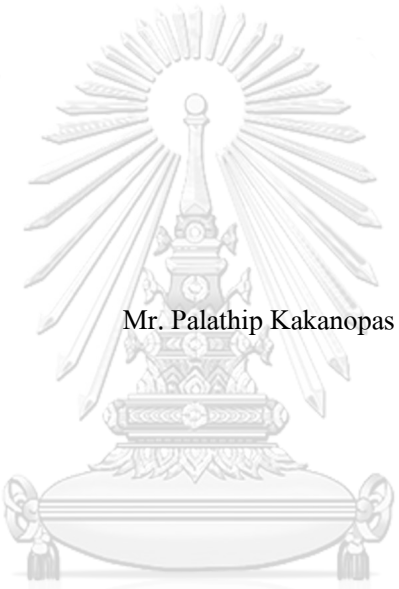
DEVELOPMENT OF RETENTION INDEX BASED SIMULATION FOR VALIDATION OF COMPOUND IDENTIFICATION IN GC×GC

Mr. Palathip Kakanopas



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การพัฒนาการจำลองด้วยรีเทนชันอินเด็กซ์สำหรับตรวจสอบความถูกต้องของการระบุชนิดสารประกอบในแก๊สโครมาโทกราฟีสองมิติแบบทั่วถึง

นายพลาธิป คัคโนภาส

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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Thesis Title	DEVELOPMENT OF RETENTION INDEX BASED SIMULATION FOR VALIDATION OF COMPOUND IDENTIFICATION IN GC×GC
By	Mr. Palathip Kakanopas
Field of Study	Chemistry
Thesis Advisor	Assistant Professor Dr. CHADIN KULSING

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พลาธิป คัคโนภาส : การพัฒนาการจำลองด้วยรีเทนชันอินเด็กซ์สำหรับตรวจสอบความถูกต้องของการระบุชนิดสารประกอบในแก๊สโครมาโทกราฟีสองมิติแบบทั่วถึง. (DEVELOPMENT OF RETENTION INDEX BASED SIMULATION FOR VALIDATION OF COMPOUND IDENTIFICATION IN GC×GC) อ.ที่ปรึกษาหลัก : ผศ. ดร.ชฎิล กุลสิงห์

แก๊สโครมาโทกราฟีแบบสองมิติชนิดครอบคลุม (comprehensive two dimensional gas chromatography, GC×GC) เป็นเทคนิคที่มีประสิทธิภาพสูงสำหรับการแยก การบ่งชี้ และการวิเคราะห์เชิงปริมาณของสารระเหยง่าย และกึ่งสารระเหยง่ายในตัวอย่างที่มีความซับซ้อน เช่น สารชีวโมเลกุล ไขมันจำเป็น อาหาร และ ปิโตรเลียม หนึ่งในเครื่องตรวจวัด (detector) ที่ได้รับความนิยมสูงสุดสำหรับใช้ในการระบุชนิดสารร่วมกับเทคนิค GC×GC คือ แมสสเปกโทรเมตรี (mass spectrometry, MS) โดยการระบุชนิดของพีคที่ถูกแยกมาแล้วจาก GC×GC โดยทั่วไปจะอาศัยการเปรียบเทียบแมสสเปกตรัมของพีกนั้นๆกับฐานข้อมูลทาง MS เพียงอย่างเดียวมักจะแสดงความน่าเชื่อถือต่ำในการระบุชนิดสาร เนื่องจากสารประกอบที่มีโครงสร้างคล้ายกัน (โดยเฉพาะไอโซเมอร์) มักจะมีแมสสเปกตรัมที่คล้ายกัน นอกเหนือจากการเตรียมตัวอย่างที่เหมาะสมแล้ว การระบุชนิดสารที่น่าเชื่อถือยังสามารถทำได้ด้วยการเลือกชนิดเฟสคงที่ และสภาวะการทดลองที่เหมาะสมที่สามารถแยกสารในแต่ละตัวอย่างได้อย่างมีประสิทธิภาพ เช่น ชนิดของคอลัมน์ อุณหภูมิ ช่วงเวลาในการมอดูเลต (modulation period P_M) และ hold up time (t_M) งานวิจัยนี้จึงได้สร้างวิธีการคำนวณเพื่อจำลองผลการทดลองที่ได้จาก GC×GC-MS โดยใช้ฐานข้อมูลรีเทนชันอินเด็กซ์ในคอลัมน์แรกและคอลัมน์ที่สอง (^1I และ ^2I) ในการคำนวณรีเทนชั่นไทม์ของสารของแต่ละสารในตัวอย่างและสร้างผลการทดลองแบบกราฟคอนทัวร์ (contour plot) สำหรับการทดลองที่ไม่ทราบค่ารีเทนชั่นไทม์ของนอร์มัลแอลเคนในทั้งสองคอลัมน์ ($^1t_{R(n)}$ และ $^2t_{R(n)}$) ขั้นตอนต่อไปนี้จะถูกนำไปใช้: (1) ใช้สมการ van den Dool และ Kratz relationship ตามลำดับเพื่อ คำนวณ $^1t_{R(n)}$ จาก ^1t_R และ ^1I ของชุดทดลองที่นำมาจากสาร ในตัวอย่างจริง (2) $^2t_{R(n)}$ ที่ $^1t_{R(n)}$ ต่างๆ จะถูกคำนวณโดยใช้ nonlinear equation ที่มีค่าคงที่ 6 ตัว เพื่อสร้าง isovolatility curve สำหรับจำลองค่า ^1t_R และ ^2t_R ของสารเป้าหมาย ($^1t_{R,sim}$ และ $^2t_{Rsim}$) ที่ทราบค่า ^1I และ ^2I จากฐานข้อมูลของสารนั้น โดยการจำลองจะใช้ $^1t_{R(n)}$ และ isovolatility curve ที่ถูกสร้างขึ้นมา จากนั้นสมการเกาส์เซียน (Gaussian equation) จะถูกใช้เพื่อสร้างรายละเอียดของ peak intensity และเมื่อรวมรายละเอียด peak intensity ของทุกสารที่สนใจเข้าด้วยกันแล้ว จะสามารถสร้างกราฟแบบคอนทัวร์ของแต่ละตัวอย่างโดยใช้โปรแกรม MATLAB โดยทุกการคำนวณและ curve fitting จะใช้ฟังก์ชัน Solver จาก Microsoft Excel วิธีการจำลองผลการทดลองที่สร้างขึ้นมาทั้งหมดนี้ได้ถูกนำไปใช้เพื่อจำลองผลการทดลองสำหรับสาร 622 ชนิดในตัวอย่างที่หลากหลาย ประกอบด้วย saffron (*Crocus sativas* L.), *Boswellia papyrifera*, acasia honey, incent powder/smoke และ perfume ผลการจำลองที่ได้มีความสอดคล้องกับผลการทดลองจริงของแต่ละตัวอย่างด้วยความสัมพันธ์เชิงเส้นตรง ที่มีค่า R^2 ในช่วง 0.975-0.999 และ 0.449-0.992 สำหรับ ^1t_R และ ^2t_R ตามลำดับ ต่อมาวิธีการนี้ ถูกนำไปประยุกต์ใช้ในการตรวจสอบความถูกต้องของการระบุสารที่มีการรายงานไว้งานวิจัยก่อนหน้านี้พบว่าอาจมีสาร 10 ชนิดที่ถูกระบุชื่อไม่ถูกต้อง ซึ่งสามารถตรวจสอบได้โดยสังเกตจากค่าความแตกต่างอย่างชัดเจนระหว่าง $^2t_{Rsim}$ จากการจำลองและ ^2t_R จากการทดลองจริง

สาขาวิชา	เคมี	ลายมือชื่อนิสิต .....
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Palathip Kakanopas : DEVELOPMENT OF RETENTION INDEX BASED SIMULATION FOR VALIDATION OF COMPOUND IDENTIFICATION IN GC×GC. Advisor: Asst. Prof. Dr. CHADIN KULSING

Comprehensive two-dimensional gas chromatography (GC×GC) is a high-performance technique for separation, identification and quantification of volatiles and semi-volatiles in complex multi-component samples such as biomolecular molecules, essential oil, foods, and petroleum. One of the most popular detectors used for peak identification with GC×GC is mass spectrometer (MS) allowing identification of separated peaks based on comparison with mass spectral library. However, only MS library comparison shows low confidence in compound identifications due to the fact that compounds with similar structures (especially for isomers) often have similar mass spectra. Apart from sample preparation, a great challenge is to effectively select types of stationary phase and experimental condition for improved separation of each sample (i.e. column selection, temperature program, modulation period and hold up time). This research established the computational approach to simulate GC×GC results by using first and second dimensional retention index (^1I and ^2I) based calculation approach is established to simulate retention times (^1t_R and ^2t_R) and contour plots of samples from (GC×GC-MS). For the result without ^1t_R and ^2t_R data of alkane references ($^1t_{R(n)}$ and $^2t_{R(n)}$), the following steps were applied: (1) curve fitting based on van den Dool and Kratz relationship in order to simulate $^1t_{R(n)}$ using a training set of volatile compounds in a sample with their experimental ^1t_R data, and (2) simulation of $^2t_{R(n)}$ at different $^1t_{R(n)}$ to construct their isovolatility curves based on a nonlinear equation with six constants. These parameters were obtained by performing curve fitting according to the experimental ^2t_R data of the same training set. Simulation of ^1t_R and ^2t_R of target analytes ($^1t_{R,sim}$ and $^2t_{R,sim}$) with known ^1I and ^2I were performed using $^1t_{R(n)}$ and the simulated isovolatility curves. Gaussian equations were then applied to generate the peak intensity profiles, and summation of peak profiles of all the analytes was performed in order to simulate the contour plot for each sample using MATLAB. All the calculations and curve fittings were carried out by using Solver in Microsoft Excel. The approach was applied to simulate results for 622 compounds in several samples including saffron (*Crocus sativas* L.), *Boswellia papyrifera*, acacia honey, incense powder/smoke and perfume. These were compared with the experimental data showing good correlation with the R^2 of 0.975-0.999 and 0.449-0.992 for ^1t_R and ^2t_R, respectively. This approach was then applied to propose 10 compounds which may be incorrectly identified from the literatures based on the great differences between $^2t_{R,sim}$ and the experimental ^2t_R.

Field of Study:	Chemistry	Student's Signature .....
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Palathip Kakanopas

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CHAPTER I

INTRODUCTION

1.1 Problem definition

Comprehensive two-dimensional gas chromatography (GC×GC) is one of most powerful techniques for separation, detection and identification of volatile and semi-volatile compounds in many complex samples [1]. However, there is no guarantee that a truly best column set has been selected for each separation. At least 150 stationary phases have been synthesized and proposed for different applications in GC. For example, with 100 analytical runs related to temperature program, column length or flow rate optimization for each sample analysis, the possible number of experiments required in order to obtain the best conditions in GC×GC could be >200,000,000 experiments a year [2]. One of the most popular detectors used for peak identification with GC×GC is mass spectrometer (MS) allowing identification of separated peaks based on comparison with mass spectral library [3]. However, only MS library comparison shows low confidence in compound identifications due to the fact that compounds with similar structures (especially for isomers) often have similar mass spectra.

To enhance the peak identification, GC retention database such as that obtained from Gibbs energy additivity [4], linear solvation energy relationship (LSER) [2] and Kovatś and van den Dool relationship [5] could be taken into account. A desirable goal is to establish approach for simulation of retention times in first and second dimensional separations (^1t_R and ^2t_R) for a compound of interest in GC×GC result in order to confirm the peak identity obtained from the MS library match. ^1t_R and ^2t_R are related to properties of each compound leading to different interactions, *e.g.*, dispersity-related, dipolarity-type, hydrogen bond and dispersion/cavity formation, with stationary phase. t_R in GC can be predicted according to three approaches:

(1) the Gibbs energy additivity method can be used to correlate t_R with compound functionalities, the strength of this method is accuracy in prediction based on curve fitting approach with six thermodynamic constants (five out of six could be directly applied to other columns of the same stationary phase without curve fitting) [6]. However, prediction of t_R from the thermodynamic constants has not been widely applied due to the limited amount of database and the complexity in database construction (*e.g.*, prediction of 10 compounds on 10 types of columns under a certain condition requiring up to 100 sets of the thermodynamic constants)

(2) Linear solvation energy relationship (LSER) can be used to predict capacity factor (k), that governs t_R [7]. This method has larger databased (~4,000 compounds and ~140 columns) and with smaller sets of thermodynamic constants (*e.g.*, prediction of 10 compounds on 10 types of columns under a certain condition requiring only 20 sets of LSER constants), albeit with the lower precision in t_R prediction.

(3) LSER method is thus more suitable for bulk analysis systems. Apart from these, Kovatś and van den Dool relationship were used for retention index calculation which has been the most widely used database for comparison of retention order within among different research groups and to support peak identification with MS library. Calculation of retention indices in first and second-dimensional separation (^1I and ^2I) for a compound can be performed based on direct alkane reference injection and construction of isovolatility curve of the alkanes, respectively [8].

These allow calculation of ^1I and ^2I for a given set of ^1t_R and ^2t_R, which has been well established. Interestingly, reverse calculation approach (calculation of t_R for given I) has not been reported, mainly due to the complex calculation and construction of the isovolatility curves of the alkanes. This thesis thus establishes such approach which will be validated by comparison between the simulated and experimental ^1t_R and ^2t_R of the volatile compounds in the sample of saffron (*Crocus sativus* L.) [8], *Boswellia papyrifera* [9], acacia honey [10], incense powder and smoke [11] with known the GC×GC result and the alkane isovolatility curve obtained from literature. The study will then move to simulation of the experimental GC×GC results for samples without the data of alkane isovolatility curves. To this end, Microsoft Excel based curve fitting approach will be developed and used to obtain the curves based on Kovatś and van den Dool relationship equation. In addition, the thesis will propose the approach for: (1) prediction of t_R from I database to validate peak identification reported from literature, and (2) development of simulation software to support experimental design in GC×GC with >10,000 compounds from the retention index library based on three types of columns (polar, semi-polar and non-polar column).

1.2 Literature review

1.2.1 Comprehensive two-dimensional gas chromatography

One dimensional gas chromatography (1DGC) provides low separation performance and peak capacity in the analysis of complex samples (containing several more than a hundred

compounds) resulting from using only one separation column as shown in the example of the worst separation zone (compound no. 5-9) in **Figure 1A**.

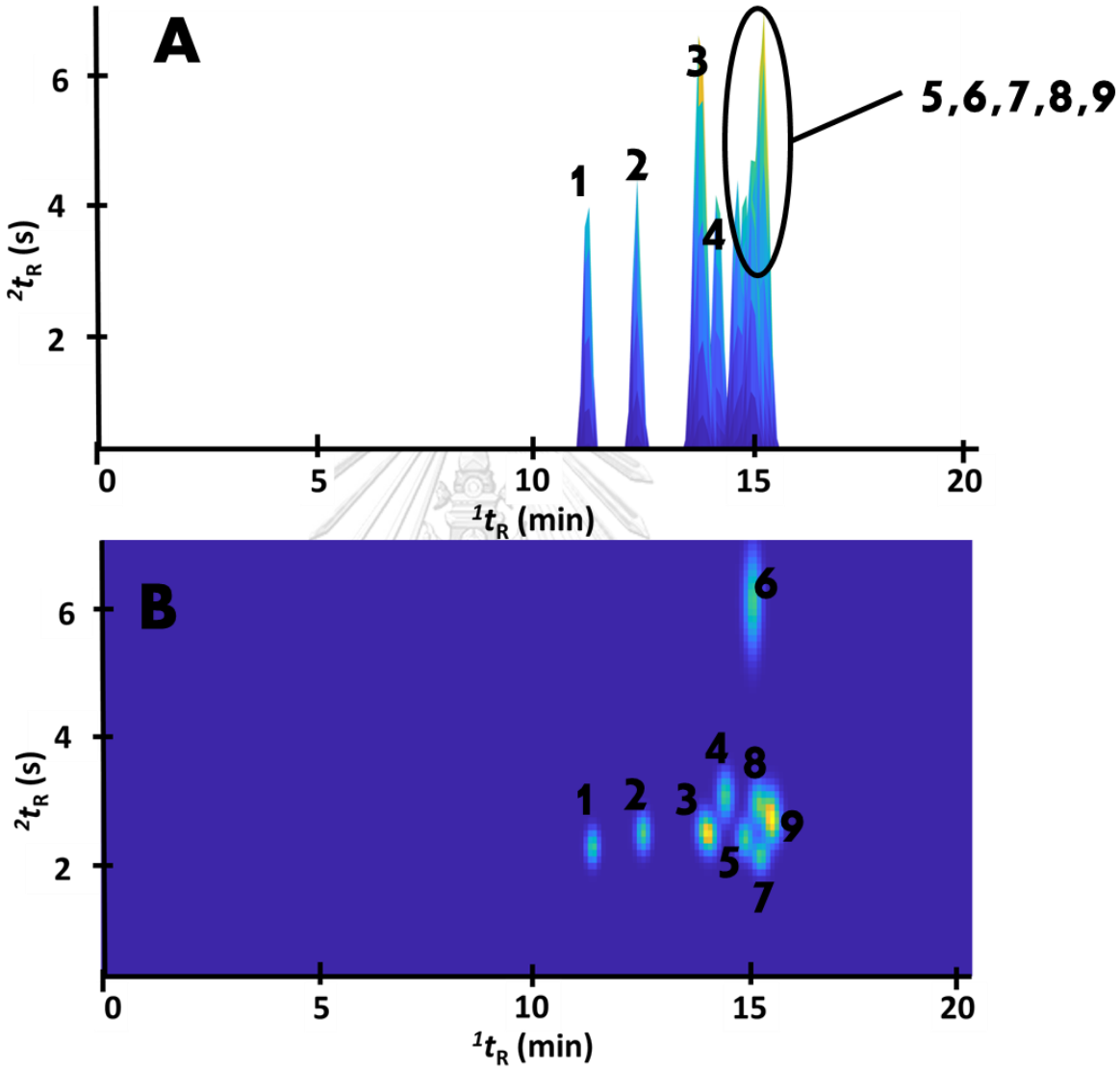


Figure 1 Simulation chromatogram of the 9 organic compounds 1) Hexanal, 2) Ethylbenzene, 3) Heptanal, 4) 2-Propenoic acid, butyl ester, 5) 2,3,7-Trimethyldecane 6) Butanoic acid, butyl ester, 7) 1-Ethyl-4-methylbenzene, 8) 2-Pentylfuranand and 9) 2-Methyl-6-heptanone. 1DGC chromatograms: (A) on polar SUPELCOWAX 10 (30 m × 0.25 mm inner diameter (I.D.) × 0.25 μm film thickness; Supelco, Bellefonte, PA) and GC × GC contour plot and (B) on polar SUPELCOWAX 10 as a ^{1}D column (30 m × 0.25 mm inner diameter (I.D.) × 0.25 μm film

thickness; Supelco, Bellefonte, PA) and a non-polar Rxi-5Sil MS as a ^{2}D column (1.0 m× 0.1 mm I.D. × 0.1 μm; Restek Corporation, Bellefonte, PA), respectively.

Among different approaches, multidimensional gas chromatography (MDGC) is one of the most effective techniques for enhancing separation performance and peak capacity since this approach employs two separation columns with different stationary phases offering peak capacity approximated as the product of the capacity obtained from each dimensional separation. Therefore, it can provide reliable volatile compound profiles (^{1}D and ^{2}D separation) in multicomponent samples. MDGC comprises of the two sub techniques which are 1) comprehensive two-dimensional GC (GC×GC or 2DGC) and 2) comprehensive heart-cut two dimensional GC (H/C 2DGC) [12].

The "comprehensive" technique separates all volatile compounds in the sample. Conventional GC×GC technique mainly consists of a carrier gas tank, an injector, a long ^{1}D column (30-60 m), a modulator, a short ^{2}D column (1-5 m) and a detector [13] as shown in the following schematic diagram of **Figure 2**.

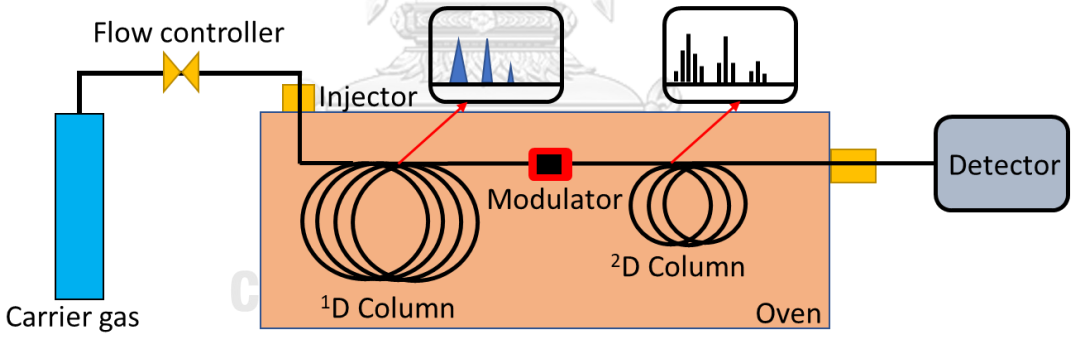


Figure 2 Schematic diagram of GC×GC technique.

For comprehensive H/C 2DGC, it comprises of three main devices (**Figure 3**): 1) two independent long capillary columns (60 m), 2) Deans Switch (DS) as a modulator and 3) Restrictor, the small diameter uncoated deactivated fused silica column which connected between dean switch and detector. The function of restrictor is monitoring of the compound eluting from ^{1}D column to detector [12].

The important device of GC×GC system to transfer analytes from a long ^{1}D column to a short ^{2}D column is called "modulator" [14, 15]. The most popular modulator used in this technique

is thermal modulator. Its duty is periodical involving 1) trap of eluents from a long ^{1}D column outlet by using liquid nitrogen to freeze all of eluents (cryogenic) 2) release of the trapped effluent onto a short ^{2}D column by using hot stream pulse and 3) separation of the compounds in the effluent onto a short ^{2}D column. [16]. Comprehensive H/C2DGC employs DS as a modulator which is an electronic switching device for controlling the microfluidic flow by directly supplying the excess pressure from pressure control module (PCM). The concept of DS is to deliver all separated compounds eluting from ^{1}D column to a long ^{2}D column.

The results of GC×GC and comprehensive H/C 2DGC represent in a 2D contour plot as shown in **Figure 1B**. Compared with 1DGC approach, both GC × GC and comprehensive H/C 2DGC provide greater peak capacity and higher resolution and detection limit as well as higher confidence in compound identification [17].

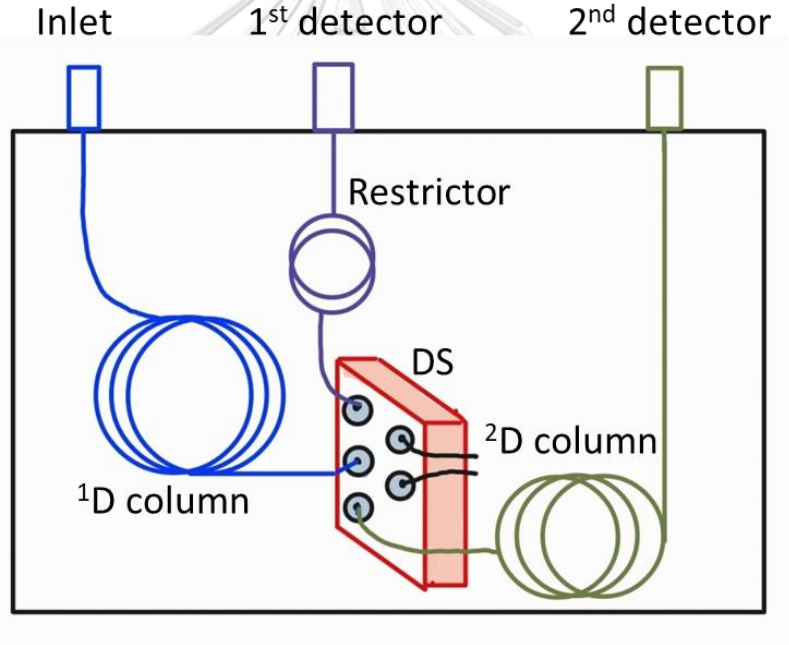


Figure 3 The schematic diagram of comprehensive H/C 2DGC technique.

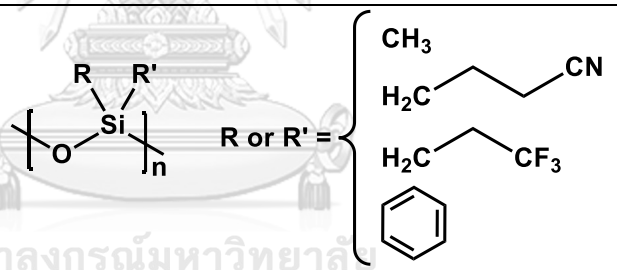
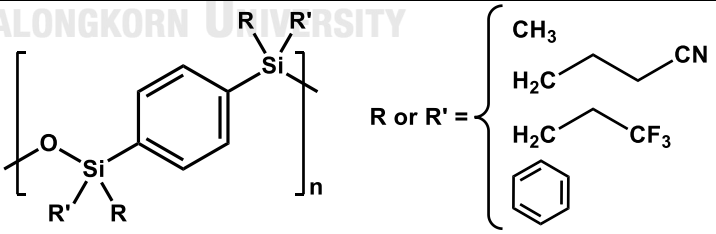
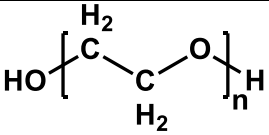
1.2.2 Stationary phase in GC

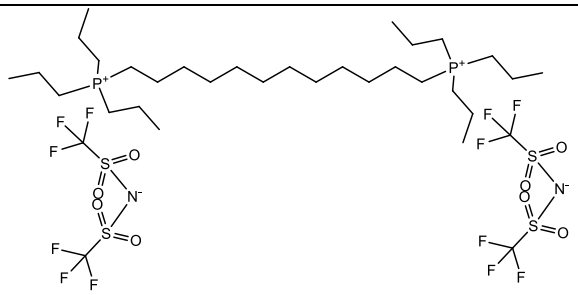
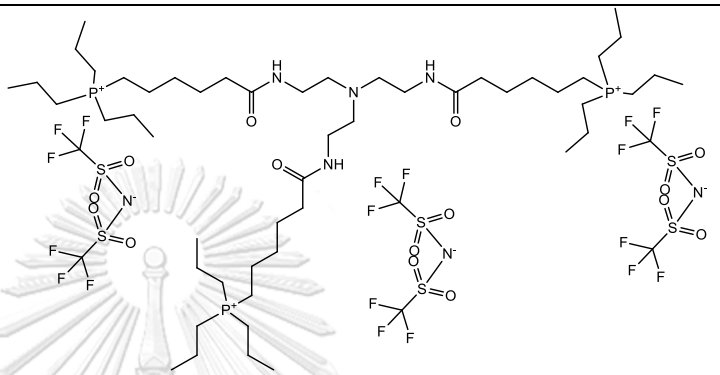
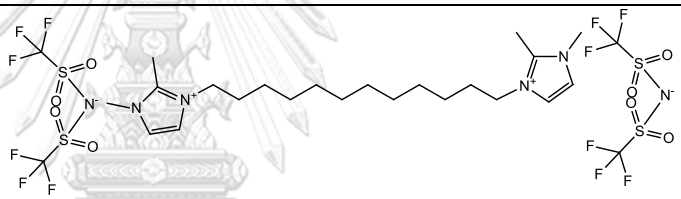
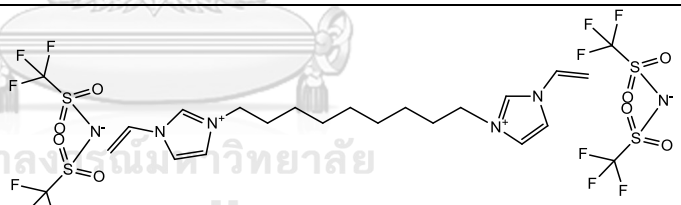
A desirable goal in GC is to obtain appropriate distribution of analytes in chromatograms. Ideally, if target analytes can be moved to a zone free from interfering signals, this will permit unambiguous determination and quantification of target analytes. Apart from difference in analyte vapor pressures, tuneability in GC is obtained by variation of experimental conditions, most commonly temperature, and stationary phase type; column dimensions and flow normally affect efficiency (narrowness) of the GC peak. With altered temperature, retentions of different analytes

with a given stationary phase alter. Variation of the temperature program in GC is thus a simple and straightforward approach to adjust selectivity tuning together with carrier gas flow optimization enhancing theoretical plate number in separation, albeit usually only a small variation is possible. Variation of stationary phase chemistry can significantly redistribute analyte positions depending on different interactions between each analyte and the stationary phase. Stationary phases can be referred to as the 'heart' of the analytical gas chromatography experiment [18], as it critically affects the separation quality.

Several types of stationary phases have been developed for capillary GC, for different separation purposes. Conventional stationary phases provide separation mainly based on polar/non-polar interactions and analyte vapour pressure differences. Some common GC phases, the polarities of which are indicated by the number of phenyl, fluorinated alkyl, or other functional groups contained in each phase, are summarized in **Table 1.**

Table 1. GC stationary phase.

Category	**Structure**
R,R'-polysiloxane	
Arylene **(Low bleed)**	
Poly(ethylene glycol) **(PEG)**	

IL59	
IL76	
IL82	
IL100	

Ionic liquids – salts in a liquid state – have found a wide range of applications in chemistry mainly because of their characteristic adaptable properties. The potential 'green' application of ILs as solvents to dissolve almost any chemical was identified as the innovation "most likely to shape the 21st century". The combination of hundreds of cationic and anionic species enables the tuneability of nearly every property of the IL, from thermal stability, variable dielectric constant of the medium, to the aggregation state. IL have become attractive stationary phase materials for GC, offering several advantages; their high polarity, high viscosity and low vapour pressure arising from their ionic nature which facilitates GC column coating, chemical flexibility of their organic part,

and thermal stability of their inorganic part all suggest the possibility of fruitful R&D for construction of phases based on IL.

1.2.2 Linear solvation energy relationship model (LSER)

LSER is the theoretical concept based on the interaction between molecular structures of stationary phases and the separated compounds. [19] This theory has been applied for column classification and improved understanding of retention mechanisms and experimental designs in various modes of chromatography including normal and reversed phase liquid chromatography [20], ion exchange chromatography [21] and GC. LSER studies variables involving retention mechanisms. The experimental design in GC can be accomplished based on modification of this concept for simulation of separated volatile compound results depending on several experimental parameters such as column sets, column lengths, flow rates, and temperature programs. The solvation model purposed by Abraham, [22] as shown in equation 1.

$$\boldsymbol{logk = eE + sS + aA + bB + lL + c} \quad \textbf{(1)}$$

where k is retention factor and c is an intercept constant. The values of *eE, sS, aA, bB*, and *lL* (the products between analyte compounds and stationary phase descriptors) represent overall interactions with analytes and stationary phase contributions (represented by the upper and lower cases of the descriptors, respectively). The interactions involve dispersity, dipolarity, H-bond with an acid analyte, H-bond with a basic analyte and dispersion/ cavity formation. The lowercase and the uppercase letters involve interactions contributed from the stationary phase and the separated compound, separately [23].

1.2.3 Retention factor; k

t_R is the time that a solute or compound spends from the column inlet to the detector depending on the interaction of the analyte and stationary phase. The compounds with the stronger interactions will have higher t_R. Retention factor can then be expressed as

$$\boldsymbol{k = \frac{t_R - t_0}{t_0}} \quad \textbf{(2)}$$

where t_0 is unretained peak time. The corresponding oven temperature at t_R is called as elution temperature (T_R).

