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SYNCHRONIZED LASER ABSORPTION AND OPTICAL EMISSION SPECTROSCOPY OF PLASMA WITH COPPER VAPOUR ADMIXTURES

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In this paper, a DC arc discharge plasma with copper vapour admixtures is studied by synchronized laser absorption (LAS) and optical emission spectroscopy (OES). The spatial and spectral characteristics of the arc discharge plasma between copper electrodes in an argon flow at atmospheric pressure were analysed. The emission spectra were recorded by the OES methods and the excitation temperatures and population of the energy levels of the copper atom corresponding to the upper levels of optical transitions with the wavelengths studied in this work were determined. In turn, the LAS method was used to determine the population of the lower energy level of one of the optical transitions under study. The synchronous application of both methods makes it possible to determine the radial distributions of the excitation temperatures and the number density of copper atoms. The consistency of the obtained results confirms the possibility of using synchronized laser absorption and optical emission spectroscopy in diagnostics of plasma with copper vapour admixtures.

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INTRODUCTION

Plasma diagnostics play an important role in understanding the complex processes occurring in plasma of discharges, which are widely used in various industrial, biomedical, and environmental applications. Laser Absorption Spectroscopy (LAS) and Optical Emission Spectroscopy (OES) are the most demanded methods of such diagnostics [1, 2].

OES has long been established as a versatile, non-perturbing diagnostic technique that uses the radiation emitted by excited plasma species to characterize its parameters such as excitation temperatures, electron densities, and species number densities. This technique has proven invaluable in studies of plasmas under various conditions, including low-pressure discharges and atmospheric plasma jets, due to its simplicity, cost-effectiveness, and ability to provide real-time measurements of active species and energy states [3, 4]. However, OES often encounters limitations, such as self-absorption and reliance on realisation of local thermodynamic equilibrium (LTE), which can lead to complications when studying non-equilibrium plasmas or regions with low emissivity [5].

On the other hand, LAS offers high spectral resolution and sensitivity by measuring the absorption of a narrow-band laser beam as it passes through the plasma. Unlike OES, LAS is free from self-absorption effects and can probe regions with weak emission intensities, making it particularly suited for diagnosing the periphery of plasma discharges or other non-equilibrium regions [3, 6]. LAS also allows for the precise determination of specific plasma parameters, such as the density of atomic or molecular species and line broadening effects caused by collisional and Doppler mechanisms, even in spatially resolved configurations [5].

Despite their individual advantages, the combined application of LAS and OES has shown promise in overcoming their respective limitations.

This study focuses on the synchronized use of LAS and OES techniques to investigate the plasma of a DC arc discharge with copper vapour admixtures. By integrating the strengths of both techniques, it aims to analyse the spatial and spectral characteristics of the discharge, including radial distributions of excitation temperature, and the copper number density.

1. INVESTIGATION METHODS

A DC arc discharge at a current of 3.5 A between single-component copper electrodes (6 mm diameter) in an argon flow (7 SLPM) were investigated. A discharge gap was 8 mm. Synchronous combination of LAS and OES is realized according to the scheme of the experimental setup shown in Fig. 1.

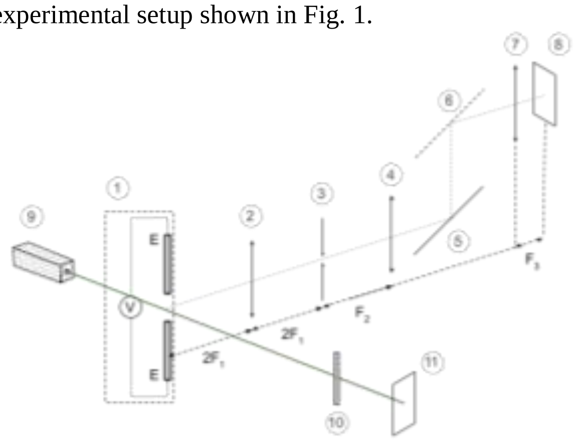

Fig. 1. Scheme of the combined simultaneous plasma emission and absorption registration

The scheme consists of: 1 – vertically-oriented electrodes E with a power source V; 2 – lens with a focal length F_1 = 200 mm; 3 – horizontal entrance slit of the spectrograph; 4 – collimator with a focal length F_2 = 150 mm; 5 – mirror; 6 – diffraction grating; 7 – lens with a focal length F_3 = 50 mm; 8 – registration device; 9 – probing laser; 10 – neutral density filter; 11 – registration device synchronised with 8.

