# DETERMINATION OF VOLATILE COMPOUNDS IN YELLOW CURRY PASTE USING FROM-TWO-TO-ONE DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY

Miss Natsuda Singtothog



A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science in Chemistry
Department of Chemistry
FACULTY OF SCIENCE
Chulalongkorn University
Academic Year 2021

# การตรวจวัดสารระเหยง่ายในพริกแกงเหลืองโดยใช้แก๊สโครมาโทกราฟี-แมสสเปกโทรเมตรีจากสองมิติไปหนึ่งมิติ

น.ส.ณัฐสุดา สิงห์โตทอง



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาเคมี ภาควิชาเคมี
คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2564

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| Thesis Title | DETERMINATION OF VOLATILE COMPOUNDS IN YELLOW CURRY PASTE USING FROM-TWO-TO-ONE DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY |
| By | Miss Natsuda Singtothog |
| Field of Study | Chemistry |
| Thesis Advisor | Associate Professor THUMNOON NHUJAK, Ph.D. |
| Thesis Co Advisor | Assistant Professor Chadin Kulsing, Ph.D. |

Accepted by the FACULTY OF SCIENCE, Chulalongkorn University in Partial Fulfillment of the Requirement for the Master of Science

..... Dean of the FACULTY OF SCIENCE
(Professor POLKIT SANGVANICH, Ph.D.)

THESIS COMMITTEE

..... Chairman
(Professor VUDHICHAI PARASUK, Ph.D.)

..... Thesis Advisor
(Associate Professor THUMNOON NHUJAK, Ph.D.)

..... Thesis Co-Advisor
(Assistant Professor Chadin Kulsing, Ph.D.)

..... Examiner
(Assistant Professor Puttaruksa Varanusupakul, Ph.D.)

..... External Examiner
(Assistant Professor Natthida Sriboonvorakul, Ph.D.)

ณัฐสุดา สิงห์โตทอง : การตรวจวัดสารระเหยง่ายในพริกแกงเหลืองโดยใช้แก๊สโครมาโทกราฟี-แมสสเปกโทรเมตรีจากสองมิติไปหนึ่งมิติ. ( DETERMINATION OF VOLATILE COMPOUNDS IN YELLOW CURRY PASTE USING FROM-TWO-TO-ONE DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY) อ.ที่ปรึกษาหลัก : รศ. ดร.ธรรมนูญ หนูจักร, อ.ที่ปรึกษาร่วม : ผศ. ดร.ชฎิล กุลสิงห์

ในงานวิจัยนี้ ได้พัฒนาวิธีการวิเคราะห์ด้วยแก๊สโครมาโทกราฟี-แมสสเปกโทรเมตรีแบบหนึ่งมิติ (1D GC-MS) สำหรับการวิเคราะห์เครื่องแกงเหลือง วิธีการนี้เกี่ยวข้องกับการประยุกต์ที่ตั้งต้นจากการวิเคราะห์ด้วยแก๊สโครมาโทกราฟี-แมสสเปกโทราเมตรีแบบสองมิติชนิด comprehensive heart-cut (CH/C 2D GC-MS) ที่ได้รูปแบบสารระเหยง่ายทั้งหมดโดยเปรียบเทียบแมสสเปกตรัมและรีเทนชั่นอินเด็กซ์ของสารที่ได้จากการทดลองกับค่าอ้างอิงที่ได้จากฐานข้อมูล จากนั้นใช้รูปแบบสารระเหยง่ายที่ได้เพื่อเป็นข้อมูลสำหรับวิธี selected ion monitoring (SIM) ซึ่งต่อมาประยุกต์กับ 1D GC-MS ที่ใช้ SIM ได้นำวิธีการนี้สำหรับปรับปรุงการวิเคราะห์ตัวอย่างเครื่องแกงเหลือง ค่า peak capacity ที่ได้เป็น 1207 สำหรับ 1D GC-MS และ 2080 สำหรับ CH/C 2D GC-MS อย่างไรก็ตามค่า peak capacity จาก 1D GC-MS ที่น้อยกว่าก็เพียงพอสำหรับการวิเคราะห์ตัวอย่างเครื่องแกงเหลือง แต่การวิเคราะห์ด้วย 1D GC-MS ที่ใช้ SIM ในการิเคราะห์ซึ่งมีความซับซ้อนน้อยกว่าใช้เวลาในการวิเคราะห์และการทำซ้ำที่ดีกว่า วิธีการพัฒนาขึ้นนี้ให้ประสิทธิภาพและง่ายสำหรักการวิเคราะห์ตัวอย่างที่ซับซ้อนได้



สาขาวิชา เคมี ลายมือชื่อนิสิต .....

ปีการศึกษา 2564 ลายมือชื่อ อ.ที่ปรึกษาหลัก .....

ลายมือชื่อ อ.ที่ปรึกษาร่วม .....

# # 6171954123 : MAJOR CHEMISTRY

KEYWORD: 2D separation, GC-MS, method translation, Thai food, volatile compounds

Natsuda Singtothog : DETERMINATION OF VOLATILE COMPOUNDS IN YELLOW CURRY PASTE USING FROM-TWO-TO-ONE DIMENSIONAL GAS CHROMATOGRAPHY-MASS SPECTROMETRY. Advisor: Assoc. Prof. THUMNOON NHUJAK, Ph.D. Co-advisor: Asst. Prof. Chadin Kulsing, Ph.D.

In this work, an approach to allow improved analysis with one-dimensional GC-MS (1D GC-MS) was established and demonstrated for analysis of a pool of yellow curry paste samples. The approach involved initial application of comprehensive heart cut two-dimensional GC-MS (CH/C 2D GC-MS) to obtain a full volatile profile by comparing the experimental mass spectrum and retention index of each compound with the mass spectra and retention indices of standard compounds from a database. The obtained volatile profile was then used to generate a selected ion monitoring (SIM) method, which was then applied with 1D GC-MS using a SIM mode. This approach was further applied for improved analysis of several yellow curry paste samples. The peak capacity was approximated as 1207 for 1D GC-MS with a SIM mode, and 2080 for CH/C 2D GC-MS. However, the lower peak capacity from 1D GC-MS was sufficient for analysis of yellow curry paste samples. The analysis times and repeatability could also be expected to be better with less complicated experimental setup of the 1D GC-MS with a SIM mode analysis. The established approach provided a simple and effective approach for the analysis of complex samples in the future.



Field of Study: Chemistry

Academic Year: 2021

Student's Signature .....

Advisor's Signature .....

Co-advisor's Signature .....

# ACKNOWLEDGEMENTS

First of all, I would like to thank my thesis advisor, Associate Professor Dr. Thumnoon Nhuajak, and co-advisor Assistant Professor Dr. Chadin Kulsing for help, support, knowledge, and advice throughout the thesis.

I would like to thank all thesis examiners, Professor Dr. Vudhichai Parasuk, Assistant Professor Dr. Puttaruksa Varanusupakul, Assistant Professor Dr. Natthida Sriboonvarakul for useful suggestions and comments

I would like to thank members of Chromatography and Favor Chemistry Research Group and ChromatoKikTaNie Lab for help, support, knowledge, and friendship.

I would like to thank Department of Chemistry, Faculty of science, Chulalongkorn University for support instruments and facilities in this thesis.

Finally, I would like to thank my parents and family, who support, encouragement, and behind the successful of my education and works.

Natsuda Singtothog

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# CHAPTER I

# INTRODUCTION

## 1.1 Problem definition

In general, food consists of many chemical groups, for example, amino acids, organic acid, protein, aroma compounds and nutrients food contains proteins, carbohydrates, fats, vitamins, and fibers. These compounds have a mass range, polarity and a large number of molecules. Profile of curry paste has been identified and quantified as complex food with the requirement for development of analytical methods for improved food analysis. The ingredient of curry paste includes chili, garlic, shallot, and curcumin [1-3], which has difference volatile compound profile such as Beta-caryophyllene, Allicin, Diallyl disulfide, and Curcuminoid. The characteristics of food aroma are very complex matrix mostly consisting of volatile and semi-volatile compounds [3]. Normally, the conventional analysis method is gas chromatography-mass spectrometry (GC-MS). The GC-MS can separate volatile compounds in food or herbs in the curry paste because GC-MS has a high separation performance using one column separated by boiling point, volatile and semi-volatile compounds. The commonly applied detector is mass spectrometry (MS) which can predict types of compounds by comparing characteristic mass and specific fragmentation pattern from the National Institute of Standards and Technology (NIST) 2017. Application of GC-MS includes environmental analysis, identification of unknown samples, foodstuff, and trace elements in materials.



The advanced analytical technique involves comprehensive heart-cut multidimensional gas chromatography (CH/C MDGC) of thousands of compounds in food in a single analysis. This technique is simple for separation of analytes from a large number of sample matrix components. CH/C MDGC has high sensitivity, selective mass spectrometry and reduced interference background.

However, the expense of analysis cost and time for additional chromatographic separation is often required for improved analysis of various compounds. Thus, in this study, we developed the technique of GC-MS to enable to separate compounds with the capability comparable to two-dimensional gas chromatography-mass spectrometry (2D GC-MS) in order to avoid a complicate system and difficulty in repeated analysis.

**1.2 Literature review**

The major ingredients of yellow curry paste include garlic, shallot, pepper, and curcumin, which have different volatile components. Positive properties of garlic include anti-bacterial, anti-oxidant, anti-microbial, and anti-asthmatic agents [4]. Volatile compound profiles of fresh and black garlic samples contained 51 volatile compounds tested by using HS-GC-MS analysis. The main components were thiosulfinates and sulfur volatiles, as well as the characteristic aroma compounds of garlic including diallyl sulfide, dimethyl trisulfide, diallyl disulfide, diallyl trisulfide, and 2-butenal. Besides, the composition of garlic included amino acids with the major components of glutamic acid (Glu 29%), aspartic acid (Asp 17%), serine (Ser 11%), and so on [5, 6].

GC-MS is an analytical technique used to separate and identify volatile or semi volatile compounds. Applications of GC-MS range from food analysis to the areas of environmental, drug, essential oil, biological, petroleum, forensic, pharmaceutical, and perfume. When combined with MS, MS enables fragmentation of components and their identification is based on the mass to charge ratios, *e.g.* by using the NIST library program [7-10].

