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Influence of Electrochemical Oxidation on the Maturation Process of the Distilled Spirit

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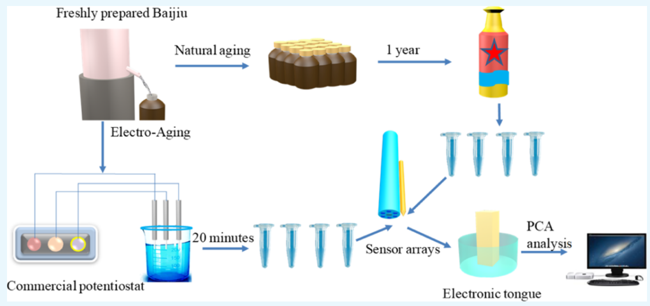
ABSTRACT: Optimizing the aging process is urgently required in the distilled spirit industry because of the time-consuming and expensive procedure of natural aging. Herein, the componential changes of the liquor sample are confirmed by the component analysis (e.g., gas chromatograph), and the effect of electrochemical oxidization treatment on the overall properties of typical Chinese liquor (Baijiu) is investigated. The key finding is that high oxidative potential can be used to catalyze the oxidation of alcohols, and the reaction rate is dramatically faster than that in the process of natural aging. The present study reveals the influence of electrochemical oxidation on the contents of compounds (particularly, the alcohols) in Baijiu and offers a perspective into the utilization of electrochemical oxidization treatment as an alternative strategy for artificial maturation of Baijiu.



1. INTRODUCTION

Baijiu, otherwise known as Chinese liquor, one of the world's top six distilled spirits, plays a big role in the Chinese diet structure and is an important carrier of world diet culture.[1,2] Liquor has a complex aroma mainly because of the esters.[3,4] Chinese Jiuqu provides multiple saccharifying enzymes for the simultaneous saccharification and fermentation processes.[5] By taking Jiuqu as the saccharification and fermentation starter, Baijiu is made by the major steps that involves cooking, saccharification, fermentation, distillation, aging, and blending.[6] The freshly produced liquor has a pungent taste and is only semifinished. Similar to brandy and whiskey, for liquor, a certain storage process is also required for the maturation, irritation, and spiciness reduction, so that it will have a better taste.[7] Such a phenomenon is called "maturation" or "aging" in the liquor-making industry. A period of 3−5 years or even 10 years are required for aging.[8,9] Long aging greatly increases the liquor-making cost, as well as the sales price of liquor. Therefore, the aging process urgently needs to be optimized in the international distilled spirits industry. In recent years, many artificial maturation techniques have been reported.[10−12] For example, ozone with a strong oxidicability is used to accelerate the oxidation reaction of liquor, and microwave irradiation is used to catalyze the esterification reaction to shorten the aging time.[13,14] Although artificial maturation techniques have made some progress,[15] there are still some problems in the research and application process, for example, ozone oxidation mainly acts on the gas−liquid interface, leading to the uneven liquor body and affecting the quality. The research on the catalytic reaction mechanism of the microwave radiation method is not clear enough. After treatment, the liquor samples of different batches are quite different and the process is uncontrollable. Compared with artificial maturation, natural aging is still the main technology for producing high-quality liquor.[16]

It is generally believed that the aging process can improve the quality of liquor for two main reasons:[17] first, the freshly produced liquor contains some spicy and volatile compounds, such as hydrogen sulfide, allyl alcohol, and propionaldehyde, which will be volatilized during the aging, making the liquor taste from spicy to soft. Second, there are some slow chemical reactions during the aging, such as oxidation, esterification, and alcohol aldehyde condensation, producing a variety of flavor substances. In recent years, the electrochemical techniques, in particular, differential pulse voltammetry and cyclic voltammetry (CV) using either metal- or carbon-based electrodes, have been developed for understanding the mechanisms of flavor perception, which is the determinant factor of the quality of liquor.[18,19] As has been reported, the peaks in the cyclic voltammograms of wines correspond to certain phenolics with higher oxidation potentials, which provides a qualitative measurement of wine phenolics based on reduction current.[20]

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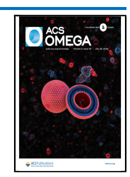

