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Discrimination of 11 Chinese Materia Medica from *Umbelliferae* by Electronic Nose

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Abstract

In this paper, electronic nose (E-nose) was used to discriminate the 11 Chinese Materia Medica (CMM) from *Umbelliferae* by the difference of their odors. The E-nose generated data were analyzed by discriminant function analysis (DFA) and the responses of 18 sensors of E-nose were evaluated by CA analysis. Results showed that a rapid evaluation of complex response of the samples could be obtained, in combination with DFA, SQC and the CA analysis of the E-nose was given better results in the recognition values of the odor of the 11 CMM. All the 11 CMM could be distinguished by E-nose coupled with DFA, sensor 2, 3, 4, 5, 11, 13 and 15 were found to be able to better discriminate between the CMM samples. The CMM from Umbelliferae produced from different areas and processed with different methods could be distinguished by the E-nose, too. The results of the similarity of fingerprints of the E-nose are fitted with the TCM records about the property (yaoxing), channel tropism (guijing), function and usage of the CMM. The E-nose is a technology that can reflect the holistic odor of a CMM and is relevant to the TCM doctor's practical identification. The odor of CMM can be expressed by objective data instead of subjective sense by human nose. Based on the sensor`s intensity of E-nose, the fingerprint of a CMM can be established, too. Although the E-nose has so many advantages, only use E-nose technology is not enough to control the quality of a CMM. It must be combined with the other macroscopic discriminating technology, such as the E-tongue, the E-eye, to have a holistic evaluation of a CMM.

Keywords: Chinese Materia Medica from Umbelliferae, Electronic Nose, Discrimination, Odor

1. Introduction

Chinese Materia Medica (CMM) are materials, which the Traditional Chinese Medicine (TCM) doctors used to treat diseases of the human being for thousand years. In ancient China, macroscopic characteristics, such as shape, size, color, smell and taste were used by TCM doctors used to identify CMM and to evaluate their quality. Macroscopic identification relies on the naked senses, and is therefore a simple, fast and easy way to authenticate CMM [1].The odor of CMM refers to the olfactory stimuli, such as aromatic, distinctive, or unpleasant smells [2]. Each CMM has its own special odor to some extent, especially those containing volatiles, such as Szechwan lovage rhizome (Rhizoma chuanxiong, chuanxiong, RCX), Chinese angelica (Radix angeicace sinensis, danggui). Traditionally, for the same CMM, samples with strong odors are considered to be superior in quality. In the modern day, it is understood that the strength of the odor often reflects the volatiles` content. As the CMM from Umbelliferae is considered, each CMM contains many kinds of volatiles, such as, coumarins, phenols，acids, etc [3]. The odor is reflecting all the volatiles of the CMM. Most of the CMM from Umbelliferae have strong odors, and their odors are mostly xin (pungent) in nature, they are classified as balmy by TCM doctor. That is why traditionally odor was used as an important standard to evaluate the quality of the CMM from Umbelliferae.

Usually, CMM are used as whole plant and/or combination of several herbs, and multiple constituents are responsible for the therapeutic effects. Therefore, quality control of CM is very difficult. To date, the valid method for quantitatively evaluating the quality of the CMM is poor [4]. Today, in China Pharmacopea, chemical analy-

sis of volatiles which have odors, by HPLC and TLC, are used to control quality of the CMM from Umbelliferae. And the volatiles, such as, ferulic acid, is used as a reference compound to control the quality of RCX, *Radix angelicae ainensis* (*danggui*) and *Rhizoma et Radix ligustici* (gaoben) [5]. We think this method can not objecttively reflect the quality of a CMM from *Umbelliferae*. First of all, the method based on the chemical component analysis has no relationship with the traditional TCM doctor's experience identification, a technology based on the macroscopic characteristics of a CMM, including appearance, color, odor and taste. The second is that there are many components in a CMM, only use one or two component(s) can not reflect the holistic quality of a CMM. For example, RCX contains more than fifty kinds of chemical components. It contains 40 kinds of volatile oil, such as ligustilide (58%), 3-butylphthalide (5.29%), etc. And it contains lactones, alkloids, phenols and acids, too [3]. But only ferulic acid was used as a reference compound to control the quality of RCX in China Pharmacopoeia [5]. The ferulic acid is not the main active component of this CMM, why is it used as a reference compound? Because although it is known that the main active component of RCX is ligustilide, but this component is not stable, it is very easy to break down when exposed to air or light. Even use ligustilide as a reference compound can not reflect the whole odor of RCX, because the odor of RCX is made up of the volatile oil, the lactones, the phenols and the acids. Another example is ginseng (*Radix ginseng*, renshen). In traditional experiences, ginseng of a large size is thought to be of superior quality. However, modern studies have indicated that the content of ginsenoside in the fiberous roots is higher than that in the main root [6]. It seems that not all the ancient statements on the genuineness and quality based on macroscopic characteristics are correct. But the actual explanation for this phenomenon is that only use ginseside as reference compounds can not reveal the genuineness of the ancient statement about ginseng. Why? Because ginseng has many components and the superior quality of ginseng is based on the macroscopic characteristics that all the components contained in ginseng displayed.

