Characterization of flavor frame in grape wines detected by HS-SPME-GC-MS coupled with HPLC, electronic nose, and electronic tongue

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Abstract

To analyze the flavor components in 17 commercially available wine samples from seven grape varieties (Cabernet Sauvignon, Cabernet Gernischt, Shiraz, Merlot, Pinot Noir, Tempranillo and Chardonnay), comprehensive flavor characterization, volatile and non-volatile compounds of grape wines were evaluated by headspace solid phase micro-extraction (HS-SPME) coupled with gas chromatography-mass spectrometry (GC-MS), electronic nose (E-nose), electronic tongue (E-tongue), high performance liquid chromatography (HPLC) and automatic amino acids analyzer. According to GC-MS analysis, a total of 86 volatile compounds were identified, mainly including alcohols, esters, phenols, terpenes and norisoprenoids. Results showed that significant differences of contents of free amino acids and radar fingerprint chart of E-tongue technology were recorded for the 17 grape wines. Moreover, principal component analysis (PCA) of E-nose and E-tongue were used to distinguish the different grape wines effectively, with the cumulative contribution rate accounting for 92.33% and 91.78%, respectively. The results prove that sensors W2S and W1W in the E-nose for wines have a higher influence in the current pattern file. The most abundant phenol in 17 wine samples is catechin. The differences in species and contents of volatile and non-volatile substances give the unique flavor of different grape wines. The results demonstrated that the above mentioned equipment are useful for in-depth grape wine flavor analysis.

Introduction

Grape wine is one of the most global widely known and appreciated alcoholic beverages. Moderate consumption may have some beneficial effects on human health due to the high antioxidant activity of wine[1]. Aroma, taste, and appearance are three important indicators to evaluate food quality[2]. Among them, the aroma profile of wine is one of the key factors influencing its quality[3]. Understanding consumer preferences and predicting their behavior is a difficult task for the wine industry. Previous studies[4–10] have documented the organoleptic characteristic such as aroma appreciated by wine consumers. Grape wine is a complex matrix consisting of a wide range of volatile and non-volatile compounds[11]. Although the overall composition of most grape cultivars is very similar, there are distinct aroma and flavor differences between most varieties. These differences can mostly be attributed to relatively minor variations in the proportion of the compounds that constitute the aroma profile of the grape[12]. Especially, the varietal component derived from grape aroma and aromatic precursors, impart specific aroma depending on the cultivars characteristics[13,14] Further, wine flavor is also dependent on fermentation process, storage and aging. The most important aroma substances of wine have been identified as alcohols, esters, aldehydes, ketones, acids, terpenes[15], ethers, lactones, pyrazines, phenolic compounds[16] and sulfur containing compounds. These sulfur-containing compounds can have either a positive or negative

impact on the aroma and flavor of wine, compounds such as 3-mercaptohexanol can impart fruity flavors to a wine[17]. Although some of these compounds are present at low concentrations in the grape wine, they normally have a huge impact on the overall aroma profile[18].

Grape wine is well-known for its health benefits, and most of them are, at least partially, attributed to the presence of phenolic compounds. It has been reported that moderate consumption of alcoholic beverages, especially wine, could protect from cardiovascular disease. This phenomenon defined as the French paradox was proposed for the first time by Serge Renaud[19]. The phenolic compounds originate from original grape and/or formed during alcohol fermentation. Additionally, volatile substances present in concentrations at below their perception threshold may contribute to the final wine aroma and flavor palette by interactive effects with each other in various ways other compounds in wine[20]. Studies also showed that when the ethanol concentration in wine was lowered to 7%, a significant increase in the intensities of the fruity, flowery, and acid flavors and aromas was seen[21].

Flavor is responsible for the overall distinctive sensory properties of grape wine, and is vital in the evaluation of quality. The subtle differences that distinguish one varietal wine from another may depend on the concentration and types of the volatile and non-volatile substances. The quality of wine can be evaluated through both chemical and sensory analysis. The most widely accepted chemical analytical method to

detect, identify and quantify flavor compounds is GC-MS combined with HS-SPME for its high selectivity, sensitivity and precision[22–24]. Equipments such as electronic nose and electronic tongue consisting of an array of sensors are widely applied to detect flavor of food by simulating the olfaction and taste of humans with the advantages of excellent selectivity, high sensitivity, less time-consuming and relatively lower price[25]. Among them, gas sensor arrays are referred to as electronic nose, with partial specificity and an appropriate pattern-recognition system, while chemical sensor arrays are defined as electronic tongue, identifying the five basic tastes (sweet, salty, sour, bitter, and umami)[26]. Depending on the sensing materials, gas sensors of E-nose can be classified into several types including, metal-oxide semiconductor (MOS), conducting polymers (CP), quartz crystal microbalance (QCM), and surface acoustic wave (SAW) sensors[27]. Among them, MOS gas sensor is most widely used for E-nose, it was reported that MOS sensors are sensitive to hydrogen and unsaturated hydrocarbons or solvent vapors containing hydrogen atoms[25]. The common E-tongue has the following types: potentiometry, voltammetry, and impedance spectroscopy[28]. E-tongue can detect the overall taste of food, they cannot identify specific compounds. Taste-active compounds, such as free amino acids (FAAs), were responsible for the characteristic taste of grape wines and also act as precursors to the formation of aromas. Thus, the individual taste compounds can be determined by amino acid detection. Currently, E-nose and E-tongue have been widely researched on quality evaluation of red wine. The E-Nose was revealed like a powerful tool for the objective differentiation of the wines obtained from the authorized grape variety in a Protected Denomination of Origin[29]. A multi-sensor fusion technology based on a novel low-cost E-nose and a voltammetric E-tongue was developed to classify red wines that differ in geographical origins, brands, and grape varieties[30]. Compared to GC-MS, E-noses do not provide information on the quantity of the individual volatile compounds but rather a global analysis of the volatile chemical profile so-called 'fingerprints', which is more similar to the human olfactory perception[31,32].

There is a growing interest in developing rapid methods for the analysis of organoleptic properties of grape wine such as aroma and taste which play a crucial role in consumer preferences and choices[33]. Therefore, accurately and efficiently identifying different wines are of particular importance. In addition, it is important for quality control, storage, and brand recognition as well. In the literature, different methods for wine age prediction[34,35], the influence of grape maturity on wine volatiles and the optimum drying time of the grape to produce sweet wines of higher aromatic quality[36] were investigated. However, there are no systematic studies describing the combined application of HS-SPME-GC-MS, E-nose, E-tongue, HPLC and amino acids analyzer in grape wines flavor studies. Hence, we set up a comprehensive method to analyze the flavor of commercially available grape wines (Cabernet Sauvignon, Cabernet Gernischt, Shiraz, Merlot, Pinot Noir, Tempranillo and Chardonnay). Principal component analysis (PCA) of E-nose and E-tongue was applied to analyze the difference in volatile and non-volatile organic compounds of grape wines. The combination of flavor chemistry with sensory analysis techniques could provide a comprehensive odor and taste characterization of wines, which could provide an effective method for consumers to choose their preferred grape wines. The information obtained in this study would have important referential value for the flavor research of grape wines.

Materials and methods

Materials

By researching the types of grape wines sold in the local supermarket in Nanjing, China, 17 commercially available grape wines from seven different grape varieties (Cabernet Sauvignon, Cabernet Gernischt, Shiraz, Merlot, Pinot Noir, Tempranillo and Chardonnay) were studied as experimental samples (Table 1). HPLC grade methanol, acetic acid, ethyl acetate and phenolic acid standards (gallic acid, protocatechuic acid, vanillic acid, catechin, caffeic acid, syringic acid, *p*-coumaric acid and ferulic acid) were purchased from Sigma-Aldrich Chemical Company (St. Louis, MO, USA). Water was purified on Simplicity system (Millipore) to prepare the aqueous solutions.

Methods

HS-SPME-GC-MS analysis

The volatile compounds of grape wine were determined using HS-SPME-GC-MS according to the reported methods[37] with slight modification. The methods have been proved to develop a derivatization protocol for untargeted GC-MS analysis.

Grape wine (10 mL) was mixed with 2.0 g sodium chloride. The mixture was placed in a 20 mL headspace vial, and stirred at 40 °C for 30 min. To extract volatile compounds from grape wine, a 50/30 μm (DVB/CAR/PDMS) fibre (Supelco, Bellefonte, USA) was used which was preconditioned at 250 °C for 10 min. The fibre was exposed to the sample headspace and extracted at 40 °C for 40 min. After extraction, the fibre was inserted into the splitless injector of the GC-MS (7890A-5975C, Agilent, USA) to identify the volatile compounds. The gas chromatograph was equipped with a 5% phenylmethyl

Table 1. The details of the grape wines utilized in the experiment.

