

DEPENDENCE OF GAS CHROMATOGRAPHIC RETENTION DATA OF HYDROCARBONS ON THE FILM THICKNESS OF THE POLYDIMETHYLSILOXANE STATIONARY PHASE

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Kovats indices of cyclic and aromatic hydrocarbons, separated by capillary gas liquid chromatography on polydimethylsiloxane capillary columns, were found to increase with increasing stationary phase film thickness. This effect is explained in terms of adsorption of the stationary phase on the active sites of the inner surface of the capillary column. Since the number of active sites is limited, the overall polarity of the polydimethylsiloxane stationary phase is better defined in columns with thick stationary phase films. Interlaboratory reproducibility of retention indices of cyclic and aromatic hydrocarbons is therefore also better when using capillary columns with thick films of the polydimethylsiloxane stationary phase. Retention data obtained on such thick-film columns are influenced by adsorption of the stationary phase on the column walls to a lesser extent than in columns with thinner films.

Samples of volatile hydrocarbons are usually analyzed by high resolution gas chromatography with nonpolar polydimethylsiloxane stationary phases coated on the inner surfaces of glass or fused silica capillaries. Recent advances in column technology are connected with a very high reproducibility of manufactured fused silica capillary columns containing chemically bonded and cross-linked polydimethylsiloxane stationary phases. Such columns are flexible, show very low bleeding, have long lifetimes at relatively high temperatures, and exhibit very low catalytic and adsorption activities. Standardization of a capillary column production is connected with a very high degree of reproducibility of retention data. When such columns are placed in an oven with a precise and reliable set-up and a controlled working temperature and carrier gas column inlet pressure, the retention data can be used with a relatively high reliability for identification purposes. Such data can be employed in automated analysis of multicomponent samples using microprocessor-controlled GC instruments. HRGC analysis of paraffins, olefins, naphthenes and aromatics (PONA) in various samples is an example of this approach¹.

Lubeck and Sutton^{2,3} have published hundreds of Kovats retention indices for branched, cyclic, aromatic and olefin hydrocarbons chromatographed on commercially available fused silica capillary columns coated with polydimethylsiloxane stationary phases. The data, however, reveal a statistically significant dependence of the retention indices on the thickness of the polydimethylsiloxane stationary phase film over the region at 0.2 – 1.0 μm , namely such that the Kovats indices (I) of cyclic and aromatic hydrocarbons as well as their temperature coefficients (dI/dT) increase with increasing film thickness of the polydimethylsiloxane stationary phase. This finding, however, disagrees with the results of Johansen and Ettre⁴, who observed no dependence of the Kovats indices of hydrocarbons separated on columns coated with a polydimethylsiloxane stationary phase of different film thickness. One of the reasons of this discrepancy may be in the different precision of the retention index measurement. Lubeck and Sutton^{2,3} measured the retention indices of each individual hydrocarbon with a relatively high repeatability (standard deviation of measurement below 0.1 index units), whereas Johansen and Ettre⁴ measured retention data for hydrocarbons in mixtures where the peaks overlapped, and moreover, they failed to report the repeatability of their measurements.

The following conclusions have been drawn from studies of how the GLC retention data are affected by the adsorption of polar solutes separated on glass capillary columns with nonpolar as well as polar stationary phases of different film thickness:

- retention indices of polar solutes separated on nonpolar stationary phases (e.g. Apiezon L, OV-101) decrease with increasing stationary phase film thickness⁴⁻⁹,
- retention indices of polar solutes separated on polar stationary phases (e.g. Carbowax 20 M) increase with increasing stationary phase film thickness^{7,9}.

Farkas et al.¹⁰ as well as Zhao Guoliang and Chi Rixiao⁸ have found that the adsorption of alkanes and naphthalene on capillary columns with chemically bonded polydimethylsiloxane stationary phases is negligible. The evaluation of the dependence of the Kovats indices of very polar solutes on the film thickness for nonpolar and moderately polar stationary phases leads to the following statement: *the overall column polarity of capillary columns decreases with increasing film thickness in the case of nonpolar stationary phases and increases with increasing film thickness in the case of polar stationary phases*^{5,11}. This statement, however, is only valid if the polarity of solute is much higher than that of the stationary phase and the adsorption on the liquid surface has virtually no effect on the solute retention.

The dependence of the retention indices on the thickness of the stationary phase film is more complex if the polarities of the stationary phase and the solutes do not differ substantially, as in the case of hydrocarbons separated on capillary columns coated with polydimethyl stationary phases.

The aim of this contribution is: (i) to explain why the Kovats retention indices of hydrocarbons depend on the film thickness of the polydimethylsiloxane stationary phase, and (ii) to predict reliable retention data for identification purposes.

