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Oxygen Transfer Rate of Shaoxing Rice Wine Jars

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Abstract Traditional Shaoxing rice wine was stored in the pottery jar for aging because the jar are porous and allow oxygen in the air to permeate into the wine, and oxygen plays a key role in the wine aging as it affects the color, aroma and stability of the wine. In this paper we evaluated how much oxygen penetrated into the pottery jar during the rice wine storage. Iron (Ⅱ) solution as the reducing agent was stored in Shaoxing rice wine jars for 30 days. During this period some iron (Ⅱ) was oxidized into iron (Ⅲ) by the oxygen penetrated into the pottery jars. The mass concentrations of the iron (Ⅲ) were determined by a KSCN colorimetric method, thus the oxygen transfer rate (OTR) of the pottery jars was calculated. The result showed that the OTR value is 0.106 mg/L per day, and this value is an important reference for designing the large stainless container with micro-oxygeneration devices for Shaoxing rice wine.

Key words Shaoxing rice wine; Pottery jar; Oxygen transfer rate

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Shaoxing rice wine is a traditional Chinese alcoholic beverage that has been consumed in China for centuries [1]. The wine is made from rice and stored in the pottery jar for a long time for aging or maturing [2]. The pottery jar is an ideal container for Shaoxing rice wine because it is cheap, easy to obtain, permeable to oxygen, and befitting to form the special flavor of the rice wine [3], but the its disadvantages are also obvious: (1) result in a high labor cost and require a large wine library because it needs about 44 pottery jars to store per ton wine; (2) wine loss from 0.5% to 1.0% per year during storage; (3) it is difficult to blend and fill. Therefore, it is important to develop the large stainless steel tanks with the micro-oxygenation device to store Shaoxing rice wine, but as a prerequisite, the designer should know how much oxygen will permeat into the pottery jars during the rice wine storage.

For above purposes, we try to evaluate the oxygen transfer rate (OTR) of the pottery jars. Fe^{2+} solution as a reductant was stored in the hermetically sealed pottery jars. During 30 days storage, some Fe^{2+} ions were oxidized into the Fe^{3+} by the oxygen permeated into the jars. The OTR value was calculated by the mass concentration of Fe^{3+} which can be measured by a KSCN colorimetric method.

1 Materials and Methods

1.1 Apparatus

UV6001PCS spectrophotometer, 100 mL beaker, 10 mL colorimetric tube, 1 mL cuvette,

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electric furnace, 25 mL burette, glass pipette, and three selected 24 L Shaoxing pottery wine jars made in Zhuji city.

1.2 Reagents

HCl (10 mol/L), $FeCl_2$, H_2O_2 ($\varphi=30\%$), KSCN, iron powder reduced, and deionized water.

Iron (Ⅲ) standard stock solution (1.0 g/L): weighed 0.100 0 g iron powder reduced and put into 100 mL beaker, added 10 mL of HCl (10 mol/L) and 1 mL H_2O_2 ($\varphi=30\%$). After the iron powder was entirely dissolved, boiled the solution for 5 min to remove excess hydrogen peroxide. When the solution cooled to room temperature, placed it into 100 mL volumetric flask, diluted with deionized water to 100 mL, and mixed by inversing the flask. This standard solution contains 1.0 g iron per liter.

Iron (Ⅲ) standard work solution (10 mg/L): pipetted 1 mL iron standard stock solution into 100 mL volumetric flask, diluted with deionized water to 100 mL, and mixed, then diluted this solution with different mass concentration for making the calibration curve.

Iron (Ⅱ) work solution: poured boiling water into 3 new pottery jars which are randomly selected with a volume of 24 L, sealed with plastic sheeting, after cooled to room temperature, added 24 g $FeCl_2$ and 20 mL HCl (10 mol/L) in each jar, and sealed again. The mass concentration of the iron (Ⅱ) work solution is about 1 g/L. Placed this solution for 5 days to measure the iron (Ⅲ) mass concentration as the initial one.

KSCN Solution: dissolve 30 g KSCN (potassium thiocyanate) in deionized water and make up the solution to 100 mL with deionized water.

Calibration curve: added 1 drop (about 0.05 mL) of KSCN solution (300 g/L) in each iron standard solution, and then mixed, placed under room temperature (10－35 ℃) for 5 minutes, poured into 1 cm cuvette for detection. The mass concentration of iron (Ⅲ) standard solution are: 2 mg/L, 4 mg/L, 6 mg/L, 8 mg/L, 10 mg/L. Absorbance was measured at 500 nm with deionized water as a reference (10 mL containing a drop of KSCN solution). The calibration curve was shown in Fig. 1, and the regression equation is: $A=0.058\,5c+0.007\,9$ ($R^2=0.999$).

