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Enhanced Raman spectroscopic discrimination of the geographical origins of rice samples via transmission spectral collection through packed grains

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ABSTRACT

Transmission Raman spectroscopy has been effectively utilized for the discrimination of rice samples according to geographical origin. Since the constituents of rice are heterogeneously distributed and/or localized in a grain, the collection of Raman spectra providing a better compositional representation of packed rice grains is an essential requirement for accurate analysis. The optimal packing thickness yielding the most reproducible transmission spectra was initially determined. Internal propagation of radiation was more sensitively influenced by random packing when a packing was thinner; while, a thicker packing largely attenuated transmitting Raman signal and eventually degraded the signal-to-noise ratio of collected spectra. At the determined packing thickness, transmission spectra of all rice samples were collected, and discrimination into two different geographical origins was performed using principal component analysis (PCA) combined with linear discriminant analysis (LDA). For comparison, back-scattering Raman spectra of the same samples were also collected. The discrimination accuracy was improved when Raman spectra collected directly through the packed rice grains were used. Since the constituents of rice were not homogeneously distributed in a grain as confirmed using Raman microscopy, the transmission measurement enabling transversal sampling across a packing of rice grains was better for compositional representation of individual grains in the packing and able to recognize minute spectral differences between two groups, ultimately leading to more accurate discrimination of geographical origin.

1. Introduction

In our previous publication, we demonstrated that the Raman spectra collected over a large area of rice grains improved the differentiation of rice samples according to geographical origin compared to using a conventional measurement scheme illuminating a laser into a tiny spot on the rice grains [1]. The motivation of this research was to develop a fast and non-destructive analytical method to identify geographical origins, especially at-site, for establishment of order in the circulation distribution. However, it was still based on a back-scattering Raman measurement, which could produce spectra containing relatively more weighted information on constituents localized on the outer part of the grain. Rice constituents, such as the embryo, endosperm, and bran, are quite localized in the grain, and their distribution is not homogenous [2,3]. Therefore, a spectral collection method capable of sampling across the rice grain is necessary to represent the whole chemical composition. Moreover, packed granular samples are routinely measured in many practical non-destructive spectroscopic analyses [4–16,20], so a transmission spectral collection scheme [13–19] that is better able to sample a grain as well as represent packed grains could be greatly beneficial for reliable analysis [20].

It is known that a polished rice grain is primarily composed of endosperm (80–85 wt%), which is mostly starch with a low protein content [2,3]. It also contains a small amount of embryo (mainly fat), although the embryo is largely removed during the course of grain polishing. Overall, the weight percentages of carbohydrate, crude protein, crude fat, and water in a polished rice grain are approximately 70–80%, 7–8%, 1–2% and 11–12%, respectively [21–27]. The Raman spectral features of amylose and amylopectin (the constituents of starch) are quite similar to each other due to structural similarity, since these are simply large chains of glucose units in a linear or branched form, respectively. The spectral feature of starch would provide only minor selectivity for geographical discrimination of rice samples, unless their starch contents are substantially different from each other. Embryo (composed largely of fat and protein) would provide better spectral discrimination due to its larger compositional variability, while its content is fairly low after polishing. Thus,

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the spectral differences between rice samples with different geographical origins are not substantial. Since only minute compositional differences among polished rice samples are present, a collection of representative and reproducible Raman spectra of rice samples is a minimal prerequisite for recognizing differences and enabling discrimination.

Here, both back-scattering and transmission measurements were compared to discriminate polished rice samples with two different geographical origins. For the back-scattering spectral collection, a wide area illumination (WAI) scheme was also employed [28]. For the acquisition of transmission spectra, a laser was irradiated on a rice packing, and the transmitted Raman signal crossing the packing was collected at the opposite side [15]. For a reliable transmission measurement, an optimal thickness yielding reproducible spectra of packed rice samples with much less variability to random packing was initially established. Using each back-scattering and transmission spectral dataset acquired from the same rice samples, a principal component analysis (PCA)-linear discriminant analysis (LDA) was performed for discrimination, and the resulting accuracies were compared. Finally, the inhomogeneous distribution of constituents within a rice grain was investigated by collecting microscopic Raman spectra at different spots on the surface of sliced grains and examining possible variations among the acquired spectral features.

2. Experimental

Thirty imported and 30 domestic polished rice samples were kindly supplied by the National Agricultural Products Quality Management Service (NAQS), Seoul, Korea. Imported rice samples came mostly from diverse regions in China. The polished grain samples were directly measured without further grinding into powder. The rice samples were simply transferred into a circular cell (diameter: 2 cm) for both back-scattering and transmission Raman spectral collection.

