



# Regression algorithm for calculating second-dimension retention indices in comprehensive two-dimensional gas chromatography



D.M. Mazur<sup>a,d</sup>, I.G. Zenkevich<sup>b</sup>, V.B. Artaev<sup>c</sup>, O.V. Polyakova<sup>a</sup>, A.T. Lebedev<sup>a,d,\*</sup>

<sup>a</sup> Lomonosov Moscow State University, Organic Chemistry Department, 119992 Moscow, Russia

<sup>b</sup> St. Petersburg University, Institute for Chemistry, Universitetskii prospect 26, St. Petersburg, 198504, Russia

<sup>c</sup> LECO Corporation, 3000 Lakeview Avenue, St. Joseph, MI, USA

<sup>d</sup> Lomonosov Northern (Arctic) Federal University, Core Facility Center Ärkтика, nab. Severnoy Dviny 17, Arkhangelsk, 163002, Russia

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## ABSTRACT

Gas chromatography–mass spectrometry (GC–MS) is one of the most accurate, well developed, and reliable analytical tools for the analysis of volatile and semivolatile compounds. The GC–MS data have been extensively improved by enhancing the separation capacity via comprehensive two-dimensional gas chromatography (GC×GC). The reliability of the identification of the analytes in GC×GC–MS can be notably improved by applying the second-dimension retention index (<sup>2</sup>I) as additional analytical parameter along with the commonly used first dimension retention index (<sup>1</sup>I) and mass spectrum. A novel approach for calculating second-dimension retention indices (<sup>2</sup>I) for semivolatile organic compounds is proposed. It is noteworthy that the standards used in calculations are the same compounds recommended as internal standards by US EPA 8270 Method for analysis of semivolatile organic compounds. The new algorithm takes into account the analyte retention time and its retention temperature at the secondary column, (<sup>2</sup>t<sub>R</sub>) and (<sup>2</sup>T<sub>R</sub>), respectively. The experimental data collected with different primary oven temperature ramp rates and carrier gas flow rates have shown that the calculated by the proposed approach <sup>2</sup>I values remain the same for each evaluated compound, drifting in a very narrow range. The proposed approach was tested using 100 organic compounds from various chemical classes including alkanes, phenols, nitrobenzenes, chlorinated hydrocarbons, anilines, polycyclic aromatic hydrocarbons (PAHs), phthalates, etc. The important advantage of the proposed <sup>2</sup>I values for compounds of the same chemical origin (reference standards and analytes) involves applicability of well-known Lee's indices for non-polar phases. Therefore, the proposed approach can be used in targeted and non-targeted analysis of a wide range of organic compounds. The reduced version of the second dimension retention indices provides a valuable mapping of the homologues series of organic compounds, making their detection and identification easy and reliable.

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## 1. Introduction

Gas chromatography–mass spectrometry (GC–MS) is one of the most accurate, well developed, and reliable analytical tools for analysis of volatile and semivolatile compounds. For example, GC–MS is widely used in environmental studies for detecting, identifying and quantifying numerous pollutants [1]. The success of GC–MS with electron ionization (EI) in the reliable identification of organic compounds was made possible largely due to two non-correlated analytical parameters: retention index (<sup>1</sup>I) and mass

spectrum [2,3]. Both parameters are included in the databases widely used for identification of organic compounds, namely NIST [4] and WILEY [5] libraries of mass spectra. However, in case of analysis of complex mixtures (oils, plant extracts, metabolomics samples) full separation of analytes using one-dimensional GC even with highly efficient capillary columns is not always possible. Further increase of the separation efficiency implies using the comprehensive two-dimensional gas chromatography coupled to mass spectrometry, GC×GC–MS [6,7], which provides greater peak capacity and becomes more and more popular in analysis of complex samples [8–13].

Despite the active use of multidimensional GC techniques, some limitations of this approach still exist. Effective data processing implies using GC retention indices measured not only for the first dimension column, but also those attributed to the secondary

\* Corresponding author at: Lomonosov Moscow State University, Organic Chemistry Department, 119992 Moscow, Russia.

E-mail address: [a.lebedev@org.chem.msu.ru](mailto:a.lebedev@org.chem.msu.ru) (A.T. Lebedev).

dimension column ( $^2I$ ). The commonly used graphical presentation of GC  $\times$  GC chromatograms seems to be not acceptable for accurate mathematical processing of the retention data. There were several studies previously carried out on this topic. Beens [14], as well as Marriott and Western [15,16] introduced “iso-volatility” curves for standards (*n*-alkanes and fatty acid methyl esters) by using a non-heated PTV injector or by timed sequential solution injections. Construction of a plot with the first- and second-dimension retention times ( $^1t_R$  and  $^2t_R$ ) resulted in several curves. These curves were obtained by multiple injections of the mentioned standards at different times and temperature conditions within a single oven temperature program. The  $^2I$  of an analyte of interest may be determined if its corresponding parameters position on the plot is between the relevant *n*-alkanes “iso-volatility” curves. The method was further improved by Antle et al. [17], but, in contrast with the previous studies, the alkane standards were employed to estimate the  $^2I$  values of the aromatic targets using PAH as bracketing compounds. Zhao et al. [18], as well as Wang et al. [19], have proposed a novel empirical  $^2t_R - ^2T_e$  function to construct an adjusted second dimension retention time map, which could cover all second dimension timescale for further calculations of  $^2I$ . Since the second dimension column can be considered as being under pseudo-isothermal conditions, the authors used Kovats retention index formula:

$$z = 100n + 100 \frac{\log(t_{R,x}) - \log(t_{R,n})}{\log(t_{R,n+1}) - \log(t_{R,n})} \quad (1)$$

where  $^2I_x$  and  $t_{R,x}$  are the retention index and adjusted retention time of the target compound in the second dimension column, respectively, and  $t_{R,n}$  and  $t_{R,n+1}$  are the adjusted retention times of two *n*-alkanes eluted off the second dimension column immediately before and after the target analyte, and *n* refers to the number of C-atoms in the corresponding alkanes.

