Using Bezier Curves for the Calculation of Retention Indices of Polycyclic Aromatic Hydrocarbons in the So-Called Lee's Scale in Temperature-Programmed Gas Chromatography with Mass Spectrometry Detection

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Abstract

The retention indices of some polycyclic aromatic hydrocarbons (PAHs) separated by temperature-programmed gas chromatography are computed by smoothing reference data with Bezier curves of orders 6 are more consistent with the scheme of this retention parameter, and they present standard deviations systematically smaller than those associated with classical retention indices. The Bezier curve possesses the property of local control, (i.e., their graphs are modified only in the neighbourhood of the displaced point). The values thus obtained were compared with the corresponding ones calculated in a classical way. Detailed statistical analysis is presented to describe the retention indices of PAHs expressed in the so-called Lee's scale as a function of retention temperatures (in °C). As a training set, experimental retention data of PAHs obtained on a PE-5 phase is used for correlation. As prediction sets, literature experimental retention indices expressed in the so-called Lee's scale obtained on a DB-5 slightly polar stationary phase are applied for comparison. The method developed is successfully used for estimating and predicting the capillary gas chromatography retention index of PAHs.

Introduction

Polycyclic aromatic hydrocarbons (PAHs) represent a complex mixture of compounds originating from the incomplete combustion of organic matter. Environmental exposure to PAHs occurs primarily from the inhalation of engine exhausts and tobacco smoke, as well as from ingestion of smoked and barbecued foods (1,2). Occupational exposures to PAHs occur in several industries, notably those involving the production of aluminum, iron, and steel (3). In the steel industry, coke-oven workers are heavily exposed to PAHs both by inhalation and through skin contact (4–6).

Occupational exposure to PAH mixtures have been associated with lung, skin, and bladder cancers of humans (4,7–9). Several specific 5-ring PAHs, including benzo(a)pyrene, are classified as probable or possible human carcinogens by the International Agency for Research on Cancer and by the US Environmental Protection Agency (7,10). However, 2- and 3-ring PAHs tend to be much more abundant than the 5-ring compounds in a given environment and may also be hazardous to health. Naphthalene, the simplest and most volatile PAH, produces respiratory tumors in mice and rats (11,12).

Because of the known hazards associated with the increasing emission of PAHs into the environment and the developing social environmental awareness, there is a need for both further structural identification and more accurate quantitative measurement of these substances. By using the hyphenated gas chromatography (GC) mass spectrometry (MS) technique it is possible to obtain information on the composition of very complex samples. The availability of different and specialized commercial libraries have made numerous mass spectra available, which should facilitate the identification of unknown components in many different matrices. The identification of "unknowns" is usually limited to the comparison of the spectra obtained during the analysis of our sample with that reported in the library, selecting those spectra that are most similar or very close to that of the "unknown".

The identification performed by GC–MS using commercial libraries can be rendered difficult for different reasons, such as: the similarity of the spectra of many different compounds; the inaccurate experimental conditions used for the acquisition of the library spectra; and the presence of different spectra in the same component but with different common or systematic names. Therefore, an additional tool for differentiation of the spectra among the analyzed components is required. The chro-

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matographic information on retention time can support the MS results. In fact, it is possible to determine the relative retention time of target components by analyzing these under identical analytical conditions used for a reference solute, usually a solution of the homologous series of *n*-paraffin hydrocarbons. This approach was first used by Kovats (13–14) for isothermal analysis. In this case, the log of the adjusted retention time is proportional to the carbon number of the homologues.

The use of retention indices rather than retention times allows one to avoid chromatographic variations (vector gas flow, temperature program, and column length) in the determination of compounds. It could also be interesting to calibrate results obtained in different laboratories using columns of the same polarity. Van den Dool and Kratz (15) have shown, empirically, that the identification scheme based on logarithmic relationships among isothermal net retention times, developed by Kovats (13–14), may be transferred to temperature-programmed gas chromatography (TPGC) in terms of linear relationships among retention temperatures.

