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Determination of Volatile Components in Ginger Using Gas Chromatography−Mass Spectrometry with Resolution Improved by Data Processing Techniques

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Ginger is widely used as either a food product or an herbal medicine in the world. In this paper, a method was developed for determining volatile components in essential oils from both dried and fresh ginger by use of gas chromatography−mass spectrometry (GC-MS) and chemometric approaches. With the resolution improvement by chemometric methods upon two-dimensional data from GC-MS, the drifting baseline can be corrected. In addition, the peak purity can be assessed and the number of chemical components and their stepwise elution in the peak clusters can be identified. The peak clusters investigated are then resolved into pure chromatograms and related mass spectra for each of the components involved. Finally, with the pure chromatograms and related mass spectra obtained, the chemical components can be qualitatively identified based on the similarity searches in the MS databases and the chromatographic retention times. Quantitative determination can be conducted using the overall volume integration approach. The results showed that 140 and 136 components were separated and that 74 and 75 of them were tentatively identified, which accounted for about 62.82 and 47.11% of the total relative content for dried and fresh ginger, respectively. In comparison with the chromatographic fingerprints of essential oils from dried and fresh ginger, 60 of the volatile components determined match with each other. The study demonstrated that the use of chemometric resolution based on two-dimensional data can mathematically enhance the separation ability of GC-MS and assist qualitative and quantitative determination of chemical components separated from complicated practical systems such as foods, herbal medicines, and environmental samples.

KEYWORDS: GC-MS; chemometrics; ginger; volatile component

INTRODUCTION

In China, Japan, America, and other countries, ginger is commonly used as either a food product or an herbal medicine. The essential oil, which is one of the products from ginger, has been internationally commercialized as flavoring agents and additives for food and pharmaceutical processing (*1*, *2*). The chemical components in the essential oil might affect the characteristic flavor and quality of ginger. On the other hand, there are substantial differences among chemical components of ginger oils from different sources. Even oils from the same region can differ significantly because several varieties are cultivated. Thus, there is a growing interest in research on methods for qualitative and quantitative analysis of components from ginger oils. The chemical investigations carried out in the past showed that monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, and nonterpenoid compounds were the main constituents in ginger oils (*3*−*8*).

Because gas chromatography (GC) is featured by its powerful separation ability, it is commonly used to conduct qualitative and quantitative analysis of essential oils from ginger (*3*−*8*). However, as there are a larger number of chemical components present in ginger oils and many of them are low in concentration, it is impossible to separate all constituents using GC in a single chromatographic run. Thus, the results obtained from a gas chromatography−mass spectrometry (GC-MS) study based on direct similarity searches in the MS libraries might produce false identification of chemical components because of the presence of overlapping peaks and small components. To improve the reliability of qualitative identification, new analytical approaches should be developed. During the past decades, the combined method of GC-MS with chemometric resolution has been

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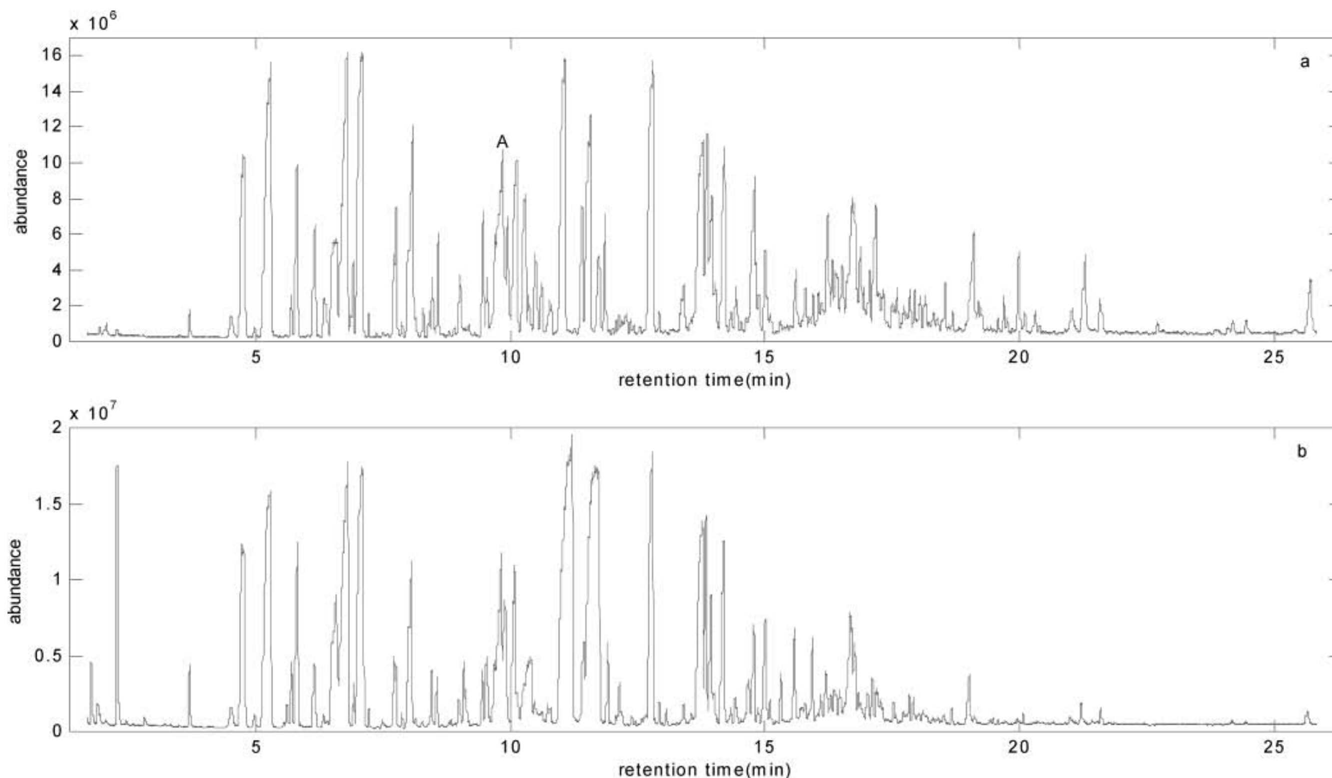

