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THE MONOCHROMATIZATION EFFECT – AN APPROACH TO SURFACE ANALYSIS BY GLOW DISCHARGE – OPTICAL EMISSION SPECTROSCOPY

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Over 20 years ago, our group reported on the selective emission of a single or very few spectral lines under certain plasma conditions. This was called the Monochromatisation effect (the M effect) and was observed experimentally in the visible region of the spectra. We report here for the first time on the wavelengths of Ne, Ar, Kr, Xe that present M-effect at 100 Torr total pressure. In this paper it is shown that this effect could play a major role in dc and rf glow optical emission spectroscopy (GD-OES) used as surface analytical tool. This work is intended to contribute to the optimization of this analytical technique for a better accuracy of surface analysis.

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1. Introduction

In-depth resolved analysis of layered materials using dc-glow discharge optical emission spectroscopy (GD-OES) or rf-GD-OES have attracted a great interest as analytical tool. Discharges in pure inert gases (especially argon) are currently employed in analytical GD sources.

Special attention has been recently devoted to investigate spectral changes due to the presence of hydrogen to the argon dc-GD. Hydrogen, along with other light gases inherently present in the surface analysis chamber was found to alter radiation emission yields of the analyte and of the carrier gas and also to decrease sputtering rate, causing losses in the accuracy of the method [1-4]. These phenomena have not been explained up to now.

Hydrogen traces were detected in GDS especially at the beginning of the analysis. They come from residual moisture in the analysis chamber and on the sample surface, hydrocarbons from vacuum oil pumps, hydrogen compounds present in the sample etc.

Spectral changes caused by the presence of hydrogen in d.c. glow discharges (dc-GD) and in dielectric barrier discharges (DBD) were investigated by our group. We have previously reported on the selective emission of very few (or, in some cases, of just one) intense spectral lines observed in certain plasma conditions. This was called the Monochromatisation effect (M-effect) [5-7]. We have reasons to believe that the M-effect can explain, at least partially, the effect of hydrogen on GD-OES analysis. This is based on the fact that, as will be shown later, excited and metastable atoms formed as a result of the M-effect can transfer energy to the analyte atoms and also to the carrier gas present in the GD plasma, changing their emission spectrum. Also, the equation governing the M-effect uses up the ions of the carrier gas decreasing the sputtering yield.

In this study, the impact of the M-effect on neon, argon, krypton and xenon, usually employed in GD-OES analysis as carrier gases was investigated.

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2. Experimental setup

A DBD discharge was used for analysis of the selective emission of neon, argon, krypton and xenon on addition of hydrogen.

Identical optical and electrical conditions were used for all gas combinations. The DBD was ignited in a plasma display pannel type reactor of 0.15 mm narrow-gap at 100 torr total gas pressure. The discharge was ignited using a 35 KHz square wave power supply having 1 kV peack to peack voltage. The emission spectra was acquired using an Optical Multichannel Analyser (OMA).

In order to characterise the M-effect, the M parameter of a spectral line was defined. This parameter was taken as the ratio of the intensities of two intense emission spectral lines in the spectrum of the plasma, the line at the denominator being taken as reference. It must be mentioned that any line in the spectrum can be taken as reference.

The emission lines that present M-effect were put in evidence by introducing the ratio μ of the M parameter calculated for the mixture with hydrogen of a certain pure gas and the M parameter of the pure gas. The emission lines with high values of μ (>2) are said to present M-effect. The evolution of the μ parameter with hydrogen addition in Ne, Ar, Kr and Xe discharges was investigated.

3. Results and discussion

The emission spectra of DBD discharges in four inert gases (Ne, Ar, Kr and Xe) and their mixture with hydrogen are discussed in the following. In order to compare the spectra before and after addition of hydrogen, the spectra were normalized to the maximum value of the line intensity.

It should be noted that the absolute values of all line intensities of all gases studied decreased on hydrogen addition. This effect is due to an electron cooling process in the plasma. It is also interesting to observe that there are lines in the spectrum that remain intense even after hydrogen addition. As will be shown in the following figures, a single line in the Ne, Ar and Kr spectrum was found to have this behaviour.

3.1. Emission spectra of DBD in Ne-H2

An illustration of the M-effect in Ne is given in Fig. 1, where the emission spectra of the DBD in pure neon and also in neon - hydrogen are presented.

