A Quantitative Study for Determination of Sugar Concentration Using Attenuated Total Reflectance Terahertz (ATR-THz) Spectroscopy

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ABSTRACT

The objective of our research was to use ATR-THz spectroscopy together with chemometric for quantitative study in food analysis. Glucose, fructose and sucrose are main component of sugar both in fresh and processed fruits. The use of spectroscopic-based method for sugar determination is well reported especially using visible, near infrared (NIR) and middle infrared (MIR) spectroscopy. However, the use of terahertz spectroscopy for sugar determination in fruits has not yet been reported. In this work, a quantitative study for sugars determination using attenuated total reflectance terahertz (ATR-THz) spectroscopy was conducted. Each samples of glucose, fructose and sucrose solution with different concentrations were prepared respectively and their absorbance spectra between wavenumber 20 and 450 cm^{-1} (between 0.6 THz and 13.5 THz) were acquired using a terahertz-based Fourier Transform spectrometer (FARIS-1S, JASCO Co., Japan). This spectrometer was equipped with a high pressure of mercury lamp as light source and a pyroelectric sensor made from deuterated L-alanine triglycine sulfate (DLTGS) as detector. Each spectrum was acquired using 16 cm^{-1} of resolution and 200 scans for averaging. The spectra of water and sugar solutions were compared and discussed. The results showed that increasing sugar concentration caused decreasing absorbance. The correlation between sugar concentration and its spectra was investigated using multivariate analysis. Calibration models for glucose, fructose and sucrose determination were developed using partial least squares (PLS) regression. The calibration model was evaluated using some parameters such as coefficient of determination (R^2), standard error of calibration (SEC), standard error of prediction (SEP), bias between actual and predicted sugar concentration value and ratio prediction to deviation (RPD) parameter. The cross validation method was used to validate each calibration model. It is showed that the use of ATR-THz spectroscopy combined with appropriate chemometric can be a potential for a rapid determination of sugar concentrations.

Keywords: ATR-THz Spectroscopy, sugar solution, calibration model, PLS regression

1. INTRODUCTION

Quantitative analysis of sugar in solution is not only important in fermentation and brewing processes but also in the manufacture of soft drinks. Recently the use of spectroscopic method for sugar determination is becoming popular. Among the available spectroscopic method, visible-near infrared (NIR) spectroscopy and middle infrared (MIR) spectroscopy have been well established technology (Lanza & Li, 1984; Kemsley et al., 1992). However, it is not yet been reported, the use of terahertz (THz) spectroscopy for quantitatively measuring sugar concentration. Not only has quantitative analysis, THz spectroscopy had potential to be used as qualitative analysis tool in food industry. For example, we can investigate the influence of temperature of sample to the spectrum of THz.

Terahertz (THz) spectroscopy can be referred as the study on interaction between matter and electromagnetic wave in the terahertz spectral region from 300 GHz (λ = 1 mm) to 10 THz (λ = 30 μm) (Dexheimer, 2007). The development of THz technology including device for generating and detecting THz wave has opened the possibility to bring THz spectroscopy in more practical manner. Since water has strong absorption in THz region, a special sample preparation so called attenuated total reflectance (ATR) was used to obtain spectroscopic information of glucose solution. This ATR method was also used previously for glucose concentration measurement in MIR spectroscopy (Sivakesava and

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Irudayaraj, 2000). In this study, we will show the potential of ATR-THz spectroscopy as an analytical method for the determination of glucose concentrations in aqueous solutions.

2. MATERIALS AND METHOD

2.1 Materials

In this study, a number of 50 samples of glucose concentration were prepared by dissolving appropriate amounts of glucose powder in distilled water. The ranges of concentrations were from 0.5 to 30% (w/w). The samples then divided into two sets, calibration and validation sample set, randomly. Calibration sample set was used to develop calibration model. The developed model will be validated using validation sample set. The prepared samples were stored in room temperature one day prior to spectra measurement.