Figure 1. TIC profiles of volatile components from dried (**a**) and fresh (**b**) ginger. The peak cluster A is investigated within 9.60–10.05 min.

developed rapidly. Two-dimensional data become available with the mass spectral information from a mass selective detector and the chromatographic information on retention times, peak heights, and peak areas from GC. In comparison with the conventional one-dimensional GC, qualitative and quantitative determination of chemical components can be conducted more reliably using GC-MS, as the information obtained from both the spectral and the chromatographic directions can be used. Furthermore, chemometric approaches can be used to extract much more chemical information from the huge amount of two-dimensional data obtained. Among the chemometric tools, the evolving approaches, such as heuristic evolving latent projections (HELP) (*9*−*11*), evolving factor analysis (EFA) (*12*−*14*), windows factor analysis (WFA) (*15*, *16*), subwindow factor analysis (SFA) (*17*, *18*), and orthogonal projection resolution (OPR) (*19*, *20*), have grown rapidly in recent years. These chemometric techniques have been shown to apply successfully to many real complex systems (*21*−*23*).

In this study, the volatile components of essential oils from dried and fresh ginger were determined by GC-MS at first to collect the two-dimensional data set. Next, several suitable chemometric approaches were used to conduct data processing on the two-dimensional data obtained so as to resolve targeted chromatograms and mass spectra as from pure chemical components. On the basis of the resolved chromatograms and related mass spectra, tentatively qualitative identification was performed with assistance from the mass spectra and chromatographic retention times of chemical components. In addition, quantitative analyses were carried out using the overall volume integration technique (*21*−*23*). Finally, the results obtained were compared to chromatographic fingerprints of essential oils from dried and fresh ginger.

MATERIALS AND METHODS

Materials. Dried and fresh ginger were from pharmaceutical stores and supermarkets in Hong Kong, China.

Extraction of Essential Oils. About 200 g of dried ginger and 865 g of fresh ginger were added to a special extractor with over 1000 mL of distilled water till the samples were all swollen, and they were allowed to stand for 30 min under room temperature. Then, about 100 mL more of distilled water was added. Next, the volatile components were extracted by steam distillation, as it was found to give a simple and effective method to obtain essential oils from herbs (*24*). The yields of essential oils from dried and fresh ginger are 0.25 (g/g) and 0.15% (g/g), respectively.

Instruments and Working Conditions. In this study, a GC-17A Gas Chromatograph and QP-5000 Mass Spectrometer from Shimadzu Company were employed. An OV-17 capillary column [30 m × 0.25 mm (i.d.), 0.25 μm (film thickness), manufactured by J&W Scientific, Folsom, CA] was used. Initially, the column temperature was set at 60 °C and then programmed from 60 to 250 °C at a rate of 10 °C/min and kept at 250 °C for several minutes. The inlet temperature was kept at 230 °C. Helium carrier gas was used at a constant flow rate of 1 mL/min. In the mass spectrometer, electron impact (EI^+) mass spectra were recorded using 70 eV of ionization energy in full scan mode in the 20−350 amu mass range with 0.1 s/scan velocity. The ionization source temperature was set at 230 °C.

Data Analysis. Data analyses were performed on a Pentium-based IBM compatible personal computer. All programs on chemometric resolution approaches were coded in MATLAB 5.3 for Windows. The library searches and spectral matching of the resolved pure components were conducted by comparison to mass spectra from the National Institute of Standards and Technology and Wiley MS databases with about 180 000 compounds.

