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Molecular absorption measurements with an optical fibre coupled array of ultra-violet light-emitting diodes

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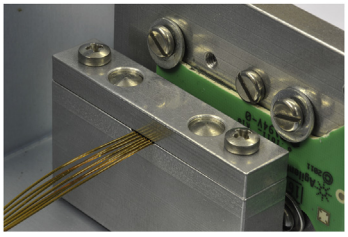
HIGHLIGHTS

- The detector features 8 LEDs covering the wavelength range from 255 to 350 nm.
- The use of optical fibres allows the coupling of all sources to a single photometric cell.
- Switching of LEDs is entirely electronic.

GRAPHICAL ABSTRACT



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ABSTRACT

A photometric detector based on eight different light-emitting diodes covering the ultraviolet range from 255 nm to 350 nm is described. These are coupled with fused silica optical fibres to a conventional cuvette with 1 cm optical path length or to a low volume flow through cell for detection in high-performance liquid chromatography. Photodiodes are employed for the measurement of the transmitted intensity as well as of a reference signal and the photocurrents are processed with a log-ratio amplifier to obtain a voltage proportional to absorbance values. The wavelength desired for the measurement at hand is selected by electronically switching on the requisite light-emitting diode. The detector was found to have a low noise level of 80 μAU. In batch-wise measurements as well as in detection for high-performance liquid chromatography dynamic ranges of 2–3 orders of magnitude were possible. Reproducibilities in peak areas for the latter application were better than 1%.

1. Introduction

Light-emitting diodes (LEDs) are appealing light sources for molecular absorption measurements and other spectroscopic methods. Their relatively narrow emission bands are a good match to the absorption bands of molecules so that no monochromators are needed. Other advantages are a stable intensity, low power consumption, limited heat production, small size and generally long lifetimes. For these reasons LEDs for the visible, the near infrared and the near ultraviolet (UV) ranges have been widely adopted for analytical instruments. Recent reviews are available [1,2]. A shortcoming of LEDs is the lack of wavelength flexibility. It is, of course, possible to mechanically exchange the LED in an instrument for different tasks, but this is not convenient when frequent or rapid changeovers are required. For this reason, the use of white LEDs covering a wide wavelength range has been

Abbreviations: UV, ultraviolet; LED, light-emitting diode; AU, absorbance unit; ACN, acetonitrile; MeOH, methanol; NADH, β-nicotinamide adenine dinucleotide; FWHM, full width at half maximum.

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suggested for analytical devices [3]. This approach retains most of the advantages of the LEDs, but reintroduces the need for a monochromator. A different route to wavelength flexibility is the use of an array of LEDs of different colours, as has been reported by several authors [4–10]. A difficulty in this approach arises when measurements are to be carried out in a cell with dimensions which are smaller than the size of the array of LEDs. This was solved by Hauser and coworkers for LEDs in the visible wavelength range by employing a commercially available star-coupler based on polymeric optical fibres [9,10] and by Fonseca and Raimundo by creating a bundle from 32 individual thin polymeric optical fibres [7]. The plastic cases of the visible LEDs were shortened and polished in these cases to get close access of the fibres to the emitting substrates in order to achieve efficient coupling.

In recent years LEDs for the deep-UV range down to 240 nm have also become commercially available. This is significant in that many organic molecules absorb light at these short wavelengths, but not in the near UV or the visible wavelength ranges. Several reports have indeed appeared on the evaluation of deep-UV LEDs at wavelengths below 300 nm for analytical purposes. Schmid et al. [11] and Bomastyk et al. [12] reported detectors for HPLC with standard columns using LEDs emitting at the often used detection wavelengths of 255 and 280 nm, while Li et al. [13], Sharma et al. [14] and Bui et al. [15] reported such detectors for HPLC and ion-chromatography with narrow bore columns. Macka and co-workers [16] as well as Bui and Hauser [17] extended the approach to UV-detection in capillary electrophoresis. The use of deep-UV LEDs for the detection of gaseous species, such as ozone [18,19] as well as the BTEX compounds (benzene, toluene, ethylbenzene and xylene) [20], has also been reported. Kraiczek et al. described the use of an array of 8 UV LEDs covering the wavelength range from 255 nm to 350 nm in a detector for HPLC [5]. Efficient coupling of the light from all individual UV-LED chips was achieved by placing these at the focal plane of an optical grating, in the reverse arrangement of a photodiode array detector. Herein a new fused silica fibre-coupled instrument based on multiple UV-LEDs is reported. It has been evaluated as a photometer for use with standard cuvettes, and as an absorption detector in HPLC.