Back-scattering Raman spectra were collected using the WAI scheme (PhAT system, Kaiser Optical Inc.) as previously published [28]. It was able to cover a large sample area (28.3 mm^2) with a laser illumination diameter of 6 mm. Transmission Raman spectra were collected by directly illuminating laser radiation (785 nm, Invictus, Kaiser Optical Inc.) onto the packed rice samples housed in the circular cell [15]. The diameter of laser illumination was approximately 6 mm, and the power of the laser beam at the packing was approximately 400 mW. Transmitted Raman signals were collected at the opposite side using the same WAI probe (in other words, the same spectrometer used to collect the back-scattering spectra). Triplicate spectra were collected at room temperature. At each spectral collection, rice samples were reloaded into the circular cell to ensure random packing.

A rice grain was sectioned and positioned on a microscope stage connected to a Raman spectrometer, and a laser beam (approximately 80 μm in diameter) was focused on the face using an objective lens (10 × /0.25 numerical aperture) for spectral collection. All calculations and multivariate analyses, including baseline correction, intensity normalization, PCA and LDA, were conducted using MATLAB version 7.0 software (The Math-Works Inc., MA, USA).

3. Results and discussion

3.1. Determination of the optimal packing thickness for transmission measurement

The transmission Raman feature of rice samples may be influenced by the random packing of the grains as well as the packing thickness, as was shown in a previous publication [20]. The thinner packing of granular samples resulted in transmission spectra with higher intensity (sensitivity), while the spectral features varied quite sensitively upon reloading of samples due to relative increase in randomness of grain packing when the packed volume was smaller. Transmission spectra were relatively more reproducible under random packing when the packing volume was larger (thicker packing), while the intensity of transmitted Raman signals was greatly attenuated. Therefore, for a given laser power, it is necessary to determine the optimal packing thickness of rice grains for reliable transmission spectral collection. Transmission Raman spectra were collected by varying the packing thickness from 0.5 to 3.0 cm in increments of 0.5 cm. All spectra were collected by illuminating laser radiation for 2 s with an accumulation of 60 scans (total acquisition time: 120 s). Five replicate transmission spectra were acquired at each packing thickness, and rice grains were randomly re-packed at every replicate spectral collection.

Since the shape of a rice grain is approximately an oval, there is considerable void space inside a packing, which could directly influence internal propagation of transmitting radiation. Simultaneously, reflections would occur at the surface of individual granules without full interaction with the grains. Transmission Raman spectra of a domestic rice sample collected at different packing thicknesses over the 1700–390 cm^{-1} range are shown in Fig. 1(a). As expected, when the packing was thinnest (0.5 cm), the intensity of Raman peaks as well as baselines of replicate spectra varied largely. When the thickness increased to 1.0 cm, the vertical baseline variation among the replicate spectra was still substantial and the band intensities decreased due to the larger attenuation of Raman signal by the thicker packing. Replicate spectra became more reproducible at a packing thickness of 1.5 cm, while the corresponding intensity decreased synchronously. When the packing becomes thicker, the relative variation in the distribution and size of void space in a packing decreases statistically; therefore, the resulting transmission spectral feature could be relatively less influenced by random packing. Moreover, when laser radiation hits a packing, it isotropically diffuses through the packed grains and interacts more with the neighboring grains. This increased sample coverage volume is obviously advantageous for better compositional representation of a sample packing. In the case of packing thicknesses at 2.5 and 3.0 cm, the corresponding baselines become considerably stable; the intensities largely decreased, which eventually degraded the signal-to-noise ratio of the collected spectra.

To examine the reproducibility of replicate transmission spectra collected at each packing thickness, normalized spectra in the 1700–390 cm^{-1} range as shown in Fig. 1(b) were investigated. For normalization, the baselines of spectra were corrected at 1700, 1185, 975, 813, 692, 552 and 390 cm^{-1}, and these baseline-corrected spectra were divided by the corresponding peak areas under the 1700–390 cm^{-1} range. The spectra acquired at different packing thicknesses are offset for suitable comparison. The shaded box corresponds to the 692–552 cm^{-1} range, where the reproducibility is easily recognizable by visual observation.