RESULTS AND DISCUSSION

Resolution of Two-Dimensional Data from Volatile Components of Dried and Fresh Ginger. Figure 1 shows the total ion chromatograms (TICs) of volatile components in essential oils extracted from dried and fresh ginger. In appearance, the two chromatographic fingerprints are quite similar except for the presence of a few species at the beginning of **Figure 1b** and the quantitative difference of some chemical components appearing after 18 min. The similarity coefficient between

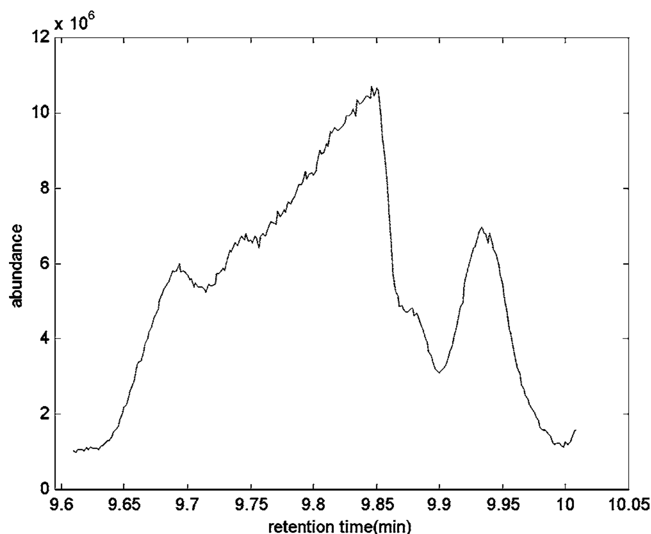

Figure 2. TIC profile of a cluster of peaks before baseline correction.

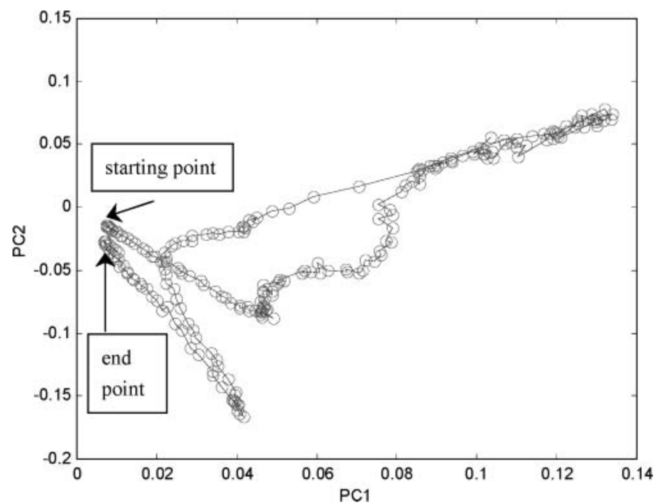

Figure 3. ELPG of a cluster of peaks before baseline correction.

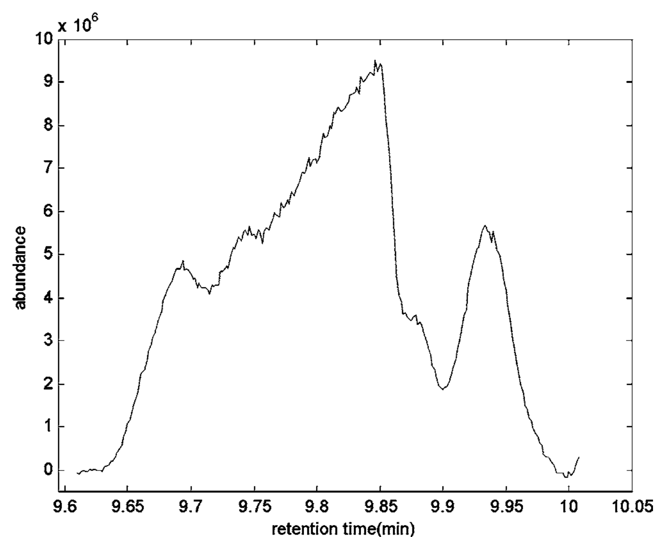

Figure 4. TIC profile of a cluster of peaks after baseline correction.

Figure 1a,**b** is 0.8272. About 80 and 72 chromatographic peaks were present in **Figure 1a**,**b**, respectively. However, in the case of complex mixtures, as shown in previous work (*21*−*23*, *25*), many of the peaks actually corresponded to several overlapped components. On the other hand, the baseline drifts associated with residual gases and column backgrounds were clearly shown during chromatographic runs.

In fact, for most of the chromatographic peaks shown in **Figure 1a**,**b**, the similarity indices obtained from direct searching of the MS databases are quite low. To make things worse, the same component is possibly hit at different chromatographic scan points because it is a mixture of mass spectra from overlapping peaks used in the similarity search. All of these indicate a great complexity of the system investigated, or simply stated, most of the chromatographic peaks are not pure and are mixed with background noise. Thus, before qualitative and quantitative determination, the correction should be made on the baseline and the overlapping peak clusters should be resolved into pure chromatograms and mass spectra for each of the components involved. **Figure 2** represents a cluster (A) in **Figure 1a** within the retention times of 9.60−10.05 min. From **Figure 2**, the baseline shifts upward to an abundance higher than zero and there are at least three chemical components present, suggesting an overlapping situation for the peak cluster under study.