Sample number	Grape wine varieties	Country of origin	Alcohol content (V/V %)
1	Cabernet Sauvignon-A	China	12.0
2	Cabernet Sauvignon-B	China	13.0
3	Cabernet Sauvignon-C	China	12.5
4	Cabernet Sauvignon-D	China	12.0
5	Cabernet Sauvignon-E	France	12.0
6	Cabernet Gernischt-A	China	12.5
7	Cabernet Gernischt-B	China	12.5
8	Shiraz-A	China	13.0
9	Shiraz-B	Australia	14.5
10	Pinot Noir-A	China	13.0
11	Pinot Noir-B	China	12.0
12	Merlot-A	Australia	13.5
13	Merlot-B	Australia	14.0
14	Merlot-C	Australia	13.8
15	Merlot-D	China	12.5
16	Tempranillo	Spain	13.0
17	Chardonnay	Australia	13.0

silicone capillary column (HP-5, 30 m × 0.25 mm × 0.25 μm, Agilent, USA). The injector temperature was 250 ℃. The carrier gas was helium at a constant flow rate of 1.0 mL/min. Analysis was carried out in the electronic impact mode at 70 eV. The temperature of ionization source and quadrupole was 250 ℃ and 150 ℃, respectively. Detection was performed in full scan mode, from 29 aum to 550 aum. The identification was determined using the NIST.08 libraries and the minimum matching requirement was 80%. The relative content was calculated on the basis of peak area percentage. Each sample was measured in triplicate.

Analysis of phenolic compounds using HPLC

The extraction method of phenolic compounds referred to Caceres-Mella et al.[16]. Phenol analysis was carried out with HPLC (LC-20AD, Shimadzu, Japan).The HPLC system consists of a diode array detector (SPD-M20A), autosampler (SIL-20A) and a column oven (CTO-20A). HPLC assay was conducted as described by Beta et al.[38] with some modifications. Their analysis results verify the validity and universality of the method. 250 mm × 4.6 mm, 5 μm ZORBAX SB-C18 (Agilent, USA) was used for separation. The mobile phase consisted of A (0.1% acetic acid in water) and B (0.1% acetic acid in methanol), and the flow rate was 0.9 mL/min. The contents of phenolic compounds were quantified using external calibration curves. The gradient elution program was as follow: 91%–86% A for 0–11 min, 86%–85% A for 11–17 min, 85%–81% A for 17–28 min, 81%–72% A for 28–38 min, 72%–60% A for 38–46 min, 60%–30% A for 46–65 min, and 30%–91% A for 65–75 min. The column oven temperature was held at 30 ℃. The injection volume was set to 20 μL and detection wavelength was 280 nm. Analyses were performed in triplicate.

Analysis of free amino acids

The procedures were conducted according to the published literature by Xia et al.[39]. Ten mL grape wine sample was mixed with 10 mL sulfosalicylic acid (10%) to precipitate protein and then centrifuged at 4 ℃ for 20 min (10,000 rpm/min). Subsequently, the supernatants were filtered with a 0.45 μm micro-pore filter membrane. The content of free amino acids in grape wines was detected by automatic amino acid analyzer (L-8900, Hitachi Ltd., Tokyo, Japan) with a column packed with Hitachi custom ion-exchange resin 2622 (4.6 mm × 60 mm, particle size 5 μm) and then calculated by calibrating with standard amino acids (0.1 μmol/mL). Twenty μL sample solution was injected into the automatic analyzer to obtain the peak area of each amino acids in grape wine. Each sample was measured in triplicate. Quantitation was analyzed by an external standard method and the content of amino acids in the sample was calculated by the formula as follows:

$$M_i = \frac{X_i \times (V_W + V_S)}{V_0 \times V_w}$$

Where M_i (mg/L) is the content of amino acid 'i' in samples, V_s (mL) is the volume of sulfosalicylic acid, X_i (ng) is the concentration of amino acid 'i' detected by the instrument, V_0 (μL) is the injection volume, and V_w (mL) is the volume of the wine sample.

Analysis of E-nose

The analysis of grape wine was performed with a portable electronic nose PEN 3, (Airsense Analytics GmbH, Germany) which was composed of an array of 10 metal oxide semiconductors (MOS). The response characteristics of each sensor were shown as follows: W1C (aromatic compounds); W5S (nitrogen oxide); W3C (ammonia and aromatic compounds); W6S (hydrogen); W5C (olefin and aromatic compounds); W1S (hydrocarbons); W1W (hydrogen sulphide); W2S (alcohols and partially aromatic compounds); W2W (aromatic compounds and organic sulphides); W3S (alkanes (methane, etc.). E-nose was applied to identify different volatile species. The pattern recognition software (Win Muster v.1.6.2) was used for data recording and elaboration.

The E-nose analysis was conducted according to a method of Liu et al.[40], 10 mL grape wine was injected into a headspace vial of 40 mL volume and equilibrated at 25 ± 2 ℃ for 30 min to reach a steady state. The headspace gas was pumped through the sensor array for 80 s (injection time) with a flow rate of 300 mL/min. After sample analysis, the system was purged for 100 s with filtered air to enable the signals to return to the baseline. Each sample was measured in triplicate.

Analysis of E-tongue

This experiment was conducted with the Taste-Sensing System SA402B (Intelligent Sensor Technology Co. Ltd. Japan) according to the method from Liu et al.[40]. This E-tongue system was comprised of reference electrodes (Ag/AgCl), auto-sampler, and sensor array. Taste sensors used in this experiment include sourness, bitterness, astringency, umami and saltiness. In this experiment, all the wine bottles were opened on the same day, and samples were stored at a constant temperature of 25 ℃ before measurement. After centrifugation at 12,000 rpm for 15 min, 80 mL grape wine was filtrated, and the supernatant was gained for electronic tongue determination. Each sample was repeated four times, and the last three stable sets of data were retained.

Data analysis

All the assays were performed in triplicate for each of grape wine and the experimental data was expressed as mean values. The PCA data were organized by Origin 95. Radar fingerprint chart was organized by Excel. Electronic nose measurement of grape wine sample was performed using Win Muster software (Winmuster1.6.2) for loading analysis. Least significant difference (LSD, defined when $P < 0.05$) were used to analyze the significant differences among 17 wine samples via SAS (V8.0, the SAS Institute, USA).

Results and discussion

HS-SPME-GC-MS analysis

A total of 86 volatile flavor compounds were identified in 17 samples from seven kinds of grape wines using HS-SPME-GC-MS, including 10 alcohols, 44 esters, 14 terpenes and norisoprenoids, eight hydrocarbons, five acids, one aldehyde, two phenols, and two other compounds (Supplemental Table S1). About 46, 41, 45, 45, 59, 16 and 13 kinds of volatile compounds were identified on Cabernet Sauvignon, Cabernet Gernischt, Shiraz, Merlot, Pinot Noir, Tempranillo and Chardonnay, respectively. As shown in Fig. 1, the sum content of esters and alcohols made up the most of total volatile content. Alcohols were the predominant flavor substances in
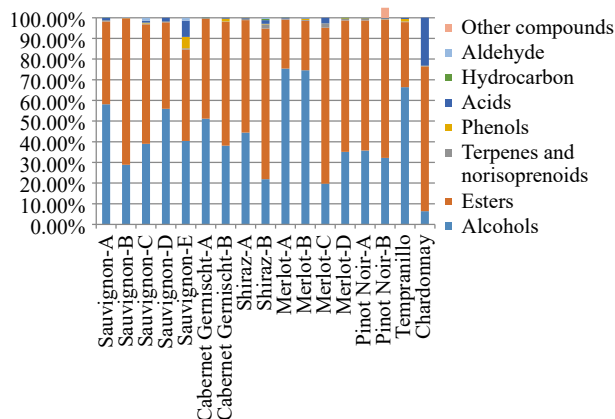
Fig. 1 The relative contents of volatile compounds classes of seventeen wine samples.