Moreover, ln k is linearly related to number of carbons of an *n*-alkane standard under isothermal separation condition (Equation 3),

$$\ln k = an + b \quad (3)$$

where a and b are constants defining slope and y axis-intercept in the linear equation, respectively.

By substituting the k value of $\frac{t_R - t_0}{t_0}$ into equation 3, t_R of n of each compound can be determined as

$$n = \left(\ln\left(\frac{t_R - t_0}{t_0}\right) - b\right)/a \quad (4)$$

1.2.3 Quantitative structure retention relationship (QSRR)

Quantitative structure retention relationship (QSRR) is the approach to describe the numerical characteristics associated with chemical structures that are derived from the mathematical procedure for calculation of the molecular descriptors. This model defined the molecular descriptors by transformation of the various chemical properties (topology, geometry, wave function, potential energy surface or some combination of these properties for given a chemical structure) into symbolic representation of a molecule. Therefore, the approach can exhibit significant information on the effect of molecular structure about the possible mechanism of retention [24, 25].

For example, Gibbs free energy difference (ΔG) of each compound distributing between the solution onto the stationary phase and the gas phases can be related to a specific physical property correlated with its chemical structure on each stationary phase. The ΔG additivity based QSRR method was used to estimate t_R of compounds at different temperatures from their structures. Martin et. Al. [26] divided the molecule into n parts and a set of ΔG_i values was assigned to each divided part as shown in equation 5.

$$\Delta G^0 = \Delta G_f + n\Delta G_i + \Delta G_d \quad (5)$$

, where ΔG_f is the ΔG of functional group, ΔG_i is the ΔG of carbon number related part of molecule, ΔG_d is ΔG of compound (containing double bond), and n is a number of carbon atoms [25].

1.2.4 Thermodynamic model

Thermodynamic model was used as a tool to predict experimental GC × GC results because the thermodynamic functions: Gibbs energy (G), enthalpy (H) and entropy (S), are correlated to the interaction between compounds and stationary phases with the important parameter of ΔG. The study of linear relationship between log k and reciprocal of the absolute column temperature ($1/T$)

can be further applied for prediction of GC × GC results by using thermodynamic model (equation 6) [27].

This model was used to investigate the interaction between analyte and carrier gas inside capillary column with a specific stationary phase, expressed by the relationship between ΔG and k. The temperature dependence of ΔG can be established by the basic thermodynamic relationship as mentioned in equation 7 [28-30].

$$\ln k = -\ln \beta - \frac{\Delta G}{RT} \quad (6)$$

$$\ln k = -\ln \beta + \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (7)$$

Where β is the column phase ratio (volumetric ratio of mobile phase to stationary phase), T is an absolute temperature, R is the gas constant and ΔS is a change of entropy.

Equation 2 was substituted into equation 7 to generate equation 8 representing the relationship between t_R and thermodynamic parameters used to directly calculate t_R in isothermal separation with known values of t_M, β, ΔS and ΔH.

$$t_R = t_M\left(1 + e^{\left(-\ln \beta + \frac{\Delta S}{R} - \frac{\Delta H}{RT}\right)}\right) \quad (8)$$

t_R in temperature program can be calculated from the linear relationship between k and $1/T$, within a short temperature range. Equation 7 was modified to equation 8, 9 and 10 to extend the relationship [31-33].

$$\ln k = A + \frac{B}{T} + CT \quad (9)$$

$$\ln k = A + \frac{B}{T^{\alpha}} \quad (10)$$

$$\ln k = A + \frac{B}{T} + \ln T \quad (11)$$

Where A is $\frac{\Delta S}{R} - \ln \beta$, B is $\frac{-\Delta H}{R}$ and C and α are constants.

T_R can be directly calculated by equation 11 in only isothermal condition. Therefore, ΔH and ΔS can be replaced by the change of molar isobaric heat capacity (ΔC_p) (equations 12 and 13) for calculation of t_R in temperature program [29, 34, 35], as shown in equation 14.

$$\Delta H_t = \Delta H(T_o) - C_p(T_t - T_0) \quad (12)$$

$$\Delta S_t = \Delta S(T_o) - C_p(\ln T_t - \ln T_0) \quad (13)$$

$$t_M = \int_0^{t_R} \frac{1}{1 + a \times e^{(b/(T_0 + r(t - t_0)) + c \ln n}} dt \quad (14)$$

where a, b, and c are constants, determined by the curve fitting method, T_0 is the initial temperature, r is the linear temperature program rate, t is time in minutes, and t_0 is the hold time of the initial isothermal temperature.

Equations 8, 12, 13 and 14 were combined to derive the equation for calculation of peak position in isothermal and temperature program [36], as shown in equations 15 and 16, respectively.

$$t_R = t_M\left(1 + e^{a+bz+e+\frac{c+dn+f}{T}}\right) \quad (15)$$

Where $a = \frac{\Delta S_f}{R} - \ln\beta, b = \frac{\Delta S_i}{R}, c = -\frac{\Delta H_f}{R}, d = -\frac{\Delta H_i}{R}, e = \frac{\Delta S_d}{R}$, and $f = -\frac{\Delta H_d}{R}$

$$t_R = \sum_{i=1}^{m} \frac{t_M[1+g(\theta_i - T_i)]}{m}\left[1 + e^{\left(a+bz+e+\frac{c+dz+f}{\theta_i}\right)}\right] \quad (16)$$

, where m is the number of the elements of the column, g is the temperature gradient of t_M, T_i is the initial temperature (K), and θ_i is the temperature (K) of i^{th} element.

1.3 Purpose of the study/objective and scope of the study

This project will illustrate the capability of computational program to predict peak positions (^1t_R and ^2t_R) and peak intensity from I and improve identification and experimental design of GC×GC with gradient temperature elution.

CHAPTER II

THEORY

2.1 Retention index

Apart from the established approach for t_R prediction from Introduction section, I of a chemical compound is a scale of retention time relative to two adjacent internal standards (*n*-alkane), ones immediate elutie before and after the target peak. The range of the employed *n*-alkanes must cover the expected retention period range of all target analytes (*e.g.* C_8 - C_{24} for untargeted analysis of monoterpenes in a perfume sample). In order to calculate I in 2D separation for a peak of interest, generation of positions of reference n-alkanes in a 2D plot (isovolatility curve, **Figure 16**) using temperature programed GC×GC is required. This can be performed using relevant information from isothermal results at different T under the same experimental column arrangement. The first-dimensional retention indices of compounds (^1I) are straightforward calculated by using ^{1}D elution time (^1t_R) of target compounds [37]. However, second-dimensional retention index (^2I) calculation is influenced by several experimental condition such as the second column length and elution temperature at ^1t_R, because the *n*-alkanes and sample separation are complete in the ^{1}D column (longer column), but compounds with poor interaction with both columns eluted to detector before the others. This affects elution temperature of both alkane and the analyte peaks on the ^{2}D column.

Jiang et al. [38] presented the approach for construction of isovolatility curves, by direct multiple injections of alkanes in GC×GC. First, sample and the reference *n*-alkanes were injected (range of the employed *n*-alkanes should cover the expected ^1t_R and ^2t_R time ranges of all target compounds). Then, target compounds and *n*-alkanes underwent ^{1}D separation, moved to the modulator and underwent ^{2}D separation. Delayed multiple injections of the alkanes were then performed in order to vary the alkane ^2t_R and generate the isovolatility curves. Because the ^2t_R is much shorter than ^1t_R, compounds were eluted under pseudo-isothermal condition in ^{2}D column. ^2I values were then calculated by using Kovatś index (Equation 17) [39]. The analytes eluted on the ^{1}D column under linear temperature program, ^1I values were then calculated according to van den Dool and Kratz relationship (equation 18).

$$I = 100n + 100\left(\frac{\log {}^2t_{R(i)} - \log {}^2t_{R(n)}}{\log {}^2t_{R(n+1)} - \log {}^2t_{R(n)}}\right) \quad (17)$$

$$I = 100n + 100\left(\frac{t_{R(i)} - t_{R(n)}}{t_{R(n+1)} - t_{R(n)}}\right) \quad (18)$$

where I is the retention index of the analyte, and n and n+1 are the index for carbon numbers of alkane standards which bracket the analyte i.

2.2 A regression model for calculating the second-dimension retention time

For 1DGC, the n-alkane standards were used as references for calculation of ${}^{1}I$ of the compounds. Due to the restriction of the polarity, length, temperature of the ^{2}D column and operation of modulator, this approach cannot be directly applied to calculate ${}^{2}I$. Thus, Wang et al. [40] developed the ${}^{2}t'_{R}$-${}^{2}T_{e}$ regression model to depict the relationship among adjusted second dimensional retention time (${}^{2}t'_{R}$), temperature of ^{2}D column (${}^{2}T_{e}$) and carbon number of n-alkanes by using an exponential nonlinear function with only five parameters (p_1-p_5). This model can be applied to construct the isovolatility curves for ${}^{2}I$ calculation. The step to derive the ${}^{2}t'_{R}$-${}^{2}T_{e}$ regression model starts from the equation to calculate ${}^{2}t_{R}$ in isothermal condition (equation 19) [41, 42].

$$ {}^{2}\boldsymbol{t_R} = \boldsymbol{p_1} + \mathbf{exp}\left(\boldsymbol{p_2} \times \boldsymbol{N} + \boldsymbol{p_3}\right) \quad \textbf{(19)} $$

Where ${}^{2}t_{R}$is the second-dimensional retention time of each n-alkane, p_1-p_3 are coefficients of the model, and N is the carbon numbers of the n-alkane.

Because the hold-up time in ^{2}D column (${}^{2}t_{M}$) depends on ${}^{2}T_{e}$ and head pressure, both parameters were fixed as constants to calculate ${}^{2}t_{M}$ from the retention times of three alkane homologues with equidistant carbon number (equation 20) [43].

$$ {}^{2}\boldsymbol{t_M} = \frac{\boldsymbol{t_{R1}t_{R3}-t_{R2}^2}}{(\boldsymbol{t_{R3}-t_{R2}})-(\boldsymbol{t_{R2}-t_{R1}})} \quad \textbf{(20)} $$

where t_{R1}, t_{R2} and t_{R3} are the retention times of three homologues with the adjacent carbon numbers such as C_{n-1}, C_n and C_{n+1} alkanes [44].

Mean ${}^{2}t_{M}$ at different temperatures were fitted as following:

$$ {}^{2}\boldsymbol{t_M} = \boldsymbol{0.000004} \times ({}^{2}\boldsymbol{T_e})^2 - \boldsymbol{0.0025} \times {}^{2}\boldsymbol{T_e} + \boldsymbol{1.6184} \quad \textbf{(21)} $$

where t_M is the fitted hold-up time on the ^{2}D column and ${}^{2}T_{e}$ is the ^{2}D column elution temperature in ˚C.

Therefore, ${}^{2}t_{R}$ could be transformed to ${}^{2}t'_{R}$ after ${}^{2}t_{M}$ subtraction [41] and can be expressed as

$$ {}^{2}\boldsymbol{t'_R} = \boldsymbol{exp}\left(\mathbf{a}({}^{2}\boldsymbol{T_e}) \times \boldsymbol{n} + \mathbf{b}({}^{2}\boldsymbol{T_e})\right) \quad \textbf{(22)} $$

where ${}^{2}t'_{R}$ is the adjusted second dimensional retention time of n-alkanes; ${}^{2}T_{e}$ is the elution temperature on the ^{2}D column; n is the alkane number of carbon atom; a(${}^{2}T_{e}$) and b(${}^{2}T_{e}$) are

dependent variables of ${}^2T_e$, whose values could be calculated using the basic model at different temperatures.

Two variables of a(${}^2T_e$) and b(${}^2T_e$) in equation 22 were fitted to generate the equation depending on ${}^2T_e$, as shown in equations 23 and 24.

$$\ln\left(a\left({}^2T_e\right)\right) = p_1 \times {}^2T_e + p_2 \quad (23)$$

$$\ln\left(b\left({}^2T_e\right) + p_1\right) = \left(p_2 - {}^2T_e\right) \times p_3 + p_4 \quad (24)$$

where p_1-p_4 are parameters of the fitting function which can be calculated by using minimum square error criterion [42].

Equations 22, 23 and 24 were combined to generate multiple fitting model as

$${}^2t'_R = \exp\left(\exp\left(p_1 \times {}^2T_e + p_2\right) \times N + \exp\left(p_3 + {}^2T_e + p_4\right) + p_5\right) \quad (25)$$

where p_1- p_4 are parameters of the fitting function, and N is the carbon number of *n*-alkane.

2.3 Gaussian or normal distribution

Gaussian distribution or normal distribution is a bell-shaped curve, which is normally used in statistics to represent the probability density function of a normally distributed random variable. The graph of Gaussian distribution is characterized by the maximum value of the graph (mean; μ) and the amount of dispersion from mean (standard deviation;σ) [4]. This function is applied in this study to represent a peak intensity profile in ^{1}D and ^{2}D results expressed as

$$g(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2} \quad {}^1\text{D Gaussian function in } {}^1\text{D GC} \quad (26)$$

$$f(x,y) = A\, exp\left(-\left(\frac{(x-x_0)^2}{2{\sigma_x}^2} + \frac{(y-y_0)^2}{2{\sigma_y}^2}\right)\right) \quad {}^2\text{D Gaussian function in } {}^2\text{D GC} \quad (27)$$

where *g(x)* and *f(x,y)* are intensity coordinates, *A* is intensity constant, *x* and *y* are time coordinates, σ_x and σ_y are peak standard deviations, and x_0 and y_0 are retention times of analytes in 1DGC and GC × GC techniques (*x* and *y* for separation in ^{1}D and ^{2}D columns), respectively. The values that calculated by ^{1}D and ^{2}D Gaussian functions are peak width and intensity of ^{1}D and ^{2}D chromatograms at various retention times.

2.4 Standard deviation (Peak width); σ

σ is used to describe unequally distributed velocity of each molecule of a compound within a normal Gaussian distribution curve, which depends on plate height (H), t_R and column length (L). The shape of the symmetry peak in a chromatogram (**Figure 4**) depends on a peak width at baseline (w_b). Broader peaks are generally observed from compounds spending longer t_R inside

the stationary phase of a separation column. w_b is equal to four times of the standard deviation as seen in equation 28 [45].

$$w_b = 4\sigma = 1.699 w_h \tag{28}$$

$$w_h = \sqrt{5.545 \frac{Ht_R}{L}}$$

$$\sigma = \frac{1.699}{4} w_h$$

$$\sigma = \sqrt{\frac{Ht_R{}^2}{L}} \tag{29}$$

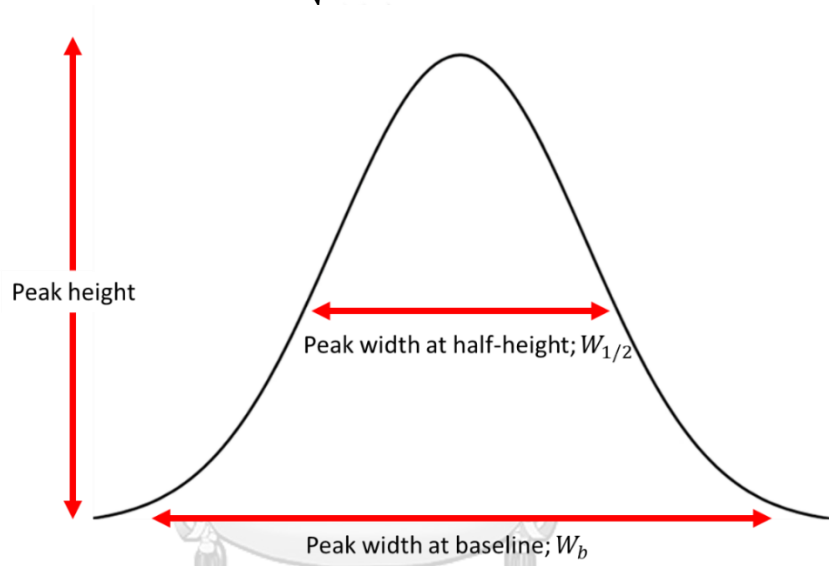


Figure 4 Component of a normal distribution peak.

CHAPTER III

EXPERIMENTAL

3.1 Reagents and materials

Perfume was purchased from a local supermarket, Thailand, and kept in a refrigerator at 4 °C prior to use. *n*-alkane standards (C8-C22) were purchased from Sigma–Aldrich (St. Louis, MO).

3.2 Instrumental

2.3.1 CH/C MDGC-MS

Perfume was diluted in ethanol (10% v/v) prior to CH/C MDGC-MS analysis. The sample was analysed using An Agilent 7890A gas chromatograph hyphenated with an Agilent 5975C QMS (Agilent technologies Inc., US). A ^{1}D semi-nonpolar DB-1MS column (60 m × 0.25 mm I.D. × 0.25 μm) and a ^{2}D polar DB-Wax (60 m × 0.25 mm × 0.25 μm) were used for separation. A restrictor column (1.5 m × 0.1 mm) was applied to balance the flow with the ^{2}D column with a Deans Switch device (DS, Agilent technologies Inc.) as an interface. The outlets of the restrictor and the ^{2}D columns were connected to flame ionization detector (FID) and MS, respectively. Carrier gas (99.999% He) flow rates in ^{1}D and ^{2}D separations were 2.0 and 4.0 mL min^{-1}, respectively. The GC oven temperature program was set at 60 °C and increased to 250 °C (4 °C min^{-1}). The MS ion source temperature, electron ionization voltage and *m/z* range were set at 250 °C. -70 eV and 28–550, respectively. The cyclic multiple H/C approach with the constant window of 0.2 min was performed [46] with the repetitive H/C period of 300 s. This required 25 injections in order to enable comprehensive analysis heartcutting all the components from ^{1}D column.

3.3 Data collection and processing

This study simulated GC×GC results compared with the experimental data ($^{1}t_{R}$ and $^{2}t_{R}$) for separation of saffron [8], *Boswellia papyrifera* [9], acacia honey [10], incense powder/smoke [11] and perfume [46] samples which were obtained from literature. Literature data of ^{1}I and ^{2}I of the corresponding ^{1}D and ^{2}D columns were taken from NIST library or from literature [47]. Microsoft Excel was used to simulate isovolatility curve profiles based on a training set of known compounds and the ^{1}I and ^{2}I data. $^{1}t_{R}$ and $^{2}t_{R}$ were then calculated according to the simulated isovolatility curves [4].

3.4 Collection of ${}^{1}t_{R,lit}$, ${}^{2}t_{R,lit}$, ${}^{1}I_{lit}$, ${}^{2}I_{lit}$ and experimental condition from previous works

Simulation of ${}^{1}t_{R}$ and ${}^{2}t_{R}$ for all compounds in a training set required ${}^{1}I_{lit}$ and ${}^{2}I_{lit}$ and experimental conditions as temperature ramp rate, hold up time, starting modulation time, and starting modulation period from previous studies [8-11] as the input data into the related cells generated in a Microsoft Excel spreadsheet with the example shown in **Figure 5A**.

Figure 5 Spreadsheet for simulation of ${}^{1}t_{R}$ and ${}^{2}t_{R}$, with ${}^{1}I_{lit}$, ${}^{2}I_{lit}$ and experimental conditions (temperature ramp rate, hold up time, starting modulation time, and starting modulation period) input in A.

3.5 Simulation of *n*-alkanes ${}^{1}t_{R}$, analyte ${}^{1}t_{R}$ and ${}^{1}I$ from curve fitting

3.5.1 In the case that *n*-alkane ${}^{1}t_{R}$ (${}^{1}t_{R(n)}$) data were not available from literature, equation 30 was input into Microsoft Excel to generate function for calculation of ${}^{1}t_{R(n)}$ and ${}^{1}I$ from curve fitting (${}^{1}I_{fitting,i}$) for a given set of literature ${}^{1}I$ (${}^{1}I_{lit,i}$), ${}^{1}t_{R}$ of each analyte *i* in a selected training set (${}^{1}t_{R(train,i)}$) and the reported ${}^{1}t_{R}$ values of known analytes in each sample obtained from literatures.

$$ {}^{1}I_{fitting,i} = 100n + 100\left(\frac{{}^{1}t_{R(train,i)} - {}^{1}t_{R(n)}}{{}^{1}t_{R(n+1)} - {}^{1}t_{R(n)}}\right) \qquad (30) $$

where $I_{fitting,i}$ is the retention index of the analyte, and *n* and *n*+1 are the index for carbon numbers of alkane standards which bracket the analyte *i*.

3.5.2 Set up the appropriate range of carbon numbers with the retention time data that cover all peaks of interests observed from ${}^{1}I_{lit}$ values. For example, the optimal range of carbon

numbers from 7 to 24 was selected for the minimum and maximum of ${}^{1}I_{\text{lit}}$ values of 800 and 2,300, respectively.

3.5.2 Input the data of ${}^{1}t_{\text{R(train,i)}}$, ${}^{1}I_{\text{lit}}$ and experimental conditions (**Appendix 1-4**) into the related cells in Microsoft Excel (**Figure 5A**).

3.5.3 According to equation 30, The corresponding ${}^{1}t_{\text{R(n)}}$ and ${}^{1}t_{\text{R(n+1)}}$ of each analyte in the training set were iteratively adjusted by using Solver in Microsoft Excel (**Figure 6**) until sum of the differences between ${}^{1}I_{\text{fitting}}$ and ${}^{1}I_{\text{lit}}$ of all the analytes ($\sum_{i=1}^{m}\left| {}^{1}I_{\text{lit,i}} - {}^{1}I_{\text{fitting,i}}\right|$) were minimized ($\pm$ 20) [8] where m is number of analytes in the training set). This process was performed until correct ${}^{1}t_{\text{R}}$ of all the alkanes (${}^{1}t_{\text{R(n),corr}}$) were obtained. Simulation of ${}^{1}t_{\text{R}}$ of an analyte of interest (${}^{1}t_{\text{R,sim,i}}$) was then performed according to equation 31, all of the steps mention above were shown in **Figure 7**.

$$\mathbf{{}^{1}t_{R,sim,i} = \frac{{}^{1}I_{lit,i} - 100n}{100}\left({}^{1}t_{R(n+1)} - {}^{1}t_{R(n)}\right) + {}^{1}t_{R(n)}} \qquad \textbf{(31)}$$

To facilitate the curve fitting, suitable value of starting ${}^{1}t_{\text{R(n)}}$ was input into the variable cell for each compound which was close to the compound ${}^{1}I_{\text{lit}}$ at various C_n. For example, peak i (${}^{1}t_{\text{R,lit}} = t_{\text{R,i}}$ min and ${}^{1}I_{\text{lit}} \approx 100\text{n}$) should be close to ${}^{1}t_{\text{R(n)}}$ and ${}^{1}t_{\text{R(n+1)}}$. The values slightly more and less than $t_{\text{R,i}}$ were thus input for ${}^{1}t_{\text{R(n),start}}$ and ${}^{1}t_{\text{R(n+1),start}}$, respectively.

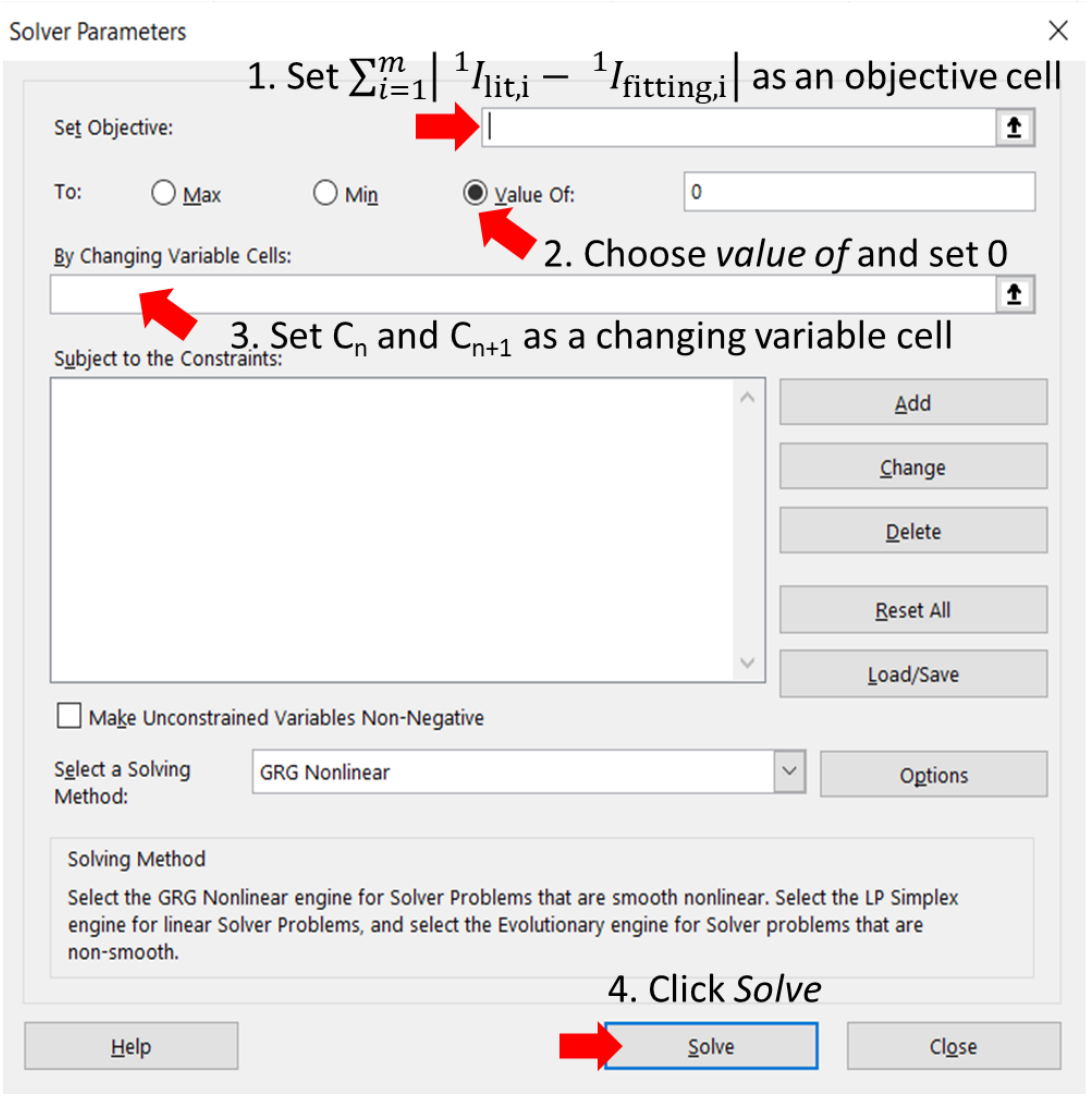


Figure 6 Curve fitting steps for calculation of ${}^{1}I_{\text{fitting,i}}$ and ${}^{1}t_{\text{R(n),corr}}$ carried out by using Solver in Microsoft Excel. $\sum_{i=1}^{m}|{}^{1}I_{lit,i} - {}^{1}I_{fitting,i}|$ were set as the Set Objective cell that were minimized by selecting ${}^{1}t_{\text{R(n)}}$ as the Changing Variable Cell.

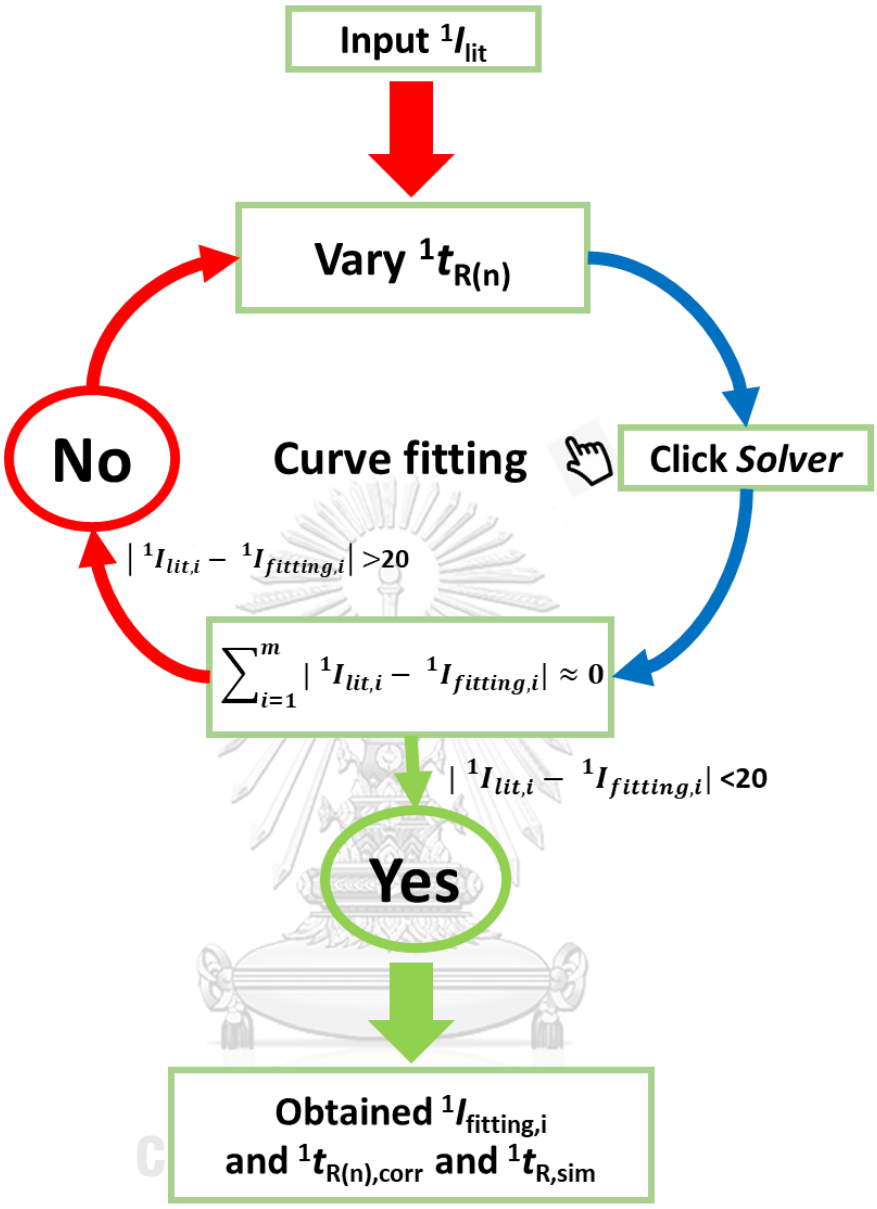


Figure 7 Overall process for simulation of $^1I_{fitting,i}$ and $^1t_{R(n)}$ starting from $^1I_{lit}$ and $^1t_{R,lit}$ input, adjustment of $^1t_{R(n),i}$ and $^1t_{R(n+1),i}$ for each analyte in the training set to calculate $^1I_{fitting,i}$ by using Solver in Microsoft Excel. The iterative process was performed until $\sum_{i=1}^{m}|\,^1I_{lit,i} - {}^1I_{fitting,i}|$ was minimized to be $\leq$20.

3.6 Simulation of ${}^2t_R$ of alkanes and ${}^2I$ from curve fitting

3.6.1 Generate formular to calculate ${}^2t'_R$ from equation 25.

$$ {}^2t'_R = \exp\left(\exp\left(p_1 \times {}^2T_e + p_2\right) \times n + \exp\left(p_3 + {}^2T_e + p_4\right) + p_5\right) \quad (25) $$

where ${}^2t'_R$ is equal to ${}^2t_R$+ constant applied to simulate all the results in this thesis. $p_{1\text{-}5}$ are parameters of the fitting function, n is the carbon number of n-alkane.

