Non-destructive measurement system for process control using combined spectroscopic data

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Abstract Raw sugar manufacture from sugarcane is one of the important industries in the southern part of Japan. The possibility for predicting chemical components of cane juice samples was investigated using visible to near-infrared (Vis-NIR) and mid-infrared (MIR) spectroscopic data in order to develop a rapid and accurate measurement system. The combined spectra of cane juice were measured with two types of spectrometers. Calibration models for the prediction of pol and ion components were developed using PLSR (partial least squares regression) analysis. Most of calibration models using the combined spectroscopic data showed higher correlation than that using only NIR instrument data. The efficient optimisation of process control in sugar mills can be expected through the timely feedback of chemical information obtained from the spectroscopic measurement system.

Key words Process control, near-infrared spectroscopy (NIRS), mid-infrared spectroscopy (MIRS), juice component

INTRODUCTION

Near-infrared (NIR) spectroscopy has been widely used for the measurement of sugar content in many agricultural and food products (Osborne et al. 1993). This method is a non-destructive and rapid technique that allows the determination of multiple properties at the same time without any sample preparation or reagents. These features make this technique suitable for the on-line monitoring of plants, i.e. ripening of fruit. In sugarcane production, NIR methods have been also used for determining quality parameters in cane (Berding et al. 1991; Taira et al. 2013). Many studies have previously reported the analysis of sugarcane juice samples using NIR spectroscopy. Pol value is conventionally used as a quality index in the sugar industry and this is the most important parameter in the evaluation of cane quality and/or maturity in sugarcane production. In addition, information on ion components is also important for diagnosis of cane status and also for sugar manufacturing in the raw sugar mill processes. However, rapid and simultaneous measurement for quality and ion components in cane juice by NIR spectroscopy has not been reported. Mid-IR (MIR) spectroscopy also has been used for qualitative and quantitative analysis in general. MIR spectra have information for vibration of molecules and the spectrum of a liquid sample is measured easily with an ATR accessory.

In this paper, we describe the possibility of predicting sugar and ion component using two types of spectroscopic data.

MATERIALS AND METHODS

Sample and preparation

We collected 100 cane samples from 10 sugar mills in Japan during the 2012/2013 harvest season. The cane samples were shredded using cutter grinder (CG03, Jeffress Engineering Pty. Ltd). Approximately 550 g of the shredded sample were collected, and 25.5 MPa pressure was applied in the press device to extract the juice.

NIR analysis

Visible and NIR (Vis-NIR) measurements were performed using a NIR instrument (InfraXact, Foss Co. Ltd.) equipped with a slurry cup and a 0.5 mm thick gold reflector. The visible to NIR spectra were measured from 54230 to 17544 cm\(^{-1}\) (570 to 1848 nm in 2 nm increments). MIR spectra were measured using FT-IR (Thermo Fisher Scientific, iS5 FT-IR) with ATR attachment from 550 to 4000 cm\(^{-1}\) in 2 cm\(^{-1}\) increments. The temperature of samples was controlled with a water bath at 20°C. The time for Vis-NIR spectrum measurement was 40 sec and for MIR spectra was 20 sec in each sample.
Reference analysis

The soluble solid content (SSC) and polarimeter readings were measured using a refractometer and polarimeter (MCP500, Anton Paar GmbH), respectively. The Pol value was calculated from the Pol reading and SSC value. Ion chromatography was used for ion component analysis (Na⁺, K⁺, Mg²⁺, Ca²⁺, Cl⁻, PO₄³⁻, SO₄²⁻). The measured datasets of Pol, SSC and ion components were provided to develop the calibration models.

Data analysis

Combined spectra (visible, NIR and MIR spectra) and reference data were used to develop calibration models. Data analyses were performed with the Matlab (The Mathworks Inc., USA). Partial least square regression (PLSR) was employed to develop suitable calibrations. The maximum number for PLS factors was set to 15. Calibration models were performed using each visible-NIR range, MIR range and combined spectra to evaluate the effective range.

RESULTS AND DISCUSSION

Spectra of cane juice in Vis-NIR and MIR ranges

Figure 1 shows the Vis-NIR and MIR spectra after SNV (Standard Normal Variate) treatment for cane juice samples measured with two types of spectrometer. SNV is one of the methods for correcting the baseline shift of spectra. Four dominant peaks in the spectra were observed at 660, 1630, 3300, and 6900 cm⁻¹ – these are due to the water absorption band.

Calibration for Pol and ion components

The calibration models for chemical components were made using 197 cane juice spectra. Table 1 shows the results of calibrations for Pol, SSC and ion components. The accuracy of calibration models using MIR spectra are higher than the models using Vis-NIR spectra, except for Cl⁻. Especially, the models using MIR spectra of SO₄²⁻ and PO₄³⁻ gave higher coefficients of determination (R²) than the models using Vis-NIR. As a next step, calibration models using combined spectra were developed. The accuracy of the calibration models for Pol, SSC, K⁺, Mg²⁺ and Ca²⁺ were improved compared to the
models developed with separate instrument data. The measurement of spectroscopic data using NIR and MIR were taken easily and rapidly without any chemicals. The technique using combined spectroscopic data could be measured cane quality and ion components.

