High power deep UV-LEDs for analytical optical instrumentation

Yan Li [a,1], Miloš Dvořák [a,b,c,1], Pavel N. Nesterenko [a], Nantana Nuchtavorn [a,d], Mirek Macka [a,*]

[a] School of Physical Sciences and Australian Centre for Research on Separation Science (ACROSS), University of Tasmania, Private Bag 75, Hobart 7001, Australia
[b] Materials Research Centre, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
[c] Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 967/97, 602 00 Brno, Czech Republic
[d] Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Mahidol University,447 Sri-Ayudhaya Rd., Rajathevee, Bangkok 10400, Thailand

# Spectrophotometry
<paper review>

Antonio Osamu Katagiri Tanaka
A01212611@itesm.mx

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LEDs offer a better alternative to traditional UV sources (low-cost, small size, robustness, portability, and low noise).

Li et al. intention was to report the performance newly deep UV-LEDs and investigate their feasibility for analytical applications.

- With increasing input current the ratio of VIS parasitic emission to the deep UV emission decreases

- The performance was demonstrated by detecting four parabens.
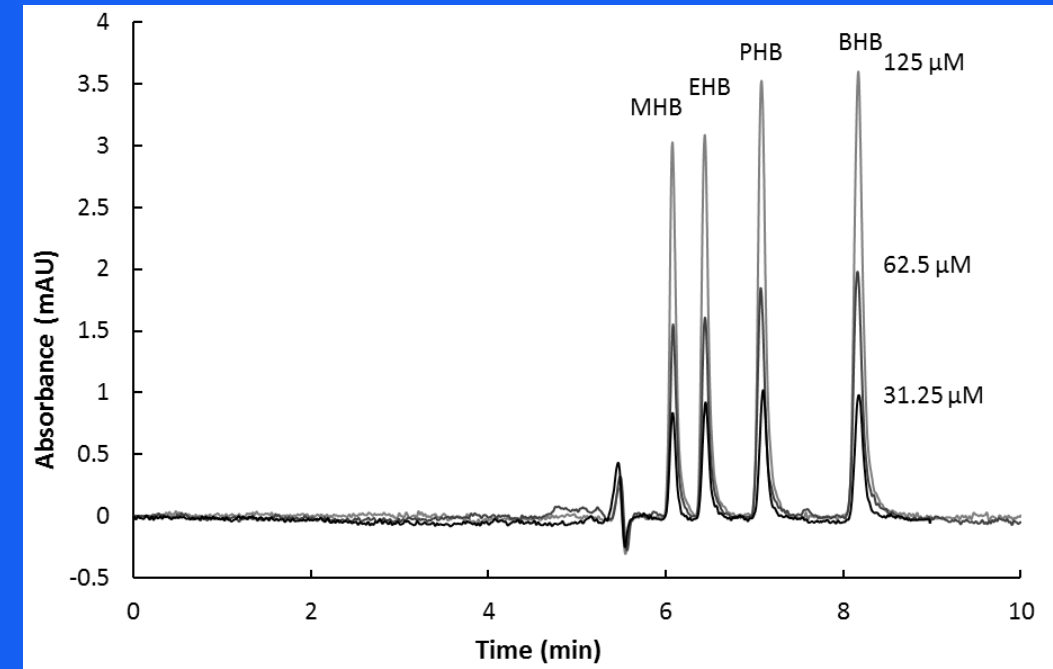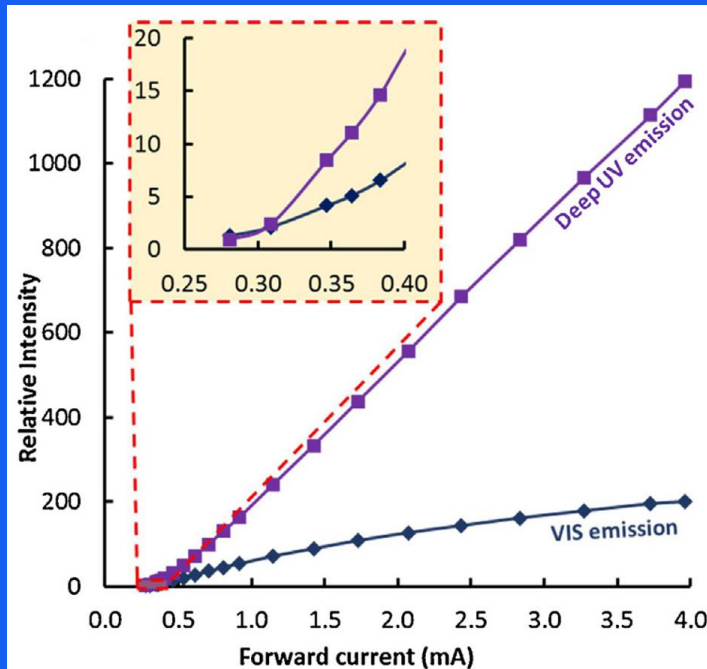
The new deep UV-LED noise was low, which is approximately 10 times lower than the noise using the old generation deep UV-LEDs

UV-Vis Spectroscopy — Paper Review

Antonio Osamu Katagiri Tanaka[1]*

[1] *ITESM, Av. Eugenio Garza Sada 2501 Sur, N.L., Monterrey, Mexico*

1   UV Spectrophotometry

Currently, there is a growing interest in the application of deep UV spectrophotometry for gas sensing applications, such as diagnosis of several diseases, environmental analyzes in the stratosphere, and indoor air quality (1). UV absorption spectrometry is a popular characterization technique and has been used in analytical applications due to its simplicity, flexibility, low cost, and convenience (2). A typical UV spectrophotometer is mainly composed of a UV emission source, chromator, and UV photodetector, as summarized in Figure 1.
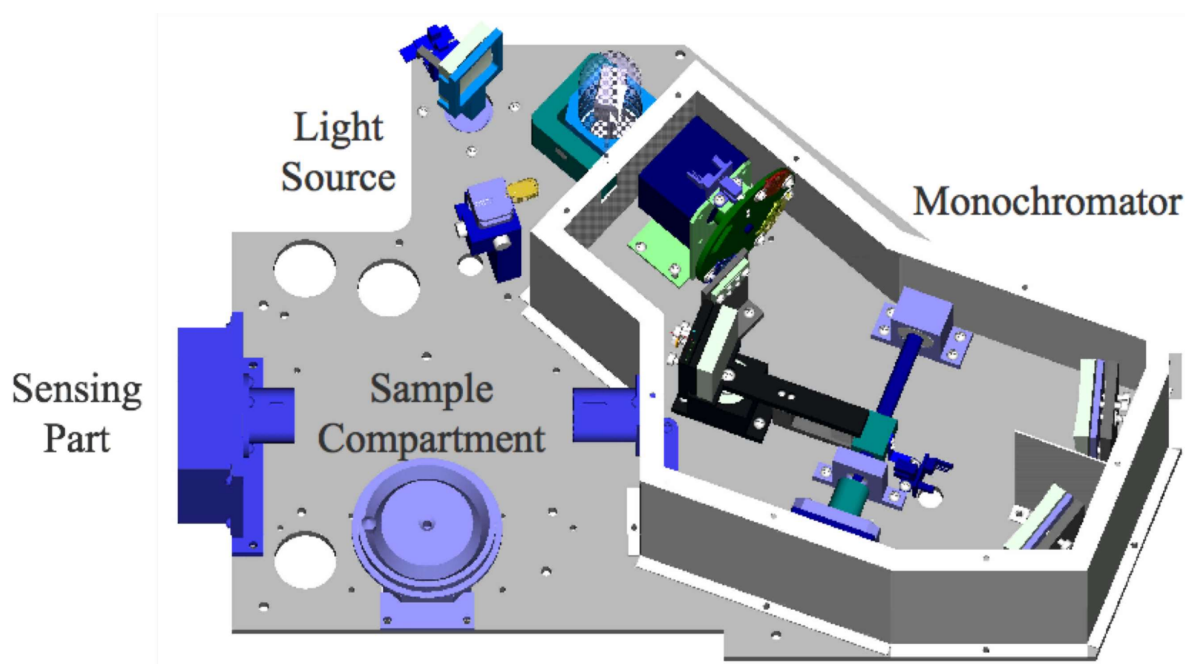

