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Final LDRD Report: Ultraviolet Water Purification Systems for Rural Environments and Mobile Applications

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Abstract

We present the results of a one year LDRD program that has focused on evaluating the use of newly developed deep ultraviolet LEDs in water purification. We describe our development efforts that have produced an LED-based water exposure set-up and enumerate the advances that have been made in deep UV LED performance throughout the project. The results of E. coli inactivation with 270-295 nm LEDs are presented along with an assessment of the potential for applying deep ultraviolet LED-based water purification to mobile point-of-use applications as well as to rural and international environments where the benefits of photovoltaic-powered systems can be realized.

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1. Introduction

Ultraviolet (UV) disinfection is a well established, cost-competitive technology. In the late 1800's researchers first discovered the germicidal effects of sunlight, and systems based on fluorescent tube technology have been operating since the 1950's. More recently, UV disinfection has been attracting a lot of attention due to the discovery of chlorinated Disinfection Byproducts (DBP), and new measurements confirming the effectiveness of UV to inactivate *Cryptosporidium*. It is well know that chlorination is not effective in treating *Cryptosporidium.* The physical mechanism of UV disinfection is different from chlorination. UV light causes physical changes to the DNA structure preventing replication, where as chlorination directly damages the cellular structure causing cell death. UV is also effective in disinfecting water containing *Giardia,* E. coli, viruses, spores, and other bacteria. *Cryptosporidium* and *Giardia* are waterborne pathogenic protozoa implicated in major public health crises throughout the world. In light of this, UV disinfection systems based on fluorescent tube technology are being installed in many large-scale municipal systems. A few systems, coupled with PV power sources, have been installed in rural environments. These installations have been met with many challenges due to maintenance, reliability, and the fragile nature of the fluorescent tube sources. In addition, the higher power requirements result in larger, more costly photovoltaic systems. These limitations also make UV purification systems based on fluorescent tube technology impractical for mobile point-of-use applications.

In the past two years, Sandia researchers have demonstrated up to milliwatt output powers from AlGaN-based LEDs in the 275-290 nm region of the spectrum. *This development has enabled, for the first time, a solid-state light source in the germicidal region of the spectrum (230-300 nm) with output powers that are nearing relevant levels for water purification.* For example, *Giardia* has been shown to be effectively inactivated at doses on the order of 2 mJ/cm^2 (2mW *sec/cm^2). A few 100s of μWs up to mW level is typical of deep UV LED power output levels (physical dimensions of these devices are on the order of a piece of sand), even in this early stage of their development. More mature visible LED technology, based on related nitride semiconductor alloys, can achieve 1 Watt output powers with good packaging and large area LED device design and it is anticipated that significant performance advances will be also achieved in the deep UV devices with further development. In contrast to UV fluorescent lamps, LEDs are very compact, shock-resistant, require low power DC operation, can be tailored to emit in a range of wavelengths in the 250-300 nm region, and have the potential to exhibit very long operational lifetimes (up to 100,000 hrs, or greater than 10 years). A typical lifetime of UV fluorescent tubes is on the order of 4000-10,000 hours, or about one year. Long-life is particularly important for rural applications, where maintenance and repair are problematic.

Our focus in this one year LDRD project has been to explore UV water purification systems concepts that would take advantage of the cost, size, robustness, and energy saving potential of this emerging solid-state deep UV LED technology. This LDRD project had three major tasks. The first task was to perform an assessment of rural and international UV water purification systems including design considerations for an LED based system. The second

task was to perform an assessment of mobile, point-of-use UV purification systems, once again including designs considerations for an LED-based system. The third task was to perform UV inactivation studies of E. coli contaminated water samples using Sandia-developed deep UV LEDs. This task required the additional parallel efforts of optimizing the deep UV LED performance for water purification as well as developing an optical system for delivering relatively uniform UV light to the water sample. Recognizing the relatively low output powers of deep UV LEDs at this early stage of development, our purpose in this task was not to aspire to achieve a more efficient water purification system using LEDs in place of lamps. Rather, our goal was to perform proof-of-concept experiments to evaluate the effectiveness of UV LEDs in E. coli inactivation, and to reveal the distinctive benefits and challenges in the application of solid-state LEDs to water purification. The ultimate goal of this project is to combine the results of our applications assessments and experimental studies to provide a recommended technical path for potential follow-on programs that would seek to realize an LED-based water purification system. Below we summarize our accomplishments in this project.

2. Water Purification Systems for Rural Off-Grid Locations Based on Ultraviolet Light Emitting Diodes and Powered by Photovoltaic Modules

Introduction

It is estimated that one third of the world's population or two billion people do not have access to electricity and two billion people lack clean drinking water. Most of all of those lacking clean water are also those without electricity. Diarrhea, cholera, hepatitis, and other diseases caused by contaminated water kill roughly five million people a year. Many times more that number of people become ill, and the growth of 60 million children is stunted because of recurring diarrhea and other illnesses. Water purification systems exist based on ultraviolet (UV) radiation that is sourced by a mercury vapor lamp. UV-based systems do not remove objects from the water, but rather they kill organic material that causes illness. The lamps have limitations, especially in rural settings. However, the use of solid-state light emitting diodes (LEDs) as the source of UV light have features that make them superior to mercury tubes or lamps.

As for power, the distributed nature of the households in the world without access to electricity makes the use of photovoltaic (PV) technology an appropriate option to power the water

purifying systems. They are reliable (no moving parts), have a lifetime of more than 25 years, and the resource that they depend on (sunshine) is sufficiently available almost everywhere in the world making PV a universal choice. This report looks at the efficient combination of PV to power UV water purification systems and the advantage of LEDs over mercury lamps as sources of the UV radiation. An emphasis is placed on solutions that are effective, reliable, cost-efficient, safe and sustainable for use in rural off-grid areas mainly in the developing world.

Ultraviolet Radiation

Ultraviolet radiation is similar to visible light in all-physical aspects. It has a shorter wavelength just before the violet end of the visible colors. In scientific terms, UV radiation is electromagnetic radiation just like visible light, microwaves and x-rays (see Figure 1). Electromagnetic radiation is transmitted in the form of waves that are described by their wavelength or frequency as well as their amplitude (strength or intensity). For radiation in the UV region of the spectrum, wavelengths are measured in nanometers (nm). The intensity of UV radiation is measured in the units of milliwatts per square centimeter (mW/cm^2), which is energy per square centimeter received per second. Also, it is measured in the units of millijoules per square centimeter (mJ/cm^2), which is energy received per unit area in a given time.

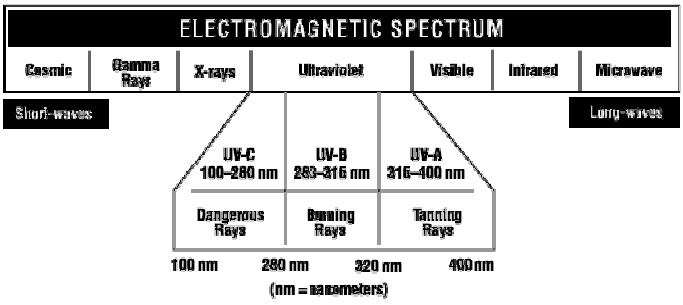


Figure 1 – *Electromagnetic Spectrum.*

UV radiation is divided into three wavelength ranges: A, B and C. The shortest wavelength of UV radiation (UV-C), between 100 and 280nm, poses the maximum risk to living organisms. This is considered the germicidal UV wavelength range. The sun emits UV-C, but it is absorbed in the ozone layer of the atmosphere before reaching the earth – thus it is safe to walk outside during the day. Other than the sun, there are man-made UV sources that emit UV-C and they are well regulated for safety.

UV Water Purification

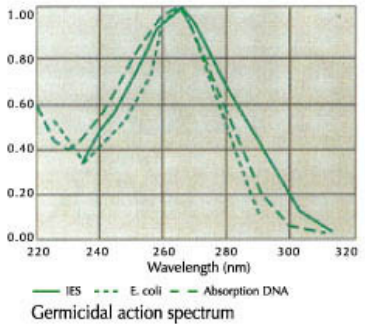


Figure 2 – *Germicidal spectrum.*

UV-C light disinfects water by permanently de-activating bacteria, spores, molds, viruses and other pathogens, thus destroying their ability to multiply and cause disease. The most effective single wavelength is typically UV at 265nm (see Figure 2), however recent research has shown that UV radiation at wavelengths 271nm and 263nm are the most effective for the deactivation of particular target organisms.

The mechanism of kill is well documented and unlike chemical disinfectants the organism is unable to develop any immune mechanisms. The mechanism of kill involves the absorption of photons of UV energy by the DNA, which fuses the DNA and prevents replication. The ability to effectively disinfect water is a function of both time and intensity.

Ultraviolet light for water purification is most typically generated from a low pressure or a medium pressure lamp. Low Pressure lamps are the most common lamp type and are the oldest source of man-made ultraviolet light. They consist of a quartz envelope that separates two tungsten filaments. The lamp is evacuated to <10torr and anywhere from 10 to 60mg of mercury is introduced into the quartz envelope. The spectral output of this lamp type is monochromatic, a single line output at 253.7nm. A fluorescent lamp is a low-pressure lamp that has the inner surface of the lamp coated with phosphors to absorb all of the 253.7nm light, and only emit the longer wave visible light. This lamp has an output that is temperature dependent and can take up to 400 seconds to get to full output in cool or hot water.

