Current Optics and Photonics
Vol. 3, No. 4, August 2019, pp. 336-341

ISSN: 2508-7266(Print) / ISSN: 2508-7274(Online)
DOI: https://doi.org/10.3807/COPP.2019.3.4.336

Real-time Spectroscopic Methods for Analysis of Organic Compounds in Water

Chihoon Kim and Taeksoo Ji*

*Laboratory of Semiconductor Device Research, School of Electronics and Computer Engineering,
Chonnam National University, Gwangju 61186, Korea*

(Received April 26, 2019 : revised June 14, 2019 : accepted June 28, 2019)

This paper proposes an optical system where the organic compound content in water is determined by using an ultraviolet (UV) LED (280 nm) and photodetector. The results obtained by the proposed prototype LED spectroscopy system, which includes a single photodetector and two parallel sample holders, are calculated by applying partial least square regression; the values are highly correlated with the actual concentrations of potassium hydrogen phthalate solutions, with an adjusted coefficient of determination about 0.996. Moreover, the total organic carbon values derived from the UV-Vis spectrometer of real samples (lake, river and sea water) differed little from those obtained by the LED spectroscopy. We confirm that the fast, sensitive, and compact LED sensor system can be readily configured for real-time monitoring of organic compounds in water.

Keywords : LED sensor, UV absorbance, Total organic carbon, Spectroscopy, Organic pollution
OCIS codes : (300.0300) Spectroscopy; (120.0120) Instrumentation, measurement, and metrology; (120.4820) Optical systems; (300.6390) Spectroscopy, molecular

I. INTRODUCTION

Biochemical oxygen demand, chemical oxygen demand, and total organic carbon (TOC) tests have been used simultaneously to assess the contamination of clean water by wastewater discharged from industrial, agricultural or urban areas [1-3]. Physicochemical and biological variables must be considered simultaneously with respect to optimal assessment of water quality. Among the environmental indicators of water quality mentioned above, the TOC is more relevant because TOC measurement uses smaller amounts of reagents, and can be performed rapidly and easily. To determine the concentration of organic carbons in water, carbon compounds need to be oxidized and converted to a single molecule for quantitative measurement. The instruments commercially available for TOC analysis first convert organic carbon to carbon dioxide (CO2) by applying heat, ultraviolet (UV) irradiation, and/or chemical oxidants. The CO2 generated during oxidation is then monitored using analytical tools such as infrared spectrometry, thermal conductivity measurement, conductometry, coulometry [4-6].

In general, oxidation systems can be categorized according to the process temperature as low-temperature photochemical systems (below 100°C), which contain UV irradiation, heated persulfate, and UV/persulfate methods, and high-temperature pyrolysis systems (between 600 and 1200°C), which contain platinum (Pt) catalyst. The use of these low-temperature methods is, however, restricted to less polluted water that contains no suspended solids, whereas high-temperature pyrolysis systems, which typically use a platinum catalyst to facilitate oxidation, are more commonly employed in TOC analysis. This is because this high-temperature method possesses greater oxidation efficiency than most other methods. Despite its high oxidation efficiency, the high-temperature approach has disadvantages such as poor reproducibility and low accuracy, which are caused by contamination during sample manipulation and sampling. Moreover, most high-temperature systems are equipped with relatively expensive columns that use Pt-based catalysts to ensure complete oxidation of organic carbon. These limitations associated with the high-temperature method make it difficult to manufacture a

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*Corresponding author: tji@chonnam.ac.kr, ORCID 0000-0003-4748-9141

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low-cost and portable TOC analysis system for real-time measurement. Therefore, there has been increasing need for the development of simple and valid diagnostic methods for determining the TOC of polluted water [7-10].

We previously reported an optical system capable of detecting organic compounds in polluted water [11]. However, this optical system for TOC analysis was bulky, because it consisted of a heavy optic spectrometer and photodetector to monitor the UV absorption. It also required a post-calibration process for accurate measurement that needs to be done manually. Both of these factors hamper the compact and real-time TOC analysis system. In this paper, we present a compact and reliable optical measurement system that utilizes a UV light-emitting diode (LED) emitting at 280 nm as a light source, a single photodetector for measuring the organic concentration, and two sample holders, one for reference and the other for sample measurement. This two-parallel-sample-holder-configuration provides accurate and automatic calibration so that it can be applied in the field. In the system, the processed absorbance signal can be obtained in real-time using LabVIEW software. To ensure reliability, the optimal variables for yielding accurate TOC values were extracted from the UV absorbance spectra using a nonlinear regression model, and the optimal variables were used as quantitative indicators of the TOC values [12].

