2

Experimental Setup: DBD based Excilamp and Plasma Sources Fabrication, Diagnostic Techniques, and UV and far UV-C based Milk Sterilization Systems

2.1 Introduction

This chapter outlines the design, development, and characterization of dielectric barrier discharge (DBD)-based excimer and plasma sources, with a focus on their application in milk treatment. It introduces innovative devices, such as DBD-based coaxial excilamps emitting at 222 nm and 253 nm, and a cold plasma source, alongside the design of an annular UV reactor for continuous large-scale milk processing. The chapter also discusses diagnostic techniques for characterizing these excilamps, including power consumption, UV output, and electrical-to-optical conversion efficiency. Additionally, it covers methods for assessing milk properties —such as pH, conductivity, titratable acidity, fat/SNF content, methylene blue reduction test (MBRT), and bacterial load analysis. Finally, it describes the experimental setups used to evaluate the performance of these devices and their effects on milk's physicochemical properties.

2.2 Design and Development of DBD-based Plasma Source and Excilamps

2.2.1 Dielectric Barrier Discharge based KrCl* and XeI* Excilamps

In the presented studies, volume discharge DBD configurations, which consist of double barrier coaxial geometries, have been used. A cross-sectional view of the used DBD configuration has been shown in Figure 2.1. Different shapes of metal electrodes, i.e., mesh, rod, helical, and strip, have been used, and they are made from different materials, such as copper, aluminum, and stainless steel. The dielectric barriers made from quartz have been used in the experiments. The thickness of different dielectric barriers varied from 1.5 mm to 2 mm. A schematic and original (not operational) view of the electrode configurations of these developed sources is shown in Figure 2.2 (a) and 2.2 (b).

To fabricate a sealed-off coaxial quartz DBD tube, two tubes of different dimensions have been used to maintain the required gas gap. These tubes are sealed by glass blowing technique from both sides while maintaining the required gas gap. The outer surface of the quartz tubes is wrapped by a stainless-steel sheet electrode having equidistant holes of 5 mm, and the inner electrode of copper wire (helical shaped with pitch 2.1 mm) has been inserted into the coaxial tubes in close proximity to the inner wall. The inner or live electrode is a copper wire molded in a helical shape with a 0.3 mm diameter and length of 150 mm with an optimized pitch of 2.1 mm to get a uniform discharge with minimal gas heating. A high voltage signal is applied on the inner electrode while the outer mesh electrode is grounded. The outer mesh electrode acts as a cathode, while the inner helical copper electrode acts as an anode. The gas gap is kept at 1.5 mm in the DBD tubes shown in Figure 2.1 and 2.2 (a). The inner radius of the outer quartz tube is 13 mm, and the thickness is 1.5 mm, while the inner radius of the inner quartz tube is 7 mm. The thickness is 1.5 mm for the DBD tubes, as shown in Figure 2.1 and 2.2 (a). The total length of the tubes and the length of wrapping of the outer mesh and the inner helical electrode are 160 mm and 150 mm, as shown in Figure 2.2 (b). The gases used are krypton, chlorine, xenon, and argon, a combination

of rare gas and halogen to produce the required wavelength of UV radiation. The UV-C transmittance of the quartz used for wavelength 222 nm is about 70%, and 253 nm is 75% (Kedar Scientific, Mumbai, India). The live electrode is hermetically sealed using Teflon sealing for electrical isolation.

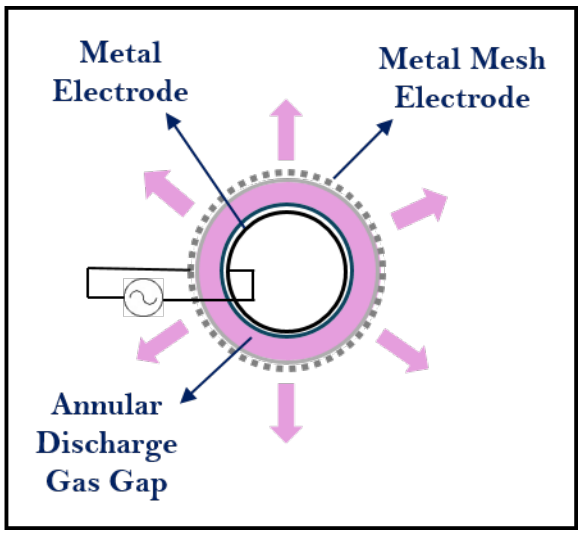


Figure 2.1: Cross sectional view of the designed far UV-C (222 nm) and UV-C (253 nm) excimer lamps.

