

THE EFFECT OF HYDROGEN ON THE SPATIAL INTENSITY  
DISTRIBUTION OF IRON LINES IN ANALYTICAL  
GLOW DISCHARGES

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**Abstract.** Analytical glow discharges running in pure Ar are commonly used for direct solid analysis and depth profiling. The analytical results can be very significantly affected by molecular gases (H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>) which are very often present in the discharge for various reasons. One approach to understanding of the processes involved when a small amount of H<sub>2</sub> is present in the discharge is to investigate the spatial intensity distribution of emission lines and the effect of H<sub>2</sub> on this distribution. Different processes take place in different parts of the discharge volume and affect thus different lines in various ways. The aim of this study was to investigate the effect of H<sub>2</sub> on spatial intensity distribution of different Fe and Zn emission lines but only Fe results are discussed in this paper.

## 1. INTRODUCTION

Analytical glow discharges (GD) in the so-called Grimm-type configuration have been used for direct solid sample analysis and for depth profile analysis of coated materials for several decades (Jakubowski et al. 2007). Elements present in the sample (the cathode of the GD source) are sputtered, excited and ionised in the discharge and information about the elemental composition of the sample is obtained either by an optical emission spectrometer (GD-OES) or by a mass spectrometer (GD-MS).

One of the areas of great importance is the effect of molecular gases (H<sub>2</sub>, N<sub>2</sub> and O<sub>2</sub>) on the characteristics of the analytical glow discharge (Martín et al. 2007, and references cited therein). These gases can be present in the discharge due to contamination of the gas, source and/or sample or as a constituent in the sample. The presence of a very small amount of molecular gas, in particular H<sub>2</sub>, affects the electrical characteristics of the discharge, the sputtering rate of samples and the intensities of emission lines sample and working gas atoms and ions. Such changes have a serious impact on analytical results. Therefore, it is necessary to study the discharge processes involved in order to interpret the analytical results correctly.

It has been shown recently that ionic emission lines of the sample with the total excitation energy<sup>1</sup> close 13.6 eV can be selectively excited in the Ar-H<sub>2</sub> discharge by an asymmetric charge transfer (ACT) reaction between the metallic atom and hydrogen ion (Steers *et al.* 2006). Furthermore, it has been observed that those Fe II lines which are in pure Ar excited by ACT with Ar ions are suppressed in the intensity in the presence of H<sub>2</sub>. Very recently, it has been also shown that some Fe atomic lines with the excitation energy close to 5.3 eV can be also selectively excited in the presence of hydrogen (Šmíd *et al.* 2008). In the standard configuration, the GD source is viewed ‘end-on’ and the light emitted from the end of the source is imaged on the entrance slit of the spectrometer. This means that an integrated intensity from the whole discharge volume is recorded. However, different discharge processes take place in different distances from the cathode; therefore, it is very useful to view the source ‘side-on’ and to study the spatial intensity distribution of sample emission lines.

In this paper, results obtained in the experiments with a modified Grimm-type glow discharge source for ‘side-on’ observations will be presented. Emission spectra in different distances from the cathode were recorded using Fe and Zn as a cathode material and mixtures of Ar with various H<sub>2</sub> concentrations were used as working gas; only the results on Fe emission lines are shown and discussed here.

## 2. EXPERIMENTAL

For the study of the spatial intensity distribution of emission line, a modified Grimm-type GD source was used; the anode tube has a longitudinal slot which can be observed via two viewing ports in a block inserted between the cathode plate and the anode body. The inner diameter of the anode tube is 8 mm. The gas was introduced into the source via a mixing unit consisting of a set mass flow controllers (5 ml/min, 50 ml/min and 500 ml/min, Bronkhorst) – which allowed mixing of pure argon with a premixed mixture of Ar with 2% v/v of H<sub>2</sub>. The source was powered by a dc power supply (MCN 350-2000, FuG) and run in the mode with constant voltage and constant current – 700 V & 10 or 20 mA. Pure Fe and pure Zn were used as cathode materials.