EXPERIMENTAL

Apparatus

A HP 5980 gas chromatograph (Hewlett–Packard, Waldbronn, Germany) equipped with an FID and an all-glass inlet splitter was used. Hydrogen at a flow rate of 40 cm/s served as the carrier gas. Samples were injected by using a 10 μ l Hamilton syringe. Chromatograms were evaluated by using an integrator (HP 3396, Hewlett–Packard). Injection of methane was applied to determine the gas hold-up time. The hydrocarbon sample, which was prepared by Dr P. Cellar, at the Laboratory for Chromatography, Slovnaft, Bratislava, consisted of a mixture of 100 μ l volumes of 40 compounds listed in Table I.

The repeatability of retention index measurement was estimated by evaluating three chromatograms obtained on column E at 60 °C. The standard deviation of the retention indices was lower than: (i) 0.03 index units for branched alkanes, (ii) 0.05 index units for cyclic hydrocarbons, and (iii) 0.07 index units for aromatic hydrocarbons.

Column Characteristics

Columns A (0.25 μ m) and C (1.0 μ m) (DB-1 from J&W Scientific, Rancho Cordova, CA) were fused silica capillary columns containing cross-linked and chemically bonded polydimethylsiloxanes whose McReynolds constants were similar to those of other polydimethylsiloxane stationary phases (SE-30, OV-101 and SP-2100).

Columns B (0.5 μ m) and E (0.5 μ m) (PONA from Hewlett–Packard, Avondale, CA) were fused silica capillary columns with cross-linked polydimethylsiloxane, designed for hydrocarbon type analyses (PONA-paraffins, olefins, naphthenes and aromatics).

Column D (0.2 μ m) was a glass capillary column 278 m long, prepared by us by connecting three capillary columns with a shrinkable Teflon tube. The glass columns were all made of soft glass (Unihost, Kavalier, Teplice, The Czech Republic). Prior to coating with the stationary phase, the inner surface of the columns was treated with gaseous HCl by applying a static procedure described elsewhere¹². The stationary phase was deposited on the column wall dynamically by using 0.3 ml of 15% polydimethylsiloxane (OV-101, Carlo Erba, Milan, Italy) in methylene chloride at a velocity of 2 cm/s. The stationary phase solution was pushed through the column by means of compressed nitrogen with an Hg plunger in a way similar to that described by Schomburg et al.¹³. The stationary phase film thickness was determined by using the equation:

$$d_f = \frac{r_c}{2} \sqrt{\frac{u\eta_s}{\gamma_s}}, \quad (1)$$

where d_f is the film thickness, r_c is the capillary inner diameter, u is the coating solution velocity, η_s is the viscosity of the coating solution, and γ_s is its surface tension¹⁴. The number of theoretical plates found for column D by injecting n-alkane with a capacity factor of 2.56 was $7.5 \cdot 10^4$.

TABLE I

Kovats indices found at 60 °C for sample I constituents in capillary column coated with polydimethylsiloxane stationary phases

| No. | Name | Column ^a | | | | | |
|-----|---|---------------------|-------|-------|-------|-------|-------|
| | | A | B | C | D | E | F |
| 1 | Pentane | 500 | 500 | 500 | 500 | 500 | 500 |
| 2 | 2,2-Dimethylbutane | 538.0 | 538.0 | 537.9 | 537.9 | 538.2 | – |
| 4 | Cyclopentane | 567.8 | 568.0 | 568.3 | 568.4 | 568.0 | 568.1 |
| 5 | 2,3-Dimethylbutane | – | – | – | 568.4 | 567.3 | 567.3 |
| 6 | 2-Methylpentane | 569.8 | 569.8 | 569.7 | 568.4 | 569.7 | 569.8 |
| 7 | 3-Methylpentane | 584.4 | 584.6 | 584.5 | 584.2 | 584.5 | 584.4 |
| 8 | Hexane | 600 | 600 | 600 | 600 | 600 | 600 |
| 9 | 2,2-Dimethylpentane | 625.7 | 625.7 | 625.6 | 625.7 | 625.6 | 625.5 |
| 10 | 2,4-Dimethylpentane | 631.0 | 631.0 | 630.9 | 630.7 | 630.8 | 630.7 |
| 11 | Methylcyclopentane | 630.4 | 630.5 | 630.8 | 630.7 | 630.6 | 629.9 |
| 12 | Benzene | 653.8 | 654.2 | 654.4 | 653.5 | 654.2 | 655.8 |
| 13 | 3,3-Dimethylpentane | 658.1 | 658.0 | 658.0 | 657.9 | 658.1 | 657.6 |
| 14 | 2-Methylhexane | 667.8 | 667.8 | 667.8 | 667.7 | 667.8 | 667.5 |
| 15 | 2,3-Dimethylpentane | 671.1 | 671.1 | 671.2 | 671.0 | 671.0 | 670.6 |
| 16 | 1,1-Dimethylcyclopentane | 675.9 | 676.0 | 676.1 | 675.8 | 676.8 | 675.4 |
| 17 | 1- <i>cis</i> -3-Dimethylcyclopentane | 685.5 | 685.6 | 685.8 | 685.3 | 685.6 | 685.2 |
| 18 | 3-Ethylpentane | 687.0 | 687.4 | 687.4 | 687.9 | 687.4 | 686.7 |
| 19 | 1- <i>trans</i> -2-Dimethylcyclopentane | 690.0 | 691.0 | 691.2 | 690.7 | 691.0 | 690.6 |
| 20 | Heptane | 700 | 700 | 700 | 700 | 700 | 700 |
| 21 | 2,2-Dimethylhexane | 722.9 | 722.8 | 722.8 | 723.2 | 722.8 | 723.5 |
| 22 | Methylcyclohexane | 724.0 | 724.1 | 724.4 | 723.2 | 724.2 | 723.9 |
| 23 | 2,5-Dimethylhexane | 732.5 | 732.5 | 732.4 | 732.8 | 732.4 | 732.2 |
| 24 | 2,4-Dimethylhexane | 734.9 | 734.9 | 734.9 | 734.8 | 734.8 | 734.6 |
| 25 | Ethylcyclopentane | 734.3 | 734.5 | 734.8 | 734.8 | – | 733.9 |
| 26 | 3,3-Dimethylhexane | 742.9 | 743.0 | 743.0 | 743.0 | 742.8 | – |
| 27 | Toluene | 756.2 | 756.5 | 756.7 | 756.5 | 756.6 | 758.0 |
| 29 | 2,3,3-Trimethylpentane | 761.4 | 761.4 | 761.4 | 761.4 | 761.3 | 761.1 |
| 30 | 3,4-Dimethylhexane | 770.5 | 770.5 | 770.5 | 770.6 | 770.6 | 770.5 |

