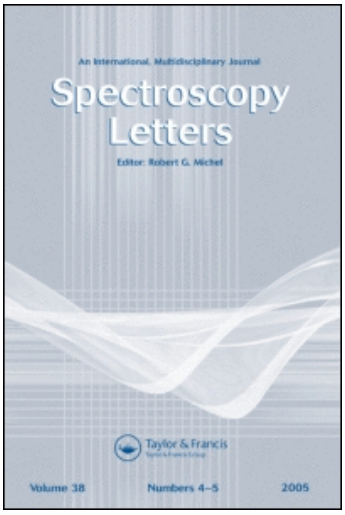

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A Spectroscopic Investigation of Spatial Symmetry of Radiation in the U-shaped DC Argon Plasma with Aerosol Supply

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ABSTRACT Radial distributions of plasma parameters, temperature, and electron number density, together with radial distribution of analyte absorption and emission, were investigated in order to obtain insight into the radial symmetry of low-current ($\leq$10 A), atmospheric pressure, argon stabilized arc with tangential introduction of the aerosol. For plasma diagnostics, several methods were used: measurements of H_β line profile, absolute intensity measurements of the argon 430.01-nm line, and of the spectrally adjacent continuum and power interruption technique. It was found that the inevitable asymmetry in aerosol introduction has negligible influence on basic plasma parameters but influences considerably the spatial distribution of the analyte particle spectral absorption and emission.

KEYWORDS Argon plasma, DC arc, plasma diagnostics, radial symmetry

INTRODUCTION

Argon-stabilized, DC current, U-shaped arc, with continual aerosol supply, is a spectrochemical source with low detection limits[1,2] suitable for trace metal analysis. The combined gas vortex and wall stabilization ensures stable excitation conditions while elimination of electrode areas from the observation direction made possible a good spectral intensity to background ratio. Relatively long horizontal part of the arc column (33 mm) is also suitable for atomic absorption applications where it serves as a free atom reservoir. Because of the arc plasma temperature, particularly good results are accomplished for elements that create refractory oxides.

The sample is introduced into the arc discharge as a water aerosol through argon stream (usually about 2.8 L/min) that enters tangentially into the central segment thus forming a gas vortex that additionally stabilizes the horizontal part of the arc column. However, this argon stream causes distortion of the radial symmetry of the analyte spectral emission. For the same reason, along the direction of arc axis, some asymmetry is expected to exist for the sections near the aerosol injection hole. Because of construction of this arc device, the influence of emission from near the electrodes regions is eliminated from the observation direction (Fig. 1a).[3,4] Upright parts of

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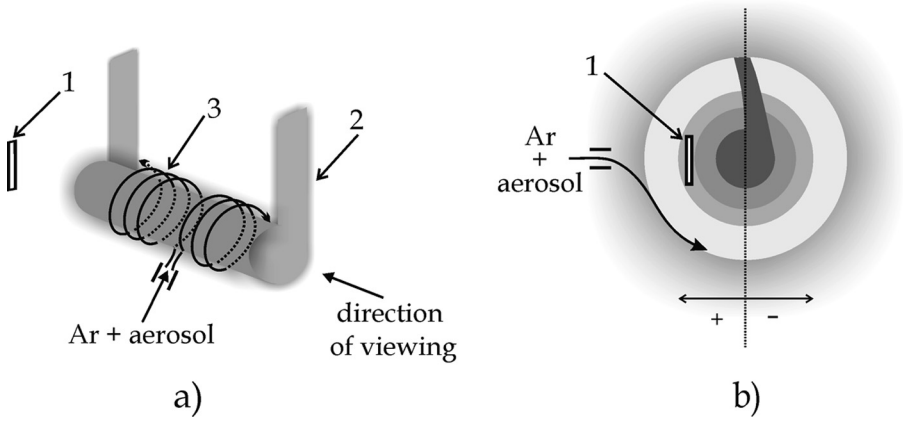

FIGURE 1 **(a) Off-axis view. 1, entrance slit; 2, arc column; 3, gas vortex carrying aerosol. (b) Horizontal part of arc column image projected on the entrance slit of the monochromator. Axis of the horizontal part of the arc column is parallel to the optical axis of the monochromator.**

the arc column also contribute to the emission asymmetry when observation is made in "end-on" direction.