II. METHODS

Figure 1 shows a schematic of the optical absorbance system equipped with a UV-LED (UVLED280TO46L, Sensor Electronic Technology Inc.) for TOC analysis. Continuous light at a central wavelength of 280 nm from the UV-LED passes directly through two stages (reference and sample stage) in a quartz cell to minimize the loss of the transmitted light by a 1 × 2 fiber coupler. The light transmitted from both cells is simultaneously sent to the photodetector (APD120A, Thorlabs) by a 2 × 1 fiber coupler. Potassium hydrogen phthalate (KHP, white acidic salt compound, C8H5KO4) solutions with various concentrations [high, 10~200 mg/L; medium, 2~8 mg/L; low, 0.3~0.9 mg/L) were used as standard samples for measuring organics in water using the proposed LED spectroscopy system.

The light intensity absorbed by samples can be determined according to the Beer-Lambert law, which can be applied to quantify the concentration of unknown materials dissolved in a solution using the observed intensity variation of the light due to absorption or scattering. The absorbance can be expressed as the ratio of the incident and transmitted light:

$$A = -\log_{10}\left(\frac{I_s - I_D}{I_R - I_D}\right) \tag{1}$$

where A is the absorbance, and I_s, I_R, and I_D are the light intensity measured from the sample, the reference, and the dark signal, respectively. The dark and reference signals are types of background noise signals coming from the photodetector and a deionized (DI) water sample, respectively [14, 15].

III. RESULTS

Figure 2(a) shows the magnified transmittance spectra for different references such as single DI (only one inserted) and double DI (both inserted) in both sample stages. From these spectra, we can see that the spectral intensity of single DI and double DI have no difference.

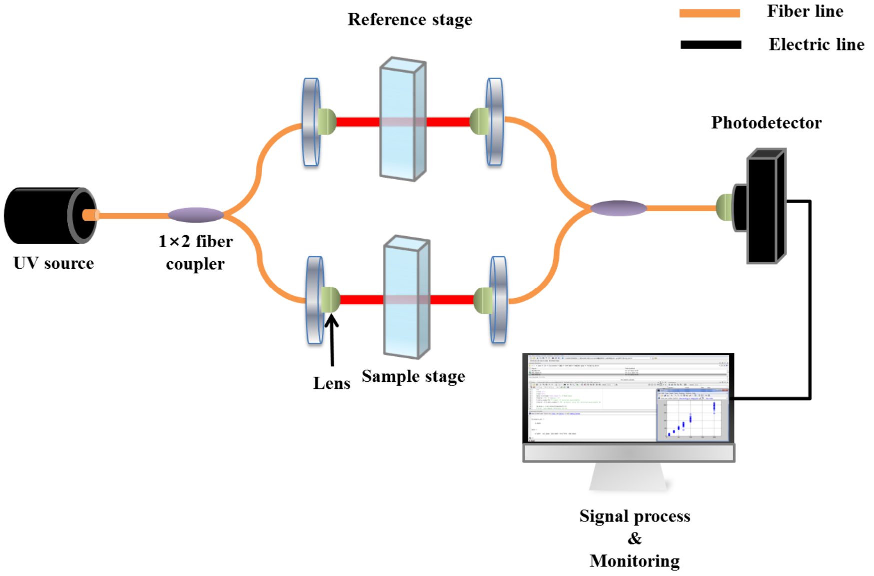

FIG. 1. Schematic of a prototype of the proposed LED spectroscopy system.

Accordingly, the insertion of DI's into two sample stages was defined as a basis for the measurements. Figure 2(b) shows the absorbance spectra obtained for different KHP concentrations ranging from 0.3 to 100 mg/L using an elaborate UV-NIR spectrometer (Bayspec Inc.) equipped with a UV-LED light source. In this case, the absorbance reaches a maximum at a wavelength of approximately 272 nm that increases with increasing KHP concentration. It is well known that organics with unsaturated bonds, such as aromatic compounds, strongly absorb UV light in the optimal wavelength range of 270 to 290 nm, giving rise to variation in the absorbance depending on the concentration, whereas saturated molecules such as inorganic compounds show little absorption at wavelengths of 250 to 300 nm [11]. The obvious absorbance change in the UV region according to the KHP concentration in Fig. 2(b) confirms the possibility that the absorption spectra can be used to quantify the concentrations of organic compounds in water. Thus, we can apply it to LED spectroscopy based on concentration measurement using UV-NIR spectrometer.