ANSI/NSF Standard 55

The latest ANSI/NSF Standard 55, which deals with Ultraviolet Microbiological Water Treatment Systems, was revised in January 2002. Standard 55 was written to establish the minimum requirements a manufacturer would need to certify a Class A or B ultraviolet (UV) system. Depending on the class that a manufacturer would like to claim, systems certified to this standard may be used on either microbiologically safe or unsafe water.

Class A point-of-entry and point-of-use (POU/POE) devices are designed to disinfect and/or remove microorganisms, including bacteria and viruses, from contaminated water to a safe level. They are not intended for treatment of water that has an obvious contamination source such as raw sewage; nor are systems intended to convert wastewater to microbiologically safe drinking water. Class A systems are capable of delivering a UV dose, at a wavelength of 254 nanometers (nm), to at least 40 millijoules per square centimeter (mJ/cm^2) at the alarm set point - the point where a manufacturer will set its UV sensor to activate the system alarm.

Class B POU systems are designed for supplemental bactericidal treatment of treated and disinfected public drinking water or other drinking water tested and deemed acceptable for human consumption by the state or local health agency having jurisdiction. Class B systems are not intended for disinfection of microbiologically unsafe water but are designed to reduce normally occurring nonpathogenic or nuisance microorganisms only. The systems are capable of delivering a UV dose, at 254 nm, to at least 16 mJ/cm^2 at 70 percent of the normal UV lamp output or alarm set point.

For systems in rural areas of developing countries Class A is what we need to address. The previous version of this standard had a minimum of 38 mJ/cm^2. The increase to 40 was to bring this requirement in line with current international requirements. Please note that it corresponds specifically to 254nm, the common emission wavelength of mercury vapor lamps. If a LED-based system at 265nm meets the same dose requirement of 40 mJ/cm^2, then it should be more effective at disinfection.

LED Advantages

Disadvantages of mercury vapor lamps are compounded in rural isolated areas of the developing world. They include a relatively short lifetime (usually one year), local non-availability of lamps when time to replace, and the improper disposal of the lamps when they are no longer effective. This is what is seen now when vapor lamps are used in rural areas.

Advantages of UV LEDs as the source of UV radiation resolve two of the major disadvantages of the vapor lamps listed above assuming that UV LEDs will have a longer life span than the lamps and will approach the lifetime of visible light LEDs. The longer life of such a source of UV in a water purification system will make for a more sustainable system. There will still be the issue of local availability, but at least the frequency of replacement will be significantly reduced. LEDs do not contain mercury, which is a hazardous material.

Additional advantages of UV LEDs in general include: distributed and conformal layout of point sources in the system; possibility to use the preferred wavelength of 265nm instead of 254nm; more durable in transit and handling (no filaments or glass); faster startup time; ability to turn on and off with higher frequency; lower voltages; and less auxiliary electronics.

Although the LED has a longer lifetime than fluorescent lighting, there is still the solarization effect that is the major limiting factor for the lifetime of the mercury vapor lamps. The UV LED should still suffer from solarization, but at a level lower than that of the lamp due to a lower amount of ultraviolet radiation intensity.

The cost of an LED-based system should be lower overall. It may be that the total amount of UV LEDs has a lower cost than the equivalent mercury vapor lamp in a similar purification system. However, other cost savings will come from longer lifetimes and less breakage in transit and handling. In terms of sustainability in rural areas, a higher cost for the overall system would be justified for a longer lifetime of the UV source and added overall reliability of the system. This is due to the tendency of not replacing lamps annually or when they fail.

Design Considerations

Purification

The ANSI/NSF Standard 55 for Class A systems mentions having a UV sensor to make sure that UV radiation is actually reaching the water stream. This is very important for use in rural areas, where information is scarce. This is for the factor of safety. The design of a system using LEDs, a distributed source of radiation, should incorporate a technique that takes this distributed nature into account. A mercury vapor tube is a single line source and probably one measurement is sufficient to alert the system of an adequate level of UV radiation reaching the water stream. A distributed system of sources may need a distributed layout of sensors, depending on the design.

Also, in terms of safely, there are several items that must be in working order as designed for the water purification system to pass water to the output: 1) adequate power for the system to function; 2) adequate UV radiation reaching the extent of the water stream; and 3) water quality input meets certain requirements.

The first two items calls for the incorporation of sensors that measure proper operating voltages and UV radiation in the water stream (or far side of the water stream) and operate a "fail safe" (normally closed unless conditions are met) valve on the output of the system. The third item relates to turbidity and particle size that would hamper the effectiveness of the system by blocking UV radiation from reaching all particles in the passing water. The system would require a filter or series of filters on the input. Of course, this introduces another element that would need maintenance and periodic replacement. A sediment filter of 5 microns is a common size at the input.

As for sustainability of such systems in the rural environment, the longer the lamp life and the ease of lamp replacement are key. The first one is the most important for sustainability – as long as other components have long life spans and/or are easy to repair. Another factor is the routine maintenance issue: cleaning of input filters and buildup of residue on the internal components, especially the lamps. The distributed nature of LEDs may pose a challenge for lamp replacements. The easiest solution would be to create a replacement line source of LEDs that imitate a central mercury vapor lamp tube.

Present lifetimes for mercury vapor lamps are one year. If LEDs can offer at least a doubling of lifetime at a similar cost and an ease of replacement, then sustainability may be met. A five-year lifetime would be a great achievement and worth an extra cost. Sustainability during the five-year period would simply depend on routine maintenance, assuming other component failures do not occur.

A simple design would encourage reliability – the fewer components that can fail, the better. A certain pressure may be required for proper operation. Most UV water purifications systems today have minimum or constant pressure requirements that call for a pump in the system.
A design that uses gravity to pass the water through the system would be the most reliable. The internal pathway may have to be such to encourage a natural turbidity to allow for all water particles to receive sufficient radiation.

Power Source

Since the sun shines everywhere and photovoltaic (PV) modules produce reliable electricity with warranties up to 30 years, we will consider PV technology to power the UV water purification system. The efficiency of such an overall system is optimal if the water purification component is made to operate on direct current (DC). In this manner inverters will not be necessary (added cost, loss of reliability, loss of energy).

There are two approaches of design depending on storage. If clean potable water is not going to be stored, the energy storage will be necessary. However, if water storage is available,

then energy storage can be eliminated. Of course, you can have both energy and water storage as a luxury design. Water storage only would be the most economical and reliable solution, however water would only be purified while the sun is shining and the storage container must be kept free of potential contaminants. A chlorine-based periodic cleaning is recommended of the storage container. Energy storage would require a battery and charge controller. These are added components that increase the cost and lower the reliability (more components that can fail). The system with energy storage would stabilize the voltages on the water purification system, especially as the sunshine comes and goes. Without the energy storage, we would have a situation of wild PV that would have to be accounted for in the design. In this case water would only be purified when adequate power is available.

LEDs offer an advantage over mercury lamps in terms of off-on cycles. The higher the off-on frequency of mercury lamps (arc fired), the faster they burn out. Thus, "wild" PV (and wind) system designs are not suitable with the mercury lamps. In rural areas a wild energy source design offers cost savings (less components) and higher reliability (less components). This is now possible with a solid-state source of UV – the germicidal LED. The LED also has a significantly shorter activation (start-up) time than the mercury lamp.

The purchase cost of a LED-based UV water purification system may not be cheaper than one based on mercury vapor lamps. However, if a LED-based system consumes less energy, then a smaller amount of PV modules would be necessary. As an example, if 20% less electricity were required, then using the general figure of $5 per watt, a 40-watt panel would offer a savings of $50 compared to that of a 50-watt panel. Another cost savings would come in the calculation of life-cycle costs, assuming that the UV LED, like their visible light cousins, will have extended lifetimes of 5 to 10 times longer. Additional cost savings would come in the form of less overall components of the overall system (power + water purification). LEDs will allow higher on-off cycles without penalty, which opens the possibility of the use of "wild" or direct drive (no energy storage) PV (or small wind) designs, thus reducing the need for absolute energy storage and higher-end controlling electronics.

Sizing

There is not one configuration suitable for all situations. Currently available UV water purification units come in all various designs and are usually differentiated by the amount of water that can be disinfected per unit time. The more water volume per minute the more energy required.

An example of a commonly available design is shown in Figure 3. The mercury vapor lamp is positioned as a linear element in the center of a tube. Water enters at Point 1, passes along the outer circumference of the lamp (Point 2) exposed to intense UV radiation, and exits at Point 4. The power required seems to be a DC voltage as outlined by a 120V AC transformer at Point 3. Systems in off-grid areas usually use 12V DC,

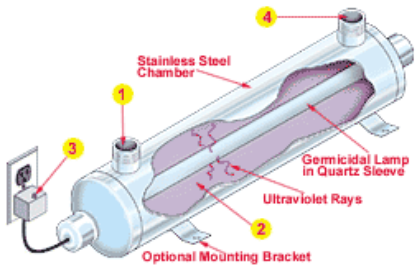


Figure 3: *Commonly available design of a UV water purification product on the market today.*

which is the voltage supplied by an automotive or deep-cycle battery. In a PV system a deep-cycle type of battery is normally used to handle daily deep discharges of energy.

