

## A Pair of Light Emitting Diodes for Absorbance Measurement

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Light emitting diodes (LEDs) have a semiconductor chip (~1 mm<sup>2</sup> area) mounted on a concave mirror and emit narrow band of wavelengths when forward biased.<sup>1</sup> LEDs have been widely used in many fields. Conventional light bulbs are being replaced by LED bulbs. They are also used as indicator lights, display panels, traffic signals, and flash lights due to their low power consumption and long life time.<sup>2</sup> LED costumes and dresses are also becoming popular.<sup>3</sup> City farming is getting more attention due to the fact that more population live in and near a city. LEDs are one of the most fascinating light sources in case of growing vegetables inside a building. Gwangju (one of the metropolitan cities in South Korea) built a LED based vegetable farming facility.<sup>4</sup> In terms of energy conversion efficiency (electricity to light), LEDs are ranked in third among many different kinds of light sources. They are covering very broad range of wavelengths from infrared (IR) to ultraviolet (UV). In addition, their emitting intensities are getting increased.<sup>5</sup> These features make LEDs ideal light sources for making much smaller and more convenient light therapy devices.<sup>6</sup>

In analytical chemistry, their small size, low cost and intrinsic stability in terms of light intensity fluctuation make them attractive to be used in many different types of spectroscopic instruments especially in absorbance and fluorescence measurement systems.<sup>5</sup> Olajos *et al.* used a LED induced fluorescence technique to evaluate various sample preparation methods for multi-capillary gel electrophoresis.<sup>7</sup> UV-LEDs are even used to decompose NO<sub>2</sub> to NO photochemically. Sadanga *et al.* measured atmospheric NO<sub>2</sub> continuously using a LED based NO<sub>2</sub> photolytic converter.<sup>8</sup> Eom also developed and evaluated several different designs of UV-LED based NO<sub>2</sub> photolytic converter.<sup>9</sup>

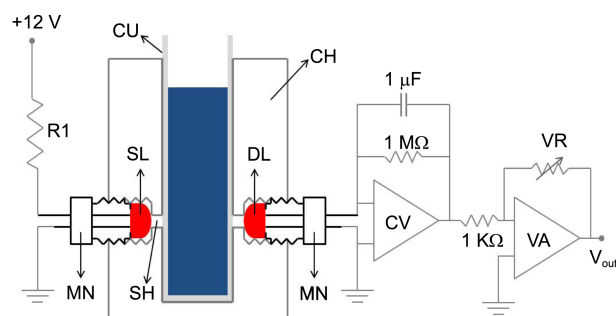
Even though LEDs are mostly using as light sources, they could be used as photo sensors. Mim *et al.* monitored UV radiation from the sun by using a LED as a photo sensor.<sup>10</sup> Ryu *et al.* applied red and IR LEDs to measure reflected sun lights from agricultural and forest vegetations to monitor their metabolism, structure, and function.<sup>11</sup> Berr *et al.* used a LED in colorimetric measurement with a tungsten halogen lamp.<sup>12</sup> Lau *et al.* developed a pared light emitting diode detector to be used in optical sensing measurement.<sup>13</sup> A forward biased LED was a light source emitter while a reverse biased LED (*i.e.* detector LED) was used as a photo sensor. Instead of measuring a photocurrent registered on a detector LED, they adopted a timer circuit to measure dis-

charging time of the reverse biased LED. The discharging time is faster, the more intensive light illuminated on the detector LED.

Meanwhile, Dasgupta *et al.* suggested that two LEDs of adjacent wavelengths could be used to construct a dual wavelength detector by operating two LEDs alternatively as an emitter and a photodiode.<sup>14</sup> In this report, a pair of LEDs was used to make absorbance measurement. The first LED was a light source as a solid-state light source (*i.e.* emitter LED) and the other was used as a photodiode (*i.e.* detector LED). When light illuminates the emitting chip of an LED, small amount of current (~nA level) can be produced. We were using an operational amplifier to amplify photocurrents registered on the detector LED directly. Compared to other light transducers like silicone based photodiodes, a LED is known to be more sensitive to the same wavelength which the LED emits. Bromothymol blue (BTB) was used as a test dye. The red LED's emission spectra and relative sensitivity in terms of wavelength was also reported here. The test dye's absorption spectra, linear range of the calibration curve, and limit of detection were also measured.