MS provides a powerful detector for GC, which is sensitive, selective, and offers superior qualitative analysis. In general, MS can operate in full scan and selected ion monitoring (SIM) mode, a full scan is set with a wide mass scan range such as 35-500 Da and results in data of total ion chromatogram (TIC). SIM mode selects only specific *m/z* values of ions. SIM mode improves selectivity and resolution and reduces interferences [11-14]. Applications of GC-MS with SIM mode include food flavoring compounds, organic compounds, biological and environment [15-18].

MDGC is a technique using two different capillary columns. This technique provides confidence in compound identification, improved resolution, enhanced peak capacity, reliable analysis of a complex sample, and low detection limit. However, MDGC with high separation efficiency requires a long analysis time and complicated setup system [7, 19-21].

**1.3 Aim, Scope and expected benefits of this work**

The aim of this work is to improve analysis of volatile and semivolatile compounds in yellow curry using 1D GC—MS with a SIM mode. First, CH/C 2D GC-MS was established for the analysis of yellow curry paste samples. Then, the selected m/z values of the separated compounds were further applied in a SIM mode in 1D GC-MS. This is performed based on the information obtained from CH/C 2D GC-MS providing total volatile profile which was used to generate 1D GC-MS with a SIM mode. This technique provided identification performance, capability of mass spectrometry for identified compounds in a SIM mode compared with 1D GC-MS full scan. The benefit of this work is to improve and expect repeatability compared with CH/C 2D GC-MS reduces injections of 2D GC-MS and analysis time.

# CHAPTER II

# THEORY

## 2.1 Gas chromatography (GC-MS)

Gas chromatography (GC) is an analytical technique in used for vaporizing and separating compounds without decomposition. Figure 1 shows an example of a GC diagram. When a sample solution is injected into the GC system, the compounds in the samples are heated and vaporized within one injection. GC system consists of carrier gas *e.g.* nitrogen, helium, or hydrogen gas, which passes the sample components passing through the column (stationary phase). The GC column contains a liquid or solid phase material as stationary phase. The sample components should have different boiling points or interactions (*e.g.* polar and/or nonpolar) with the stationary phase, such as the more polar eluting later on a polar column. The detector is placed at the column outlet, which responses the signals of the sample and shows a chromatogram (a plot between signal vs retention time) containing peaks of volatile compounds in the sample. The signal intensity will be proportional to the amount of each analyte that elutes from the column with the overall process.

There are various types of detectors used in GC have such as mass spectrometry (MS), nitrogen-phosphorous detector (NPD), electron capture detector (ECD), flame ionization detector (FID), mass selective detector (MSD) operated in full scan mode, and atomic emission detector (AED). All detectors provide high sensitivity, efficiency, fast response, low detection limit and linearity range [22].

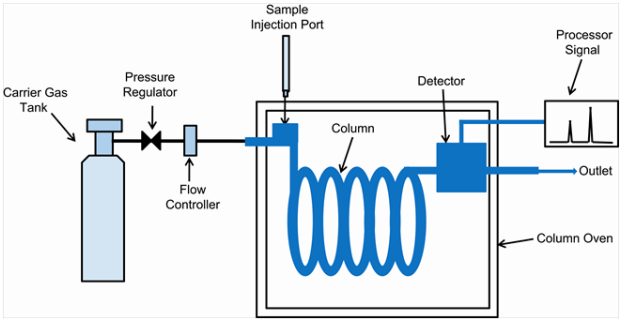


Figure 1 GC diagram. Reproduced from [23].

**2.2 Gas chromatography-mass spectrometry (GC-MS)**

Gas chromatography-mass spectrometry (GC-MS) is a hyphenated technique used in analytical chemistry, combining the benefits of two different analytical techniques. GC provides separation of volatile organic compounds in a complex sample, and MS is for detection, identification and/or quantification. This technique offers high specificity and sensitivity which is very useful in the field of untargeted analysis. in many branches such as analyses of food, medical, environmental, biological and others.

Compounds in a sample mixture analyzed and identified by GC-MS must be volatile and thermally stable which are detected as peaks in a chromatogram. After the compounds vaporization pass through the column by inert carrier gas and are separated inside the column, and/or polar and nonpolar. Each compound is expected to have different retention time as shown in Figure 2.

performance of the GC method can be adjusted by changing experimental conditions such as temperature program, flow rate, type of column, film thickness, diameter and length of column, and type of stationary phase.

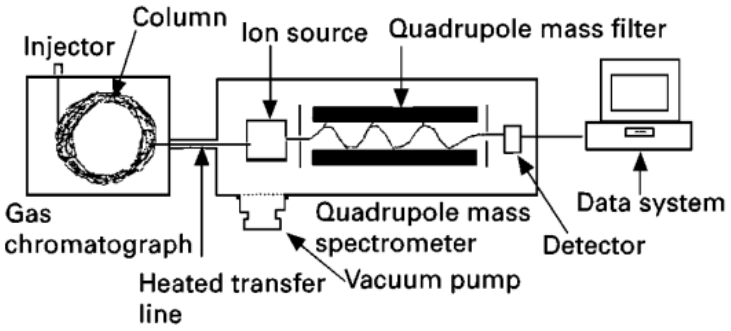


Figure 2 GC-MS instrument. Reproduced from [14].

**2.3 Multidimensional gas chromatography (MDGC)**

Multidimensional gas chromatography (MDGC), as shown in Figure 3, refers to two different GC columns assigned as first dimensional ($^1$D) and second dimensional ($^2$D) columns with different selectivities such as $^1$D non-polar/$^2$D polar or $^1$D polar/$^2$D non-polar. The $^1$D and $^2$D columns with different lengths are connected via an interface called a modulator. MDGC can be divided into two types which are comprehensive two-dimensional GC (GC×GC) and comprehensive heart cut MDGC (CH/C MDGC). The GC×GC technique is performed using a single injection to complete a whole sample analysis using a short $^2$D column. On the other hand, the CH/C MDGC technique is performed using multiple injections with a longer $^2$D column of about 30 to 60 m. In CH/C analysis, Dean switch (DS) [24, 25] is used as the interface, which allows analyte to transfer from $^1$D column and controls analyte to release onto $^2$D column or a restrictor column used to balance flows between both columns. A cryogenic trapping device can be applied with either or GC×GC or CH/C MDGC using a cryogen such as cryogenic liquid nitrogen, which focuses, traps and releases analytes into $^2$D column increasing prior to the detection [26-29].

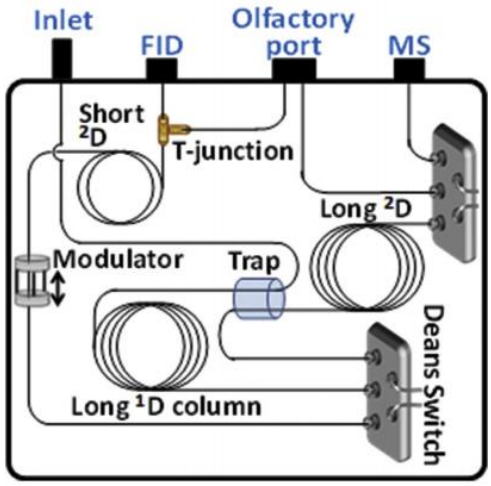


Figure 3 MDGC instrumentation. Reproduced from [28].

**2.4 Mass spectrometry**

Mass spectrometry (MS) is a technique used to identify unknown compounds in samples. This technique is highly sensitivity which can separate and detect ions in the gas phase. MS is based on fragmentation and ionization of sample molecules in the gas phase. Molecules can undergo ionization becoming odd-electron ion, [M+● ] or even-electron ion [M+], and can be detected by the detector. In addition, fragmented ions are observed depending on the characteristic of compounds. In general, MS has instrumental components consisting of ion source, mass analyzer, detector, and data system under vacuum system as shown Figure 4. Ions within a sample are produced in the ion source. Then, mass analyzer separates ions according to their mass-to-charge (m/z) ratios. Detector detects and records the ion intensities as well as data system recording and the signal amplifying.

**2.4.1 Ion source (Electron ionization, EI)**

After separation in GC, the separated components from the column are transferred into an ion source of MS via a heated transfer line where they are converted to ions. Electron Ionization (EI) is the most common ionization technique used for GC-MS. An EI source consists of a heat filament that produces electron accelerated towards an anode. Analyte molecules produce molecular ions (M+•) with high amount of internal energy. Since the ionization is produced by a single electron

that is accelerated to 70 V (corresponding to the energy of -70 eV), this is enough energy to cause extensive fragmentation which is useful for untargeted compound identification by comparison with MS spectrum data from the libraries. The positive charges attract and accelerating direct to the mass analyzer.

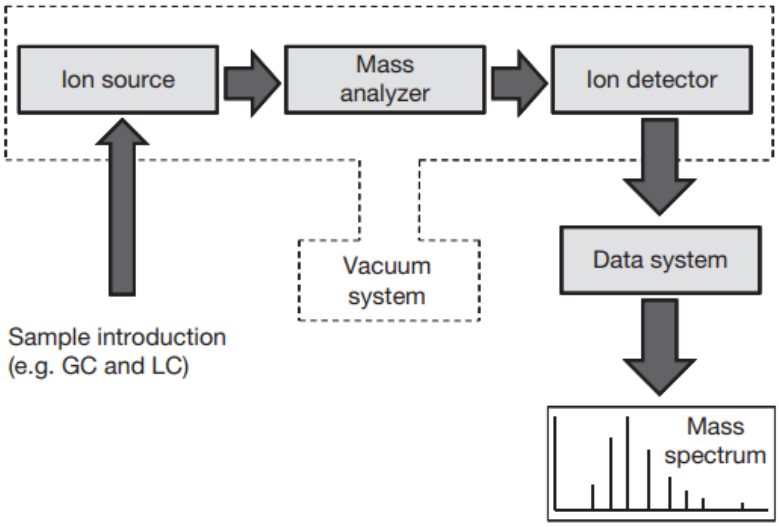


Figure 4 Diagram showing the components of mass spectrometry. Reproduced from [17].