In our previous work [11], a multiple linear regression (MLR) model was employed to analyze the absorbance signal at several selected wavelengths and to determine the correlation between the absorbance and the organic compounds concentration. In the MRL model, the relationship between an independent (X_{ik}, the predictor) and dependent variable (Y_i) is given by

$$Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \cdots + \beta_k X_{ik} + \epsilon_i, i = 1, 2, \ldots, n \tag{2}$$

where ϵ_i and β_0 are the error term and the intercept, respectively. β_j, j = 0, 1,…, k, is the regression coefficient of the j-th predictor. However, MLR is less suited for modeling non-linear data as ours in this study. On the other hand, partial least square (PLS) regression can be used when the number of data points is less than the number of independent variables, or when there is considerable multicollinearity among independent variables. The general idea of PLS is to try to extract latent factors that account for as much of the predictor variation as possible, and model the responses well [12, 13]. Therefore, the PLS regression model has been chosen in this study to calibrate the nonlinear data as well as to find the existence of multicollinearity among independent variables. Based on the maximum absorbance value measured with the UV-NIR spectrometer, we arbitrarily chose eleven reliable wavelengths (270.102, 270.663, 271.224, 271.784, 272.345, 272.908, 273.466, 274.027, 274.587, 275.148 and 275.709 nm) for PLS analysis. We analyzed the absorbance data collected at the selected wavelengths in the statistical package for the social sciences (IBM, SPSS Statistics 23) program and then determined the optimal number of parameters among the eleven wavelength sets that give rise to the highest adjusted determination R^2_{adj} and the coefficient of determination R^2, which is defined as follows:

$$R^2 = 1 - \frac{SSE}{SST},\ R^2_{adj} = 1 - \frac{\dfrac{SSE}{n-k-1}}{\dfrac{SST}{n-1}} \tag{3}$$

where SSE, SST, n, and k are the error sum of squares, the total sum of squares, the sample size, and the total number of regressors in the linear model, respectively. Figure 3 compares the known KHP concentrations of the synthetic solutions to the calculated KHP concentrations in a range of low to high concentrations for before averaging (Fig. 3(a)) and after averaging KHP concentration (Fig. 3(b)). The R^2_{adj} values of the before averaging concentration and the after averaging concentration were found to be 0.952 (R^2: 0.953) and 0.976 (R^2: 0.977), respectively, implying that the sample concentrations can be determined with accuracies of 95.2 and 97.6% from the absorbance data. The high similarity of R^2_{adj} and R^2 values indicates that the PLS model is well fitted [16]. To clarify the analysis, all reliable wavelengths were selected for further PLS modeling because these wavelengths were found to be included in all the optimal sets. The regression coefficients (β_i, i = 0, 1,…, 11) extracted from 11 wavelengths were found to be -15.945, 4929.223, -338.063, -3180.751, -331.285,

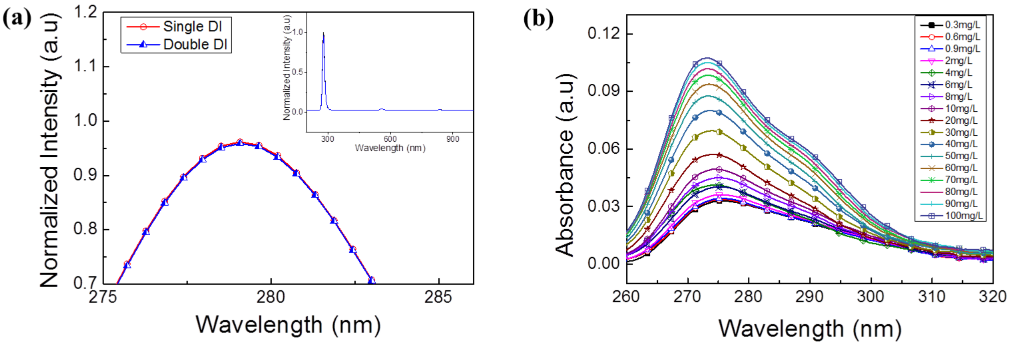

FIG. 2. Transmittance spectra of solutions with different reference situations (a) and absorbance spectra of the solution with different KHP concentrations measured by (b) a UV-NIR spectrometer (Bayspec Inc) using a UV-LED light source at a wavelength of 280 nm. The transmittance intensities are normalized with respect to the highest intensity value.

244.3, 131.571, 313.433, -762.211, 512.743, -556.183, and 347. TOC values then can be determined based on the coefficients as follows:

$$\begin{aligned} TOC\,(mg/L) = & -15.945 + 4929.223(I_{270.102}) \\ & -338.063(I_{270.663}) - 3180.751(I_{271.224}) \\ & -331.285(I_{271.748}) + 244.3(I_{272.345}) \\ & +131.571(I_{272.908}) + 313.433(I_{273.466}) \\ & -762.211(I_{274.027}) + 512.743(I_{274.587}) \\ & -556.183(I_{275.148}) + 347.417(I_{275.709}) \end{aligned} \tag{4}$$

where from $I_{270.102}$ to $I_{275.709}$ are the absorbance intensities at each wavelength.