In a datasheet from MINIPURE five models are available ranging from 1 to 9 gallons per minute (GPM) flow rates. Power consumption ranges from 14 watts for the 1 GPM model to 34 watts for the 9 GPM one. The power figures include ballast lost, which is estimated to be 2 to 5 watts. All provide a dosage rate in excess of 30,000 mW/cm^2, which is short of Class A approval. Prices are $340 for the smallest unit and $619 for the largest. Quartz sleeves range from $40 to $55 and all lamps are about $100 per unit.

Sizing of the PV system components would depend on the selected water purification unit along with design criteria such as energy storage or not; the amount of solar irradiance for the site; how many days of autonomy; energy demand from other system components; etc. Proper sizing can be accomplished using Sandia publication entitled, "Stand-Alone Photovoltaic Systems: A Handbook of Recommended Design Practices." Cost will depend on the energy demand of the system. The more energy efficient a water purification unit will be, the smaller the size of the PV modules (in watts) and thus the cost (currently at $4 - 5/watt).

Conclusion

LEDs producing ultraviolet light in the germicidal wavelength region, especially at 265nm, offer many advantages compared to the conventional mercury vapor tube lamp for use in water purification systems based on UV disinfection. Certain advantages are especially important for designs that will be used in rural areas of developing parts of the world, where grid electricity is not available, safe drinking water is hard to come by, infrastructure for replacement parts is far away, and general expertise is not common. They include longer lifetimes of the UV sources (LEDs) before replacement and the ability to include more frequent on-off cycles in the overall design. These benefits are related to lower life-cycle costs, more reliable designs and overall sustainability of the complete water purification solution (purifier + energy source).

3. Photovoltaic-Powered UV-light Water Disinfection Systems for Mobile/Military Applications

Strong sunlight disinfects water by permanently de-activating bacteria, spores, molds and viruses. Over a century ago, scientists identified the part of the electromagnetic spectrum responsible for this well-known effect; wavelengths between 200nm and 300nm, often called UV-C. The most effective single wavelength is typically UV at 265nm, however recent research in the USA has shown that 271nm light and 263nm light are the most effective UV wavelengths for the deactivation of particular target organisms.

The mechanism of kill involves the absorption of photons of UV energy by the DNA, which fuses the DNA and prevents replication. DNA (Deoxyribonucleic acid) consists of a linear chain of nitrogen bases known as purines (adenine and guanine) and pyrimidines (thymine and cytosine). These compounds are linked along the chain by sugar-phosphate components. The DNA of most forms of life is double stranded and complimentary; the adenine in one strand is always opposite thymine in the other, and linked by a hydrogen bond, and guanine is always paired with cytosine by a hydrogen bond. The purine and pyrimidine combinations are called base pairs. When UV light of a germicidal wavelength is absorbed by the pyrimidine bases (usually thymine) the hydrogen bond is ruptured. The dimer that is formed links the two bases together, and this disruption in the DNA chain means that when the cell undergoes mitosis (cell division) the DNA is not able to replicate. The most effective wavelengths to achieve this effect are found between 263nm to 275nm, and the peak wavelength distribution is dependent on the target organism.

Ultraviolet light is most typically generated from a low pressure or a medium pressure Mercury vapor UV lamp. These lamp types are different in character and performance, and are described below:

Low Pressure lamps are the most common lamp type and are the oldest source of ultraviolet light. They consist of a quartz envelope that separates two tungsten filaments. The lamp is evacuated to <10torr and approximately 60mg of mercury is introduced into the quartz envelope. The spectral output of this lamp type is monochromatic, a single line output at 253.7nm. A fluorescent lamp is a low-pressure lamp that has the inner surface of the lamp coated with phosphors to absorb all of the 253.7nm light, and only emit the longer wave visible light. This lamp type is typically 1 meter (3 feet) in length. This lamp has an output that is temperature dependent and can take up to 400 seconds to get to full output in cool or hot water.

The optimal operating temperature is 15^{o}C, and the lamp output will fall off rapidly as the lamp temperature migrates from this condition. These lamps should not be used if the water is hot or cold, or if the water flow is intermittent as the temperature build up will cause the lamp output to decrease. Frequent switching of these lamps will have a detrimental effect on lamp life, and the most probable failure mode will be failure of the filaments, which become brittle. Typically these lamps have an **efficiency of 25-30%**, which is temperature dependent. The lamp life is typically **8000 hours.** Amalgam lamps have been developed recently to overcome the problems associated with traditional low-pressure technology. This type of lamp contains a mercury amalgam, and typically up to 120mg of mercury is contained in each lamp. The Amalgam lamp is typically very long, and not unusually can be more than 1.5 m (5 feet) in length. Once switched on, the Amalgam lamp output is not affected by water temperature fluctuations, however the large size of the lamp does mean that they can take up to 800 seconds to get to full power, and the warm up time is temperature dependent.

These lamps are monochromatic in output, and only produce UV light at 253.7nm. Amalgam lamps have a typical power of **300watts**, and can have up to **35% efficiency**, however the

lamp life is often below the expected **10,000 hours** due to failure caused by the filaments becoming brittle and deposits of mercury oxide causing the ends to become black, which leads to poor heat dissipation and is the most probable failure mode.

The medium pressure lamp is designed to have a spectral output that is specifically enhanced in the germicidal region. These lamp types are often called polychromatic, as they have a continuous output from 200nm up to the long wave visible light. Medium pressure lamps have a higher pressure within the quartz envelope (typically 1000 torr) and a **3.5kW** lamp will contain approximately 300mg of mercury. These lamps have an efficiency typically between 15% to 20%, depending on lamp type, and typically 15 low pressure lamps or 6 amalgam lamps will be required to have a comparable UV intensity output. The medium pressure lamp is hot running and typically the lamp surface will reach 800^{o}C, however the protective sleeve that separates the lamp from the fluid being treated will not usually rise above 60^{o}C. An overtemperature detector will power down the lamp should the water flow stop for an extended period. Medium pressure lamps are typically from 20cm to 1.5m in length and a variety of quartz types are selected depending on the required spectral output, with pure fused silica used for disinfection.

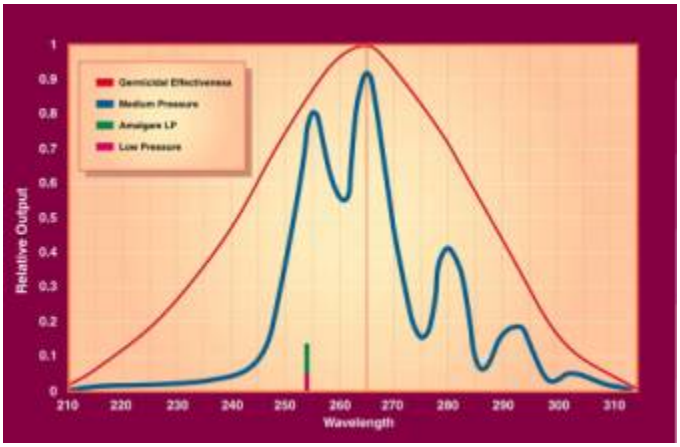


Figure 4: *Graph of germicidal effectiveness vs. wavelength. To be most effective, the UV source should emit light near 265 nm. An LED wavelength of 280 nm should be almost as effective as that of low-pressure Hg-vapor lamps which emit primarily at 254 nm.*

The use of a monitoring system to measure the fluence being emitted by the lamp allows the operators to have confidence in the integrity of the system. Systems should be designed to be fail safe and the control protocols that are used will not allow untreated water to be sent forward. The dedicated UV monitor measures the output from each lamp. The monitors are sealed and do not allow any operator adjustment. The monitor measures intensity in absolute units of mw/cm^2. An online transmittance monitor measures the transmittance of the fluid being treated, and not unusually surface water can have a very high fluctuation in transmittance. Use is made of data logging facilities to demonstrate the adequacy of treatment, and to provide a permanent record of disinfection.

The US military (Office of Naval Research - Marine Corps Systems Command) has initiated a research program to develop a compact UV water purification module for use by small

groups of soldiers in the field. The module needs to filter and sterilize drinking water on demand. The required attributes of the system are:

- Destroys 99.99% of Bacteria, Viruses, Protozoa
- Fast, Small, Lightweight, Rugged
- Economical and Long Lasting
- Non-chemical, Adds No Taste or Toxicity
- Portable, requires no external electricity source.

The requirement of longevity precludes the use of Mercury vapor UV lamps. In the disinfection system, the UV lamp is the component with the shortest life: Mercury lamps become unreliable after about 8,000 hours of continuous operation. The useful life of Mercury vapor lamps is limited by the degradation of the electrode material. The decrease in UV radiation is caused by the deposit of evaporated electrode material on the inner surface of the lamp tube. Frequent ignition accelerates this electrode wear and reduces lamp life significantly. Because of the portable nature of the system and the use of PV-generated electricity to power it, the system is likely to experience intermittent usage, which would reduce the useful life of a Mercury vapor lamp to unacceptable levels.

The other part of the system with the most limited life span is the electronic ballast (transformer), required to boost the voltage necessary for the Hg vapor lamp. Both of these elements would be eliminated in a UV-LED disinfection system.

1. How much drinking water is provided per person per day?

The requirement of drinking water is estimated at 4 liters (1 gallon) per person per day for direct use. In a hot, arid environment, more would be necessary. Our design goal is 10 liters (2 and a half gallons) per person per day. For a group of 10 soldiers, at least 25 gallons per day should be produced.

