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REPRODUCIBILITY OF TEMPERATURE-PROGRAMMED GAS CHROMATOGRAPHIC RETENTION INDICES WITH NON-POLAR GLASS CAPILLARY COLUMNS

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SUMMARY

The reproducibility of linear temperature-programmed gas chromatographic retention indices has been assessed with non-polar persilanized and OV-1-coated capillary columns. Measurements of the short- and long-term reproducibility of retention indices obtained under nominally constant chromatographic conditions have been performed. Conditions were assessed that have to be met if chromatographic parameters (carrier gas inlet pressure, temperature programming rate, column length and/or diameter) are to be changed without changing retention indices.

INTRODUCTION

Temperature-programmed gas chromatographic (TPGC) retention indices are increasingly applied in the analysis of complex mixtures¹⁻⁷. We have applied TPGC retention indices to environmental organic analysis^{4,5} by capillary column TPGC and TPGC-mass spectrometry (MS). In this field, the differentiation of many compounds, such as positional isomers (*e.g.*, alkylbenzenes, terpenes), requires an accuracy and reproducibility of TPGC retention indices of better than one index unit.

The use of capillary columns and modern chromatographic equipment increases the accuracy and reproducibility of TPGC retention times in principle to a few hundredths or even thousandths of a minute and, hence, of TPGC retention indices to even better than 0.1 index unit, provided that the chromatographic conditions are not modified and, in particular, the stationary phase does not change and the amounts of solute injected do not exceed the limits given by the linear portions of the gas-liquid distribution isotherms. The advent of persilanized non-polar and moderately polar glass and fused-silica capillary columns with high stationary phase stability^{8,9}, which can be manufactured in a very reproducible way gives additional promise for increased reproducibility of TPGC retention indices^{2,6,7}.

As the practical usefulness of precision TPGC retention indices depends strongly on their long-term and inter-column reproducibility and also on the amount of standardization of chromatographic parameters (*e.g.*, carrier flow-rate or column inlet pressure, temperature programming rate and column dimensions) required in

TABLE I
COMPOSITION OF THE TEST MIXTURE AND COMPOUND ABBREVIATIONS

<i>Abbreviation</i>	<i>Compound name</i>	<i>Concentration (ng/μl)</i>	<i>Abbreviation</i>	<i>Compound name</i>	<i>Concentration (ng/μl)</i>
C ₆	<i>n</i> -Hexane	62	TMB	1,3,5-Trimethylbenzene	122
C ₇	<i>n</i> -Heptane	72	DMA	N,N-Dimethylaniline	126
C ₈	<i>n</i> -Octane	123	DMP	2,6-Dimethylphenol	163
C ₉	<i>n</i> -Nonane	98	NAP	Naphthalene	132
C ₁₀	<i>n</i> -Decane	102	ANT	Anthracene	120
C ₁₁	<i>n</i> -Undecane	112	ALK1	Branched C ₁₅ alkane (in diesel oil)	
C ₁₂ to C ₂₄	<i>n</i> -Alkanes in diesel oil	600	ALK2	Branched C ₁₇ alkane (in diesel oil)	
BENZ	Benzene	107	ALK3	Pristane (in diesel oil)	
TOL	Toluene	104			
XYL	<i>o</i> -Xylene	124			

order to reproduce TPGC retention indices, we have investigated these aspects with persilylated OV-1-coated glass and fused-silica capillary columns.

EXPERIMENTAL

TPGC retention indices were determined with the test mixture given in Table I. Volumes of 1 μ l of the mixture were injected in the split mode with a splitting ratio of 10:1. Retention times were measured with a Hewlett-Packard 5880 A gas chromatograph and GC terminal, equipped with a flame-ionization detector. Calculations of retention indices (see below) were performed with a Finnigan INCOS GC-MS data system, which could be interfaced to the GC terminal in order to allow for the transfer of GC report data after each analysis. During all experiments, the temperature was isothermal at 35°C for 5 min and was subsequently programmed to 280°C (our standard conditions for the analysis of volatile environmental organics). The injec-

TABLE II
CAPILLARY COLUMN SPECIFICATIONS

<i>Column No.</i>	<i>Material</i>	<i>Length (m)</i>	<i>I.D. (mm)</i>	<i>Phase ratio</i>
1	Fused silica	50	0.2	450
2	Borosilicate	25	0.31	67
3	Borosilicate	25	0.31	67
4	Borosilicate	25	0.31	67
5	Borosilicate	23	0.31	67
6	Borosilicate	24.8	0.29	67
6A	Borosilicate	22.4	0.29	67
6B	Borosilicate	20.0	0.29	67
6C	Borosilicate	17.7	0.29	67