Among the presentations of GC data for polycyclic aromatic compounds, the temperature-programmed retention indices (15) in so-called Lee's scale (16) based on PAH internal standards (naphthalene, phenanthrene, chrysene, and picene) is preferred because of its much better reproductibility compared with other forms of retention data. In some cases, the highly hazardous properties or unavailability of the PAHs may limit a chemist's access to a pure standard for comparisons with unknowns. In these cases, it would be helpful to have a method to obtain a first approximation of the retention indices of the compound of interest.

The Lee retention index (I_L) (16) of an unknown compound is calculated by linear interpolation:

$$I_x^T = 100(n) + \left[100 \times \frac{(T_{Rx} - T_{Rn})}{(T_{Rn+1} - T_{Rn})}\right] \qquad \text{Eq. 1}$$

T_R denotes retention temperatures. T_{Rx} is the elution temperature of the unknown compound; T_{Rn} and T_{Rn+1} are the retention temperatures that elute before and after the unknown: $n = 2$ for naphthalene, $n = 3$ for phenanthrene, $n = 4$ for chrysene, and $n = 5$ for bezo(ghi) perylene. The Lee retention indices of hundreds of compounds have been published in the literature (16–18), and they may be used directly to confirm or refute matches from computerized mass spectral library searching.

The calculation of the linear TPGC retention index was generally based on the linear interpolation between the retention temperatures of neighboring compounds homolog, and the presence of a complete homologue series of compounds in the sample was required. In view of the complexity of many samples, it was often impossible to add the PAH internal standards to the sample without creating interferences with the sample itself.

On the other hand, the relationship between the number of rings in the PAH standard and their elution temperatures was not strictly linear as supposed by linear interpolation. To avoid these drawbacks and to gain precision in non-linear interpolations, the Bezier curves (19) have been used to compute programmed retention indices. Otherwise, this method does not require the presence of a complete series of homologue

straight-chain alkyl compounds as references for the calculation of retention indices.

Finally, it must be emphasise that the linear interpolation method is sensitive to the choice of interpolation nodes, and it does not allow for the anticipation of variation of retention indices when the set of standards is modified.

To avoid this global dependence on local properties, it is suggested to use other technique, such the Bezier curves (20–22).

In this work, the smoothing of the curves of Bezier of order 6 was applied to the calculation of retention indices (Bezier curves I_{Be}) of 18 PAHs of a test mixture, eluted in temperature programming on a slightly polar PE-5 by raising the temperature of the column at three different speeds. The retention indices thus obtained, by referring the PAH internal standards (naphthalene, phenanthrene, chrysene, and picene), will be compared with the retention indices determined with a classic way (I_L), using the Van den Dool and Kratz's relation.

The description ability of the model was tested using the following statistical parameters: coefficient of determination (R^2), Fisher ratio (F), residual error (SD), and the sum of squares second divided differences (Σ_M). The predictive ability was characterized with cross-validation tests.

Theoretical: Bezier Curves

The Bernstein's polynomials permit, by the definition of a polygonal line, to construct a curve joining the first point to the last point of the line, and the intermediate tops used to pattern the shape of the curve. Such curves are called Bezier curves.

Let (Tj, Ij), $j = 0, ..., m$ be a given set of points. The Bezier curve of m order was definite by the parametric equation:

$$\begin{cases} T(t) = \sum_{j=0}^{m} B_{(j,m)}(t)T_j \\ I(t) = \sum_{j=0}^{m} B_{(j,m)}(t)I_j \end{cases} \qquad \text{Eq. 2}$$

t varying from 0 to 1, and B(j,m) was a polynomial of Bernstein:

$$B(j,m) = C_j^m \, t_j \, (1-t)^{m-1} \qquad \text{Eq. 3}$$

The coefficients of the binomial:

$$C_j^m = \frac{m!}{j!(m-j)!} \qquad \text{Eq. 4}$$

being calculated by the recurrence relation:

$$C_j^m = C_j^{m-1} + C_{j-1}^{m-1} \qquad \text{Eq. 5}$$

Where I_R was the temperature-programmed retention index, and T was the elution temperature. The calculations were done using a program written in MAPLE V (Maplesoft, Ontario, Canada).

Experimental

A Perkin Elmer GC (Boston, MA) equipped with a programmable cool on-column inlet and a mass selective detector (MSD) was used. The MSD operated in electron impact mode with electron energies of 70 eV. The GC column was a 20 m PE-5, 0.18-mm i.d., capillary column coated with 0.18-μm film thickness, 5% cross-linked phenyl methyl siloxane stationary phase.