### 2.4.2 Mass analyzer

From the ion source, the fragment ions are differently accelerated into the mass analyzer according to their *m/z* values. The several types of mass analyzers including magnetic sector, time-of-flight, quadrupole, ion trap, and tandem have been developed. The selection of a mass analyzer depends on a mass range, resolution, scan rate, a linearity range, or detection limit. Quadrupole mass spectrometer (QMS) is the most common mass analyzer in GC-MS. As shown in Figure 5 [30], a typical quadrupole mass analyzer consists of four rods with a hyperbolic cross section with a pair of positive and negative rods with the application of fixed Direct Current (DC) and alternating Radio Frequency (RF) potentials. Ions produced in the source of the instrument then travel through the Q, and they are filtered according to their m/z value so that only ions with a single m/z value survive from the Q and strike the detector. The RF is varied to bring ions of different m/z into

focus at the Q center and allow them to reach the detector resulting in a mass spectrum. Most quadrupole instruments are limited to unit *m/z* resolution and have a mass range up to *m/z* of 1000. The most selective mode with a single quadrupole MS is called selected ion monitoring (SIM) where a fixed set of DC and RF voltages is applied to the quadrupole allowing only ions with a single *m/z* to pass through. Ions with different m/z are filtered out.

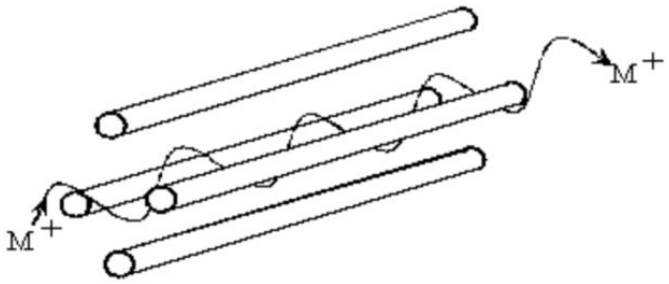


Figure 5 Quadrupole mass analyzer. Reproduced from [30].

**2.4.3 Ion detector**

Ions passing through the mass analyzer are accelerated and detected when they are collided with the multiplier surface emitting electrons. Their signals are transformed by the detector based on their charge or momentum. A detector can generate electric current proportional to ion abundance. The performance of a detector depends on geometry, gain, velocity, dynamic range, and sensitivity. The most commonly used ion detector in GC-MS is the electron multiplier (EM) due to its signal amplification ability and being cost effective.

# CHAPTERE III

# EXPERIMENTAL

## 3.1 Instruments, equipment and apparatus

A CH/C 2D GC-MS system was performed using GC—QqQMS system (7890A-7000, Agilent technologies Inc.), while Gerstel MPS 7890B-5977B MSD was used for a 1D GC-MS system (Agilent technologies Inc.). Both systems consist of autosampler and column oven couple with a mass spectrometry operated by electron impact ionization (EI), triple quadrupoles, and MassHunter software processing.

In CH/C 2D GC-MS with a restrictor column (1.5 m x 0.1 mm; Agilent technologies Inc, USA), an HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness; J&W Scientific, USA), and a DB-WAX capillary column (60 m x 0.25 mm x 0.25 μm; J&W Scientific, USA) were used as the $^{1}$D and $^{2}$D columns, respectively. For 1D GC-MS, the HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness; Agilent technologies Inc.) was used

The following equipment and apparatus were used: GC glass vial of 2 mL (Agilent technologies USA), syringe of 10 μL, (Agilent technologies USA), Micropipettes 100-1000 μL, (Eppendorf (Germany)), PTFE 0.20 μM, (National scientific, U.K), Vortex mixer (Scientific Industries, USA), A 4 digits-Balance (Mettler Toledo, USA), and Dean switch (Agilent technologies USA).



## 3.2 Chemicals and Samples

The mixture of *n*-alkanes C8-C20 CAS: 110-54-3 (Sigma Aldrich, Bellefonte, PA) was used as a reference to calculate retention index (I) of the chemical compounds. *n*-Hexane was purchase from RCL Labscan Limited CO., Ltd. USA. Three samples of yellow curry paste were purchased from Thai supermarket.

For sample preparation, 1 g of yellow curry paste sample was weighted and dissolved in hexane with 2 mL for CH/C 2D GC-MS and 1 mL for 1D GC-MS. Then the hexane extract was filtered by a 0.20 µm-PTFE syringe filter prior to GC-MS analysis.

**3.3 Analysis of volatile compounds**

**3.3.1 CH/C 2D GC-MS**

With a splitless mode, injection port temperature of 240 ℃ and injection volume of 1 µL were set with helium (99.999%) flow rate of 2.0 and 4.0 mL/min. FID and MS temperatures were set at 300 ℃ and 240 ℃ respectively. The GC temperature program for $^{1}$D nonpolar HP-5MS column was set at 40 ℃ held for 6 min$^{-1}$ and then increased to 250 ℃ at a rate of 6 ℃/min. The restrictor column was applied to balance flow with $^{2}$D column, then the outlets of restrictor column and $^{2}$D column connected to FID and MS, respectively. DS was operated in ON/OFF (ON into FID and OFF into MS) set time between OFF about 5 min and 0.2 min for ON and then transfer to $^{1}$D column connected to FID, and MS, respectively. The mass spectrometry operated by electron Impact -70 eV and the mass range of 28-550 m/z was applied. The temperature was set at 250 ℃.

**3.3.2 1D GC-MS with a SIM mode**

With a splitless mode, injection port temperature of 240 ℃ and injection volume of 0.5 µL were set with helium (99.999%) flow rate of 1.8 mL/min. MS temperature was set at 240 ℃. The initial temperature of a HP-5MS capillary column began at 40 ℃ held for 5 min and increased to 200 ℃ at a rate of 5 ℃/min then raised to 240 ℃ at a rate of 10 ℃/min held for 5 min. The mass spectrometry operated by electron impact -70 eV. Selected ion monitoring set Dwell time 50 ms. The temperature of quadrupole and ion source in MS was set at 150 ℃ and 230 ℃ respectively. The m/z values and compounds were as shown in Table 2.

**3.4 Data processing**

Data presentation and identification of volatile compounds in GC-MS were performed using Agilent MassHunter software. A peak of interest was identified by

the comparison of the MS spectrum with that from the NIST17 library. The identification criteria were a match score >650 and difference of ±20 units between experimental retention index (RI) and the literature values on the semi nonpolar column. The experimental RI was obtained by comparison of a peak retention time with that of the alkanes eluting just before and after this peak under the same separation conditions. The results were further processed using Microsoft Excel.

For calculation of $^{1}I$ in CH/C 2DGC, *n*-alkane standards were injected under the same experimental conditions as that applied for the Yellow Curry paste samples with DS off. Van den Dool and Kratz equation was used to calculate *I* for a peak according to [31]

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

$^{1}t_{R(i)}$ is retention time of the peak on the $^{1}$D column. *n* and *n*+1 are the numbers of carbons of alkanes with the elution times bracketing $^{1}t_{R(i)}$. In this study, $^{1}t_{R}$ is calculated from $t_{H/Cmid}$ as

$$^{1}t_{R} = t_{H/Cmid} = \frac{t_{H/Cstart} + t_{H/Cend}}{2} \quad (2).$$

$t_{H/Cmid}$, $t_{H/Cstart}$ and $t_{H/Cend}$ are H/C center time, start time and end time of the H/C, respectively. Note that calculation of *I* in 1DGC-SIM MS was also performed using Equation 1 albeit with $t_{R}$ was applied instead of $^{1}t_{R}$. $^{2}t_{R}$ in CH/C 2DGC can be calculated as

$$^{2}t_{R} = t_{observed} - {}^{1}t_{R} \quad (3).$$

$t_{observed}$ is the peak time observed with MS after elution through $^{1}$D and $^{2}$D columns. In the case of a peak of compound split into different H/C fractions,

calculation of ${}^{1}t_{R}$ and ${}^{2}t_{R}$ of a compound was based on weight average of each sub-peak area.

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 CH/C 2D GC-MS analysis of a pool of yellow curry samples

The analysis of volatile compounds in yellow curry used a development 1D GC-MS operated with SIM mode as a simple approach providing similar result to that of CH/C-2DGC. Initial CH/C-MDGC result was obtained from a pool of samples contain all the expected compounds in yellow curry.

The sample pool was analyzed using cryogenic free CH/C MDGC approach. With this approach, all the peaks obtained from $^{1}$D separation were H/C with the constant window of 0.2 min prior to $^{2}$D separation. Cyclic multiple H/C strategy and multiple injections were applied $^{1}$D with $^{2}$D separation time of 5 min. This applied 25 injections with the total analysis time of 25 h. The example result is shown in Figure 6 with all the identified compounds profile and odor description shown in Table 1. In general, the sample pool contained 119 volatile compounds identified based on $^{1}$I and MS library match. Their peak area percentages were obtained based on the total peak areas (combining all the sub-peaks of the same compound caused by the CH/C process) in MS full scan mode. The major components based on the peak area percentages were 2,2,3,4-tetramethyl pentane (18 %), α,α-dimethyl-benzene methanol (6 %) and 2-ethyl-6-methylphenol (8 %) which contributed to the smells of not available, green, sweet and not available, respectively. Other compounds with their odor descriptors were provided in Table 1.