The presence of a drifting baseline, purity of peaks, number of chemical components, and their stepwise elution can be confirmed using the so-called evolving latent projection graph (ELPG; see **Figure 3**) in chemometrics (*9*−*11*, *21*−*23*). ELPG is, in practice, a principal component projective curve from chromatographic or spectral spaces. From the ELPG derived from the chromatographic space, if the starting and end segments of ELPG are not superposed completely, the peak cluster investigated will surely contain a drifting baseline. On the other hand, a straight segment of ELPG will represent the selective region of one pure component while the curving section indicates an overlapping region with at least two constituents. From results given in **Figure 3**, ELPG of the peak cluster A is extremely complex. It is difficult to identify the number of chemical components and the stepwise elution of the peak cluster A directly. Moreover, the starting and end points are not superposed, indicating the existence of a shifting baseline. Thus, before performing further data processing, the baseline should be corrected.

For the commercial GC-MS instruments, background subtraction is directly performed by the MS software as follows. First, a scan point, which contains only the background mass spectrum, is subjectively found. Then, the abundance of the same intermass numbers appearing in the target spectrum is subtracted from the background spectrum to obtain a practical target mass spectrum. Obviously, whether the selection of the background point is reliable can affect the real target mass spectrum obtained. However, with the help of local rank analysis in chemometrics, the zero component regions, which contain no eluting components before the appearance of the first chemical component and after the disappearance of the last chemical constituent, can be identified. After the zero component regions are identified, useful information on the background noise might be determined conveniently (*9*−*11*, *21*−*23*). As the result, a much better baseline correction could be obtained using chemometric techniques. **Figures 4** and **5** show a peak cluster A and its ELPG after baseline correction, respectively. In comparison with **Figures 2** and **4** and **Figures 3** and **5**, the drifting baseline might be corrected efficiently as the abundance of the baseline approximates zero in **Figure 4** and the starting and end segments of ELPG have been superimposed completely in **Figure 5**.

The peak purity and the number of chemical components together with their stepwise elution can be further identified by

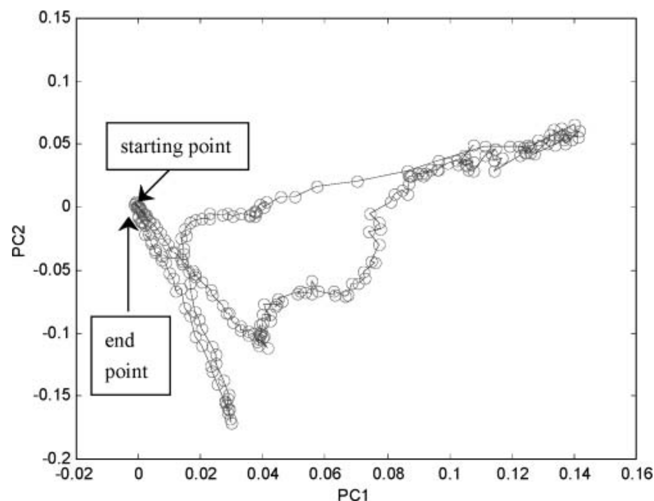

Figure 5. ELPG of a cluster of peaks after baseline correction.

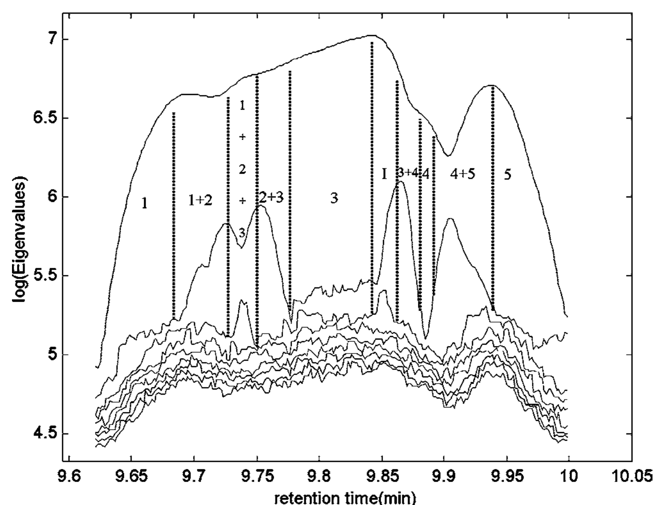

Figure 6. FSWM plot of a cluster of peaks before correction of heteroscedastic noise.