2.2 Spectral acquisition method

Spectra of each sugar solution were acquired using a terahertz-based Fourier Transform spectrometer (FARIS-1S, JASCO Co., Tokyo, Japan). This spectrometer was equipped with a high pressure of mercury lamp as light source and a pyroelectric sensor made from deuterated L-alanine triglycine sulfate (DLTGS) as detector (Figure 1). All spectra measurements were conducted on 150 Pa of pressure. Spectrum of air was used as reference and was repeated for every five samples. Each spectrum was acquired using 16 cm^{-1} of resolution and 200 scans for averaging both for sample and reference. Software of spectral manager for windows (JASCO Spectral Manager, JASCO co., Tokyo, Japan) was used to control the spectral acquisition. The absorbance spectra of samples were acquired three times for each samples and its average value was used for ATR correction. The corrected values then were imported to the Unscrambler for further analysis.

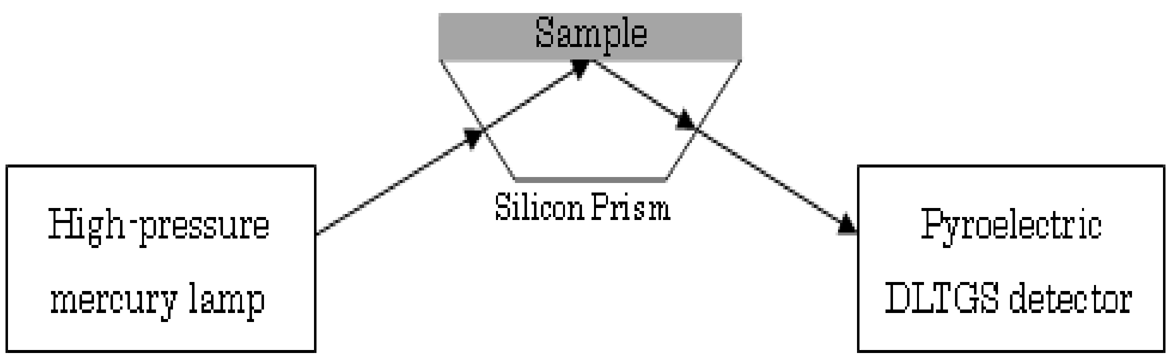

Figure 1. The schematic diagram of spectral measurement using ATR-THz spectroscopy.

2.3 Spectral analysis

The average spectra from 3 replicates were processed using different pre-processing methods. Spectral pre-processing is required to remove any irrelevant information such as noise and scattering effect. Recently many pre-processing method are available in the commercial chemometric analysis tools. Here in our study, some pre-processing method will be used including smoothing (moving average and Savitzky-Golay smoothing), multiplicative scatter correction (MSC), standard normal variate (SNV), Norris derivative and Savitzky-Golay first and second derivative.

The averaging technique is used to reduce the number of wavelengths or to smooth the spectrum of sugar solutions. It s also used to optimize the signal-to-noise ratio (Cen and He, 2007). Calculation of derivation spectra based on Savitky-Golay is very popular and improve the calibration model. Principal component analysis (PCA) was performed before developing model to determine any relevant and interpretable structure in the data and to detect outliers (Naes et al., 2002; Adams, 1995). PCA searches for directions of maximum variability in sample grouping and uses them as new axes called principle components that can be used as new variables, instead of the original data, in following calculations (Blanco and Villarroya, 2002). All of these analyses were performed using The Unscrambler® version 7.01 (CAMO, Oslo, Norway), statistical software for multivariate analysis. A student's t-test was performed using Statistical Package for the Social Science (SPSS) version 11.0 for Windows in order to evaluate the significance level of the model.

Quality of the calibration model was evaluated using following statistical parameters such as coefficient of determination between predicted and measured sugar (R^2), standard error of calibration (SEC), standard error of prediction (SEP), bias between actual and predicted glucose concentration and ratio prediction to deviation (RPD) value.

