Development of near-infrared absorption spectrometry system by using NIR wideband glass phosphor LED

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Abstract. We developed a NIR absorption spectrometry system for detection of toxic substances by using a glass phosphor based LED. Using this NIR absorption spectrometry system, phosphoric acid solution samples were measured by molybdenum-blue method. Absorption band around 900 nm and that around 960 nm were observed. The absorption band around 900 nm increased with increasing of the phosphoric acid concentration. Partial least squares (PLS) analysis was revealed that a lower phosphoric acid concentration limit of 0.01 ppm. Furthermore, Cu dilute solutions were measured. Although there was no clear absorption band related to Cu, PLS analysis was revealed that a lower Cu concentration limit of 0.1 ppm. These results indicated that this NIR absorption spectrometry system is useful for practical applications.

1. Introduction

In Japan, a “Positive list system” was introduced for the regulation of residual agricultural chemicals, pesticides, feed additives and veterinary drugs in 2006. This regulation prohibits the distribution of food containing agricultural chemicals above their maximum residue limits (MRLs). Furthermore, if the MRL has not been set, maximum upper limit of 0.01 ppm was applied. Additionally, agrochemicals are regulated by many countries and Codex Alimentarius Commission [1,2]. Therefore, rapid and reliable measurement method is required for the detection of hundreds of agrochemicals. In general, a liquid or gas chromatography and a mass-spectroscopy combination system (LC/MS or GC/MS) are used [3-9]. However, it is necessary to comminute samples. In addition to it, a long measurement time (typically, > 60 minutes) is required.

A Near-infrared (NIR) absorption spectroscopy is used in applications of agricultural field [10-12]. Since the NIR absorption spectroscopy is known as rapid and non-destructive method [10], it is suitable for the total inspection. In general, a wide-band light source is desirable for absorption spectrometry for measuring a broad region of the absorption spectrum. Thus, halogen lamps or...
light-emitting diodes (LEDs) are usually used as NIR light sources. Halogen lamps have a wide spectral width, but are big and have a short lifetime. On the other hand, LEDs are small and have a long lifetime, but have a narrow spectral width. Therefore, we have proposed a new-type light sources that emits NIR region with a wideband spectrum, and have the long-lifetime. To realize this light source, we synthesized a wideband NIR phosphor and combined with an LED in one package. The detail has reported in our previous papers [13-17]. Therefore, we tried the development the prototype of NIR absorption spectrometry system by using this light source for analysis of agrochemicals.

2. Prototype of NIR absorption spectrometry system

Figures 1(a), (b), and (c) show photos of the NIR absorption spectrometry system, an inside this system and wideband NIR glass phosphor combined LED, respectively. The size of this system is W500 ×H170 ×D300 mm. This system has enough space to change optical configurations. The basic configuration is consisted from our wideband NIR light source, a sharp-cut filter (SURUGASEIKI Co., LTD, IR-62), a sample holder (Ocean Optics, Inc., CUV-VAR), an integrating sphere (Opto Sirius Co., FOIS-1), and a multi-channel spectrometer (Hamamatsu Photonics K.K., C9405B). The temperature of above optical components is able to keep at constant by a Peltier device and a temperature controller. The light source is a Pr$^{3+}$-doped glass phosphor stacked on a Sm$^{3+}$-doped glass phosphor combined with a high-power blue LED in one package, and it has the luminescence from 760 to 1100 nm and has the maximum output power of 1.1 mW. Figure 2 shows the schematic diagram of this system. The multi-channel spectrometer is connected to the PC by USB cable, and spectra are displayed on the monitor in real time. After correcting spectra, a partial least squares (PLS) analysis was carried out on the PC. In general, a detection of sub-ppm level of toxic substances is difficult due to low light absorption. Thus, we used the PLS method for the analysis of a small spectrum changing.

![Figure 1](image1.png)

**Figure 1.** Photos of the prototype of (a) NIR absorption measurement system, (b) inside the system, and (c) glass phosphor combined LED as the light source.