a fixed size moving window EFA (*13*) or the so-called eigenstructure tracking analysis (*11*). In the fixed size window method (FSWM) plot, the noise level is characterized by eigenvalue curves, which have similar numerical values and appear together at the bottom. Eigenvalue curves higher than the noise level represent the presence of new components. For a system with only one species, only one eigenvalue curve is higher than the noise level in its FSWM plot. From the FSWM plot of a peak cluster A given in **Figure 6**, there are three eigenvalue curves higher than the noise level. Thus, the peak cluster A is surely not pure. In **Figure 6**, the region i represents the pure region of the i-th component while the region $i + j$ or $i + j + k$ denotes the overlapping ones containing the i-th and j-th or even the i-th, j-th, and k-th components (here, i, j, k = 1, 2...5). However, it is unreasonable if three components elute within the I region in **Figure 6** because of the appearance of the third eigenvalue curve higher than the noise level. In fact, the third eigenvalue curve higher than the noise level within this region is produced by the so-called heteroscedastic noise, which is usually present during GC-MS runs (*26*). Unlike the common noise, the heteroscedastic noise is proportional to the chromatographic signals. After a special data pretreatment as described in reference (*26*) has been conducted on the heteroscedastic noise, a new FSWM plot is obtained (see **Figure 7**). From **Figure 7**, the I region only consists of the 3rd and 4th

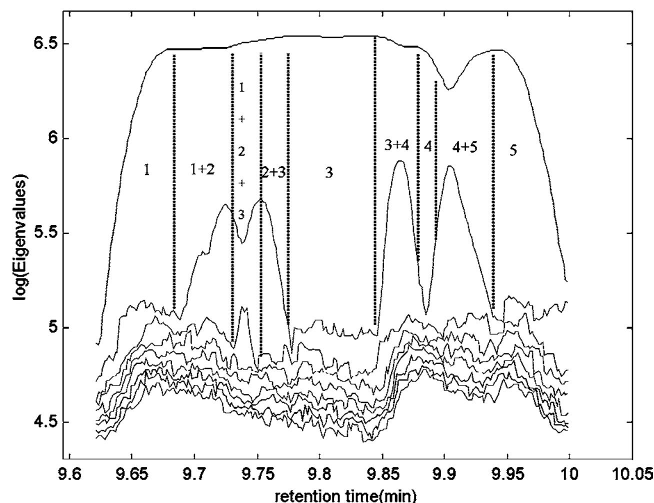

Figure 7. FSWM plot of a cluster of peaks after correction of heteroscedastic noise.

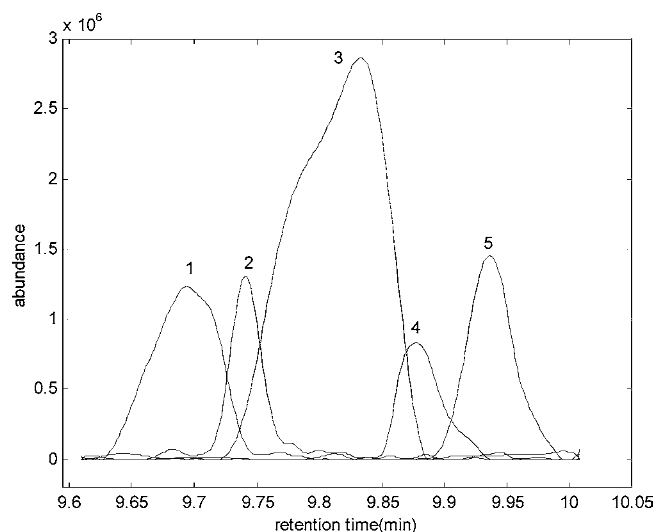

Figure 8. Resolved chromatograms for a cluster of peaks containing five components.

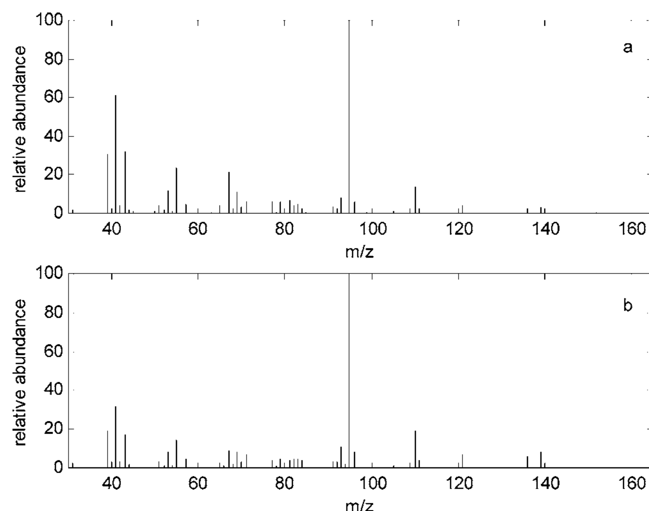

Figure 9. Resolved mass spectrum (**a**) of component 3 and standard mass spectrum (**b**) of borneol ($C_{10}H_{18}O$).