As mentioned above, the features of replicate spectra collected at the 0.5 cm packing vary largely. At a 1 cm packing thickness, reproducibility started to improve rather substantially as is seen by the relatively decreased variability in the replicate spectra. Reproducibility was maximized when the packing thickness was either 1.5 or 2 cm, but started to worsen at a 2.5 cm-thickness packing. The degraded reproducibility in the measurements with the thicker packings (2.5 and 3.0 cm) is mainly attributed to the lowered signal-to-noise ratio of collected spectra due to the large attenuation of Raman signal by the packings themselves.

Using the replicate spectra collected at each packing thickness, relative standard deviations (RSDs) of intensities at each wavenumber

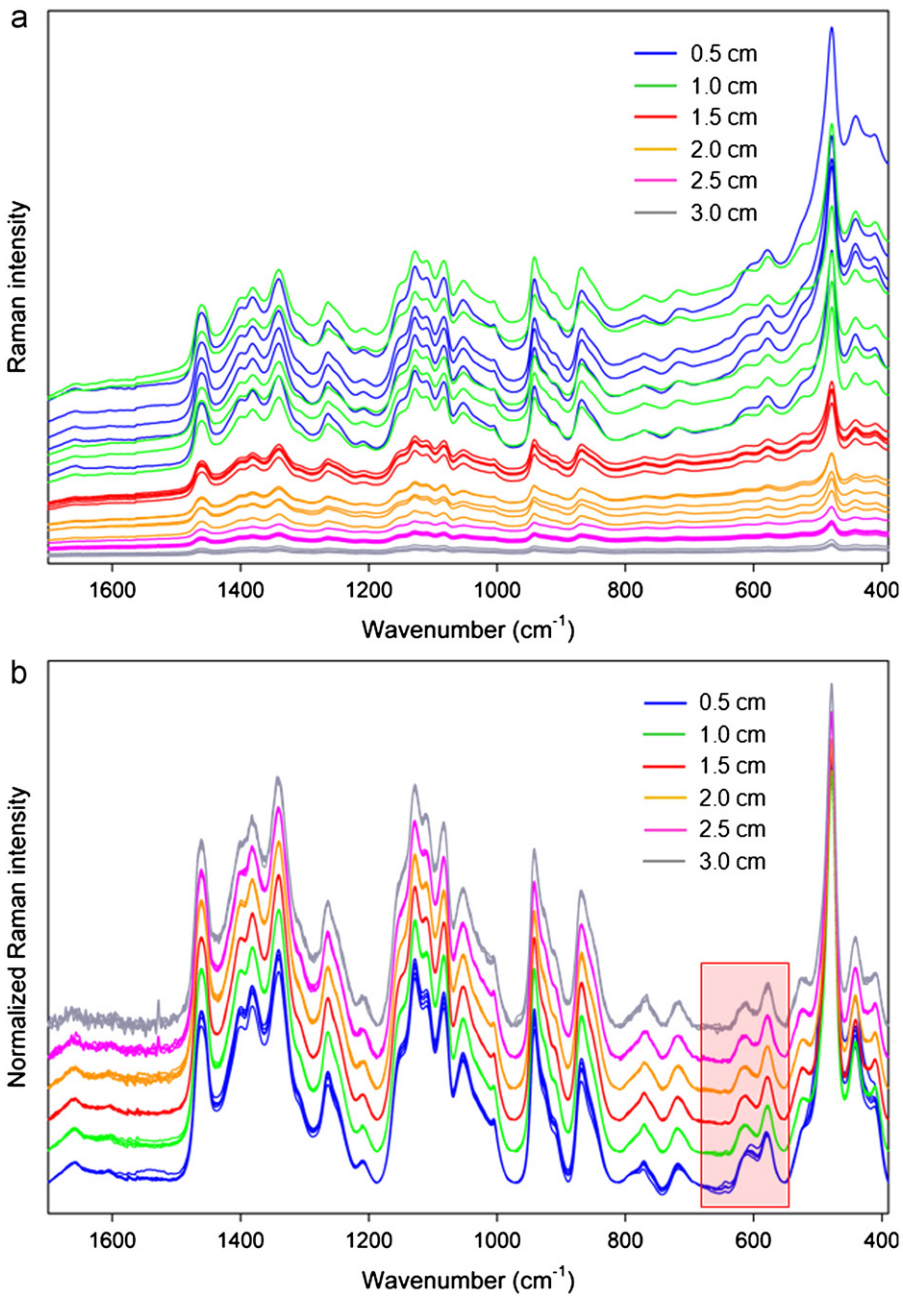

Fig. 1. Raw (a) and normalized (b) transmission Raman spectra of a domestic rice sample collected at different packing thicknesses over the 1700–390 cm^{-1} range. Before normalization, the baselines of raw spectra were corrected.