2. How clear must the inlet water be?

The UV transmittance of inlet water determines how well the UV light penetrates and disinfects the water column (for a broad review and many technical references, see Wolfe, 1990). Transmittance decreases with increasing turbidity and dissolved salts. The transmittance is measured with an "extinction coefficient." The larger the extinction coefficient, the faster the UV intensity is attenuated as it travels through the water. Water with a large extinction coefficient for UV will prevent microorganisms farthest away from the UV light source from being inactivated. The extinction coefficient of tap water is 0.1 cm^{-1} for 254 nm UV light. In our design, we assume the inlet water to have the extinction coefficient of 0.3 cm^{-1}, as large as that of the average water discharged from US waste-water treatment plants. More turbid water would need to be pumped through a filter before entering the disinfection unit.

3. How much electrical power is required?

Ultraviolet (UV) rays with a wavelength 254 nm will effectively kill bacteria, viruses, yeast, molds and algae. The UV radiation breaks through the outer membranes of the organisms, destroying or inactivating the DNA (Deoxyribonucleic Acid) thus preventing them from reproducing. This safely and effectively purifies water without changing its pH, color, taste, odor or temperature.

Germicidal UV dose is a measure of germicidal energy, multiplied by the exposure time, multiplied by the area within the treatment chamber, and adjusted for UV transmission. The amount of energy to reduce the viable population of individual pathogens by a factor of ten is commonly referred to as a D-10 value. A list of D-10 values for most common microorganisms is well known. By doubling the exposure energy to twice the pathogen's D-10 value, another factor of 10 reduction is achieved; i.e. 99% killed. Standard industrial disinfection commonly uses 30mWsec/cm2 to achieve a three-log, or 99.9% disinfection rate. The power required from the UV LED light source would need to be 30mW/cm^2 if the flow rate of the water was such that each volume of water was irradiated for at least one second. The area of the light source, water flow rate and UV power density need to be adjusted to meet the 3-log dose requirement. In practice, water enters a highly polished stainless steel chamber at a predetermined flow rate where it passes along one or more quartz sleeves containing ultraviolet radiation generating lamps. In a properly sized UV sterilizer, any common microorganisms present are exposed to 30,000 μws/cm^2 of germicidal UV energy, effectively killing them.

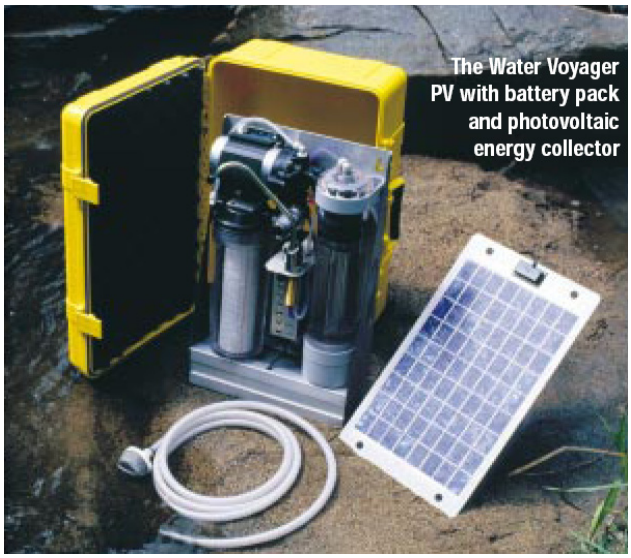


Figure 5: *Typical portable PV-powered UV disinfection system with a self-contained filtration/UV/Ozone water treatment system capable of producing safe, potable water from microbiologically-contaminated sources.*

The unit above can work with pressurized or non-pressurized water supplies, and contains its own battery storage and PV charging system. The specifications for this commercially available, portable, PV-powered system are given below.

- Power requirements: 12-18 VDC, 60 Watts maximum (power from internal batteries or external supply) to provide power for low-pressure Hg-vapor lamp.
- Flow: up to 1/2 GPM continuous.
- Contaminant reduction: Lead (>99%), cysts (>99.95%), Turbidity (>99%), microbial (bacteria and viruses) reduction, including >99.999% E-coli reduction.
- UV exposure intensity: In excess of 22,500 $\mu Ws/cm^2$
- Single battery-charge performance: 2.5 hours or 75 gallons
- Photovoltaic input: Up to two 10 Watt panels (20W) provide approximately 3 hours (90 gallons per day) of usage on solar power alone while keeping the batteries fully charged
- Physical dimensions: 9.5" x 21.5" x 15"
- Weight (dry): 49 lbs., including case.

If we assume the electrical to light conversion efficiency of UV-LEDs is only one-third that of the lamp-based system shown above (10% compared to 30%), 20 Watts of PV power should be enough to disinfect one-third of the specified amount, or 30 gallons/day, sufficient for our 10 soldier scenario with enough for a prudent reserve.

If gravity flow or hand pumping is used to input the water, electricity is needed only for the production of the UV light. This would keep the total power required to about 20 Watts. Another possible implementation of a PV power source could use flexible, lightweight thin-film amorphous Si photovoltaic panels, such as those shown below in the solar tent. Even if the conversion efficiency of these panels is only 2%, typical of amorphous Si PV, in bright sunshine of 1000 W/m^2 only 1 m^2 of panel area is required to generate the necessary 20 Watts of power.

Figure 6: *A 1-m^2 Powerfilm Solar lightweight flexible PV tent can provide about 20 watts in AM1.5 sunlight (solar noon), sufficient to power a system capable of disinfecting 90 gallons of water in three hours for a Hg-lamp based system, or 30 gallons for an LED-based system.*

Figure 7: *Typical PV-powered UV disinfection system in use.*

SteriPEN™ (Hydrophoton) is another commercial product that uses Ultraviolet (UV) light to destroy waterborne microbes. SteriPEN™ destroys viruses, bacteria and protozoa–including Girardia and Cryptosporidium– from one liter of water in 90 seconds. It uses 5W to power the low-pressure UV lamp inside. The lamp output is about 1mW/cm^2. The lamps cost $10-$20. They are fragile and likely to break if dropped without the protective cap in place.

Figure 8: *Example of lightweight, portable UV-sterilization device that can purify 32oz. of clear water in a minute and a half. (SteriPEN™ from Hydrophoton)*

Conclusions

For this portable, military-type application, a reasonable goal for the UV LED research program is to develop LEDs with energy conversion efficiencies about 10% at a wavelength as close as possible to 265 nm for maximum germicidal effectiveness. We anticipate benefits such as longer life and significantly lower cost, based on similarities to LEDs made of very similar semiconductor materials with outputs at longer wavelengths (e.g. near-UV wavelengths), which have 100, 000 hour lifetimes and cost about 10 cents apiece.

LEDs should significantly increase purifier durability, since they are clearly less fragile than lamps. Their increased durability will be especially important when used with intermittent power sources such as PV, which would tend to degrade lamp lifetime further. In addition, LEDs can be more easily integrated into various systems due to their small size which makes them amenable to flexible designs as long as they have outputs near 1mW/cm^2.

4. Deep Ultraviolet LED Development

A new and expanding area of research is the exploration of nitride-based semiconductor materials and device structures for electroluminescence at wavelengths shorter than 300 nm. While most near-UV (380-400 nm) light emitting diodes (LEDs) employ InGaN quantum well structures with GaN barriers, reaching deep-UV wavelengths requires AlGaN alloys with aluminum concentrations of 50% and higher. These wide bandgap alloys suffer from a number of materials issues which complicate their implementation into high efficiency LEDs, including high dopant ionization energies and tendency for dopant compensation[1,2], high densities of threading dislocations (typically greater than $5x10^9$ cm^{-2}) which can act as non-radiative recombination centers, and large internal fields due to spontaneous polarization and piezoelectric effects. Despite these challenges, notable advances have recently been made in the performance of deep UV LEDs[3-9]. In particular, our group at Sandia has succeeded in demonstrating milliwatt level output powers from 1 mm x 1mm devices at 275-290 nm[10] and has further achieved electroluminescence from LEDs at wavelengths as short as 237 nm[11].

A goal of this LDRD was to further develop these relatively immature deep UV LEDs and to specifically optimize their performance for water purification studies. An important parameter for this application is the emission wavelength, which is tunable with the implementation of appropriate AlGaN ternary alloys in the structure. Our target for this parameter was the 255-275 nm region, which defines a wavelength range that is particularly effective in microbial inactivation (germicidal effectiveness of 80% or higher, with peak performance at 265 nm). It should be noted that the performance of typical AlGaN LEDs drops rather sharply with decreasing wavelengths, due to the increased materials challenges of the higher bandgap alloys. Thus, while 265 nm is approximately the best wavelength for germicidal inactivation, the higher powers that can be achieved from LEDs at 275 nm would most likely offset the slightly reduced germicidal effectiveness at that wavelength. In the E. coli inactivation studies described in the following section, we evaluated LEDs with wavelengths as long as 295 nm, which were still of interest due to their relatively higher powers.