The scheme of emission registration 2-8 was calibrated earlier [7] to measure absolute emission intensities of spectral lines. The emission spectra were registered in the range of 430…650 nm. Typical emission spectrum in the range of 505…525 nm (such a range is chosen to present the both spatial and spectral distribution of emission intensities of most intensive copper spectral lines) with spatial resolution and taking into account spectral sensitivity of the registration scheme is shown in Fig. 2. Cu I spectral lines observed in the emission spectrum, as well as the energies of the upper and lower atomic level, configuration and term of the corresponding transition are given in Table.

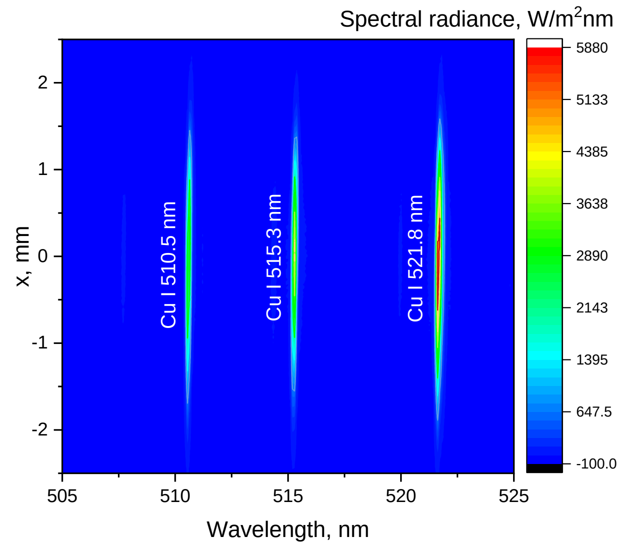

Fig. 2. Typical spatially resolved emission spectrum of the plasma in the range of 505…525 nm with taking into account spectral sensitivity of the registration scheme

The list of the observed Cu I spectral lines (with wavelength λ) with the energies of the upper (E_k) and lower (E_i) atomic level, configuration and term of the corresponding transition ($k \to i$) [8]

λ, nm	Transition $k \to i$ Configuration and term	E_k, eV	E_i, eV
465.1	$3d^9 4s5s\ ^4D_{7/2} \to 3d^9 4s4p\ ^4P_{9/2}$	7.74	5.07
510.5	$3d^{10} 4p\ ^2P_{3/2} \to 3d^9 4s^2\ ^2D_{5/2}$	3.82	1.39
515.3	$3d^{10} 4d\ ^2D_{3/2} \to 3d^{10} 4p\ ^2P_{1/2}$	6.19	3.79
521.8	$3d^{10} 4d\ ^2D_{5/2} \to 3d^{10} 4p\ ^2P_{3/2}$	6.19	3.82
570.0	$3d^{10} 4p\ ^2P_{3/2} \to 3d^9 4s^2\ ^2D_{3/2}$	3.82	1.64
578.2	$3d^{10} 4p\ ^2P_{1/2} \to 3d^9 4s^2\ ^2D_{3/2}$	3.79	1.64

The spatial radiance distributions *I(x)* of the Cu I 510.5, 515.3, and 521.8 nm spectral lines, shown in Fig. 3, were obtained by Gaussian approximation of the spectral distribution of each spectral line at each considered spatial point *x*, as shown in [7].

The spatial distributions of the brightness of the spectral lines were converted into radial intensity distributions by the Bockasten's method [9], taking into account the axial symmetry of the arc discharge. The radial distributions of the emission intensities were further utilize to determine the excitation temperature and number density of copper atoms by Boltzmann plot technique [7].