Cabernet Sauvignon-A, Cabernet Sauvignon-D, Cabernet Gernischt-A, Merlot-A, Merlot-B and Tempranillo with relative contents of 58.16%, 55.96%, 51.13%, 75.44%, 74.61% and 66.57%, respectively. However, in Cabernet Sauvignon-B, Cabernet Sauvignon-C, Cabernet Sauvignon-E, Cabernet Gernischt-B, Shiraz-A, Shiraz-B, Merlot-C, Merlot-D, Pinot Noir-A, Pinot Noir-B and Chardonnay, esters were found to be the main volatile compounds. The most abundant volatile compounds of 17 samples were 3-methyl-1-butanol, phenylethyl alcohol, butanedioic acid diethyl ester, hexanoic acid ethyl ester and octanoic acid ethyl ester, decanoic acid, ethyl ester. 3-methyl-1-butanol is major contributor to the alcoholic fraction and it is formed by the deamination and decarboxylation of leucine. 2-Phenylethanol, an alcohol that gives a pleasant rose aroma can be considered as a component of the primary aroma. The esters are the largest class of volatile compounds present in wine. They are responsible for the secondary and the tertiary aroma of wines. The main volatile compounds in Cabernet Sauvignon-A and Cabernet Sauvignon-D were 3-methyl-1-butanol, hexanoic acid ethyl ester (apple, fruity, sweetish notes), butanedioic acid diethyl ester. 3-methyl-1-butanol and octanoic acid ethyl ester (ripe fruits, pear, sweety notes) were found to be the major volatile compounds contributing to the flavor of Cabernet Gernischt-A. Hexanoic acid, 2-methylpropyl ester and 1-Isopropyl-2-methoxy-4-methylbenzene were the two unique flavor compounds of Shiraz-A. 3-methyl-1-butanol accounts for a relatively high proportion in Merlot-A, Merlot-B and Tempranillo and high levels of 3-methyl-1-butanol (smokey and unpleasant aroma) might contribute negatively to the grape wine aroma profile. Terpenoids and norisoprenoids have great benefits for the human body and they contribute to some highly desirable descriptors such as floral and citrus notes[41]. In the present study, 14 different terpenoids and norisoprenoids were identified for the seventeen samples. 6, 5, 5, 6 and 6 kinds of terpenoids and norisoprenoids were identified on Cabernet Sauvignon-A, Shiraz-A, Merlot-C, Pinot Noir-A and Pinot Noir-B, respectively. 1,2-dihydronaphthalene-1,1,6-trimethyl (TDN) which is described as petroleum, kerosene and diesel was generally detected in all samples except Cabernet Sauvignon-B. Among 17 grape wines, the variety of volatile compounds in Pinot Noir was the most abundant. Hydrocarbons in wine result from the waxy components of

the grape surface, appear in very small quantities and participate in the varietal aroma but without any special organoleptic significance[42]. Phenolic compounds play a key role in defining the quality of a red wine, because they participate directly in color, the antioxidant properties, astringency and bitterness of the wine[16]. 3-ethylphenol and 2,4-bis(1,1-dimethylethyl)phenol were detected among the 17 wines. The proportion between the different volatile compounds is fundamental in order to impress a harmonious equilibrium to the grape wine profile. For example, the presence of alcohols in too high concentrations could be a negative feature since they may hide the positive contribution of esters or aldehydes (floral and fruity).

HPLC analysis

Phenolic acids also contribute to the taste of grape wines. In this study, eight phenolic acids including gallic acid, protocatechuic acid, vanillic acid, catechin, caffeic acid, syringic acid, p-coumaric acid and ferulic acid were analyzed and the quantitative results were shown in Table 2. In total, the highest concentration of phenolic compounds was observed in Pinot Noir-A (167.743 ± 2.395 mg/L), while the lowest was in Chardonnay (48.321 ± 1.628 mg/L). The most abundant phenols in sixteen red wine samples were gallic acid and catechin. Wine made from Pinot Noir grape variety had the highest concentration of catechin compared to the other sixteen wine samples, which is in accordance with the results published by Krstonosic et al.[43]. Concerning other abundant phenols, protocatechuic acid was detected in a relatively high concentration (8.658−27.230 mg/L) in seventeen wines. The observed differences in the phenolic content could be attributed to many factors, including terroirs, grape maturity, and varietal characteristics, as well as the applied winemaking technology.

Free amino acids analysis

The amino acids can not only provide nitrogen for the growth of microorganisms, but also they can bring nice color for the wine[44]. As one of the essential components of grape wine, amino acids supply diverse tastes which were umami (monosodium glutamate, MSG)-like (including Asp and Glu), bitter (including Val, Met, Ile, Leu, Phe, His and Arg) and sweet (including Thr, Ser, Gly and Ala)[45]. In this study, 17 kinds of free amino acids (FAAs) in seventeen grape wines were detected. The total content of amino acids varied from 144.702 ± 8.589 to 510.153 ± 6.708 mg/L as shown in Table 3. The top five grape wines with the highest total amino acids were Pinot Noir-A, Tempranillo, Cabernet Sauvignon-A, Pinot Noir-B and Merlot-B. There was a significant difference ($P < 0.05$) in MSG-like amino acids content among Pinot Noir-A, Chardonnay, Cabernet Sauvignon-D, Cabernet Sauvignon-B, Cabernet Gernischt-B and Shiraz-B. However, no notable difference in bitter amino acids was observed among Cabernet Sauvignon-A, Cabernet Sauvignon-D and Cabernet Sauvignon-E. The content of essential amino acids among Merlot-D, Pinot Noir-A and Chardonnay were significantly different from each other. Cabernet Sauvignon-E, Shiraz-A, Merlot-B and Pinot Noir-B had little difference in the content of sweet amino acids. Further, our results revealed that among these amino acids, glutamic acid, proline, lysine, arginine and alanine predominated. Glutamic acid which has the umami taste

Table 2. Phenolic acids in seventeen grape wines using HPLC.

Phenolic acids	Contents of phenolic acids (mg/L)																
	Cabernet Sauvignon-A	Cabernet Sauvignon-B	Cabernet Sauvignon-C	Cabernet Sauvignon-D	Cabernet Sauvignon-E	Cabernet Gernischt-A	Cabernet Gernischt-B	Shiraz-A	Shiraz-B	Merlot-A	Merlot-B	Merlot-C	Merlot-D	Pinot Noir-A	Pinot Noir-B	Tempranillo	Chardonnay
gallic acid	22.322 ± 2.408fg	19.224 ± 2.945h	19.187 ± 0.882h	30.553 ± 4.171cd	34.722 ± 0.512b	22.912 ± 0.691f	18.660 ± 1.355h	39.721 ± 1.848a	32.877 ± 0.162bc	23.673 ± 0.179f	27.293 ± 0.031e	28.391 ± 0.055de	31.806 ± 0.626c	41.739 ± 1.206a	15.424 ± 0.126i	19.900 ± 0.039gh	3.108 ± 0.068j
protocatechuic acid	21.171 ± 1.289bc	9.788 ± 1.216kl	12.985 ± 0.209fgh	19.860 ± 2.938cd	10.796 ± 0.168jk	11.607 ± 0.127hijk	14.315 ± 1.597f	10.949 ± 1.008ijk	27.230 ± 1.376a	8.658 ± 0.114l	17.858 ± 0.134e	18.319 ± 0.021de	26.639 ± 0.207a	22.171 ± 0.631b	12.739 ± 0.985fghi	13.551 ± 0.056fg	12.295 ± 0.163ghij
vanillic acid	6.851 ± 0.202h	8.362 ± 0.201g	9.792 ± 0.756f	2.150 ± 0.151j	4.939 ± 0.042i	2.117 ± 0.368j	9.495 ± 1.301f	2.832 ± 0.225j	14.841 ± 0.188d	2.980 ± 0.150j	22.551 ± 0.327a	16.620 ± 0.201c	17.987 ± 1.514b	17.272 ± 0.975bc	9.006 ± 0.515fg	11.034 ± 0.133e	5.999 ± 0.705h
catechin	34.540 ± 2.871h	20.991 ± 1.712l	29.309 ± 1.03i	33.886 ± 1.693h	55.238 ± 0.983c	45.555 ± 0.632d	24.244 ± 1.062k	46.814 ± 0.439d	40.728 ± 0.448ef	34.660 ± 0.965h	42.315 ± 0.987e	37.839 ± 0.482g	39.583 ± 1.280fg	58.853 ± 0.347b	63.725 ± 1.595a	26.547 ± 0.947j	13.135 ± 0.109m
caffeic acid	1.565 ± 0.293i	1.498 ± 0.106ij	3.313 ± 0.029h	9.050 ± 0.149b	11.735 ± 0.008a	6.262 ± 0.557d	5.050 ± 0.430f	7.807 ± 0.480c	3.991 ± 0.281g	7.644 ± 0.026c	5.588 ± 0.469e	7.342 ± 0.243c	4.098 ± 0.249g	6.198 ± 0.201d	1.026 ± 0.149j	6.008 ± 0.428de	2.010 ± 0.045i
syringic acid	10.954 ± 1.501d	9.369 ± 0.537ef	10.348 ± 1.127de	15.011 ± 0.497b	8.751 ± 0.007f	17.211 ± 0.249a	12.294 ± 0.786c	13.370 ± 0.877c	9.908 ± 0.359edf	5.360 ± 0.019g	5.755 ± 0.133g	9.205 ± 0.283ef	8.966 ± 0.623f	14.902 ± 0.713b	3.925 ± 0.372h	5.416 ± 0.070g	6.217 ± 0.683g
p-coumaric acid	6.128 ± 0.305cde	4.327 ± 0.495fg	5.560 ± 0.233e	7.353 ± 0.480b	6.309 ± 0.024cd	6.351 ± 0.657cd	4.311 ± 0.306fg	7.897 ± 0.469b	1.420 ± 0.301h	5.828 ± 0.143de	8.792 ± 0.055a	4.733 ± 0.079f	4.879 ± 0.013f	4.229 ± 0.622fg	6.697 ± 0.630c	3.848 ± 0.087g	0.741 ± 0.042i
ferulic acid	1.444 ± 0.250f	0.643 ± 0.101h	0.956 ± 0.078g	0.954 ± 0.075g	1.023 ± 0.022g	1.616 ± 0.079ef	1.612 ± 0.164ef	1.876 ± 0.131de	1.596 ± 0.035f	3.080 ± 0.177b	1.903 ± 0.172d	2.063 ± 0.054d	2.011 ± 0.030d	2.377 ± 0.171c	0.999 ± 0.070g	2.517 ± 0.191c	4.817 ± 0.347a
Total	104.975 ± 3.850g	74.204 ± 5.231j	91.450 ± 2.602i	118.816 ± 0.709e	133.513 ± 0.701bc	113.631 ± 1.378f	89.982 ± 3.098i	131.267 ± 3.470c	132.591 ± 1.132bc	99.539 ± 1.254h	132.055 ± 1.331bc	124.512 ± 0.298d	135.969 ± 1.285b	167.743 ± 2.395a	113.542 ± 2.107f	88.821 ± 1.140i	48.321 ± 1.628k