In addition, we have identified a prediction interval for a sample which gives a photodetector response of 0.16953 is 0.000301 mg/L. Accordingly, the 95% confidence interval for 15 degrees of freedom is 0.000642 mg/L [17].

Figure 4 insets show the electrical signals for the same sample sets obtained again using a single photodetector for 73 seconds, which makes the spectroscopy system real-time capable and easier to integrate. However, as seen in the plots, the raw signals detected by the photodetector cannot be easily distinguished to each other. For the case of the low KHP concentration set with a 0.3 mg/L difference and the medium KHP concentration set with a 2 mg/L difference

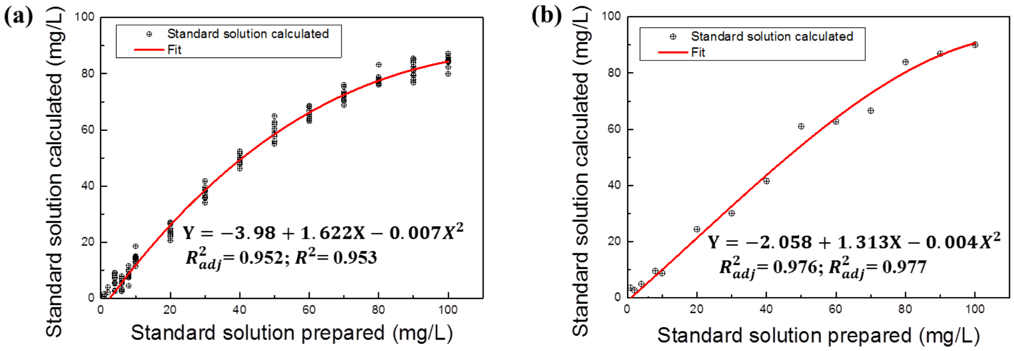

FIG. 3. Relationship between the prepared KHP concentrations (standard solution prepared) and concentrations calculated by PLS analysis for (a) low to high KHP concentrations (R^2_{adj} : 0.952; R_2: 0.953) before averaging and (b) after averaging KHP concentrations (R^2_{adj} : 0.976; R_2: 0.977).

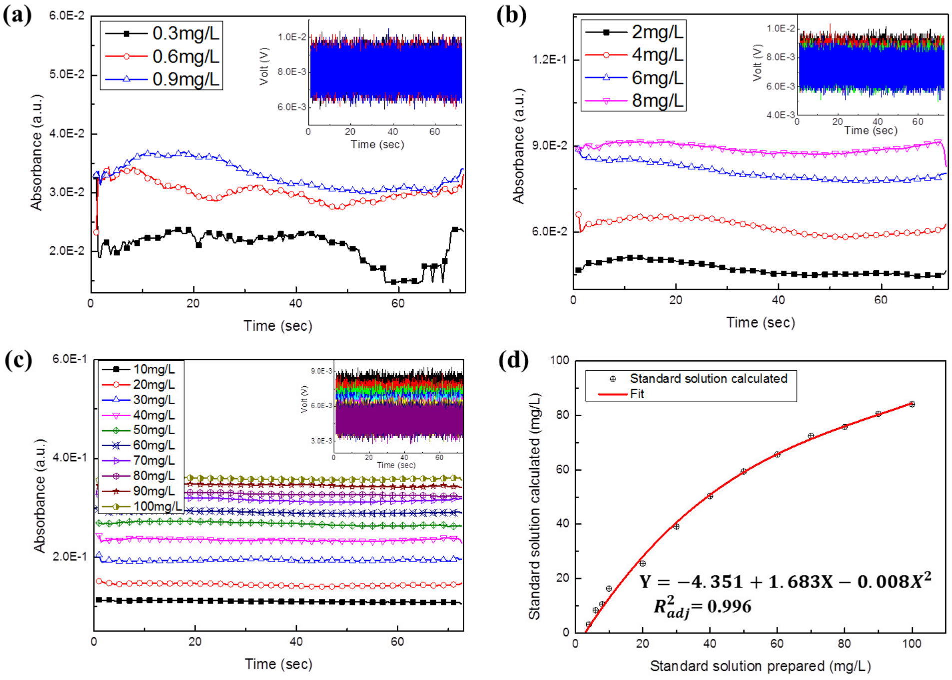

FIG. 4. Absorbance values measured by a single photodetector (Si avalanche photodetector) for (a) low KHP concentrations, (b) medium KHP concentrations, (c) high KHP concentrations, and (d) calculated by analysis for low to high KHP concentrations (R^2_{adj} : 0.996). The signal before signal processing can be seen on the insets and based on a 500 sample rate for the program.

