Comparison of active and passive spectroscopic methods to investigate atmospheric inductively coupled plasmas

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Abstract

A comparison of Thomson and Rayleigh scattering, diode laser absorption and line emission measurements is performed on a 100 MHz atmospheric argon-flowing inductively coupled plasma. The parameters, which are measured in two or more ways, are the electron density, the electron temperature and the heavy particle temperature. The optimized diagnostics show the same behavior for the electron density and temperature. Nevertheless, the Thomson scattering diagnostic is the best at retrieving the radial profile. The heavy particle temperature, as measured by using both Rayleigh scattering and diode laser absorption, is identical within the estimated errors. The technique of measuring the temperature during power interruption, with both Thomson scattering and emission spectroscopy, shows that the electron and heavy particle temperatures are not equal during the period of power interruption.

Keywords: Diode laser absorption; Inductively coupled plasma; Plasma diagnostics; Pulsed plasmas; Thomson scattering

1. Introduction

Inductively coupled plasmas are widely used for spectrochemical analysis and material treatment and might be used in future as light sources. Since the knowledge on the fundamental behavior of the inductively coupled plasma (ICP) will improve its applicability, information on the temperatures and particle densities in the plasma is indispensable. In this article we present a study on a 100 MHz argon-flowing atmospheric ICP. The three main parameters, the electron density \(n_e\), electron temperature \(T_e\) and heavy particle temperature \(T_h\) are measured using several techniques. Such a comparative study allows the estimation of the quality of the techniques used and gives more insight into the plasma itself. Moreover, once the validity region of the various techniques is known, they can be used for other plasmas with comparable plasma conditions.

Recently, a new set of diagnostic methods has been developed and implemented in our laboratory. The techniques can be divided into active techniques, Thomson and Rayleigh scattering (TS and RS) and diode laser absorption (DLA), and passive techniques, H\(_2\)-line broadening (HB) and absolute line emission intensity (ALI) measurements. Thomson and Rayleigh scattering make it possible to measure \(T_e\), \(n_e\) and \(T_h\) locally \[1\]. A second way to determine \(T_h\) is the method of Thomson scattering in combination with power interruption of the generator (TSPI) \[2\]. The diode laser absorption diagnostic \[3\] is built to measure \(n_e\) and \(T_h\). Beside these active methods,
earlier implemented passive techniques like ALI and HB are expected to be useful as well. Absolute line emission spectroscopy [4] is used to calculate $n_e$ and $T_e$. A combination of this method with the power interruption [5–7] (LIPI) can be used to estimate $T_h$. Finally, the HB method [8] is applied for measuring $n_e$. In this article, we will first briefly explain the used diagnostics and then continue with a comparison and discussion of the results. The results of the power interruption experiment makes a discussion on the behavior of $T_e$ during the switch-off period necessary. This can be found in Section 4.4.

2. Applied diagnostics

The laboratory is equipped with several techniques which can be applied to various kinds of small plasmas. These plasmas are placed on a table which can be moved horizontally and vertically. The main advantage of moving the plasma is that the diagnostics have a fixed detection volume and realignment is not required. An exception is the DLA diagnostic, for which a stepper motor-controlled moving mirror is used to measure at each lateral position. The different diagnostics can be controlled using one single PC486 computer and no changes in the setup are necessary when switching to another experimental technique. This makes a fast data acquisition possible and implies that all techniques can be used within 1 day, which is desirable in order to reduce errors due to the non-reproducibility and instability of the plasma itself. In Fig. 1 the experimental setup is depicted, showing all the diagnostics used. The detection volume and the relative position of the instruments can be easily recognized.

An overview on the experimental methods used, together with their measured parameters is given in Table 1. These methods will be briefly introduced now, but for a detailed description we refer you to corresponding earlier publications.