Each value is expressed as mean ± SD (n=3) and data in the same row with different letters are significantly different (P < 0.05).

can improve the taste of grape infusions. Pinot Noir-A had the highest content of total amino acids, taste-active amino acids (MSG-like, bitter and sweet components) and essential amino acids among seventeen grape wines. Since free amino acids are precursors of flavor compounds, the different contents of free amino acids were highly correlated to the complex synthesis of flavor compounds in grape wines. Free amino acids are closely related to the taste of the grape wines, which determines the quality of the grape wines.

E-nose analysis

The E-nose was a good method to analyze aroma, as it could offer a fast and non-destructive method to sense volatile substances[46]. PCA was a statistical tool that explained the differentiation between samples as well as the relationship between the objects[47–49]. A clear separation of the samples into 17 groups was found according to the PCA plot of the different grape varieties as shown in Fig. 2a. The principal components PC1 and PC2 represented 73.58% and 18.75% of the total variance, respectively, with the cumulative contribution rate accounting for 92.33%. In general, when the accumulated contribution of certain principal compounds (PCs) is over 85%, the PCs can represent the original data. The clusters of the data were divided into three groups labeled A, B and C. Group A was composed of ten subclusters without being overlapped. However, they were closer to each other, indicating that similar volatile ingredients existing in these ten samples (Cabernet Sauvignon-B, Cabernet Sauvignon-C, Cabernet Sauvignon-D, Cabernet Sauvignon-E, Merlot-B, Merlot-C, Merlot-D, Cabernet Gernischt-B, Shiraz-B and Pinot Noir-B). Related to HS-SPME-GC-MS analysis, the difference in the aroma profile among Chardonnay and other wines, Chardonnay located in the left-bottom area labeled B and clearly isolated from the other 16 red wines in PCA plot of E-nose. Group C was made up of six wine samples including Cabernet Sauvignon-A, Shiraz-A, Pinot Noir-A, Cabernet Gernischt-A, Merlot-A, and Tempranillo, clearly isolated from each other. All of them generate special aroma because of their unique fermentation process and raw materials. E-nose is sensitive for obtaining smell information, and slight changes of flavor could result in different sensors response. The results illustrate that this non-destructive method by E-nose is an effective assay for grape wine discrimination.

Linear discriminant analysis (LDA) is frequently used for classification in food field and its main aim is to find the linear combinations of noted attributes that can well separate two or more than two classes of objects[50]. The classification results of the 17 grape wines on the coordinates based on first linear discriminant (LD1) and second linear discriminant (LD2) represented 76.84% and 18.72% of the total variance, respectively, with the discriminant accuracy accounting for 95.56% are shown in Fig. 2b. The results indicate that the PEN 3 E-nose with LDA is an effective instrument to distinguish the 17 grape wines via their odors.

Loading analysis is useful to check for the influence of a sensor on the distribution of data sets. The loading factor associated to PC1 and PC2 for each sensor is represented in Fig. 2c. The points in the plot represent the sensors used in the experiment. The sensor with loading parameters close to zero for a particular principal component has a low contribution to the total response of the array, whereas high values

Table 3. Comparison of free amino acids (FAAs) in different kinds of grape wines.

Contents of FAAs (mg/L)

