Effect of composition of electrolyte cathode on emission intensity of metal atoms in the discharge plasma at atmospheric pressure

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Abstract. The emission spectra and the plasma parameters of discharges were investigated. Water solutions of copper and nickel chlorides with additions of sodium chloride were used as electrolyte cathodes. The change of the relative intensities of the emission lines of the elements (Cu and Ni) with increasing NaCl concentrations in the solution is shown. The gas temperature and the reduced electric field strength in the plasma were founded. The electron energy distribution function and the excitation rate coefficients for emitting states of copper and nickel atoms by the numerical solution of the Boltzmann equation were obtained. It was shown that in plasma emission spectroscopy measuring it is necessary to consider the correlation between rates of excitation and composition of the sample solution in order to determine the concentration of metal ions in the water solutions.

1. Introduction
Determination of metal ion concentrations in drinking water and wastewater industry is a crucial challenge associated with the problems of health and environmental protection. Several studies have shown that in order to control the composition of aqueous solutions the direct current discharge excited between the cathode electrolyte (analyzed solution) and metal anode can be used [1-5]. At that the lines of the metal atoms were registered in the emission spectra of the discharge. The method has a high sensitivity (up to 10^{-9} \text{ gl}^{-1} [2]), low-power [3], does not require expensive equipment and allows analysis under atmospheric pressure without using an inert atmosphere. The experiments with solutions of salts showed that the intensity of the analyzed lines corresponding cations concentration in solutions is linear in a wide concentration range (0.1 to 100 \text{ mgl}^{-1}) [4]. However, it is known that the emission intensity of atoms strongly depends on the pH of the solution [5]. Furthermore it is established that various additives to the solutions have the great influence on the line intensity of atoms [2].

Reliable basis of the method requires solving a number of questions. It is necessary to define the mechanism of occurrence of analyzed atoms in the gas phase, mechanisms of the excitation and deactivation of the emitting states, the influence of the transfer of liquid cathode components to the gas phase on the physical parameters of the plasma. The concentration of the metal atoms in the plasma is determined by the transport processes of the liquid components of the cathode due to ion bombardment, as well as all the chemical processes that lead to the formation and expenditure of atoms [6]. If atoms go into emission state due to electron impact, it is necessary to know the excitation rate coefficients that depend on the electron energy distribution function (EEDF). In turn, EEDF depends on reduced electric field strength in the plasma ($E/N$) and a full set of electron collisions. The
transfer processes alters the composition of the gas phase and they lead to a change of discharge characteristics. Thus, it can be expected that the composition of the cathode liquid electrolyte (solution) will affect the intensity of emission lines analyzed metals even at constant concentration of the corresponding ions in solution.

The aim of this work is experimental study of the effect of electrolyte composition of the cathode on the intensity of the emission lines of copper and nickel atoms and influence on the rates of excitation coefficients of the emission states.

2. Experimental part
Simplified scheme of experimental set-up is shown in Figure 1. Direct current (DC) discharge ($i = 10 – 50$ mA) was excited by applying high voltage between the surface of aqueous cathode and copper cathode which placed at the position 1–10 mm above the liquid surface. Water solutions of copper and nickel chlorides with concentrations of $(1–5) \times 10^{-3}$ mol l$^{-1}$ were used as cathodes. Solution of sodium chloride ($c = 0.05 – 0.5$ mol l$^{-1}$) is used as an additional electrolyte. The electric field strength in plasma ($E$) and the cathode voltage drop ($U_c$) were calculated from dependences of the discharge voltage on the inter-electrode distance. These dependencies are approximated by a linear function with a correlation coefficient is not less than 0.99. The emission spectra of the positive column ($\lambda = 200 – 950$ nm) were recorded by the AvaSpec-2048 spectrometer (grating 600 lines mm$^{-1}$). Gas temperature was found from the intensity distribution in the radiation band of $N_2 (C^3\Pi_u \rightarrow B^3\Pi_g, 0–2)$ transition as described in [7]. To evaluate the reproducibility of the results were performed five independent measurements. Limits of the confidence intervals were calculated with a confidence level 0.9.

3. Results and discussions
The dependences of the relative intensity of Cu atoms emission lines ($\lambda = 324.7$ nm, $\epsilon_{ex} = 3.82$ eV) and Ni atoms emission lines ($\lambda = 361.9$ nm, $\epsilon_{ex} = 3.54$ eV) on the concentration of the corresponding salts in solution at different concentrations of the additional electrolyte NaCl are shown in Figure 2. The emission intensity is directly proportional to the concentration of respective cations in the liquid cathode, but the angular dependency coefficients are significantly various for different concentrations of sodium chloride. Minimum slope of the straight line $I = f(c)$ is observed without of NaCl in the solution, the maximum is observed in additional electrolyte concentration 0.05 mol l$^{-1}$. At least there are two reasons of influences of the sodium chloride additive in liquid cathode on the intensity of emission analyzed atoms.
The intensities of the lines of copper (a) and nickel (b) atoms at various concentrations of sodium chloride in solution: 0 (1), 2 – 0.05 (2), 0.1 (3), 0.2 (4), 0.5 mol l\(^{-1}\) (5). \(i = 50\) mA.