3. RESULTS AND DISCUSSIONS

3.1 Typical ATR spectra of glucose solution in THz region

Figure 2 shows the typical ATR spectrum of glucose solution (glucose+water) in the THz region. The peak of absorbance was identified at about 150.42 cm^{-1} (about 6THz) and the valley at about 250 cm^{-1} (about 8 THz). This result was well confirmed with previous reports. Ogawa et al. (2009) in the previous study showed the peak at 4 THz and valley at 8 THz of water absorbance. The presence of glucose in the water in our study has shifted the peak and valley location of water absorbance to lower frequency.

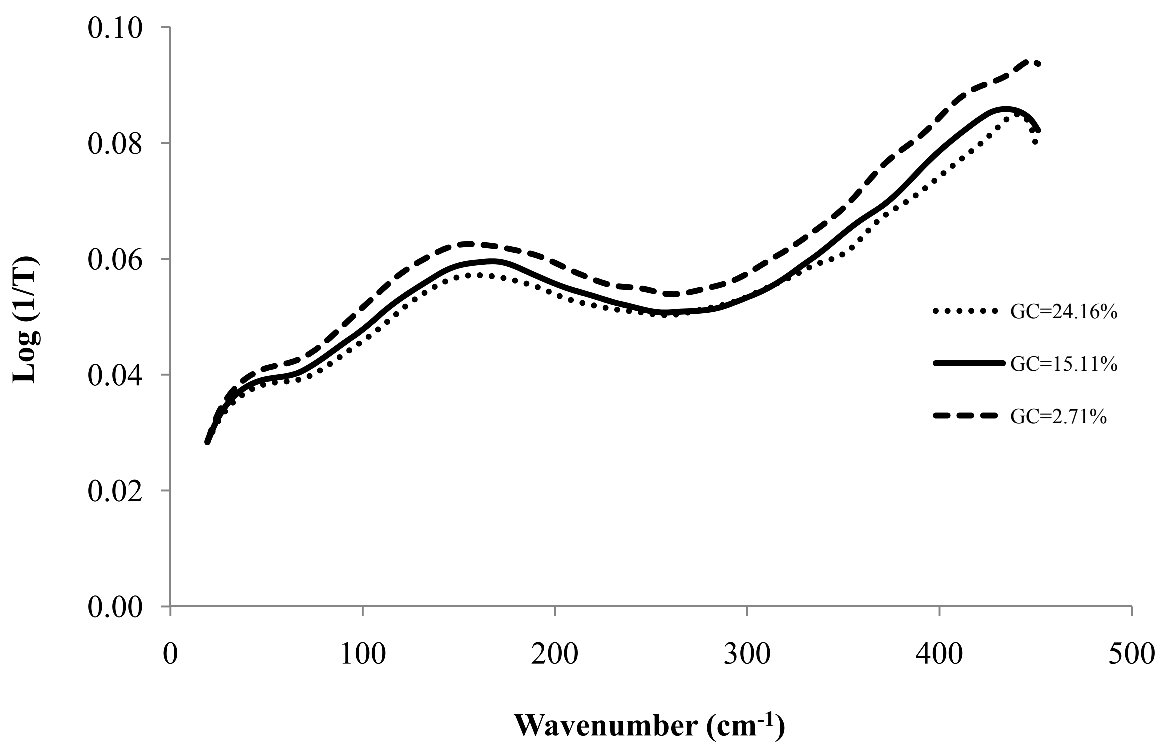

Figure 2. Typical ATR spectra of glucose solution with different concentration in THz region.

3.2 Developing calibration model for glucose concentration determination

Using the PLS regression method the calibration and validation was performed for original pre-processing spectra. Calibration model using the PLS method should have enough number of factors (F) to optimize the prediction model and to avoid over-fitting. Furthermore, the best calibration model can be characterized as follows. These are low number of factors (F), high coefficient of determination (R^2), low standard error of calibration (SEC), low standard error of prediction (SEP) and low bias. The ratio of standard error of prediction to standard deviation (RPD) value was the other parameter used for evaluating the performance of calibration model. For good prediction model, it is desirable that high RPD value is required (Williams, 1987).