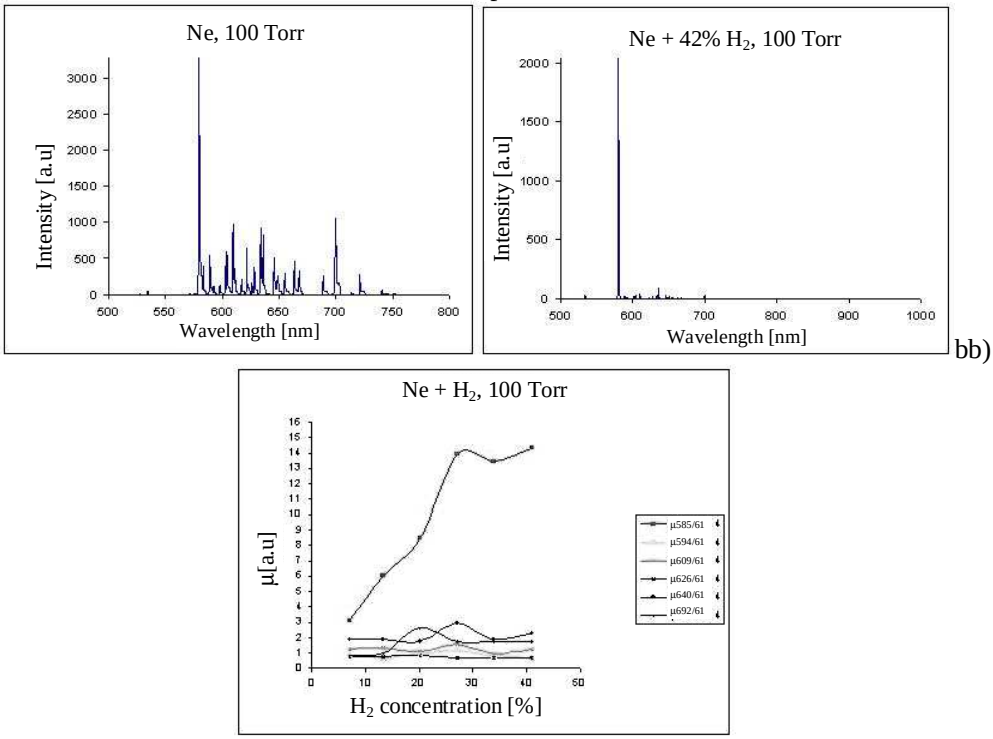
a) 
 bb)

Fig. 1. a) DBD emission spectra of pure Ne and its mixture with 42% H_2, total pressure 100 Torr. b) The dependence of the μ parameter on the H_2 concentration at 100 Torr total pressure.

As can be seen in these figures, on addition of hydrogen, a drastic change of the emmision spectrum of Ne takes place. The rich spectrum of pure Ne becomes a single, intense, line spectrum. This shows that Ne presents M-effect and the value of the wavelength is 585 nm. It is also interesting to compare the evolution of μ for this spectral line as well as those for the most intense lines of the pure Ne spectrum. The value of μ for the 585 nm line had a fast increase to up to about 25% H_2 and steady values thereafter, this showing a saturation process of the M-effect with H_2 addition.

3.2. Emission spectra of DBD in Ar-H2

Similar behaviour of the emission spectra on hydrogen addition was also observed for argon (see Fig. 2). The 750 nm spectral line of Ar showed M-effect. On addition of hydrogen to argon, the value of μ for this line increased. It can also be observed that the M-effect was higher for Ne than for Ar.