The aim of this work was to investigate radial symmetry of the arc core and its periphery with regard to the parameters that are important for the spectrochemical viewpoint, such as electron number density, temperature, analyte absorption, and emission distributions. In U-shaped arc plasma, investigation of analyte atoms distribution[1,3] and its diagnostics[4–6] was the subject of several publications, but the arc symmetry was not considered. In accordance with the aim of this work, we used plasma diagnostic techniques suitable for radial distribution measurements. We assumed that the plasma column is cylindrically symmetric and homogeneous along the arc axis. Our results are integrally averaged along the direction of the arc axis, so possible nonuniformity in this direction was not taken into account. There are indications that in some cases axial asymmetry may also be important.[7,8] Our main goal was to obtain the most reliable relative relations of plasma parameters along the radial direction, not to discuss their exact values.

Electron number densities were determined by measuring the Stark-broadening of hydrogen H I 486.13 nm (H_β) line and by measuring the absolute intensity of continuum radiation. The H_β line broadening method is a very useful diagnostic tool: H_β line is rather intense even with small hydrogen concentration in plasma, it is isolated from the argon spectra, and what is particularly important is that it does not require thermal equilibrium conditions and temperature dependence is minor. The method is not experimentally demanding, H_β line profiles are such that high-resolution optics is not essential, and the attained accuracy ranging from 5% to 7% for argon plasma is excellent. Many authors considered determination of electron number density from measured H_β line profiles, and in this work, the model proposed in publication Ref. [9] was used.

Continuum emission in pure argon plasma, at atmospheric pressure and in spectral interval 400–500 nm, is dominantly determined by recombination of electrons and Ar^+ ions. For multicomponent plasma like the one investigated (besides argon, hydrogen and oxygen are present), all ions will contribute to the continuum.[10,11] Their relative contribution depends on the value of free-bound continuum factor (ζ), Eq. (1). For this equation to be applied, concentration of all ionic species present (n_j) must be known and these concentrations are highly temperature dependent. For the purpose of this work, the method was simplified by calibrating the continuum intensity at the arc axis, for 430 nm, with the electron number density obtained from H_β line profile measurements using the same experimental conditions. The weakness of this approach lies in the assumption that relative concentrations of Ar^+, H^+, and O^+ ions are independent of the plasma radial position, which is not true because of the radial distribution of temperature. Nevertheless, electron number densities obtained in this way, although not exact, are acceptable for validation of radial symmetry distribution.

$$\varepsilon_c(\lambda) = \frac{1.63 \cdot 10^{-34} n_e \sum_j n_j \xi_j}{\lambda^2 \sqrt{T_e}} \ (\mathrm{W\ m^{-3}\ nm^{-1}\ sr^{-1}}) \tag{1}$$

Problems concerning definition and measurement of temperature and its relation to plasma thermodynamic equilibrium state are discussed in Refs. [12,13] in detail. Contrary to some other plasma (for instance He, H_2), argon plasma diagnostics is disadvantaged by large error (about 30%) in determination of argon lines transition probabilities. Radial distribution of excitation temperature (T_{exc}) was determined by measuring the absolute emissivity of Ar I 430.01 nm line. This line was chosen because the value of the transition probability is one of the most accurate in the Ar spectrum. The value $3.77 \times 10^5\,s^{-1}$ was taken from Ref. [14]. Argon line absolute emissivities were determined with a carbon arc anode as a radiation standard. Care was taken to measure the integral intensity by taking into account the spectral bandpass.[15] For large slit widths, bandpass can be calculated from the slit width and linear reciprocal dispersion.

