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PROBLEMS WITH THE REPRODUCIBILITY OF RETENTION DATA ON CAPILLARY COLUMNS WITH HYDROCARBON C₈₇ AS THE STATIONARY PHASE

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SUMMARY

The reproducibility of retention data on hydrocarbon C₈₇ stationary phase coated on soda lime glass capillary columns was systematically studied. For mixtures of *n*-alkanes and of alkylbenzenes it was found that the selectivity of the stationary phase is higher and the retention indices of alkylbenzenes and their temperature coefficients are higher compared to those obtained on OV-101. The reproducibility of the column preparation was good, the differences in retention indices measured on several columns being of the order of several decimals of index units. The columns were stable at lower temperatures (100, 120°C) within a certain time interval (14 days). In the course of longer measurements, the stationary phase slowly increases in polarity; a rapid change in polarity was observed at elevated temperatures (180°C).

INTRODUCTION

The largest amount of retention data published for hydrocarbons was obtained on squalane which is generally accepted as the standard non-polar stationary phase¹⁻³. Squalane, however, suffers from the obvious disadvantage that, due to its volatility, the temperature limit of its use in glass capillary columns is about 90°C^{4,5}. At higher temperatures there is considerable column bleeding. Mixtures of diastereoisomers do not fulfil the demands concerning the purity of the stationary phase and the reproducibility of retention data⁶. Therefore the use of methylsilicones has been advanced as a standard or as one of a set of preferred phases^{7,8}, as they are almost non-polar and stable at higher temperatures⁹. This choice may also be criticized for several reasons, in respect of the stability and performance¹⁰.

The requirements of an hydrocarbon for use at high temperature have been considered by Huber and Kováts¹¹, who deduced that a molecular weight in excess of 1100 would allow an upper limit of 300°C. Riedo *et al.*¹⁰ synthesized the hydrocarbon 24,24-diethyl-19,29-dioctadecylheptatetracontane of formula C₈₇H₁₇₆, and provided a possible solution to the problem of the non-polar standard stationary phase between the temperature limits of 30 to 250°C. The properties of this phase have been described in several papers^{10,12-16}. Prolonged use in columns with silanized packing material at 180°C was possible without any significant increase in the phase constants or deterioration of the peak shape¹³.

Comparing the Mc Reynolds constants on hydrocarbon C₈₇ and on squalane, it was shown that the values for benzene, *n*-butanol, 2-pentanone, 2-nitropropane, pyridine were higher on hydrocarbon C₈₇, the largest differences being found for benzene and pyridine¹⁴.

Some authors have accepted hydrocarbon C₈₇ as a standard non-polar stationary liquid, having the commercial name Apolane-87¹⁷. Its use as well as retention data were reported for packed columns^{10,15,16,19-22}. Only a few papers deal with the application of hydrocarbon C₈₇ as a stationary phase in support-coated open-tubular (SCOT)²³ and wall-coated open-tubular (WCOT)^{24,25} columns. Soják *et al.*²⁴ used this stationary phase with success; they prepared highly efficient capillary columns with very thin film (SLP) for the separation of isomers of linear pentadecenes and compared the results with those obtained on squalane. The retention indices of *n*-pentadecenes on C₈₇ differed from those on squalane by less than +2 index units (i.u.). A slight difference has been found between the selectivity of C₈₇ hydrocarbon and that of squalane. This selectivity, in combination with an efficient separation system, made it possible to separate *n*-pentadecene isomers more rapidly and more completely. The authors also published the retention indices of C₈ alkylbenzenes which were higher than on squalane (the difference was from 16.3 to 20.9 i.u.), but the reproducibility of retention data and the column stability was not described.

The aim of our work was to use capillary columns with hydrocarbon C₈₇ as a standard non-polar stationary liquid for the identification of alkylbenzenes. In the course of long isothermal experiments under routine laboratory conditions, changes in retention data were observed. Therefore a systematic examination of the reproducibility of retention characteristics of alkylbenzenes was undertaken on several glass capillary columns with dynamically or statically coated stationary phases (with various inner surface pretreatments).

