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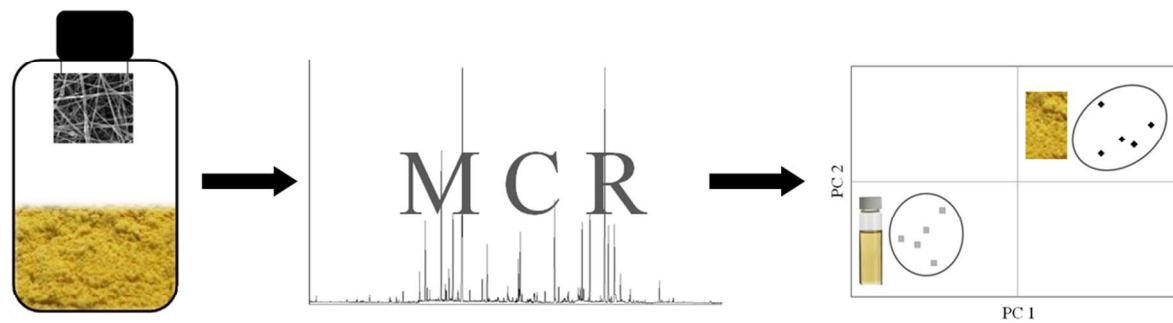
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Graphical abstract:

Polyaniline-nylon-6 nanocomposite for headspace adsorptive microextraction together with GC-MS and chemometrics were utilized as a novel procedure for comprehensive and comparative analysis of oregano fragrance and its essential oil.



Application of polyaniline-nylon-6 nanocomposite, GC-MS and chemometrics for rapid and comprehensive analysis of *Zingiber officinale* fragrance components

M. Asadollahi-Baboli<sup>\*,a</sup>, A. Aghakhani<sup>b</sup>

<sup>a</sup> Department of Science, Babol University of Technology, Babol 47148-71167, Mazandaran, Iran

<sup>b</sup> Department of Semiconductors, Materials and Energy Research Center, Karaj 31787-316, Iran

### Abstract

Ginger (*Zingiber officinale*) headspace has been extracted using novel polyaniline-nylon-6 (PANI-N6) nanocomposite, fabricated by electrospinning. GC-MS (gas chromatography-mass spectrometry) and chemometrics have been used to identify the components of the fragrance. Chemometric resolution techniques were utilized to improve the resolution, qualification and quantification of co-eluted compounds in GC-MS. In this way, chromatographic problems such as baseline/background contribution, low S/N peaks and co-elution occurred during chromatographic analysis are solved using the proposed strategy. Moreover, principal component analysis (PCA) was used to determine hidden structure and to identify those volatiles which were most differentiating between the fragrance and the essential oil of ginger. The results show that the fragrance and the essential oil of ginger are different enough in term of chemical composition to put them in two distinct classes using 17 components which account for the most of the variation. Among 62 identified components of ginger fragrance,  $\alpha$ -phellandrene (18.14%),  $\alpha$ -zingiberene (16.45%), (*E,E*)- $\alpha$ -farnesene (7.21%), camphene (5.47%) and geranial (4.38%) are the major components. The results proved that the present procedure may be useful for comprehensive analysis of complex natural aroma such as ginger fragrance.

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\* Corresponding author: Tel.: +981113232071(ext.1721); fax: +981113234201.

E-mail address: [asadollahi@nit.ac.ir](mailto:asadollahi@nit.ac.ir) (M. Asadollahi-Baboli).

**Keywords:**

Polyaniline-nylon-6 nanocomposite, Chemometrics, Fragrance analysis, GC-MS, *Zingiber officinale*

**1 Introduction**

Ginger (*Zingiber officinale*) is a commonly used spice, flavoring agent and herbal medicine. It is extensively used in the formation of compounded aromas for flavoring confectionery, bakery products, perfumes, condiments, sauces and carbonated beverages. Ginger is one of the most ancient spice plants in most tropical and subtropical regions of the world and is used to spice food in most of Middle East and Asian cuisines.<sup>1</sup> In addition, ginger has some medicinal properties including an anti-emetic effect, prevention of coronary artery disease, healing and prevention of arthritic conditions and stomach ulcers, useful against tumour growth, rheumatism and migraine.<sup>2</sup> Volatile composition of ginger has been studied using essential oil obtained from hydrodistillation.<sup>3-5</sup> However, the produced oil in this process has different composition from the original fragrance due to the heat applied during extraction. However, by applying an appropriate headspace preconcentration step, it is possible to analyze the ginger fragrance directly as limit of detection has lowered. Recent approaches based on the headspace adsorptive microextraction, provide advantages of being lower sample consumption, higher sample preparation speed, ease of operation and little solvent usage.<sup>6</sup> To improve the sensitivity of the headspace adsorptive microextraction, nanostructured materials can be used because the interactions between the desired analytes and the sorbent are increased. This could be due to the enhancement of surface to volume ratio as the size of the sorbent particles is reduced extensively. In this work, polyaniline (PANI) was synthesized inside the nylon-6 (N6) solution as a carrier polymer, and a

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3 composite of polyaniline-nylon-6 (PANI-N6) was electrospun into the fibrous sheet with nano-  
4 scale dimensions.<sup>7</sup> Then, the prepared composite was applied for the headspace adsorptive  
5 microextraction of ginger fragrance because of high surface to volume ratio, suitable functional  
6 groups and high porosity.  
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11 The complexity of natural samples means that separation technique is necessary together with  
12 mass spectrometry. Thus, gas chromatography-mass spectrometry (GC-MS) has been used due  
13 to the high sensitivity and the low limit of detection. Nevertheless, presence of different  
14 chromatographic problems, such as baseline drift, low S/N peaks and co-elution, makes isolation  
15 and identification difficult.<sup>8</sup> Multivariate chemometric methods can overcome these problems  
16 and improve the qualification and quantification of co-eluted compounds.<sup>9</sup> In the present  
17 contribution, a new strategy based on headspace adsorptive nanocomposite microextraction, GC-  
18 MS and chemometric methods was proposed for the comprehensive analysis of ginger fragrance.  
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20 (1) PANI-N6 nanocomposite was applied for the headspace adsorptive microextraction under the  
21 optimum analytical conditions. (2) GC-MS was used to generate the informative second-order  
22 data. (3) Multivariate curve resolution-alternation least square (MCR-ALS) together with other  
23 chemometric methods was used to improve the resolution, qualification and quantification of co-  
24 eluted compounds in GC-MS.<sup>10</sup> (4) Principal component analysis (PCA) was used to represent  
25 changes in chemical compositions of the fragrance and the essential oil of ginger among different  
26 samples.<sup>11</sup>  
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## 50 **2 Experimental**

### 51 *2.1. Materials and reagents*

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3 Rhizomes of ginger were sliced into small pieces and air-dried in a shaded place at ambient  
4 temperature (25 °C) until constant weight. Plant materials were collected from the zone of  
5 Tabriz, Northwest Iran. The air-dried plant material was grinded to obtain a homogenous fine-  
6 grade powder and was kept at 4 °C in the absence of light. Acetone, chloroform, ethanol,  
7 ethylacetate, formic acid, hexane, Aniline and Ammonium peroxodisulphate were purchased  
8 from Merck Co. Nylon-6 (N6) was obtained from Kolon Industries Inc. (Seoul, Korea).  
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## 20 *2.2. Electrospinning of PANI-N6 nanocomposite*

