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Bezier Curves for the Calculation of Retention Indices in Temperature-Programmed Gas Chromatography

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Abstract: Although the programmed retention index is not theoretically justified, as the Kováts index system, it is of more general use. It could serve as additional parameter for a more precise identification of organic compounds during GC/MS analyses. So, one gains to define it precisely. A method has been described for the calculation of linear programmed retention indices based on Bezier curves smoothing, which shows some advantages in comparison with the Van den Dool and Kratz's method. For the mathematical procedure the standards do not necessary have to belong to a homologous series.

Key words: Gas chromatography, temperature programming, smoothing of reference data, independent of local properties function

INTRODUCTION

At its introduction, the Kováts retention index (1958) represented an important concept in compound identification. However, the introduction and universal use of Temperature Programming (TPGC) for the analysis of Complex, wide boiling range samples seriously restricted the use of the classical retention indices because their theory is based on isothermal chromatography. To bridge this gap Van and Kratz (1963) suggested to calculate a similar value, by replacing the logarithm of the adjusted retention times in the Kováts (isothermal) index calculation by the direct numerical values of the gross retention times or retention temperatures (polygonal interpolation). In theory, this is strictly valid when an ideal temperature program is selected, i.e., when are the retention temperatures (or retention times) of the n-alkanes to behave linearly as function of the carbon number, i.e., when the difference between the retention temperature (or retention time) of two adjacent homologues is the same in the whole programmed analysis. However, it is commonly used for any TPGC analysis. The use of gross retention times may be an advantage because the measure or calculation of the gas hold-up time is not necessary; however when capillary columns with carrier gas hold-up times, great with respect to the retention of the first eluted peaks, are used, or multi-linear temperature programming is set, this approach may lead to large errors.

Golovnya *et al*. (1997) demonstrated that the non-linear behaviour of the retention of n-alkane homologues in TPGC depends on the considerable differences in temperature increments of sorption parameters. They suggested the use of a non-linear fourth parameter equation for extrapolation and interpolation calculations of retention indices, which shows some advantages in comparison with the Van den Dool and Kratz's method mainly when some members of the n-alkane series are missing.

The investigation of a generalized non-linear TPGC retention index generated several proposals (Gloovhya *et al*., 1997; Erdey *et al*., 1970; Keupcik *et al*., 1998; Messadi *et al*., 1990; Paoli *et al*., 1991; Ali *et al*., 1992; Messadi *et al*., 1993; Ferchichi and Messadi, 1994; Girard, 1996; Grigorieva *et al*., 1997; Didaoui *et al*., 1997; Iousici *et al*., 1999a,b; 2000; 2001) and the aim presently persists.

In this study, we treated the calibration data with Bezier curves, functions which possess the property of local control, that is, which graphs are modified only around the point that one displaces (Martin, 1989; Gerald and Wheathy, 1994; Demengel and Pouget, 1998).

We applied this technique to the calculation of retention indices (I_{Be}) of 7 components of a test mixture, eluted in temperature programming on a packed column (Tenax-GC coated with SE-30). The retention indices thus obtained, will be compared to the retention indices determined with a classic way I_L using the Van den Dool and Kratz's relation and a complete set of standard hydrocarbons.

Theoretical: Martin (1989) Gerald and Wheathy (1994) Demenyl and Pouget (1998). The Bernstein's polynomials permit, by the definition of a polygonal line to construct

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a curve joining the first point to the last point of the line, the intermediate tops used to pattern the shape of the curve. Such curves are called Bezier curves.

