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Rapid identification of high-temperature *Daqu* Baijiu with the same aroma type by UV-VIS sensor of HBT combined with Zn^{2+}

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Abstract

Aim: Baijiu adulteration has always been a hot spot of social concern, especially high-temperature *Daqu* Baijiu, because of its better flavor quality and high value, it faces a challenge from illegal adulteration of high-grade Baijiu bottles with low-grade Baijiu.

Methods: A new ultraviolet-visible spectroscopy (UV-VIS) sensor method based on 2-(2-hydroxyphenyl) benzothiazole (HBT) combined with Zn^{2+} was constructed. The specific mechanism of light signal change was mainly based on the competitive coordination effect of pyrazines and other nitrogen-containing compounds in high-temperature *Daqu* Baijiu and small molecular probe HBT on Zn^{2+} and the excited state intramolecular proton transfer (ESIPT) mechanism of HBT itself.

Results: The random forest results showed that the prediction set classification accuracy was improved from 62.37% to 100%. The accuracy of the data driven-soft independent modelling of class analogies (DD-SIMCA) model was between 90% and 100%, indicating that the array sensor had a good recognition effect on the adulteration of the same aroma type of Baijiu. Twelve kinds of Maillard reaction products such as tetramethylpyrazine, 2,6-dimethylpyrazine, and furfural in Baijiu were predicted successfully, and the deviation between the real value and the predicted value was less than 1.8746% ± 1.4515%.

Conclusions: This method not only improves the specificity of spectral detection, and the amount of information extracted from Baijiu samples, but also the detection time is shortened to less than 3 min, and the accurate identification of high-temperature *Daqu* Baijiu with the same aroma type was realized. This method can provide reliable help for the rapid identification of high-temperature *Daqu* and other precious Baijiu, even traditional fermented food.

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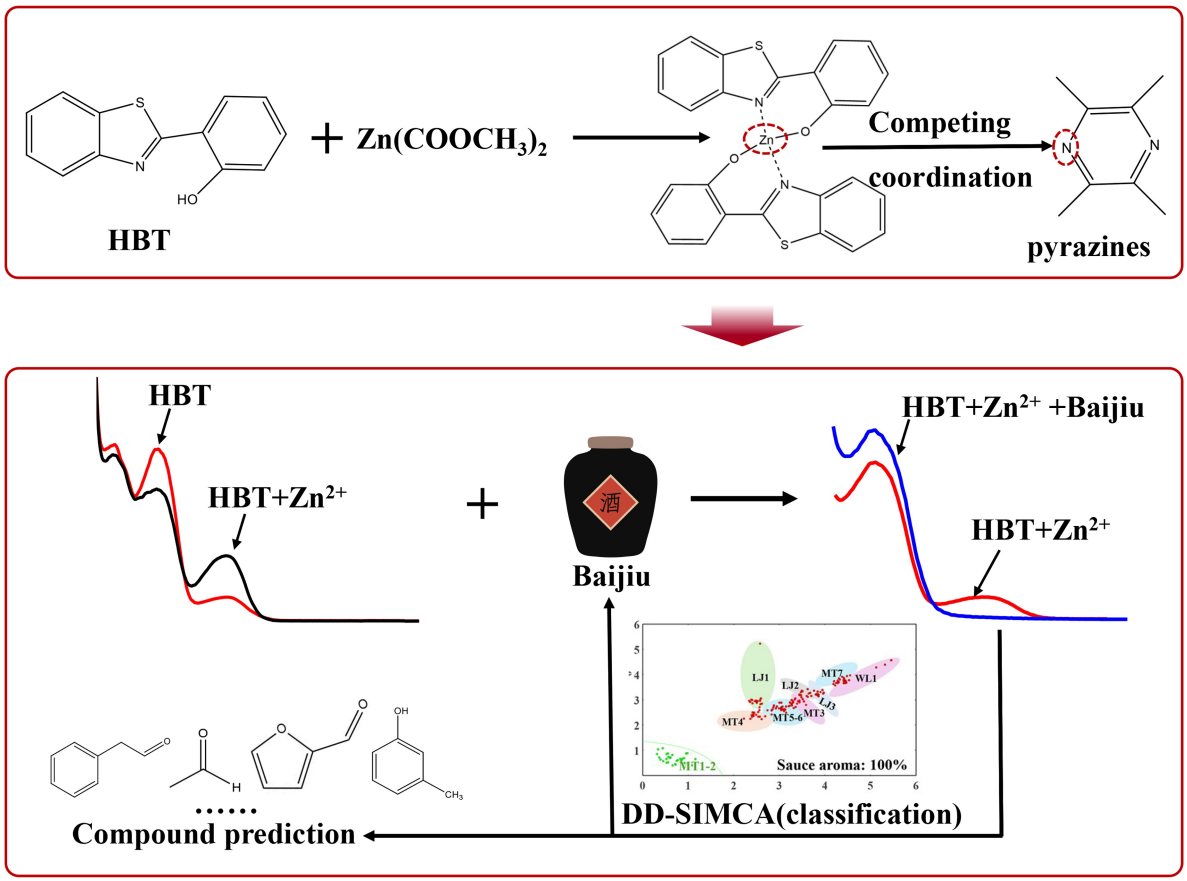

Graphical abstract. Accurate identification of same aroma type high-temperature *Daqu* Baijiu by ultraviolet visible spectral sensing of HBT combined with Zn^{2+}. HBT: 2-(2-hydroxyphenyl) benzothiazole; DD-SIMCA: data driven-soft independent modelling of class analogies; "....." indicates that pyrazine and other (Maillard reaction products) are landmark compounds that affect the classification of Baijiu

Keywords

High-temperature *Daqu* Baijiu, 2-(2-hydroxyphenyl) benzothiazole, ultraviolet-visible spectroscopy, authenticity identification

Introduction

Chinese Baijiu is a typical representative of traditional Chinese wine and one of the six distilled wines in the world [1]. Baijiu is made of grain as raw material, *Daqu* as saccharification starter, and then through fermentation, distillation, aging, blending, bottling, and finally the factory sales. Unique microbial solid (semi-solid) fermentation, distillation, and other production processes create different styles of Baijiu. About 2,000 flavor components have been detected in Baijiu, and there are 12 aroma types in Chinese Baijiu based on the proportion of style and flavor components [2]. The three main aroma types are sauce aroma type, mixed aroma type, and strong aroma type, most of which are brewed by the high-temperature *Daqu* process with the temperature of more than 60°C. High-temperature fermentation results in a relatively high content of Maillard reaction products, such as pyrazines, aldehydes, furans, thiophenes, and other Maillard reaction products and acids, esters, alcohols, phenols, terpenes produced by microbial metabolic pathways. The flavor compounds together give Baijiu its unique body style [3, 4]. In general, high-temperature *Daqu* fermentation and distillation make this kind of Baijiu have the characteristics of a long-brewing cycle, high cost, rich aroma, and mellow taste, etc., and more than 70% of the expensive Baijiu on the market are brewed by high-temperature *Daqu* process [5–7]. Due to the excellent quality and high value of high-temperature *Daqu* Baijiu, it is often filled by illegal traders through high-grade bottles of low-grade Baijiu with the same flavor to be shoddy, and consumers are not easy to distinguish when purchasing.

