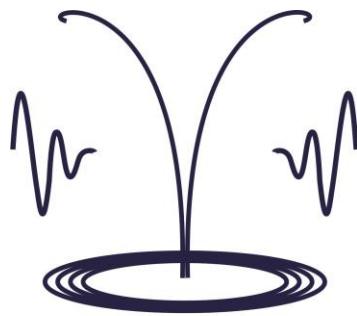


Radio Physics Faculty of Taras  
Schevchenko National University of Kyiv



## ATOMIC DATA AND STARK BROADENING OF CuI AND AgI SPECTRAL LINES: SELECTION AND ANALYSIS



9<sup>th</sup> SCGLSA  
Banja Koviljača  
May 13-17, 2013  
Serbia

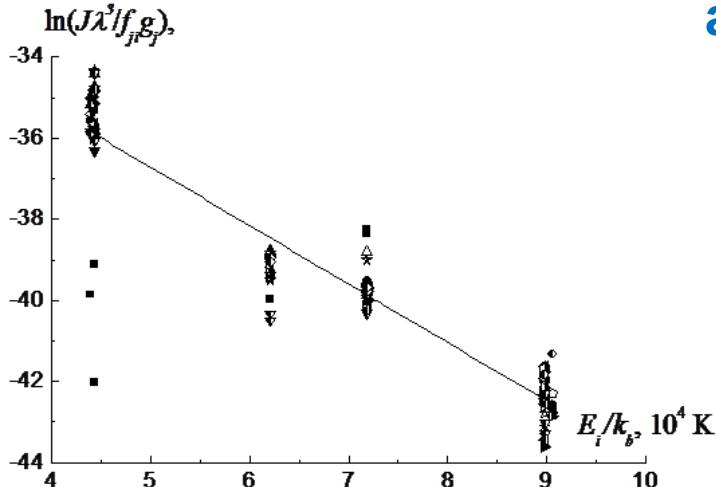
IX Serbian conference on  
spectral line shapes in  
astrophysics

R. V. Semenyshyn,  
I. L. Babich,  
V. F. Boretskij,  
A. N. Veklich



# Optical emission spectroscopy

## Selection of Cul spectral lines and their atomic data



Boltzmann plot obtained by Cul spectral lines at arc current 3.5 A using large variety of up-to-date atomic data.

$\lambda, \text{ nm}$	$g_j f_j$	References	Legend
427.5	0.9097	[1]	☆
465.1	1.4218	[1]	☆
510.5	0.0197	[2]	▼
515.3	1.6466	[3]	●
521.8	1.9717	[4]	▲
570.0	0.0057	[5]	◆
578.2	0.0130	[6]	△
793.3	0.4246	[3]	●
809.3	0.6120	[7]	■

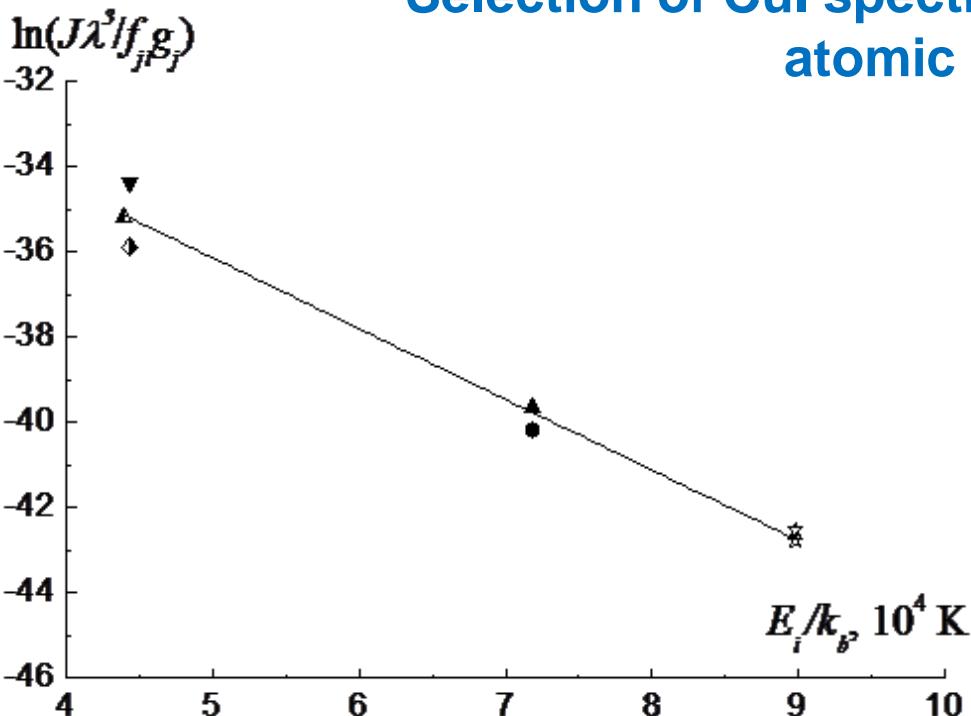
Selected Cul spectral lines and their atomic data.