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22 The polymeric solution was obtained by dissolving 0.25 g of N6 and 0.1 g of ammonium  
23 peroxodisulphate salt in 1 mL of formic acid. Then aniline monomer (0.5 g) was added to the  
24 solution to obtain a homogenous solution. The aluminum foil (10× 10 cm) collector and the  
25 polymer containing syringe needle were connected to the high voltage power supply terminals. A  
26 voltage of 16 kV was applied for the nanofibers production while a flow rate of 1.5  $\mu\text{L min}^{-1}$   
27 was set for the syringe pump to deliver the polymer solution. All the electrospinning processes  
28 were performed under the ventilation for 12h. After the electrospinning experiment, a sheet with  
29 a typical dimension of 1×1 cm, was cut from the central part of the Al foil employed for  
30 headspace adsorptive microextraction. The procedure, chemical characteristics and physical  
31 properties of the PANI-N6 nanocomposite was described in the work of Bagheri and  
32 Aghakhani.<sup>7</sup>  
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## 51 *2.3. Headspace adsorptive microextraction and essential oil extraction*

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53 Rhizomes of ginger (5 g) were placed into a 50 mL glass vial with PANI-N6 nanocomposite  
54 above it to collect fragrance volatiles for 30 min at room temperature (25 °C). The  
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3 nanocomposite was conditioned in ethanol for 10 min prior to the extraction. After the headspace  
4 adsorptive microextraction, the nanocomposite was folded and inserted inside a 5 mL glass vial  
5 for solvent desorption and was concentrated by a gentle flow of nitrogen up to 0.5 mL. The final  
6 organic extracts were stored at 4 °C in the absence of light. For essential oil extraction, A 30 g  
7 sample of air-dried powdered ginger was extracted by the hydrodistillation technique during 3  
8 hours in a full glass Clevenger-type apparatus. The extracted crude essential oil (yield 1.45%,  
9 w/w) was dried over anhydrous sodium sulphate and stored in a sealed vial with a rubber lid,  
10 covered with aluminum foil to protect the contents from photo-conversion, and kept under  
11 refrigeration at 4 °C until analysis. Eventually an aliquot of the 1 µL for each organic extract and  
12 the essential oil was injected into the GC-MS.  
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#### 29 *2.4. Apparatus*

31 An aliquot of the 1 µL for each organic extract and the essential oil was injected into an Agilent  
32 HP-6890 gas chromatograph coupled with Agilent HP-5973 mass selective detector equipped  
33 with a 30 m×0.25 mm HP-5MS fused silica column (0.25 µm film thickness). The MS was  
34 operated in the EI mode (70 eV). Helium (99.999%) was employed as carrier gas and its flow  
35 rate was adjusted to 1 mL min<sup>-1</sup>. The GC column temperature was programmed from 60 to 220  
36 °C at 3 °C/min and held for 20 min. The injector temperature was set at 230 °C in the split ratio  
37 of 1:5. Mass range scanned from 40 m/z to 440 m/z. A Brandenburg (West Midlands, England)  
38 regulated power supply and a KDS100 syringe pump (KdScientific Co., Holliston, MA, US)  
39 were used for electrospinning and the polymer solution delivery in the electrospinning process,  
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## 2.5. Chemometric analysis

In this work, chemometric resolution techniques were utilized to extract the pure mass spectrum and chromatographic profile of each co-eluted component from decomposition of two-way data of the original GC-MS data matrix. The detailed theories behind these powerful and handy procedures are given elsewhere.<sup>9-12</sup> However, the chemometric resolution procedure is described briefly in this work to make the article more consistent and understandable. First, some preprocessing methods such as baseline/background correction, denoising and smoothing should be done for each peak cluster. Congruence analysis and least square fitting method developed by Liang and Kvalheim<sup>11</sup> were used for the baseline/background correction. The method of morphological score<sup>13</sup> is used for denoising because it is able to discriminate the signal from the noise. The Savitsky-Golay filter is also used for smoothing filter. Second, essential steps of morphological score and FSMW-EFA techniques<sup>14</sup> were applied to assess chemical rank determination and local rank analysis, respectively. The morphological score is based on the fact that the ratio of the norm of a spectrum to the norm of its first difference is higher for a profile of a component than a profile generated only by noise. In this method, in order to avoid accumulation of noise and obtaining reliable results, only some key factors are analyzed instead of the full rank matrix. In FSMW-EFA technique, PCA analyses are performed on fixed size windows moved row by row downwards along the elution direction. The FSMW-EFA plot shows the eigenvalues obtained in all the PCA analyses as it was done in EFA. This representation contains the information on the compound overlap in the elution direction. In FSMW-EFA plots, the logarithmic of eigenvalues higher than the noise level shows the presence of a new component. Next, MCR-ALS algorithm was applied for resolving the co-eluted GC-MS peak clusters into pure chromatograms and mass spectra after applying proper constraints. This



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3 algorithm starts with initial estimates obtained by the SIMPLISMA until the concentration and  
4 pure spectra optimally fit in the experimental data matrix.<sup>15</sup> Finally, resolved mass spectra were  
5 compared with those of mass libraries in order to confirm the quality and reliability of results.  
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10 The above procedure was performed for every overlapped peak cluster. MCRC software was  
11 used for preprocessing, chemical rank determination, local rank analysis and MCR-ALS.<sup>16</sup> Other  
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14 programs for the chemometric resolution methods were coded in MATLAB 7 by the authors.  
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### 20 **3 Results and discussion**

#### 21 *3.1. Headspace adsorptive microextraction using PANI-N6 nanocomposite*

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Headspace adsorptive microextraction has been employed in order to extract the volatiles of ginger fragrance. In this work, PANI-N6 nanocomposite was employed for headspace adsorptive microextraction because of its high surface to volume ratio, porosity and suitable functional groups. Low polar compounds such as hydrocarbon monoterpenes and hydrocarbon sesquiterpenes can be easily extracted through  $\pi$ - $\pi$  and hydrophobic interactions with conjugated structure in PANI. Additionally, high polar compounds such as oxygenated monoterpenes, oxygenated sesquiterpenes and esters can be extracted through polar and hydrophilic interactions with NH and C=O functional groups in N6. The web-like structure of the nanocomposite with size of around 10 nm makes the nanocomposite very porous with high surface area, which should result in a significantly increased surface area availability and higher mass transfer during the extraction as well as the analyte desorption process. In the next step, effects of desorption solvent (acetone, chloroform, ethanol, ethylacetate, and hexane,) on the extraction efficiency were investigated to facilitate the best performance. The height of the bars in Fig. 1 represents the relative composition of volatiles of ginger fragrance quantities in each desorption solvent in

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3 terms of peak area. Volatiles were classified into five chemical groups consisting of monoterpene  
4 hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpene  
5 and miscellaneous compounds. The last group contains aliphatic hydrocarbons, aromatic  
6 compounds, alcohols, esters and ketones. As shown in Fig. 1, hexane was acting as the best  
7 solvent for the desorption process in headspace adsorptive microextraction. It should be noted  
8 that PANI-N6 was stable in these organic solvents.  
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### 20 *3.2. Chemometric analysis of ginger fragrance*