Using original spectra, calibration model resulted in high coefficient of determination (R^2=0.99). The pre-processing of spectra was effective in improving the calibration model, except for MSC and SNV spectra. For smoothing spectra, calibration model was improved both using moving average and Savitzky-Golay. Using derivative spectra, all pre-processing including first, second Savitzky-Golay and Norris derivative significantly improved the quality of calibration model. The best calibration model could be identified for Savitzky-Golay second derivative spectra with lowest SEP and highest RPD value (Table 2). This calibration model was comparable to that reported by Sivakesava and Irudayaraj (2000) for individual glucose concentration determination with R^2 = 0.99 and SEC = 0.5~0.7%. The scatter plot between actual and predicted glucose concentration in the best calibration model is presented in Figure 3.

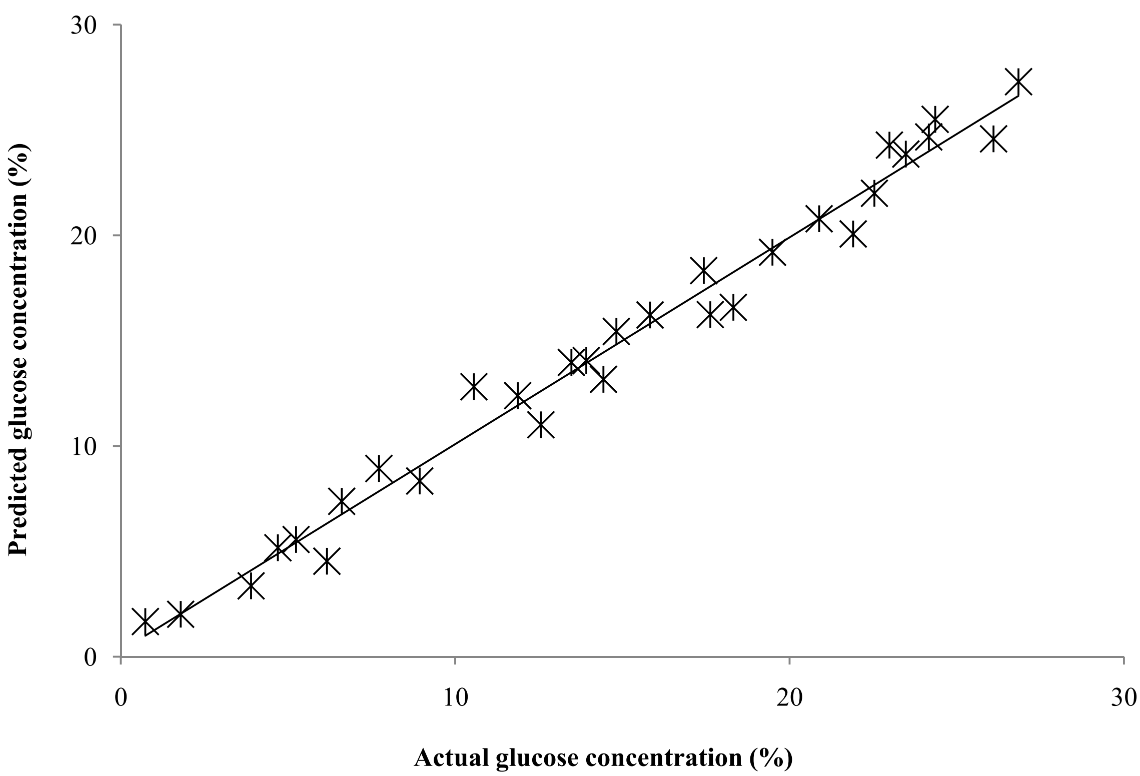

Figure 3. Scatter plot between actual and predicted glucose concentration of the best calibration model.

3.3 Validation of calibration model

The validation of original and pre-processing calibration model resulted in low SEP except for MSC and SNV spectra. The performance of the validation using the best calibration model of Savitzky-Golay second derivative spectra was very excellent with lowest SEP and highest RPD value. Scatter plot of validation result between actual and predicted values using the best calibration model is presented in Figure 4. By a 95% confidence pair t-test, there were no significant differences between measured and predicted glucose concentration. This result showed that a calibration model for determination of glucose concentration using ATR-THz spectroscopy could be successfully developed and well validated.