FIGURE 1

Schematic diagram of a typical UV-Vis spectrophotometer (3)

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*E-mail: A01212611@itesm.mx

1.1 UV Sources

Open arcs, fluorescent, incandescent, lasers, and LEDs are the typical UV sources. In spectroscopy implementations, the UV source shall be stable (commonly characterized by fluctuation or short-term stability) and with sufficient power intensity (usually quantified by the ratio of variation in the intensity of emitted light to the mean intensity of the emitted light) for the desired wavelength. The short-term stability and power intensity are essential factors in defining the accuracy and reliability of a spectrophotometer (1).

Deuterium UV lamps are relatively more stable than other alternatives, due to their extended lifetime and relativity high-intensity light output. However, the major drawbacks of deuterium lamps are the need of a highly stable power supply, and a warm-up time of approximately 30 minutes for thermal equilibrium. Low-pressure mercury lamps are also popular for spectrophotometric sensing of ozone, benzene, toluene, ethyl-benzene, and xylenes as the emission spectrum strongly follows the absorption spectra of these molecules. However, mercury lamps require high power input and has low output stability (1). Among the available UV sources, LEDs are an attractive option for future spectrophotometric devices die to portability, low cost, and low power consumption. Different UV sources arer55r5r5 summarized inTable 1.

TABLE 1

Collation of UV sources for spectrophotometry (1).

	LED	Deuterium Lamp	Xenon Flash Lamp	Mercury Lamp
Wavelength	Single peak	Relatively wide spectrum 120–400 nm	Broad-spectrum 160–2000 nm	Broad-spectrum 185–2000 nm
Stability of light output	Excellent temporal and spatial stability.	Good. Fluctuation <0.005%	Relatively poor. Fluctuation <3%	Relatively poor. Fluctuation <2%
Warm-up time	Instantaneous	20–30 min	Instantaneous	1–15 min
Life [hrs]	3000–10,000	2000–4000	400–5000	500–3000
Input wattage [W]	DC powered 6–10 V	5–150	2–60	5–150

Table 1 continued

	LED	Deuterium Lamp	Xenon Flash Lamp	Mercury Lamp
Thermal effect on samples	None	Sample can be affected by the heat from the lamp	None	Sample can be affected by the heat from the lamp
Cost	Low	High	High	Low
Drive electronics	Simple	Complex	Complex	Complex
Safety	Low voltage and cold light source	High power supply (Input wattage 5–150 W) and hot lamp surface	High voltage supply (Input wattage 2–300 W): sparking risk	High voltage supply (Input wattage 50–500 W) and contains mercury in fragile quartz envelop

1.2   UV-LED based spectroscopy

LEDs are semiconductor diodes, which emit light due to the hole-electron interaction, as the energy of an emitted photon depends on the band gap of the semiconductor. LEDs are small and portable with low optical noise, which can be easily incorporated into absorbance measurement detectors. LEDs have lower intensity drifts, low cost, long lifetime (104 h), and low heat generation (1). These features made them suitable for low-power portable applications.

2   Paper Review: High power deep UV-LEDs for analytical optical instrumentation (4)

LEDs have been implemented as light sources in various applications of optical sensing and chemical analyzes, as they offer a better alternative to traditional light sources (low-cost, small size, robustness, portability, and low noise). However, the lack of rapid, facile and accurate radiometric analysis of LEDs is a major limiting factor which constrains their practical use (5).

Li et al. intention was to report the performance of three new deep UV-LEDs (OPTAN255H, OPTAN255J and OPTAN280J), and investigate their feasibility for analytical applications. The LEDs selection was based on the maximum emission wavelength and maximum optical power (4).

2.1   Chemicals and reagents

As stated in Li et al.'s article, chromate in 50 mM NaOH solution was used as absorbing probe. The capillary was firstly flushed with water or the chromate standard solution with approximately 10 capillary volumes, then the flow was stopped and the absorbance was measured under static conditions. Each test solution was measured three times and in increasing concentration. Sodium hydroxide and sodium chromate were purchased from Sigma-Aldrich (St. Louis, MO, USA). The solutions were prepared fresh weekly and stored at 4 ∘C when not in use (4).

2.2   Instrumentation & Method

Li et al. used an USB2000 + XR1-ES miniature fiber optic based spectrometer (OceanOptics, Dunedin, FL, USA) with integration time set at 3 ms to measure the spectra of the deep UV-LEDs. The spectrometer used has a bandwidth of 2 nm. The spectrophotometer and LEDs were mounted into an optical bench (ACH-CUV-VAR, Ocean Optics, Dunedin, FL, USA) without additional optical fibers or lens. The data acquisition and processing of the emission spectra of deep UV-LEDs was processed with SpectraSuite software (Ocean Optics, Dunedin, FL, USA) (4). Li et al.'s paper assess the effects of input current and voltage on the intensities of the visible parasitic emission and the desirable UV emission.

2.3   Results

2.3.1   *Emission spectrum*

Li et al. experimental results show that while the parasitic emission still exists with the new generation deep UV-LEDs, with increasing input current the ratio of undesirable parasitic emission to the main deep UV emission rapidly decreased to values as low as 0.1% at the maximum forward current (100 mA) Figure 2 (4).