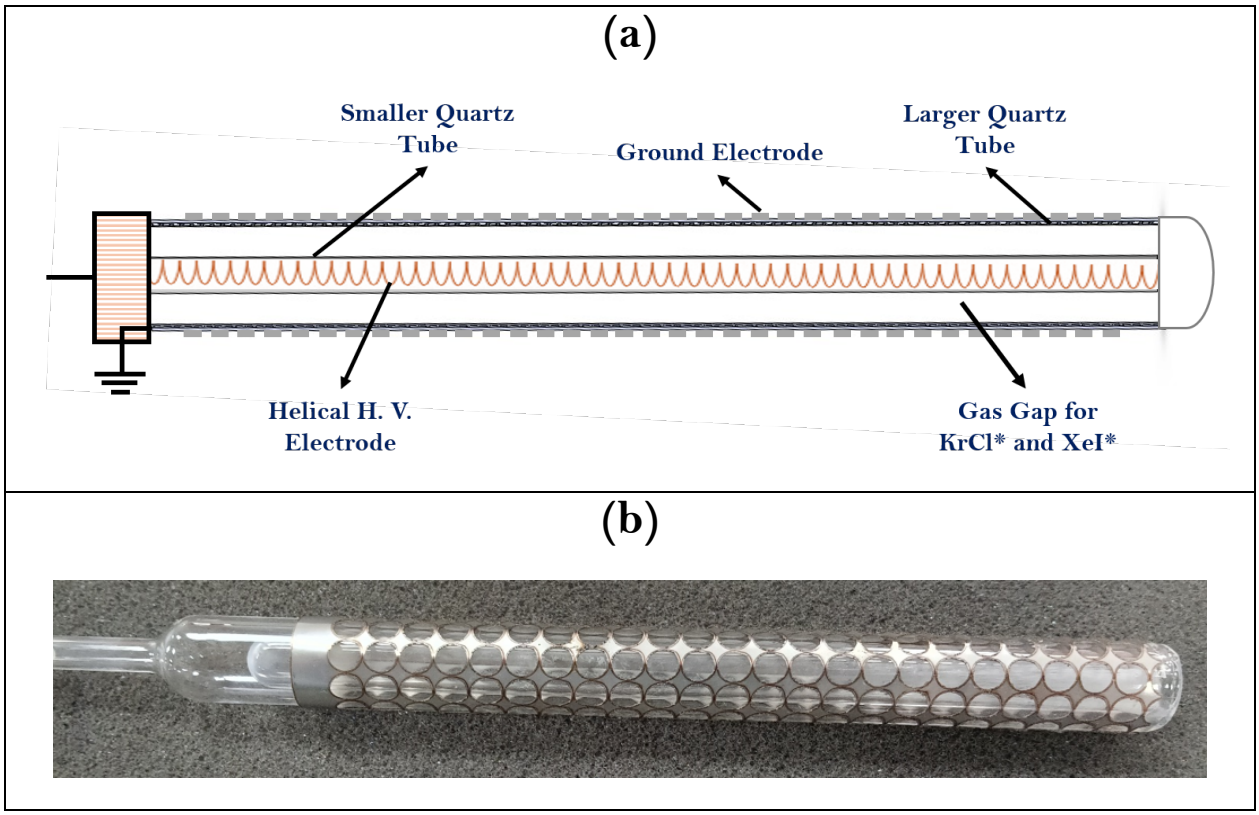


Figure 2.2: (a) Schematic view, and **(b)** original view (not operational) of the far UV-C (222 nm) and UV-C (253 nm) excimer lamps.

2.2.2 Dielectric Barrier Discharge Plasma Reactor

We have designed and developed a DBD plasma source which comprises a coaxial DBD arrangement, as shown in Figure 2.3. An aluminium rod of diameter 12 mm with a length of 95 mm acts as a central high voltage (or powered) electrode. The grounded electrode is made of a food grade stainless steel wire mesh having a thickness of 1 mm. A cylindrical glass tube with an outer diameter of 16 mm, a glass thickness of 1.85 mm and a length of 100 mm is used as a dielectric barrier between the powered and grounded electrode. The aluminium rod is shielded hermetically into the glass tube, and the wire mesh is tightly fitted on the outer electrode. One side of the glass tube has been pinched completely, and on the other side, a Teflon structure of length 15 mm is used as an end cap for insulation purposes.

This developed cold-plasma source has shown quite useful results on the milk sterilization application, particularly increasing MBRT of raw milk while maintaining its physicochemical properties such as pH, conductivity, titratable acidity, fat/SNF content etc. The details are discussed in the subsequent chapters.

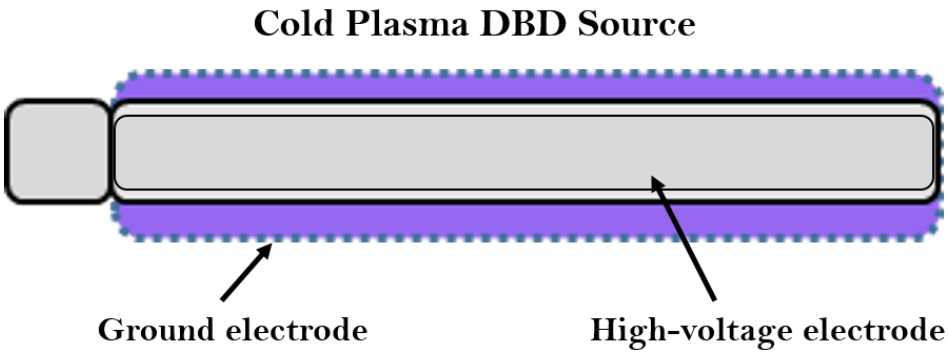


Figure 2.3: Schematic view of co-axial DBD plasma source.

2.2.3 Annular UV Reactor

For continuous treatment of milk at a small scale by farmers, an annular UV photo reactor has been designed and developed using an 11 W UV-C lamp and housed in a Teflon cylindrical vessel. The Teflon cylindrical vessel has an inner diameter (ID) of 16.2 mm and a total length of 22.6 cm and also has a spiral screw inside with a pitch of 6 mm and a depth of 2 mm. A UV-C lamp (253.7 nm) having a diameter of 16 mm and length of 226 mm, emitting UV-C radiation of intensity 2.6 mW/cm^2, has been fitted inside the Teflon cylinder. Most of the milk flow happens through thread gapping that allows the milk to follow the same flow pattern. The used lamp has a special grade quartz (Phillips, India) which filters out the 185 nm wavelength that is generally considered the ozone-generating wavelength.

The unprocessed milk has been exposed to different dosages of UV light by adjusting the number of flows through the UV reactor. Milk was pumped through the designed UV-C reactor using a peristaltic pump at a flow rate of 1 L/hr for conducting physicochemical and microbiological analysis. Before the experiment, the UV-C lamp was switched on for 2.5 minutes as a warm-up time and to ensure no external contamination was present within the experimental reactor. In addition, the unit was disinfected by flushing ethanol (50% vol/vol) through it for 3-4 minutes, followed by flushing sterilized water for an additional 4-5 minutes to eliminate any remaining ethanol residue. Following the application of UV-C treatment to milk, the Oxonia solution is then passed through the reactor for 5 minutes.

Oxania is utilized as it is a well-recognized disinfectant that utilizes hydrogen peroxide/peracetic acid. It effectively disinfects surfaces by rendering a variety of microorganisms inactive [André et al., 2012]. Figure 3.3 (a) and 3.3 (b) shows a schematic

representation and actual view of the milk treatment system that utilizes annular UV reactor design.

