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Laser induced fluorescence on Nitrix Oxide in an atmospheric pressure plasma jet

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Laser induced fluorescence on Nitric Oxide in an atmospheric pressure plasma jet

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Abstract

In this research NO density and temperature measurements are performed in a cold atmospheric plasma jet with the use of laser induced fluorescence. The plasma is generated in an admixture of 1 slm Argon with 2% air. On the plasma jet a plate electrode or a ring electrode is attached, which is grounded. An important perspective application of the plasma jet is wound treatment. Nitric oxide is one of the radicals present in the plasma jet. NO is argued to have a beneficial effect for wound healing. Since it is important to know why this plasma jet stimulates wound healing research to NO in the plasma jet is valuable.

With a dye laser the NO ground state is excited. When the molecule de-excites by radiative decay a photon is emitted. This fluorescence light is collected by a monochromator (set on 247 nm) and a photomultiplier which is mounted on the monochromator. By scanning the dye laser an NO excitation spectrum can be measured. Now the LIF intensity can be determined and consequently the NO density obtained after a calibration measurement with a known NO density.

The first measurement is a position scan. For this scan the NO density is measured for different axial and radial positions in the plasma. For both electrodes there is still NO present at the tip of the plasma. For the plate electrode there is NO present up to 14 mm above the tip of the plasma in concentration larger than 0.5 ppm.

Secondly the influence of the power on the NO density is investigated. For the plate electrode the length of the plasma increases for higher power. The position corresponding to the maximum NO density shifts upwards when the power is increased. The NO density at this maximum position also increases. For the plate electrode the density varies from 0.3 ppm to 0.9 ppm. For the ring electrode the maximum NO density is right above the tube. The NO density is higher for higher powers and varies from 0.2 to 1 ppm. The error margin in the measured NO densities is 50%.

For a tissue treatment the plasma shouldn’t be too hot. Therefore the temperature is determined by measuring an NO excitation spectrum and make a fit through this spectrum. For the plate electrode the temperature is 420 ± 20 Kelvin for all different conditions. For the ring electrode the temperature reaches a maximum of 500 ± 20 Kelvin for high powers. Although the temperature is lower for the plate electrode it is still too hot for tissue treatments.
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1 Introduction

A cold atmospheric plasma jet (APPJ) is a well known source of a non-equilibrium, atmospheric pressure and low temperature plasma. The low temperature makes it possible to treat heat sensitive surfaces with the APPJ, for example polymers and tissue. This leads to some important biomedical applications, like wound treatment, antimicrobial treatment and dental applications. The bacteria killing characteristic is based on direct interaction of the plasma with micro organisms. Just UV radiation or heat results in lower reduction rates, which indicates that the interaction of the chemically active molecules and radicals in the plasma with the bacteria contributes to the bacteria killing. [5]

One of the chemically active molecules which is produced in the plasma jet is Nitric Oxide. NO is very important in biological processes such as wound healing, skin cell development and division or cell signalling. It also turned out that NO kills micro-organisms when directly administered in vitro. The antimicrobial activity of NO works for many pathogenic microorganisms like viruses, bacteria and parasites. These characteristics make research to NO in APPJ’s valuable. [6] For tissue treatment the gas temperature has to be below 315 Kelvin to prevent cell destruction. Therefore accurate gas temperature and power measurements are important. [9] Research about NO in a cold atmospheric pressure plasmas is surprisingly rare, which makes it even more relevant.

The plasma jet can be investigated by spectroscopic methods like Optical Emission Spectroscopy and Laser Induced Fluorescence. In Optical Emission Spectroscopy the optical emission from an excited atom or molecule is measured to determine concentrations. Pipa et al. investigated the influence of varying the Argon flow and the percentage air in the flow on the NO concentration in an APPJ with the use of OES. It is found that for an Ar flow from 5 to 15 slm the maximum NO density is at 0.2 - 0.4 % air. Changing the Ar flow changes the NO emission signal as a function of the percentage air in the Argon flow. For a smaller Ar flow the emission signal is higher, the maximum is broader and the decay is slower. [6]

In this research NO densities are measured with the use of Laser Induced Fluorescence. In laser induced fluorescence a molecule or atom is excited by a tunable laser. After some time the molecule de-excites and emits a photon. This fluorescence light is detected in a LIF measurement. An advantage of LIF over Optical Emission Spectroscopy is that the ground state is probed directly. Moreover it is possible to measure absolute densities by performing a calibration measurement, while with OES only relative densities can be measured.