For temperature determination in argon plasma, a method described in Ref. [12] that uses previously determined electron number density to calculate the temperature assuming the plasma is in local thermodynamic equilibrium (LTE) is often proposed. The temperature determined in this way is denoted as T_{LTE}. In this work, T_{LTE} was evaluated using the electron number densities determined from Stark broadening of H_β line and from measured continuum intensity.

The power interruption technique[5,6,16] is used for measuring the ratio of line intensities before (I_0) and after (I) power interruption. In case when excited level, whose relaxation is responsible for emitted spectral line, is predominately populated by three particle recombination and depopulated by ionization in collisions with free electrons, the power interruption will cause intensity jump (microsecond timescale) described by Eq. (2). Ratio of electron (T_e) to heavy particle (T_h) temperature is denoted by γ (T_e/T_h). It is assumed that after the power interruption, on a microsecond time scale, T_e drops to a T_h value.

$$\ln\frac{I}{I_0} = \frac{\gamma - 1}{kT_e}(I_{ion} - E_{exc}) + \frac{3}{2}\ln\gamma \qquad (2)$$

In systems that are far from LTE, Eq. (2) should be used only for transitions involving levels that are close to ionization energy level in order to justify the approximation of the excitation temperature by the electron temperature. These levels are predominately populated by a previously described mechanism. The higher the excitation state is (closer to ionization energy), the conditions for validity of Eq. (2) are more fulfilled. For lower lying levels, other processes may significantly contribute to level population, mainly ground-state atom collisions with free electrons, and departure from Eq. (2) occurs.

If electron temperature is known (from some other measurements), Eq. (2) may be used for T_h determination. De Regt and co-workers[17] have shown that in inductively coupled argon plasma, T_e does not decrease quickly to T_h, which makes Eq. (2) problematic for T_h determination. Considering the precision, effort, and, sometimes, cost for other spectroscopic techniques available for T_h determination (molecular band emission, Doppler spectral line profiles, laser scattering), power interruption technique is competitive. In this work, power interruption technique is used only as indication of radial asymmetry of excitation equilibrium and difference between T_e and T_h (measured as radial distribution of I/I_0). For that purpose, we measured Ar I 696.54 nm and H_α 656.28 nm line for which it may be expected not to be in complete equilibrium with free electrons, but their sensitivity and extent of intensity jump makes them appropriate to refine measurements of radial asymmetry, especially at lager displacements from the arc axis.

MATERIALS AND METHODS

In the current work, measurements were carried out with the U-shaped DC argon arc with combined gas vortex and wall stabilization, which construction details are described elsewhere.[1,5,6] The arc was operating in current intensity range 6 to 10 A (81 to 74 V). The discharge chamber (diameter 16 mm) consists of water-cooled, electrically insulated copper diaphragms. The arc column, 33 mm long, was aligned parallel to the optical axis of the monochromator (Fig. 1a), and its end-on image was projected, by achromatic lens, at a magnification of 1:1 on the entrance slit of the monochromator. Argon stream (2.8 L/min) carrying water aerosol was introduced into the central segment of the arc chamber (at atmospheric pressure) tangentially to the arc column, forming a gas vortex, which additionally stabilizes the discharge. The argon stream produces

small shift of the arc column in respect to the axis of the central segment opening, Fig. 1b. It was found from the argon flow and nebulizer efficiency that plasma gas is approximately comprised of 88 mol% argon and of 8% elementary hydrogen and 4% elementary oxygen originating from the dissociation of nebulized water.

Radial distributions were obtained by moving the arc device perpendicularly to the optical axis. Radial distances on the same side where plasma gas is introduced into the central segment are marked by a (+) sign, whereas the opposite side is marked as (–). The arc axis was accurately defined as a position of maximal continuum emission around 430 nm.

