

Determination of Water Content in Ethanol by Miniaturized Near-Infrared (NIR) System

Soohwa Cho, Hoeil Chung,* Young-Ah Woo,[†] and Hyo-Jin Kim[†]

Department of Chemistry, College of Natural Sciences, Hanyang University, Seoul 133-791, Korea

*E-mail: hoeil@hanyang.ac.kr

[†]College of Pharmacy, Dongduk Women's University, Seoul 136-814, Korea

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The miniaturized NIR (Near-infrared) spectrometer has been utilized for the determination of water content (1-19% range) in ethanol that is the most popular organic solvent in pharmaceutical industries. It has many potential capabilities that can replace the conventional analyzers especially for the on-line measurement since it is compact, versatile and cost-effective. By using two dimensional (2D) correlation spectroscopy, it was preliminarily investigated to find any unforeseen spectral distortion among the spectra collected from the miniaturized spectrometer. The 2D study revealed that the spectral variation clearly followed the variation of water concentration without any spectral distortion or abnormality. PLS (Partial Least Squares) was employed to build the calibration model and the resulting prediction performance was acceptable and stable over several days. Even though the miniaturized NIR system was evaluated to fairly simple chemical matrix, the overall study demonstrates the sufficient feasibility for diverse practical and industrial applications.

Key Words : Near-infrared spectroscopy, Miniaturized spectrometer, Ethanol solution, 2D correlation spectroscopy

Introduction

Ethanol is one of the most popular organic materials in the pharmaceutical industry for use as a general solvent as well as an extraction agent. Due to its heavy usage, it is usually purified and regenerated by recycling used ethanol. The majority of the used ethanol stream contains methanol and water as impurities. Therefore, for optimal recycling of ethanol, the continuous monitoring of the water content is very important. Karl Fisher titration has been employed at large for this purpose. However, this method is very slow, destructive and easily subject to human errors. Near-infrared (NIR) spectroscopy^{1,2} is an excellent analytical tool used to replace the wet analysis method because it is fast, non-destructive and capable of continuous on-line measurement.^{3,4} In addition, it has been applied for the analysis of various alcoholic beverages such as beer, wines and distilled liquors.¹ Recently, the development of the small-scale NIR instrument has gained widespread attention since it is compact, relatively cheap and versatile in use.

In this study, a miniaturized NIR spectrometer has been developed and investigated for the determination of water content in the methanol/ethanol matrix. This system is composed of a tungsten-halogen lamp, a transmittance-type fiber optic sample probe, a non-moving self-focusing grating and a photo-diode array (PDA) detector. There are no moving components in this system. The detailed instrumental description can be found in the previous publication.⁵ NIR spectra were collected for the samples (1% to 19% water content) and quantitative analysis was performed using the partial least squares (PLS) regression method.⁶⁻¹⁰ Additionally, two dimensional (2D) correlation spectroscopy¹¹⁻¹³ was employed to confirm the systematic spectral variation based on the concentration dependence. Overall results demonstrate that our miniaturized NIR system has a strong potential for use in many industrial on-line applications.

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Experimental Section

Sample preparation: High purity anhydrous ethanol and methanol (99.9% purity) were used. Initially, an ethanol/methanol mixture (of constant concentration) was prepared along with samples of various water concentrations. Ten samples from 1% to 10% (in 1% increments) and five samples from 11% to 19% (in 2% increments) were prepared. In total, 15 samples were prepared and used as the calibration sets. For validation, 3%, 5% and 7% samples were newly prepared each day and predicted over 5 days. All the NIR spectra were collected at room temperature.

Miniaturized NIR system and data processing: The overall schematic diagram of the miniaturized spectrometer is shown in Figure 1 and the more in-depth instrumental description is available elsewhere.⁵ The major component was the micro-spectrograph including the self-focusing diffraction grating with fiber fixing grooves fabricated by the combined use of lithography and micro-molding technologies. The light launched from the optical fiber is illuminated to the surface of the grating. An InGaAs photo-diode array (PDA) with a 450 sidewall at the focus line was used for the signal detection. The spectral resolution of approximately 7 nm is achieved with the grating constant of 2-5 μm and the step height of 0.2-0.6 μm . The size of spectrograph was 2.5 cm \times 1.5 cm \times 0.1 cm. The overall

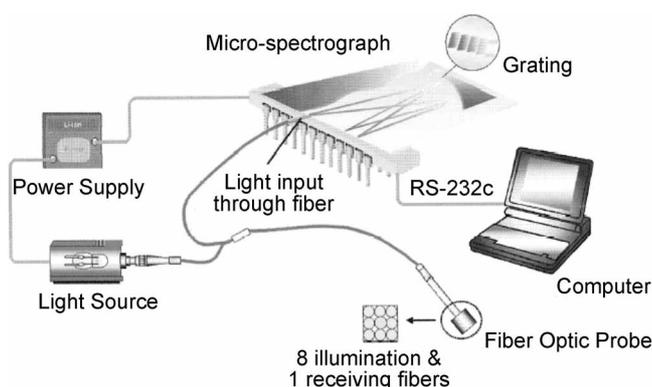


Figure 1. The schematic diagram of the miniaturized spectrometer.

system included a tungsten halogen lamp as a light source, a photodiode array for micro-spectrograph, and an external power supply (or internal battery). The necessary software was installed for data collection. The RS-232c cable was used to connect the NIR system with a computer.