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22 Total ion chromatogram (TIC) of the volatiles of ginger fragrance obtained from GC-MS is  
23 shown in Fig. 2. From this figure, it is clear that the chemical composition of the ginger  
24 fragrance is pretty complicated. Therefore, direct searching of mass spectrum library may lead to  
25 incorrect identifications without further data processing. For example, different compounds  
26 could be obtained at different scan points of a co-eluted peak using direct library searching. As  
27 well, it is difficult to identify low concentration components since two-way GC-MS data usually  
28 contains some peaks associated with column background. These problems can be solved by  
29 resolving co-eluted components into pure chromatograms and mass spectra using chemometric  
30 resolution techniques. The TIC was divided into chromatographic segments using zero  
31 component regions along elution sequence. According to the morphological score method some  
32 of these chromatographic segments are single component peaks. These peaks can be easily  
33 identified and quantified by direct library searches. However, the main difficulties are in the case  
34 of peak clusters with overlapping compounds. In order to illustrate the resolution procedure  
35 using chemometric resolution techniques, peak cluster A was selected as an example from Fig. 2.  
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3 Peak clusters **A** has scan number range from 8283 (51.35 min) to 8370 (51.78 min) and its local  
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5 TIC is shown as a subset in this figure.  
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8 The chemical rank of the peak cluster **A** was determined using morphological score plot after  
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10 performing denoising, baseline correction and smoothing. It is clear from Fig. 3 that there are  
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12 five components in this peak cluster having the number of singular vectors with the  
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14 morphological scores upper than that of the noise levels. Then, peak purity of two-way data can  
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16 be determined using FSMW-EFA rank map as shown in Fig. 4. In this rank map plot, the  
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18 logarithmic curve of eigenvalues higher than the noise level represents the presence of a new  
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20 component. From this plot one may obtain some information about the number of zero  
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22 components, overlap and selective regions. This plot also shows that there are five components  
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24 for the peak cluster **A** (marked by numbers) which confirms the results obtained from chemical  
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26 rank determination. Finally, the peak cluster **A** has been uniquely resolved into chromatographic  
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28 profiles and mass spectra of related components using MCR-ALS. Moreover, SIMPLISMA  
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30 method was used for initial estimation together with non-negativity, unimodality, and selectivity  
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32 constraints. The resolved chromatogram of the peak cluster **A** is shown in Fig. 5. The  
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34 components of the resolved peak cluster **A** can be identified by similarity searches using the  
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36 NIST database. The components in the peak cluster **A** are bicyclosquiphellandrene,  $\gamma$ -  
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38 gurjunene, germacreneD,  $\gamma$ -curcumene and  $\alpha$ -curcumene with high reverse match factor (RMF)  
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40 of 942, 980, 954, 981 and 958, respectively. RMF is calculated in the same way as the match  
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42 factor. However, all peaks in the sample spectrum that are not in the library spectrum are  
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44 disregarded when it is calculated. This is especially useful when the spectrum represent more  
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46 than a single compound. Finally, the reliability of the results was confirmed by comparing the  
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48 Kovats retention indices of the resolved components with those of the pure ones. The  
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3 components in other peak clusters are resolved in a similar way. In order to evaluate the  
4 performance of the resolution technique, resolved and standard mass spectra for two components  
5 ( $\alpha$ -phellandrene and  $\alpha$ -zingiberene) are shown in Fig. 6, as examples. As this Figure shows there  
6 is a good agreement between resolved and standard mass spectra. Table 1 shows the 62 identified  
7 components for volatiles of ginger fragrance using GC-MS combined with chemometrics.

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9 For each component, the outer product of the concentration and spectrum vectors shows the total  
10 two-way response. The total amount of each component is proportional to the overall volume of  
11 its two-way response. Overall volume integration (OVI) was applied for computing the quantity  
12 of each component after implementing chemometric resolution techniques.<sup>17</sup> The advantage of  
13 this method over the general peak area integration is that all mass spectra absorbing points are  
14 taken into consideration and much more accurate results can be reached. As well, it avoids the  
15 disadvantage that general peak area approximately treated by peak split. It should be noted that  
16 the relative amount of the extracted compounds is expressed as a percentage of the obtained peak  
17 area relative to the total area of all peaks of the TIC. The final relative quantitative results of the  
18 volatile components of ginger fragrance are listed in Table 1 having concentrations higher than  
19 0.1%. It should be noted that it is not possible to perform quantitative analysis for co-eluted  
20 peaks without using chemometric resolution techniques. In the peak cluster **A**, the relative  
21 percentages of bicyclosesquiphellandrene,  $\gamma$ -gurjunene, germacreneD,  $\gamma$ -curcumene and  $\alpha$ -  
22 curcumene are 0.52, 0.28, 0.43, 3.32 and 0.32, respectively.

### 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 *3.3. Comparative analysis of the fragrance and the essential oil*

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Ginger essential oil was analyzed using hydrodistillation and GC-MS as described in  
experimental section. The chromatographic profiles of the overlaid TICs of the essential oil and

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3 the fragrance were depicted in Fig. 2. The chemical composition of the essential oil was also  
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5 obtained using chemometrics and was tentatively identified using NIST. In addition, PCA was  
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7 used to identify inherent patterns in the data in an unbiased way and to highlight the similarities  
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9 and differences amongst the fragrance and the essential oil of ginger. This technique helps  
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11 determine hidden structure and to determine those volatiles which were most differentiating  
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13 within the entire data. PCA method was performed using the final relative areas of the well  
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15 resolved peaks. Fig. 7a and b depicts the score and loading plots for ten samples. The PC1 and  
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17 PC2 explained 58.26% and 21.08% of the total variance, respectively. It can be seen from Fig. 7a  
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19 that the fragrance and the essential oil of ginger are easily distinguishable as two distinct classes,  
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21 and the variation within each class is well within acceptable limits. The loading plot (Fig. 7b)  
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23 reveals the influence of each component in differentiating between the fragrance and the  
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25 essential oil of ginger. Those components that account for maximum variance in the data set are  
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27 given more weight or loading. The 17 components which account for the most of the variance  
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29 are represented on the loadings plot. These results show that the fragrance and the essential oil of  
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31 ginger are different enough in term of chemical composition to put them in two distinct classes.  
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33 Table 1 shows the volatile components and the relative percentage of each component in the  
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35 fragrance and the essential oil of ginger. The reproducibility in peak responses was investigated  
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37 using three replicate experiments ( $n = 3$ ) for the fragrance and the essential oil samples. Kovats  
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39 retention index (RI) for each component in HP-5MS was calculated and can be used as a  
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41 complementary tool for the identification. The RIs of all the components were calculated by  
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43 logarithmic interpolation between bracketing n-alkanes. The relative standard deviations (RSD),  
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45 RMF and RI for the components in both samples are presented in Table 1. The results show that  
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47  $\alpha$ -phellandrene (18.14%) is the main component followed  $\alpha$ -zingiberene (16.45%), (*E,E*)- $\alpha$ -  
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3 farnesene (7.21%), camphene (5.47%) and geranial (4.38%) in ginger fragrance. Ginger essential  
4 oil contains  $\alpha$ -zingiberene (26.60%) as main component followed by  $\gamma$ -curcumene (9.12%),  
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6 (*E,E*)- $\alpha$ -farnesene (8.50%), camphene (7.46%) and  $\beta$ -bisabolene (4.31%). There are some studies  
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8 reports these major compounds in the essential oil as important pesticides, antibacterial,  
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10 antioxidant, antiproliferative and antilipase, yet this is the first study on the fragrance using  
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12 headspace adsorptive microextraction and chemometrics tools.<sup>18-20</sup> As shown in Table 1, ginger  
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14 fragrance has less volatile components (62 components) than ginger essential oil (76  
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16 components). The volatile components of ginger fragrance belong to monoterpene hydrocarbons  
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18 (34.05%), oxygenated monoterpenes (14.25%), sesquiterpene hydrocarbons (42.75%),  
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20 oxygenated sesquiterpene (2.47%) and miscellaneous groups (4.12%). The fragrance has more  
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22 light volatiles with higher percentage. On the other hand, the essential oil contains both light and  
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24 heavy volatiles because of high temperature and long extraction time during extraction. These  
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26 differences are probably due to production of thermal artifacts such as oxidization,  
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28 decomposition and rearrangement during hydrodistillation.  
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#### 39 **4 Conclusion**