The entrance slit height was 1 mm and width was up to 200 μm. A specific feature of this plasma source is that it allows one to perform direct measurement of the radial distributions by end-on observation.[4]

Water aerosol was produced with Meinhard concentric glass nebulizer (Meinhard Glass Products, Colorado, USA) in conjunction with laboratory made double-pass spray chamber. The Carl Zeiss (Jena, Germany) PGS-2, 2-m focal length spectrograph with photoelectrical detection (high efficiency R928 photomultiplier tube) was equipped with two interchangeable diffraction gratings to obtain higher dispersion (approximately 0.1 nm/mm) for H_β line profile measurements and lower dispersion (approximately 0.7 nm/mm) for integral intensities measurements. Power interruption and time-resolved intensity measurement setup were described in detail in a previous paper.[5]

Radial distribution of analyte absorption in arc plasma was measured using the same PGS-2 spectrograph. Emission from appropriate hollow cathode lamp as a source was focused through the central part of the arc column while secondary analyte emission from the plasma was discriminated by using mechanical chopper (placed between hollow cathode lamp and the arc device) and lock-in amplifier. Signal from photomultiplier was carried to phase-sensitive amplifier and then to PC via AD converter. Absorption measurements were performed with single-beam configuration.

RESULTS AND DISCUSSION

Radial distribution of electron number density evaluated from measured H_β profile and absolute emissivity of continuum near 430 nm are presented in Fig. 2. Only the arc core was considered because at larger displacements, electron number density is not high enough for accurate evaluation. Measured electron number densities are in the range 1×10^{20} to $1.5 \times 10^{21}\,m^{-3}$. The values obtained from continuum emissivity are somewhat higher, which is expected considering the discussion given in Section 1. At lower temperatures, contributions from

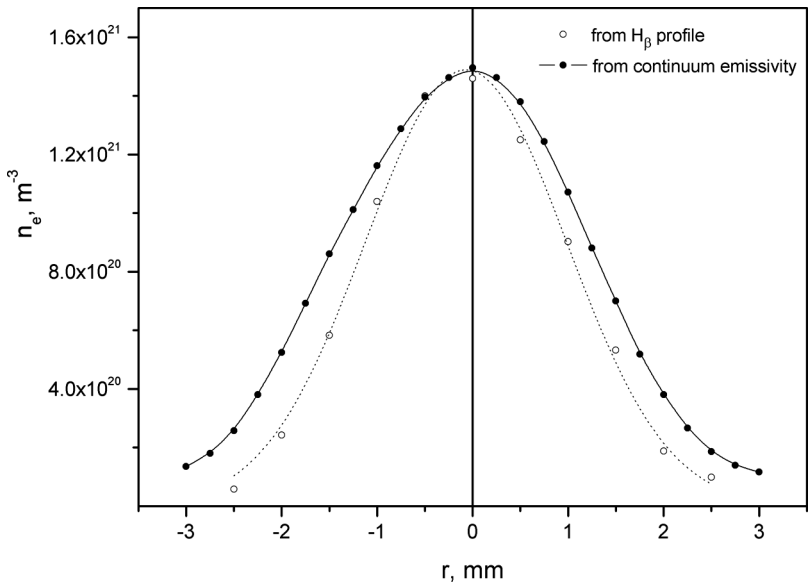

FIGURE 2 **Radial distribution of electron number densities obtained from Stark broadening of H_β line and from absolute continuum intensity; arc current was 6 A.**