FAAs	Cabernet Sauvignon-A	Cabernet Sauvignon-B	Cabernet Sauvignon-C	Cabernet Sauvignon-D	Cabernet Sauvignon-E	Cabernet Gernischt-A	Cabernet Gernischt-B	Shiraz-A	Shiraz-B	Merlot-A	Merlot-B	Merlot-C	Merlot-D	Pinot Noir-A	Pinot Noir-B	Tempranillo	Chardonnay
Aspartic acid (Asp)	21.525 ± 1.519c	13.433 ± 1.031f	17.666 ± 0.575d	14.921 ± 0.762e	25.437 ± 0.502b	15.846 ± 1.601e	11.094 ± 0.09g	15.391 ± 0.05d	13.668 ± 0.06f	8.076 ± 0.168h	22.347 ± 0.339c	7.850 ± 0.210h	6.347 ± 0.451i	33.736 ± 0.464a	24.744 ± 0.267b	7.291 ± 0.152hi	24.332 ± 1.113b
Threonine (Thr*)	16.269 ± 1.056c	12.063 ± 0.853ef	10.578 ± 0.714g	11.488 ± 0.61gf	13.503 ± 0.262d	12.406 ± 0.507ef	8.693 ± 1.461h	13.749 ± 0.110d	9.002 ± 0.039h	8.181 ± 0.056h	13.022 ± 0.231de	5.339 ± 0.144i	3.458 ± 0.251j	27.163 ± 0.401b	13.234 ± 0.121de	6.562 ± 0.139i	31.053 ± 2.011a
Serine (Ser)	16.291 ± 0.906c	10.945 ± 0.827g	12.117 ± 1.050f	10.472 ± 0.498g	14.156 ± 0.282d	12.004 ± 0.791f	8.572 ± 0.105h	13.099 ± 0.113e	7.701 ± 0.038hi	6.924 ± 0.119i	13.434 ± 0.189de	6.768 ± 0.180i	4.393 ± 0.314j	22.375 ± 0.321b	13.233 ± 0.142de	5.119 ± 0.095j	37.086 ± 1.283a
Glutamic acid (Glu)	49.592 ± 1.962c	29.761 ± 1.331i	37.523 ± 0.552f	33.494 ± 1.637h	42.911 ± 0.879d	36.752 ± 1.665e	29.229 ± 0.262i	40.975 ± 0.0918de	22.722 ± 0.097j	24.139 ± 0.344j	35.406 ± 0.557g	22.510 ± 0.547j	19.312 ± 1.210k	82.522 ± 0.901a	35.544 ± 0.415g	17.984 ± 0.270k	78.470 ± 1.532b
Proline (Pro)	47.364 ± 1.523c	44.537 ± 1.459d	41.971 ± 1.562e	36.592 ± 0.454f	12.211 ± 0.253j	40.114 ± 1.500e	36.604 ± 0.997f	40.966 ± 0.212e	35.376 ± 1.341fg	33.374 ± 0.677g	45.784 ± 2.334d	37.380 ± 1.495f	22.142 ± 0.251i	65.491 ± 0.840a	33.837 ± 1.868g	30.493 ± 0.151h	59.177 ± 1.503b
Glycine (Gly)	23.421 ± 2.099b	14.103 ± 0.939f	16.887 ± 0.242de	16.110 ± 0.835e	18.429 ± 0.352c	15.579 ± 1.300e	13.557 ± 0.137f	16.509 ± 0.188e	12.292 ± 0.054g	10.829 ± 0.127h	18.142 ± 0.337cd	10.299 ± 0.289h	10.842 ± 0.771h	32.777 ± 0.752a	18.313 ± 0.188c	7.6452 ± 0.142i	18.943 ± 0.631c
Alanine (Ala)	39.205 ± 1.851bc	26.972 ± 1.254g	30.702 ± 1.026e	35.004 ± 1.763d	38.996 ± 1.659bc	34.357 ± 1.659d	28.894 ± 0.451f	38.139 ± 0.197c	27.647 ± 0.134fg	22.450 ± 0.235h	40.208 ± 1.078b	20.594 ± 0.587i	18.195 ± 1.326j	75.277 ± 0.950a	37.903 ± 0.413c	16.628 ± 0.304j	16.820 ± 0.008j
Cysteine (Cys)	5.540 ± 0.104cd	1.783 ± 0.082g	1.354 ± 0.095h	2.178 ± 0.084f	1.465 ± 0.021hg	5.280 ± 0.511ed	1.401 ± 0.084hg	5.873 ± 0.100c	1.281 ± 0.025h	5.126 ± 0.084e	1.352 ± 0.148h	1.131 ± 0.061h	1.132 ± 0.62h	7.094 ± 0.151b	1.467 ± 0.039hg	5.095 ± 0.041e	9.678 ± 0.677a
Valine (Val*)	17.734 ± 0.779b	11.333 ± 0.920g	10.746 ± 0.591g	11.000 ± 0.547g	12.718 ± 0.219ef	12.414 ± 0.624f	8.266 ± 0.139h	14.721 ± 0.071c	7.854 ± 0.042h	8.522 ± 0.194h	13.401 ± 0.334de	6.770 ± 0.183i	4.781 ± 0.329j	27.156 ± 0.393a	13.798 ± 0.141d	8.534 ± 0.065h	17.712 ± 0.611b
Methionine (Met*)	8.801 ± 0.302b	4.274 ± 0.253f	3.833 ± 0.311g	4.509 ± 0.208ef	5.550 ± 0.272d	2.976 ± 0.332hi	3.393 ± 0.090h	7.962 ± 0.039c	2.733 ± 0.011j	2.167 ± 0.603k	4.914 ± 0.144e	2.118 ± 0.055k	1.543 ± 0.111	11.846 ± 0.131a	4.765 ± 0.056e	2.429 ± 0.026jk	5.465 ± 0.466d
Isoleucine (Ile*)	7.964 ± 0.353b	5.198 ± 0.235hg	5.155 ± 0.258hg	4.997 ± 0.249hg	6.017 ± 0.111de	5.337 ± 0.677fg	3.611 ± 0.044i	5.623 ± 0.045ef	3.388 ± 0.026i	1.805 ± 0.066k	6.385 ± 0.113cd	2.878 ± 0.081j	1.708 ± 0.118k	9.591 ± 0.158a	6.544 ± 0.083c	1.776 ± 0.003k	4.836 ± 0.329h
Leucine (Leu*)	17.252 ± 0.553d	16.345 ± 0.735e	14.193 ± 0.407g	15.124 ± 0.783f	21.805 ± 0.425b	11.825 ± 0.750h	10.729 ± 0.104i	14.612 ± 0.025fg	11.344 ± 0.057hi	5.575 ± 0.073k	18.994 ± 0.339c	8.527 ± 0.262j	5.383 ± 0.400k	25.117 ± 0.451a	17.209 ± 0.215d	5.225 ± 0.162k	17.531 ± 0.642d
Tyrosine (Tyr)	ND	13.138 ± 0.663d	12.427 ± 0.839e	10.907 ± 0.445g	9.98 ± 0.156h	ND	16.776 ± 0.129c	12.025 ± 0.019e	6.011 ± 0.012k	7.871 ± 0.062i	23.243 ± 0.342b	6.382 ± 0.130k	7.041 ± 0.463j	ND	10.059 ± 0.06g	4.621 ± 0.338l	28.734 ± 0.508a
Phenylalanine (Phe*)	17.956 ± 0.721d	15.889 ± 0.609f	14.612 ± 0.535g	16.983 ± 0.871e	23.974 ± 0.416c	14.005 ± 0.601g	11.978 ± 0.104h	17.690 ± 0.060de	12.123 ± 0.083h	10.386 ± 0.083i	18.076 ± 0.293d	10.289 ± 0.263i	5.070 ± 0.367j	29.293 ± 0.341b	18.266 ± 0.184	10.089 ± 0.107i	33.473 ± 1.008a
Lysine (Lys*)	25.432 ± 0.979b	17.212 ± 0680f	18.807 ± 0.749	19.639 ± 0.963e	26.293 ± 0.475b	21.102 ± 0.684d	14.359 ± 0.082h	23.706 ± 0.062c	15.486 ± 0.053g	14.371 ± 0.189h	23.719 ± 0.378c	11.691 ± 0.339i	9.576 ± 0.613j	35.700 ± 0.679a	21.965 ± 0.276d	12.052 ± 0.611i	25.346 ± 0.916b
Histidine (His)	3.439 ± 0.038j	3.164 ± 0.157j	3.604 ± 0.145i	6.410 ± 0.276g	11.158 ± 0.181b	1.513 ± 0.130l	2.186 ± 0.10k	10.079 ± 0.033c	5.502 ± 0.022h	6.711 ± 0.060fg	4.287 ± 0.052i	7.488 ± 0.195ed	7.033 ± 0.423ef	4.784 ± 0.137i	7.797 ± 0.091d	3.409 ± 0.076j	27.230 ± 1.189a
Arginine (Arg)	21.602 ± 1.500f	23.530 ± 0.928e	14.266 ± 0.564h	34.958 ± 1.719b	12.218 ± 0.282j	23.194 ± 1.510e	31.221 ± 0.515c	17.041 ± 0.141h	25.002 ± 0.318d	23.730 ± 0.317de	17.294 ± 0.242h	10.844 ± 0.304i	16.746 ± 1.144h	20.205 ± 0.315g	46.065 ± 0.512a	13.638 ± 0.313i	16.389 ± 0.768h
Essential amino acids	111.389 ± 3.63c	82.317 ± 3.414ef	77.924 ± 3.549f	83.739 ± 1.636e	109.860 ± 1.636c	80.0643 ± 3.377ef	61.030 ± 2.024g	98.063 ± 0.178d	61.931 ± 0.305g	51.007 ± 0.474h	98.511 ± 1.831d	47.612 ± 1.328h	31.519 ± 2.177i	165.887 ± 2.473a	95.782 ± 1.076d	46.668 ± 0.543h	135.415 ± 5.299b
MSG-like	71.118 ± 3.171c	43.195 ± 2.346h	55.189 ± 1.059ef	48.415 ± 2.400g	68.348 ± 1.382c	52.597 ± 3.263f	40.323 ± 0.356i	56.365 ± 0.142e	36.390 ± 0.159j	32.216 ± 0.492k	57.753 ± 0.896de	30.363 ± 0.757k	25.659 ± 1.661l	116.256 ± 1.241a	60.288 ± 0.682d	25.275 ± 0.420l	102.806 ± 2.626b
Bitter	94.728 ± 3.420d	80.185 ± 3.159f	66.410 ± 3.045h	93.981 ± 4.683d	93.439 ± 1.361d	71.264 ± 4.026g	71.264 ± 4.026g	87.728 ± 0.060e	67.946 ± 0.342gh	58.895 ± 0.430i	83.351 ± 1.516f	48.914 ± 1.343	42.264 ± 2.879k	128.010 ± 1.877a	114.444 ± 1.282c	45.101 ± 0.744jk	122.636 ± 3.935b
Sweet	95.186 ± 5.489c	64.083 ± 3.794f	70.283 ± 1.930e	73.073 ± 3.707e	85.084 ± 1.674d	74.346 ± 4.020e	59.716 ± 2.155fg	81.496 ± 0.587d	56.643 ± 0.264g	48.384 ± 0.521h	84.384 ± 1.834d	43.001 ± 1.200i	36.888 ± 2.661j	157.592 ± 2.405a	82.684 ± 0.863d	35.961 ± 0.672j	103.903 ± 3.889b
Total	339.369 ± 13.086c	264.133 ± 8.793h	266.442 ± 6.253h	284.785 ± 11.827g	296.221 ± 5.321fg	264.703 ± 12.407h	240.567 ± 4.807i	308.159 ± 0.947ef	219.133 ± 0.527j	200.237 ± 1.429k	320.009 ± 7.448de	178.862 ± 5.324l	144.702 ± 8.589n	510.153 ± 6.708a	324.744 ± 1.333d	158.597 ± 2.238m	452.296 ± 13.074b