Therefore, it is of great significance to develop a rapid detection method for the accurate identification of high-temperature *Daqu* Baijiu quality and authenticity.

Detection and screening of Baijiu flavor substances have been concentrated in the field of chromatography and mass spectrometry, such as gas chromatography-olfactory detection, gas chromatography-nitrogen, and phosphorus detection, full two-dimensional gas chromatography-time-of-flight mass spectrometry, high-performance liquid chromatography-triple quadrupole mass spectrometry, etc. [8–11]. Not only does it have the advantages of high sensitivity, high precision, and simple operation, but it also has some limitations that cannot be ignored, such as insufficient resolution, easy to be interfered with by *m/z* approximate ions, and high instrument cost. The selection of the mobile phase is also a difficult point, and many factors need to be considered. For spectral analysis, not only the analysis speed is fast, but the application range is also wide, the sensitivity and accuracy are high, there is no need for complex sample pretreatment, and the cost is relatively low. However, for the detection of Baijiu, the specificity of conventional single spectral analysis is poor, so it is necessary to improve the specificity of spectral detection by introducing sensing probes with specific optical responses to Baijiu samples.

Optical molecular probe is the use of photoinduced electron transfer, charge transfer, energy transfer, and other photophysical processes, the design of a new optical (including light absorption, fluorescence, and luminescence) probe, which is composed of the identification of binding groups, signal emission groups, linking groups. It can be used in the study of biological and environmental toxicant labeling, fluorescence microscopic analysis, etc. 2-(2-hydroxyphenyl) benzothiazole (HBT), a small molecule optical probe. Its unique optical properties have been elucidated [12], namely, the excited state intramolecular proton transfer (ESIPT) of the enol excited state molecules, which exhibits a large Stokes shift. It is mainly a process in which the hydroxyl group and the lone pair electrons on N form hydrogen bonds, and the hydrogen bonds are transferred to the adjacent heteroatoms such as N, O, and S within the molecule to form tautomers. The five-membered heterocyclic ring and the six-membered hybrid formed by hydrogen bonds form a color group that is easy to flows electrons and absorbs energy under ultraviolet light so that electronic transition occurs and produces a strong fluorescence effect. This effect exists widely in nature and is one of the basic modes of proton transfer in biological processes. Weller et al. [13] studied the ultraviolet absorption and fluorescence spectra of methyl salicylate, found that it had an unusually large Stokes shift, and explained this phenomenon. In 1956, they first proposed the ESIPT theory. Because the N and O atoms in the molecular structure of HBT are easy to form chelates with metals, they show excellent electroluminescence and electron transport properties, so chemists pay much attention to them. In 1996, professor Yuji Hamada's research group [14] synthesized four complexes of HBT-zinc (HBT_Zn^{2+}) heterocyclic chelates, among which HBT_Zn^{2+} has a wide photoluminescence spectrum, which has attracted great attention.

Previous studies in our research group have shown that Maillard reaction products are closely related to the brewing process and quality of high-temperature *Daqu* Baijiu and play a major role in the identification of the same aroma type Baijiu. Next, the ultraviolet-visible spectroscopy (UV-VIS) of furfural and other Maillard reaction products in Baijiu were studied, and it was found that the UV-VIS spectra alone could not identify different grades of the same aroma type Baijiu. Therefore, to further improve the ability of UV-VIS spectroscopy to distinguish homoaromatic Baijiu, this study combined with spectral characterization selected HBT, which can bind to Zn^{2+} and cause significant optical signal transformation. A new method for accurate identification of high-temperature *Daqu* Baijiu with the same aroma type by HBT combined with Zn^{2+} UV-VIS spectral sensor was developed. The light signal change was mainly based on the competitive coordination effect of pyrazines and other nitrogen-containing compounds in high-temperature *Daqu* Baijiu and HBT on Zn^{2+} and ESIPT mechanism of HBT itself.

HBT itself has ultraviolet absorption at 287 nm, 335 nm, and 400 nm. After adding Zn^{2+}, nitrogen on HBT heterocycle, and oxygen on the hydroxyl group form a complex centered on Zn^{2+}, restraining ESIPT effect, resulting in a significant reduction of absorption peaks near 287 nm and 335 nm, and the absorption near 400 nm is enhanced. In general, water and alcohol will form intermolecular hydrogen bonds with HBT.

In addition, nitrogen-containing compounds such as pyrazine in Baijiu will have the effect of competing with HBT for the coordination of zinc ions, which will affect the ESIPT process under multiple actions, and eventually be reflected in the dual-wavelength absorption intensity of HBT, achieving significant amplification of spectral signals. Therefore, it is feasible to select the HBT_Zn^{2+} model to identify the authenticity of Baijiu.

Materials and methods

Materials and reagents

A total of 31 varieties of Baijiu were purchased from Walmart stores (Wuhan, China). The samples were the same as "Rapid identification of high-temperature *Daqu* Baijiu with the same aroma type through the excitation emission matrix fluorescence of maillard reaction products" by Chen et al. [15] please refer to Table S1 (https://ars.els-cdn.com/content/image/1-s2.0-S0956713523003389-mmc3.docx) of the published articles [15]. The authenticity of the Baijiu was confirmed through traceable codes that were affixed to the wine boxes, as well as through Walmart's purchase records. Before conducting the analysis, the samples were stored at 4°C under controlled conditions. HBT (98%), and zinc acetate [$Zn(OAc)_2$, 99%] were purchased from Aladdin Biotechnology Co., Ltd. (Shanghai, China). *N,N*-Dimethylformamide (DMF) was provided by Sinopharm Co., Ltd. (Beijing, China). All chemicals were analytical grade and could be used directly without further purification. The ultra-pure water machine used in the laboratory was bought from Chengdu Suyuan Technology Co., Ltd. (SYS-II-10L, Chengdu, China). Its resistivity is 18.25 MΩ. The spectra of the samples were recorded on the ultraviolet spectrophotometer (UV-1800, Mapada Instruments Co., Ltd., Shanghai, China). A two-pass optical quartz colorimeter with a diameter of 10 mm.

