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Review of Rice Quality under Various Growth and Storage Conditions and its Evaluation using Spectroscopic Technology

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Abstract

Purpose: Grain quality is a general concept that covers many characteristics, ranging from physical to biochemical and physiochemical properties. Rice aging during storage is currently a challenge in the rice industry, and is a complicated process involving changes in all of the above properties. Spectroscopic techniques can be used to obtain information on the quality of rice samples in a non-destructive manner. **Methods:** The objective of this review was to highlight the factors that contribute to rice quality and aging, and to describe various spectroscopic modalities, particularly vibrational and hyperspectral imaging, for the assessment of rice quality. **Results:** Starch and protein are the main components of the rice endosperm, and are therefore key factors contributing to eating and cooking quality. While the overall starch, protein, and lipid content in the rice grain remains essentially unchanged during storage, structural changes do occur. These changes affect pasting and gel properties, and ultimately the flavor of cooked rice. In addition, grain quality is significantly affected by growing and environmental conditions, such as water availability, temperature, fertilizer application, and salinity stress. These properties can be evaluated using spectroscopic techniques, and rice samples can be discriminated by using multivariate statistical analysis methods. **Conclusion:** Hyperspectral imaging and vibrational spectroscopy techniques have good potential for determining rice quality properties in a non-invasive manner, i.e., not requiring the introduction of instruments into the rice grain.

Keywords: Hyperspectral imaging, Non-destructive measurement, Rice aging, Rice quality, Vibrational spectroscopy

Introduction

Rice is the seed of the monocot plants *Oryza sativa* (Asian rice) and *Oryza glaberrima* (African rice). As a cereal grain, it is the most widely consumed staple food for a large part of the world's human population, particularly in Asia. In addition, it is the second largest worldwide production and is the most important grain with regard to human nutrition and caloric intake, because it provides more than one fifth of the calories consumed by humans worldwide. Therefore, evaluation of the rice germplasm is an important step in meeting the high human demand for rice. Rice quality can be determined from the size, shape, and appearance of the grain, as well as the milling quality and cooking properties. Diversity in crop varieties is essential for agricultural development to increase food production, alleviate poverty, and promote economic growth. Rice is ideal for food aid because it is rich in complex carbohydrates, contains all eight essential amino acids, and is cholesterol- and sodium-free. It is used therapeutically for digestive disorders, is hypoallergenic, it transports/handles easily, and is acceptable to all cultures.

Genetic evidence has shown that modern rice originated from a single domestication event 8,200-13,500 years

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Table 1. Top five rice-producing countries in 2012–2013

Country	Highest production (million tons)
China	143
India	105
Indonesia	36.5
Bangladesh	33.3
Vietnam	27.5

ago in the Pearl River valley region of China (Huang et al., 2012). However, previous archaeological evidence has suggested that rice was first domesticated in the Yangtze River valley region in China (Molina et al., 2011). Rice was then spread from East Asia to Southeast and South Asia. Rice was introduced to Europe through Western Asia and to the Americas by European colonization. Rice is normally grown as an annual plant, although in tropical areas it can survive as a perennial and can produce a ratoon crop for up to 30 years.

According to data provided by the United States Department of Agriculture, in 2012-2013 the top five highest rice-producing countries in the world were China, India, Indonesia, Bangladesh, and Vietnam (Table 1).

The quality attributes of rice include its external appearance (size, shape, color, chalkiness, and lack of defect or decay) and internal quality (moisture, sugar, protein, and lipid content). Among the external quality attributes, shape, color, and chalkiness are considered the most important indicators of rice quality (Liu et al., 2008). Traditional analytical methods for assessing these quality measurements are complex, time-consuming, and unstable. However, the main challenge for the rice industry is to maintain the quality of rice. The objective of this review was to evaluate the factors that contribute to rice quality, and the potential of different kinds of spectral modalities, such as hyperspectral imaging and vibrational spectroscopy, for the evaluation of rice quality.