Zhu et al. [20] have extended the method in order to predict the retention indices for the constant inlet pressure analysis mode and to determine the second dimension real adjusted retention time and void times in both dimensions. Furthermore, Bieri and Marriott [21] have developed a new instrumental approach with a flow splitter to divert part of the primary column flow to a supplementary detector simultaneously generating a conventional 1D chromatogram along with GC  $\times$  GC chromatogram. This solution was intended to remove the effect of the short secondary column on derived 1D indices, as well as to avoid handling of pulsed GC  $\times$  GC peaks.

Obviously, the principal difficulty of the  $^2I$  calculation involves the necessity to compare the positions of the peaks on the different 2D-chromatograms being registered at different temperatures, while the approach based on “iso-volatility” curves implies the complex mathematical approximation of the retention time data.

An interesting approach was proposed by Veenas and Haglund [22] and it is based on co-injection of the samples and the polyethylene glycol (PEG) and *n*-alkane reference standards, which results in both first-dimension linear retention indices (LRIs) and second-dimension PEG  $^2I$  (PEG- $^2I$ ) values for all analytes in the sample.

We herein propose a simpler alternative method of  $^2I$  calculation using single injection and polycyclic aromatic hydrocarbons (PAH) as the internal standards. It is worth mentioning that PAHs are commonly used in the US EPA methods of analysis of semivolatile organic compounds. It should be noted as well that the principal goal of this paper involves the discussion of the calculation of the new  $^2I$  retention parameters in the form of Lee's indices.

## 2. Materials and methods

### 2.1. Materials and chemicals

Several standard solutions of different classes of compounds (8270 MegaMix, Grob Mix, Hydrocarbons, PAHs, Chlorinated and Brominated aromatic compounds mixtures obtained from Restek Corp., Bellefonte, PA, USA) were used. All compounds were of 95–99% purity and dissolved in dichloromethane at concentrations of 100  $\mu\text{g/mL}$ .

### 2.2. Instrumentation

All experimental data were obtained with the Pegasus<sup>®</sup> GC-HRT<sup>+</sup> 4D, a GC  $\times$  GC high resolution time-of-flight mass spectrometer (LECO Corporation, St. Joseph, MI, USA) coupled to an Agilent 7890 A Gas Chromatograph (Agilent Technologies, Palo Alto, CA, USA), equipped with the LECO Cryogenic Thermal Modulator.

For the first series of experiments Rxi-5ms column 30 m  $\times$  0.25 mm (id)  $\times$  0.25  $\mu\text{m}$  (film thickness) (Restek Corporation, Bellefonte, PA) for the first dimension separation and an Rxi-17Sil MS column 1.4 m  $\times$  0.25 mm (id)  $\times$  0.25  $\mu\text{m}$  (film thickness) (Restek Corporation, Bellefonte, PA) for the second dimension separation were used. Helium was used as carrier gas at flow rate of 1.3 mL  $\text{min}^{-1}$ . For the second series of experiments we have used the same combination of columns at helium flow rate of 1.0 mL  $\text{min}^{-1}$ .

Unless otherwise specified, all injection volumes were 1  $\mu\text{L}$ , split ratio was 100:1. The injector, transfer line, and source temperatures were 270  $^{\circ}\text{C}$ , 340  $^{\circ}\text{C}$ , and 300  $^{\circ}\text{C}$ , respectively. A two minute solvent delay was imposed for all runs. The oven temperature program for this series of experiments was as follows: 5 min isothermal at 35  $^{\circ}\text{C}$ , then primary oven temperature program ramp at 5  $^{\circ}\text{C}$   $\text{min}^{-1}$  to 325  $^{\circ}\text{C}$  or 310  $^{\circ}\text{C}$  (first and second series of experiments, respectively) and 12 min isothermal before ending the run. In the subsequent experiments the primary oven ramp rate was changed to 8, 10, 12, or 20  $^{\circ}\text{C}$   $\text{min}^{-1}$ . The secondary oven temperature was set to 20  $^{\circ}\text{C}$  higher with respect to the primary oven. The modulator temperature offset was 15  $^{\circ}\text{C}$  relative to the secondary oven and the modulation period was set to 3 s. The mass spectra for all GC  $\times$  GC runs were acquired at the rate of 200 full spectra per second with mass range set to 15–800 *m/z*. Electron ionization was performed at 70 eV electron energy. The system was controlled by ChromaTOF<sup>®</sup> software version 5.20 (LECO Corporation), which was also used for data collection and data processing.

Calculations of the 2D retention indices were carried out using Microsoft Excel software (version Microsoft Office 2007) and the “homemade” QBasic program.

## 3. Results and discussion

GC–MS analysis of the semivolatile pollutants in the environmental samples is routinely performed in the governmental and research laboratories [1]. However, our experience shows that a complex matrix may cause ambiguity in the identification of the analytes, especially in non-targeted type of analysis [23]. Identification of coeluting compounds and especially analyte isomers could be particularly challenging.

Use of GC  $\times$  GC–MS provides additional analytical parameter for even more confident and improved identification of the analytes. However, the retention index approaches proposed so far and mentioned above [14–20] are quite laborious and require additional experiments with the standards before the analytical runs. We believe that a potentially practically useful retention index method

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