3.6.2 Generate function for calculation of ${}^2I$ obtained from the curve fitting (${}^2I_{\text{fitting,i}}$) by using the relationship between ${}^2I_{\text{fitting,i}}$ and ${}^2t_R$ of each analyte i in a selected training set (${}^2t_{\text{R(train,i)}}$) expressed according to equation 32.

$$ {}^2I_{\text{fitting,i}} = 100n + 100\left(\frac{\log {}^2t_{\text{R(train,i)}} - \log {}^2t_{\text{R(n)}}}{\log {}^2t_{\text{R(n+1)}} - \log {}^2t_{\text{R(n)}}}\right) \quad (32) $$

where i is the index of the analyte, and n and n+1 are the carbon numbers of alkane standards which bracket the analyte i.

3.6.3 Input the data of ${}^2t_{\text{R,lit}}$, ${}^2I_{\text{lit}}$ and experimental conditions (**Appendix 1-4**) into the related cells in Microsoft Excel (**Figure 5A**).

3.6.4 Setup the appropriate range of carbon numbers (n) that cover all the peaks of interests.

3.6.5 Vary the values of p_1-p_5 by using function Solver in Microsoft Excel (**Figure 8**). For a given set of starting values ($p_{1,\text{start}}$ - $p_{5,\text{start}}$), p_1 - p_5 in equation 25 were iteratively varied to achieve $p_{1,\text{corr}}$ - $p_{5,\text{corr}}$ resulting in a set of the isovolatility curves with minimized $\sum_{i=1}^{m} \left| {}^2I_{\text{lit,i}} - {}^2I_{\text{fitting,i}} \right|$ ($\pm$ 20) [8]. These simulated curves were then applied for calculation of the corresponding ${}^2t_{\text{R(n)}}$ and ${}^2t_{\text{R(n+1)}}$ for a target analyte of interest ${}^2t_{\text{R,sim,i}}$ of which can be predicted as equation 33. All of the steps mentioned above were shown in **Figure 8**.

$$ {}^2t_{\text{R,sim,i}} = 10^{\left(\frac{{}^2I_{\text{lit,i}} - 100n}{100}\left(\log {}^2t_{\text{R(n+1)}} - \log {}^2t_{\text{R(n)}}\right) + \log {}^2t_{\text{R(n)}}\right)} \quad (33) $$

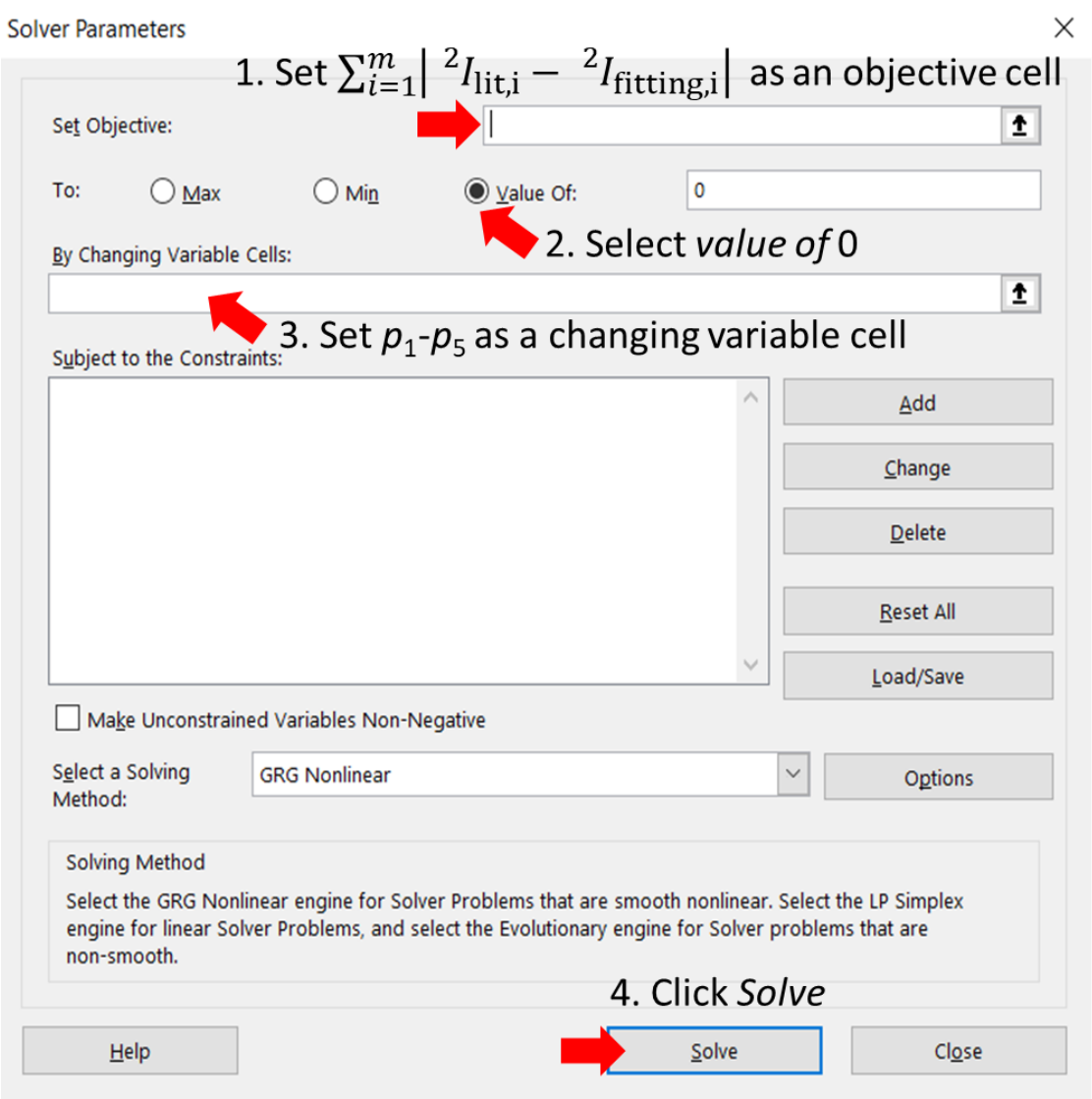


Figure 8 Curve fitting steps of ${}^{1}I_{\mathrm{fitting}}$ of each compound and ${}^{1}t_{\mathrm{R,corr}}$ of alkane carried out by using Solver in Microsoft Excel. $\sum_{i=1}^{m}\left|{}^{2}I_{lit,i}-{}^{2}I_{fitting,i}\right|$ was set as an Objective cell, that was minimized by setting of p_1-p_5 as the Changing Variable Cell.

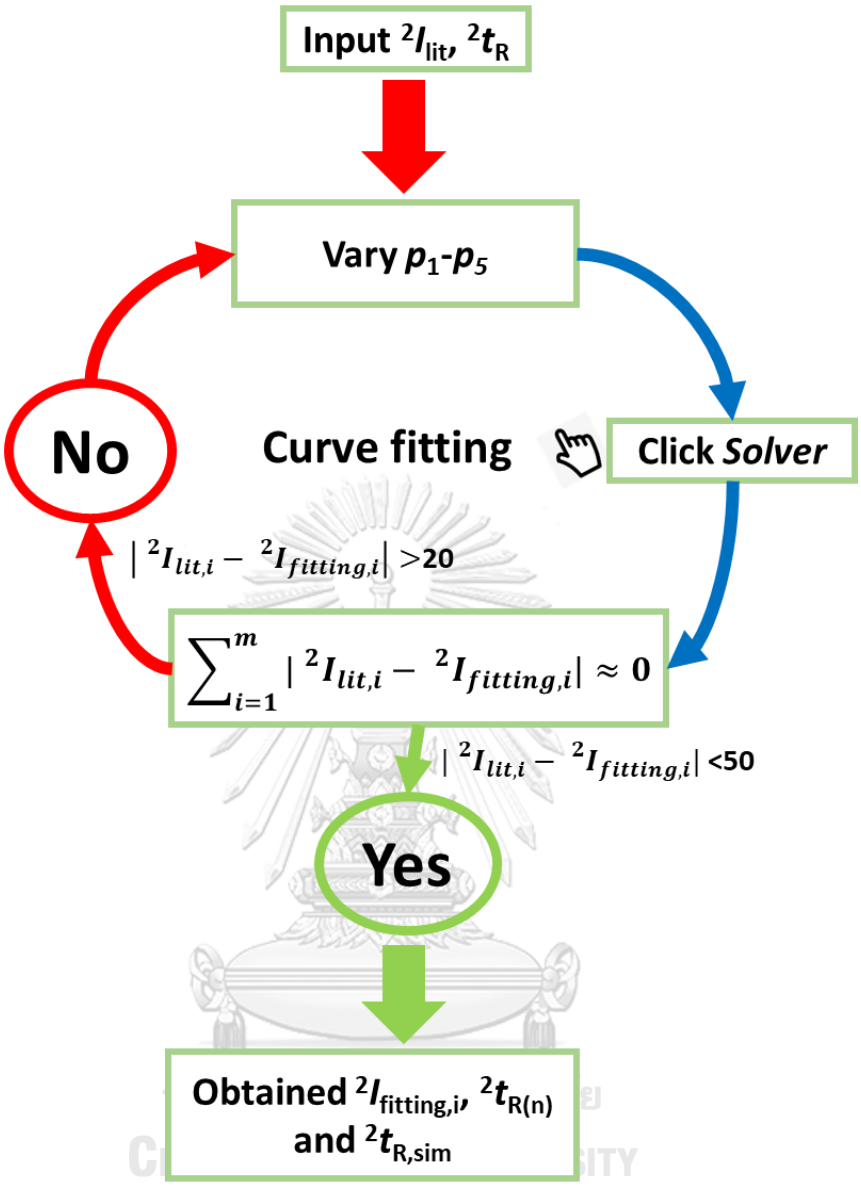


Figure 9 Overall process for simulation of $^2I_{\text{fitting,i}}$ and $^2t_{\text{R(n)}}$ starting from the input of $^2I_{\text{lit}}$ and $^2t_{\text{R,lit}}$, followed by variation of p_1-p_5 by using Solver in Microsoft Excel. This process was iteratively performed until the $\sum_{i=1}^{m}|\ ^2I_{lit,i} - {}^2I_{fitting,i}|$ was $\leq$20.

3.7 Simulation of $^{1}t_{R}$ and $^{2}t_{R}$ of each compound

3.7.1 Click function Solver in Microsoft Excel, set $|\ ^{1}\boldsymbol{I}_{\mathbf{lit,i}} - \ ^{1}\boldsymbol{I}_{\mathbf{fitting,i}}|$ of each interested compound as the Objective cell to value of 0 and $^{1}t_{R}$ of each compound set as the Changing Variable Cell (**Figure 10**).

3.7.2 Click function Solver in Microsoft Excel, set $|\ ^{2}\boldsymbol{I}_{\mathbf{lit,i}} - \ ^{2}\boldsymbol{I}_{\mathbf{fitting,i}}|$ of each interested compound as the Objective cell to value of 0 and $^{2}t_{R}$ of each compound were set as the Changing Variable Cell (**Figure 11**).

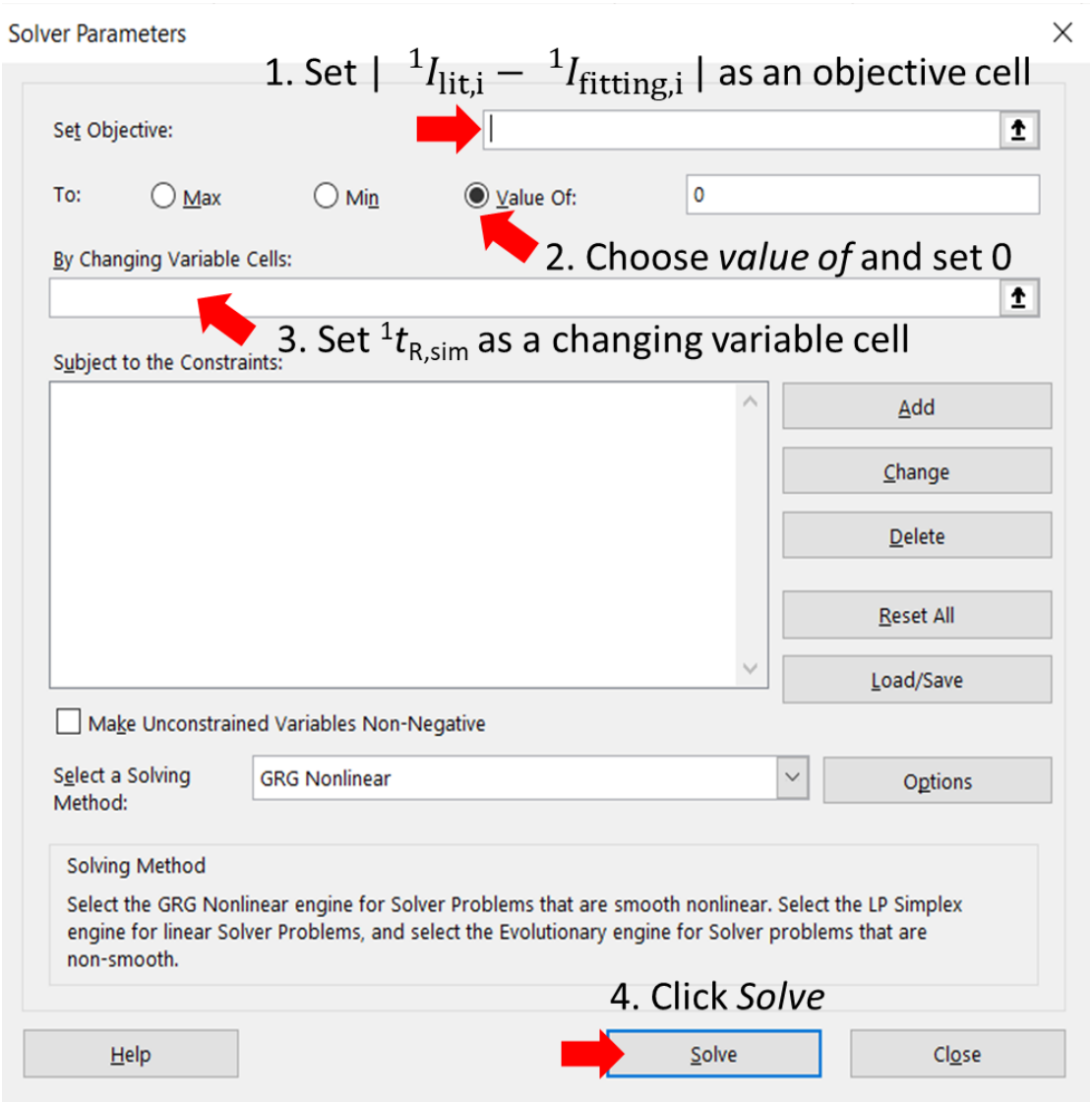


Figure 10 Curve fitting steps of $^{1}t_{R,sim}$ of each compound carried out by using Solver in Microsoft Excel. $\sum_{i=1}^{m}|\ ^{1}I_{lit,i} - \ ^{1}I_{fitting,i}|$ was set as an Objective cell, that was minimized by setting of $^{1}t_{R,sim}$ as the Changing Variable Cell.

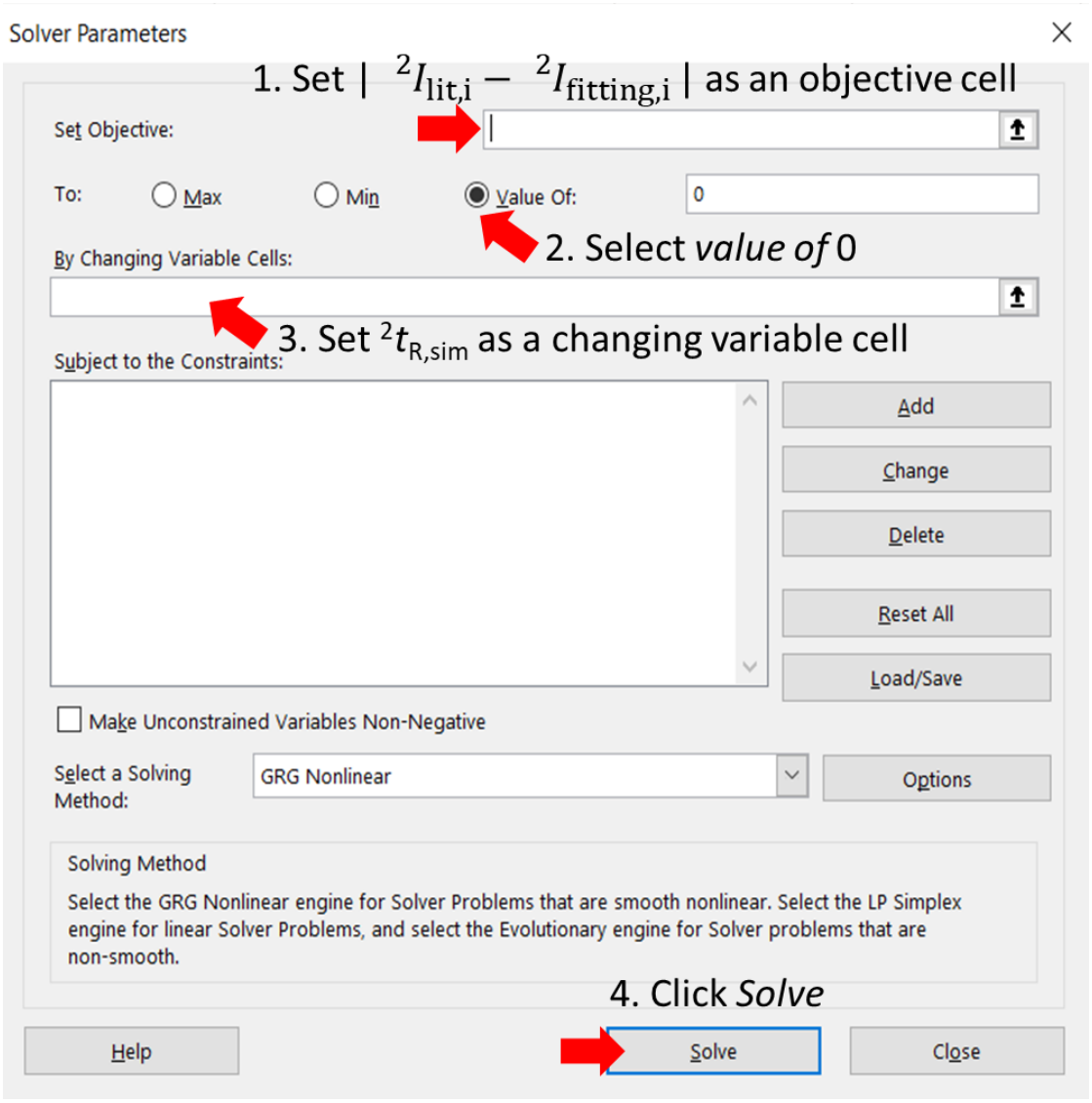


Figure 11 Curve fitting steps of $^2t_{R,sim}$ of each compound carried out by using Solver in Microsoft Excel. $\sum_{i=1}^{m}|\ ^2I_{lit,i} - {}^2I_{fitting,i}|$ was set as an Objective cell, that was minimized by setting of $^2t_{R,sim}$ as the Changing Variable Cell.

3.7 Simulation of standard deviation; σ from t_R

3.7.1 Generate σ formula in a cell in Microsoft Excel by using equation 29.

3.7.2 Input the data of ^{1}D and ^{2}D plate heights (^1H and ^2H), L and t_R into a formula for calculation of σ for each peak, as shown in **Figure 12**.

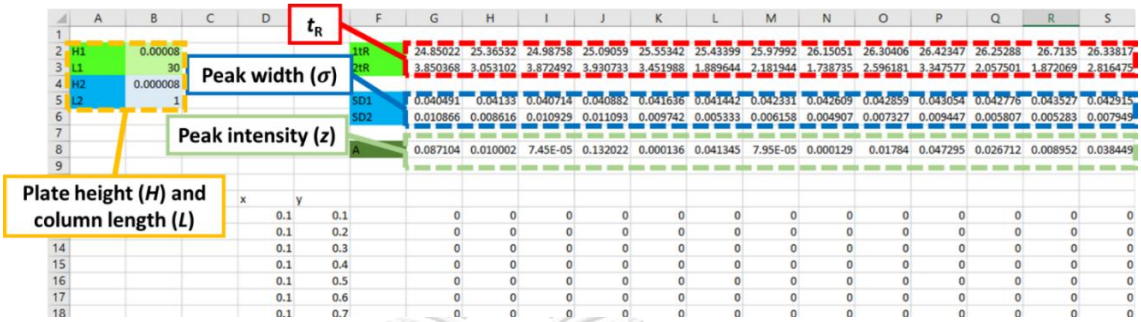


Figure 12 The formula in Microsoft Excel for calculation the standard deviation (σ) by using equation 29.

3.8 Simulation of peak profile in comprehensive two-dimensional gas chromatography by using two-dimensional Gaussian equation

3.8.1 Generate the ^{2}D Gaussian formula by using two-dimensional Gaussian equation (equation 27).

3.8.2 Set the appropriate range of ^{1}D (x) and ^{2}D (y) separation times into a Gaussian formula.

3.8.3 Input ^1t_R (x), ^2t_R (y) and $^1\sigma$ and $^2\sigma$ (from standard deviation formula) in the Gaussian function with the section 3.7.2 showing calculation of all points data of chromatogram (z) as shown in **Figure 13**.

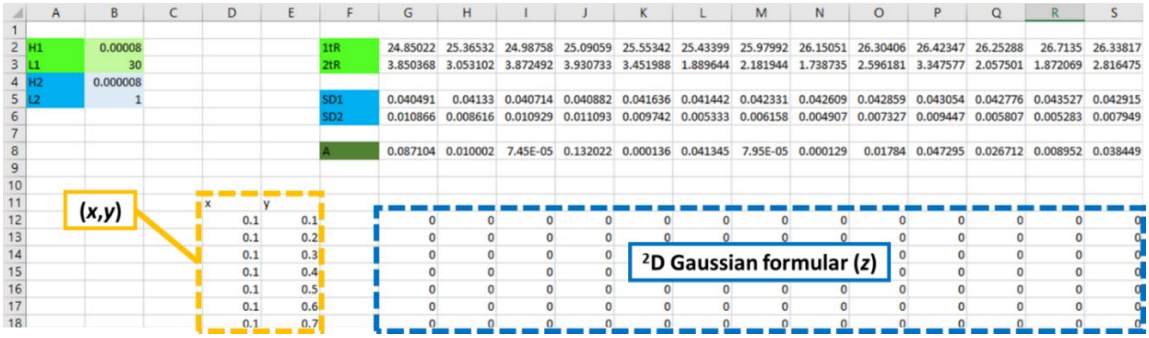


Figure 13 The formula in Microsoft Excel for calculation of t_R, σ and peak intensity (z) by using modulation method.

3.9 Generation of ^{2}D contour plots by using MATLAB

3.9.1 Generate *surface plot* function by using codes as shown in **Figure 14A**.

3.9.2 Save data of $^{1}t_{R}$ (x), $^{2}t_{R}$ (y) and z of a chromatogram that was calculated from the steps mentioned above as *filename.txt* file and then saved into the MATLAB folder.

3.9.3 Upload *.txt* file from step 3.7.2 on the program MATLAB by filling typing the command *load filename.txt;* into the command window (**Figure 14B**).

3.9.4 Generate of 3D chromatogram by typing the command *[output] = plotsurface(filename without .txt);* into command window (**Figure 14C**).

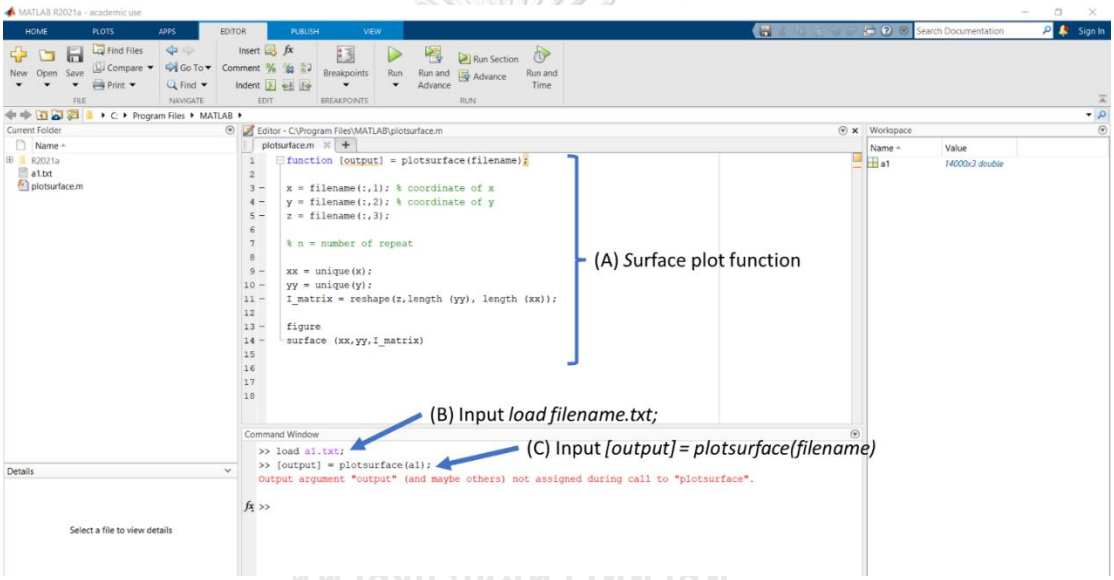


Figure 14 The related commands for generation of a 3-dimension plot in MATLAB.

Table 2 Summary of overall steps for simulation of peak position (step 1-7), σ (step 8-9) and peak intensity (step 10-11).

STEP	Equation	Function	Output
1	-	Collect ${}^1t_{R,lit}$, ${}^2t_{R,lit}$, ${}^1I_{lit}$, ${}^2I_{lit}$, and compound names from paper	-
2	$${}^1I_{fitting,i} = 100n + 100\left(\frac{{}^1t_{R(train,i)} - {}^1t_{R(n)}}{{}^1t_{R(n+1)} - {}^1t_{R(n)}}\right)$$ (30) $${}^1t_{R,sim,i} = \frac{{}^1I_{lit,i} - 100n}{100}\left({}^1t_{R(n+1)} - {}^1t_{R(n)}\right) + {}^1t_{R(n)}$$ (31)	Generate ${}^1I_{fitting}$, ${}^1t_{R(n)}$ and ${}^1t_{R.,sim,i}$ formular by using equation 30.	-
3	$${}^1I_{fitting,i} = 100n + 100\left(\frac{{}^1t_{R(train,i)} - {}^1t_{R(n)}}{{}^1t_{R(n+1)} - {}^1t_{R(n)}}\right)$$ (30)	Substitute ${}^1t_{R,lit}$ into equation 30 and vary ${}^1t_{R(n)}$ and ${}^1t_{R(n+1)}$ to calculate ${}^1I_{fitting}$. (${}^1t_{R(n)}$ and ${}^1t_{R(n+1)}$ are varied until $\lvert {}^1I_{fitting} - {}^1I_{lit}\rvert \approx 0$)	${}^1t_{R(n)}$ ${}^1I_{fitting}$
4	$${}^1t_{R,sim,i} = \frac{{}^1I_{lit,i} - 100n}{100}\left({}^1t_{R(n+1)} - {}^1t_{R(n)}\right) + {}^1t_{R(n)}$$ (31)	Input ${}^1t_{R(n)}$ and ${}^1t_{R(n)}$ into equation 31, and vary ${}^1t_{R.,sim,i}$ to calculate ${}^1I_{fitting}$. (${}^1t_{R.,sim,i}$ is varied until $\lvert {}^1I_{fitting} - {}^1I_{lit}\rvert = 0$)	${}^1t_{R.,sim,i}$
5	$${}^2t_{R(n)} = \exp\left(\exp\left(p_1 \times {}^2T_e + p_2\right) \times n + \exp\left(p_3 + {}^2T_e + p_4\right) + p_5\right)$$ (25) $${}^2I_{fitting,i} = 100n + 100\left(\frac{\log {}^2t_{R(train,i)} - \log {}^2t_{R(n)}}{\log {}^2t_{R(n+1)} - \log {}^2t_{R(n)}}\right)$$ (32)	Generate ${}^2I_{fitting}$, ${}^2t_{R(n)}$ and ${}^2t_{R.,sim,i}$ formular by substitute equation 32 into equation 25.	-
6	$${}^2t_{R(n)} = \exp\left(\exp\left(p_1 \times {}^2T_e + p_2\right) \times n + \exp\left(p_3 + {}^2T_e + p_4\right) + p_5\right)$$ (25) $${}^2I_{fitting,i} = 100n + 100\left(\frac{\log {}^2t_{R(train,i)} - \log {}^2t_{R(n)}}{\log {}^2t_{R(n+1)} - \log {}^2t_{R(n)}}\right)$$ (32)	Substitute ${}^2t_{R,lit}$ into equation 32, and vary p_1-p_5 to calculate ${}^2t_{R(n)}$, ${}^2t_{R(n+1)}$ and ${}^2I_{fitting}$ in the same time.	p_1-p_5 ${}^2t_{R(n)}$ ${}^1I_{fitting}$
7	$${}^2t_{R,sim,i} = 10^{\left(\frac{{}^2I_{lit,i} - 100n}{100}\left(\log {}^2t_{R(n+1)} - \log {}^2t_{R(n)}\right) + \log {}^2t_{R(n)}\right)}$$ (33)	Input ${}^2t_{R(n)}$ and ${}^2t_{R(n)}$ into equation 33, and vary ${}^2t_{R.,sim,i}$ to calculate ${}^2I_{fitting}$ using Solver. (${}^2t_{R.,sim,i}$ is varied until $\lvert {}^1I_{fitting} - {}^1I_{lit}\rvert = 0$)	${}^2t_{R.,sim,i}$

STEP	Equation	Function	Output
8	$\sigma = \sqrt{\frac{Ht_R^2}{L}}$ (29)	Generate σ formula by using equation 29.	-
9	$\sigma = \sqrt{\frac{Ht_R^2}{L}}$ (29)	Input ${}^1t_{R.,sim,i}$ and ${}^2t_{R.,sim,i}$ into equation 29 to calculate ${}^1\sigma$ and ${}^2\sigma$, respectively	${}^1\sigma$ ${}^2\sigma$
10	$f(x,y) = A\,exp(-(\frac{(x-x_0)^2}{2{\sigma_x}^2}+\frac{(y-y_0)^2}{2{\sigma_y}^2}))$ (27)	Generate peak intensity formula by using equation 27.	-
11	$f(x,y) = A\,exp(-(\frac{(x-x_0)^2}{2{\sigma_x}^2}+\frac{(y-y_0)^2}{2{\sigma_y}^2}))$ (27)	Input ${}^1t_{R.,sim,I}$, ${}^2t_{R.,sim,I}$, ${}^1\sigma$ and ${}^2\sigma$ into equation 27 to calculate peak intensity.	Peak intensity

3.10 Validation of possibly incorrect peak identification

3.10.1 Residual analysis

To evaluate the performance of this approach on a dataset, the ${}^{2}t_{R,sim}$ were defined residuals and examining residual plots. Residuals (e_i) are differences between the predicted value (${}^{2}t_{R,sim}$) from this approach and the observed value of the dependent variable (${}^{2}t_{R,lit}$), as shown in equation 34. The residual values of compound which out of 2×SD were suggested as the misreported compound.

$$e = \left| {}^{1}t_{R,lit} - {}^{1}t_{R,sim} \right| \quad \textbf{(34)}$$

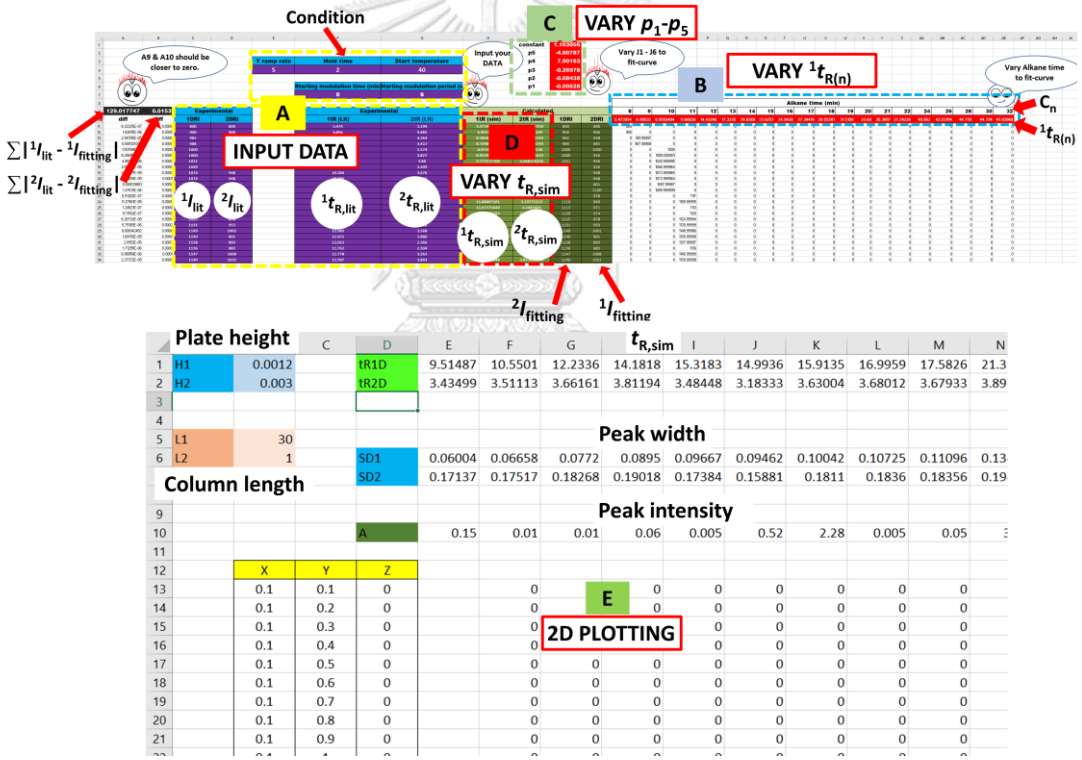
3.10.2 Leave-one-out analysis

Leave one out is the data analysis method which split a dataset into many training sets, each training set were leave one compound out and curve fitting (step 1-7 from **Table 2**) for calculation of least square values ($|{}^{2}t_{R,sim} - {}^{2}t_{R,lit}|^{2}$). All of least square value from every training set were calculated mean and standard deviation (SD). If which training set had least square value out of 2×SD, the leaving out compounds were suggested as the misreported compound.