In China, Daodiyaocai (Genuine Traditional CMM) is a most important concept in the TCM theory. In another word, a CMM produced from a special area is better than the CMM produced from the other areas. For example, RCX produced from Dujiangyan county is a Genuine Traditional CMM [7]. Another example is *Radix angelicae sinensis* (danggui), this CMM produced in Ming county, Gansu is better than produced form other areas such as Sichuan and Yunnan provinces [7]. For a long time, painstaking efforts were done to reveal the connotation of the Daodiyaocai, but there is no ideal results to this puzzle. Because except the production area difference, e.g. climate, soil, there are many other factors, such as cultivating technology, the field management, the processing method, etc, can effect the quality of the CMM, too [2]. An objective method, which is closely related with the traditionally macroscopic identification and quality evaluation is needed to express the quality of CMM changes with the variations of the factors mentioned above.

The E-nose is an instrument that mimics the TCM doctor's olfactory perception and provides an odor fingerprint of the sample, it is equipped with an array of non-selective and broad-spectrum chemical sensors useful for the analysis of headspace of liquid or solid samples [8].Therefore it is a technology that can reflect the macroscopic characteristic of a CMM. As a non-invasive method, the E-nose has gradually being applied in the quality assessment of Chinese medicine [9-13]. The E-nose has been appropriately used in the quality assessment of precious traditional Chinese medicines, such as musk, too [14].

Is the electronic nose (E-nose) can correctly explain the property (yaoxing) of the CMM? Is the E-nose can correctly explain the genuineness and quality based on macroscopic characteristics? Is the E-nose can reveal one aspects of the connotation of the Daodiyaocai? In this paper, E-nose was used to identify 11 CMM from *Umbelliferae* and the quality control of a CMM based on the holistic theory of TCM is discussed.

2. Materials and Methods

2.1. Experimental Material

9 of the CMM purchased in Chengdu Hehuachi market of CMM and 2 of the CMM collected in their produced areas were used as testing samples. The samples were identified by Professor Guangming Shu from Sichuan Academy of Chinese Medical and Materia Medica Sciences. The name, the production area, the property (yaoxing) in nature, the channel tropism (guijing), the function, the usage, the components and the reference compounds were listed in **Table 1**.

2.2. Electronic Nose

FOX-4000 (Alpha-M.O.S., France) consists of a sampling apparatus, a detector unit containing an array of 18 sensors, air generator equipment, HS-100 autosampler and pattern recognition software (SOFTV12) for data recording. The sensor array is composed of 18 metal oxide semiconductors (MOSs) chemical sensors divided into chambers as three types: T, P, and LY.

Table 1. The details of the CMM samples utilized in the experiment.

No.	Sample name [5]	Production area	Reference compound [5]	Property (odor and taste) in nature	Components [3]	Channel tropism [6]	Usage [5]	Function [5]
1	Fructus foeniculi	Neimenggu province	Trans-anethole	Pungent and balmy	trans-anethole, anisaldehyde, anisole, *α*-fenchone, methylchavicol, fenchone, limonene, *α*-pinene, xanthotoxin, *α*-amyrin, coumarins: imperatorin, bergapten, 7-hydroxycoumarin, arachic acid, behenic acid 6,7-dihydroxycoumarin, oleanolic acid, linoleic acid, petroselinic acid, palmitic acid	liver, kidney, spleen, stomach	Abdominal pain caused by invasion of the pathogenic cold, dysmenorrheal, cold pain in the lower abdomen	Clearing away cold, alleviating pain, regulating the flow of qi, normalizing the function of stomach and spleen
2	Fructus cnidii	Gansu province	Osthol	bitter, pungent and balmy	Coumarins: osthol, imperatorin, bergapten, isopimpinellin, xanthotoxin, xanthotoxol; biscoumarins: cnidimonal, cnidimarin; coumarin derivatives: 5-formylxanthotoxol, 2-deoxymeranzin hydrate, volatile oil: L-pinene, L-camphene, bornyl isovalerate, isoborneol, dihydrooroselol, columbianadin, ciniadin, palmitic acid	kidney	skin ailments (itchy, "wet" skin conditions, eczema, scabies and acne), vulval and vaginal itching and infections, sexual dysfunction, allergy, sexual Malaise, frigity and female sterility	eliminating dampness, dispersing pathogenic wind, destroying parasites, relieving itching, warming kidney and invigorating kidney-yang
3	Radix angelicae pubescentis	Sichuan province	osthol, columbianetin acetate	bitter, pungent and a little balmy	coumarins: osthol, bergapten, xanthotoxin, angelols A,B, C, D, E, F, G, H, J, angelitriol, angelin, columbianetin, columbianetin acetate, columbianadin, isoimperatorin, columbianetin-*β*-D-glucopyranoside, umbelliferone, nodakenin, angelidiol, oxypeucedaninhydrate, columbianetin propionate, isoangelol, anoupubesol; essential oil: 1-Methyl-2-isopropylbenzene, *α*-pinene, himachalol, 2,3,5,6-tetramethylphenol, longifolene, palmitic acid, *α*-phellandrene, humulene, sylvestrene	kidney bladder	Numbness caused by wind-cold-dampness, lambago, Shaoyin headache, headache due to pathogenic wind-cold-dampness	dispersing pathogenic wind, removing dampness, relieving stagnation and alleviating pain
4	Radix glehniae	Jilin province	-	sweet, a little bitter and a little balmy	Isoimperatorin, lupine, betulin, *β*-sitosterol, daucosterol, panaxynol, facarindiol, (8E)-1,8-hepta-decadiene-4,6-diyne-3,10-dioland, *α*-pinene, *β*-phellandrene, germacrene B, phellopterin, bergapten, xanthotoxin, psoralen, scopoletin, xanthotoxol, 9-geranyloxypsoralen, marmesin, bergaptin,7-O-3,3-dimethylallyl scopletin, osthenol-7-O-*β*-gentiobioside, imperatorin, isoimperatorin, alloisoimperatorin, cnidilin, poly-saccharides	lung and stomach	cough caused by lung-heat, deficiency of the stomach-yin and consumption of body fluid caused by febrile disease, thirsty	Nourishing Yin, Clearing away the lung heat, reinforcing stomach, promoting the production of body fluid

