Application of atmospheric pressure discharges with a liquid cathode for determination of alkaline-earth metal ions in aqueous solutions

N A Sirotkin¹, V A Titov¹² and O I Ignat'yev²

¹G.A. Krestov Institute of Solution Chemistry RAS, Ivanovo, 153045, Russia
²Ivanovo State University of Chemistry and Technology, Ivanovo, 15300, Russia

E-mail: alexsad8@yandex.ru

Abstract. The concentrations alkaline-earth metal ions in water solutions were determined by the method of emission actinometry of atmospheric pressure discharge plasma with a liquid cathode. The rubidium atoms were the actinometer component in plasma, whose cations with a known concentration were added to the analyzed solution. The solutions of magnesium, calcium, barium with concentrations of 10⁻⁵-10⁻⁴ g l⁻¹ were analyzed. It is established that the addition of electrolytes in the solution influence on the emission intensity of the metal atom lines. However, the use of the ratio of the intensities of the radiation of the analyzed components and the component-actinometer can improve the accuracy of the analysis. The water hardness factor of the tap water was determined using this method.

1. Introduction

The emission-spectral analysis of the content of metal ions in water is one of the areas of use of gas discharges in contact with liquids. Determining the concentration of ions in drinking water and wastewater of industrial enterprises is an important task related to the problems of health and environmental protection. DC discharge with the analyzed solution using as liquid electrolyte cathode and a metal electrode placed in the gas phase could be applied to determine the composition of water and aqueous solutions [1-3]. The lines of metals are registered in the plasma emission spectra, which are present in the solution in the form of cations due to the transfer of components of the solute into the plasma under the action of ion bombardment. The method has several advantages, including high sensitivity, low power consumption, ease of instrumentation, no need to use inert media and the ability to analyze mixtures of cations without prior separation. The advantages suggest that this method is promising for the quantitative analysis of aqueous solutions, including biological or industrial origin. The concentration of sodium, potassium, magnesium, calcium ions is determined in tap water [4–7], the concentrations of Cu, Pb and other heavy metals (Cd, Ni, Zn) ions were obtained in [6, 7]. It was noted that the intensities of the emission lines of atoms in plasma depend on the pH of the solution. The effect of various additives present in the solutions on the intensities of metal atoms lines was established in [8, 9]. The main reason for this is the effect of a change in the plasma composition on physical characteristics, in particular, on the reduced field strength and, as a result, on the energy distribution function of electrons. This makes it difficult to analyze solutions with high mineralization since the additional electrolytes can unpredictably affect the intensity of the lines of analyzed metals.
The aim of this work is to analyze the possibility of determination of the concentration of metal ions in aqueous solutions by the method of optical emission actinometry of plasma using an atmospheric pressure discharge with a liquid cathode.

2. Experimental part
A direct current discharge ($i = 50 \text{ mA}$) was excited at atmospheric pressure between the surface of the solution, which used as the electrolyte cathode, and the rod anode of copper, 2.0 mm in diameter, placed in the air above the solution (fig. 1). The emission spectra of the discharge were registered by the AvaSpec-3648 spectrometer. Details of the experimental set-up and the details of the experiment are described in [10]. Solutions of magnesium, calcium, and barium chlorides with concentrations of $10^{-6} - 10^{-4} \text{ g l}^{-1}$ in bidistilled water were used as liquid cathodes. Solution of sodium chloride ($C_b = 0.05 - 0.5 \text{ mol l}^{-1}$) is used as an additional background electrolyte. The actinometer component was rubidium atoms, the cations were added to the analyzed solution to a concentration of $10^{-2} \text{ g l}^{-1}$. To determine the concentration of the metals under analysis we used the ratio of the emission intensities of the Rb atoms ($\lambda=780.1 \text{ nm}$, transition $2^2\text{P}^0 \rightarrow 2^2\text{S}$) as an actinometer component and Mg atoms ($\lambda=285.3 \text{ nm}$, transition $1^1\text{P}^0 \rightarrow 1^1\text{S}$), Ca ($\lambda=657.3 \text{ nm}$, transition $3^3\text{P}^0 \rightarrow 1^1\text{S}$), Ba ($\lambda=553.6 \text{ nm}$, transition $1^1\text{P}^0 \rightarrow 1^1\text{S}$) as analyzed components:

$$\frac{C_{X^+}}{C_{A^+}} = \frac{I^X k^X \sum z^X A_x s_x}{I^A k^A \sum z^A A_x s_x}$$

(1)

where $C_{X^+}$ is the concentration of cations of the analyzed ions; $C_{A^+}$ is the concentration of cations of the component-actinometer in the analyzed solution; $I^X$, $I^A$ are the intensities of the emission lines of the analyzed component and the actinometer component, $k^X$, $k^A$ are the rate constants for the excitation of emission states; $A_x$, $A_x$ are the probabilities of emission transitions; $\Sigma z^X$ and $\Sigma z^A$ are total frequencies of deactivation in the processes of emission and quenching; $s_x$, $s_x$ are the transfer coefficients of the solution components into the plasma.

To calculate the coefficients of the excitation rates of the emission states by electron impact we used the energy distribution function of electrons which was found by numerical solution of the Boltzmann equation, as described in [11].

We used the experimental values of the electric field strength in plasma and the gas temperature in the calculations. The field strength in the plasma and the gas temperature are determined by the methods given in [12, 13]. We used the transfer coefficients obtained in [10].