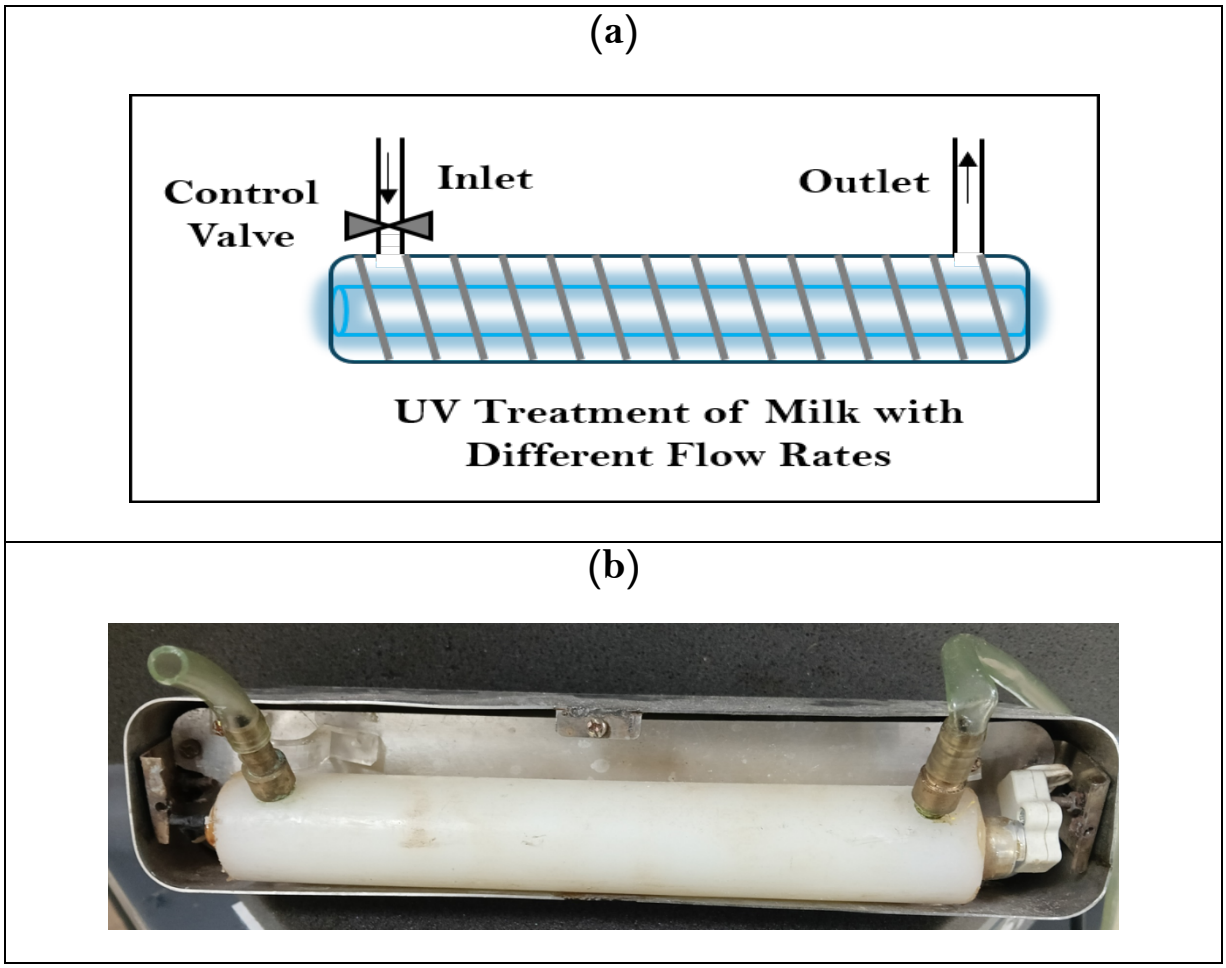


Figure 2.3: (a) Schematic view, and **(b)** original view of the annular UV reactor.

The following describes the working principles and equipment used in the development and diagnosis of DBD-based excilamps.

2.3 Vacuum System for Experimentation

The schematic view of a high vacuum chamber with mounting arrangements is shown in Figure 2.4 (a). The high vacuum chamber is made up of stainless steel (SS), which consists of the arrangement of mounting four DBD tubes simultaneously. For the development of exciplex UV light sources, firstly, the gas gap is evacuated up to 2×10^{-6} mbar of base pressure using a roughing vacuum pump (IVP 150) and the turbo molecular pump (EDWARDS Next3000 160W). The fabricated high vacuum chamber with mounting arrangement is shown in Figure 2.4 (b). After evacuating, the gas gap is flushed with argon gas at least ten times in a controlled manner before the desired pressure of Kr/Cl_2 and xenon-iodide mixture to eliminate unwanted impurities. After flushing, the source is again evacuated up to the above-mentioned base pressure, and the gases are filled up to the desired pressure by controlling the needle valves. The gas cylinders of rare gases, such as Xe, Ar, N_2 and Kr/Cl_2, are connected to the developed DBD devices through a gas-filling system. After evacuating the desired base pressure, the Xe or Kr/Cl_2 gas mixture has been filled in different DBD configurations. The pressure of the filled gas varies from 40 mbar to 500 mbar. The gas flow has been controlled using mass flow controllers (MCS-1SLPM-D-DB9M-PCA13 & MCS-10SLPM-D-DB9M).

