Establishment of Rice Freshness Evaluation System and Quick Inspection Method

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Abstract. This paper combines chemometrics methods to study the correlation between physical and chemical quality characteristics, thermodynamic properties, texture characteristics and flavour substances during rice aging, and screens for key flavour substances that characterize changes in rice aging and establish new aging degree evaluation system, develop accurate and rapid inspection methods and detection boxes for grain maturity, and promote their application. The thesis has important practical and strategic significance to realize the safe storage of rice, save energy and reduce damage, and improve the quality of stored grain.

1. Introduction
Rice is one of the most important grains in China. Due to its own characteristics and environmental impact, its quality will inevitably change with the extension of storage time, or even deteriorate, causing immeasurable economic losses to the country and enterprises. It brings severe challenges to the storage of rice. The main causes of the deterioration of rice aging are microbial invasion and lipid oxidation. Rice is a porous substance with a large specific surface area, which is easily contaminated with bacteria and mould spores. In addition, rice itself is rich in nutrients, so it is difficult to prevent the growth and reproduction of microorganisms. Microorganisms cause the deterioration of rice. Its general function is to decompose the components of rice and decompose the materials of high molecular structure into small molecules; at the same time, due to the reproduction of microorganisms in rice, a variety of intermediate products are produced, resulting in a comprehensive decline in food quality and even toxins. And stench. Although some rice has no obvious deterioration, the nutritional value has been lost, and the substrate is often poisonous. The most typical example is that after rice is infested with Penicillium islands or Aspergillus flavus, it will produce aflatoxin which strongly causes liver cancer. This is the strongest carcinogen found so far. It is 75 times stronger than dimethylnitrosamine, a cancer killer. It can still survive at 280 °C. The oxidative deterioration of lipids is also an important factor that causes deterioration and deterioration of rice quality. Although the fat content in rice is only 2%, it is chemically active and easily affected by oxygen in the air. It is hydrolysed, rancid and spoiled by auto-oxidation. After the fat is hydrolysed, low-grade fatty acids with odorous properties are produced, which increases the acidity of the rice, and also generates aldehydes and ketones, which are harmful to the human body. Rice itself is a living body, there are many active enzymes, the metabolic activities of these enzymes will also cause the rice to deteriorate. In addition, rice is also affected by pests and rodents. Not only
does it cause a loss in the quantity of stored rice, but it also contaminates the rice, resulting in a decline in quality.

Based on the previous research, it can be seen that the change of rice quality is a development and dynamic process, and the quality indicators are interrelated and mutually restrictive. At present, research on changes in rice flavour substances and quality changes during storage and methods and special equipment for detecting rice freshness are rare. Therefore, research and development of rapid detection methods and detection boxes to accurately identify the freshness of rice, timely monitoring of the aging of grain, and to eliminate the phenomenon of using the reserve characteristics of rice to "reserve the grain with the top of the old" to store grain to supplement the storage phenomenon, which is an effective The outstanding problems of quality and safety have important practical and strategic significance to realize the safe storage of rice, save energy and reduce damage, and improve the quality of stored grain.

2. Rapid detection technology of rice quality

2.1. Physical and chemical methods

During the storage of rice, the three major nutrients of starch, lipid, and protein will change. In addition, the activities of catalase and α-amylase in rice grains will also decrease with time. Changes in the components and enzyme activities in rice are used to quickly detect the quality of rice. Literature [1] developed a mixed reagent based on methyl red, bromothymol blue and sodium chloride as the main components based on the corresponding relationship between free fatty acids and pH value during the aging process of rice. The aging degree is tested quickly. After soaking with this reagent, the fresh rice extract is green and the aged rice is yellow. The greater the aging degree, the closer to orange. Although the physical and chemical methods can roughly reflect the changes in rice quality, they cannot accurately distinguish between the quality of rice and the quality of rice. It is necessary to combine other measurement methods to accurately evaluate the quality of rice.