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41 The volatile components of ginger fragrance were extracted and identified using headspace  
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43 adsorptive microextraction with PANI-N6 nanocomposite together with GC-MS and  
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45 chemometrics. High surface area, porosity and suitable functional groups make PANI-N6  
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47 nanocomposite a suitable candidate for headspace adsorptive microextraction. In addition, the  
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49 GC-MS suffer from fundamental problems such as baseline and background contribution, low  
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51 S/N peaks and co-elution. Hence, chemometrics were employed for accurate qualification and  
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53 quantification of co-eluted compounds. A total of 62 components of ginger fragrance were  
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3 identified using proposed strategy. Furthermore, the components responsible for differentiation  
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5 of the fragrance and the essential oil of ginger were also determined using PCA. Inspection of  
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7 the results confirmed the achievement of more reliable results with time and work saving using  
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9 PANI-N6 nanocomposite together with GC-MS and chemometrics.  
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**Table 1.** Volatile components of the fragrance and the essential oil of ginger using proposed procedure.

No.	Chemical name <sup>a</sup>	RI <sup>b</sup>	RMF <sup>c</sup>	Percentage			
				Ginger fragrance	RSD <sup>d</sup>	Ginger essential oil	RSD
1	Tricyclene	928	960	0.51	7.35	0.15	4.38
2	$\alpha$ -Thujene	931	942	0.32	7.44	0.12	8.47
3	$\alpha$ -Pinene	941	978	3.13	4.16	2.66	6.09
4	Camphene	953	983	<b>5.47</b>	3.60	<b>7.46</b>	2.68
5	Sabinene	974	940	-	-	0.20	3.13
6	$\beta$ -Pinene	980	960	0.38	8.86	0.19	10.71
7	Myrcene	992	970	2.10	7.18	0.86	8.83
8	$\alpha$ -Phellandrene	1007	991	<b>18.14</b>	3.45	3.46	4.35
9	$\Delta$ -3-Carene	1013	968	0.13	12.47	0.15	11.54
10	$\alpha$ -Terpinene	1022	986	0.31	9.23	0.17	3.99
11	<i>p</i> -Cymene	1026	920	0.25	8.97	0.18	5.44
12	$\beta$ -Phellandrene	1031	955	2.25	6.23	3.47	3.63
13	( <i>Z</i> )- $\beta$ -Ocimene	1040	924	0.23	9.23	0.23	10.54
14	( <i>E</i> )- $\beta$ -Ocimene	1052	948	0.11	8.66	0.23	6.45
15	$\gamma$ -Terpinene	1064	952	0.19	11.74	0.31	12.25
16	Terpinolene	1086	954	0.14	11.58	0.18	2.74
17	1,3,8-p-Menthatriene	1112	969	0.39	4.30	-	-
<b>Monoterpene hydrocarbons</b>				<b>34.05</b>		<b>20.03</b>	
18	1,8-Cineole	1036	953	1.21	5.23	0.75	7.81
19	4-Thujanol	1069	980	0.67	11.02	0.18	5.00
20	Linalool	1099	937	1.23	4.65	0.54	8.97
21	Sabinol	1138	966	0.17	10.90	0.22	9.03
22	Camphor	1144	969	0.10	8.16	0.24	2.77
23	Isopulegol	1146	978	0.12	9.80	-	-
24	Camphenehydrate	1150	954	-	-	0.22	5.72
25	Citronellal	1156	992	0.34	9.54	0.24	8.12
26	endo-Borneol	1167	950	0.46	9.22	0.85	6.08
27	Terpinen-4-ol	1177	962	0.10	8.00	0.17	8.62
28	$\alpha$ -Terpineol	1189	915	3.16	4.34	2.27	4.56
29	Nerol	1230	997	0.11	9.03	0.26	5.41
30	Citronellol	1231	960	0.30	4.44	0.40	7.74
31	Neral	1244	939	1.27	9.79	0.78	8.06
32	Geraniol	1253	920	0.63	5.07	0.55	7.68
33	Geranial	1273	962	<b>4.38</b>	3.45	1.62	5.27
<b>Oxygenated monoterpenes</b>				<b>14.25</b>		<b>9.29</b>	
34	$\Delta$ -Elemene	1340	921	0.14	12.69	0.18	6.48
35	Cyclosativene	1370	957	1.68	3.21	0.12	4.55
36	$\alpha$ -Copaene	1379	929	0.55	8.55	0.23	7.21
37	$\beta$ -Elemene	1396	958	0.10	4.43	0.64	5.34

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4	38	$\beta$ -Caryophyllene	1420	986	0.54	12.64	0.14	6.44
5	39	$\gamma$ -Elemene	1434	910	0.44	11.50	0.15	11.71
6	40	<i>trans</i> - $\alpha$ -Bergamotene	1437	916	0.26	6.25	0.18	8.05
7	41	Aromadendrene	1442	931	0.13	11.31	0.18	9.68
8	42	<i>trans</i> - $\beta$ -Farnesene	1460	935	-	-	0.17	4.64
9	43	Bicyclosesquiphellandrene	1472	942	0.52	5.82	-	-
10	44	$\gamma$ -Gurjunene	1475	980	0.28	8.44	0.17	5.94
11	45	GermacreneD	1479	954	0.43	12.82	1.15	11.50
12	46	$\gamma$ -Curcumene	1481	981	3.32	8.23	<b>9.12</b>	4.11
13	47	$\alpha$ -Curcumene	1482	958	0.34	4.18	0.24	5.93
14	48	$\alpha$ -Muuroolene	1491	963	4.13	2.45	1.21	5.27
15	49	Valencene	1493	946	0.23	3.92	1.57	9.40
16	50	$\alpha$ -Zingiberene	1495	980	<b>16.45</b>	4.80	<b>26.60</b>	3.25
17	51	$\beta$ -Bisabolene	1505	938	3.45	8.86	<b>4.31</b>	4.04
18	52	( <i>E,E</i> )- $\alpha$ -Farnesene	1516	973	<b>7.21</b>	2.76	<b>8.50</b>	2.59
19	53	$\Delta$ -Cadinene	1525	917	0.10	10.18	0.25	11.39
20	54	$\beta$ -Sesquiphellandrene	1526	943	2.45	6.64	3.70	12.07
21	55	GermacreneB	1558	930	-	-	0.45	5.31
22		<b>Sesquiterpene hydrocarbons</b>			<b>42.75</b>		<b>59.25</b>	
23	56	Elemol	1550	937	0.21	5.23	0.56	2.78
24	57	Cubenol	1561	950	-	-	0.28	3.30
25	58	Caryophyllene oxide	1587	932	-	-	0.35	6.48
26	59	Sesquisabinene hydrate	1605	961	-	-	0.14	6.06
27	60	<i>trans</i> -Nerolidol	1566	954	0.10	9.04	0.55	5.62
28	61	Zingerone	1625	916	-	-	0.17	4.52
29	62	<i>Epi</i> - $\alpha$ -muurolol	1642	912	0.11	7.83	0.43	5.67
30	63	$\beta$ -Eudesmol	1651	971	0.18	7.17	0.46	3.68
31	64	$\alpha$ -Bisabolol	1690	943	-	-	0.26	7.10
32	65	( <i>Z,Z</i> )-farnesol	1694	932	-	-	0.30	12.46
33	66	( <i>Z,E</i> )-farnesol	1699	955	1.87	3.96	1.15	7.34
34	67	( <i>E,E</i> )-farnesol	1745	919	-	-	0.31	6.08
35	68	( <i>Z</i> )-lanceol	1763	948	-	-	0.10	8.93
36		<b>Oxygenated sesquiterpenes</b>			<b>2.47</b>		<b>5.08</b>	
37	69	6-Methyl-5-hepten-2-one	984	943	0.34	12.10	0.39	5.07
38	70	n-Octanal	1002	937	0.52	10.77	0.44	5.43
39	71	n-Octanol	1072	943	0.34	4.68	0.45	3.20
40	72	2-Nonanone	1095	909	-	-	0.55	3.37
41	73	Nonanal	1104	964	0.45	5.12	-	-
42	74	Decanal	1206	958	-	-	0.13	10.54
43	75	Bornylacetate	1289	967	2.25	3.28	0.68	2.56
44	76	2-Undecanone	1294	974	-	-	0.22	9.32
45	77	Pentadecane	1500	985	0.22	3.12	0.49	8.32
46	78	Tetradecanoic acid	1768	936	-	-	0.31	7.94