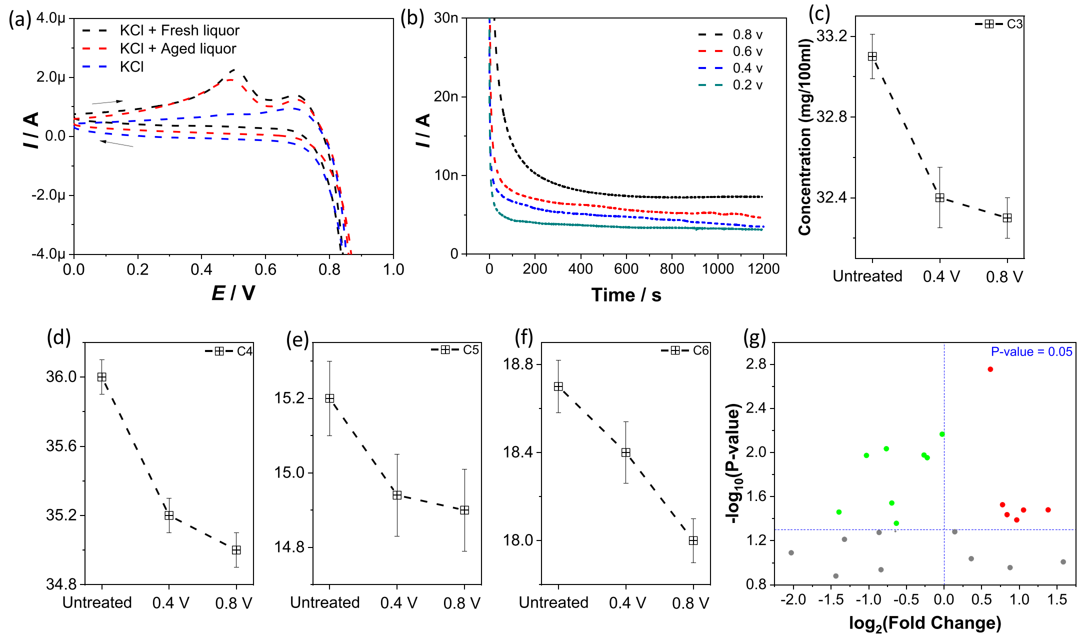

Figure 1. (a) CV performed in 0.1 M KCl, freshly produced liquor in 0.1 M KCl (20%, volume ratio), and 1-year aging liquor in 0.1 M KCl (20%, volume ratio), respectively. (b) Chronoamperometry of the freshly produced liquor, treated at different oxidation potentials: 0.2, 0.4, 0.6, and 0.8 V. The content of alcohols (determined based on three independent experiments) in the liquor sample after electrochemical treatment with the potential at 0.4 and 0.8 V: *n*-propanol (c), *n*-butyl alcohol (d), isoamyl alcohol (e), and *n*-hexanol (f), respectively. (g) Volcano plot analysis of 24 compounds before and after electrochemical oxidation at 0.8 V.

In addition, CV fingerprinting was used to monitor the "oxidation status" of white wines and to evaluate the effects of oxygen regimes and antioxidant activity.[21] As is well known, electrochemical techniques emerge as an alternative strategy for the efficient and economic analysis of food constituents when we consider some of the characteristics of traditional approaches like time consumption and use of expensive equipment and expensive reagents unfriendly to the environment.

Therefore, considering that the key substances in distilled spirits can also be oxidized or reduced on the electrode surface,[22,23] the use of electrochemical oxidation techniques to assist in the aging of liquor was discussed. Combining electrochemistry, electronic tongue classification, and principle components analysis, it is proved that electrochemical oxidative treatment can significantly change the overall properties of the typical Chinese liquor, Baijiu. It was confirmed that high oxidative potential can be used to catalyze the oxidation of alcohols, and the reaction rate is faster than that in the process of natural aging. The presented research implicates electrochemical oxidization treatment is potentially available for developing the technology for artificial maturation of Baijiu.