Let (x_j, y_j), $j = 0, \ldots, m$ a given set of points. The Bezier curve of m order is definite by the parametric equation:

$$\begin{cases} x(t) = \sum_{j=0}^{m} B_{(j,m)}(t)\, x_j \\ y(t) = \sum_{j=0}^{m} B_{(j,m)}(t)\, y_j \end{cases} \tag{1}$$

t which is varying from 0 to 1 and $B_{(j,m)}$ is a polynomial of Bernstein:

$$B_{(j,m)}(t) = C_j^m\, t^j\, (t-1)^{m-j} \tag{2}$$

The coefficients of the binomial:

$$C_j^m = \frac{m!}{j!(m-j)!} \tag{3}$$

being calculated by the recurrence relation:

$$C_j^m = C_j^{m-1} + C_{j-1}^{m-1} \tag{4}$$

The calculations were done using a program, compatible on PC, written in Turbo-Pascal. In order to facilitate the exploitation of the results we printed the values taken by Bezier curves in 200 points of the interval of interpolation.

MATERIALS AND METHODS

For chromatographic purposes, solutions were made by dissolving studied compounds in benzene and pre-set volumes of 1 µL (Hamilton syringe) were injected manually in the chromatograph.

The analyses are to make on a fused silica column (0.40 m long; 4 mm inner diameter) packed with 3.61 g of Tenax-GC coated with 0.5% of silicone SE-30, which allowed to sharpen the peaks of the solutes and to determine temperatures with a better precision. The peaks recorded at the column outlet being Gaussian in shape, retention temperature corresponded to column temperature when the peak maximum has been reached.

The chromatograph was an Philips model PU-304 equipped with temperature programming and fitted with a two-flame differential FID. The flow of nitrogen carrier gas was controlled by a constant mass-flow device and a column pressure regulator. The chromatogram and temperature were registered simultaneously on the same graph with a Graphispot (Sefram) two-channel recorder.

The temperature of the column was raised from 50 to 280°C at the rate of 5°C /min.

RESULTS AND DISCUSSION

The means of 10 experimental retention temperatures (°C) and corresponding standard deviations (in parentheses), of the reference n-alkanes with z carbon atoms (C_z) and the test compounds are assembled hereafter.

C_6: 117 (1.87) –C_7: 136 (1.22) –C_8: 152.3 (1.25)-C_9 : 163.7 (0.94)-C_{10} : 177.3 (0.47) C_{11}: 187.7 (0.94) –C_{12}: 194.3 (0.47) –C_{13}: 207.3 (0.47) –C_{14}: 215.7 (0.97) C_{15}: 223.7 (0.94) C_{16}: 231 (0.88)-C_{17}: 238.7 (1.25)-C_{18}: 247.3 (0.57)-C_{19}: 254 (0.71)-C_{20}: 260 (1.25).

Phenol: 179.3 (0.51); m-Cresol: 194.3 (0.47); 2,6-Dimethylphenol: 201 (0.90); 3,5-Dimethylphenol: 206.3 (1.41); Naphtalene: 214.3 (1.09); Thymol: 221.3 (0.82); 8-Hydroxyquinoline: 230 (1.41).

The smoothing by Bezier curve leads to the values of the third column of Table I which displays the values of the retention index of the test compounds referred to the successive n-alkanes C_{10}-C_{16}. One point outs that the difference $|I_L - I_{Be}|$ is less than 9 index unit (i.u.). This result is far from those obtained when using non-linear interpolation (natural cubic splines; polynomials of different orders) to compute programmed retention indices, the difference being more important (until 40 i.u.).

Minitab software (2003) was used to compare the means of retention indices computed according to either method (paired samples t-test(DAgnelie ., 1998), so as the associated σ_{Be} and σ_L standard deviations.

The p-value obtained for the means (P = 0.181) is superior to the risk $\alpha = 0.05$, in contrast to the corresponding σ_{Be} and σ_L ($P = 0.000 \langle\ \alpha = 0.05$). This shows that both methods produce comparable means but lead to significantly different standard deviations, σ_{Be} being systematically smaller than σ_L.