Since the forward current increases, the parasitic emission becomes saturated while the deep UV emission increases linearly, resulting to extremely low P/DUV ratio at its maximum forward current Figure 3, which overcomes the parasitic emission issue (4).
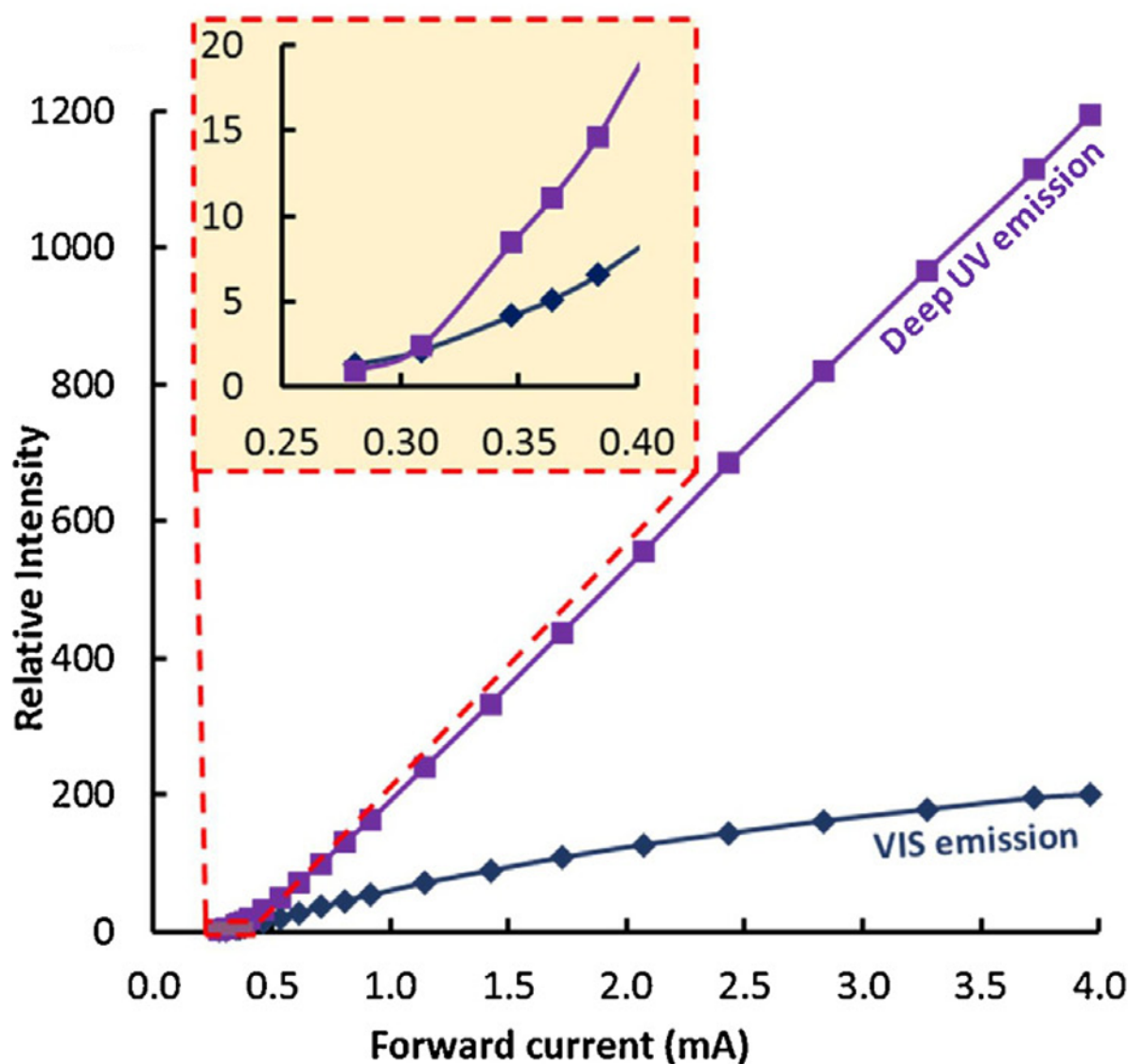
FIGURE 2

The intensity of deep UV emission and parasitic emission at different forward currents. The plots show unequal increasing rate of deep UV emission and the parasitic Vis emission (4).

Li et al. susoect that the parasitic emission can originate either in the presence of undesirable bands of lower energy in the emitting semiconductor, or by the presence of materials in the LED that exhibit fluorescence or phosphorescence behaviors (4).

2.3.2 *Detection performance and demonstration in capillary chromatography*

Li et al. implemented a new generation deep UV-LED (255 nm) as light source for a photometric on capillary detection, showing excellent linearity with stray light down to 0.8%, and effective path length above 92% of the used capillary inner diameter, and finally the perfor-
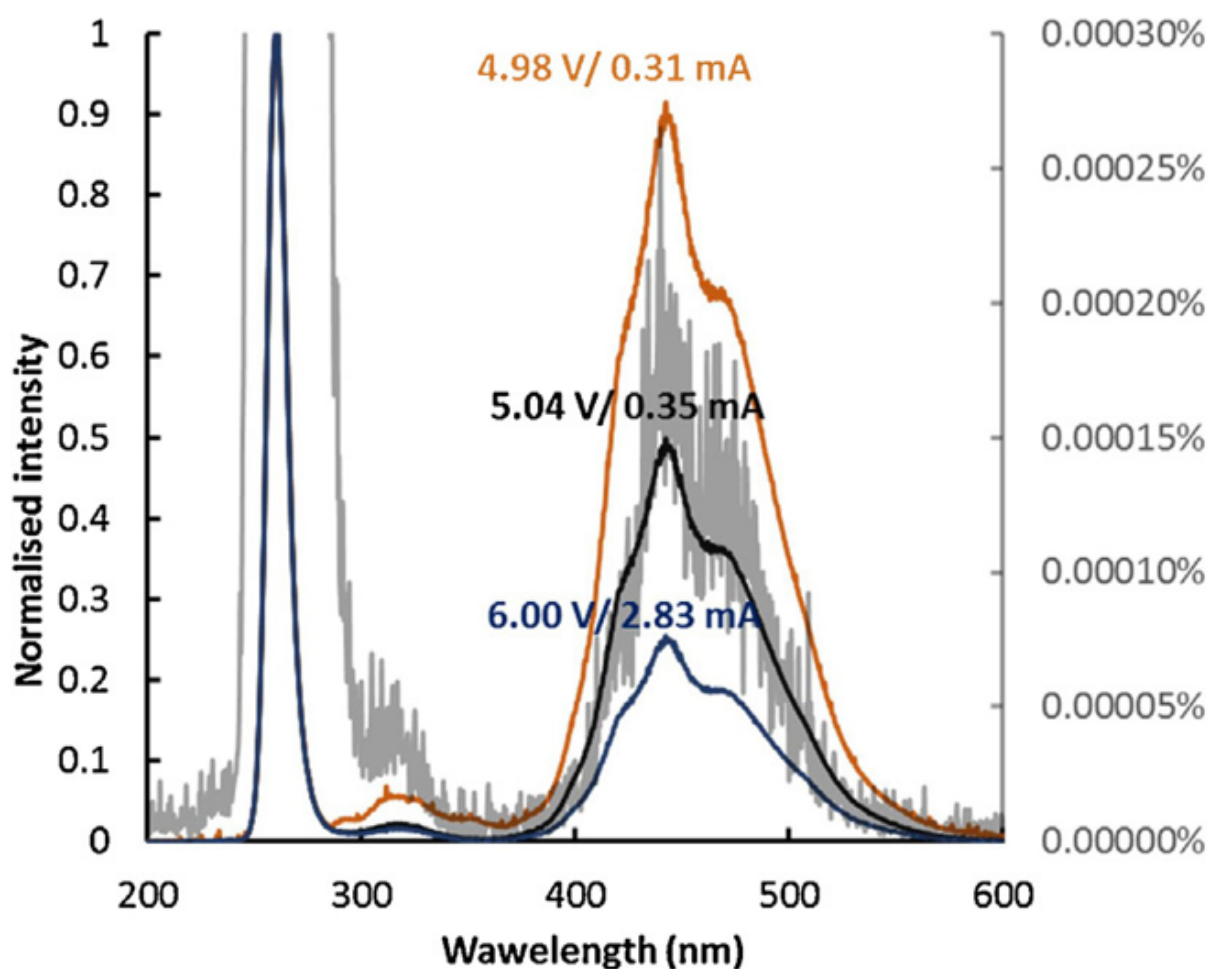
FIGURE 3