5	Radix peucedani	Guizhou province	praeruptorin a,b	bitter, pungent and a little cold	praeruptorin a,b,c,d,e, pteryxin, scopolin, 3'(S)-angeloyloxy-4′(R)-isovaleryloxy-3′,4′-dihydroseselin , decursin, peucedanocoumarin I-III, nodakenin, 5,8-dimethoxypsoralen, anchoic acid, isoscopoletin, umbelliferone, praeroside I-V	lung	cough and tachypnea due to pathogenic wind-heat, phlegm, Asthma due to excessive phlegm caused by pathogenic heat, cough and phlegm caused by pathogenic wind-heat	Depressing upward-reverse flow of qi, resolving phlegm, clearing the wind and clearing away heat
6	Radix chuanming-shinis violacei	Lanzhong Sichuan province, without cortex	-	Sweet, mild, a little balmy	5,8-dimethyoxy-psoracen, umberlliferone, 5-pentenyl-8-methoxy-psoracen, deltoin, marmesin, ammijin; feruic acid, octadecoic acid, polysaccharides	Lung, spleen, stomach	cough caused by lung-heat, consumption of yin caused by febrile disease	nourishing Yin, reinforcing the lung, invigorating spleen
7	Radix saposhnikoviae	Liaolin province	prim-O-glucosylcimicifugin, 5-O-methylvisammiosode	pungent, sweet and a little balmy	octanal, *β*-bisabolene, nonanal, imperatorin, 3'-o-acetylhamaudol, scopoletin, cimicifugin prim-o-glucasylcimifugin, anomalin, 5-O-methylvisammiosode, bergapten, psoralen, xanthotoxin	bladder, liver, spleen	wind-cold type common cold, headache, acute tonsillitis caused by pathogenic wind-cold	Promoting blood circulation, promoting the circulation of qi, dispersing pathogenic wind, and alleviating pain
8	Rhizoma chuanxiong	Dujianyan county, Sichuan province, sun dried	ferulic acid	pungent and balmy	ligustilide, ferulic acid, neocnidilide, 3-butylphthalide,3-butylidene phthalide, cnidiumlactone, 4-hydroxy-3-butylphthalide, ligustilidiol, vanillic acid, vanillin, chuanxiongzine, bis-5,5'-formylfurperyeether,spathulenl,sabinene,chuanxiongol, 2,2'-ligustilide, linoleic acid, palmitic acid, 4-hydroxy-3-methoxy styrene	liver, gallbladder, pericardium	Numbness of chest, cardialgia, sternocastal pain, amenorrhoea, dysmenorrheal, headache, irregular menstruation, abdominal pain, acute tonsillitis caused by pathogenic wind-cold, headache, swollen due to tumble	Promoting blood circulation, promoting the circulation of qi, dispersing pathogenic wind, nd alleviating pain
9	Rhizoma et Radix ligustici	Kangding county, Sichuan province	ferulic acid	pungent and balmy	ligusinenoside A,B,C, Ligusinenosides A-C, ferulaic acid, ligustilide，3-butylidene phthalide,neocnidilide, cnidilide, palmitic acid, terpineol-4, 4-terpinylacetate,*α*-cedrene, 3-butylidene-4,5-dihydrophthalide, myristicine, spathulenol, *β*-phellandrene, *β*-selinene, methyleugenol, bergapten, scopoletin , 5-Oxo-*δ*-4-decahydrobenzindene	bladder	wind-cold type common cold, headache, acute tonsillitis caused by pathogenic wind-cold	Dispersing pathogenic wind, clearing away cold, removing dampness, alleviating pain
10	Radix angelicae sinensis	Ming county, Gansu province	ferulic acid	sweet, pungent and balmy	ligustilide, n-butylidene phthalide, carvacrol, camphoric acid, anisic acid, azelaic acid, 6-methoxy-7-hydroxycoumarin, palmitic acid, ferulaic acid,angelicide,vanillic acid, brefeldin, phosphatidylcholine, poly-saccharides	liver, spleen heart	Deficiency of blood, atrophy, irregular menstruation, acute tonsillitis caused by pathogenic wind-cold, contipation	Enriching blood, promoting blood circulation, regulating menstruation, loosening the bowel and relieving constipation

11	Rhizoma et Radix notopterygh	Sichuan province	Notopterol, isoimperatorin	Pungent, bitter and balmy	α-pinene, β-pinene, α-copaene, trans-β-farnesene, benzyl benzoate, limonene, p-hydroxyphenthyl anisate, ferulic acid, oleic acid, linoleic acid, sabinene, notopterol, isoimperatorin, cnidilin, nodakenin, ehtylnotopterol, notopterol, 5-hydroxy-8-(1,1'-dimenthylallyl) psoralen, bergaptern, osthenol, phenethyl, ferulate, trans-ferulic acid	bladder	wind-cold type common cold, headache, acute tonsillitis caused by pathogenic wind-cold,	Relieving exterior syndrome, clearing away cold, dispersing pathogenic wind, removing dampness, alleviating pain
12	Radix chuanmingshinis violacei	Qingbaijiang, Sichuan, without cortex	the same as No. 6	Sweet, mild, a little balmy	the same as No. 6	Lung, spleen, stomach	the same as No. 6	the same as No. 6
13	Rhizoma chuanxiong	Penshan, Sichuan, sun dried	ferulic acid	pungent and balmy	the same as No. 8	the same as No. 8	the same as No. 8	the same as No. 8
14	Rhizoma chuanxiong	Penshan, Sichuan province, coal heated	ferulic acid	pungent and balmy	the same as No. 8	the same as No. 8	the same as No. 8	the same as No. 8
15	Radix chuanmingshinis violacei	Qingbaijiang, Sichuan province, with cortex	-	Sweet, mild, a little balmy	the same as No. 6	the same as No. 6	the same as No. 6	the same as No. 6