To perform the germicidal inactivation studies, we also needed to demonstrate sufficient powers either from individual LEDs or from an LED array. This represented the most significant challenge for our project, given the relatively small size of UV LED die and the low external quantum efficiencies at this early stage of development. While the exact power that is needed per LED die is entirely dependent on the system design, we note that a representative UV dose for 4 log reduction of E. coli is in the range of 3 mJ/cm2 (strain 0157:H7, ATCC43894[12]). As our water purification experiments were performed on stationary samples (not in a flow cell), we had the flexibility to apply fairly long exposure times to make up for lower LED powers.

The LEDs that were developed throughout this project were grown by metal-organic vapor-phase epitaxy in an EMCORE D-125 reactor. Trimethylgallium (TMG), trimethylaluminum (TMA), trimethylindium (TMI) and ammonia were used as the group III and V source materials, with silane and bis(cyclopentadienyl)magnesium (Cp_2Mg) as the dopant sources. All films were grown on sapphire substrates, in either on-axis (1000) c-plane orientation or

0.3° toward the m-plane. In Figure 9, we show a schematic of the design of our current generation of deep UV LEDs. AlN is used as a nucleation layer and is followed by an AlGaN buffer layer. The choice of Al composition of the buffer layer is dependent on the target wavelength of the LEDs and may be varied from 47-65% Al for emission wavelengths in the 295-270 nm range. The next layer in the structure is the Si-doped n-type AlGaN layer, which is on the order of 0.8-2 μm in thickness. The n-AlGaN layer is followed by a multi-quantum well active region with $Al_xGa_{1-x}N$ quantum wells and $Al_yGa_{1-y}N$ barriers. As a specific example, for 275 nm devices we employ three 2 nm thick $Al_{0.40}Ga_{0.60}N$ quantum wells with 5 nm thick $Al_{0.60}Ga_{0.40}N$ barriers. These compositional values are estimated from growth calibrations as well as x-ray diffraction, reflectivity and Hall measurements of calibration structures and are estimated to be accurate to +/- 1.5%. Finally, the p-type side of the LED structure is composed of an AlGaN current blocking layer with Al composition approximately 10% higher than that of the barrier material, and a thickness of 10-20 nm. The structure is completed with a 20-100 nm thick p-GaN cap layer. While this p-GaN layer is absorptive for our deep UV emission wavelength range, this loss is offset by the significantly improved metal contact resistance to p-GaN versus p-AlGaN.

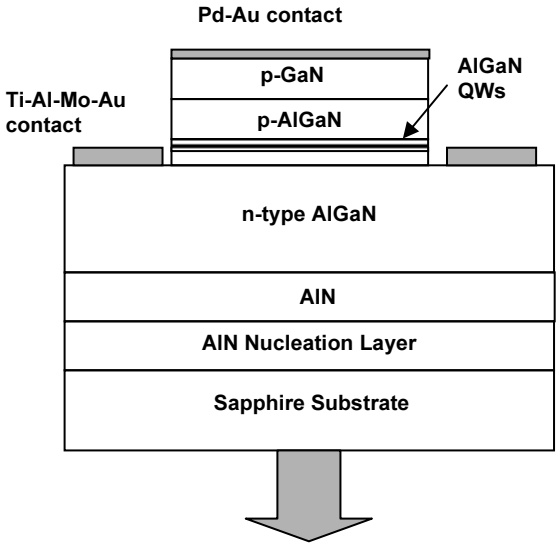


Figure 9: *Schematic of AlGaN-based deep UV LED structure.*

Device fabrication involved standard photolithography, dry etching and metal evaporation. Mesas ranging from 200 μm x 200 μm to 300 μm x 300 μm were defined by inductively coupled plasma etching in a BCl_3/Cl_2 plasma down to the n-type AlGaN layer. Ohmic n-type contacts were formed using a Ti (15nm)/ Al (60 nm)/Mo (35nm)/ Au (50 nm) multilayer structure, and a subsequent rapid thermal anneal at 825°C for 30 seconds in N_2. The p-type contact consisted of Pd (10-20 nm)/Au (200nm). The completed devices were diced into arrays and flip-chip bonded to Si submounts. The submounted chips were packaged in TO-257 headers with integrated Al reflectors, as shown in Figure 10.

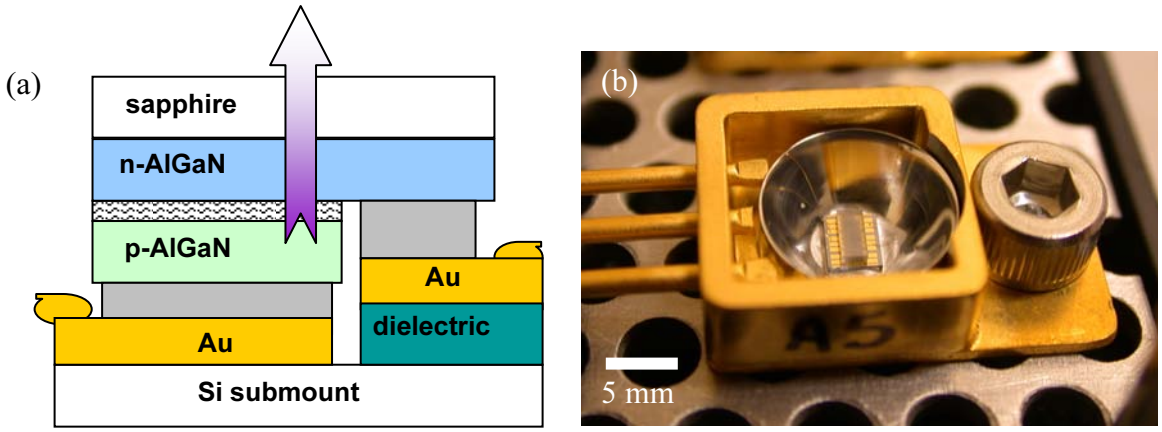


Figure 10. *(a) Schematic of flip chip bonded deep UV LED on Si submount (b) 2 x 5 element flip-chip LED array mounted in a TO-257 package. Note that the LEDs used in this project were typically 2 x 2 element arrays.*

A number of LED structures and arrays with wavelengths ranging from 270-295 nm were developed and evaluated in this project. The LEDs consisted of 2 x 2 arrays of 300 μm x 300 μm sized elements. Each of the elements was operated at 30 mA for a total input current of 120 mA. Details on the peak wavelengths, output powers and electroluminescence spectra will be provided in the following section.

5. Optical System Development

Experimental protocols for performing micro-organism inactivation versus UV dose have been established for standard Hg lamp-based measurements[13]. Typically, a "collimated beam apparatus" is used to deliver a well collimated and highly uniform beam of UV light to a water sample in a Petri dish, as depicted in Figure 11. As an example, one reported set-up utilized 3 inch diameter PVC tubing, coated with a flat-black paint, and in a length range of 10-50 inches[12]. In practice, some slight non-uniformities in the light spatial distribution remain, and stirring of the water sample is commonly performed to further improve the uniformity of UV dose. The over-riding goal of applying these protocols is to ensure that a well calibrated and uniform UV dose is applied throughout the entire water sample.

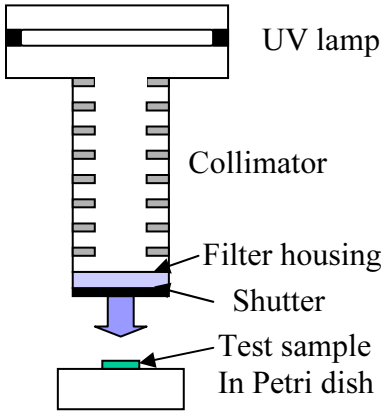


Figure 11: *Typical collimated beam apparatus for lamp-based UV dose-response measurements.*

One of the challenges of this project was to develop an optical system to deliver uniform and well calibrated UV doses from deep UV LED arrays in place of standard Hg lamps. The most limiting factor in our design considerations was the fact that, at this relatively early stage of development, deep UV LEDs have low powers (< 1 mW at operating currents consistent with acceptable device lifetimes). Therefore, the standard

collimation approaches used for Hg lamps are far too lossy to be applied successfully to our deep UV LEDs. Further, unlike most lamps that have a relatively uniform spatial distribution of light, our LED arrays are notably non-uniform, with bright spots of light emitted from each LED element of the array. Finally, our flip-chip bonded LED chips are truly three dimensional emitters, with a substantial amount of light emerging from the cleaved sides of the chip in addition to the top of the chip. To only utilize the top emission would again reduce the available optical power to levels that would be inadequate for our UV inactivation studies, and so our optical design had to attempt to capture both side and top emission, and apply a light mixing strategy to enhance the uniformity of the light output with minimal loss.

In Figure 12, we show a photograph of the design of the UV LED-based optical system that we developed in this program. As described in the previous section, we used 2x2 element LED arrays, with each element of the array being approximately 300 μm x 300 μm in size. Our custom LED packaging employed an aluminum reflector to collect side emission and to reduce the angular distribution of the UV light. We coupled this packaged LED array to an aluminum collimator tube with an inner diameter of approximately 8 mm which was compatible with the diameters of both the LED reflector as well as the well plates we used for holding water samples (described in next section). We found that the important trade-off between light throughput, in-plane spatial uniformity and collimation was largely dependent on the length of the tube and the roughness of the inner surface of the tube. While we explored a range of surface finishes, from highly polished to severely roughened by bead-blasting, our final design consisted of an intermediate surface roughness that was present in the as-purchased aluminum tubing and a tube length of six inches.