TABLE I
(Continued)

| No. | Name | Column ^a | | | | | |
|-----|---|---------------------|-------|-------|-------|-------|-------|
| | | A | B | C | D | E | F |
| 31 | 1- <i>cis</i> -3-Dimethylcyclohexane | 778.4 | 778.5 | 778.6 | 778.1 | – | – |
| 31a | 1- <i>trans</i> -4-Dimethylcyclohexane | 780.2 | 780.3 | 780.5 | 779.9 | – | 779.7 |
| 32 | 1-Methyl- <i>trans</i> -2-ethylcyclopentane | 791.8 | 791.8 | 792.2 | 791.9 | – | – |
| 33 | Octane | 800 | 800 | 800 | 800 | 800 | 800 |
| 34 | 1- <i>trans</i> -2-Dimethylcyclohexane | 797.4 | 797.5 | 797.8 | 797.5 | 797.7 | – |
| 35 | 1- <i>trans</i> -3-Dimethylcyclohexane | 803.9 | 804.1 | 804.3 | 804.1 | 804.2 | – |
| 36 | 1- <i>cis</i> -2-Dimethylcyclohexane | 826.6 | 826.8 | 827.1 | 826.7 | 826.9 | – |
| 37 | Ethylbenzene | 847.8 | 848.1 | 848.2 | 847.6 | 848.1 | – |
| 38 | 1,4-Dimethylbenzene | 857.1 | 857.4 | 857.6 | 856.9 | 857.0 | – |
| 39 | 1,3-Dimethylbenzene | 856.1 | 856.4 | 856.6 | 855.9 | 856.4 | – |
| 40 | 1,2-Dimethylbenzene | 877.6 | 877.8 | 878.1 | 877.4 | 878.0 | – |

^a For characteristics see text; column F – recalculated from data published by Johansen and Etre for the column (100 m long with 0.25 mm i.d. made of soda lime glass) coated with 0.2 μm film thickness of OV 101 stationary phase⁴.

RESULTS AND DISCUSSION

It is reasonable to assume that during a capillary gas chromatographic analysis in a nonpolar fused silica capillary column, the concentration of the stationary phase in the column is much higher than the concentration of solutes, and that the effect of retention of hydrocarbons by adsorption on the stationary phase liquid surface can be neglected. Accepting these assumptions we come to the conclusion that the overall polarity of the stationary phase (with a given film thickness of the stationary liquid spread on the inner surface of the capillary column) and the polarity of the hydrocarbons are the main factors influencing the retention indices of hydrocarbons separated by HRGC under the working conditions chosen. It is clear that normal and branched hydrocarbons can be considered as nonpolar whereas unsaturated and aromatic hydrocarbons exhibit some polar features. Polydimethylsiloxane stationary phases are generally regarded as nonpolar but the retention index of benzene on such phases ($I = 642$ at 60 °C) is substantially higher than on the nonpolar squalene (2,6,10,15,19,23-hexamethyltetracosane) phase ($I = 638$ at 60 °C), while the indices of paraffins and naphthenes are almost the same⁴.