Sample preparation

Appropriate amounts of $Zn(OAc)_2$ and HBT were weighed, dissolved in DMF, and ultrasonicated for 10 min to dissolve them uniformly. Solution of $Zn(OAc)_2$ at 5×10^{-5} mol/L and solution of HBT at 1×10^{-5} mol/L were obtained. Took 100 μL each of HBT and $Zn(OAc)_2$, 700 μL of DMF, mixed well, and then added 100 μL of Baijiu (without pretreatment) and mixed well to make the solution to be tested (in order to get the best reaction ratio of HBT, $Zn(OAc)_2$ and Baijiu and got better reaction effect, the three reaction volumes were set to be the same). To ensure the reproducibility of the experimental method, 15 parallels were made for each Baijiu.

UV-VIS spectral acquisition

After waiting for the reaction of the test solution for 5 min, it was added into a two-pass quartz cuvette with an optical diameter of 10 mm, and the spectra were scanned and recorded with a UV spectrophotometer. Parameter settings: wavelength 260–650 nm, absorbance 0.0–0.8.

Chemometrics methods

Four chemometric methods including random forest (RF), RF regression (RFR), data driven-soft independent modelling of class analogies (DD-SIMCA), and orthogonal partial least squares discriminant analysis (OPLS-DA), were applied to the classification and identification of high-temperature *Daqu* Baijiu with the same aroma type. RF is an integrated learning algorithm that performs the classification task by constructing multiple decision trees, each of which is trained and predicted independently, and the final result is derived by voting or averaging [16]. The optimal parameters of RF, including nTree and LVs were chosen by out-of-bag (OOB) error rate. RFR is mainly used to predict the content of Maillard products in Baijiu that have made great contribution to classification. It improves the performance and stability of the model by constructing multiple decision trees and averaging or weighted averaging the predicted results of these trees to obtain the final regression result [17]. The one-class classification method is usually a better choice for detecting multiple adulterations because it requires only real samples to build a classification model that can identify any sample that is different from this as adulterated [18, 19]. DD-SIMCA is a combination of PCA and SIMCA for developing a threshold that separates the target class from all other

samples. It has certain development potential in the field of food adulteration detection [20, 21]. In this study, a DD-SIMCA model was constructed to test the identification ability of the UV-VIS sensor of HBT combined with Zn^{2+} for adulteration of Baijiu with the same aroma type and different grades. OPLS-DA is a multivariable statistical analysis method, that combines partial least squares regression and orthogonal signal correction techniques to distinguish different groups of Baijiu samples and identify the key compounds that affect the classification of Baijiu through variable importance projection values (VIP) [22, 23].

Data analysis software

MATLAB (R2018b, MathWorks.Inc, USA) was used for RF, RFR, and DD-SIMCA. Origin (Pro 9.0, OriginLab, USA) was used to draw the UV spectrogram. OPLS-DA ran in SIMCA14.1 (Sartorius Stedim Data Analytics AB, Sweden).

Results

Pure UV-VIS spectral analysis of Baijiu

Baijiu contains nearly two thousand organic compounds such as aldehydes, ketones, acids, esters, alcohols, ethers, and heterocycles. Among these organic substances, there are chromophore groups such as –COOH, –CHO, –C=N that can produce ultraviolet or visible absorption, and there are also chromophore groups such as –OH, –OR, $–NO_2$ that have no absorption band in the ultraviolet and visible regions, but can undergo n-π conjugations when connected with chromophore groups, which can enhance the absorption peak of chromophore groups or redshift them. The UV-VIS spectrum of Baijiu is caused by the valence electron transition after absorption of ultraviolet or visible light by unsaturated groups in these organic molecules. These organic flavor substances only account for about 2% of Baijiu, and although the content is very small, the content of flavor substances in different flavors of Baijiu is significantly different. Based on this, the UV-VIS absorption spectrum plays a certain role in the identification of Baijiu flavor types.

Figure 1 shows the ultraviolet absorption spectra of three different flavor types of Baijiu Figure 1A: sauce aroma type (11 kinds); Figure 1B: mixed aroma type (10 kinds); Figure 1C: strong aroma type (10 kinds). The results showed that there was only one absorption band (250–300 nm) in all three aroma types, and this band was mainly the absorption peak produced by furfural and other substances. Furfural, also known as 2-furanaldehyde, is a scientific name is α-furanaldehyde, which is derived from the substitution of the hydrogen atom on the furan 2 positions by the aldehyde group. It is chemically active. When continuous wavelength ultraviolet light irradiates the Baijiu sample, the electron absorption energy in the unsaturated bond in the organic compound transitions from the low energy level to the high energy level, forming strong characteristic absorption at 276 nm [24]. Furfural and other organic substances containing unsaturated bonds in Baijiu are mainly produced by the Maillard reaction and microbial metabolism. Affected by factors such as grain quality, environmental water source, fermentation temperature and time, and microbial flora, furfural content in Baijiu with different flavor types is bound to be different [25–27]. The concentration of compounds is directly proportional to the absorbance. According to the spectral results, the content of furfural is the highest in sauce aroma type, followed by that of mixed aroma type and that of strong aroma type is the lowest. The content of flavor substances is related to the unique brewing process of sauce aroma type Baijiu, which is one of the important bases to distinguish sauce aroma type from other flavors.

OPLS-DA analysis based on UV-VIS spectrum of pure Baijiu

OPLS-DA uses partial least squares regression to establish a relationship model between supervised variables and sample classes. To achieve the prediction of the sample category. R^2Y and Q^2 are the predictive parameters of the model, which can be considered effective models when they are > 0.5. The closer their values are to 1, the better the fit of the model, which is stable and reliable, and the higher the accuracy. In this study, OPLS-DA was used to classify different grades of Baijiu with the same aroma type. Figure 1D shows that Maotai alcohol and Wuling classic Piaoxiang wine can be separated from other sauce-

