: length, 50 m; I.D., 0.25 mm; stationary phase, 1,2,3-triscyanoethoxypropane; temperature, 94.2°. Carrier gas, nitrogen. Inlet pressure, 1.0 atm. (a) Separation on 3/3/75; (b) separation on 18/3/75. Peaks: 1 = methane; 2 = n-undecane; 3 = benzene; 4 = n-dodecane; 5 = toluene; 6 = n-tridecane; 7 = ethylbenzene; 8 = 1,4-dimethylbenzene; 9 = isopropylbenzene; 10 = n-propylbenzene; 11 = n-tetradecane; 12 = 1-methyl-4-ethylbenzene; 13 = 1,3,5-trimethylbenzene; 14 = 1-methyl-3-isopropylbenzene; 15 = 1-methyl-4-isopropylbenzene; 16 = 1-methyl-2-ethylbenzene; 17 = 1,3-diethylbenzene; 18 = 1-methyl-2-isopropylbenzene; 19 = 2-methyl-2-phenylbutane; 20 = n-pentadecane; 21 = 1-methyl-2-propylbenzene; 22 = 1,4-diisopropylbenzene; 23 = 1,2,3-trimethylbenzene; 24 = n-pentylbenzene; 25 = 1,3-dimethyl-2-ethylbenzene; 26 = 1,3,5-triethylbenzene; 27 = n-hexadecane.

During one working day, a repeatibility corresponding to a mean standard deviation of 0.17 i.u. was obtained at 84.7° and 94.2° for column No. 4. The main reasons for this decrease in precision compared with squalane and acetyltributyl citrate are possibly the higher speed of analysis and certainly the very rapid ageing of the columns, as will be discussed below.

Effect of ageing of the column. During 4 days at 94.2°, the mean decrease in retention index was 2.5 i.u. for aromatic hydrocarbons, which corresponds to a decrease of 0.6 i.u. per day. Immediately after these measurements had been made, the column temperature was decreased to 84.7° for 10 days. During the last 5 days of this period, the decrease in retention index was 1.0 i.u., corresponding to a decrease of 0.2 i.u. per day. The temperature was then increased to 94.2° again. The overall decrease during the total period of 15 days was 6 i.u., corresponding to about 0.3 i.u. per day.

The effect of column ageing on the separation can be seen by comparing Fig. 3a and 3b (*e.g.*, peaks 11 and 12 and peaks 20 and 21), measured at the beginning and the end of this period respectively. The problem of ageing of the TCEP column is connected with the proper expression of retention data, and is even more significant than with acetyltributyl citrate columns.

In Table XI capacity ratios (k) and relative retention times (r) are given for some alkylbenzenes and n-alkanes at 94.2°. The standard was isopropylbenzene and the carrier was nitrogen at an inlet pressure of 1.0 atm. Contrary to the change in retention index (6 i.u.) during the period of 15 days, the change in relative retention times, based on an alkylaromatic hydrocarbon standard, was only about 0.1%. For n-alkanes, the change in relative retention times ranged from 1.9 to 4.1%. This can be explained by differences in the change in capacity ratios for aromatic hydrocarbons and n-alkanes during this period. The capacity ratios for aromatic hydrocarbons decreased considerably faster (about 4%) than those for n-alkanes. The change in the capacity ratios is about the same for all of the aromatic hydrocarbons, but for n-alkanes, the change decreases with increasing carbon number (from 2.0% for n-undecane to 0.6% for n-hexadecane). Therefore, n-alkanes are not suitable as standard compounds, either for relative retention times or for Kováts retention indices, with this phase. Another argument for not applying n-alkanes as standards for the expression of relative retention data for aromatic hydrocarbons (polar compounds) on TCEP (polar stationary phase) is the concentration dependence of the retention times. Both of these effects not only have a considerable influence on the repeatibility but also play a dominant role in the inter-laboratory agreement for such systems.

TABLE XI

INFLUENCE OF AGEING OF THE COLUMN ON THE CAPACITY RATIOS AND RELA-
TIVE RETENTION TIMES OF SOME AROMATIC HYDROCARBONS AND n-ALKANES
ON A TCEP CAPILLARY COLUMN AT 94.2°

Carrier gas: nitrogen. Inlet pressure: 1.0 atm. Number of measurements: 5.