EXPERIMENTAL

Capillary columns were made of soda lime glass (Unihost, Teplice, Czechoslovakia). Surface roughening was performed by statically etching the inner surface with gaseous hydrogen chloride at 330°C for 16 h. Two columns were further deactivated with Carbowax 20M²⁶. Two silanized columns (with dipentyltetramethyldisilazane) were leached with liquid hydrochloric acid (20%) at 140°C for 15 h²⁷. The columns were coated dynamically (15% solutions of hydrocarbon C₈₇ in toluene and OV-101 in chloroform) or statically (0.15–0.4% solutions of hydrocarbon C₈₇ in pentane) with the stationary phase.

Gas chromatographic (GC) measurements were performed on a Model 2350 gas

chromatograph (Carlo Erba, Milan, Italy) equipped with a flame ionization detector and stream splitter. Glass capillary columns were coated with hydrocarbon C₈₇ (I, 200 m × 0.25 mm I.D.; II, 100 m × 0.25 mm I.D., dynamically coated; 30 m × 0.25 mm I.D., statically coated) and OV-101 (278 m × 0.25 mm I.D. dynamically coated). The carrier gas was nitrogen (at a linear velocity of 10 cm/s) or hydrogen (30 cm/s) at 100 and 120°C. The nitrogen used for filament lamps and electrolytic hydrogen were of guaranteed purity of 99.998% and were not specially purified.

Mixed samples were prepared by alkylation reactions of benzene or alkylbenzenes with alkyl halogenides in the presence of aluminium chloride. Samples were injected after dilution in acetone and addition of *n*-alkanes (C₇–C₁₄) with 1- and 10- μ l Hamilton syringes. Methane was used for the determination of the gas hold-up time. The elution time was measured with a digital stop-watch Time Calculator RM 4111 (Tesla, Rožnov, Czechoslovakia).

NMR measurements of pure hydrocarbon C₈₇ (Supelco, Bellefonte, PA, U.S.A.) and the washed-out phase of the column were performed on a Brooker CXP 300 NMR spectrometer operated at 300 MHz for ¹³C and ¹H spectra.

RESULTS AND DISCUSSION

Hydrocarbon C₈₇ stationary phase was chosen to study the retention behaviour of alkylbenzenes with carbon atom numbers from C₇ to C₁₅. Squalane is not suitable for the analysis of alkylbenzenes with carbon atom numbers over 10 for long periods. Standards of higher alkylbenzenes were lacking, therefore mixed samples were prepared. No retention data for alkylbenzenes on hydrocarbon C₈₇ were available, so the components were identified by comparison with data on an OV-101 capillary column and by GC-mass spectrometry (MS). In Figs. 1 and 2 chromatograms are shown illustrating the separation of mixtures of *n*-alkanes and products of alkylation of 1,2-dimethylbenzene by ethyl bromide on columns of hydrocarbon C₈₇ and OV-101 at 120°C. The composition of the mixture together with the retention indices, *I*, at 120°C and *I*/10°C are given in Table I. The separation of alkylbenzene isomers was better on hydrocarbon C₈₇ (column I; effective plate number, *N*_e = 329 000; *k* = 4.0) than on OV-101 (*N*_e = 395 720; *k* = 4.4). Retention indices as well as their temperature coefficients are systematically higher on hydrocarbon C₈₇ in comparison with OV-101.

During work at 100 and 120°C over a long period it was observed that the retention indices of alkylbenzenes increased. Retention data (*I*, *k*) for alkylbenzenes on two new capillary columns (I, II) of differing film thicknesses (column II gave about capacity factors, *ca.* 50% lower) and their values after 8 months of use of column I are given in Table II.

The retention indices measured on the new columns were approximately the same, independent of the film thickness. The capacity factors on column I decreased within 8 months of use. The percentage degrees in capacity factors for *n*-alkanes and some alkylbenzenes are given in Table III. The largest decrease was observed for the *n*-alkanes (7–8%); for aromatic hydrocarbons the decrease was 1.5–3%, as expected from the increase in polarity. Also the values of the relative retentions, *r* (Table III), of *n*-alkanes and aromatics differ significantly. For *n*-alkanes the decrease in relative retention, Δr , was 4.5–6.0%, increasing with increasing carbon chain length. For alkylbenzenes, Δr slightly increased. From these results it follows that the polarity of column I has changed.

