Abstract. Following the recent introduction of AlGaN/GaN based ultraviolet Light Emitting Diodes (UV-LEDs) in the 250 nm to 350 nm wavelength region, a wide range of research activities have begun. For example, using the high levels of power of available UV-light, chemical reactions can be stimulated. However, when optical detection techniques are considered, light intensity and wavelength accuracy are more important to achieve low detection limits. Using LED-based light sources in the ultraviolet instead of the classical deuterium, xenon, mercury or metal halide sources is very attractive due to their high power conversion, relatively simple electronic driving circuitry and low power consumption. For both absorption and fluorescence detection, such LEDs and complete detection systems are powerful tools both traditional and new applications in the field and laboratory. In this work, the electrical and optical properties of these new UV-LEDs will be described. Further, the flexibility of using optical fibres for UV-light delivery will be discussed with respect to the available UV-wavelengths and UV-induced damage. To exemplify the potential of UV LEDs, a self correcting fibre optic detection system over the wavelength range 260 and 280 nm, based on such LEDs will be shown. Further, an overview discussing flexible optical fibre UV-light delivery systems will be given and applications for both will be considered.

1. Introduction
Traditionally, UV light in the 200 and 380 nm wavelength region has been generated by using deuterium, xenon, mercury, metal halide, hollow cathode light sources and expensive laser systems, for example. For stable and efficient operation, such light sources require a mains supply, complex driving circuitry and stable mechanical housings. By nature of their design, they are fragile and care has to be taken when using them in field applications. Recent innovations in the light source area have included the miniaturization of Xenon light sources [1] and high frequency operated deuterium light sources [2]. In addition to their reduced size, they have been designed for fibre optic coupling, which allow the design of a miniaturized fibre optic light delivery system. However, these white light sources still require sophisticated electronics and the required warm-up period to reach stability and their limited lifetime are also important issues.

Research into semiconductor based UV light sources has been very active in the last years. LED manufacturers have successfully pushed the minimum wavelength from 430 nm down to 350 nm for
mainstream applications. An important milestone was the design of a high-power UV-LED at 365 nm, with up to 100 mW optical power [3, 4, 5]. More recent success in UV optoelectronics have led to the development of UV light emitting diodes (LEDs) operating below 300 nm [6, 7, 8].

Fused silica/silica fibres can be used to transport UV light achieving effective UV light delivery in optical detection systems. However, fused silica fibres have a tendency to solarise as a result of the UV illumination. With deuterium lamps emitting light in the 180 nm to 350 nm region, long term research has been undertaken to study and minimize so-called E-centres influencing the 260 nm region [10, 11, 12]. In addition to All-Silica (AS-) fibres, Polymer-Clad Silica (PCS-) fibres and Polymer Optical Fibres (POFs) have been tested as UV-light delivery systems [13, 14].

The focus of this work has been to evaluate and demonstrate the applicability of UV LEDs for optical detection systems and fibre delivery systems. As LEDs have the tendency to drift in light output power, temporal and spectral studies of the output power have been performed. Uses of UV LEDs for DNA and protein detection, Thin Layer Chromatography and polymer curing are discussed.

2. Properties of light-sources

2.1. Low-power UV-LEDs

UV LEDs are based on AlGaN multiple quantum well active layer designs with up to milliwatt cw output powers at 20 mA driving current, for wavelengths in the 250 to 350 nm region. Their emission spectra show a 10 to 12 nm spectral bandwidth (FWHM). For single wavelength applications, these LEDs may be seen as “monochromatic”. A key advantage of LEDs is their small defined light emitting aperture; light can conveniently and efficiently be coupled into an optical fibre either by directly placing the fibre in front of the LED dye or by coupling via a lens. Several AlGaN/GaN UV LEDs manufactured via the “Migration Enhanced Metal Organic Chemical Vapour Deposition (MEMOCVD) technique were evaluated. UV light was coupled from the LED into a 600 µm solarisation resistant fibre [15, 16]. Light power at the fibre output was measured with a UV-sensitive photodiode and a pico-amperemeter. The spectral emission was measured with a TIDAS II spectrophotometer [17]. Results obtained from UV-LEDs with centre wavelengths of 260, 280, 305 and 365 nm, driven at 20 mA are shown in Figure 1 and Table 1, respectively.