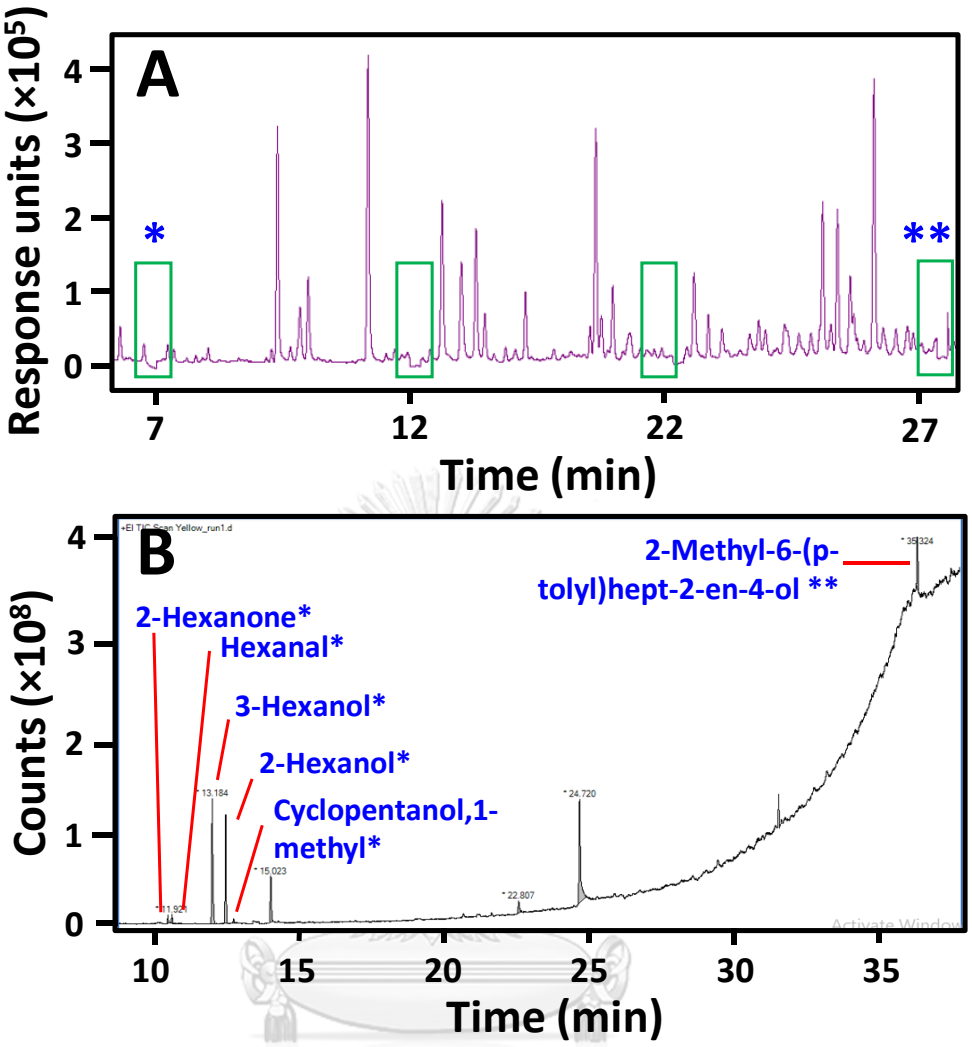


Figure 6 CH/C MDGC result (1st, 2nd and 3rd injections) using H/C window of 0.2 min of the pool of yellow curry paste sample.

Table 1 Volatile compound profiles with odor description, literature retention index on $^{1}$D nonpolar column and the compound peak areas in the pool of yellow curry paste samples analysed by CH/C 2DGC.

| Identified compound name | Odor description | CAS No. | *I* lit | CH/C 2DGC analysis of the sample pool | | |
|---|---|---|---|---|---|---|
| | | | | Peak area ($\times 10^4$) | $^{1}t_R$ (min) | $^{2}t_R$ (min) |
| 2-hexanone | Fresh green odor | 591-78-6 | 790 | 451 | 7.10 | 4.7 |
| hexanal | Aldehydic fatty oily-green fruity | 66-25-1 | 800 | 512 | 7.10 | 4.8 |
| 1-methyl-cyclopentanol | NA | 1462-03-9 | 797 | 248 | 7.10 | 6.8 |
| 3-hexanol | Fresh green odor spicy fruity fatty | 623-37-0 | 797 | 10743 | 7.12 | 6.1 |
| 2-hexanol | Fresh green odor spicy fruity fatty | 626-93-7 | 801 | 12752 | 7.18 | 6.4 |
| 2-hydroxyethyl propanoate | Sweet fruity pineapple-like ethereal-buttery | 97-64-3 | 815 | 780 | 7.50 | 13.5 |
| 2,2,3,4-tetramethylpentane | NA | 1186-53-4 | 821 | 401588 | 7.55 | 2.3 |
| 3-ethyl-2,2-dimethylpentane | NA | 16747-32-3 | 824 | 33838 | 7.90 | 2.3 |
| 2-methyl-2-pentenal | Fruity aldehydic juicy green | 623-36-9 | 837 | 2998 | 7.90 | 5.6 |
| lactic acid | NA | 50-21-5 | 838 | 684 | 7.90 | 13.1 |
| 3,4-dimethylheptane | NA | 922-28-1 | 858 | 35184 | 8.10 | 2.3 |
| 2,4-dimethyl-1-heptene | NA | 19549-87-2 | 836 | 355 | 8.10 | 3.0 |
| 3-methylbutanoic acid | Fruity acidic pungent cheesy sour | 503-74-2 | 863 | 3307 | 8.10 | 14.8 |
| 2-methylbutanoic acid | Acidic fruity dirty cheesy | 116-53-0 | 861 | 3381 | 8.30 | 14.6 |
| diallyl sulfide | Pungent sulfurous onion garlic | 592-88-1 | 861 | 2316 | 8.50 | 5.2 |
| 2,2,4-trimethylheptane | NA | 14720-74-2 | 876 | 97371 | 8.50 | 2.4 |
| 2,2,4-trimethylheptane | NA | 14720-74-2 | 876 | 97371 | 8.50 | 2.4 |
| *o*-xylene | Geranium | 95-47-6 | 887 | 2661 | 8.90 | 4.9 |
| 3-methyl-2-hexanol | NA | 2313-65-7 | 909 | 674 | 9.30 | 11.7 |
| 2-heptanol | Citrus fruity floral green herbal sweet fresh lemongrass | 543-49-7 | 900 | 559 | 9.50 | 11.5 |
| allyl methyl disulfide | Alliaceous, garlic green onion | 2179-58-0 | 920 | 4496 | 10.00 | 6.4 |
| 2,2-dimethyloctane | NA | 15869-87-1 | 916 | 31156 | 10.10 | 2.3 |
| 2,2-dimethyloctane | NA | 15869-87-1 | 916 | 31156 | 10.10 | 2.3 |
| allylbenzene | NA | 300-57-2 | 934 | 13233 | 10.27 | 4.4 |
| 2,2,6-trimethyloctane | NA | 62016-28-8 | 963 | 64467 | 10.50 | 2.5 |
| (*Z*)-1-methyl-2-(prop-1-en-1-yl) disulfane | NA | 23838-18-8 | 932 | 240 | 10.50 | 6.4 |

| Identified compound name | Odor description | CAS No. | *I* lit | CH/C 2DGC analysis of the sample pool | | |
|---|---|---|---|---|---|---|
| | | | | Peak area ($\times 10^4$) | $^1t_R$ (min) | $^2t_R$ (min) |
| (*E*)-1-methyl-2-(prop-1-en-1-yl) disulfane | NA | 23838-19-9 | 940 | 2213 | 10.53 | 6.2 |
| *3H*-1,2-dithiole | NA | 288-26-6 | 952 | 7707 | 11.13 | 10.1 |
| 1,2,6,6-tetramethyl-1,3-cyclohexadiene | NA | 514-96-5 | 985 | 4281 | 11.30 | 13.7 |
| 1-ethenyl-3-methylbenzene | NA | 100-80-1 | 979 | 7058 | 11.33 | 3.7 |
| 1-ethenyl-2-methylbenzene | NA | 611-15-4 | 975 | 6272 | 11.37 | 3.1 |
| dimethyl trisulfide | Sulfureous, alliaceous, green, onion, vegetative | 3658-80-8 | 970 | 7626 | 11.50 | 7.4 |
| 1-ethyl-4-methylbenzene | NA | 622-97-9 | 980 | 3765 | 11.90 | 3.1 |
| α-phellandrene | Green, citrus, woody, black pepper-like | 99-83-2 | 1005 | 295 | 12.30 | 4.4 |
| 2,6-dimethylnonane | NA | 17302-28-2 | 1016 | 1079 | 12.47 | 15.6 |
| 3-carene | Sweet and pungent odor citrus | 13466-78-9 | 1011 | 205 | 12.50 | 4.2 |
| 1-propenylbenzene | NA | 637-50-3 | 1011 | 11460 | 12.60 | 1.6 |
| *o*-cymene | Aromatic floral | 527-84-4 | 1022 | 532 | 12.90 | 5.1 |
| cyclopropyl benzene | NA | 873-49-4 | 1032 | 31140 | 12.93 | 14.2 |
| cyclopropyl benzene | NA | 873-49-4 | 1032 | 31140 | 12.93 | 14.2 |
| cyclopropyl benzene | NA | 873-49-4 | 1032 | 31140 | 12.93 | 14.2 |
| limonene | Piny turpentine -like odor citrus | 138-86-3 | 1030 | 286 | 13.10 | 4.4 |
| eucalyptol | Eucalyptus herbal camphor | 470-82-6 | 1032 | 1318 | 13.12 | 4.6 |
| 1-ethenyl-3-ethylbenzene | NA | 7525-62-4 | 1066 | 39526 | 13.70 | 0.4 |
| acetophenone | Sweet cherry pit vanilla-like | 98-86-2 | 1065 | 6951 | 13.84 | 8.9 |
| *n*-butylbenzene | NA | 104-51-8 | 1054 | 740 | 13.90 | 5.2 |
| 2-methyldecane | NA | 6975-98-0 | 1064 | 1286 | 13.90 | 8.2 |
| trans-Linalool oxide (furanoid) | Sweet floral | 34995-77-2 | 1086 | 205 | 14.00 | 7.3 |
| 5-ethenyltetrahydro-α,α,5-trimethyl- cis-2-furanmethanol | Earthy floral sweet woody | 5989-33-3 | 1074 | 551 | 14.30 | 6.4 |
| diallyl disulphide | Alliaceous onion and garlic-like | 2179-57-9 | 1081 | 12481 | 14.49 | 7.0 |
| 2,6-dimethyl-6-trifluoroacetoxyoctane | NA | 61986-67-2 | 1100 | 170 | 14.50 | 3.3 |
| 2,6-dimethyl-6-trifluoroacetoxyoctane | NA | 61986-67-2 | 1100 | 170 | 14.50 | 3.3 |
| α,α-dimethyl-benzene methanol | Green sweet earthy | 617-94-7 | 1090 | 133094 | 14.55 | 10.0 |
| 1-methyl-4-(1-methylethylidene)-cyclohexene | Fresh woody sweet pine citrus | 586-62-9 | 1088 | 847 | 14.70 | 4.7 |