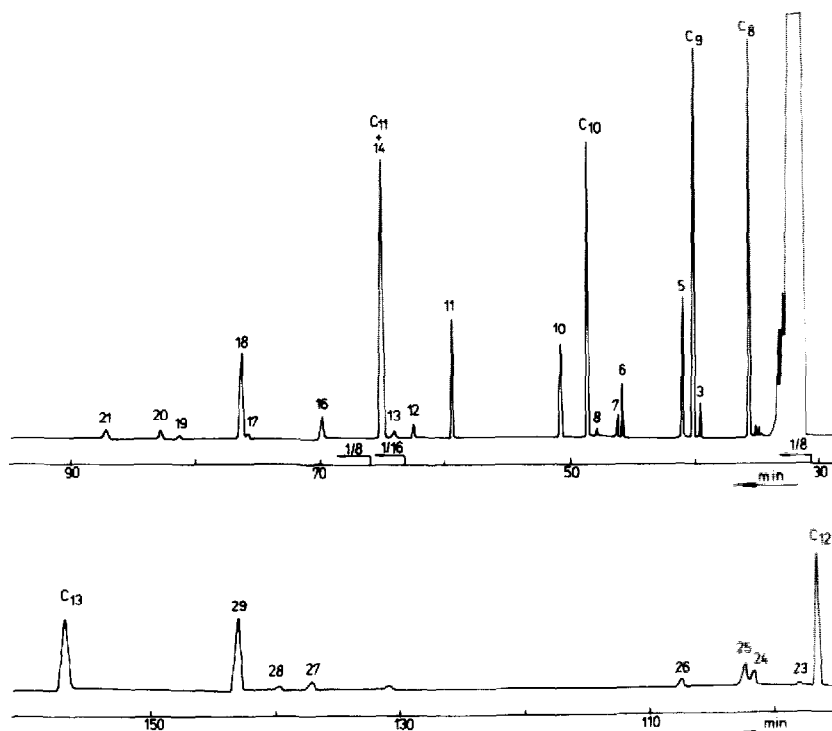


Fig. 1. Chromatogram of the separation of *n*-alkanes and products of alkylation of 1,2-dimethylbenzene by ethyl bromide on an hydrocarbon C₈₇ glass capillary column I at 120°C with nitrogen as the carrier gas. For peak designation see Table I.

According to our previous experience of the reproducibility of measurement of retention data on squalane columns (below 90°C) and OV-101 columns under the same experimental conditions (purity of carrier gas, capillary inner wall quality) and the published thermal stability of hydrocarbon C₈₇, chemical changes of this stationary

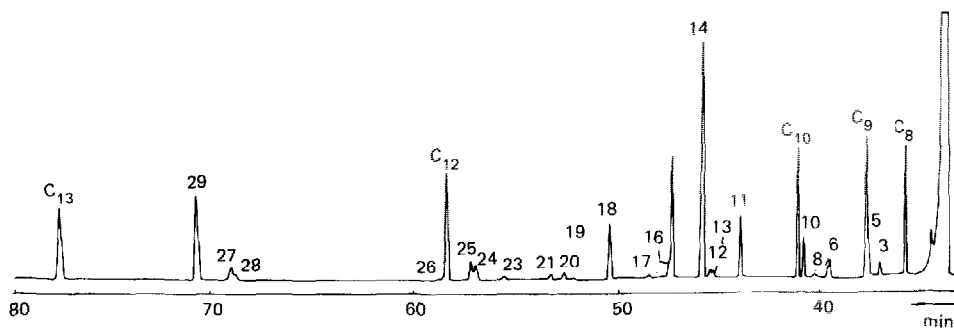


Fig. 2. Chromatogram of the separation of *n*-alkanes and products of alkylation of 1,2-dimethylbenzene by ethyl bromide on an OV-101 glass capillary column at 120°C with hydrogen as the carrier gas. For peak designation see Table I.

