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Determination of organic compounds in water using ultraviolet LED

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Abstract

This paper describes a method of detecting organic compounds in water using an ultraviolet LED (280 nm) spectroscopy system and a photodetector. The LED spectroscopy system showed a high correlation between the concentration of the prepared potassium hydrogen phthalate and that calculated by multiple linear regression, indicating an adjusted coefficient of determination ranging from 0.953–0.993. In addition, a comparison between the performance of the spectroscopy system and the total organic carbon analyzer indicated that the difference in concentration was small. Based on the close correlation between the spectroscopy and photodetector absorbance values, organic measurement with a photodetector could be configured for monitoring.

Keywords: UV absorbance, total organic carbon, spectroscopy, organic pollutant

(Some figures may appear in colour only in the online journal)

1. Introduction

Due to industrial and indiscriminate discharge of synthetic compounds, such as surfactants, volatile organic compounds (VOCs), and pesticides, the risk of water pollution has become a serious threat. Biochemical oxygen demand (BOD), chemical oxygen demand (COD), and total organic carbon (TOC) tests have been used simultaneously, with other chemical parameters, to detect the changes in the wastewater discharged from industrial or domestic sources. For an optimum assessment of water quality, the parameters should be a combination of physical, chemical, and biological factors [1–3]. Among these environmental indicators, the TOC content of water is a more useful indicator to indicate the degree of pollution. To measure the TOC in water, the carbon compounds can be oxidized and converted to a single molecule that can be measured quantitatively. The commercially available instruments for TOC measurement utilize heat, oxygen, ultraviolet

irradiation, and chemical oxidants or combinations of these oxidants, to convert the organic carbon to carbon dioxide (CO₂). The CO₂ is measured using analytical procedures such as infrared spectrometry, thermal conductivity, conductometry, coulometry, and CO₂-sensitive sensors [4–6].

Generally, there are two methods used for the oxidation process: at low temperatures (below 100 °C) using a photochemical system and at high temperatures (between 600 °C and 1200 °C) using pyrolysis. The ultraviolet irradiation, heated persulfate, and UV/persulfate methods are available for use in low temperature photochemical system. In addition, these methods are restricted to use in water with low levels of pollution and no suspended solids. Moreover, their accuracy depends on particle size because they use small orifice syringes. In comparison, the high-temperature photochemical system, which usually employs a platinum (Pt) catalyst to facilitate oxidation, has become the mainstream method for the analysis of TOC in polluted water because of its greater oxidation efficiency compared with other methods. Therefore, a number of high-temperature photochemical systems have been built and are commercially available. Even though these systems have better oxidation efficiencies than other systems,



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they are not immune to the problems of poor reproducibility, accuracy, and non-real-time measurements due to sample manipulation and contamination during sampling. Moreover, high-temperature photochemical systems have a relatively expensive sampling column and the catalytic sites may be subject to poisoning or deactivation by salt deposition. *The manufacturing of compact systems has been restricted due to these problems.* Therefore, there is a need for the development of a simple and valid method of measuring TOC in polluted water [7–12].

To achieve simplicity and reliability of the measurement system, an ultraviolet LED (UV-LED) spectroscopy system and photodetector were utilized in this paper. The system configuration is shown in figure 1. To ensure reliability, the optimum variables were obtained using multiple linear regression (MLR) [13]. According to a comparison between the spectroscopy and photodetector absorbance values, we can confirm that a photodetector could be applied for detecting organic compounds. Therefore, a compact organic measurement system could be configured.