79	Curcumenyl acetate	1807	958	-	-	0.68	3.50
80	Hexahydrofarnesyl acetone	1848	935	-	-	0.17	7.45
<b>Miscellaneous compounds</b>				<b>4.12</b>		<b>4.52</b>	

<sup>a</sup> Identification was made according to comparison of resolved mass spectra with those of standards in MS Library Database and Kovats retention indices.

<sup>b</sup> Kovats retention indices in HP-5MS column in reference to normal alkanes.

<sup>c</sup> Reverse match factor for the resolved MCR-ALS mass spectrum and the standard mass spectrum in NIST MS database.

<sup>d</sup> Relative standard deviation (RSD) for three times repetition (n = 3).

**Figure captions**

**Fig. 1.** Influence of various solvents on the desorption efficiency of volatiles of ginger fragrance categorized into five chemical groups.

**Fig. 2.** The overlaid TICs of ginger fragrance and its essential oil together with the local TIC of the peak cluster **A**.

**Fig. 3.** Morphological score plot for the peak cluster **A**.

**Fig. 4.** FSMW-EFA plot for peak cluster **A** after heteroscedastic noise ~~correction~~ reduction.

**Fig. 5.** Resolved chromatograms of peak cluster **A** using MCR-ALS method.

**Fig. 6.** Resolved (a, c) and standard mass spectra (b, d) for  $\alpha$ -phellandrene and  $\alpha$ -zingiberene, respectively.