TABLE I

RETENTION INDICES, *I*, OF PRODUCTS OF ALKYLATION OF 1,2-DIMETHYLBENZENE BY ETHYL BROMIDE AND THEIR TEMPERATURE COEFFICIENTS, $\Delta I/10^\circ\text{C}$, MEASURED ON HYDROCARBON C₈₇ AND OV-101 CAPILLARY COLUMNS

Peak No.	Compound*	Hydrocarbon C ₈₇		OV-101	
		<i>I</i> ₁₂₀	$\Delta I/10^\circ\text{C}$	<i>I</i> ₁₂₀	$\Delta I/10^\circ\text{C}$
3	1,4-DiMeB	889.7	2.95	870.9	2.50
5	1,2-DiMeB	913.7	3.50	895.0	3.20
6	1-Me3EtB	973.4	3.15	959.6	2.70
7	1-Me4EtB	977.4	3.80	962.2	2.54
8	1-Me2EtB	993.9	4.05	976.4	3.10
10	1,2,4-TriMeB	1017.4	3.65	993.0	3.10
11	1,3-DiMe5EtB	1072.8	3.00	1052.9	2.25
12	1,4-DiMe2EtB	1088.6	3.85	1073.1	2.95
13	1,3-DiMe4EtB	1096.2	4.05	1075.2	3.10
14	1,2-DiMe4EtB	1100.0	4.00	1080.8	3.05
16	1,2-DiMe3EtB	1120.5	4.60	1101.2	3.60
17	1,2,4,5-TetraMeB	1142.1	4.50	1113.2	3.55
18	1,3-DiEt5MeB	1143.5	2.75	1134.0	2.10
19	1,2-DiEt4MeB	1159.4	3.45	1149.7	3.00
20	1,4-DiEt2MeB	1163.8	3.40	1154.9	2.90
21	1,3-DiEt4MeB	1176.5	3.60	1160.2	3.00
23	TriMeEtB	1203.8	3.85	1179.9	3.45
24	TriMeEtB	1211.6	3.80	1190.0	3.30
25	TriMeEtB	1213.2	3.85	1191.6	3.40
26	TriMeEtB	1223.6	4.05	1200.0	3.40
27	DiMeDiEtB	1273.5	3.50	1260.9	3.10
28	DiMeDiEtB	1277.7	3.80	1261.8	2.95
29	DiMeDiEtB	1281.8	3.50	1269.9	3.00

* Abbreviations: Me = methyl, Et = ethyl, B = benzene.

phase under relatively mild conditions (120°C) were not expected. Therefore we have tried to find an explanation for the polarity changes of the stationary phase in columns statically coated with the defined film thickness of SLP. We have considered the influences of column ageing, properties of the inner surface of the capillary wall, film thickness of SLP, carrier gas (nitrogen, hydrogen), temperature of column conditioning.

The reproducibility of retention index measurements on six columns conditioned at 150°C was in the range of several decimals of index units, without regard to the quality of the inner walls (non-deactivated columns; deactivated Carbowax; silanized), film thickness of hydrocarbon C₈₇ (0.1–0.25 μm) and nature of the carrier gas (nitrogen hydrogen). The reproducibility on the same columns over 2 weeks was found to be of the order of 0.3 i.u. On the same columns after conditioning at higher temperature (180°C) and on the other four columns directly conditioned at 180°C, the indices measured significantly increased, but on most columns the values of the retention indices were similar to those obtained on column after 8 months used.