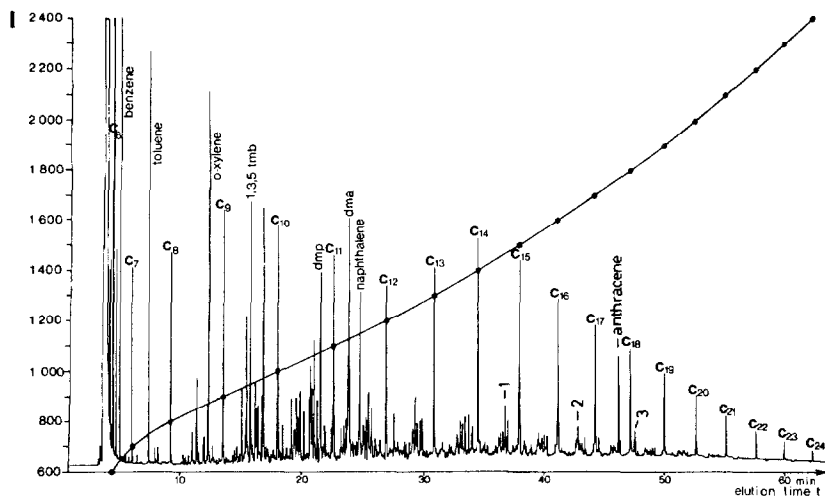


Fig. 1. Capillary column gas chromatogram of a test mixture and plot of TPGC retention indices, I , of n -alkanes vs. elution time, t . For chromatographic conditions, see Experimental. Temperature programming rate, $4^\circ\text{C}/\text{min}$. For compound name abbreviations, see Table I.

tion port and detector temperature was 300°C . All capillary columns used in this study were persilanized and coated with OV-1. The fused-silica column was supplied by Hewlett-Packard and all glass columns by MEGA capillary column laboratory. The columns are further specified in Table II.

CALCULATION OF RETENTION INDICES

Fig. 1 shows the capillary column chromatogram of a test mixture similar to that specified in Table I. In addition, the retention indices, I , of the n -alkanes are plotted against their elution times, t . The plot shows, as already pointed out by Nau and Biemann¹, that the relationship between the retention times and the number of carbon atoms of the n -alkanes is not strictly linear, as was assumed by Van den Dool and Kratz¹⁰ when they first introduced linear TPGC retention indices.

Therefore, TPGC retention indices, calculated by linear and non-linear interpolation of the I vs. t curve, show differences which, under our experimental conditions, are significant. We therefore calculated TPGC retention indices by use of a cubic spline function for interpolation. In this approach, for each retention time interval (t_n, t_{n+1}) (where t_n and t_{n+1} are the retention or relative retention times of n -alkanes with n and $n + 1$ carbon atoms, respectively), the I vs. t curve is approximated by a third-order polynomial. These polynomials are determined in such a way that they adopt the values I_n and I_{n+1} for t_n and t_{n+1} , respectively, and that the values of the first and second derivatives of polynomials of adjacent intervals coincide in the joining points. Cubic splines have the particular feature that they are the smoothest (least curved) continuous and twice differentiable functions through the points (I_n, t_n) ¹¹. A Fortran IV computer program was prepared for the calculation of the TPGC indices by spline interpolation.

TABLE III

LONG-TERM STABILITY OF TPGC RETENTION INDICES MEASURED ON COLUMN 1 (SEE TABLE II)