### Table 1

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Preferred</th>
<th>Alternative</th>
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<tbody>
<tr>
<td>$n_e$</td>
<td>TS</td>
<td>ALI, HB</td>
</tr>
<tr>
<td>$n_h$</td>
<td>RS</td>
<td>ALI</td>
</tr>
<tr>
<td>$T_e$</td>
<td>TS</td>
<td></td>
</tr>
<tr>
<td>$T_h$</td>
<td>RS</td>
<td>DLA (TSPI, ALI + LIPI)</td>
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<tr>
<td>$T_e^*$</td>
<td>TSPI</td>
<td>ALI + LIPI</td>
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TS: Thomson scattering, RS: Rayleigh scattering, TSPI: Thomson scattering during power interruption, DLA: diode laser absorption, HB: $H_2$ broadening, ALI: absolute line emission intensities, LIPI: line emission intensities during power interruption. Since the electron temperature during power interruption turns out not to be equal to the heavy particle, temperature, diagnostics for both $T_e^*$ and $T_h$ are given.

Thomson and Rayleigh scattering is the scattering of incident light on, respectively, free and bound electrons. Since the scatter efficiency is
extremely low (for Thomson scattering about $10^{-14}$), the light source has to be powerful and the detector very sensitive. In the setup used a 10 Hz pulsed Nd: YAG laser at doubled frequency (532 nm) acts as the source, having an energy of 0.45 J per pulse. The scattered light is detected by an intensified one-dimensional photo diode array, allowing quick measurements and giving spectra of the scattered signal with a resolution of 0.14 nm. Note that both Thomson and Rayleigh measurements are local measurements since the scattered signal is detected under 90° with the incident laser beam.

2.1.1. Thomson scattering (TS)

The Thomson scattered photons are broadened by the Doppler effect, so that the width of the wavelength profile gives the electron temperature. After calibration the total number of scattered photons determines the electron density. The measurements are fitted using an expression [9,10] that includes collective scattering, which is required due to the relatively high electron densities and low temperatures in the ICP. For a detailed description of the setup and calibration procedure we refer to Ref. [1].

By performing TSPI, we are able to measure the temperature of the electrons directly (5 μs) after the removal of the energy input. This temperature $T_e$ gives an indication of the steady state value of the heavy particle temperature $T_h$. The method of measuring $T_e$ has been published earlier [2].

Inaccuracies in the temperatures obtained by TS and TSPI are about 150 K. However, the reproducibility of the plasma conditions brings the total inaccuracy toward about 500 K. The inaccuracy in the electron density is about 15%, including reproducibility of the plasma.

2.1.2. Rayleigh scattering (RS)

The same setup can be used for measuring RS. This signal is in principle Doppler broadened, but since RS originates from electrons bound to heavy particles the corresponding broadening is much smaller than that of the free electrons (Thomson) and can therefore not be resolved by this setup. Nevertheless, RS can be used in atmospheric plasmas to measure $T_h$. This method has been performed by Huang and co-workers [11,12] on ICPs. The basis of the method is the ideal gas law in combination with constant atmospheric pressure.

The starting point is measuring the number of Rayleigh scattered photons on argon ($I_{off}$) at room temperature ($T_r$) when the plasma is off. If the plasma is switched on, the Rayleigh scattering intensity ($I_{on}$) will decrease since the temperature increase at constant pressure will be accompanied by a decrease in the particle density. More specifically, the ratio of the temperatures with plasma on ($T_h$) and off ($T_r$) is equal to the ratio of the particle density with plasma off ($n_h$) and on ($n_h$), that is $T_h = T_r(n_h/n_h) = T_r(I_{off}/I_{on})$, as can be found using the ideal gas law $p = nk_BT$. Since the density is directly proportional to the total number of scattered photons, i.e. the detected signal and the scattered intensity at room temperature are known, the heavy particle temperature can be calculated.

There is one important disturbing phenomena in this procedure and that is the presence of stray light generated by improper reflections on several optical components. This stray light enters the detection system in the same way as RS does and since both coincide within the apparatus profile, they cannot be distinguished from each other. Therefore, in practice, additional measurements on a different gas like He are performed to estimate the amount of stray light. It is obvious that a lot of attention is paid to reduce the stray light. Reducing the detection angle appears to be most effective, since, due to the nature of stray light, it decreases relatively more than the Rayleigh signal does. The RS method for the determination of $T_h$ has an inaccuracy of about 8%.