2. Experimental

2.1. Chemicals and materials

Deionized water with a resistivity of 18 MΩ cm was obtained from a NANO-Pure water purification system (Barnstead, IA, USA). All chemicals were of either analytical grade or HPLC gradient grade. Sodium hydroxide, 4-hydroxybenzoic acid, naproxen, vitamin B6, uracil, caffeine and fluorene were products of Fluka (Buchs, Switzerland). Methyl benzoate was obtained from Acros (Morris Plains, NJ, USA). Salicylic acid, retinyl acetate, β-nicotinamide adenine dinucleotide (NADH), retinoic acid, retinol naphthalene and fluoranthene were purchased from Sigma-Aldrich (Buchs, Switzerland). $NaHCO_3$ and Na_2CO_3 were sourced from Merck (Zug, Switzerland). Acetonitrile (ACN) was obtained from Avantor (Gliwice, Poland). Methanol (MeOH) was a product of J. T. Baker (Deventer, Holland). All solutions for HPLC measurements were degassed in an ultrasonic bath.

2.2. Instrumentation

A UV-LED-array emitting at different wavelengths from 254 to 348 nm was obtained from Sensor Electronic Technology (Columbia, SC, USA). This consisted of eight chips which were mounted directly on a printed circuit substrate and the electrical contacts were made via gold wires bonded to the tracks. The LEDs were operated with a constant current source as detailed previously [12]. The photodiodes for the UV range (S1226-18BQ) were sourced from Hamamatsu (Shizuoka, Japan). These silicon photodiodes have an active area of 1.2 mm^2 and feature a quartz glass window to allow detection in the UV-range down to 190 nm. The flow-through cuvette employed for detection in HPLC was a product of Hellma (178.313-QS, Müllheim, Germany). The fused silica ball lenses were purchased from Edmund Optics (product numbers 67387 and 67386, Karlsruhe, Germany). Multimode optical fibres for the UV-range (UM22-600, 600 μm core; UM22-400, 400 μm core diameter; UM22-300, 300 μm core diameter) from Thorlabs (Dachau, Germany) were used for the light transmission. A log-ratio amplifier (LOG102) was obtained from Texas Instruments (Austin, TX, USA). The mechanical parts, consisting of holders for the LED-array and absorption cell, and the mounting and positioning stages for the optical fibres, were made in our workshops from aluminium. Separations were performed on an Agilent HPLC system (Model 1100, Waldbronn, Germany) which incorporates a photodiode-array detector (DAD) using columns from YMC (J'sphere ODS-H80, 4 μm, 150 mm × 4.6 mm, Kyoto, Japan) and Agilent (ZORBAX SB-phenyl, 5 μm, 250 mm × 4.6 mm). An e-corder data acquisition system (model ED401) and the Chart software package from EDAQ (Denistone East, NSW, Australia) running on a personal computer were used for the digitization and recording of signals. A low pass filter with a cut-off frequency of 2 Hz was applied. The emission spectra of the LEDs were acquired with a Flame diode array spectrometer from Ocean Optics (Dunedin, FL, USA) and the absorption spectra of compounds were obtained with a conventional UV/Vis-spectrophotometer from Agilent (model 8453).

3. Results and discussion

3.1. Design of the detector

A sketch of the general arrangement is shown in Fig. 1. Eight UV-LEDs with different emission wavelengths from 254 to 348 nm

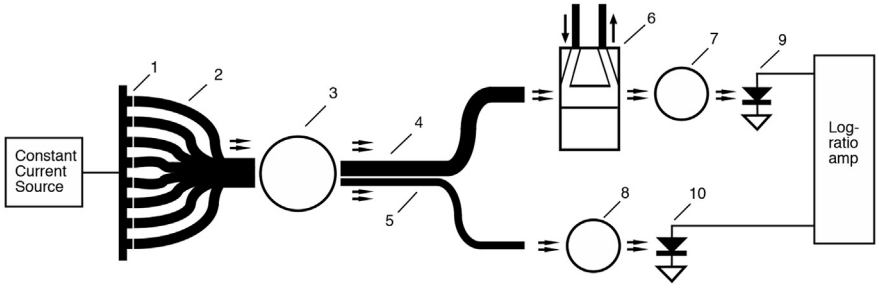

Fig. 1. Schematic drawing of the design of the detector (not to scale): (1) UV-LED array mounted on a substrate, (2) 400 μm optical fibres, (3) 6 mm ball lens, (4) 600 μm optical fibre to cell, (5) 300 μm optical fibre to a reference photodiode, (6) cuvette, (7) (8) 5 mm ball lenses, (9) (10) photodiodes.