1. Kerkhoff P. Micali G., Werner K., Wolf A., and Zimmermann P. Radiative decay and autoionization in the 4D-States of the 3d94s5s configuration in Cu I / H. Kerkhoff, // Z. Phys. A - Atoms and Nuclei – 1981. – 300. – P. 115-118.
2. Borges F. O., Cavalcanti G. H. and Trigueiros A. G. Determination of plasma temperature by a semi-empirical method // Brazilian Journal of Physics. – 2004. – 34, No 4B. – P. 1673-1676.
3. Bielski A. A critical survey of atomic transition probabilities for Cu I // J. Quant. Spectrosc. Radiat. Transfer. – 1975. – 15. – P. 463-472.
4. Pichler G. Properties of the oscillator strengths of Cu I and Ag I spectral lines // Fizika. – 1972. – 4. – P. 179-188.
5. Fu K. Jogwich M., Knebel M., and Wiesemann K. Atomic transition probabilities and lifetimes for the Cul system // Atomic Data and Nuclear Data Tables – 1995. – 61, No. 1. – P. 1-30.
6. Riemann M. Die Messung von relativen und absoluten optischen Übergangswahrscheinlichkeiten des Cul im wandstabilisierten Lichtbogen // Z. Phys. – 1964. – 179. P. 38-51.
7. Migdalek J. Relativistic oscillator strengths for some transitions in Cu(I), Ag(I) and Au(I) // J. Quant. Spectrosc. Radiat. Transfer – 1978. – 20, No. 1. – P. 81-87.



# Optical emission spectroscopy

## Selection of Cul spectral lines and their atomic data



$\lambda, \text{ nm}$	$g_i f_{ji}$	References	Legend
427.5	0.9097	[1]	☆
465.1	1.4218	[1]	☆
510.5	0.0197	[2]	▼
515.3	1.6466	[3]	●
521.8	1.9717	[4]	▲
570.0	0.0057	[5]	◆
578.2	0.0130	[6]	▲
793.3	0.4246	[3]	●
809.3	0.6120	[7]	■

Selected Cul spectral lines and their atomic data.

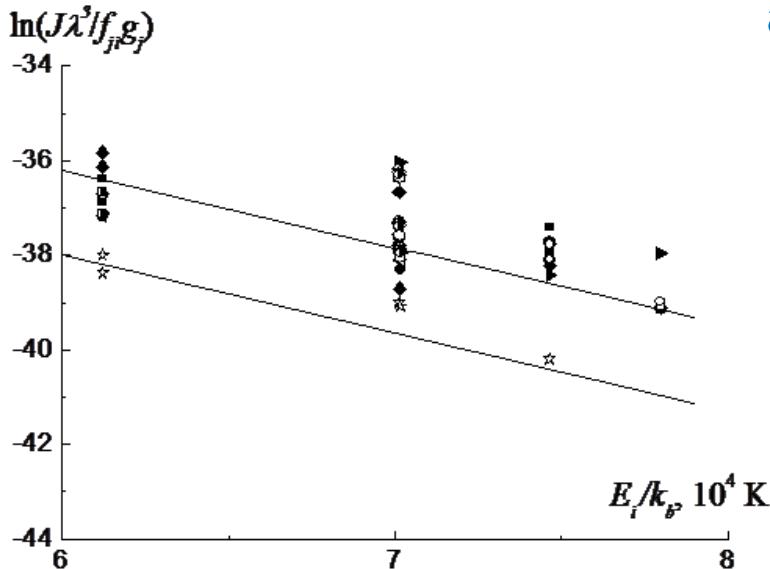
Boltzmann plot obtained by Cul spectral lines at arc current 3.5 A using selected atomic data.

Babich, I.L., Boretskij, V.F., Veklich, A.N., Ivanisik, A.I., Semenyshyn, R.V., Kryachko, L.A., Minakova, R.V., Spectroscopy of electric arc plasma between composite electrodes Ag-CuO // Electrical contacts and electrodes / Kiev: "Frantsevich Institute for Problems of Materials Science". 2010, p. 82-115 (in Ukrainian) // <http://dspace.nbuv.gov.ua/bitstream/handle/123456789/28892/12-Babich.pdf> – accessed May 14, 2013.



# Optical emission spectroscopy

## Selection of AgI spectral lines and their atomic data



Boltzmann plot obtained by AgI spectral lines at arc current 3.5 A using large variety of up-to-date atomic data.