The emission spectra of new generation deep UV-LED (OPTAN255H) at 3 selected input currents (left axis) and at the maximum current (100 mA, grey line, right axis). The parasitic emission became relatively lower with increasing forward current and at the maximum forward current (100 mA) the parasitic emission is only about 2×10^{-4}% (right axis) (4)

mance was demonstrated by detecting four parabens separated by miniaturized capillary liquid chromatography Figure 4 (4).

The measurement reproducibility is within 1–3% relative standard deviation. Due to the high optical intensity of the new generation deep UV-LED, the baseline noise was low, determined as only 13.4 μAU, which is approximately 10 times lower than baseline noise for the same on-capillary detector using the old generation deep UV-LEDs. The on-capillary detector using the new generation deep UV-LED also offered excellent linearity. The detection performance comparison of a same on-capillary detector using old generation and new generation deep UV-LED as light source is shown inTable 2.
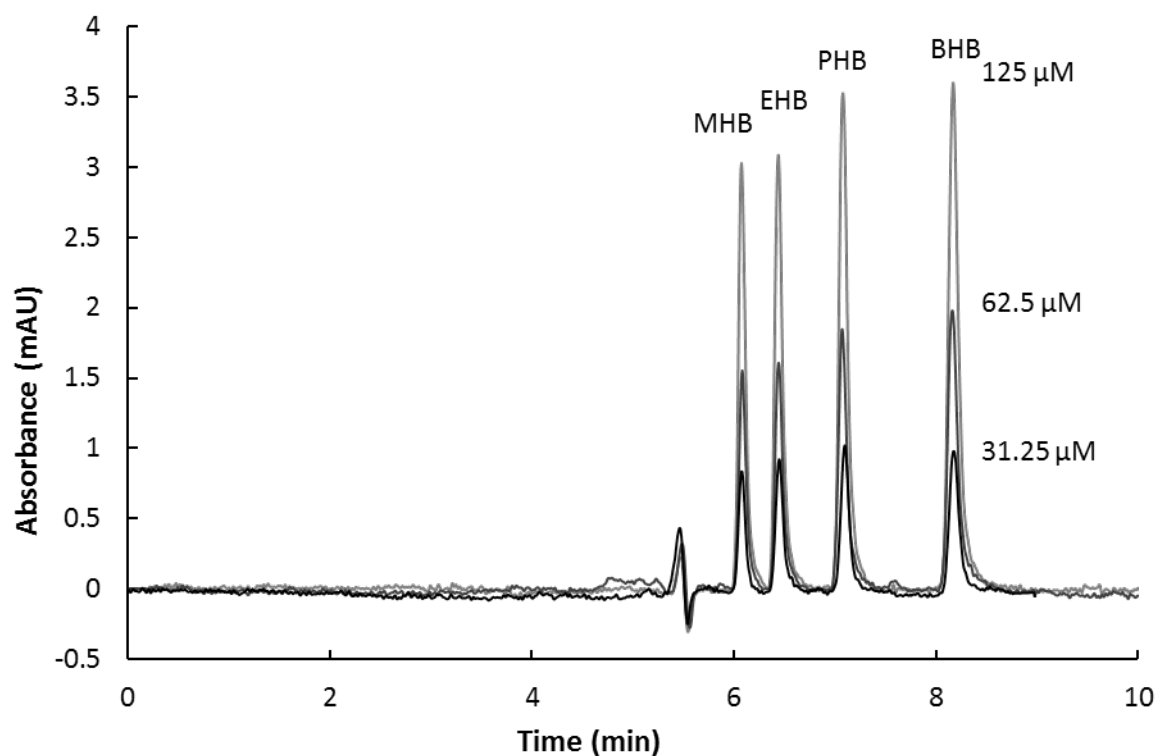
FIGURE 4

Isocratic separation of parabens of different concentrations. Conditions: Concentration of all analytes in three separations was 31.25 μM, 62.5 μM or 125 μM. methyl 4-hydroxybenzoate(MHP), ethyl 4-hydroxybenzoate (EHB), mM propyl 4-hydroxybenzoate (PHB), and butyl 4-hydroxybenzoate (BHB); Solvent: 50 mM ammonium acetate -acetonitrile 50/50 (v/v); flow rate: 0.5 mL min^{-1}; detection: 255 nm LED on-capillary photometric detector. Deep UV-LED forward current 100 mA (4).

TABLE 2

Comparison of the detection performance of on-capillary detector using old generation and new generation deep UV-LED as light source (4).