2.2. Near infrared spectroscopy detection technology

Near-infrared light is an electromagnetic wave with a wavelength of 780 to 2500 nm. Proteins, fats, water, amylase and other substances have their corresponding characteristic absorption wavelengths in this wavelength range. According to Beer's law, the logarithm of the amount of absorbed light and the sample There is a linear relationship between the percentage content of the substance that absorbs this wavelength of light, and the content and change of nutrients in the sample can be determined quickly and non-destructively. Although the near-infrared spectroscopy technology can quickly measure the quality of rice, but due to China's vast territory, rich rice varieties, different soil water quality and other factors, it is still necessary to establish a rice quality database by region and variety to establish a general data analysis Model to more quickly and accurately determine rice quality. As shown in Figure 1, it is the principle of near-infrared spectrum rice quality detection technology.

Figure 1. The principle of near-infrared spectroscopy rice quality detection technology
2.3. Rapid detection technology of electronic nose
The electronic nose is a novel biomimetic detection method that simulates biological olfaction. It is usually composed of three parts: a gas sensor array, a signal processing system and a pattern recognition system. After its surface acts, the sensor converts the information into a measurable and time-related measurable physical signal group, so that the entire electronic nose can identify different components in the gas and give an overall evaluation. Compared with traditional expert panel sensory evaluation, gas chromatography, and chromatography-mass spectrometry techniques, the electronic nose detection technology has the advantages of high accuracy, good repeatability, and no need for pre-treatment. Quick detection.

3. PH test experiment to evaluate rice freshness

3.1. Materials and methods

3.1.1 Raw materials. The samples required for this experiment were provided by the Storage Teaching and Research Section of Zhengzhou Grain College. They were from Jiangxi, Fujian, Guangxi, and Liaoning. The hulling machine is used for shelling, and the milled brown rice is sealed in a small plastic bag, placed in a refrigerator for refrigeration, and set aside.

3.1.2 Main instruments and reagents. PHS -25 digital display acidity meter; electro-optical analysis balance (divided value 0.1 mg); rack-mounted pharmaceutical balance (divided value 0.2 g); hulling machine. Test tubes, filter paper, volumetric flasks, pipettes, etc. Methyl red, analytically pure; bromothymol, analytically pure; red tetrazolium, chemically pure; guaiacol, tertiary; potassium iodide, analytically pure; absolute ethanol, analytically pure; 30% hydrogen peroxide, analytically pure.

3.1.3 How to use reagents. 0.2% TTC solution: Weigh 0.2 g of TTC drug in a 100 mL volumetric flask, first add 60 mL of absolute ethanol to dissolve it, then add distilled water to dilute the volume to 100mL. 1% guaiacol solution: Pipette 1 mL of guaiacol stock solution into a 100 mL volumetric flask, first add 60 mL of absolute ethanol to dissolve it, then add distilled water to dilute to 100mL. 0.25% KI solution: Weigh 0.25 g KI drug in a 100 mL volumetric flask, add distilled water to dissolve and dilute to 100mL. 3% hydrogen peroxide solution: Pipette 1 mL of 30% hydrogen peroxide stock solution into a 100 mL volumetric flask, dilute it with distilled water and dilute to 100mL. Preparation of acidic indicator stock solution: Weigh 0.05 g of methyl red and 0.15 g of bromothymol blue and place in a 100 mL volumetric flask. Dissolve it with 75 mL of absolute ethanol first, then add distilled water to bring the volume to 100mL.

3.2. Method
A representative set of rice samples (No. 15, No. 16, No. 19, No. 21, No. 22, No. 24) were selected for the discussion of test methods. By observing the comprehensive control and comparative analysis of the respective test phenomena and results, and choosing an ideal test method from which to conduct in-depth research and analysis of the rice's freshness.