$\lambda$ , nm	$g_{fj_i}$	References	Legend
405.5	0.2636	[8]	□
447.6	0.0300	[8]	○
466.8	0.0787	[9]	▶
520.9	1.0902	[4]	■
546.5	2.0335	[10]	★
547.2	0.3640	[11]	●
768.8	0.2392	[4]	■
827.4	0.1367	[12]	◆

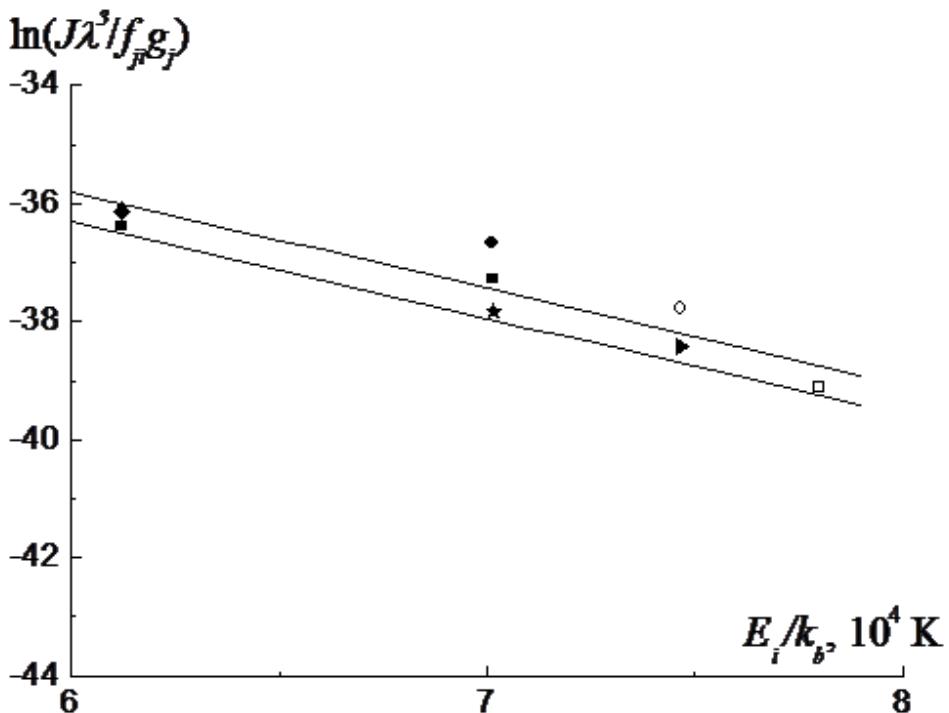
Selected AgI spectral lines and their atomic data.

8. Lavin C. Almaraz M. A., Martin I. Relativistic oscillator strengths for excited state transitions in some ions of the silver isoelectronic sequence // Z. Phys. D – 1995. – 34. – P. 143-149.
9. Plehotkina G. L. Radiative lifetimes Ag I, Ag II // Optics and Spectroscopy. – 1981. – 51, № 1. – P. 194-196.
10. Zheng N., Wang T., and Yang R. Transition probability of Cu I, Ag I, and Au I from weakest bound electron potential model theory // J. of Chem. Phys. – 2000. – 113. – P. 6169-6173.
11. Migdalek J. and Baylis W. E. Influence of atomic core polarisation on oscillator strengths for 2S1/2-2P1/2,3/2 and 2P1/2,3/2-2D3/2,5/2 transitions in Cu I, Ag I and Au I spectra // J. Phys. B: At. Mol. Phys. – 1978. – 11, No. 17. – P. L497-L501.
12. Terpstra J. and Smit J. A. Measurement of “optical” transition probabilities in the silver atom // Physica. – 1958. – 24. – P. 937-958.



# Optical emission spectroscopy

## Selection of AgI spectral lines and their atomic data



Boltzmann plot obtained by AgI spectral lines at arc current 3.5 A using selected atomic data.