Table 1: Retention indices (average of 10 measurements) computed by polygonal interpolation (I_L) and smoothing by Bezier curve of order 6 (I_{Be}^6), using successive n–paraffins (C10 to C16) as standards; and are the corresponding standard deviations

	I_L	I_{Be}^6	σ_L	σ_{Be}
Phenol	1019.4	1019.7	10.01	8.26
m-Cresol	1180.1	1174.5	7.10	4.19
2,6-Dimethylphenol	1244.0	1244.1	2.39	1.62
3,5-Dimethylphenol	1291.2	1298.2	1.19	0.77
Naphtalene	1384.3	1390.5	2.39	1.49
Thymol	1470.8	1474.1	1.79	0.77
8-Hydroxyquinoline	1568.1	1576.4	3.24	1.96
$10^2 \Sigma_M$	8.70	0.77		

According to chromatographic theory, there are linear relationships between the retention temperature of higher members of homologous series and their carbon number, provided that linear temperature programs are applied. The retention indices of the other compounds are defined on the basis of these linear relationships. In order to determine which of the two methods considered yields results more consistent with this definition, the sums of squared second divided differences (Demidovitch and Maron, 1973) were calculated for the consecutive compounds:

$$\Sigma_M = \sum_j \left[\frac{1}{T_{j+1} - T_j} \left(\frac{r^{(M)}_{j+1} - r^{(M)}_j}{T_{j+1} - T_j} - \frac{r^{(M)}_j - r^{(M)}_{j-1}}{T_j - T_{j-1}} \right) \right]^2 \qquad (5)$$

where M = L, Be. T_j designates the retention temperature of the non-standard compound and $r_j^{(L)}$, $r_j^{(Be)}$, its retention indices computed by the linear and the Bezier method, respectively.

The smoothing by Bezier curve leads to the more consistent values with the scheme of the retention index, since the sum of squared second divided differences (: Σ_M Table 1, last line) is then inferior to the one obtained for I_L.

We compared the retention indices corresponding to the smoothing by Bezier curve to the retention indices calculated by the classical way. The regression line $I_{Be} = a + b\, I_L$ fitting the N (= 7) pairs of values I_{Be}/I_L (Eq. 6) was found by the method of least squares.

$F_{obs} = \frac{s_1^2}{s_2^2}$; s_1^2 is the variance due to the regression (variation of I_{Be} with I_L) and s_2^2 the residual variance about the regression line; S is the standard error.

$$I_{Be} = 5.8\ (\pm 25.86) + 0.9994\ (\pm 0.0196)\ I_L \qquad (6)$$
$$N = 7 \ ;\ S = 9.120 \ ;\ R^2 = 99.8\ \% \ ;\ F = 2601.86.$$

The hypothesis of a slope unity and regression line not significantly far away from the origin of the coordinates is compatible with our results, for a probability P = 0.995.

The observed F value is very higher than the value given by the tables for 99.9 percent confidence level. The test is there fore highly meaningful and, thus, at a time, there is a correlation between I_{be} and I_L.

Only the m-Cresol and 2,6-Dimethylphenol (less than one third of the points on which the regression is based), could present residuals, which overpass the Standard error value (S).

When, as a testing, the reference mixture constituted of the successive normal paraffins C_6 to C_{20} is used, the order m of the Bezier curve increases from 6 to 14. In that case the difference $\left| I_L - I^{14}_{Be} \right|$ is generally amplified (until 17i.u.), while standard deviations remain comparable on the whole. The smoothing by Bezier curve, once more, leads to the retention index the most linear.

As before, standard error (Eq. 7) is exceeded by the residuals of m-Cresol and 2,6-Dimethylphenol.

$$I^{14}_{Be} = -26.15\ (\pm 23.43) + 1.0160\ (\pm 0.0177)\ I_L \qquad (7).$$
$$N = 7 \ ;\ S = 8.03 \ ;\ R^2 = 99.8\ \% \ ;\ F = 3311.24.$$

To prove an eventual influence of the order of Bezier curves (interval effect) on the regression quality, we considered the parallelism of the regression lines (6) and (7). The statistical processing don't make evident a significant difference between the ordinate values of the average points (t = 0.004), or a rotation of a straight regression line compared to another (t = 1,181). Finally one must accept the equality of variances for the lines (6) and (7) ($\sigma^2_{(6)} = \sigma_{(7)}$)on account of the experimental value F = 0.449. Thus, it there no interval effect on the quality of the regression.