Compound	Mean retention index \pm maximum deviation				June-Oct.: maximum mean difference
	June 82* (9)**	Aug. 82 (5)	Sept. 82 (6)	Oct. 82 (9)	
BENZ	645.26 \pm 0.17	645.22 \pm 0.11	645.06 \pm 0.18	645.05 \pm 0.25	0.21
TOL	755.27 \pm 0.06	755.49 \pm 0.03	755.52 \pm 0.04	755.50 \pm 0.10	0.25
XYL	874.84 \pm 0.09	874.85 \pm 0.04	874.79 \pm 0.07	874.76 \pm 0.03	0.09
TMB	953.66 \pm 0.04	953.65 \pm 0.04	953.65 \pm 0.04	953.65 \pm 0.05	0.01
DMA	1062.37 \pm 0.11	1062.16 \pm 0.10	1062.11 \pm 0.11	1062.01 \pm 0.06	0.36
DMP	1082.12 \pm 0.19	1081.42 \pm 0.29	1081.16 \pm 0.06	1080.99 \pm 0.15	1.13
NAP	1155.10 \pm 0.13	1155.12 \pm 0.02	1155.16 \pm 0.15	1155.20 \pm 0.12	0.10
ALK1	1464.20 \pm 0.15	1463.95 \pm 0.14	1463.85 \pm 0.33	1463.68 \pm 0.19	0.52
ALK2	1651.92 \pm 0.15	1651.54 \pm 0.30	1651.38 \pm 0.44	1651.31 \pm 0.32	0.61
ANT	1751.95 \pm 0.20	1751.92 \pm 0.10	1752.08 \pm 0.06	1752.12 \pm 0.23	0.20
ALK3	1813.41 \pm 0.17	1813.29 \pm 0.16	1813.15 \pm 0.23	1813.05 \pm 0.34	0.36

* Instrument shutdown in July.

** No. of values in parentheses.

RESULTS AND DISCUSSION

Reproducibility of retention indices under nominally unchanged chromatographic conditions

Short-term reproducibility. As reported elsewhere^{4,5}, the reproducibility of TPGC indices for repetitive injections was ± 0.1 to ± 0.2 index units or less.

Long-term reproducibility. The reproducibility of the indices measured on column 1 was checked over a period of 5 months. During this period, the column was used for the analysis of volatile organic air pollutants. From time to time, the test mixture was injected and analysed under nominally unvaried experimental conditions. Table III reports monthly mean values, the maximum deviations from the means and the maximum differences between mean values. Monthly deviations are approximately ± 0.5 index units, and the same is true for the deviations of the monthly mean values from one another, with the exception of DMP, a slightly acidic compound, indicating a minor change of column acidity.

Fig. 2 shows daily variations of the retention indices of the aromatic hydrocarbons contained in the test mixture, measured with a glass capillary column (column 5 in Table II). Anthracene and naphthalene, the retention indices of which depend most sensitively on elution temperature in our mixture, show the largest variations. The strong variations around points A and B (*ca.* 1.3 index units for anthracene, see Fig. 2) are probably due to stationary-phase changes at the column terminals. At point A, two heavily polluted water samples were analysed by thermal elution of the sampling columns whereby appreciable amounts of water entered the analytical column. Thus, particularly at the hot column terminals, stationary phase

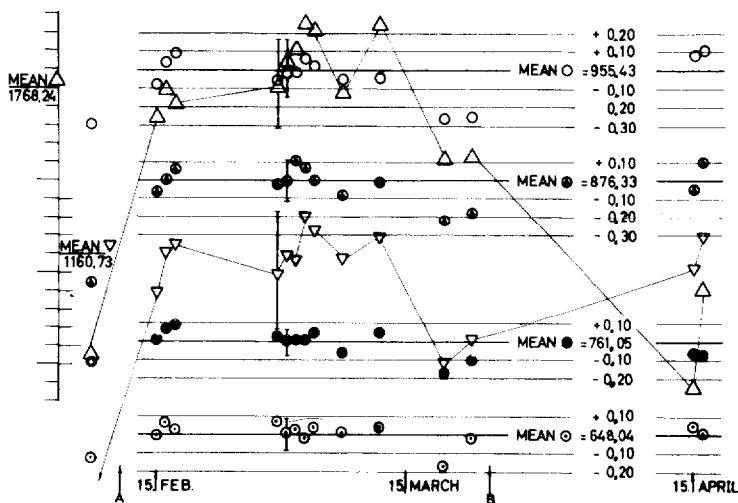


Fig. 2. Daily mean values of TPGC retention indices of the aromatic hydrocarbons contained in the test mixture described in Table I. ○ = BENZ; ● = TOL; ▲ = XYL; ○ = TMB; ▽ = NAP; △ = ANT. For other details see text.

or column surface changes may occur that influence the retention behaviour of the less volatile compounds. At point B the terminals were renewed. Between points A and B retention index changes were within ± 0.5 index units.