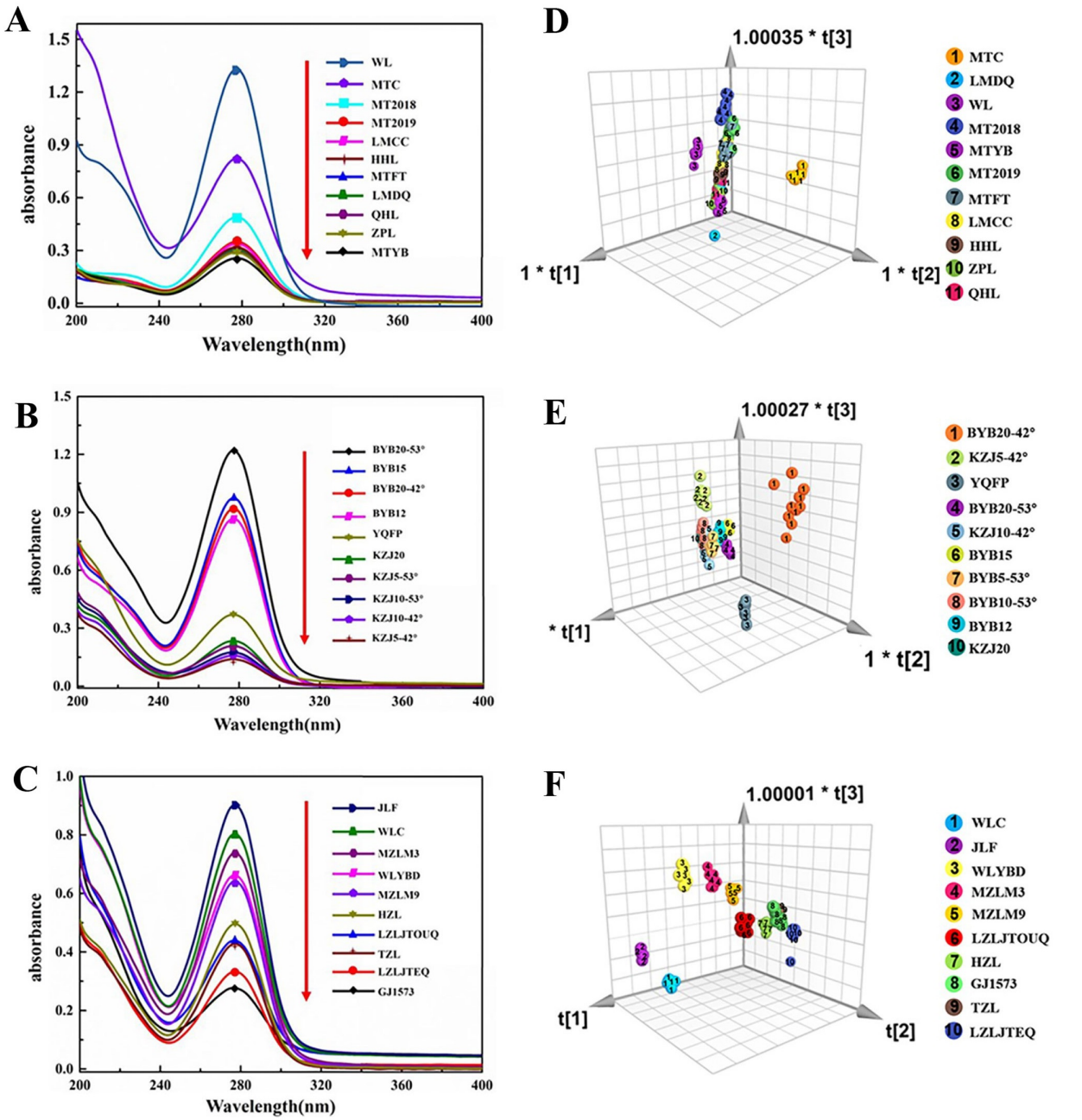

Figure 1. UV spectrum of different aroma types Baijiu (A–C) and OPLS-DA classification results of different aroma types Baijiu (D–F). A/D: sauce aroma type; **B/E:** mixed aroma type; **C/F:** strong aroma type. WLC: Wuliangye; MTC: Miaotaichun; MT2018: Maotai2018; LMCC: Laimaochuancheng; HHL: Honghualang; MTFT: Maotaifeitian; LMDQ: Laimaoduanqu; QHL: Qinghualang; ZPL: Zhenpinlang; MTYB: Maotaiyingbin; BYB20-42: Baiyunbian20-42; KZJ5-42: Kouzijiao5-42; YQFP: Yuquanfangping; JLF: Jinliufu; WLYBD: Wuliangyebadai; MZLM3: Mengzhilan_M3; LZLJTOUQ: Luzhouliaojiaotouqu; HZL: Haizhilan; GJ1573: Guojiao1573; TZL: Tianzhilan; LZLJTEQ: Luzhoulaojiaotequ

flavor wines. The brewing technology of Maotai alcohol and Wuling Piaoxiang wine produced since 2009 is quite different from that of traditional Maotai Baijiu. The production cycle of traditional Maotai Baijiu is 7 months, the steamed wine is stored in the warehouse for more than 4 years, and then nearly 200 wines of different wine ages are carefully mixed in the way “the wine is blended with more wine”, which is a special technique that involves mixing Baijiu of different quality, taste, style, and function in a certain proportion to coordinate and balance the “color, aroma, taste and style” of the Baijiu so that the Baijiu can achieve the expected style and quality standards. After five years, Maotai Baijiu has the characteristics of outstanding sauce flavor, mellow body, long aftertaste, and lasting aroma in the empty glass, which is a typical Chinese sauce aroma style [28]. Although Maotai alcohol is also a member of the Maotai family and is of the same origin as Maotai, it continues to innovate on the basis of adhering to the traditional brewing process,

adopting the Dragon Boat Festival harvest, double ninth feeding, nine cooking, eight fermentation, and seven distilling, and the production cycle is as long as 5 years. The quality of the sauce wine is more prominent, and the wine body is softer and comfortable [29]. Wuling wine is made of glutinous red sorghum grown in southern Sichuan, with solid-state fermentation and solid-state distillation as the raw material. With the essence of the production process, the original wine is produced according to three typical types of sauce flavor, mellow sweet flavor, and cellar bottom flavor, and different rounds of wine are stored for a long time (more than 3 years). Wuling wine is different from Maotai Baijiu in that it has made innovative improvements in every key point of brewing technology. For example, Wuling wine is 5 degrees higher than Maotai Baijiu in the stage of high-temperature accumulation and high-temperature makes *Daqu*, enriching the microbial system that can withstand high-temperature and produce fragrance [30]. Figure 1E results showed that Baiyunbian 20 years 42° and Yuquan square bottle wine can be significantly distinguished from other mixed aroma wines. Yuquan wine, because of its unique two-step brewing process of thick sauce and fragrance, has significant differences in flavor content and type from other mixed aroma wines, so the classification and discrimination results are the best. The classification effect of the strong aroma type is the best (Figure 1F), and all 10 types of Baijiu can be distinguished. In summary, UV absorption spectra combined with a stoichiometric pattern recognition algorithm cannot completely distinguish different grades of Baijiu with the same aroma type, so a new strategy needs to be sought.