CHAPTER IV

RESULTS AND DISCUSSION

This study established approach to simulate t_R and peak profiles of target compounds in GC×GC analysis of samples including saffron, *Boswellia papyrifera*, acacia honey, incense powder/smoke. This is based on the initial information of identities and retention indices of compounds within a selected training set, curve fitting to simulate alkane ^1t_R data and isovolatility curves, and retention index of target compounds of interest. The overall process is shown in **Figure 15**, with the detail provided in the Experimental section, which can be performed without additional injection of standard compounds. The simulated and experimental results obtained from literatures [8-11] were then compared and discussed.



H1	0.0012		tR1D	9.51487	10.5501	12.2336	14.1818	15.3183	14.9936	15.9135	16.9959	17.5826	21.3
H2	0.003		tR2D	3.43499	3.51113	3.66161	3.81194	3.48448	3.18333	3.63004	3.68012	3.67933	3.89
L1	30												
L2	1		SD1	0.06004	0.06658	0.0772	0.0895	0.09667	0.09462	0.10042	0.10725	0.11096	0.13
			SD2	0.17137	0.17517	0.18268	0.19018	0.17384	0.15881	0.1811	0.1836	0.18356	0.19
			A	0.15	0.01	0.01	0.06	0.005	0.52	2.28	0.005	0.05	

X	Y	Z								
0.1	0.1	0	0	0	0	0	0	0	0	0
0.1	0.2	0	0	0	0	0	0	0	0	0
0.1	0.3	0	0	0	0	0	0	0	0	0
0.1	0.4	0	0	0	0	0	0	0	0	0
0.1	0.5	0	0	0	0	0	0	0	0	0
0.1	0.6	0	0	0	0	0	0	0	0	0
0.1	0.7	0	0	0	0	0	0	0	0	0
0.1	0.8	0	0	0	0	0	0	0	0	0
0.1	0.9	0	0	0	0	0	0	0	0	0

Figure 15 Microsoft Excel spread sheet for calculation of $^1I_{fitting}$, $^2I_{fitting}$, $^1t_{R,sim}$ and $^2t_{R,sim}$. (A) input cells for the data of $^1I_{lit}$, $^2I_{lit}$, $^1t_{R,lit}$, $^2t_{R,lit}$, ramp rate, hold time, start temperature, starting modulation time, and starting modulation period obtained from literatures, (B) input $^1t_{R(n)}$ to be varied for minimizing $\sum_{i=1}^{m}\left|{}^1I_{lit,i} - {}^1I_{fitting,i}\right|$, (C) input p_1 - p_5 and constant to be varied for minimizing $\sum_{i=1}^{m}\left|{}^2I_{lit,i} - {}^2I_{fitting,i}\right|$, (D) $^1t_{R,sim}$ and $^2t_{R,sim}$ of each compound, and (E) input parameters for generation of a contour plot ($^1t_{R,sim}$ and $^2t_{R,sim}$, ^1H, ^2H, ^1L, ^2L and intensity profiles at position (x and y).

The developed approach requires selection of a training set for generation of alkane t_R and isovolatility curve data in order to enable simulation of ${}^1t_R$ and ${}^2t_R$ of target analytes and the contour plot of a sample. Since the selection of training set significantly affected the simulation performance [48], suitable selection should be performed in order to provide reliable simulation results. It should also be noted that compounds in the training set and the simulated target compounds should be separated under the identical experimental condition. In other words, any change in experimental condition reduces the simulation reliability. Two cases were investigated in our study. The first case is to use one sample from a literature as the training set to simulate another sample separated under the same conditions. The second case is to select a training set of compounds within the same sample (reported from the same literature) and simulated the rest of the compounds in the sample.

4.1 Selection of a training set from a sample to simulate result for another sample.

4.1.1 Curve fitting to obtain t_R and isovolatility curve

This case allows simulation of any sample containing compounds with known retention indices on ^{1}D and ^{2}D columns by injection of a known sample under the same condition. In order to demonstrate this concept, data of the saffron sample [8] was selected as a training set to simulate result for the *Boswellia papyrifera* sample separated under the same experimental condition and reported from the same group in different literature [9]. To this end, ${}^1t_{R(train,i)}$ (experimental ${}^1t_R$ data of compound *i* in the saffron sample), ${}^2t_{R(train,i)}$, ${}^1I_{lit}$ and ${}^2I_{lit}$ of each compound in the saffron sample and experimental condition (**Table 3**) were collected from the literatures [8-11] and input into the related cells in Microsoft Excel (with the interface shown in **Figure 15A**) as the training set in our study.

Table 3.Reported experimental conditions applied for different samples.

Sample	Starting temperature (°C)	Hold time at starting temperature (min)	Ramp rate (°C/min)	Starting modulation time (min)	Modulation period (s)	Reference
Saffron	40	2	5	0	6	[8]
Boswellia papyrifera	40	2	5	0	6	[9]
Acacia honey	40	10	2	0	8	[10]
Incense powder and smoke	40	2	5	0	6	[11]

${}^1t_{R(n),i}$ and ${}^1t_{R(n+1),i}$ of each analyte were then varied (**Figure 15B**) to calculate ${}^1I_{fitting,i}$ of each compound by using equation 30 until $\sum_{i=1}^{m} \left| {}^1I_{lit,i} - {}^1I_{fitting,i} \right|$ was minimized. In order to

facilitate the curve fitting, suitable value of starting $^{1}t_{R(n)}$ was input into the variable cell for each compound which was close to the compound $^{1}I_{lit}$ at various C_n. For example, hexanal peak ($^{1}t_{R,lit}$ = 11.26 min and $^{1}I_{lit}$ = 1078) in saffron should be close to $^{1}t_{R(10)}$ and $^{1}t_{R(11)}$. The values slightly more and less than 11.26 were thus input for $^{1}t_{R(10),start}$ and $^{1}t_{R(11),start}$, respectively. The isovolatility curves were then simulated and curve fitting was performed by variation of p_1-p_5 parameters (**Figure 15C**) to minimize $\sum_{i=1}^{m}\left| {}^{2}I_{lit,i} - {}^{2}I_{fitting,i}\right|$. More detail for the fitting process is provided in the Experimental section. The simulated isovolatility curves providing the best fit are plotted and compared with the experimental result in **Figure 16**, and the corresponding values of p_1-p_5 were provided in **Table 4**.

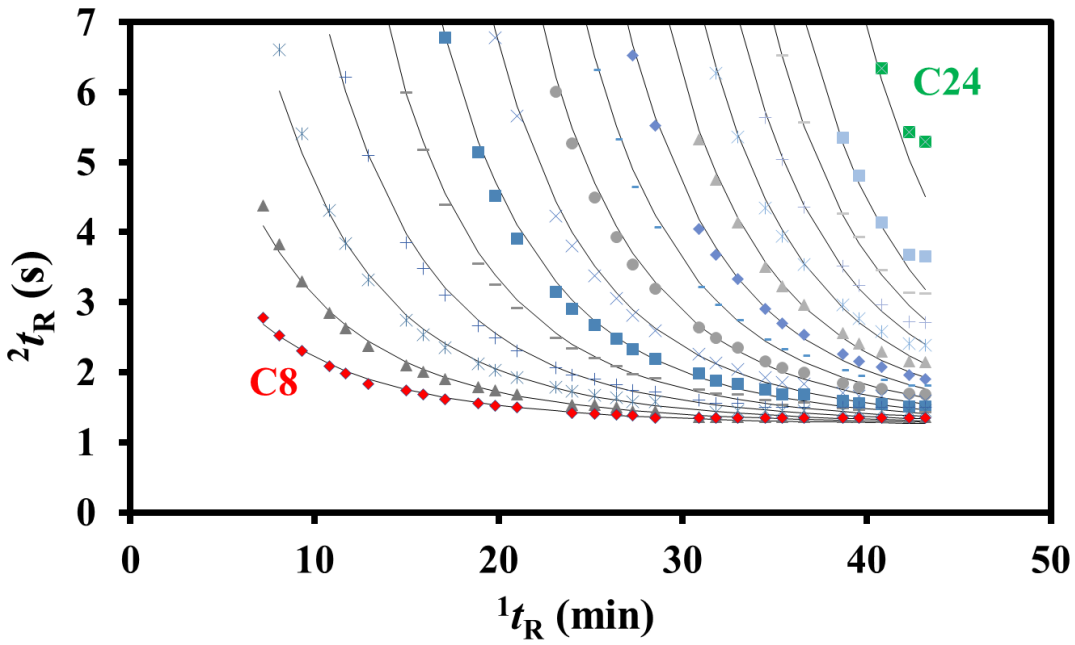


Figure 16 $^{1}t_R$ vs $^{2}t_R$ plots of alkane isovolatility curves obtained from the curve fitting result (solid lines) and the experimental data (dotted lines) of the saffron sample.

Table 4.Isovolatility curve parameters applied in this study (p_1-p_5 and a constant) and H values of different columns in ^{1}D and ^{2}D separation (^1H and ^2H, respectively, obtained by manually fitting σ data with the experimental results according to equation 32).

Column set	Figure	p_1	p_2	p_3	p_4	p_5	Const.	^1H	^2H
SUPELCOWAX 10 × Rxi-5Sil MS	20A	-0.0052	-0.0844	-0.2698	7.9016	-4.8079	1.1631	0.00200	0.00550
SUPELCOWAX 10 × Rxi-5Sil MS	20B	-0.0052	-0.0844	-0.2698	7.0916	-4.8079	1.1631	0.00150	0.00150
DB-FFAP × BPX-50	20C	0.0049	-0.0839	-0.0535	0.4940	-6.4350	1.1263	0.00200	0.00550
BPX5 × BP-20	20D	-0.0047	-0.1036	-0.2941	9.6259	-7.2976	0.9157	0.00075	0.00090

4.1.2 Comparison with the experimental result

According to all $^1t_{R(n)}$ values and the isovolatility curves obtained from GC×GC result of the saffron sample, compound profiles ($^1t_{R,sim}$ and $^2t_{R,sim}$) of the saffron and *Boswellia papyrifera* samples were simulated and the results were in agreement with the experiments as illustrated in **Figure 17A** and **17B**, respectively, with the corresponding correlations shown in **Figures 18A** and **18B**, respectively.

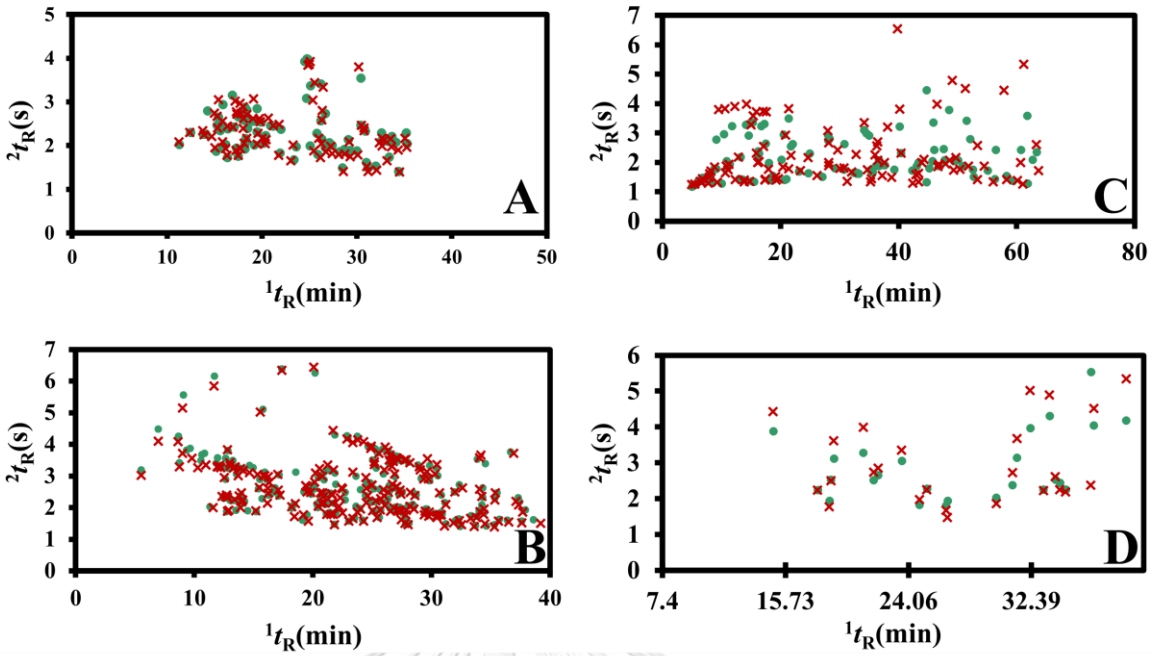


Figure 17 Experimental (green ●) vs simulated (red ×) GC×GC results for the saffron (A), *Boswellia papyrifera* (B), acacia honey (C), incense powder/smoke (D) on SUPELCOWAX 10 (30 m × 0.25 mm i.d. ×0.25 μm df) × Rxi-5Sil MS (1.0 m × 0.1 mm i.d. × 0.1 μm df), SUPELCOWAX 10 (30 m × 0.25 mm i.d. ×0.25 μm df) × Rxi-5Sil MS (1.0 m × 0.1 mm i.d. × 0.1 μm df), DB-FFAP (30 m × 0.25 mm i.d. × 0.25 μm df) × BPX-50 (1.5 m × 0.1 mm i.d. × 0.1 μm df), BPX5 (30 m × 250 μm i.d. × 0.25 μm df) × BP-20 (1.5 m × 0.1 mm i.d. × 0.1 μm df), respectively, employing different separation. The related experimental conditions and parameters are provided in **Table 4**.

4.2 Selection of a training set from a set of compounds to simulate result for other compounds within the same sample

4.2.1 Curve fitting to obtain t_R and isovolatility curve

This provides benefit of confirmation of compound identities reported in literatures and enables screening for a possible set of incorrectly identified compounds. Acacia honey and incense powder/smoke were selected as the examples. To this end, all the compounds (whether they were correctly or incorrectly identified) reported for each sample were selected as the training set with the experimental condition provided in **Table 3**. The parameters obtained from the fitting results were provided in **Table 4**.

4.2.2 Comparison with the experimental result

The simulated and experimental ${}^{1}t_{R}$ and ${}^{2}t_{R}$ of the investigated samples were plotted in **Figure 17C** and **17D**, respectively, with the corresponding correlations provided in **Figure 18C** and **18D**. It can be observed from the correlation between experimental ${}^{2}t_{R}$ obtained from literature (${}^{2}t_{R,lit}$) and ${}^{2}t_{R,sim}$ that the data of some compounds were out of the linear trend lines. With the assumption that most compounds were correctly reported from literatures, simulation based on the training set can lead to simulation results being in agreement with the experimental data. Any mismatch between the values of retention times (${}^{1}t_{R,lit}$ and ${}^{2}t_{R,lit}$) and the simulated retention times (${}^{1}t_{R,sim}$ and ${}^{2}t_{R,sim}$) indicates the possibility of compounds incorrectly identified from the literatures.

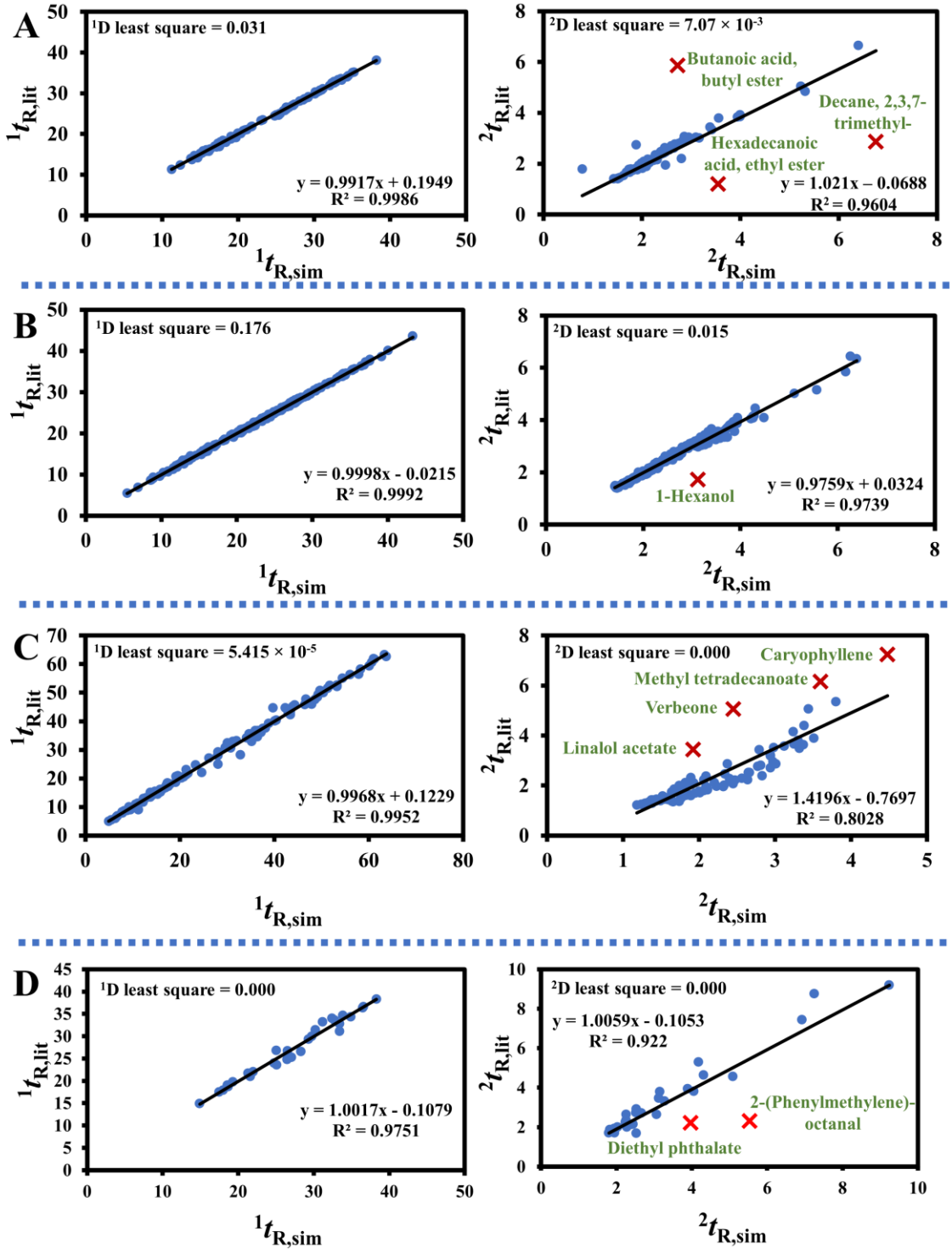


Figure 18 Correlations of ${}^{1}t_{R,lit}$ vs ${}^{1}t_{R,sim}$ (left) and ${}^{2}t_{R,lit}$ vs ${}^{2}t_{R,sim}$ (right) for all the investigated compounds in the samples of (A) saffron, (B) *Boswellia papyrifera*, (C) acacia honey and (D) incense powder/smoke. The possibly incorrectly identified compounds were represented in red ×.

4.3 Application for simulation of GC×GC contour plot chromatograms

Parameters of $^{1}t_{R}$, $^{2}t_{R}$, peak width and peak intensity from the experimental steps mentioned above were used to generate 2D contour plots by using MATLAB. This thesis applied the established approach to simulate separation results for saffron, *Boswellia papyrifera*, acacia honey, incense powder/smoke into contour plot as shown in **Figure 19**. The simulation results (left) showed similar pattern with the experimental results (right) for the focused groups of compounbds. Note that several compounds without the literature *I* data could not be simulated and were thus excluded from the simulation. This indicates the reliability of the established approach.

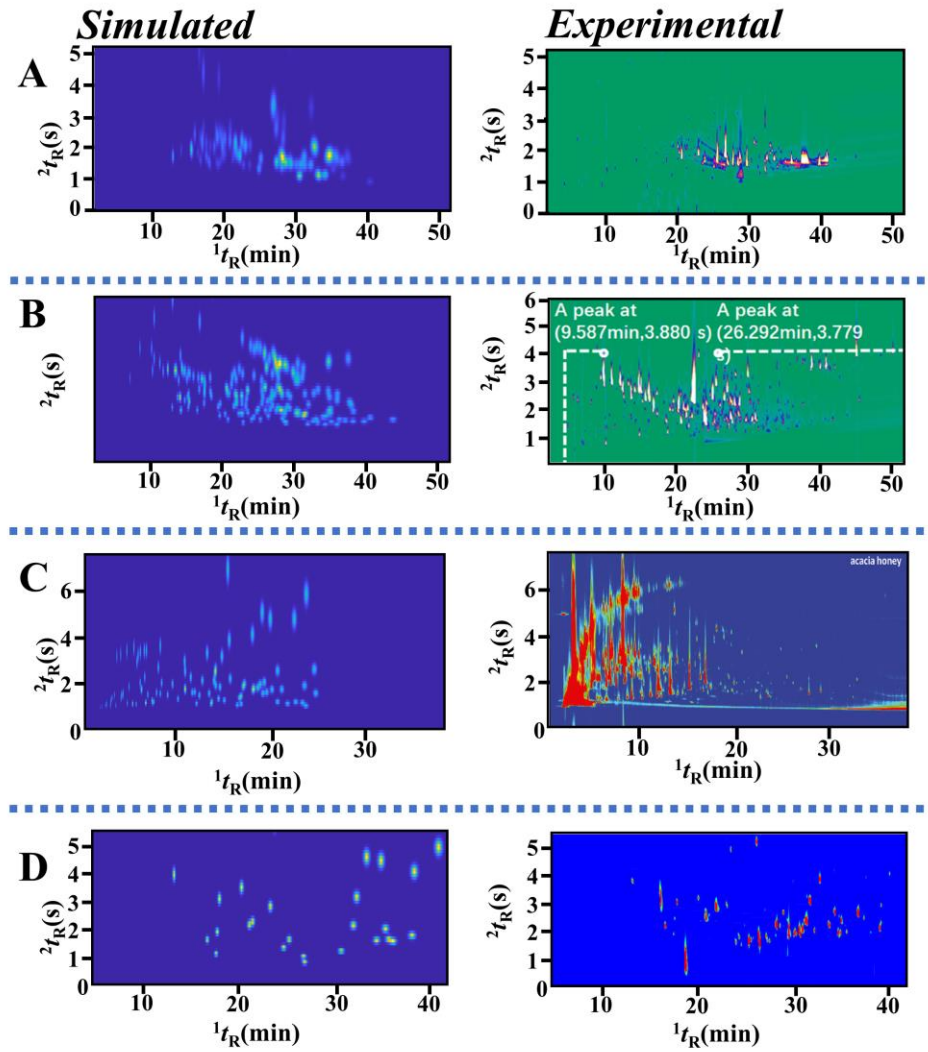


Figure 19 Simulated (left) and experimental (right) GC×GC contour plots of saffron (A), *Boswellia papyrifera* (B), acacia honey (C), incense powder/smoke (D), with the experimental results from [8], [9], [10] and [11], respectively.

4.4 Effect of wraparound

Wraparound should be taken into account prior to the conclusion of mismatch. Thus, ${}^{2}t_{R,lit}$ of a compound of interest was also added or subtracted by *n* times of modulation period (*n* = 0, 1, 2, …) prior to comparison with the simulated values. For example, the suspicious compounds in the saffron sample (modulation period = 6 s) were butanoic acid butyl ester (${}^{2}t_{R,lit}$ = 5.88, ${}^{2}t_{R,sim}$ = 2.73), hexadecanoic acid, ethyl ester (${}^{2}t_{R,lit}$ = 1.20, ${}^{2}t_{R,sim}$= 3.55) and decane, 2,3,7-trimethyl (${}^{2}t_{R,lit}$ = 2.88, ${}^{2}t_{R,sim}$ = 6.76). The addition/subtraction from the literature values could not result in any closer values to the simulated data.

In addition, column length and plate height were input for the simulation (**Figure 15E**) in order to calculate ${}^{1}\sigma$ and ${}^{2}\sigma$ by using equation 29 and to generate a contour plot, see more details in Experimental section. The related parameters for the simulation are provided in **Table 4**. The simulated results were similar (for the identified peaks with available ${}^{1}I$ and ${}^{2}I$ data) to the experimental results obtained from the literatures as shown in **Figure 19** indicating reliability of the established approach.

4.5 Example application of the developed approach for suggestion of a possible correct identity of a peak

In case of correctly reported compounds, the simulated and experimental results of the same sample separated by GC×GC under the same condition (column type, column length, ramp rate, modulation period and flow rate) should be well matched. By comparison of compound identification in the perfume (**Table 5**), it was found that 68 out of 69 were correctly identified. However, the reported name of bis(1-methyl-2-hydroxyethyl)ether and dipropylene glycol for the peak with ${}^{1}t_{R} \approx 19.6$ min from identification of compound name using only ${}^{1}I$ and both ${}^{1}I$ and ${}^{2}I$, respectively, were difference (highlighted in the grey row in **Table 5**). For further illustration of the compound confirmation, the correlation plot of experimental and simulation ${}^{1}t_{R}$ and ${}^{2}t_{R}$ were plotted in **Figure 19A** and **19B**, respectively. The results display that bis(1-methyl-2-hydroxyethyl)ether is out of the trendline as shown in **Figure 19B** (${}^{2}t_{R,lit}$ = 10.29 min vs ${}^{2}t_{R,sim}$ = 7.09 min). Accordingly, it could be noted that bis(1-methyl-2-hydroxyethyl)ether was the incorrect identity. On the other hand, dipropylene glycol could be suggested as more correct identity of this peak (**Figure 21**).

Table 5. Comparison of identified compounds in perfume sample between the two experiments under the same condition [46].