were calculated and then averaged across the full range to quantitatively evaluate reproducibility. The average RSDs for measurements with packing thicknesses of 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 cm were 6.1%, 1.0%, 0.8%, 1.2%, 1.6% and 2.8%, respectively. RSD was lowest when the packing thickness was 1.5 cm, as was expected from the spectra shown in Fig. 1(b). A packing thickness of 1.5 cm was used for further collection of transmission Raman spectra for all rice samples. It is important to note that, while the optimized packing thickness is valid within the experimental conditions in the study, it will vary depending on parameters such as granule shape, granule size, transparency of a granule, laser exposure time and laser power. If these conditions change, the optimal packing thickness for transmission Raman measurement will vary accordingly.

3.2. Comparison of back-scattering and transmission Raman spectra of packed rice samples

To examine Raman spectral features between imported and domestic rice samples, all normalized Raman spectra of samples belonging to each geographical origin were averaged, and these average spectra were used for comparison. Average back-scattering and transmission spectra of the rice samples from both origins are shown in Fig. 2. The spectra were offset for clear comparison. Raman spectra of amylose, amylopectin and starch are also shown for comparative examination. Since amylose and amylopectin correspond to linear and branched chains of repeating glucose units, respectively, the difference in their Raman spectral features is minor due to the structural similarity. Minute

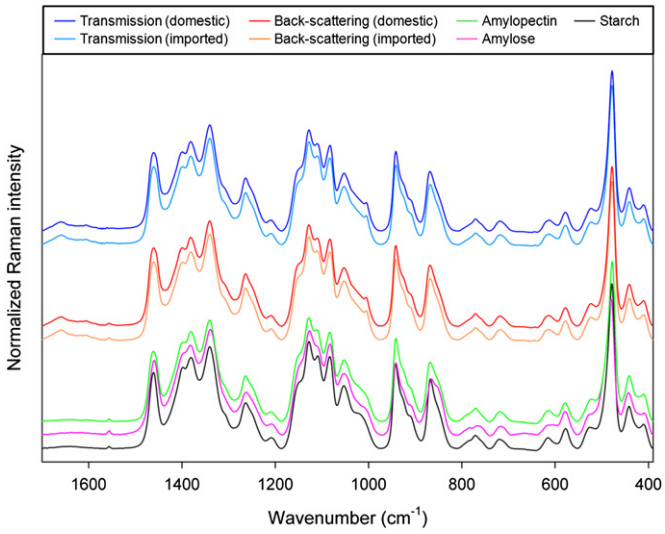

Fig. 2. Average back-scattering and transmission spectra of rice samples from both geographical origins. The spectra are offset for clear comparison. For comparative examination, Raman spectra of amylose, amylopectin and starch are also shown.

spectral differences between these two constituents are observed, such as in the 880–760 cm^{-1} range. The spectral feature of starch is relatively closer to that of amylopectin since amylopectin consists of approximately 80% of starch in the case of rice [2,3,23].

The overall spectral features of average back-scattering spectra corresponding to both geographical origins are similar to each other. Additionally, the transmission spectral features between two geographical origins are analogous to each other. Together, these results indicate that the compositions of rice samples from both origins are quite similar, so a clear Raman spectroscopic distinction would be difficult. In addition, the back-scattering and transmission spectral features are generally similar to each other, implying no significant difference in the sample representation of rice samples by either spectral collection method.

Since the spectral difference between rice samples from the two origins was not clearly visible in the spectra, it was necessary to identify possible minute differences that could help the discrimination. For this purpose, a difference spectrum between the two average spectra corresponding to both origins was acquired for each measurement as shown in Fig. 3(a). The difference in the spectral features between both origins was generally similar for both measurements, as expected, while minute differences were observed across the range. For an examination of the details of the difference spectral features, the 1500–1165 and 1165–790 cm^{-1} ranges are highlighted in Fig. 3(b) and (c), respectively. In the 1500–1165 cm^{-1} range, a difference in intensity is mainly noticeable, while the shapes of the bands in the 1395–1385 cm^{-1} and 1260–1190 cm^{-1} ranges (indicated by asterisks) are dissimilar. Interestingly, the band shapes around 1390 cm^{-1} in the spectra of amylose and amylopectin are slightly different (Fig. 2). The shape of band in the 868–840 cm^{-1} range (indicated by triangle) is quite dissimilar also (Fig. 3(c)). Similarly, a relatively larger spectral difference between amylose and amylopectin was observed around this spectral range.