components. Five components are surely in existence in the A peak cluster. As a result, the number of chemical components and their stepwise elution can be correctly determined based

Table 1. Volatile Components Tentatively Identified in Essential Oils from Dried (1)[a] and Fresh (2)[b] Ginger

		relative content (%)				relative content (%)	
no.	name of component	1	2	no.	name of component	1	2
1	acetone		0.11	46	cubebene	0.67	
2	propanol		0.33	47	2,4-decadienal	0.37	
3	butanol		1.51	48	citronellol	0.83	0.46
4	2-butanol		0.02	49	*β*-elemene		0.33
5	3-methyl-butanol		0.06	50	geraniol acetate		0.06
6	2-methyl-butanol		0.01	51	geranyl isobutyrate	4.91	3.76
7	hexanal	0.16	0.36	52	*β*-farnesene	0.11	0.12
8	3,7-dimethyl-1,3,6-octatriene	0.27	0.27	53	isocaryophyllene	0.14	
9	3,7-dimethyl-1,3,7-octatriene	1.92	1.46	54	α-farnesene	0.53	0.16
10	5-methyl-2-hexanone	0.09	0.11	55	zingiberene	4.19	4.06
11	camphene	6.39	5.90	56	farnesene	2.02	1.99
12	2,3-bis[methylene]bicyclo[3.2.1]octane		0.02	57	curcumene	1.34	1.11
13	*β*-pinene	0.03	0.48	58	α-longipinene	0.22	0.20
14	*β*-mycrene	1.68	1.88	59	α-muurolene	0.11	0.15
15	α-phellandrene	1.18	0.66	60	germacrene	0.24	0.16
16	terpinolene	0.57		61	caryophyllene	0.14	0.09
17	limonene	2.07		62	copaene	0.06	0.02
18	2-butyl-acetate	0.40	0.23	63	nerolidol	1.48	0.75
19	*p*-cineole	5.96	5.85	64	undecanoic acid	0.41	
20	4-carene	0.13	0.10	65	aceteugenol	0.30	
21	2-nonanol	0.55	0.52	66	isoeugenol	/	0.10
22	linaloloxide	1.11	0.39	67	elemol	/	1.09
23	*cis*-geraniol	0.08	0.07	68	dimethyl-phthalate	0.04	0.07
24	2-octanone	0.73	0.27	69	α-bisabolol	0.33	0.07
25	3,7-dimethyl-1,6-octadien-3-ol	2.77	1.88	70	dihydrocarveyl acetate		0.07
26	hydroxylinalool	0.19		71	*β*-eudesmol	0.05	0.03
27	citral	0.04		72	guaiol	0.29	0.11
28	perillene		0.03	73	*δ*-cadinol	0.21	0.16
29	verbenone	0.16	0.04	74	2-pentadecynol	0.45	0.22
30	2-*p*-tolylpropene	0.15	0.02	75	α-eudesmol	0.56	0.22
31	limonene oxide	0.44	0.43	76	eudesmol	0.84	0.54
32	1,3,5-tris(methylene)cycloheptane	0.03		77	α,4-dimethyl-α-[4-methyl-3-pentenyl]-3-cyclohexene-1-methanol	0.12	0.52
33	isopinocamphenol	0.71	0.30	78	diethyl phthalate	0.25	0.19
34	dipentene dioxide	0.03	0.04	79	farnesal	0.13	0.11
35	2-pinanol		0.04	80	patchulane	0.12	
36	benzeneacetaldehyde	0.04		81	2-methyl-5-[1,2,2-trimethylcyclo-pentyl]phenol	0.29	0.05
37	isoborneol	0.35	0.59	82	propylur	0.13	0.11
38	hydrate camphene	1.06	0.81	83	pentadecanoic acid	1.63	0.46
39	borneol	2.86	0.32	84	cyclopentaneundecanoic acid	0.24	0.04
40	camphor	0.43	0.90	85	3,7,11,15-tetramethylhexadeca-1-3,6,10,14-pentaene		0.04
41	myrcenol	0.85	0.25	86	9-octadecenal	0.18	0.05
42	α-terpineol	2.76	2.07	87	9,12-octadecadienal	0.88	0.15
43	myrtenol	0.18		88	9,12,15-octadecatrienal	0.25	0.11
44	cryptone	0.15	0.13	89	linalyl 2-methylpropanoate	0.06	

[a] Blank entries mean not determined. [b] All of the components were tentatively identified, and the relative content was approximate.

on the ELPG and FSWM plots in chemometrics. After information on the number of chemical species and the stepwise elution were obtained as shown above, the overlapping peak cluster A might then be uniquely resolved into pure chromatographic profiles and mass spectra of all five components. Here, several chemometric resolution approaches such as HELP (*9−11*), EFA (*12−14*), WFA (*15*, *16*), SFA (*17*, *18*), and/or OPR (*19*, *20*) can be used.