In this report first the theoretical background of the plasma and LIF is explained (chapter 2), than the experimental setup including the plasma source and the laser system is described (chapter 3). In chapter 4 the results are discussed and in the last chapter a conclusion is given.
2 Theoretical background

2.1 Atmospheric plasmas

A plasma is a collection of free charged particles, moving in random directions. A plasma is, on the average, electrically neutral. Plasma is a state of matter, like solid, fluid and gas. Although the solid, fluid and gas state are much more known 99% of the universe is believed to be plasma. A plasma is a complex medium with many technological applications and is therefore an important research subject in science.

Plasma science includes for example space plasmas, fusion plasmas and technological plasma. It also ranges over many variations of parameters like pressure, distance and energy. One way of distinguishing different plasmas is using the terms hot or cold plasmas. The characteristics hot and cold depend on the relative value of the heavy particle temperature compared to the electron temperature. In this research a cold atmospheric pressure plasma is used, also shortly called an atmospheric plasma jet (APPJ). The electron temperature of an APPJ is only a few electron volt while the gas temperature is typically below 500 Kelvin. This makes the plasma source able to create reactive and charged species, metastable atoms and UV photons. One of the molecules produced in the APPJ is NO.

2.2 NO energy scheme

Within an atom or a molecule electrons exist in different energy levels. An electron absorbing or emitting energy can move from one level to another. The energy needed for an electron transition is at least the energy difference between two energy levels. In this research the transitions from the ground state NO $X^2\Pi$ to the electron excited state NO $A^2\Sigma$ and vice versa are studied. The energy states are subdivided in vibrational states with vibrational quantum number $\nu$. A picture of the NO energy scheme with its vibrational states is in figure 1. The vibrational states are subdivided in rotational states with rotational quantum number $J$. $J$ is the total angular momentum with components of the electron spin angular momentum $S$ (with the projection along the internuclear axis $\Sigma$), the electronic orbital angular momentum $L$ (with the projection along the internuclear axis $\Lambda$) and the angular momentum of the nuclear rotation $N$. For NO $J$ is half-integral, because NO has an odd number of electrons.

2.3 Laser induced fluorescence

In a Laser induced fluorescence (LIF) measurement a laser is shot on an atom, ion or molecule in, for example, a plasma. The examined specie will be excited by absorbing a photon when it is a the appropriate frequency in its ground state. After some time, depending on the life-time of the excited state, the ion, atom or molecule will be de-excited and emits a photon. The wavelength of the emitted photon can be different than the wavelength of the laser. By scanning the
dye laser along rotational transitions an absorption spectrum can be measured. An advantage of using Laser induced fluorescence is that the ground state is probed directly in contrast to for example optical emission spectroscopy.

For the energy transfers in the LIF process a two-level system is introduced. The Einstein balance equations of this system are

\[
\frac{dn_1}{dt} = -n_1 B_{12} E_l + n_2 (A_{21} + B_{21} E_l + Q_{21}),
\]

(1)

\[
\frac{dn_2}{dt} = n_1 B_{12} E_l - n_2 (A_{21} + B_{21} E_l + Q_{21}),
\]

(2)

where \(n_2\) and \(n_1\) are respectively the number densities of the upper and the lower level of the energy transition. \(A_{21}\) is the Einstein coefficient and \(B_{21}\) and \(B_{12}\) are the absorption and stimulated emission rates. \(Q_{21}\) is the collisional quenching rate and \(E_l\) is the laser energy in \(\text{Js}^{-2}\). \([10]\). The two-level LIF model is shown in figure 2. The transition in this figure is a transition between two vibrational energy levels.

With the use of this model an equation for the detected fluorescence can be derived. After Uddi et al. \([8]\) the detected fluorescence can be written as a function of the vibrational transition \(\nu\):

\[
S_{LIF} = \frac{C_{opt} E_l A_{\nu'=0\rightarrow\nu''=2}}{\sum_{\nu'} A_{\nu'\nu''} + Q} \cdot \sum_{i} \{f_{B_i(T)} B_i g_i\} \cdot n_{NO},
\]

(3)
where the summation is over all transitions $i$ which are excited by the laser. $C_{opt}$ is a product of constant factors which describe the optical collection, $E_l$ is the total laser energy per pulse, $A$ and $B_i$ are Einstein coefficients, $f_{Bi}(T)$ is the equilibrium Boltzmann fraction based on the rotational temperature, $Q$ is the quenching rate, $g_i$ is the line shape function and $n_{NO}$ is the NO density. For equation 3 it is assumed that the quenching rate is independent of the rotational quantum number. The quenching rate is described further in section 2.4 and the Boltzmann distribution and the line shape function are described further in section 2.5.