2. RESULTS AND DISCUSSION

CV performed in 0.1 M KCl, freshly produced liquor in 0.1 M KCl (20%, volume ratio), and 1 year aging liquor in 0.1 M KCl (20%, volume ratio) are shown in Figure 1a. As seen, there is no redox peak shown in the CV scanned in 0.1 M KCl which accords with the typical CV observation for the polycrystalline gold disc electrode.[24] It indicates that the gold surface is stable, and no oxygen adsorption occurs as the electrolyte solution is cleaned by injecting nitrogen gas before recording the voltammogram, which is necessary for the subsequent CV tests. The CV scanned in 0.1 M KCl containing 20% freshly produced liquor presented two broad peaks: peak I at [0.45, 0.58 V] and peak II at [0.63, 0.72 V]. Such broad peaks suggest that a wide range of compounds in the liquor are oxidizable and contribute to the total current. The CV scanned in 0.1 M KCl containing 20% 1-year aging liquor also presented two broad peaks, differentiated only by the decreased peak currents. This is reasonable because the spontaneous chemical oxidation of alcohols to aldehydes or carboxylic acids by dissolved O_2 is a very slow process.[25,26] Kilmartin et al. have reported that the polyphenols in wine are the redox-active compounds that are easily oxidized at metal or carbon electrodes.[27] However, in the case of Baijiu, it has been reported that the alcohols in Baijiu can be oxidized by the oxygen.[25,26] Thus, we next consider the influence of electrochemical oxidation on the alcohols in Baijiu.

The freshly produced liquor was treated by the increasing oxidation potentials and recorded by chronoamperometry. As shown in Figure 1b, all the current curves had a rapid current change (within the first 200 s), after which they were small and there were only small fluctuations. In the second half, the higher the applied potential, the higher the platform current. The content of alcohols in the Baijiu sample after electrochemical treatment was determined by gas chromatography, as shown in Figure 1c−f. It can be seen that after electrochemical oxidation treatment, the contents of n-propanol (abbreviated as C3), *n*-butyl alcohol (C4), isoamyl alcohol (C5), and *n*-hexanol (C6) in liquor samples decreased. At the same time, the content of alcohols decreased even more when treated with higher potential. The consumption rate of alcohols in the process of natural aging is less than 5×10^{-8} mg mL^{-1} min^{-1} in general. The corresponding consumption rates of C3, C4, C5, and C6, with the aid of electrochemical oxidation, are 4.1 $\times 10^{-4}$, 5.1×10^{-4}, 1.5×10^{-4}, 3.9×10^{-4} mg mL^{-1} min^{-1}, respectively. It has been reported that parallel reaction pathways occur during the electrochemical oxidation of

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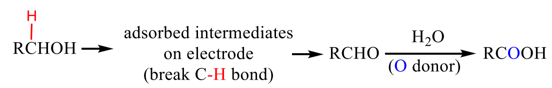
alcohols.[28] The parallel pathways have been demonstrated, producing aldehydes or carboxylic acids as soluble products, to an extent that depends on system parameters like electrode roughness, time of electrolysis, and concentration of alcohols. The electrochemical oxidation of alcohols can be formulated as follows (Scheme 1).

Scheme 1. Schematic Representation of the Electrochemical Oxidation Process of Alcohols



The gold electrode biased at a certain potential serves as the catalyst for breaking the C−H bond, and the carboxylic acids formation step requires dissociation of water, which is the oxygen donor of the step.

In the aging process of Baijiu,[29] the containers used to store Baijiu samples are usually earthenware made of natural clay, which is characterized by a slight breathability. During the aging process, enough oxygen from the outside enters the interior of the pottery to make up for the oxygen consumed by the oxidation reaction, ensuring that dissolved oxygen is maintained at a state of saturation. Although the aging process relies on dissolved oxygen to oxidize alcohols, the reaction rate is extremely slow. As can be seen, in the electrochemical oxidation of alcohols, high potential is used to accelerate the oxidation of alcohols; thus, the reaction rate of artificial aging is faster.

Therefore, the oxidation potential of 0.8 V was selected to promote Baijiu "aging" and the 24 compounds in treated samples before and after electrochemical oxidation were analyzed by the volcano plot. In the volcano plot, each dot refers to a compound, the abscissa $\log_2$ fold change indicating the logarithm of the content ratio of the corresponding compounds in the treated group to the nontreated group. The greater the change of abscissa, the greater the content differences between groups of compounds. Longitudinal coordinates represent the negative logarithmic conversion of P values of content differences. The larger the negative logarithmic transformation, the more significant the differential level. As shown in Figure 1g, the dots in green indicate that the corresponding compounds have decreased, while the dots in red indicate that the corresponding compounds have decreased. The above results confirm the influence of electrochemical oxidation on the contents of compounds (particularly the alcohols) in Baijiu and suggest that electrochemical oxidization treatment is potentially available for developing the technology for artificial aging of Baijiu.