2.3. Experiment Procedure

Experiments were performed on FOX-4000. The samples were accurately weighed for 0.5 g and placed in 10 ml sealed headspace vials and loaded into the autosampler tray; then 1000 μl of headspace air was automatically injected into E-nose by a syringe and flow-injected into the carrier gas flow.

In the testing process, distilled water was used to adjust the carrier gas humidity. The synthetic dry air was pumped into the sensor chambers with a constant rate of 150 ml/min via an air transformer connected to a syringe during the measurement process. The injection volume was 1ml, injection rate of 1ml/s, the total syringe volume of 2.5 ml, while the syringe temperature was maintained at 35˚C. The time of acquisition parameters and the time between injections are respective 120 s and 600 s. Each sample was measured four times based on highly accurate repeatability. The maximum response points automatically recorded for each 18 sensors were used as the E-nose response.

2.4. Data Analysis

The responses of the electronic nose were at first analyzed by DFA to investigate the presence of classes inside the samples population. The DFA results were discussed in details according to the property, the chemical components, the channel tropism, the function and the usage, production areas and processing methods of the samples to characterize the CMM by the electronic nose. CA was employed to examine the sensorial data and test the relationships of various CMM. Finally, SQC was used to perform the classification of the CMM samples [15]. All calculations were performed in SOFTV 12 and SPSS software.

3. Results and Discussion

3.1. The Common Characteristics among the 11 CMM from *Umbelliferae*

There are many common characteristic among the 11

CMM from *Umbelliferae* as shown in **Table 1**. There exist differences between the TCM and the Western medicine, such as the yaoxing (property), the guijing (channel tropism), the function and the usage, etc. The yaoxing (property) and guijing (channel tropism) are the unique characteristics of TCM.

First, we can find that all the 11 species have pungent and bitter odors, their yaoxing (property) are mostly balmy or a little balmy in nature, only *Radix peucedani* (qianhu, N5) has a property of a little cold in nature. In TCM theory, the CMM which has strong pungent or sweet odors and dispersing characteristics has a yaoxing (property) of mostly balmy or hot in nature [16], such as RCX (N8, N13 and N14). Traditionally, for the same CMM, sample with the strongest odor is considered to be superior in quality [2].

Second, it can be found in **Table 1**, there are many components in the sample of the 11 CMM from *Umbelliferae* [4]. Furthermore, there are many common components, e.g. volatile oils, coumarins , phenols, acids and lactones in the 11 CMM as listed in **Table 1**. For example, coumarins can be found in all of the 11 CMM except RCX; sample 1, 2, 3, 4, 8, 10 contain α-pinene; sample 1, 2, 3, 4, 7, 8 contain bergapten, etc. It is understood that the odor reflects all volatiles contained in a CMM and the strength of the odor often reflects the content of all the volatiles. The odor is a holistic expression of all the volatiling components which can be smelled by nose and the E-nose, such as volatile oils, courmins, lactones, phenols and acids, etc. In China, quality assessment of the CMM from Umbelliferae based on macroscopic characteristics, such as odor, is widely used in the CMM markets. Similarly, medicinal vendors classify and price CMM from *Umbelliferae* based on the strength of the odor of the CMM from *Umbelliferae*, and consumers also primarily evaluate the quality of CMM from *Umbelliferae* on the basis of the odor of them. Therefore, use the holistic odor of the CMM from *Umbelliferae* as a standard to evaluate its quality is better than just only use one or a few components as standards. Because there is no relationship between the analysis of a CMM based on the component(s) and the doctor's practical identification. On the contrary, the use of the odor as a standard to evaluate a CMM is relevant to the doctor's practical identification and it is more close to the holism of the TCM theory. The E-nose technology can identify the different odors of volatiles, such as, musk, vinegar, etc [14, 17]. That is why we use E-nose as a tool to discriminate the 11 CMM from *Umbelliferae*.

Third, there are also some common phenomenon of the guijing (channel tropism) of the 11 CMM. In TCM theory, there are 18 invisible channels (jinluo) [16], such as kidney channel, bladder channel, heart channel, lung channel, etc, in the human body. The CMM has special property and can go into the special channel, such as kidney channel. This characteristic of the CMM is called guijing (channel tropism). Three of the CMM (*Fructus foeniculi*, xiaohuixiang, *Fructus cnidii*, shechuangzi, *Radix angelicae pubescentis*, duhuo) can go into the kidney channel, four of the CMM (*Radix angelicae pubescentis*, duhuo, *Radix saposhnikoviae*, fangfeng; RCX, *Radix angelicae sinensis*, danggui) can go into the bladder channel. And four of the CMM (*Fructus foeniculi*, xiaohuixiang, RCX, *Rhizoma et Radix ligustici*, gaoben, *Radix angelicae sinensis*, danggui, *Rhizoma et Radix notopterygh*, qianghuo) can go into the spleen channel. Off course, there are other channels that the 11 CMM can go into, such as, liver channel, lung channel, heart channel and the gallbladder, etc.