Qualitative Determination of Volatile Components in Essential Oils from Dried and Fresh Ginger. As the pure chromatographic curve and related mass spectrum of each component involved in the A peak cluster are resolved, qualitative determination can be directly performed by means of similarity searches in the MS libraries. At the same time, information on chromatographic retention times is also useful for the identification of chemical components. The results indicate that components 1, 3, 4, and 5 are tentatively identified as hydrate camphene ($C_{10}H_{18}O$), borneol ($C_{10}H_{18}O$), camphor ($C_{10}H_{16}O$), and myrcenol ($C_{10}H_{18}O$), respectively. The resolved chromatographic profiles are shown in **Figure 8**. There are five chemical components in the A peak cluster. **Figure 9** represents the resolved mass spectrum and the standard mass spectrum from the MS libraries of borneol. Comparing **Figure 9a**,**b**, one can easily see that the resolved results are quite reasonable. Unfortunately, the second component cannot be qualitatively identified because of the absence of its standard mass spectrum in the MS databases. However, it might be deduced that its molecular formula is also $C_{10}H_{18}O$ based on the resolved mass spectrum.

Quantitative Analysis of Volatile Components in Essential Oils from Dried and Fresh Ginger. In general, quantitative analysis of GC-MS is carried out by means of peak areas and overlapping peaks are approximately treated by the peak splitting approach. Clearly, the results thus obtained might be unreliable and even wrong for some serious overlapping peak clusters. In this study, the overall volume integration approach is used for quantitative determination. If the pure chromatogram and mass spectrum of each component are resolved by use of chemometric resolution techniques, its overall volume can be calculated (*21−23*). Denoting the pure chromatogram and mass spectrum of the *i*-th component to be c_i and s_i, respectively, the term $c_i\, s_i^{\,t}$ will be taken as its overall volume integration value. Similar to the quantitative approach in relating the peak area to the concentration generally used in one-dimensional GC, $c_i\, s_i^{\,t}$ is directly proportional to the amount of the *i*-th constituent. Taking the sum of the overall volume integration of all chemical components to be one, the relative amount of each species could

be approximately quantified. Here, no internal standard and/or reference compound is needed.

In the same way, data treatment with chemometric resolution approaches is also conducted for other peak clusters. One hundred forty and 136 chemical components have been separated, and 74 and 75 of them are identified, which represent about 62.82 and 47.11% of the total content for dried and fresh ginger, respectively (see **Table 1**). However, as no reference compound is used, the identification of chemical components is merely tentative and the relative content is approximate, as shown in **Table 1**.

In comparison with other chemical investigations for ginger oils (*3*−*8*), the present study could separate and identify many more chemical components by use of the combined approach of GC-MS with chemometric techniques. Results from **Table 1** show that 60 chemical constituents are identical in essential oils from dried and fresh ginger. It might just explain a good similarity between the chromatographic fingerprints in **Figure 1a**,**b** and the similarity coefficients up to 0.8272.

In conclusion, as volatile components in essential oils from dried and fresh ginger are real analytical systems with high complexities, it is very difficult to separate all chemical components during GC-MS analysis. In this study, the combined approach of GC-MS with chemometric resolution has been successfully applied to correct the drifting of the baseline, identify peak purity and the number of chemical components together with the stepwise elution, enhance the resolution of pure chromatograms and mass spectra, and thus tentatively enable qualitative and quantitative determination of chemical components by making use of the advantages of two-dimensional data. The method developed in this work not only greatly enhances the separation ability of GC-MS but also increases its accuracy in qualitative and quantitative identification.

In the view of herbalists, dried and fresh ginger might be different in their pharmacological activities. However, the results in this study show that most of their volatile components in essential oils are the same as to each other.

LITERATURE CITED

(1) Kelly, C. Z.; Marcia, O. M. M.; Ademir, J. P.; Angela A. M. M. Extraction of ginger (*Zingiber officinale* Roscoe) oleoresin with CO_2 and cosolvents: A study of the antioxidant action of the extracts. *J. Supercrit. Fluids* **2002**, *24*, 57−76.

(2) Alexander, G. B.; Gordon, T. W.; Byung-Soo, C. Extraction of Australian ginger root with carbon dioxide and ethanol entrainer. *J. Supercrit. Fluids* **1998**, *13*, 319−324.

(3) Shao, Y. J.; Marriott, P.; Shellie, R.; Hugel, H. Solid-phase microextraction−comprehensive two-dimensional gas chromatography of ginger (*Zingiber officinale*) volatiles. *Flavour Fragrance J.* **2003**, *18*, 5−12.

(4) Chen, C. C.; Ho, C. T. Gas chromatographic analysis of volatile components of ginger oil *(Zingiber officinale* Roscoe) extracted with liquid carbon dioxide. *J. Agric. Food Chem.* **1988**, *36*, 322−328.