2. Experimental setup

2.1. System setup

The setup for the absorbance system is shown in figure 1(a). All optical parts and two detectors are included which has a dimension of $30 \times 20 \text{ cm}^2$. A UV-LED with a continuous light source at 280 nm was passed directly through a sample in order to minimize the loss of light, and the reduced light source was sent to a 1×2 fiber coupler. The spectrometer (SV2100, resolution: 1 nm) and photodetector (PDA10A, Si transimpedance amplifier) then converted the light into electronic signals which could be used for data analysis. Potassium hydrogen phthalate (KHP, white and acidic salt compound, $\text{C}_8\text{H}_5\text{KO}_4$) used in official test methods of water quality, ES 04311.1, was used to measure the organics in the water with the absorbance system. A variety of concentrations of the samples was obtained: high concentration (10, 30, 50, 70, and 100 mg l^{-1}), medium concentration (1–9 mg l^{-1} , respectively) and low concentration (0.2, 0.4, 0.6, and 0.8 mg l^{-1}). In addition, figure 1(b) shows the TOC measurement using a combustion catalytic oxidation process and a nondispersive infrared sensor (NDIR), which is used in this commercial system. A small amount of acid is added to the sample which generates CO_2 gas as a result of the reaction between inorganic carbon and acid. The CO_2 produced is removed; however, a small amount of purgeable organic carbon (POC) is lost in this process. The sample is then put in the catalytic combustion chamber at 850°C . The organic carbon present decomposes and forms CO_2 gas which is then measured using the NDIR sensor to measure the TOC content. Before the measurement process, the gas is dehumidified to remove any water content. The whole process requires expensive components such as membranes to remove CO_2 gas, water vapor, and heating elements to achieve high temperature for catalytic combustion [10].

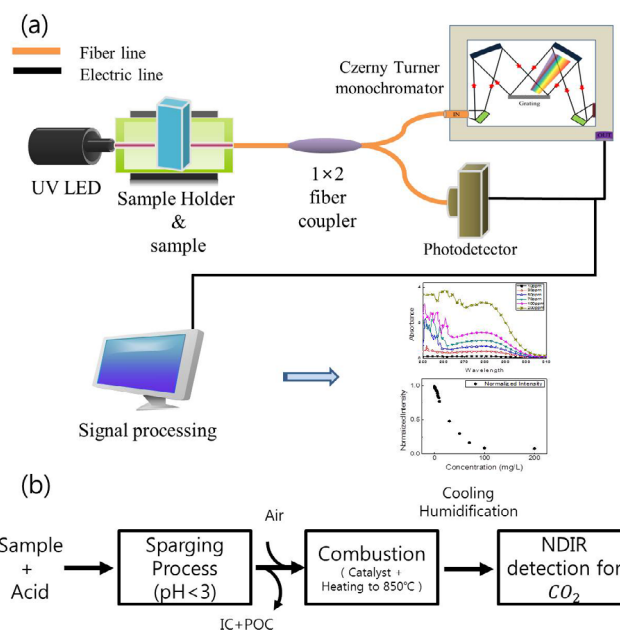


Figure 1. (a) Schematic diagram of the UV-LED spectroscopy system, (b) process for TOC analyzer sample measurement.

2.2. Principle of operation

When light passes through a sample, the absorbed light is detected according to the Beer–Lambert law. This law implies that the concentration of an unknown sample dissolved in a solution is quantified by monitoring the intensity change (i.e. absorption and scattering). After measuring the dark signal intensity, that is the noise coming from the spectrometer and the reference signal from the deionized (DI) water, the absorbance of the prepared samples was determined over an integration time of 150 ms. The absorbance can be expressed as the ratio of the incident and transmitted light, given by

$$A = -\log \left(\frac{I_S - I_D}{I_R - I_D} \right), \quad (1)$$

where A is the absorbance; and, I_S , I_R , and I_D are the measured intensities of the sample, reference, and dark signals, respectively [14, 15].

3. Results

The transmittance spectra for different KHP concentrations are shown in figure 2. As shown in figure 2(a), the transmission spectra were obtained by using a deuterium–tungsten lamp, and the transmission spectra using the LED is shown in figure 2(b). The absorbance values for the concentrations of the samples from high to low are plotted in figure 3. The absorbance change in the UV region was clearly measured by spectrophotometer (Cary 5000, resolution: 0.05–0.5 nm), thus confirming the quantification of the organics as shown in figures 3(a)–(c). Among these results, the properties of the organics with unsaturated bonds, such as the aromatic compounds that strongly absorb UV light in the optimum wavelength range of 270–290 nm, showed a clear variation