Based on the observation of difference spectra, it is reasonable to draw two conclusions. First, the characteristics of back-scattering and transmission measurements for spectral representation of packed rice samples differ slightly, as confirmed by the dissimilar features in the marked bands seen in Fig. 3. Second, variations in relative concentration between amylose and amylopectin in starch could be a valuable source for the differentiation of rice samples, although the corresponding spectral variation is tiny.

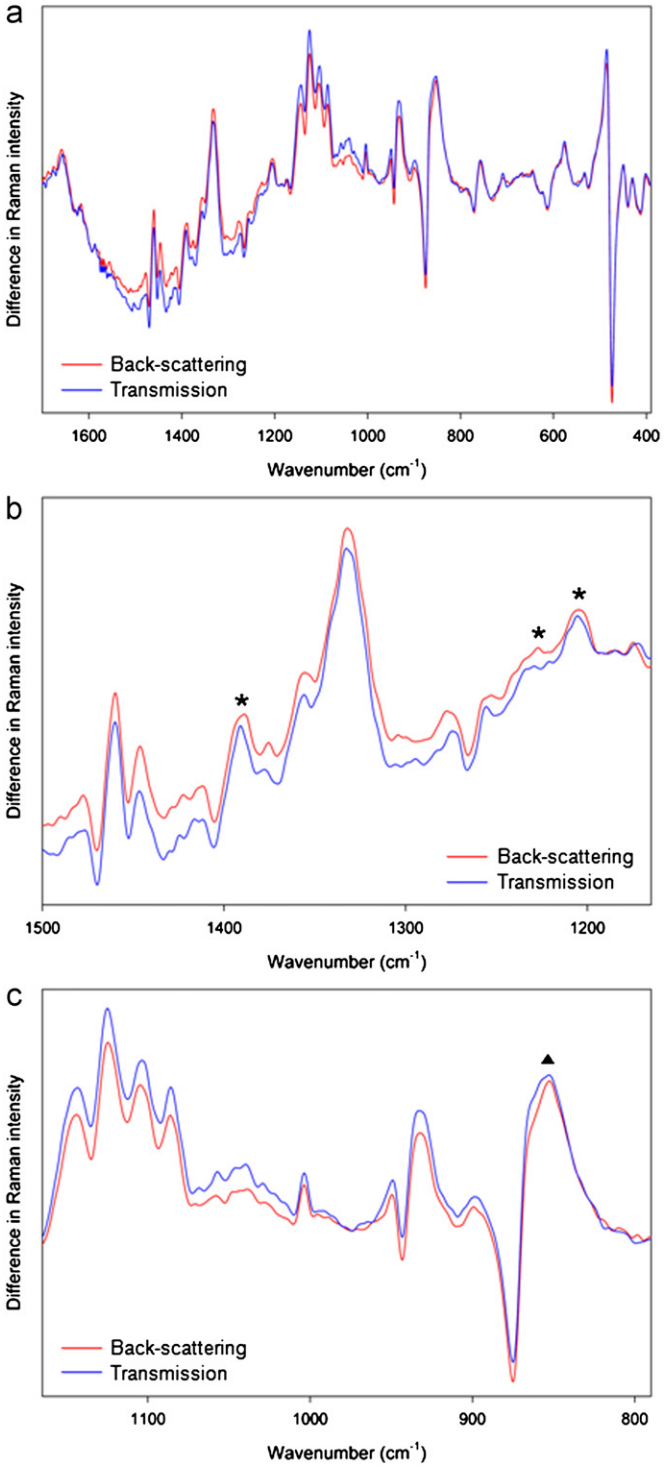

Fig. 3. Difference spectra acquired by subtracting the average spectra of imported samples from the average spectra of domestic samples for both back-scattering and transmission measurements (a). For detailed examination, the differences in spectral features are highlighted in the 1500–1165 (b) and 1165–790 cm^{-1} (c) ranges.