Each value is expressed as mean ± SD (n = 3) and data in the same row with different letters are significantly different (P < 0.05). [a] ND: not detected. * Means essential amino acids.
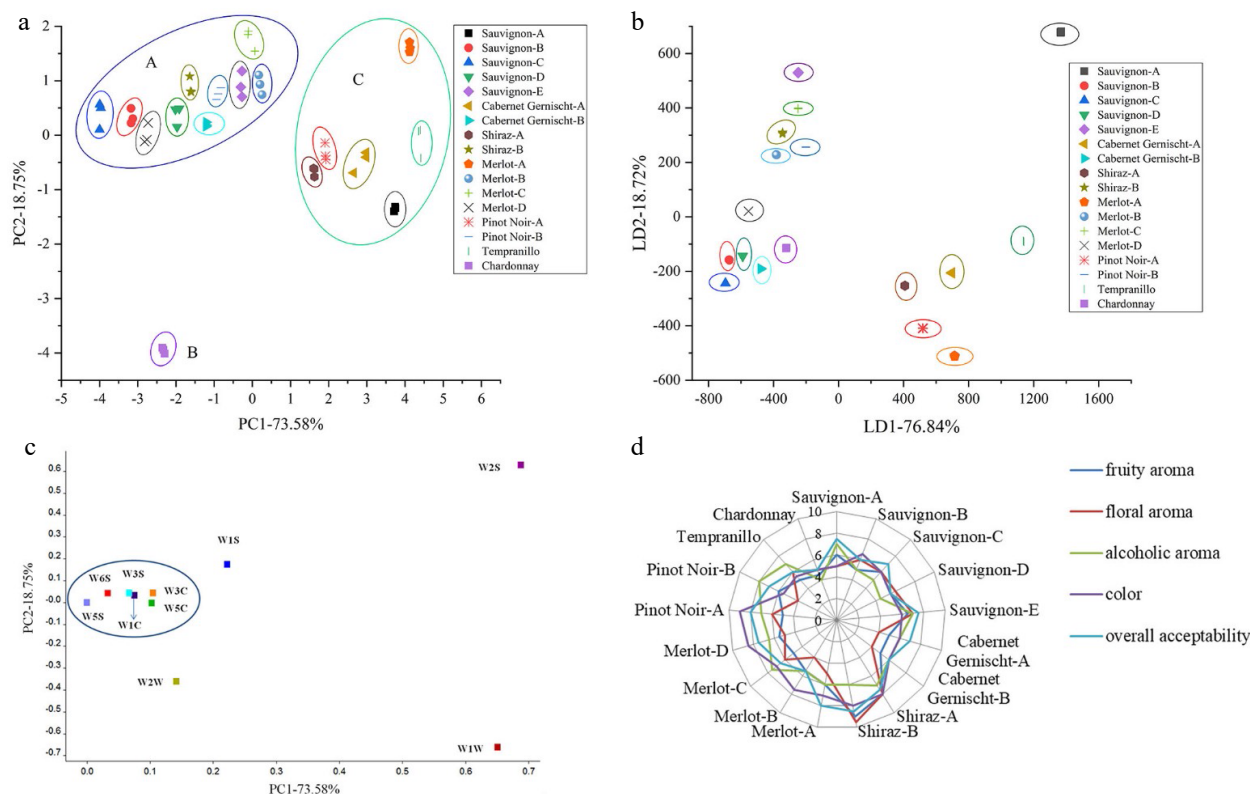
Fig. 2 (a) PCA plot, (b) LDA plot, (c) loading analysis of E-nose for 17 grape wines and (d) graph of sensory scores of the 17 grape wines.

indicates a discriminating sensor[51]. It is shown that sensors W2S and W1W have a higher influence in the current pattern file while sensors W1S and W2W have relatively low influence. The detectable compounds by sensors W2S and W1W were alcohols and sulfur-containing organics. Sensors W1C, W3S, W5C, W3C, W5S and W6S have closer influence so that they might be represented by one of the group member and this group has a minor influence in the current pattern file.

Fifty mL grape wine was put into a beaker of 250 mL volume, and they were randomly offered to panelists, the aroma descriptors of samples were recorded by panelists. Panelists agreed that the aroma of grape wine samples could be described using five attributes: fruity aroma, floral aroma, alcoholic aroma, color, and overall acceptability. The intensities of the aroma attributes were scored using a scale from 0 to 10, the higher scores, the stronger intensities. Each sample was evaluated three times by each panelist. Data were expressed as mean. A trained panel quantitated the intensity of the aroma attributes of tea samples were evaluated by ten panelists (six females and four males), with aged between 20 and 30 years old. Panelists were trained by a series of important grape wine aroma compounds.

The scores of human aroma sensory evaluation analysis are plotted on the radar chart and shown in Fig. 2d. The result analysis demonstrated that fruity aroma, alcoholic aroma and overall acceptability showed significant differences among Chardonnay and other 16 kinds of red wines in the sensory evaluation scores. This is consistent with the results analyzed by E-nose. Shiraz-B exhibited higher level of floral aroma and fruity aroma which may be related to high relative content of higher alcohols and esters detected by HS-SPME-GC-MS. In addition, Pinot Noir-A and Merlot-D have beautiful color, which perhaps due to their relatively high phenolic contents detected by HPLC.

E-tongue analysis

The radar fingerprint chart of E-tongue with different grape varieties was presented in Fig. 3a. The mainly typical taste of grape wine includes astringency and sourness. Significant difference ($P < 0.05$) was observed in aftertaste-B and sour taste. However, there was a minor difference on the flavor from bitterness, astringency, aftertaste-A richness and umami among 17 grape wines. Further, there was a great correlation between the E-tongue and the human sensory evaluation score[52]. The values of saltiness and richness of Tempranillo and Chardonnay were lower than 15 other grape wines. Astringency taste intensity based on the E-tongue measurement ranged from 1.147 ± 0.045 to 4.400 ± 0.046. The bitterness and astringency of grape wines are mainly correlated to the phenol profile[16,53]. Pinot Noir-A exhibited the highest sourness intensity with a score of -9.733 ± 0.207. Cabernet Sauvignon-E with the highest umami taste levels also appeared to have the highest saltiness scores. It can therefore be concluded that E-tongue could be a rapid method for taste evaluation in wineries. Consumers can easily choose their preferred grape wines according to the satisfactory taste results offered by E-tongue.