For comparison, light output power levels of the high power LED described in the next section are shown. As expected, the output power is seen to be increasing with increasing wavelength, using the same coupling and processing conditions. Relative spectral intensity distributions of the UV LEDs as a function of wavelength were measured with a spectrophotometer [15]. The resolution of the spectrometer was confirmed to be 2.5 nm using a mercury spectral calibration lamp at 253.7 nm wavelength. Although their Full width at Half Maximum (FWHM) values appear similar, ranging up
to 12 nm, these LEDs exhibit a trailing edge, making them unsuitable for methods with a 10 nm bandwidth requirement (Figs. 1, 2).

Table 1: Total output power (600 µm AS-fibre output) of the LEDs under test.

| Wavelength [nm] | 265 | 285 | 305 | 365 | 365 |
|-----------------|-----|-----|-----|-----|-----|
| Output power [µW] | 55  | 125 | 150 | 450 | >5000 |

The light output power was found to increase linearly with driving current, from 5 mA to 20 mA. Although the LED is heated up with increasing driving current, the spectral shape and therefore the spectral bandwidth is stable within an accuracy of 0.1 nm (Fig. 2), a margin of error negligible for most applications. In comparison to broadband lamps, the warm-up times of UV LEDs are very short: even with 20 mA driving current, saturation can be observed after 5 minutes (Fig. 3). In some cases, however, the stability in a free-run operation is not sufficient [18], measured with ASTM-standard E685-93 [19] for light-sources: the noise value of 2 mAU can be reduced to < 1 mAU by stabilizing the UV-LEDs [17,18].

2.2. High-power UV-LEDs

High power UV LEDs in the UV A region are very promising light sources for illumination and optical detection applications [3]. A fibre optic based illumination system based on such LEDs has been developed [4,5,6]. For optimization of the light output, wavelength stability and lifetime, the temperature of the LED chip is TEC-cooled, and regulated by a PID-closed loop system. For operating the LED at different light output power levels, a precision current source is used.

Fig. 4: Photograph of the UV-LED light source, with imaging system.

Fig. 5: Block diagram of the UV-LED light source (electro-optical parameters)

The current source is able to operate in a cw mode or analogue AC-mode modulated by an external signal generator up to 10kHz. The output power (up to 100mW) for the UV-LED light source is controlled by the external control voltage $U_i$, (Fig. 4). The mechanical setup and a block diagram of
the electronic circuit and the optics are shown (Fig.5), as well. Further, such systems are also available with a 250 mW optical output. More information about this UV LED light source is given elsewhere [4,5].

3. Fibres for UV-applications

Originally designed for telecommunications uses, fibre-optic systems have been studied in medical and industrial applications, including new applications in chemistry or biology over the last decade. In the spectral region between approximately 200 nm and 1.6 µm, synthetic silica is the most widely used material for the fabrication of light-guiding fibres. Silica-based fibres are used for light delivery as well as in dipping probes, reflectance probes, external cuvette holders, flow cells and long path sample cells. This allows placing the sample cell closer to the sample site and separating expensive sampling equipment from potentially corrosive or hazardous samples [9]. Information on improvements to all silica fibre as light guides for wavelengths as low as 180 nm have been published elsewhere [10-12,15,16].

However, for the UV-A and UV-B regions, there are other alternatives [5, 14]. Above 330 nm, the attenuation of PMMA-based plastic optical fibres (POF) is acceptable: at the 365 nm wavelength, the basic attenuation less than 0.8 dB/m. Results for POFs with different core diameter and POF-bundles have been published recently [5,14]. However, UV-damage found in such fibres leads to a reduction in transmission, which depends strongly on the light-source, the intensity or power, and the time of irradiation. Two effects are obvious: in the wavelength-region below 325 nm, the loss in the POF increases. On the other hand, there is a gain in transmission between 335 and 400 nm wavelengths.

Above 280 nm, Polymer Clad Silica Fibres (PCSF) with standard 200 or 600 µm core can be used, as its spectral attenuation and UV-damage is significantly smaller. For the shortest UV-LED wavelength available (255 nm), only All-Silica fibres [10-12,15,16], micro-structured silica-based high-NA fibres [20] or Teflon-coated silica fibres [15] are suitable.

4. Proposed systems and applications

4.1. Protein Detection with UV LED at 280 nm

UV LEDs have been used in several sensing applications. Fluorescence lifetime measurements in the pulsed regime have already demonstrated that using high frequency modulation (200 MHz), 340 nm and 280 nm LEDs can be used to detect four basic biological autofluorophores. Coenzymes nicotinamide adenine dinucleotide NADH, riboflavin, aromatic amino acids tyrosine and tryptophan are responsible for the major part of auto fluorescence from live cells. An UV-LED detection system for the determination of DNA and RNA via absorption spectroscopy has recently been developed [18].

