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The study of fingerprint characteristics of the emanations from human arm skin using the original sampling system by SPME-GC/MS

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Abstract

An efficient and noninvasive method consisting of an original sampling device, solid phase microextraction (SPME) and gas chromatography–mass spectrometry (GC–MS) was developed to analyze volatile organic emanations from the skin of human arms. The emanations were sampled by SPME connected with the active sampling device for 30 min and transferred into GC–MS immediately for the consequent analysis. The sampling projects for 15 candidates were scheduled in both winter and spring with the same optimized conditions. Thirty-five compounds were finally identified according to various degrees of certainty. Different emission behaviors specified with principal component analysis (PCA) and similar fingerprint characteristics were observed clearly by comparisons of chromatograms of different seasons. Top ten emanations contributing to characteristics in different seasons were attempted to be described using comparisons based on common model strategy. The large amounts of experimental data were all handled by the corresponding chemometrics strategies with the homemade chromatographic data processing system. The results suggest that the analysis based on fingerprint characteristics of human skin emanations could provide useful and important clues to reveal biomarkers among the mixture of human skin emanations.

Keywords: Human emanations; Fingerprint characteristics; Original sampling system; SPME

1. Introduction

It is well known that volatile organic compounds (VOCs) synthesized by metabolism and emanations of human skin make up human odors. Hundreds of different kinds of substances appear in human odors, which can be classified into several groups according to their functional groups such as carboxylic acids, alcohols, aldehydes, aliphatics, esters, ketones, amines, heterocyclics, and so on [1]. The alternant actions between both skin gland and excreting organic compounds achieve individual human odors. Special regulations of individual emission behaviors of human odors are interlinked to human hormonal control and bacterial populations localized at skin surfaces surviving by metabolizing and transforming organic compounds absorbed from the external environment [2]. Any changes of metabolism equilibrium cause alteration of human emanations. Therefore, the variety of individuals results in different characteristics of human odors, also called “fingerprint” characteristics by analogy with the real dactylograms. Fingerprint characteristics of human odors are actually a kind of informative biomarkers [3] and have been successfully used to train sleuthhounds, identify criminals and diagnose diseases. Modern analytical instruments provide a good platform to obtain fingerprint characteristics of human odors. Especially, potential fingerprint information of human emanations can be extracted easily from fingerprint chromatograms through corresponding chromatographic methods such as gas chromatography–mass spectrometry (GC–MS). Great efforts have gone into identifying specific emanations in human breath, [4,5] axillae [6,7] and other parts of human body [8] using corresponding presampling and chromatographic methodologies.

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Because human body odors contain informative biomarkers, using proper analytical technique to identify components of human body odors has been placed on the agenda. However, the difficulties emerge during the pre-sampling procedure to obtain such trace emanations. The emanations from human body have been considered as a valid and harmless method for mosquito surveillance, since mosquitoes seek livestock and humans related to the attraction of skin emanations [9]. Tentative attractants for Aedes Aegypti (a kind of mosquitoes) have been detected using handled glass followed with cryofocused GC–MS analysis [1]. Therefore, it is possible to describe the fingerprint characteristics of human odors, if proper sampling techniques are applied to collect the emanations of human odors.

Solid phase microextraction (SPME) is an excellent presampling method, simple, sensitive, selective, efficient, accurate and solvent-saving. SPME has been widely used in environmental, biological, pharmaceutical and other field analyses since this innovative technique was developed by Pawliszyn and co-workers [10,11]. Several SPME reviews, including environmental analysis, [12] biological analysis, [13] biomedical analysis [14] and field analysis, [15] attempt to highlight and specify the virtues and progresses in different aspects such as theory, fiber coating, application, and the like. In VOCs analysis, SPME is also considered as a suitable and rapid sampling method. Especially, headspace solid phase microextraction (HSSPME) ensures high sensibility and good selectivity owing to the extremely low blank in the analysis of VOCs. Grote and Pawliszyn [4] and Hyspler et al. [5] quantified isoprene, ethanol and acetone in the human expired breath. Other papers about bovine breath analysis by HSSPME [16,17] have been introduced in recent years. However, there are still few reports about combining HSSPME with the active sampler to directly extract and sample the emanations from human skin. The main difficulties exist in the low concentrations of analytes, complex ambient blanks and continued programs for data analysis. On the surface of the human arm skin there are many kinds of aerobic bacteria, which can decompose and change the long-chain metabolins into short-chain and small-molecular volatile organic compounds such as aldehydes, ketones, alcohols, esters and so on. Most of them possess typical scents and contribute to one of the most typical emitting sources in human body. Because most emanations among human odors possess high volatility, it is convenient to sample the emanations from candidate's arm skin without any embarrassing body exposures by HSSPME.