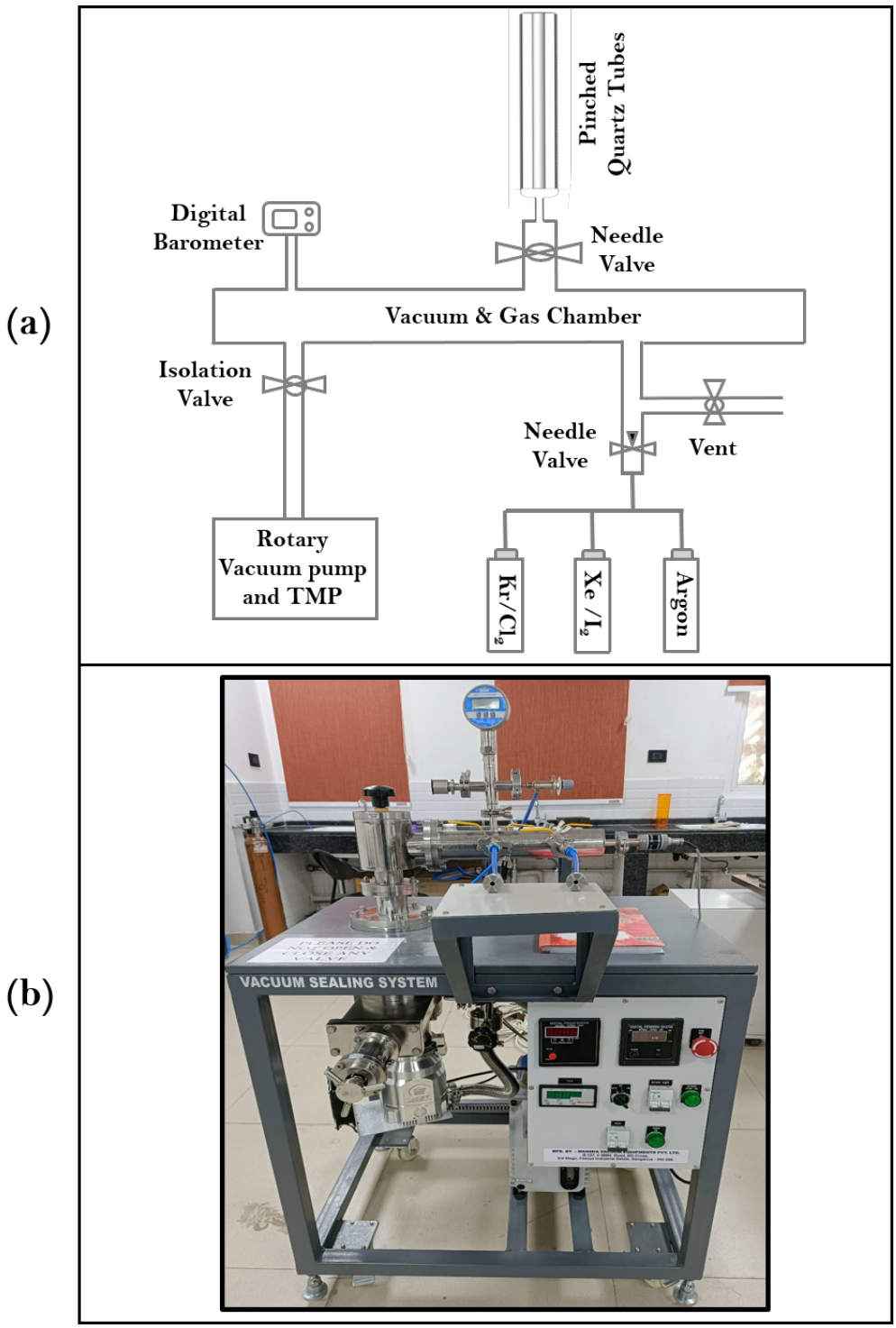


Figure 2.4 (a) Schematic view of the high vacuum system **(b)** Pictorial image of the high vacuum system.

To obtain precise measurements of the overall gas pressure, a digital pressure gauge (Equinox EQ-DPG-801) is utilized, displaying the pressure within the chamber. As a main discharge gas in the case of KrCl* excilamp, Kr and Cl_2 with a ratio of 100:1 (99.999%, Alchemie Gases & Chemicals Pvt. Ltd., Mumbai, India) have been used for all the experiments. In the 253 nm exciplex lamp, research grade xenon gas (99.99%, Phoenix Gases Pvt. Ltd.) was used and a fractional amount of iodine was introduced for plasma formation in the lamp. The iodine concentration is optimized experimentally by changing it from 5% to 0.0005% of xenon for maximum absolute UV-C irradiation. These high-purity gases produce excimer light emissions in

the coaxial DBDs. After the pressure optimization, the lamps were pinched at optimized pressure for further experimentations.

2.4 Experimental Setup for Electrical and Optical Measurements

The designed plasma source and exciplex UV lamps are operated by a microsecond pulsed power source [1-25 kV, 5-50 kHz pulse repetition frequency, 1 A, 2 μs pulse width] at different power settings. A four-channel mixed domain oscilloscope (Tektronix MDO3014, 100 MHz, 2.5 GS/s) is coupled with a 1:1000 high voltage probe (Tektronix P6015A, 1000X, 75 MHz bandwidth) and a current monitor (Pearson 110, 0.1 V/A, 1-20 MHz, 20 ns usable rise time) for the visualization of voltage and current waveforms. The oscilloscope is interfaced with a personal computer for real-time analysis and recording of the voltage and current waveforms. The input power is calculated using these waveforms, as discussed in Chapter 3. Both the current and voltage measurement systems must be adjusted to have the same time delay. A simple method has been used to synchronize both measurement systems by adjusting the cable length. The IR camera is utilized to capture the temperature of the excilamp surfaces.

In this section, the experimental setup for the measurement of the UV-C emission spectrum and absolute irradiance intensity are also presented. For equilibrium parameter measurements in DBD based plasma sources, sophisticated but modest optical emission spectroscopy has been used. The light emitting from the excimer sources has been used to monitor and diagnose the excimer source through spectral analysis. Usually, the most intense radiation emitted from the DBD based excimer sources originates due to bound-bound, free-bound, Bremsstrahlung, and molecular radiations, etc. [Cooper, 1966]. To detect these optical emissions, the main apparatus used is a grating monochromator, which disperses the light emanating from plasma. The light emitted from the excimer sources is conveyed to the entrance slit of the monochromator through a set of optics, including an optical fiber cable to image the light. After the dispersion of light from the grating of the monochromator, the light emerging from the exit slit is detected by Photomultiplier Tube (PMT) and stored in the computer.