For the identification of the eventual chemical changes in the composition of the stationary phase, the NMR spectra of pure hydrocarbon C₈₇ and of washed-out

TABLE II

RETENTION INDICES, I , AND CAPACITY FACTORS, k , OF ALKYL BENZENES MEASURED ON HYDROCARBON C₈₇ COLUMNS I, II AT 120°C

Compound*	Column I				Column II	
	I	k	I^{**}	k^{**}	I	k
1,2-DiMeB	913.7	0.32	924.4	0.32	913.3	0.15
1-Me3EtB	973.4	0.48	982.9	0.47	973.1	0.22
1-Me4EtB	977.4	0.49	986.7	0.48	978.1	0.23
1-Me2EtB	993.9	0.55	1003.6	0.54	993.9	0.26
1,2,4-TriMeB	1017.4	0.64	1027.1	0.63	1017.0	0.30
1,3-DiMe5EtB	1072.8	0.92	1081.6	0.90	1072.4	0.43
1,4-DiMe2EtB	1088.6	1.02	1097.3	1.00	1088.5	0.48
1,2-DiMe4EtB	1100.0	1.10	1109.3	1.08	1100.0	0.52
1,2-DiMe3EtB	1120.5	1.26	1130.4	1.24	1120.3	0.59
1,3-DiEt5MeB	1143.5	1.47	1152.1	1.43	1143.2	0.68
1,2-DiEt4MeB	1159.4	1.63	1168.1	1.59	1158.9	0.76
1,4-DiEt2MeB	1163.8	1.68	1172.6	1.64	1163.5	0.78
1,3-DiEt4MeB	1176.5	1.82	1185.6	1.78	1176.1	0.85
TriMeEtB	1203.8	2.18	1213.3	2.14		
TriMeEtB	1211.6	2.29	1220.9	2.25	1211.1	1.08
TriMeEtB	1213.2	2.32	1222.6	2.27		
TriMeEtB	1223.6	2.48	1233.2	2.43	1223.1	1.16
DiMeDiEtB	1273.5	3.45	1282.8	3.36	1273.0	1.60
DiMeDiEtB	1277.7	3.53	1286.6	3.44	1277.4	1.65
DiMeDiEtB	1281.8	3.63	1291.3	3.55	1281.3	1.69

* Abbreviations as in Table I.

** Values measured on column I after 8 months of use.

TABLE III

CAPACITY FACTORS, k , RELATIVE RETENTIONS, r , OF n -ALKANES AND ALKYL-BENZENES MEASURED ON COLUMN I AT 120°C AND THEIR DIFFERENCES, Δk , Δr , AFTER 8 MONTHS OF COLUMN USE

Compound*	k	r	k^{**}	r^{**}	Δk (%)	Δr (%)
n -C ₉	0.29	0.20	0.27	0.19	6.89	-4.50
1-Me4EtB	0.49	0.34	0.48	0.34	2.04	+0.89
n -C ₁₀	0.57	0.39	0.53	0.37	7.02	-5.14
1,2,4-TriMeB	0.64	0.44	0.63	0.44	1.56	+0.92
n -C ₁₁	1.10	0.75	1.02	0.71	7.27	-5.33
1,3-DiEt5MeB	1.47	1.00	1.43	1.00	2.72	
n -C ₁₂	2.13	1.45	1.96	1.37	7.98	-5.59
TriMeEtB	2.29	1.57	2.25	1.57	1.75	+0.06
n -C ₁₃	4.09	2.79	3.76	2.62	8.07	-5.92

* Abbreviations as in Table I.

** Values measured on column I after 8 months of use.

stationary phase were compared. Since from one column after the change in SPL polarity it was possible to wash out 3–6 mg of stationary phase, no changes in the composition or structure of the stationary phase were determined by NMR spectroscopy.

CONCLUSIONS

According to the results obtained glass capillary columns made of soda lime glass and containing the stationary phase hydrocarbon C₈₇ underwent column ageing. The stationary phase is stable at lower temperatures (100, 120 °C) over a certain time interval (14 days). In the course of longer measurements, the stationary phase slowly increases in polarity, or a rapid change in polarity occurs at elevated temperatures (180°C) due to chemical changes in the thin film of the stationary phase. Since no special purification of the carrier gases was employed, this is most probably a result of oxidation caused by the catalytic activity of the glass surface and by trace oxygen impurities in the carrier gas. Under these conditions, however, OV-101 and SE-54 capillary columns are perfectly stable with respect to the reproducibility of retention index measurements.

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