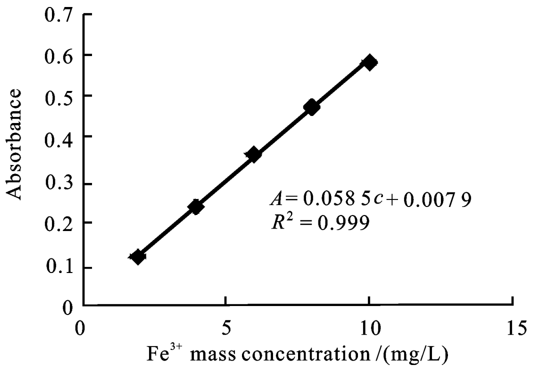

Fig. 1 Calibration curve

1.3 Preparation sample and measurements

The three selected jars labeled A, B and C were filled with boiled water, after cooled to room temperature (25 ℃) added with 3.5 g $FeCl_2$ and 20 mL HCl (10 mol/L, role as a stabilizer) per liter. Then sealed with plastic films, and stored under 25 ℃ for measurements. After the $FeCl_2$ solutions (about 1 g/L) had been made in pottery jars for 5 days, pipetted 2.0 mL sample solution from upper, middle and lower parts of the pottery jar respectively, diluted to 10 mL in the colorimetric tube (dilution factor is 5), added 1 drop (about 0.05 mL) solution of KSCN (300 g/L), and mixed, placed under room temperature (10－35 ℃) for 5 minutes, then poured into 1 cm cuvette, measured the absorbance at a wavelength of 500 nm with deionized water (10 mL containing a drop of the KSCN solution) as a reference. Calculated the iron (Ⅲ) mass concentration as the initial one, and then used the same method to measure the iron (Ⅲ) mass concentration once every five days in a month (30 days).

2 Results and Analysis

Pottery jars are made of clay which are porous and allow oxygen slowly to permeat into the chamber of the jar, resulting that the iron (Ⅱ) is oxidized into the iron (Ⅲ). Therefore, by measuring the iron (Ⅲ) mass concentration we are able to calculate how much oxygen has been penetrated into the pottery jar during a given period.

Iron (Ⅲ) mass concentration were calculated with the regression equation $A = 0.0585c + 0.0079$ ($R^2 = 0.999$). The data was listed in Table 1 and 2.

The equivalent mass concentration of oxygen permeated into the pottery jar chambers was calculated with the following formula:

$$C_{O_2} = \frac{C_{Fe} \times 15.999}{55.84 \times 2}$$

In which:

C_{O_2}: Oxygen permeated into pottery jar, mg/L.

C_{Fe}: Fe(Ⅲ) mass concentration, mg/L.

15.999: mass of molecule of oxygen.

55.84: mass of molecule of iron.

2: each oxygen atom needs to gain 2 electrons.

Variations of the iron (Ⅲ) mass concentration and the equivalent mass concentrations of oxygen in a month are listed in table 3, and the trend is illustrated in Fig. 2.

Table 1 Initial Fe^{3+} and equivalent oxygen mass concentration

Sample	A			B			C			$\bar{x}$	*SD*	*RSD*/%
	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower			
Absorbance	0.160	0.142	0.148	0.148	0.158	0.143	0.156	0.171	0.142	0.152	0.010	6.537
Fe^{3+}/(mg/L)	13.000	11.462	11.974	11.974	12.829	11.547	12.658	13.940	11.462	12.316	0.849	6.895
O_2/(mg/L)	1.863	1.642	1.716	1.716	1.838	1.655	1.814	1.998	1.642	1.765	0.115	6.904

Note: A, B and C are three repetitions, sample dilution factor is 5, the same as table 2.

Table 2 Fe^{3+} and equivalent oxygen mass concentration after 30 days

Sample	A			B			C			$\bar{x}$	*SD*	*RSD*/%
	Upper	Middle	Lower	Upper	Middle	Lower	Upper	Middle	Lower			
Absorbance	0.435	0.417	0.411	0.398	0.381	0.395	0.407	0.428	0.434	0.412	0.019	4.512
Fe^{3+}/(mg/L)	36.504	34.966	34.453	33.342	31.889	33.085	34.111	35.906	36.419	34.519	1.498	4.603
O_2/(mg/L)	5.231	5.011	4.937	4.778	4.57	4.741	4.888	5.145	5.219	4.947	0.215	4.602