Forth, the functions of most of the 11 CMM are somewhat similar to each other. In **Table 1**, Sample 2, 3, 6, 7, 8, 10 have the same function of "dispersing pathogenic wind"; sample 1, 3, 6, 7, 8, 10 have the same function of "alleviating pain".

Fifth, the usages of the 11 CMM are similar, too. For example, sample 6, 7, 8, 9, 10 have the usage to cure acute tonsillitis caused by pathogenic wind-cold; sample 1, 2, 3, 6, 7, 8, 9, 10 have the usage to cure many kinds of pain caused by pathogenic wind-cold, such as headache, lambago and knee pain, etc. Sample 7 and 10 have the usage to cure cold due to pathogenic wind-cold.

Last, from Table 1, it can be found that some reference compounds are used to control the quality of two or three CMM. For example, ferulic acid is used as reference compound to control the quality of RCX, *Rhizoma et Radix ligustici* and *Radix angelicae sinensis*; and Osthol is used as reference compound to control the quality of *Fructus cnidii* and *Radix angelicae pubescentis* [5].

3.2. E-Nose Responses to Samples of the 11 CMM from *Umbelliferae*

Figure 1 shows the typical responses of sensors with RCX (N8). Each line represented the average signal variation of RCX (N8), respectively for one sensor of the 18 sensors. The curves represented the intensity of each sensor against time due to the electro-valve action when the volatiles reached the measurement chamber [15]. In the initial period, the intensity of each sensor was low, then increased continuously, and finally stabilized after a few seconds or minutes. The horizontal axis was the timeline, a total of 120 s; the vertical axis was the intensity of the response, each curve on behalf of a sensor in response to the changes within 120 s. In this study, the maximum response values of each sensor was extracted and analyzed individually. In this way, response values

represented in different curves were explored and other response values with little significance were discarded.

By CA analysis, the relative importance of the sensors in the array was identified. As shown in **Figure 2**, Sensor 2, 3, 4, 5, 11, 13 and 15 have the highest influence on the discrimination of the 11 CMM from *Umbelliferae* family. When compared this result with that of the musk, shexiang [15], senor 2, 3, 5, 15 are the common senors which have the highest influence on the intensity of the E-nose on the two kinds of CMM. While the senor 4, 11, 12, 13, 17 are the different highest influence sensors that can discriminate the CMM from *Umbelliferae* family with the musk, shexiang. Sensor 6 (T30/1) is misclassified to have strong influence on the discrimination of the 11 CMM from *Umbelliferae* family, because its intensity is very low as shown in **Figure 1**. For example, the intensity of sensor 6 (T30/1) of RCX, Dujiangyan (N8) is only 0.0781. In contrast, the intensity of sensor 3 of RCX, Dujiangyan (N8) is –1.481. Therefore sensor 6 (T30/1) can not have strong influence on the discrimination of the CMM from *Umbelliferae*.

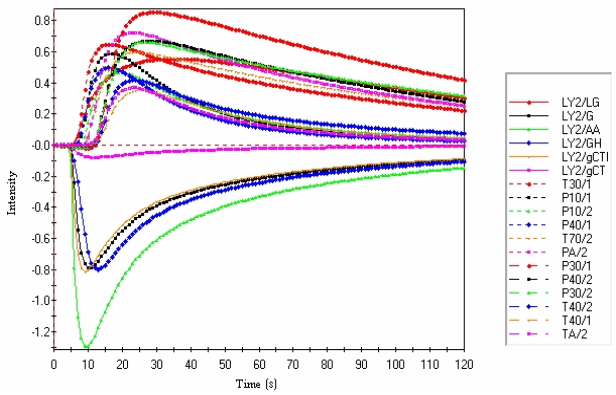

Figure 1. A typical response of 18 sensors during the measurement of RCX (N8).

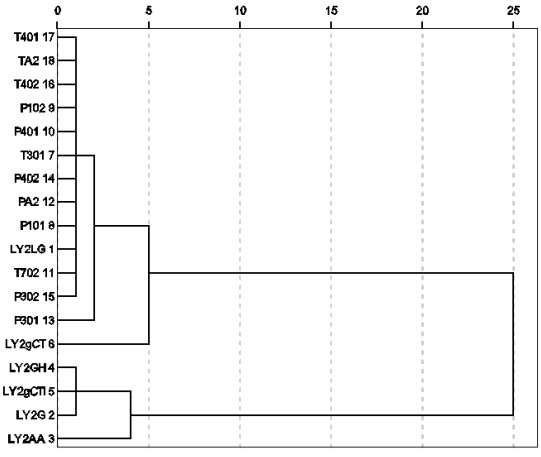

Figure 2. CA dendrogram based on the response intensity of the 18 sensors to the 11 CMM from *Umbelliferae*.

3.3. The Similarity of the Fingerprint of the 11 CMM from *Umbelliferae*

The influence of different odors of the 11 CMM from *Umbelliferae* on the responses of the E-nose was analyzed by dynamic headspace methods. As it is illustrated in **Figure 3**, the odors of the 11 CMM from Umbelliferae samples did not show any significant differences, indicating the composition of the samples in the performance being of the similar odor. The results showed that it was impractical to use a radar map to distinguish the odors of the 11 CMM directly.

