TECHNEAU

Development of UV-LED Disinfection

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Report within WP2.5: Compact Units for Decentralised Water Supply.

Colofon

Title
Development of UV-LED disinfection

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Glossary – preliminary definitions

Fluence (H'; often called UV dose) : total amount of radiant energy from all directions passing through an infinitesimally small sphere of cross-sectional area dA, divided by dA. The fluence is the *fluence rate* times the *irradiation time* in seconds [SI unit: J / m²]. [1]

The term fluence has commonly been called the UV dose. Dose is a term that is used to describe the total absorbed energy. In the case of microorganisms, only a few percent of the ultraviolet light are absorbed, the rest of it just passes through the organism. The term fluence is thus more appropriate, since it relates to the incident UV energy, rather than the absorbed UV energy[1]. [1, 2]

Fluence rate (E') is the radiant power passing from all directions through an infinitesimally small sphere of cross-sectional area dA, divided by dA [SI unit: W / m²]. *Fluence rate,* instead of *intensity* or *irradiance,* is the appropriate term for UV disinfection, since UV-light can penetrate the microorganism from any direction. [1]

Irradiance is the appropriate term when a surface is irradiated by UV light coming from all directions above the surface. The radiometer that is used with a UV apparatus measures the irradiance. In a well-designed bench setup, the fluence rate and the irradiance are almost the same. [2]

[1] For aspects influencing the fluence see chapter 4.1

1 Introduction

TECHNEAU WP2.5 targets the development of new technologies for decentralised water treatment. One important aspect is to have low-energy consuming systems. In that regard, the UV disinfection using LEDs (Light-Emitting Diode) seems a promising technology.

Research activities on this cutting-edge technology were organised in collaboration with the Ferdinand-Braun Institute in Berlin, which works on innovative applications in the fields of microwaves and optoelectronics, and the Technical University of Berlin. That includes a state-of-the-art of the current challenges with UV-LEDs, the characterisation of the commercial offers, the design and construction of UV-LED disinfection modules and the completion of biodosimetric tests to evaluate their efficiencies. The different results reported in this report.

2 State-of-the-art on UV Light Emitting Diodes

2.1 The Dawn of Solid State Lighting

GaN-based blue, green, and white light emitting diodes (LEDs) can be found in an increasing number of applications. Initially starting with niche applications like backlighting of mobile phones, GaN LEDs are penetrating a number of new markets, e.g. LCD backlighting of laptops and TVs, street lighting, and car headlights. The world market for light emitting diodes is expected to grow from six billion (10^9) US$ in 2007 to 21 billion US$ in 2013.

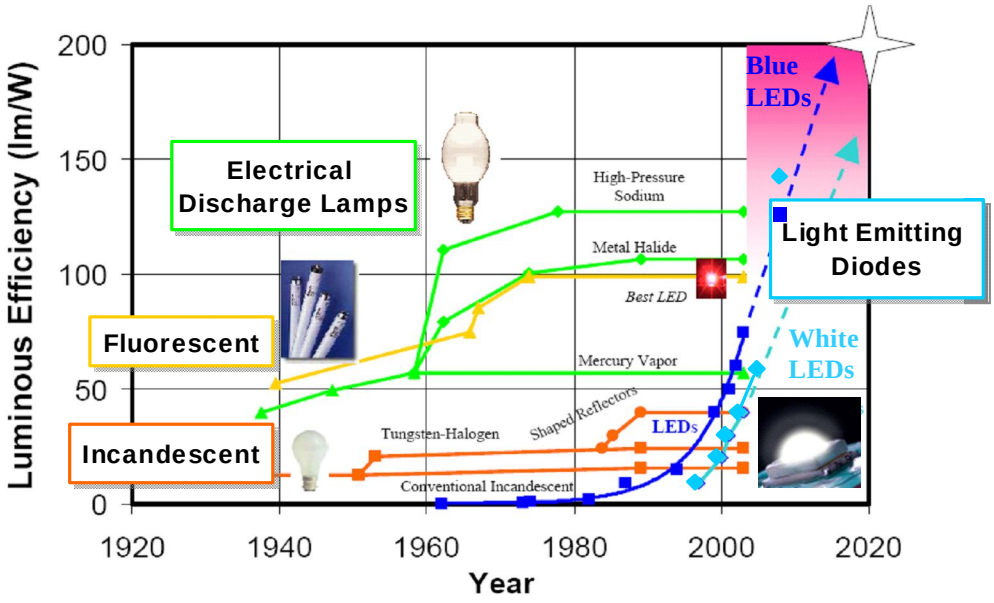


Fig. 1: Luminous efficiency of GaN-based blue and white light emitting diodes (LEDs) in comparison to traditional light sources [data courtesy of M. Krames, Philips-Lumileds Lighting].

The increasing market penetration of blue, green, and white GaN-based LEDs is driven by the rapid and continuing improvements in performance. Fig. 1 shows the efficiency of LEDs compared to conventional light sources. Today nitride LEDs have surpassed all traditional light sources in terms of efficiency. In the laboratory record results for wall-plug efficiencies (WPE) for blue LEDs are currently more than 60%, that means that 60% of the electric power is converted into usable blue light.

2.2 Materials for UV light emitting diodes (LEDs)

There are a number of semiconductor materials capable of emitting light in the ultraviolet wavelength range. The graph in Fig. 2 shows the bandgap energies of various semiconductor materials plotted vs. the lattice spacing. The

bandgap energy determines the emission wavelength of the LED devices. For a emission at 265 nm a bandgap energy of 4.68 eV is required.

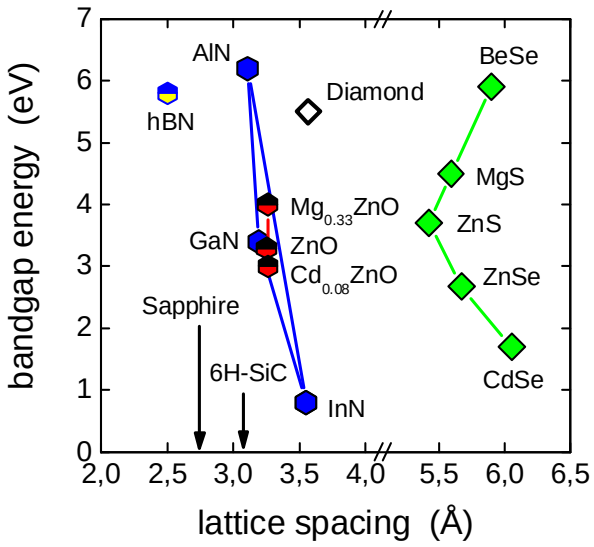


Fig. 2: Bandgap energy vs. lattice spacing for different semiconductor materials.

ZnS/MgS/BeSe compounds can be grown on GaAs substrates and would allow accessing the UVB and UVC spectral range. Problems: These materials are very “soft” and develop defects when generating light. This leads to early failure of LEDs and lasers. Another challenge is to find appropriate p-dopants for the wide-bandgap compounds. Summary: A possible candidate with a number of fundamental questions that still need to be solved. So far no UV LED has been demonstrated with this materials system.

Diamond: An indirect semiconductor and therefore fundamentally limited regarding the efficiencies that can be achieved. There is also no other wide-bandgap compound that would allow the fabrication of heterostructures for efficient carrier injection and confinement. Summary: Due to fundamental physical limitations, diamond is not a suitable candidate for high efficiency UV emitters.

ZnO/MgO compounds would allow accessing the UVB and parts of the UVC spectral range. However, up to now no reliable p-dopant has been found for these materials. Controlled p-doping is critical to realize pn-junctions for light emitting diodes. Although there are several reports in literature about p-doping of ZnO and even demonstrations of LED devices, none of these reports makes a convincing case. Summary: It may be still possible that ZnMgO compounds will one day yield functioning UV LED devices, but considering the huge effort and meager results so far, a successful outcome is becoming increasingly doubtful. In addition, MgZnO is undergoing a transition from wurtzite to rock-salt crystal structure at Mg mole fractions in the range of 30% - 50%, which would limit the accessible UV wavelength range.

GaN/AlN are the most promising compound materials to realize LEDs in the UVB and UVC wavelength range. GaN-based high efficiency LEDs have been already demonstrated in the near UV (EQE of ~40% at 365nm and EQE of ~60% at 400nm) and there is no fundamental physical limit to achieving similar efficiencies in the deep UV. Furthermore, GaN materials and devices can build on the already existing technology infrastructure that has been established for blue / green LEDs and provide high volume, low cost production.

