



# A regression model for calculating the second dimension retention index in comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry



Bing Wang<sup>a,b,c</sup>, Hao Shen<sup>a</sup>, Aiqin Fang<sup>d</sup>, De-shuang Huang<sup>a</sup>, Changjun Jiang<sup>a</sup>, Jun Zhang<sup>e,\*</sup>, Peng Chen<sup>f,\*</sup>

<sup>a</sup> College of Electronics and Information Engineering, Tongji University, Shanghai 201804, China

<sup>b</sup> The Advanced Research Institute of Intelligent Sensing Network, Tongji University, Shanghai 201804, China

<sup>c</sup> The Key Laboratory of Embedded System and Service Computing, Tongji University, Shanghai 201804, China

<sup>d</sup> Bioproduct and Biosystem Engineering, University of Minnesota, Twin Cities, MN 55108, USA

<sup>e</sup> College of Electrical Engineering and Automation, Anhui University, Hefei, Anhui, China

<sup>f</sup> Institute of Health Sciences, Anhui University, Hefei, Anhui, China

## ARTICLE INFO

### Article history:

Received 16 January 2016

Received in revised form 21 April 2016

Accepted 25 April 2016

Available online 26 April 2016

### Keywords:

GC × GC/TOF-MS

Regression model

Retention time

Retention index

Second dimension retention time

## ABSTRACT

Comprehensive two-dimensional gas chromatography time-of-flight mass spectrometry (GC × GC/TOF-MS) system has become a key analytical technology in high-throughput analysis. Retention index has been approved to be helpful for compound identification in one-dimensional gas chromatography, which is also true for two-dimensional gas chromatography. In this work, a novel regression model was proposed for calculating the second dimension retention index of target components where *n*-alkanes were used as reference compounds. This model was developed to depict the relationship among adjusted second dimension retention time, temperature of the second dimension column and carbon number of *n*-alkanes by an exponential nonlinear function with only five parameters. Three different criteria were introduced to find the optimal values of parameters. The performance of this model was evaluated using experimental data of *n*-alkanes (C<sub>7</sub>–C<sub>31</sub>) at 24 temperatures which can cover all 0–6 s adjusted retention time area. The experimental results show that the mean relative error between predicted adjusted retention time and experimental data of *n*-alkanes was only 2%. Furthermore, our proposed model demonstrates a good extrapolation capability for predicting adjusted retention time of target compounds which located out of the range of the reference compounds in the second dimension adjusted retention time space. Our work shows the deviation was less than 9 retention index units (iu) while the number of alkanes were added up to 5. The performance of our proposed model has also been demonstrated by analyzing a mixture of compounds in temperature programmed experiments.

© 2016 Elsevier B.V. All rights reserved.

## 1. Introduction

Mass spectrometry (MS) coupled with chromatographic separation techniques has become a key analytical technology in high-throughput analysis of small molecules [1]. In 1990s, Liu and Phillips invented comprehensive two-dimensional gas chromatography (GC × GC) with a modular between two distinctly different capillary columns of different polarities [2]. The first dimension column has a length of 15–30 m, while the second dimension column

is only 0.5–2 m [3–5], which means the separation in the second dimension column is so fast that it can be treated as in pseudo-isothermal conditions [6]. Compared with one-dimensional gas chromatography (1-D GC), GC × GC has great improvement in column capacity and compounds separation [3,7]. In recent years, comprehensive two-dimensional gas chromatography/time-of-flight mass spectrometry (GC × GC/TOF-MS) has been extensively applied in analyzing complex mixtures such as oil, food, drug, metabolical and biological samples [8–13].

Currently, compound identification through searching spectrum library is the most popular method in analyzing experimental spectra generated from GC × GC/TOF-MS system [14–16]. However, this method produces many false-positive identifications,

\* Corresponding authors.

E-mail address: [wangbing@ustc.edu](mailto:wangbing@ustc.edu) (B. Wang).

especially for complex mixtures analysis. For example, two compounds with similar structure may have similar fragment of mass spectra, and homologous compounds may have very similar mass spectra too [17]. Therefore, more information, such as separation status of molecule, should be involved to increase identification confidence. Retention index (RI), a standardized retention time which calculated by *n*-alkanes in 1-D GC, are widely used to aid compound identification [18,19]. For this purpose, lots of retention index libraries have been developed for 1-D Gas Chromatography [15,16,20–23].

In addition, there are also a few works focusing on 2-D retention index for GC × GC/TOF-MS. Beens et al. first constructed a 2-D retention map with continuous injection of *n*-dodecane, and mentioned three strategies in estimating the second column hold-up time ( $^2t_M$ ) [24], and used five alkanes (C<sub>9</sub>–C<sub>13</sub>) as reference compounds later [25]. Western and Marriott made further study with different injection methods, initial temperatures, temperature ramp rate, and reference compounds. They also calculated the second dimension retention index with 2-D retention map to identify compounds [6,26]. Zhu et al. used a similar strategy as Western and Marriott to identify the unknown compounds in cigarette essential oil [27]. Pang et al. made a change of columns set order to identify unknown compounds in tobacco leaves and adopted regression function to extend the coverage of 2-D retention map [28]. Bieri and Marriott proposed the solid-phase microextraction (SPME) method [29] and a double injection system to study the elution range covered by reference compounds C<sub>10</sub>–C<sub>21</sub> [30]. Zhao et al. proposed a novel function to construct an adjusted second dimension retention time map [31]. More information about retention indices in GC × GC can be found in Mühlen and Marriott's review paper [32]. However, the application of 2-D RI based on *n*-alkanes was limited in GC × GC/TOF-MS because of the polarity of the second column. Many polar compounds experimentally eluted after reference compounds C<sub>9</sub>–C<sub>22</sub> in the second dimension column, which exceed the coverage of 2-D reference map [26]. Therefore, new calculation methods which can expand the coverage of second dimension RI are needed. Another limitation of previous studies is that the calculation models are very complicated. For example, there are ten parameters have to be determined in a polynomial adjusted retention time fitting model proposed by Zhao et al., which raises the computational difficulty and the likelihood of falling into overfitting problem. To overcome the coverage and computational complexity limitations, a practical method with better extrapolation capability for calculating the second dimension retention index is needed.