The GC temperature was held at 50°C for 1.5 min then ramped to 345°C at 6°C/min. The final temperature was held for 10 min. The injector port temperature was maintained at 280°C. The MSD was run in selected ion monitoring (SIM) mode. The SIM programs were designed to monitor primary and secondary ions of a group of analytes that elute at times near one of the PAH internal standards. Phenanthrene, chrysene, picene, and benzo[c]picene were used as bracketing compounds. The retention indices were recalculated and linearized by the use of four indices determinators before further calculations. Naphtalene was given a retention index of 200, phenanthrene of 300, chrysene of 400, and picene of 500.

Results and Discussion

The retention temperatures (in °C) of the PAH internal standards, and the test PAH, measured in triple with three different temperature gradients are reported in Table I.

It is known that the temperature programs of commercial devices could deviate considerably from the supposed linearity. These deviations, which were important in the beginning and in the end of programming, were also because of the variations of the ambient temperature. The dependence, "flow temperature",

increases the non-linearity of retention temperature of a homologue set of compounds.

In these conditions, any linear interpolation of the whole of standardization data was maladjusted because of the important errors that it could generate. The simplest standardization curve was obtained by joining the reference data by a polygonal line (polygonal interpolation I_L). Note that the irregularities in the shape delineated were attenuated by using the Bezier curve.

According to chromatographic theory, there are linear relationships between the retention temperature of higher members of homologous series and their ring number, provided that linear temperature programs were applied. The retention indices of the other compounds were defined on the basis of these linear relationships. In order to determine which methods considered yield results more consistent with the definition, the sum of squares second divided differences (23) were calculated for the consecutive PAH:

$$\sum_m = \sum_j \left[\frac{1}{T_{j+1} - T_{j-1}} \left(\frac{r_{j+1}^{(M)} - r_j^{(M)}}{T_{j=1} - T_j} - \frac{r_j^{(M)} - r_{j-1}^{(M)}}{T_j - T_{j-1}} \right) \right]^2 \qquad \text{Eq. 6}$$

Where M = L, Bz; T_j designates the retention temperature of the PAH, whose retention indices was calculated by linear interpolation and the Bezier method, respectively. Table II condenses the average values of the indices of retention and the corresponding standard deviations, obtained in a traditional way (I_L) and with smoothing by Bezier curve of order 6 (I^6_{Be}) by bringing back the compound tests to seven internal standards of PAH.

The interpolation by the Bezier curve led to more consistent values with the scheme of the retention index because the sum of squared second divided differences (Σ_M) was then systematically inferior to the one obtained for I_L.

The retention indices thus obtained were compared to the retention indices calculated in the classical way. The regression line $I_{Be} = a + bI_L$ fitting the pairs of values I_L/I_{Be} was found by the method of least squares (24). The calculation of the parameters a and b and the subsequent variance analysis (25) were done for every case. The standard deviations (SD), SD (a) and SD (b), measure the precision with which the parameters a and b were obtained if one takes into account the number of degrees of freedom ($N = 2$); N was the number of paired values I_B, I_L.

$$F_{obs} = \frac{S_1^2}{S_2^2} ; S_1^2 \qquad \text{Eq. 7}$$

is the variance because of the regression (variation of I_{Be}, with I_L), and S_2^2 was the residual variance about the regression line, which measures the scattering of the values of I_{Be} about the regression line. The values of calculated F (Table III) were much higher than the value given by the tables for a level of confidence of 99.9%. The test was, therefore, highly meaningful, and thus there

Table I. Temperature of Retention (°C) of the PAH of Reference and the Made-up Tests Measured in Triple