Discussion on the mechanism of the HBT_Zn^{2+} UV-VIS sensor

HBT is a compound with typical ESIPT properties. During proton transfer, enol-type and keto-type tautomerism occur, showing dual-wavelength absorption in the UV-VIS spectrum. As shown in Figure 2, there are two strong absorption peaks and one weak absorption peak in the absorption spectrum of HBT, which are about 287 nm, 335 nm, and 400 nm respectively. In general, HBT is dominated by a stable enol form, and the two strong absorption peaks at 287 nm and 335 nm are represented by π-π* transitions of carbon-carbon double bonds in the enol form [31]. In addition, Zheng et al. [32] concluded that the absorption peak of ketone configuration should be located in the long band at 400 nm by studying the spectral rules of HBT under different polar conditions. According to literature reports [19], Zn^{2+} was easy to coordinate with compounds such as pyrazines containing nitrogen and oxygen, but there was no obvious optical signal change. In this study, the combination of Zn^{2+} and HBT could significantly amplify the spectral signal. Figure 2A shows that after the addition of Zn^{2+} to HBT, the double absorption peak of the enol configuration near 287 nm and 335 nm is significantly reduced, while the absorption of the ketone configuration near 400 nm is enhanced. It was concluded that Zn^{2+} and nitrogen on the 2-molecule HBT heterocyclic ring and oxygen on the hydroxyl group form a complex centered on Zn^{2+}, which hindered the ESIPT process, resulting in significant changes in UV absorption of the two configurations (Figure 3). After Baijiu was added to the mixture of HBT+Zn^{2+}, the absorption peak of the enol configuration near 335 nm increased significantly, while the absorption peak of the ketone configuration near 400 nm disappeared. Since Baijiu is mostly water and ethanol, the comparison of alcohol and water with different degrees of alcohol showed that the absorption peak of the enol configuration near 335 nm was also significantly increased, while the absorption of the ketone configuration near 400 nm was weakened to different degrees (Figure 2B), which was different from the absorbance presented when Baijiu was added. It might be that water and alcohol formed intermolecular hydrogen bonds with HBT, and the pyrazines and other compounds containing nitrogen and oxygen in Baijiu competed with HBT to coordinate Zn^{2+}, which affected the ESIPT process under multiple actions, and finally significantly amplified the spectral signal [19, 31]. It is similar to the UV-VIS spectra shown in Figure 1, all Baijiu has a response under this method, but the difference in the spectrum is very subtle (Figure S1). Therefore, it was difficult to directly identify each group of Baijiu samples from the peak shape and peak position of the spectrum, and chemical information hidden in the UV-VIS spectra should be extracted by the stoichiometric method. The classification model was established to identify 31 kinds of Baijiu samples.

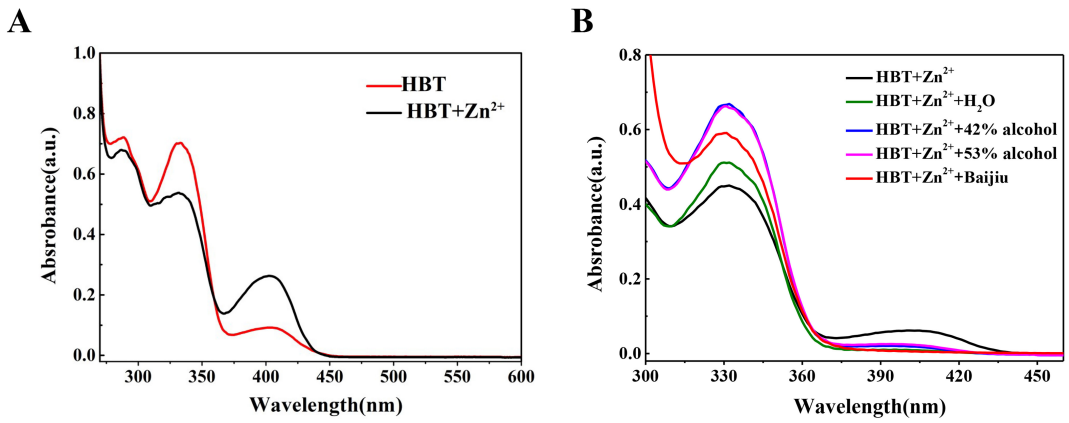

Figure 2. Spectral response of HBT_Zn^{2+} UV-VIS sensor to Baijiu. A: UV absorption pattern of the reaction of HBT with Zn^{2+}; **B:** UV absorption profiles of HBT_Zn^{2+} in response to Baijiu/water/ different alcohol concentrations. UV-VIS: ultraviolet-visible spectroscopy; HBT: 2-(2-hydroxyphenyl) benzothiazole

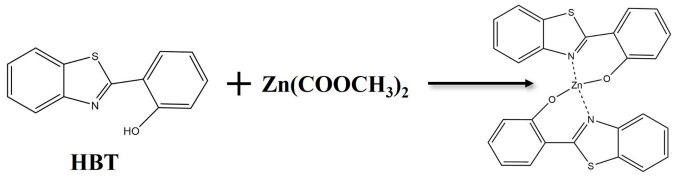

Figure 3. Reaction mechanism between HBT and Zn^{2+}. HBT: 2-(2-hydroxyphenyl) benzothiazole

Classification and discrimination of Baijiu by RF

RF is a powerful ensemble learning algorithm based on multiple decision trees, each of which is trained and predicted independently of each other. By averaging the prediction results of multiple decision trees, the risk of overfitting can be effectively reduced, and the overall prediction accuracy can be improved. In order to better evaluate the recognition ability of HBT_Zn^{2+} UV-VIS sensor for high-temperature *Daqu* Baijiu, a discrimination model of high-temperature *Daqu* Baijiu was established by using a chemometrics RF algorithm. First, we used the RF constructed by the "TreeBagger" function in Matlab2018b to model the sensor data and set "oobvarimp" in this function to enable the variable importance assessment of samples outside the bag, in which the number of decision trees nTree was optimized from 1 to 100 according to the sensor data for cross-validation. Then, based on the optimized nTree, samples accounting for 80% of the total sample volume were randomly selected as the training set, and the remaining samples were used as the prediction set to build an RF model. Finally, classification and prediction were made according to the accuracy of the training set and prediction set of the model. It could be seen from Table 1 that in the identification of different brands of Baijiu with the same aroma type, the result of the sensor system was better than the original spectrum of Baijiu, compared with the single UV-VIS spectrum of Baijiu, the identification accuracy of this method was improved from 62.37% to 100%. It was successfully used in the identification of high-temperature *Daqu* Baijiu.

Table 1. Discrimination of high-temperature *Daqu* Baijiu by random forest algorithm

Method	Sort	Accuracy rate (%)		Number of errors	
		Training set	Prediction set	Training set	Prediction set
UV-VIS	Sauce	100	93.94	0	2
	Mixed	100	93.33	0	2
	Strong	100	96.67	0	1
	Total	97.24	62.37	5	33
HBT_Zn^{2+} UV-VIS	Sauce	100	100	0	0
	Mixed	100	100	0	0
	Strong	100	100	0	0
	Total	100	100	0	0

UV-VIS: ultraviolet-visible spectroscopy; HBT: 2-(2-hydroxyphenyl) benzothiazole

Prediction of the content of Maillard reaction products by RFR

In order to further verify the contribution weight of Maillard reaction products in Baijiu to this classification and discrimination method, the absorbance data of high-temperature *Daqu* Baijiu under this method and the concentration of Baijiu flavor compounds identified by HS SPME-GC-MS (headspace solid phase microextraction-gas chromatogra-phy-mass spectrometry) were regression analyzed by RFR algorithm. Table 2 shows that this method can accurately predict the contents of Maillard reaction products such as pyrazines and furfural, and the deviation between the real value and the predicted value is less than 1.8746% ± 1.4515%. Further indicating that the Maillard reaction products such as pyrazines were markers affecting the classification of Baijiu.