### 2.4 Quenching

Quenching refers to processes reducing the fluorescence intensity during the LIF measurement. Examples of quenching processes are excited state reactions and collisional quenching. Quenching depends highly on the pressure and temperature of the examined substance.

To determine the quenching rate the total LIF intensity is measured time resolved. [7] An example of this time resolved LIF measurement is pictured in figure 3. The intensity decays exponentially after the laser pulse with decay time $\tau = \frac{1}{\sum_{\nu_{\nu',\nu'}} A_{\nu_{\nu',\nu'}} + Q}$. 

![Figure 2: Schematic view of the two-level LIF model.](image)
Figure 3: Time resolved LIF intensity. The LIF signal occurs at 120 ns and decays exponentially. The plate electrode is used and the power in the plasma is 2.3 Watt. The axial position in the plasma is 2 mm. The decay time of the exponential decay in the intensity is 25 ns.

2.5 Temperature fit

As showed in section 2.3 the LIF signal is depending on the temperature. The $f_{Bi}(T)$ Boltzmann term in equation 3 can be written as

$$f_{Bi}(T) = \frac{(2J_i + 1)}{N} e^{-\frac{E_i}{kBT}}, \quad (4)$$

where $J_i$ is the rotational number of the lower state and $E_i$ is the energy of the lower state of transition $i$ and $N$ is the rotational partition function given by

$$N = \sum_i (2J + 1)e^{-\frac{E_i}{kBT}} \approx \frac{k_B T}{B_v}, \quad (5)$$

where $B_v$ is the rotational constant.

With the use of the equation 3 and the knowledge that the quenching coefficient $Q$ and the Einstein $A$ coefficient are independent of the transition $i$ the intensity $I_i$ of a line of transition $i$ can be shortly written as

$$I_i \propto B_i \cdot (2J_i + 1)e^{-\frac{E_i}{kBT}}, \quad (6)$$

where $B_i$ is the Einstein absorption coefficient corresponding to transition $i$, induced by the laser and $T$ is the temperature in Kelvin. Above equation is valid if there is no saturation, if the vibrational energy transfer is negligible or at least independent of the rotational state, if the rotational energy transfer is faster than the lifetime of the excited state, if quenching is independent of the
rotational state and if the plasma is optically thin (the absorbed laser energy should be negligible compared to the total laser energy).

To calculate the total spectrum we add a constant background $C$ and multiply the intensity with a line profile $g(\lambda)$. This results in the following equation

$$S(\lambda) = C + \sum_i I_i \cdot g(\lambda - \lambda_i).$$  \hspace{1cm} (7)

Mostly the line profile can be approached by a Voigt profile, so

$$g(\lambda) = G(\lambda, \Delta_G) \otimes L(\lambda, \Delta_L),$$  \hspace{1cm} (8)

where $G$ is a Gaussian curve with width $\Delta_G$ and $L$ is a Lorentzian curve with width $\Delta_L$. Now the resulting spectrum function is $S(\lambda; I_0, T, C, \Delta_G, \Delta_L)$, since the other variables are known from literature. The function can be programmed into a computer and fitted to a measured spectrum. The fitted spectrum will give a value for the temperature. The parameters $E_i, A$ and $B_i$ and the fitting process are used as in [3].
3 Experimental setup

In this chapter the experimental setup is described and the measurement methods are explained. With laser induced fluorescence it is possible to determine absolute densities, how these densities are determined is also described in this chapter.

3.1 Plasma source

The plasma source is an atmospheric pressure plasma jet. The plasma jet contains a plastic cover. In this cover a glass tube is placed, through which a carrier gas, Argon mixed with air, flows. The flow rate of Argon is 1 slm and the flow rate of air is 20.2 sccm, which corresponds with 2% of the Argon flow. The glass tube contains a needle which is connected to an E&I A075 RF power supply (75 Watt) driven at 13.9 MHz via a home made matching circuit. The matching circuit consist of a coil with 21 windings. To extend the plasma a second grounded electrode is attached. This electrode is a ring electrode or a plate electrode. In figure 5 the plasma is pictured with both the ring electrode and the plate electrode. The plasma is pulsed with 20 kHz with the use of a hp function generator and a BNC pulse generator. The duty cycle is set at 20% by setting the pulse width on the BNC pulse generator at 10 µs. A schematic picture of the plasma and the matching circuit is shown in figure 4. The plasma source is placed on a movable table to measure at different X- and Y-positions in the plasma. The zero-position is chosen at the glass tube as shown in figure 5. The distance between the plate and the glass tube is 2.7 mm, the thickness of the plate is included in this distance.