An Andor make Photomultiplier tube (PMT)-based monochromator (SR-500i-B1, focal length 500 mm, grating 2400 groves/mm, resolution 0.05 nm) equipped with an optical fibre (200 μm, ocean optics) has been used for analyzing the optical properties of the developed plasma and exciplex sources. Accordingly, the optical properties are analyzed for the developed excimer lamps, including band position and full width half maxima (FWHM) of it. For the measurement of absolute UV intensity (in mW/cm^2) emitted by exciplex light sources, a Hamamatsu make UV power meter (C9536) has been used with different sensor heads (H9535-222 & H9535-254) pre-calibrated at the 222 nm and 254 nm wavelengths. Figure 2.5 shows the schematic view of the experimental set-up for the electrical and optical characterization of DBD based plasma source and excilamps.

2.5 Electrical and Optical Characterization of the Plasma Source and Excilamps

The input power and power consumed in one duty cycle (DC) (P_{in} *and* P_{DC}) is calculated using V-I characteristics (equation 2.1 to 2.3) as reported in our previous works [Jangra et al., 2023a] [Jangra et al., 2023b].

$$Electrical\ Energy\ (E) = \int_0^T V(t)I(t)dt \tag{2.1}$$

$$Discharge\ Power\ (P_{in}) = \frac{1}{T}\int_0^T V(t)I(t)dt \tag{2.2}$$

$$Duty\ ratio = \frac{T_{ON}}{T_{ON} + T_{OFF}} \tag{2.3}$$

$$P_{DC} = Duty\ ratio \times P_{in} \tag{2.4}$$

P_{in} represents the power input in Watts, $v(t)$ represents the applied voltage as a function of time, and $i(t)$ represents the current profile as a function of time.

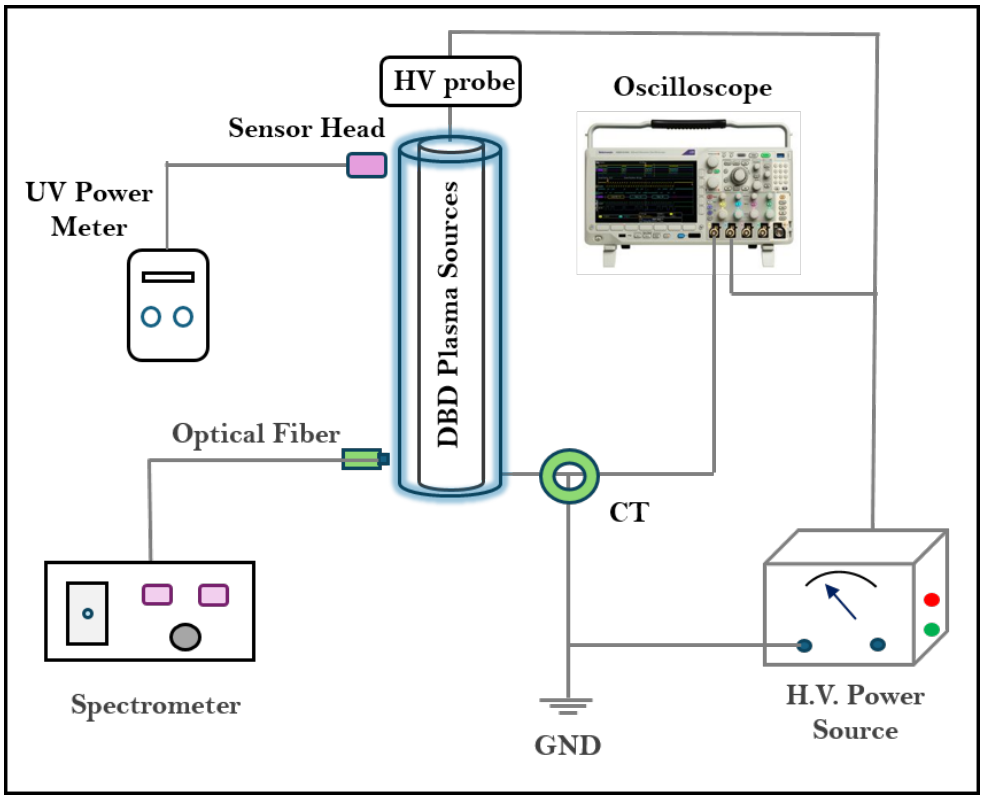


Figure 2.5: Complete experimental setup for electrical and optical measurements of developed DBD based plasma and excimer sources.

The Keitz formula has been used to estimate the optical output power (P_{out} in mW) of the exciplex sources [Zhu et al., 2023] as,

$$P_{out} = \frac{2\pi^2 DL}{2\alpha + sin2\alpha} \tag{2.5}$$

Where E = measure irradiance intensity (in mW/cm^2)

D = Distance (in cm) from the center of the excilamp to the UV photodetector

L = Arc length (in cm) of excilamp

α = The half angle (in radians), at which the excilamp is subtended from the photodetector position [see Figure 2.6 (b)], i.e.,

$$\tan\ \alpha = \frac{L}{2D} \tag{2.6}$$

One of the essential conditions is that the UV photodetector's cosine response must be appropriate for the lamp length and distance employed. Cosine response indicates that the UV power meter's output should be proportional to the cosine of the angle between the input beam and the UV power meter's surface normal. Furthermore, it is necessary for D to exceed 2L in order for the photodetector to have a full view of the entire arc length of the lamp. A metallic sliding frame slides the UV power meter at a fixed angle to measure the UV irradiation at varying distances and the same angle from the lamp. The pictorial image of the UV Power meter with a photodetector head is shown in Figure 2.6 (a).