The purpose of this study is to identify emanations from the skin of human arms, clarify fingerprint characteristics of human odors and prepare to specify the biomarkers in human emanations. The method consisting of SPME, the original sampling system and GC–MS analysis is simple, efficient and noninvasive. A special "chromatographic data processing system" based on Matlab 6.5 is programmed to manage the mass of chromatographic data in order to distill the potential but useful information. In a word, this piece of work tentatively explores the useful fingerprint characteristics of human odors and makes the adequate preparation for the next phase study on the biomarkers of human odors in detail.

2. Experimental

2.1. Emanations sampling device

The original active sampling device was made up of a sampling canister, two gas-flow circuits and a power system (Fig. 1). Whole-stainless-steel-and-glass design, not containing any organic materials was adopted to reduce influences induced by other organic compounds. Two gas-flow circuits, an inner circuit and an outer circuit, were created in this sampling device, which were separated from each other by stainless steel pipes. The two gas-flow circuits had different functions. The outer circuit was created for the purging and cleaning protocol, while the inner circuit sampled target compounds. The inner volume of the glass-sampling canister was about 6 L. Both the inner and outer circuits were connected with this glass canister, which was sealed naturally with the entrance of the human arm. One-way pump and filters were installed inside the device to provide the power for the gas flow and remove the residue gases. Particularly, the design of the sampling point was given a lot of care about the exposing length and position for SPME fiber. The interface including a silicon septum (Agilent Scientific, USA) allowed the SPME to connect with the sampling system simply and efficiently, which was similar to the GC foreline injector.

All parts of the active sampling system except for the one-way pump and filters were cleaned thoroughly with laboratory detergent and warm tap water followed by rinsing with deionized water before sampling. During continuous sampling procedures highly pure nitrogen (purity >99.995%, Xicheng Air Product Ltd. Co., China) purged the system to sweep out the emanation residues. The blanks caused by the sampling device and the ambient were taken into consideration in this work. A single SPME was progressed for 30 min in the sealed active sampling system before intraday experiments to get the blank chromatogram. The blanks were used to evaluate the cleaning protocol and identify contamination stemming from the sampling device. In short, great efforts were dedicated to decline the sampling system blanks from both the device and ambient. First, whole-stainless-steel-and-glass design provided the precondition to lower the device background; secondly, two separated gas-flow circuits and the nitrogen-purging procedure proved to be valid on reducing the ambient blanks; the last but not the least, a special "chromatographic data processing system" was coded to subtract the background from the corresponding sampling chromatogram, which guaranteed to obtain final purified chromatograms based on chemometrics strategies.

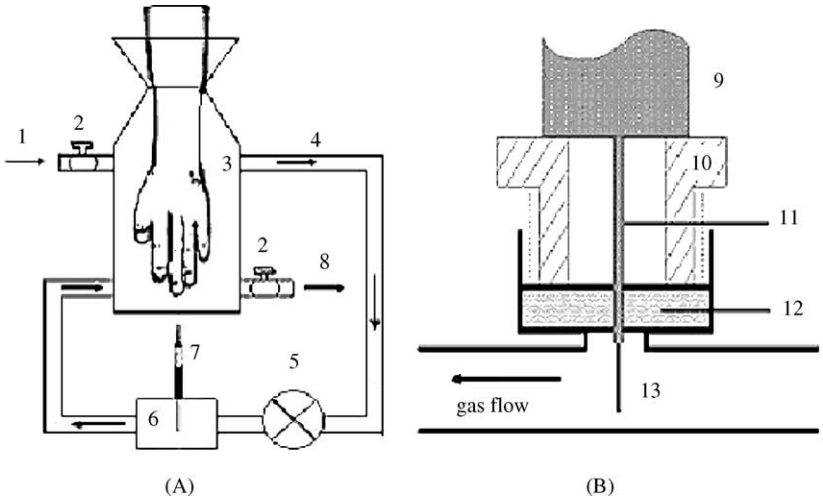

Fig. 1. Schematic of the active sampling device for emanations from the skin of the human arm with SPME. Part A is the profile of the sampling device. The purge gas, N_2, enters the system from the entrance (1) and is drained out of the device through the exit (8). Valves (2), the sampling jar (3), stainless steel pipes (4) and one-way pump (5) make up of inner and outer gas-flow circuits. SPME (7) samples emanations at the appointed position (6), which is demonstrated in more detail in the enlarged part B. The core of the sampling position contains the interface (10) connected with the adjustable depth gauge (9) of SPME, which steers septum piercing needle (11) of SPME through the septum (12) smoothly. When SPME fiber coating (13) is exposed amid gas flow, pre-sampling begins.