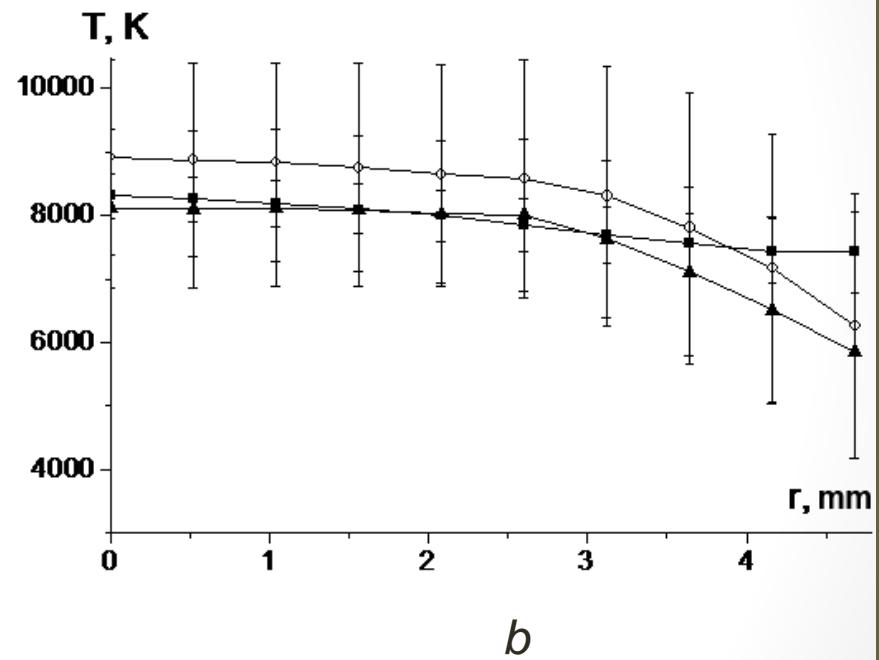
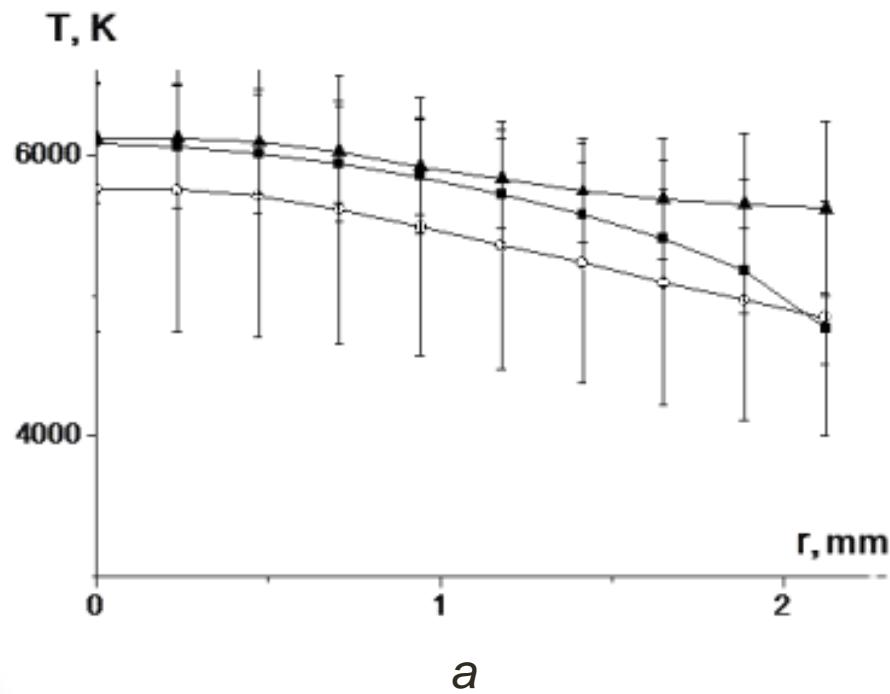
$\lambda, \text{ nm}$	$g f_{ji}$	References	Legend
405.5	0.2636	[8]	□
447.6	0.0300	[8]	○
466.8	0.0787	[9]	►
520.9	1.0902	[4]	■
546.5	2.0335	[10]	★
547.2	0.3640	[11]	●
768.8	0.2392	[4]	■
827.4	0.1367	[12]	◆

Selected AgI spectral lines and their atomic data.



# Optical emission spectroscopy

## Temperature measurement



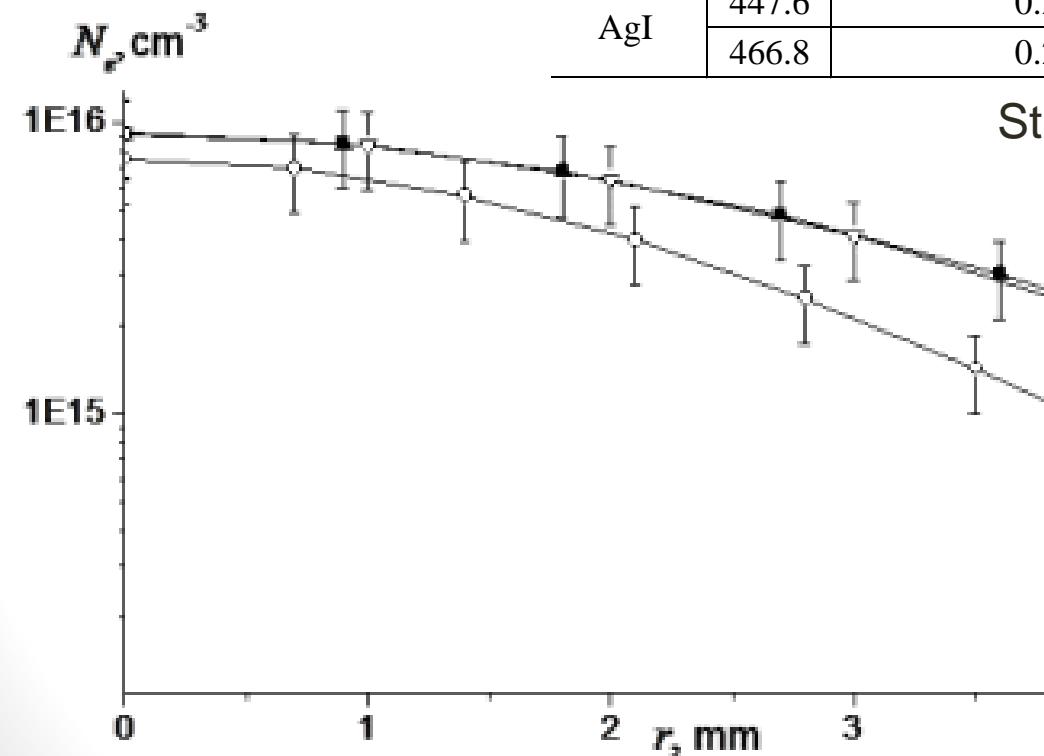
Radial profiles of electric arc plasma temperatures in air, obtained by Boltzmann plot technique using CuI ( $\blacksquare$ ), AgI ( $\circ$ ) spectral lines and by relative intensities of AgI 405.5 – 768.8nm ( $\blacktriangle$ ), arc currents 3.5 A (a) and 30 A (b).