2.2. Diode laser absorption (DLA)

A diode laser is used to measure the absorption profile of an argon line [13]. By selecting a diode laser with a wavelength corresponding to a transition, like the measured 4s$^2$P$_2$ → 4p$^3$D$_3$ (811.53 nm), the wavelength of the laser can be scanned around the line by varying the current through the laser. Pointing the laser beam through the plasma and detecting the intensity, the absorption coefficient...
can be obtained as a function of wavelength. Note that Abel-inversion is needed to obtain local values of the absorption coefficient. The measured absorption profile can be fitted with a Voigt function, containing a pressure broadened Lorentzian-shape profile and a Doppler broadened Gaussian profile. The width of the latter profile can easily be used for determination of the heavy particle temperature as a function of the radius of the plasma. The resulting temperature is accurate to within 10%, except in the center of the plasma (r < 3 mm), where due to Abel-inversion the inaccuracies are higher. In principle, the Lorentzian part of the profile obtained by diode laser absorption can be used for the determination of \( n_e \) if other broadening mechanisms than Stark broadening can be neglected. However, in the open ICP, Van der Waals broadening turns out to be important as well and using DLA for \( n_e \) determination becomes difficult. For further details concerning the absorption diagnostic and the Van der Waals broadening effect we refer to Ref. [3].

### 2.3. Optical emission spectroscopy

Optical emission spectroscopy presents a class of techniques for which the plasma is not probed by an external source. The setup consists of a set of lenses and mirrors that images the plasma on the entrance slit of the 1 m monochromator. This slit has a width of 100 \( \mu \)m for line intensity measurements (absolute (ALI) and during power interruption (LIPI)) and 10 \( \mu \)m for the H\textsuperscript{\textsc{ii}} measurements (HB). For the ALI and HB measurement a two-dimensional CCD-array (SBIG, type ST6-UV) is used. The CCD-array, cooled at \(-28^\circ\text{C}\), allows the measurement of the emission intensity as a function of wavelength of the whole radius of the plasma (8.8 mm) at once, as is depicted in Fig. 2. The wavelength window is 5 nm broad whereas the resolution of 0.02 nm is determined by the size of one pixel (25 \( \mu \)m). This setup is calibrated absolutely using a tungsten ribbon lamp. For the LIPI experiments we use another detector mounted on the same monochromator, namely a photomultiplier (Hamamatsu R376) in combination with a multichannel scaler to measure time-resolved emission information with a resolution of 2 \( \mu \)s. Note that the lateral data of the absolute line emission and HB experiments has to be Abel-inverted in order to obtain radial information on the parameters.

#### 2.3.1. Absolute line emission intensities (ALI)

The intensity measurements of several emission lines together with their transition probabilities yield absolute values for the number densities \( \eta(p) \) of the corresponding states. The \( \eta(p) \) values as a function of ionization potential show the atomic state distribution function (ASDF). If the population of these levels obey Saha’s law [4,14], the ASDF can be used to calculate \( T_e \) via the slope. Under the assumption that \( n_e = n_i \) (\( n_i \) the ion density), \( n_e \) can be determined using the Saha equation,

\[
\eta(p) = \frac{h^3}{2g_+ (2\pi m_e k_B)^{3/2}} \frac{n_e^2}{T_e^{3/2}} e^{\left(\frac{T_e}{k_B T_e}\right)}
\]

The constants \( k_B, m_e \) and \( h \) have their usual meaning, \( g_+ \) is the degeneracy of the ion ground state and \( I_p \) is the ionization potential of state \( p \). In the present experiment the 8d–4p (506.0 nm), 7s–4p (588.9 nm), 5d–4p (518.8 nm) and 7d–4p (531.8 nm) transitions are measured and the corresponding levels are verified to be in Saha-equilibrium [15,16]. However, the results have an inaccuracy of about 15% in \( T_e \) and \( n_e \).