Factors and Conditions during Storage

At present, rice is the main food source for two-thirds of the world's population. Production was expected to keep pace with demand until about 2005, but the long-term forecasts give cause for concern (International Rice Commission, Food and Agriculture Organization). Many Asian countries are expected to move away from self-sufficiency and become net importers of rice over the next 10 to 20 years. A small amount of the rice crop is used as ingredients in processed foods and as feed, but the bulk is consumed as cooked rice. This pattern of usage results in the need to store rice over a long period. Moreover, some markets (e.g., India) prefer stored rice, while others (e.g., China and Japan) favor fresh rice. Freshness is a major consideration in the Japanese market, and specific tests for freshness have been devised for its measurement (Matsukura et al., 2000). During storage, a number of physicochemical and physiological changes occur, which are collectively termed aging, including changes in pasting properties, color, flavor, and composition, which all affect rice quality (Suzuki et al., 1999). Aging commences before harvest, and increases with time, temperature, and moisture (Okabe, 1979; Perdon et al., 1997).

Interactions among these variables are also important. Polynomial models that include these interactions (Perdon et al., 1997) suggest that rice aging is a complex process in several forms of rice (Barber, 1969; Chrastil, 1990; Daniels et al., 1998). Storage conditions are important in the aging process. Nitrogen has been found to be superior to air for preserving the palatability of cooked rice during brown rice storage at 10°C for two years; however, no significant difference in quality was found between brown rice stored in nitrogen and that stored in carbon dioxide (Juliano, 1985a). Storage in nitrogen has little effect on the texture of rice, in comparison with storage in air (Perez and Juliano, 1981). The hermetic storage of milled rice at 30°C for three months under vacuum or in nitrogen, carbon dioxide, or ambient conditions has little effect on sugar levels, fat acidity, texturometer hardness, or the adhesiveness of cooked rice at 14.7% storage moisture (Yanai et al., 1979). At 15°C, aging effects are most significant during the first three to four months of storage (Perez and Juliano, 1981). Tensile strength, crushing, breaking hardness, and resistance to grinding increase after aging (Kondo and Okamura, 1937; Kunze and Choudhury, 1972).

One of the most sensitive indices of the aging process in rice is the change in pasting properties, as measured by thermoviscometry and amylography (Perdon et al., 1997). Rice exhibits a very wide range of cooking quality and rheological properties, which are largely determined by the swelling, gelatinization, and retrogradation characteristics of its starch. The viscosity of rice paste increases dramatically after storage (Shibuya et al., 1974; Shoji and Kurasawa, 1981). Viscosity increases at high temperatures during the first three months of storage and then plateaus (Juliano, 1985b). Contradictory data have been reported on the effects of aging on amylograph peak viscosity. Villareal et al. (1978) reported the opposite effect, although Lin et al. (1979) found that the amylograph peak viscosity of slurries prepared from aged rice was lower than that obtained from fresh rice. After an initial increase in amylograph peak viscosity during the first six months of storage of rough and milled rice, a steady decrease was noted over the subsequent three years of storage.

Properties and interactions between rice components during storage

Most attempts to explain the changes in functional properties associated with aging have focused on rice components (starch, protein, and lipids) and their interactions (Chrastil, 1990). As with functionality, changes in starch, lipid, and protein components have been shown to be most apparent at an elevated storage temperature (Chrastil, 1990), whereas gross changes in starch, amylose, and protein content during storage are minimal (Villareal et al., 1976; Sowbhagya and Bhattacharya, 1978).

Starch and amylose

The cooking quality of rice is associated with the starch gelatinization temperature. Starch gelatinization is a process that involves the breaking down of starch molecules in the presence of water and heat, thereby allowing the hydrogen-bonding sides (hydroxyl hydrogen and oxygen) to engage more water. Rice genotypes with a low gelatinization temperature were probably selected for their preferred cooking quality during domestication. Amylose content is the main factor that determines taste panel scores for the cohesiveness, tenderness, color, and gloss of cooked rice and is directly related to the water absorption, volume expansion, fluffiness, and separability of cooked grains (Delwiche et al., 1996). Amylose acts as both a diluent and an inhibitor of swelling, particularly in the presence of lipids. Variations in gel consistency exist among varieties with a similarly high amylose content (more than 25%), and the gel consistency of rice with less than 24% amylose is usually soft. The amount of leached amylose, which depends on the total rice content, correlates positively with the texture of cooked rice, with total amylose content in the range 18.4-29.5% (Ong and Blanshard, 1995).