Inter-column reproducibility. A major advantage of persilylated non-polar capillary columns is that they can be manufactured in a very reproducible manner. Table IV reports retention indices, determined with three new glass capillary columns (columns 2, 3 and 4 in Table II) having identical specifications. The GC conditions were

TABLE IV
REPRODUCIBILITY OF TPGC RETENTION INDICES WITH DIFFERENT BUT NOMINALLY IDENTICAL COLUMNS

Compound	TPGC retention index		
	Column 2	Column 3	Column 4
BENZ	642.70	642.73	642.73
TOL	754.08	753.96	753.96
XYL	874.32	874.37	874.40
TMB	953.27	953.31	953.32
DMA	1062.07	1062.18	1062.19
DMP	1077.41	1077.41	1077.43
NAP	1156.84	1156.94	1156.95
ALK1	1464.58	1464.63	1464.66
ALK2	1652.32	1652.30	1652.42
ANT	1757.74	1758.04	1758.06
ALK3	1813.88	1813.90	1813.93

TABLE V

REPRODUCIBILITY OF TPGC RETENTION INDICES WITH DIFFERENT SETS OF TEMPERATURE PROGRAMMING RATES AND COLUMN INLET PRESSURES, YIELDING THE SAME ELUTION TEMPERATURE

GC parameter	Column 5			Column 6			
	r ($^{\circ}\text{C}/\text{min}$)	4.0	3.5	3.5	4.00	3.56	3.03
P_i/P_0	1.88	1.77	1.88	2.00	1.88	1.75	1.75
a	0.875	0.999	0.875	0.778	0.875	1.027	1.027
ra	3.50	3.50	3.08	3.11	3.12	3.11	4.11
<i>Compound</i>	<i>Retention index</i>						
BENZ	647.91	647.65	647.72	643.35	643.60	644.68	644.80
TOL	760.94	760.24	760.75	754.79	754.22	753.85	753.66
XYL	875.77	876.15	875.41	874.71	875.08	875.45	876.41
TMB	955.14	955.32	954.79	953.62	953.74	953.91	954.85
DMA	1066.10	1066.23	1065.06	1062.75	1062.90	1063.09	1065.09
DMP	1086.71	1086.73	1086.09	1078.66	1078.72	1078.83	1079.86
NAP	1159.05	1159.10	1157.01	1157.44	1157.62	1157.87	1161.62
ALK1	1464.36	1464.34	1464.34	1464.60	1464.55	1464.59	1464.67
ALK2	1652.24	1652.46	1652.48	1652.46	1652.46	1652.45	1652.48
ANT	1766.82	1766.97	1762.39	1759.14	1759.30	1759.44	1769.22
ALK3	1813.12	1813.24	1813.06	1813.88	1813.87	1813.81	1813.23

also nominally identical. The temperature programming rate was $4^{\circ}\text{C}/\text{min}$ and the column pressure ($p_i - p_0$) was 13 p.s.i. For other conditions, see experimental. The reproducibility of the retention indices is equal to that obtained with repetitive injections on the same column.

Reproducibility of retention indices with varying chromatographic conditions and/or column specifications

Although the retention indices reported in Tables III, IV and V and in Fig. 2 were all determined with persilylated and OV-1-coated columns, they vary for some compounds by up to 20 index units. The reasons for these changes are complex. A rationale for an understanding of at least an important part of these differences is provided by an equation given by Harris and Habgood¹²:

$$\frac{r}{\bar{F}_{T_0}} = \int_{T_0}^{T_R} \left(\frac{T_0}{T}\right)^{1.7} \frac{dT}{A \exp(\Delta H/RT) + 273 \cdot \bar{v}_{ds}^T/T} \quad (1)$$

This equation describes implicitly the elution temperature T_R with linear temperature programming and a constant column inlet pressure as depending on various parameters: r is the temperature programming rate, \bar{F}_{T_0} the column flow-rate at the initial temperature T_0 , expressed at standard temperature (273°K) divided by the weight of the stationary phase liquid (or gum) and corrected for the pressure gradient in the column according to

$$F_{T_0} = jF_{0T_0} \quad (2)$$

where F_{0T_0} is the carrier flow-rate at the column outlet at initial temperature T_0 , expressed at standard temperature. The pressure gradient correction factor is¹²

$$j = \frac{3}{2} \cdot \frac{(P^2 - 1)}{(P^3 - 1)} \quad (3)$$

where $P = p_i/p_0$, *i.e.*, the ratio of the column inlet and outlet pressures. A and ΔH are constants characteristic of a solute-solvent pair. For any given solute they will change only if the stationary phase type is changed (provided the ideal gas law applies to the solvent-carrier gas interaction. \bar{v}_{ds}^T is the dead volume, corrected for the pressure gradient at column temperature T (*i.e.*, the actual column void volume, V_{col}) divided by the weight of the stationary phase:

$$\bar{v}_{ds}^T = \frac{V_{col}}{gV_{phase}} = \beta/g \quad (4)$$

where $\beta = V_{col}/V_{phase}$ is the phase ratio of the column and g is the specific weight of the liquid phase at the coating temperature.