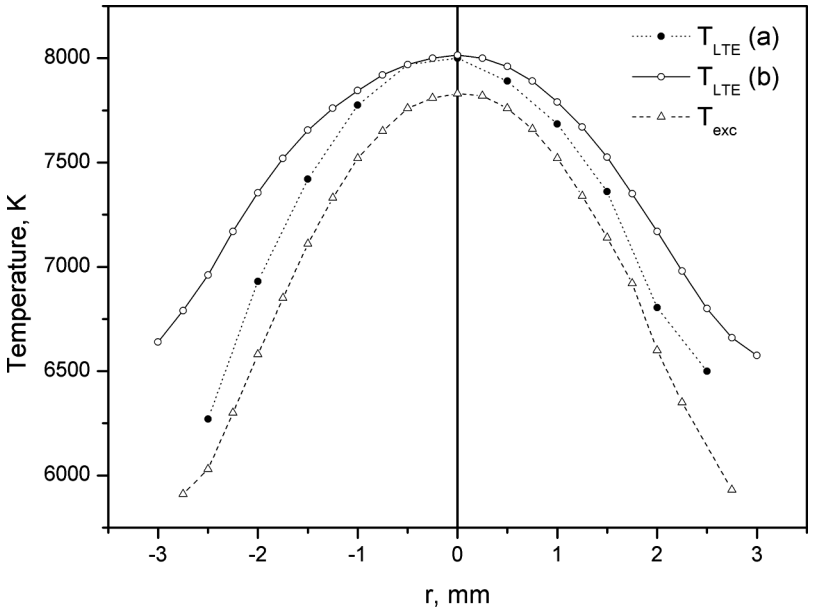

FIGURE 3 **Radial distribution of LTE and excitation temperature; $I = 6$ A. T_{LTE} (a) calculated from electron number densities obtained from Stark broadening of H_β line and T_{LTE} (b) with electron number densities obtained from absolute continuum intensity.**

the presence of O and H are larger due to their lower ionization energies (for O and H 13.614 and 13.595, respectively, compared with 15.775 eV for Ar). In Fig. 2 it is seen that noticeable asymmetry is present; electron number densities are somewhat higher on the (–) side of the arc column, especially outside the interval between -1.5 to 1.5 mm.

Radial distribution of T_{LTE} presented in Fig. 3 shows the same asymmetry as in Fig. 2 because the latter is calculated with electron number densities obtained from H_β profiles. Radial distribution of excitation temperature is obtained from the spatially resolved measurements of integral emissivity of Ar I 430.01-nm line.

In contrast with T_{LTE}, radial distribution of T_{exc} shows a radial symmetry within the experimental error. Measured temperatures are in the 8000 to 6000 K range, depending on the radial position. Considering the difference in obtained values of T_{LTE} and T_{exc}, it is worth considering their relation to T_e. In case the plasma is in the LTE state, all temperatures T_{LTE}, T_{exc}, and T_e should be equal. In wall-stabilized arcs, it is expected that, due to ambipolar diffusion, transport of electrons occurs. As a result of that, in central plasma zones, there will be electron underpopulation with respect to T_e, and therefore T_{LTE} will be smaller than T_e. On the other hand, T_{exc} will be equal to T_e only if the excitation level considered is in equilibrium with free electrons,[10] otherwise T_{exc} will differ from T_e. For given electron number density, in arc core, excited Ar levels are more underpopulated the higher their ionization energy is (for Ar 430.01-nm line, ionization energy is 1.725 eV). Consequently, T_{exc} will be smaller than T_e.

Bydder and Miller[18] have shown that the intensity ratio I/I_0 (i.e., T_e/T_b), obtained from power interruption experiment, is a much more sensitive indication of plasma asymmetry than is information acquired from line-intensity measurements. By power interruption technique, we have measured I/I_0 for Ar I 696.54-nm and H_α 656.25-nm lines with excited level ionization energies 2.46 and 1.51 eV, respectively. Although it may be expected that these levels are not in complete equilibrium with free electrons,[5] their sensitivity and extent of intensity jump (Eq. (2)) make them appropriate for refined measurements of radial asymmetry, especially at larger displacements from the arc axis. Because of high ionization energies of these lines (and absence of complete equilibrium between excited states and free electrons), exact evaluation of T_b from these measurements is not possible, but nevertheless they truly represent the extent of T_e to T_b difference and its variations in excitation conditions. As it may be seen from Fig. 4 in the interval -2 to 2 mm from the arc axis, I/I_0 increases toward plasma periphery,