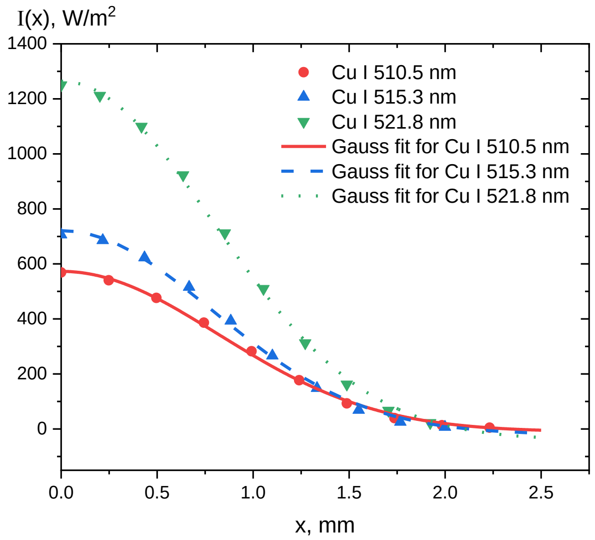

Fig. 3. Typical spatial distributions of the radiance of Cu I 510.5, 515.3 and 521.8 nm spectral lines (dots) with the corresponding Gauss fit (curves)

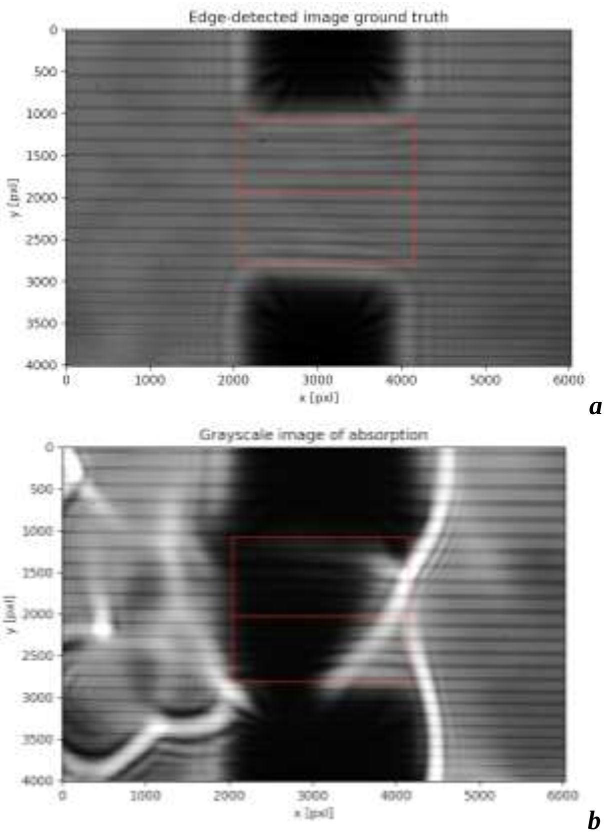

Fig. 4. Spatial distribution of the intensity of (a) the reference laser beam and (b) the probe beam passing through the plasma

A copper vapour laser "Kriostat 1" was used in LAS as a radiation source, which generates two Cu I 510.5 and 578.2 nm spectral lines. The radiation power of the laser was 1 W. The pulse frequency was 10 kHz with a repetition period of 0.1 ms and a duration of 20 ns. A diffraction grating was additionally used in the optical scheme to isolate one of them. Since, according to [10], the Cu I 510.5 nm line is characterized by a slight spectral shift in a wide range of temperatures and electron densities of the plasma, it is advisable to use it for probing this plasma object. The width of this spectral line is approximately $1.8\cdot10^{-3}$ nm.

The image of the electrode assembly in the parallel laser beam was recorded using a CMOS matrix of 6036×4020 pixels (23.5×15.6 mm) with subsequent processing on a PC (Fig. 4).

By measuring the intensity of the reference laser beam $I_0(x)$ (without the arc) and the intensity of the probe beam $I(x)$ (that was partially absorbed in the arc plasma) at each spatial point, one can obtain the spatial distribution of the optical thickness at the centre of the spectral line $\tau_0(x)$ of such a plasma by Eq. (1):

$$\tau_0(x) = \ln\left(\frac{I_0(x)}{I(x)}\right). \quad (1)$$

Since the width of the spectral line of laser radiation is smaller than that of the spectral line of plasma emission, it can be assumed that absorption occurs exactly at the centre of the spectral line. The radial distribution of the optical thickness $\tau_0(x)$ obtained by Eq. (1) is shown in Fig. 5.