The spectra were collected using a fiber optic trans-reflectance probe. The probe consisted of eight illuminating fibers, a receiving fiber, and a reflecting mirror. The distance between the optical fibers and the reflecting mirror was 1 mm, providing an actual pathlength of a 2 mm. Each spectrum corresponds to an accumulation of 30 scans in the 1100-1750 nm range with 2 nm data interval. Temperature of the detector was controlled at 30 °C.

A PLS regression and second derivative algorithm were performed using GRAMS/32 software with an add-on PLS algorithm (Galactic Industries Corporation, Salem, NH).

Results and Discussion

Spectral features: Figure 2 (top) shows the NIR spectra of water mixtures taken by the miniaturized spectrometer. From the bottom spectra to the top spectra, the water concentration increased from 1% to 19%. Water band (OH) at 1450 nm (6900 cm^{-1}) was clearly observed to have increased with concentration. This band is the first overtone band of the OH stretching mode in the infrared region (*e.g.* $\approx 3450\text{ cm}^{-1} \times 2 = 6900\text{ cm}^{-1} = 1450\text{ nm}$) that can be assigned to the hydrogen bonded OH peak. The band at 1580 nm is the free OH which is the first overtone peak from the methanol/ethanol mixture as well as water. The bands at 1180 and 1700 nm correspond to the second and first overtone of the CH stretching mode. As shown in this figure, the water band intensity at 1450 nm increased with the increase of water concentration.

To enhance the spectral features as well as to reduce the baseline variations, all the spectra were converted to their second derivative spectra.¹⁴ The corresponding second derivative spectra are shown in Figure 2 (bottom). The baseline variations were effectively removed and spectral features were enhanced while keeping the same qualitative information. The spectral variations based on water concentration were observed and the isosbestic point at 1476 nm

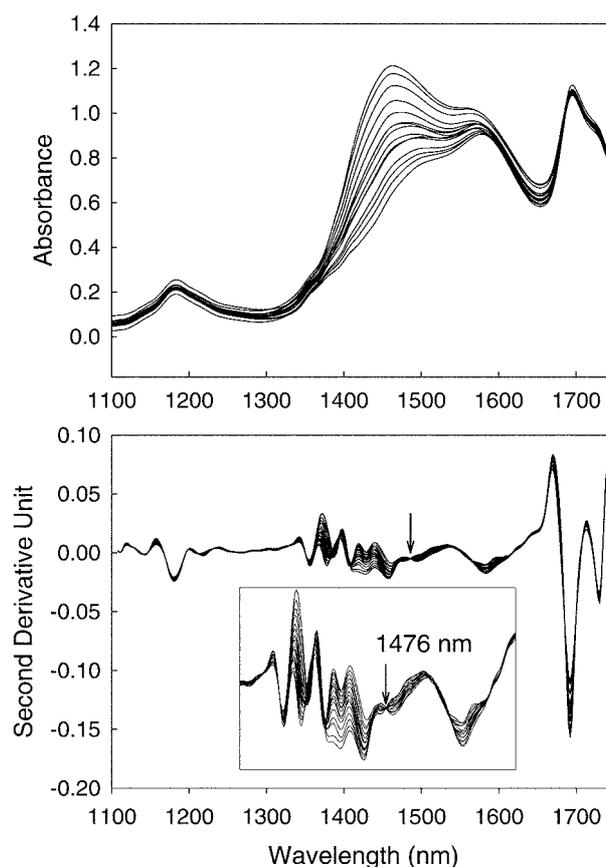


Figure 2. The raw NIR (top) and second derivative spectra (b) of 1% to 19% water content acquired from the miniaturized spectrometer.

between water and the methanol/ethanol mixture was identified (marked as arrow in the figure).

Two dimensional (2D) correlation spectroscopy: To investigate the performance of miniaturized spectrometer in more detail, two dimensional (2D) correlation spectroscopy¹¹⁻¹³ was employed. This method is very effective in finding the systematic correlations in a given system under external perturbation. The external perturbation in this study was the variation of water concentration. Figure 3 shows the resulting contour map of synchronous 2D spectrum. The synchronous spectrum represents the concurrent change of spectral intensity at the 1100-1750 nm range. The spectral intensity variation on the diagonal line (centered at 1450 nm, designated as A) is called “autopeak” that indicates the greater spectral change based on the concentration variation. The autopeak had consistent positive correlation (in this case, an increase with concentration). Three cross peaks (off-diagonal positions) were also observed (B, C and D). A solid line (B) and dotted lines (C and D) correspond to the positive and negative cross peaks, respectively. The peak B had a positive correlation with the increase in water concentration. This peak position is near the free OH band from the methanol/ethanol mixture as well as water.¹⁵ It increased with the decrease of concentration of the ethanol/methanol mixture. This indicates that the variation of water absorption is more dominant than those from the ethanol/