Protein

The characteristics of rice containing low protein levels have been reported previously (Juliano and Delmundo, 1965), and it was subsequently demonstrated that protein content is inversely related to adhesiveness (Juliano, 1985a). Levels of free amino acids increase during the storage of milled rice (Dhaliwal et al., 1991) but protein content does not change during storage, although its general solubility is reduced (Barber, 1972; Chrastil, 1990), with a particularly large decrease in albumin (a water-soluble protein) solubility (Barber, 1972; Villareal, 1976). This effect is greatest in medium- and long-grain rice, in which the number of disulfide bridges increases during storage. The rice-storage protein oryzenin (glutelin) is the prevailing protein in medium-grain rice (Juliano and Delmundo, 1985), and contains 0.2% sulfur (as -SH) before storage and 0.14% sulfur (as -SH) after storage. A similar trend was found for oryzenin from long-grain rice. During the storage of both the varieties, low-molecular weight peptides decrease and high-molecular weight peptides increase. However, these changes in the distribution of peptide subunits in the oryzenin fraction during storage are smaller than those in the average molecular weight of the whole oryzenin molecule, which almost doubles during storage (Chrastil, 1990).

Lipids

Rice lipids are usually stable in intact cellular spherosomes. However, if the lipid membrane is destroyed by phospholipase, lipid hydrolysis is initiated by lipases (Takano et al., 1989). Oleic and linoleic acids are the most important fatty acids in various lipid fractions. Shin et al. (1986) found that the lipid content of brown rice was stable during storage for 12 months at 5°C, but significantly decreased during storage at 35°C. The proportion of oleic acid in each lipid fraction increased slightly during the storage period at the expense of linoleic acid. However, the absolute amounts of both oleic and linoleic acids in the neutral lipid fraction decreased during the storage period, whereas they increased in the free fatty acid fraction. Nishiba et al. (2000) reported the degradation of triacyglycerides during rice storage. Furthermore, the peroxide value (Barber et al., 1972) and free fatty acid and carbonyl levels (Sowbhagya and Bhattacharya, 1976) increase during the storage of milled rice as the pH of the cooking water decreases (Shoji and Kurasawa, 1981). The peroxide value of non-starch lipids increases in conjunction with a decrease in the iodine value (Barber et al., 1972). These changes observed during storage suggest that at least two processes affect lipids in rice, one involving the hydrolysis of lipids to produce free fatty acids, and the other is lipid oxidation (including free fatty acids) that produces hydroperoxides. Temperature and light conditions during storage are particularly important for both hydrolytic and oxidative reaction rates (Sowbhagya et al., 1976).

Phenolic acids

Regarding the minor components of the rice grain, phenolic acids are of particular interest because of their involvement in the plant cell wall. Their physiological activity and potential dietary uses have received much attention (Osawa, 1999). Grains contain various phenolic acids (Garcia-Conesa et al., 1999), including hydroxycinnamic acids. Among these, ferulic acid (FA) and p-Coumaric acid (PCA) are the main phenolic acids present in the cell walls of monocots, particularly those of the Gramineae family (Hartley et al., 1990; McCalluma and Walker, 1990; Lam et al., 1992; Zupfer et al., 1998). Phenolic acids are usually concentrated in the outer aleurone layer of the seed, which is rich in arabinoxylans (Salomonsson et al., 1980). Phenolic compounds exert a significant effect on the properties of the cell wall, which is mechanically strengthened by cross-linking (Saulnier and Thibault, 1999). Tsugita et al. (1983) found that the free phenolic acid content increased during the storage of milled rice. Furthermore, bound phenolic acids were released by enzymatic reaction, and large increases in the concentrations of p-hydroxybenzoic acid, vanillic acid, syringic acid, caffeic acid, PCA, and FA were observed when rice was stored at 40°C (80% relative humidity) for 60 days compared with storage at 4°C. The authors suggested that changes in the phenolic acid concentration contribute to changes in the cooking properties of aged rice. In another study, Zupfer et al. (1998) demonstrated that changes in the FA concentration could be used to predict end-use grain quality.