Taking into account the axial symmetry of the arc discharge plasma, the radial distribution of absorption coefficient at the centre of the spectral line $\kappa_0(r)$ is related to the optical thickness of the plasma by the Eq. (2):

$$\kappa_0(r) = -\frac{1}{\pi}\int_r^{r_0}\frac{\tau_0'(x)dx}{\sqrt{x^2-r^2}}, \quad (2)$$

where $\tau_0'(x)$ is the spatial derivative of the optical thickness and r_0 is the absorption boundary. The method proposed by Bockasten [9] was also used to solve this integral. Radial distribution of the absorption coefficient in the centre of Cu I 510.5 nm spectral line obtained by Eq. (2) is shown in Fig. 6.

In turn, the absorption coefficient at the centre of the spectral line $\kappa_0(r)$ is related to the number density of absorbing particles $n_k(r)$ by Eq. (3):

$$n_k(r) = \frac{\kappa_0(r)\Delta\lambda(r)}{\rho f_{ik}\lambda^2}, \quad (3)$$

where ρ is the numerical coefficient depended on the spectral line contour, f_{ik} is the oscillator strength for the optical transition with wavelength λ, $\Delta\lambda$ is the full width at half maximum (FWHM) of the spectral line profile. Since the copper vapour laser "Kriostat 1" emits at exactly the same wavelength as the plasma with copper vapour admixtures, $n_k(r)$ in Eq.(3) will correspond to the population of the lower level of the optical transition with wavelength Cu I 510.5 nm (see Table 1). The FWHM of this spectral line is determined by its broadening due to Doppler's effect [11], which can be estimated by Eq.(4):

$$\Delta\lambda(r) = \Delta\lambda_D(r) = 7.67\cdot10^{-7}\lambda\sqrt{\frac{T_g(r)}{\mu}}, \quad (4)$$

where $T_g(r)$ is a radial distribution of temperature of heavy particles (gas temperature), μ is the atomic mass.

Numerical coefficient ρ is $8.19\cdot10^{-20}$ for the Doppler contour [12]. The oscillator strength f_{ik} for the corresponding optical transition is taken from previous work [13].

Thus, to determine the population of the lower energy level of the optical transition with wavelength λ by LAS it is necessary to determine the temperature of heavy particles T_g. Under the assumption of local thermodynamic equilibrium (LTE), this temperature will be equal to the temperature of plasma and the excitation temperature of the energy levels T_e, which can be determined using the OES methods

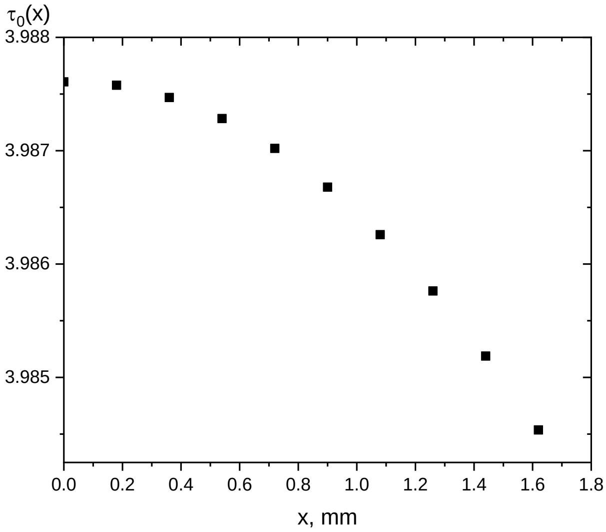

Fig. 5. Spatial distribution of optical thickness at the centre of Cu I 510.5 nm spectral line