3.2.1 TTC colour rendering method. There are dehydrogenases in the rice germ cells with vitality. The hydrogen released by the dehydrogenase during the rice grain respiration can undergo a redox reaction with the colourless TTC to produce a stable red toluidine Hydrazonyl substance. Take 40 complete brown rice samples in test tubes, add 1.6 mL of 0.2% TTC solution and soak for half an hour, pour off the solution, spread the rice grains on the filter paper, and observe whether there is red reaction in the rice grain embryo. Fresh brown rice has a strong vitality, and the embryo is all coloured: the aged brown rice has a weak vitality, and the embryo cannot be completely coloured, and the red reaction can only occur locally. By observing the proportion of red grains in the embryo part, the freshness of the rice can be inferred [2].
3.2.2 The guaiacol colour method. Peroxidase is widely present in plant tissues. Peroxidase activity is strong in fresh rice and rice, but peroxidase activity in aged grain is weakened. Various polyphenols or aromatic amines can be coloured by hydrogen peroxide under the action of peroxidase. Such as guaiacol, pyrogallic acid, p-diaminobenzene hydrochloride, etc., to judge the ageing of food according to the degree of colour development. Take the japonica rice stored under normal conditions, crush it with a grinder after shelling, take brown rice powder 2.0g, add 20mL of distilled water, shake it about 10 times, let it stand for 10min, collect the filtrate 10mL with a colorimetric tube, add 2% guaiac Phenol 2mL, add 5 drops of 2% hydrogen peroxide, cover and observe the degree of colour development in a static state. The colour changes from colourless to red. The darker the colour, the stronger the enzyme activity, indicating the greater the freshness of the food. Determination: The red substance has a maximum absorption wave at a wavelength of 470 nm, so the peroxidase activity can be determined by measuring the absorbance at 470 nm. Taking the diluted filtrate as the reference solution, the absorbance value A of the solution was measured at a wavelength of 470 nm in a 1 cm cuvette, and several sets of data were used as the measured values. As shown in Figure 2, the basic principle of the guaiacol colour method was shown.

3.2.3 KI colour rendering method. The reaction of iodine precipitation using potassium iodide, and iodine appears purple when meeting starch. After adding hydrogen peroxide, the weaker the peroxidase activity, the more purple the rice grains, and the stronger the activity, the slower the coloration of the rice grains, and the lighter the colour. Draw 1.6 mL of 0.25% KI solution, add two drops of 3% hydrogen peroxide solution, shake and shake, put 40 grains of complete brown rice sample, then shake for a while, then pour off the solution, spread the rice grains on the filter paper Observe the colouring. The activity of fresh brown rice peroxidase is stronger. After adding hydrogen peroxide, potassium iodide does not decompose, so it cannot produce iodine-starch reaction, so the colour development is slow and the colour is lighter; while the aged brown rice peroxidase After the addition of hydrogen peroxide, potassium iodide is decomposed to generate iodine, and the iodine appears purple when meeting starch. By observing the colouring speed and the colour depth of the rice grains, the freshness of the rice can be inferred.
3.3. Analysis of test results
The test results show that the pH value of the brown rice water infusion of new rice and old rice is generally in the range of 6.0 ~ 7.5. Due to the different storage time and storage method, the pH value of the brown rice water infusion of new rice and old rice is not the same, there is a certain gap between the two, about 0.6 ~ 0.8. The pH value of brown rice water infusion of rice with shorter storage time is larger, generally around 7.0; while the pH value of brown rice water infusion of rice with longer storage time is lower, generally around 6.4, and the With the extension of storage time, the degree of aging of rice is increased, and the acidity is increased, which causes the pH value of the brown rice water infusion to drop significantly, generally around 6.0. Tables 1 to 3 are the results of three different experimental methods. Moreover, rice samples with good storage conditions (such as underground storage, low temperature storage, etc.) have a slow aging rate, and the pH value of the brown rice water infusion is large; however, the storage conditions are poor (such as normal temperature storage). Figure 3 shows the test results of rice grains [3].