2.2. SPME procedure and sampling strategy

Choosing a proper SPME fiber coating is crucial to the effectiveness of the individual analysis. Some useful and specific factors should be taken into consideration, such as polarity, matrix, etc. Compared with other SPME fiber coatings (100 μm polydimethylsiloxane, 65 μm carbowax-divinylbenzene and 85 μm polyacrylate, Supelco, USA), 65 μm polydimethylsiloxane-divinylbenzene (PDMS-DVB) fiber coating can sample more species and amounts of human emanations. Therefore, the type of commercial SPME fibers recommended in this study was 65 μm conditioned PDMS-DVB since most emanations from human body were non- or weak-polar VOCs and the concentrations were pretty low. On the other hand, extraction time is another important factor affecting the sensitivity of HSSPME analysis. In this experiment the different extraction time (15, 30, 45, 60 and 90 min) were performed to obtain the optimized analytical sensitivity. Due to the complexity of the emanations from human arm skin, the shorter sampling time (15 min) resulted in incomplete absorption and reduced SPME sensitivity; however, the longer sampling time (45, 60 and 90 min) enabled competitive absorption and also caused lower sampling effectiveness. Finally, the sampling time of 30 min was strongly preferred in the work, because it could achieve the excellent analytical sensitivity and comfort the candidates simultaneously.

The sampling procedure began with the nitrogen purging the system for 10 min; then, the candidate inserted his arm through the device entrance and sealed it, while the N_2 kept going for five more minutes to sweep out the contaminants from the ambient with the entrance of the human arm; after that, the outer circuit was closed when the SPME fiber coating was exposed to sample for 30 min. At this moment the inner circuit was in the inert ambient created by N_2, so some unstable emanations would be protected and sampled finally by SPME. The SPME fiber coating containing target emanations was inserted into the GC foreline injector and thermally desorbed for 5 min at the temperature of 250 °C following by analysis of GC–MS.

The sampling was performed in two different seasons (winter in 2003 and spring in 2004) in the analytical lab of Sun Yat-Sen University, Guangzhou, China. All the candidates were invited to the laboratory for sampling so that after sampling the SPME fiber coating could be transferred and desorbed in the GC injector immediately, avoiding extra trip blanks. The behavior of VOCs' volatility was strongly affected by relative humidity and temperature. In this study, the simultaneous measurements of emanation samplings in both moist and warm season (spring in Guangzhou) and dry and cold season (winter in Guangzhou) were processed to evaluate the effect of relative humidity and temperature and estimate the stability and reproducibility of fingerprint characteristics of human odors.

Fifteen candidates were invited to give assistance in this study, and five of them joined the two-season sampling project. Each candidate was asked for personal information such as blood type, age and smoking-habits. The candidates were required to wash their arms with tap water and air-dry naturally before sampling. No special diet was required as long as the candidates were in healthy condition. The candidates were sampled twice randomly within 7 days at each sampling season.

2.3. Chromatographic data processing system

In this research an original "chromatographic data processing system" based on the Matlab 6.5 was specially coded to manage the mass of research data. It was "principal com-

ponent analysis (PCA)", "common model" and "comparison of chromatograms" that were three main functions used in the work. The original data of both background and sample total ionization chromatograms (TIC) acquired from the GC/MS were exported and transformed to an "$m \times 2$" matrix ("m" represented frequencies of MS data-collecting). The first column in this "$m \times 2$" matrix represented the time of MS data-collecting, and the second column was on behalf of corresponding detector's responses. The second column in the matrix was managed in order to subtract the blank. After directly comparing the sample to the blank, the system displayed and reformed the final chromatograms. These chromatograms were purified and represented emission behaviors of skin emanations, because the background effects had been removed in the previous procedures. The chemometrics strategies of wavelet transform and polynomial smoothing were applied to smooth the purified chromatograms in this system. The system also fulfilled the function of "peak-auto-seeking" so that every peak in the final chromatogram was able to be identified and labeled, if the "S/N" was more than 3. After the retention time and MS responses were corrected and compared, the data from all the purified chromatograms were merged into an "$m \times n$" matrix ("n" represented the numbers of the purified chromatograms). Finally, PCA analysis and common model were based on this "$m \times n$" matrix. In brief, the data processing system was a special and important tool to decline the sampling backgrounds in this study.