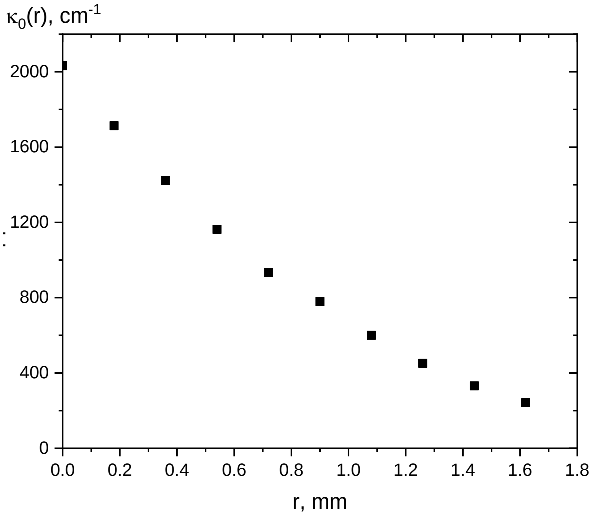

Fig. 6. Radial distribution of the absorption coefficient at the centre of Cu I 510.5 nm spectral line

2. RESULTS AND DISCUSSIONS

Typical Boltzmann plots (at different spatial points) based on emission intensities $\varepsilon(r)$ determined from spatial radiance distribution (see Fig. 3) of observed Cu I spectral lines are shown in Fig. 7

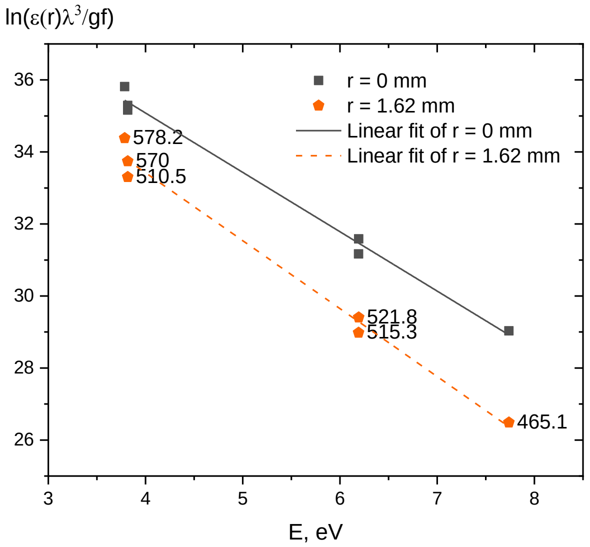

Fig. 7. Typical Boltzmann plots based on the emission intensities of Cu I spectral lines obtained at different radial points of the arc discharge

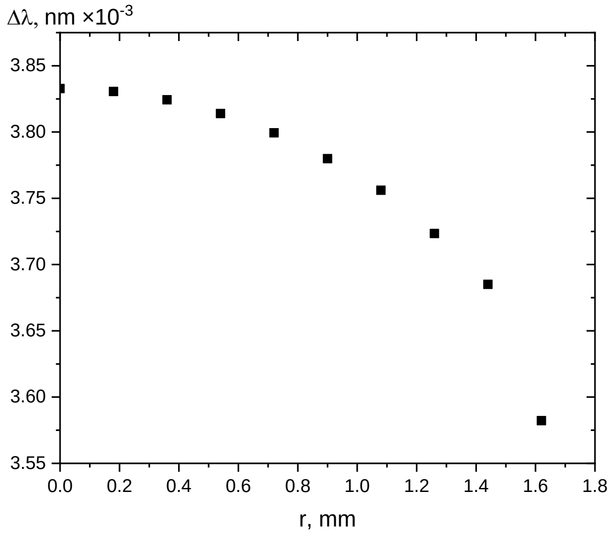

Fig. 9. Radial distributions of FWHM of Cu I 510.5 spectral line determined by its broadening due to Doppler's effect