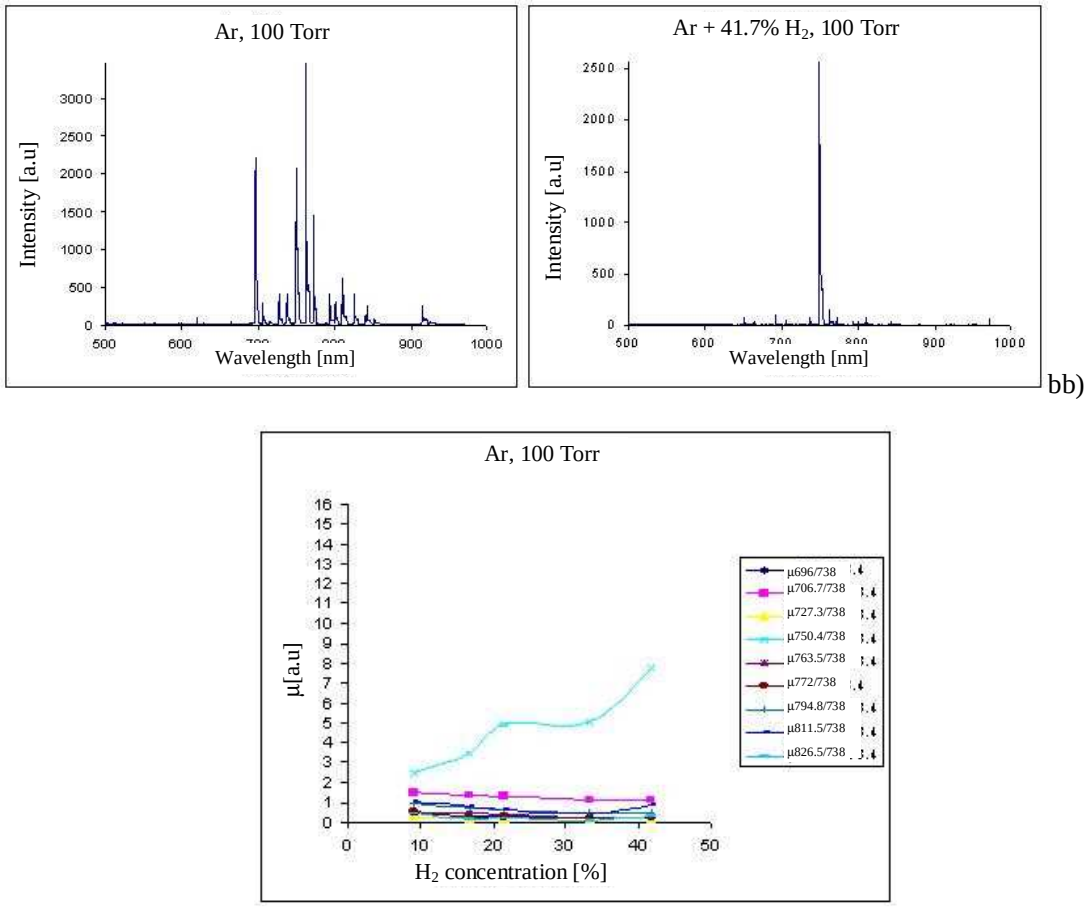


Fig. 2.a) DBD emission spectra of pure Ar and its mixture with 41.7% H_2, total pressure 100 Torr. b) The dependence of the μ parameter on the H_2 concentration at 100 Torr total pressure.

3.3. Emission spectra of DBD in Kr-H2

The emission spectra of Kr + H2 mixture discharge showed the appearance of the M-effect at 758 nm. The effect was lower than for argon.

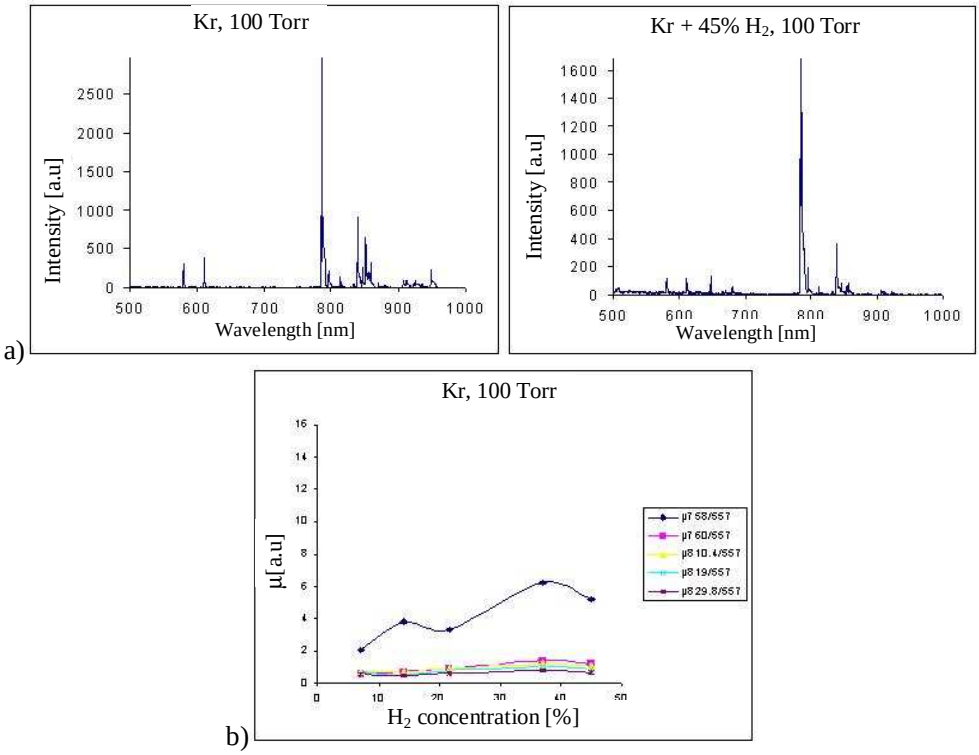


Fig. 3.a) DBD emission spectra of Kr and its mixture with 45% H_2, total pressure 100 Torr.
b) The dependence of the μ parameter on the H_2 concentration at 100 Torr total pressure.

