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Short communication

A concept of dual optical detection using three light emitting diodes

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ABSTRACT

In this paper a concept of very simple measurement system dedicated for simultaneous photometric and fluorometric detection is presented. Only three ordinary unmodified light emitting diodes (LEDs) can be applied in this analytical device: one of them is used in the conventional way as a source of nearly monochromatic light inducing fluorescence, whereas two others are applied as photometric and fluorometric detectors of light. In this study quinine is chosen as a model analyte. The reported device enables simultaneous detection of this analyte in the micromolar range of concentration. The practical utility of prototype dual detector for complex sample analysis is illustrated by its application for determination of quinine in tonic water samples.

1. Introduction

Although optical detection dominates in analytical chemistry, for many practical applications highly advanced and expensive spectrophotometers as well as spectrofluorometers are not necessary. For many dedicated analytical uses simple optical detectors based on economic optoelectronic components are sufficient.

Light emitting diodes (LEDs) are used very often in analytical photometric methods as extremely cheap, low-power, high efficiency, robust, long lifetime and very stable sources of nearly monochromatic light [1,2]. They are also suitable as excitation light sources inducing analytically useful fluorescence [2–5]. The role of LEDs as light sources for optical methods of analysis is well established.

On the other hand, it is known, that the internal photoelectric effect (opposite to electroluminescence phenomena) allows the use of LED as light detector [6,7]. Absorbance detectors exploring LEDs as light detectors are reported in the analytical literature [8–17]. As analytically useful signal generated by LED-based light detectors the discharging time [8–12] or electric potential [13–17] can be applied. Pairing of two LEDs, playing role of light emitter and detector, leads to construction of complete photometric devices useful in analytical chemistry. These are very simple photometers dedicated for educational purposes [17] as well as more advanced absorbance detectors for chromatography [8–10] and flow injection analysis [11–16].

In this communication the first-time example of the utility of LED as fluorescence detector is demonstrated. Moreover, the ability of simultaneous absorbance and fluorescence measurements using extremely simple three-LED-based device without any additional optical and optoelectronic components is presented.

2. Experimental

Quinine (as sulphate salt) was obtained from Sigma-Aldrich (Germany). All other reagents were of analytical grade and were obtained from POCh (Poland). Doubly distilled water was used throughout. The set of quinine standards was prepared in 0.05 M sulphuric acid. The oxygen from quinine solutions was removed immediately before measurements by 5 min bubbling with argon. Disposable acrylic cuvettes (1 cm optical pathlength) were obtained from Sarstedt (product no. 67.755, Germany). The cuvettes with solutions were thermostated (usually at 30 °C) using water bath. The anionite resin Amberlite IRA-904 used in the course of real sample (drinks contained quinine) analysis was obtained from Bio Rad Laboratories. Drink samples were diluted with 0.1 M sulphuric acid. For each sample the measurements performed using the prototype device were six times replicated.

The prototype of dual photo/fluorometer is show in Fig. 1. The holder for 1 cm × 4 cm × 4 cm cuvettes has been constructed using Technic™ LEGO® bricks. Typical holes in Lego bricks are suitable for LED mounting. In the course of measurements the holder was additionally isolated from incident light using ordinary black box. The holder enables mounting of one LED emitter, one LED-absorbance detector and two LED-fluorescence detectors. Optionally, fiber optic coupling the cuvette with conventional fluorometer can be mounted. Similar constructions have been shown in our previous papers [13,17].

Declared nominal powers of 365, 370 and 375 nm UV LEDs applied in this investigation were 3, 6 and 11 mW, respec-

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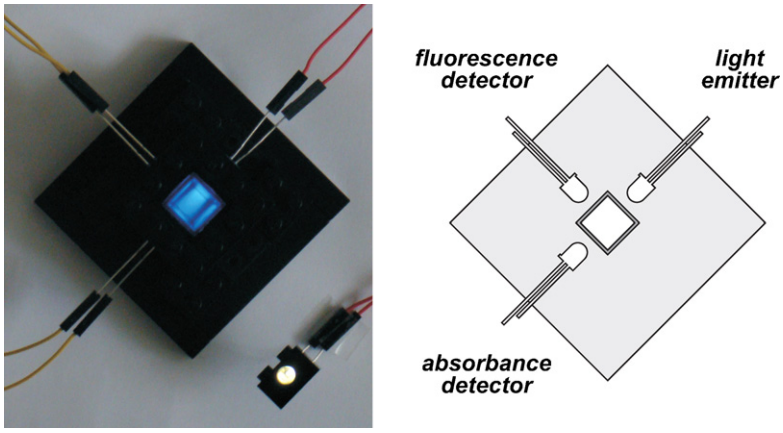

Fig. 1. The prototype of three-LED-based device for cuvette measurements.

tively. These 5 mm LEDs were supplied by Amecam (product numbers: LED365003-40AWOM06, LED3700006-50AWOM06 and LED375011-50AWOM06, respectively). 5 mm blue (470 nm) and red (630 nm) LEDs were obtained from Optosupply Honkong (product numbers OSUB5131A-PQ and OSHR53E1A-LM, respectively).

