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Sensors and Actuators B 114 (2006) 819–825
SENSORS AND ACTUATORS B CHEMICAL
www.elsevier.com/locate/snb

Quantitative colorimetric analysis of dye mixtures using an optical photometer based on LED array

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Received 18 March 2005; received in revised form 4 July 2005; accepted 7 July 2005
Available online 20 December 2005

Abstract

A disco photometer which was an optical sensing array based on multiple LEDs was constructed for colorimetric analysis. This approach has been used to analyse single dyes and dye mixtures containing up to three dye components. This technique made use of the inherent well-defined LED emission band to provide selectivity for chromophors, which have equally well-defined absorbance band to give very good analytical data. The results showed that this LED array configuration could be used to reduce the complexity of data obtained from the mixtures and also improve the quality of the output.

Keywords: Colorimetric analysis; Optical sensing; LED detector; Multivariate analysis

1. Introduction

In the area of chemical sensing it has always been a big challenge to analyse complex mixtures containing multiple components, which gives cross-sensitivities that interfere with the sensor performance. An ideal solution to this problem is to find sensors with very high selectivity, e.g. enzyme-like specificity, to provide good analytical information from samples containing complex mixtures. Unfortunately, in general, a chemical sensor or even a reagent-based sensing scheme can only achieve partial selectivity. To circumvent this problem, multiple sensors have been used to form sensor arrays that would provide a multi-dimensional information to describe the chemical signature of analytes. This information would be included into a reference library for the quantitative/determination of unknown samples. This multivariate approach is generally combined with a certain statistical method, normally a data reduction technique based on either linear or non-linear algorithms, such as principal component analysis [1] and neural networks [2,3], to simplify and improve the quality of the output. These approaches have been used successfully in chemical analysis and research efforts have continuously been made to improve the accuracy and reliability of the output [4–6].

Chemical analysis using array-sensing approach mainly includes electrochemical [7–9], mass [10,11] and optical sensors [12–18]. In the electrochemical sensing category a large proportion of the work has been in the area of gas sensing that is based on conductometric techniques. Sensors fabricated from inherently conducting polymers such as polypyrrole and polyaniline [19]; polymer composites prepared from blending a conducting element such as carbon powder with a non-conducting polymeric binder [20] and semiconductors such as tin oxide [21–24] have been extensively studied. Mass sensors are generally based on quartz crystals fabricated in a specific way so that they oscillate under applied voltage. The crystal is then coated with a sorbent material. The mass increase due to analyte being absorbed on the coating causes a frequency shift in the oscillator. Optical sensing using

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0925-4005/$ – see front matter © 2005 Published by Elsevier B.V.
doi:10.1016/j.snb.2005.07.054

multivariate approach includes the use of fibre optics [3–5] and chemochromic dyes [13,15]. Recent approaches include combining different sensors such as optical and capacitive in an array in an attempt to improve the reliability of the data [25,26]. These techniques normally provide qualitative rather than quantitative information, usually resulted in classification of chemicals.

Recently we have developed a simple optical sensor platform that used LEDs as both the light source and light detector. To function as a light sensor the LED is reverse biased at a specific voltage to generate photocurrent upon incident light. This photocurrent then discharges the LED at a rate that is proportional to the intensity of light reaching the detector. A simple threshold detection/timer circuit is used to indirectly measure the photocurrent at the detector LED to give digital output [27]. This LED emitter–light sensor combination is very versatile and can be configured to measure absorbance or reflectance and has been successfully used for colour measurements, and for monitoring colorimetric reactions and for metal detection [28,29].

This paper present the work on chemical sensing using a disco photometer fabricated from LEDs. A series of LEDs with different emission bands were used as light sources, and a low band gap IR LED was used as a universal light detector. LED array was used as light source because they offer flexibility in emission wavelength from UV to IR range with variable spectral widths (emission band widths). An important criterion in constructing a sensing array is to achieve optimal selectivity. In this design we envisage to use the well-defined emission band of the light source, in this case the LEDs, to provide selectivity for the sensor array that measures absorbance or reflectance. The degree of overlapping between the absorption bands of the analytes and the emission band of the light source therefore determines selectivity of the sensing array. This simple concept makes use of the fact that the two parameters are both constant and well-defined therefore the discrimination power of the array for target analytes can be tuned by selecting appropriate LED light sources to enhance selectivity. This approach does not rely on chemical selectivity of reagents such as chromophore receptors or fluorescent probes, which may become unstable over time. An array of LEDs that covered a broad spectral range from UV to IR region was selected to demonstrate this flexible multivariate approach for quantitative analysis.

2. Experimental

2.1. Disco photometer

Super bright infrared, red, orange, yellow, green, blue and UV LEDs were purchased from Kingbright, USA. The characteristics of the LEDs are shown in Table 1 and Fig. 2. The electronic circuitry used in this disco photometer has been described elsewhere [27]. The LEDs were arranged such that the emitter LEDs were encircling a centre detector LED protected by a black heat shrink to exclude the light coming in from the side as shown in Fig. 1(a). The emitter LEDs were inclined towards the centre so that all light beams merged at a spot approximately 1 cm in diameter and 2 cm from edge of the detector LED (Fig. 1(b)).

Table 1
Emission characteristics of the LEDs used in the fabrication of the disco photometer and the absorption characteristics of the dyes used

LED (no.)	Spectral line half-width (nm)	Peak emission wavelength (nm)
IR sensor (1)	–	940
IR (2)	50	880
Red (3)	20	660
Orange red (4)	20	630
Yellow (5)	35	590
Green (6)	30	565
Blue (7)	25	465
UV (8)	26	400
Dye	Spectral half width of absorption (nm)	Peak absorption wavelength (nm)
Methyl red	150	520
Bromocresol purple	100	430
Aniline blue	100	600

2.2. Optical cell

An optical cell was made up from a commercial black film canister ($d = 3$ cm, $h = 5$ cm) as shown in Fig. 1(b). A hole was cut on the top cover of the canister onto which the disco photometer was secured using epoxy glue. To promote light reflection a white polypropylene sheet cut to size to fit the bottom of the canister was fixed in with epoxy glue. The distance from the tip of the LEDs to the bottom of the optical cell was 2 cm where optimum reflection was obtained.

2.3. Dye solution measurement

Methyl red (MR), bromocresol purple (BCP) and aniline blue (AB) were obtained from Aldrich, Dublin.

Three dye stock solutions, 0.05 mM BCP, 0.05 mM MR and 0.01 mM AB were made up in 0.1 M HCl. Mixing the dye stock solutions in various proportions made up multiple component samples that contained a mixture of dyes.

A fixed amount of 5 ml solution was used for all measurements. For single component measurements, various dilutions were made up by mixing a predefined amount of the stock solution with 0.1 M HCl to make up a final total volume of 5 ml. For multiple component analysis, various ratios of stock solutions were used to make up a final volume of 5 ml. One exception was that of the 1:1:1 mixture of the three dyes which was made up by mixing 1 ml of each stock solution and made up to 5 ml with 0.1 M HCl.

A 5 ml sample of each solution to be investigated were pipetted into the optical cell and the top cover that was fitted with the disco photometer was then replaced. Three repeats