2.3 Applications of UV light emitting diodes (LEDs)

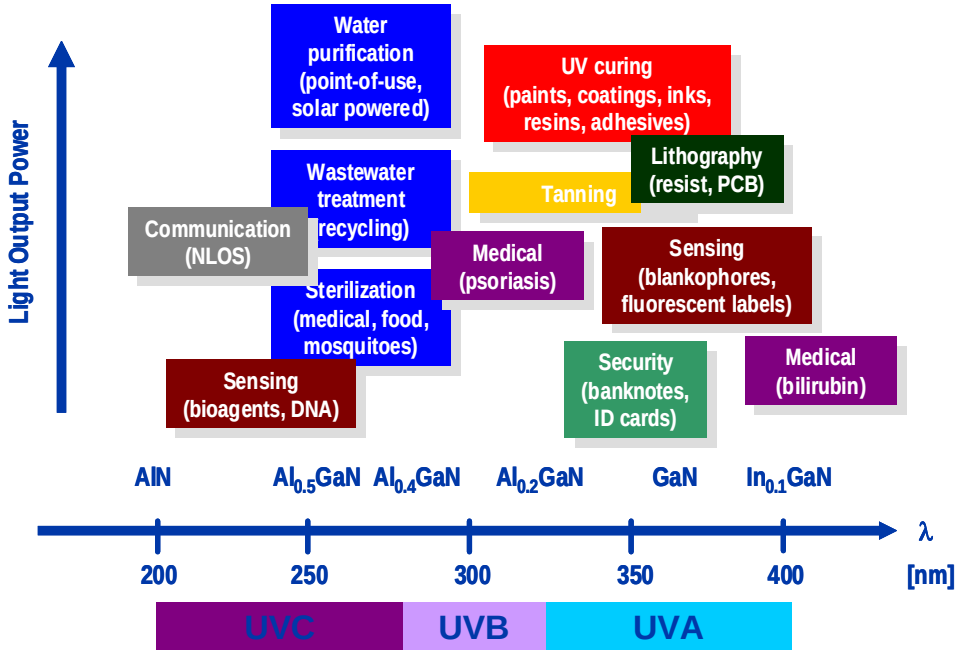


Fig. 2: Applications for LEDs in the UVA, UVB, and UVC wavelength range.

Figure 2 shows a number of possible applications for UV emitters and the respective required wavelength range. The core application for the Techneau project are water disinfection, requiring emitters in the 250 nm to 282 nm wavelength range.

Other applications for UV LEDs are

- Sensing (UVC, UVA)
- UV curing (UVB, UVA)
- Medical (e.g. treatment of psoriasis, UVB)
- Tanning (UVB)
- Lithography (UVA)
- Non-line-of-sight communication (UVC)
- Sterilization (e.g. food, medical, mosquitoes, UVC)

2.4 Water purification with UV LEDs

UV light at the proper *fluence* and *wavelength* inactivates microorganisms by disrupting their DNA or RNA molecules, rendering them unable to reproduce.

DNA absorbs UV light with wavelengths between 200 and 300 nm. The maximum of UV-light absorption through DNA is typically reached at a wavelength around 260 nm [3]. The peak wavelength distribution is dependent on the target organism [4]. Chen et al [2009] presented that Bacillus *subtilis* spores (the target organism of this research) have an absorption maximum below 240 nm and around 270 nm. The fluence-inactivation response for 254 nm and 279 nm wavelengths were shown to be similar. [3]

Different wavelengths are emitted depending on the UV-source: Conventionally, UV-light is generated from mercury lamps. Low pressure mercury lamps emit nearly monochromatic UV light at a wavelength of 254 nm whereas medium pressure lamps emit a polychromatic spectrum with various wavelengths [5]. A relatively new method to generate UV light is the use of UV LEDs [6]. UV LEDs offer the possibility to use a preferred wavelength instead of the 254 nm emitted by low pressure mercury lamps [6].
Further benefits of UV-LEDs in applications for water purification were assessed by Crawford et al. [7]. They summarised the following advantages of UV LEDs compared to conventional mercury lamps:

- no disposal problem (LEDs do not contain mercury)
- compact and robust design: more durable in transit and handling (no glass or filaments)
- faster start-up time
- ability to turn on and off with higher frequency
- lower voltages, low power requirements
- high energy efficiency (in future)
- reduced frequency of replacement because of longer lifetime (in future).

2.5 Challenges regarding the UV device structure

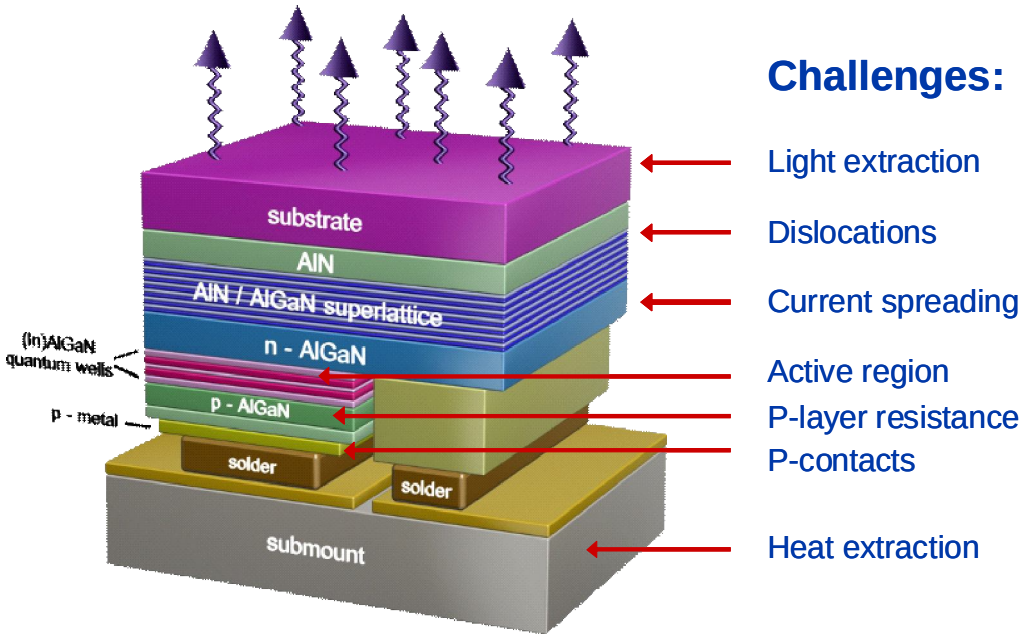


Fig. 3: Heterostrucutre and chip design for a InAlGaN deep UV LED.

Figure 3 shows a flip-chip mounted LED device for deep UV emission. The light is extracted through the UV-transparent AlGaN and AlN layers and sapphire substrate. The light emitting region is comprised of AlGaN or InAlGaN multiple quantum wells.

A number of key challenges remain to realize high efficiency UV emitters:

- Enhancing light extraction from the chip
- Reducing the high dislocation density in the AlN / AlGaN buffer layers
- Reducing the series resistance of the Si-doped AlGaN current spreading layer
- Improving the internal quantum efficiency of the InAlGaN MQWs
- Reducing the series resistance of the Mg-doped AlGaN layers
- Reducing the p-contact resistance
- Enhancing heat extraction from the chip.

3 Characterisation of commercial UV-LEDs at 265 and 280 nm

Five LEDs from Sensor Electronic Technology (SET) [1] and three LEDs from Seoul Semiconductor (SSC) [2] with emission wavelength of 265 nm and 280 nm were characterized. All LEDs were housed in TO-18 packages.

3.1 Spectra

The emission spectra of the 265 nm and 280 nm LEDs from SET are shown in Fig. 4. The spectra were measured under continuous-wave (cw) conditions at 20 mA with an optical fiber spectrometer. The “265 nm” LEDs have an emission peak around 269 nm, the “280 nm” LEDs are emitting between 282 nm and 283 nm. A typical spectral emission full-width at half-maximum (FWHM) between 10 nm and 11 nm was found.

Three LEDs from SSC were investigated for every emission wavelength. It was found that the “265 nm” LEDs have an emission peak between 267 nm and 269 nm, the “280 nm” LEDs are emitting between 279 nm and 282 nm. A similar FWHM of the emission spectrum around 10 nm was found.