Only ^1I			^1I and ^2I		
Compound	^{1}D time (min)	^{2}D time (min)	Compound	^{1}D time (min)	^{2}D time (min)
2-Methyl-2-buten-1-ol	10.40	4.92	2-Methyl-2-buten-1-ol	10.40	4.92
1-Hexanol	12.95	4.53	1-Hexanol	12.80	4.67
3-Methyl-2-buten-1-ol	14.60	3.54	3-Methyl-2-buten-1-ol	14.60	3.54
Benzaldehyde	15.84	5.34	Benzaldehyde	15.80	5.20
α-Pinene	16.00	2.73	α-Pinene	16.00	2.73
β-Myrcene	17.60	3.04	β-Myrcene	17.60	2.90
β-Pinene	17.62	2.90	β-Pinene	17.60	3.04
cis-3-Hexenyl acetate	17.84	3.51	cis-3-Hexenyl-1-acetate	17.80	3.54
Benzenemethanol	18.62	10.28	Benzenemethanol	18.60	10.29
Limonene	19.41	3.14	Limonene	19.40	3.14
Eucalyptol	19.49	3.15	Eucalyptol	19.40	3.23
α-Methylbenzyl alcohol	19.80	8.41	Benzenemethanol, α-methyl-	19.80	8.41
trans-3,7-Dimethyl-1,3,6-Octatriene	19.94	3.09	trans-3,7-Dimethyl-1,3,6-Octatriene	19.80	3.21
Bis(1-methyl-2-hydroxyethyl)ether	19.54	10.29	Dipropylene glycol	19.60	9.77
1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	20.60	3.09	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	20.60	3.09
2,6-Dimethyl-7-octen-2-ol	20.74	3.92	2,6-Dimethyl-7-octen-2-ol	20.60	4.04
Methyl benzoate	21.40	5.44	Methyl benzoate	21.20	5.57
trans-Linalool oxide	21.31	4.00	trans-Linalool oxide	21.40	4.17
Linalool	21.90	4.28	Linalool	21.80	4.37
β-Phenethyl formate	23.60	6.42	β-Phenethyl formate	23.60	6.42
trans-Rose oxide	22.40	3.45	trans-Rose oxide	22.40	3.45
3,5-Dimethylanisole	22.20	4.14	3,5-Dimethylanisole	22.20	4.14
1,2-Dihydrolinalool	23.20	4.00	1,2-Dihydrolinalool	23.20	4.00

Only ^{1}I			^{1}I and ^{2}I		
Compound	^{1}D time (min)	^{2}D time (min)	Compound	^{1}D time (min)	^{2}D time (min)
Fenchol	22.80	4.57	Fenchol	22.80	4.57
β-Terpineol	23.80	4.75	β-Terpineol	23.80	4.75
cis-p-Menthan-3-one	24.35	3.75	cis-p-Menthan-3-one	24.20	3.64
Ethyl benzoate	24.51	5.01	Ethyl benzoate	24.40	5.10
2,6-Dimethyl-3,7-octadiene-2,6-diol	25.00	7.45	2,6-Dimethyl-3,7-octadiene-2,6-diol	25.00	7.45
1-Methyl-4-(1-methylethyl) cyclohexanol	25.01	4.60	1-Methyl-4-(1-methylethyl) cyclohexanol	25.00	4.61
Isomenthol	25.20	4.56	Isomenthol	25.20	4.56
Benzenemethanol, α-methyl-, acetate	25.20	5.00	Benzenemethanol, α-methyl-, acetate	25.20	5.00
Methyl salicylate	25.60	5.83	Methyl salicylate	25.40	5.98
Dihydrocitronellol	25.70	4.40	Dihydrocitronellol	25.60	4.49
α-Citronellol	25.64	4.90	α-Citronellol	26.60	4.87
Cyclohexanol, 1-methyl-4-(1-methylethylidene)-	26.00	4.78	Cyclohexanol, 1-methyl-4-(1-methylethylidene)-	26.00	4.78
cis-Geraniol	27.01	5.25	cis-Geraniol	27.00	5.26
Isogeraniol	27.29	5.20	Isogeraniol	27.00	5.36
β-Phenethyl acetate	27.60	5.50	β-Phenethyl acetate	27.60	5.50
trans-Geraniol	27.96	5.32	trans-Geraniol	27.80	5.45
Linalyl acetate	28.07	3.62	Linalyl acetate	28.00	3.68
α-Citral	28.30	4.63	α-Citral	28.20	4.71
Hydroxycitronellal	28.80	6.02	Hydroxycitronellal	28.80	6.02
Dihydro-5-pentyl-2(3H)-furanone	31.40	6.44	Dihydro-5-pentyl-2(3H)-furanone	31.40	6.44
Anethole	29.20	4.93	anethole	29.20	4.93
benzyl 2-methylpropanoate	29.40	4.76	benzyl 2-methylpropanoate	29.40	4.76
Methyl anthranilate	31.00	8.95	Methyl anthranilate	31.00	8.95
Anethole	29.20	4.93	anethole	29.20	4.93

Only ^{1}I			^{1}I and ^{2}I		
Compound	^{1}D time (min)	^{2}D time (min)	Compound	^{1}D time (min)	^{2}D time (min)
benzyl 2-methylpropanoate	29.40	4.76	benzyl 2-methylpropanoate	29.40	4.76
Citronellol acetate	31.56	3.66	Citronellol acetate	31.20	3.85
Eugenol	31.80	7.47	Eugenol	31.80	7.47
Geranyl acetate	32.71	3.92	Geranyl acetate	32.60	4.01
1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	33.00	4.15	1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	33.00	4.15
3-Methyl-2-(cis-2-penten-1-yl)-2-cyclopenten-1-one	33.20	5.29	3-Methyl-2-(cis-2-penten-1-yl)-2-cyclopenten-1-one	33.20	5.29
3-Phenyl-2-propenyl acetate	34.79	6.23	3-Phenyl-2-propenyl acetate	34.60	6.37
Nopyl acetate	34.80	4.00	Nopyl acetate	34.80	4.00
5-Hexyldihydro-2(3H)-furanone	35.40	6.19	5-Hexyldihydro-2(3H)-furanone	35.40	6.19
β-Chamigrene	36.00	3.57	β-Chamigrene	36.00	3.57
Pentyl benzoate	36.28	4.67	Pentyl benzoate	36.20	4.75
α-Selinene	36.80	3.53	α-Selinene	36.80	3.53
β-Ionone	36.90	4.47	β-Ionone	36.80	4.54
Methyl (2-pentyl-3-oxocyclopentyl) acetate	42.20	5.19	Methyl (2-pentyl-3-oxocyclopentyl) acetate	42.20	5.19
cis-3-Hexenyl salicylate	43.23	5.08	cis-3-Hexenyl salicylate	43.20	5.11
1-(2,6,6-Trimethylcyclohex-2-en-1-yl)-1-pentene-3-one	38.20	4.14	1-(2,6,6-Trimethylcyclohex-2-en-1-yl)pent-1-en-3-one	38.20	4.14
Isoamyl salicylate	38.70	4.70	Isoamyl salicylate	38.60	4.79
α-(Trichloromethyl)benzyl acetate	39.30	5.23	α-(Trichloromethyl)benzyl acetate	39.20	5.25
3-Buten-2-one, 3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-	37.00	4.07	3-Buten-2-one, 3-methyl-4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-	37.00	4.07
α-(Trichloromethyl)benzyl acetate	39.30	5.23	α-(Trichloromethyl)benzyl acetate	39.20	5.25
3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	39.60	4.24	3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	39.60	4.24

Only ^{1}I			^{1}I and ^{2}I		
Compound	^{1}D time (min)	^{2}D time (min)	Compound	^{1}D time (min)	^{2}D time (min)
Diethyl Phthalate	39.90	6.46	Diethyl Phthalate	39.80	6.53
1-Acetonaphthone	41.20	7.95	1-Acetylnaphthalene	41.20	7.95
Benzyl Benzoate	46.17	7.48	Benzyl Benzoate	46.00	7.60
Benzyl salicylate	49.84	9.65	Benzyl salicylate	49.80	9.67

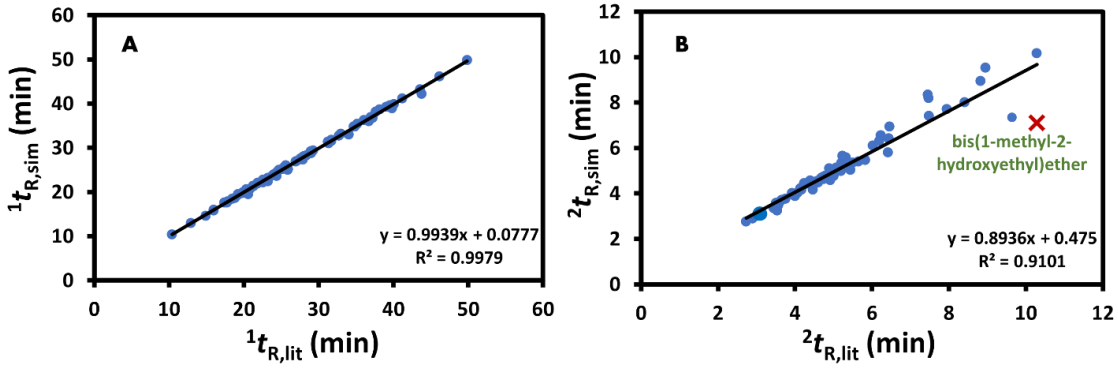


Figure 20 Correlations of $^1t_{R,lit}$ vs $^1t_{R,sim}$ (A) and $^2t_{R,lit}$ vs $^2t_{R,sim}$ (B) for all the investigated compounds in the perfume sample. The possibly incorrectly identified compound was represented in red ×.

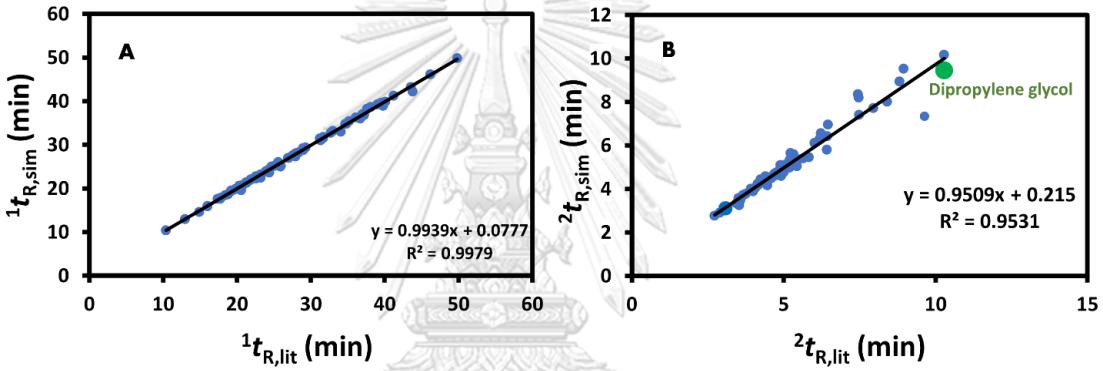


Figure 21 Correlations of $^1t_{R,lit}$ vs $^1t_{R,sim}$ (A) and $^2t_{R,lit}$ vs $^2t_{R,sim}$ (B) for all the investigated compounds in the perfume sample. The suggested compound as more correct identity was represented in green ●.

4.6 Validation of the screening approach using residual and leave one out analysis

The residual analysis (**Figure 22**) and leave-one-out (**Appendix 6-10**) approaches were further performed in order to validate the compounds with suspected identities. The outliner data were set to be outside ±2 times of the values of standard deviations (2×SD) in the residual analysis and 2×SD of the least square values in the leave-one-out analysis.

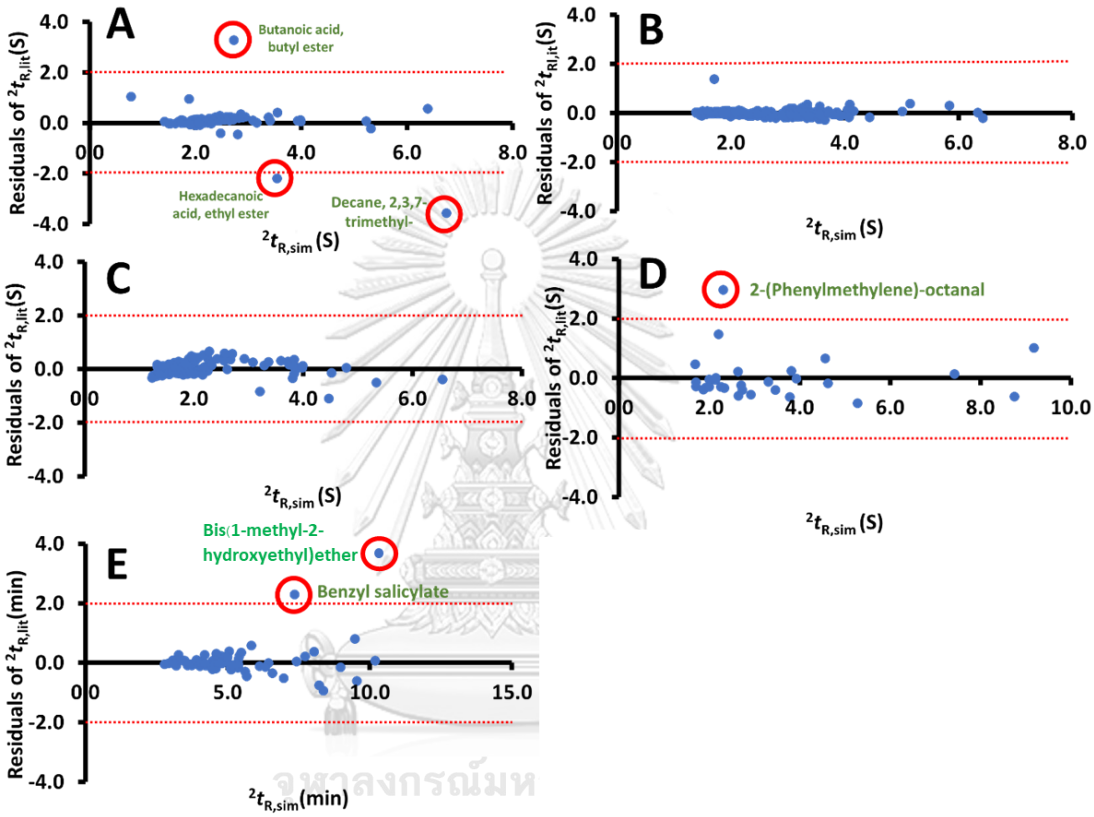


Figure 22 Evaluation of the simulation uncertainty: residual analysis results for the corresponding correlation plots from **Figure 18** and **20**. The data of the suspected compounds were indicated by the red circles.

4.7 Validation of possibly correct suggestion for identifying compound

The corresponding correlations ${}^1t_R$ and ${}^2t_R$ of the perfume samples were plotted in **Figure 20** and **21**. This revealed bis(1-methyl-2-hydroxyethyl)ether (${}^1t_R$ = 19.54 min and ${}^2t_R$ = 10.29 min) as the incorrectly identified compounds and the suggestion of correct peak identities could be obtained from the MS library which were dipropylene glycol. Due to the retention index data could not be applied to suggest the new compound because there are many compounds in the NIST library having similar retention index values. However, this thesis provided the validation of the suggestion of possible correct compound identity based on the *n*-alkane data obtained in our laboratory for analysis of the perfume sample. In order to illustrate the capability to simulate alkane retention times, alkane standards were experimentally injected under the same separation condition compared with the simulated data showing the errors provided in **Table 6**.

Table 6 The fitting curve parameters of the isovolatility curves of *n*-alkanes from perfume sample.

${}^1t_{R(n)\ experimental}$	${}^2t_{R(n)\ experimental}$	${}^1t_{R(n)sim}$	${}^1t_{R(n)sim}$	$\lvert {}^1t_{R(n)lit} - {}^1t_{R(n)sim} \rvert$	$\lvert {}^1t_{R(n)lit} - {}^1t_{R(n)sim} \rvert$
9.18	2.31	9.90	2.41	0.72	0.10
11.40	2.40	10.73	2.49	0.66	0.09
14.55	2.50	14.83	2.57	0.29	0.07
18.34	2.60	18.33	2.64	0.01	0.04
22.40	2.69	22.36	2.70	0.04	0.01
26.47	2.77	26.52	2.75	0.05	0.02
30.42	2.83	30.31	2.79	0.11	0.04
34.21	2.89	34.25	2.83	0.04	0.06
37.83	2.94	37.52	2.86	0.31	0.08
41.31	2.99	41.52	2.89	0.21	0.09
44.85	2.81	46.17	2.91	1.32	0.10
46.34	3.06	46.17	3.02	0.17	0.04
51.41	3.09	56.36	2.95	4.95	0.14
54.67	3.40	56.30	2.95	1.63	0.45

CHAPTER V

CONCLUSION

New approaches for prediction of peak positions ($^1t_{R,sim}$ and $^2t_{R,sim}$) and the contour plots in GC×GC without the requirement of alkane reference injection were established and applied to simulate the results for separation of chromatogram from different samples; saffron, *Boswellia papyrifera*, acacia flowers, honey, and incense powder/smoke. The approaches were based on Kovatś index and van den Dool and Kratz relationship equations. The results (see **Figure 16** in Chapter IV**)** revealed the similar pattern of peaks chromatogram between literatures and simulations with the good correlation plots (**Figure 18**) between $t_{R,lit}$ and $t_{R,sim}$ of ^{1}D separation providing the R^2 (0.9791-0.9992) and acceptable R^2 ranges (0.8028-0.9220) of ^{2}D separation with some of the compounds being significantly out of the trendline.

Applications for confirmation of compound identification for different samples reported from the literature were demonstrated via their ^2t_R correlation plots. Solver has been found to be a useful tool to vary p_1-p_5 minimizing the difference between $^2I_{lit}$ and $^2I_{fitting}$ leading to simulation of the results based on the assumption that the compound identities reported from the literature were mostly correct. Thus, the observation of some compounds being out of the correlation trendline (mismatching between $^2I_{lit}$ and $^2I_{fitting}$) suggests that there is an error for the compound identification. For this application, there is 10 suspected compounds from the 4 papers, which may be identified incorrectly. It should be noted that the information of MS data is required if the higher numbers of compounds are aimed for identifications (it is not available in this thesis). The retention index data could not be applied to suggest the new compound since there are many compounds in the NIST library having similar retention index values. However, this thesis presents the example case for suggestion of a more correct compound identity based on the data obtained in our laboratory for analysis of perfume samples based on the possible set of compounds that obtained from the available MS data of the suspected peak.

Furthermore, the contour plots of GC×GC were successfully generated by means of plate theory, Gaussian equations and using of MATLAB. This work applied the established approach to provide the simulation similar to the experimental results of saffron, *Boswellia papyrifera*, acacia flowers, honey, and incense powder/smoke samples (see **Figure 19** in Chapter IV).

To this end, the proposed concepts are expected to be useful to support experimental design, simulation of a contour plot for a known set of compounds (*e.g.* for teaching in a lecture class), confirmation of peak identities obtained from two dimensional GC hyphenated with MS.

Thus, the developed approach can provide more reliable compound identification results in diverse samples. However, this application requires the training from the specialist before use, or the established application need to simplify especially for reducing complexity of the approach to be more user friendly in the future.

APPENDICES

Appendix 1 Reported compound profile and the ^{1}I and ^{2}I data in saffron [8] analysed by GC×GC-MS.

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
1	Hexanal	11.26	11.26	2.10	2.04	1078	1078	812	802
2	Ethylbenzene	12.39	12.46	2.31	2.31	1138	1140	871	872
3	2-Propenoic acid, butyl ester	13.91	13.76	2.26	2.28	1189	1184	902	905
4	Heptanal	13.76	14.06	2.35	2.27	1184	1194	912	900
5	Benzene, tert-butyl-	14.68	14.27	2.22	2.81	1215	1201	992	996
6	Decane, 2,3,7-trimethyl-	14.24	14.74	2.88	6.76	1200	1217	1200	1212
7	Butanoic acid, butyl ester	14.86	14.97	5.88	2.73	1221	1225	998	991
8	2-Hexenal, (E)-	14.97	15.16	2.76	1.89	1225	1231	865	845
9	Benzene, 1-ethyl-4-methyl-	15.03	15.27	1.96	2.48	1227	1235	994	961
10	Furan, 2-pentyl-	15.27	15.37	2.68	2.66	1235	1238	996	994
11	2-Heptanone, 6-methyl-	15.30	15.56	2.41	2.36	1236	1245	957	948
12	5-Dodecene, (Z)-	15.42	15.61	5.06	5.24	1240	1247	1180	1189
13	Pyridine, 2,6-dimethyl-	16.18	15.86	1.94	1.99	1266	1255	890	902
14	Mesitylene	15.83	15.87	2.57	2.47	1254	1255	996	981
15	1,3,6-Octatriene, 3,7-dimethyl-, (Z)-	15.42	15.87	3.06	2.95	1240	1256	1041	1030
16	Styrene	15.83	16.16	2.09	2.04	1254	1265	915	905
17	Pyrazine, methyl-	16.33	16.35	1.78	1.74	1271	1272	845	831
18	Benzene, 1-ethyl-2-methyl-	16.36	16.37	2.46	2.40	1272	1272	994	984
19	Cyclohexene, 4-methyl-3-(1-methylethylidene)-	17.15	16.88	3.03	3.16	1299	1290	1088	1103
20	Cyclohexane, hexyl-	17.53	17.01	4.86	5.32	1312	1294	1237	1261
21	Octanal	16.92	17.07	2.43	2.44	1291	1296	1005	1006
22	Cyclohexanone	17.24	17.26	1.90	1.96	1302	1303	903	917
23	Pyridine, 3-methyl-	17.47	17.46	1.79	1.77	1310	1309	874	868
24	Benzene, 1-methyl-2-propyl-	17.33	17.47	2.78	2.67	1305	1310	1063	1048
25	Benzene, 1,4-diethyl-	17.77	17.67	2.74	2.73	1320	1317	1070	1068
26	Benzene, butyl-	17.36	17.77	2.74	2.66	1306	1320	1058	1048
27	Benzene, 2-ethyl-1,4-dimethyl-	18.38	18.07	2.72	2.60	1341	1330	1086	1068
28	Pyrazine, 2,6-dimethyl-	17.74	18.16	1.94	1.93	1319	1333	925	923
29	2-Heptenal, (Z)-	18.09	18.16	2.07	2.05	1331	1333	964	961
30	Benzene, (1-methylbutyl)-	17.68	18.17	2.97	2.89	1317	1334	1098	1088
31	5-Hepten-2-one, 6-methyl-	18.38	18.26	2.18	2.17	1341	1337	998	997
32	Benzene, 1-methyl-2-propyl-	18.06	18.37	2.63	2.65	1330	1341	1063	1066

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
33	Benzene, (1,1-dimethylpropyl)-	18.00	18.37	2.89	2.83	1328	1341	1098	1089
34	Benzene, 1,2,3-trimethyl-	18.03	18.47	2.40	2.41	1329	1344	1028	1029
35	Benzene, 2-ethyl-1,4-dimethyl-	19.06	18.87	2.63	2.58	1364	1358	1093	1085
36	Pyridine, 2,4,6-trimethyl-	19.47	19.16	2.04	2.03	1378	1368	996	993
37	1,3,8-p-Menthatriene	19.73	19.17	2.63	2.57	1387	1368	1113	1105
38	Indane	19.58	19.47	2.29	2.32	1382	1378	1051	1057
39	Benzene, 1,3-diethyl-5-methyl-	19.08	19.47	3.08	2.86	1365	1378	1150	1125
40	Nonanal	19.82	19.87	2.56	2.55	1390	1392	1105	1105
41	Pyrazine, trimethyl-	20.36	20.16	2.05	2.07	1413	1403	1021	1024
42	3-Octen-2-one	19.99	20.26	2.18	2.12	1396	1408	1040	1028
43	3-Cyclohexen-1-one, 3,5,5-trimethyl-	20.41	20.36	2.15	2.24	1416	1413	1044	1064
44	Benzene, 1,2,3,4-tetramethyl-	20.68	20.87	2.64	2.47	1430	1440	1142	1115
45	1-Octen-3-ol	20.90	21.04	1.80	0.79	1442	1449	960	0
46	Benzene, 1,2,3,5-tetramethyl-	21.17	21.17	2.47	2.46	1456	1456	1129	1128
47	2,4-Heptadienal, (E,E)-	21.75	21.86	1.79	1.85	1487	1492	980	1002
48	Ethanone, 1-(1,4-dimethyl-3-cyclohexen-1-yl)-	21.81	21.97	2.49	2.38	1490	1498	1152	1133
50	1,6-Octadien-3-ol, 3,7-dimethyl-	23.27	23.56	2.03	1.98	1537	1545	1098	1085
51	Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-, (-)-	24.85	24.49	3.85	3.94	1583	1573	1423	1431
52	Megastigma-4,6(Z),8(E)-triene	25.37	24.68	3.05	3.10	1598	1578	1354	1360
53	Longifolene	24.99	24.70	3.87	4.00	1587	1578	1430	1441
54	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-	25.09	24.80	3.93	3.99	1590	1581	1439	1445
55	γ-Elemene	25.55	25.09	3.45	3.39	1607	1590	1410	1403
56	Isophorone	25.43	25.06	1.89	2.01	1600	1589	1118	1155
57	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	25.98	25.77	2.18	2.29	1632	1620	1220	1245
58	Benzaldehyde, 4-methyl-	26.15	25.86	1.74	1.81	1642	1625	1080	1110
59	Naphthalene, 1,2,3,4-tetrahydro-1,8-dimethyl-	26.30	26.17	2.60	2.58	1651	1643	1318	1316
60	γ-Elemene	26.42	26.19	3.35	3.42	1658	1644	1430	1438
61	1,3-Cyclohexadiene-1-carboxaldehyde, 2,6,6-trimethyl-	26.25	26.27	2.06	2.16	1648	1649	1197	1223

No.	Name	$^1t_{R,lit}$	$^1t_{R,sim}$	$^2t_{R,lit}$	$^2t_{R,sim}$	$^1I_{lit}$	$^1I_{fitting}$	$^2I_{lit}$	$^2I_{fitting}$
62	2-Hydroxy-3,5,5-trimethyl-cyclohex-2-enone	26.71	26.66	1.87	1.97	1675	1672	1149	1184
63	2-Octenal, 2-butyl-	26.34	26.68	2.82	2.75	1653	1673	1355	1344
64	Benzaldehyde, 2,5-dimethyl-	27.26	27.06	1.99	2.08	1705	1696	1208	1234
65	Heptadecane	27.14	27.14	6.67	6.40	1700	1700	1700	1686
66	2,6,6-Trimethyl-2-cyclohexene-1,4-dione	27.39	27.36	1.83	2.01	1710	1709	1152	1219
67	2(5H)-Furanone	28.56	28.46	1.41	1.51	1758	1754	924	1012
68	2-Cyclopenten-1-one, 4-hydroxy-3-methyl-2-(2-propenyl)-	28.12	28.16	1.81	1.87	1740	1742	1168	1196
69	Naphthalene	28.74	28.66	1.82	1.92	1765	1762	1193	1231
70	2-Cyclohexen-1-one, 2-hydroxy-3-methyl-6-(1-methylethyl)-	29.20	29.07	2.09	2.15	1784	1778	1304	1320
71	1,4-Cyclohexanedione, 2,2,6-trimethyl-	29.27	29.26	1.76	1.91	1787	1786	1183	1243
72	Acetic acid, 2-phenylethyl ester	30.11	29.96	1.80	1.89	1825	1818	1226	1265
73	2-Butanone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	30.46	30.37	2.47	2.48	1842	1838	1444	1446
74	Benzene, (1-butylheptyl)-	30.17	30.39	3.81	3.56	1828	1839	1633	1606
75	5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	30.75	30.67	2.41	2.41	1856	1852	1442	1442
76	α-Ionone	30.77	30.87	2.35	2.35	1857	1862	1429	1428
77	2,3-Dihydro-5-hydroxy-6-methyl-4(H)-pyran-4-one	31.04	30.96	1.53	1.63	1870	1866	1104	1166
78	Benzyl alcohol	31.18	31.16	1.42	1.50	1877	1876	1002	1080
79	Phenylethyl Alcohol	32.06	31.96	1.45	1.54	1922	1916	1052	1138
80	3-Buten-2-ol, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	32.37	32.57	2.07	2.13	1939	1950	1412	1428
81	trans-β-Ionone	32.63	32.57	2.18	2.31	1953	1950	1452	1491
82	4-(2,6,6-Trimethyl-cyclohexen-1-yl)-butan-2-ol	32.87	32.87	2.14	2.18	1966	1966	1449	1463
83	Naphthalene, 2-ethyl-	32.63	32.97	2.00	2.12	1953	1971	1396	1435
84	Naphthalene, 1,6-dimethyl-	33.62	33.27	1.99	2.11	2006	1988	1427	1471
85	1-Hydroxymethyl-7,7-dimethylbicyclo[2.2.1]heptan-2-one	33.18	33.36	1.66	1.75	1983	1993	1255	1307

No.	Name	$^1t_{R,lit}$	$^1t_{R,sim}$	$^2t_{R,lit}$	$^2t_{R,sim}$	$^1I_{lit}$	$^1I_{fitting}$	$^2I_{lit}$	$^2I_{fitting}$
86	3-Buten-2-one, 4-(2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl)-	33.53	33.67	2.16	2.22	2002	2008	1484	1503
87	Naphthalene, 1,4-dimethyl-	34.37	34.07	1.91	2.09	2041	2027	1424	1495
88	2,5-Dimethyl-4-hydroxy-3(2H	34.50	34.36	1.41	1.43	2047	2040	1077	1100
89	Cyclohexanemethanol, 4-ethenyl-α,α,4-trimethyl-3-(1-methylethenyl)-, [1R-(1α,3α,4β)]-	35.07	35.17	2.17	2.31	2074	2079	1548	1589
90	5-Methyl-2-phenyl-2-hexenal	35.27	35.27	1.97	2.06	2083	2083	1486	1520
91	Hexadecanoic acid, ethyl ester	38.19	38.19	1.20	3.55	2227	2227	1975	1984

Appendix 2 Reported compound profile and the ^{1}I and ^{2}I data in *Boswellia papyrifera* [9] analysed by GC×GC-MS.