Table 2. Prediction results of the content of Maillard reaction products in Baijiu by HBT_Zn^{2+} UV-VIS sensor method

Category	Compounds	True value	Predicted value	The difference
Pyrazines	2,6-dimethylpyrazine	0.2490 ± 0.2192	0.2489 ± 0.2188	0.3430% ± 0.9530%
	2,6-dimethyl-5-ethylpyrazine	0.3762 ± 0.2491	0.3759 ± 0.2481	0.8731% ± 1.4945%
	Tetramethyl pyrazine	0.2241 ± 0.2383	0.2240 ± 0.2382	0.2374% ± 0.1861%
	2,5-dimethyl-3-amyl-pyrazine	0.3299 ± 0.2353	0.3302 ± 0.2353	0.5187% ± 0.0081%
Aromatics	1,2-dimethoxybenzene	0.2377 ± 0.1904	0.2376 ± 0.1905	0.7460% ± 2.0487%
	2-acetyl-5-methylfuran	0.3697 ± 0.2581	0.3699 ± 0.2581	0.7212% ± 1.1937%
	2-methylphenol	0.2379 ± 0.1703	0.2380 ± 0.1703	1.8746% ± 1.4515%
Aldoketones	Phenylacetaldehyde	0.3342 ± 0.2218	0.3342 ± 0.2219	0.7663% ± 1.4843%
	α-ethylenephenylacetaldehydeydeyde	0.3867 ± 0.2597	0.3868 ± 0.2598	0.4586% ± 0.6471%
	5-methyl-2-furanaldehyde	0.3140 ± 0.2216	0.3139 ± 0.2217	0.6599% ± 1.4408%
	Furfural	0.3881 ± 0.2605	0.3881 ± 0.2603	0.7600% ± 1.6048%
	1-(2-furanyl)-ethyl ketone	0.3967 ± 0.2555	0.3965 ± 0.2555	0.4951% ± 0.6270%

UV-VIS: ultraviolet-visible spectroscopy; HBT: 2-(2-hydroxyphenyl) benzothiazole

Method validation is generally evaluated by the performance index and stability index of the model. Model performance is the accuracy of the model prediction. To ensure the high stability and reproducibility of the method, we made 15 batches of each Baijiu sample using the same experimental conditions to obtain a 465 (samples 15 × 31) × 300 (data points) data matrix, which was then cross validated to assess its performance. It divided the data set into subsets, used 20% of the samples as the validation set and the rest as the training set, repeated the process 95 times, and finally averaged the results of the 95 experiments to evaluate the performance of the model. From the results, the prediction accuracy of the four models reached 100%. The regression model relied on the root mean square error (RMSE) to predict, and Table 2 shows that the RMSE of the predicted compound content is less than 1%. The performance of the model was stable, and the prediction accuracy was high, which further indicated the high precision of the experiment and the good data quality.

Identification of the same aroma type Baijiu

In order to further explore the recognition ability of HBT_Zn^{2+} UV-VIS sensor system for adulteration of the same aroma type Baijiu, a DD-SIMCA model was constructed. First of all, the ultraviolet sensing spectral data was imported into MATLAB (Baijiu with higher prices in the same aroma type and brand were used as real samples, and others were used as adulterated samples for identification), then run DDSGUI in the command window, input the spectral data of real samples and adulterated samples successively in the pop-up window, and finally obtained the identification diagram of the three flavors. After beautification and modification of the format, the DD-SIMCA results of three fragrances were obtained, as shown in Figure 4. It shows the DD-SIMCA acceptance diagram of the same aroma type adulteration of three kinds of Baijiu. Overall, it could be seen that the same aroma type low-grade Baijiu adulteration of high-grade Baijiu could be accurately identified. The green line was the discriminant line, which referred to the threshold value belonging to the real sample. The real sample was marked as a green dot on the acceptance diagram, which was in the lower left corner of the green discriminant line. Other samples, known as adulterated samples,