The bar chart of the 11 CMM from *Umbelliferae* (**Figure 4**) are similar to the radar fingerprint. This result is reasonable because the same volatiles have the same odor. As we can find in **Table 1** that some of the 11 CMM from Umbelliferae contain many common components, for example, sample 1, 2, 3, 4, 8, 10 contain *α*-pinene; sample 1, 2, 3, 4, 7, 8 contain bergapten, etc.

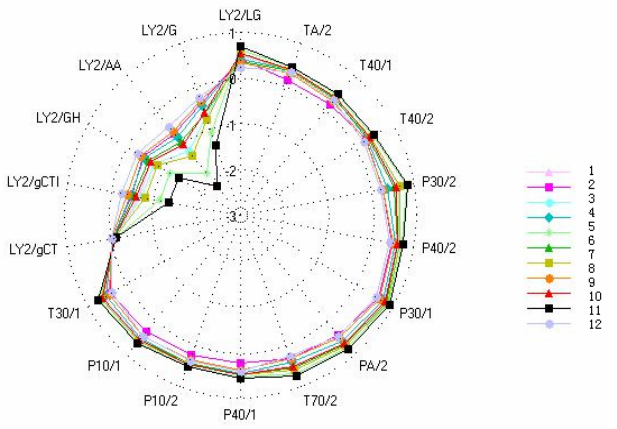

Figure 3. Radar fingerprint of 11 CMM from *Umbelliferae*.

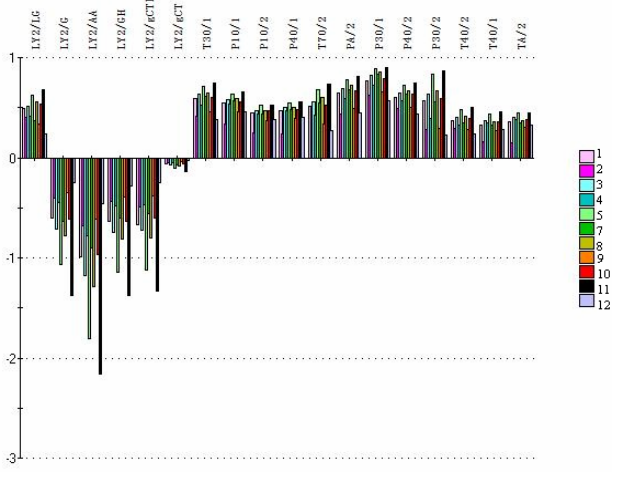

Figure 4. Bar fingerprint of 18 sensors during the measurement of the 11 CMM from *Umbelliferae*.

And this result is fitted with the records of the property, functions and usages of the 11 CMM from *Umbelliferae*, too [5]. Maybe there exists relationship between the similarity of the odor fingerprint with the some of the same property, function and the usages among some of the CMM.

As shown in **Table 1**, *Radix peucedani*, qianhu (N5) has a property (yaoxing) of a little cold in nature, but there has no apparent difference between N5 and other CMM samples in the radar map and in the bar fingerprint (**Figure 3** and **Figure 4**), which has a property (yaoxing) of balmy or a little balmy in nature. That means the odor captured by the electric nose can not reflect the difference between CMM with different property (cold, cool, warm or hot in nature).

In China, Genuine Traditional CMM (Daodiyaocai) is a most important concept of the TCM theory. In another word, a CMM produced from a special area is better than the CMM produced from other areas. For example, RCX produced from Dujiangyan county (Sample 8) is a Genuine Traditional CMM, its quality is generally accepted by the TCM doctors as the best, while RCX produced from other areas, such as Penshan county (Sample 12 and 13) and Penzhou county is not as better as the one produced from Dujiangyan county. The comparison of 18 sensors' intensity of the three samples of RCX, produced from Dujiangyan county and Penshan county is shown in **Figure 5**. The fingerprints of the 3 samples are similar to each other. The coefficient between N8 and N13 is 73%, the coefficient between N8 and N14 is 89.8% and the coefficient between N13 and N14 is 80.7%. The intensity of all the 18 sensors of Dujiangyan county (N8) is weak than that of Penshan county (N13, N14). This result is conflict with the traditional knowledge: RCX produced in Dujianyan is better in quality and RCX with strong aroma is superior in quality [7]. Further research is needed to reveal the genuineness of RCX. Based on the intensity of the E-nose, a fingerprint of the Genuine Traditional CMM (Daodiyaocai), such as RCX can be set up.

3.4. The Comparison between the 11 CMM from *Umbelliferae*

Discriminant function analysis is a supervised classification method aimed at finding a formal decision boundary between classes. The idea is to find linear discriminant functions (S1, S2,…, Sn), which are linear combinations of the original variables. The classification model (DFA) was built on the first four PC, which normally account for over 90% of the variance (information) of the original data matrix. In each case, the DFA model was cross- validated as follows. Data from individual samples (culture or sputum) were withheld, and a DFA model was built on the remaining data set (training set). The data from the withheld samples (testing set) were then inserted into the discriminant functions and subsequently assigned to the class for which the centroid had the smallest Euclidean distance to the unknown sample. The result could be visualized by plotting the individual discriminant functions against each other [18]. **Figure 6** shows the DFA results of the 11 CMM from Umbelliferae data projected onto their first four PCs.