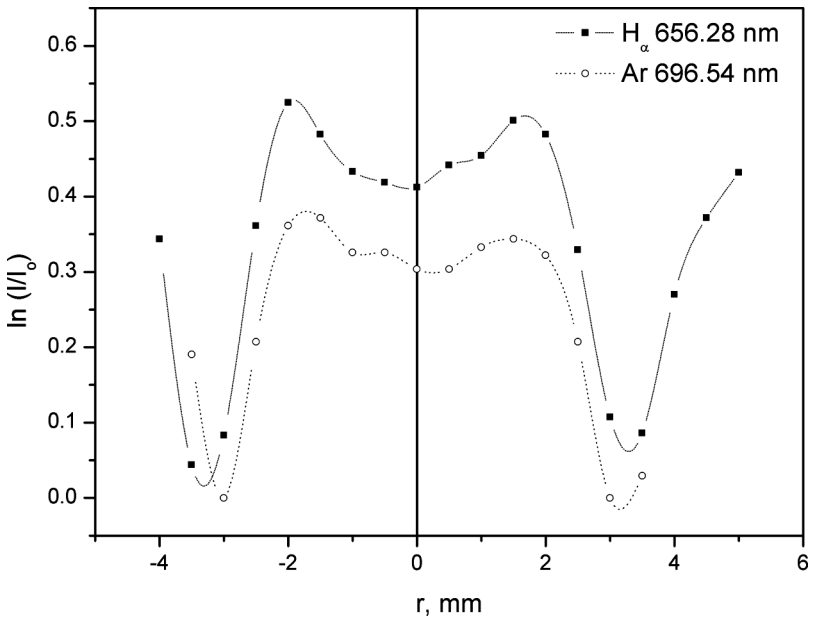

FIGURE 4 **Radial distribution of measured cooling jump for Ar I 696.54 nm and H_α 656.25 nm; $I = 10$ A.**

obviously because T_e/T_b increases as a result of electron number density lessening.[19]

In literature, there is a lack of data on the I/I_0 radial distribution for low-current argon arc, notably the one with the water aerosol introduction. At displacements larger than 2 mm from the arc axis (Fig. 4), intensity jump first declines (on both sides of the axis) to zero level and then rises again. It is worth noting that even at outer regions (distances beyond 4 mm from the arc axis), intensity jump is still positive, which implies that these lines are predominately excited by three-particle recombination.[5,16] The observed I/I_0 trend implies that excitation mechanism and state of thermal equilibrium are dependent on radial position, though such trend is hard to explain for periphery discharge zones. In any case, radial distribution of I/I_0 shows considerable asymmetry and that applies for the arc core as well as for the arc periphery. These values, similar to the electron number densities, are somewhat larger on the (–) side of the arc column.

It is well-known that low-current argon arc exhibits pronounced demixing effect.[3,20] Depending on their ionization energy, analyte atoms more or less penetrate to the arc core. By comparing the optical absorbances, which are proportional to the number of absorbing atoms along the absorption path, in the arc core and in its periphery (Fig. 5), it is evident that Zn as an element with high ionization energy (9.39 eV) more efficiently penetrates to the arc core than do the elements with lower ionization energies such as Mn (7.43 eV) and K (4.34 eV). Because the absorbance primarily depends on analyte atom concentration and very weakly on temperature, distribution of absorbance truly represents analyte concentration distribution. Absorbance measurements are thus suitable as an indicator of analyte radial distribution asymmetry, even more as they are not very sensitive to variations in excitation conditions. It may be concluded that radial distribution of analyte concentration shows large asymmetry and that this asymmetry is related to asymmetrical transport of analyte particles. Lowering of absorbance on the faraway periphery is a consequence of insufficient temperature, which facilitates formation of stable refractory oxides and hydroxides.

Radial distribution of analyte emission is associated with radial distribution of analyte concentration and with radial distribution of temperature and other parameters responsible for excitation process. Elements with higher ionization energies have emission maximum closer to the arc axis. Figure 6 confirms the previous assumption that analyte distribution is asymmetrical, the emission asymmetry being even more pronounced.