Using eqns. 2, 3 and 4, eqn. 1 can be transformed into

$$\frac{r}{F_{0T_0}} \cdot \frac{2}{3} \cdot \frac{(P^3 - 1)}{(P^2 - 1)} \cdot \frac{g \cdot v_{col}}{\beta} = \int_{T_0}^{T_R} \left(\frac{T_0}{T}\right)^{1.7} \frac{dT}{A \exp(\Delta H/RT) + 273\beta/(gT)} \quad (5)$$

Eqn. 5 allows a series of interesting conclusions to be drawn concerning the reproducibility of TPGC retention indices, as these depend only on the elution temperatures of a compound and of the two neighbouring *n*-alkanes (or other homologous compounds). As long as the elution temperatures do not change, the retention indices do not change either. According to eqn. 5, this is the case for *all* components of a mixture if two conditions are fulfilled: (1) the integrand in eqn. 5, including the programme start temperature, T_0 , is constant; and (2) the left-hand side of eqn. 5 does not change.

Condition 1 is fulfilled if, besides T_0 , the stationary phase type (*i.e.*, A , ΔH and g) and the phase ratio, β , remain unchanged. These parameters should be standardized if standard indices are to be determined.

Condition 2 is of particular interest, as it requires only the constancy of the expression as a whole. As F_{0T_0} , P and V_{col} are not independent variables, it may be preferable to express F_{0T_0} by means of Poiseuille's law for compressible gases:

$$F_{0T_0} = \frac{\pi D^4 p_0}{16^2 \eta(T_0) L} \cdot (P^2 - 1) = K_1 (P^2 - 1) D^4 / L \quad (6)$$

where K_1 is constant as long as the column outlet pressure p_0 (in general ambient pressure) and the carrier gas type [*i.e.*, $\eta(T_0)$] are not changed. D and L are the (free) column inner diameter and the column length, respectively. Using

$$V_{col} = \pi D^2 L / 4$$

and summarizing all constants in a new constant K , Condition 2 takes the following form:

$$raL^2/D^2 = K \quad (7)$$

where $a = (P^3 - 1)/(P^2 - 1)^2$ is a function of $P = p_i/p_0$ alone; a decreases with increasing P . In principle, all of the parameters of eqn. 7 may be changed without changing any T_R values, if others are changed simultaneously in an appropriate way. The following cases are of greatest practical interest: (a) r and a are changed in an inversely proportional manner; (b) L is changed and the change is compensated for by an appropriate change of r and/or a ; and L and D are changed proportionally. In the following, we report on a few experiments aimed at verification of cases (a) and (b).

It should be mentioned that eqn. 1 does not consider non-linearities of the solute distribution isotherm. Moreover, it should be kept in mind that changes of the stationary phase may happen accidentally (*e.g.*, by oxidation or polymerization) and that β may change by bleeding.

Simultaneous changes of r and a . Table V reports TPGC retention indices determined with columns 5 and 6 (see Table II). With column 5, retention indices were determined for two sets of values of r and a , giving the same product. With column 6, three sets of r and a values were tested. In order to show the variations in retention indices induced by a change of the product ra , retention indices were determined for the lower values of r and a with column 5 and for the highest of both values with column 6. The data reported in Table V lead to the following conclusions:

(1) For all compounds eluted later than *o*-xylene, retention indices are reproduced within less than 0.5 index units. A fine adjustment of r could even improve the reproducibility. It should be noted that adjustment of the column pressure has a limited precision of about 2–5% of the p_i-p_0 value.

(2) *o*-Xylene and compounds eluted earlier are either eluted during the isothermal portion of the gas chromatograms or are still influenced by it. Moreover, this influence varies for different r and a values. Eqns. 5 and 7 do not apply to this part of the chromatogram. As already noted by Perrigo and Peel³, reproducibility of the retention indices is therefore worse. Chromatographic conditions should be chosen in such a way that no compound of interest is eluted at the starting portion of the chromatogram.

(3) A comparison of the matched and unmatched retention indices in Table VI reveals the varying degrees to which the retention indices change with the elution temperature, *i.e.*, the degree to which the temperature dependence of a compound's retention time differs from that of the neighbouring *n*-alkanes. As may be expected, there is virtually no such difference for alkanes 1 and 2, and pristane shows only a small difference. The differences are largest for anthracene and naphthalene.