The electrical to optical conversion efficiency (η) of the KrCl* and XeI* excilamps at different gas pressures and optimized electrical parameters has been calculated using the following relationship;

$$\eta(\%) = \frac{P_{out}}{P_{in}} \times 100 \tag{2.7}$$

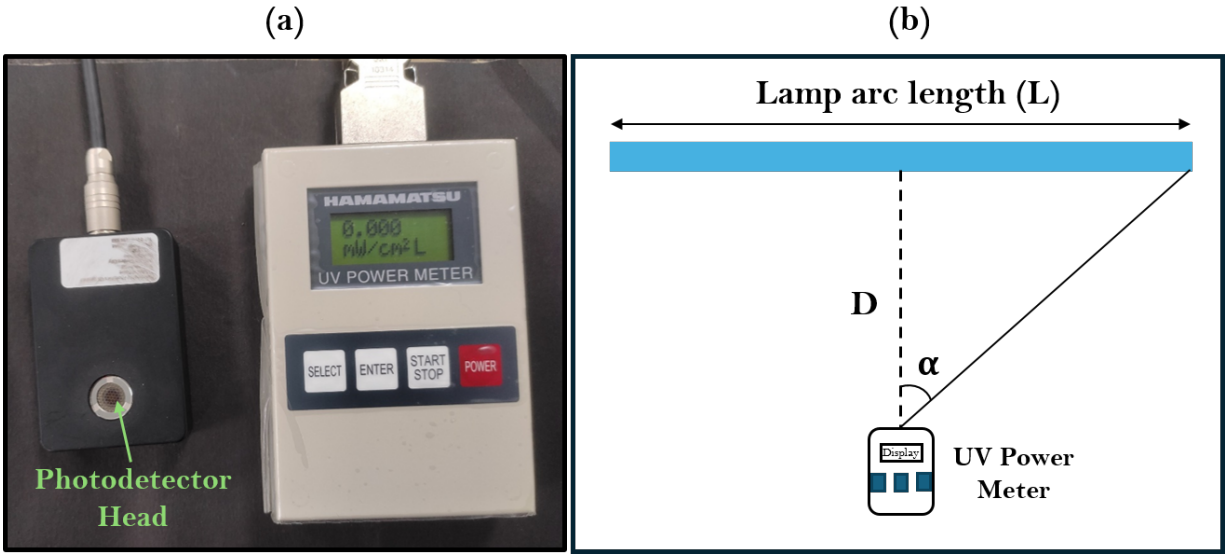


Figure 2.6: (a) Pictorial image of the UV power meter with photodetector head and **(b)** Geometry of the measured UV output system.

2.6 UV Dosage Measurements using Actinometry Method

Actinometry is used to determine the UV dose delivered to milk samples as described by Muller et al. [Müller et al., 2017]. It has been performed by exposing an aqueous solution of 0.6 M potassium iodide (KI) and 0.1 M potassium iodate (KIO_3) in 0.01 M borate buffer (pH 9.20) to the exciplex UV sources at various time intervals used in the experimentation. The UV dose (J/L) delivered to the milk samples was calculated using the following equation [Müller et al., 2017]:

$$UV\ Dose = \frac{A_{352\,nm} \times P_{222/253\,nm}}{pl \times \emptyset \times \varepsilon_{352\,nm}} \tag{2.8}$$

Where $A_{352\,nm}$ is the absorbance of the aqueous solution at 352 nm, $P_{222/253\,nm}$ is the number of Joules/Einstein photons at 222 nm and 253 nm (5.405×10^5 J/einst and 4.716×10^5 J/einst, respectively), pl is the path length of the cuvette (10 mm), Φ is the quantum yield (mol/einst), $\varepsilon_{352\,nm}$ is the molar absorption coefficient of triiodide at 352 nm (27,600 dm^3/mol). A

quantum yield correction was implemented by utilizing the initial temperature (°C) and iodide concentration ($A_{300\,nm}$ × 1.061^{-1}).

2.7 DBD Plasma and Exciplex UV Source based Milk Treatment System

Raw milk used for the treatment was procured from a local milk vendor in Jodhpur, Rajasthan, India. To ensure no homogenization or standardization of milk during the experiment, unprocessed milk was utilized. These processes alter the fat content and other constituents of milk, potentially affecting the pathogen inactivation and reducing the MBRT value. This is because fats can envelop pathogens, thereby providing protection.

Unprocessed milk was exposed to plasma and different doses of 222 nm and 253 nm exciplex UV light. To ensure that the UV light could pass through the milk, potassium iodide was dissolved in DI water, and the solution was passed through the container while the UV lamp was on. The white solution became yellow, and the UV–vis absorption spectra confirmed the UV dose when compared with the calibration curve. The radiometry method (as described in section 2.5) was also utilized for the measurement of absolute UV radiation with and without milk. A complete schematic of the exciplex UV source–based milk treatment system is shown in Figure 2.7 (a). All milk handling and sample collection are done in a biosafety cabinet (BSC) to prevent contamination before and after plasma/UV treatment. The transfer and filling of treated milk into test tubes are also carried out in BSC. In another system, milk was pumped through the designed UV-C reactor using a peristaltic pump at a flow rate of 1 L/hr for the continuous treatment. Figure 2.7 (b) depicts a detailed schematic representation of the continuous milk treatment system that utilizes a UV source.