Generation of deep UV-LEDs	Stray light	Baseline noise [μAU]	Measured effective pathlength [percentage of the capillary ID]	Upper LOD linearity (mAU)
Old (sapphire substrate based)	30.5%	100	79%	31
New (AlN substrate based)	0.8%	13.4	95%	745

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Author biography
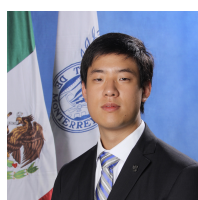
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High power deep UV-LEDs for analytical optical instrumentation

Yan Li [a,1], Miloš Dvořák [a,b,c,1], Pavel N. Nesterenko [a], Nantana Nuchtavorn [a,d], Mirek Macka [a,*]

[a] School of Physical Sciences and Australian Centre for Research on Separation Science (ACROSS), University of Tasmania, Private Bag 75, Hobart 7001, Australia
[b] Materials Research Centre, Faculty of Chemistry, Brno University of Technology, Purkyňova 118, 612 00 Brno, Czech Republic
[c] Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Veveří 967/97, 602 00 Brno, Czech Republic
[d] Department of Pharmaceutical Chemistry, Faculty of Pharmacy, Mahidol University,447 Sri-Ayudhaya Rd., Rajathevee, Bangkok 10400, Thailand

ABSTRACT

Optical detection systems for portable analytical instrument require commercially available, miniaturized, robust and well performing light sources. Light emitting diodes (LEDs) have been extensively used in portable analytical devices as they are exceptionally stable light sources offering a number of advantages over traditional light sources including robustness, small size and low-cost. In the analytically more significant deep UV spectral range, LEDs suffer from low optical power and parasitic emissions in the visible wavelength range. Recently, newly developed deep UV-LEDs based on aluminium nitride (AlN) substrates have been introduced claiming improved performance, however there is little in terms of systematic evaluation of their performance parameters when used as light sources in chemical sciences. The aim of this work was to investigate the performance of these new generation deep UV-LEDs, and assess their analytical applicability. Three AlN substrate based LEDs (OPTAN255H, OPTAN255J and OPTAN280J) were selected based on their maximum emission wavelength and maximum optical power. Their emission spectra, optical output power values and energy conversion efficiency (electrical/optical) were investigated. This work shows effects of forward current and voltages on the ratio of intensities of the visible parasitic emission to the desirable deep UV emission. Experimental results show that while the parasitic emission still exists with the new generation deep UV-LEDs, with increasing forward current the ratio of undesirable parasitic emission to the main deep UV emission rapidly decreased to values as low as 0.1% at the maximum forward current (100 mA). The new generation deep UV-LED (255 nm) was then applied as a light source for a photometric on-capillary detection, showing excellent linearity with stray light down to 0.8%, and effective pathlength above 92% of the used capillary inner diameter, and finally the performance was demonstrated by detection of four parabens separated by miniaturised capillary liquid chromatography.

1. Introduction

LEDs as light sources have been widely used in research, technology and general lighting [1] with their impact in all areas dramatically increasing especially during the last two decades. For analytical optical instruments, Flaschka et al. in 1973 had pioneered to apply LEDs in photometric detection systems [2]. Since then,

LEDs have become frequently used as light sources for absorbance and fluorescence measurements [1,3]. The advantages of implementing LEDs for analytical optical instrumentations include: (i) Quasi-monochromatic emission, therefore additional optical filters are not required in photometric detection [4–6]; (ii) High output intensity that introduces less noise to the measurements data over conventional light sources [1]; and (iii) Robustness, compact size, light weight, low power consumption and low cost, which make them desirable for the use in portable, low-cost devices [7–10]. The applications of LEDs for analytical purposes have been extensively reviewed in the last two years [1,11].

Most UV-absorbing analytes have the maximum absorptivity below 300 nm [12], therefore LEDs emitting in the deep UV

range have the highest analytical significance. For deep UV-LEDs, group-III-nitride materials, aluminium nitride (AlN) and gallium nitride (GaN), are normally used as the semiconductor material. The bandgap energies are 3.43 eV for GaN and 6.04 eV for AlN at room temperature. Therefore, by changing the content ratio of Ga and Al in the semiconductors material, a 200–300 nm wavelength range can be achieved. Through the last decades, LEDs have been advanced in respect to lowering emission wavelength and increasing optical power. Since late 20th century, deep UV-LEDs offering high optical output power have been reported at research level [13–16], and sapphire substrate based deep UV-LEDs with emission maxima down to ca. 240 nm appeared on the market from 2008 [17,18]. Schmid et al. [19] pioneered the application of this generation of deep UV-LEDs for optical detector on a common high performance liquid chromatography (HPLC) system. Since then, several studies of optical detectors based on the same generation of 255 and/or 280 nm deep UV-LEDs were reported, for capillary electrophoresis (CE) [20], HPLC [21–23] and capillary LC [8,9,24,25].

Though these studies are application oriented, some issues of this generation of deep UV-LED were found and reported [19,20,22,24]. Firstly, the output optical power of deep UV-LEDs is substantially lower than most visible –range LEDs. The low optical power leads to more noise, therefore in real applications a focusing lens sometimes was considered [21,24]. The second concern is the lack of complete monochromaticity. Not only the bandwidth of the UV emission peak is relatively broad (ca. 25 nm half-height bandwidth) [20], but also UV-LEDs generally have a parasitic broadband emission in the visible range [8,19,22,24]. This parasitic broadband emission issue is well-known in physics and attracted great attention during the last decade, with many comprehensive studies having been conducted [13,26–31]. For analytical optical devices, the parasitic emission band would increase stray light effect and consequently degrade the linearity and detection sensitivity [20]. Therefore, short pass filters [8] or special UV-selective photodiodes [19] were employed in the previous studies, which increased the cost and complexity of the entire device. UV-selective photodiode also prevents the deep UV-LED from being used in multi-wavelength detection systems.

Deep UV-LEDs technology progressed over recent years, especially the substrate growing techniques. Deep UV-LEDs based on AlN substrate (instead of sapphire) became commercially available since 2014 [32]. In theory, the new AlN substrate should give rise to lattice mismatch between the substrate and the AlN layers to a lesser degree, which allows the LEDs to deliver higher output power and achieve increased lifetimes [33]. This new generation high power deep UV-LEDs have been so far used in only few publications oriented on analytical and detection science, showing favourable performance including ca. 100 times improved optical output [7,11,34,35] and negligible amount of parasitic emission band [36]. These studies clearly showcased the great applicability of this new generation of deep UV-LEDs, indicating their possibility to be the next ordinarily used deep UV-LEDs for analytical devices. However, despite these encouraging results, there is little, if any, information available for analytical scientists allowing comparison of the analytically relevant properties and performance for the old and new generations of UV-LEDs.

This paper aims at filling this knowledge gap in regard to analytically relevant properties of the new generation of deep UV-LEDs, which have become widely used in analytical instrumentation applications. The emission spectra, optical power (also termed radiant power) and energy conversion efficiencies of new (AlN substrates) and old (sapphire substrates) generations of deep UV-LEDs were investigated and compared. Special attention in this study was paid to the parasitic visible region emission, in respect to its origin and its intensity ratio to the main deep UV emission (P/DUV). This is the first time the properties and analytical applicability of the

new generation of LEDs being comprehensively studied for analytical purposes, which is highly significant and valuable specifically in the area of optical sensing.

2. Materials and methods

2.1. Chemicals and reagents

Analytical or higher grade reagents and deionised water (Millipore, Bedford, MA, USA) were used for preparing all solutions. Sodium hydroxide and sodium chromate were purchased from Sigma-Aldrich (St. Louis, MO, USA). These solutions were prepared fresh weekly and stored at 4 °C when not in use.