3.3. Discrimination of rice samples according to geographical origin

Using both normalized back-scattering and transmission spectra, discrimination between imported and domestic rice samples was attempted using LDA. Initially, PCA was performed using each spectral dataset, and the resulting scores were used for LDA. A combination of the two principal components was tested since

the performance of discrimination was easily recognizable in the two-dimensional domain. Of the first to fourth principal components, an optimal combination of two principal components yielding the best discrimination accuracy was searched. The resulting errors were obtained by the following procedure. Initially, 48 and 12 samples were randomly assigned to the calibration and validation sets, respectively, and PCA–LDA was performed in the 1700–390 cm^{-1} range. This procedure was repeated 200 times, and the resulting discrimination error was acquired.

The score scatter plots for the discrimination of rice samples using back-scattering and transmission measurements, respectively, are shown in Fig. 4(a) and (b), where red and blue circles correspond to the imported and domestic rice samples. In each plot, the corresponding boundary line determined by LDA is also shown. The combination of the first and second principal components provided the best discrimination accuracy for both back-scattering and transmission measurements. In the case of the back-scattering measurement, two groups were discernible with a slight overlap around the boundary line; the differentiation of the two groups was more distinct with the use of transmission measurement. The discrimination errors were 9.97 and 1.61% for the back-scattering and transmission measurements, respectively, confirming that transmission spectra collected through packed rice samples provide more descriptive information for the identification of each geographical origin. Although Raman spectral features of rice samples between two geographical origins are minute, PCA is effective to recognize them for the discrimination as found in several previous publications [29–31].

To investigate the improved accuracy in the transmission measurement further, the loadings used in both PCA models were investigated. Fig. 5 shows the first loadings used for both back-scattering (red) and transmission (blue) measurements in the 1500–1165 (a) and 1165–790 cm−1 (b) ranges. The same spectral ranges used to show the difference spectra in Fig. 3(b) and (c) are also displayed for consistency in comparison. The shapes of the loadings are quite different each other, although the spectral features of raw spectra acquired using both measurements are similar as shown in Fig. 2(a). This indicates that the spectral information representing the composition of rice samples minutely differs for both measurements, although the same samples were measured. This result would suggest that the distribution of constituents in a grain is not homogeneous, such as different compositions between inner and outer part of a grain. If rice constituents are homogeneously distributed, the resulting back-scattering and transmission spectral features suppose to be nearly identical.

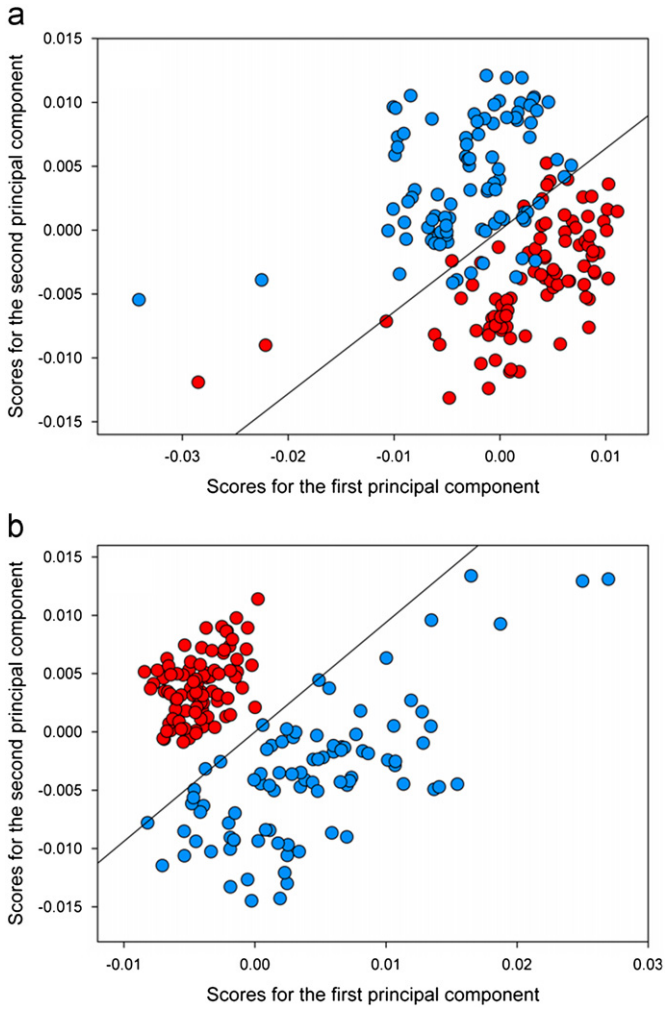

Fig. 4. Score scatter plots (the first vs. second principal components) for the discrimination of rice samples using back-scattering (a) and transmission (b) measurements. Red and blue circles correspond to the imported and domestic rice samples, respectively. In each plot, the corresponding boundary line determined by LDA is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

