Characterisation of an Ar-H$_2$-O$_2$ ICP by OES:
Measurement of the atomic concentrations of H and O

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Abstract. In order to characterize an inductively coupled plasma torch used in refining of metallurgical silicon, we have developed a spectroscopic method based on absolute emissivity measurements and Abel inversion. This method permitted to measure the concentrations of atomic hydrogen and atomic oxygen, which are among the reactive species involved in the purification process. Assuming LTE, the temperature profiles are deduced from the emissivity of the Argon lines. The concentration of atomic oxygen is deduced from the intensity ratio O/Ar. The hydrogen concentration measurement has to take into account the Stark broadening and the Doppler broadening of the hydrogen lines. The comparison between experimental and simulated line profiles permits to determine this concentration. The method has been tested on 2 kW and 30 kW inductively coupled plasma torches at atmospheric pressure. The results show that the concentrations of atomic oxygen and atomic hydrogen can be measured with an accuracy of 25%. The main disadvantage of this method is that, using emission, it does not permit to measure the concentration in the “cold” zone of the plasma, i.e. at the edges.

1. Introduction
Today the major part of silicon for solar cells is purified by the Siemens process. Since this process is energy and cost intensive there is a lot of research is being performed with the goal of replacing it by cheaper and energy saving methods. Segregation works well for removing metallic impurities but boron segregates only very little. For this reason the laboratory SIMAP is working on a purification process for metallurgical silicon which reduces especially the boron concentration.

The process (see Figure 1) uses electromagnetic stirring to transport the impurities to the surface (i). There the impurities react with the reactive gases (ii) forming volatile reaction products, which are evacuated with the gas flow (iv). The plasma torch (iii) heats up the gases argon (~96%), hydrogen (~3%) and oxygen (~1%) to about 10000K and generates so the reactive gases. J Degoulange studied the reaction paths of the boron with the reactive gases [1].

He found that the radicals, which are likely to be important for the purification, are atomic hydrogen H, atomic oxygen O and the hydroxyl radical OH. He also found that the way of injecting the gases into the different flows changes the reactivity of the plasma on a carbon target [2]. By optimizing the temperature and concentration profiles one can so improve the efficiency of the process. Our laboratory is therefore developing a numerical model for the simulation of the plasma. In parallel we do measurements in order to improve the model but also to improve the process directly by comparing temperature and concentration profiles with the purification efficiency.
There are different ways to measure the temperature and the concentration which are compared in a paper of Wiese [3]. We apply a method based on atomic emission spectroscopy with Abel inversion for the measurement of the radial temperature profile and the radial concentration profiles of atomic oxygen and atomic hydrogen.

The spatially resolved concentration measurement by emission spectroscopy was yet applied in the 1970’s to measure the spatial resolution of atoms in small plasma torches which are used for chemical analyses [4]. The interest of the research was focused more on the plasma parameters such as temperature, electron density and excited states density than on the concentration of the gases [5][6][7][8]. Therefore, and because of the assumption of LTE and symmetry, there are only a few papers using emission spectroscopy with Abel inversion for the measurement of the concentration. Other techniques like absorption spectroscopy and laser induced fluorescence (LIF) are often applied for the measurement of the concentration. The concentration of atomic oxygen and atomic hydrogen can be measured by two photons absorption laser induced fluorescence (TaLIF). This technique needs very high laser fluxes because the two photon absorption probability is weak and the spontaneous fluorescence which screens the TaLIF signal is high.

2. The method:

For the measurement of the temperature and the concentration we use the emissivity of atomic lines. We assume that the post-discharge zone of the plasma is in local thermal equilibrium (LTE). We will validate this assumption later with our results. In LTE one single temperature describes all energy modes (translational, electronic, ionization) for each coordinate. In plasmas this estimation is often false because of the high temperature gradients. Transport phenomena heat up and cool down the different energy modes differently. For example, electronic modes can be cooled down by emission of radiation for example. In atmospheric plasmas the collision rate is very high so that an LTE can be established between the different energy modes. For the establishment of LTE the transfer of energy by collisions must be much higher than the transfer of energy by electromagnetic radiation.
In LTE the Boltzmann distribution describes the distribution of the atoms on different electronic energy levels. The atoms in higher energy levels make spontaneous transitions to lower energy levels by emission of a photon. The emissivity of such a transition is the product of the concentration of the level, the transition probability $A_{ul}$ and the energy of the photon $\frac{hc}{\lambda}$:

$$
\varepsilon_{\text{line}} = n_u \cdot A_{ul} \frac{hc}{4\pi \lambda} = n_u \cdot g_u \cdot \exp\left(\frac{-E_u}{kT}\right) \cdot A_{ul} \frac{hc}{4\pi \lambda}
$$

Thus, the emissivity depends so only on the concentration of the atoms and on the temperature. We know the concentration of argon which is very close to 100%. Therefore we measure the total emissivity of the argon line at 420.07 nm to calculate the temperature. Then we measure the emissivity of the oxygen line at 436.82 nm and the hydrogen line at 486.13 nm. We use the ratio between the emissivities of the oxygen line and the argon line for the calculation of the relative concentration of oxygen. We use the same method for the hydrogen concentration. For the choice of the lines we took care to avoid interference, self-absorption and low emissivity. The parameters of the lines can be found on the NIST website [9]. We use the Abel inversion [10] to calculate the emissivity profile from the lateral intensity profile of the plasma. The absolute intensity of light is only rarely used because of the difficulty of precise calibration. In our case this is not a problem because a high error of a factor two on the calibration gives only a low error of 4% on the temperature and 11% on the concentration as we calculated by multiplying the emissivity by two at a temperature of 9000 K and an arbitrary concentration of atomic oxygen.

3. The experimental setup

3.1. The plasma torches

The two plasma torches each consist of three concentric tubes. The diameters are given in Table 1. The two outer tubes of the small torch a) are quartz tubes and the injector is made of alumina. The two inner tubes end at the height of the first turn of the inductor and the outer tube ends just above the last turn of the inductor and release the plasma into the air. We use a nebulizer to inject water into the small plasma torch and we can also inject oxygen. The inner and the outer tube of the big torch are water cooled copper tubes and the middle tube is a quartz tube. The outer tube is segmented in 8 parts so that it does not shield the magnetic field. It releases the plasma into a reactor chamber. The length of the injector can be adjusted to inject the gas directly into the plasma. We can inject argon, oxygen and hydrogen into the big torch.

| Table 1 Geometry of the two plasma torches |
|------------------------------------------|
| a) b)                                      |
| D1 external 30 mm 60 mm                   |
| D1 internal 27 mm 40 mm                   |
| D2 external 25 mm 37.5 mm                 |
| D2 internal 22 mm 33.5 mm                 |
| D3 external 4 mm 16 mm                    |
| D3 internal 2 mm 7 mm                     |
| D coil 37 mm 90 mm                        |
| L 41 mm 45 mm                             |
| Coil 5 turns 4 turns                      |
| $P_{max}$ 2 kW 30 kW                      |
| Flow 12 l/min 40 l/min                    |
3.1.1. The optical system
The light from the plasma is reflected by a mirror perpendicularly towards the monochromator. (See Figure 2) A lens focuses the light onto the entry slit of the monochromator. By turning the mirror we obtain a lateral intensity profile of the plasma. The distance between the mirror and the plasma is large compared to the diameter of the plasma. The small step size of the turning mirror allows us to measure get a lateral intensity profile of about 200 values for the small torch, which is good for the Abel inversion. For the calibration of the optical system we used a tungsten filament lamp after each measurement.

We opened the slits of the monochromator very wide (100µm) so that line broadening in the plasma is much smaller than the instrumental line broadening (FWHM=0.06nm). This works for the argon line and for the oxygen line. The Doppler broadening and the Stark broadening of the hydrogen line is large compared to the instrumental broadening. We used the assumption of LTE to calculate the width of the line with the measured temperature. For the Stark broadening we use the Saha equation for the electron density and a formula given by Griem [11] to calculate the line width. We assume that other broadening mechanisms are negligible.