Compounds	5°C/min			8°C/min			10°C/min		
	1	2	3	1	2	3	1	2	3
Naphtalene	99	100	99	109	109	109	116	116	116
Acenaphtylene	141	142	141	152	153	153	160	159	160
Acenaphtene	146	147	146	159	159	158	166	165	165
Fluorene	160	159	160	173	173	173	180	180	179
Phenanthrene	186	186	186	200	200	201	207	208	207
Anthracene	186	187	188	201	202	201	209	208	208
Fluoranthene	216	217	217	232	233	233	241	241	241
Pyrene	222	222	222	238	238	238	247	247	247
Benzo[ghi]fluoranthene	248	248	248	266	266	266	275	276	276
Benzo[c]phenanthrene	249	249	249	267	267	267	277	276	277
Benzo[a]anthracene	254	254	254	272	272	272	282	282	282
Chrysene	255	254	255	273	274	273	284	283	283
Naphtacene	258	257	257	276	275	275	285	285	286
Benzo(b)fluoranthene	279	279	278	298	297	297	308	309	308
Benzo(k)fluoranthene	280	279	280	297	298	298	309	309	309
Benzo(e)pyrene	286	285	285	304	303	303	315	314	314
Benzo(a)pyrene	286	286	286	303	304	304	315	315	315
Picene	312	311	312	330	330	329	342	343	342

was a correlation between I_{Be} and I_L. Note that the best correlation was obtained for the interpolation by the Bezier curve.

The highest scattering about regression lines were observed with the Bezier curve, which led to better correlations with PAH ISs, which was practical for smoothing the Bezier curve and gave the best possible compromise between the values of Fobs, S^2_2, and Σ_M. To avoid correlation by chance and to increase the quality of description well above the level common in the literature and to find the best empirical fitting equation for predictive purposes to discriminate among the possible relevant models, the results were compared with experimental data of Lundsted et al. (26) and Takada et al (27) both obtained with a stationary phase DB-5. The corresponding relative errors (E%) are listed in Table IV. Here E% was computed according to:

$$E\% = \frac{|residual|}{|experimental\ value|} \times 100 \qquad \text{Eq. 8}$$

Table II. Retention Indices of Some PAH Eluted in Temperature Programming Using Polygonal Interpolation (IL, Average of three Measurements) and the Smoothing with Bezier Curves (Order 6) as well as Corresponding Standard Deviations (σ) and the Sum of Squared Second Divided Differences (Σ_M)

Compounds	5°C/min		8°C/min		10°C/min	
	$I_L (\sigma_L)$	$I^6_{Be} (\sigma_B)$	$I_L (\sigma_L)$	$I^6_{Be} (\sigma_B)$	$I_L (\sigma_L)$	$I^6_{Be} (\sigma_B)$
Naphtalene	200 (0)	200 (0)	200 (0)	200 (0)	200 (0)	200 (0)
Acenaphtene	254.2 (0.2)	254.7 (0.2)	254.4 (0.2)	254.8 (0,2)	254 (0.4)	255 (0.3)
Phenanthrene	300 (0)	300.6 (0.1)	300 (0)	300.8 (0.3)	300 (0)	301.5 (0.2)
Pyrene	352.4 (0.4)	351.5 (0.1)	351.6 (0.4)	351.3 (0)	352.2 (0.4)	354.4 (0)
Chrysene	400 (0)	401.2 (0)	400 (0)	401.4 (0.2)	400 (0)	402.0 (0.2)
Benzo(a)pyrene	454.4 (1.8)	454.1 (0.1)	453.67 (0.5)	453.8 (0.5)	453.1 (1.3)	453.0 (0.5)
Picene	500 (0)	500 (0)	500 (0)	500 (0)	500 (0)	500 (0)
$10^5\Sigma_M$	3.42	2.12	5.05	2.91	4.38	3.63

Table III. Coefficients of the Least Square Straight Line $I_{Be} = a + bI_L$ When the PAHs Are Referred to PAH Internal Standards

	5°C/min	8°C/min	10°C/min
a	0.0459	–0.1406	–0.0701
b	1.0008	1.0018	1.0028
SE (a)	0.6444	0.8926	1.2424
SE (b)	0.0017	0.0024	0.0033
R	0.99997	0.99990	0.99991
S^2_2	0.365	0.701	1.356
SE(I)= $\sqrt{S^2_2}$	0.604	0.837	1.164
Fobs	334716.0	174279.9	89774.8