Optical emission spectra were studied using an Echelle spectrometer with CCD detection (ESA 3000, LLA Instruments GmbH). This spectrometer can record spectra in the spectral range between 200 and 1000 nm with resolution 5 pm at 200 nm and 27 pm at 600 nm. An ICCD (intensified charge-coupled device) camera was used as a detector. The image of the slit of the anode tube was focused with an achromatic lens on the entrance connector of an optical fibre. The lens and the optical fibre were firmly connected together and mounted on a stage whose position could be adjusted using a micrometer screw to view different positions along the anode slot. The spectra were always recorded in 12 positions from the cathode, the step was 0.5 mm close to the cathode (up to 4 mm from the cathode) and 1 mm further away (up to 7 mm from the cathode).

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<sup>1</sup>The total excitation is a sum of the excitation energy of the ion and the ionisation energy.

### 3. RESULTS

#### 3. 1. Fe I LINES

The axial distribution of intensities of Fe I lines is shown in Figure 1 (a) for selected lines and the discharge in pure argon at 700 V and 20 mA, the overall pressure was 4.0 mbar. The selection of the lines was made to cover the whole range of the excitation energies found in the spectra. The intensities were normalised to the maximum intensity of the corresponding line in the plot.

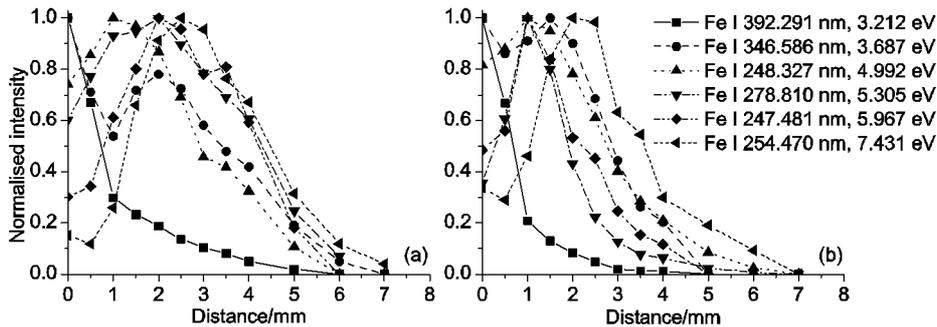


Figure 1: Axial intensity distribution of Fe I lines; (a) pure Ar, (b) Ar+0.3% v/v H<sub>2</sub>, the discharge conditions 700 V & 20 mA.

It is apparent that lines coming from different excitation energies show different intensity distribution. The line with the lowest excitation energy (Fe I 392.291 nm, 3.212 eV) has its maximum near to the cathode after which the intensity monotonically decreases. In the intensity distribution of the next two lines (Fe I 370.556 nm, 3.397 eV and Fe I 346.586 nm, 3.687 eV), the maximum intensity is still at the cathode but a second local maximum is developing approx. 2 mm from the cathode. The maximum intensity of the line with even higher excitation energy (Fe I 381.296 nm, 4.209 eV) is no longer at the cathode but approx. 1–2 mm from the cathode. The same is true for the next two lines (Fe I 248.327 nm, 4.992 eV and Fe I 278.810 nm, 5.305 eV). The intensity distribution of the last two lines shown in this plot (Fe I 247.481 nm, 5.967 eV and Fe I 254.470 nm, 7.431 eV) is different in that the intensity at the cathode is relatively lower than for the other lines and the maximum intensity is furthest away from the cathode (approx. 2.5 mm) compared to the other lines in this plot.

The different axial intensity distributions of various lines are most probably linked with different excitation processes involved in the population of the energy levels of the iron atoms. It has been reported (Bogaerts et al. 2000) that in the glow discharge atomic emission lines can be excited by two main excitation processes depending on the distance from the cathode: heavy particle excitation (fast argon ions and fast argon neutrals) and electron impact excitation. The first process appears mainly close to the cathode where heavy particles have enough energy whereas the latter process can only take place in the negative glow because there are few electrons present in the cathode dark space. Clearly, individual emission lines investigated have different

sensitivity to these two excitation processes. The lines with lower excitation energy can be easily excited by heavy particles (higher intensity near the cathode) whereas the lines with higher excitation energy can be excited mainly by collisions with electrons (higher intensity in the negative glow). The relative importance of these two processes gradually changes as the excitation energy increases.