![Test results of rice grains](image)

**Figure 3.** Test results of rice grains

**Table 1.** Absorbance value measured by TTC colour method

| year | Series 1 | Series 2 |
|------|----------|----------|
| 2016 | 0.199    | 0.221    |
| 2017 | 0.262    | 0.281    |
| 2018 | 0.340    | 0.365    |
| 2019 | 0.869    | 0.903    |

**Table 2.** Absorbance value measured by guaiacol colour method

| years | Series 1 | Series 2 | Series 3 | Series 4 | average |
|-------|----------|----------|----------|----------|---------|
| 2016  | 0.303    | 0.299    | 0.289    | 0.282    | 0.293   |
| 2017  | 1.073    | 1.085    | 1.094    | 1.104    | 1.089   |
| 2018  | 0.631    | 0.630    | 0.628    | 0.627    | 0.629   |
| 2019  | 1.776    | 1.800    | 1.824    | 1.829    | 1.807   |
Table 3. Absorbance values measured by KI colour method

| Year | Series 1 | Series 2 |
|------|----------|----------|
| 2016 | 0.420    | 0.498    |
| 2017 | 0.281    | 0.361    |
| 2018 | 0.423    | 0.503    |
| 2019 | 0.763    | 0.872    |

4. Infrared non-destructive testing method for determining rice freshness

4.1. Materials and methods

4.1.1 Raw materials. From 2017, 2018, and 2019 of a certain grain depot, 40 rice samples (200g each) of 120 rice samples were taken each year. Packaging in ziplock bags for near infrared detection.

4.1.2 Methods and instruments. Near-infrared spectrometer, spectrum acquisition wavelength range: 950 - 1650nm, resolution 5.0nm, sample cup: diameter 75mm, loading sample twice, scanning twice; UNSCRAMBLER9.7: CAMO company; SPSS18. The light source was preheated for 30 min before analysis. Make sure the sample is representative and well mixed, fill the sample cup, try to make the sample surface smooth, and use a straight edge tool (ruler) to scrape off the excess rice. The sample cup should be kept full and flat to ensure repeated measurement accuracy.

4.2. Results

It can be seen from Figure 4 that the spectrum of rice with different degrees of freshness is not much different. Rice has multiple absorption peaks in the swept wave band. The spectral change trends of all samples are approximately the same but do not overlap. The different content of groups leads to different absorption peak sizes. By analysing the main absorption peaks of this graph, selecting different spectral bands to establish mathematical models, and judging the optimal spectral range by correlation coefficients and root mean square error (RMSEP), we can see that the full spectrum and the 1100.1 ~ 1300.0 nm The correlation coefficient is good and the rms prediction error is small, but considering the impact on the results and the number of factors, the full spectrum band is selected when the next model is established [4].

Figure 4. Infrared spectrum of rice with different degrees of freshness
5. Evaluation system of rice freshness

Using the principle of stepwise regression analysis, the following formula is obtained by performing stepwise regression calculation on each rice index. In the following formula, Y is the storage time, a; X1 is the germination rate of rice, %; X2 is the fatty acid value of rice, KOH · (100g) -1; X3 is the reducing sugar content of rice, %; X4 is the non-performing Reducing sugar content, %; X5 is the viscosity of rice, s / mm2; X6 is the drop value of rice, s. So, there is a significant factor analysis of the quality index of rice (mixed sample of Indica rice and japonica rice)

\[ Y = 3.3936 - 0.1170X_1 - 0.0585X_2 + 0.0005X_2^2 + 0.00016X_2^3 + 0.2355X_1X_3 \]  

(1)

An F test was performed on the significance of the equation. Set \( \alpha = 0.001 \), \( N_1 = 5 \), \( N_2 = 53 \), check F distribution table, get \( F_\alpha = 5.13 \). Because \( F = 54.4075 \) and \( F_\alpha = 5.13 \), the equation returns significantly under the condition of significance level \( \alpha = 0.001 \), and the equation is meaningful. Figure 5 shows the evaluation system of rice freshness.