# Optical emission spectroscopy

## Electron density measurement

Element	$\lambda, \text{ nm}$	$w, \text{ nm}$ $T = 10\,000\text{K}, N_e = 10^{17} \text{ cm}^{-3}$	$K = N_e / w,$ $10^{24} \text{ cm}^{-4}$	Reference
CuI	448.0	0.422	2.370	[13]
	515.3	0.346	2.890	[13]
AgI	447.6	0.209	4.785	[14]
	466.8	0.230	4.348	[14]



Radial distributions of electron density obtained by AgI 447.7 (■), AgI 466.8 (▲), CuI 448.0 (○) and CuI 515.3 (▽) nm in arc current 30 A

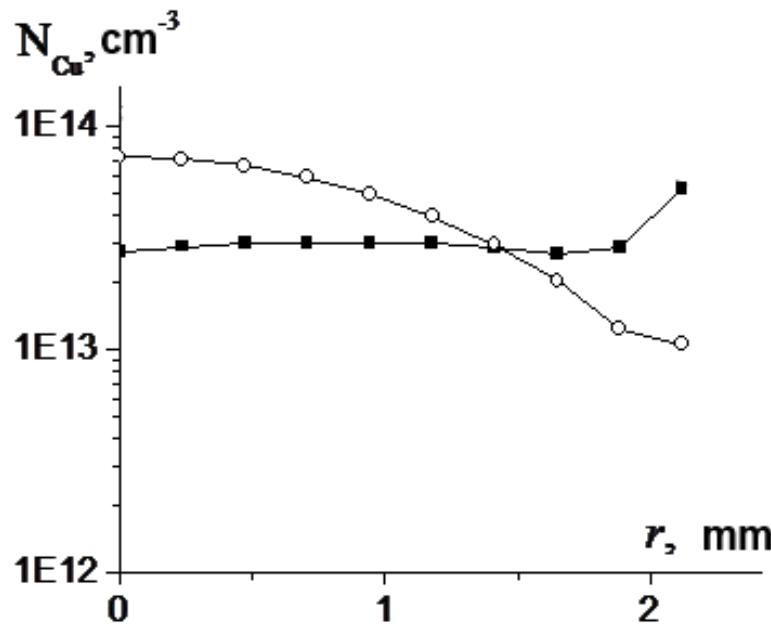
13. Konjevich R., Konjevich N. Stark broadening and shift of neutral copper spectral lines // Fizika. – 1986. – 18, No. 4. – p. 327-335.

14. Dimitrijevic M. S., Sahal-Brechot S. Atomic Data and Nuclear Data Tables. – 2003. – 85. – P. 269-290.



# Laser absorption spectroscopy

# Comparison of copper density measurement



*Radial profiles of cooper atoms density of electric arc discharge plasma obtained using OES (■) and LAS(○), arc current 3.5 A.*

# Conclusions

- Atomic data of CuI and AgI spectral lines were carefully analyzed and selected. Namely, oscillator strength of these elements are recommended for spectroscopic diagnostics of plasma sources with copper and/or silver vapours.
- Stark broadening of CuI and AgI spectral lines and parameters of this mechanism are testified.