One of the chemically active molecules in the plasma is nitric oxide (NO). Even when a pure Argon flow is used NO is produces due to air impurities in the gas. From Pipa et al. it is known that mixing air through the argon flow increases the NO production up to a maximum, which is at 0.2 - 0.4 % air. [5] From this article it is also shown that changing the Ar flow leads to different NO concentrations for increasing air admixture. A smaller Ar flow leads to a higher NO concentration, a broader maximum and a slower decay. Since in this research the used Ar flow is much less than in the research of Pipa et al., a percentage of 2% air is used.
Figure 4: A schematic picture of the plasma with the RF E&I power supply, the pulse generator, the amplifier research PM2002 power meter and the Rogowski coil. The latter is used to measure the current. In this picture the ring electrode is attached.

Figure 5: The plasma with both the ring electrode and the plate electrode. The flow is 1 slm Ar with 2% air.
Figure 6: The power as a function of the rms current, when the plasma is off. The system is pulsed with 20 kHz and a duty cycle of 20%.

### 3.2 Power measurements

To measure the power in the matching circuit and the plasma an amplifier research PM2002 with PH2000 dual diode power heads is used. To know the exact power in the plasma, we need to know the power through the matching circuit for each current and each condition. The result of a plasma-off measurements is shown in figure 6. The system was pulsed on 20 kHz with a duty cycle of 20%. The current is measured with the use of a Rogowski coil. The measurement is performed for both the plasma with the plate electrode and the plasma with the ring electrode. The equation for the fits are respectively

\[
P_{\text{plate}} = -2.3354 + 0.0036 \cdot I + 7.88265 \cdot 10^{-7} \cdot I^2 \quad (9)
\]

\[
P_{\text{ring}} = -0.70324 + 5.4967 \cdot 10^{-4} \cdot I + 2.48849 \cdot 10^{-6} \cdot I^2, \quad (10)
\]

where \( P \) is the power and \( I \) is the root mean square (rms) current. Because there are a lot of conditions influencing the power through the circuit, for example changes in the position of the cables, a plasma-off power measurement is performed each time a measurement is performed. To given an idea of the power through the circuit while the plasma is on two current-power plots for both the plate and the ring electrode are pictured in figure 7.

To investigate the influence of the power on the intensity and thereby the NO density a small scan from 226.125 nm to 226.145 nm is made on different positions in the plasma for both the ring electrode and the plate electrode. The small scan range is chosen to reduce the measurement time. The measured spectrum is shown in figure 8.
Figure 7: The power as a function of the rms current for the plasma generated in 1 slm Ar with 2 % air, pulsed with 20 kHz and a duty cycle of 20 %

(a) plate electrode  
(b) ring electrode

Figure 8: The spectrum measured for the power measurements and the position scan. The first peak corresponds with $J = 2.5$, the second peak corresponds with $P21, J = 8.5 \ Q21, J = 8.5$ and the third peak corresponds with $R22, J = 12.5$. 
3.3 LIF setup

The excitation of NO is realized with a dye laser tunable from about 221-227 nm. The laser is a Sirah cobra dye laser with a Coumarin 2 dye, pumped with an Edgewave IS6III-E YAG laser at 355 nm. To create the UV, the frequency of the light of the dye laser is doubled with a BBO crystal. The laser is pulsed with 2000 Hz or 4000 Hz, depending on the desirable laser energy per pulse, since a lower frequency results in a higher energy per laser pulse. The laser beam is focused with a lens or attenuated with a pinhole, depending on the desirable size and laser energy per unit area of the laser spot. It is important to prevent saturation, which is discussed in detail in section 3.5. The bandwidth of the laser light is 1.4 pm before doubling by the BBO crystal, which is in the specification of the laser. The laser energy is measured by an Ophir photodiode energy sensor.

The fluorescence light is collected perpendicularly to the laser beam by two quartz lenses. A mirror is used to focus the fluorescence light on the entrance slit of a UV monochromator. The monochromator is used to collect just one wavelength of the fluorescence light. This wavelength is set at 247 nm. The monochromator is a McPherson 234/302 with 0.2 m focal length and a range of 50-500 nm FWHM. To control the bandwidth the slit width of the entrance slit of the monochromator can be adjusted. A photomultiplier is placed behind the exit slit of the monochromator to collect the fluorescence light. The photomultiplier is a Hamamatsu R8486, which is optimized for UV wavelengths and is connected to an Ortec 1 GHz pre-amplifier. A computer with a Fast Comtec P7888 time digitizer is connected to the photomultiplier to count the amount of pulses. The time resolution of the time digitizer is 1 ns.