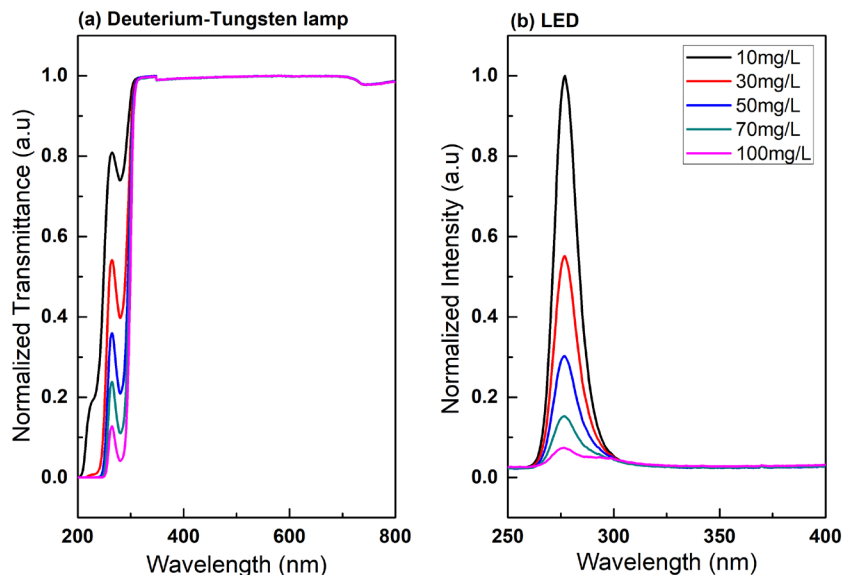


Figure 2. (a) UV-vis transmission spectra of different concentrations of KHP using a Deuterium-Tungsten lamp and (b) LED transmission spectra at 280 nm.

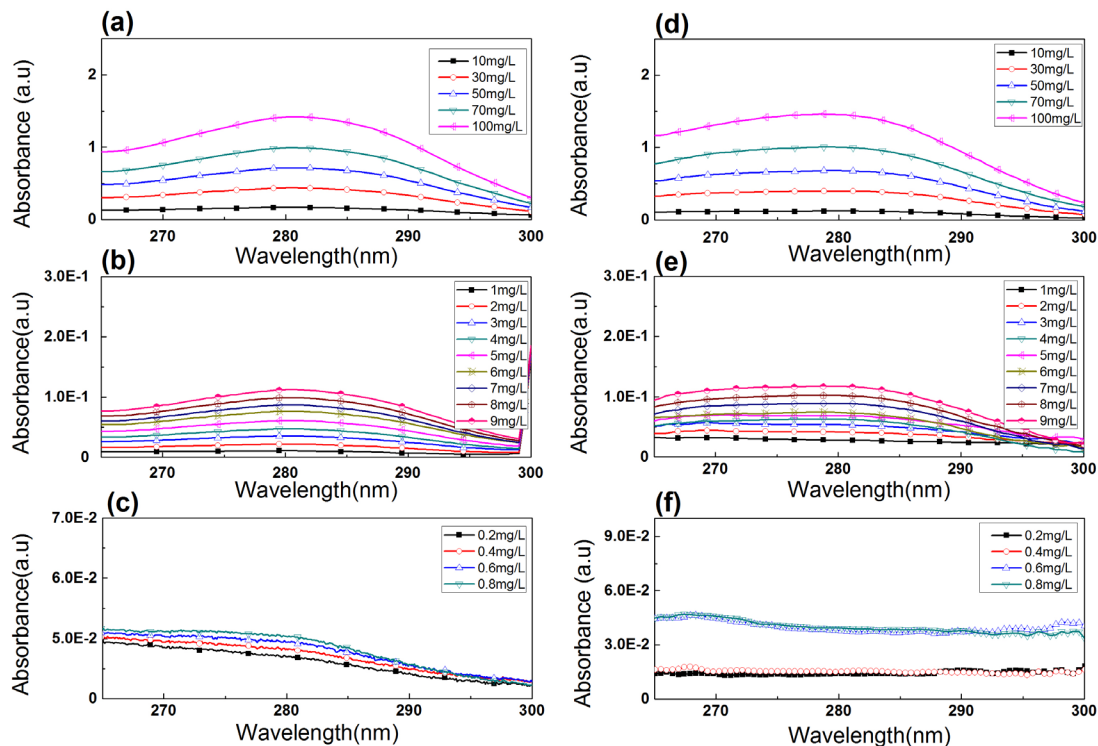


Figure 3. UV spectra of samples with different concentrations of KHP. Panels (a)–(c) were derived from the measurements of the spectrophotometer (Cary 5000, resolution: 0.05–0.5 nm). Panels (d)–(f) were obtained from the prototype spectroscopy system and UV-LED with different concentrations of KHP.

in absorbance for different concentrations. Moreover, saturated molecules such as inorganic compounds which are not detected in the wavelength range of 250–300nm were also considered [16]. The absorption spectra measured ten times for each sample in the UV-LED spectroscopy system are shown in figures 3(d)–(f). The absorbance variations within the wavelength range of 270–290nm for the different concentrations of the samples are also shown. It can be seen that the absorbance value measured by our system are clearly

distinguishable, thus demonstrating the possibility of quantifying the organic compounds in the water.