Table 1 Continues

| Identified compound name | Odor description | CAS No. | *I* lit | CH/C 2DGC analysis of the sample pool | | |
|---|---|---|---|---|---|---|
| | | | | Peak area ($\times 10^4$) | $^1t_R$ (min) | $^2t_R$ (min) |
| 4-ethenyl-1,2-dimethylbenzene | Floral | 27831-13-6 | 1100 | 356 | 14.70 | 6.3 |
| (*Z*)-1-allyl-2-(prop-1-en-1-yl) disulfane | NA | 122156-03-0 | 1107 | 5230 | 14.90 | 6.6 |
| linalool | Fresh floral-woody sweet citrus | 78-70-6 | 1099 | 737 | 14.90 | 7.1 |
| (*E*)-1-allyl-2-(prop-1-en-1-yl) disulfane | NA | 122156-02-9 | 1103 | 7729 | 15.10 | 6.7 |
| dipropyl disulfide | Sulfurous alliaceous fresh green onion | 629-19-6 | 1107 | 230 | 15.30 | 5.4 |
| 1-ethyl-4-methoxybenzene | Anise | 1515-95-3 | 1110 | 66893 | 15.50 | 9.1 |
| α,4-dimethyl-benzenemethanol | Menthol-like floral sweet | 536-50-5 | 1132 | 30335 | 15.90 | 8.7 |
| allyl methyl trisulfide | Creamy garlic onion | 34135-85-8 | 1142 | 45717 | 16.24 | 7.8 |
| methyl propyl trisulfide | Sulfureous onion garlic green metallic | 17619-36-2 | 1150 | 1343 | 16.50 | 6.9 |
| pentyl benzene | NA | 538-68-1 | 1157 | 1308 | 16.70 | 5.2 |
| 1-phenyl-1,2-propanedione | Green plastic buttery honey pepper | 579-7-0 | 1175 | 4847 | 17.01 | 5.8 |
| 3-vinyl-1,2-dithiacyclohex-4-ene | NA | 62488-52-2 | 1198 | 3591 | 17.50 | 9.3 |
| N,N-diethyl-2-methylbenzenamine | NA | 606-46-2 | 1193 | 1959 | 17.60 | 6.5 |
| N,N-diethyl-2-methylbenzenamine | NA | 606-46-2 | 1193 | 1959 | 17.60 | 6.5 |
| dodecane | Alkane-like | 112-40-3 | 1200 | 1692 | 17.70 | 3.3 |
| benzoic acid, hydrazide | NA | 613-94-5 | 1205 | 2321 | 17.70 | 5.1 |
| 2-vinyl-4*H*-1,3-dithiine | NA | 80028-57-5 | 1206 | 18559 | 17.70 | 9.1 |
| benzaldehyde dimethyl acetal | Fruity green winey | 1125-88-8 | 1200 | 72224 | 17.90 | 6.7 |
| 3,6-dimethylundecane | NA | 17301-28-9 | 1210 | 441 | 18.50 | 3.8 |
| 4-ethyl-3-methylphenol | NA | 1123-94-0 | 1237 | 5001 | 18.58 | 6.7 |
| 2-ethyl-6-methylphenol | NA | 1687-64-5 | 1236 | 177772 | 18.67 | 6.0 |
| 2-propenyl ester benzoic acid | Sweet floral banana-like cherry | 583-04-0 | 1254 | 2567 | 18.90 | 3.9 |
| (1-methylenebutyl) benzene | NA | 5676-32-4 | 1236 | 13931 | 18.90 | 4.8 |
| 1,3-bis(1,1-dimethylethyl) benzene | NA | 1014-60-4 | 1249 | 6694 | 19.21 | 4.5 |
| 1-phenyl-1-butanone | Camphor cherry walnut hazelnut | 495-40-9 | 1263 | 5266 | 19.51 | 3.3 |
| 3-methyl-1-phenyl-1-butanone | NA | 582-62-7 | 1271 | 5513 | 19.71 | 3.1 |
| 2,6,11-trimethyldodecane | NA | 31295-56-4 | 1275 | 4302 | 19.76 | 8.8 |
| 2-butyl-1-octanol | NA | 3913-02-8 | 1277 | 2424 | 19.94 | 9.5 |
| 1,3,5,5-tetramethyl-1,3-cyclohexadiene | NA | 4724-89-4 | 1292 | 4528 | 19.95 | 5.0 |

Table 1 Continues

| Identified compound name | Odor description | CAS No. | *I* lit | CH/C 2DGC analysis of the sample pool | | |
|---|---|---|---|---|---|---|
| | | | | Peak area ($\times 10^4$) | $^1t_R$ (min) | $^2t_R$ (min) |
| phenol, 2-(1-methylethyl)-, acetate | NA | 1608-68-0 | 1277 | 564 | 20.10 | 5.5 |
| anethole | Sweet anise licorice | 104-46-1 | 1286 | 417 | 20.10 | 8.3 |
| N,N-diethyl-3-methylbenzenamine | NA | 91-67-8 | 1290 | 509 | 20.30 | 3.4 |
| α-oxo-benzeneacetic acid methyl ester | NA | 15206-55-0 | 1318 | 2824 | 20.42 | 2.3 |
| α-oxo-benzeneacetic acid methyl ester | NA | 15206-55-0 | 1318 | 2824 | 20.42 | 2.3 |
| (*E,E*)-2,4-decadienal | Fatty aldehydic citrus fatty | 25152-84-5 | 1317 | 1295 | 20.70 | 7.8 |
| (*E*)-1-(prop-1-en-1-yl)-3-propyltrisulfane | NA | 23838-27-9 | 1345 | 4275 | 20.90 | 11.0 |
| 2-methyl-6-propylphenol | NA | 3520-52-3 | 1320 | 48747 | 21.10 | 3.5 |
| (*E*)-1-allyl-3-(prop-1-en-1-yl) trisulfane | NA | 382161-78-6 | 1346 | 736 | 21.10 | 7.8 |
| N,N-diethyl-4-methylbenzenamine | NA | 613-48-9 | 1343 | 664 | 21.50 | 2.4 |
| 2-(4-methoxyphenyl) ethanol | Aroma fresh citrus | 702-23-8 | 1374 | 15291 | 21.90 | 2.8 |
| 5-methyl-1,2,3,4-tetrathiane | NA | 116664-30-3 | 1364 | 3057 | 22.30 | 10.7 |
| 1-phenyl-1-pentanone | Balsamic vinegar-like | 1009-14-9 | 1374 | 3442 | 22.40 | 0.3 |
| 1-(4-methoxyphenyl)-2-propanone | Sweet fruity spicy | 122-84-9 | 1384 | 41527 | 22.45 | 2.2 |
| tetradecane | Odor threshold for n-butanol | 629-59-4 | 1400 | 8547 | 22.53 | 5.8 |
| alloaromadendrene | Woody | 25246-27-9 | 1461 | 2673 | 23.70 | 4.9 |
| (*E*)-β-famesene | Woody citrus herbal sweet | 18794-84-8 | 1457 | 895 | 24.10 | 4.7 |
| 5-methyltetradecane | NA | 25177-32-2 | 1453 | 2327 | 24.30 | 8.9 |
| 1-methyl-4-(6-methylhept-5-en-2-yl) cyclohexa-1,3-diene | NA | 451-55-8 | 1480 | 1739 | 24.70 | 5.1 |
| pentadecane | Waxy | 629-62-9 | 1500 | 1202 | 24.90 | 3.8 |
| 1-(1,5-dimethyl-4-hexenyl)-4-methylbenzene | Herbal | 644-30-4 | 1483 | 16446 | 24.90 | 5.5 |
| [*S*-(*R**,*S**)]-5-(1,5-dimethyl-4-hexenyl)-2-methyl-1,3-cyclohexadiene | Spicy fresh sharp | 495-60-3 | 1495 | 16113 | 25.10 | 5.1 |
| 2-hexyl-1-decanol | NA | 2425-77-6 | 1504 | 4138 | 25.16 | 5.4 |
| 2,4-di*tert*-butylphenol | NA | 96-76-4 | 1519 | 6955 | 25.30 | 10.3 |
| β-bisabolene | Balsamic woody | 495-61-4 | 1509 | 3607 | 25.50 | 4.9 |
| (*R*)-1-Methyl-4-(6-methylhept-5-en-2-yl)cyclohexa-1,4-diene | NA | 28976-67-2 | 1514 | 1150 | 25.50 | 5.1 |

Table 1 Continues

| Identified compound name | Odor description | CAS No. | *I* lit | CH/C 2DGC analysis of the sample pool | | |
|---|---|---|---|---|---|---|
| | | | | Peak area ($\times 10^4$) | $^1t_R$ (min) | $^2t_R$ (min) |
| [*S*-(*R**,*S**)]-3-(1,5-dimethyl-4-hexenyl)-6-methylene-cyclohexene | Herbal fruity woody | 20307-83-9 | 1524 | 18448 | 25.80 | 5.2 |
| 1,2,3,4,4*a*,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene | NA | 16728-99-7 | 1533 | 15255 | 25.90 | 4.3 |
| 3,7,11-trimethyl-1-dodecanol | NA | 6750-34-1 | 1571 | 2538 | 26.30 | 3.6 |
| 5-nitro-1,2,3,4-tetrahydro-naphthalene | NA | 29809-14-1 | 1589 | 925 | 26.70 | 4.2 |
| 2-methyl-6-(p-tolyl) hept-2-en-4-ol | NA | 38142-57-3 | 1583 | 3819 | 27.10 | 8.2 |
| a*R*-turmerone | NA | 532-65-0 | 1664 | 126223 | 28.90 | 8.2 |
| eudesma-4(15),7-dien-1β -ol | NA | 119120-23-9 | 1688 | 2421 | 29.10 | 0.3 |
| (*Z*)-γ-atlantone | NA | 108549-48-0 | 1699 | 49843 | 29.10 | 7.3 |
| (*E*)-γ-atlantone | NA | 108549-47-9 | 1712 | 83020 | 29.70 | 7.8 |
| (*E*)-atlantone | NA | 108645-54-1 | 1773 | 14519 | 31.10 | 8.3 |

Table 1 Continues

From Tables 1 most of the compounds were characteristically observed from the ingredient of yellow curry dish. For example, limonene observed in the extracted lemongrass oil [32, 33]. Linalool was identified with HS-SPME GC-MS analysis as the major volatile compounds in Kaffir lime leaf, *Citrus hystrix* (DC.) with the characteristic odor of citrus [34]. Limonene, and linalool, were reported as the components in the extracted oil of Kaffir lime leaf [35]. Limonene was also reported in swingle essential oil, with the characteristic smell of citric [36, 37].