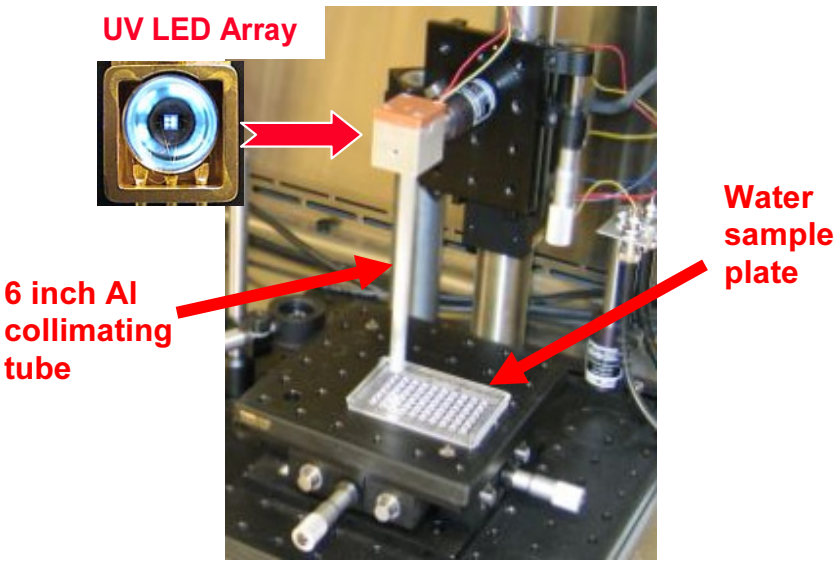


Figure 12: *Beam collimation set-up for deep UV LED array.*

The six inch tube length enabled an optical throughput of approximately 24% while significantly eliminating the strong non-uniformity inherent in our 2 x 2 array emission. The intensity profile of the UV light after the collimation tube is shown in Figure 13 for a 270 nm 2x2 LED array. As we lacked the apparatus to do a full 2D map of the intensity, we instead show line scans in two orthogonal directions, anticipating a fairly symmetric pattern. For the z = 0 conditions (directly at the exit of the tube), we see that we have approximately 15% variation of the intensity across

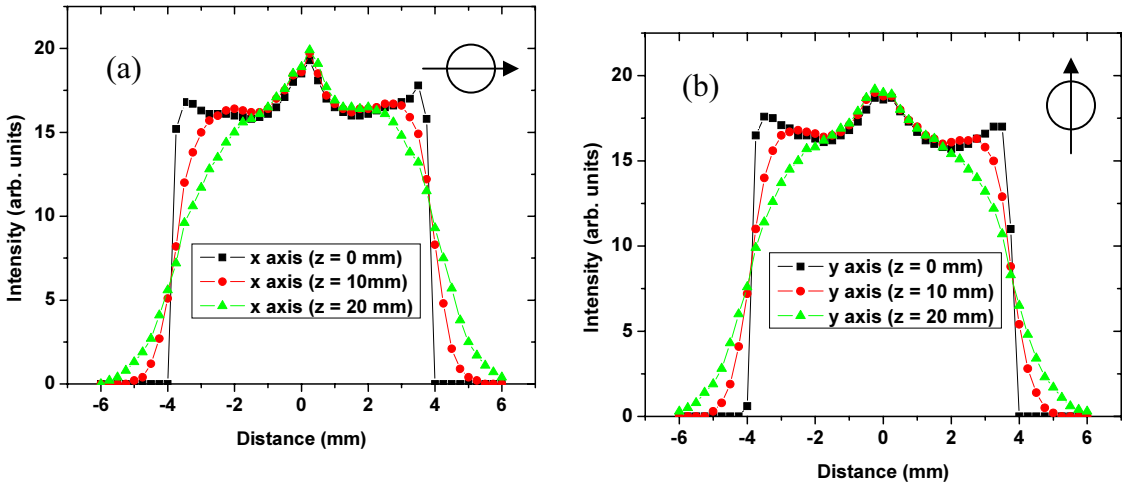


Figure 13: *UV LED spatial intensity line scans in two orthogonal in-plane directions (x-axis and y-axis). Z-axis refers to the vertical distance from exit of collimating tube.*

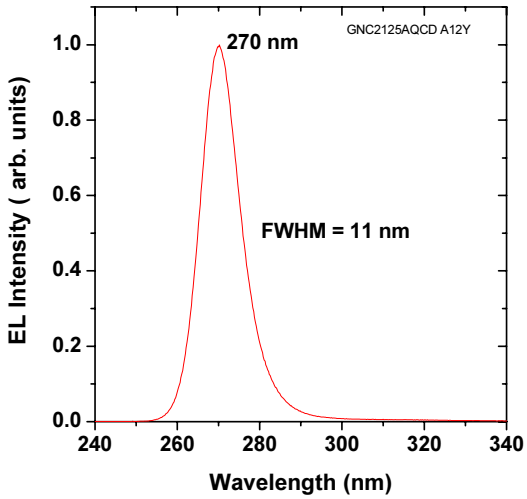
an 8 mm diameter, for both the x and y in plane directions. This variation could be improved with longer tube lengths, but at a cost of reduced throughput. To demonstrate the collimation of the beam, we also show the beam profiles at 1 cm and 2 cm distance from the

exit aperture of the tube. The data show that the edges of the pattern are particularly sensitive to distance from the tube. For the water sample containers, we employ a 6 mm diameter sample cell with a depth of approximately 1 cm and 190 µl volume. The data in Figure 13 show that the beam profile is largely unchanged through the 1 cm depth of the sample, assuming a 6 mm diameter. Therefore while the collimation is not ideal, it is well suited to the sample container employed in our experiments.

A number of LED arrays were developed and characterized throughout this project. In Table 1, we list the die designation, peak wavelength, and output powers at the exit of the collimating tube for several arrays. Output powers were measured using a calibrated Si photodetector (Newport 818-UV) and with 30 mA applied to each element of the 2x2 array. Our earliest devices near 272 nm (GNC1972 A2) had very low output powers, on the order of 20 µW. (Note that the power levels reflect the optical losses from the collimating system). Through optimizing the materials quality of our deep UV LEDs, we made substantial progress in improving this output power by the end of the project. This progress is reflected in the 170 µW output powers from the 270 nm GNC2125A A12Y array.

LED Array	Peak Wavelength (nm)	Power after Collimating Tube (µW)
GNC1972 D4	272.0	20
GNC1117A D4	295.0	120
GNC2125A A12Y	270.2	170
GNC2126B A10X	272.0	123
GNC2126B B10X	272.4	98

Table 1: *Wavelength and output power of deep UV LED arrays evaluated for water purification studies.*



In Figure 14, we show a representative electroluminescence spectrum of our GNC2125A A12Y 2x2 LED array. The spectrum was taken under the 30 mA per element current injection conditions. We note a peak wavelength at 270 nm, with a full width at half maximum spectral width of 11 nm.

Figure 14: *Electroluminescence of a 2x2 AlGaN-based LED array operated at 30 mA per element.*

6. E. coli Inactivation Studies

The efficacy of SNL developed deep UV LEDs were tested using two different *Escherichia coli* (E. coli) strains previously characterized and tested with monochromatic low pressure UV lamps by the Environmental Protection Agency (EPA). In the following, we describe the experimental details of the E. coli inactivation studies performed in this project. The most extensive studies were performed using the higher power GNC2125 270 nm arrays, and we will therefore focus on those particular experiments. A brief description of earlier studies using lower power 272 nm, 277 nm and 295 nm LEDs will be presented at the end of this section.

6.1 E. coli Inactivation Studies using 270 nm GNC2125A LED Array

Preparation of E. coli:

Two different strains of E. coli, used by the EPA for their UV efficacy testing, were obtained from ATCC. E. coli strain 23229 (shown to have high sensitivity to UV exposure) and 15596 (shown to have medium sensitivity to UV exposure). They arrived in lyophilized form (freeze dried with a protective protein coat). Both strains were prepared in the same manner.

Lyophilized E. coli were extracted and transferred into TSB (Tryptic Soy Broth, formula in Appendix A), which was freshly prepared and autoclaved. Transfer was done by aseptically pipetting 100 ml of TSB into lyophilized stock and then extracting into 500ml of TSB for each strain (Finntip pipettes were used throughout experiment). Inoculated broth was subjected to incubation for 24 hours at 37 degrees C ($\pm$ 1 degree). Colonies were enumerated on TSA and confirmation of E. coli was done by culturing a each sample on EMB (Eosin Methylene Blue Agar, formula in Appendix A), which showed the characteristic lactose fermentation and green metallic sheen of growth by E. coli (EMB is a selective and differential agar, only growing enteric bacteria and showing specific characteristics for E. coli). Further identification was done with typical Gram staining methods, which verified the E. coli as a Gram negative rod. A fresh batch of each confirmed E. coli strain was cultured in newly made 500 ml of TSB, incubated at 37 degrees for 24 hours. 1 ml of each broth strain was then transferred to a fresh batch of TSB (500 ml) and incubated for 2 hours at 37 degrees C (beakers shaken every 15 minutes), then removed to keep them in an early growth phase.