2.4. Parameters for gas chromatography–mass spectrometry (GC–MS)

The fiber with targeted analytes was analyzed by a Hewlett-Packard (HP) 6890 gas chromatography with a HP 5973 mass detector. The splitless injector was operated at 250 °C with the purge flow of 80 mL/min. The injection port was closed for 5 min during extracted analytes desorbing. Ultra-pure helium (purity >99.999%, constant flow: 1 mL/min, Xicheng Air Product Ltd. Co., China) served as carrier gas. For separations, a 60 m length × 0.32 mm i.d. × 1.8 μm film thickness HP-VOC column (Agilent Scientific, USA) was used. The oven was programmed as following rates. The initial temperature of the column was 60 °C (2 min hold) followed by a ramp of 8 °C/min to 200 °C (15 min hold) and a second ramp of 5 °C/min to 260 °C, and finally ramped to 270 °C with a post-run for 3 min. The parameters of HP 5973 mass detector were: ion mass/charge ratio, 20–550 m/z; quadrupole temperature, 150 °C; electron impact ionization (EI); EI source temperature, 230 °C; interface temperature 280 °C; electron multiplier voltage, 1780 ev; scan model, 2.41 scans/s.

2.5. Emanation identification and data analysis

Potential emanations were identified by matching sample mass spectrum with those of the National Institute of Standards and Technology (NIST) MS spectral library for peaks presented in the chromatograms. When available, some of important potential emanations were interpreted further comparing the retention time with corresponding standards. Emanations were considered "identified", when their mass spectral fit values were at the default value of 85 or above or the retention time matched the relative standard retention time within 0.05 min. Besides "identified" VOCs, some discernable peaks in the chromatogram would be finally sure to be "identified" if relative standards could be available. The chromatographic data processing system was contributed to eliminating blanks from the skin of the arm emanation chromatograms. Thus, relatively pure emanation chromatograms were achieved at the same time, in which the related peak area counts for compounds would be integrated. The method for data management would be probably more precise than comparing peak area counts directly. Typical chromatograms of an emanation sample and its corresponding blank sample are illustrated in Fig. 2. The final chromatogram is the result of comparing the sample chromatogram to the related blank chromatogram. The peak numbers represent the eluted order of identified compounds.

3. Results and discussions

3.1. The profile of human arm skin emanations

Human skin emanations thermally desorbed from the SPME fiber coating, acquired in EI mode, are listed in Table 1. Analysis using this method results more than 100 discernable peaks in the chromatograms (Fig. 2), 35 of which are identified according to the various degrees of certainty. Most of the identified peaks are clear labeled in the enlarged chromatogram (Fig. 3). Due to the strong volatility of emanations, the fingerprint characteristics carried by these VOCs, namely some reproducible peaks and relatively similar ratios of peak area counts, are clearly apparent during the period of 15–30 min. The detected emanations consist of mainly six groups according to the diverse functional groups, which are alkenes, alcohols, alkanes, aldehydes, esters and other organic compounds. Some of presented emanations, such as 3,7-dimethyl-6-octanol, benzyl alcohol, phenylethyl alcohol, octanal, nonanal, decanal, benzyldehyde, pentadecane and hexadecane, have been identified in the previous work [1].

The frequency of detection of these emanations is calculated and displayed in Table 2. Benzaldehyde, eicosane and cedrol are detected almost in all candidates' chromatograms, with a high percentage distribution about 90%. Most of long-chain alkenes, namely camphene, 1,3,5,7-cyclooctene, 3-dodecene and hexadecene, are only presented one time with a percentage 2.56%. The tentative reason is related with the instability of this group of alkenes. These alkenes are easily decomposed and oxidized in the low concentration levels, even if the ambient and status of candidates change