**Fig. 7.** PCA plot of the fragrance and the essential oil of ginger samples. (a) Score plot and (b) loading plot.

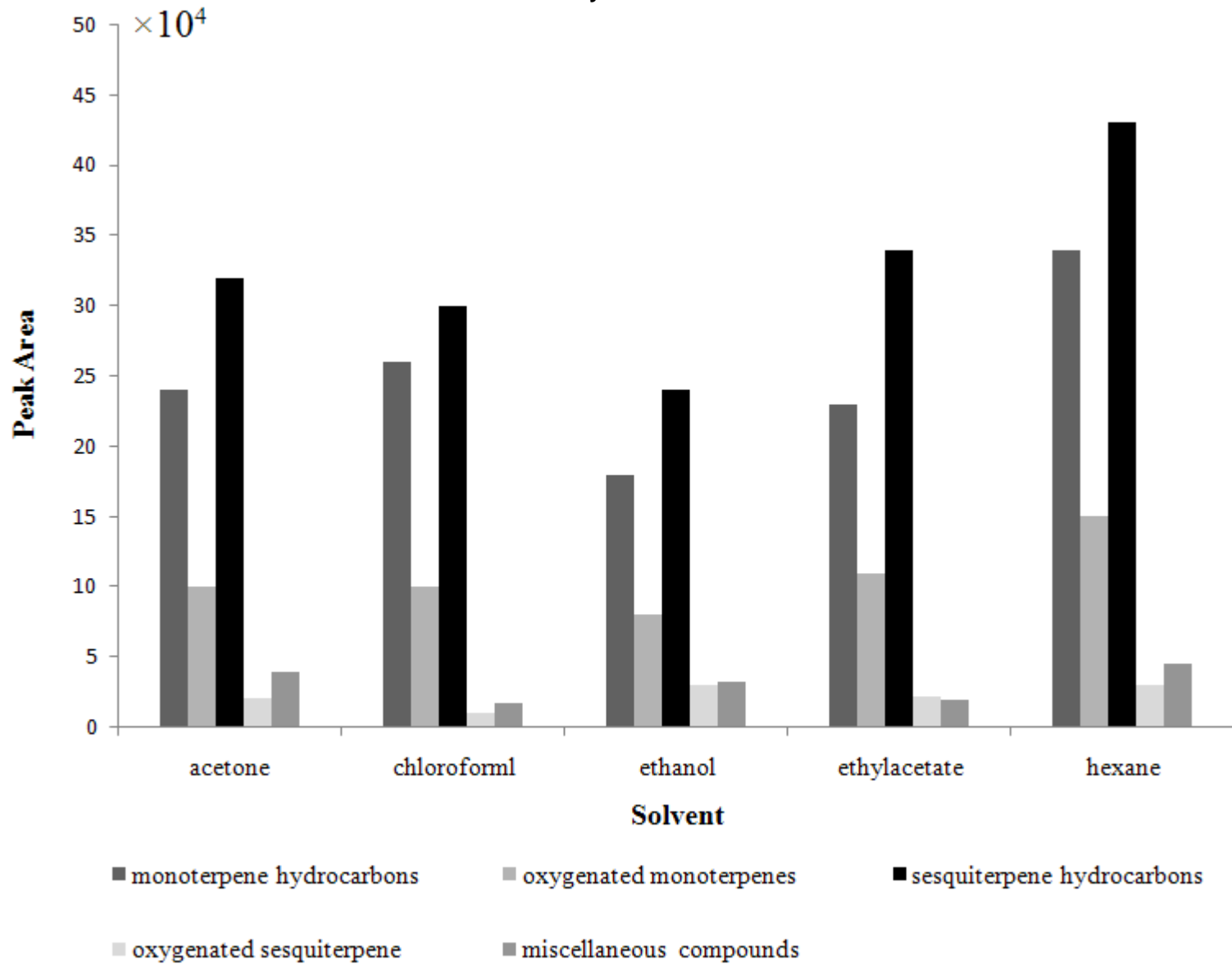


Fig. 1