Two 45 ml portions from this fresh batch of each strain were aliquoted into 50 ml conical tubes (BD Falcon polypropylene) to prepare samples for washing, keeping them stationary in this early growth phase. Samples were centrifuged at 3000 rpm (10 degrees C) for 1 hour. Supernatant was pored off and replaced with PBS (Phosphate Buffered Saline, formula in Appendix A), then vortexed at 1 minute. Samples were centrifuged again (this process was done 3 times to completely wash and remove all nutrients from samples) and stored at 6 degrees C. This 'washed' E. coli was used for UV exposures.

Final washed samples were also cultured on EMB to re-confirm E. coli. Appropriate serial dilutions were made and plated out on both TSA (pour plate for plate counts) and Petrifilm Aerobic Count Plate (3M). Identical numbers for each dilution on both plating methods was confirmed. Petrifilm was used for plating of samples exposed to UV light (Petrifilm was chosen for ease of plating and bacterial colony counting.

The dilution of each E. coli strain that had 10^5 cells was determined and put aside for UV exposure. Characterization of UV absorbance of each strain from this dilution was done using a HP 8452A Diode Array Spectrophometer using BrandTech UV disposable cuvets and a detector setting of 270nm (UV LED used had a wavelength of 270.2nm). The results yielded an absorption coefficient of 1.36E-2 cm^{-1} and 2.34E-2 cm^{-1} for E. coli ATCC# 15597 and ATCC#23229, respectively.

UV Exposure of E. coli:

Exposure of E. coli was done using 96 well plates (Figure 15) from Costar (half area flat-bottom polystyrene plates, Corning 3690), which hold 190 µl of sample per well. For each sample, one well was used for UV exposure (A1) and one for a control (A12). Note that a dilution factor of 5.26 was calculated in the results to show the number of Colony Forming Units per ml (CFU/ml) in the result chart. All of the UV exposure equipment was located in a Labconco Biological Laminar Flow Hood, which had all materials in contact and around exposure area decontaminated with a solution of 10% bleach. Once each sample was exposed, both exposed and control samples were aseptically transferred and serial diluted from 10^1 to 10^6 (there was no 10^0 as the full 190ul became part of the 10^1 dilution). Each dilution was plated in triplicate on Petri Film, which were all incubated at 37 degrees C for 24 hours with no light (to minimize light repair of organisms).

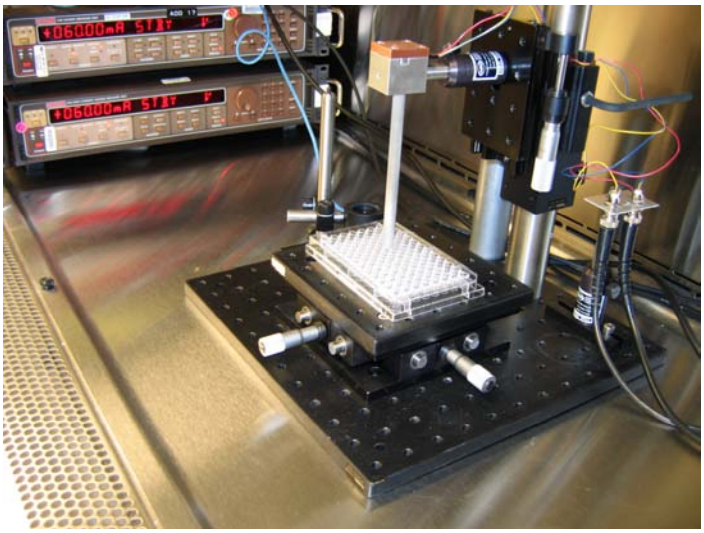


Figure 15: *Experimental UV exposure set up showing UV LED optical set up, 96 well plate for water samples and LED power supplies.*

An important aspect of our exposure studies was the determination of the UV dose applied to the water samples as well as a selection of the range of doses we would apply in our exposure studies. Our 270 nm LED array was measured to deliver an average power density of 0.44 mW/cm^2 to the water sample surface. Applying our previously described absorption coefficients, we determine that ~2.3% of the incident UV light is absorbed in the E. coli ATCC#23229 sample, and ~1.4% in the E. coli ATCC# 15597 sample. These values result in a power density of 0.01 mW/cm^2 and 0.006 mW/cm^2 being absorbed in the E. coli ATCC#23229 and ATCC# 15597 samples, respectively. As an aside, we note that these very low absorption values result in a very inefficient use of the UV LED output for these sample volumes. In a practical water purification system, photon recycling to enable multiple-passes of transmitted light would most likely be used. Here we apply a single pass to most accurately calibrate the UV dose.

In calculating the range of UV doses to employ in our studies, we referenced E. coli inactivation studies reported for Hg lamp based exposures. In particular, we found that a 4 log inactivation is reported to require a dose of 9.5 mJ/cm^2 for E. coli ATCC# 15597 sample, while a dose of < 0.2 mJ/cm^2 is reported for the more UV sensitive E. coli ATCC#23229 strain[12]. As these experiments were performed using a low pressure Hg lamp at 254 nm, we estimate that these dose values reflect a germicidal effectiveness of ~85% (compared to ~95% for our 270 nm devices, see Figure 4). With these considerations, we estimate that the more UV resistant E. coli ATCC# 15597 sample will require an exposure time of up to 24 minutes using our 270 nm LED array for 4 log inactivation, while the significantly more UV sensitive E. coli ATCC#23229 strain should only require an exposure time of up to 18 seconds.

Given that the effectiveness of a more broad-band UV LED versus a monochromatic LP Hg lamp has never before been determined, we planned a series of exposure time sequences to cover a range of UV doses well beyond our estimated values. The exposures for the UV resistant ATCC# 15597 strain were kept at 10 minutes and below to minimize any degradation of the LED array, and we therefore expect to achieve less than 4 log reduction. Below we show the exposure times that were applied in our studies. We note that each time listed applies to the exposure of a distinct water sample (and *not* sequential exposure to the same sample).

For E. coli ATCC #23229:

Series 1) 1 sec, 2 sec, 3 sec, 4 sec, 5 sec, 6 sec
Series 2) 5 sec, 10 sec, 15 sec, 20 sec, 25 sec, 30 sec
Series 3) 0.5 min, 1 min, 1.5 min, 2 min, 2.5 min, 3 min

For E. coli ATCC #15597:

Series 1) 0.5 min, 1 min, 1.5 min, 2 min, 2.5 min, 3 min
Series 2) 2 min, 3 min, 4 min, 6 min, 8 min, 10 min

Colony counts were done after the 24 hour incubation.

Results:

The exposure of E. coli ATCC# 15597 to our 270 nm LED array resulted in a 1.9 log reduction at 10 minutes (equating to 8.93E4 cells killed for this exposure), which was the longest exposure time employed. The log reduction of other test times for this strain are as follows:

Exposure time (min)	Log Kill
0.5	0.04
1	0.17
1.5	0.18
2	0.42
2.5	0.52
3	0.59

Exposure time (min)	Log Kill
2	0.48
3	0.58
4	0.76
6	1.85
8	1.85
10	1.89

Table 2: *Series 1 and 2 E. coli inactivation results for E. coli ATCC # 15597 and 270 nm LED exposure.*

As seen in Table 2, we observe good consistency in the 3 minute exposure results for the two time sequences. Our 10 minute exposure time translates to an effective UV dose of ~ 3.6 mJ/cm^2. Further, the 6 minute exposure condition, consistent with a dose of 2.2 mJ/cm^2, yields a similar log reduction. As a comparison, we reference a 2 log reduction dose value of 6 mJ/cm^2 that has been reported for Hg lamp-based measurements[12]. Our UV doses for approximately 99% inactivation are therefore ~ 3X lower than reported lamp based values for this E. coli strain.

For the more UV sensitive E. coli ATCC#23229 strain, we achieved the following results:

Exposure time (sec)	Log Kill
1	0.011
2	-0.12*
3	0.15
4	0.10
5	0.16
6	0.09

Exposure time (sec)	Log Kill
5	0.17
10	0.14
15	0.12
20	0.22
25	0.20
30	0.24

Exposure time (min)	Log Kill
0.5	0.16
1	0.19
1.5	0.34
2	0.36
2.5	0.79
3	0.65

Table 3: *Series 1, 2 and 3 E. coli inactivation results for E. coli ATCC # 23229 and 270 nm LED exposure. * denotes a questionable data point where the control sample had lower E. coli counts than the exposed sample.*

We see that the inactivation of this E. coli strain is far lower than expected and we further observe some inconsistencies in the results for the same exposure times in different trials. The maximum log reduction is in the 0.65-0.79 range for the 2.5-3 minute exposures. For the 3 minute exposure in particular, we calculate a dose of 1.8 mJ/cm^2, which is significantly higher than the < 0.2 mJ/cm^2 dose that has been reported to achieve 4 log reduction with LP Hg lamps. At this stage, we have no clear explanation for this discrepancy, and further exposure studies with this E. coli strain are needed.

6.2 Preliminary Microorganism Inactivation Studies using 272 nm, 277 nm and 295 nm LED Arrays

In the early stages of the project, we performed microorganism inactivation test runs using lower power LEDs with emission at 272 nm, 277 nm and 295 nm. Lacking absorbance data, these studies were not calibrated to absolute dose, but were performed to map out the best experimental approach. These studies were done using two different bacterial strains: E. coli ATCC# 11229 and Bacillus subtilis ATCC# 19659. The smaller B. subtilis endospores are anticipated to have a higher UV dose requirement, with up to 29 mJ/cm^2 reported for 4 log reduction[12]. Both bacterial strains were prepared from frozen glycogen stock cultures, enumerated in TSB with a second fresh stock being double washed in PBS as in the above bacterial preparations.