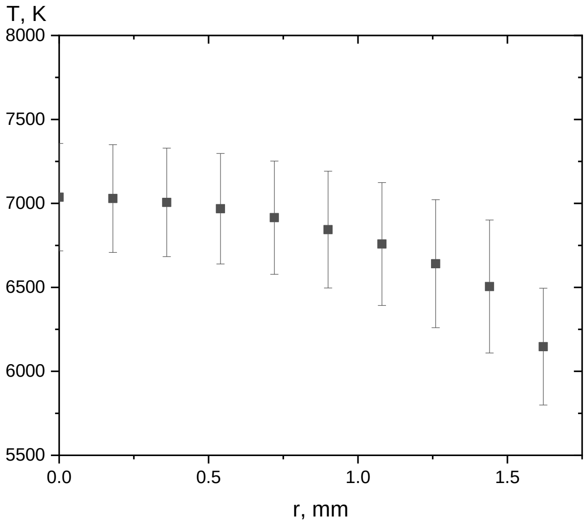

Fig. 8. Radial distribution of excitation temperature obtained by Boltzmann plot technique based on emission intensities of Cu I spectral lines

One can see that the points on the Boltzmann plots in a good agreement with linear fit which in turn indicates a low error in determining the excitation temperature (within ~5%). The excitation temperature obtained by Boltzmann plot technique (see Fig. 7) is shown in Fig. 8.

Radial distribution of FWHM ($\Delta\lambda$) of Cu I 510.5 spectral line was determined according Eq. (4) assuming realisation of LTE in the investigated plasma (Fig. 9).

One can see that FWHM of the spectral line in the plasma is at least twice as large as that emitted by the laser. Thus, it can be concluded that the statement about the absorption of probe laser radiation in the centre of the spectral line can be justified.

Thus, using Eq. (3), the radial distribution of the population $n_k(r)$ of the level $3d^94s^2\ ^2D_{5/2}$, which corresponds to the lower level of the optical transition with wavelength 510.5 nm was calculated.

In addition, using Eq. (5), the populations of the upper levels of optical transitions with wavelengths 465.1, 510.5, 515.3, 521.8, 570.0, and 578.2 were also calculated (see Table).

$$\varepsilon(r) = \frac{hc}{4\pi\lambda} A_{ki} n_k(r), \qquad (5)$$

where h is the Planck constant; c is the speed of light; A_{ki} is the probability of the electron transition from the k^{th} to the i^{th} energy level (the Einstein coefficient for spontaneous emission) [7]. The probabilities of the electron transition A_{ki} of all investigated spectral lines are taken from [13].

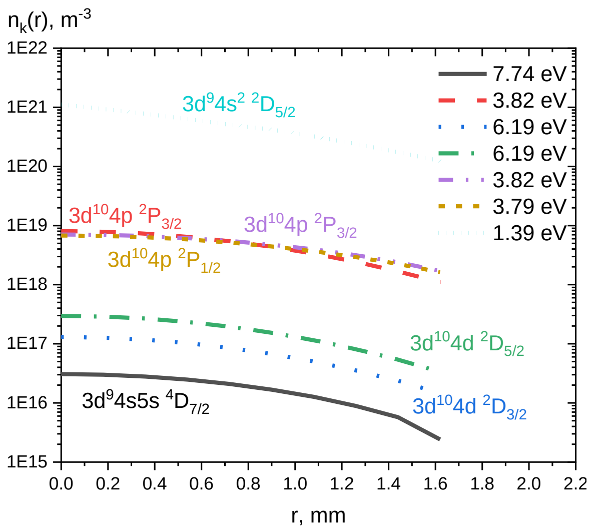

Fig. 10. Radial distributions of the population of different energy levels of copper atoms in the plasma

Radial distributions of population of the energy levels $3d^94s5s\ ^4D_{7/2}$, $3d^{10}4p\ ^2P_{3/2}$, $3d^{10}4d\ ^2D_{3/2}$, $3d^{10}4d\ ^2D_{5/2}$, $3d^{10}4p\ ^2P_{3/2}$, $3d^{10}4p\ ^2P_{1/2}$, and $3d^94s^2\ ^2D_{5/2}$ (see Table), obtained by Eq. (3) and (5) are shown in Fig. 10.