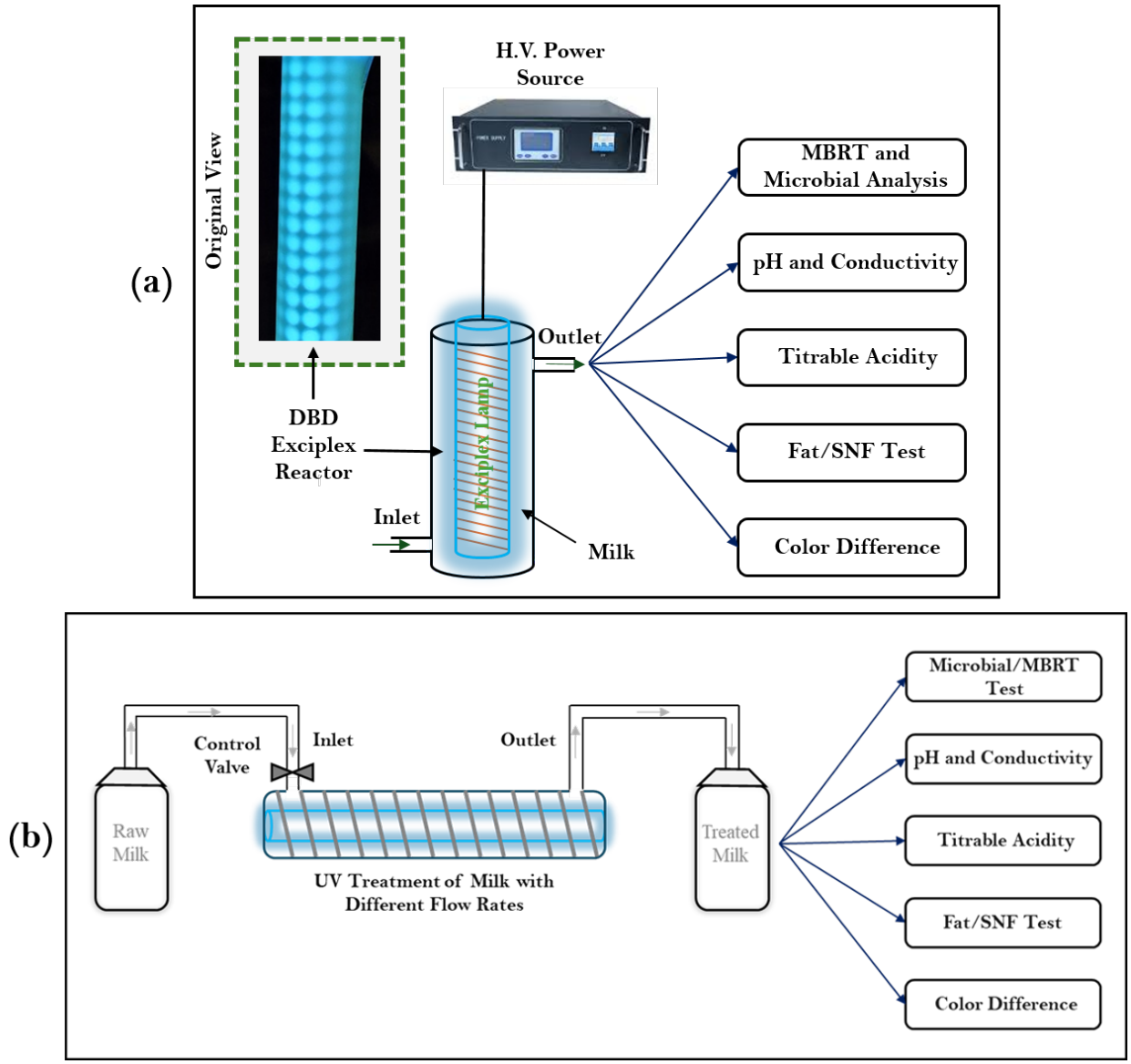


Figure 2.7: (a) Schematic view of the exciplex UV light-based milk treatment system. Enlarge pictures show the original view of developed exciplex source and reactor and **(b)** Schematic diagram of UV light-based continuous milk treatment system.

2.7.1 Investigation of Physicochemical Properties of Milk

It is important to analyze the physical and chemical parameters of milk after plasma and exciplex UV treatment to set better parameters for process standardization. In this work, different physicochemical parameters, such as pH, conductivity, temperature, color, titratable acidity, and fat/SNF content, have been evaluated after plasma and exciplex UV treatment of whole milk. All parameters are recorded before treatment (control), immediately after treatment (0 min), and then after a fixed interval of time.

The pH, conductivity, and temperature are measured using a pH and conductivity meter (Mettler Toledo) after transferring the treated milk samples into a 100 ml beaker and immersing the electrodes until a consistent value is achieved. Before taking the pH and conductivity readings, the pH and conductivity meters were calibrated using standard pH (pH 4.0, pH 7.0, and pH 10.0) and conductivity (84, 1413, and 12880 µS/cm) solutions. Conductivity is a crucial tool for microbial proliferation.

The titratable acidity was measured using the AOAC method (AOAC 947.5) to analyze the effect of acidity due to the exciplex UV treatment. Titratable acidity was tested with phenolphthalein (HPh, Qualigens) indicator; HPh was added to untreated and treated milk and titrated with N/10 $NaOH$ solution. To do so, 10 ml of the treated milk sample, 10 ml of distilled water, and 1 ml of HPh indicator were mixed well in a glass beaker. Finally, it was titrated with N/10 $NaOH$ solution for 30 s until a faint pink color persisted. The results are shown as % lactic acid using the following relationship: 1 ml of N/10 $NaOH$ = 0.009 g lactic acid.

Fat and solids not fat (SNF) contents are measured using a lactoscan milk analyzer before and after treatment.

The color of food is an essential component that plays a crucial role in influencing its acceptance. Therefore, it is important to determine how exciplex UV treatment affects the color change in milk, and the same has been analyzed using a colorimeter (3nh Global, CR6). Before analyzing the milk samples, the colorimeter was calibrated by placing black and white plates. The color difference was obtained from the color variation formula defined by the International Commission on Illumination (CIE) [Pathare et al., 2013].

$$\Delta E_{ab}^{*} = \sqrt{(L^{*} - L)^2 + (a^{*} - a)^2 + (b^{*} - b)^2} \tag{2.9}$$

Where, ΔE_{ab}^{*} = color variation

L^{*}, L = luminosity of exciplex UV–treated and untreated samples, respectively

a^{*}, a = difference between red and green

b^{*}, b = difference between yellow and blue

2.7.2 MBRT and Bacterial Analysis

For assessing the quality of milk, the Methylene Blue Reduction Test (MBRT) is commonly used. This test works on the principle that the quality of milk can be evaluated by observing the colour change after adding a dye, such as methylene blue. Methylene blue acts as a redox indicator and loses its colour under low oxygen conditions. This is because of the synthesis of reducing chemicals as a result of bacterial metabolism, and accordingly, the amount of oxygen in milk decreases [De Silva et al., 2016]. The number of microorganisms in milk and the metabolism of oxygen in the test tube determine how long it takes for the milk to become white again. Lomas et al. provide a comprehensive description of the specific procedure used for the MBRT study [Pérez-Lomas et al., 2020]. The detailed process adopted for the MBRT analysis is shown in Figure 2.8. The following steps are used for conducting the MBRT analysis:

1. Take 10 ml of milk sample in a sterile glass test tube
2. Adding 1 ml of standardized (0.05%) MBRT dye and mixing it well
3. Closing the tube with a sterilized vacuum tight rubber cap
4. Placing the test tube in a water bath maintained at 37°C
5. Noting the time taken for decolourization.