Flavor

The flavor of cooked rice tends to be influenced by the aging process during storage. In some cultures, rice is consumed within a month of milling, because off-flavor can be noted after two to four weeks of storage. Carbonyl compounds, particularly hexanal, are thought to be the major contributors to the off-flavor because they increase in content during storage (Villareal et al., 1976). During storage at 40°C, linoleic acid and linolenic acid levels decrease with the emergence of a stale flavor, which indicates high levels of propanal, pentanal, and hexanal (Yasumatsu et al., 1966). Under these conditions, lipids are hydrolyzed and oxidized to form free fatty acids or peroxides that cause an increase in acidity, which significantly reduces the taste and flavor of rice. Protein oxidation (between sulfhydryl groups) also reduces levels of volatile sulfur compounds, and the amount of hexanal is linearly proportional to that of oxidized linoleic acid (Shin et al., 1986).

Enzyme activity

Activity of alpha-amylase and beta-amylase in rough rice samples significantly decreases during storage (Dhaliwal et al., 1991), and corresponds with a decrease in soluble protein. Alpha-amylase is concentrated in the bran fraction; therefore, the alpha-amylase content of milled rice is low and has a negligible effect on amylograms, except for waxy milled rice, which contains appreciable amounts of alpha-amylase in the endosperm and exhibits a low amylogram viscosity. Peroxidase and catalase activities also rapidly decrease during rice storage; as these are easily measured, they are commonly used in Japan as indices of rice quality deterioration during storage (Matsukura et al., 2000). Dhaliwal et al. (1991) reported that protease, lipase, and lipoxygenase activities increase in stored samples.

Molecular Basis of Grain Quality in Rice

Comparisons of quality traits have revealed a significant variation among rice cultivars grown even in the same environment (Adu-Kwarteng et al., 2003; Cameron and Wang et al., 2005; Kang et al., 2006; Vidal et al., 2007), which specify that the decisive factors controlling starch and protein contents. Therefore, grain quality resides in the rice genome itself, i.e., in the loci that encode starch synthetases and seed-storage proteins, as well as their cis- and trans-acting regulators.

Characteristics of amylose and amylopectin in the endosperm

Starch in the endosperm is the dominant carbohydrate reserve in the grain. There are two different types of storage starch: amylose and amylopectin. Amylose is a linear polymer of d-glucose units, and amylopectin is a highly branched polymer of glucose. A series of enzymes are involved in the biosynthesis of starch in the rice grain. Most of these enzymes are represented by different isoforms and are encoded by multiple genes, leading to a highly complex biosynthesis and accumulation process. In rice, four different isozymes are expressed in different tissues (Chan et al., 1990). Three genes have been cloned, and their expression patterns characterized (Wang et al., 1992a, b, 1999; Huang et al., 1996). The biosynthesis of starch in the developing rice grain starts with the conversion of sucrose into glucose and fructose.

Protein composition of rice grains

Storage proteins in rice grain can be grouped into four main types, according to their solubility: water-soluble albumin, salt-soluble globulin, alkaline-soluble glutelin, and alcohol-soluble prolamin. Unlike other crops, up to 80% of the total storage protein in rice is glutelin (Yamagata et al., 1982), whereas prolamin accounts for a maximum of only 20-30%. Although four storage proteins are initially synthesized on the endoplasmic reticulum membrane and then trans-located into the endoplasmic reticulum lumen, they are stored in two different PBs, PB-1 and PB-2, which are mainly stored in the starchy peripheral part of the endosperm. Glutelin in rice is synthesized as a 57-kDa precursor and then cleaved into a 37 to 39-kDa acidic subunit and 22 to 23-kDa basic subunits (Yamagata et al., 1982). Glutelins are encoded by approximately 15 genes per haploid genome, and can be classified into four subfamilies: GluA, B, C, and D. GluA has four members and GluB is the largest with eight members. To date, only two members of GluC and one member of the GluD subfamily have been identified (Takaiwa et al., 1987; Okita et al., 1989). Because of the redundancy of glutelin and prolamin genes in rice, it is difficult to identify naturally occurring cultivars with obviously altered storage protein levels. The only relevant study published to date was based on a selection of 19 cultivars among 1,400 accessions from Russia, Northern China, and North Korea, which reported increased levels of the 57-kDa glutelin precursor with markedly decreased levels of the acidic and basic subunits (Satoh et al., 1995).

Overlapping expression patterns of starch synthetase and seed-storage protein genes

Most starch synthetase genes are expressed in the seeds during the grain-filling stage of rice development, and peak at either six or ten days after flowering (DAF), and then decline gradually towards maturation. Rice glutelin and prolamin genes are exclusively expressed during seed development. Similar to starch synthetase, the majority of the seed-storage protein genes in rice are developmentally regulated. A recent transcriptional profiling study of six members of the GluA and GluB subfamilies revealed no detectable expression level in any gene at 3 DAF, but peak activity was observed at 10 DAF before decreasing again towards maturation (20 DAF) (Duan and Sun et al., 2005).