Simultaneous changes of r , a and L . Table VI reports TPGC indices for column 6 (see Table II) at its original length (24.8 m) and at the reduced lengths 22.4 m (6A.1; 6A.2), 20 m (column 6B) and 17.7 m (column 6C). The column inlet pressure, p_i , and the temperature programming rate, r , were adjusted so as to reproduce the retention indices measured at the original length of column 6. For 6A.1 r and a were chosen so as to reproduce the product raL^2 of column 6. The resulting retention

TABLE VI

REPRODUCIBILITY OF TPGC RETENTION INDICES WITH DIFFERENT COLUMN LENGTHS

GC parameter	Column No.				
	6	6A.1	6A.2	6B	6C
$p_i - p_0$ (p.s.i.)	14.7	13	13	11.2	10
a	0.778	0.875	0.875	1.018	1.126
r ($^{\circ}\text{C}/\text{min}$)	4.00	4.32	4.21	4.12	3.77
L (m)	24.8	22.4	22.4	20.0	17.7
raL^2	1913	1913	1848	1687	1330
<i>Compounds</i>	<i>Retention index</i>				
BENZ	643.35	643.51	643.46	643.37	643.50
TOL	754.79	755.15	755.13	754.92	754.26
XYL	874.71	874.66	874.58	874.67	874.96
TMB	953.62	953.69	953.63	953.57	953.65
DMA	1062.75	1062.88	1062.75	1062.71	1062.84
DMP	1078.66	1078.72	1078.69	1078.71	1078.63
NAP	1157.44	1157.78	1157.51	1157.42	1157.48
ALK1	1464.60	1464.61	1464.52	1464.56	1464.70
ALK2	1652.46	1652.64	1652.46	1652.40	1652.56
ANT	1759.14	1760.17	1759.25	1759.16	1759.09
ALK3	1813.88	1814.00	1813.85	1813.79	1814.97

indices are higher than for column 6 at its original length, suggesting that the elution temperatures were too high. Therefore, the temperature programming rate was reduced in order to match the retention indices of column 6. The same happened for columns 6B and 6C. Only at raL^2 values of 1678 and 1330, respectively, could the retention indices of column 6 be reproduced within ± 0.1 index unit or better, with the exception of benzene, toluene, and *o*-xylene, for which the reproducibility was worse for the reasons discussed in the preceding paragraph. For the time being, we do not have an explanation for this deviation from eqn. 7.

Anyway, the results confirm that even with changing column length it is possible to readjust the TPGC indices of all compounds to their original values, with the exception of those of compounds which are eluted either in the isothermal part of the chromatogram or near the start (approximately during the first 10 min at a rate of $4^{\circ}\text{C}/\text{min}$) of the temperature programme.

CONCLUSION

The usefulness of TPGC retention indices for the analysis of complex mixtures depends on their accuracy and reproducibility. For persilylated OV-1-coated (non-polar) capillary columns, which are most promising with respect to stationary-phase stability and inter-column reproducibility, we have shown that short- and inter-column reproducibility of TPGC retention indices, measured with modern chromatographic equipment, is better than ± 0.5 index units and typically in the region of ± 0.1 index unit. Long-term index stability without any adjustment of parameters is typically better than ± 0.5 index units.

Starting from the principle that retention indices will change only if the elution temperature changes, it has been pointed out that reproducible retention indices can be obtained simultaneously for all components of a mixture if columns with the same stationary phase and phase ratio and a fixed starting temperature for the temperature programme are used.

It has been pointed out further that the temperature programming rate, r , the column inlet to outlet pressure ratio, P , and the column geometry need not be standardized in order to obtain standard TPGC indices. The only requirement is that, if one of these parameters is changed, the others are appropriately adjusted.

In particular, it has been theoretically shown and experimentally verified that simultaneous changes of r and P do not change the TPGC retention indices if the product ra remains constant, where a is a function of P alone, which decreases with increasing P .

The theoretically predicted constancy of the TPGC retention indices when the column length L is changed but the product raL^2 remains constant, could not be experimentally confirmed. For the time being, we have no explanation for this finding. It was, possible, however, to adjust r and a so that all retention indices of a mixture were reproduced for different column lengths. It could also be verified that the elution temperatures increase if either of the parameters r , a or L are increased and *vice versa*.

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