To meet these needs, this work proposed a novel computational model to calculate the second dimension retention index ( $^2I$ ) with better robustness, which even works for some compounds located out of the range of reference compounds in the adjusted second dimension retention time map. Generally,  $^2I$  can be calculated with Kováts Retention Index function even in temperature programmed experiments because the second dimension column can be seen as pseudo-isothermal [6,33,34]. In our work, a new simple second dimension adjusted retention time–second column temperature ( $^2t_R' - ^2T_e$ ) function was developed to fit adjusted experimental retention times of the reference *n*-alkanes based on an adjusted second dimension retention time map which was constructed by using experimental data from the GC × GC/TOF-MS runs at various second dimension temperatures with *n*-alkanes as reference compounds. In this work, three different criteria were introduced to find optimal parameters of the regression function. It can be found from our experiments that with the proposed  $^2t_R' - ^2T_e$  function and criteria, adjusted retention time of *n*-alkanes in the second dimension can be predicted more accurately. In addition, retention index of target compounds, no matter eluted before or after reference *n*-alkanes, can also be calculated. A standard mixture of differ-

ent compounds and reference *n*-alkanes were used to evaluate the performance of our proposed model.

## 2. Experimental materials

### 2.1. Reagents

Dichloromethane and C<sub>7</sub>–C<sub>40</sub> *n*-alkane mixture were purchased from Sigma-Aldrich (St. Louis, MO). 8270 MegaMix (76 components) were obtained from Restek Corp. (Bellefonte, PA). Alkane mixture was prepared in dichloromethane with a concentration 2.5 µg/mL per compound.

### 2.2. Instrumentation and operational conditions

An Agilent Technologies 6890 gas chromatograph (Santa Clara, CA) was hyphenated to a LECO Pegasus III TOF MS (St. Joseph, MI). The instrument was outfitted with the commercially available Gerstel MPS2 autosampler (Baltimore, MD)

In the GC × GC configuration, a 30 m × 0.25 mm ID × 0.25 µm film thickness, DB-5 ms (Agilent Technologies, Santa Clara, CA) GC capillary column, was used as the primary column for the GC × GC/TOF-MS analysis. A second column 1.8 m × 0.10 mm ID × 0.10 µm film thickness, DB-17 (Agilent Technologies, Santa Clara, CA), was placed inside the LECO secondary GC oven after the thermal modulator. The helium carrier gas flow rate was set to 1.0 mL min<sup>-1</sup> at a corrected constant flow via pressure ramps. A 2 µL split liquid injections (the split ratio was set at 100:1) were made with the injection port temperature set at 260 °C. The thermal modulator was set to +20 °C relative to the primary oven and the second oven was +5 °C to the primary oven. A modulation time of 6 s was used for temperature programmed experiments and 9 s for isothermal experiments. The MS mass range was *m/z* 45–800 with an acquisition rate of 200 spectra per second. The ion source chamber was set at 230 °C with the MS transfer line temperature set at 225 °C and the detector voltage was 1700 V with an electron energy of 70 eV. In isothermal experiments, alkane mixture was analyzed with first column temperature constantly at 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 220, 230, 240, 250, 260, 265, 270 and 280 °C, respectively. The total analysis time was 60 min for each run. In temperature programmed experiments, the analysis of alkane and MegaMix mixture was performed with primary column initial temperature at 60, 80, 100, 120, 140, and 160 °C for 0.5 min, respectively. Then the column temperature ramped to 280 °C at 5 °C/min with a hold time 20 min.

### 2.3. Raw data reduction

The LECO ChromaTOF software (version 4.21), equipped with the National Institute of Standards and Technology (NIST) MS database (NIST MS Search 2.0, NIST/EPA/NIH Mass Spectral Library; NIST 2002), was used for instrument control, spectrum deconvolution, and compound identification. By manually visualizing the raw data, the peak width on the first dimension column was estimated to range from 2 to 3 modulation periods, while ranges from 0.2–0.5 s on the second dimension column. Manufacturer recommended parameters for ChromaTOF were used to reduce the raw instrument data into a compound peak list, and were set as follows: baseline offset = 0.5; smoothing = auto; peak width in first dimension = 6s; peak width in the second dimension = 0.1s; signal-to-noise ratio = 100; match required to combine peaks = 500; R.T. shift = 0.08s; minimum forward similarity match = 600. The true peak spectrum was also exported as part of the information for each peak in absolute format of intensity values.

Download English Version:

<https://daneshyari.com/en/article/1198461>

Download Persian Version:

<https://daneshyari.com/article/1198461>

[Daneshyari.com](https://daneshyari.com)