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
1	Octane	5.47	5.47	3.20	3.03	800	800	800	812
2	Nonane	6.90	6.91	4.49	4.09	900	899	897	918
3	Cyclohexane,propyl-	8.59	8.59	4.26	4.08	982	982	931	948
4	Cyclopentene,1-(2-methylpropyl)-	8.68	8.71	3.42	3.30	988	986	889	902
5	Decane	9.02	8.96	5.57	5.16	1000	1002	996	1015
6	Tricyclo[2.2.1.0(2,6)]heptane,1,7,7-trimethyl-	9.29	8.96	3.83	3.72	1000	1012	926	933
7	α-Pinene	9.59	9.78	3.88	3.57	1031	1024	939	956
8	Cyclohexene,3-(1-methylethyl)-	10.48	10.25	3.50	3.27	1049	1058	941	943
9	α-Fenchene	10.58	10.92	3.68	3.35	1074	1061	955	972
10	Camphene	10.79	10.92	3.73	3.35	1074	1069	964	976
11	Hexanal	11.26	11.55	2.04	2.00	1098	1087	803	808
12	Undecane	11.63	11.61	6.17	5.84	1100	1101	1095	1111
13	(-)-α-thujene	11.78	12.09	3.41	3.34	1117	1106	971	984
14	Sabinene	11.88	11.89	3.59	3.30	1110	1110	988	993
15	2H-Pyran,2-ethenyltetrahydro-2,6,6-trimethyl-	12.08	11.97	3.28	3.29	1113	1117	970	970
16	(-)-β-Pinene	12.28	12.17	3.34	3.27	1120	1124	981	980
17	1-Butanol,3-methyl-,acetate	12.36	12.31	2.31	2.36	1125	1127	874	870
18	Thuja-2,4(10)-diene	12.57	12.48	2.91	2.96	1131	1134	951	948
19	(+)-4-Carene	12.58	12.99	3.57	3.33	1149	1135	1007	1020
20	3-Penten-2-one,4-methyl-	12.66	12.74	1.89	1.89	1140	1137	800	800
21	2-n-Butyl-furan	12.66	12.68	2.37	2.40	1138	1137	891	888
22	p-Xylene	12.76	12.62	2.30	2.34	1136	1141	884	876
23	3-Carene	12.78	12.93	3.26	3.42	1147	1141	990	995
24	Cyclohexene,1-(2-methylpropyl)-	12.79	12.74	3.80	3.83	1140	1142	1028	1029
25	Benzene,1,3-dimethyl-	12.96	12.74	2.24	2.33	1140	1148	877	868
26	(+)-2-Carene	13.18	13.25	3.49	3.25	1158	1156	1016	1021
27	3-Heptanone	13.26	13.36	2.23	2.25	1162	1159	883	882
28	2-Butenal,2-ethyl-	13.46	12.88	1.93	1.91	1145	1165	825	811
29	β-Myrcene	13.48	13.67	3.07	3.01	1173	1166	993	997
30	α-Phellandrene	13.58	13.42	3.30	3.29	1164	1170	1016	1011
31	Acetic-acid,pentyl-ester	13.76	13.75	2.28	2.37	1176	1176	904	901
32	Benzene,(1-methylethyl)-	13.86	13.92	2.40	2.47	1182	1180	923	922

No.	Name	${}^{1}t_{R,lit}$	${}^{1}t_{R,sim}$	${}^{2}t_{R,lit}$	${}^{2}t_{R,sim}$	${}^{1}I_{lit}$	${}^{1}I_{fitting}$	${}^{2}I_{lit}$	${}^{2}I_{fitting}$
33	7-Oxabicyclo[2.2.1]heptane,1-methyl-4-(1-methylethyl)-	13.88	13.87	3.24	3.23	1180	1180	1019	1017
34	2-Heptanone	14.06	13.98	2.15	2.18	1184	1187	888	883
35	1,3-Cyclohexadiene,1-methyl-4-(1-methylethyl)-	14.08	14.09	3.23	3.19	1188	1187	1024	1022
36	Heptanal	14.16	14.04	2.21	2.24	1186	1190	902	896
37	Cyclopentanone,2-methyl-	14.46	13.87	1.90	2.00	1180	1201	839	825
38	D-Limonene	14.58	14.61	3.34	3.11	1206	1205	1039	1045
39	Eucalyptol	14.88	15.30	3.27	3.05	1230	1215	1041	1058
40	2-Hexenal	15.16	15.16	1.89	1.91	1225	1225	849	849
41	Furan,2-pentyl-	15.37	15.45	2.60	2.64	1235	1232	993	990
42	1,3,6-Octatriene,3,7-dimethyl-,(Z)-	15.47	15.77	2.90	3.01	1246	1236	1030	1034
43	2-Heptanone,6-methyl-	15.66	16.14	2.29	2.14	1259	1242	950	960
44	5-Dodecene,(E)-	15.71	15.51	5.11	5.02	1237	1244	1187	1186
45	γ-Terpinene	15.88	16.20	3.13	2.98	1261	1250	1066	1070
46	1,3,7-Octatriene,3,7-dimethyl-	16.07	15.88	2.88	3.01	1250	1257	1045	1035
47	3-Octanone	16.17	16.20	2.40	2.45	1261	1260	983	980
48	Acetic-acid,hexyl-ester	16.47	16.17	2.46	2.61	1260	1270	1001	988
49	m-Cymene	16.67	16.26	2.63	2.79	1263	1277	1030	1015
50	p-Cymene	16.77	17.04	2.63	2.56	1290	1281	1032	1035
51	Octanal	17.07	17.19	2.38	2.40	1295	1291	1004	1004
52	Cyclohexene,1-methyl-4-(1-methylethylidene)-	17.08	17.01	3.04	3.05	1289	1291	1093	1085
53	Tridecane	17.33	17.33	6.39	6.34	1300	1300	1295	0
54	2-Heptenal,(Z)-	18.16	18.17	1.99	2.02	1331	1331	943	949
55	5-Hepten-2-one,6-methyl-	18.36	18.47	2.11	2.13	1342	1338	979	985
56	1-Hexanol	18.48	18.39	3.13	1.71	1339	1342	848	827
57	2-Cyclopenten-1-one	19.05	19.58	1.61	1.58	1383	1364	827	1090
58	Benzene,4-ethyl-1,2-dimethyl-	19.17	19.47	2.51	2.49	1379	1368	1081	1096
59	Acetic-acid,heptyl-ester	19.37	19.33	2.57	2.70	1374	1375	1098	917
60	2-Cyclopenten-1-one,2-methyl-	19.46	19.17	1.78	1.77	1368	1379	906	1065
61	2-Nonanone	19.77	19.77	2.44	2.49	1390	1390	1086	1112
62	Octanoic-acid,methyl-ester	19.77	19.44	2.62	2.67	1378	1390	1117	1118
63	2,4,6-Octatriene,2,6-dimethyl-	19.97	20.09	2.73	2.81	1402	1398	1141	1120
64	Thujone	20.07	20.58	2.61	2.47	1421	1401	1128	0

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
65	Tetradecane	20.13	20.04	6.27	6.44	1400	1404	1393	1029
66	2-Octenal,(E)-	20.26	20.68	2.12	2.14	1425	1409	1036	1017
67	Benzene,1-methoxy-4-methyl-	20.36	20.43	2.00	2.04	1415	1412	1009	1178
68	Hexanoic-acid,butyl-ester	20.38	20.19	2.96	3.09	1406	1413	1189	1081
69	Furan,3-(4-methyl-3-pentenyl)-	20.57	20.84	2.36	2.34	1431	1420	1099	1182
70	Octanoic-acid,ethyl-ester	20.88	20.76	2.89	2.99	1428	1432	1197	1209
71	n-Octanoic-acid-isopropyl-ester	20.88	20.53	3.13	3.24	1419	1433	1224	1038
72	2-Octenal,(E)-	20.96	20.89	2.11	2.15	1433	1436	1050	1111
73	1,3,8-p-Menthatriene	20.97	20.79	2.41	2.47	1429	1436	1119	960
74	1-Octen-3-ol	21.06	21.12	1.81	1.79	1442	1439	954	1068
75	trans-Linalool-oxide(furanoid)	21.16	21.59	2.16	2.14	1460	1443	1069	980
76	1-Heptanol	21.26	21.49	1.80	1.78	1456	1447	957	1137
77	2,6-Dimethyl-1,3,5,7-octatetraene,E,E-	21.27	21.59	2.46	2.40	1460	1448	1137	1240
78	Butanoic-acid,3-methyl-,hexyl-ester	21.28	21.20	3.18	3.35	1445	1448	1241	990
79	5-Hepten-2-ol,6-methyl-	21.36	21.69	1.86	1.79	1464	1451	984	1142
80	Limonene-oxide,cis-	21.47	21.54	2.46	2.43	1458	1455	1142	1077
81	Bicyclo[3.1.0]hexan-2-ol,2-methyl-5-(1-methylethyl)-,(1α,2α,5α)-	21.66	22.16	2.15	2.05	1482	1463	1081	839
82	Furfural	21.75	21.77	1.49	1.46	1467	1466	807	1238
83	Isopentyl-hexanoate	21.78	21.69	3.11	3.19	1464	1467	1249	1344
84	α-Cubebene	21.80	21.64	4.31	4.44	1462	1468	1355	999
85	2,4-Heptadienal,(E,E)-	21.86	22.44	1.85	1.83	1493	1470	992	1213
86	Acetic-acid,octyl-ester	21.87	22.37	2.75	2.63	1490	1471	1207	1123
87	α-Campholene-aldehyde	22.67	22.26	2.25	2.32	1486	1502	1128	1165
88	2-Decanone	22.67	22.44	2.49	2.60	1493	1502	1187	1370
89	.alfa.-Copaene	22.80	22.83	4.28	4.17	1509	1507	1390	1379
90	Bourbonene	22.90	23.34	4.22	4.05	1531	1512	1390	925
91	2,5-Hexanedione	22.95	22.97	1.58	1.58	1515	1514	888	970
92	Benzaldehyde	23.46	23.32	1.69	1.66	1530	1536	959	1104
93	Linalool	23.56	23.97	2.05	1.96	1558	1540	1106	1300
94	Propanoic-acid,octyl-ester	23.58	23.32	3.00	3.13	1530	1541	1299	1401
95	1H-Cycloprop[e]azulene,1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl-,[1aR-(1aα,4α,4aβ,7bα)]-	23.70	23.76	4.26	4.14	1549	1546	1422	1098

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
96	1-Octanol	23.86	23.71	1.98	1.87	1547	1553	1045	1227
97	Linalool,formate	23.97	24.46	2.58	2.61	1579	1558	1241	970
98	2-Furancarboxaldehyde,5-methyl-	24.16	24.25	1.61	1.58	1570	1566	934	1210
99	3-Cyclohexene-1-acetaldehyde,α,4-dimethyl-	24.37	24.60	2.39	2.37	1585	1575	1216	1293
100	Acetic-acid,nonyl-ester	24.48	24.43	2.80	2.95	1578	1580	1300	1416
101	Tricyclo[2.2.1.0(2,6)]heptane,1,7-dimethyl-7-(4-methyl-3-pentenyl)-,(-)-	24.59	24.22	3.94	4.08	1569	1585	1431	1168
102	Pinocarvone	24.67	24.48	2.20	2.15	1580	1588	1179	1288
103	Bornyl-acetate	24.78	24.94	2.80	2.72	1600	1593	1308	1434
104	Longifolene	24.79	24.83	3.94	3.87	1595	1594	1438	1389
105	β-Elemene	24.99	25.13	3.51	3.45	1608	1602	1406	1110
106	6-Methyl-3,5-heptadiene-2-one	25.06	24.99	1.89	1.90	1602	1605	1095	1275
107	2-Undecanone	25.07	24.92	2.61	2.72	1599	1605	1285	1188
108	Terpinen-4-ol	25.17	25.25	2.19	2.22	1613	1609	1190	1439
109	β-copaene	25.19	24.87	3.87	3.94	1597	1610	1447	1363
110	Hexanoic-acid,hexyl-ester	25.28	25.13	3.26	3.37	1608	1614	1386	1423
111	Aromandendrene	25.39	25.54	3.74	3.72	1625	1619	1443	1043
112	2-Acetyl-5-methylfuran	25.56	25.38	1.70	1.69	1618	1626	1018	1214
113	Pulegone	25.57	25.69	2.24	2.29	1631	1626	1215	1298
114	4-Terpinenyl-acetate	25.57	25.90	2.60	2.57	1640	1626	1300	1146
115	cis-p-Mentha-2,8-dien-1-ol	25.66	25.64	1.93	1.93	1629	1630	1126	1453
116	γ-Gurjunene	25.79	26.07	3.85	3.92	1647	1635	1469	1382
117	Decanoic-acid,ethyl-ester	25.88	25.98	3.07	3.19	1643	1639	1385	1216
118	Bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde,6,6-dimethyl-	26.07	26.00	2.16	2.07	1644	1647	1209	1243
119	2-Decenal,(E)-	26.27	25.98	2.28	2.37	1643	1655	1247	1459
120	2-Isopropenyl-4a,8-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene	26.29	26.29	3.78	3.80	1656	1656	1482	1304
121	Bicyclo[3.1.0]hexan-3-ol,4-methylene-1-(1-methylethyl)-,acetate	26.37	26.34	2.52	2.48	1658	1659	1309	1336
122	6-Octen-1-ol,3,7-dimethyl-,acetate	26.37	26.67	2.70	2.74	1672	1660	1343	1447
123	Octanoic-acid,3-methylbutylester	26.39	26.62	3.42	3.31	1670	1660	1447	1183
124	trans-Pinocarveol	26.46	26.53	1.98	1.88	1666	1663	1160	1441
125	cis-β-Farnesene	26.49	26.38	3.41	3.50	1660	1664	1451	1468

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
126	Alloaromadendrene	26.49	26.46	3.71	3.66	1663	1664	1484	1465
127	Spiro[5.5]undec-2-ene,3,7,7-trimethyl-11-methylene-,(-)-	26.59	27.01	3.65	3.57	1686	1669	1482	1466
128	β-Humulene	26.69	26.72	3.47	3.47	1674	1673	1465	1183
129	5,7-Octadien-2-ol,2,6-dimethyl-	26.76	27.06	1.97	1.91	1688	1676	1166	1212
130	Estragole	26.86	26.77	2.03	2.00	1676	1680	1189	1339
131	α-Terpinyl-acetate	26.87	26.98	2.63	2.65	1685	1680	1347	1405
132	Acetic-acid,decyl-ester	26.88	26.84	2.99	3.06	1679	1681	1410	1479
133	γ-Muurolene	26.99	27.15	3.64	3.52	1692	1685	1497	1317
134	Myrtenyl-acetate	27.17	27.37	2.44	2.43	1701	1693	1317	1486
135	Spiro[4.5]dec-7-ene,1,8-dimethyl-4-(1-methylethenyl)-,[1S-(1α,4β,5α)]-	27.19	27.08	3.52	3.55	1689	1693	1491	1210
136	α-Terpineol	27.26	27.27	2.02	1.93	1697	1697	1197	1482
137	α-Muurolene	27.29	27.70	3.52	3.51	1716	1698	1495	1359
138	α-Terpinyl-acetate	27.37	27.06	2.55	2.67	1688	1701	1349	1189
139	endo-Borneol	27.46	27.34	1.95	1.88	1700	1705	1179	1334
140	Dihydrocarvyl-acetate	27.47	27.32	2.49	2.55	1699	1706	1339	1484
141	α-Selinene	27.49	27.83	3.51	3.52	1722	1707	1502	1167
142	Bicyclo[3.1.0]hexan-3-ol,4-methylene-1-(1-methylethyl)-,(1α,3α,5α)-	27.56	27.79	1.83	1.78	1720	1710	1135	954
143	2-Furanmethanol,5-methyl-	27.75	27.98	1.46	1.46	1729	1719	915	1086
144	2(3H)-Furanone,5-ethyldihydro-	27.76	27.41	1.64	1.62	1703	1719	1044	1233
145	Bicyclo[3.1.1]hept-3-en-2-one,4,6,6-trimethyl-,(1S)-	27.96	27.85	2.06	1.92	1723	1728	1222	1497
146	β-Bisabolene	27.99	28.14	3.44	3.42	1736	1729	1513	1009
147	2(5H)-Furanone,3-methyl-	28.06	27.74	1.52	1.50	1718	1732	963	1258
148	2-Cyclohexen-1-one,3-methyl-6-(1-methylethyl)-	28.37	28.14	2.11	2.04	1736	1746	1263	1253
149	D-Carvone	28.46	28.49	2.05	1.96	1752	1751	1244	1370
150	2,6-Octadien-1-ol,3,7-dimethyl-,acetate,(Z)-	28.47	28.16	2.47	2.49	1737	1751	1369	1344
151	2-Undecenal	28.67	28.56	2.40	2.38	1755	1760	1359	1515
152	δ-Cadinene,(+)-	28.79	28.93	3.36	3.29	1772	1765	1534	1522
153	γ-Cadinene	28.89	29.02	3.30	3.19	1776	1770	1529	1474
154	Benzene,1-(1,5-dimethyl-4-hexenyl)-4-methyl-	29.08	29.33	2.93	2.91	1790	1779	1483	1222

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
155	Bicyclo[3.1.1]hept-2-ene-2-methanol,6,6-dimethyl-	29.36	29.35	1.85	1.77	1791	1791	1193	1222
156	m-Ethylacetophenone	29.46	29.73	1.84	1.73	1809	1796	1195	1280
157	Benzaldehyde,4-(1-methylethyl)-	29.46	29.42	1.96	1.88	1794	1796	1244	1507
158	Dodecanoic-acid,methyl-ester	29.48	29.59	3.04	3.14	1802	1797	1517	1274
159	Benzene,1,4-dimethoxy-2-methyl-	29.56	29.77	1.96	1.86	1811	1801	1247	1492
160	2-Tridecanone	29.78	29.71	2.86	2.91	1808	1811	1497	1558
161	Octanoic-acid,hexyl-ester	29.79	29.63	3.34	3.55	1804	1812	1572	1223
162	trans-Carveol	30.26	30.44	1.82	1.75	1845	1836	1212	1579
163	Dodecanoic-acid,ethyl-ester	30.39	30.42	3.26	3.37	1844	1842	1588	1543
164	(-)-Calamenene	30.48	30.28	3.02	3.06	1837	1847	1553	1214
165	Benzenemethanol,α,α,4-trimethyl-	30.56	30.42	1.76	1.69	1844	1851	1187	1268
166	3,5-Dimethoxytoluene	30.76	30.81	1.87	1.77	1864	1861	1246	1444
167	5,9-Undecadien-2-one,6,10-dimethyl-,(E)-	30.77	30.65	2.41	2.47	1856	1862	1437	1249
168	cis-Carveol	30.86	30.69	1.81	1.77	1858	1867	1223	1377
169	Butyl-benzoate	31.07	31.17	2.16	2.11	1882	1877	1374	1079
170	Benzyl-alcohol	31.16	31.07	1.50	1.42	1877	1882	1022	1476
171	Butylated-Hydroxytoluene	31.87	31.93	2.51	2.49	1919	1916	1503	1179
172	Phenylethyl	31.96	31.82	1.60	1.52	1914	1920	1126	1210
173	3,7-Octadiene-2,6-diol,2,6-dimethyl-	32.26	32.30	1.66	1.60	1936	1934	1182	1572
174	α-Calacorene	32.28	32.56	2.74	2.62	1948	1935	1573	1029
175	Heptanoic-acid	32.36	32.51	1.41	1.46	1946	1939	1076	1285
176	Benzaldehyde,4-methoxy-	33.26	33.25	1.75	1.66	1980	1981	1269	1081
177	Phenol,2-methyl-	33.66	33.57	1.44	1.40	1995	1999	1022	1315
178	p-Mentha-1,8-dien-7-ol	33.76	33.77	1.74	1.69	2005	2005	1278	1762
179	Octanoic-acid,octyl-ester	33.79	34.02	3.54	3.57	2020	2007	1768	1414
180	Methyleugenol	33.96	34.07	1.92	1.87	2023	2017	1405	1482
181	Naphthalene,1,4-dimethyl-	34.17	34.38	2.09	1.96	2041	2029	1458	1565
182	1,6,10-Dodecatrien-3-ol,3,7,11-trimethyl-	34.27	34.19	2.33	2.36	2030	2035	1545	1630
183	Caryophyllene-oxide	34.28	34.02	2.63	2.58	2020	2035	1627	1384
184	Benzene,4-ethenyl-1,2-dimethoxy-	34.36	34.36	1.85	1.78	2040	2040	1355	1772
185	Tetradecanoic-acid,ethyl-ester	34.49	34.14	3.40	3.66	2027	2048	1782	1082
186	Octanoic-acid	34.56	34.46	1.42	1.49	2046	2052	1157	1139
187	p-Cresol	35.26	35.27	1.46	1.39	2093	2093	1077	1597

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
188	Benzoic-acid,hexyl-ester	35.27	35.30	2.30	2.24	2095	2094	1575	1643
189	Cubenol	35.47	35.33	2.48	2.47	2097	2105	1636	1312
190	p-Cymen-7-ol	35.66	35.63	1.63	1.57	2113	2115	1267	1311
191	Nonanoic-acid	36.36	36.48	1.62	1.55	2159	2153	1272	1925
192	Cembrene	36.60	36.89	3.77	3.72	2181	2165	1934	1670
193	2.α-epi-Cadinol	37.27	37.07	2.32	2.20	2191	2201	1660	1639
194	Eudesmol	37.37	37.32	2.19	2.09	2203	2205	1618	1348
195	Thymol	37.56	37.55	1.59	1.51	2212	2211	1274	1565
196	Benzene,1,2,3-trimethoxy-5-(2-propenyl)-	37.87	37.60	1.94	1.86	2214	2222	1526	1389
197	1,2-Cyclohexanediol,1-methyl-4-(1-methylethenyl)-	38.56	39.00	1.63	1.51	2268	2247	1330	1462
198	n-Undecoic-acid	40.06	40.04	1.65	1.64	2371	2400	1481	1545
199	Dodecanoic-acid	43.57	42.83	1.72	1.59	2525	2537	1549	1685

Appendix 3 Reported compound profile and the ^{1}I and ^{2}I data in acacia honey [10] analysed by GC×GC-MS.

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
1	a-Pinene	9.07	9.51	2.79	3.81	1039	1027	947	885
2	Camphene	10.4	10.55	2.98	3.84	1068	1064	961	911
3	b-Pinene	11.73	12.23	3.25	3.92	1110	1101	986	947
4	3-Carene	14.13	14.18	3.3	3.99	1146	1145	1013	973
5	a-Phellandrene	14.4	15.32	3.32	3.60	1167	1150	1006	989
6	Myrcene	14.53	14.99	2.94	3.29	1161	1152	983	956
7	a-Terpinene	15.2	15.91	3.37	3.73	1178	1165	1019	1000
8	Limonene	16.67	17.00	3.26	3.75	1198	1192	1032	1004
9	b-Phellandrene	17.2	17.58	3.33	3.73	1209	1202	1037	1015
10	Terpinolene	21.33	21.36	3.51	3.84	1280	1279	1088	1067
11	1,2-Dihydrolinalool	36.67	36.00	2.09	2.26	1509	1523	1114	1085
12	Linalool	37.47	37.62	1.93	2.01	1543	1540	1088	1070
13	Linalol acetate	37.6	38.15	1.92	3.22	1554	1543	1243	1074
14	4-Terpinenol	40.4	40.40	2.34	2.33	1601	1601	1173	1174
15	Caryophyllene	44.67	39.76	4.48	6.56	1588	1666	1433	1347
16	a-Terpenol	45.73	44.32	2.06	2.12	1661	1683	1184	1172
17	Verbenone	46	47.91	2.45	1.96	1720	1687	1195	1282
18	Borneol	46.8	46.80	1.9	1.95	1699	1699	1178	1165
19	Carvone	47.6	48.60	2.47	2.09	1733	1714	1228	1294
20	a-Farnesene	48.53	49.12	3.8	4.80	1743	1732	1496	1433
21	b-Damascenone	52.13	53.32	2.81	2.59	1820	1800	1372	1402
22	Nerol	52.53	51.79	1.77	1.89	1794	1807	1221	1189
23	Geraniol	55.07	54.48	1.74	1.89	1839	1849	1253	1210
24	Nerolidol	63.33	63.33	2.37	2.61	2010	2010	1517	1476
25	2-Methyl-but-3-en-2-ol	10	9.23	1.29	1.32	1031	1053	599	573
26	Pentan-3-ol	12.93	12.34	1.43	1.41	1112	1123	677	685
27	Pentan-2-ol	13.47	13.80	1.42	1.41	1139	1133	687	696
28	Butan-1-ol	15.07	13.80	1.36	1.35	1139	1162	649	659
29	1-Penten-3-ol	15.47	14.78	1.35	1.35	1157	1170	663	661
30	3-Methylbutan-1-ol	18.4	17.42	1.39	1.43	1206	1224	725	710
31	2-Methylbutan-1-ol	18.4	17.37	1.4	1.41	1205	1224	716	714
32	Hexan-2-ol	18.67	19.12	1.55	1.52	1238	1229	782	794
33	3-Methylbut-3-en-1-ol	20.67	19.23	1.4	1.41	1240	1267	730	727

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
34	Pentan-1-ol	20.93	19.60	1.44	1.45	1247	1272	754	749
35	Heptan-3-ol	23.07	21.36	1.71	1.80	1280	1310	879	857
36	Heptan-2-ol	24.67	23.36	1.65	1.73	1315	1336	884	859
37	Hexan-1-ol	27.07	26.18	1.52	1.56	1360	1374	854	840
38	Octan-3-ol	29.2	28.13	1.82	2.00	1391	1407	988	948
39	Octan-2-ol	30.67	30.76	1.78	1.83	1430	1429	978	965
40	Oct-1-en-3-ol	32.4	30.07	1.67	1.81	1420	1454	966	928
41	Heptan-1-ol	33.2	32.00	1.64	1.69	1448	1465	953	937
42	2-Ethyl-hexan-1-ol	35.6	34.68	1.68	1.76	1487	1501	1003	977
43	Nonan-2-ol	36.67	36.48	1.9	2.08	1519	1523	1089	1051
44	2-Furanmethanol	44.67	42.36	1.33	1.29	1631	1666	835	872
45	Nonan-1-ol	45.2	43.93	1.82	2.01	1655	1675	1157	1113
46	Phenylmethanol	56.27	56.05	1.43	1.34	1865	1869	1013	1083
47	Decan-1-ol	50.8	49.70	1.89	2.17	1754	1775	1257	1199
48	1-Phenylethanol	52.67	53.32	1.52	1.41	1820	1809	1039	1108
49	2-Phenylethanol	58.27	58.27	1.54	1.41	1903	1903	1091	1171
50	Phenol	61.87	61.04	1.28	1.26	1992	2003	950	990
51	Butan-2-one	6.67	6.67	1.38	1.32	908	908	573	610
52	3-Methylbutanal	6.8	6.78	1.49	1.45	915	916	637	653
53	Pentan-2-one	7.87	7.87	1.59	1.49	984	984	665	702
54	Butane-2,3-dione	8.27	7.78	1.33	1.29	978	1004	560	593
55	2-Methyl-3-pentanone	8.67	8.23	1.79	1.72	1003	1015	733	746
56	Hexanal	11.33	11.12	1.95	1.77	1084	1090	773	809
57	Heptan-2-one	16.13	16.13	2.23	2.00	1182	1182	866	902
58	Heptanal	16.27	16.35	2.33	2.04	1186	1185	874	915
59	Hex-2-enal	18	17.95	2	1.77	1216	1217	840	886
60	Octan-2-one	21.73	21.73	2.56	2.26	1287	1287	960	998
61	Octanal	22	24.68	2.64	2.18	1336	1292	981	1035
62	6-Methylhept-5-en-2-one	24.93	28.13	2.32	1.91	1391	1340	968	1035
63	Nonan-2-one	28	28.13	2.77	2.68	1391	1389	1077	1087
64	Nonanal	28.27	32.82	2.83	2.29	1460	1393	1082	1144
65	Furfural	32.93	35.23	1.66	1.33	1495	1462	815	976
66	Decanal	34.53	36.43	3.01	2.71	1518	1485	1175	1206
67	Benzaldehyde	36.13	37.24	1.89	1.55	1535	1512	954	1057

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
68	5-Methylfurfural	39.2	38.81	1.77	1.48	1568	1576	939	1043
69	Benzeneacetaldehyde	43.07	42.95	1.89	1.58	1640	1642	1022	1120
70	Acetophenone	43.33	43.40	2.01	1.65	1647	1646	1052	1150
71	Methyl acetate	5.47	5.47	1.24	1.26	813	813	518	499
72	Ethyl acetate	6	6.37	1.38	1.35	886	856	595	607
73	Methyl butanoate	8.27	7.96	1.63	1.63	990	1004	711	711
74	Methyl 2-methylbutanoate	8.8	8.84	1.81	1.86	1020	1019	767	757
75	Methyl pentanoate	9.07	11.23	1.8	1.95	1087	1027	810	782
76	Butyl acetate	10.8	10.80	2.06	1.88	1075	1075	795	821
77	3-Methylbutyl acetate	13.2	12.83	2.2	2.20	1121	1128	860	860
78	Methyl hexanoate	16.13	15.86	2.4	2.33	1177	1182	910	917
79	Methyl octanoate	28	28.00	2.94	3.09	1389	1389	1114	1103
80	Methyl nonanoate	34.13	34.13	3.12	3.37	1479	1479	1208	1188
81	Methyl decanoate	40.13	40.14	3.24	3.83	1596	1596	1315	1270
82	Methyl undecanoate	45.87	46.47	3.38	4.00	1694	1685	1411	1364
83	Benzyl acetate	47.73	46.67	2.09	1.87	1697	1716	1154	1207
84	Methyl phenylacetate	49.33	49.33	2.07	1.75	1747	1747	1150	1233
85	Methyl salicylate	50	50.38	2.1	1.78	1767	1760	1175	1251
86	Methyl dodecanoate	51.47	51.32	3.44	4.53	1785	1788	1513	1436
87	Methyl tridecanoate	56.4	57.87	2.45	4.48	1895	1871	1610	1414
88	Methyl tetradecanoate	61.73	61.17	3.6	5.35	1996	2002	1713	1597
89	Butyrolactone	42.27	43.40	1.74	1.33	1647	1630	885	1085
90	c-Nonanolactone	62.67	63.74	2.11	1.73	2012	2007	1320	1429
91	2-Ethylhexanoic acid	59.33	60.11	1.37	1.38	1962	1937	1085	1079
92	Furan	4.93	4.93	1.18	1.24	786	786	492	400
93	Dimethyldisulfide	10.93	10.66	1.83	1.66	1071	1079	743	782
94	Propylbenzene	17.47	17.10	2.66	2.56	1200	1207	946	955
95	Styrene	20.13	20.35	2.11	1.85	1261	1257	881	925
96	p-Cymene	20.53	20.83	2.97	2.93	1270	1264	1021	1024
97	p,a-Dimethylstyrene	30.8	29.65	2.65	2.44	1414	1431	1066	1093
98	3-Furaldehyde	32.93	31.24	1.64	1.36	1437	1462	805	930
99	Camphor	34.93	36.29	2.94	2.57	1515	1491	1156	1198
100	2-Acetylfuran	35.2	35.37	1.76	1.44	1497	1495	889	1008
101	Biphenyl	60.67	60.67	2.45	2.02	1980	1980	1365	1451

Appendix 4 Reported compound profile and the ^{1}I and ^{2}I data in incense powder/smoke [11] analyzed by GC×GC-MS.

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
1	Benzaldehyde	14.90	3.89	14.90	4.43	962	962	1550	1547
2	Benzyl alcohol	17.50	9.24	17.50	11.63	1036	1036	1864	1865
3	2,6-Dimethyl-7-octen-2-ol	17.90	2.24	18.02	2.24	1064	1057	1473	1464
4	3,7-Dimethyl-3-octanol	18.70	1.94	18.70	1.77	1100	1100	1415	1418
5	3,7-Dimethyl-1,6-octadien-3-ol	26.80	2.53	25.04	2.51	1257	1295	1541	1877
6	Benzoic acid,methyl ester	19.00	3.12	18.59	3.61	1094	1108	1654	1635
7	Phenylethyl alcohol	19.80	6.92	19.29	8.40	1116	1130	1895	1900
8	Acetic acid,phenylmethyl ester	21.00	3.28	21.59	3.99	1178	1162	1762	1734
9	3,7-Dimethyl-1-octanol	21.70	2.52	21.33	2.74	1171	1181	1680	1659
10	Menth-1-en-8-ol	22.00	2.66	22.00	2.85	1189	1189	1705	1697
11	Acetic acid,2-phenylethyl ester	23.60	3.06	25.08	3.36	1258	1226	1822	1819
12	4-Methoxy-benzaldehyde	24.00	5.09	24.76	6.22	1251	1235	2014	2011
13	10-Undecanal	24.80	1.83	26.47	1.97	1288	1252	1682	1601
14	Benzenemethanol,a,a-dimethyl-, acetate	25.30	2.28	27.06	2.25	1302	1263	1755	1758
15	p-tert-Butylcyclohexyl acetate cis	26.60	1.8	28.30	1.67	1360	1291	1675	1654
16	5-Methyl-2-(1-methylethenyl)-4-hexen-1-ol, acetate	26.70	1.95	26.51	1.48	1289	1293	1609	1721
17	2H-1-Benzopyran-2-one	29.30	7.25	29.30	11.48	1441	1441	2457	2399
18	Butylated hydroxytoluene	30.00	2.03	29.74	1.86	1513	1528	1871	1894
19	2-Hydroxy-benzoic acid pentyl ester	31.10	2.38	33.43	2.73	1650	1594	2095	2046
20	a-(Trichloromethyl)-benzenemethanol acetate	31.40	3.15	30.21	3.67	1541	1604	2222	2207
21	Diethyl phthalate	38.30	3.97	38.30	5.01	2103	2103	2378	2718
22	Cedrol	33.20	2.26	31.17	2.22	1598	1645	2110	2119
23	Benzophenone	33.60	4.31	32.76	4.89	1635	1654	2443	2463
24	a-Cadinol	34.00	2.53	32.41	2.61	1627	1663	2224	2230
25	n-Hexyl salicylate	34.30	2.44	34.91	2.25	1683	1669	2171	2225
26	Patchouli alcohol	34.70	2.26	33.88	2.19	1660	1678	2177	2198
27	2-(Phenylmethylene)-octanal	36.40	5.54	36.49	2.38	1755	1749	2309	2739
28	Benzyl benzoate	36.60	4.05	36.60	4.52	1762	1762	2593	2619
29	2-Hydroxy-benzoic acid phenylmethyl ester	32.80	4.18	33.43	5.34	1650	1636	2796	2405

Appendix 5 Reported compound identification in perfume [46] analyzed by GC×GC.