First, NaCl additive changes the value of the cathode voltage drop which in its turn determines the average energy of positive ions bombarding the surface of liquid cathode and the rate of cathode sputtering. Second, the electric field strength in plasma and character of the EEDF are changed and as a result the rates of excitation of the emitting states by electron impact are altered.

Experiments showed that the rotational temperature of \(N\_2 (C^3I\_L\_u)\), which can be identified with the temperature of the gas is \((1600 \pm 100)\) K and weakly depends on the discharge current and on the composition of the electrolyte cathode. At once, the reduced electric field strength in plasma is decreased with increasing concentration of sodium chloride in the solution (Figure 3). As a result, it changes behavior of EEDF and the rate coefficients of threshold processes including processes of electron impact excitation states Cu and Ni atoms. The rate coefficients of the electron impact excitation of Cu \((4p^3P^o_3/2)\) and Ni \((4s^2D)\) were calculated by using EEDF (Table 1). The electron energy distribution function was obtained by numerical solution of the Boltzmann equation (software package BOLSIG+) [8]. The collisions of the electrons with the molecules \(N\_2, O\_2\) (at a ratio of mole fraction \(y(N\_2):y(O\_2) = 4:1\)), \(H\_2O\) and NO were taken into account in our calculations with using cross-sections from [9, 10]. The mole fraction of water in plasma \((\sim 0.01)\) was evaluated by the rate of accumulation of condensate in a trap, and for NO molecules \((\sim 2.5 \times 10^{-3})\) by using data obtained by means of numerical modeling of processes in plasma [6].

The calculations showed the nearly twofold decrease in the rates of excitation coefficients of the emission states with the addition of sodium chloride in solution-cathode. However, it does not fully explain the changes observed in the emission intensity. It is clearly seen that for further analysis of the results one should take into account the change in the rate of transfer of the solution components in plasma, as well as the mechanisms of excitation and deactivation of the emitting states of analyzed atoms. Changing the efficiency of the liquid cathode components transfer in the plasma can be explained by the dependence of the cathode voltage drop \((U\_c)\) on the composition of the electrolyte cathode. For example, the value of cathode voltage drop is \((615 \pm 20)\) V in discharge with liquid cathode without sodium chloride but at a concentration of NaCl 0.05 mol l\(^{-1}\) \(U\_c\) is \((490 \pm 10)\) V and weakly increases with increasing concentration of additional electrolyte.
The dependences of the reduced electric field strength in the plasma of the discharge current at different concentrations of electrolyte solutions: 1, 3, 5, 7 – cathode – solution of CuCl₂, 2, 4, 6, 8 – cathode – solution of NiCl₂. Concentration of NaCl – 0 (1, 2), 0.05 mol l⁻¹ (3, 4), 0.1 mol l⁻¹ (5, 6), 0.5 mol l⁻¹ (7, 8).

**Figure 3.**

**Table 1.** The rate coefficients of the electron-impact excitation of Cu (4p²P°₃/₂) and Ni (4s₂D)

| i (mA) | Cu       | Ni       |
|--------|----------|----------|
|        | k (cm³s⁻¹) | Concentration of NaCl in solution (mol l⁻¹) |                   |
| 0      | 0        | 0        | 0.05     | 0.5     | 0        |
| 30     | 2.68×10⁻¹⁰ | 1.72×10⁻¹⁰ | 1.49×10⁻¹⁰ | 2.64×10⁻¹⁰ | 1.69×10⁻¹⁰ | 1.46×10⁻¹⁰ |
| 40     | 2.16×10⁻¹⁰ | 1.42×10⁻¹⁰ | 1.21×10⁻¹⁰ | 2.12×10⁻¹⁰ | 1.41×10⁻¹⁰ | 1.19×10⁻¹⁰ |
| 50     | 2.07×10⁻¹⁰ | 1.24×10⁻¹⁰ | 1.09×10⁻¹⁰ | 1.97×10⁻¹⁰ | 1.22×10⁻¹⁰ | 1.06×10⁻¹⁰ |

**Acknowledgments**
The study was supported by Russian Foundation for Basic Research according to the research project 16–33–60061 mol_a_dk.

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