2.2. Instrumentation

The deep UV-LEDs with integrated hemispherical lens (OPTAN255H, OPTAN255J and OPTAN280J) were purchased from Crystal IS (Green Island, NY USA). Blue LED (OVLGB0C6B9, 470 nm) was sourced from OPTEK (Carrollton, TX, USA). More detailed specifications of each LED are shown in Table 1. The optical output power was measured with a silicon photodiode (active area 100 mm^2; UV enhanced response; Edmund Optics, York, UK) using its optical vs. electric power calibration graph. A DC Power Supply PS-3005D (Wavecom Instruments, Findon, SA, Australia) was employed to power the LEDs when constant voltage (0 – 10 V) was required, while an in-house made constant current power supply was used when the constant current (0 – 100 mA) was applied. The details of the in-house made constant current power supply can be found in Johns et al. [4]. Multimeter Digitech QM1535 (Jaycar, NSW, Australia) was employed for the measurement of the forward current and voltage applied onto LEDs. Multimeter Tenma 72-7740 (Springboro, Ohio, USA) was used to measure the optical output power collected by the silicon photodiode. The LED-based on-capillary photometric detector used an Agilent optical interface (Alignment interface, 50 μm coded green, Agilent Technologies, Waldbronn, Germany), housed in an in-house designed black nylon holder, the design of the on-capillary detector was described in detail earlier [5]. The detectors were interfaced using an eDAQ e-corder data acquisition system (Model ED401, Denistone East, New South Wales, Australia). A miniaturised LC system reported previously [7] was employed for the demonstration separation of parabens. A 300 mm × 100 μm i.d. Chromolith CapRod RP-18 monolith column (Merck KGaA, Darmstadt, Germany) was used on the miniaturised LC system [7].

The spectra of the deep UV-LEDs were measured using an USB2000 + XR1-ES miniature fibre optic based spectrometer (OceanOptics, Dunedin, FL, USA) with integration time set at 3 ms. The spectrometer used has a bandwidth of 2 nm. The spectrophotometer and LEDs were mounted into an adjustable optical bench (ACH-CUV-VAR, Ocean Optics, Dunedin, FL, USA) without additional optical fibres or lens. Spectroscopy software SpectraSuite (Ocean Optics, Dunedin, FL, USA) was used for data acquisition and processing of the emission spectra of deep UV-LEDs. The presented chromatograms of separation of parabens were online processed by mains digital filter (50 Hz) and a low-pass digital filter with a cut-off frequency of 0.5 Hz showing a negligible effect on peak heights.

2.3. Effective pathlength and stray light measurement procedure

Detection linearity as sensitivity (absorbance divided by concentration) *vs.* absorbance graph for on-capillary detector was converted from the measurement of absorbance to concentration relationship [4]. Chromate in 50 mM NaOH solution was used as absorbing probe. The capillary was firstly flushed with water or the chromate standard solution (approx. 10 capillary volumes), then

Table 1

LEDs parameters (manufacturer specified/measured or used) of three new generation deep UV-LEDs (OPTAN255H, OPTAN255J and OPTAN280J), one old generation (UVTOP255-HL-TO39) deep UV-LED and a visible LED (OVLGB0C6B9) for comparison.

Name of LEDs		Maximum current (mA)	Voltage at maximum current (V)	Electrical Power (mW)	Emission maximum (nm)[a]	Optical Power (mW)[a]	Half-height emission bandwidth (nm)	Lifetime (Hours)[b]	Substrate	Price (USD$)	Energy conversion efficiency
Deep UV-LED	OPTAN255H	100/100	7.7	765	255/260	0.5–1.0/0.55	6	3000	AlN	300	0.072%
	OPTAN255J	100/100	8.1	812	255/257	1.0–2.0/0.79	6	3000	AlN	300	0.097%
	OPTAN280J	100/100	9.0	902	280/279	1.0–2.0/1.48	6	3000	AlN	300	0.183%
	UVTOP255-HL-TO39[c]	20/30	N.A/6.5	265	255/257	0.040/0.014	25	100	Sapphire	300	0.015%
Visible LED	OVLGB0C6B9	20/20	3.1	62	470/469	N.A/5.14	22	100,000	InGaN	0.5	8.277%

[a] Calculated for peak wavelength at maximum of intensity using forward current.

[b] Continuous mode, 50% maximum forward current.

[c] Parameters taken from manufacturer datasheets or measured by Krčmová et al. [20].

the flow was stopped and the absorbance was measured under static conditions. Each test solution was measured in triplicate and in order of increasing concentration. From the sensitivity vs. absorbance curve effective pathlength and% of stray light values were calculated.

3. Results and discussions

3.1. Emission spectrum

One of the key parameters of LEDs is the emission spectrum, which shows the maximum emission wavelength, emission bandwidth and the monochromaticity [8,20,36]. In optical detection systems, the maximum forward current is usually applied to obtain the highest possible light intensity and thus optimal signal-to-noise ratio. The spectrum of the new generation of deep UV-LEDs at the maximum forward current is shown in Fig. 1 (solid line). The main feature of new generation deep UV-LEDs is the low intensity ratio of the parasitic emission to the deep UV emission (P/DUV) (0.0002%),as compared to the P/DUV ratio of old generation deep UV-LEDs (8%; Fig. 1, dashed line). In addition, the emission bandwidth (half-height) is only 6 nm, compared to 25 nm for the old generation deep UV-LED (see Fig. 1 and Table 1). The narrow emission bandwidths implies that this deep UV-LED can be more effectively used in optical spectrophotometric detectors as a monochromatic light source without the need for an additional optical filter [34], which significantly reduces the complexity, size and cost of the instrumentation. A more detailed overview of the data is provided in Table 1.
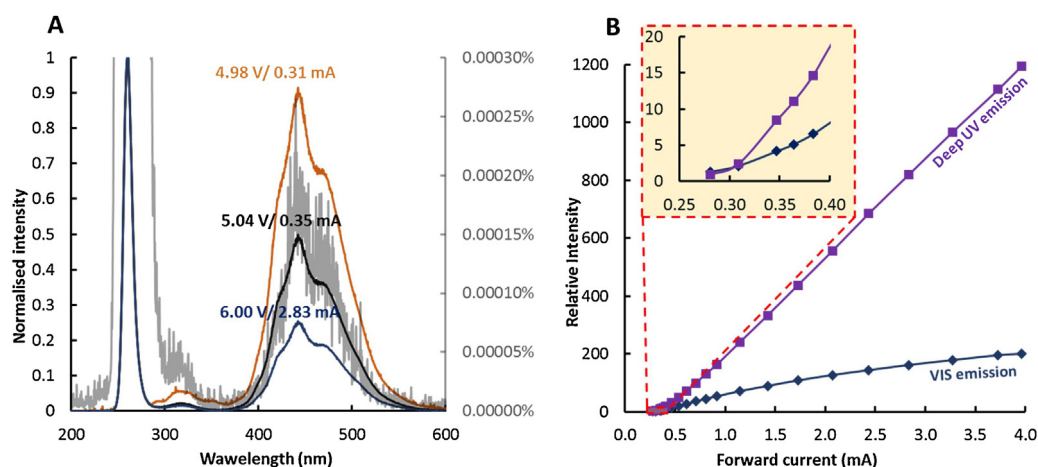
As the new generation deep UV-LED at its maximum operating current shows a low P/DUV ratio, further investigation focused on the factors that affect the P/DUV ratio. The parasitic emission can originate either in the presence of undesirable (parasitic) bands of lower energy in the emitting semiconductor, or it can be caused by presence of materials in the LED that exhibit fluorescence/phosphorescence. According to previous reports [22,28,37], the sapphire based deep UV-LEDs produced higher P/DUV ratio at low forward current values (<5 mA), which was due to a deep neutral acceptor levels assisted radiative recombination in the p-AlGaN layer [27,28]. In addition, the parasitic emission was also thought to be due to the fluorescent contaminants in the LED package [23]. Therefore, the performance of the new generation AlN based LED at low forward currents was studied (Fig. 2). The results of the new generation deep UV-LED (OPTAN255H) shows that the P/DUV ratio was relatively high at low forward current values (<5 mA), but the UV emission increased much more rapidly with the increase of forward current than the parasitic emission, resulting to lower P/DUV (Fig. 2B). This means that the recombination issue in the p-AlGaN layer still exists for the new generation deep UV-LED. Also, this indicated that the fluorescent contaminants at least were not the main reason for the parasitic emission. The AlN substrate provides the new generation deep UV-LED with very high maximum forward current (100 mA, comparing to about 30 mA for the old generation [20]). Since the forward current increases, the parasitic emission becomes saturated while the deep UV emission increases linearly, resulting to extremely low P/DUV ratio (0.0002%) at its maximum forward current (Fig 2A), which indirectly overcome the parasitic emission issue.

