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Research note

Comparison of excitation mechanisms in the analytical regions of a high-power two-jet plasma

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ABSTRACT

Excitation mechanisms in the analytical regions of a high-power two-jet plasma were investigated. A new plasmatron recently developed was applied in this work. The Boltzmann population of excited levels of Fe atoms and ions was observed in both analytical regions, before and after the jet confluence, as well as in the jet confluence, which proves excitation of atoms and ions by electron impact. The disturbance of local thermodynamic equilibrium in all regions of the plasma flow was deduced on the basis of considerable difference in Fe atomic and ionic excitation temperatures. Such a difference is most likely to be caused by contribution of metastable argon to atom ionization. The region before the jet confluence has the greatest difference in Fe atomic and ionic excitation temperatures and is more non-equilibrium than the region after the confluence due to comparatively low electron and high metastable argon concentrations. Low electron concentration in this region provides lower background emission than in the region after the jet confluence, which leads to better detection limits for the majority of elements.

1. Introduction

A two-jet plasma (TJP) is a high-power excitation source for atomic emission spectrometry (AES). The TJP-AES is mainly used for analysis of various powders, but this method can be also applied for analysis of solutions [1]. There are two analytical regions in the plasma flow—before and after the jet confluence. The region of the jet confluence is not used in analysis because of high background emission (Fig. 1). Relatively weak matrix effects are an important feature of the TJP. This makes it possible to use the same calibration samples for analysis of different samples. For instance, calibration samples based on graphite powder were applied for analysis of gallium [2], indium and tellurium oxides [3,4], bone [5], dried animal organs and whole blood [6,7] after their 2–10-fold dilutions with graphite buffer. However, such an approach does not always give valid results due to different behavior of calibration and analyzed samples in the plasma. For correct interpretation of the results, it is necessary to know the thermodynamic state of the plasma and processes which mainly determine the population of energy states.

In the previous paper [8] excitation mechanisms in the region before the jet confluence employed for analysis of different biological samples [5–7] and high-purity substances [2–4,9] were considered. The plasmatron of old design developed in the mid-1970s was applied in that work. The present investigation has been performed using a new plasmatron recently developed. The aim of this work was to compare the Boltzmann plot behavior and excitation temperatures of Fe atoms and ions in both analytical regions of the TJP and discuss possible excitation mechanisms on the basis of the results obtained.

2. Experimental

2.1. Samples

For construction of Boltzmann plots, the samples of graphite powder containing 0.03 and 0.3 wt.% Fe were prepared.

2.2. Instrumentation

A high-power (10–12 kW) two-jet arc plasmatron designed at "VMK-Optoelektronika" (Russia) was used. Argon plasma jets were generated in two electrode units (tungsten cathode and copper anode) connected to power supply, gas delivery, and water cooling systems. The jets joined at the output to form an arc plasma discharge (Fig. 1). The power supply system of the plasma generator fabricated using state-of-the-art solid state components, the gas flow control and automatic sample introduction systems were computer controlled.

A Grand spectrometer [10] equipped with a concave diffraction grating (2400 lines/mm) and two multichip photodiode arrays, which were a key component of a multichannel analyzer of emission spectra (MAES), allowed spectrum registration in two spectral ranges: 185–350 and 385–460 nm. The photodiode arrays include twelve and eight crystals, each containing 2580 photodiodes of 12.5 × 1000 µm. The MAES system is supplied with ATOM software for processing spectral data.

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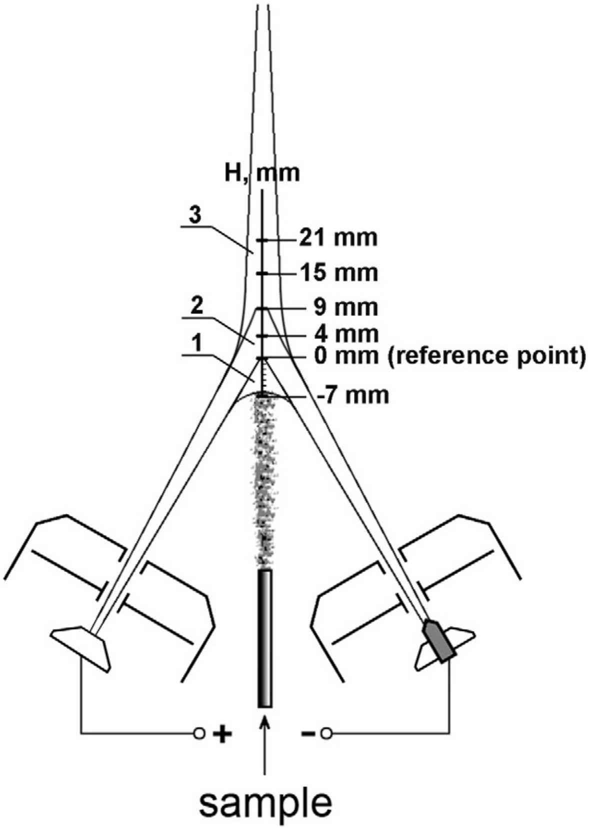

Fig. 1. Plasma torch and regions of the plasma flow: 1) before the jet confluence, 2) the jet confluence and 3) after the jet confluence. H = 0 mm is a reference point for observation zone locations.