The BNC pulse generator is used to time the laser pulse. This can be accomplished by adjusting the delay time. Because it is hard to correct for the variable background of the plasma it is important to limit the background as much as possible. This can be accomplished by timing the laser pulse after the plasma pulse, during the plasma off time. This means that the delay time of the laser should be more than 10 µs. In figure 9 the timing of the laser pulse is shown for a delay time of 5 µs and 30 µs. For measurement with a delay time shorter than 10 µs it is possible reduce the background by measuring just above the plasma. For the power measurements and the position scan a laser delay time of 30 µs is used.

As mentioned before a measurement is performed by scanning the dye laser along rotational transitions to measure an absorption spectrum. For each point of the spectrum a time resolved histogram of counts is accumulated over a number of laser shots, in this case set on 1000 shots. Now it is possible to measure time resolved, wavelength resolved and both at the same time. In figure 10 a result of such a measurement is shown. In figure 11 one can see a photograph of the setup and in figure 12 a schematic picture of the setup is shown.
Figure 9: By changing the laser’s delay time the laser pulse is timed during the plasma on time (5 $\mu$s) or during the plasma on time (10 $\mu$s). The plasma is driven at 13.9 MHz and pulsed with 20 kHz. The duty cycle is 20%.

Figure 10: The LIF signal time and wavelength resolved of the plasma with the plate electrode. The power in the plasma is 3.9 Watt and the position from the glass tube is 8 mm.
Figure 11: A picture of the setup with the plasma with the plate electrode. At the right one can see the monochromator and the photomultiplier.

Figure 12: Schematic picture of the experimental setup with the plasma and the LIF system. The LIF system consist of a dye laser system and a detection system with a monochromator and a photomultiplier (PMT).
3.4 Determining the NO density

During a LIF measurement a wavelength resolved NO spectrum is measured. This spectrum needs to be corrected for the background. The value of this background is determined by the time resolved LIF measurement shown in figure 13c and equals the data in this figure from 0 to 120 seconds and from 250 to 2048 seconds. The LIF signal equals the data from figure 13c from 120 to 250 seconds. Now a background corrected spectrum can be calculated by subtracting the background from the LIF signal. Both a spectrum with background and a background corrected spectrum are shown in figure 13. In this case the background is constant, but a variable background is possible too. To correct for this a polynomial fit is made through the background. Since this fit is not always perfect a constant background is desirable. This can be accomplished by shooting the laser just above the plasma or by setting the laser delay time to more than 10 µs which is discussed earlier in section 3.3.

Now the spectrum is corrected for the background the LIF signal can be described with equation 3.

From this equation one can see that to calculate the density it is necessary to correct for the laser energy and for quenching. Both parameters can be different each measurement. For the laser energy this is because for example the dye is running down and for the quenching coefficient the cause can be a different temperature. To perform the correction the obtained LIF signal is divided by both the laser energy and the decay time ($\tau = \frac{1}{\sum_{\nu'} A_{\nu'\nu''} + Q}$). This results in the following equation

$$S_{\text{LIF,corrected}} = C_{\text{opt}} A_{\nu'=0\rightarrow\nu''=2} \cdot \sum_i \left\{ f_{B_i}(T) B_i g_i \right\} \cdot n_{\text{NO}}.$$ (11)

The spectrum is not corrected for temperature. In figure 14 the intensity of the measured lines (shown in figure 8) is plotted as a function of the temperature. The temperature of the calibration measurement is 300 Kelvin (room temperature). From figure 14 one can see that not correcting for the temperature leads to a maximum error margin of 30%, since the gas temperature differs from 300 Kelvin for the calibration measurement to a maximum of 500 Kelvin for the measurements. (The results of gas temperature measurements in the plasma are shown in section 4.3)
Figure 13: An NO spectrum with and without background correction. The plasma is an Ar plasma with 2% air with the plate electrode attached. The delay time was set on 5 µs. The power is 3.9 Watt. The position in the plasma is 5 mm above the plate electrode.

To determine absolute NO densities a calibration measurement is needed. In this research the calibration measurement is done with a mixture of He with 2.79 ppm NO. The NO densities for different conditions are shown in table 1. The uncertainty in the NO density is approximately 20% due to errors in the exponential decay fit and due to temperature differences discussed before. Since all other parameters in equation 11 are identical for both the measurement and the calibration measurement the NO density can be determined by the following equation

$$n_{NO, measurement} = n_{NO, calibration} \frac{S_{LIF, corrected, measurement}}{S_{LIF, corrected, calibration}}, \quad (12)$$

where $n_{NO, calibration}$ is 2.79 ppm.
It is recommended to perform a calibration measurement each measurement day. Due to circumstances that was not possible in this research. Densities discussed in chapter 4 are determined by using the densities from table 1 corresponding to the same plasma conditions used in the discussed measurement.