3.2. Optical output power and energy conversion efficiency

Optical output power and energy conversion (electrical/optical) efficiency are important characteristics of an LED. Deep UV-LEDs have relatively low optical power output compared to LEDs in the visible range [1], and the self-heating is a common issue of deep
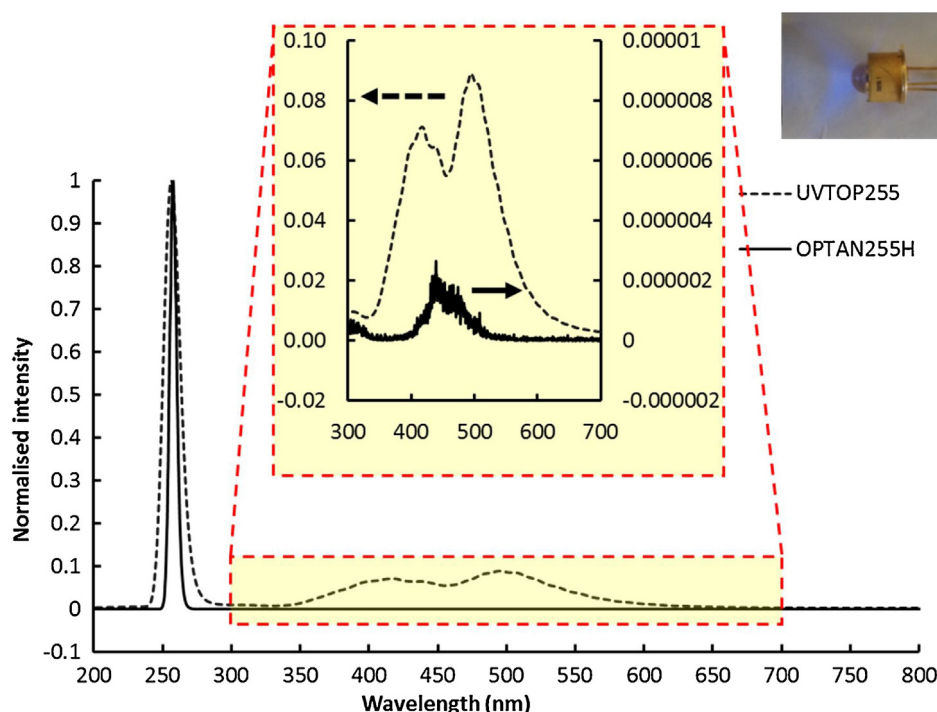
Fig. 1. Emission spectrum of the new type LED (OPTAN255H as the example, solid line) and the old type LED (UVTOP255-HL-TO39, dashed line) at their maximum forward current. Intensities are normalised based on the maximum emission peak. The zoomed area shows the P/UV ratio is 0.0002% for the new generation deep-UV LED (right axis), while 8% for the old generation of deep-UV LED (left axis). An image of UVTOP255-HL-TO39 with its typical visible light emission is shown in the insert, clearly showing the strong parasitic emission in the visible spectrum region. Conditions: as in Table 1 and Experimental Section.

Fig. 2. A The emission spectra of new generation deep UV-LED (OPTAN255H) at 3 selected low forward currents (0.31, 0.35 and 2.83 mA, coloured lines with labels, left axis) and at the maximum current (100 mA, grey line, right axis). The parasitic emission became relatively lower with increasing forward current and at the maximum forward current (100 mA) the parasitic emission is only about 2×10^{-4}% (right axis). B: The intensity of deep UV emission and parasitic emission at different forward currents. The plots show unequal increasing rate of deep UV emission and the parasitic emission. Details of conditions see Experimental.

Table 2

Comparison of the detection performance of on-capillary detector using old generation and new generation deep UV-LED as light source.

Generation of deep UV-LEDs	Stray light	Baseline noise (µAU)	Measured effective pathlength (percentage of the capillary ID)	Upper LOD linearity (mAU)
Old[a] (sapphire substrate based)	30.5%	100	79%	31
New (AlN substrate based)	0.8%	13.4	95%	745

[a] Parameters taken from manufacturer datasheets or measured by Krčmová et al. [20].