Element	$\lambda, \text{ nm}$	$w, \text{ nm}$ $T = 10\ 000K, N_e = 10^{17} \text{ cm}^{-3}$	$K = N_e / w,$ $10^{24} \text{ cm}^{-4}$	Reference
CuI	448.0	0.422	2.370	[13]
	515.3	0.346	2.890	[13]
AgI	447.6	0.209	4.785	[14]
	466.8	0.230	4.348	[14]

CuI:

$\lambda, \text{ nm}$	$g_{fj_i}$	References
427.5	0.9097	[1]
465.1	1.4218	[1]
510.5	0.0197	[2]
515.3	1.6466	[3]
521.8	1.9717	[4]
570.0	0.0057	[5]
578.2	0.0130	[6]
793.3	0.4246	[3]
809.3	0.6120	[7]

AgI:

$\lambda, \text{ nm}$	$g_{fj_i}$	References
405.5	0.2636	[8]
447.6	0.0300	[8]
466.8	0.0787	[9]
520.9	1.0902	[4]
546.5	2.0335	[10]
547.2	0.3640	[11]
768.8	0.2392	[4]
827.4	0.1367	[12]

# Thank you for your attention

More detailed information concerning experiment organization and measurement techniques will be described during report:

“Spectroscopy peculiarities of thermal electric arc discharge plasma between composite electrodes Ag-SnO<sub>2</sub>-ZnO”  
(15.40 p.m., 16<sup>th</sup> of May)

# References

1. Kerkhoff P. Micali G., Werner K., Wolf A., and Zimmermann P. Radiative decay and autoionization in the 4D-States of the 3d94s5s configuration in Cu I / H. Kerkhoff, // Z. Phys. A - Atoms and Nuclei – 1981. – 300. – P. 115-118.
2. Borges F. O., Cavalcanti G. H. and Trigueiros A. G. Determination of plasma temperature by a semi-empirical method // Brazilian Journal of Physics. – 2004. – 34, No 4B. – P. 1673-1676.
3. Bielski A. A critical survey of atomic transition probabilities for Cu I // J. Quant. Spectrosc. Radiat. Transfer. – 1975. – 15. – P. 463-472.
4. Pichler G. Properties of the oscillator strengths of Cu I and Ag I spectral lines // Fizika. – 1972. – 4. – P. 179-188.
5. Fu K. Jogwich M., Knebel M., and Wiesemann K. Atomic transition probabilities and lifetimes for the CuI system // Atomic Data and Nuclear Data Tables – 1995. – 61, No. 1. – P. 1-30.
6. Riemann M. Die Messung von relativen und absoluten optischen Übergangswahrscheinlichkeiten des CuI im wandstabilisierten Lichtbogen // Z. Phys. – 1964. – 179. P. 38-51.
7. Migdalek J. Relativistic oscillator strengths for some transitions in Cu(I), Ag(I) and Au(I) // J. Quant. Spectrosc. Radiat. Transfer – 1978. – 20, No. 1. – P. 81-87.
8. Lavin C. Almaraz M. A., Martin I. Relativistic oscillator strengths for excited state transitions in some ions of the silver isoelectronic sequence // Z. Phys. D – 1995. – 34. – P. 143-149.
9. Plehotkina G. L. Radiative lifetimes Ag I, Ag II // Optics and Spectroscopy. – 1981. – 51, № 1. – P. 194-196.
10. Zheng N., Wang T., and Yang R. Transition probability of CuI, AgI, and AuI from weakest bound electron potential model theory // J. of Chem. Phys. – 2000. – 113. – P. 6169-6173.
11. Migdalek J. and Baylis W. E. Influence of atomic core polarisation on oscillator strengths for  $2S_{1/2}$ - $2P_{1/2,3/2}$  and  $2P_{1/2,3/2}$ - $2D_{3/2,5/2}$  transitions in Cu I, Ag I and Au I spectra // J. Phys. B: At. Mol. Phys. – 1978. – 11, No. 17. – P. L497-L501.
12. Terpstra J. and Smit J. A. Measurement of “optical” transition probabilities in the silver atom // Physica. – 1958. – 24. – P. 937-958.
13. Konjevich R., Konjevich N. Stark broadening and shift of neutral copper spectral lines // Fizika. – 1986. – 18, No. 4. – p. 327-335.
14. Dimitrijevic M. S., Sahal-Brechot S. Atomic Data and Nuclear Data Tables. – 2003. – 85. – P. 269-290.

# Supplementary information

$\lambda$ , nm	$g f_{ji}$	References	Legend
427.5	0.9097	[1]	☆
465.1	1.4218	[1]	☆
510.5	0.0197	[2]	▼
515.3	1.6466	[3]	●
521.8	1.9717	[4]	▲
570.0	0.0057	[5]	◆
578.2	0.0130	[6]	△
793.3	0.4246	[3]	●
809.3	0.6120	[7]	□

Table.1. Selected CuI spectral lines and their atomic data.