Compound	Capacity ratio (k)				Relative retention time (r)			
	3/3	18/3	Δk	(rel.-%)	3/3	18/3	Δr	(rel.-%)
n-Undecane	0.151	0.148	2.0		0.260	0.265	1.88	
Benzene	0.206	0.197		4.5	0.355	0.356		0.28
n-Dodecane	0.254	0.249	2.0		0.439	0.449	2.22	
Toluene	0.336	0.322		4.3	0.579	0.579		0.00
n-Tridecane	0.432	0.425	1.6		0.745	0.765	2.61	
p-Xylene	0.529	0.507		4.2	0.913	0.912		−0.11
n-Tetradecane	0.749	0.732	1.2		1.276	1.318	3.18	
1,3,5-Trimethyl-benzene	0.849	0.814		4.3	1.462	1.464		0.13
1-Methyl-2-ethyl-benzene	1.002	0.960		4.4	1.727	1.728		0.05
n-Pentadecane	1.280	1.275	0.4		2.205	2.300	4.10	
1,3,5-Triethylbenzene	2.049	1.967		4.1	3.533	3.536		0.08
n-Hexadecane	2.232	2.219	0.6		3.845	3.999	3.85	

Finally, it can be concluded that these problems will be greatly reduced for aromatic hydrocarbons when the n-alkane standards are replaced with a homologous series of aromatic compounds that have similar structures to those of the compounds to be identified.

Influence of temperature. It was shown above that ageing of the column results in time-dependent retention indices, and this effect must be carefully considered in the

measurement of the temperature dependence of retention indices. Therefore, in this work retention indices were measured at two temperatures during 1 day. The measured dI/dT values on TCEP given in Table XIII are very high, ranging from 1.94 to 3.60 i.u. per °C, which necessitates extremely careful temperature measurement and control for confirmation of the identities of alkylbenzenes on TCEP by means of dI/dT values.

    Influence of the nature of the carrier gas and the inlet pressure. In Table XII, retention indices for some aromatic hydrocarbons, representing a mixture of 17 compounds on a TCEP capillary column, are compared for nitrogen and hydrogen as carrier gases at inlet pressures between 1 and 2 atm and 84.7°. Increasing the inlet pressure from 1 to 2 atm resulted in an average increase in the retention index of 1.2 i.u. for nitrogen. Comparing the difference in retention index for hydrogen and nitrogen a similar result was obtained. It seems that the influence of the nature of the carrier gas and the inlet pressure on retention indices increases with increasing polarity of the stationary phase for aromatic hydrocarbons.

TABLE XII

INFLUENCE OF PRESSURE DROP AND NATURE OF THE CARRIER GAS ON THE RETENTION INDICES OF SOME AROMATIC HYDROCARBONS, REPRESENTING A MIXTURE OF 17 COMPOUNDS, ON TCEP AT 84.7°

Compound	Nitrogen (14/3)			Inlet pressure 1.0 atm (17/3)		
	2.0 atm	1.0 atm	Δ	Nitrogen	Hydrogen	Δ
Toluene	1229.7	1228.7	1.0	1228.6	1226.9	1.7
o-Xylene	1370.4	1369.2	1.2	1368.8	1367.6	1.2
1,2-Diethylbenzene	1478.0	1476.8	1.2	1476.4	1474.9	1.5
n-Pentylbenzene	1519.3	1517.9	1.4	1517.4	1516.3	1.1
1,2,3,5-Tetramethylbenzene	1579.9	1578.6	1.3	1577.8	1576.7	1.1

    Separation of alkylbenzenes. The most important property of TCEP for the separation of aromatic hydrocarbons is its selectivity, which can be used for their separation from other hydrocarbons. For example, benzene is eluted between n-undecane and n-dodecane in the temperature range used in this study. The pair 1-methyl-2-isopropylbenzene and 1,4-diethylbenzene are difficult to separate on this phase, as also are sec.-butylbenzene, 1-methyl-3-ethylbenzene, 1-methyl-4-ethylbenzene and tert.-butylbenzene.