### Experimental

A common acid-base indicator, bromothymol blue (BTB, Reagent grade, Samchun Chemicals, Korea) in 0.10 M NaOH was used as a test dye. Two red LEDs (nominal  $\lambda_{\text{max}} = 660$  nm, MS-L512CRHU, Moksan, Korea) were used as a light



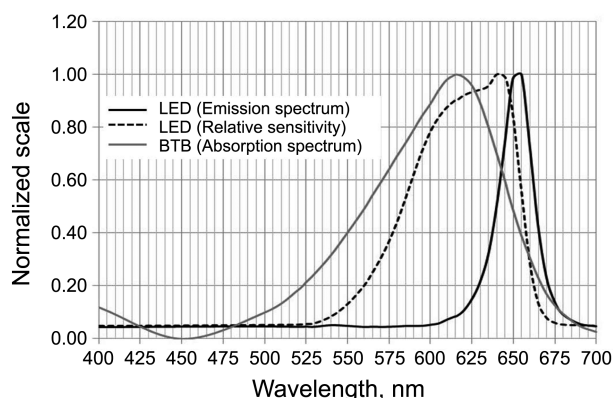
**Figure 1.** Schematic diagram of two LED absorbance measurement system; R1: current limiting resistance, MN: male nut, CU: sample cuvet, SL: source LED, SH: slit hole, DL: detector LED, CH: cuvet holder, CV: current-voltage converter, VA: voltage amplifier, VR: variable resistor (10 K $\Omega$ ). The photocurrent on DL was amplified through two stage op-amplifier. See text for details.

source and a photodiode. The standard solution of the dye was prepared in the concentration of 10.0 mM. NaOH solution (0.10 M) was used for proper dilution of BTB to prepare working solutions. Deionized water (Direct-Q3, Millipore, France) was used for the preparation of all aqueous solutions. A commercial spectrometer (Thermo 9423QA2200E, Thermo, UK) was used to measure the spectra of BTB solution (in 0.1 M NaOH).

The schematic diagram of the absorbance measurement system using two identical red LEDs is shown in Figure 1. Two red LEDs were aligned to face each other through a standard 1-cm path disposable cuvet (Kartell, Italy) where placed in a cuvet holder (CH) machined with aluminum. The holder was dark sprayed inside and outside to minimize stray light. Two threaded holes were drilled on the cuvet holder (CH) placing both an emitter LED (SL) and a detector LED (DL) facing each other. Two small id (1.5 mm) holes were served as a slit. The emitter LED was powered by +12 volt with a driving current of 10.4 mA (with a current limiting resistor, R1). Lights emitted from the emitter LED travel BTB solution in a cuvet and then reach the detector LED. The photocurrent registered on the detector LED was several nA level which is too weak for signal processing so the current was amplified using an operational amplifier (TL082CP, TX instrument, TX, USA). The op-amp was assembled in the author's laboratory. The photocurrent was first converted to voltage (1 volt/ $\mu$ A, current-to-voltage converter, CV) and then further amplified using a voltage-voltage amplifier (VA) having an adjustable gain knob (max. gain = 10 with variable resistor, VR).

The op-amp's final output (*i.e.* photocurrent level,  $V_{out}$ ) was collected by a desktop PC via analogue-digital converter card (16 bit IO/DO, SCXI-1122, National Instruments, USA). Data acquisition was done through a software (Labview2011 SP1, National Instrument) provided from the manufacturer. The equation of  $A = -\log\{(V_s - V_d)/(V_r - V_d)\}$  was used to convert measured photocurrent (*i.e.* transmittance) to absorbance unit where  $V_s$  and  $V_r$  are source light intensities measured from sample (*i.e.* BTB solution) and reference solutions (*i.e.* 0.1 M NaOH), respectively and  $V_d$  is the dark signal recorded when the emitter LED was turned off. Each photocurrent was measured for 5 minutes and averaged those data points after cut off the initial and the last ~1 minute data points. For calibration curve, data collection frequency was 100 Hz and moving averaged 100 data points for the study of absolute noise level of the system and limit of detection (LOD).