#### 2.3.2. Line emission response to power interruption (LIPI)

The response of the line emission intensity to the power interruption of the generator can be used to determine the ratio \( \gamma^* = T_e/T_e^* \), in which \( T_e^* \) is the
temperature of the electrons just after the power interruption. Performing these measurements using a photomultiplier in combination with a multichannel scaler, the emission is registered as a function of time, showing a nearly instantaneous jump upward at the moment of power interruption. This jump is induced by the sudden change in temperature of the electrons from $T_e$ to $T_e^*$, while the electron density stays more or less constant during this cooling period of about 5 $\mu$s. Assuming Saha before ($t = 0$ s) and 5 $\mu$s after the elimination of the electromagnetic field, the size of the jump, i.e. the ratio of the intensity with power on ($\eta(p)$) and off ($\eta(p)^*$) will give the ratio $\gamma^* = T_e/T_e^*$, since [5,6]

$$\ln\left(\frac{\eta(p)}{\eta(p)^*}\right) = \frac{\gamma^* - 1}{k_B T_e} I_p + \frac{3}{2} \ln \gamma^*$$  \hspace{1cm} (2)

which can be obtained by taking the ratio of Eq. (1) for power off and the steady state (on). This method is introduced by Gurevich and Podmoshenski [17] and is among others used by Fey et al. [6]. Just as in the case of ALI measurements, the data has to be Abel-inverted. For the measured plasma conditions the inaccuracy in $T_e/T_e^*$ turns out to be better than 10%. Unless there are other mechanisms which heat the electrons during the off period, we may assume that $T_e^* = T_h$.

2.3.3. $H_\beta$ broadening (HB)

In an open ICP hydrogen lines are always present. These lines can be used to measure the electron density with an $f = 1$ m monochromator since they are more broadened than the width of the apparatus profile of this setup. For the $H_\beta$ line (486.13 nm), the Stark broadening mechanism dominates over the Doppler and other broadening processes. An example of an HB measurement is shown in Fig. 3. With the same setup the emission from a pure argon closed ICP [18] (likely to contain significantly less hydrogen) is measured. This might indicate that the presence of a background emission on the right side causes the asymmetry of the profile. Using the Stark broadening theory of Griem [19], and work of Vidal et al. [20] and Czernichowski and Chapelle [21] the width of the $H_\beta$ line can be converted to electron density.

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**Fig. 3.** An example of the $H_\beta$ profile representing an electron density of $1.28 \times 10^{21}$ m$^{-3}$ measured at $r = 6$ mm and $h = 7$ mm ALC. The dotted line is the emission as obtained from a pure argon-filled, closed ICP, presumably without the presence of hydrogen, so probably indicating the origin of the asymmetry of the $H_\beta$ profile.
The ICP is created by the inductive coupling of energy into an argon gas flow. The quartz torch, with an inner diameter of 18 mm, has three concentric tubes and is positioned in a coil of two windings, see Fig. 4. The coil is fed by a 100 MHz RF generator developed by Philips and operates at a typical input power of 1.2 kW. The three flows can be controlled separately. The outer flow (12 l/min) serves as the main gas supply and avoids the contact between the plasma and the quartz torch. The intermediate flow (0.3 l/min) lifts the plasma a few millimeters, whereas the central flow (0.6 l/min) can be used to introduce nebulized analytical solutions into the plasma. Although we used this central flow, no nebulized water was introduced in the present work, and all measurements were performed on a “dry” argon plasma. The measurements were performed at 7 mm above the load coil (ALC) as a function of the radius (0 < r < 9 mm).

4. Results and discussion

The measurements were carried out at 7 mm above the load coil (ALC), i.e. 2 mm above the end of the quartz torch. The advantage of measuring just above instead of through the torch is clear for all diagnostics, but certainly important for Thomson and Rayleigh scattering. However, it should be realised that since the plasma operates in open air, a small contamination of nitrogen and water vapor will be present especially near the edge of the plasma. A point of attention is the reproducibility of the ICP itself. The inaccuracy is limited in both power ($\delta P = 0.1$ kW) and radial position ($\delta r = 0.4$ mm). A change in power of 0.1 kW has a significant influence on the electron temperature (300 K) as measured by Thomson scattering experiments. The inaccuracy in the radial position limits the accuracy in the plasma parameters if gradients are large, e.g. for $n_e$ at the edge of the plasma. To determine the quality of the various diagnostics we will discuss the determination of each parameter successively and finish with a discussion on the behaviour of $T_e$ during power interruption.