In **Figure 6**, all the 11 CMM samples from Umbelliferae can be isolated from each other by the electronic nose. That means there has difference between the odors of the CMM samples from Umbelliferae. The electronic nose can be used as method to identify the 11 CMM from Umbelliferae. Although the 11 CMM samples from Umbelliferae contain some common components, but most of the components of them are different and furthermore, the contents of the common components is not

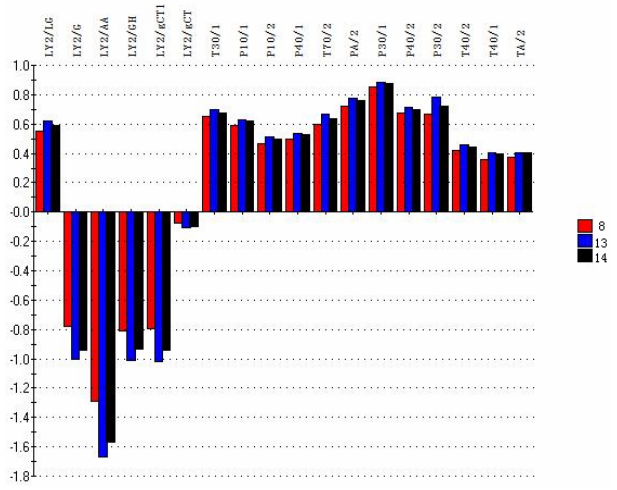

Figure 5. Bar fingerprint of 18 sensors during the measurement of three samples of RCX from different production areas.

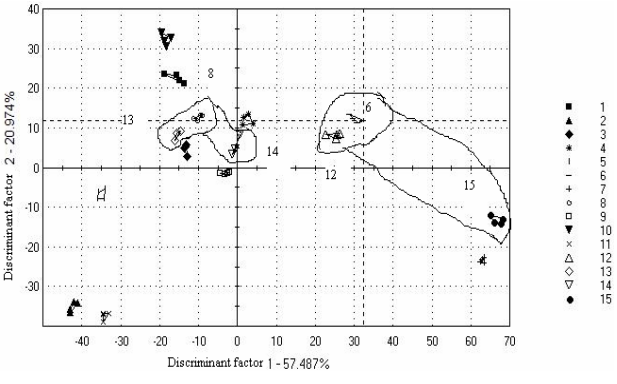

Figure 6. DFA results of the 15 samples of the 11 CMM from Umbelliferae.

the same. This result is fitted with the TCM records of the 11 CMM from Umbelliferae. For example, there exists difference between their characteristics, such as, property (yaoxing), channel tropism, functions and usages, etc, as shown in **Table 1**. Consequently, it is scientific that the TCM doctor uses the smell (odor) as a standard to discriminate the CMM from *Umbelliferae*. The E-nose can reflect the holistic characteristics of the odor of the CMM from *Umbelliferae*, it is more scientific and is more relevant to the practical identification method used by the TCM doctor.

The CMM from *Umbelliferae* which are produced from different areas can easily be discriminated from each other by E-nose, as shown in **Figure 6**. RCX, produced from Dujiangyan county (N8) and Penshan county (N13) can be discriminated with each other in **Figure 6**, *Radix chuanmingshinis violacei*, chuanmingshen, produced from Langzhong county (N6) and Qingbaijian county (N12) can be discriminated with each other, too.

Processing method is very important in the TCM theory. By using different processing methods, the odor of a CMM is changed, consequently the property, function and usage of a CMM is changed, too. In fact, processing method has some effects on the quality of a CMM. The CMM from *Umbelliferae* which are processed with different methods can easily be discriminated from each other by E-nose. RCX, produced from Penshan county, are processed with two methods, sun-dried (N13) and coaled-heated (N14) can be discriminated with each other in **Figure 6**. Therefore the processing method has some effects on the quality of CMM. Sample 14 is coal-heated RCX from Penshan county, its intensity of 18 sensors is decreased than the sun-dried RCX (N13) from Penshan county. As RCX is concerned, the quality of sun-dried one is better than the coal-heated one, as shown in **Figure 5**. It is coherent with the traditional processing method, sun-drying.

Radix chuanmingshinis violacei, chuanmingshen, produced from Qingbaijian county, which are processed with two different methods, cuticle-peeled (N12) and cuticle-keeping (N15) can be discriminated with each other, too.

The difference between the samples with different processing methods (N8, N14 and N6, N15) is more signifycant than the difference between the samples from different production areas (N8, N13; N6, N12).This result indicates that the processing method has more influence on the quality of the CMM from Umbelliferae than the production areas, as shown in **Figure 7**.

Generally speaking, CA can yield a data description in terms of clusters or groups of data points that possess strong internal similarities. CA is a more direct tool to find subclasses than PCA. We used CA analysis to study the relationships and the scale of each affecting factor, such as production areas, Genus, processing method, when the CMM from *Umbelliferae* were surveyed by the electronic nose. The Euclidean metric was used in the CA with an "average between groups" method of linkage. Considering the large amount of the measurements, the average responses of four measurements to each of 15 CMM samples were applied to CA analysis and the CA dendrogram is shown in **Figure 7**.

As shown in **Figure 7**, two different groups could be seen in the dendrogram, the first group included samples 1, 5, 7, 10, 8, 13, 14. The three samples of RCX (N8, N13, N14), can be found in this group. The Euclidean distance between the two sun-dried and coal-heated chuanxiong (N8 and N14) was close and satisfied. The Euclidean distance between N8 and N14 is near than the distance between N8 and N13. This result is contrary with the DFA result. *Radix peucedani*, Qianhu (N5) was misplaced in the first group with N8 and N14 in **Figure 7**. And sample 2, 4, 9, 6, 12, 15 formed the second group. It is shown that the *Radix chuanmingshinis violace*, Chuanmingshen with cuticle, Qingbaijiang were more similar to each other and the Euclidean distance between them (N6, N12) was close and satisfied, this result is similar with the DFA result.