For variable reduction and separation into classed, PCA was used applied[54]. PCA of non-volatile compounds of 17 samples from seven kinds of grape varieties were presented in Fig. 3b. It was observed that variance contribution rates of PC1 and PC2 were 64.65% and 27.13%, respectively. The
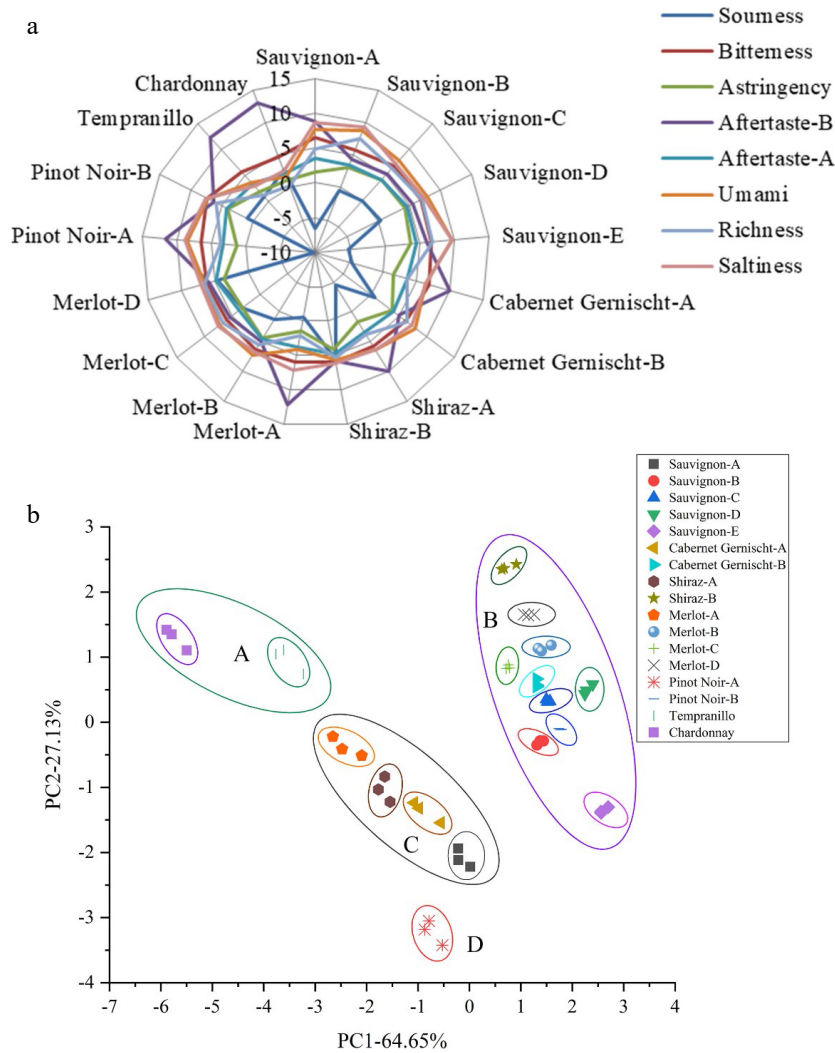
Fig. 3 (a) Radar fingerprint chart of the sensory score, (b) PCA plot of E-tongue data for 17 grape wines.

accumulative variance contribution rate of the first two PCs was 91.78% (> 85%), which were considered most information to represent the entire samples. In the PCA plot, a better separation effect of 17 grape wines was shown. Tempranillo, Chardonnay, Shiraz-B, Cabernet Sauvignon-E and Pinot Noir-A were clearly separated from other wines. Shiraz-A, Merlot-A, Cabernet Gernischt-A and Cabernet Sauvignon-A were slightly clustered in the centre of the PCA plot. A group comprised of Cabernet Sauvignon-B, Cabernet Sauvignon-C, Cabernet Sauvignon-D, Pinot Noir-B, Merlot-B, Merlot-C, Merlot-D and Cabernet Gernischt-B was located close together, all eight samples had positive score values at PC1. For E-tongue results, the PCA was able to distinguish the 17 wines from seven grape types completely.

Conclusions

In this study, the volatile and non-volatile flavor components of grape wines were analyzed by HS-SPME-GC-MS, E-nose, E-tongue, HPLC, and automatic amino acids analyzer techniques. The phenolic substances detected by HPLC are related to the color of the wine and the content of amino

acids and phenols affect the taste of the wine, such as bitterness and astringency detected by E-tongue. Meanwhile, the combined use of HS-SPME-GC-MS and electronic nose technology analyzes the volatile flavor of 17 wines. The floral aroma and fruity aroma of the wine are closely related to alcohols and esters. Pinot Noir-A had the highest content of bitter amino acids, phenols and it was clearly separated from other wines in the PCA plot of E-tongue. The flavor and taste of Chardonnay showed great significance compared to 16 other kinds of red wines. Shiraz-B exhibited higher scores of floral aroma and fruity aroma in sensory evaluation, which may be related to its relative amount of volatile aroma substance. A total of 86 volatile compounds were identified among the 17 samples from seven kinds of wine samples. Alcohols and esters were the main flavor substances. The results clearly show that it is possible to classify grape wines from seven varieties by using E-nose and E-tongue. Sensors W2S and W1W in the E-nose for wines have a higher influence in the current pattern file. In addition, the PCA results of E-nose and E-tongue were obtained with the cumulative contribution rate accounting for 92.33% and 91.78%, respectively. Additionally, the content of free amino acids especially the

taste-active amino acids, exhibited significant difference ($P <$ 0.05). Gallic acid and catechin made up a large percentage of the grape wines. This study highlighted the usefulness of combining aroma and taste analysis techniques of grape wines, which could effectively instruct consumers to choose their preferred wines. Meanwhile, this research also provided some efficient methods to monitor grape wine quality in the actual process of industrialization. The beverage industry can certainly follow the protocols and parameters presented in this work in order to make use and apply the techniques immediately.

Acknowledgments

Conflict of interest

The authors declare that they have no conflict of interest.

Dates

References

1. Garaguso I, Nardini M. 2015. Polyphenols content phenolics profile and antioxidant activity of organic red wines produced without sulfur dioxide/sulfites addition in comparison to conventional red wines. *Food Chemistry* 179:336−42
2. Wang YR, Luo RM, Wang SL. 2022. Water distribution and key aroma compounds in the process of beef roasting. *Frontiers in Nutrition* 9:978622
3. Styger G, Prior B, Bauer FF. 2011. Wine flavor and aroma. *Journal of Industrial Microbiology & Biotechnology* 38(9):1145
4. García M, Aleixandre M, Gutiérrez J, Horrillo MC. 2006. Electronic nose for wine discrimination. *Sensors and Actuators B - Chemical* 113:911−16
5. Aleixandre M, Santos JP, Sayago I, Cabellos JM, Arroyo T, et al. 2015. A wireless and portable electronic nose to differentiate musts of different ripeness degree and grape varieties. *Sensors* 15:8429−43
6. Keyzers RA, Boss PK. 2010. Changes in the volatile compound production of fermentations made from musts with increasing grape content. *Journal of Agricultural and Food Chemistry* 58:1153−64
7. Forde CG, Cox A, Williams ER, Boss PK. 2011. Associations between the sensory attributes and volatile composition of Cabernet Sauvignon wines and the volatile composition of the grapes used for their production. *Journal of Agricultural and Food Chemistry* 59:2573−83
8. Sáenz-Navajas MP, Avizcuri JM, Ballester J, Fernández-Zurbano P, Ferreira V, et al. 2015. Sensory-active compounds influencing wine experts' and consumers' perception of red wine intrinsic quality. *LWT - Food Science And Technology* 60:400−11
9. Tempere S, Pérès S, Espinoza AF, Darriet P, Giraud-Héraud E, et al. 2019. Consumer preferences for different red wine styles and repeated exposure effects. *Food Quality and Preference* 73:110−16
10. Zhang X, Wang K, Gu X, Sun X, Jin G, et al. 2022. Flavor Chemical Profiles of Cabernet Sauvignon Wines: Six Vintages from 2013 to 2018 from the Eastern Foothills of the Ningxia Helan Mountains in China. *Foods* 11(1):22
11. Marigliano LE, Yu R, Torres N, Medina-Plaza C, Oberholster A, et al. 2023. Overhead photoselective shade films mitigate effects of climate change by arresting flavonoid and aroma composition degradation in wine. *Frontiers in Plant Science* 14:1085939
12. Polásková P, Herszage J, Ebeler SE. 2008. Wine flavor: chemistry in a glass. *Chemical Society Reviews* 37:2478−89
13. Parker M, Barker A, Black CA, Hixson J, Williamson P, et al. 2019. Don't miss the marc: phenolic-free glycosides from white grape marc increase flavor of wine. *Australian Journal of Grape Wine Research* 25:212−23
14. Antalick G, Šuklje K, Blackman JW, Meeks C, Deloire A, et al. 2015. Influence of grape composition on red wine ester profile: Comparison between cabernet sauvignon and shiraz cultivars from Australian warm climate. *Journal of Agricultural and Food Chemistry* 63:4664−72
15. Yang Y, Jin GJ, Wang XJ, Kong CL, Liu JB, et al. 2019. Chemical profiles and aroma contribution of terpene compounds in Meili (*Vitis vinifera* L.) grape and wine. *Food Chemistry* 284:155−61
16. Delgado Cuzmar P, Salgado E, Ribalta-Pizarro C, Olaeta JA, López E, et al. 2018. Phenolic composition and sensory characteristics of Cabernet Sauvignon wines: effect of water stress and harvest date. *International Journal of Food Science and Technology* 53(7):1726−35
17. Fretz CB, Luisier JL, Tominaga, T, Amadò R. 2005. 3-mercaptohexanol: An aroma impact compound of Petite Arvine wine. *American Journal of Enology and Viticulture* 56(4):407−10
18. Liang Z, Zhang P, Zeng X, Fang Z. 2021. The art of flavored wine: Tradition and future. *Trends in Food Science and Technology* 116:130−45
19. Biagi M, Bertelli AAE. 2015. Wine alcohol and pills:What future for the French paradox? *Life Sciences* 131:19−22
20. Liu G, Xu S, Wang X, Jin Q, Xu X, et al. 2016. Analysis of the volatile components of tea seed oil (*Camellia sinensis O. Ktze*) from China using HS-SPME-GC/MS. *International Journal of Food Science And Technology* 51:2591−602
21. Saha B, Longo R, Torley P, Saliba A, Schmidtke L. 2018. SPME method optimized by Box-Behnken design for impact odorants in reduced alcohol wines. *Foods* 7(8):127
22. Liu YQ, Liu HX, Lin WL, Xue YZ, Liu MQ, et al. 2022. SPME-GC−MS combined with chemometrics to assess the impact of fermentation time on the components, flavor, and function of Laoxianghuang. *Frontiers in Nutrition* 10:3389
23. Fan X, Liu G, Qiao Y, Zhang Y, Leng C, et al. 2019. Characterization of volatile compounds by SPME-GC-MS during the ripening of Kedong Sufu a typical Chinese traditional bacteria-fermented soybean product. *Journal of Food Science* 84:2441−48
24. Capone S, Tufariello M, Francioso L, Montagna G, Casino F, et al. 2013. Aroma analysis by GC/MS and electronic nose dedicated to *Negroamaro* and *Primitivo* typical Italian Apulian wines. *Sensors and Actuators B: Chemical* 179:259−69
25. Tan JZ, Xu J. 2020. Applications of electronic nose (e-nose) and electronic tongue (e-tongue) in food quality-related properties determination: A review. *Artificial Intelligence in Agriculture* 4:104−15
26. Di Rosa AR, Leone F, Cheli F, Chiofalo V. 2017. Fusion of electronic nose electronic tongue and computer vision for animal source food authentication and quality assessment-A review. *Journal of Food Engineering* 210:62−75