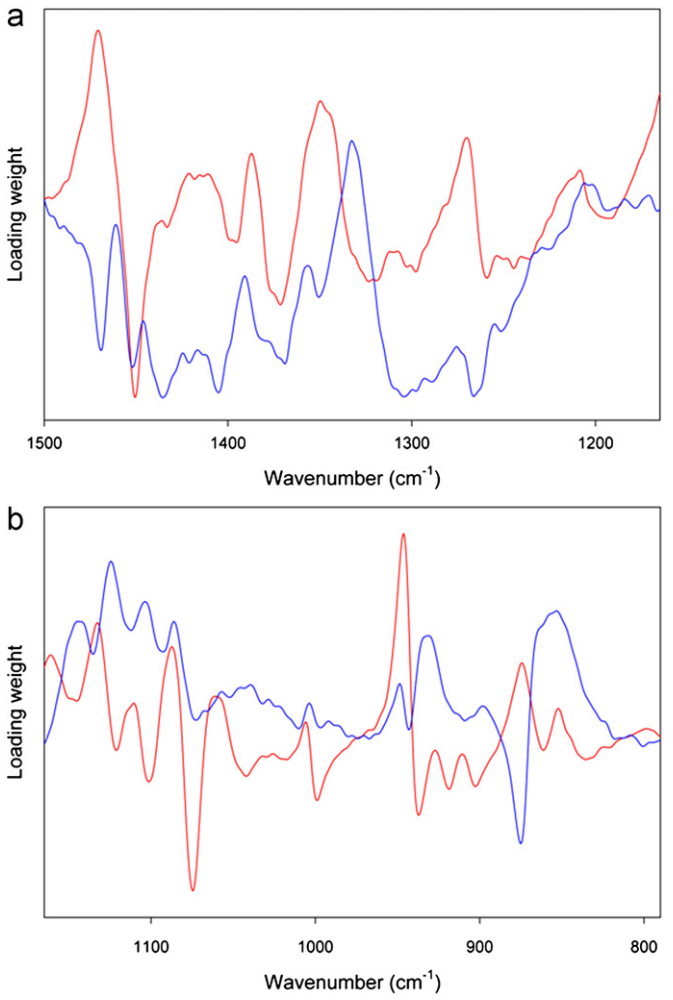

Fig. 5. First loadings used for both back-scattering (red) and transmission (blue) measurements in the 1500–1165 (a) and 1165–790 cm^{-1} (b) ranges. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

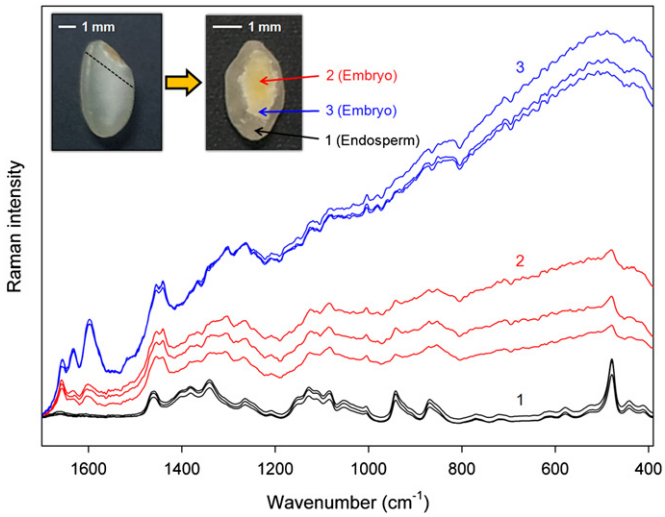

Fig. 6. Raman spectra (1700–390 cm^{-1} range) collected at the 3 different spots on the sectioned face indicated by the arrows on the right picture. The left picture shows a grain used for investigation, and the dashed line indicates the sectioned line. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