**4.2 1D GC-MS with a SIM mode analysis of yellow curry samples**

1D GC-MS with a SIM mode approach has been set up for all the compounds obtained from the CH/C 2DGC-MS analysis (Table 1). This was based on the compound spectra from NIST library (instead of the experimental spectra) in order to avoid selection of false positive *m/z* values caused by the coeluting components, such as column bleeding or any other coeluting peaks, in 2D separation. The selected *m/z* values were characteristic of each compound with high intensity (major abundant within each characteristic group) in order to support compound identification and lead to significantly high peak areas in SIM results. Four *m/z* values were selected for each compound which resulted in the total 1D SIM analysis consisting of 111 *m/z* values of all the compounds observed with the 2D analysis. Since the applied instrument allowed only 4 m/z values per injection, the overall 1DGC-MS with a SIM mode analysis of each sample was obtained by performing 5 injections. In order to provide reliable quantitative analysis as shown Figure 7 in 1D GC-MS with a SIM mode, the selected set of *m/z* values should also result in peak areas showing correlation with that in CH/C 2D GC-MS analysis.

The developed 1D approach was applied for analysis of three yellow curry paste samples. A volatile compound profiles were shown in Table 2 with the peak areas based on summation of the areas obtained from all four selected SIM *m/z* values of each compound. The example chromatograms obtained from the SIM analysis of 3-hexanol with the retention time of 6.4 min were provided in Figure 8.

Table 2 Volatile compound profiles of different yellow curry paste samples analyzed by 1D GC-MS with a SIM mode detecting four characteristic m/z values for each compound.

| Identified compound name | 1D GC-MS analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_R$ [a] (min) | Characteristic m/z | | | | Sum of characteristic peak areas (×10$^4$) | | |
| | | 1 | 2 | 3 | 4 | Sample 1 | Sample 2 | Sample 3 |
| 2-hexanone | 6.42 | 85 | 77 | 58 | 43 | 419.7 | 616.7 | 460.0 |
| hexanal | 6.42 | 82 | 72 | 56 | 43 | 441.9 | 643.7 | 485.1 |
| 1-methyl-Cyclopentanol | 6.58 | 72 | 43 | 39 | 27 | 3450 | 777.6 | 4490 |
| 3-hexanol | 6.41 | 73 | 58 | 55 | 31 | 2.58 | 41.56 | 45.27 |
| 2-hexanol | 6.50 | 69 | 55 | 41 | 27 | 279.2 | 319.2 | 284.7 |
| 2-hydroxyethyl propanoate | 6.93 | 75 | 45 | 29 | 27 | 1926 | 166.7 | 99.75 |
| 2,2,3,4-tetramethylpentane | 7.28 | 57 | 43 | 39 | 27 | 137.8 | 353.0 | 244.9 |
| 3-ethyl-2,2-dimethylpentane | 7.98 | 71 | 57 | 43 | 29 | < 0.01 | 28.57 | 18.49 |
| 2-methyl-2-pentenal | 7.84 | 98 | 69 | 43 | 39 | 222.9 | 13.85 | 7.434 |
| lactic acid | 7.70 | 56 | 43 | 29 | 27 | < 0.01 | 626.3 | 12.99 |
| 3,4-dimethylheptane | 7.98 | 70 | 57 | 43 | 29 | < 0.01 | 23.00 | 15.29 |
| 2,4-dimethyl-1-heptene | 8.00 | 71 | 70 | 55 | 43 | 1543 | 2593 | < 0.01 |
| 3-methylbutanoic acid | 7.98 | 56 | 43 | 41 | 39 | < 0.01 | 19.52 | 14.01 |
| 2-methylbutanoic acid | 7.98 | 73 | 57 | 29 | 27 | < 0.01 | 20.40 | 7.929 |
| diallyl sulfide | 8.22 | 99 | 77 | 69 | 55 | < 0.01 | 0.28 | 1.05 |
| 2,2,4-trimethylheptane | 7.99 | 85 | 71 | 56 | 57 | 13.31 | 17.33 | 13.85 |
| 2,2,4-trimethylheptane | 7.99 | 85 | 71 | 56 | 57 | 13.31 | 17.33 | 13.85 |
| *o*-xylene | 7.72 | 65 | 64 | 63 | 39 | 11.58 | 1.89 | < 0.01 |
| 3-methyl-2-hexanol | 7.80 | 70 | 55 | 43 | 27 | 122.4 | 29.67 | 11.80 |
| 2-heptanol | 7.80 | 70 | 55 | 43 | 27 | 122.4 | 29.67 | 11.80 |
| allyl methyl disulfide | 6.85 | 120 | 79 | 45 | 41 | 293.7 | 2605 | < 0.01 |
| 2,2-dimethyloctane | 7.59 | 85 | 71 | 57 | 41 | 68.03 | 6036 | 14.23 |
| 2,2-dimethyloctane | 7.59 | 85 | 71 | 57 | 41 | 68.03 | 6036 | 14.23 |
| allylbenzene | 7.94 | 119 | 115 | 103 | 75 | 1.197 | 0.75 | 0.43 |
| 2,2,6-trimethyloctane | 8.00 | 85 | 71 | 57 | 43 | 1831 | 2622 | 1645 |
| (*Z*)-1-methyl-2-(prop-1-en-1-yl) disulfane | 8.45 | 82 | 77 | 70 | 69 | < 0.01 | 0.21 | < 0.01 |
| (*E*)-1-Methyl-2-(prop-1-en-1-yl) disulfane | 7.80 | 85 | 72 | 57 | 39 | 44.68 | 7.49 | 6.06 |
| *3H*-1,2-dithiole | 14.0 | 103 | 80 | 77 | 39 | < 0.01 | 0.14 | 0.44 |
| 1,2,6,6-tetramethyl-1,3-cyclohexadiene | 14.0 | 136 | 121 | 105 | 91 | < 0.01 | 0.20 | 0.72 |
| 1-ethenyl-3-methylbenzene | 14.0 | 92 | 91 | 78 | 77 | < 0.01 | 0.32 | 0.97 |
| 1-ethenyl-2-methylbenzene | 14.0 | 92 | 91 | 78 | 77 | < 0.01 | 0.32 | 0.97 |
| dimethyl trisulfide | 14.0 | 80 | 79 | 78 | 65 | < 0.01 | 0.10 | 0.37 |

| Identified compound name | 1D GC-MS analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_R$ [a] (min) | Characteristic m/z | | | | Sum of characteristic peak areas (×10$^4$) | | |
| | | 1 | 2 | 3 | 4 | Sample 1 | Sample 2 | Sample 3 |
| 1-ethyl-4-methylbenzene | 14.0 | 118 | 117 | 115 | 91 | < 0.01 | 0.27 | < 0.01 |
| α-phellandrene | 15.4 | 136 | 93 | 77 | 41 | < 0.01 | 1.04 | 1.30 |
| 2,6-dimethylnonane | 16.9 | 85 | 70 | 71 | 55 | < 0.01 | 0.79 | 0.86 |
| 3-carene | 15.1 | 121 | 107 | 93 | 79 | 0.03 | 0.27 | 1.24 |
| 1-propenylbenzene | 14.0 | 105 | 91 | 78 | 41 | < 0.01 | 0.19 | 0.62 |
| *o*-cymene | 15.7 | 134 | 119 | 91 | 77 | < 0.01 | 3.39 | 3.16 |
| cyclopropyl benzene | 14.0 | 119 | 103 | 91 | 79 | < 0.01 | 0.18 | 0.62 |
| cyclopropyl benzene | 14.0 | 119 | 103 | 91 | 79 | < 0.01 | 0.18 | 0.62 |
| cyclopropyl benzene | 14.0 | 119 | 103 | 91 | 79 | < 0.01 | 0.18 | 0.62 |
| limonene | 14.0 | 136 | 107 | 93 | 65 | < 0.01 | 0.26 | 1.05 |
| eucalyptol | 15.0 | 136 | 108 | 93 | 81 | 0.05 | 0.24 | 0.99 |
| 1-ethenyl-3-ethylbenzene | 14.0 | 106 | 91 | 77 | 63 | < 0.01 | 0.20 | 0.67 |
| acetophenone | 14.0 | 105 | 77 | 51 | 39 | < 0.01 | 0.15 | 0.48 |
| *n*-butylbenzene | 14.0 | 105 | 91 | 92 | 65 | < 0.01 | 0.28 | 0.82 |
| 2-methyldecane | 14.0 | 77 | 65 | 41 | 39 | < 0.01 | 0.14 | 0.50 |
| trans-Linalool oxide (furanoid) | 14.8 | 80 | 77 | 41 | 39 | < 0.01 | 0.09 | 4.22 |
| 5-ethenyltetrahydro-α,α,5-trimethyl- cis-2-furanmethanol | 14.0 | 81 | 79 | 41 | 39 | < 0.01 | 0.11 | 0.42 |
| diallyl disulphide | 14.8 | 105 | 81 | 41 | 39 | < 0.01 | 0.06 | 2.78 |
| 2,6-dimethyl-6-trifluoroacetoxyoctane | 14.8 | 81 | 51 | 41 | 39 | < 0.01 | 0.06 | 2.76 |
| 2,6-dimethyl-6-trifluoroacetoxyoctane | 14.8 | 81 | 51 | 41 | 39 | < 0.01 | 0.06 | 2.76 |
| α,α-dimethyl-benzene methanol | 14.8 | 121 | 118 | 77 | 43 | < 0.01 | 0.13 | 2.70 |
| 1-methyl-4-(1-methylethylidene)-cyclohexene | 15.3 | 136 | 121 | 93 | 79 | 0.03 | 0.24 | 0.14 |
| 4-ethenyl-1,2-dimethylbenzene | 14.6 | 105 | 103 | 91 | 78 | < 0.01 | 0.17 | 2.29 |
| (*Z*)-1-Allyl-2-(prop-1-en-1-yl) disulfane | 14.8 | 107 | 105 | 81 | 41 | < 0.01 | 0.09 | 2.47 |
| linalool | 14.8 | 121 | 107 | 93 | 39 | < 0.01 | 0.25 | 7.60 |
| (*E*)-1-Allyl-2-(prop-1-en-1-yl) disulfane | 16.0 | 105 | 79 | 41 | 39 | < 0.01 | 0.56 | 1.75 |
| disulfide dipropyl | 15.7 | 43 | 41 | 39 | 27 | < 0.01 | 0.51 | 2.81 |
| 1-ethyl-4-methoxybenzene | 15.7 | 136 | 121 | 91 | 77 | < 0.01 | 3.63 | 4.90 |
| α,4-dimethyl-benzenemethanol | 16.1 | 136 | 121 | 93 | 43 | 0.03 | 2.97 | 7.28 |
| allyl methyl trisulfide | 16.9 | 111 | 79 | 45 | 39 | < 0.01 | 0.77 | 1.67 |
| methyl propyl trisulfide | 16.9 | 154 | 79 | 43 | 41 | < 0.01 | 1.79 | 2.37 |
| pentyl benzene | 16.7 | 105 | 91 | 78 | 65 | < 0.01 | 2.49 | 1.05 |
| 1-phenyl-1,2-propanedione | 18.2 | 77 | 43 | 39 | 27 | < 0.01 | 1.52 | 0.35 |
| 3-vinyl-1,2-dithiacyclohex-4-ene | 17.6 | 85 | 71 | 70 | 57 | < 0.01 | 0.10 | 0.06 |