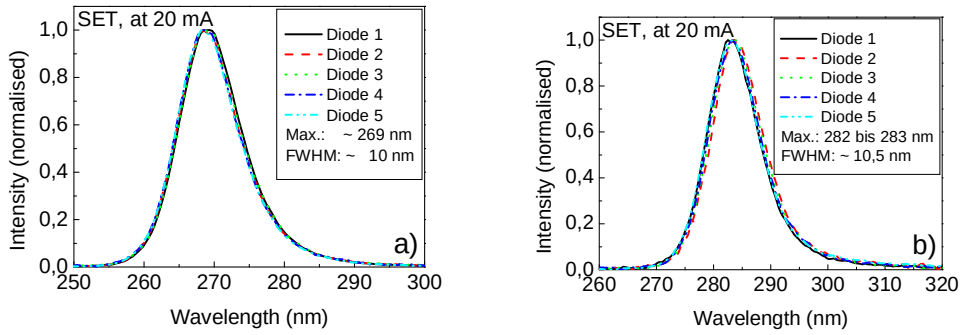


Fig. 4: Emission spectra of the a) 265 nm and b) 280 nm LEDs from SET.

3.2 Current-Voltage Characteristics

The current-voltage characteristics were measured with an Agilent power supply and a Keithley 2000 multimeter under cw conditions. Figure 5 shows the current-voltage characteristics of the LEDs from SET. All tested LEDs had a very similar current-voltage characteristic with operating voltages of ~5.8 V

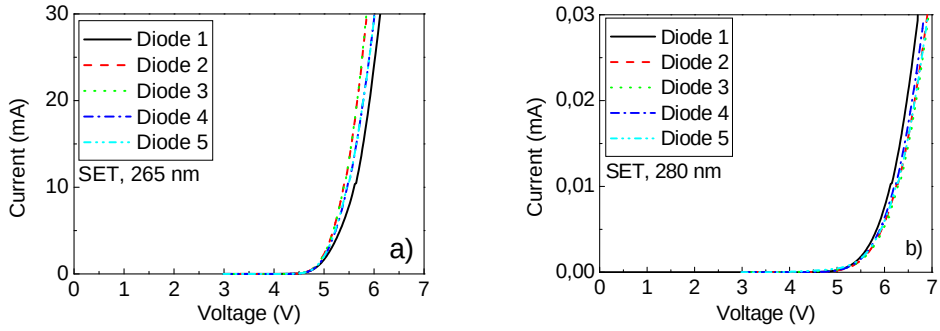


Fig. 5: Current-voltage characteristics of the a) 265 nm and b) 280 nm LEDs from SET.

for the 265 nm LEDs and ~6.5 V for the 280 nm LEDs (at 20 mA).
For the SSC LEDs a typical operating voltage of ~6.2 V was found for all wavelengths.

3.3 Emission Power

For the measurement of the emission power a Si-Photodiode with a detector area of 100 mm² was used. In Fig. 6 the emission power vs. current (LI) characteristics for the SET LEDs is plotted. All tested LEDs exhibit similar L-I characteristics. The emission power at 20 mA initially was always higher than specified in the data sheet (0.35 mW for the 265 nm LEDs and 0.5 mW for the 280 nm LEDs according to specifications).
For the LEDs from SSC similar results were found. All tested LEDs also initially showed a higher emission power than specified in the data sheet.

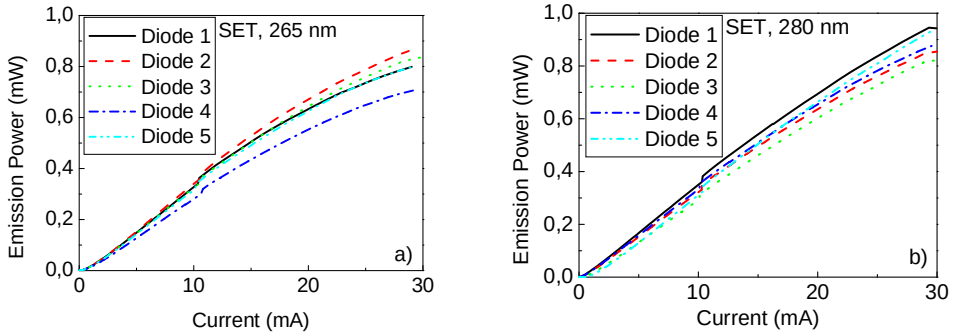


Fig. 6: Emission power-current characteristics of the a) 265 nm and b) 282 nm LEDs from SET.

Maintaining a constant output power is an important factor for a water disinfection module. Fig. 7 shows the development of the power at a current of a 20 mA for a 265 nm LED. After 100 hours the emission power has decreased by 40%. The series resistance increased from 11.8 Ohm (0 hours) to 12.9 Ohm (after 100 hours) while we observe no change in the emission wavelength. The degradation of the emission power makes it necessary to monitor this parameter during all test and keep it constant by increasing the current as required.

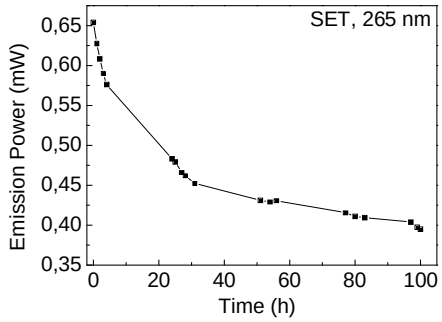


Fig. 7: Emission power over 100 hours of a 265 nm SET LED at 20 mA.

4 Design of a UV-LED disinfection module

4.1 Design constraints for biodosimetry trials in bench-scale reactors

Researchers have made considerable headway in standardising protocols for conventional mercury lamps to investigate UV disinfection on bench-scale. They have found that factors as e.g. the water quality and contact time influence the delivered fluence and various correction factors have to be considered when calculating the fluence. These factors are described in more detail in this section, to design an adequate disinfection module for UV-LEDs.

The water quality has a major effect on the transmitted fluence and the resulting level of inactivation, since the incoming water quality determines how well the UV light penetrates the water [8]. The UV transmittance of the unfiltered water measures the amount of UV light absorbed by UV-absorbing water components, reducing its availability to inactivate microorganisms [5].

In a flow-through UV disinfection system, contact time (cumulative exposure to UV light) is a crucial parameter affecting the fluence received by the microorganisms. In contrast to chemical disinfection systems, the contact time in UV disinfection cannot be monitored directly. It is influenced by the flow rate and UV reactor hydraulics, determining the specific path of the organism through the reactor [9, 10]. This complexity of the factors influencing UV disinfection performance in flow-through reactors led to the development of a method to calibrate the expected performance of full-scale units. This method called biodosimetry, was originally proposed by Qualls and Johnson [11]. Today there are several norms in Europe and USA that specify this analysis protocol with different types of microorganisms.

During biodosimetry tests bench-scale and field-scale tests are conducted with a biological test organism. The relationship between UV fluence and the inactivation of a test organism is established under carefully controlled laboratory conditions in bench scale tests. The field scale test is conducted at design flow and under conditions designed to represent a conservative simulation of full-scale operation. The disinfection fluence received by the unit, called reduction equivalent fluence (REF), is then determined by the fluence that accomplishes the same level of inactivation under bench scale conditions [9].

Experimental protocols for performing microorganism inactivation versus fluence have been established for mercury lamp based measurements [2]. These protocols include a “collimated beam apparatus” to deliver a highly uniform beam of UV-light to a water sample in a Petri dish. This conventional design limits the use of UV LEDs because conventional collimated beam approaches need high power output sources, to compensate for losses between the UV light source and the water sample. Since UV LEDs have a low output power a LED array composed of a number of LEDs is needed, which has to be placed as close as possible to the water sample.

According to Bolton and Linden [2] it is not necessary to completely standardise a bench scale apparatus, but basic guidelines should be considered when designing a modified apparatus for a specific application. Amongst other aspects, the design has to ensure that the beam irradiating the water

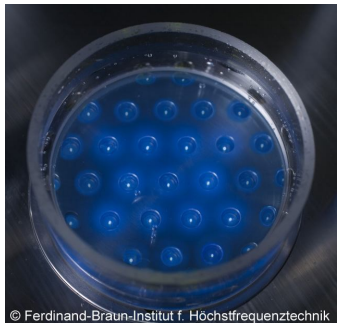
sample is reasonably uniform and the divergence is small enough to ensure accurate sensor readings. The average fluence for all microorganisms in the suspension has to be kept equal by carefully controlled stirring (no vortex) [2].
The delivered average fluence differs from the measured irradiance, caused by a number of factors. The sensor reading gives the incident irradiance, from which the average irradiance is derived. The average irradiance is an estimate for the average fluence rate; the average fluence rate multiplied by the exposure time gives the delivered average fluence [2]. The measured irradiance is influenced by [2]:

- the refraction and reflection that occurs when UV light passes from one medium to an other,
- the inhomogeneous distribution of the UV light over the Petri dish and
- the absorption of the UV light by water components.