For analyzing the absorbance signals at selected wavelengths which vary in accordance with the concentration of the samples, a MLR model was adopted, which represents the relationship between an independent variable (X_{ki} , predictor) and a dependent variable (Y_i):

$$Y_i = \beta_0 + \beta_1 X_{i1} + \beta_2 X_{i2} + \dots + \beta_k X_{ik} + \varepsilon_i, \quad i = 1, 2, \dots, n, \quad (2)$$

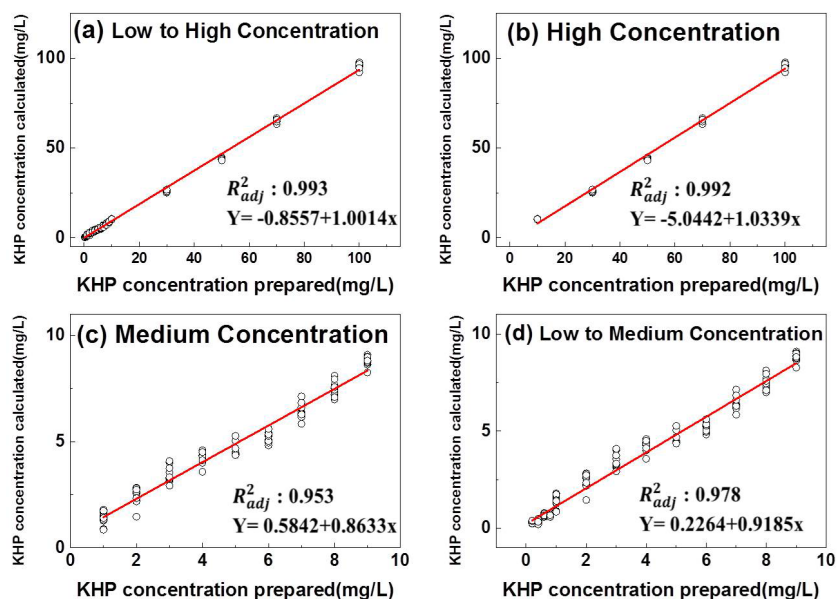


Figure 4. Relationship between the concentrations of the prepared KHP and those calculated using a MLR analysis. (a) Low to high concentration. (b) High concentration. (c) Medium concentration. (d) Low to medium concentration.

where ε_i and β_0 are the error term and the intercept, respectively, and $\beta_j, j = 0, 1, \dots, k$ are the regression coefficients of the j th predictors [17].

A MLR analysis was performed by analyzing the influence of more than two independent variables on a dependent variable, and to acquire accurate quantification, the number of independent variables was determined based on the optimum analysis model. Primarily, from the measured values, 12 reliable wavelengths (278.1, 278.5, 279, 279.5, 280.4, 280.9, 281.4, 281.8, 282.3, 282.8, 283.2, and 283.7 nm) were selected for the MLR. The absorbance data collected at the selected wavelengths were analyzed using the stepwise method in the Statistical Package for the Social Sciences (IBM, SPSS Statistics 21). However, the analysis in figure 4(a) involved five parameters of the wavelength: 278.5, 279, 281.8, 283.2, and 283.7 nm, whereas in figures 4(b)–(d) there were more than two parameters; therefore, the wavelengths 281.8 and 283.7 nm were included in all data, and the two wavelengths were used to conduct the MLR analysis. The best regression coefficients (β_0 : -0.554 , β_1 : 1151.109 , and β_2 : -1112.144) are extracted by applying two wavelengths (281.8 and 283.7 nm), indicating that the TOC can be calculated by equation (2):

$$\text{TOC (mg l}^{-1}\text{)} = -0.554 + 1151.109(I_{281.8}) - 1112.144(I_{283.7}), \tag{3}$$

where $I_{281.8}$ and $I_{283.7}$ are the intensities of the absorbance at the wavelengths 281.8 and 283.7 nm, respectively. In figure 4, a best-fit line was drawn through the points of the calculated concentrations. In addition, each adjusted coefficient for the determination of R^2_{adj} was calculated by MLR for: low to high concentration (R^2_{adj} : 0.993, figure 4(a)), high concentration (R^2_{adj} : 0.992, figure 4(b)), medium concentration (R^2_{adj} : 0.953, figure 4(c)), and low to medium concentration (R^2_{adj} : 0.978, figure 4(d)), implying that the concentrations

of the samples can be determined with accuracies of 99.3%, 99.2%, 95.3%, and 97.8%, respectively [16, 18].