The polarity of polydimethylsiloxanes is due to the different electroaffinity of the atoms (H, C, Si, O) bound in the polydimethylsiloxane polymers. Since the amount of polydimethylsiloxane in the capillary column is much higher than that of the hydrocarbons analyzed, the stationary phase is preferentially adsorbed on the active sites of the capillary column walls. As the adsorption energy depends, *inter alia*, on the adsorption activity of the active sites, the most active sites are occupied preferentially, followed by the less and least active sites. Therefore the overall polarity of polydimethylsiloxane stationary liquids depends on the film thickness, namely so that it is lowest for thin films and highest for very thick films. This is why in the analysis of hydrocarbons, the overall polarity of capillary columns coated with polydimethylsiloxane stationary liquids increases with increasing film thickness. This statement, however, does not apply to polar compounds on polar surfaces (particularly in columns with thinner films) where the compounds are adsorbed before the polydimethylsiloxane stationary phase.

The increase in the overall column polarity depends appreciably on the adsorption activity of the capillary wall surface, and for chemically bonded or cross-linked phases also on the nature of the compound used for these types of reaction⁷. The more polar groups and active sites occur on the surface, the more significant is the dependence of the overall column polarity on the polydimethylsiloxane film thickness. This conclusion can also be derived from Table I, where the Kovats indices of some hydrocarbons are listed for different capillary columns coated with a polydimethylsiloxane stationary liquid of different film thickness. The following conclusions can be drawn from the data for columns A–C:

- the retention data of branched alkanes, except for 3-methylpentane and 3-ethylpentane, are nearly independent of the stationary phase film thickness,
- the retention indices of cycloalkanes and aromatic hydrocarbons increase with increasing thickness of the stationary phase film. This dependence, however, is not linear, the differences between the data obtained for columns B–A are higher than for columns C–B, although the stationary phase film thickness increases from 0.25 μm in column A to 0.50 μm for column B to 1.0 μm for column C. This conclusion is consistent with the results obtained for alcohols separated on columns coated with Carbowax 20 M stationary phases¹¹.

A reasonable agreement is found between the published² (columns A–C) and measured (columns D–E) retention indices of hydrocarbons in columns with matching film thickness. Comparison of data in corresponding columns (A with D, B with E) indicates the reproducibility of the retention index measurements. A very good reproducibility is observed for columns B and E with a stationary phase film thickness of 0.5 μm , where the published and experimental retention indices differ less than 0.3 index units. The reproducibility for columns with films 0.25 μm thick (columns A, D and F) is poorer than for columns with films 0.50 μm thick (columns B and E). It is clear that the contribution of the column wall surface activity to the retention indices is

minimized in columns with relatively thick films of the polydimethylsiloxane stationary phase. This leads to the conclusion that the interlaboratory reproducibility of retention indices of hydrocarbons obtained on capillary columns coated with polydimethylsiloxane stationary phases will be the better, the thicker is the film of the polydimethylsiloxane stationary phase. Films 0.50 μm thick, however, provide a reproducibility which is acceptable for the identification of hydrocarbons in refinery products.

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REFERENCES

1. *The Sadtler Capillary GC Standard Retention Index Library*. Sadtler Research Laboratories, Philadelphia 1989.
2. Lubeck A. J., Sutton D. L.: *J. High Resolut. Chromatogr.* 6, 328 (1983).
3. Lubeck A. J., Sutton D. L.: *J. High Resolut. Chromatogr.* 7, 542 (1984).
4. Johansen N. G., Ettore L. S.: *Chromatographia* 15, 625 (1982).
5. Matisova E., Krupcik J., Garaj J.: *Chromatographia* 16, 169 (1982).
6. Berezkin V. G., Korolev A. A.: *Chromatographia* 20, 482 (1985).
7. Sojak L., Berezkin V. G., Janak J.: *J. Chromatogr.* 209, 15 (1981).
8. Zhao Guoliang, Chi Rixiao: *Chromatographia* 29, 575 (1990).
9. Berezkin V. G.: *J. Chromatogr.* 159, 359 (1978).
10. Farkas P., Sojak L., Kovac M., Janak J.: *J. Chromatogr.* 471, 251 (1989).
11. Krupcik J., Matisova E., Garaj J., Sojak L., Berezkin V. G.: *Chromatographia* 16, 166 (1982).
12. Krupcik J., Kristin M., Valachovicova M., Janiga S.: *J. Chromatogr.* 126, 147 (1975).
13. Schomburg G., Husmann H., Weeke F.: *J. Chromatogr.* 99, 63 (1974).
14. Ettore L. S.: *Open Tubular Columns in Gas Chromatography*, p. 58. Plenum Press, New York 1965.

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