It can be seen that the radial distributions of levels populations determined with good accuracy. The populations of the $3d^{10}4p\ ^2P_{3/2}$ (which is determined from emission intensity of both Cu I 510.5 and 570.0 nm spectral lines) and $3d^{10}4p\ ^2P_{1/2}$ levels do not differ, which, taking into account their practically identical energy values (3.82 and 3.79 eV, respectively), indicates the correctness of the calculations. As for the $3d^{10}4d\ ^2D_{3/2}$ and $3d^{10}4d\ ^2D_{5/2}$ levels, the energies of which differ by less than 0.001 eV, some divergence of their populations is noticeable. The reasons for this discrepancy may lie in minor inaccuracies in determining the spectral sensitivity of the registration scheme in a given spectral range or in the inaccuracy of spectroscopic data (in particular, A_{ki}). Nevertheless, the difference in the populations of these levels is still insignificant.

Using the obtained radial distributions of energy level populations determined by both LAS and OES methods, a Boltzmann plot is constructed using Eq. (6). This diagram, unlike the one shown in Fig. 7, takes into account not only the upper energy levels of optical transitions, but also the lower level of optical transition with a wavelength of 510.5 nm. According to Boltzmann distribution [7]:

$$\ln\left(\frac{n_k(r)}{g_k}\right) = -\frac{E_k}{k_B T(r)} + \ln\left(\frac{n(r)}{\Sigma_a}\right), \quad (6)$$

where g_k is the statistical weight of the k^{th} energy level, E_k is the energy of k^{th} level, k_B is the Boltzmann constant, *n(r)* is the radial distribution of the total number density of the emitting element (copper) and Σ_a is the partition function of the emitting element. The Boltzmann plots at different radial points of arc discharge obtained by Eq.(6) are shown in Fig. 11.

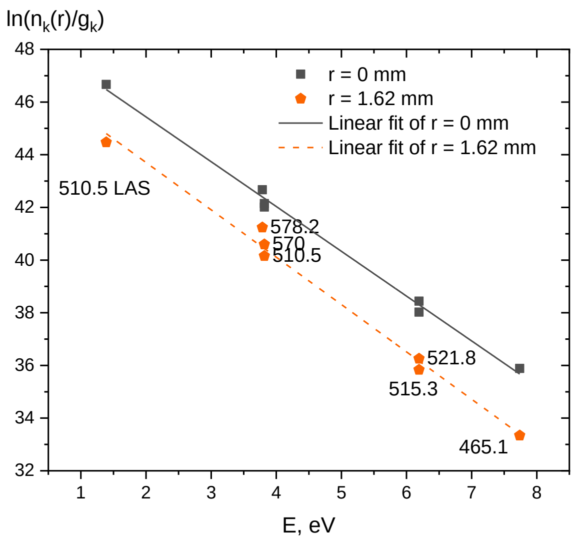

Fig. 11. Typical Boltzmann plots based on the obtained populations by LAS and OES

As can be seen, despite the combination of results obtained by different techniques, the points on the plots still match well with the linear approximation (the error is still within ~5%). The addition of one more point (510.5 LAS) compared to Fig. 7, hardly changes the slope of the approximating line, indicating that the temperature does not change much. In order to verify this, Fig. 12 shows the radial distributions of temperatures determined by the Boltzmann plots technique shown in Fig. 7 (OES) and 11 (LAS+OES).

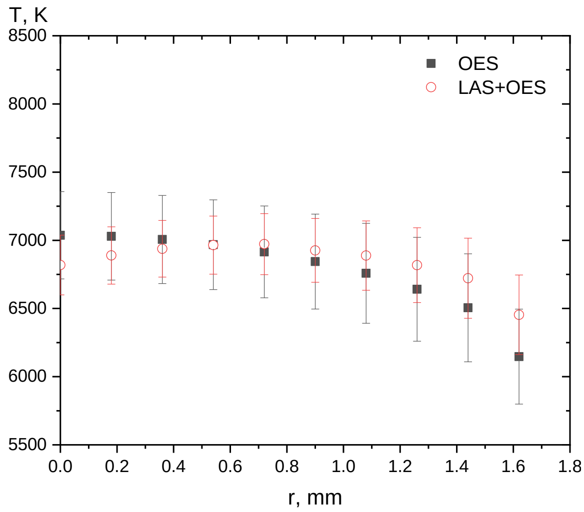

Fig. 12. Radial distributions of the excitation temperatures obtained by Boltzmann plot technique using results from OES (black) and both LAS and OES (red)