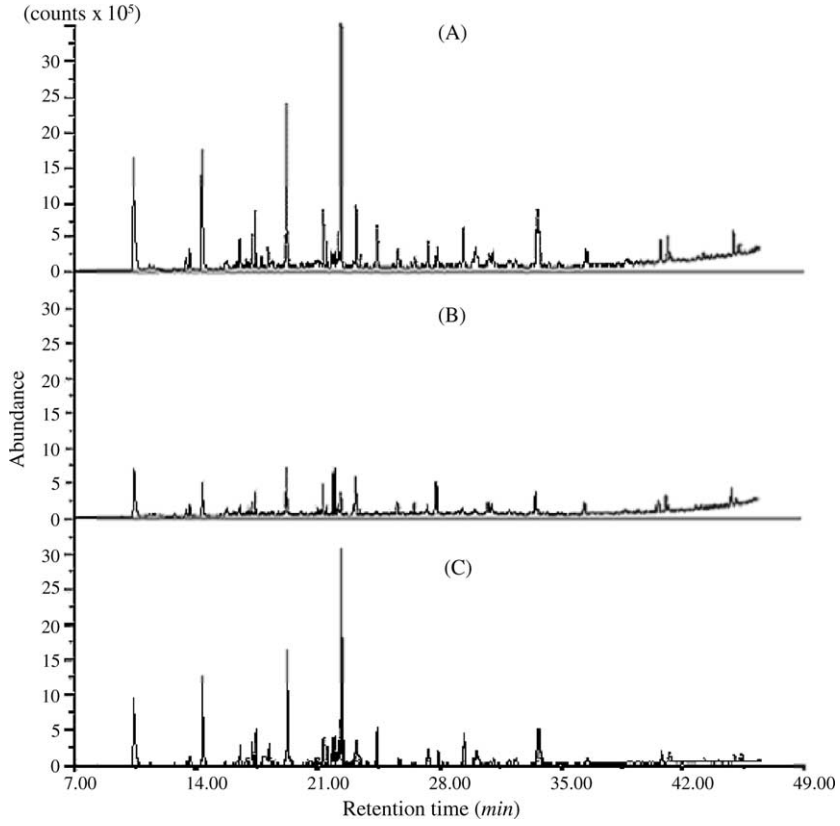

Fig. 2. (A) The chromatogram of the candidate's emanations. (B) The chromatogram of sampling blanks. (C) The purified chromatogram subtracted the blanks from the chromatography of the candidate's emanations using the "chromatographic data processing system".

slightly. Lilial, undecane, 2-methyl dodecane and cyclopentadecane are also observed only once in this work. Alcohols, alkanes and aldehydes accounted constitute mainly 64% of the detected emanations listed in Table 1. Especially, some of these compounds, such as 2-ethyl hexanol, 5-methyl-2-isopropyl cyclohexanol, benyl alcohol, tetradecane, pentadecane, hexadecane and decanal, have relatively high displaying frequencies around 50%. More attention should be paid to methyl salicylate and tetramethyl thiourea. Although the two compounds presented in the chromatograms more often than many other compounds, they were only detected in the winter of 2003. Guangzhou experiences warm and moist climatic conditions in spring. Although the high temperature benefits the accelerating volatilization of emanations, the moist ambient would weaken the volatility of emanations, pile the excreting grease and result the pore jam. In addition methyl salicylate behaves easier trend of hydrolyzation in the moister ambient. Making a comprehensive consideration, the absence of methyl salicylate and tetramethyl thiourea in the spring could be probably explained. Siloxanes believed from the capillary column stationary phase and phthalate contaminants from the ambient are considered as main background interferences, which are finally ruled out with general knowledge.

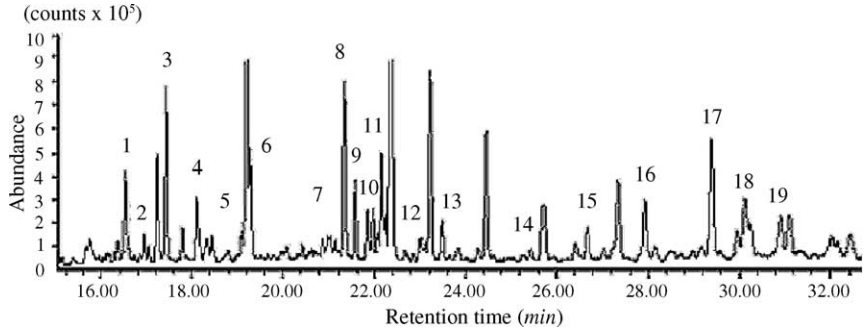

Fig. 3. The enlarged chromatogram for the retention time from 15 to 30 min. The peak numbers correspond to those listed compounds in Table 1.