Post-Transcriptional regulation of genes in grain development

Regulation of starch synthetase and seed-storage protein genes not only occurs at the transcriptional level but also at the post-transcriptional level. Both proteins have been detected in 10 DAF seeds, and their levels steadily increase throughout seed development. However, previous studies have reported that the molar ratio of glutelin to prolamin proteins decreased from 1.7 at 10 DAF to 1.2 at 25 DAF, whereas the amounts of glutelin and prolamin transcripts increased from nearly equal at 5 and 10 DAF to a 40% excess of prolamin transcripts during grain maturation (Kim et al., 1993; Li et al., 1993). This indicates that the expression levels of the glutelin and prolamin multigene families are differentially regulated, not only at the transcriptional level but also at the post-transcriptional level.

Environmental and Culture-System Effects on Rice Quality Traits

Effects of water shortage and drought

Water is one of the most essential factors in crop production, and among all of the cereals, rice requires the most water irrigation. Different water management treatments, namely plastic film mulching, water-saving irrigation, and conventional irrigation, significantly affect the growth rate of brown rice, head rice, chalky rice, as well as their nutrient components. Of all of the relevant variables, water treatment has the greatest effect on protein content (Cheng et al., 2003). However, flooding just before harvest induces visible changes to the physical appearance of grains. Kernels in flood-affected samples become soft and develop fissures, which contribute to low head rice recovery rates, and milled rice has a lower kernel weight and protein content, but higher amylose and ash levels (Singh et al., 1990). Growing rice in upland, non-flooded environments affects grain quality. A recent study compared several cooking and nutrient quality traits, including amylose content, gel consistency, gelatinization temperature, and protein content, under upland and lowland conditions. The phenotypic values of all four traits were significantly higher in the upland environment than in the lowland environment (Guo et al., 2007).

Fertilizer

The nitrogen level in the soil is another factor that strongly affects yield and grain quality. The current hypothesis is that yield is related to the nitrogen-supplying capacity of the soil, which in turn determines the grain protein content (Perez et al., 1996). The application of nitrogen fertilizer at different stages, from panicle initiation to flowering and the grain-filling stages, significantly increases the seed-storage protein content (Nangju and De Datta, 1970; Taira et al., 1970; Nagarajah et al., 1975). It also improves protein content-related traits such as the growth rate of milled and head rice (Wopereis-Pura et al., 2002; Leesawatwong et al., 2005), and translucency (Perez et al., 1990). Potassium is another essential fertilizing agent in rice production (Fageria et al., 1990a, b). The effect of potassium on rice kernel quality was not well understood until a recent study demonstrated that potassium fertilizer application increases gel consistency and grain protein content, but has no significant effect on gelatinization temperature and amylose content (Bahmaniar and Ranjbar et al., 2007).

Soil salinity

Salinity is another important condition of the soil that can strongly affect grain quality. A comparison of rice cultivars grown in low-salinity and high-salinity regions revealed that an increased level of salinity significantly lowered the protein content of seven out of nine cultivars, but had no effect on amylose content and the alkali spreading value (Juliano and El-Shirbeeny, 1981). Another study found that grains grown on saline soils have a higher storage protein content, but less translucent grain and lower starch and amylose levels than those grown on normal soil (Siscar-Lee et al., 1990).

Seasonal effects and temperature

Rice is largely grown as a transplanted crop. Delays in sowing and transplantation may affect grain quality, due to differences in temperature and solar radiation. Late planting delays flowering and results in the partial filling of spikelets, thereby lowering the milling yield and head rice recovery rate during processing (Shahi et al., 1975; Dhaliwal et al., 1986). Grain dimensions (length and width) are also affected by late sowing and transplantation, which result in a higher protein content. However, under these conditions, amylose levels decrease (Dhaliwal et al., 1986), possibly because of high temperatures during grain filling caused by late sowing and transplantation.