    In comparison with literature data[21], we found a reversed order for 1,4- and 1,3-dimethylbenzene; the latter result can be confirmed by considering the dI/dT values for these substances.

CONCLUSION

    Kováts retention indices and the corresponding temperature coefficients for 47 alkylbenzenes up to C_{15} on squalane, acetyltributyl citrate and 1,2,3-triscyanoethoxypropane at 80° are listed in Table XIII. For these phases, the repeatibility of the retention indices decreases with increasing polarity (standard deviations 0.03, 0.07 and 0.17, respectively). For squalane and acetyltributyl citrate columns, the re-

TABLE XIII

RETENTION INDICES OF ALKYLBENZENES ON SQUALANE, ACETYLTRIBUTYL CITRATE AND 1,2,3-TRISCYANOETHOXYPROPANE AT 80.0° AND THEIR TEMPERATURE COEFFICIENTS

Carrier gas: for squalane, hydrogen; for acetyltributyl citrate and TCEP, nitrogen. Inlet pressure: for squalane, 4.0 atm; for acetyltributyl citrate, 1.0 atm.

Compound	Squalane		Acetyltributyl citrate		TCEP	
	$I_{80°}$	dI/dT	$I_{80°}$	dI/dT	$I_{80°}$	dI/dT
Benzene	644.42	0.240	780.66	0.192	1128.2	1.96
Toluene	751.68	0.245	882.60	0.213	1219.1	2.03
Ethylbenzene	841.56	0.265	973.52	0.225	1289.8	2.14
p-Xylene	855.73	0.251	980.48	0.214	1302.1	2.14
m-Xylene	857.76	0.245	983.96	0.213	1306.1	2.07
o-Xylene	877.26	0.284	1010.94	0.253	1357.5	2.42
Isopropylbenzene	901.00	0.264	1032.42	0.214	1319.5	2.11
n-Propylbenzene	929.74	0.282	1059.99	0.245	1349.9	2.22
1-Methyl-3-ethylbenzene	943.07	0.242	1070.53	0.213	1370.4	2.23
1-Methyl-4-ethylbenzene	945.26	0.269	1071.02	0.207	1372.1	2.24
1-Methyl-2-ethylbenzene	958.25	0.282	1092.09	0.268	1415.4	2.37
1,3,5-Trimethylbenzene	962.70	0.239	1084.45	0.206	1387.9	2.20
tert.-Butylbenzene	967.08	0.290	1099.32	0.255	1372.7	2.21
1,2,4-Trimethylbenzene	979.70	0.288	1107.43	0.264	1435.5	2.38
Isobutylbenzene	982.35	0.301	1108.74	0.263	1363.1	2.21
sec-Butylbenzene	983.15	0.308	1112.10	0.262	1371.7	2.21
1-Methyl-3-isopropylbenzene	997.41	0.216	1124.76	0.180	1396.4	2.07
1,2,3-Trimethylbenzene	1004.31	0.337	1140.56	0.312	1493.1	2.65
1-Methyl-4-isopropylbenzene	1004.39	0.267	1129.57	0.228	1403.2	2.13
1-Methyl-2-isopropylbenzene	1010.42	0.264	1145.13	0.224	1439.4	2.26
1,3-Diethylbenzene	1023.18	0.244	1151.40	0.201	1428.4	2.19
1-Methyl-3-propylbenzene	1027.78	0.255	1153.38	0.217	1425.0	2.21
n-Butylbenzene	1029.42	0.284	1160.26	0.251	1431.3	2.29
1,3-Diethylbenzene	1032.95	0.289	1167.31	0.253	1465.4	2.36
1-Methyl-4-propylbenzene	1033.02	0.282	1157.01	0.246	1430.3	2.25
1,4-Diethylbenzene	1033.82	0.277	1160.42	0.244	1439.4	2.23
1-Methyl-2-propylbenzene	1039.41	0.298	1171.86	0.265	1467.5	2.37
1,3-Dimethyl-5-ethylbenzene	1043.46	0.218	1166.87	0.182	1447.8	2.18
1,4-Dimethyl-2-ethylbenzene	1054.29	0.260	1182.94	0.229	1486.9	2.32
1-Methyl-3-tert.-butylbenzene	1051.12	0.236	1185.93	0.183	1444.4	2.14
1,3-Dimethyl-4-ethylbenzene	1060.40	0.281	1188.53	0.249	1492.7	2.46
tert.-Pentylbenzene	1062.21	0.369	1192.72	0.330	1447.0	2.34
1,2-Dimethyl-4-ethylbenzene	1064.95	0.286	1194.04	0.253	1499.3	2.49
1,3-Dimethyl-2-ethylbenzene	1064.97	0.309	1201.77	0.287	1527.0	2.63
1-Methyl-4-tert.-butylbenzene	1069.11	0.292	1195.38	0.261	1455.4	2.11
sec.-Pentylbenzene	1071.59	0.286	1200.61	0.260	1437.0	2.32
1,2-Dimethyl-3-ethylbenzene	1080.77	0.329	1217.51	0.303	1543.5	2.73
1,2,4,5-Tetramethylbenzene	1099.53	0.341	1229.04	0.298	1558.3	2.74
1,2,3,5-Tetramethylbenzene	1105.05	0.338	1235.59	0.309	1565.0	2.77
1,3-Diisopropylbenzene	1115.13	0.195	1241.46	0.137	1458.8	1.94
n-Pentylbenzene	1128.58	0.286	1257.89	0.233	1506.4	2.37
1,2,3,4-Tetramethylbenzene	1125.98	0.395	1266.14	0.370	1618.6	3.07
1,3-Dimethyl-5-tert.-butylbenzene	1146.85	0.167	1272.43	0.119	1512.9	2.05
1,4-Diisopropylbenzene	1148.55	0.247	1274.07	0.197	1494.4	2.07
1,3,5-Triethylbenzene	1188.34	0.167	1314.30	0.117	1547.0	2.20
Pentamethylbenzene	1251.20	0.452	1389.91	0.432	1737.9	3.60
1,3,5-Triisopropylbenzene	1282.82	0.015	1406.21	−0.074	1556.0	1.28