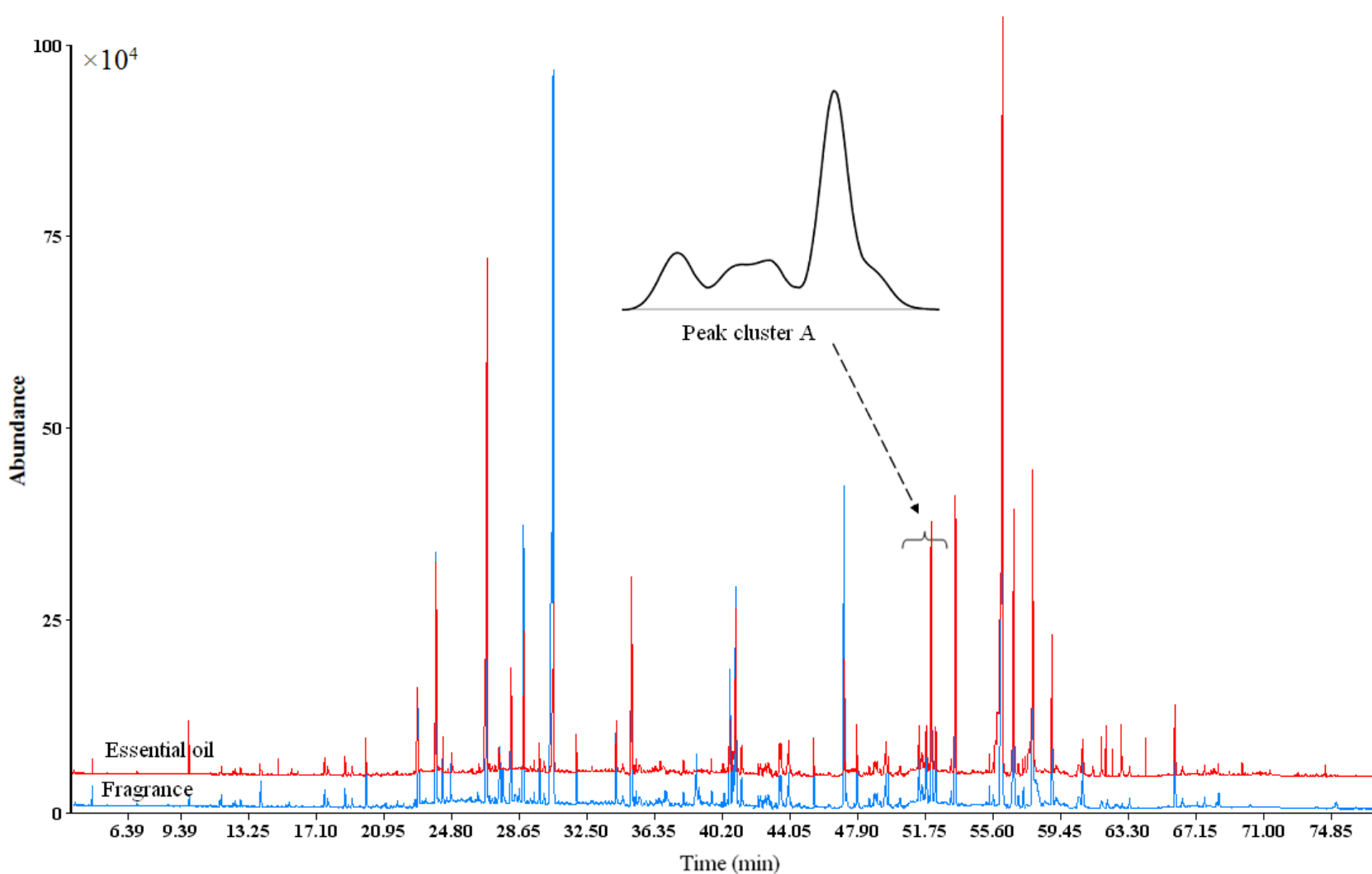


Fig. 2

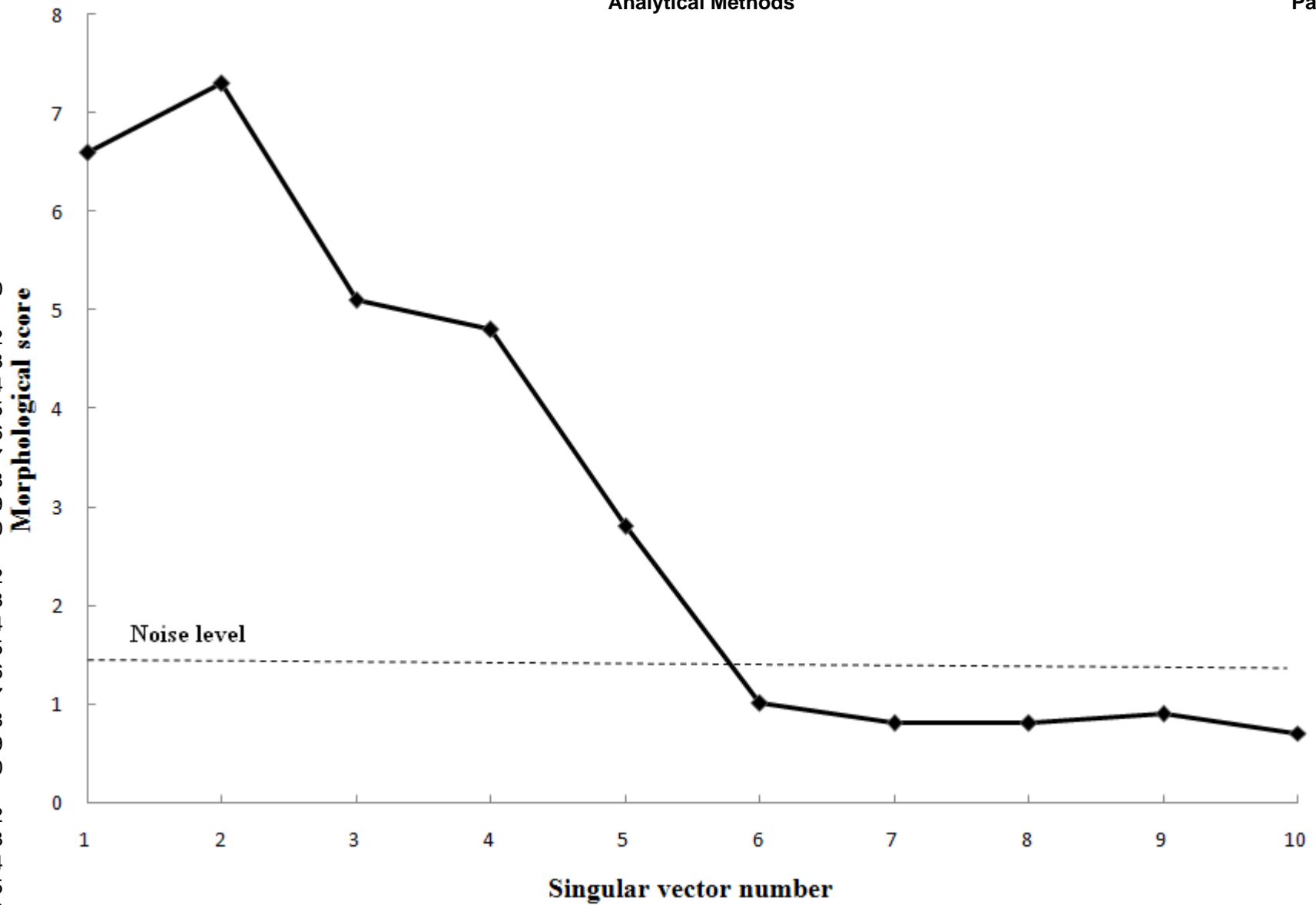


Fig. 3

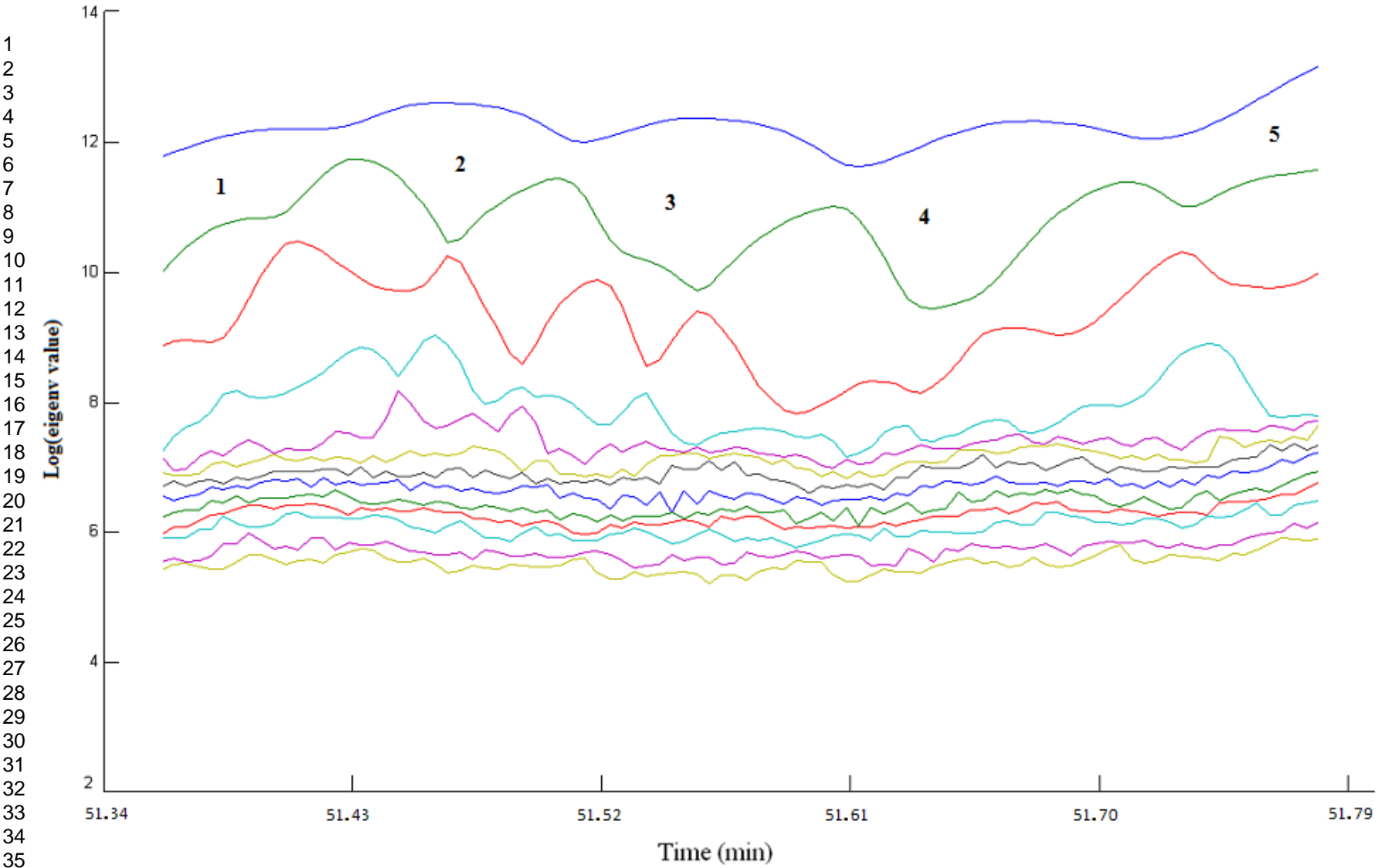
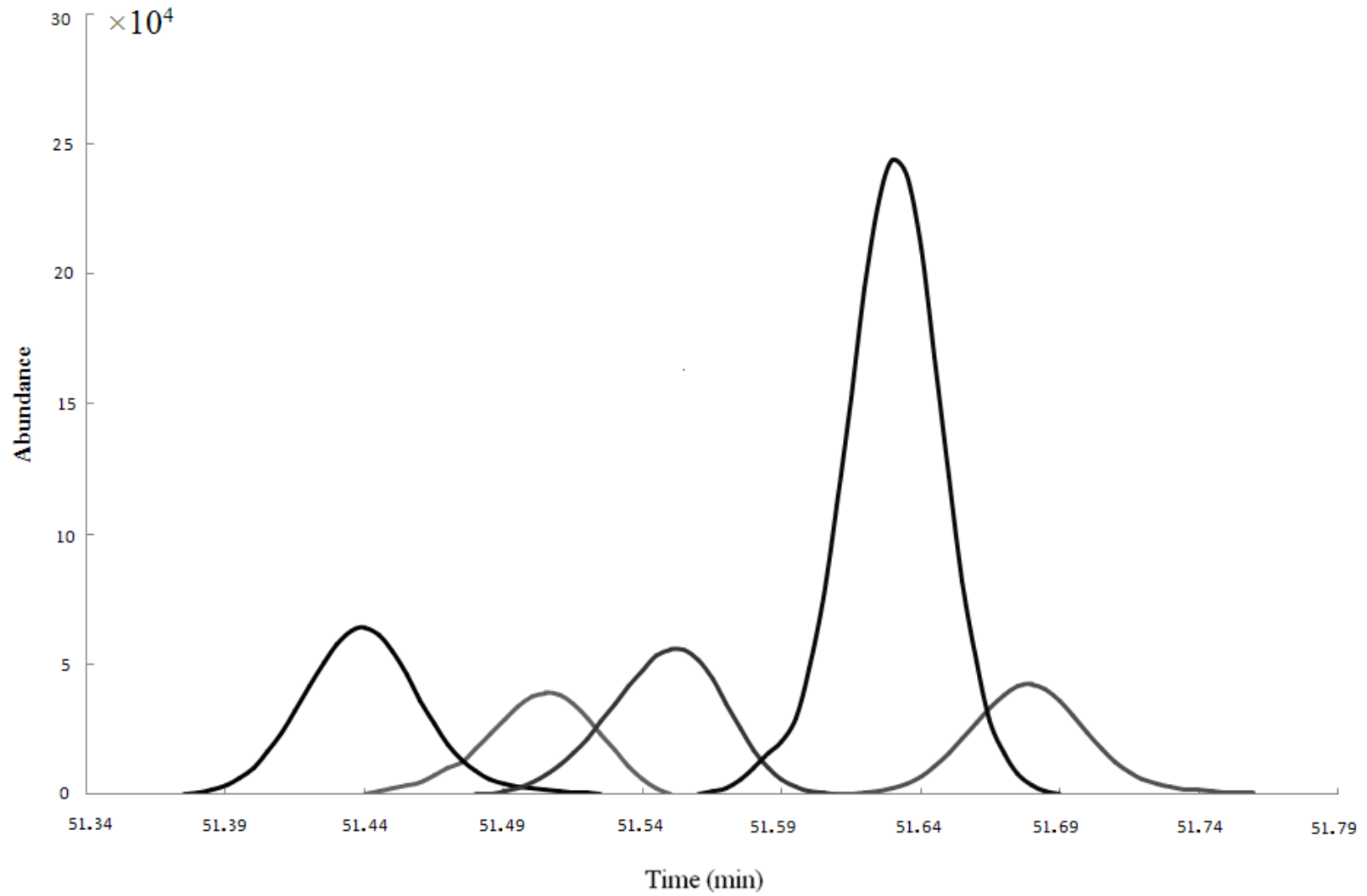