Table 2 Continues

| Identified compound name | 1D GC-MS analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_R$ [a] (min) | Characteristic m/z | | | | Sum of characteristic peak areas (×$10^4$) | | |
| | | 1 | 2 | 3 | 4 | Sample 1 | Sample 2 | Sample 3 |
| N,N-diethyl-2-methylbenzenamine | 16.9 | 134 | 119 | 108 | 69 | < 0.01 | 1.67 | 1.40 |
| N,N-diethyl-2-methylbenzenamine | 16.9 | 134 | 119 | 108 | 69 | < 0.01 | 1.67 | 1.40 |
| dodecane | 17.6 | 85 | 71 | 57 | 43 | < 0.01 | 0.13 | 0.07 |
| benzoic acid, hydrazide | 18.2 | 136 | 105 | 77 | 51 | < 0.01 | 3.23 | 0.57 |
| 2-vinyl-4*H*-1,3-dithiine | 16.9 | 111 | 103 | 97 | 72 | < 0.01 | 0.52 | 0.63 |
| benzaldehyde dimethyl acetal | 17.7 | 121 | 105 | 77 | 75 | < 0.01 | 3.31 | 1.26 |
| 3,6-dimethylundecane | 16.2 | 113 | 99 | 71 | 57 | 186.1 | 815.9 | 425.6 |
| 4-ethyl-3-methylphenol | 18.6 | 136 | 121 | 91 | 77 | < 0.01 | 5.58 | 0.94 |
| 2-ethyl-6-methylphenol | 18.6 | 136 | 121 | 91 | 77 | < 0.01 | 5.58 | 0.94 |
| 2-propenyl ester benzoic acid | 18.6 | 106 | 105 | 103 | 77 | < 0.01 | 1.68 | 0.22 |
| (1-methylenebutyl) benzene | 18.6 | 91 | 77 | 51 | 27 | < 0.01 | 2.59 | < 0.01 |
| 1,3-bis(1,1-dimethylethyl) benzene | 20.3 | 91 | 65 | 50 | 39 | < 0.01 | 0.08 | < 0.01 |
| 1-phenyl-1-butanone | 20.4 | 105 | 77 | 51 | 50 | < 0.01 | 0.08 | < 0.01 |
| 3-methyl-1-phenyl-1-butanone | 18.6 | 120 | 105 | 78 | 77 | < 0.01 | 1.72 | 0.21 |
| 2,6,11-trimethyldodecane | 19.9 | 55 | 43 | 41 | 39 | < 0.01 | 1.10 | 0.51 |
| 2-butyl-1-octanol | 20.7 | 97 | 69 | 55 | 39 | < 0.01 | 0.21 | 0.19 |
| 1,3,5,5-tetramethyl-1,3-cyclohexadiene | 18.6 | 91 | 77 | 55 | 41 | < 0.01 | 2.85 | < 0.01 |
| phenol, 2-(1-methylethyl)-, acetate | 20.7 | 107 | 95 | 91 | 79 | < 0.01 | 0.32 | 0.21 |
| anethole | 20.7 | 91 | 77 | 65 | 39 | < 0.01 | 0.11 | 0.28 |
| N,N-diethyl-3-methylbenzenamine | 20.7 | 91 | 81 | 65 | 51 | < 0.01 | 0.23 | 0.21 |
| α-oxo-benzeneacetic acid methyl ester | 20.3 | 77 | 73 | 65 | 51 | < 0.01 | 0.18 | < 0.01 |
| α-oxo-benzeneacetic acid methyl ester | 20.3 | 77 | 73 | 65 | 51 | < 0.01 | 0.18 | < 0.01 |
| (*E,E*)-2,4-decadienal | 20.7 | 95 | 81 | 41 | 39 | < 0.01 | 0.66 | 0.35 |
| (*E*)-1-(prop-1-en-1-yl)-3-propyltrisulfane | 20.7 | 69 | 55 | 41 | 39 | < 0.01 | 0.36 | 0.42 |
| 2-methyl-6-propylphenol | 12.1 | 150 | 91 | 77 | 51 | 1354 | 682.4 | 1019 |
| (*E*)-1-allyl-3-(prop-1-en-1-yl) trisulfane | 20.7 | 81 | 55 | 41 | 39 | < 0.01 | 0.46 | 0.38 |
| N,N-diethyl-4-methylbenzenamine | 20.3 | 163 | 148 | 120 | 91 | < 0.01 | 0.46 | < 0.01 |
| 2-(4-methoxyphenyl) ethanol | 20.7 | 91 | 77 | 55 | 41 | < 0.01 | 0.28 | 0.42 |
| 5-methyl-1,2,3,4-tetrathiane | 20.3 | 108 | 91 | 80 | 41 | < 0.01 | 0.40 | 0.23 |
| 1-phenyl-1-pentanone | 27.0 | 79 | 77 | 65 | 41 | < 0.01 | 1.09 | 0.08 |
| 1-phenyl-1-pentanone | 27.0 | 79 | 77 | 65 | 41 | < 0.01 | 1.09 | 0.08 |

Table 2 Continues

| Identified compound name | 1D GC-MS analysis | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | $t_R$ [a] (min) | Characteristic m/z | | | | Sum of characteristic peak areas (×$10^4$) | | |
| | | 1 | 2 | 3 | 4 | Sample 1 | Sample 2 | Sample 3 |
| 1-(4-methoxyphenyl)-2-propanone | 20.7 | 91 | 77 | 65 | 51 | < 0.01 | 0.08 | 0.22 |
| tetradecane | 22.5 | 70 | 56 | 43 | 41 | < 0.01 | 0.11 | 0.40 |
| alloaromadendrene | 20.9 | 70 | 57 | 43 | 41 | < 0.01 | 0.16 | < 0.01 |
| (*E*)-β-famesene | 23.8 | 71 | 70 | 43 | 41 | < 0.01 | 0.16 | < 0.01 |
| 5-methyltetradecane | 26.0 | 154 | 85 | 57 | 43 | < 0.01 | 0.12 | < 0.01 |
| 1-methyl-4-(6-methylhept-5-en-2-yl) cyclohexa-1,3-diene | 25.5 | 146 | 104 | 94 | 41 | < 0.01 | 0.45 | 0.04 |
| pentadecane | 24.0 | 85 | 71 | 57 | 43 | 0.06 | 0.22 | 0.21 |
| 1-(1,5-dimethyl-4-hexenyl)-4-methyl benzene | 25.5 | 146 | 104 | 94 | 41 | < 0.01 | 0.45 | 0.04 |
| [*S*-(*R**,*S**)]-5-(1,5-dimethyl-4-hexenyl)-2-methyl-1,3-cyclohexadiene | 26.9 | 204 | 119 | 93 | 41 | < 0.01 | 0.96 | 0.20 |
| 2-hexyl-1-decanol | 24.0 | 85 | 71 | 57 | 43 | 0.06 | 0.22 | 0.21 |
| 2,4-di*tert*-butylphenol | 25.0 | 147 | 73 | 75 | 57 | < 0.01 | 0.10 | < 0.01 |
| β-Bisabolene | 25.9 | 133 | 105 | 57 | 43 | < 0.01 | 0.13 | < 0.01 |
| (*R*)-1-methyl-4-(6-methylhept-5-en-2-yl) cyclohexa-1,4-diene | 25.9 | 133 | 105 | 57 | 43 | < 0.01 | 0.13 | < 0.01 |
| [*S*-(*R**,*S**)]-3-(1,5-dimethyl-4-hexenyl)-6-methylene-cyclohexene | 25.0 | 147 | 112 | 71 | 57 | < 0.01 | 0.04 | < 0.01 |
| 1,2,3,4,4*a*,7-hexahydro-1,6-dimethyl-4-(1-methylethyl)-naphthalene | 25.9 | 159 | 129 | 71 | 57 | < 0.01 | 0.10 | < 0.01 |
| 3,7,11-trimethyl-1-dodecanol | 22.9 | 97 | 83 | 69 | 55 | 240.4 | 5145 | 2614 |
| 5-nitro-1,2,3,4-tetrahydro-naphthalene | 27.4 | 159 | 128 | 115 | 91 | 186.5 | 5062 | 764.2 |
| 2-methyl-6-(p-tolyl) hept-2-en-4-ol | 27.5 | 119 | 117 | 91 | 77 | 0.05 | 0.93 | < 0.01 |
| a*R*-turmerone | 29.3 | 132 | 119 | 91 | 83 | 0.29 | 4.11 | 3.31 |
| eudesma-4(15),7-dien-1β -ol | 29.0 | 177 | 159 | 81 | 41 | < 0.01 | 0.66 | < 0.01 |
| (*Z*)-γ-atlantone | 29.2 | 119 | 105 | 83 | 55 | 0.29 | 3.74 | 2.13 |
| (*E*)-γ-atlantone | 29.7 | 119 | 105 | 83 | 55 | 0.25 | 3.74 | 2.40 |
| (*E*)-atlantone | 31.2 | 135 | 120 | 105 | 77 | < 0.01 | 0.24 | < 0.01 |

Table 2 Continues

[a] The average retention time of four *m/z* values were selected for each compound.