Table 1
Identified compounds of the skin of the human arm emanations from thermal desorption of SPME fibers

Compounds	Identified peak no.	Retention time (min)	Fit[a]	Notes[b]
Alkenes				
1,3,5,7-Cyclooctene	20	14.364	96	B
Alpha-pinene	21	15.293	90	A
Camphene	22	15.955	95	B
D-limonene	23	17.774	92	B
3-Dodecene	26	20.828	97	B
Caryophyllene	18	30.217	96	B, C
Pentadecene	28	30.374	96	B
Hexadecene	29	33.411	94	B
Alkanes				
Undecane	25	18.750	90	A
Dodecane	7	20.947	96	A, C
Tridecane	13	23.478	93	B, C
2-Methyl dodecane	14	25.382	89	B
Tetradecane	15	26.642	95	A, C
Pentadecane	19	30.860	91	B, C
Cyclopentadecane	30	35.143	90	B
Hexadecane	32	36.491	97	B
2-Methyl hexadecane	33	39.607	96	B, D
Eicosane	35	41.209	90	B
Alcohols				
2-Ethyl hexanol	3	17.378	86	A, C
5-Methyl-2-isopropyl cyclohexanol	8	21.314	91	B, C
Benyl alcohol	4	18.096	89	A, C
Phenylethyl alcohol	24	18.125	86	B, D
3,7-Dimethyl-6-octanol	10	22.044	96	B, C
3,7-Dimethyl-2,6-octandiol	27	22.833	90	B, C
Cedrol	34	40.727	97	B
Aldehydes				
Benzaldehyde	1	16.491	96	A, D
Octanal	2	16.905	94	B, C
Nonanal	6	19.231	91	A, C
Decanal	9	21.548	88	B
Lilial	31	35.363	86	B, C
Esters				
Methyl salicylate	11	22.137	93	A
Isobornyl propionate	16	27.882	87	B
Miscellaneous				
Acetophenone	5	19.050	87	A, D
Tetramethyl thiourea	12	22.989	94	B
Diphenyl ether	17	29.394	94	B, C

[a] Fit value is referred to what degree the target spectrum matches the standard spectrum in the NIST library (100 relates to a perfect fit).
[b] (A): The compound is identified with both the corresponding standard and the NIST. (B): The compound is identified with the standard spectrum in the NIST. (C): The compound has a higher emitting amount in winter than it does in spring. (D): The compound has a higher emitting amount in spring than it does in winter.

3.2. *Fingerprint characteristics of emanations based on comparisons between various seasons*

From Tables 1 and 2, it is clear that emission behavior of human odors in the moist season varied from those taken in the dry season, although all the collections were progressed with the same optimized experimental conditions. The dry climate in winter yields better volatile efficiency than the moist one, because some compounds would be easily hydrolyzed and decomposed by the propagating bacteria in spring. Aldehydes, esters and alcohols have been considered as staple energetic source of the bacteria, so amounts of these compounds decrease more than other compounds in spring. Fig. 4 is a typical comparison of two-season sampling project with one of the five candidates. To our surprise, although the climate affected the emission behavior, the ratios of many crucial fingerprint peaks did not fluctuate very much in the different seasons. Therefore, the reproducibility of fingerprint characteristics could be also evaluated from the chromatograms of all the five candidates in the two-season sampling project. The four random sampling results of every candidate (two times in winter and two times in spring) confirmed the good reproducibility and stability of fingerprint chromatograms of human arm skin emanations. The

Table 2
Summary of identified emanations of human arm skin

Compounds	Winter	Spring	Total detection	Percentage distribution[a]
Alkenes				
1,3,5,7-Cyclooctene		1	1	2.56
Alpha-pinene	8	3	11	28.21
Camphene		1	1	2.56
D-limonene		3	3	7.69
3-Dodecene	1		1	2.56
Caryophyllene	5	1	6	15.38
Pentadecene	2		2	5.13
Hexadecene	1		1	2.56
Alkanes				
Undecane		1	1	2.56
Dodecane	2	4	6	15.38
2-Methyl dodecane	1		1	2.56
Tridecane	6	3	9	23.08
Tetradecane	9	10	19	48.72
Pentadecane	10	11	21	53.85
Cyclopentadecane	1		1	2.56
Hexadecane	20	2	22	56.41
2-Methyl hexadecane	5	1	6	15.38
Eicosane	20	17	37	94.87
Alcohols				
2-Ethyl hexanol	18	8	26	66.67
5-Methyl-2-isopropyl cyclohexanol	21	1	22	56.41
Benyl alcohol	17	4	21	53.85
Pheylethyl alcohol	1	3	4	10.26
3,7-Dimethyl-6-octanol	6		6	15.38
3,7-Dimethyl-2,6-octandiol	1		1	2.56
Cedrol	18	17	35	89.74
Aldehydes				
Benzaldehyde	21	15	36	92.31
Octanal	3	2	5	12.82
Nonanal	9	4	13	33.33
Decanal	19	2	21	53.85
Lilial	1		1	2.56
Esters				
Methyl salicylate	22		22	56.41
Isobornyl propionate	11	5	16	41.03
Miscellaneous				
Acetophenone	4		4	10.26
Tetramethyl thiourea	14		14	35.90
Diphenyl ether	16	10	26	66.67

[a] One sampling round is interrupted by an instrumental error. Totally 39 sampling rounds are performed with 20 person-times (15 candidates).

two characters, namely various emission behavior and special fingerprint information maintaining, are simultaneously demonstrated in the Fig. 4.