The constituent analysis of the naturally aged liquors (without electrochemical treatment) was primarily performed by gas chromatography. These compounds were selected and detected for these reasons: (1) compounds that have a comparatively higher content, (2) the main compounds that contributed to the aroma and flavor of the Baijiu sample, and (3) the compounds related to the safety indicators according to national standards of Baijiu. As shown in Figure 2a, changes in the contents of the main volatile compound in the aged liquors (from six aging times, 1, 2, 3, 4, 5, and 10 years) can be divided into three groups based on the cluster analysis of the heat map, which visually reflects the content changes of the 24 quantified compounds. The volatile compounds in the three clusters showed similar trends to those of isobutyric acid (cluster 1), isoamyl alcohol (cluster 2), and ethyl butyrate (cluster 3), respectively, as shown in Figure 2b. The results illustrate the constituent changes in Baijiu during the naturally aging process. Some researchers reported the changes in the

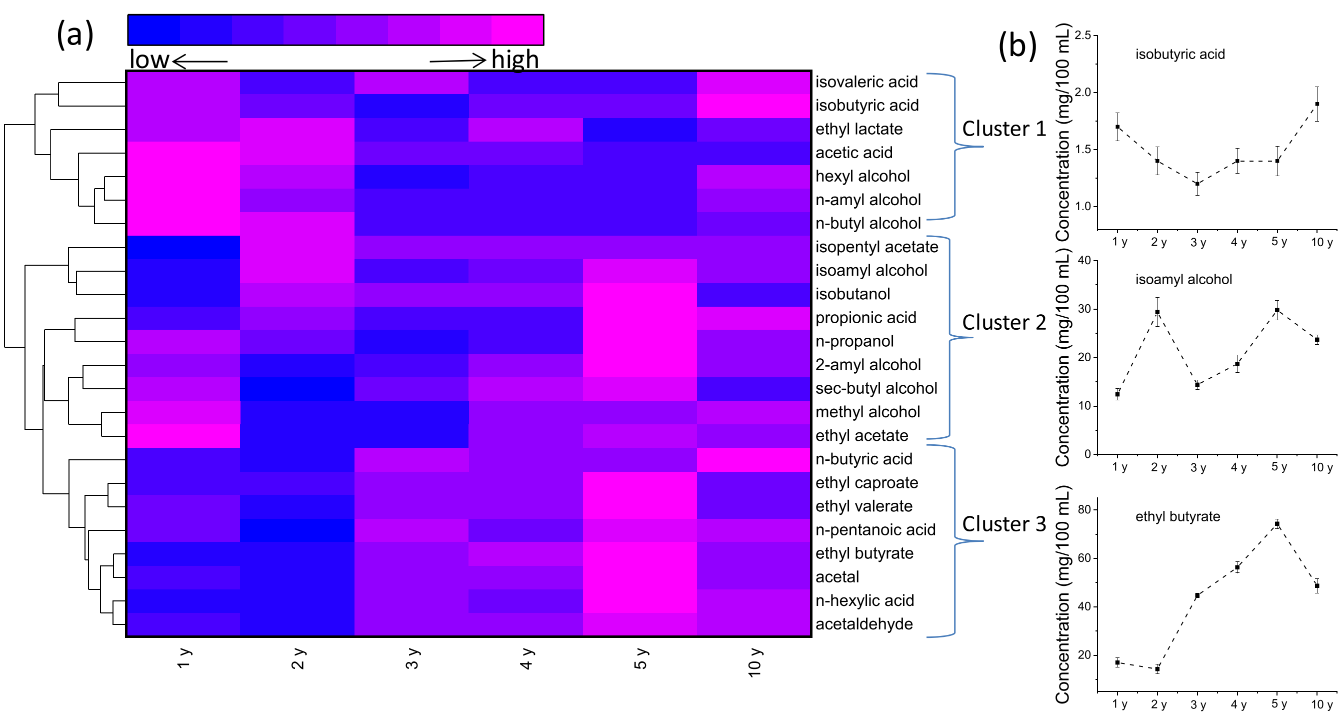


Figure 2. (a) Heat map of 24 volatile compound contents in aged Baijiu (from six aging times, 1, 2, 3, 4, 5, and 10 years). The contents were determined based on three independent experiments. Red and blue patches indicate high and low contents of the volatile compounds. (b) Cluster analysis of the heat map: isobutyric acid, isoamyl alcohol, and ethyl butyrate represent three different types of trends.