The challenge of this project was to develop an optical system to deliver uniform and well-calibrated UV fluences to the water sample from deep UV LED arrays. The design had to enhance the uniformity of the inhomogeneous light output distribution while reducing UV light losses.

4.2 Module I

Figure 8 shows the first generation UV LED water disinfection module produced to perform the biodosimetry trials. The UV LED array consists of 33 devices with an emission wavelength of 269 nm. The LEDs for this investigation were obtained from Seoul Semiconductor [2]. The LEDs were placed on the base of the water disinfection module with a pitch of one cm in order to obtain a sufficiently high power density and a nearly homogeneous UV light distribution. Because of the low emission power of 0.3 mW per LED at 20 mA an array of 33 LEDs (28.5 LEDs were considered to be active) was used to provide sufficiently high emission intensity of around 8.5 mW at 20 mA.
A Petri dish with a diameter of 6 cm was placed on the top of the UV LED array with a 2 mm thick suprasil base, that allows over 90% of the deep UV light to be transmitted. On top of the disinfection module a UV sensitive silicon photodiode and a stirrer were mounted. The photodiode was used to monitor the emission power of the LED module in order to guarantee the same irradiation fluence during all microbiological tests. In order to obtain a homogeneous irradiation of the entire water volume the water was stirred during the tests.
An external power supply was used for the operation of the water disinfection module.



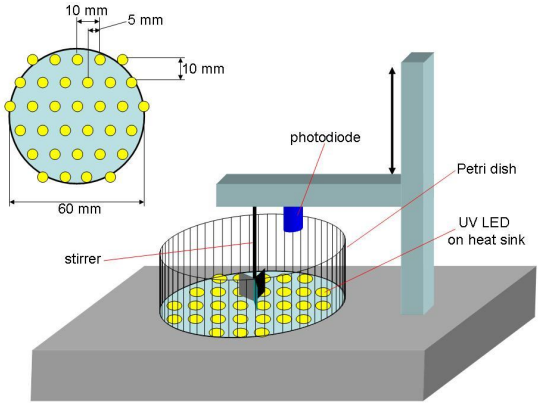


Fig. 8: UV LED water disinfection module generation I.

4.3 Module II

Figure 9a shows the second generation UV LED water disinfection module produced to perform biodosimetry trials. In this module the layout of the LED array was optimized. The 35 LEDs from SET [1] were concentrically located in three circles with diameters of 1.8 cm, 3.5 cm and 5.2 cm. A reference LED from the same batch was placed in front of an UV sensitive silicon photodiode to monitor the emission power of the LED module in order to guarantee the same irradiation fluence during all microbiological tests. The integration of this reference LED in the module has the advantage that now it is not necessary to shade the setup from the surrounding area light. Other improvements were the compact setup of the module with an integrated power supply and the possibility for a manual or computer control of the disinfection module. In this module LEDs with emission at 282 nm were used that had shown a slightly higher output power and less thermal roll-over than the 269 nm ones (see fig. 6).
For this second illumination unit also a simple flow reactor had been designed. It can replace the Petri dish and has a potential flow rate of ~12 cm^3/min. The flowing module is shown in Fig. 6b. It consists of aluminium with a milled water canal for a good reflection of the UV light. As window a 2 mm suprasil plate was used.

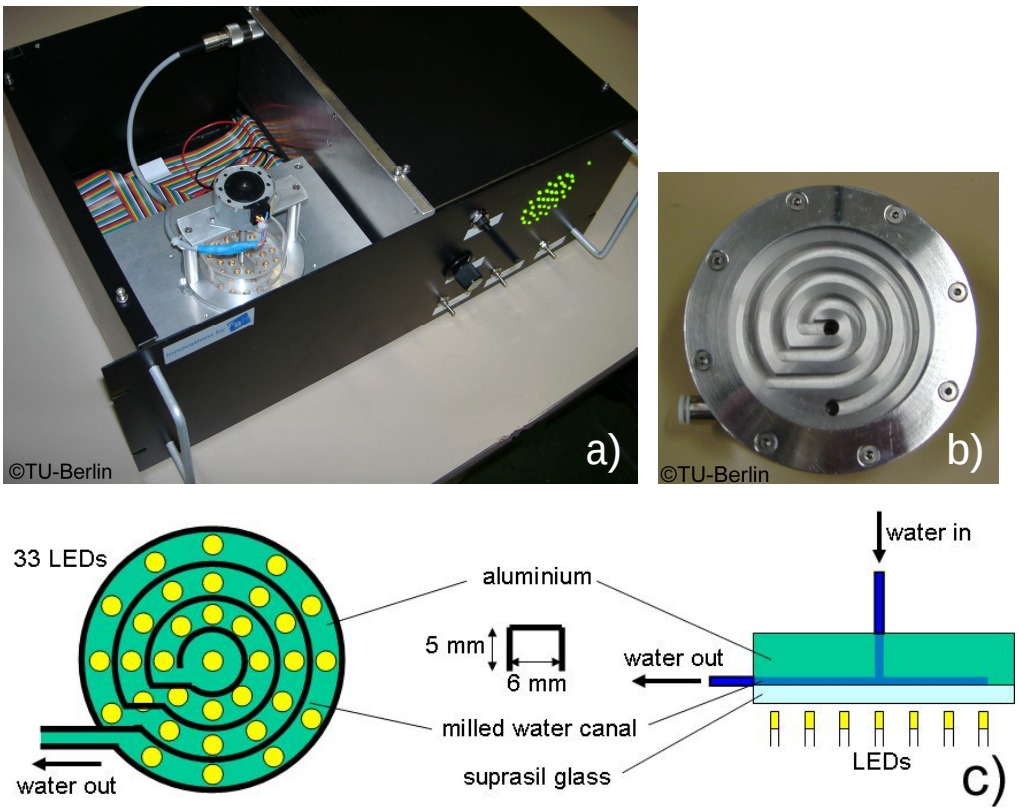


Fig. 9: a) UV LED water disinfection module generation II with control electronics. b) Optional flow module. c) Desing geometry of the flow module.

5 UV-LED Disinfection Performance Tests

The disinfection capacity of 269 and 282 nm emitting LEDs was investigated during this research. The following sections provide information about the materials and methods used, a presentation and discussion of the generated results and first conclusions.

5.1 Material and Methods

Disinfection Tests

A UV fluence-response curve of Bacillus *subtilis* was generated with a laboratory apparatus especially designed for UV LEDs. The test organism was obtained from the Institute of Hygiene and Public Health (University of Bonn), where it was cultivated and characterised according to the German standard [13] with monochromatic low pressure UV lamps [12]. It was delivered in deionised water with a concentration of 10^9 cfu / ml.

For the exposure tests the applied test organism was suspended in the test water according to [13] to obtain a concentration of 10^6 cfu / ml. Tests were conducted at room temperature (23 ± 2 °C).

The tests were performed with stationary samples of 30 mL, exposed successively to increasing UV fluences (0, 100, 250, 400, 600 J / m²). During tests with the 269 nm LEDs, samples (sample volume: 1,5 mL) were taken after 0, 62, 155, 248 and 372 seconds. Samples of the tests conducted with the 282 nm LEDs were taken after 0, 43, 106, 170 and 255 seconds.

Eight tests were performed with the flow through cell at various flow rates (0.028; 0,18; 0,13 ± 0,01 cm³ / s). The experiments were performed based on [12]. The LED (282nm) power was varied The experiment applying the highest fluence was conducted first. Tubes were changed between tests and the test cell was flushed with sterile deionised water. Table 1 summarises the performed tests. Results presented in section 5.2 are averaged values.

In a first run of flow through experiments, the test protocol included the following steps:

1. initialising the system (adjustment of flow rate and UV-power),
2. sampling before UV-exposure (reservoir),
3. starting flow, discarding five test cell volumes,
4. sampling before UV-exposure (after flow through test cell),
5. turning on UV light,
6. sampling after UV-exposure (after 1, 2, 3 and 4 minutes),
7. sampling before UV-exposure (reservoir),
8. flushing with deionised water.

After first test results were obtained, the test protocol was changed to the following procedure:

1. initialising the system (adjustment of flow rate and UV-power),
2. sampling before UV-exposure (reservoir),
3. turning on UV light,

4. starting flow, discarding five test cell volumes,
5. sampling after UV-exposure (after 1, 2, 3 and 4 minutes),
6. sampling before UV-exposure (reservoir).