peatibility is of the same order as for other hydrocarbons using the same high-precision gas chromatographic system.

Ageing of the column results in a decrease in retention indices for polar columns, while for apolar columns the retention index will increase. The influence of this factor on the repeatibility increases with increasing polarity of the stationary phase, even at temperatures far below the allowed maximum temperature. For instance, the retention index for aromatic hydrocarbons on TCEP decreased by 6 i.u. during 15 days at temperatures between 81.7° and 94.2°. At the same time, the relative retention times, using isopropyl benzene as the standard, were constant within $\pm$ 0.1 %. This striking difference is caused by a four-fold faster decrease of the capacity ratio for aromatic hydrocarbons compared with n-alkanes. Therefore, the influence of ageing of the column on the repeatibility depends fundamentally on the proper expression of retention data (choice of standards). For aromatic hydrocarbons separated on a polar phase, the Kováts retention index is not the most convenient means of expressing retention data, as it is based on n-alkane standards.

The effect of column ageing can have a considerable influence on the results of the estimation and application of dI/dT values, and this effect must be carefully considered in studies concerning confirmation of identity. The relatively high dI/dT values of between 0.2 and 3.0 for the phases studied in this work require accurate measurement and control of temperature.

The influence of the nature of the carrier gas and the inlet pressure on the retention index increases with increasing polarity of the stationary phase for aromatic hydrocarbons. For different types of hydrocarbons, the influence of this factor increases in the order alkanes $<$ alkenes $<$ cycloalkanes $<$ aromatic hydrocarbons. For instance, comparing retention indices on TCEP obtained with hydrogen as carrier gas at 1.0 atm with those obtained with nitrogen as carrier gas at 2 atm, a difference of about 3 i.u. can be expected. When comparing retention data between laboratories, this factor should be taken into account.

The separation of all of the alkylbenzenes up to C_{10} can be achieved with two high-resolution capillary columns of different polarity.

The application of this study to fine-structure retention correlations will be discussed in a later paper.

ACKNOWLEDGEMENTS

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