### 3.5 Saturation

In order to measure NO densities saturation of the LIF signal must be prevented. This means that $n_2 \ll n_1$, where $n_2$ and $n_1$ are the number densities of respectively the upper and the lower energy state of the transition. Now stimulated emission can be neglected. To check for saturation the LIF intensity is measured as a function of the laser pulse energy. When the LIF intensity is proportional to the laser energy there is no saturation. For both the pinhole and the lens a saturation check is done. The results are shown in figure 15.

As one can see both relations are linear, which means that there is no saturation and it is possible to measure the NO density. For the measurements the laser is set at maximum power. This means that the laser energy was approximately $1.05 \ \mu J$. For the lens the laser bundle has an area of approximately $0.066 \pm 0.02 \ \text{mm}^2$ and for the pinhole this area is approximately $0.79 \pm 0.2 \ \text{mm}^2$. This means that the energy per mm$^2$ is $16 \ \mu J/\text{mm}^2$ for the lens and $1.3 \ \mu J/\text{mm}^2$ for the pinhole.
Table 1: The NO densities for different conditions of the plasma

(a) plate electrode

<table>
<thead>
<tr>
<th>axial position (mm)</th>
<th>power (Watt)*</th>
<th>NO density (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.6</td>
<td>1.6</td>
<td>0.64</td>
</tr>
<tr>
<td>10</td>
<td>2.6</td>
<td>0.79</td>
</tr>
<tr>
<td>11.5</td>
<td>3.4</td>
<td>1.0</td>
</tr>
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<td>13.7</td>
<td>4.4</td>
<td>1.4</td>
</tr>
<tr>
<td>13.9</td>
<td>4.8</td>
<td>1.5</td>
</tr>
</tbody>
</table>

(b) ring electrode

<table>
<thead>
<tr>
<th>axial position (mm)</th>
<th>power (Watt)*</th>
<th>NO density (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.9</td>
<td>0.74</td>
<td>0.19</td>
</tr>
<tr>
<td>3.3</td>
<td>1.1</td>
<td>0.30</td>
</tr>
<tr>
<td>3.7</td>
<td>2.4</td>
<td>0.38</td>
</tr>
<tr>
<td>3.8</td>
<td>4.0</td>
<td>0.82</td>
</tr>
<tr>
<td>4.1</td>
<td>5.8</td>
<td>0.80</td>
</tr>
</tbody>
</table>

*The uncertainties in the power are ± 0.2 Watt.

Figure 15: The intensity of the LIF signal as a function of the laser energy for both the pinhole and the lens. For the pinhole the spotsize of the laser is 0.79 ± 0.2 mm² and for the lens the spotsize is 0.066 ± 0.02 mm².
4 Results and discussion

Different conditions of the APPJ are changed to investigate the influence of these conditions on the LIF intensity and the NO density. In section 4.1 a position scan of the plasma is shown, in section 4.2 the influence of the input power is explained and in the last section of this chapter the results of the temperature measurements are shown.

4.1 Position scan

To get an idea of the distribution of the NO in the plasma a position scan for both plasma with the ring electrode and the plate electrode is made. The LIF intensity is measured at different axial and radial positions in the plasma. A position scan of the plasma with the plate electrode is pictured in figure 16 and a position scan of the plasma with the ring electrode is pictured in figure 17.

![Position scan of a plasma generated in 1 slm Ar with 2% air and the plate electrode attached. The power in the plasma is 4.4 Watt. The length of the plasma is approximately 14 mm and the width is 1 mm. The values of the colorbar correspond to the NO density in ppm. The plate is positioned at the X-axis.](image)

Figure 16: Position scan of a plasma generated in 1 slm Ar with 2% air and the plate electrode attached. The power in the plasma is 4.4 Watt. The length of the plasma is approximately 14 mm and the width is 1 mm. The values of the colorbar correspond to the NO density in ppm. The plate is positioned at the X-axis.
Figure 17: Position scan of a plasma generated in 1 slm Ar with 2% air and the ring electrode attached. The power in the plasma is 7.3 Watt. The length of the plasma is approximately 5 mm and the width 1 mm. The values in the colorbar correspond to the NO density in arbitrary units.