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
1	2-Methyl-2-buten-1-ol	10.40	10.40	4.92	4.59	760	760	1320	1320
2	1-Hexanol	12.95	12.95	4.53	4.45	854	854	1348	1355
3	3-Methyl-2-butenyl acetate	14.60	14.90	3.54	3.25	902	902	1225	1182
4	Benzaldehyde	15.84	15.99	5.34	5.37	933	933	1520	1520
5	α-Pinene	16.00	15.99	2.73	2.76	933	933	1033	1028
6	β-Myrcene	17.60	17.74	3.04	3.02	983	983	1169	1161
7	β-Pinene	17.62	17.39	2.90	2.90	973	973	1128	1112
8	cis-3-Hexenyl acetate	17.84	17.84	3.51	3.58	986	986	1317	1315
9	1-Methyl-4-methoxybenzene	18.45	18.45	4.46	4.17	1003	1003	1461	1434
10	Benzenemethanol	18.62	18.81	10.28	10.17	1012	1012	1864	1870
11	Limonene	19.41	19.26	3.14	3.04	1023	1023	1216	1200
12	Eucalyptol	19.49	19.22	3.15	3.09	1022	1022	1227	1213
13	α-Methylbenzyl alcohol	19.80	19.82	8.41	8.01	1037	1037	1801	1801
14	trans-β-Ocimene	19.94	19.86	3.09	3.17	1038	1038	1251	1250
15	Dipropylene glycol	19.54	20.59	10.29	7.10	1056	1056	1892	1767
16	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	20.60	20.34	3.09	15.37	1050	1050	1259	2073
17	2,6-Dimethyl-7-octen-2-ol	20.74	20.83	3.92	3.98	1062	1062	1473	1455
18	Methyl benzoate	21.40	21.23	5.44	5.04	1072	1072	1654	1612
19	trans-Linalool oxide	21.31	21.31	4.00	3.90	1074	1074	1461	1452
20	Linalool	21.90	21.79	4.28	4.42	1086	1086	1541	1547
21	3,5-Dimethylanisole	22.20	22.56	4.14	4.21	1105	1105	1533	1533
22	trans-Rose oxide	22.40	23.23	3.45	3.34	1121	1121	1383	1367
23	Phenylethyl Alcohol	22.10	21.87	8.82	8.94	1088	1088	1895	1906
24	Fenchol	22.80	22.56	4.57	4.53	1105	1105	1580	1582
25	1,2-Dihydrolinalool	23.20	23.23	4.00	3.99	1121	1121	1520	1512
26	β-Phenethyl formate	23.60	24.40	6.42	5.81	1149	1149	1771	1771
27	β-Terpineol	23.80	23.90	4.75	4.63	1137	1137	1627	1627
28	Benzyl ethanoate	23.97	23.98	5.65	5.40	1139	1139	1762	1720
29	cis-p-Menthan-3-one	24.35	24.35	3.75	3.77	1148	1148	1528	1496
30	Ethyl benzoate	24.51	24.44	5.01	4.76	1150	1150	1698	1658
31	2,6-Dimethyl-3,7-octadiene-2,6-diol	25.00	25.89	7.45	8.35	1185	1185	1945	1995
32	1-Methyl-4-(1-methylethyl) cyclohexanol	25.01	24.69	4.60	4.49	1156	1156	1650	1627
33	Isomenthol	25.20	25.93	4.56	4.53	1186	1186	1667	1664
34	α-Methylbenzyl acetate	25.20	25.10	5.00	4.85	1166	1166	1687	1687
35	Methyl salicylate	25.60	25.44	5.83	5.46	1174	1174	1795	1765

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
36	Dihydrocitronellol	25.70	25.77	4.40	4.57	1182	1182	1680	1666
37	α-Terpineol	25.64	25.48	4.90	4.85	1175	1175	1705	1697
38	γ-Terpineol	26.00	25.60	4.78	4.77	1178	1178	1684	1690
39	Citronellol	26.93	26.93	4.89	5.10	1211	1211	1761	1765
40	cis-Geraniol	27.01	27.01	5.25	5.35	1213	1213	1815	1797
41	Isogeraniol	27.29	27.92	5.20	5.34	1237	1237	1812	1820
42	β-Phenethyl acetate	27.60	27.58	5.50	5.36	1228	1228	1822	1813
43	trans-Geraniol	27.96	27.92	5.32	5.59	1237	1237	1854	1847
44	Linalyl acetate	28.07	28.07	3.62	3.65	1241	1241	1563	1555
45	α-Citral	28.30	28.37	4.63	4.56	1249	1249	1732	1732
46	Hydroxycitronellal	28.80	29.02	6.02	6.11	1266	1266	1929	1929
47	Anethole	29.20	28.94	4.93	5.07	1264	1264	1817	1817
48	Benzyl 2-methylpropanoate	29.40	29.28	4.76	4.75	1273	1273	1784	1784
49	Methyl anthranilate	31.00	31.33	8.95	9.53	1326	1326	2194	2232
50	Dihydro-5-pentyl-2(3H)-furanone	31.40	31.25	6.44	6.42	1324	1324	2024	2024
51	Citronellol acetate	31.56	31.69	3.66	3.72	1335	1335	1668	1660
52	Eugenol	31.80	31.69	7.47	8.20	1335	1335	2168	2169
53	Geranyl acetate	32.71	32.71	3.92	4.01	1361	1361	1764	1752
54	1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	33.00	34.05	4.15	4.22	1395	1395	1830	1830
55	3-Methyl-2-(cis-2-penten-1-yl)-2-cyclopenten-1-one	33.20	32.99	5.29	5.30	1368	1368	1964	1961
56	3-Phenyl-2-propenyl acetate	34.79	34.84	6.23	6.55	1418	1418	2176	2150
57	Nopyl acetate	34.80	34.67	4.00	3.88	1413	1413	1777	1777
58	5-Hexyldihydro-2(3H)-furanone	35.40	35.16	6.19	6.31	1428	1428	2119	2138
59	β-Chamigrene	36.00	36.71	3.57	3.48	1475	1475	1737	1725
60	Pentyl benzoate	36.28	36.08	4.67	4.65	1456	1456	1987	1963
61	α-Selinene	36.80	37.23	3.53	3.44	1491	1491	1751	1725
62	β-Ionone	36.90	37.23	4.47	4.49	1491	1491	1971	1971
63	α-Cetone	37.00	37.00	4.07	4.03	1484	1484	1877	1875
64	1-(2,6,6-Trimethylcyclohex-2-en-1-yl)-1-pentene-3-one	38.20	37.64	4.14	4.22	1503	1503	1933	1933
65	Isoamyl salicylate	38.70	38.12	4.70	4.70	1515	1515	2033	2033
66	β-Methyl ionone	38.90	39.80	4.17	4.17	1557	1557	1988	1988
67	α-(Trichloromethyl)benzyl acetate	39.30	39.04	5.23	5.65	1538	1538	2197	2197

No.	Name	$^{1}t_{R,lit}$	$^{1}t_{R,sim}$	$^{2}t_{R,lit}$	$^{2}t_{R,sim}$	$^{1}I_{lit}$	$^{1}I_{fitting}$	$^{2}I_{lit}$	$^{2}I_{fitting}$
68	3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	39.60	39.56	4.24	4.44	1551	1551	2020	2033
69	Diethyl Phthalate	39.90	40.08	6.46	6.95	1564	1564	2378	2366
70	Methyl (2-pentyl-3-oxocyclopentyl) acetate	42.20	43.80	5.19	4.98	1649	1649	2264	2264
71	cis-3-Hexenyl salicylate	43.23	43.57	5.08	5.13	1644	1644	2280	2280
72	1-Acetonaphthone	41.20	41.20	7.95	7.71	1592	1592	2471	2471
73	Benzyl salicylate	49.84	49.84	9.65	7.33	1836	1836	2784	2784

Appendix 6 Reported least square after leave one out of compound in saffron [8] analyzed by GC×GC-MS with p_1-p_5 parameters and a constant (Mean and SD of least square after leaving out are 30.4121 and 1.7308, respectively).

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
1	Hexanal	30.4118	-0.0053	-0.0818	-0.2698	7.9016	-4.8458	1.1957
2	Ethylbenzene	30.4121	-0.0053	-0.0851	-0.2698	7.9016	-4.8448	1.1746
3	2-Propenoic acid, butyl ester	30.4121	-0.0053	-0.0825	-0.2698	7.9016	-4.8468	1.1857
4	Heptanal	30.4063	-0.0053	-0.0826	-0.2698	7.9016	-4.8474	1.1326
5	Benzene, tert-butyl-	30.1461	-0.0053	-0.0834	-0.2698	7.9016	-4.8469	1.1989
6	Decane, 2,3,7-trimethyl-	17.7755	-0.0053	-0.0848	-0.2698	7.9016	-4.8474	1.1658
7	Butanoic acid, butyl ester	20.8218	-0.0053	-0.0844	-0.2698	7.9016	-4.8491	1.1385
8	2-Hexenal, (E)-	29.8928	-0.0053	-0.0813	-0.2698	7.9016	-4.8462	1.1229
9	Benzene, 1-ethyl-4-methyl-	29.7663	-0.0052	-0.0812	-0.2698	7.9016	-4.8459	1.1385
10	Furan, 2-pentyl-	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8459	1.1999
11	2-Heptanone, 6-methyl-	30.4119	-0.0053	-0.0812	-0.2698	7.9016	-4.8450	1.1990
12	5-Dodecene, (Z)-	30.3866	-0.0053	-0.0842	-0.2698	7.9016	-4.8447	1.1979
13	Pyridine, 2,6-dimethyl-	30.4120	-0.0053	-0.0814	-0.2698	7.9016	-4.8442	1.1200
14	Mesitylene	30.4099	-0.0053	-0.0813	-0.2698	7.9016	-4.8456	1.1854
15	1,3,6-Octatriene, 3,7-dimethyl-, (Z)-	30.4065	-0.0053	-0.0812	-0.2698	7.9016	-4.8453	1.2001
16	Styrene	30.3989	-0.0052	-0.0847	-0.2698	7.9016	-4.8463	1.1900
17	Pyrazine, methyl-	30.4121	-0.0053	-0.0839	-0.2698	7.9016	-4.8458	1.1900
18	Benzene, 1-ethyl-2-methyl-	30.4119	-0.0053	-0.0825	-0.2698	7.9016	-4.8458	1.1987
19	Cyclohexene, 4-methyl-3-(1-methylethylidene)-	30.4118	-0.0053	-0.0845	-0.2698	7.9016	-4.8457	1.1228
20	Cyclohexane, hexyl-	30.4117	-0.0053	-0.0846	-0.2698	7.9016	-4.8433	1.2381
21	Octanal	30.4121	-0.0053	-0.0848	-0.2698	7.9016	-4.8439	1.1896
22	Cyclohexanone	30.4121	-0.0053	-0.0844	-0.2698	7.9016	-4.8389	1.1443
23	Pyridine, 3-methyl-	30.2182	-0.0052	-0.0813	-0.2698	7.9016	-4.8460	1.1221
24	Benzene, 1-methyl-2-propyl-	30.4119	-0.0053	-0.0812	-0.2698	7.9016	-4.8466	1.1256
25	Benzene, 1,4-diethyl-	30.4120	-0.0053	-0.0812	-0.2698	7.9016	-4.8469	1.1398
26	Benzene, butyl-	30.4076	-0.0053	-0.0812	-0.2698	7.9016	-4.8474	1.1357
27	Benzene, 2-ethyl-1,4-dimethyl-	30.4116	-0.0053	-0.0842	-0.2698	7.9016	-4.8491	1.1998
28	Pyrazine, 2,6-dimethyl-	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8462	1.1669
29	2-Heptenal, (Z)-	30.4121	-0.0053	-0.0842	-0.2698	7.9016	-4.8459	1.1167
30	Benzene, (1-methylbutyl)-	30.4115	-0.0053	-0.0814	-0.2698	7.9016	-4.8459	1.1200
31	5-Hepten-2-one, 6-methyl-	30.3335	-0.0053	-0.0813	-0.2698	7.9016	-4.8450	1.1395
32	Benzene, 1-methyl-2-propyl-	30.4089	-0.0052	-0.0812	-0.2698	7.9016	-4.8447	1.1967

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
33	Benzene, (1,1-dimethylpropyl)-	30.3932	-0.0053	-0.0847	-0.2698	7.9016	-4.8442	1.2150
34	Benzene, 1,2,3-trimethyl-	30.4121	-0.0053	-0.0839	-0.2698	7.9016	-4.8456	1.1701
35	Benzene, 2-ethyl-1,4-dimethyl-	30.4117	-0.0053	-0.0825	-0.2698	7.9016	-4.8453	1.1977
36	Pyridine, 2,4,6-trimethyl-	30.2865	-0.0053	-0.0818	-0.2698	7.9016	-4.8463	1.2002
37	1,3,8-p-Menthatriene	30.4094	-0.0053	-0.0851	-0.2698	7.9016	-4.8458	1.1228
38	Indane	30.4080	-0.0053	-0.0825	-0.2698	7.9016	-4.8458	1.1658
39	Benzene, 1,3-diethyl-5-methyl-	30.4104	-0.0053	-0.0826	-0.2698	7.9016	-4.8457	1.1385
40	Nonanal	30.4121	-0.0053	-0.0834	-0.2698	7.9016	-4.8468	1.1229
41	Pyrazine, trimethyl-	30.4120	-0.0053	-0.0848	-0.2698	7.9016	-4.8474	1.1385
42	3-Octen-2-one	30.3959	-0.0053	-0.0844	-0.2698	7.9016	-4.8469	1.1999
43	3-Cyclohexen-1-one, 3,5,5-trimethyl-	30.4121	-0.0053	-0.0813	-0.2698	7.9016	-4.8474	1.1990
44	Benzene, 1,2,3,4-tetramethyl-	30.3950	-0.0053	-0.0812	-0.2698	7.9016	-4.8491	1.1979
45	1-Octen-3-ol	29.3877	-0.0053	-0.0812	-0.2698	7.9016	-4.8462	1.1357
46	Benzene, 1,2,3,5-tetramethyl-	30.4121	-0.0052	-0.0812	-0.2698	7.9016	-4.8459	1.1998
47	2,4-Heptadienal, (E,E)-	30.4120	-0.0053	-0.0842	-0.2698	7.9016	-4.8459	1.1669
48	Ethanone, 1-(1,4-dimethyl-3-cyclohexen-1-yl)-	30.4120	-0.0053	-0.0814	-0.2698	7.9016	-4.8450	1.1167
49	Benzaldehyde	30.4121	-0.0053	-0.0813	-0.2698	7.9016	-4.8447	1.1200
50	1,6-Octadien-3-ol, 3,7-dimethyl-	30.3746	-0.0053	-0.0842	-0.2698	7.9016	-4.8442	1.1395
51	Tricyclo[2.2.1.0(2,6)]heptane, 1,7-dimethyl-7-(4-methyl-3-pentenyl)-, (-)-	30.4110	-0.0053	-0.0812	-0.2698	7.9016	-4.8456	1.1967
52	Megastigma-4,6(Z),8(E)-triene	30.4121	-0.0053	-0.0842	-0.2698	7.9016	-4.8453	1.2150
53	Longifolene	30.4070	-0.0052	-0.0814	-0.2698	7.9016	-4.8450	1.1701
54	Bicyclo[3.1.1]hept-2-ene, 2,6-dimethyl-6-(4-methyl-3-pentenyl)-	30.4117	-0.0053	-0.0813	-0.2698	7.9016	-4.8447	1.1443
55	γ-Elemene	30.4114	-0.0053	-0.0812	-0.2698	7.9016	-4.8442	1.1221
56	Isophorone	30.4120	-0.0053	-0.0847	-0.2698	7.9016	-4.8456	1.1256
57	1-Cyclohexene-1-carboxaldehyde, 2,6,6-trimethyl-	30.4114	-0.0052	-0.0839	-0.2698	7.9016	-4.8453	1.1398

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
58	Benzaldehyde, 4-methyl-	30.4120	-0.0053	-0.0825	-0.2698	7.9016	-4.8463	1.1326
59	Naphthalene, 1,2,3,4-tetrahydro-1,8-dimethyl-	30.4121	-0.0053	-0.0818	-0.2698	7.9016	-4.8458	1.1989
60	γ-Elemene	30.4095	-0.0053	-0.0851	-0.2698	7.9016	-4.8458	1.1658
61	1,3-Cyclohexadiene-1-carboxaldehyde, 2,6,6-trimethyl-	30.4121	-0.0053	-0.0825	-0.2698	7.9016	-4.8457	1.1385
62	2-Hydroxy-3,5,5-trimethyl-cyclohex-2-enone	30.4117	-0.0053	-0.0826	-0.2698	7.9016	-4.8468	1.1229
63	2-Octenal, 2-butyl-	30.4080	-0.0053	-0.0834	-0.2698	7.9016	-4.8474	1.1385
64	Benzaldehyde, 2,5-dimethyl-	30.4121	-0.0053	-0.0848	-0.2698	7.9016	-4.8469	1.1999
65	Heptadecane	30.3860	-0.0053	-0.0844	-0.2698	7.9016	-4.8474	1.1990
66	2,6,6-Trimethyl-2-cyclohexene-1,4-dione	30.4121	-0.0053	-0.0813	-0.2698	7.9016	-4.8491	1.1979
67	2(5H)-Furanone	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8462	1.1200
68	2-Cyclopenten-1-one, 4-hydroxy-3-methyl-2-(2-propenyl)-	30.4097	-0.0053	-0.0812	-0.2698	7.9016	-4.8462	1.1854
69	Naphthalene	30.4121	-0.0052	-0.0812	-0.2698	7.9016	-4.8459	1.2001
70	2-Cyclohexen-1-one, 2-hydroxy-3-methyl-6-(1-methylethyl)-	30.4119	-0.0053	-0.0842	-0.2698	7.9016	-4.8459	1.1900
71	1,4-Cyclohexanedione, 2,2,6-trimethyl-	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8450	1.1900
72	Acetic acid, 2-phenylethyl ester	30.4116	-0.0053	-0.0842	-0.2698	7.9016	-4.8447	1.1987
73	2-Butanone, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	30.4121	-0.0053	-0.0814	-0.2698	7.9016	-4.8442	1.1228
74	Benzene, (1-butylheptyl)-	30.4099	-0.0053	-0.0813	-0.2698	7.9016	-4.8456	1.2381
75	5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8453	1.1896
76	α-Ionone	30.4121	-0.0052	-0.0847	-0.2698	7.9016	-4.8450	1.1443
77	2,3-Dihydro-5-hydroxy-6-methyl-4(H)-pyran-4-one	30.4121	-0.0053	-0.0839	-0.2698	7.9016	-4.8447	1.1221
78	Benzyl alcohol	30.4121	-0.0053	-0.0825	-0.2698	7.9016	-4.8442	1.1256
79	Phenylethyl Alcohol	30.4121	-0.0053	-0.0818	-0.2698	7.9016	-4.8456	1.1398
80	3-Buten-2-ol, 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-	30.4121	-0.0053	-0.0851	-0.2698	7.9016	-4.8453	1.1357

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
81	trans-β-Ionone	30.4121	-0.0053	-0.0825	-0.2698	7.9016	-4.8463	1.1987
82	4-(2,6,6-Trimethyl-cyclohexen-1-yl)-butan-2-ol	30.4120	-0.0053	-0.0826	-0.2698	7.9016	-4.8466	1.1228
83	Naphthalene, 2-ethyl-	30.4117	-0.0052	-0.0834	-0.2698	7.9016	-4.8469	1.2381
84	Naphthalene, 1,6-dimethyl-	30.4119	-0.0053	-0.0848	-0.2698	7.9016	-4.8474	1.1896
85	1-Hydroxymethyl-7,7-dimethylbicyclo[2.2.1]heptan-2-one	30.4120	-0.0053	-0.0844	-0.2698	7.9016	-4.8491	1.1443
86	3-Buten-2-one, 4-(2,2,6-trimethyl-7-oxabicyclo[4.1.0]hept-1-yl)-	30.4121	-0.0053	-0.0813	-0.2698	7.9016	-4.8462	1.1221
87	Naphthalene, 1,4-dimethyl-	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8459	1.1256
88	2,5-Dimethyl-4-hydroxy-3(2H	30.4121	-0.0053	-0.0844	-0.2698	7.9016	-4.8459	1.1398
89	Cyclohexanemethanol, 4-ethenyl-α,α,4-trimethyl-3-(1-methylethenyl)-, [1R-(1α,3α,4β)]-	30.4121	-0.0053	-0.0813	-0.2698	7.9016	-4.8450	1.1357
90	5-Methyl-2-phenyl-2-hexenal	30.4121	-0.0053	-0.0812	-0.2698	7.9016	-4.8447	1.1998
91	Hexadecanoic acid, ethyl ester	25.2875	-0.0053	-0.0812	-0.2698	7.9016	-4.8442	1.1669

Appendix 7 Reported least square after leave one out of compound in *Boswellia papyrifera* [9] analyzed by GC×GC-MS with p_1-p_5 parameters and a constant (Mean and SD of least square after leaving out are 4.5590 and 0.1456, respectively).

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
1	Octane	4.3928	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1718
2	Nonane	4.2695	-0.0053	-0.0844	-0.2698	7.9016	-4.8084	1.1837
3	Cyclohexane,propyl-	4.3879	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1818
4	Cyclopentene,1-(2-methylpropyl)-	4.4057	-0.0053	-0.0845	-0.2698	7.9016	-4.8083	1.1738
5	Decane	4.2477	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1698
6	Tricyclo[2.2.1.0(2,6)]heptane,1,7,7-trimethyl-	4.4096	-0.0053	-0.0844	-0.2698	7.9016	-4.8082	1.1718
7	α-Pinene	4.3245	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1708
8	Cyclohexene,3-(1-methylethyl)-	4.3692	-0.0053	-0.0849	-0.2698	7.9016	-4.8087	1.1718
9	α-Fenchene	4.3140	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1764
10	Camphene	4.2749	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1718
11	Hexanal	4.4203	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1724
12	Undecane	4.3152	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1720
13	(-)-α-thujene	4.4173	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
14	Sabinene	4.3392	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1728
15	2H-Pyran,2-ethenyltetrahydro-2,6,6-trimethyl-	4.4215	-0.0052	-0.0846	-0.2698	7.9016	-4.8083	1.1724
16	(-)-β-Pinene	4.4172	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
17	1-Butanol,3-methyl-,acetate	4.4193	-0.0052	-0.0847	-0.2698	7.9016	-4.8083	1.1718
18	Thuja-2,4(10)-diene	4.4193	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1718
19	(+)-4-Carene	4.3627	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1712
20	3-Penten-2-one,4-methyl-	4.4217	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1713
21	2-n-Butyl-furan	4.4208	-0.0053	-0.0853	-0.2698	7.9016	-4.8083	1.1717
22	p-Xylene	4.4201	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1729
23	3-Carene	4.3960	-0.0053	-0.085	-0.2698	7.9016	-4.8083	1.1737
24	Cyclohexene,1-(2-methylpropyl)-	4.4211	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1708
25	Benzene,1,3-dimethyl-	4.4140	-0.0053	-0.0848	-0.2698	7.9016	-4.8083	1.1730
26	(+)-2-Carene	4.3602	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.2001

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
27	3-Heptanone	4.4213	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1200
28	2-Butenal,2-ethyl-	4.4215	-0.0053	-0.0845	-0.2698	7.9016	-4.8083	1.1737
29	β-Myrcene	4.4189	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1718
30	α-Phellandrene	4.4216	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1708
31	Acetic-acid,pentyl-ester	4.4138	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1718
32	Benzene,(1-methylethyl)-	4.4161	-0.0053	-0.0849	-0.2698	7.9016	-4.8084	1.1764
33	7-Oxabicyclo[2.2.1] heptane,1-methyl-4-(1-methylethyl)-	4.4217	-0.0053	-0.0847	-0.2698	7.9016	-4.8087	1.1718
34	2-Heptanone	4.4208	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1724
35	1,3-Cyclohexadiene,1-methyl-4-(1-methylethyl)-	4.4196	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1720
36	Heptanal	4.4210	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1718
37	Cyclopentanone,2-methyl-	4.4125	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1728
38	D-Limonene	4.3668	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1724
39	Eucalyptol	4.3722	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
40	2-Hexenal	4.4213	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
41	Furan,2-pentyl-	4.4201	-0.0052	-0.0847	-0.2698	7.9016	-4.8083	1.1718
42	1,3,6-Octatriene,3,7-dimethyl-,(Z)-	4.4104	-0.0053	-0.0852	-0.2698	7.9016	-4.8084	1.1712
43	2-Heptanone,6-methyl-	4.3995	-0.0052	-0.0853	-0.2698	7.9016	-4.8083	1.1718
44	5-Dodecene,(E)-	4.4127	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1728
45	γ-Terpinene	4.3986	-0.0053	-0.085	-0.2698	7.9016	-4.8083	1.1724
46	1,3,7-Octatriene,3,7-dimethyl-	4.4050	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
47	3-Octanone	4.4195	-0.0053	-0.0848	-0.2698	7.9016	-4.8083	1.1718
48	Acetic-acid,hexyl-ester	4.3989	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1718
49	m-Cymene	4.3946	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1712
50	p-Cymene	4.4172	-0.0053	-0.0845	-0.2698	7.9016	-4.8083	1.1713
51	Octanal	4.4213	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1717
52	Cyclohexene,1-methyl-4-(1-methylethylidene)-	4.4217	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1729
53	Tridecane	4.4193	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1737
54	2-Heptenal,(Z)-	4.4208	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1708

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
55	5-Hepten-2-one,6-methyl-	4.4211	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1730
56	1-Hexanol	2.4250	-0.0053	-0.0860	-0.2698	7.9016	-4.8564	1.2055
57	2-Cyclopenten-1-one	4.4204	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1200
58	Benzene,4-ethyl-1,2-dimethyl-	4.4214	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1737
59	Acetic-acid,heptyl-ester	4.4043	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
60	2-Cyclopenten-1-one,2-methyl-	4.4216	-0.0053	-0.0849	-0.2698	7.9016	-4.8084	1.1708
61	2-Nonanone	4.4193	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
62	Octanoic-acid,methyl-ester	4.4192	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1764
63	2,4,6-Octatriene,2,6-dimethyl-	4.4159	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
64	Thujone	4.4030	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1724
65	Tetradecane	4.3928	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1720
66	2-Octenal,(E)-	4.4216	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1718
67	Benzene,1-methoxy-4-methyl-	4.4199	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1698
68	Hexanoic-acid,butyl-ester	4.4050	-0.0053	-0.0846	-0.2698	7.9016	-4.8087	1.1718
69	Furan,3-(4-methyl-3-pentenyl)-	4.4216	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1708
70	Octanoic-acid,ethyl-ester	4.4109	-0.0053	-0.0844	-0.2698	7.9016	-4.8082	1.1718
71	n-Octanoic-acid-isopropyl-ester	4.4097	-0.0053	-0.0851	-0.2698	7.9016	-4.8084	1.1764
72	2-Octenal,(E)-	4.4199	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1718
73	1,3,8-p-Menthatriene	4.4182	-0.0053	-0.0853	-0.2698	7.9016	-4.8083	1.1724
74	1-Octen-3-ol	4.4216	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1720
75	trans-Linalool-oxide(furanoid)	4.4212	-0.0053	-0.085	-0.2698	7.9016	-4.8083	1.1718
76	1-Heptanol	4.4214	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1728
77	2,6-Dimethyl-1,3,5,7-octatetraene,E,E-	4.4185	-0.0052	-0.0849	-0.2698	7.9016	-4.8083	1.1724
78	Butanoic-acid,3-methyl-,hexyl-ester	4.3938	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
79	5-Hepten-2-ol,6-methyl-	4.4173	-0.0052	-0.0845	-0.2698	7.9016	-4.8083	1.1718
80	Limonene-oxide,cis-	4.4213	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1718
81	Bicyclo[3.1.0]hexan-2-ol,2-methyl-5-(1-methylethyl)-,(1α,2α,5α)-	4.4116	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1712
82	Furfural	4.4212	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1724
83	Isopentyl-hexanoate	4.4155	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1720
84	α-Cubebene	4.4030	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
85	2,4-Heptadienal,(E,E)-	4.4213	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1728
86	Acetic-acid,octyl-ester	4.4087	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1724
87	α-Campholene-aldehyde	4.4164	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
88	2-Decanone	4.4091	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
89	.alfa.-Copaene	4.4082	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1718
90	Bourbonene	4.3943	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1712
91	2,5-Hexanedione	4.4217	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1713
92	Benzaldehyde	4.4210	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1717
93	Linalool	4.4137	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1729
94	Propanoic-acid,octyl-ester	4.4070	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1737
95	1H-Cycloprop[e]azulene,1a,2,3,4,4a,5,6,7b-octahydro-1,1,4,7-tetramethyl-,[1aR-(1aα,4α,4aβ,7bα)]-	4.4079	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1708
96	1-Octanol	4.4093	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1730
97	Linalool,formate	4.4207	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1698
98	2-Furancarboxaldehyde,5-methyl-	4.4207	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
99	3-Cyclohexene-1-acetaldehyde,α,4-dimethyl-	4.4214	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1708
100	Acetic-acid,nonyl-ester	4.3994	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
101	Tricyclo[2.2.1.0(2,6)]heptane,1,7-dimethyl-7-(4-methyl-3-pentenyl)-,(-)-	4.4009	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1764
102	Pinocarvone	4.4195	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1718
103	Bornyl-acetate	4.4156	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1724
104	Longifolene	4.4177	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1720
105	β-Elemene	4.4176	-0.0053	-0.0853	-0.2698	7.9016	-4.8084	1.1718
106	6-Methyl-3,5-heptadiene-2-one	4.4215	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1728
107	2-Undecanone	4.4100	-0.0053	-0.085	-0.2698	7.9016	-4.8083	1.1724
108	Terpinen-4-ol	4.4209	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
109	β-copaene	4.4156	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1718
110	Hexanoic-acid,hexyl-ester	4.4105	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
111	Aromandendrene	4.4211	-0.0053	-0.0845	-0.2698	7.9016	-4.8082	1.1712
112	2-Acetyl-5-methylfuran	4.4217	-0.0053	-0.0852	-0.2698	7.9016	-4.8084	1.1713
113	Pulegone	4.4190	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1717
114	4-Terpinenyl-acetate	4.4208	-0.0052	-0.0847	-0.2698	7.9016	-4.8083	1.1729
115	cis-p-Mentha-2,8-dien-1-ol	4.4217	-0.0053	-0.0849	-0.2698	7.9016	-4.8082	1.1737
116	γ-Gurjunene	4.4171	-0.0052	-0.0847	-0.2698	7.9016	-4.8084	1.1708
117	Decanoic-acid,ethyl-ester	4.4076	-0.0053	-0.0847	-0.2698	7.9016	-4.8087	1.1730
118	Bicyclo[3.1.1]hept-2-ene-2-carboxaldehyde,6,6-dimethyl-	4.4129	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.2001
119	2-Decenal,(E)-	4.4129	-0.0053	-0.0846	-0.2698	7.9016	-4.8082	1.1200
120	2-Isopropenyl-4a,8-dimethyl-1,2,3,4,4a,5,6,7-octahydronaphthalene	4.4213	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1737
121	Bicyclo[3.1.0]hexan-3-ol,4-methylene-1-(1-methylethyl)-,acetate	4.4201	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1718
122	6-Octen-1-ol,3,7-dimethyl-,acetate	4.4203	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1708