The absorbance values were measured using a Si photodetector as shown in figure 5. The best linear fits of this data are shown as red lines in figure 5. In addition, each adjusted coefficient of determination (R^2_{adj}) was calculated for: low to high concentration (R^2_{adj} : 0.998 figure 5(a)), high concentration (R^2_{adj} : 0.997, figure 5(b)), medium concentration (R^2_{adj} : 0.97, figure 5(c)), and low to medium concentration (R^2_{adj} : 0.97, figure 5(d)), and the absorbance values had accuracies of 99.8%, 99.7%, 97%, and 97%, respectively. In order to evaluate the correlation between the absorbance and the photodetector sensitivity, the absorbance calculated by the Beer–Lambert law was analyzed using linear fitting as shown in figure 5. All of the obtained adjusted coefficient values (R^2_{adj}) were greater than 0.97 (accuracy of 97%). This implied that the absorbance values could be clearly characterized, even though the concentration of KHP was lower than 1 mg l^{-1} . Therefore, the correlation of these results with the UV-absorption of the photodetector showed that the absorption spectra are in agreement with those obtained using the spectroscopy system.

Several samples were prepared: S1 (tap water), S2 (river water), S3 (lake water), and S4 (seawater), to compare the results of the UV-LED spectroscopy system with the TOC analyzer (Vario TOC cube, Germany). Figure 6(a) shows the absorbance spectrum of the samples measured by the UV-LED spectroscopy system and figure 6(b) shows the comparison between the concentrations calculated by UV absorption and the TOC analyzer. The maximum difference between the concentrations calculated with the TOC analyzer and UV-LED spectroscopy system was 0.5 mg l^{-1} . The results were in agreement, thereby verifying the correctness of the UV absorption method. This comparison clearly shows that

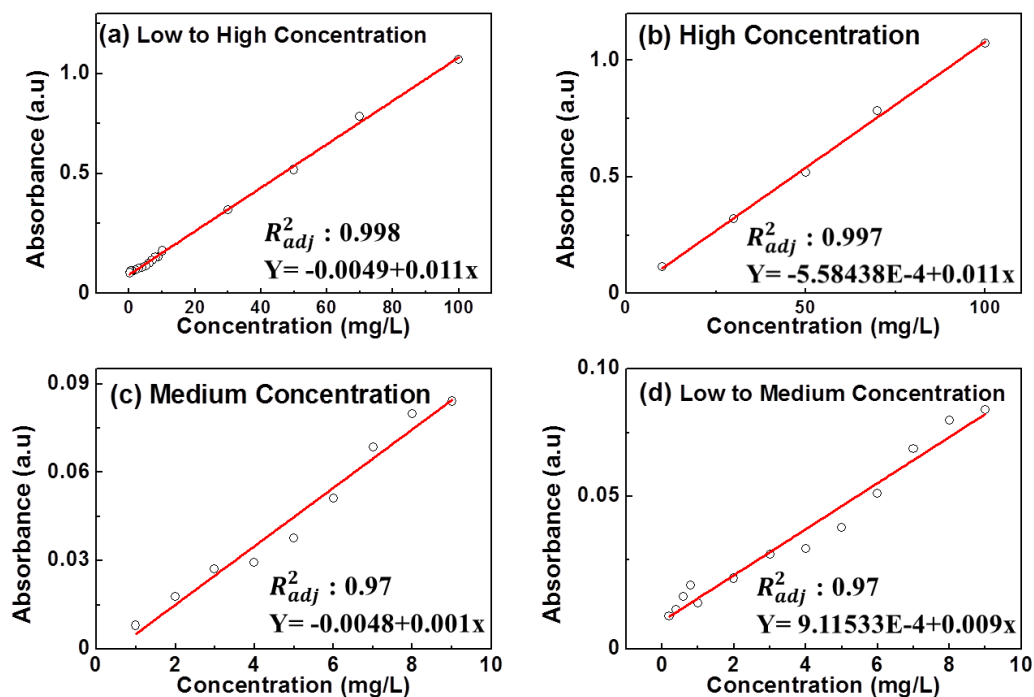


Figure 5. Absorbance spectra values as measured by the photodetector (Si transimpedance amplifier). Different concentrations of KHP prepared and measured using the Beer–Lambert law. (a) Low to high concentration. (b) High concentration. (c) Medium concentration. (d) Low to medium concentration.