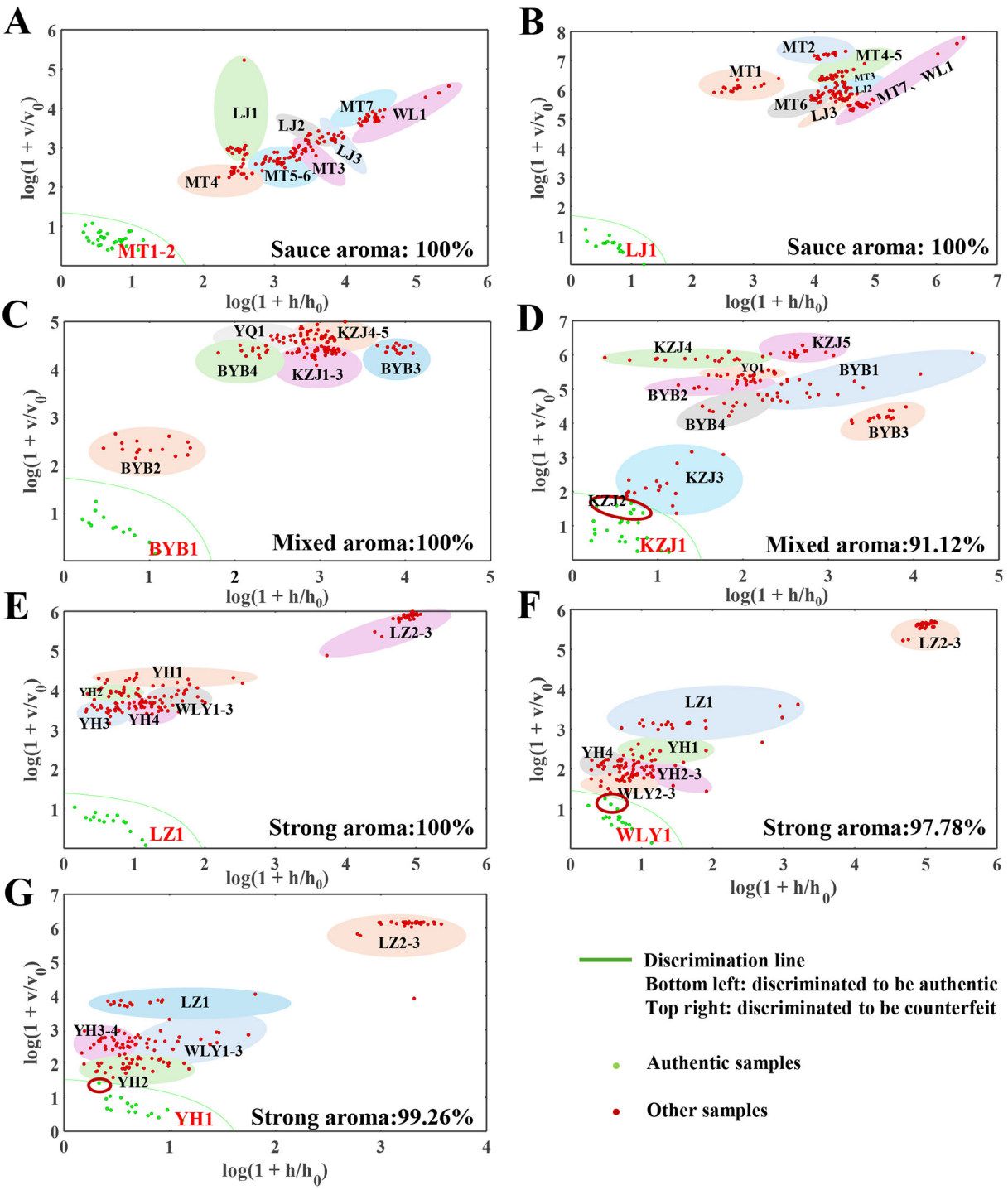

Figure 4. DD-SIMCA acceptance diagram of HBT_Zn^{2+} UV-VIS sensor identification of different grades of Baijiu with the same aroma type. (**A**) Sauce aroma type (MT1, MT2); (**B**) sauce aroma type (LJ1); (**C**) mixed aroma type (BYB1); (**D**) mixed aroma type (KZJ1); (**E**) strong aroma type (LZ1); (**F**) strong aroma type (WLY1); (**G**) strong aroma type (YH1). The abbreviations and corresponding full names of the Baijiu samples used in this experiment are listed in detail in Table S1 (please refer to https://ars.els-cdn.com/content/image/1-s2.0-S0956713523003389-mmc3.docx in the published articles [15])

were marked with red dots in the upper right corner of the green line. Figure 4A shows that MT1 (Maotaifeitian 2019) and MT2 (Maotaifeitian 2018) are real samples, and other sauce aroma type Baijiu are adulterated samples. Figure 4B shows that LJ1 (Qinghualang) is the true sample and other sauce aroma type Baijiu is the adulterated sample. In Figure 4C, BYB1 (Baiyunbian 20 year-53%vol) is the real sample, and the other mixed aroma type wines are the adulterated samples. In Figure 4D, KZJ1 (Kouzijiao 20 year) is the true sample, and the other mixed aroma type wines are the adulterated samples. In Figure 4E, F, and G, LZ1 (Guojiao 1573), WLY1 (Wuliangyebadai), and YH1 (Yanghe Mengzhilan_M9) are taken as real samples respectively, and other strong aroma types are adulterated samples. According to the results, the

results showed that the identification accuracy of sauce aroma type could reach 100%. The discriminant accuracy rate of mixed aroma type was above 90%. Strong aroma type was greater than 97%. The reason was that the Baijiu of the same aroma type and brand was similar in brewing process and flavor, and the error of human operation in the experiment might have caused misjudgment. In general, the accuracy of the model was between 90% and 100%, indicating that the array sensor had a good recognition effect on the adulteration of the same aroma type Baijiu.

Discussion

In this study, the changes of optical signals generated by pyrazines and other differential markers in high-temperature *Daqu* Baijiu, the competitive coordination of HBT to Zn^{2+}, and the effect on the ESIPT mechanism of HBT itself were studied. A new method for accurate identification of same-flavor high-temperature *Daqu* Baijiu by HBT combined with Zn^{2+} UV-VIS spectral sensor was developed. Combined with the RF, the high-temperature *Daqu* Baijiu of the same aroma type and different grades was successfully identified. Compared with the single UV-VIS spectrum of Baijiu, the identification accuracy of this method was improved from 62.37% to 100%. The accuracy of the DD-SIMCA model was between 90% and 100%, indicating that the array sensor had a good recognition effect on the adulteration of the same aroma type Baijiu. Finally, the RFR was used to predict the contents of 12 Maillard reaction products successfully, and the deviation between the real value and the predicted value was less than 1.8746% ± 1.4515%, which further indicated that pyrazine Maillard reaction products were markers affecting the classification of Baijiu. In summary, from the perspective of reaction mechanism and accuracy indexes of RF, RFR, and DD-SIMCA models, the applicability of HBT_Zn^{2+} sensor method for Baijiu authenticity identification has been verified. The method established in this chapter provides another new way of thinking about the identification of Baijiu.

Abbreviations

DD-SIMCA: data driven-soft independent modelling of class analogies

DMF: *N,N*-Dimethylformamide

ESIPT: excited state intramolecular proton transfer

HBT: 2-(2-hydroxyphenyl) benzothiazole

HBT_Zn^{2+}: 2-(2-hydroxyphenyl) benzothiazole-zinc

OPLS-DA: orthogonal partial least squares discriminant analysis

RF: random forest

RFR: random forest regression

RMSE: root mean square error

UV-VIS: ultraviolet-visible spectroscopy

$Zn(OAc)_2$: zinc acetate

Supplementary materials

The supplementary figures for this article are available at: https://www.explorationpub.com/uploads/Article/file/101067_sup_1.pdf.

Declarations

Author contributions

YZ: Methodology, Investigation, Writing—original draft. YS: Methodology, Investigation. YC: Methodology. HC: Methodology, Writing—review & editing, Funding acquisition. W Long: Formal analysis. W Lan: Formal analysis. XJ: Supervision, Funding acquisition. HF: Conceptualization, Funding acquisition, Supervision.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent to publication

Not applicable.

Availability of data and materials

The datasets that support the findings of this study are available from the corresponding author upon reasonable request.

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References

1. Tu W, Cao X, Cheng J, Li L, Zhang T, Wu Q, et al. Chinese Baijiu: The Perfect Works of Microorganisms. Front Microbiol. 2022;13:919044. [DOI] [PubMed] [PMC]
2. Liu H, Sun B. Effect of Fermentation Processing on the Flavor of Baijiu. J Agric Food Chem. 2018;66:5425–32. [DOI] [PubMed]
3. Wang L, Chen S, Xu Y. Distilled beverage aging: A review on aroma characteristics, maturation mechanisms, and artificial aging techniques. Compr Rev Food Sci Food Saf. 2023;22:502–34. [DOI] [PubMed]
4. Hong JX, Zhao DR, Sun BG. Research progress on the profile of trace components in Baijiu. Food Rev Int. 2023;39:1666–93. [DOI]
5. Yi Z, Jin Y, Xiao Y, Chen L, Tan L, Du A, et al. Unraveling the Contribution of High Temperature Stage to Jiang-Flavor Daqu, a Liquor Starter for Production of Chinese Jiang-Flavor Baijiu, With Special Reference to Metatranscriptomics. Front Microbiol. 2019;10:472. [DOI] [PubMed] [PMC]
6. Xiao C, Lu Z, Zhang X, Wang S, Ao L, Shen C, et al. Bio-Heat Is a Key Environmental Driver Shaping the Microbial Community of Medium-Temperature Daqu. Appl Environ Microbiol. 2017;83:e01550–17. [DOI] [PubMed] [PMC]
7. Wang M, Yang J, Zhao Q, Zhang K, Su C. Research Progress on Flavor Compounds and Microorganisms of Maotai Flavor Baijiu. J Food Sci. 2019;84:6–18. [DOI] [PubMed]