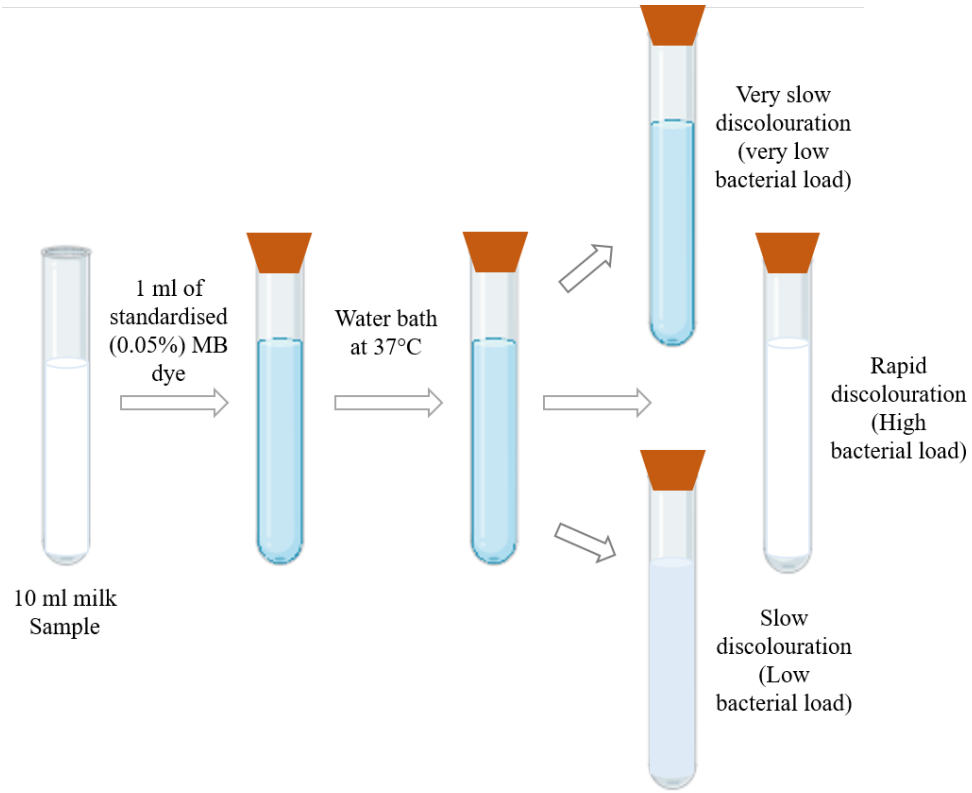


Figure 2.8: Detailed process for the MBRT analysis of whole milk.

For specific bacterial analysis, gram-negative (*E. coli*) and gram-positive (*S. aureus*) bacterial inactivation is analyzed in the untreated and treated milk samples in the case of UV excimer treated raw milk. Gram-negative (*Salmonella typhi.*) and gram-positive (*Staphylococcus aureus*) bacteria are analysed in the control and UV-treated milk samples for specific bacterial analysis in the case of annular UV reactor. For *E. coli* counts, 1 mL of untreated and treated milk samples was placed on a petri dish and approximately 15 mL of Tryptone Bile X-glucuronide Agar (TBX, HiMedia, M1591) at 44 – 47 °C was poured over it. Subsequently, the petri dishes were incubated at 44±1 °C for 18–24h and the number of blue colonies formed after incubation was counted. For *S. aureus* counts, surface plating was performed on pre-poured Baird-Parker Agar (HiMedia, M043) with egg yolk-tellurite emulsion enrichment. The plates were incubated at 37±1 °C for 48 h and the number of black glossy colonies with transparent zones after incubation was counted. For the *Salmonella typhi.* counts, 1 mL of treated milk samples were taken and diluted by adding 9 mL of autoclaved MilliQ. The 50 µl of diluted culture was spread on Xylose Lysine Deoxycholate Agar (XLD agar, Himedia, M031). Then, petri plates were incubated for 24 hours at 37 °C. The colonies that typically form at the end of the incubation period are counted, and the results are reported as log CFU/ml.

2.8 Limitations of the used Diagnostics

In electrical measurements of DBD plasma and exciplex sources, several parameters can influence the input electrical signals. The primary parameter is the power supply, which provides the input power to the DBD sources. In DBD systems, micro-discharges occur in a few nanoseconds and can transition to a diffuse discharge if the applied voltage is sufficiently high. Although diffuse discharges can be achieved at low voltages and high frequencies, increasing the frequency leads to ionization effects that perturb the DBD discharge, resulting in a non-thermal plasma state. In pulsed DBD systems, high-voltage pulses with short rise and fall times drive the plasma discharge, necessitating equipment with wide bandwidth and resistance to electromagnetic interference. Voltage and current pulses are measured using a high-voltage probe

(Tektronix P6015A) and a current probe (Pearson 110), where the high-voltage probe has a bandwidth of 0-75 MHz suitable for capturing fast signals with rise and fall times of over 4 ns. Both probes are capable of measuring signals with a rise time of approximately 20 nanoseconds. The total current and applied voltage waveforms are visualized using a four-channel Tektronix digital oscilloscope (Model: MDO 3014), which has a bandwidth of up to 100 MHz, an input impedance of 1 MΩ, and a maximum sampling rate of 2.5 GS/s. The length of the cables for the measurement equipment is carefully adjusted to ensure that the delay times for voltage and current measurements are synchronized, enabling precise calculation of the total electrical input power.

Spectroscopy measurements are primarily constrained by three key factors: the characteristics of the light-emitting source, the resolution of the spectrometer, and the sensitivity of the detector. Each of these factors must be carefully selected and optimized to ensure accurate spectroscopic results. Moreover, plasma, being an intricate chemical environment, presents additional challenges. It encompasses vast spectroscopic features on an atomic scale, which can complicate the interpretation of data. In particular, phenomena such as collisional radiative processes are not always fully understood, leading to potential errors in the analysis. Therefore, it is essential to exercise caution and incorporate these complex effects into the interpretation of observed spectral features to minimize inaccuracies and improve the reliability of spectroscopic measurements. Sincere efforts have been made to minimize the errors in all measurements wherever possible otherwise statistical errors have been worked out.