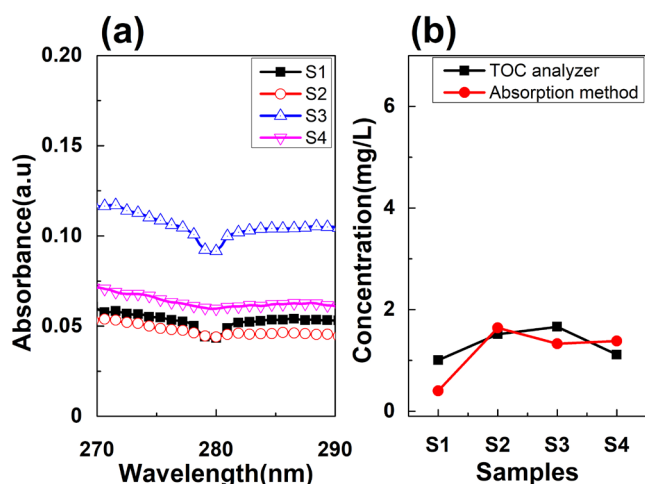


Figure 6. The four samples, S1 (tap water), S2 (river water), S3 (lake water), and S4 (seawater), were measured using a UV-LED spectroscopy system and TOC analyzer. In panel (a), the UV absorption was measured from 270–290 nm, each sample had a different absorbance trend near 280 nm. Panel (b) shows a comparison of the concentrations calculated by the absorption method and TOC analyzer.

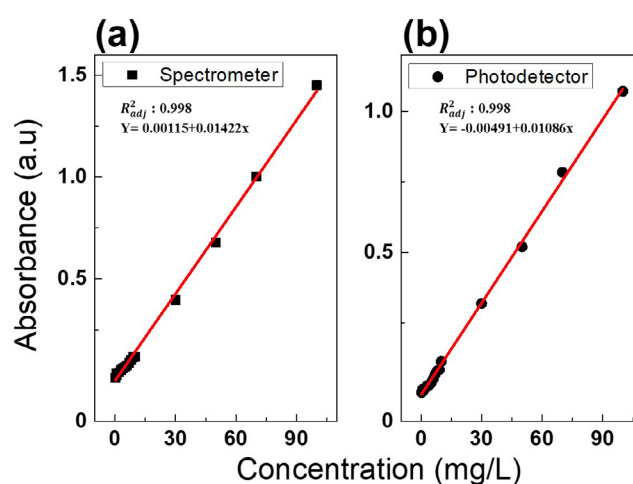


Figure 7. Comparison of the KHP absorbance measured by the UV-LED spectroscopy system (a) and the photodetector (b).

the results of the two methods have a good correlation, which offers a simple means for the monitoring of organic compounds in water.

In order to evaluate the correlation between the LED (figure 7(a)) and photodetector absorptions (figure 7(b)), the adjusted high coefficient values (R^2_{adj}) were obtained by using a linear fit analysis. In addition, the slope of the LED absorption calculated by the linear fit analysis was greater

than the corresponding photodetector slope, because the spectroscopy system was more sensitive than the photodetector. However, the photodetector method was less sensitive and the adjusted coefficient value was too high (0.998), so the photodetector method should only be used in correlation with the absorbance. Using this method, the photodetector is the easiest instrument to use to detect organic compounds in water.

4. Conclusion

In this paper, we proposed a simple optic system that uses UV-LED as a high efficiency light source that is able to

monitor organic carbon in water. A MLR analysis showed that a high degree of correlation (R_{adj}^2 : 0.992–0.978) was observed for the UV absorption and TOC concentrations. Moreover, a high degree of correlation (R_{adj}^2 : 0.998) for both UV absorption and the photodetector was shown. By utilizing the UV-LED source and the correlation between the spectroscopy and photodetector absorbance, stable and highly sensitive measurements were achieved. These findings could significantly widen the scope of TOC research in both the laboratory and the field, including the possibility of continuous *in situ* monitoring.

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