Research Paper

EAEF 5(3) : 90-95, 2012

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

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Abstract

In this work, a quantitative study for glucose concentration determination was conducted using ATR-THz spectroscopy. Glucose solutions with different concentrations were prepared and their absorbance spectra between wavenumber 19.285 cm^{-1} and 451.261 cm^{-1} were acquired using a terahertz-based Fourier transform spectrometer. The spectra of glucose solutions in different concentrations were compared and discussed. The results showed that increasing glucose concentration caused decreasing absorbance. Calibration models for glucose determination were developed using partial least squares (PLS) regression for original and pre-processing spectra. The calibration model using Savitzky-Golay second derivative spectra gave satisfactory results. The use of ATR-THz spectroscopy combined with an appropriate chemometric method has potential for a rapid determination of glucose concentrations in aqueous solution.

[Keywords] ATR-THz spectroscopy, terahertz wave, glucose solution, calibration model, PLS regression, quantitative analysis

I Introduction

Quantitative analysis of sugar in solution is not only important in fermentation and brewing processes but also in the manufacture of soft drinks. High Pressure Liquid Chromatography (HPLC) method can measure accurately sugar components like glucose, fructose and sucrose (Shaw, 1988). However it is difficult to apply to production line measurement. Recently the use of a spectroscopic-based method for sugar determination is becoming popular. Among the available spectroscopic methods, visible-near infrared (Vis-NIR) spectroscopy and mid-infrared (MIR) spectroscopy have been well established, with advance development of instrumentation and a broad range of its application, including the food industry (Lanza & Li, 1984; Kemsley *et al*., 1992; Giangiacomo & Dull, 1986; Sivakesava & Irudayaraj, 2000). Both the NIR and MIR spectroscopic methods are faster than HPLC, no or little sample preparation is necessary and they are more suitable for process control applications.

In MIR spectroscopy, the use of attenuated total reflectance (ATR) method together with chemometric method for analysis of sugars in solution or powder samples have been well reported (Wilson & Tapp, 1999). De Lene Mirouze *et al*. (1993) used principal component regression (PCR) and partial least squares (PLS) regression to determine glucose concentration in glucose syrup. Quantitative analysis of glucose and other sugars (maltose, maltotriose, and maltodextrines) using PLS regression was also reported by Bellon-Maurel *et al*. (1995a; 1995b). Dupuy *et al*. (1993) also used PLS regression to quantify the glucose concentration in powdered sugar.

In the terahertz (THz) region, Hirori *et al.* (2004) showed the possibility of using the ATR method in the THz region to study distilled liquid water. Later Jepsen *et al*. (2007) used terahertz reflectance time-domain spectroscopy (THz-TDS) in the low frequency range (0.1-1.0 THz) to show the potential of this region for the determination of sugar (sucrose) concentration. However the use of ATR-THz spectroscopy especially in the low and high frequency (0.6 to 13.5 THz) together with chemometric method for measuring glucose concentration has not yet been reported. This region, especially in low frequency (0.3- 6 THz, or 10-200 cm^{-1}) has rich information with intramolecular and intermolecular vibrational modes of biological molecules (Laman *et al.*, 2008). While NIR and MIR spectroscopy utilize electromagnetic waves which correspond to stretching or bending motions of individual bonds in the molecule, in contrast, in far infrared or the THz region electromagnetic waves correspond to motions

* Partly presented at the 124th JSAM Kansai Branch Annual Meeting at Okayama University in August 2010 and at SPIE Defense Security and Sensing 2011 at Orlando Florida USA in April 2011

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of the entire structure (Laman *et al.*, 2008).