![Figure 2](image2.png)

**Figure 2.** Schematic diagram of the prototype of the NIR absorption spectrometry system.

3. Experimental

Phosphoric acid solution samples were measured by a molybdenum blue method, since phosphorus-based agrochemical is used for a growth of agro-products. The molybdenum blue method is well known as a practical technique for measuring phosphoric acid in a few ppm levels [18]. Samples were prepared by diluting the 1000 ppm phosphoric acid standard solution (Wako Pure Chemical Industries, Ltd.) with ultrapure water. Phosphoric acid concentration was set to 0.01 to 0.1 ppm, and ultrapure water was used as a zero ppm sample. NIR spectra of these samples were measured by using a ten mm quarts cell. An integration time of multi-channel spectrometer was set to
50 msec, and absorption spectra were averaged by 50 times. Therefore, total measurement time for one spectrum is 2500 msec. The absorption spectrum \(A_\lambda\) was calculated from the transmission spectrum \(S_\lambda\), spectrum of light-source \(L_\lambda\) and dark spectrum \(D_\lambda\) by using following equation,

\[
A_\lambda = -\ln \left( \frac{S_\lambda - D_\lambda}{L_\lambda - D_\lambda} \right).
\]  

We also measured the Cu diluted solutions as the preliminary experiment of Cu based agrochemicals. Samples were prepared by diluting the 1000 ppm Cu standard solution (Wako Pure Chemical Industries, Ltd.) with methanol. Cu concentration was set to 0.1 to 1.0 ppm, and methanol was used as a zero ppm sample.

4. Results and Discussion

4.1 Phosphoric acid

Absorption spectra of samples are shown in Figure 3 (indicated in every 0.02 ppm). These spectra were smoothed by the Savitzky-Golay (SG) method (5 points). In Fig. 3, a large absorption band corresponding to the second overtone of the O-H stretching of water is observed around 960 nm. Moreover, it is observed that a small absorption band around 900 nm increases with increasing the phosphoric acid concentration. This result is in agreement with Ref 18.

PLS method is applied for quantitative phosphoric acid concentration analysis. The second derivative spectra with SG method (23 points) were used for PLS analysis to remove both baseline and linear trend. In this study, Unscrambler X (version 10.2, CAMO) was used for PLS analysis. Figure 4 shows the relationship between the nominal and predicted phosphoric acid concentrations by PLS analysis. Nominal and predicted phosphoric acid concentration show good agreement. In this analysis, the values of \(R^2\) (determination coefficient) and RMSEP (root-mean-square-error of prediction) are 0.981 and 0.004 ppm, respectively. These values indicate the high correlativity and accuracy. From these results, it is estimated that the lower detection limit of phosphoric acid is 0.01 ppm.

4.2 Cu solutions

Absorption spectra and regression coefficient spectrum of second derivative spectra are shown in Figures 5 (a) and (b), respectively. In Fig. 5 (a), spectra indicated in every 0.2 ppm. These spectra were smoothed by the SG method (5 points). The strong absorption around 900 and 1000 nm corresponding to the third overtone of C-H stretching and the second overtone of O-H stretching are observed, respectively. Therefore, clear absorption related to Cu was not observed. The second derivative with SG method (23 points) was carried out and used for the PLS analysis. The regression coefficient spectrum is one of the PLS analysis result, and it shows the correlation between Cu concentration and spectrum change. In Fig. 5 (b), strong correlation is observed around 820 nm, which should be due to the d-d transition of Cu [19].

Figure 6 shows the relationship between the nominal and predicted Cu concentrations by PLS analysis. Nominal and predicted Cu concentration show good agreement. In this analysis, the values of \(R^2\) and RMSEP are 0.986 and 0.037 ppm, respectively. These values indicate the high correlativity and accuracy. From these results, it is estimated that the lower detection limit of Cu is 0.1 ppm.
5. Summary
In this study, the prototype of the NIR absorption spectrometry system by using our novel light source was developed and verified by using phosphoric acid and Cu diluted solutions. By using molybdenum blue method, phosphoric acid concentration of 0.01 ppm was detected. In the case of Cu solution, lower limit of Cu concentration was 0.1 ppm. It is concluded that the prototype of the NIR absorption spectrometry system has enough accuracy for the practical application.

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