![Figure 2 The optical system](image)

4. Measurement of the line broadening:
We measured the line shape of the lines we used for our measurement ([11]). The argon lines and the oxygen line have exactly the same shape which is the shape of the instrumental broadening. The shape of the hydrogen line is the convolution of the Lorentzian profile from the Stark broadening, the Gaussian profile from the Doppler broadening and the profile of the instrumental broadening. For the measurement of the Stark broadening we calculated the emissivity at different wavelengths and fitted a convolution of the unknown Stark broadening with the known Doppler and instrumental broadening. In this way we obtain the full width at half maximum of the Stark broadening (Figure 4).
We can see that the measured line broadening is consistent with the calculated line broadening, especially at high temperature where line broadening is large. The small differences may be due to the measurement method. As we know exactly the line broadening of all the lines we can calculate the total emissivity of each line directly from the emissivity at the central wavelength of the line. We need this total emissivity for the concentration and temperature measurement.

5. Results
All measurements were made at the outlet of the torches. We began the measurements on the small plasma torch (2 kW). First we measured the temperature for two different argon lines with different transition probabilities (415.9 nm and 420.1 nm). If there was a radiative depopulation of these energy levels we could see a difference between the two temperature profiles (Figure 5). As there is no difference between the two temperature profiles the radiative depopulation of the energy levels is negligible. The error bars are due to the uncertainty in the transition probability which is better than 25%. For small temperatures the emissivity is very low and stray light makes the measurement impossible. Therefore our spectroscopic measurement is limited to a minimum temperature which is about 2000K below the maximum temperature.

We also injected water into the auxiliary flow in order to see if we can measure the concentration (Figure 6). The profiles are flat, which shows us that the gases are well diluted. The ratio of the two concentrations is close to two which shows us that the assumption of LTE is good. The increase of the concentrations at the edge of the plasma is probably due to the dilution with ambient air but also deviations from LTE may play a role. The error bars represent the difference between the right side and the left side of the lateral profile. It is due to temporal variations and to small deviations from the symmetry.
We also tried to measure a concentration gradient. For this purpose we injected a high flow of a mix of argon and oxygen in the injector. The effect is a strong cooling of the centre of the plasma and a bigger diameter of the plasma (Figure 7) and a concentration gradient (Figure 8). The measurement is not very precise in the centre of the plasma, because of the low emissivity and the high temporal variations.

We continued the measurement with the big torch. When we injected a relatively small oxygen flow in the injector we also saw a concentration gradient (Figure 10) but the cooling of the centre is less important (Figure 9). Since the concentration of oxygen in the measurement is very low the error bars are large. This is because of the high intensity of the background and of temporal variations. The measurement shows us that, with the injection of the reactive gases direct into the plasma, even a small flow rate results in a higher concentration in the centre. A higher concentration of reactive gases in the centre of the plasma is probably not good for the purification. We can use the method to study how we can get a better dilution of the gases.
In order to check the precision on the absolute concentration we injected a homogenous mix of argon and oxygen in all flows of the plasma torch so that we can compare the measured concentration to the injected concentration. We adapted the voltage of the generator so that the power injected rest constant. We show in Figure 11 the measured concentration for several different injected concentrations. The measured values are very close too the injected concentrations. This shows us that the plasma is very close to local thermal equilibrium and that our method works.

The differences can be due to different effects:
- the imprecision of the flow meters (rotameter)
- deviations from the symmetry
- temporal variations
- deviations from LTE

Figure 11 Concentration profiles of atomic oxygen for different injected ratios (Big torch, Ar+O₂)
6. Conclusion
The results showed that the examined plasma torches are very close too LTE. Therefore the method presented here permits the measurement of the concentration of the gases in an inductively coupled plasma torch with an absolute precision of better than 25%. The method is limited by stray light to the hot part of the plasma where the emissivity is high. The main sources of stray light are the backside of the reactor chamber and the mirror. These stray light sources can be reduced so that a study of the colder zones is possible. We showed that the gases in the process torch are not well diluted. Therefore it should be possible to use the method to optimize the dilution for the purification process.

References
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