In order to specify the different emission behavior statistically between spring and winter sampling data, this research has attempted to classify the chromatograms of total 20 sampling rounds (15 candidates) according to chromatographic fingerprints obtained by pattern recognition based on PCA. The profile matrix consisted of 20 rows and 6724 columns was processed in the chromatographic data processing system. The first three principal components, PC1, PC2 and PC3, were used to provide a convenient visual aid for identifying inhomogenity in the data sets. Fig. 5 shows the principle component projection plot of PC1 to PC3 from 20 chromatographic fingerprints investigated. The emission characteristic seasonal variety emerged and inspired our best interest to explore the possible reasons. The conceivable reasons are that the human being's metabolic equilibrium changes when the climate conditions are dramatically different. The alterations of metabolic equilibrium cause the difference of excreting emanations both in species and in amounts.

3.3. Tentative discussions of the clues of mosquito surveillance

To further specify idiographic compounds inducing the obvious segregations between two seasons, the strategy of common model was performed to compare the chro-

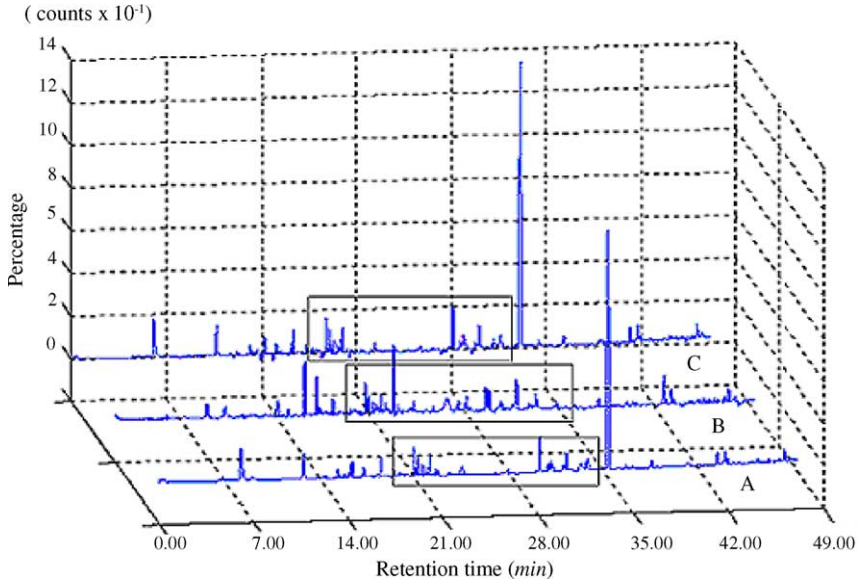

Fig. 4. Comparison chromatograms of winter and spring samples. (A) The typical chromatogram of candidate's emanations in winter. (B) The typical chromatogram of candidate's emanations in spring. (C) The final comparison of chromatogram A and B using "chromatographic data processing system". All of the peak area counts in the chromatograms are normalized in this data processing system in order to draw out the potential fingerprint information. The rectangular areas represent tentative fingerprint characteristics because of the regular peaks presenting regularly with similar ratios of peak area counts.

matograms of two respective groups of data from total 20 sampling rounds in the data processing system. The top ten compounds which made great contributions to the characteristics for various seasons were exported in the Table 3. Two main factors, probabilities and mean peak area counts, were taken to evaluate the contribution of each discernible peak. The statistic data showed that aldehydes, alcohols, eaters and long-chain alkanes formed the primary distinction