A powder-introduction device was employed to transfer the powders into the plasma. A 20-mg sample placed in a Plexiglas beaker was inserted into the device where a spark between zirconium electrodes over the surface of the powder initiated blast waves agitating the powder. A resulting aerosol was delivered into the plasma with a carrier gas.

A new experimental setup provides working conditions similar to those of the old plasmatron, but it has a more precise control of operating parameters and wider spectral range.

2.3. Experimental conditions

For construction of Boltzmann plots in different zones of the plasma flow, the spectra were registered under optimal conditions for each analytical region (Table 1).

For the region before the jet confluence, spectra were measured on a distance of 0–7 mm lower than the reference point with 1 mm-step. The reference point (H = 0) corresponds to the top of the region 1 depicted in Fig. 1.

For the region after the jet confluence, spectra were registered on a distance of 8–9, 14–15, and 20–21 mm above the reference point.

Table 1
Working conditions of the two-jet plasma.

Parameter	Region before the jet confluence	Region after the jet confluence/confluence
Current strength	85 A	85 A
Plasma gas	4 L min^{-1}	3 L min^{-1}
Carrier gas	0.75 L min^{-1}	1 L min^{-1}
Angle between jets	60°	60°

2.4. Construction of Boltzmann plots and temperature measurement

The classical Boltzmann plot method was used [11,12]. The Boltzmann distribution equation is transformed to the following form:

$$\log\ (K_i I_i) = aE_i + b \tag{1}$$

where I_i is line intensity, E_i is the excitation energy of the upper level, and K_i is a factor including statistical weight (g_i), wavelength (λ_i), and transition probability (A_i).

$$K_i = \lambda_i / g_i A_i \tag{2}$$

The excitation temperature of Fe atoms and ions was determined from the slope of the Boltzmann plot (Eq. (1)):

$$T = \text{-}5040/a. \tag{3}$$

3. Results

3.1. Region before the jet confluence

3.1.1. Characteristics of Boltzmann plots

In the previous paper [8] the Boltzmann plot behavior was studied in the analytical region before the jet confluence using the plasmatron of old design where the distance between the nozzles (D) was 22 mm. In the present work the Boltzmann plots were constructed for plasma torches of different size, "large" (D = 22 mm) and "small" (D = 17 mm); other experimental conditions remained the same. For Fe I lines, the E_{exc} range was 3.2–7.1 versus 3.9–7.1 eV in [8].

The Boltzmann plots for excited levels of Fe atoms and ions obtained in the optimal observation zones of the "large" and "small" plasmas (4–5 and 3–4 mm lower than the reference point (Fig. 1), respectively) are presented in Fig. 2. It is seen that all excited Fe I and Fe II levels well follow the plots. The Boltzmann population for Fe I and Fe II lines was found to exist on different distances from the jet confluence. The group of Fe I and Fe II lines, their atomic constants and excitation energies taken from [13] are given in Table S1 (Appendix A) and Table S2, respectively.

3.1.2. Excitation temperature of Fe atoms and ions

Estimating the temperature from the slope of the Boltzmann plots showed the considerable difference in Fe atomic and ionic excitation temperatures, T_{atom} and T_{ion}, respectively. The distribution of T_{atom} and T_{ion} along the analytical region for the "large" and "small" plasmas is presented in Fig. 3. It is seen that $\Delta T = T_{ion} - T_{atom}$ is higher for the "small" plasma than for the "large" one. T_{atom} and T_{ion} gradually reduce when moving away from the confluence; however, the considerable enhancement of T_{ion} is observed in the lower zone of the region where ΔT is about 3000 and 5500 K for the "large" and "small" plasmas, respectively. For other zones, which are nearer to the confluence, the ΔT values are in the range of 1700–2600 K for the "large" plasma and 2500–3500 K for the "small" one.

The temperature standard deviation was calculated through the adequacy dispersion of regressive equation $y = ax + b$ (Eq. (1)). The deviation of about 250 K is observed near the jet confluence for atomic lines, and it does not exceed 100 K in the optimal observation zones for both atomic and ionic lines.

3.2. Region of the confluence and after one

3.2.1. Characteristics of Boltzmann plots

For studying these regions, the "large" plasma having better evaporation efficiency and weaker matrix effects than the "small" one was applied. The observation zone in the region of the confluence was