Introduction

NIR spectroscopy is a simple and non-destructive analytical tool employed in diverse fields. Acquired NIR spectra are well representative of samples’ organic constituents. NIR bands are generally broad and their component-specificities are thereby not high. The combination of NIR data with other spectroscopic data could be a versatile choice to potentially improve accuracy of target analysis. First, NIR spectroscopy was combined with laser-induced breakdown spectroscopy (LIBS) to enhance the discrimination of soybean paste samples according to geographical origin. Second, NIR and Raman spectroscopy were adopted together for the discrimination of red pepper powder samples according to geographical origin. In these studies, various strategies for the data combination (fusion) and their characteristics will be discussed.

Materials and methods

Collection of soybean paste and red pepper samples

Commercially available soybean paste and red pepper samples provided from the National Agricultural Products Quality Management Service (NAQS) in Gimcheon, Korea.

- A total of 97 soybean paste samples; 35 imported samples and 62 domestic samples
- A total of 103 red pepper powder samples included 52 domestic, 51 imported samples

LIBS and NIR measurements of soybean paste samples

- Each LIBS spectrum was recorded by accumulating optical emissions from 160 laser exposures over an 8 mm line-scan, and 30 LIBS spectra were obtained by performing separate 8 mm line-scans per sample.
- Diffuse reflectance NIR spectra (range: 6050-4000 cm⁻¹, resolution: 8 cm⁻¹, 64 scans) of the powder samples were collected using a MB-3600 FT-NIR spectrometer.

Raman and NIR measurements of red pepper samples

- Raman spectra (range: 1704-804 cm⁻¹, resolution: 1 cm⁻¹), were obtained by Cora 5001 Raman spectrometer with 1064nm laser due to fluorescence of red pepper.
- Each Raman spectrum was collected by accumulating 30 scans with a laser exposure time of 5 s at each scan
- The NIR spectra were measured in the same way as the soybean paste sample.

Results

NIR spectroscopy combined with LIBS to discriminate geographical origin of soybean paste

A. NIR-based discrimination of geographical origins of soybean paste samples

B. LIBS-based discrimination of geographical origins of soybean paste samples

C. Combination of LIBS and NIR spectral features for discrimination

NIR spectroscopy combined with Raman spectroscopy to discriminate origin of red pepper

A. NIR and Raman spectra of red pepper samples and discrimination result

B. Application of hetero 2D Raman/NIR spectroscopy correlation and discrimination result

Discrimination result by k-NN

<table>
<thead>
<tr>
<th>PC scores for k-NN</th>
<th>Accuracy</th>
<th>Specificity</th>
<th>Sensitivity</th>
</tr>
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<tbody>
<tr>
<td>NIR spectra</td>
<td>93.6±1.5%</td>
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</tr>
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<td>Raman spectra</td>
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</tr>
<tr>
<td>hetero 2D slice</td>
<td>97.4±0.6%</td>
<td>96.2±1.1%</td>
<td>96.6±4.6%</td>
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- As a result of discrimination using Raman or NIR spectra, the accuracies were less than 94%
- When hetero correlation was applied, the accuracy was increased to 97 ±4.0%

Conclusion

- LIBS or Raman data were combined with NIR data, the discrimination accuracy was higher than before.
- Elemental information obtained from LIBS spectra was complementary to NIR spectra.
- Information of different vibration bonds from Raman and NIR was also complementary.
- In addition, these combination methods can be used for discrimination analysis on food and agricultural samples.
Results
NIR spectroscopy combined with LIBS to discriminate geographical origin of soybean paste

A. NIR-based discrimination of geographical origins of soybean paste samples

- **Average NIR raw spectra**
  - Imported sample
  - Domestic sample

- **PC scores of NIR raw spectra**
  - Accuracy: 83.6%

- **Asynchronous 2T2D slice spectra**

- **PC scores of 2T2D spectra**
  - Accuracy: 89.2%

B. LIBS-based discrimination of geographical origins of soybean paste samples

- **Average LIBS spectra**
  - Normalized intensity
  - Wavelength (nm)

- **Distribution of $A_{Ca}$ and $A_{C}$ values**
  - Accuracy: 95.4%
  - $p$-value < 0.0001

- **$A_{Ca} / A_{C}$ values in the two groups**

C. Combination of LIBS and NIR spectral features for discrimination

- **$A_{Ca} / A_{C}$ and 2nd PC score of 2T2D slice spectra in narrow range**
  - Accuracy: 99.6%

- **In NIR spectra data, when 2T2D correlation analysis was used, the discrimination accuracy increased to 95.3%**.
- **In LIBS data, among the area of 8 elements (Ca, K, Mg, Na, C, H, O, N), $A_{Ca}$ and $A_{C}$ were efficient in discrimination**.
- **The $A_{Ca} / A_{C}$ is combined with NIR 2T2D spectra in narrow range, the discrimination accuracy increased to 99.6%**.
**NIR spectroscopy combined with Raman spectroscopy to discriminate origin of red pepper**

**A. NIR and Raman spectra of red pepper samples and discrimination result**

**B. Application of hetero 2D Raman/NIR spectroscopy correlation and discrimination result**

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**Discrimination result by k-NN**

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- The NIR spectra were measured in the same way as the soybean paste sample.

Results

NIR spectroscopy combined with LIBS to discriminate geographical origin of soybean paste

A. NIR-based discrimination of geographical origins of soybean paste samples

- The average spectrum of imported samples was adopted as the reference spectrum to perform 2T2D correlation analysis.
- The difference was highlighted using the range 5203-4929 cm⁻¹.
- When using raw NIR spectra, the accuracy was 84.3%.
- When 2T2D slice spectra was used, the accuracy increased to 91.5±1.8%.
- In case of 2T2D spectra in narrow range, the accuracy improved to 95.0±1.7%.

B. LIBS-based discrimination of geographical origins of soybean paste samples

- Area normalization was performed.
- Among the area of 8 elements (Ca, K, Mg, Na, C, H, O, N), A_Ca and A_K were efficient in discrimination.
- The p-value by t-est for A_Ca was smaller than 0.0001. The accuracy was 95.4±1.1%.

C. Combination of LIBS and NIR spectral features for discrimination

- AsL5 was used to remove background caused by fluorescence.
- In both PC scores of Raman & NIR, some samples overlapped.

NIR spectroscopy combined with Raman spectroscopy to discriminate origin of red pepper

A. NIR and Raman spectra of red pepper samples and discrimination result

- AsL5 was used to remove back
- ground caused by fluorescence.
- In both PC scores of Raman & NIR, some samples overlapped.

B. Application of hetero 2D Raman/NIR spectroscopy correlation and discrimination result

- Hetero 2D correlation is used, difference between in two groups is highlighted.
- When the PC scores of asynchronous and synchronous slice spectra were combined, the classification between the two groups was improved.

Conclusion

1. LIBS or Raman data were combined with NIR data, the discrimination accuracy was higher than before.
2. Elemental information obtained from LIBS spectra was complementary to NIR spectra.
3. Information of different vibration bonds from Raman and NIR was also complementary.
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