Table 1: Summary of the performed static and dynamic tests.

Test Mode	Test Water[1)]	Wavelength 269 nm	Wavelength 282 nm
static	DI	6 x	3 x
	TW	3 x	3 x
	SW	2 x	2 x
	SE	1 x	2 x

	Flow cm^3/s	LED Power mW / LED	Calculated Fluence J/m^2
Dynamic 282 nm	DI: 0,293	0,6	1 x 358
	DI: 0,283	0,9	1 x 556
	DI: 0,185	0,5	1 x 507
	DI: 0,180	0,7	1 x 681
	DI: 0,173	0,9	1 x 851
	DI: 0,133	0,35	1 x 462
	DI: 0,135	0,49	1 x 635
	DI: 0,123	0,59	1 x 843

[1)] DI: deionised water, TW: tap water, SW: surface water, SE: secondary effluent

Microbiological Analysis

Determination of spores was performed according to [12]. The viable micro-organisms were enumerated by diluting the samples, plating and incubating the dilutions and counting the colonies that arise as colony-forming units (CFU) on plates with 1 to 300 colonies.

Samples obtained during tests conducted with the 269 nm LEDs were analysed as follows: Test rows a) to d) conducted with deionised water and samples obtained from tests with different water qualities were determined in a single assay. Test rows e) and f) were cultivated in three replicates at each dilution. Samples obtained with the 282 nm LEDs were all cultivated in triplicates.

The log inactivation ($\log(N_0/N)$) was plotted against the fluence to derive a fluence-effect relation. In case of the flow through tests, N_0 was calculated by averaging the test results of the three samples taken before UV-exposure.

Water Quality

Tests were performed with different water qualities: deionised water (DI), tap water (TW), surface water (SW) and secondary effluent (SE).

The absorption coefficient (A), which reduces the available disinfection fluence and the UV transmittance (UVT) of the filtered (cellulose nitrate filters, Sartorius AG) and unfiltered test waters was measured with a two beam spectrometer (model Lambda 12, Perkin Elmer) in a five cm quartz cuvette.

The absorbance at 254 nm is relating to a one m path length. UV transmittance is defined as the percent transmittance in the medium when the path length is one cm and the wavelength is 254 nm. Since tests were performed with UV-LEDs emitting at 269[2] and 282 nm, A and UVT were also determined for these wavelengths.
The turbidity was measured with a turbidity meter (2100 N IS HACH). The detector, placed at 90° from the incident 860 nm beam, measured the scattered light. The sample was homogenised by shaking before every measurement. Table 2 summarises the measured water quality parameters.

Table 2: Water quality parameters (mean values) of the applied test waters.

	Parameter	Unit	Deionised Water (DI)	Tap Water (TW)	Surface Water (SW)	Secondary Effluent (SE)
269 nm	A[1] (254)	[1/m]	1.1	8.8	19.0	29.2
unfiltered	A (269)	[1/m]	n.a.[3]	7.7	17.1	26.6
unfiltered	UVT[2] (254)	%	97.5	81.7	64.6	51.0
filtered	A (254)	[1/m]	0.8	8.5	17.6	28.2
filtered	A (269)	[1/m]	n.a.	7.5	15.7	25.7
282 nm	A[1] (254)	[1/m]	2,7	10,8	18,4	28,7
unfiltered	A (282)	[1/m]	2,3	8,2	13,4	22,1
unfiltered	UVT[2] (254)	%	94,1	78,0	65,5	51,7
filtered	A (254)	[1/m]	0,69	7,9	15,9	23,6
filtered	A (282)	[1/m]	0,43	5,4	11,0	17,6

[1] A: absorption coefficient
[2] UVT: UV transmission
[3] n.a.: not available

5.2 Results and Discussion

The disinfection capacity of 269 and 282 nm emitting LEDs was investigated by running disinfection tests with deionised water on the specially designed UV-LED disinfection modules described in section 3. The obtained results were then compared to the inactivation response curve of a conventional collimated beam apparatus to quantify the disinfection capacity of the UV LEDs. In order to verify the application of UV-LEDs for varying water disinfection applications, experiments were conducted with different water qualities and a bench-scale flow through cell.

Static Tests with 269 nm LEDs and Deionised Water

Microorganism inactivation tests were performed with arrays of UV LEDs emitting at 269 nm (test module I). Bacillus *subtilis* spores, suspended in deionised water, were used as test organism and exposed successively to UV

[2] This wavelength was specified by the manufacturer. During this research a wavelength of 268 was determined, for the applied LEDs.

light. Fig. 10 presents the results of the exposure tests with the 269 nm LEDs. Samples of test rows a) to d) were determined in a single assay. Test rows e) and f) were cultivated in three replicates at each dilution.

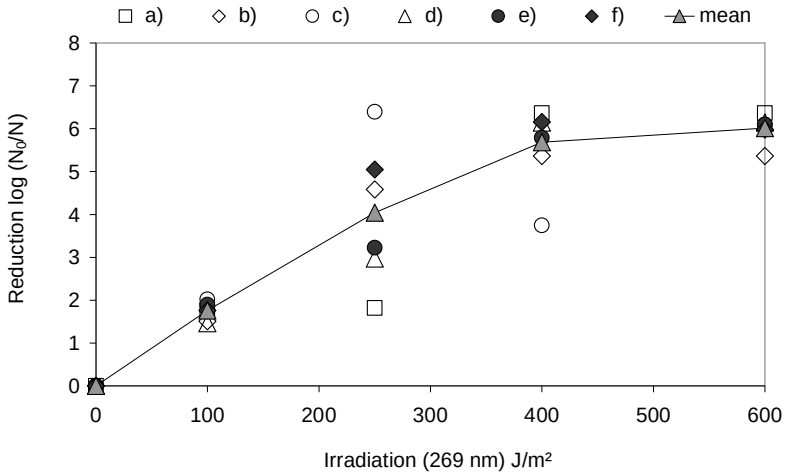


Fig. 10: Fluence-inactivation response of Bacillus *subtilis* spores in deionised water for 269 nm LEDs. Test rows a) to d) were analysed in a single assay. Test rows e) and f) were cultivated in triplicates.

The inactivation increases with increasing fluence. It is noticeable that a high dispersion of reduction factors was found at a fluence of 250 J/m²: The log reduction varies between 1.8 and 6.4. These variations could be caused by the construction of the UV-module or the microbiological analysis.
Test rows e) and f) (black series) were therefore analyzed in triplicates. A maximum standard deviation of 0.3 of triplicate measurement cannot explain the observed variation of 4.6 log scales. The curve progression of test row c) (circles) suggests that there is an influence of the physical construction of the UV-module. At a fluence of 250 J/m², a total inactivation was found and therefore the limit of quantification was reached. In the samples exposed to a fluence of 400 J/m², the inactivation was again reduced to 3.7.
This reduced inactivation could be ascribed to not inactivated microorganisms attached to the Petri dish wall, which are resuspended by mixing and lead to a recontamination. On the other hand, the recontamination could also be a consequence of the inhomogeneous distribution of the UV fluence in the Petri dish, which is not compensated for by stirring. Since UV LED arrays are composed of various radiation sources, the UV light is emitted inhomogeneously. Adequate mixing of the test water is therefore crucial to obtain a homogeneous water sample, where every microorganism is exposed to the same fluence. Results indicate that stirring is not adequate to obtain homogeneous water in the Petri dish, hindering representative sampling.

The applicability of UV LEDs for water disinfection was further investigated with the same experimental set-up, using various types of waters, as tap water, surface water and secondary effluent. Via these experiments, the influence of different water matrixes on the disinfection capacity was investigated.

Static Tests with 269 nm LEDs and Different Water Qualities

Disinfection results obtained with test module I (269 nm LEDs) generated with different water qualities are presented in Fig. 11.