Table 3 Fe^{3+} and equivalent oxygen mass concentration measured once every 5 days

Item	0 d	5 d	10 d	15 d	20 d	25 d	30 d
Fe^{3+}/(mg/L)	12.316	12.316	19.068	20.265	23.598	28.214	34.519
O_2/(mg/L)	1.765	2.304	2.732	2.904	3.382	4.043	4.947

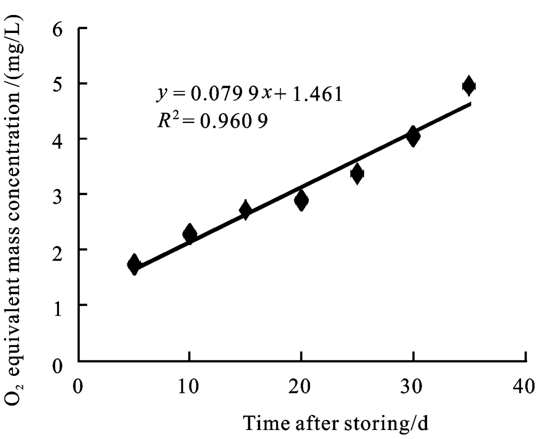

Fig. 2 Relationship between equivalent oxygen mass concentration and times

Since initial equivalent oxygen mass concentration is 1.765 mg/L, and the cumulative amount of oxygen permeated into pottery jar in 30 days is: (4.947 − 1.765) mg/L = 3.182 mg/L, the oxygen transfer rate of hermetically sealed pottery jars is 0.106 mg/L per day, or 38.69 mg/L per year.

3 Discussion

Shaoxing rice wine is a unique non-distilled alcoholic drink in the world. It is characterized with the saccharificated rice with fungoids and the wine is stored in the pottery jar for aging.

Nowdays many new wine making techniques and facilities have been widely used in Shaoxing rice wine breweries, such as computer monitoring and mechanical transporting, but the rice wine is still stored in the ancient jars which critically suppress the automatization of Shaoxing rice wine industries. Ever Shaoxing winemakers believe that the rice wine must be stored in pottery jars to form its unique odors and tastes, but no one knows the detail mechanisms. Coincident with the continually increasing labor costs it seems inevitable to develop the large tank devices for the rice wine storage.

It is well known that the traditional grape wine is stored in oak barrels which are porous, allow traces of oxygen continually penetrating into the barrel, benefit oxidization to occur and promote the mature of the wine. Therefore, in order to decrease the cost many wine manufacturers now have used stainless steel tanks instead of the barrels to store wines [4-7]. Because the steel tanks are airtight containers, a technique named micro-oxygenation was developed in 1991 in France, which involves the controlled introduction of a low mass concentration of oxygen during wine maturation [8]. It is claimed that micro-oxygenation can reproduce the benefits of barrel-aging but in a much shorter time and at a fraction of the cost.

Several researchers have evaluated the oxygen transfer rate (OTR) of oak barrels filled with wine, this value ranging from 0.7 to 45 mg/L per year in new oak barrels [9]. Cai *et al*[10] in 2014 had taken a preliminary study of the oxygen permeability of Shaoxing pottery wine jar and they concluded that the OTR of the wine jar was 0.35 mg/L, but in their paper the initial oxygen content was measured by iodometric method, which would entirely neglect the Fe^{3+} preexisted in the $FeCl_2$ solution. For this reason we carried out this study, and calculated that the OTR of the pottery jars was 38.69 mg/L per year. This value is very similar to that of the oak barrels for the grape wine, and can be taken as an important reference for designing the container with micro-oxygeneration devices for Shaoxing rice wine.

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绍兴黄酒陶坛氧传递速率研究

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摘　要　传统绍兴黄酒贮存于陶坛，因陶坛透气，进入陶坛的氧气可促进黄酒成熟，并影响黄酒的颜色、风味和稳定性。为研究黄酒贮存过程中陶坛的氧传递速率，以 Fe^{2+} 溶液为还原剂，绍兴黄酒密封于陶坛贮存 30 d后，进入陶坛的 O_2 会将 Fe^{2+} 氧化为 Fe^{3+}，采用硫氰酸钾比色法测定 Fe^{3+} 质量浓度，可估算出贮存期进入陶坛的氧气量及氧传递速率。结果表明，传统陶坛的日均氧传递速率(OTR)为0.106 mg/L，为设计带有微氧化装置的黄酒专用大型不锈钢贮酒罐提供理论依据。

关键词　绍兴黄酒；陶坛；氧传递速率

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