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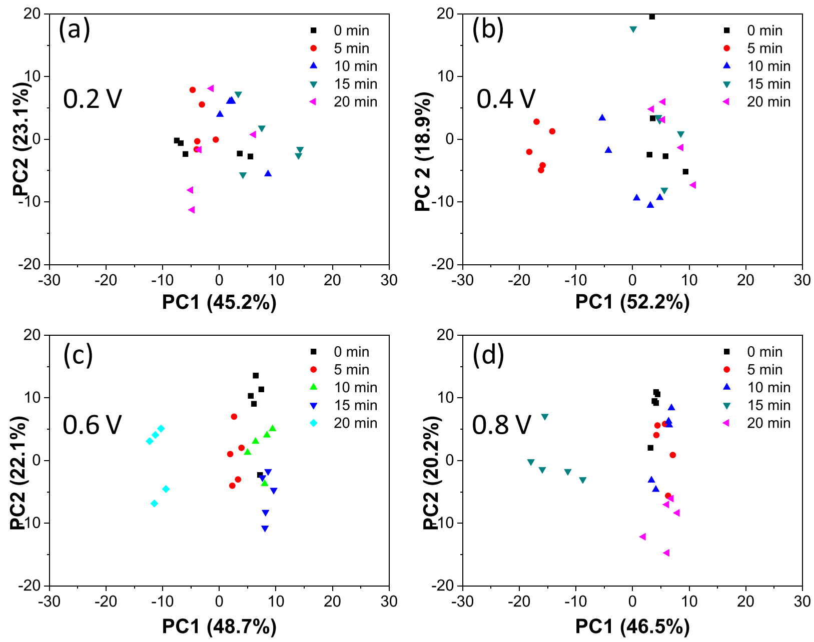

Figure 3. PCA diagrams from samples processed at different time points: 0, 5, 10, 15, and 20 min, with different oxidation potentials: 0.2 (a), 0.4 (b), 0.6 (c), and 0.8 V (d).

constituent profiles of Baijiu which are consistent with the above results. Niu's group analyzed Wuliangye Baijiu that had been aged for 1 year, 15 years, and 30 years by liquid−liquid extraction combined with gas chromatography−mass spectrometry.[30] They reported that there was positive correlation between the aging aroma and the content of ethyl hexanoate (r = 0.998). Fan's group analyzed the constituent difference between freshly produced liquor and aged liquor (Yanghe Daqu Baijiu, aging more than 5 years) and found that the flavor dilution values of most volatile compounds became larger in the aged liquor than in the freshly produced liquor.[31] Zhu et al. characterized Baijiu components during different aging times using gas chromatography, and the principal component analysis (PCA) results indicated that the young liquor and aged liquors were well separated from each other, which is consistent with the evolution of liquor components during the aging process.[32]

On the other hand, Ma et al. reported a multistage-spraying rotating packed bed for liquor aging and the treated liquor had qualities equivalent to the naturally aged liquors (aged more than two years)[10] and proposed a mechanism involving the weak interaction among liquor compounds. Studies performed using electrochemical impedance spectroscopy found that quantity and particle size of colloid increase with the increase in the aging process.[33] The redox properties change significantly, which are closely related to colloid structure, colloid size, and cluster compound environment.[33] Li et al. reported that Fe^{3+} cations can be used to oxidize the colloidal substances in Baijiu and reduce the entropy of the Baijiu colloidal system.[34] In this case of electrochemical oxidization treatment, the Baijiu colloidal system is directly treated with high oxidization potential. With the aid of high oxidization potential, the electron transfer and polarity change occurs and reduces the entropy value of the Baijiu colloidal system,[34] maintaining the stability of the Baijiu colloidal system. Herein, it can be suggested that the overall properties of Baijiu during maturation are not only affected by the componential changes but also affected by the structural changes which could be induced by treating with high oxidization potential.