As one can see the maximum NO density is at 11 mm for the plate electrode and equals 1.6 ppm. For the ring electrode the maximum NO density is 0.5 mm above the glass tube. For both electrodes the maximum is at 0 mm radial position, which corresponds to the middle of the plasma. An explanation for the higher maximum NO position in the plasma with the plate electrode can be that the plasma is drawn out of the glass tube by the plate electrode.

The lengths of the visible part of the plasma are 14 mm and 5 mm respectively for the plasma with the plate electrode and the ring electrode. From the position scans one can see that there is still NO present at these positions. For the plate electrode 1.3 ppm NO is present at the tip of the plasma, this is a reduction of approximately 20% compared to the NO density at the maximum. For the ring electrode the NO density is reduced by a factor 2 at the tip of the plasma compared to the maximum. For the plate electrode the NO density 14 mm above the tip of the plasma is 0.6 ppm NO, this is a reduction of a factor 3 compared to the maximum. For the ring electrode the NO is reduced by a factor 8 at 11 mm above the tip of the plasma compared to the maximum. The densities in ppm are just an indication of the order of magnitude, since the calibration measurement is performed another day. The difference in the plasma conditions for both days are about 10%. The fact that a temperature correction isn’t performed also contributes to the large inaccuracy. The error margin of the densities is estimated at 40%. Relatively the densities are more accurate, since relative densities don’t depend on the calibration measurement. Due to the temperature the error margin of the relative densities has a maximum of 30%.
4.2 Power measurements

To investigate the influence of the power on the NO density a scan from 226.125 nm to 226.145 nm is made at different positions in the plasma. For the plate electrode these positions are 5, 6, 8, 10 and 12 mm from the glass tube and for the ring electrode these positions are 1, 2, 3, 4, 5 and 7 mm from the glass tube. The result of the measurements for the plate electrode is shown in figure 18a and the result for the ring electrode in figure 18b.

For the plate electrode the plasma gets longer when the power is increased. As one can see from figure 18a the position corresponding to the maximum NO density shifts upwards when the power is increased. This is probably a result of the growing length of the plasma. The value of the maximum NO density also increases when the power is increased. For the ring electrode the maximum NO density is right above the glass tube as shown earlier in section 4.1. The NO density is again higher for higher powers. The length of the plasma with the ring electrode varies just a little bit for different powers. In figure 19 a plot of the length of the visible part of both plasmas as a function of the power is shown. At the tip of the plasma, which will be in contact with the tissue during a treatment, a higher power leads to a higher NO density. An explanation for this phenomenon can be that at higher powers there is more energy for the production of NO in the plasma.

The error in the densities is estimated at 40% for the same reasons mentioned in section 4.1. The error margin for the densities measured for the ring electrode at powers higher than 4 Watt is estimated at 50%, since the temperature and therefore the error caused by not correcting for the temperature is higher.

Figure 18: The NO density measured for different positions and different powers. The used flow is 1 Argon plasma with 2% air.
4.3 Temperature measurements

The rotational temperature turns out to be a good approximation for the gas temperature (the heavy particle translational temperature). The reason for this is that rotational energy transfer is mainly caused by collisions with heavy particles. It is also often assumed to be fast enough to create thermodynamic equilibrium between the heavy particles and the rotational distribution.

To measure the temperature in the plasma an excitation scan from 226.3 nm to 226.95 nm is measured. This large scan range is chosen, because this makes it easier to make a fit through the measured spectrum. The fits of two spectra (one for the plasma with ring electrode and one for the plasma with plate electrode) are pictured in figure 20 and figure 21. From the fitted spectrum the temperature is determined following the procedure described in section 2.5.

The temperature is measured for different conditions of the power and the delay time. The results of these measurements are shown in figure 22. The error margins pictured in this figure are the 95% intervals (2σ) given by the Matlab fit function. For the plate electrode the temperatures are the same within the uncertainties for each condition. The measured temperatures for the plate electrode are compared to Rayleigh scattering measurement performed by Sven Hofmann et al in a pure Argon plasma. [9] The temperatures were equal within the error margin. This is shown in figure 23. For the ring electrode the temperature seems to increase for different powers. More data points are desirable to confirm this assumption. A possible explanation for the increasing relation is that the length of the plasma doesn’t change much as a function of the power, which leads to a higher power density compared to the plate electrode. This is shown in figure 24, where the power density is plotted as a function of the length of the plasma. The measured temperatures can deviate from the real gas temperature. Rotational peaks in the spectrum are assumed to be distributed
according to a Boltzmann distribution, but the peaks do not always perfectly fit to the theoretical Boltzmann distribution.