For supplying the LED emitter a home-made circuit was constructed using a solderless board and typical electronic components obtained from TME (Poland). As instrument measuring analytical signal (voltage generated by LED-based detectors) a digital pH-meter from Radelkis (model OP208/1, Hungary) was applied. The scheme of complete device for dual optical measurements is depicted in Fig. 1.

The reference measurements of fluorescence were performed using fiber optic fluorometer (model USB2000FLG from Ocean Optic Inc. (OOI), USA). The reference photometric measurements were performed using a UV–vis Shimadzu spectrophotometer (model 2401/PC, Japan).

3. Results and discussion

3.1. Selection of LED emitter

In this study quinine, often applied for educational demonstrations of fluorescence phenomenon [18–21], has been chosen as a model analyte. Quinine is easily detectable by both, absorbance and fluorometric methods. In sulphuric acid solutions, quinine has two analytically useful absorption/excitation wavelengths, 250 and 350 nm. Regardless of which excitation wavelength is used, the wavelength of maximum fluorescence is 450 nm. Thus, as a light source, UV LEDs were applied.

In primary experiments the LED induced fluorescence was measured using OOI fluorometer. For these experiments the silica fiber optic connecting the instrument with the cuvette holder was mounted in place of LED-fluorescence detector. The highest fluorescence intensity of quinine (0–50 μM) was induced by 375 nm LED with the slope of 19.6 ± 0.2 [counts per μM] ($R^2 = 0.9996$). For comparison, the sensitivities for 370 and 365 nm LEDs were 8.8 ± 0.1 ($R^2 = 0.9985$) and 4.3 ± 0.1 ($R^2 = 0.9998$), respectively. The results suggest that the intensity of LED emitter is more significant parameter than the compatibility of light source spectrum with absorption spectrum of quinine. In the other words, due to straightforward energy transfer mechanism, quinine absorbs reasonable strongly up to 375 nm and as long as it happens and the LED intensity is greater, then there will be more energy transferred and the emission will be enhanced. As expected, longer-wavelength red and blue LEDs did not induced fluorescence of quinine. Obviously, the emission spectrum of fluorescence-induced-LED is compatible with absorption spectrum of quinine. This way the selected LED can also play the role of light source in the course of absorbance mode measurements.

3.2. Selection of LED-fluorescence detector

LEDs could play a role as non-selective detectors for light of higher energy than the light emitted by them. Additionally, halfwidths of the emission spectra of the LEDs used in the course of investigations are ±10 nm. Thus, potentially all tested LEDs can detect light generated by 375 nm LED emitter, whereas only blue and red LED detectors could measure quinine fluorescence. As expected UV LEDs are insensitive for fluorescence. Useful calibration graphs for fluorometric quinine detection are shown in Fig. 2. Analytically useful calibration graphs for photometric quinine detection are given in Fig. 3. According to the operation theory of paired LED-absorbance detectors based on compilation of Shockley equation and Lambert–Beer law [13], for absorbance mode of measurements the voltage signal is directly proportional to quinine concentration. As the intensity of fluorescence is directly proportional to the analyte concentration, the fluorometric calibration curves are expected to be linear in the logarithmic scale of concentration.

Fluorometric measurements with red LED detector allow wider linear range of determination, whereas blue LED detector offers higher sensitivity but worse detection limit and reproducibility. Moreover, the graphs shown in Fig. 2 illustrate effect from the intensity of light inducing fluorescence. In both cases for lower intensities worse detection limits are observed caused by limited sensitivity of LEDs as light detectors.

3.3. Selection of LED-absorbance detector

For absorbance measurements only data for red and 365 nm LEDs detectors are shown (Fig. 3) because analytical signals generated by other LEDs were out of scale of the used pH-meter (the electromotive force generated by illuminated LEDs was higher than 1999.9 mV). As it was shown in our previous paper [14] only high impedance pH-meters offer ideal currentless conditions for measurements of voltage signal generated by LED detectors. Simpler electronic circuits give no ability to demonstrate real characteristics and phenomena of linear LED response, what is intention of this paper. On the other hand, pH-meters are common laboratory equipment. Thus, the suggested way of experiments is acceptable for analysts without experience in electronics.

For red LED detector surprising inversion of calibration graph was obtained (Fig. 3). Apparently, with an increase of quinine