LEDs have the tendency to drift in light output power as a function a temperature caused by self-heating. To evaluate an improved system, initially baseline, drift and noise were measured. Using a UV LED with a single channel detector, drifts of up to 20 mAU per hour were detected, even after the initial warm-up period. However, after correcting the signal with a reference channel, baseline drifts below 0.5 mAU/hour and peak to peak noise below 0.05 mAU were observed (Fig. 7). To reduce the trailing edge of the 280 nm UV LED and therefore the spectral bandwidth of the LED, an interference filter with a centre wavelength of 280 nm having a bandwidth (FWHM) of 10 nm was used. For evaluation, concentrations of Bovine Albumin (BSA) in the region up to 8 mg/L were prepared by gravimetric dilution in ultrapure water. For comparison, absorbance at 280 nm versus concentration was measured (Fig. 8) with the LED detection system (with and without the interference filter) and the spectrophotometer TIDAS II (T2). The system with T2 exhibits linear behaviour between 0 and 2.3 AU at 280 nm; then the stray light of the detector limits the detection range. The LED detection system without the 280 nm interference filter shows a strongly non linear behaviour. This can be explained by the fact that the 280 nm LED emits light up to 310 nm at its trailing edge, where there is
only minor absorbance of BSA and therefore the portion of light in this region stays constant reducing the total absorbance signal (Fig. 8). By contrast, the LED detection with the interference filter in place performed exceptionally, as absorbance readings up 3.5 AU could be reliably detected [17, 18].

The output of the 365 nm UV LED high power module described earlier can be closely controlled by stabilizing its temperature, a constant current supply and optical feedback making it attractive for illumination and detection applications. With Plastic Optical Fibres (POF) being optically stable down to the 365 nm wavelength even at such high light power levels, UV light can be transported through these flexible and inexpensive light guides. The permissible bend radii of 5-10 cm are small in contrast, using silica-based optical fibres which are far less flexible (required bending radii > 40 cm) or more. Coupling efficiencies of up to 65% were obtained; in recent experiments with 250 mW UV LEDs, up to 135 mW could be detected at the output of such a fibre. Focusing light from several UV-LEDs into a fibre-bundle based on 2000 µm POFs, the total output power could be increased to, for example, 900 mW with a 7 LED arrangement. However, power homogeneity over the fibre bundle output still has to be optimized. On the other hand, the output power of the LED can be split into different arms of similar power density. Using for example 7 arms of 1000 µm POF, a 365 nm light output of up to 20 mW could be obtained in each arm.

High power UV-LED-modules have been used for fluorescence processes, optically-supported curing of adhesives, as well as photo catalysis, bio-analysis, general applications in medical technology and for various UV illumination applications. Further, they can be used as drop-in replacements for high power mercury and metal halide light sources; e.g. the replacement of conventional metal-halide lamps in CTS (computer to screen) printers are an interesting application.

4.2 Usage of UV LEDs in Thin Layer Chromatography

Absorption and fluorescence are traditional techniques used in Thin Layer Chromatography (TLC). Recently, fibre optic bundles with cross section type converters were developed to improve detection and simplify the measurement system [21, 23].

A typical measurement setup includes fibre-optic assemblies, aligned linearly in three rows in the detection head located at the TLC plate. They are sequentially divided into three SMA terminated bundles on the opposite end. One arm (row) is used for detection of the light and light-delivery to the spectrometer, while the two other arms can be used for light-delivery from different light-sources. As an example, glucosamine has been quantified by absorption and fluorescence [22]. The method presented was very sensitive and reliable; with fluorescence, the resolution limit was improved by a factor of > 5.
5. Summary

The goal of this work was to evaluate the optical and electrical performance of UV LEDs in UV light delivery systems and fibre optic UV detection systems. It was shown that high power UV 365 nm LEDs could be successfully and reliably coupled into Plastic Optical Fibres (POFs) for light delivery. Further, the spectral bandwidth, peak wavelength and output power of AlGaN/GaN UV LEDs in the 250 nm to 350 nm were investigated and a dual channel detection system introduced, which automatically compensates for any light output power drift. The detection range and achievement of high stability were demonstrated. This renders the instrument valuable for such demanding applications protein detection, TLC and HPLC.

For specific applications, deuterium and visible light sources and the high quality spectrometer that typically could be used could be replaced by a far less expensive UV or visible detection scheme based on UV or visible LEDs of similar performance (see above), when the wavelength range is defined

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