Spectroscopic Measurement of Rice Quality

Given that rice is one of the most extensively cultivated cereals in the world and is consumed as a staple food by more than half of the world's population (Kato et al., 2000), the regular monitoring of rice quality is imperative. Although rice classification can be conducted by visual inspection based on color, production area, hardness, etc., such a visual inspection method has disadvantages. For example, some classes may look similar but their quality attributes can vary significantly, which affects product quality (Brosnan and Sun, 2004). The eating quality of cooked rice is closely monitored by the rice processing and milling industry, which considers both its external appearance and internal quality. Thus far, this review has discussed the many parameters that affect rice quality. For the effective monitoring of quality using spectral imaging, a multi-disciplinary approach is required to unite physics, chemistry, instrument development, and concepts in applied mathematics related to data analysis and data management. To date, several studies have been conducted on rice quality using spectroscopic techniques, which will be reviewed below.

Hyperspectral imaging (HSI) technique

HSI, also known as spectral imaging, is an innovative technique that combines spectroscopy and digital imaging (computer-assisted vision), making it useful for obtaining both spectral and spatial information (numerous pixels of information) from a tested object (Figure 1). Therefore, HSI, described as $I(x, y, \lambda)$ or $I(\lambda, x, y)$, can be considered either as a detached spatial image $I(x, y)$ at each single wavelength (λ), or as a spectrum $I(\lambda)$ at each individual pixel (x, y) (Sun et al., 2010). HS images are composed of

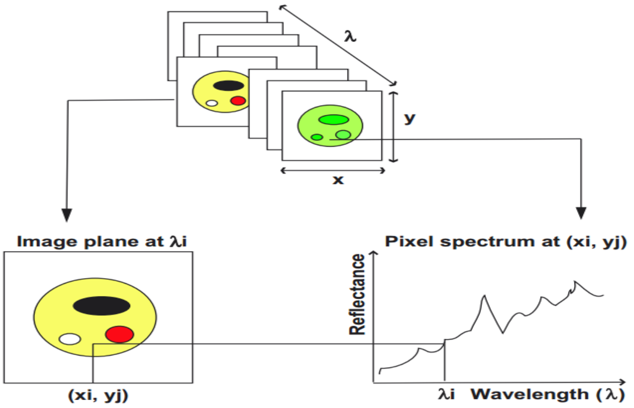

Figure 1. Schematic representation of a hyperspectral imaging hypercube showing the relationship between spectral and spatial dimensions (Gowen et al., 2007).

hundreds of contiguous wavebands for each spatial location of a targeted object. Consequently, each pixel in a hyperspectral image contains the spectrum of that specific position. As in the case with other spectroscopic techniques, HSI can be conducted in reflectance, transmission, or fluorescence modes. In addition, HSI is a non-destructive and rapid technique that enables sample measurement without contact (Kim et al., 2001).

In recent years, the HSI technique has been utilized in either reflectance or transmittance modes (Ariana and Lu, 2008) in the range of visible and near-infrared (NIR) wavelengths (400-2500 nm) for quality classifications of food and agricultural products (Kim et al., 2002; Zhang et al., 2012). HSI is used in the quality inspection, classification, and evaluation of a wide range of agricultural food products (Monteiro et al., 2007). Because of the large size of hyper cubes (that can exceed 50 MB, depending on image resolution, pixel binning, and spectral resolution), complex multivariate analytical tools are usually employed for classification, such as principal component analysis (PCA), partial least squares (PLS), linear discriminant analysis (LDA), multi-linear regression (MLR) and artificial neural network (ANN). HSI has also been widely used in the evaluation of cereal quality, including wheat grade identification (Mahesh et al., 2008) and maize kernel hardness classification (Williams et al., 2009).

Vibrational spectroscopies

Raman spectroscopy

Raman spectroscopy is a technique that is used to measure the vibrational and rotational spectra of sample molecules. For the measurement of Raman spectra, laser light excites the sample and this light is then scattered in all directions. Some of this scattered light is directed toward the detector, which records the Raman spectrum. The phenomenon was first observed by C.V. Raman in 1928, who received the Nobel Prize for this discovery in 1931. Raman spectroscopy offers several benefits, including its sensitivity, high information content, and non-destructive nature, which allows the sample to be used for further analysis and there is no need for sample preparation. Aqueous samples are easily analyzed, because there is no interference from atmospheric CO_2 or H_2O. Furthermore, instead of visible excitation lasers, a Fourier transform (FT)-Raman spectrometer uses a laser in the NIR range, usually at 1,064 nm. Since fluorescence is almost absent at this wavelength, a major advantage of FT-Raman is the absence of fluorescence interference. Due to its higher spectral resolution and distinct features, Raman spectroscopy techniques are applicable for determinations of grain quality.