shown in Figs. 4(a) and 4(b), respectively, the electrical signals appear like one signal without any noticeable gap in the adjacent signals. Although the signals are slightly distinguishable in the high concentration set as seen in Fig. 4(c) inset, we need data processing to interpret and utilize the signal clearly. For processing, the mean function of LabVIEW was employed as a function of averaging of real-time sequence data, which is defined as follows:

$$\mu = \frac{1}{n}\Sigma_i^{n-1} X_i \tag{5}$$

where μ is mean and n is the number of elements in X. The absorbance values calculated by the above function are plotted in Figs. 4(a)~4(c) from the low to high concentration samples. From the values, the adjusted coefficient of determination (R^2_{adj}) was calculated giving rise to 0.996 (Fig. 4(d)). The high adjusted coefficient value (exceeding 0.996, i.e., accuracies of 99%) over the entire range of low to high concentrations implies that TOC concentrations can be clearly estimated by the method, and the correlations of the TOC with the UV absorption by the photodetector are in good agreement with those obtained by the spectrometer detector.

To confirm the validity of the LED spectroscopy method for TOC measurement, we collected three real samples, A (lake water), B (river water), and C (sea water), and compared the TOC values of the samples determined by PLS analysis with those measured by the spectrometer. Figure 5(a) shows the absorbance of the three samples measured by the prototype LED spectroscopy system using a single photodetector for 73 seconds, and Fig. 5(b) compares the concentrations calculated from the UV-LED absorption and measured by the spectrometer. As can be seen in Fig. 5(b), the values are in good agreement with small deviations, thereby confirming the applicability of the LED spectroscopy for monitoring organic compounds in water. The high adjusted coefficient value (0.996) extracted from the absorbance spectra of the single photodetector is the same as that of the sophisticated spectrometer (0.952 and 0.976, before and after averaging concentrations); thus, the photodetector method is still an attractive way to build a compact, portable spectroscopy system capable of real-time detection of organic compounds in water.

IV. CONCLUSION

We propose a real-time and reliable optical system that uses a UV-LED as a high-efficiency light source and a single photodetector as a tool for UV absorbance measurement and is capable of monitoring organic compounds in water. The high degree of correlation (R^2_{adj}: 0.996) obtained through PLS analysis using the prototype LED spectroscopy system with the single photodetector indicates that the UV absorption and TOC concentration for concentrations ranging from 0.3 to 100 mg/L are highly correlated. The values were demonstrated to be comparable to those obtained using a sophisticated spectrometer. Thus, by simply adopting a single photodetector rather than using an expensive and bulky spectrometer, a compact, portable spectroscopy system can be readily built that is capable of real-time detection of organic compounds in water.

ACKNOWLEDGMENT

This work was supported by the Basic Science Research Program through the National Research Foundation of Korea funded by the Ministry of Education (NO. 2018048610).

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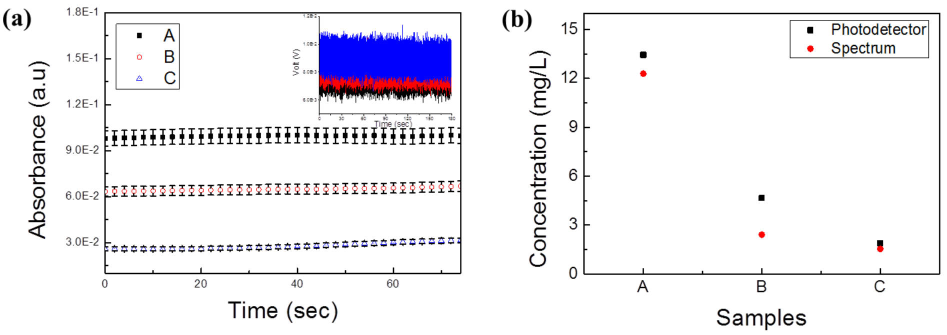

FIG. 5. (a) Absorbance spectra including 5% error bar for three samples by the prototype LED spectroscopy system (A: lake water, B: river water, and C: sea water). The signal before signal processing can be seen on the insets. (b) Comparison of the TOC values calculated from the LED spectroscopy with those measured by the spectrometer detector. B and C were collected from the Gwangju stream and South Sea in Korea, respectively.

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