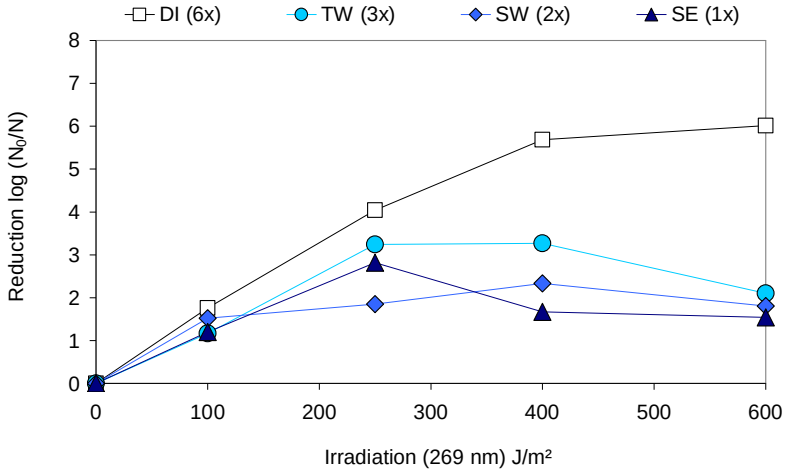


Fig. 11: Fluence-inactivation response of Bacillus *subtilis* spores in waters (DI: deionised water, TW: tap water, SW: surface water, SE: sweage effluent) with different qualities for 269 nm LEDs; in parentheses are the number of conducted experiments.

As observed for the experiments with deionised water, results are influenced by the construction of the UV-module, causing recontamination and inhomogeneous distribution of UV-light.
All curves for all waters besides deionised water have a disinfection maximum. The highest applied fluence of 600 J/m² has a lower disinfection capacity as for example a fluence of 250 J/m². With e.g. SE a higher reduction of 2,8 is found at 250 J/m² compared to a lower reduction of 1,5 at 600 J/m².
The smoothed mean value of the deionised water was generated from six experiments, indicating that variations are reduced statistically, the more often the tests are conducted. Just one experiment as performed with the secondary effluent is not sufficient to draw reliable conclusions.
Disregarding these influences, a trend is visible: Results indicate that UV-absorbing compounds in the various waters reduce the disinfection capacity. The log reduction in deionised water reaches a maximum quantifiable value of 6,0 compared to a maximum value of 3,2 in tap water.

The presented results underline the assumption of recontamination and inhomogeneous dispersion of UV-light. Therefore, to reduce these variations caused by the module construction, an improved experimental set-up was designed and constructed. The UV test module II was equipped with LEDs emitting at 282 nm.

Static Tests with 282 nm LEDs and Deionised Water

Microorganism inactivation tests were also performed with arrays of UV LEDs emitting at 282 nm. Bacillus *subtilis* spores, suspended in deionised water, were used as test organism and exposed successively to UV light. Results generated with test module II (282 nm LEDs) are presented in Fig. 12.

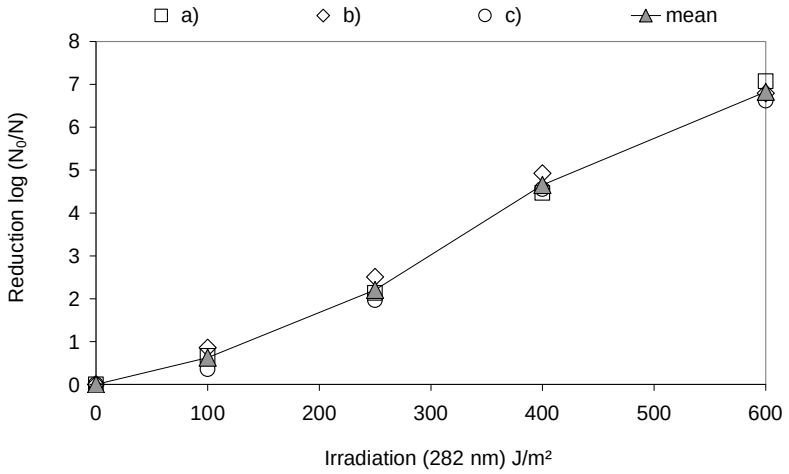


Fig. 12: Fluence-inactivation response of Bacillus *subtilis* spores in deionised water for 282 nm LEDs. Test rows were cultivated in triplicates.

The inactivation increases clearly with higher applied fluences. The maximum variation between the test runs (0,5 log reduction) were in the same order of magnitude as the standard deviation of the triplicate analysis (0,4 log reduction). The test set-up of module II therefore admits more reproducible results than test module I, reducing influences of the physical construction.

Static Tests with 282 nm LEDs and Different Water Qualities

Disinfection results obtained with test module II (282 nm LEDs) generated with different water qualities are presented in Fig. 13.

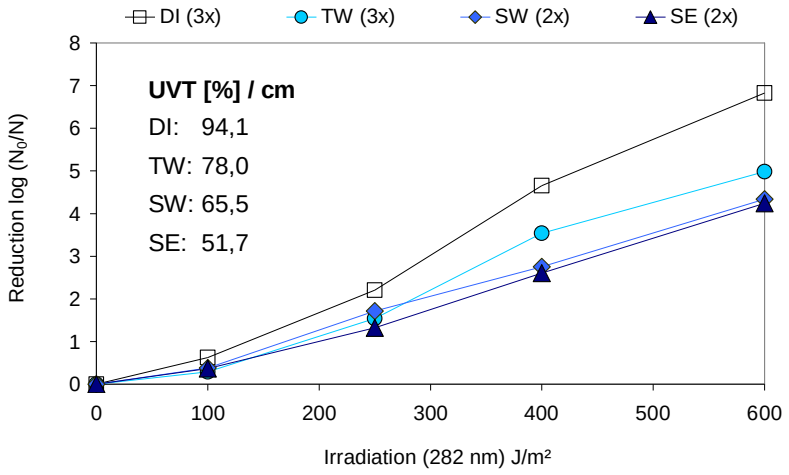


Fig. 13: Fluence-inactivation response of Bacillus *subtilis* spores in waters (DI: deionised water, TW: tap water, SW: surface water, SE: sewage effluent) with different qualities (UVT as representative parameter) for 282 nm LEDs; in parentheses are the numbers of conducted experiments.

The disinfection capacity is decreased with higher contents of UV-absorbing compounds. The highest difference was observed for DI, which is nearly free of UV-absorbing compounds (UVT 94,1 %), and TW, which contains UV-absorbing compounds (UVT 78,0 %). A further increase of absorbing com-

pounds reduces the inactivation capacity; but the decrease is not linearly dependant on the concentration.

Comparison of 269 and 282 nm LEDs

Figure 14 presents the inactivation curves derived from the results obtained with the apparatus' designed for UV LEDs.

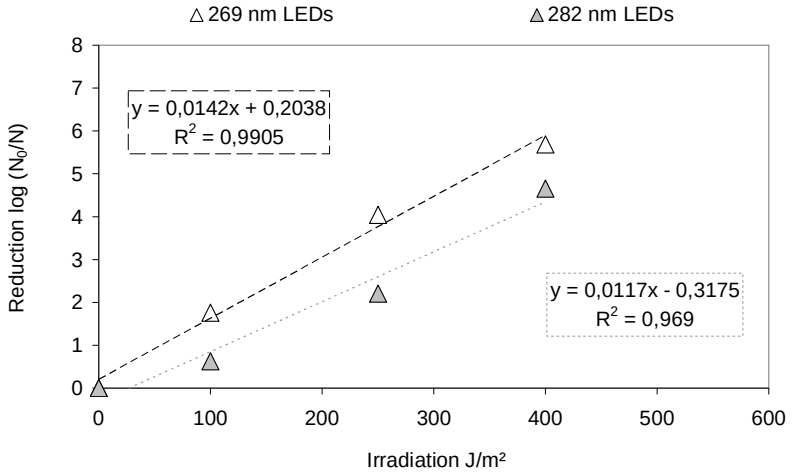


Fig. 14: Comparison of fluence-inactivation response of Bacillus *subtilis* spores in deionised water, obtained with the apparatus' designed for UV LEDs.

The results indicate a higher disinfection capacity for the 269 nm LEDs than for the 282 nm LEDs. This enhanced disinfection capacity could be attributed to the higher germicidal effectiveness at this wavelength. Chen et al. [2009] published an absorption maximum of Bacillus *subtilis* spores at 270 nm.

The inactivation performances of the UV-LEDs compared to a conventional mercury lamp are presented in Table 3. The results were calculated by linear regression of the fluence-inactivation response of Bacillus *subtilis*.

Table 3: Comparison of inactivation curves obtained with the apparatus' designed for UV LEDs and a conventional bench-scale mercury lamp apparatus.