Fourier transform-near infrared (FT-NIR) spectroscopy

FT-NIR spectroscopy records the intensity of absorbance across the entire spectrum as a function of the optical path difference between two NIR beams in an interferometer. The two beams are created by splitting the measurement beam, i.e., the beam that is transmitted through or reflected from the specimen. One split beam travels over a different optical path length via a moving mirror, and it is recombined with a second beam to create an interference signal. The total interference signal results from the mirror travelling through a range of wavelengths, and it is then transformed to spectral components via a fast Fourier transform.

FT-NIR spectroscopy has the advantages of high resolution, fast and accurate frequency (conforming exactly to fact), higher signal-to-noise ratios, no sample preparation, and non-destructive testing. Furthermore, FT-NIR spectroscopy has its own unique characteristic, which is that the functional groups of every molecule generate a characteristic absorption or transmission spectrum that can be used for identification, like a fingerprint. Therefore, FT-NIR spectroscopy can also be successfully used to analyze grain properties such as rice lipid content, moisture content, and optimal cooking time.

Application of Spectroscopic Techniques to Rice Quality Assessment

Shen et al. (2010) investigated 16 free amino acids in Chinese rice wine using FT-NIR within the range 800-2,500 nm. Ninety-eight samples of Chinese rice wine with different aging periods were tested by FT-NIR spectroscopy with PCA and partial least square regression (PLSR) and high-performance liquid chromatography. The absorption band found at 1,460 nm was water or carbohydrate, and was related to the first overtone of the O-H group, and that at 1,934 nm represented the combination of stretching and deformation of O-H in water and ethanol. An absorption band at 1,692 nm may have been related to the stretch of the first overtone or C-H groups in aromatic compounds, and the absorption band at 1,776 nm was related to the C-H stretch of the first overtone. Absorption at 2,266 nm was related to the C-H combination and O-H stretch overtones. Absorption at 2,302 nm was mainly related to the C-H overtones of ethanol. The score plot of the first two principal components obtained from the raw spectra accounted for 99.6% of the total variation. The correlation coefficients of the calibration were larger than 0.94, and the residual predictive deviation was larger than 1.5 for amino acids. In another study, Deora et al. (2014) obtained moisture measurements of gluten-free rice-based pasta using FT-NIR spectroscopy in the spectral region 4,000-12,000 cm^{-1}, and the data were analyzed by PLSR. The water absorption bands were observed at around 5,155 cm^{-1} for O-H stretching and at 7,000 cm^{-1} for O-H deformation. The vibration of the second overtone of the carbonyl group was the most intensive band in the spectrum at 5,784 cm^{-1} for C-H stretching and at 6,912 cm^{-1} for C-H deformation vibration. The overtones obtained for and were at 5,528 cm^{-1} and 5,808 cm^{-1}, respectively, and the PLSR found a correlation of 0.9775 for calibration. The root mean square error of cross validation value was 0.83.

Wang et al. (2014) evaluated rice variety and quality using HSI within the range 400-1,000 nm. Samples of three paddy rice varieties were used for visible and NIR HSI with PCA and a back propagation neural network (BPNN) measurement. The average accuracy obtained, based on merging the BPNN spectral and image data, was 94.45%, which was higher than the accuracy obtained from the PCA spectral model (89.18%) and the BPNN spectral model (89.19%) alone. Kong et al. (2013) explored the feasibility of cultivar identification using NIR HIS and multivariate data analysis in the range 874-1,734 nm. Four cultivars of rice seeds were analyzed using PCA, partial least square discriminant analysis (PLS-DA), soft independent modeling of class analogy (SIMCA), K-nearest neighbor algorithm (KNN), support vector machine (SVM), and random forest (RF). The score plot obtained by PC1 and PC2 explained 98.59% of the total variation, which indicates that global classification models can be constructed for cultivar identification. The PLS-DA and KNN models were relatively ineffective, with a classification accuracy of prediction of more than 80%. The SIMCA, SVM, and RF models obtained classification rates of 100% in both the calibration set and the prediction set, which indicates that rice seed cultivars can be accurately identified. In another study, Hwang et al. (2012) investigated the geographical origins of rice samples by transmission spectral collection through packed grains,