3.4. Emission spectra of DBD in Xe-H2

As shown in Fig. 4, no line in the spectra of Xe + H2 could be observed.

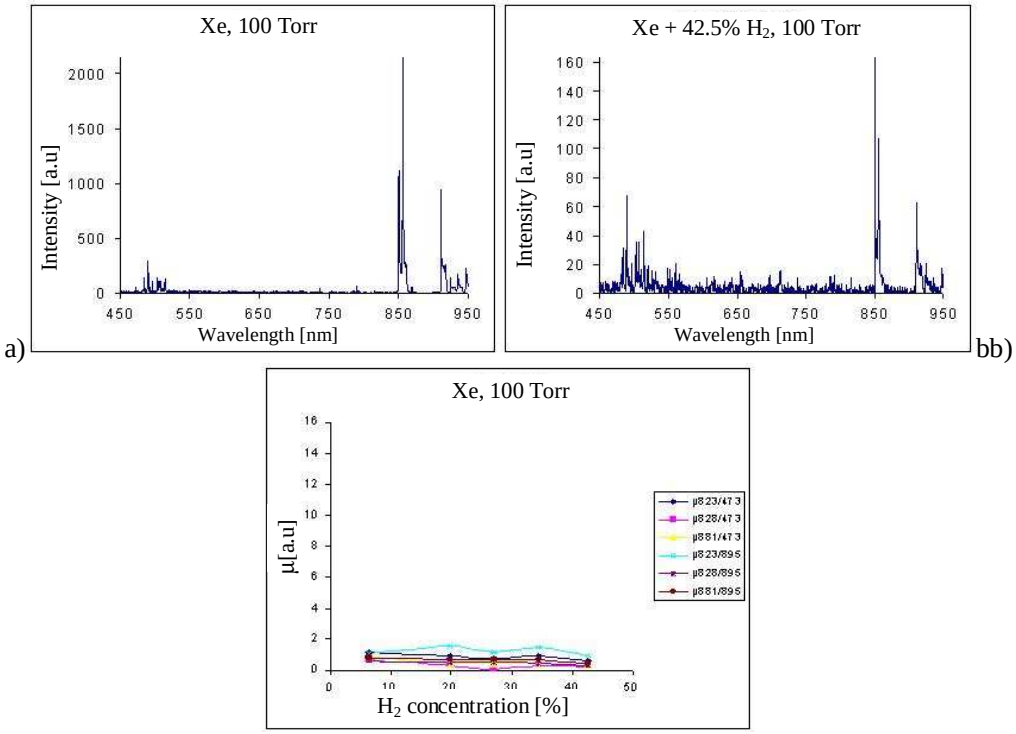


Fig. 4. DBD emission spectra of pure Xe and its mixture with 42.5% H_2, total pressure 100 Torr.
b) The dependence of the μ parameter on the H_2 concentration at 100 Torr total pressure.

3.5. The influence of the M-effect on the GD-OES analysis

We believe that all conditions necessary for the appearance of the M-effect are met in GD-OES analysis. The reaction products of this effect may play in important role in the spectral changes reported by many authors in current literature.

The reaction governing the M-effect [8] in the case of argon for example is given in equation 1 and 2 where λ_M is the wavelength of the emission line that presents M-effect. The means of the appearance of the reactants in the plasma during GD-OES analysis is presented in the following.

The argon ions (Ar^+) bombarding the sample remove surface particles as well as hydrogen inherently present on the sample surface. Thus, hydrogen atoms excited on the n=2 level appear in the plasma. At high pressures, usually greater than 1 torr, due to capture of resonance radiation, hydrogen atoms excited on the n=2 level are continuously created. As their lifetime is comparable with that of metastable atoms, these excited hydrogen atoms can be regarded as metastable. Once all conditions necessary for reaction (1) are met, the reaction takes place and the reaction products appear in the plasma. These excited species can transfer their energy to the sputtered atoms of the sample also present in the plasma, via Penning processes. This phenomenon can result in *spectral changes of the analyte*, also reported by different authors in current literature [2]. Furthermore, the effective *quenching of the argon ion signal* can also be explained by equation 1. This phenomenon results in a decrease of the sputtering yield.

4. Conclusions

The mechanisms resulting in the appearance of the M-effect have been previously published. We report here for the first time on the wavelengths of Ne, Ar, Kr, Xe that present M-effect at 100 torr total pressure.

It is shown here that the M-effect together with the Penning effect may be at the origins of the processes responsible for the changes in the GD-OES spectra observed by many authors, changes due to the existence of hydrogen in the analysis chamber during surface analysis. This paper is intended to open further studies on the optimisation of this analytical tool. The fact that the M-effect was found to decrease with the atomic number of the element from Ne to Xe, may also be important for the developpment of this analytical tool.

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