Fluence	**269 nm UV LED**	**282 nm UV LED**	**Mercury Lamp**
[J/m²]	[log RF]	[log RF] ± 0,2	[log RF] ± 0,1
100	1.6 ± 0,2	0,9	0.8
250	3.7 ± 1,4	2,7	1.9
400	5.8 ± 0,7	4,5	2.9

When comparing the inactivation curves obtained with the UV LED-modules to the inactivation curve obtained with a conventional mercury UV bench-scale apparatus, higher inactivation results are obtained. It is noticeable that both UV LEDs perform better than the conventional mercury lamp. According to Chen et al. [2009] the inactivation of Bacillus subtilis spores should be comparable at the wavelengths of 254 nm and 279 nm [3].
Various factors as for example the condition of the test suspension (agglomerated spores), the fluence calculations and/or the different constructions of the LED-apparatus and the conventional apparatus might influence the test

results. Schoenen et al. (1994) investigated the influence of the set-up design on the inactivation kinetics of different microorganisms.
They found that smallest differences in the irradiation geometry cause variations of various orders of magnitude [14]. Experiments conducted with different apparatus might therefore not be comparable. However, at this stage, a clear explanation for this much higher disinfection capacity, compared to the conventional UV-source still has to be investigated.

Flow Through Tests with 282 nm LEDs and Deionised Water

Dynamic tests were performed with a flow-through cell, to obtain first results for the applicability of UV LEDs under real conditions. The flow rate was adjusted to 0,28 ± 0,01 cm³/s, 0,18 ± 0,01 cm³/ and 0,13 ± 0,01 cm³/, while the UV-LED power was varied (see 5.1). Results are presented in Figure 15.

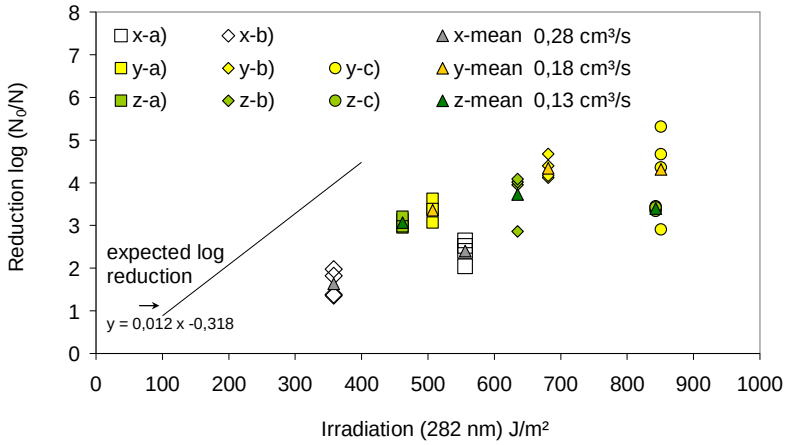


Fig. 15: Fluence-inactivation response of Bacillus *subtilis* spores in deionised water, obtained with the apparatus' designed for 282 nm UV LEDs in static tests (expected log reduction) compared to results obtained during flow through tests.

As expected, the reduction equivalent fluence (REF) highly differs from the calculated fluence. The inactivation of Bacillus *subtilis* in the flow through test cell is much lower than in the static tests, theoretically applying the same fluence. This is a common phenomenon, when up-scaling UV-reactors and constructing flow through reactors instead of static reactors. These results indicate that the flow conditions lead to areas of lower UV irradiation and short-circuiting in the flow through test cell, reducing the overall performance of the UV-LEDs.
The considerably lower reduction in test run x could therefore possibly be ascribed to the higher flow-rate, which could have increased dead volumes, reducing the disinfection capacity. On the other hand, these results could also be caused by the test procedure. During test run x the spore suspension was passed through the test unit without turning on the UV-LEDs. The test cell was therefore flushed with Bacillus *subtilis* in a very high concentration (10^6 cfu/ml). Subsequently flushing the unit, while the UV-LEDs were turned on, could probably not avoid a contamination of the sample. For the following test runs y and z the test procedure was therefore adapted, to avoid contamination of the test cell before the start of the test run. Results show a better performance of the test runs y and z using the adapted procedure.

Results at high fluences around 850 J/m² cannot be evaluated, because of a high variation of the test results. This effect might be forced by experimental artefacts as e.g. spore clumping. However, an increase of the applied fluence leads to a higher inactivation, indicating a promising design of the UV LED configuration in the flow through cell.

5.3 Conclusions

First test results indicate an effective inactivation of Bacillus *subtilis* spores through UV LEDs emitting at the wavelengths of 269 and 282 nm, even considering the low optical power of the LEDs. However, water purification applications, where water has to be disinfected within a few seconds, are still limited by long exposure times of up to 3 to 4 minutes.

6 Overall Conclusion and Perspectives

This report presented recent developments in the field on the UV-LED disinfection. This technological field is very recent and further interests - along with rapid and continuing improvements in performance (especially in terms of emission power) – are expected within the next years.

After the physical characterisation of the few UV-LEDs - at 269 and 282 nm - that are currently available on the market, their disinfecting action was to be measured via biodosimetric tests. They show an increase of the inactivation with an increasing fluence using different types of raw water, although some early static tests tend to highlight potential recontamination and inhomogeneous distribution of UV-light – which may be explained by the module configuration. Main other results indicate that UV-absorbing compounds in the various waters reduce the disinfection capacity.

Morevoer, a more effective disinfection is observed at 269 nm than at 282 nm for a similar fluence. However, the emission output is better with 282 nm - UV-LEDs. Therefore, an interesting aspect, worth being investigated in the future is to ensure an optimized configuration, which balances the input power, which is necessay to run the UV-LED module, and its disinfecting action.

With potential enhanced emission powers, new developments for UV-LED water purification applications would enable to perform larger-scale tests and shorten UV exposure times.

7 References

1. Bolton, J.R., *Calculation of ultraviolet fluence rate distributions in an annular reactor: Significance of refraction and reflection.* Water Research, 2000. 34(13): p. 3315-3324.
2. Bolton, J.R. and K.G. Linden, *Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments.* Journal of Environmental Engineering-Asce, 2003. 129(3): p. 209-215.
3. Chen, R.Z., S.A. Craik, and J.R. Bolton, *Comparison of the action spectra and relative DNA absorbance spectra of microorganisms: Information important for the determination of germicidal fluence (UV dose) in an ultraviolet disinfection of water.* Water Research. In Press, Corrected Proof.
4. Bolton, J.R. and C.A. Cotton, *The Ultraviolet Disinfection Handbook*. 1 ed. 2008, Denver: American Water Works Association.
5. DVGW, *Arbeitsblatt W 294-1: UV-Geräte zur Desinfektion in der Wasserversorgung Teil 1: Anforderungen an Beschaffenheit, Funktion und Betrieb*. 2003 a, Deutsche Vereinigung des Gas- und Wasserfaches, Bonn.
6. Vilhunen, S., H. Särkkä, and M. Sillanpää, *Ultraviolet light-emitting diodes in water disinfection.* Environmental Science and Pollution Research, 2009. 16(4): p. 439-442.
7. Crawford, M.H., M.A. Banas, M.P. Ross, D.S. Ruby, J.S. Nelson, R. Boucher, and A.A. Allerman, *Final LDRD Report: Ultraviolet Water Purification Systems for Rural Environments and Mobile Applications*. 2005, Sandria National Laboratories: Albuquerque, New Mexico. p. 1-37.
8. Caron, E., G.C. Jr., B. Barbeau, P. Payment, and M. Prévost, *Impact of microparticles on UV disinfection of indigenous aerobic spores.* Water Research, 2007. 41: p. 4546-4556.
9. MWH, *Water Treatment: Principles and Design* 2nd ed. 2005, Hoboken, NJ: John Wiley & Sons, Inc.
10. Blatchley, E.R., C. Shen, O.K. Scheible, J.P. Robinson, K. Ragheb, D.E. Bergstrom, and D. Rokjer, *Validation of large-scale, monochromatic UV disinfection systems for drinking water using dyed microspheres.* Water Research, 2008. 42(3): p. 677-688.
11. Qualls, R.G. and J.D. Johnson, *Bioassay and Dose Measurement in UV Disinfection.* Applied and Environmental Microbiology, 1983. 45(3): p. 872-877.
12. DVGW, *Arbeitsblatt W 294-2: UV-Geräte zur Desinfektion in der Wasserversorgung Teil 2: Prüfung von Beschaffenheit, Funktion und Desinfektionswirkung*. 2003 b, Deutsche Vereinigung des Gas- und Wasserfaches, Bonn.
13. DVGW, *Arbeitsblatt W 294-3: UV-Geräte zur Desinfektion in der Wasserversorgung Teil 3: Messfenster und Sensoren zur radiometrischen Überwachung von UV-Desinfektionsgeräten - Anforderungen, Prüfung und Kalibrierung*. 2003 c, Deutsche Vereinigung des Gas- und Wasserfaches, Bonn.
14. Schoenen, D., J. Gebel, A. Kolch, O. Hoyer, R. Sommer, A. Cabaj, P. Karanis, W. Maier, H.M. Seitz, A. Wiedenmann, T. Hahn, and K. Botzenhart, *F + E Verbundvorhaben: Untersuchungen zur Sicherheit des technischen Einsatzes von UV-Strahlen zur Trinkwasserdesinfektion - Mik-*

robiologische Untersuchungen zur UV-Desinfektion von Trinkwasser. 1994, Arbeitsgemeinschaft Trinkwasser Talsperren e.V. : Siegburg.