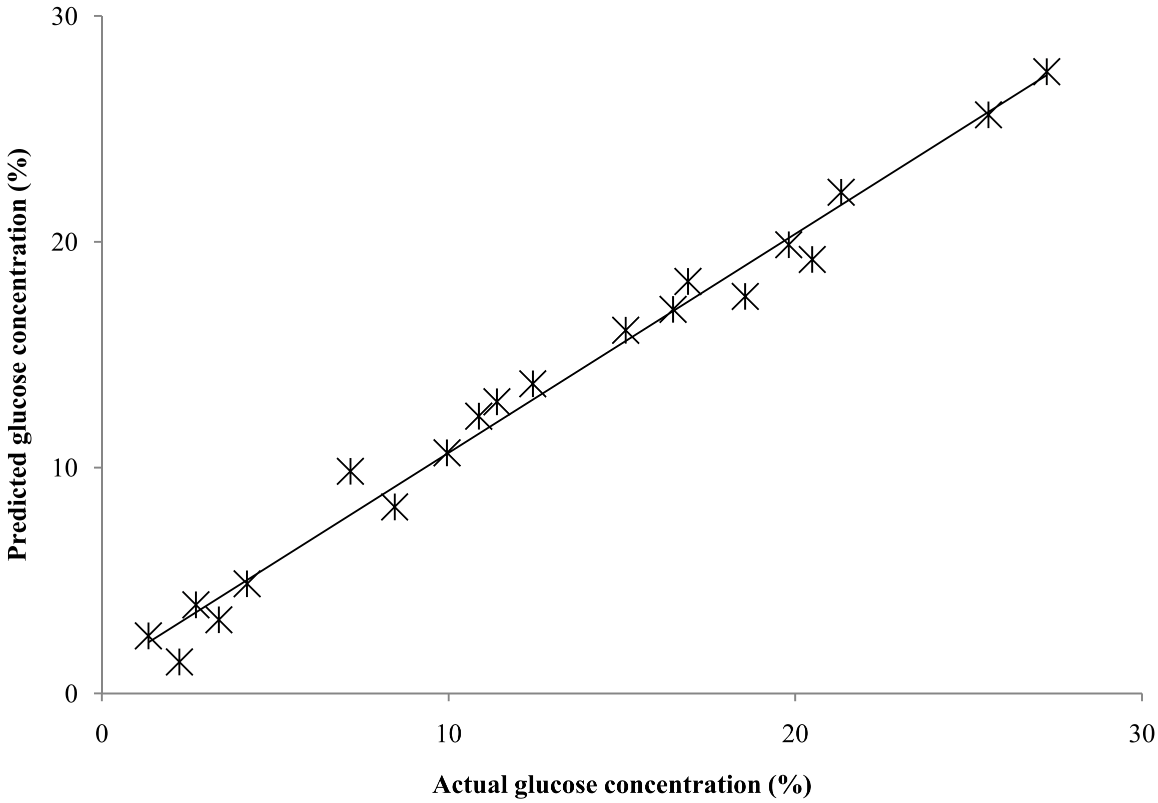

Figure 4. Scatter plot between actual and predicted glucose concentration in validation step.

4. CONCLUSIONS

The ATR-THz spectroscopy provides an easy, direct but reliable method to obtain glucose solution spectra in THz region. The potential use of ATR-THz spectroscopy together with appropriate chemometric for glucose concentration determination has been successfully demonstrated. The calibration model for glucose concentration determination was successfully developed and well validated. The best calibration model using Savitzky-Golay second derivative spectra resulted in lowest SEP and very high of RPD value. This promising result can be applied for rapid analysis of glucose concentration and open the application of THz spectroscopy in food analysis. In next future works, it is very important to evaluate the possibility of using this method for concentration determination of other sugars such fructose and sucrose and in mixture solution. The influence of temperature of sugar is also very interesting to be investigated. It is very common that in lower temperature, some sugar may taste sweeter than that in higher temperature.

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