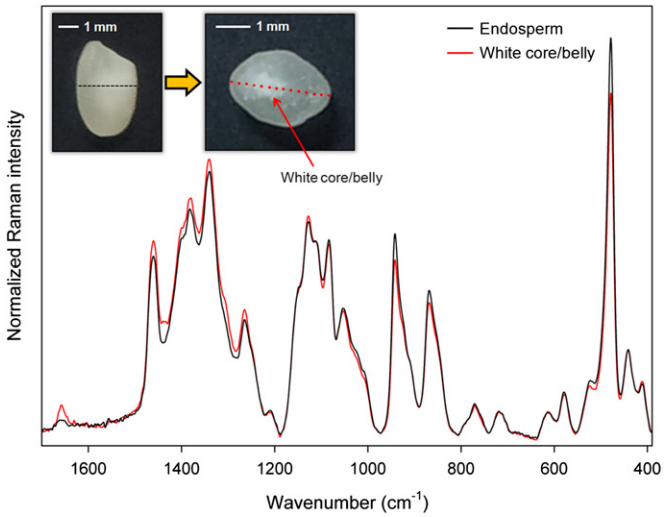

Fig. 7. Raman spectra (1700–390 cm^{-1} range) representing white core/belly (red) and endosperm (black). The arrow on the right picture indicates the region of white core/belly. The red dots indicate where the laser is irradiated for the spectral collection. The left picture shows a grain used for the investigation, and the dashed line indicates the sectioned line. The sectioned grain is different from that shown in Fig. 6. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.4. Investigation of inhomogeneous distribution of constituents inside a grain

Heterogeneous distribution of constituents inside a polished rice grain was investigated by observing the Raman spectral features acquired at different local spots on the sectioned face of a grain. For this purpose, a rice grain was cut as described in Fig. 6; the dashed line indicates the sectioned line, and the right picture shows the sectioned face of the grain. As shown, the embryo (yellowish color inside) and endosperm (translucent white color) are clearly apparent. On the sectioned face, Raman spectra were collected using a microscope at 3 different spots indicated by the arrows in Fig. 6. Triplicate spectra were collected around each spot. The feature of spectra ♯1 acquired at the endosperm is similar to that of starch, which is not surprising as the endosperm is composed mostly of starch. The spectral features collected at the embryo (♯2 and 3) are dramatically different compared to that of the endosperm, since the major component of the embryo is fat. The spectral features collected at two different locations in the embryo were also different, and the underlying fluorescence intensities varied, clearly indicating a larger compositional variation in embryos.

Another sectioned sample was prepared by slicing out the middle part of a grain (left picture, Fig. 7) and Raman line mapping across the center of a sectioned face (right picture, Fig. 7) was performed. The red dots in the right picture indicate where the laser was irradiated for the spectral collection. In this case, the region of opaque white color was observed inside the sectioned face as indicated by the arrow corresponding to the white core/belly (alternatively, chalky endosperm), which is less condensed starch formed inside the grain [32–34]. Other than white core/belly, the rest of the grain is endosperm (translucent white color).

Out of the total 14 mapping spectra, 5 and 9 spectra were collected in white core/belly and endosperm sections, respectively, and the spectra collected in the same section were averaged for comparison. Raman spectra (1700–390 cm^{-1} range) representing white core/belly (red) and endosperm (black) are shown in Fig. 7. Both spectra were normalized as described above. The spectral features of both constituents are similar since these are very similar carbohydrates with only minute structural differences. Other than the difference in band intensities, tiny differences in the band shape were observed in the 1500–1420, 1280–1230, 1160–1100 and 1080–1000 cm^{-1} ranges.

As shown in Figs. 6 and 7, the heterogeneous distribution of rice constituents in a grain can be clearly confirmed based on the results. Therefore, transmission Raman measurement enabling transverse sampling across a packing of rice grains should be a proper choice for representative spectral sampling of the packing, thereby eventually leading to a more accurate discrimination of the geographical origins of rice samples.

4. Conclusions

Since the constituents of rice were not homogeneously distributed in a grain as confirmed using Raman microscopy, transmission Raman measurement was advantageous for a better spectral representation of packed rice samples due to its transverse sampling capability across a packing. Isotropically diffused laser radiation inside a packing also helped to improve the sample representation by interacting with a larger number of grains. If the use of a higher power laser or longer laser exposure is allowable, transmission spectral collection through the thicker packing of granular samples is feasible. This could result in further improvements in spectral representation for a batch of samples. When fast non-destructive spectroscopic analysis of packed granular samples is desired, diffuse reflectance near-infrared (NIR) spectroscopy [35] has been most frequently utilized. In the future, transmission Raman spectroscopy may be a highly comparable analytical method since it could improve the accuracy of analysis due to the availability of more selective and less moisture-insensitive spectral features compared those provided by NIR spectroscopy. The proposed analytical scheme could be also adoptable to a portable Raman spectrometer for at-site measurement in an actual field.

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