8. He X, Yangming H, Górska-Horczyczak E, Wierzbicka A, Jeleń HH. Rapid analysis of Baijiu volatile compounds fingerprint for their aroma and regional origin authenticity assessment. Food Chem. 2021;337:128002. [DOI] [PubMed]
9. Zong XY, Zhou XJ, Wen L, Gan S, Li L. Identification of Baijiu based on the Raman spectroscopy and back-propagation neural network optimized using genetic algorithm. J Food Compos Anal. 2023;126: 105917. [DOI]
10. Jiang X, Xie Y, Wan D, Chen M, Zheng F. GUITAR-enhanced facile discrimination of aged Chinese Baijiu using electrochemical impedance spectroscopy. Anal Chim Acta. 2019;1059:36–41. [DOI] [PubMed]
11. Hu SQ, Wang L. Age discrimination of Chinese Baijiu based on midinfrared spectroscopy and chemometrics. J Food Quality. 2021;2021:5527826. [DOI]
12. Xu HB, Shao KY, Hu WX. Synthesis and Spectroscopy of 2-(2-Hydroxyphenyl) benzothiazole. Microwave Chem. 2020;4:13–21. Chinese. [DOI]
13. Weller A. Intramolecular proton transfer in excited states. Z Elektrochem Angew Phys Chem. 1956;60: 1144–7. German. [DOI]
14. Hamada Y, Sano T, Fujii H, Nishio Y, Takahashi H, Shibata K. White-light-emitting material for organic electroluminescent devices. Jpn J Appl Phys. 1996;35:L1339. [DOI]
15. Chen HY, Zhu YM, Xie YF, Long WJ, Lan W, She YB, et al. Rapid identification of high-temperature Daqu Baijiu with the same aroma type through the excitation emission matrix fluorescence of maillard reaction products. Food Control. 2023;153:109938. [DOI]
16. Azizan NI, Mokhtar NFK, Arshad S, Sharin SN, Mohamad N, Mustafa S, et al. Detection of lard adulteration in wheat biscuits using chemometrics-assisted GCMS and random forest. Food Anal Method. 2021;14:2276–87. [DOI]
17. Chung HT, Tsai CC, Jen KK, Huang YS, Ferng YC, Lo CY, et al. Optimization of process parameters of selective laser melted nickel-based superalloy for densification by random forest regression algorithm and response surface methodology. Results Eng. 2024;22:102182. [DOI]
18. Pagani AP, Camargo G, Ibañez GA, Olivieri AC, Pomerantsev AL, Rodionova OY. Data-Driven Version of Multiway Soft Independent Modeling of Class Analogy (N-Way DD-SIMCA): Theory and Application. Anal Chem. 2024;96:4845–53. [DOI] [PubMed]
19. Zhu Y, Xiang F, Su Y, Jiang X, Cang Y, Long W, et al. Authenticity identification of high - Temperature Daqu Baijiu through multi-channel visual array sensor of organic dyes combined with smart phone App. Food Chem. 2024;438:137980. [DOI] [PubMed]
20. Onça L, Koljančić N, Furdíková K, Khvalbota L, Špánik I, Gomes AA. A digital image smartphone-based approach to Slovak Tokaj wine authentication chemometric assisted. Food Chem. 2024;456:140075. [DOI] [PubMed]
21. Reis-Pereira M, Mazivila SJ, Tavares F, Neves dos Santos F, Cunha M. Early plant disease diagnosis through handheld UV–Vis transmittance spectrometer with DD-SIMCA one-class classification and MCR-ALS bilinear decomposition. Smart Agric Technol. 2024;9:100631. [DOI]
22. Ju Y, Liu H, Niu S, Kang L, Ma L, Li A, et al. Optimizing geographical traceability models of Chinese *Lycium barbarum*: Investigating effects of region, cultivar, and harvest year on nutrients, bioactives, elements and stable isotope composition. Food Chem. 2024;467:142286. [DOI] [PubMed]
23. Kuligowski J, Moreno-Torres M, Quintás G. Improving insights from metabolomic functional analysis combining multivariate tools. Anal Chim Acta. 2024;1323:343062. [DOI] [PubMed]
24. Wang X, He M, Zheng J, Ma Y, Hou C, Hou D. Methodology and optimization research for discrimination of different brands of Baijiu based on multispectral techniques. Food Measure. 2024;18:7855–67. [DOI]
25. Nowak A, Janoszka B, Szumska M, TyrpieÅ„-Golder K. FURFURAL, HYDROXYMETHYLFURFURAL AND FUROSINE AS MAILLARD REACTION MARKERS IN FRUIT BASED FOODS INCLUDING JAMS AND BABY FOOD. JMBFS. 2021;11:e1384. [DOI]

26. Xu HY. Study on the relationship between furfural content and flavor type in Baijiu. Liquor Making. 2002;29:37–9.
27. Zhu XQ, Lei WH, Huang YY. Research progress of 5 – hydroxymethyl furfural in food and its safety. J Food Saf Qual. 2022;15:4983–991.
28. Li L. A preliminary study on the characteristics of Maotai Baijiu that cannot be copied. Changjiang Series. 2019;89–90.
29. Niu J, Yang S, Shen Y, Cheng W, Li H, Sun J, et al. What are the main factors that affect the flavor of sauce-aroma Baijiu. Foods. 2022;11:3534. [DOI]
30. Ling Y, Li W, Tong T, Li Z, Li Q, Bai Z, et al. Assessing the Microbial Communities in Four Different Daqus by Using PCR-DGGE, PLFA, and Biolog Analyses. Pol J Microbiol. 2020; 27–37. [DOI]
31. Wang AH, Zhang H, Abou-Zied OK, Yu C, Romesberg FE, Glasbeek M. Femtosecond fluorescence upconversion studies of excited-state proton-transfer dynamics in 2-(2′-hydroxyphenyl)benzoxazole (HBO) in liquid solution and DNA. Chem Phys Lett. 2003;367:599–608. [DOI]
32. Zheng J, Zhang G, Wu F, Ma L, Chen W. The spectra properties of 2-(2'-hydroxyphenyl)benzothiazole in different solvents. Guang Pu Xue Yu Guang Pu Fen Xi. 2008;28:970–3. [PubMed]