Sample 4 and sample 6, 12, 15 are clustered as in the second group. This result is relevant to the TCM theory. Sample 4 (*Radix Glehniae*) is also called beishashen in China, and sample 6 (*Radix chuanmingshinis violacei*) is called chuanmingshen in China [8]. When a CMM is called "shen", like renshen (Radix ginseng), it has a function to nourish yin of the body. *Radix chuanmingshinis violacei* and *Radix glehniae* have the functions to nourish yin of the body, as shown in **Table 1**.

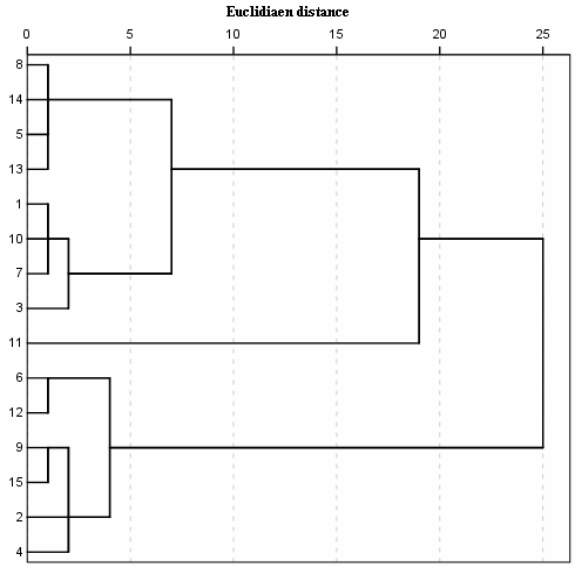

Figure7. CA dendrogram based on the average responses of 18 sensors to the 11 CMM samples from *Umbelliferae*.

3.5. The Comparison between the Two Species of *Radix Chuanmingshinis Violacei*, and *Rhizoma Chuanxiong*

Statistica1 quality control (SQC) is a set of statistical tools used by quality professionals to evaluate organizational quality. Descriptive statistics are used to describe quality characteristics and relationships between the samples. Statistical process control (SPC) involves inspecting a random sample of the output from a process and deciding whether the process is producing products with characteristics that fall within a predetermined range. Acceptance sampling is the process of randomly inspecting a sample of goods and deciding whether to accept the entire lot based on the results. As shown in **Figure 8**, the 3 samples of Radix *Chuanmingshinis violacei*, chuanmingshen (N6, N12, N15) and the 3 samples of RCX (N8, N13, N14) can be easily classified into two types. RCX (N8, N13, N14) formed a group which is up the average line (1.3). On the contrary, the three samples of Radix *chuanmingshinis violacei*, chuanmingshen (N6, N12, N15) formed a group which is below the average line (1.3). Therefore, SQC is a very useful tool to classify the samples of the CMM and find the differences between the CMM.

4. Conclusions

The odor of the CMM is a holistic reflection of all the volatile components which can be smelled by nose and E-nose. The E-nose is a technology that can reflect the holistic odor of a CMM and is relevant to the TCM doctor's practical identification. The odor of CMM can be expressed by objective data instead of subjective sense.

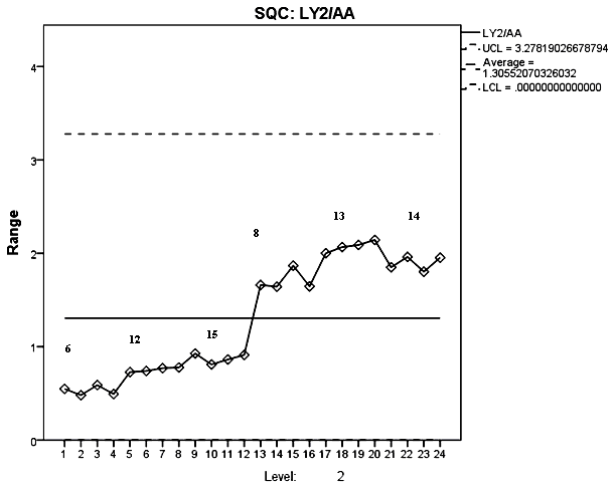

Figure 8. SQC of *Radix chuanmingshinis violacei*, chuanmingshen (N6, N12, N15) and RCX (N8, N13, N14).

The results of the E-nose are fitted with the TCM records about the property (yaoxing), channel tropism (guijing), function and usage of the CMM.

The E-nose can discriminate the CMM without prejudice, and has been demonstrated as a sensitive, fast and non-invasive technology. Moreover, the other advantages of E-nose are like sample is analyzed without reference compound and requiring no pretreatment, etc. These advantages of E-nose show its further application in the quality control of CMM.

The E-nose can be effectively used to discrinimate the CMM from different production areas, different processing methods, storage time, etc. After further research, it maybe a useful tool to reveal the connotation of the Genuine Traditional CMM (Daodiyaocai). Based on the sensor`s intensity of E-nose, the fingerprint of a CMM can be established, too.

Although the E-nose has so many advantages, only use E-nose technology is not enough to evaluate the property (yaoxing) and to control the quality of CMM, it must be combined with the other macroscopic technology, such as the E-tongue, the E-eye [19], to have a holistic analysis of a CMM.

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