$\lambda$ , nm	$g f_{ji}$	References	Legend
405.5	0.2636	[8]	□
447.6	0.0300	[8]	○
466.8	0.0787	[9]	►
520.9	1.0902	[4]	■
546.5	2.0335	[10]	★
547.2	0.3640	[11]	●
768.8	0.2392	[4]	■
827.4	0.1367	[12]	◆

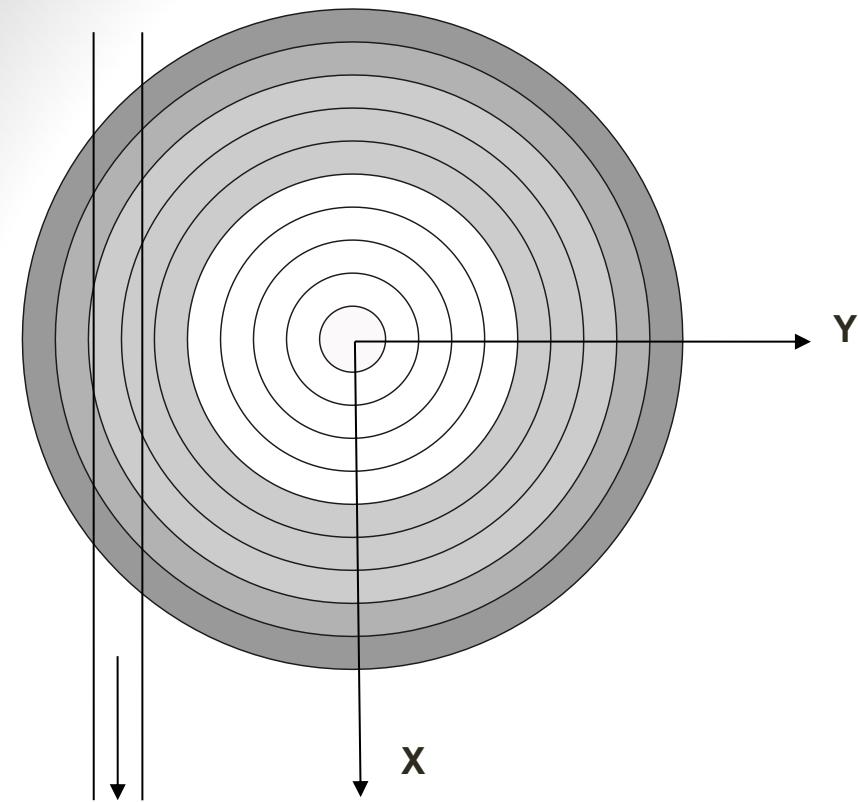
Table.2. Selected AgI spectral lines and their atomic data.

Element	$\lambda$ , nm	$w, nm$ $T = 10\ 000 K, N_e = 10^{17} cm^{-3}$	$K = N_e / w,$ $10^{24} cm^{-4}$	Reference
CuI	448.0	0.422	2.370	[13]
	515.3	0.346	2.890	[13]
AgI	447.6	0.209	4.785	[14]
	466.8	0.230	4.348	[14]

Table.3. Stark broadening data.

### References

- 1.Kerkhoff P. Micali G., Werner K., Wolf A., and Zimmermann P. Radiative decay and autoionization in the 4D-States of the 3d94s5s configuration in Cu I // H. Kerkhoff, // Z. Phys. A - Atoms and Nuclei – 1981. – 300. – P. 115-118.
- 2.Borges F. O., Cavalcanti G. H. and Trigueiros A. G. Determination of plasma temperature by a semi-empirical method // Brazilian Journal of Physics. – 2004. – 34, No 4B. – P. 1673-1676.
- 3.Bielski A. A critical survey of atomic transition probabilities for Cu I // J. Quant. Spectrosc. Radiat. Transfer. – 1975. – 15. – P. 463-472.
- 4.Pichler G. Properties of the oscillator strengths of Cu I and Ag I spectral lines // Fizika. – 1972. – 4. – P. 179-188.
- 5.Fu K. Jogwich M., Knebel M., and Wiesemann K. Atomic transition probabilities and lifetimes for the CuI system // Atomic Data and Nuclear Data Tables – 1995. – 61, No. 1. – P. 1-30.
- 6.Riemann M. Die Messung von relativen und absoluten optischen Übergangswahrscheinlichkeiten des CuI im wandstabilisierten Lichtbogen // Z. Phys. – 1964. – 179. P. 38-51.
- 7.Migdalek J. Relativistic oscillator strengths for some transitions in Cu(I), Ag(I) and Au(I) // J. Quant. Spectrosc. Radiat. Transfer – 1978. – 20, No. 1. – P. 81-87.
- 8.Lavin C. Almaraz M. A., Martin I. Relativistic oscillator strengths for excited state transitions in some ions of the silver isoelectronic sequence // Z. Phys. D – 1995. – 34. – P. 143-149.
- 9.Plehotkina G. L. Radiative lifetimes Ag I, Ag II // Optics and Spectroscopy. – 1981. – 51, № 1. – P. 194-196.
- 10.Zheng N., Wang T., and Yang R. Transition probability of CuI, AgI, and AuI from weakest bound electron potential model theory // J. of Chem. Phys. – 2000. – 113. – P. 6169-6173.
- 11.Migdalek J. and Baylis W. E. Influence of atomic core polarisation on oscillator strengths for  $2S_{1/2}-2P_{1/2,3/2}$  and  $2P_{1/2,3/2}-2D_{3/2,5/2}$  transitions in Cu I, Ag I and Au I spectra // J. Phys. B: At. Mol. Phys. – 1978. – 11, No. 17. – P. L497-L501.
- 12.Terpstra J. and Smit J. A. Measurement of “optical” transition probabilities in the silver atom // Physica. – 1958. – 24. – P. 937-958.
- 13.Konjevich R., Konjevich N. Stark broadening and shift of neutral copper spectral lines // Fizika. – 1986. – 18, No. 4. – p. 327-335.
- 14.Dimitrijevic M. S., Sahal-Brechot S. Atomic Data and Nuclear Data Tables. – 2003. – 85. – P. 269-290.