For an example of 3-hexanol, 4 m/z values of 73, 58,55 and 31 were selected and 4 chromatograms with the different particular $t_R$ and peak area were displayed as shown in Figures 8A-D. The peak area value of this compound in Table 2 was obtained by summation of the areas of all the peaks at the average $t_R$ of 6.4 min in Figures 8A-D, were the average $t_R$ from 4 chromatograms. Since several compounds could share the same *m/z* value, each SIM analysis selecting a *m/z* value resulted in several peaks in Figure 8A. This caused difficulty in identification of all the SIM peaks of each compound. Note that the $^1t_R$ in the 2D analysis could not be accurately applied as the reference for peak identification with the 1D GC-SIM MS analysis due to the retention time shift caused by different inlet and outlet pressures of the applied nonpolar columns. However, reliable identification of SIM peaks of a compound could be performed according to retention index of this compound. To this end, retention indices of all the peaks observed in Figure 8 were calculated. The SIM peaks at 6.4 min in Figures 8A-D were identified for 3-hexanol since they were observed with the same retention time and peak shape and showed the calculated values closely to the target value of 3-hexanol.

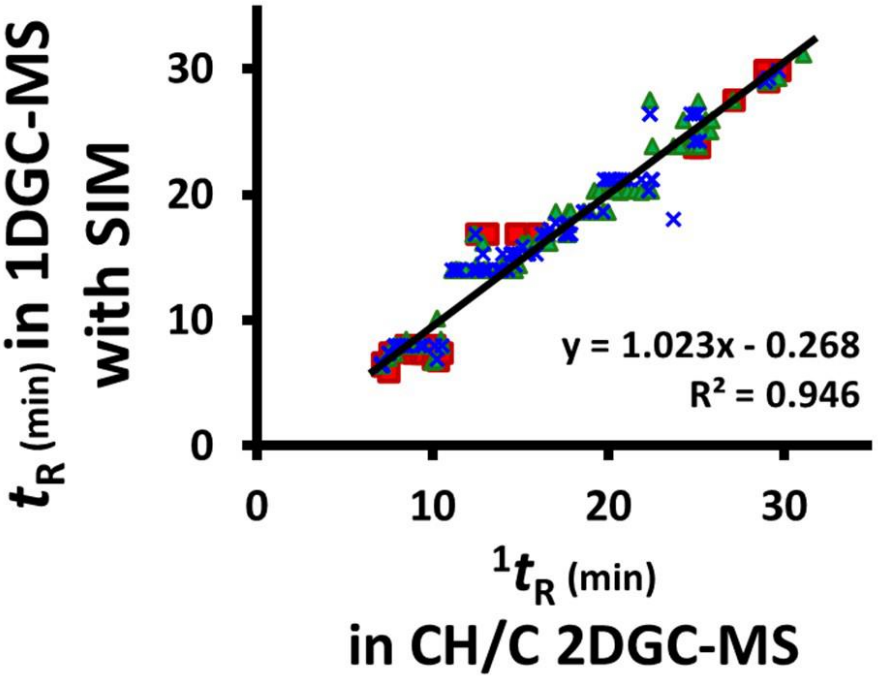


Figure 7 Correlation between x-axis: $^1$D retention time values obtained from CH/C 2D GC analysis of a volatile compounds in the pool sample and y-axis: retention time values obtained from 1D GC-MS with a SIM mode analysis of the same compounds in the yellow curry paste sample 1-3 (□, X and Δ, respectively).

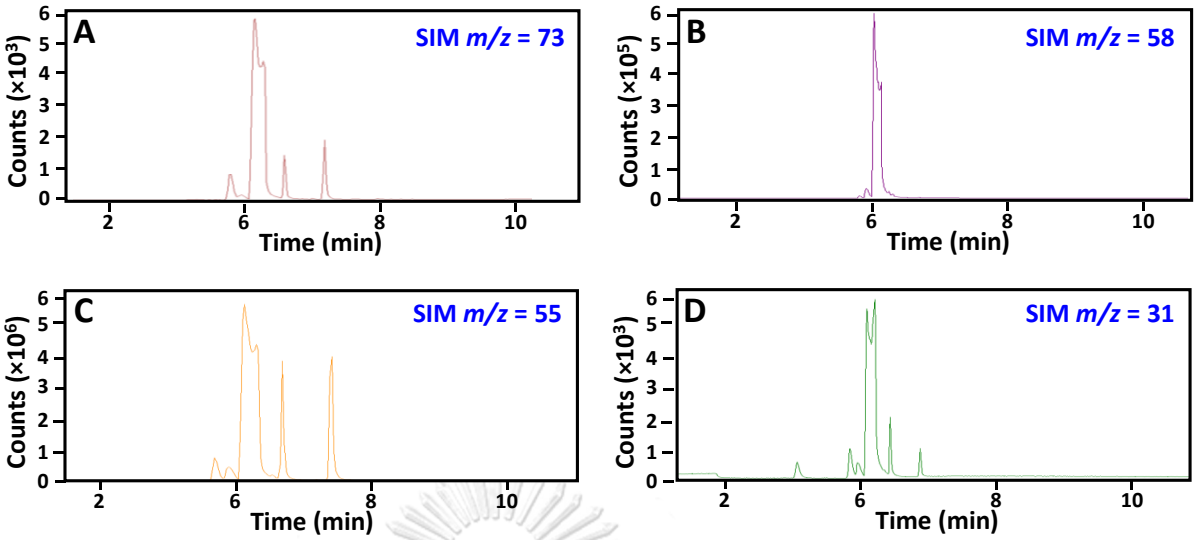


Figure 8 GC-SIM MS results of a yellow curry paste sample using different m/z values of 73 58 55 31, A-D respectively.

From Figure 6, the total peak capacity from CH/C 2D GC-MS analysis was approximated as 2080. This is calculated from ${}^{1}n_{c}$ of 52 (with average peak width, maximum $t_R$, and minimum $t_R$ of 0.4, 22.00 and 1.60 min, respectively) and ${}^{2}n_{c}$ of 40 (with average 2D peak width and ${}^{2}t_R$ range of 0.13 and 5.00 min, respectively). The peak capacity of 52 was also approximated for the conventional 1D full scan GC-MS analysis. From 1D GC-MS with a SIM mode shown in Figure 8 the peak capacity from can be approximated as 1207. This contributed from 17 (from total number of SIM divided by 4 m/z per each compound) times 71 (from average peak width of 0.35 min, the first and latest eluting peak retention times of 6.41 and 31.20, respectively).

Although lower peak capacity was approximated from 1D GC-MS with a SIM mode, this was sufficient for analysis of the samples Although the same number of compounds could be obtained analyzed compared with the CH/C 2D GC-MS analysis, the analysis times and repeatability could also be expected to be better with less complicated experimental setup of the 1D GC-MS with a SIM mode analysis. in this study.

# CHAPTER V

# CONCLUSION

In this thesis, the 1DGC approach combined with mass spectrometry with selected ion monitoring (SIM) operation was developed and applied for analysis of volatile compounds in yellow curry pastes. In order to improve analysis of analytes**.** Firstly, CH/C 2D GC-MS with a restrictor column (1.5 m x 0.1 mm) was established for the analysis of yellow curry paste samples using an HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness), and a DB-WAX capillary column (60 m x 0.25 mm x 0.25 μm) as the $^{1}$D and $^{2}$D columns, respectively. Based on retention index from the DB-WAX capillary column and mass spectra from MS library match, The total profiles and were obtained 119 identified volatile compounds in the yellow curry paste sample were obtained in an MS full scan mode. The major components based on the peak area percentages were 2,2,3,4-tetramethyl pentane (18 %), α,α-dimethyl-benzene methanol (6 %) and 2-ethyl-6-methylphenol (8 %) which contributed to the smells of not available, green, sweet and not available, respectively.

Secondly, 1D GC-MS with a SIM mode was performed using the HP-5MS capillary column (30 m x 0.25 mm i.d., 0.25 μm film thickness). Using the information from CH/C 2D GC-MS, the selected *m/z* values for 1D GC-MS were characteristic of each compound with high intensity (major abundant within each characteristic group) in order to support compound identification and lead to significantly high peak areas in SIM results. Four *m/z* values were selected for each compound which resulted in the total 1D SIM analysis consisting of 111 *m/z* values of all the compounds observed with the 2D analysis. This offers effective untargeted analysis performance similar to that provided by high performance CH/C 2D GC-MS technique. This 1D GC-MS with a SIM mode clearly improves the performance of the separation increasing the capability of mass spectrometry with larger number of identified compounds using SIM mode compared with conventional 1D GC-MS

approach with full scan operation. Furthermore, this reduces analysis times from 25 injections with the CH/C 2D GC-MS to 5 injections for 1D GC-MS because of performance of the program in GC-MS with a SIM mode was set at 20 m/z /rounds and reduced the weight of sample from 2g (CH/C 2D GC-MS) in order to increase concentration of sample and observe profile of yellow curry paste to 1g (1D GC-MS with a SIM mode). This is also expected to provide improved repeatability compared with the CH/C 2DGC technique. In addition, 1D GC-MS with a SIM mode along with information from CH/C 2D GC-MS with a full scan mode may be applied to other samples.

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# VITA

| | |
|---|---|
| **NAME** | Natsuda Singtothong |
| **DATE OF BIRTH** | 09 Dec 1994 |
| **PLACE OF BIRTH** | Bangkok |
| **INSTITUTIONS ATTENDED** | Ramkhamhaeng University |
| **HOME ADDRESS** | 42/141 Casaleena2 Nimitmai Road. Nimitmail20 Soi. Saikongdin Klong Sam Wa Bangkok 10510. |