CONCLUSION

A method has been described for the calculation of linear programmed retention indices based on Bezier curve smoothing. For the mathematical procedure the standards do not necessary have to belong to a homologous series.

The method was applied for the determination of linear programmed retention indices of 7 analytes of a test mixture, referred to different sets of n- alkanes, eluted on a column packed with modified Tenax- GC. Independently of the Bezier curve order, we observed that:

- The two types of index are in correlation for a p- value 〉0.999;
- The Bezier curve technique leads to the most consistent values with the scheme of retention index;
- There is no significant difference between the means I_{be} and I_L, in contrast to the corresponding σ values (systematically: $\sigma_{Be} \langle \sigma_L$).

The described method must be confirmed with other classes of separated compounds, in different conditions (initial temperature, heating rate), on columns (packed or capillary) with various retention mechanisms.

REFERENCES

Ali-Mokhnache, S., L. Ferchichi and D. Messadi, 1992. J. Soc. Alg. Chim., 3: 111.

Dagnélie, P., 1998. Statistique Théorique et Appliquée: Influence Statistique à Une et à deux Dimensions, Tome 2, De Boeck Université, Paris, Bruxelles.

Demengel, G. and J.P. Pouget, 1998. Modèles de Bezier, des B-Splines et des Nurbs, Editions Ellipses, Paris.

Démidovitch, B. and I. Maron, 1973. Eléments de Calcul Numérique, Editions Mir, Moscou.

De Paoli, M., M.T. Barbina and G. Bontempelli, 1991. J. Chromatogr., 547: 355.

Didaoui, L., A. Touabet and B.Y. Meklati, 1997. J. High Res. Chromatogr, 20: 605.

Erdey, L., J. Takács and E. Szalanczy, 1970. J. Chromatogr., 46- 29.

Ferchichi, L., D. Messadi, 1994. Analusis, 22: 311.

Gerald, G.F. and P.O. Wheatly, 1994. Applied Numerical Analysis, Addison-Wesley Publishing Company, Paris, (5th Edn.).

Girard, B., 1996. J. Chromatogr. A 721: 279.

Grigorieva, D.N., R.V. Golovnya, L.A. Syomina, 1997. Russ. Chem. Bull., 46: 309.

Golovnya, R.V., L.A. Syomina and A.L. Samusenko, 1997. J. High Res. Chromatogr, 20: 611.

Kováts, E., 1958. Helv. Chim. Acta, 41: 1915.

Krupcik, J., D. Repka, E. Benicka, T. Hevesi, J. Nolte, B. Paschold and H. Mayer, 1988. J. Chromatogr. pp: 448- 203.

Martin, D., 1989. Informatique: Méthodes et Applications, Edition Ellipses, Paris.

Messadi, D., F. Helaimia, S. Ali-Mokhnache, M. Boumahraz, 1990. Chromatographia, 29: 429.

Messadi, D., S. Ali-Mokhnache and C.R. Acad, 1993. Sci. Paris, 316: 605.

Lourici, L., M.L. Souici and D. Messadi, 1999. Analusis, 27: 249.

Lourici, L., M.L. Souici, D. Messadi,1999. C.R. Acad. Sci. Paris, t.2, Série II_c pp: 107.

Lourici, L., M.L. Souici, D. Messadi, 2000. C.R. Acad. Sci. Paris, Série II_c, 3: 309.

Lourici, L., M. L. Souici, A. Tahar, D. Messadi, 2001. J. Soc. Alg. Chim., 11: 131.

Van den Dool, H. and P. D. Kratz, 1963. J. Chromatogr, 11: 463.