4.1. Comparison of the $n_e$ values

In Fig. 5 the electron density profiles are shown
Fig. 5. The electron density as a function of radial position measured by Thomson scattering, absolute line intensities and H_β broadening. The measurements are performed at 7 mm ALC with an input power of 1.2 kW.

As obtained by TS, ALI and HB methods. The inaccuracies are shown as error bars. It is found that for 3 < r < 6 mm the $n_e$ values of TS, ALI and HB reasonably agree with each other within the error bars. However, from Fig. 1 it can be seen that the $n_e$ values as obtained by ALI and HB in the center (0 < r < 3 mm) are either not available (ALI) or lie systematically lower than the results of TS (HB). This is due to the Abel-inversion. In contrast with TS, ALI and HB measurements have to be Abel-inverted, so that the accuracy of these techniques decreases toward the center of the plasma. Therefore, $n_e$ can hardly be determined with these techniques in the center of the plasma at 7 mm ALC, and TS is expected to be the most powerful since the TS setup directly gives local values for $n_e$.

Of course, there are limitations in the accuracy for all three diagnostics. Thomson scattering provides electron densities with an accuracy mainly determined by the calibration. This results in a systematic inaccuracy which is the same for all positions. Moreover, at the edge of the plasma ($r > 7.5$ mm), the Thomson scattered profile itself will be disturbed by the presence of air. The temperatures at the edge of the plasma are low enough to keep the molecules intact. These molecules are responsible for a Raman scattered signal. Both Thomson and Raman signals are weak since the temperatures and densities of the species are low, making it impossible to discern RS from TS. As a result, the electron densities by TS are always overestimated at the edge of the plasma. A third inaccuracy in $n_e$ obtained by TS is introduced by the instability of the setup. An in-time changing laser beam alignment directly influences the $n_e$ determination. In the present results this influence is estimated to be smaller than 10%.

The electron density as determined by ALI requires the assumption of $n_e = n_i$, where $n_i$ represents the number density of argon ions. If there are other ions present than Ar^+, this assumption will be invalid and leads to an underestimation of $n_e$ by
Fig. 6. The electron temperature as a function of radial position measured by Thomson scattering and absolute line intensities. The measurements are performed at 7 mm ALC with an input power of 1.2 kW. Note that the complete radial structure is only obtained with Thomson scattering.

4.2. Comparison of the $T_e$ values

The electron temperature values are shown in Fig. 6. Thomson scattering provides accurate values for $T_e$ ($\Delta T_e < 150$ K), which are only affected by RS at the edge of the plasma ($r > 8$ mm). Another problem at the plasma edge is the presence of large gradients. These are not easily measurable since the detection volume (a radius of about 0.5 mm) of the diagnostic is rather large.

Compared with TS, $T_e$, as obtained by ALI, does not give a smooth radial profile. This can be partially due to the applied Abel-inversion routine. Since $T_e$ is estimated by the slope of the Boltzmann plot (the logarithm of the density versus ionization potential), which equals $1/k_B T_e$, the temperature is very sensitive to a small variation in the slope, especially if $T_e$ is high. The slope is strongly influenced by taking levels into account which are not populated according to Saha. In order to be sure that levels are in partial Local Saha Equilibrium (pLSE) only those levels are involved which are...
4.3. Comparison of the \( T_h \) values

As shown in Fig. 7, the heavy particle temperature measured using diode laser absorption and RS shows good agreement. Rayleigh scattering shows the most accurate profile of which the accuracy is limited by the influence of possible stray light. However, after minimizing, the amount of stray light turns out to be negligible as is verified by measuring RS on helium gas, having a 61 times smaller cross-section than argon. The uncertainty in this measurement together with the stability in alignment of the system determines the final inaccuracy of the RS method to about 8%.