8 Annex

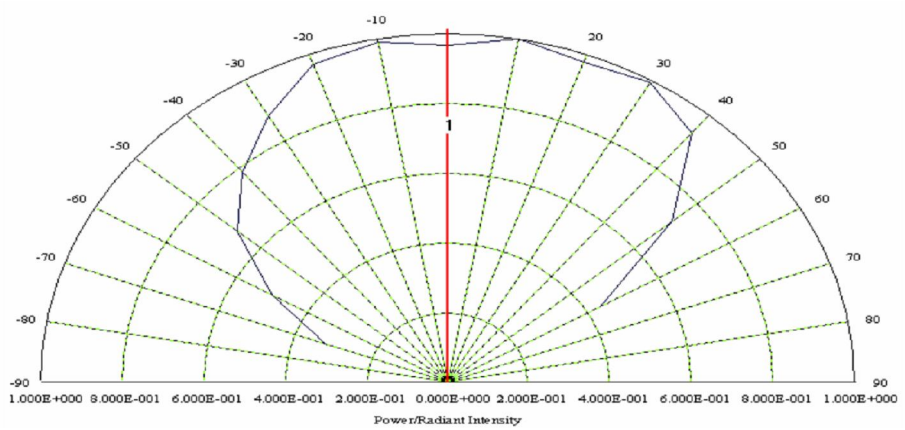


Fig. A. 1: Typical angular diagram of the UV LEDs.

The following tables summarize the results obtained with test module I equipped with 269 nm LEDs.

Table A. 1: Results obtained with 269 nm LEDs in static tests with deionised water (DI). Bacillus *subtilis* analysis of test run a) to d) were conducted in a single assay. Test run e) and f) were analised in triplicates.

Fluence	**test run a)**	**test run b)**	**test run c)**	**test run d)**
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	2300000	230000	2500000	1400000
100	39000	7100	24000	48000
250	35000	6	n.d.	1500
400	n.d.	n.d.	450	n.d.
600	n.d.	n.d.	2	n.d.

Fluence		**test run e)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1200000	1400000	1100000
100	20000	11000	16000
250	1200	500	500
400	4	n.d.	2
600	n.d.	n.d.	n.d.

Fluence		**test run f)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	880000	1000000	1000000
100	17000	17000	16000
250	8	10	8
400	2	n.d.	n.d.
600	n.d.	n.d.	n.d.

n.d.: not detectable

Table A. 2: Results obtained with 269 nm LEDs in static tests with tap water (TW). Bacillus *subtilis* analysis were conducted in a single assay.

Fluence [J/m²]	**test run a)** [cfu/ml]	**test run b)** [cfu/ml]	**test run c)** [cfu/ml]
0	25000	1300	18000
100	830	980	230
250	1	1	110
400	n.d.	3	30
600	n.d.	730	400

n.d.: not detectable

Table A. 3: Results obtained with 269 nm LEDs in static tests with surface water (SW). Bacillus *subtilis* analysis were conducted in a single assay.

Fluence [J/m²]	**test run a)** [cfu/ml]	**test run b)** [cfu/ml]
0	25000	14000
100	800	400
250	260	270
400	50	150
600	100	850

Table A. 4: Results obtained with 269 nm LEDs in static tests with sewage effluent (SE). Bacillus *subtilis* analysis were conducted in a single assay.

Fluence [J/m²]	**test run a)** [cfu/ml]
0	33000
100	2100
250	50
400	710
600	950

The following tables summarize the results obtained with test module II equipped with 282 nm LEDs.

Table A. 5: Results obtained with 282 nm LEDs in static tests with deionised water (DI). Bacillus *subtilis* analysis was conducted in triplicates.

Fluence		**test run a)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	27000000	25000000	19000000
100	5700000	4400000	5400000
250	170000	170000	180000
400	756	784	878
600	n.d.	4	2
Fluence		**test run b)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	35000000	33000000	44000000
100	4700000	5800000	5100000
250	120000	98000	130000
400	498	360	466
600	6	4	8
Fluence		**test run c)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	16000000	15000000	19000000
100	5700000	8800000	7700000
250	170000	170000	200000
400	476	402	502
600	n.d.	10	2

Table A. 6: Results obtained with 282 nm LEDs in static tests with tap water (TW). Bacillus *subtilis* analysis was conducted in triplicates.

Fluence		**test run a)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1500000	1100000	1300000
100	1000000	820000	800000
250	33000	24000	37000
400	624	984	756
600	32	20	24
Fluence		**test run b)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1100000	1300000	2100000
100	500000	640000	710000
250	38000	45000	47000
400	536	400	506
600	10	14	8
Fluence		**test run c)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1600000	1500000	1300000
100	800000	760000	590000
250	57000	41000	54000
400	256	52	236
600	6	14	16

Table A. 7: Results obtained with 282 nm LEDs in static tests with surface water (SW). Bacillus *subtilis* analysis was conducted in triplicates.

Fluence		**test run a)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1800000	2100000	2100000
100	470000	630000	540000
250	28000	33000	29000
400	2600	2900	3000
600	60	54	58
Fluence		**test run b)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1100000	2500000	1900000
100	1000000	1400000	1100000
250	48000	44000	43000
400	4100	4000	4100
600	104	164	130

Table A. 8: Results obtained with 282 nm LEDs in static tests with sewage effluent (SE). Bacillus *subtilis* analysis was conducted in triplicates.

Fluence		**test run a)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1700000	2000000	1900000
100	800000	950000	770000
250	100000	87000	84000
400	7200	7400	8000
600	220	172	142
Fluence		**test run b)**	
[J/m²]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1500000	3100000	1800000
100	780000	1100000	770000
250	100000	110000	90000
400	2000	4200	3500
600	16	92	114

Table A. 9: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,283 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run x-a)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	730000	660000	540000
0	1000000	950000	1100000
0	1300000	1300000	1400000
0,6	42000	42000	41000
0,6	11000	9500	11000
0,6	42000	48000	42000
0,6	13000	19000	13000

Table A. 10: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,293 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run x-b)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	2200000	1900000	2000000
0	3000000	3300000	3800000
0	300000	290000	310000
0,9	19000	19000	14000
0,9	5500	5800	5900
0,9	4700	4000	4100
0,9	7500	7900	7100

Table A. 11: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,185 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run y-a)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	810000	960000	1100000
0	720000	790000	630000
0,5	773	736	651
0,5	394	338	356
0,5	210	186	204
0,5	320	390	325

Table A. 12: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,180 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run y-b)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	960000	960000	1300000
0	830000	550000	680000
0,7	82	56	62
0,7	30	34	42
0,7	16	22	18
0,7	60	40	80

Table A. 13: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,173 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run y-c)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	580000	470000	540000
0	610000	570000	510000
0,9	12	20	40
0,9	2	2	4
0,9	15	12	8
0,9	690	720	630

Table A. 14: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,133 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run z-a)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1400000	1500000	1600000
0	1300000	1500000	1600000
0,35	980	1080	1160
0,35	1060	880	840
0,35	1840	1540	1600
0,35	1500	1620	1580

Table A. 15: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,135 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run z-b)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1200000	1500000	1400000
0	1200000	1100000	980000
0,49	90	149	173
0,49	136	114	108
0,49	88	95	117
0,49	1720	1820	1570

Table A. 16: Results obtained with 282 nm LEDs in flow through tests with deionised water (DI); flow rate: 0,123 cm³/s; Bacillus *subtilis* analysis was conducted in triplicates.

LED Power		**test run z-c)**	
[mw/LED]	[cfu/ml]	[cfu/ml]	[cfu/ml]
0	1100000	1500000	1400000
0	1200000	1200000	1300000
0,59	460	700	620
0,59	380	540	460
0,59	625	521	453
0,59	484	521	453