These results show the similarity of both models. Table IV shows the observed values, predicted values, residuals, and relative error of compounds in the validation group. In all cases, the relative error was less than 0.5%. From Tables III and IV, it be might concluded that the suggested Bezier curve could be successfully used for prediction purposes considering:

$$\sqrt{S^2_2} \qquad \text{Eq. 9}$$

Table IV. Comparison Experimental Retention Indices, Calculated According to the Literature (26,27) and Predicted Values by Bezier Curves of PAH

Compounds	$I_{exp}[24]$ DB5 8°C/min	$I_{exp}[25]$ DB5 30°C/min	I_{exp} (σ_L) 8°C/min	I^6_{Be} (σ_B) 8°C/min	E%
Naphtalene	–	–	200.0 (0)	200.0 (0)	0.00
Acenaphtylene	247.4	–	247.8 (0.5)	247.6 (0.1)	0.08
Acenaphtene	253.3	–	254.4 (1.0)	254.8 (0.2)	0.15
Fluorene	269.6	–	270.1 (0.4)	270.8 (0)	0.26
Phenanthrene	–	–	300.0 (0)	300.8 (0.3)	0.26
Anthracene	301.4	301.1	301.4 (1.4)	301.8 (0.2)	0.13
Fluoranthene	344.9	340.1	344.3 (0.4)	345.4 (0.3)	0.31
Pyrene	352.8	348.0	351.6 (0,4)	351.3 (0)	0.08
Benzo[ghi]fluoroanthene	390.9	389.6	390.0 (0.7)	391.2 (0.8)	0.31
Benzo[c]phénanthrene	–	–	391.3 (0.7)	392.8 (0.2)	0.38
Benzo[a]anthracene	398.6	398.4	398.2 (0.8)	399.5 (0.2)	0.32
Chrysene	–	–	400 (0)	401.4 (0.2)	0.35
Naphtacene	–	–	403.5 (1.7)	405.6 (0.2)	0.52
Benzo(b)fluoranthene	442.1	442.7	442.6 (1.4)	441.8 (0.2)	0.18
Benzo(k)fluoranthene	442.8	443.5	443.2 (1.3)	442.7 (0.1)	0.11
Benzo[e]pyrene	451.8	449.9	453.3 (1.3)	453.3 (0.5)	0.00
Benzo(a)pyrene	453.4	454.3	453.7 (0.5)	453.8 (0.5)	0.03
Picene	–	–	500.0 (0)	500.0 (0)	0.00

Although the experiment retention data used in prediction sets were obtained on different temperature programmes than the data used in the training set. This indicated that the small variations in the starting temperature and applied temperature run have little influence on the retention data.

Conclusion

Beyond the parameters that influence the determination of the Kovats index, the precision of the retention index in programmed elution depends on the determination of the retention temperatures, and it is conventional to add the standard to the sample, prior to any analysis. Some convenient considerations (complexity of the sample and availability of the successive homologues set) could render this precaution null and void. The interpolating functions used in the literature (polygonal, natural cubic spline, and polynomial) depend on the nodes of interpolation, and it is not possible to foresee the variation of the retention index when changing the set of standards.

To avoid this inconvenience, the calibration data were treated with smoothing by Bezier curve, which posses the property of local control, by which graphs were modified only around the point that is displaced.

The application was made on a test mixture of 18 PAHs separated on a capillary column (PE-5), and it referred to different mixtures of PAH internal standards proposed by Lee et al. The smoothing by the Bezier curve always leads to the retention index that is "the most linear": it is, apparently, its sole interest. The sum of squared second divided differences of the retention indices calculated by this technique was inferior to the one obtained for I_L.

These results were used in order to suggest a method of calculation of retention index in temperature programming that does not necessitate the utilization of a complete set of homologues, and which allowed the ability to recover the classical retention index (the standard error being inferior to 2 i.u.). This method, based on the Bezier curve, allowed data from the literature to be brought back, often obtained in heterogeneous conditions, to the norms fixed by the International Union of Pure and Applied Chemistry (compounds related to set of contiguous standards hydrocarbons treated by the classical Van Den Dool and Kratz method).

The described method must be confirmed with other classes of separated compounds, in different conditions (initial temperature, heating rate), on columns with various retention indices, according to one method or another, and the standard deviations must be compared. On the basis of the prediction sets, it could be concluded that the suggested model could be used for predictive purposes on similar stationary phases under different temperature programmes.

Acknowledgments

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