Fig. 4



**Fig. 5**

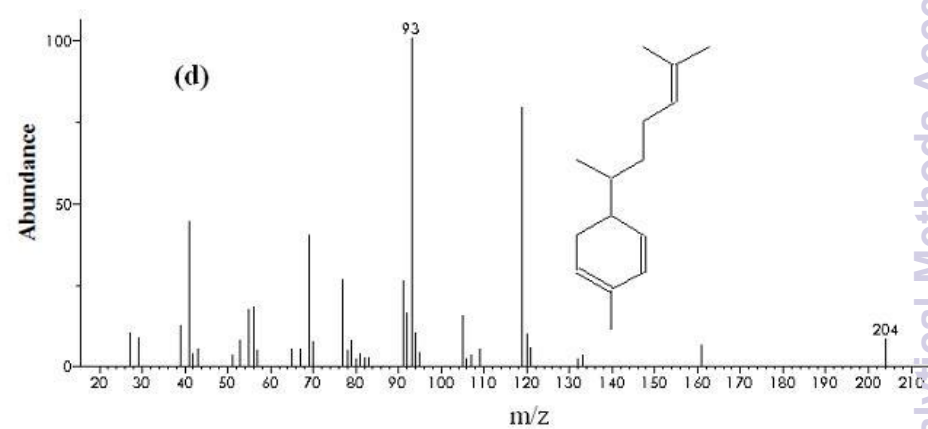
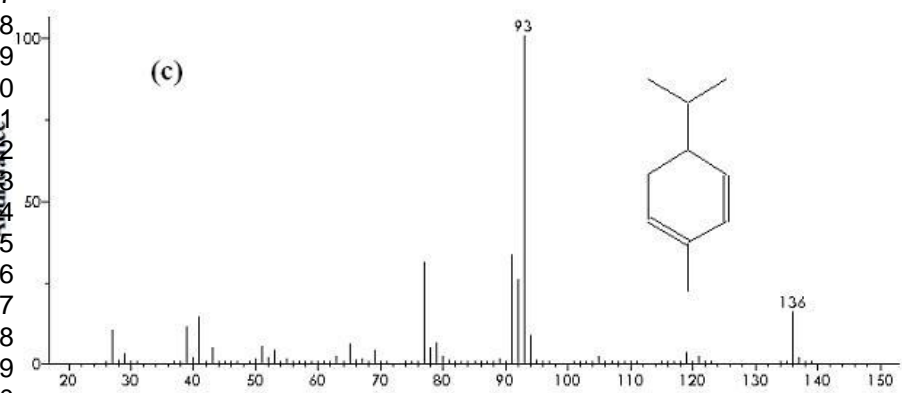
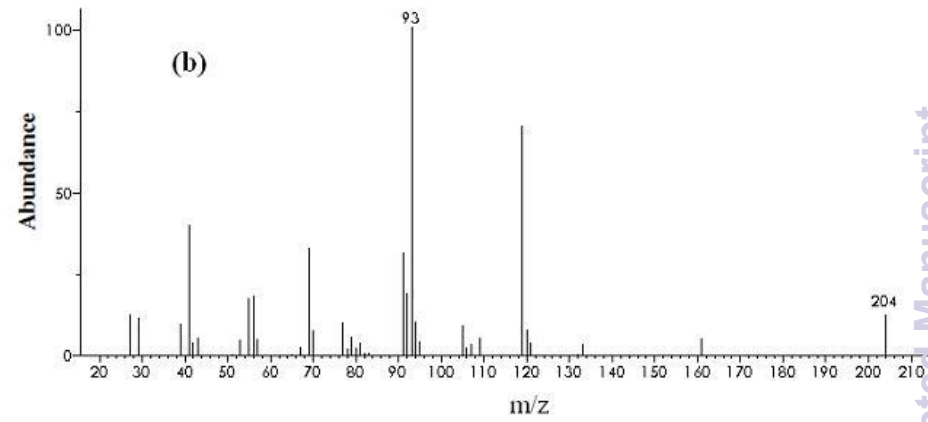
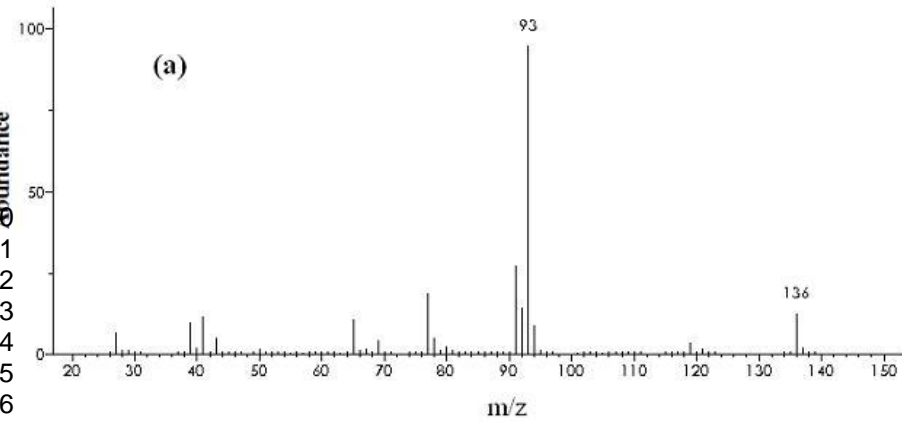
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Fig. 6

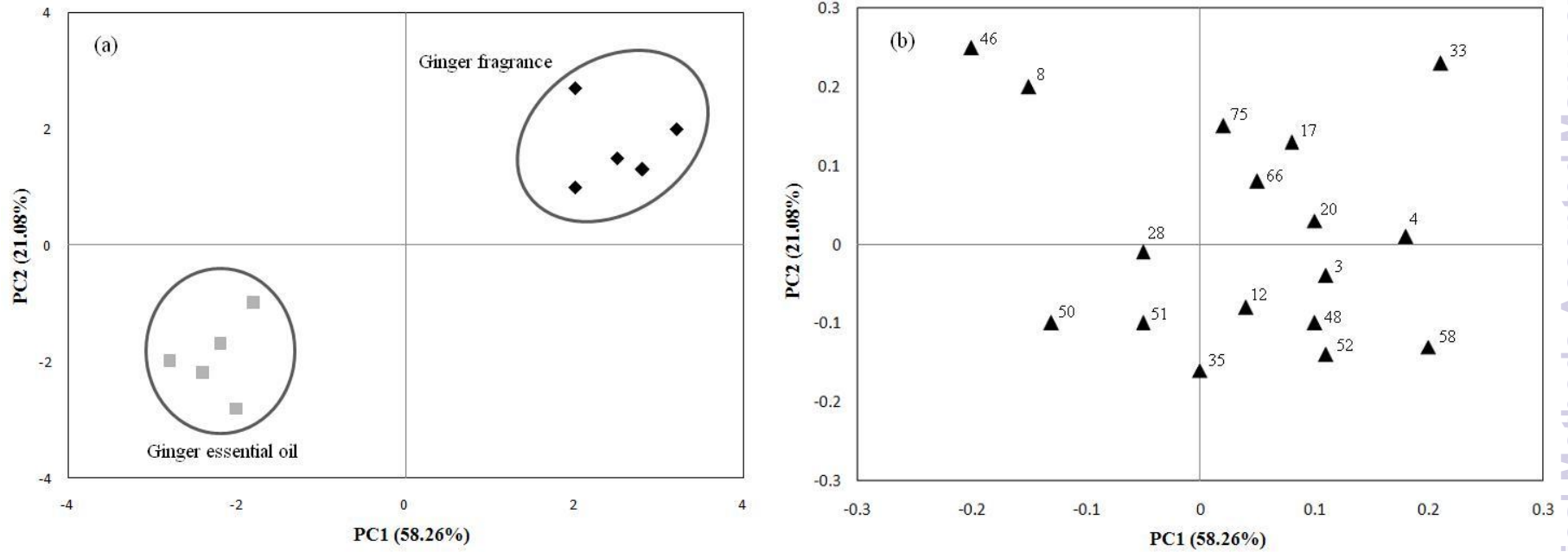


Fig. 7