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
123	Octanoic-acid,3-methylbutylester	4.4102	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
124	trans-Pinocarveol	4.4136	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1764
125	cis-β-Farnesene	4.4136	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1717
126	Alloaromadendrene	4.4183	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1729
127	Spiro[5.5]undec-2-ene,3,7,7-trimethyl-11-methylene-,(-)-	4.4153	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1737
128	β-Humulene	4.4217	-0.0053	-0.0845	-0.2698	7.9016	-4.8083	1.1708
129	5,7-Octadien-2-ol,2,6-dimethyl-	4.4184	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1730
130	Estragole	4.4211	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.2001
131	α-Terpinyl-acetate	4.4213	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1200
132	Acetic-acid,decyl-ester	4.4161	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1737
133	γ-Muurolene	4.4070	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
134	Myrtenyl-acetate	4.4216	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1708
135	Spiro[4.5]dec-7-ene,1,8-dimethyl-4-(1-methylethenyl)-,[1S-(1α,4β,5α)]-	4.4204	-0.0052	-0.0847	-0.2698	7.9016	-4.8084	1.1718
136	α-Terpineol	4.4145	-0.0053	-0.0846	-0.2698	7.9016	-4.8087	1.1764
137	α-Muurolene	4.4217	-0.0052	-0.0846	-0.2698	7.9016	-4.8084	1.1718
138	α-Terpinyl-acetate	4.4090	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1724
139	endo-Borneol	4.4163	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1720
140	Dihydrocarvyl-acetate	4.4185	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
141	α-Selinene	4.4217	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1698
142	Bicyclo[3.1.0]hexan-3-ol,4-methylene-1-(1-methylethyl)-,(1α,3α,5α)-	4.4188	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1718
143	2-Furanmethanol,5-methyl-	4.4217	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1708
144	2(3H)-Furanone,5-ethyldihydro-	4.4213	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1718
145	Bicyclo[3.1.1]hept-3-en-2-one,4,6,6-trimethyl-,(1S)-	4.4023	-0.0053	-0.0853	-0.2698	7.9016	-4.8083	1.1718
146	β-Bisabolene	4.4214	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1708

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
147	2(5H)-Furanone,3-methyl-	4.4213	-0.0052	-0.085	-0.2698	7.9016	-4.8083	1.1718
148	2-Cyclohexen-1-one,3-methyl-6-(1-methylethyl)-	4.4176	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1764
149	D-Carvone	4.4149	-0.0052	-0.0848	-0.2698	7.9016	-4.8084	1.1718
150	2,6-Octadien-1-ol,3,7-dimethyl-,acetate,(Z)-	4.4214	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1724
151	2-Undecenal	4.4211	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1720
152	δ-Cadinene,(+)-	4.4168	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
153	γ-Cadinene	4.4105	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1728
154	Benzene,1-(1,5-dimethyl-4-hexenyl)-4-methyl-	4.4213	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1724
155	Bicyclo[3.1.1]hept-2-ene-2-methanol,6,6-dimethyl-	4.4160	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1723
156	m-Ethylacetophenone	4.4100	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
157	Benzaldehyde,4-(1-methylethyl)-	4.4149	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
158	Dodecanoic-acid,methyl-ester	4.4126	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1712
159	Benzene,1,4-dimethoxy-2-methyl-	4.4124	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1713
160	2-Tridecanone	4.4191	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1717
161	Octanoic-acid,hexyl-ester	4.3745	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1729
162	trans-Carveol	4.4167	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1737
163	Dodecanoic-acid,ethyl-ester	4.4100	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1708
164	(-)-Calamenene	4.4201	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1730
165	Benzenemethanol,α,α,4-trimethyl-	4.4167	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1764
166	3,5-Dimethoxytoluene	4.4116	-0.0053	-0.0853	-0.2698	7.9016	-4.8083	1.1718
167	5,9-Undecadien-2-one,6,10-dimethyl-,(E)-	4.4180	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1724
168	cis-Carveol	4.4199	-0.0053	-0.085	-0.2698	7.9016	-4.8083	1.1720
169	Butyl-benzoate	4.4184	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
170	Benzyl-alcohol	4.4156	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1728
171	Butylated-Hydroxytoluene	4.4216	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1724
172	Phenylethyl	4.4155	-0.0053	-0.0845	-0.2698	7.9016	-4.8083	1.1723
173	3,7-Octadiene-2,6-diol,2,6-dimethyl-	4.4181	-0.0052	-0.0852	-0.2698	7.9016	-4.8083	1.1718
174	α-Calacorene	4.4093	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1718
175	Heptanoic-acid	4.4197	-0.0052	-0.0847	-0.2698	7.9016	-4.8083	1.1712
176	Benzaldehyde,4-methoxy-	4.4135	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1713
177	Phenol,2-methyl-	4.4202	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1717
178	p-Mentha-1,8-dien-7-ol	4.4195	-0.0053	-0.0847	-0.2698	7.9016	-4.8084	1.1729
179	Octanoic-acid,octyl-ester	4.4207	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1737
180	Methyleugenol	4.4201	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1708
181	Naphthalene,1,4-dimethyl-	4.4035	-0.0053	-0.0847	-0.2698	7.9016	-4.8082	1.1730
182	1,6,10-Dodecatrien-3-ol,3,7,11-trimethyl-	4.4210	-0.0053	-0.0852	-0.2698	7.9016	-4.8084	1.2001
183	Caryophyllene-oxide	4.4195	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1200
184	Benzene,4-ethenyl-1,2-dimethoxy-	4.4179	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1737
185	Tetradecanoic-acid,ethyl-ester	4.3575	-0.0053	-0.0849	-0.2698	7.9016	-4.8083	1.1718
186	Octanoic-acid	4.4164	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1708
187	p-Cresol	4.4167	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1720
188	Benzoic-acid,hexyl-ester	4.4181	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1718
189	Cubenol	4.4217	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1698
190	p-Cymen-7-ol	4.4179	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
191	Nonanoic-acid	4.4166	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1708
192	Cembrene	4.4191	-0.0053	-0.0846	-0.2698	7.9016	-4.8083	1.1718
193	2.α-epi-Cadinol	4.4072	-0.0053	-0.0846	-0.2698	7.9016	-4.8084	1.1718
194	Eudesmol	4.4105	-0.0053	-0.0847	-0.2698	7.9016	-4.8083	1.1708
195	Thymol	4.4161	-0.0053	-0.0844	-0.2698	7.9016	-4.8083	1.1718
196	Benzene,1,2,3-trimethoxy-5-(2-propenyl)-	4.4157	-0.0053	-0.0851	-0.2698	7.9016	-4.8083	1.1764

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
197	1,2-Cyclohexanediol,1-methyl-4-(1-methylethenyl)-	4.4087	-0.0053	-0.0852	-0.2698	7.9016	-4.8082	1.1718
198	n-Undecoic-acid	4.4216	-0.0053	-0.0853	-0.2698	7.9016	-4.8084	1.1724
199	Dodecanoic-acid	4.4067	-0.0053	-0.0852	-0.2698	7.9016	-4.8083	1.1720

Appendix 8 Reported least square after leave one out of compound in acacia honey [10] analyzed by GC×GC-MS with p_1-p_5 parameters and a constant (Mean and SD of least square after leaving out are 32.2350 and 0.4853, respectively).

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
1	a-Pinene	31.91	-0.0047	-0.0829	-0.9984	7.9616	-6.4388	1.1398
2	Camphene	32.02	-0.0047	-0.0839	-0.9984	7.9616	-6.4350	1.1253
3	b-Pinene	32.14	-0.0048	-0.0829	-0.9984	7.9616	-6.4250	1.1296
4	3-Carene	32.04	-0.0048	-0.0819	-0.9984	7.9616	-6.4240	1.1285
5	a-Phellandrene	32.39	-0.0049	-0.0829	-0.9984	7.9616	-6.4244	1.1280
6	Myrcene	32.31	-0.0049	-0.0828	-0.9984	7.9616	-6.4234	1.1390
7	a-Terpinene	32.30	-0.0048	-0.0818	-0.9984	7.9616	-6.4224	1.1390
8	Limonene	32.14	-0.0046	-0.0754	-0.9984	7.9616	-6.4164	0.9917
9	b-Phellandrene	32.21	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1153
10	Terpinolene	32.18	-0.0043	-0.0869	-0.9984	7.9616	-6.6881	1.1576
11	1,2-Dihydrolinalool	32.28	-0.0048	-0.0755	-0.9984	7.9616	-6.4275	1.1133
12	Linalool	32.39	-0.0047	-0.0896	-0.9984	7.9616	-6.4285	1.1145
13	Linalol acetate	31.04	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1264
14	4-Terpinenol	32.44	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
15	Caryophyllene	29.82	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
16	a-Terpenol	32.38	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
17	Verbenone	32.17	-0.0048	-0.0796	-0.9984	7.9616	-6.3702	1.1163
18	Borneol	32.40	-0.0046	-0.0811	-0.9984	7.9616	-6.4345	1.0006
19	Carvone	32.29	-0.0047	-0.0829	-0.9984	7.9616	-6.4345	1.0053
20	a-Farnesene	31.03	-0.0047	-0.0755	-0.9984	7.9616	-6.4406	1.0442
21	b-Damascenone	32.55	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1390
22	Nerol	32.34	-0.0048	-0.0838	-0.9984	7.9616	-6.4102	0.9917
23	Geraniol	32.30	-0.0049	-0.0840	-0.9984	7.9616	-6.4410	1.1153
24	Nerolidol	32.07	-0.0049	-0.0755	-0.9984	7.9616	-6.4184	1.1576
25	2-Methyl-but-3-en-2-ol	32.55	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1133
26	Pentan-3-ol	32.52	-0.0046	-0.0829	-0.9984	7.9616	-6.4184	1.1145
27	Pentan-2-ol	32.53	-0.0048	-0.0839	-0.9984	7.9616	-6.4184	1.1264
28	Butan-1-ol	32.53	-0.0043	-0.0829	-0.9984	7.9616	-6.4184	1.1264
29	1-Penten-3-ol	32.55	-0.0048	-0.0819	-0.9984	7.9616	-6.4184	1.1285
30	3-Methylbutan-1-ol	32.52	-0.0047	-0.0829	-0.9984	7.9616	-6.4184	1.1280
31	2-Methylbutan-1-ol	32.55	-0.0048	-0.0828	-0.9984	7.9616	-6.4184	1.1390
32	Hexan-2-ol	32.53	-0.0048	-0.0818	-0.9984	7.9616	-6.4184	1.1390
33	3-Methylbut-3-en-1-ol	32.54	-0.0048	-0.0754	-0.9984	7.9616	-6.4184	0.9917
34	Pentan-1-ol	32.54	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1153
35	Heptan-3-ol	32.46	-0.0047	-0.0831	-0.9984	7.9616	-6.4449	1.1377

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
36	Heptan-2-ol	32.45	-0.0046	-0.0755	-0.9984	7.9616	-6.4184	1.1133
37	Hexan-1-ol	32.49	-0.0047	-0.0896	-0.9984	7.9616	-6.4184	1.1145
38	Octan-3-ol	32.32	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
39	Octan-2-ol	32.45	-0.0047	-0.0896	-0.9984	7.9616	-6.4184	1.1264
40	Oct-1-en-3-ol	32.36	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
41	Heptan-1-ol	32.46	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
42	2-Ethyl-hexan-1-ol	32.42	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1163
43	Nonan-2-ol	32.29	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.0006
44	2-Furanmethanol	32.54	-0.0048	-0.0796	-0.9984	7.9616	-6.4184	1.0053
45	Nonan-1-ol	32.26	-0.0046	-0.0811	-0.9984	7.9616	-6.4184	1.0442
46	Phenylmethanol	32.50	-0.0048	-0.0829	-0.9984	7.9616	-6.4184	1.1133
47	Decan-1-ol	32.14	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1145
48	1-Phenylethanol	32.49	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1264
49	2-Phenylethanol	32.47	-0.0048	-0.0838	-0.9984	7.9616	-6.4184	1.1264
50	Phenol	32.55	-0.0048	-0.0840	-0.9984	7.9616	-6.4184	1.1285
51	Butan-2-one	32.47	-0.0046	-0.0755	-0.9984	7.9616	-6.4184	1.1280
52	3-Methylbutanal	32.46	-0.0047	-0.0755	-0.9984	7.9616	-6.4184	1.1390
53	Pentan-2-one	32.40	-0.0047	-0.0829	-0.9984	7.9616	-6.4184	1.1390
54	Butane-2,3-dione	32.50	-0.0048	-0.0839	-0.9984	7.9616	-6.4184	0.9927
55	2-Methyl-3-pentanone	32.39	-0.0048	-0.0829	-0.9984	7.9616	-6.4184	1.1153
56	Hexanal	32.31	-0.0048	-0.0819	-0.9984	7.9616	-6.4184	1.1576
57	Heptan-2-one	32.30	-0.0047	-0.0824	-0.9984	7.9616	-6.4288	1.1353
58	Heptanal	32.23	-0.0048	-0.0896	-0.9984	7.9616	-6.4244	1.1264
59	Hex-2-enal	32.32	-0.0047	-0.0755	-0.9984	7.9616	-6.4234	1.1264
60	Octan-2-one	32.28	-0.0048	-0.0755	-0.9984	7.9616	-6.4224	1.1398
61	Octanal	32.14	-0.0048	-0.0755	-0.9984	7.9616	-6.4164	1.1253
62	6-Methylhept-5-en-2-one	32.19	-0.0048	-0.0839	-0.9984	7.9616	-6.4345	1.1296
63	Nonan-2-one	32.55	-0.0049	-0.0829	-0.9984	7.9616	-6.6881	1.1285
64	Nonanal	32.10	-0.0049	-0.0819	-0.9984	7.9616	-6.4275	1.1280
65	Furfural	32.25	-0.0048	-0.0829	-0.9984	7.9616	-6.4285	1.1390
66	Decanal	32.41	-0.0046	-0.0828	-0.9984	7.9616	-6.4345	1.1390
67	Benzaldehyde	32.26	-0.0048	-0.0818	-0.9984	7.9616	-6.4184	0.9917
68	5-Methylfurfural	32.31	-0.0043	-0.0754	-0.9984	7.9616	-6.4184	1.1153
69	Benzeneacetaldehyde	32.29	-0.0048	-0.0811	-0.9984	7.9616	-6.4184	1.1576
70	Acetophenone	32.25	-0.0047	-0.0829	-0.9984	7.9616	-6.3702	1.1133
71	Methyl acetate	32.55	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1145
72	Ethyl acetate	32.49	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1264
73	Methyl butanoate	32.47	-0.0048	-0.0838	-0.9984	7.9616	-6.4406	1.1264

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
74	Methyl 2-methylbutanoate	32.50	-0.0048	-0.0840	-0.9984	7.9616	-6.4285	1.1576
75	Methyl pentanoate	32.49	-0.0048	-0.0755	-0.9984	7.9616	-6.4345	1.1133
76	Butyl acetate	32.29	-0.0043	-0.0755	-0.9984	7.9616	-6.4184	1.1145
77	3-Methylbutyl acetate	32.47	-0.0048	-0.0829	-0.9984	7.9616	-6.4184	1.1264
78	Methyl hexanoate	32.43	-0.0047	-0.0839	-0.9984	7.9616	-6.4184	1.1264
79	Methyl octanoate	32.29	-0.0048	-0.0829	-0.9984	7.9616	-6.3702	1.1264
80	Methyl nonanoate	32.11	-0.0046	-0.0819	-0.9984	7.9616	-6.4345	1.1264
81	Methyl decanoate	31.66	-0.0048	-0.0829	-0.9984	7.9616	-6.4345	1.1163
82	Methyl undecanoate	31.56	-0.0043	-0.0828	-0.9984	7.9616	-6.4406	1.0006
83	Benzyl acetate	32.42	-0.0048	-0.0818	-0.9984	7.9616	-6.4345	1.0053
84	Methyl phenylacetate	32.31	-0.0047	-0.0754	-0.9984	7.9616	-6.4102	1.0442
85	Methyl salicylate	32.32	-0.0048	-0.0755	-0.9984	7.9616	-6.4410	1.1153
86	Methyl dodecanoate	30.96	-0.0048	-0.0869	-0.9984	7.9616	-6.4184	1.1372
87	Methyl tridecanoate	29.97	-0.0047	-0.0929	-0.9984	7.9616	-6.4188	1.1373
88	Methyl tetradecanoate	30.25	-0.0047	-0.0876	-0.9984	7.9616	-6.4388	1.1372
89	Butyrolactone	32.18	-0.0046	-0.0839	-0.9984	7.9616	-6.4184	1.1253
90	c-Nonanolactone	32.27	-0.0048	-0.0829	-0.9984	7.9616	-6.4184	1.1296
91	2-Ethylhexanoic acid	32.51	-0.0043	-0.0819	-0.9984	7.9616	-6.4184	1.1285
92	Furan	32.51	-0.0048	-0.0829	-0.9984	7.9616	-6.3702	1.1280
93	Dimethyldisulfide	32.33	-0.0047	-0.0828	-0.9984	7.9616	-6.4345	1.1390
94	Propylbenzene	32.42	-0.0048	-0.0818	-0.9984	7.9616	-6.4345	1.1390
95	Styrene	32.30	-0.0048	-0.0754	-0.9984	7.9616	-6.4406	0.9917
96	p-Cymene	32.54	-0.0048	-0.0811	-0.9984	7.9616	-6.4285	1.1153
97	p,a-Dimethylstyrene	32.43	-0.0048	-0.0829	-0.9984	7.9616	-6.4345	1.1576
98	3-Furaldehyde	32.30	-0.0048	-0.0755	-0.9984	7.9616	-6.4184	1.1133
99	Camphor	32.32	-0.0046	-0.0755	-0.9984	7.9616	-6.4184	1.1145
100	2-Acetylfuran	32.27	-0.0047	-0.0838	-0.9984	7.9616	-6.4184	1.1264
101	Biphenyl	32.26	-0.0047	-0.0840	-0.9984	7.9616	-6.3702	1.1264

Appendix 9 Reported least square after leave one out of compound in incense powder/smoke [11] analyzed by GC×GC-MS with p_1-p_5 parameters and a constant (Mean and SD of least square after leaving out are 4.4122×10^{-15} and 5.2784×10^{-16}, respectively).

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
1	Benzaldehyde	4.53E-15	-0.0048	-0.0860	-0.2851	-8.1570	-7.5961	1.2540
2	Benzyl alcohol	4.23E-15	-0.0048	-0.1045	-0.2951	-8.1570	-7.4178	1.1726
3	2,6-Dimethyl-7-octen-2-ol	4.59E-15	-0.0048	-0.1046	-0.2951	-8.1570	-7.4051	1.2083
4	3,7-Dimethyl-3-octanol	4.59E-15	-0.0048	-0.1056	-0.2951	-8.1570	-7.4021	1.1954
5	3,7-Dimethyl-1,6-octadien-3-ol	4.54E-15	-0.0048	-0.1051	-0.2951	-8.1570	-7.3936	1.2104
6	Benzoic acid,methyl ester	4.54E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4136	1.2101
7	Phenylethyl alcohol	4.57E-15	-0.0048	-0.1044	-0.2951	-8.1570	-7.4146	1.2222
8	Acetic acid,phenylmethyl ester	4.57E-15	-0.0048	-0.1045	-0.2951	-8.1570	-7.4136	1.2252
9	3,7-Dimethyl-1-octanol	4.59E-15	-0.0048	-0.1045	-0.2951	-8.1570	-7.4156	1.2260
10	Menth-1-en-8-ol	4.59E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4166	1.2291
11	Acetic acid,2-phenylethyl ester	4.55E-15	-0.0048	-0.1053	-0.2951	-8.1570	-7.4166	1.2321
12	4-Methoxy-benzaldehyde	4.56E-15	-0.0048	-0.1037	-0.2951	-8.1570	-7.4266	1.2291
13	10-Undecanal	4.59E-15	-0.0048	-0.1052	-0.2951	-8.1570	-7.4066	1.2222
14	Benzenemethanol,a,a-dimethyl-, acetate	4.46E-15	-0.0048	-0.1056	-0.2951	-8.1570	-7.3966	1.2291
15	p-tert-Butylcyclohexyl acetate cis	4.57E-15	-0.0048	-0.1052	-0.2951	-8.1570	-7.4066	1.2104
16	5-Methyl-2-(1-methylethenyl)-4-hexen-1-ol, acetate	4.46E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4366	1.2252
17	2H-1-Benzopyran-2-one	4.58E-15	-0.0048	-0.1044	-0.2951	-8.1570	-7.4266	1.2222
18	Butylated hydroxytoluene	4.59E-15	-0.0048	-0.1046	-0.2951	-8.1570	-7.4266	1.2291
19	2-Hydroxy-benzoic acid pentyl ester	4.57E-15	-0.0048	-0.1046	-0.2951	-8.1570	-7.4066	1.2260
20	a-(Trichloromethyl)-benzenemethanol acetate	4.28E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4266	1.2291
21	Diethyl phthalate	1.85E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4136	1.2252
22	Cedrol	4.53E-15	-0.0048	-0.1044	-0.2951	-8.1570	-7.4146	1.2260
23	Benzophenone	4.59E-15	-0.0048	-0.1045	-0.2951	-8.1570	-7.4136	1.2291
24	a-Cadinol	4.58E-15	-0.0048	-0.1045	-0.2951	-8.1570	-7.4156	1.2321
25	n-Hexyl salicylate	4.59E-15	-0.0048	-0.1049	-0.2951	-8.1570	-7.4166	1.2291

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
26	Patchouli alcohol	4.59E-15	-0.0048	-0.1053	-0.2951	-8.1570	-7.4166	1.2222
27	2-(Phenylmethylene)-octanal	3.49E-15	-0.0048	-0.1037	-0.2951	-8.1570	-7.4266	1.2291
28	Benzyl benzoate	4.59E-15	-0.0048	-0.1052	-0.2951	-8.1570	-7.4066	1.2104
29	2-Hydroxy-benzoic acid phenylmethyl ester	4.59E-15	-0.0048	-0.1056	-0.2951	-8.1570	-7.4066	1.2252

Appendix 10 Reported least square after leave one out of compound in perfume [46] analyzed by GC×GC-MS with p_1-p_5 parameters and a constant (Mean and SD of least square after leaving out are 14.5607 and 0.3275, respectively).

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
1	2-Methyl-2-buten-1-ol	14.4666	-0.0038	-0.6266	-26.4775	5.5559	-3.8917	2.1445
2	1-Hexanol	14.7181	-0.0038	-0.6260	-26.4775	5.5559	-3.8872	2.1455
3	3-Methyl-2-butenyl acetate	14.5083	-0.0038	-0.6271	-26.4775	5.5559	-3.9102	2.1435
4	Benzaldehyde	14.6955	-0.0038	-0.6281	-26.4775	5.5559	-3.9001	2.1468
5	α-Pinene	14.6924	-0.0038	-0.6276	-26.4775	5.5559	-3.8817	2.1451
6	β-Myrcene	14.7475	-0.0038	-0.6252	-26.4775	5.5559	-3.8742	2.1463
7	β-Pinene	14.7260	-0.0038	-0.6240	-26.4775	5.5559	-3.8900	2.1424
8	cis-3-Hexenyl acetate	14.6606	-0.0038	-0.6245	-26.4775	5.5559	-3.8900	2.1421
9	1-Methyl-4-methoxybenzene	14.5075	-0.0038	-0.6271	-26.4775	5.5559	-3.8713	2.1436
10	Benzenemethanol	14.6870	-0.0038	-0.6260	-26.4775	5.5559	-3.9087	2.1448
11	Limonene	14.7007	-0.0038	-0.6261	-26.4775	5.5559	-3.9238	2.1447
12	Eucalyptol	14.7350	-0.0038	-0.6250	-26.4775	5.5559	-3.9122	2.1401
13	α-Methylbenzyl alcohol	14.3994	-0.0038	-0.6271	-26.4775	5.5559	-3.9012	2.1437
14	trans-β-Ocimene	14.6452	-0.0038	-0.6306	-26.4775	5.5559	-3.9132	2.1441
15	Bis(1-methyl-2-hydroxyethyl)ether	13.9636	-0.0038	-0.6302	-26.4775	5.5559	-3.8217	2.1439
16	1,4-Cyclohexadiene, 1-methyl-4-(1-methylethyl)-	14.7120	-0.0038	-0.6266	-26.4775	5.5559	-3.9017	2.1440
17	2,6-Dimethyl-7-octen-2-ol	14.6666	-0.0038	-0.6266	-26.4775	5.5559	-3.8844	2.1438
18	Methyl benzoate	14.3953	-0.0038	-0.6273	-26.4775	5.5559	-3.8800	2.1450
19	trans-Linalool oxide	14.6996	-0.0038	-0.6280	-26.4775	5.5559	-3.8882	2.1450
20	Linalool	14.5839	-0.0038	-0.6293	-26.4775	5.5559	-3.8900	2.1451
21	3,5-Dimethylanisole	14.6583	-0.0038	-0.6279	-26.4775	5.5559	-3.8900	2.1414
22	trans-Rose oxide	14.6860	-0.0038	-0.6271	-26.4775	5.5559	-3.9102	2.1435
23	Phenylethyl Alcohol	14.6015	-0.0038	-0.6281	-26.4775	5.5559	-3.9001	2.1468
24	Fenchol	14.7610	-0.0038	-0.6276	-26.4775	5.5559	-3.8817	2.1451
25	1,2-Dihydrolinalool	14.7388	-0.0038	-0.6252	-26.4775	5.5559	-3.8742	2.1463
26	β-Phenethyl formate	14.1860	-0.0038	-0.6240	-26.4775	5.5559	-3.8900	2.1424
27	β-Terpineol	14.6751	-0.0038	-0.6245	-26.4775	5.5559	-3.8900	2.1421
28	Benzyl ethanoate	14.5442	-0.0038	-0.6271	-26.4775	5.5559	-3.8713	2.1436
29	cis-p-Menthan-3-one	14.7077	-0.0038	-0.6260	-26.4775	5.5559	-3.9087	2.1448

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
30	Ethyl benzoate	14.5494	-0.0038	-0.6261	-26.4775	5.5559	-3.9238	2.1447
31	2,6-Dimethyl-3,7-octadiene-2,6-diol	13.8227	-0.0038	-0.6250	-26.4775	5.5559	-3.8742	2.1401
32	1-Methyl-4-(1-methylethyl) cyclohexanol	14.6849	-0.0038	-0.6271	-26.4775	5.5559	-3.8900	2.1437
33	Isomenthol	14.7573	-0.0038	-0.6306	-26.4775	5.5559	-3.8900	2.1445
34	α-Methylbenzyl acetate	14.6467	-0.0038	-0.6302	-26.4775	5.5559	-3.8713	2.1455
35	Methyl salicylate	14.4289	-0.0038	-0.6250	-26.4775	5.5559	-3.9087	2.1435
36	Dihydrocitronellol	14.5542	-0.0038	-0.6271	-26.4775	5.5559	-3.9238	2.1468
37	α-Terpineol	14.7451	-0.0038	-0.6306	-26.4775	5.5559	-3.9122	2.1451
38	γ-Terpineol	14.7338	-0.0038	-0.6302	-26.4775	5.5559	-3.9012	2.1463
39	Citronellol	14.5174	-0.0038	-0.6266	-26.4775	5.5559	-3.9132	2.1424
40	cis-Geraniol	14.6254	-0.0038	-0.6266	-26.4775	5.5559	-3.8217	2.1463
41	Isogeraniol	14.5877	-0.0038	-0.6273	-26.4775	5.5559	-3.9238	2.1424
42	β-Phenethyl acetate	14.6547	-0.0038	-0.6280	-26.4775	5.5559	-3.9122	2.1421
43	trans-Geraniol	14.4519	-0.0038	-0.6293	-26.4775	5.5559	-3.9012	2.1436
44	Linalyl acetate	14.6938	-0.0038	-0.6279	-26.4775	5.5559	-3.9132	2.1448
45	α-Citral	14.7273	-0.0038	-0.6271	-26.4775	5.5559	-3.8217	2.1447
46	Hydroxycitronellal	14.6368	-0.0038	-0.6281	-26.4775	5.5559	-3.9017	2.1401
47	Anethole	14.5855	-0.0038	-0.6271	-26.4775	5.5559	-3.8844	2.1437
48	Benzyl 2-methylpropanoate	14.7377	-0.0038	-0.6281	-26.4775	5.5559	-3.8800	2.1441
49	Methyl anthranilate	14.1478	-0.0038	-0.6276	-26.4775	5.5559	-3.8882	2.1439
50	Dihydro-5-pentyl-2(3H)-furanone	14.7498	-0.0038	-0.6252	-26.4775	5.5559	-3.8900	2.1440
51	Citronellol acetate	14.6659	-0.0038	-0.6240	-26.4775	5.5559	-3.8742	2.1438
52	Eugenol	13.9985	-0.0038	-0.6245	-26.4775	5.5559	-3.8900	2.1439
53	Geranyl acetate	14.6311	-0.0038	-0.6271	-26.4775	5.5559	-3.8900	2.1440
54	1-(2,6,6-Trimethyl-1-cyclohexen-1-yl)-2-buten-1-one	14.6521	-0.0038	-0.6260	-26.4775	5.5559	-3.8713	2.1438
55	3-Methyl-2-(cis-2-penten-1-yl)-2-cyclopenten-1-one	14.7175	-0.0038	-0.6261	-26.4775	5.5559	-3.9087	2.1450
56	3-Phenyl-2-propenyl acetate	14.4025	-0.0038	-0.6250	-26.4775	5.5559	-3.9238	2.1450
57	Nopyl acetate	14.6802	-0.0038	-0.6271	-26.4775	5.5559	-3.9122	2.1451

No.	Name	least square after leaving out	p_1	p_2	p_3	p_4	p_5	constant
58	5-Hexyldihydro-2(3H)-furanone	14.6081	-0.0038	-0.6306	-26.4775	5.5559	-3.9012	2.1414
59	β-Chamigrene	14.7061	-0.0038	-0.6302	-26.4775	5.5559	-3.9132	2.1435
60	Pentyl benzoate	14.7451	-0.0038	-0.6250	-26.4775	5.5559	-3.8217	2.1468
61	α-Selinene	14.7019	-0.0038	-0.6271	-26.4775	5.5559	-3.9017	2.1451
62	β-Ionone	14.7034	-0.0038	-0.6250	-26.4775	5.5559	-3.9102	2.1463
63	α-Cetone	14.7599	-0.0038	-0.6271	-26.4775	5.5559	-3.9001	2.1424
64	1-(2,6,6-Trimethylcyclohex-2-en-1-yl)-1-pentene-3-one	14.6427	-0.0038	-0.6306	-26.4775	5.5559	-3.8817	2.1421
65	Isoamyl salicylate	14.7277	-0.0038	-0.6302	-26.4775	5.5559	-3.8742	2.1455
66	β-Methyl ionone	14.7227	-0.0038	-0.6250	-26.4775	5.5559	-3.8900	2.1435
67	α-(Trichloromethyl)benzyl acetate	14.3017	-0.0038	-0.6271	-26.4775	5.5559	-3.8900	2.1468
68	3,7,11-Trimethyl-1,6,10-dodecatrien-3-ol	14.5242	-0.0038	-0.6306	-26.4775	5.5559	-3.8713	2.1451
69	Diethyl Phthalate	14.2376	-0.0038	-0.6302	-26.4775	5.5559	-3.9087	2.1463
70	Methyl (2-pentyl-3-oxocyclopentyl) acetate	14.5844	-0.0038	-0.6266	-26.4775	5.5559	-3.9238	2.1424
71	cis-3-Hexenyl salicylate	14.6762	-0.0038	-0.6266	-26.4775	5.5559	-3.8742	2.1421
72	1-Acetonaphthone	14.5562	-0.0038	-0.6273	-26.4775	5.5559	-3.8900	2.1436
73	Benzyl Benzoate	14.7221	-0.0038	-0.6280	-26.4775	5.5559	-3.8900	2.1448
74	Benzyl salicylate	12.3134	-0.0038	-0.6265	-26.4775	5.5559	-3.8916	2.1382

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