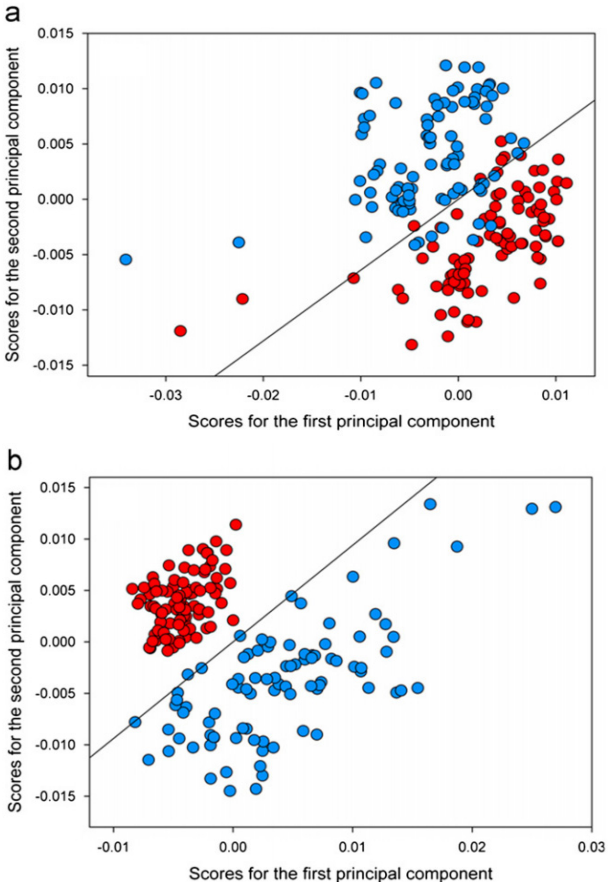

Figure 2. Score scatter plots (first vs. second principal components) for the discrimination of rice samples using back scattering (a) and transmission (b) measurements. Red and blue circles correspond to imported and domestic rice samples, respectively. In each plot, the corresponding boundary line determined by linear discriminant analysis is shown (Hwang et al., 2012).

using Enhanced Raman spectroscopy in the range 1,700-390 cm^{-1}. Thirty imported and domestic polished rice samples were analyzed with PCA using each spectral data set, and LDA was used for the resulting scores (Figure 2). The combination of the first and second principal components provided the best discrimination accuracy for both back scattering and transmission measurements.

Protein is an important component of food, and milled rice has an average protein content of 8-13%. Globulin is a protein fraction that also affects the quality of rice. Guo et al. (2013) compared data obtained from infrared (400-4,000 cm^{-1}) and Raman spectroscopy (400-1,700 cm^{-1}) with respect to changes in interactions between proteins and starch, and structural changes involving the secondary and tertiary structures of proteins induced by rice aging. Milled Japonica rice samples were analyzed by an analysis of variance and Duncan's multiple range test, at a significance level of $P < 0.05$. The globulin and starch association was strengthened whereas that between glutelin and starch had diminished, probably because of structural differences and interactions with starch that could be responsible for dissimilar pasting properties between fresh and aged rice. In another study, Feng et al. (2013) used several multivariate data analysis methods to analyze Raman spectral data for the discrimination of Indica and Japonica rice samples, and the paraffin detection in adulterated rice samples; paraffin is added to rice to achieve a desirable translucent appearance and to increase its marketability. They achieved 90% accuracy using a multivariate statistical analysis method for geographical classification in both cases, and PCA was successful in discriminating between paraffin-adulterated samples and non-adulterated samples.

Conclusions

This review describes the effects of different components of rice (such as starch, lipids, and proteins), interactions between these different components, and environmental factors on rice quality during storage, as well as its texture and cooking quality. The use of different spectral modalities, such as HSI and vibrational spectroscopies (FT-NIR and Raman), has been very successful, and has good potential for the detection of rice quality. In contrast to conventional methods that are time consuming, labor intensive, expensive, and require sample destruction, these spectral modalities are non-destructive, accurate, and convenient for the quantitative and qualitative analysis of rice quality.

Conflict of Interest

The authors have no conflicting financial or other interests.

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