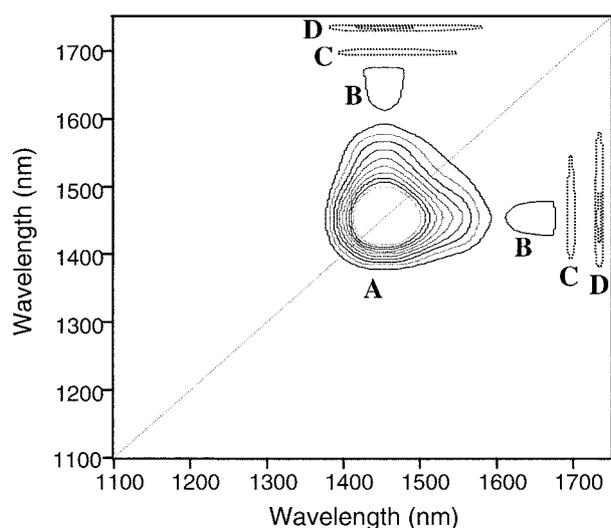


Figure 3. The contour map of synchronous two dimensional correlation spectrum.

methanol mixture due to the higher molar absorptivity of water. If the molar absorptivity of water is lower than those of ethanol/methanol, it would show negative correlation from the decrease of ethanol/methanol concentration. Peaks C and D (hydrocarbon peaks of ethanol/methanol located around 1700 nm) show the apparent negative correlation from the decrease of ethanol/methanol concentration and increase of water concentration, simultaneously. Overall, the spectra collected from the miniaturized spectrometer depicted the expected spectral variation without a sign of spectral distortion. If spectral distortion were present, it could be easily detected by ambiguous correlation using 2D correlation spectroscopy.

PLS models: PLS regression⁶⁻¹⁰ was used to build a calibration model. In the application of the PLS algorithm, it is generally known that the spectral range and the number of PLS factors are important parameters.¹⁶ In this research, the 1120-1730 nm range including the hydrocarbon and hydroxyl information was used. Then, PLS regression was performed using the second derivative spectra.

The optimum number of factors were identified as those that gave a minimum SECV (standard error of cross validation) and 3 PLS factors, in this case. The achieved SECV was 0.16%. To validate the calibration model, three samples (3%, 5% and 7%) were prepared new each day and predicted over 5 days (totaling 15 spectra: 3 samples \times 5 days). The concentration range from 3% to 7% was solely chosen for the prediction since the concentration variation is

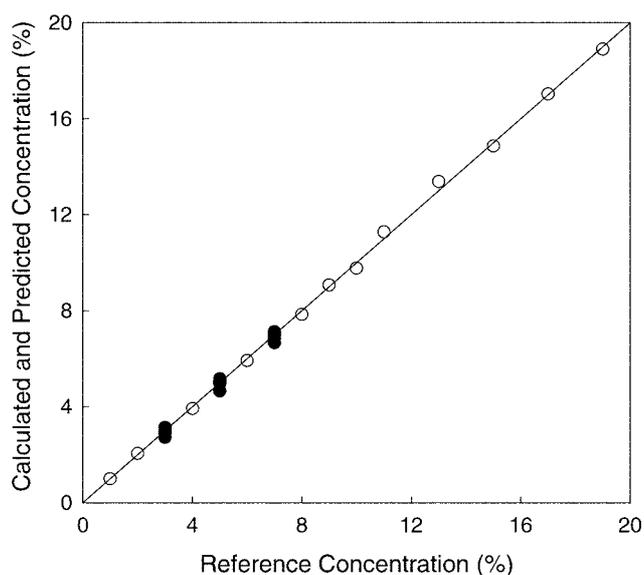


Figure 4. The scatter plot showing correlation between reference and NIR analyses. Open and filled circles represent the calibration and prediction data.

actually within this range. The prediction results are summarized in Table 1.

The prediction of each concentration over five days was nearly repeatable, with the standard deviation range from 0.15% to 0.19%. As shown, there was no bias in the prediction with SEP (Standard Error of Prediction) of 0.16%. The corresponding scatter plot showing correlation between reference and NIR analyses is shown in Figure 4. Open and filled circles represent the calibration and prediction data, respectively. The calibration and prediction data correlate very well with the reference data.

Conclusions

The overall results demonstrate the applicability of miniaturized NIR spectrometer in diverse fields, particularly in an on-line manner. The compact and cost-effective miniaturized NIR system could relieve the economic burden for end-users. This study was based on a fairly simple chemical matrix. Future research will be directed to investigate its performance on highly complex chemical matrices such as refinery products (*e.g.* gasoline, diesel fuel, etc.).

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Table 1. PLS prediction results (3%, 5%, 7% water concentration) over 5 days

Unit: %

Reference Concentration	Day 1	Day 2	Day 3	Day 4	Day 5	Average	Standard Deviation
3.0	2.9	2.7	3.1	3.0	2.9	2.9	0.15
5.0	5.2	4.7	5.0	5.0	5.0	5.0	0.19
7.0	7.1	6.7	7.0	7.0	7.0	7.0	0.17

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