The first test run had sample exposures performed directly on Petrifilm, using 100ul of bacterial suspension (for both E. coli and B. subtilis). Both controls and exposed samples were treated in this manner. Three different UV LED's were evaluated (272nm, 277nm, and 295nm) using exposure times of 2, 3, 4, 6, 8 and 10 minutes. We noted, however, that simply using a water droplet on the Petrifilm surface resulted in a spreading of the droplet throughout the exposure time. Some of the sample extended beyond our exposure beam, resulting in a spatially uncontrolled exposure of the sample. In a second test run, we resolved this issue by replacing the Petrifilms with 60 well plates (MicroWell Mini Trays, 60) having a sample volume of 15µl and a concentration of 10^6. Only E. coli ATCC # 11229 was used in the second test run, given the lower expected UV dose requirement. UV exposure was done using the 295 nm 2x2 LED array at three different power levels: P1 (~0.10 mW), 0.5P1(~0.05 mW) and 0.2P1 (~0.02 mW). Samples were brought up to 1ml and then serial diluted from 10^1 to 10^5. Colony counts were done after 24 hour incubation.

In Table 4 and Figure 16, we present the results of these 295 nm exposure studies. We observed a 5.9 log reduction at 10 minutes (which was a total kill) using a power level of P1 and 0.5P1 (equating to 8.73E05 CFU). As previously mentioned, the lack of absorbance data prohibited a direct calculation of the applied UV dose. However, several interesting trends of relative performance were noted. First, we observed a relatively poor inactivation at the shortest times (2 min), almost independent of incident power. This is most clearly seen in the 0.29 log kill for 0.2 P1 at 10 minutes versus only 0.07 log kill at P1 with a 2 minute exposure. Second, we note that both the P1 and 0.5P1 power conditions achieved a nearly complete 6 log kill after 10 minutes

P1 = 0.1 mW

Exposure time (min)	Log Kill
2	0.07
5	1.7
10	5.9

0.5 P1 = 0.05 mW

Exposure time (min)	Log Kill
2	0.10
5	0.48
10	5.9

0.2P1 = 0.02 mW

Exposure time (min)	Log Kill
2	0.03
5	0.20
10	0.29

Table 4: *E. coli inactivation results for E. coli ATCC # 11229 and 295 nm LED exposure. Studies were done for three different LED powers, P1, 0.5P1 and 0.2 P1.*

despite a significant difference at 5 minutes. This second result revealed that more exposure data points would be needed in future experiments to clearly delineate the strongly non-linear UV dose dependent behavior. Overall, these experiments established the effectiveness of using the sample plates but the very small 15 µl sample volumes were thought to be non-optimal. Specifically, they required a relatively large dilution factor, which could be a possible source of error, and yielded a very short path length for UV absorption. The water samples in these small wells also had a highly domed surface which would affect optical reflection and transmission and would be difficult to simulate in an absorbance measurement. We therefore implemented larger sample wells with 190 µl capacity for our final experiments, described previously in section 6.1. A remaining problem in our experimental approach is the inability to mix these very small volumes during exposure to assure more uniform exposure throughout the sample. The relatively low LED powers have prevented the use of large sample volumes thus far.

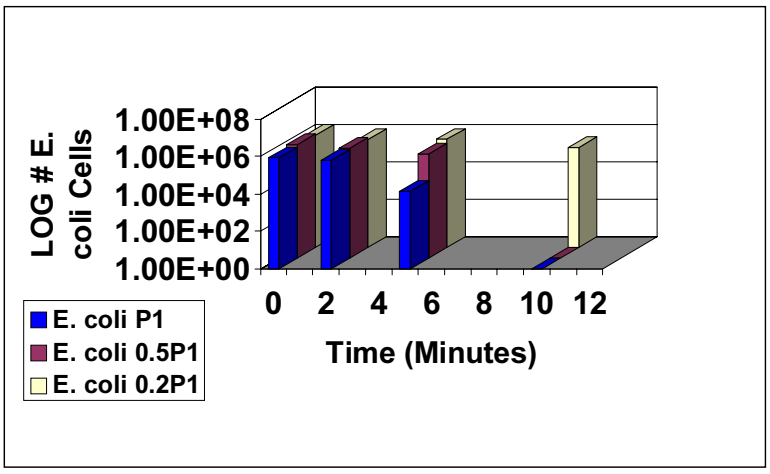


Figure 16: *E. coli inactivation results for E. coli ATCC # 11229 and 295 nm LED exposure. Studies were done for three different LED powers, P1, 0.5P1 and 0.2 P1.*

7. Conclusions

In this LDRD project, we evaluated the potential of applying newly developed AlGaN-based deep UV LED technology to the timely and critical need for effective global water purification solutions. We specifically analyzed the systems issues and potential benefits of LEDs for water purification systems in rural, off-grid environments, including developing countries. Our research identified several potential advantages of employing LEDs over lamp based systems, including potential for longer lifetimes of the UV sources (LEDs) before replacement and the ability to include more frequent on-off cycles in the overall design. These benefits are related to lower life-cycle costs, more reliable designs and overall sustainability of the complete water purification solution (purifier + energy source). We further evaluated systems design issues for compact, PV-powered water purification systems for mobile and/or military environments. Increased durability when used with intermittent power sources such as PV, integratability, and mechanical robustness were identified as beneficial attributes of LEDs over lamps. We further estimated that achieving a wallplug efficiency of approximately 10% for 265 nm LEDs would be a reasonable performance goal to impact mobile/military water purification applications.

Given the clear potential benefits that we have identified for LED-based water purification systems, a remaining task was to evaluate what state-of-the-art deep UV LEDs are capable of at this early stage of development. Our work in this area consisted of development efforts to specifically optimize LED performance for water purification. Toward that end, we demonstrated a significant increase (~8X) in output power of 270 nm LEDs; a wavelength that can provide ~95% germicidal effectiveness. We identified some of the optical challenges of collecting and uniformly distributing UV light from small area LED arrays, and designed a beam collimation set up for improving the spatial uniformity of light from a multi-element LED array. We applied this collimation set up to the demonstration of E. coli inactivation using 270-295 nm LEDs. While we succeeded in demonstrating between 99.0 and 99.9999% E. coli inactivation from SNL-developed deep UV LEDs, the required exposure times on the order of 10 minutes revealed that single pass exposures from small LED arrays are not practical for the majority of water purification scenarios.

With these insights, we propose future directions for developing effective LED-based water purification systems. First, the aforementioned performance goal of 10% efficiency should be pursued through further optimization of AlGaN-based materials. Key areas for improvement include the relatively high threading dislocation densities and the inefficient p-type doping. The best results that have been reported for deep UV LEDs to date include a wallplug efficiency of 2% at 280 nm[14], although the efficiency at 265 nm is anticipated to be at least a factor of two lower. These values give a rough estimate of the level of improvement that is needed.

Although the required improvements seem daunting, we look toward both the rapid progress that has been seen in deep UV performance to date, as well as the > 30% efficiency of related InGaN visible LEDs to provide rationale for optimism. While device lifetime issues have not been stressed in this report, we note that most deep UV LEDs to date are at best in the 1000's of hour lifetime range, and not the 100,000 hour range of the more mature InGaN visible

LEDs. The proposed emphasis on reducing defects, including threading dislocations, as well as improving p-doping in these materials is anticipated to also enhance robustness in future generations of devices.

A second thrust in future efforts should be the development of novel optical systems concepts that specifically address the distinctive challenges as well as advantages of LEDs. In particular, LEDs provide a design flexibility that is far superior to lamp based systems, providing the opportunity of innovative purification systems where the fluid handling system and optical system have a high level of integration. A future compact water purification system should be designed for the distinct challenges of LED light collection and distribution, and apply advanced photon recycling concepts to most efficiently utilize the available LED power. In all optical design considerations, the goal of maintaining a highly reliable, compact and robust system must be met to ensure that the most beneficial attributes of LEDs compared to lamps are preserved.

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Appendix A

TSB (Tryptic Soy Broth) Formula:
(BD 211825)
Soybean-Casein Digest:

Pancreatic Digest of Casein	17.0g
Enzymatic Digest of Soybean Meal	3.0g
Dextrose	2.5g
Sodium Chloride	5.0g
Dipotassium Phosphate	2.5g

Added in 1 lit of deionized water and autoclaved for sterility.

PH 7.3 $\pm$ 0.2

PBS (Phosphate Buffered Saline) Formula:

Sodium Chloride	80.0g
Potassium Chloride	2.0g
Sodium Phosphate Dibasic	14.4g
Potassium Phosphate monobasic	2.4g

Added to 1 lit of deionized water and filter-sterilized (0.2um).

PH 7.4 $\pm$ 0.2

EMB (Eosin Methylene Blue Agar):

Pancreatic Digest of Gelatin	10.0g
Lactose	10.0g
Dipotassium Phosphate	2.0g
Eosin Y	0.4g
Methylene Blue	0.065g
Agar	15.0g

Added to 1 lit of deionized water and autoclaved for sterility.

PH 7.1 $\pm$ 0.2

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