UV-LEDs [20,36,38]. The optical output power and the energy conversion efficiency of three new generation deep UV-LEDs and a blue LED (470 nm) were compared at different forward currents as shown in Fig. 3. The blue LED was selected as a comparison, due to its high optical output power and stability. As expected, the results showed that the deep UV-LEDs could deliver 0.55-1.48 mW optical output power at their maximum forward current (100 mA), which is 39–106 times higher than the old generation deep UV-LED
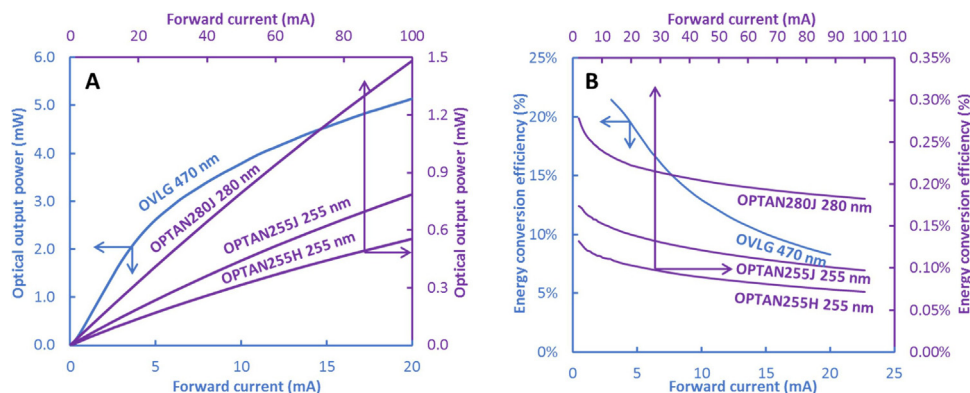
Fig. 3. A. Forward current to optical output power relationship and B. Energy conversion efficiency at different forward currents of three new generation deep UV-LEDs (Optan255H, Optan255J and Optan280) and one blue LED (470 nm) as a comparison. The energy conversion efficiency of all the LEDs decreased with increase of electrical power, while the decreasing rate is lower for the deep UV-LEDs than the blue LED.

(0.014 mW), and those experimental obtained values are close to the manufacturer values (Fig. 3A and Table 1). The forward current has an inverse-proportional effect on energy conversion efficiency for all the LEDs (Fig. 3B), indicating considerable self-heating at higher forward current. Interestingly, the influence of forward current on energy conversion efficiency is less pronounced for deep UV-LEDs as compared to the blue LED, which is likely due to a combined effect of a higher carrier generation and recombination ability of the deep UV-LEDs, and different thermal conductivities of the used materials in the body of the LED and therefore different heat dissipation and self-heating. The InGaN semiconductor in the blue LED (470 nm) has a bandgap energy of 2.64 eV, while the AlGaN semiconductor in the deep UV-LED (255 nm) has a bandgap energy of 4.87 eV. Therefore, with high energy pumped, the carrier generation and recombination of blue LED quickly became saturated, resulting to lower energy conversion efficiency. Overall, though the optical output power of the new generation deep UV-LEDs is orders of magnitude higher than the old generation deep UV-LED, the energy conversion efficiency is still much lower than the blue LED (Fig. 3B and Table 1). Therefore, an active/passive heat sink should be considered in practical applications for these deep UV-LEDs to maintain a higher performance. The demonstration of time dependence change of the optical output power for a new generation deep UV-LED with and without a passive heat sink is detailedin our previously published report [36].

3.3. Detection performance and demonstration in capillary chromatography

A 255 nm new generation deep UV-LED (Optan255H) was selected to demonstrate its detection performance in an on-capillary detector, previously used with a number of visible and deep UV-LEDs [4,7,20]. Due to the low P/DUV ratio of the deep UV-LED, there was no need for additional optical filter. A detection sensitivity (AU/mol L^{-1}) vs. absorbance graph (ESI, Fig. S1) was plotted to experimentally determine the effective pathlength, stray light and linearity, as demonstrated previously [4,6,36,39]. Absorbing substance here was chromate, which absorbs strongly at 255 nm (molar absorptivity at 255 nm: 2624 L mol^{-1} cm^{-1}), but not at visible wavelength where the parasitic emission occurs (ESI, Fig. S2). An upper limit of detection (LOD) linearity [4], determined as the absorbance corresponding to 95% sensitivity, was calculated as 745 mAU, while the dynamic linear range extends up to about 2000 mAU. The measured effective pathlength was 95 μm, which is 95% of the used capillary ID (100 μm). Importantly, only 0.8% stray light was determined, compared to 30.5% in the previous study using old generation deep UV-LED that exhibiting strong parasitic emission

[20]. The low stray light level confirmed the low P/DUV ratio of the new generation deep UV-LED. Then to demonstrate the detection performance practically, this on-capillary detector was applied for detection in a miniaturised capillary LC for the separations of parabens (ESI, Fig. S3). The run-to-run reproducibility is within 1–3% relative standard deviation (RSD) (n = 6) in peak heights. Due to the high optical intensity of the new generation deep UV-LED, the baseline noise was low, determined as only 13.4 μAU, which is significantly lower (approx. 10x) than baseline noise for the same on-capillary detector using the old generation deep UV-LEDs (100 μAU) [20]. The on-capillary detector using the new generation deep UV-LED also offered excellent linearity [7]. The detection performance comparison of a same on-capillary detector using old generation and new generation deep UV-LED as light source is shown in Table 2. This new generation deep UV-LED has been used in several applications, including in CE [35], capillary LC [7,36] and absorption detector for gas detection [34]. Overall, the experimentally measured detection parameters of the new generation deep UV-LED on-capillary detector, including effective pathlength, stray light and baseline noise, were superior to previously used similar designed detector using old generation deep UV-LEDs.

4. Conclusions

The evaluated new generation deep UV-LEDs based on AlN substrate have ca. 100 times stronger intensity of optical power than the old UV-LEDs based on sapphire substrates. This increase in the emission output at the desired UV emission band also correlates with a corresponding decrease in the parasitic visible range emission P/DUV ratio: at the maximum forward current, while the old sapphire substrate based deep UV-LEDs had a P/DUV ratio of 8%, the newer AlN substrate based deep UV-LEDs show a P/DUV ratio of only 0.0002%. Importantly, the higher driving current, the lower is the P/DUV ratio, therefore higher driving currents are to be preferred. This leads to an expected further improvement for rapidly pulsed deep UV-LEDs driven at multiples of the steady current. Due to the low P/DUV ratio, the new generation deep UV-LEDs can be employed in photometric detection without any additional optical filters. The demonstrated properties are very important for the future of optical detection using deep UV-LEDs in miniaturised, low cost analytical devices.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.snb.2017.08.085.

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Biographies

Yan Li, is currently a graduate student at the School of Physical Sciences, University of Tasmania. His research interests include liquid chromatography, portable analytical devices and optical detections.

Miloš Dvořák, received his PhD from the Brno University of Technology, and is currently a postdoctoral fellow at the Institute of Analytical Chemistry, Academy of Sciences of the Czech Republic, Brno, conducting research in capillary separations.

Pavel N. Nesterenko, is a professor at the University of Tasmania. His research evolves primarily around novel stationary phases for liquid chromatography.

Nantana Nuchtavorn, received her PhD from Mahidol University, Thailand, where she has a position of lecturer, conduction research in separation science.

Mirek Macka, is an Australian Research Council Future Fellow and Professor at the Australian Centre for Research on Separation Science (ACROSS), University of Tasmania. His research encompasses areas of separation and detection science with focus on miniaturisation.