During the electrochemical oxidation of the working electrode (gold electrode with 1 mm radius), there will be an equal amount of electrolysis taking place at the counter electrode (platinum electrode) that also contributes to the change in composition, and there are hundreds of detectable substances in Baijiu. Thus, the content change of several alcohols is not enough to reflect the change of Baijiu quality. Therefore, we explored whether the overall properties of Baijiu would be changed after electrochemical treatment, which is as follows: a common three-electrode electrochemical system was used to mature liquor samples at an appropriate oxidation potential (samples were from the common commercial liquor), and then, an electronic tongue was used to compare the differences of the samples before and after maturation.[35,36] Liquor samples were first processed with an oxidation potential of 0.2 V. PCA[37] diagrams from samples processed at different time points were shown in Figure 3a: data points in each group were distributed separately. However, for samples processed at different time points, the data points were not completely separated. For example, there was no significant difference between the 20 min treatment group and the 0 min treatment group (untreated group). Further, liquor samples were processed with an oxidation potential of 0.4 V. PCA diagrams from samples processed at different time points were shown in Figure 3b. Compared with the results processed with the 0.2 V oxidation potential, the data points were more concentrated, and for samples processed at different time points, the boundaries between data points were clearer. Similarly, when the samples were treated by the increased oxidation potential, as shown in Figure 3c,d, with the increase of oxidation potential, the data points became more concentrated and the boundaries of the samples processed at different times became clearer. For example, when processing the samples with an oxidation potential of 0.8 V, compared with the data points of the 0 min treatment group, the 20 min treatment group had clear boundaries. In addition, The PC1 and PC2 in Figure 3

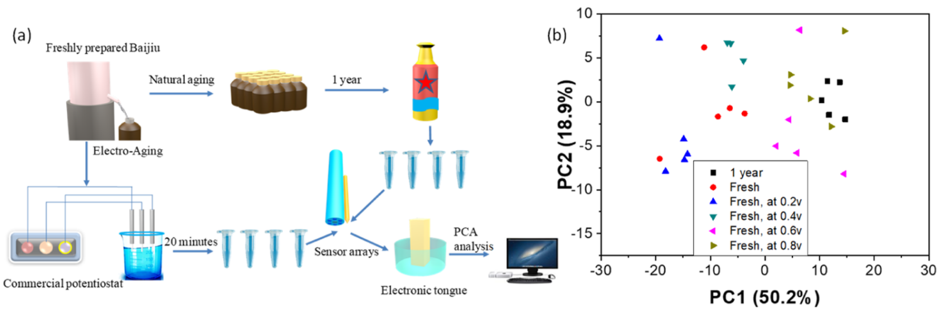

Figure 4. (a) Schematic representation of the conventional three-electrode electrochemical system used to mature the liquor samples (Baijiu). The electronic tongue-based PCA analysis was used to verify the reliability of the proposed technique. (b) PCA diagrams from 1-year aging liquor (in black) and freshly produced liquor (in red). PCA diagrams from freshly produced liquor processed at 20 min, with different oxidation potentials: 0.2, 0.4, 0.6, and 0.8 V.

capture the high percentage of the total variance (45.2, 23.1; 52.2, 18.9; 48.7, 22.1; and 46.5, 20.2% respectively). Thus, two conclusions could be drawn from the above results. First, the higher the oxidation potential used for processing the samples, the greater the difference between the samples in the treatment group and in the control samples. Second, at the same potential (such as 0.6 V), the longer the oxidative treatment time, the greater the difference between the samples in the treatment group and in the control group.

Based on the above results, a simple and practical electrochemical technique was proposed to accelerate the maturation of Baijiu. As shown in Figure 4a (scheme): freshly produced samples were selected for the accelerated maturation of Baijiu and the 1-year-old liquor was used as the control. The conventional three-electrode electrochemical system was used to mature the samples at appropriate oxidation potentials. The electronic tongue was used to compare the matured samples with those of 1-year-old to verify the reliability of the assisted maturation technique. As shown in Figure 4b, the data points of the freshly produced liquor samples and those of the aged ones were clearly separated. After treated by low oxidation potential (0.2, 0.4 V), the data points of the freshly produced liquor samples and those of the aged ones were still clearly separated. However, after a higher oxidation potential, there was a tendency for the distribution of data points of freshly produced liquor samples to coincide with those of old ones. As seen, after treated by oxidation potential of 0.8 V, there was no significant difference between the treated new and the aged samples. Clearly, an alternative approach for artificial maturation of Baijiu has been developed in this study.

3. CONCLUSIONS

Using electronic tongue classification, it is proved that electrochemical oxidative treatment can significantly change the overall properties of liquor. There is no significant difference between the freshly produced liquor and the 1-year-old liquor after treated by 0.8 V oxidation potential for 20 min. This study displayed that the oxidation degree of liquor (Baijiu) could be improved at a higher oxidation potential by using the conventional three-electrode system, thereby achieving the purpose of maturation. In view of the scale of production of aged Baijiu, the mechanisms for the chemical changes during aging is of a potential significant impact. The gas chromatograph results confirm the componential changes in the process of oxidative treatment. High oxidative potential can be used to catalyze the oxidation of alcohols, and the reaction rate is faster than that in the process of natural aging. However, further research studies are needed to explore how the colloidal structural change during maturation for further understanding the Baijiu chemistry.