6. Analysis and discussion

6.1. Determination by colour rendering method

The acid indicator method is based on a series of physiological and chemical changes in the internal chemical organization of rice grains, especially lipids, proteins, starches and melds during the storage process, resulting in changes in the pH of brown rice water infusion. The solution prepared by the agent’s methyl red and bromothymol blue is used as the original solution for detecting the rice freshness, and the research on the judgment and evaluation of the rice freshness is carried out. By observing the colour change of the acidic colour developing solution and the colouring of the rice grains, the degree of rice maturity was identified, and their storage time was estimated. The test results show that as the acidity of the brown rice water infusion increases, the colour of the acidic colour developing solution changes in the order of a - b - c - d - e - f - g - h. For rice with a shorter storage time, the colour of the brown rice
6.2. Determination by infrared method
For rice samples of different particle sizes and types, a neural network based on near infrared spectroscopy was used to predict the content of rice amylose, and a correlation study was conducted with the iodine blue value determined by the conventional iodine colorimetric method. The correlation coefficient between the predicted value obtained by the established amylose detection model in rice and the measured value by iodine colorimetry reached 0.95, and the time required was greatly reduced. In addition to proteins, fats, moisture, amylose and other substances in rice can be accurately quantified by near infrared spectroscopy, the physical, chemical properties such as brightness, accuracy, transparency, flavour, etc. can be evaluated by establishing different prediction models. Near-infrared spectroscopy was used to detect inorganic arsenic content in rice, and multiple linear regression analysis, principal component regression analysis and partial least squares regression analysis were used to establish mathematical models for testing. The results showed that the modified partial least squares method was used to establish regression the prediction results obtained by the model are more accurate.

6.3. Research on paddy preservation methods
The issue of paddy preservation involves many disciplines such as chemistry, physics and microbiology. To solve the problems of mildew, yellowing and sourness and odor of rice worms, it is necessary to comprehensively use the technology of multiple disciplines to kill molds such as Alternaria alternate, Aspergillus griseus, Penicillium and Green mould; Lipase activation, preventing non-enzymatic browning, etc. The other cause of the deterioration of the aged rice is the metabolic activity of the rice's own enzymes, and the nutrients, especially fat, are oxidized. Using biological or physical methods to inhibit the enzymes in the rice, inactivate its activity, put the rice in hibernation, and reduce the life activity of the rice to the lowest point. Using its film-forming, antibacterial and functional properties to produce pure natural rice biological preservatives sprayed on the surface of the rice to form a protective film to isolate the air from the rice, thereby inhibiting the growth of bacteria on the surface of the rice and the reproduction of insect eggs to achieve preservation effect [6].

7. Conclusion
The thesis clarifies the changes of physical and chemical quality, thermodynamic characteristics, texture characteristics and flavour substances of rice under different storage times. It uses stoichiometry to analyse the correlation between rice flavour substances and the storage period, that is, the maturity of the rice, and screens out the characteristics. The key flavour substances in the changes of rice freshness, establish a food freshness evaluation system, develop accurate fast food freshness detection methods and rapid detection boxes, quickly and accurately identify food freshness, realize safe storage of rice, save energy and reduce damage, improve the quality of grain storage and guide the scientific use of grain.

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References
[1] N. Sreedhar Reddy, Y. Prem Santhi, K. Ramya Sree, K. Ch. S. Sai Kiran, & S. Vishnu Vardhan. Performance testing and evaluation of on-farm mobile paddy dryer. current journal of applied science & technology, 28(1) (2018) 1-9.
[2] Price, M. J., Horner, P. J., & Ades, A. E. Risk of reproductive complications following chlamydia
testing. The Lancet Infectious Diseases, 16(11) (2016) 1223-1224.

[3] Chalotra, J. & Sooch, S. S.  Design, development and testing of screw press machine for paddy straw under ground digester. International Journal of Current Microbiology and Applied fences, 8(3) (2019) 138-144.

[4] Wu, J. Cui, T. Ban, T., Guo, S., & Cui, L.  Paddyfrog: systematically detecting confused deputy vulnerability in android applications. Security and Communication Networks, 8(13) (2015) 2338-2349.

[5] Monica, N. & Choi, K. S. Temporal and spatial analysis of water quality in saemangeum watershed using multivariate statistical techniques. Paddy and Water Environment, 14(1) (2016) 3-17.

[6] Price, M. J. Horner, P. J. & Ades, A. E. Risk of reproductive complications following chlamydia testing. Lancet Infectious Diseases, 16(11) (2016) 1223-1224.