Abel transformation:

$$I(y) = 2 \int_0^{\sqrt{R^2 + y^2}} \varepsilon(r) dx = 2 \int_y^R \frac{\varepsilon(r) r dr}{\sqrt{r^2 - y^2}}$$

$\varepsilon(r)$  – local emissivity

$$\varepsilon(r) = -\frac{1}{\pi} \int_r^R \frac{\partial I(y)}{\partial y} \frac{dy}{\sqrt{r^2 - y^2}}$$

[\*] proposed a method of representation of the this integral equation as a system of linear equations

$$\varepsilon(r) = \sum_{k=1}^n \beta_{ik} I(y_k)$$

---

\* Bockasten K. Transformation of Observed Radiances into Radial Distribution of the Emission of a Plasma // Journal of the optical society of America. – 1961. – V. 51, – P. 943-947.

# Model of local thermal equilibrium

$$dn(v) = n4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} \exp\left(-\frac{mv^2}{2k_B T}\right) v^2 dv$$

- distribution law of velocities of plasma particles (atoms, molecules, ions) is subordinate to Maxwell

$$\frac{n_i}{n_k} = \frac{g_i}{g_k} \exp\left(-\frac{\Delta E_{ik}}{k_B T}\right)$$

- value of concentrations of particles in the i-th and k-th state are from the Boltzmann formula

$$\frac{n^+ n_e}{n_a} = \frac{2 \sum^+}{\sum_a} \left( \frac{2\pi m k_B T}{h^2} \right)^{3/2} \exp\left(-\frac{E_1}{k_B T}\right)$$

- concentrations of plasma components (electrons, atoms and ions) linked Saha equation of ionization

# Technique of relative intensities of spectral lines

$$I_{ki} = N_k A_{ki} h \nu_{ki}$$

- Intensity of spectral lines

$$I = \int I_\nu d\nu = \frac{1}{4\pi} \frac{g_k A_{ki}}{\sum_a} n h \nu \exp\left(-\frac{E_k}{k_B T}\right)$$

- for optically thin plasma the intensity of spectral lines

$$\frac{I_1}{I_2} = \frac{A_1 g_1 n_1 \lambda_2 \sum_2}{A_2 g_2 n_2 \lambda_1 \sum_1} \exp\left(-\frac{E_1 - E_2}{k_B T}\right)$$

- the ratio of intensities of two spectral lines

$$\frac{I_1}{I_2} = \frac{A_1 g_1 \lambda_2}{A_2 g_2 \lambda_1} \exp\left(-\frac{E_1 - E_2}{k_B T}\right)$$

- if two lines belong to the same atom or ion

$$T[K] = \frac{E_2 - E_1}{k_B \left( \ln \frac{I_1}{I_2} - \ln \frac{A_1 g_1 \lambda_2}{A_2 g_2 \lambda_1} \right)}$$

- temperature of plasma from method of relative intensities of spectral lines

# Electron density in case of dominating Stark broadening of spectral lines

$$N_e = K \cdot \Delta\lambda$$

$K$  – proportionality coefficient, which reflects the electrons density normalized to the half-width of the spectral line

## Method of calculation electron density in case with current 3.5A

$$N_e = \sum N_j ; \quad j \rightarrow Cu, Zn, N, O$$

$$N_e N_{j^+} = 4.85 \cdot 10^{15} N_j \frac{U_{j^+}}{U_j} T^{3/2} e^{-E_j^i/kT}$$
$$N_e^2 = 4.85 \cdot 10^{15} T^{3/2} \sum \left( N_j \frac{U_{j^+}}{U_j} e^{-E_j^i/kT} \right)$$

$$N_e^2 = 4.85 \cdot 10^{15} T^{3/2} N_{Cu} \sum \left( \frac{U_{j^+}}{U_j} e^{-E_j^i/kT} \right)$$

$$B \approx \frac{N_{Cu}}{I_{5153} U_{Cu} \cdot e^{E_{5153\_up}/kT}} \Bigg|_{I=30A}^{r=0}$$

$$N_{Cu} = B \cdot I_{5153} U_{Cu} \cdot e^{E_{5153\_up}/kT}$$