4. EXPERIMENTAL SECTION

4.1. Materials. The commercial liquor (3 years of aging time), freshly produced liquor, and 1, 2, 3, 4, 5 and 10-year-old liquor were collected from the manufacturer Xiangjiao Group Ltd., Shaoyang, China. All liquor samples (Baijiu) used in this study were directly collected from storage containers without any additive. KCl and ethanol were purchased from Aladdin (Shanghai, China), used without further purification. KCl solutions were freshly prepared by ultrapure water (with a resistivity of 18.2 $M\Omega\cdot cm^{-1}$).

4.2. Electrochemistry. The working electrodes were polished using the alumina slurries (in different sizes: 1, 0.3, and 0.05 mm) to achieve mirror-like surfaces, followed by ultrasonic cleaning in ethanol and water. Electrochemistry was performed with a commercial electrochemical workstation (CHI660C) at room temperature ~298 K. All the electrodes were purchased from CH Instruments, Shanghai, China. Chronoamperometry was used for the electrochemical oxidation of Baijiu. In the three-electrode electrochemical system, the polycrystalline gold electrode with a radius of 1 mm was used as the working electrode, a platinum wire was used as the counter electrode, and an Ag/AgCl electrode was used as the reference electrode. An electrolytic cell with a volume of 2 mL was used. The pure liquor (1 mL in volume) was used as the electrolyte of the three-electrode electrochemical system.

4.3. PCA Performed with the Electronic Tongue. PCA was performed with an electronic tongue. The sensing element of the electronic tongue is a working electrode array (six inert electrodes: platinum, gold, tungsten, titanium, nickel, and silver electrodes). The standard three-electrode systems of the electronic tongue is composed of the working electrode array, an Ag/AgCl electrode reference electrode, and a platinum counter electrode. More details about the parameters of electronic tongue are shown in Supporting Information (Figure S1). PCA was performed with Origin 2019 (OriginLab Co., Northampton, USA).

4.4. Constituent Analysis of Liquor Samples Performed by Gas Chromatography. The constituent analysis of liquor samples from different aging times (1, 2, 3, 4, 5, and 10 years) was performed by Agilent 7890B gas chromatography (Agilent Technologies Co. Ltd.). The pressure of nitrogen gas was maintained between 0.35 and 0.50 MPa. The

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4.9 mL Baijiu sample was added with 0.1 mL internal standard with an Agilent CP-Wax 57 CB capillary column (0.25 mm × 50 m × 0.2 μm) and a flow rate of 1.0 mL/min. Temperature programming: initial temperature 40 °C for 5 min, raised to 50 °C by 3 °C/min and maintained for 6.5 min; then, it was raised to 90 °C by 6 °C/min and maintained for 5 min; again, it was raised to 130 °C by 10 °C/min and maintained for 2 min; once again, it was raised to 190 °C by 5 °C/min and maintained for 1.4 min; finally, the temperature was increased to 195 °C by 10 °C/min and maintained for 20 min. The chemical standards for the 24 compounds were purchased from Merck (Germany), and the qualitative analysis was performed by comparing the retention times between the targeted analytes and the reference standards. 2-Ethylbutyric acid and *n*-pentyl acetate (chemically similar to the analytes of interest) were used as the internal standards, and the concentrations were 18.122 and 17.316 mg/100 mL, respectively.

The analytical precision was determined in triplicate for both intra- and interday precision and expressed as the relative standard deviation (RSD),[38] as shown in Table S1 in Supporting Information. As seen, the RSD values for quantification of the 24 compounds in this study are at a comparatively low level.

4.5. Statistical Analysis of Experimental Data. The reported result is the mean value of triplicate measurements, and the data are expressed as the means of triplicate analysis (±S.E.M). $*P < 0.05$ and $**P < 0.01$ compared with the control, as estimated by one simple *t* test. Statistical analysis was performed with Origin 2019 (OriginLab Co., Northampton, USA).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c02090.

Scheme of the electronic tongue and analytical precision for both intra- and interday precision (PDF)

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Notes

The authors declare no competing financial interest.

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