For both plasma a different delay time results in the same measured temperature. A possible explanation for this result is that the time scale of a pulse is much shorter than the time scale of the gas flow. Therefore measurements performed during the plasma on time and during the plasma off time give the same result.

In figure 25 the influence of the temperature on the NO density is shown. For the plasma with the plate electrode attached there is no obvious relation between the temperature and the NO density. For the ring electrode the density seems to be higher for higher temperatures. Again more data points are desirable to confirm this.

Figure 20: LIF spectrum of NO in an Argon plasma with 2% air and the plate electrode attached. The power in the plasma is 5.3 Watt and the axial position is 7 mm. The rotational temperature is $420 \pm 13$ K.
Figure 21: LIF spectrum of NO in an Argon plasma with 2\% air and the ring electrode attached. The power in the plasma is 5.4 Watt and the axial position is 1 mm. The rotational temperature is 506 ± 11 K.

Figure 22: The temperature measured for different powers and different delay times for both the plate electrode and the ring electrode. The temperatures and uncertainties are determined by fitting the spectrum with Matlab. The plasma is an Argon plasma with 2\% air. The axial position is the position with the maximum amount of NO.
Figure 23: The temperature measured for different powers by the use of LIF for a plasma generated in Ar with 2% air and by the use of Rayleigh scattering for a pure argon plasma by Hofmann et al.

Figure 24: The power density as a function of the length for both the plasma with the plate electrode and the plasma with the ring electrode.
Figure 25: The NO density as a function of temperature for both the plasma with the plate electrode and the plasma with the ring electrode. The delay time was set at 30 µs. The plasma was generated in a mixture of Argon with 2% air. The errors in the NO density (in arbitrary units) are caused by not correcting for temperature.
5 Conclusion

In this research NO densities in an atmospheric pressure plasma jet are measured by using laser induced fluorescence. Several conditions are changed to investigate the effect on the NO density. The density is determined with the use of the measured LIF intensities. A calibration measurement is needed to determine absolute densities. Every measurement is executed for both the plasma with the ring and the plasma with the plate electrode.

From the position scans one can see that the NO maximum is just above the glass tube for the ring electrode and higher in the plasma for the plate electrode. For both plasmas there is still NO at the tip of the plasma. (The lengths are 5 mm and 14 mm for respectively the plasma with ring electrode and plate electrode). This is desirable for wound treatment, since NO stimulates wound healing and the tip of the plasma is in contact with the tissue during a treatment. When the plate electrode is used the NO density is decreased by 20% at the tip of the plasma compared to the maximum and when the ring electrode is used this density is decreased by a factor 2.

For the plate electrode the position with the maximum intensity depends on the power. For higher powers the plasma is longer and the position corresponding to the NO maximum is positioned higher in the plasma. The absolute NO density increases when the power increases from the maximum density position. For the ring electrode the maximum position is right above the glass tube. For every position the NO density is higher for higher powers. For the plate electrode the NO density varies from 0.25 ppm for 0.6 Watt to a maximum of 0.9 ppm for 3 Watt. For the ring electrode the densities vary from 0.2 ppm for 1 Watt to 1 ppm for 6 Watt. The error margin of the absolute densities is about 50%. An important result of the power measurements is that the NO density can be adjusted by adjusting the power of the plasma jet in both geometries.

Accurate temperature measurements are important, since the time averaged temperature should be below 315 K for the application. For the plate electrode the temperature seems to be constant for different powers. The gas temperature is approximately 420 Kelvin at the position corresponding to the maximum NO density. This is too hot for a wound treatment. For the ring electrode the power has influence on the temperature. For a power of 5.4 Watt the temperature runs up to even 500 Kelvin, which is way too hot for a wound treatment.

It is desirable to have a high NO density in the plasma for wound treatment, since NO improves wound healing. For the ring electrode more NO can be accomplished by increasing the power, but increasing the power seems to increase the temperature too. For the plate electrode it is possible to increase the power, without changing the temperature too much. In the plasma with the plate electrode the temperature has no obvious effect on the NO density, but in the plasma with the ring electrode the NO density seems to be higher for higher temperatures. The plasma conditions used in this research are not suitable for wound treatment since all measured temperatures are above 315 Kelvin. The relation between the axial position and the temperature is not investigated, so it is not known if there is a position in or above the plasma where the temperature
is suitable for a wound treatment. The measured temperatures can deviate from the real gas temperatures since the assumption of a Boltzmann distribution is used to fit the spectrum while the peaks in the spectrum do not always perfectly fit to the theoretical Boltzmann distribution.
References