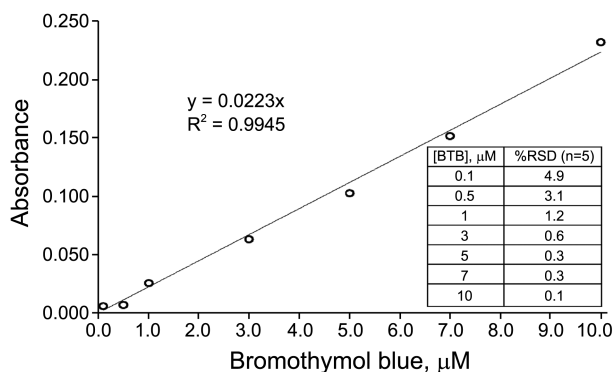
Figure 2 shows the emitter LED's emission spectrum, its relative sensitivity as a function of wavelength, and absorption spectrum of bromothymol blue dye in 0.1 M NaOH. The deprotonated BTB's absorption spectrum (absorbs broad band of visible lights ranging from 450 nm to 700 nm, absorption  $\lambda_{max} = 615$  nm) overlaps partly the emission spectrum of the emitter LED (emission  $\lambda_{max} = 655$  nm). This overlap was quite enough to perform absorbance measurement consequently. More interesting finding is that the relative sensitivity of the emitter LEDs as a photodiode. It is



**Figure 2.** Red LED's emission spectrum, its relative sensitivity as a function of wavelength, and absorption spectrum of bromothymol blue dye in 0.1 M NaOH. See text for details.

known that a LED is more sensible to the same band of wavelength which the LED emits. The Figure 2 clearly shows that the band of wavelength sensed by the red LED is blue-shifted and ~3 times broader to the corresponding emission spectrum emitted by the red LED. This figure suggests that sporting relative sensitivities versus wavelength is necessary for distinct LEDs to be used in colorimetric sensing protocols in more precise manner.

Even though the emitter LED's emission band is not quite matched with the absorption band of the dye, the paired red LED system shows a good linearity for the concentration range of 0.100–10.0  $\mu$ M shown in Figure 3. Each standard BTB solution was measured five times and averaged. The cuvet was removed and placed right before every single measurement to contain systematic errors. Reproducibility is quite good with %RSD of as high as of ~5% at 0.1  $\mu$ M concentration. Please note that this two LED-based photometer is designed to use a conventional sample cuvet so measured absorbance errors caused by a measurement is more dominating factors rather than any other error functions such as a long-term stability. Especially, for the absorbance measurement with a single sample cuvet, the long-term stability would not be an issue due to the fact that a LED is



**Figure 3.** Calibration curve of BTB working solutions in NaOH. Each concentration was measured five times and then averaged. The inset table shows %RSD for each concentration measurement. See text for details.

one of the most stable light sources in terms of the light intensity fluctuation stated at the beginning of this report. Otherwise, a long-term stability could be an issue with the current proposed photometer design in such a case of experiment (*i.e.* kinetic study), the proposed system can be modified to use a ratiometry by monitoring the light intensity of the source red LED directly from its backside with a second photodiode. The adoption of a second photodiode is a well-known technique to improve a long-term stability of a LED-based system.<sup>5</sup> Absolute noise level was found to be 0.0002 Abs and the limit of detection (LOD, S/N = 3) of BTB is 0.03  $\mu\text{M}$ . It is well known that source light's emission band should be much narrower compared to the test dye's absorption spectrum to extend dynamic concentration range due to the fact that Beer's law is working best theoretically under that experimental condition. Later, choosing an emitter LED having a narrow band of emission wavelength could improve linearity and a dynamic concentration range.

In conclusion, two same wavelength LEDs (*i.e.* an emitter LED and a detector LED, respectively) were successfully used to measure absorbance of BTB solution. A linear calibration with r-squared value of 0.9945 was achieved. 0.03  $\mu\text{M}$  of LOD was observed with a noise level of  $2 \times 10^{-4}$  absorbance unit. We are now examining relative sensitivities of different LEDs with distinct wavelength. In the future, building a spectrophotometer equipped with LEDs is quite interesting both in scientifically and pedagogically (*i.e.* undergraduate lab course).

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