27. Shi H, Zhang M, Adhikari B. 2018. Advances of electronic nose and its application in fresh foods: A review. *Critical Reviews in Food Science and Nutrition* 58(16):2700–10

28. Jiang H, Zhang M, Bhandari B, Adhikari B. 2018. Application of electronic tongue for fresh foods quality evaluation: a review. *Food Reviews International* 34:746–69

29. López de Lerma MDLN, Bellincontro A, García-Martínez T, Mencarelli F, Moreno JJ. 2013. Feasibility of an electronic nose to differentiate commercial Spanish wines elaborated from the same grape variety. *Food Research International* 51:790–796

30. Han F, Zhang D, Aheto JH, Feng F, Duan T. 2020. Integration of a low-cost electronic nose and a voltammetric electronic tongue for red wines identification. *Food Science & Nutrition* 8:4330–39

31. Xiang X, Wang Y, Yu Z, Ma M, Zhu ZH, et al. 2019. Non-destructive characterization of egg odor and fertilization status by SPME/GC-MS coupled with electronic nose. *Journal of the Science of Food and Agriculture* 99:3264–75

32. Pérez-Navarro J, Izquierdo-Cañas PM, Mena-Morales A, Martínez-Gascueña J, Chacón-Vozmediano JL, et al. 2019. First chemical and sensory characterization of Moribel and Tinto Fragoso wines using HPLC-DAD-ESI-MS/MS GC-MS, and Napping® techniques: comparison with Tempranillo. *Journal of the Science of Food and Agriculture* 99:2108–23

33. Campos MP, Sousa R, Pereira AC, Reis MS. 2017. Advanced predictive methods for wine age prediction: Part II - A comparison study of multiblock regression approaches. *Talanta* 171:132–42

34. Astray G, Mejuto JC, Martínez-Martínez V, Nevares I, Alamo-Sanza M, et al. 2019. Prediction models to control aging time in red wine. *Molecules* 24:826

35. Lopez de Lerma N, Bellincontro A, Mencarelli F, Moreno J, Peinado RA. 2012. Use of electronic nose validated by GC-MS, to establish the optimum off-vine dehydration time of wine grapes. *Food Chemistry* 130:447–52

36. Ziółkowska A, Wąsowicz E, Jeleń HH. 2016. Differentiation of wines according to grape variety and geographical origin based on volatiles profiling using SPME-MS and SPME-GC/MS methods. *Food Chemistry* 213:714–720

37. Picard M, de Revel G, Marchand S, Marchand S. 2017. First identification of three p-menthane lactones and their potential precursor menthofuran, in red wines. *Food Chemistry* 217:294–302

38. Shao Y, Xu F, Sun X, Bao J, Beta T. 2014. Phenolic acids anthocyanins, and antioxidant capacity in rice (*Oryza sativa* L.) grains at four stages of development after flowering. *Food Chemistry* 143:90–96

39. Xia Q, Wang L, Xu C, Mei J, Li Y. 2017. Effects of germination and high hydrostatic pressure processing on mineral elements amino acids and antioxidants in vitro bioaccessibility, as well as starch digestibility in brown rice (*Oryza sativa* L.). *Food Chemistry* 214:533–42

40. Men H, Shi Y, Fu S, Jiao Y, Qiao Y, et al. 2017. Mining feature of data fusion in the classification of beer flavor information using E-tongue and E-nose. *Sensors* 17:1656

41. Cao Y, Wu Z, Weng P. 2020. Comparison of bayberry fermented wine aroma from different cultivars by GC-MS combined with electronic nose analysis. *Food Science and Nutrition* 8:830–40

42. Karimali D, Kosma I, Badeka A. 2020. Varietal classification of red wine samples from four native Greek grape varieties based on volatile compound analysis color parameters and phenolic composition. *European Food Research and Technology* 246:41–53

43. Krstonošić MA, Hogervorst JC, Mikuli ć M, Gojkovi ć-Bukarica L. 2020. Development of HPLC method for determination of phenolic compounds on a core shell column by direct injection of wine samples. *Acta Chromatographica* 32:134–38

44. Wang P, Ma J, Meng X, Li X, Liu Y, et al. 2014. Changes in Flavor characteristics and bacterial diversity during traditional fermentation of Chinese rice wines from Shaoxing region. *Food Control* 44:58–63

45. Li B, Kimatu BM, Pei F, Chen S, Feng X, et al. 2017. Non-volatile flavour components in *Lentinus edodes* after hot water blanching and microwave blanching. *International Journal of Food Properties* 20:S2532–S2542

46. Ghasemi-Varnamkhasti M, Apetrei C, Lozano J, Anyogu A. 2018. Potential use of electronic noses electronic tongues and biosensors as multisensor systems for spoilage examination in foods. *Trends in Food Science & Technology* 80:71–92

47. Yu H, Wang J. 2007. Discrimination of LongJing green-tea grade by electronic nose. *Sensors and Actuators B: Chemical* 122:134–40

48. Liu M, Han X, Tu K, Pan L, Tu J, et al. 2012. Application of electronic nose in Chinese spirits quality control and flavour assessment. *Food Control* 26:564–70

49. Dong WJ, Hu RS, Long YZ, Li HH, Zhang YJ, et al. 2019. Comparative evaluation of the volatile profiles and taste properties of roasted coffee beans as affected by drying method and detected by electronic nose electronic tongue, and HS-SPME-GC-MS. *Food Chemistry* 272:723–31

50. Narayan Y. 2021. Hb vsEMG signal classification with time domain and Frequency domain features using LDA and ANN classifier. *Materials Today: Proceedings* 37:3226–30

51. Gómez AH, Hu G, Wang J, Pereira AG. 2006. Evaluation of tomato maturity by electronic nose. *Computers and Electronics in Agriculture* 54:44–52

52. Fang D, Yang W, Kimatu BM, Zhao L, An X, et al. 2017. Comparison of flavour qualities of mushrooms (*Flammulina velutipes*) packed with different packaging materials. *Food Chemistry* 232:1–9

53. Merkyte V, Morozova K, Boselli E, Scampicchio M. 2018. Fast and simultaneous determination of antioxidant activity total phenols and bitterness of red wines by a multichannel amperometric electronic tongue. *Electroanalysis* 30:314–19

54. Parra V, Arrieta ÁA, Fernández-Escudero JA, García H, Apetrei C, et al. 2006. E-tongue based on a hybrid array of voltammetric sensors based on phthalocyanines perylene derivatives and conducting polymers:Discrimination capability towards red wines elaborated with different varieties of grapes. *Sensors and Actuators B: Chemical* 115:54–61