In Figure 1 (b), the axial intensity distributions of the same set of lines in the same format are shown for Ar+0.3% v/v H<sub>2</sub> in the discharge at 700 V and 20 mA, the overall pressure was 4.7 mbar (compared to 4.0 mbar in case of pure Ar). The most obvious difference between the intensity distributions in pure Ar and in Ar+0.3% v/v H<sub>2</sub> is an overall shift of the intensity maxima closer to the cathode. Also, the peaks of the intensity distributions of the lines which have their intensity maxima further away from the cathode seem to be narrowed down in the presence of hydrogen. Furthermore, when the axial intensity distributions of the line selectively excited in the presence of hydrogen (Fe I 278.810 nm, 5.305 eV) were compared for pure Ar and Ar+0.3% v/v H<sub>2</sub>, it turned out that the maximum enhancement of this line was observed in the region between the cathode and 2 mm away from the cathode.

### 3. 2. Fe II LINES

Axial intensity distribution (normalised as in the Fe I case) of Fe II lines is shown in Figure 2 (a) and (b) for the discharge in pure Ar and in Ar+0.3% v/v H<sub>2</sub>, respectively. The discharge conditions were the same as those used for Fe I lines in the previous part.

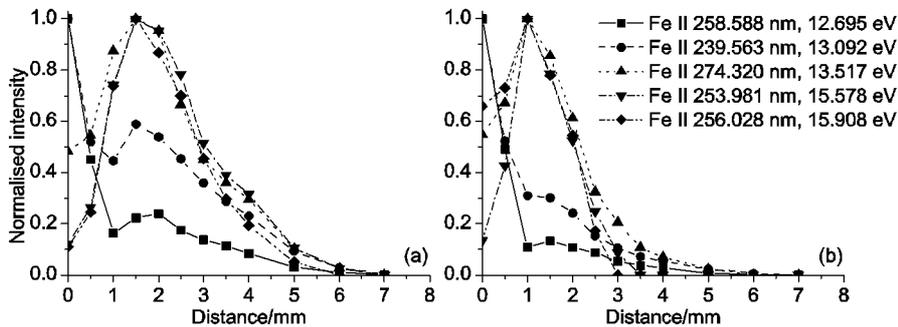


Figure 2: Axial intensity distribution of Fe II lines; (a) pure Ar, (b) Ar+0.3% v/v H<sub>2</sub>, the discharge conditions 700 V & 20 mA.

One can see in Figure 2 (a) a similar pattern to that observed in the case of Fe I lines, but the intensity drop at distances of 5-7 mm is more marked. The lines with relatively low excitation energy (Fe II 258.588 nm and 239.563 nm) have their intensity maximum near the cathode with a second peak at about 1–2 mm away from the cathode. For the other lines, the proportion between the intensities of the two peaks in the intensity distributions is changing in favour of the second peak further away from the cathode and the relative intensity of the lines near the cathode decreases with the increasing excitation energy. This again suggests that the relative importance of different excitation processes (heavy particle excitation and electron

impact excitation) changes with the excitation energy in similar way as in the case of Fe I lines.

When H<sub>2</sub> is present in the discharge (Figure 2 (b)), all axial intensity distributions are shifted closer to the cathode. Furthermore, the last three Fe II lines in the plot are in pure Ar discharge excited by ACT with Ar ions. It has been shown that hydrogen suppresses this reaction significantly (Steers et al. 2006). If the intensity distributions are plotted in arbitrary units, it can be shown that in Ar-H<sub>2</sub> discharge the intensities of these lines are dramatically reduced and this reduction mainly occurs between 1.5 and 2.0 mm from the cathode.

#### 4. CONCLUSION

The study of the axial intensity distribution of iron emission lines in the analytical glow discharge showed that the relative importance of different excitation processes differs depending on the excitation energy of the lines involved. The lines with relatively low excitation energies (up to 3.7 eV) can be easily excited by collisions with heavy particles (maximum intensity close to the cathode) whereas the lines with higher excitation energy are predominantly excited by collisions with electrons (the maximum intensity further away from the cathode). It has been also shown that the intensity distribution of the lines is shifted closer to the cathode in the presence of H<sub>2</sub>. A similar pattern has been observed for zinc emission lines.

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