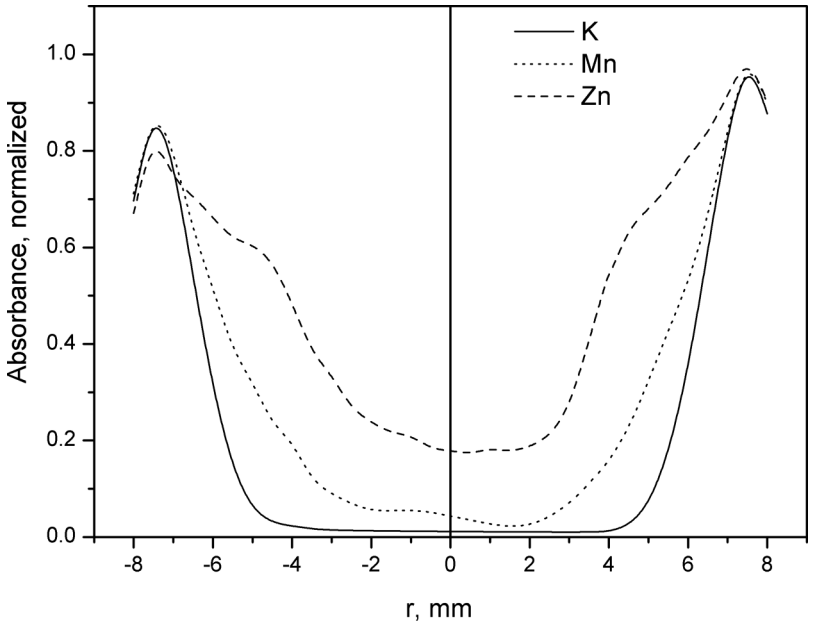

FIGURE 5 **Radial distribution of absorbance for Zn 213.86 nm, Mn 279.48 nm, and K 766.49 nm line; $I = 9$ A.**

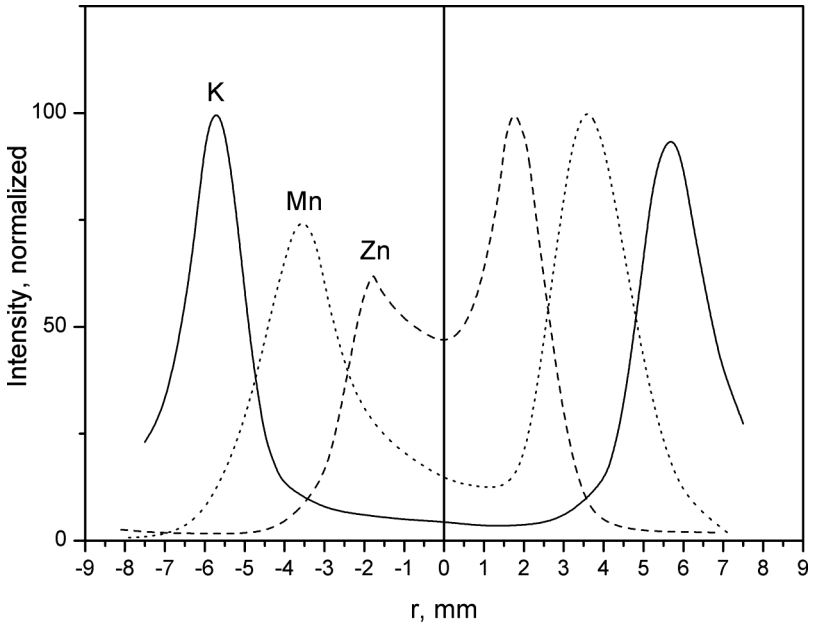

FIGURE 6 **Radial distribution of emission for Zn 213.9 nm, Mn 403.08 nm, and K 766.49 nm line; $I = 9$ A.**

CONCLUSION

Temperature and electron number density, as basic plasma parameters (governed by the argon as a main gas), show noticeable radial asymmetry, (i.e., the arc column cannot be considered as completely cylindrically symmetrical). On the other hand, radial distributions of analyte emission and absorption show larger asymmetry as the principal consequence of asymmetrical analyte transport. Obviously, unavoidable asymmetry in argon stream introduction is the main cause of the observed asymmetry of the arc column.

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