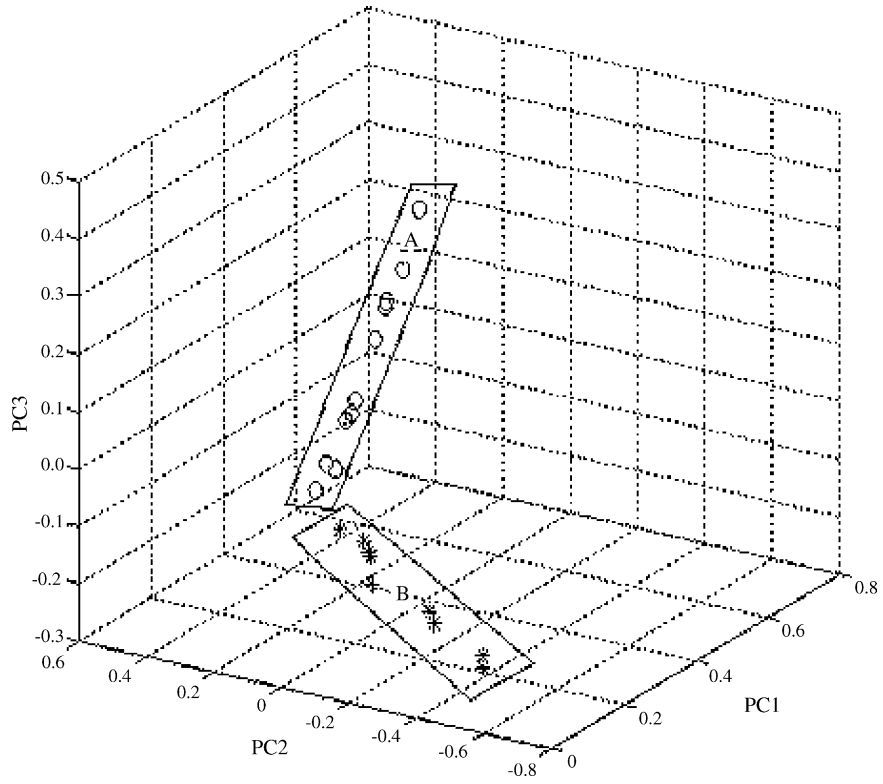

Fig. 5. Pattern recognition based on PCA. The rectangular area (A) represents the segregation of the spring sampling data cluster. The rectangular area (B) represents the segregation of the winter sampling data cluster.

Table 3
Top 10 compounds contributing to characteristics in different seasons

Compounds	Contribution percentage	Peak number
Nonanal	6.07	6
Diphenyl ether	3.33	17
3,7-Dimethyl-6-octanol	2.96	10
2-Ethyl hexanol	2.94	3
Eicosane	1.80	35
Tridecane	1.58	13
Octanal	1.23	2
Decanal	1.23	9
Isobornyl propionate	0.84	16
3, 7-Dimethyl-2, 6-octandiol	0.63	27

of the emission behavior in the different seasons. Previous works have proposed some potential chemical attractants of mosquitoes such as carbon dioxide, L-lactic acid, octanal, nonanal, decanal, butanone, 3,7-dimethyl-6-octanol, 1-octen-3-ol, phenol, honey extract, limburger cheese flavor, etc. [1,18–22]. It is remarkable that most of emanations contributing to seasonal characteristics in our study have been regarded as potential mosquito's attractants in the previous works. It is expected that the suitable compositive ratios of the identified emanations have the possibility to be attractants for mosquitoes. On the other hand, the alteration of metabolic equilibrium caused by diseases would change the normal emission behaviors of human odors. Therefore, if the fingerprint characteristics of human odors could be studied and specified in detail, informative biomarkers presented in the human odors would also benefit the diagnostics of human being's diseases and criminal identifications.

4. Conclusions

A simple and efficient method consisting of SPME-based sampling system and GC–MS analysis was created to identify volatile organic emanations from the human arm skin and expose fingerprint characteristics of human odors. Great efforts have taken to reduce backgrounds in the sampling procedure, including the special-designed active sampling device and chemometrics-based data processing system. The method is noninvasive and comfortable, appreciated by all candidates, under the optimizing experimental conditions: 65 μm PDMS-DVB SPME fiber coating, 30 min sampling time and room temperature. Especially, the sampling time of 30 min achieves the excellent analytical sensitivity and comforts the candidates at the same time. The developed chromatographic data processing system based on Matlab proves suitable and powerful to manage the mass of both chromatographic and MS data in this work. The variety of emanation characteristics in different seasons apparently emerged when PCA was performed to extract the useful information from the data of two season samplings. Ten compounds among 35 identified emanations do great contributions to the seasonal characteristics of emission behaviors of human odors based on comparisons of related chromatograms. The results suggest that the analysis based on fingerprint characteristics of human emanations from the arm skin could be valid to obtain important biomarkers with some corresponding biological strategies [3]. It is strongly believed that fingerprint characteristics of human emanations would change when diseases of human beings cause the variations of human odors. Therefore, the informative fingerprint characteristics of human odors possess the possibility to be a simple, efficient and noninvasive tool not only for biological use but also for the diagnostics of human being's diseases and criminal identifications.

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