The method of diode laser absorption has also proved to be a powerful tool for obtaining \( T_h \). However, with this method the scatter in \( T_h \) is large compared with the scatter in temperatures as measured by RS. This scatter originates from inaccuracies in the measured absorption profiles which are enlarged by the Abel-inversion process.

The third method of obtaining \( T_h \) is TSPI using the assumption that immediately after the power is interrupted \( T_e \) drops down to \( T_h \). This technique gives too high values for \( T_h \) (see Fig. 7), which cannot be due to the inaccuracies in the methods. Therefore, remarkably, we have to conclude that during the power interruption period the temperature of the electrons is not equal to the temperature of the heavy particles, but stays, depending on the radial position, 1000–2000 K higher (see next section). Note that the gradient in \( T_e \), the value of \( T_e \) just after the cooling period, is small compared to the gradient in \( T_e \) and \( T_h \).

4.4. Behavior of \( T_e \) during power interruption

In the last section it was found by TSPI that the
The electron temperature during power interruption ($T_e^*$) is not equal to $T_h$. The technique of LIPI shows the same behavior. The ratios $T_e/T_e^*$ obtained by TSPI and LIPI are shown in Fig. 8; error bars are included. The agreement of these two methods is within the experimental error. However, the ratio $T_e/T_e^*$ proves to be certainly not equal to the ratio $T_e/T_h$ as obtained by TS and RS (see Fig. 8). Therefore, we may state that after switching off the generator there are other sources of energy which keep the electrons at a higher temperature than the heavy particles. The three-particle recombination process is presumably responsible for the significant heating of the electrons during power interruption and is subject of future research [23].

The difference between the ratio $T_e/T_e^*$ and $T_e/T_h$ is striking and we can conclude that TSPI and LIPI can only be used for the determination of an upper limit for $T_h$. Unfortunately, the inaccuracies in $T_e$ as determined by ALI, and in $T_e/T_e^*$ as determined by LIPI are too large to give an acceptable value for $T_e^*$. For an estimation of the temperature of the electrons while the power is interrupted TS is the most accurate tool.

In Fig. 9 an overview is given of the temperatures of the different species in a stationary plasma and for the electrons at 5 μs after the power is switched off. The results in this figure are all obtained using the TS and RS diagnostics.

4.5. Heavy particle densities and ionization degree

Rayleigh scattering can also be used for measuring the heavy particle density $n_h$, as it is linear with the scattered intensity. The results are shown in Fig. 10. Of course, the radial profile is the inverted heavy particle temperature profile. Combining this information with the measured electron density we are able to calculate the ionization degree as a function of radial position. This is shown in Fig. 11. At 7 mm ALC the ionization degree is roughly 0.1% at
Fig. 9. Temperatures in the ICP as a function of radial position measured by Thomson and Rayleigh scattering. Shown are the steady state electron and heavy particle temperatures and the electron temperature during power interruption. Note that $T_e$ stays higher than $T_h$ during this period. The measurements are performed at 7 mm ALC with an input power of 1.2 kW.

Fig. 10. The heavy particle density as a function of radial position. The measurements are performed at 7 mm ALC with an input power of 1.2 kW.
Fig. 11. The ionization degree of the ICP as a function of radial position, obtained by a combination of the Rayleigh and Thomson scattering measurements.

5. Conclusions

The results of Thomson and Rayleigh scattering, diode laser absorption, $H_3^+$-broadening and absolute line intensity measurements are all in agreement within the experimental accuracy with respect to the electron density, electron temperature and heavy particle temperature. The scattering techniques turn out to be the most powerful in retrieving the shape of the radial profile since they measure locally. Nevertheless, the emission and absorption technique are quite useful due to their easy requirements with respect to the setup. Besides, the extensive mutual comparison of the results of the different techniques proves that the power interruption method can be applied for measuring the temperature of the electrons during power interruption. However, this temperature differs from the temperature of the heavy particles. This implies that the electrons remain at higher temperatures than the heavy particles when the power is interrupted, presumably by the energy gain of three-particle recombination processes.

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