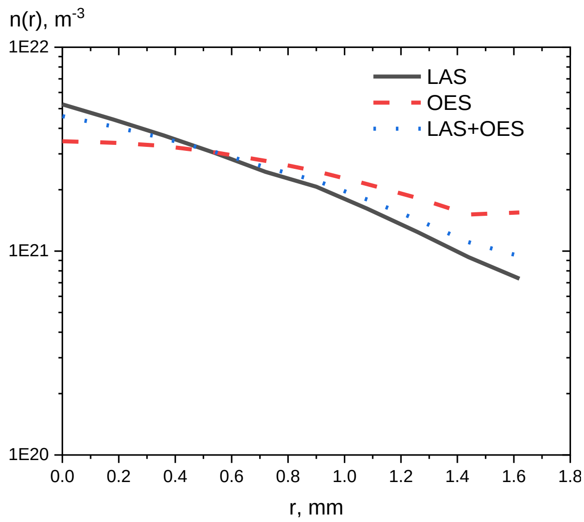

Fig. 13. Radial distributions of number densities of copper atoms in plasma of electric arc discharge obtained by LAS (black), OES (red) and combined LAS and OES (blue)

It can be seen that the radial temperature distributions coincide completely within the frame of error bars. This indicates the validity of the assumptions made in the calculations and the possibility of using the combined LAS and OES technique to investigate the plasma with copper vapour admixtures.

In addition, the radial distributions of the total number densities of copper atoms in the plasma of the investigated discharge were also determined using the LAS, OES methods, and their combination (Fig. 13). In the case of OES, the atom number density was determined by the Boltzmann plot technique according to [7]. In the case of LAS, the number density of atoms was determined in accordance with the Boltzmann distribution from the population of the lower energy level of the optical transition with a wavelength of 510.5 nm based on temperature obtained by Boltzmann plot technique (see Fig. 7). In the case of the combination of the LAS and OES methods, the number density was obtained similarly to the OES case, but using Eq. (6).

One can see that the radial distributions of number densities of copper atoms obtained by three different methods almost completely coincide along the entire radius. This, in turn, also indicates the possibility of using the combined LAS and OES technique to investigate the plasma with copper vapour admixtures.

CONCLUSIONS

The synchronized LAS and OES technique are proposed to investigate the plasma of a DC arc discharge with copper vapour admixtures. The possibility of using the simultaneous combination of the techniques has been proved by the coinciding the radial distributions of the excitation temperatures and copper number densities obtained by OES, LAS separately and by combination of both.

The proposed complex technique will make it possible to investigate the thermodynamic state of the plasma. In particular, it will be possible to examine the population distribution of energy levels in the copper atom in the investigated electric arc discharge plasma.

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СИНХРОНІЗОВАНА ЛАЗЕРНА АБСОРБЦІЙНА ТА ОПТИЧНА ЕМІСІЙНА СПЕКТРОСКОПІЯ ПЛАЗМИ З ДОМІШКАМИ ПАРІВ МІДІ

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Досліджено плазму дугового розряду постійного струму з домішками парів міді методом синхронізованої лазерної абсорбційної (ЛАС) і оптичної емісійної спектроскопії (ОЕС). Проаналізовано просторові та спектральні характеристики плазми дугового розряду між мідними електродами в потоці аргону при атмосферному тиску. Методами ОЕС зареєстровані спектри випромінювання і визначені температури заселення та заселеності енергетичних рівнів атома міді, які відповідають верхнім рівням оптичних переходів із довжинами хвиль, які досліджувались у цій роботі. Також методом ЛАС визначено заселеність нижнього енергетичного рівня одного із досліджуваних оптичних переходів. Синхронне застосування обох методів дозволяє визначити радіальні розподіли температур заселення та концентрації атомів міді. Узгодженість одержаних результатів підтверджує можливість використання синхронізованої лазерної абсорбційної та оптичної емісійної спектроскопії для діагностики плазми з домішками парів міді.