We conclude that Pol, SSC and ion measurement for cane juice using the MIR instrument with ATR accessory is possible. Moreover, combined spectroscopic data (Vis-NIR and MIR) could be used to predict the chemical components with more accuracy.

**Table 1.** Calibrations for Pol, SSC and ion components.

<table>
<thead>
<tr>
<th>Component</th>
<th>VIS-NIR</th>
<th>MIR</th>
<th>VIS-NIR and MIR</th>
</tr>
</thead>
<tbody>
<tr>
<td>R²</td>
<td>SECV</td>
<td>R²</td>
<td>SECV</td>
</tr>
<tr>
<td>Pol (%)</td>
<td>0.95</td>
<td>0.96</td>
<td>0.27</td>
</tr>
<tr>
<td>SSC (%)</td>
<td>0.96</td>
<td>0.94</td>
<td>0.32</td>
</tr>
<tr>
<td>K⁺ (mg/kg)</td>
<td>0.46</td>
<td>0.54</td>
<td>479.5</td>
</tr>
<tr>
<td>SO₄²⁻ (mg/kg)</td>
<td>0.23</td>
<td>0.94</td>
<td>103.2</td>
</tr>
<tr>
<td>Cl (mg/kg)</td>
<td>0.72</td>
<td>0.44</td>
<td>274.7</td>
</tr>
<tr>
<td>PO₄³⁻ (mg/kg)</td>
<td>0.27</td>
<td>0.85</td>
<td>125.6</td>
</tr>
<tr>
<td>Mg²⁺ (mg/kg)</td>
<td>0.29</td>
<td>0.48</td>
<td>51.8</td>
</tr>
<tr>
<td>Ca²⁺ (mg/kg)</td>
<td>0.29</td>
<td>0.56</td>
<td>57.2</td>
</tr>
<tr>
<td>Na⁺ (mg/kg)</td>
<td>0.16</td>
<td>0.27</td>
<td>28.8</td>
</tr>
</tbody>
</table>

**CONCLUSIONS**

Calibration models using combined spectroscopic data of Vis-NIR and MIR ranges were developed to predict the chemical components in cane juice. MIR spectra may be more suited for pol and ion component predictions. Furthermore, combined spectra could improve the calibration accuracy for Pol, K⁺ and some other components compared to calibrations using separate Vis-NIR and MIR.

**REFERENCES**


**Système de mesure non destructif pour le contrôle de la fabrication à l’aide de combinaisons des données spectroscopiques**

Résumé. La fabrication du sucre brut de canne est l’une des industries importantes dans le sud du Japon. La possibilité de prédire les composants chimiques des échantillons de jus de canne a été étudiée à l’aide du visible au proche infrarouge (Vis-NIR) et des données de spectroscopie infrarouge moyen (MIR) afin de développer un système de mesure rapide et précis. Les spectres combinés du jus de canne ont été mesurées avec deux types de spectromètres. Les modèles de calibration pour la prédiction du pol et des ions, ont été développés en utilisant l’analyse statistique PLSR. La plupart des modèles d’étalonnage à l’aide de la combinaison des données spectroscopiques a montré une corrélation plus élevée que celle utilisant uniquement des données de l’instrument NIR. L’optimisation du contrôle de fabrication dans les usines est prévue grâce aux informations chimiques, en temps réel, obtenues à partir du système de mesure spectroscopique.

Mots-clés: Contrôle de fabrication, spectroscopie proche infrarouge (NIRS), spectroscopie infrarouge moyen (MIRS), composant de jus
Sistema de medición no destructivo para control de procesos usando datos de espectroscopia combinada

Resumen. La fabricación de azúcar crudo a partir de caña de azúcar es una de las industrias importante en la región sur de Japón. Se investigó la posibilidad de predecir componentes químicos de muestras de jugo de caña usando espectroscopia visible-infrarrojo cercano (Vis-NIR) e infrarrojo medio (MIR) en orden de desarrollar un sistema de medición rápido y preciso. Los espectros combinados de jugo de caña se midieron con ambos tipos de espectrómetros. Los modelos de calibración para la predicción de pol y componentes iónicos se desarrollaron usando análisis de regresión de cuadrados mínimos parciales (PLSR). La mayoría de los modelos de calibración usando los datos espectroscópicos combinados mostraron correlaciones más altas que usando solo datos obtenidos por NIR. La optimización eficiente del control de procesos en fábricas de azúcar se puede esperar a través de la retroalimentación oportuna de la información química obtenida del sistema de medición espectroscópico.

Palabras clave: Control de procesos, espectroscopia de infrarrojo cercano (NIRS), espectroscopia de infrarrojo medio (MIRS), componentes del jugo.