(5) Nishimura, O. Identification of the characteristic odorants in fresh rhizomes of ginger *(Zingiber oficinale* Roscoe) using aroma extract dilution analysis and modified multidimensional gas chromatography−mass spectroscopy. *J. Agric. Food Chem.* **1995**, *43*, 2941−2945.

(6) Teris, A. v. B.; Maarten, A. P.; Gerrit, P. L.; Hoàng, V. P.; Bùi, T. Y. Investigation of the essential oil of Vietnamese ginger. *Phytochemistry* **1987**, *26*, 3005−3010.

(7) Alexander, J. M.; Nirmala, M. P. Volatile aroma constituents of Sri Lankan ginger. *Phytochemistry* **1984**, *23*, 353−359.

(8) Roger, M. S.; Janet, M. R. The essential oil of ginger from Fiji. *Phytochemistry* **1981**, *20*, 203−206.

(9) Kvalheim, O. M.; Liang, Y. Z. Heuristic evolving latent projections: resolving two-way multicomponent data. 1. Selectivity, latent-projective graph, datascope, local rank, and unique resolution. *Anal. Chem.* **1992**, *64*, 936−945.

(10) Liang, Y. Z.; Kvalheim, O. M.; Keller, H. R.; Massart, D. L.; Kiechle, P.; Erni, F. Heuristic evolving latent projections: Resolving two-way multicomponent data. 2. Detection and resolution of minor constituents. *Anal. Chem.* **1992**, *64*, 946−953.

(11) Liang, Y. Z.; Kvalheim, O. M.; Rahmani, A.; Brereton, R. G. Resolution of strongly overlapping 2-way multicomponent data by means of heuristic evolving latent projections. *J. Chemom.* **1993**, *7*, 15−43.

(12) Maeder, M. Evolving factor analysis for the resolution of overlapping chromatographic peaks. *Anal. Chem*. **1987**, *59*, 527−530.

(13) Keller, H. R.; Massart, D. L. Peak purity control in liquid-chromatography with photodiode-array detection by a fixed size moving window evolving factor-analysis. *Anal. Chim. Acta* **1991**, *246*, 379−390.

(14) Keller, H. R.; Massart, D. L.; Liang, Y. Z.; Kvalheim, O. M. A comparison of the heuristic evoling latent projections and evolving factor analysis methods for peak purity control in liquid chromatography with photodiode array detection. *Anal. Chim. Acta* **1992**, *267*, 63−71.

(15) Malinowski, E. R. Window factor-analysis−Theoretical derivation and application to flow-injection analysis data. *J. Chemom*. **1992**, *6*, 29−40.

(16) Den, W.; Malinowski, E. R. Investigation of copper(II) ethylendiaminetetraacetate complexation by window factor-analysis of ultraviolet-spectra. *J. Chemom*. **1993**, *7*, 89−98.

(17) Manne, R.; Shen, H. L.; Liang, Y. Z. Subwindow factor analysis. *Chemom. Intell. Lab. Syst.* **1999**, *45*, 171−176.

(18) Shen, H. L.; Manne, R.; Xu, Q. S.; Chen, D. Z.; Liang, Y. Z. Local resolution of hyphenated chromatographic data. *Chemom. Intell. Lab. Syst*. **1999**, *45*, 323−328.

(19) Lorber, A. Error propagation and figures of merit for quantification by solving matrix equations. *Anal. Chem*. **1986**, *58*, 1167−1172.

(20) Liang, Y. Z.; Kvalheim, O. M. Diagnosis and resolution of multiwavelength chromatograms by rank map, orthogonal projections and sequential rank analysis. *Anal. Chim. Acta* **1994**, *292*, 5−15.

(21) Gong, F.; Liang, Y. Z.; Chau, F. T. Combination of GC-MS with local resolution for determining volatile components in si-wu decoction. *J. Sep. Sci.* **2003**, *26*, 112−122.

(22) Gong, F.; Liang, Y. Z.; Cui, H.; Chau, F. T.; Chan, C. Determination of volatile components in peptic powder by gas chromatography−mass spectrometry and chemometric resolution. *J. Chromatogr. A* **2001**, *909*, 237−247.

(23) Gong, F.; Liang, Y. Z.; Xu, Q. S.; Chau, F. T. Gas chromatography−mass spectrometry and chemometric resolution applied to determination of essential oil in *Cortex Cinnamomi*. *J. Chromatogr. A* **2001**, *905*, 193−205.

(24) Chinese Pharmacopoeia Committee. *Chinese Pharmacopoeia*; Publishing House of People's Health: Beijing, 2000.

(25) Davis, J. M.; Giddings, J. C. Statistical theory of component overlap in multicomponent chromatograms. *Anal. Chem*. **1983**, *55*, 418−424.

(26) Keller, H. R.; Massart, D. L.; Liang, Y. Z.; Kvalheim, O. M. Evolving factor-analysis in the presence of heteroscedastic noise. *Anal. Chim. Acta* **1992**, *263*, 29−36.

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