THz waves had not been studied practically for a long time because of the difficulty of generating and detecting THz waves compared with the better-established technologies of optics and electronics. However, the recent development of THz devices has opened the possibility to apply THz waves in many fields (Mantsch & Naumann, 2010). THz spectroscopy is the study of interactions between matter and electromagnetic waves in the terahertz spectral region from 300 GHz (λ = 1 mm) to 10 THz (λ = 30 μm) (Dexheimer, 2007). The THz region is located between microwave and far infrared waves. THz waves have properties of both sides of the electromagnetic spectrum. Like microwaves, THz wave can be transmitted through a wide variety of substances such as paper, cloth, ceramics, plastics, and wood. Like infrared, THz wave can easily be propagated through space and reflected using THz optical devices.

Since water has strong absorption in the THz region, attenuated total reflectance (ATR) method was used as sample presentation to obtain spectroscopic information of glucose in solution. In this study, we will show the potential of using ATR-THz spectroscopy coupled with appropriate chemometric methods as an analytical method for the determination of glucose concentrations in aqueous solutions especially in monocomponent solutions.

II Materials and Methods

1. Materials

Fifty samples of various glucose concentrations were prepared by dissolving appropriate amounts of glucose powder (Grade: Guaranteed Reagent (GR); Nacalai Tesque, Inc., Kyoto, Japan) in distilled water. The ranges of concentrations were from 0.5 to 30% (mass percent, w/w). For each sample, 300 μL of glucose solution were used for spectral acquisition. The samples were then divided randomly into two sets, calibration and validation sample sets. The calibration sample set was used to develop a calibration model. The developed calibration model was validated using the validation sample set (known as external validation). The characteristics of the two samples are explained in Table 1.

Table 1 Properties of calibration and validation sample sets used for glucose concentration determination

Items	Calibration set	Validation set
Number of samples	30	20
Maximum value	26.85	27.26
Minimum value	0.73	1.34
Mean	14.65	12.78
Standard deviation (SD)	7.73	7.93
Units	%(w/w)	%(w/w)

2. Spectral acquisition method

Spectra of glucose solutions were acquired using a terahertz-based Fourier Transform spectrometer (FARIS-1S, JASCO Co., Tokyo, Japan). This spectrometer was equipped with a high pressure mercury lamp as light source and a pyroelectric sensor made from deuterated L-alanine triglycine sulfate (DLATGS) as detector. The whole system was vacuumed and all spectra measurements were conducted under 150 Pa of air pressure. The spectrum of air was used as a reference and was repeated for every five samples. Each spectrum was acquired using 16 cm^{-1} of resolution and 200 scans for averaging both the sample and the reference. Using this parameter, the interval for each spectral acquisition is 3.857 cm^{-1}. During THz spectral measurement, the temperature and the related humidity were kept around 25°C and 70% respectively. The software 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 sample and its average value was used for ATR correction. The corrected ATR absorbance values then were imported to The Unscrambler® version 9.8 (CAMO, Oslo, Norway), a statistical software for multivariate analysis.

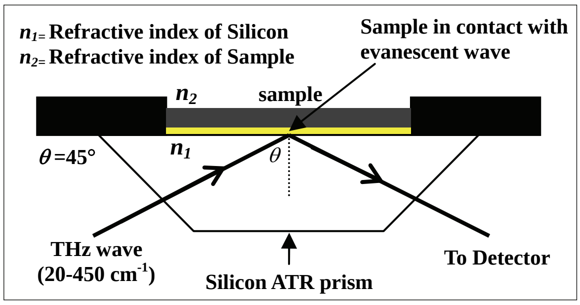

Fig. 1. The schematic diagram of spectral measurement using ATR-THz spectroscopy

3. Attenuated total reflectance (ATR) in THz region

In the past the transmission method of infrared spectroscopy was very popular and widely used. However, since water has strong absorbance in the THz region, it is difficult to obtain a good spectrum of a solution sample using the transmission method. Instead of using the transmission method, for our sample solutions we used the ATR method. Here, the main part of ATR is a silicon ATR prism that has a higher refractive index than the sample (Figure 1). THz waves generated from the high-pressure mercury lamp go to the silicon prism and generate evanescent waves. Evanescent waves then penetrate the sample. The penetration depth of our ATR system can be calculated using the following equation