![Figure 1. Experimental setup: 1 — metal anode, 2 — discharge, 3 — optical fiber, 4 — liquid cathode, 5 — glass condensate trap, 6, 7 — inlet and outlet of the solution from the peristaltic pump, 8 - reverse refrigerator.](image)
3. Results and discussions
The metal cations transfer the gas phase from the electrolyte-cathode due to ion bombardment and the emission lines of metal atoms are registered in the discharge spectra. The experimental results show that the intensities of the lines of the analyzed metals are directly proportional to the concentration of the corresponding cations in the liquid cathode, but the angular coefficients of the straight lines differ at different concentrations of the additional background electrolyte (NaCl). Minimum slope of the straight line is observed without of NaCl in the solution, the maximum is observed in additional electrolyte concentration 0.05 mol l⁻¹. Thus, the additional cation can affect the reliability of the obtained concentrations of the analyzed ions using the plasma emission spectroscopy method for the analysis of solutions. Using the method of optical actinometry of the plasma is one of the ways to solve the problem. In this case, the component-actinometer with a known concentration is added to the analyzed solution. Concentrations of the analyzed cations are determined by the relation (1) using the transfer coefficients of the components. The results of the analysis of solutions containing ions of magnesium, calcium or barium, are presented in table 1. The average error in determining the concentration of cations is 7%.

| Table 1. The results of the analysis of aqueous solutions containing ions of magnesium, calcium or barium by the method of emission actinometry of the plasma. |
|--------------------------------------------------|
| Experimental conditions | Concentration | Measured value | Precision, % |
|-------------------------|---------------|----------------|--------------|
| i = 70 mA, C₅= 0 mol l⁻¹ | 5×10⁻⁴ | (4.5±0.4)×10⁻⁴ | 10 |
| i = 70 mA, C₅= 0.05 mol l⁻¹ | 1×10⁻⁶ | (1.2±0.6)×10⁻⁶ | 2 |
| i = 70 mA, C₅= 0.1 mol l⁻¹ | 5×10⁻⁴ | (4.7±0.3)×10⁻⁴ | 6 |
| i = 70 mA, C₅= 0 mol l⁻¹ | 5×10⁻⁶ | (4.5±0.8)×10⁻⁶ | 10 |
| i = 70 mA, C₅= 0.05 mol l⁻¹ | 5×10⁻⁴ | (4.7±0.4)×10⁻⁴ | 6 |
| i = 70 mA, C₅= 0.1 mol l⁻¹ | 1×10⁻⁶ | (9.6±0.5)×10⁻⁷ | 4 |
| i = 70 mA, C₅= 0 mol l⁻¹ | 5×10⁻⁴ | (4.5±0.8)×10⁻⁴ | 10 |
| i = 70 mA, C₅= 0.05 mol l⁻¹ | 5×10⁻⁶ | (4.5±0.7)×10⁻⁶ | 10 |
| i = 70 mA, C₅= 0.1 mol l⁻¹ | 5×10⁻⁴ | (4.8±0.3)×10⁻⁴ | 4 |
| i = 70 mA, C₅= 0 mol l⁻¹ | 1×10⁻⁶ | (9.5±0.5)×10⁻⁷ | 5 |
| i = 70 mA, C₅= 0.05 mol l⁻¹ | 5×10⁻⁴ | (4.5±0.6)×10⁻⁴ | 10 |
| i = 70 mA, C₅= 0.1 mol l⁻¹ | 5×10⁻⁶ | (4.6±0.5)×10⁻⁶ | 8 |

Samples of tap water taken from centralized drinking water supply systems of the Ivanovo city (Russia) were analyzed. To provide the necessary electrical conductivity, nitric acid was added to the samples to pH 1. The actinometer component was rubidium, which cations were added to the analyzed solution to a concentration of 10⁻² g l⁻¹. The lines of sodium, potassium, magnesium, calcium and rubidium atoms, as well as the lines of hydrogen and oxygen atoms and the bands of NO, N₂ molecules and OH radicals were registrated in the discharge emission spectra (Fig. 2).
According to the results of the experiments, the total concentration of calcium and magnesium ions in water (water hardness factor) is $5.6 \pm 0.4$ °GH ($0.28 \pm 0.02$ g l$^{-1}$). In accordance with this criterion, drinking water is quite hard but is consistent with the standards established by the Sanitary Regulations and Norms (2.1.4.1074-01).

Thus, the method of optical actinometry of plasma discharges of atmospheric pressure with a liquid cathode can be used for the quantitative determination of the content of various ions in water and aqueous solutions.

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

References
[1] Pohl P, Jamroz P, Swiderski K, Dzimitrowicz A, Lesniewicz A. 2017 TrAC Trend. Anal. Chem. 88 119
[2] Marcus R K, Manard BT, Quarles CD. 2017 J. Anal. At.Spectrom. 32 704
[3] Mezei P, Cserfalvi T. 2012. Sensors. 12 6576
[4] Mezei P, Cserfalvi T, Janossy M, Szöcs K, Kim H J. 1998 J. Phys. D: Appl. Phys. 31 2818
[5] Mezei P, Cserfalvi T, Jánossy M. 1997 J. Anal. At. Spectrom. 12 1203
[6] Kim H J, Lee J H, Kim M Y, Cserfalvi T, Mezei P. 2000 Spectrochim. Acta, Part B. 55 823
[7] György K, Bencs L, Mezei P, Cserfalvi T. 2012 Spectrochim. Acta, Part B. 77 52
[8] Zhang Z, Wang Z, Li Q, Zou H, Shi Y. 2014 Talanta. 119 613
[9] Shekhar R, Madhavi K, Meeravali N N, Kumar S J. 2014 Anal. Method. 6 732
[10] Sirotkin N A, Titov V A. 2017 Plasma Chem. Plasma Process. 37 1475
[11] Sirotkin N A, Titov V A, Smirnov S A. 2018 J. Phys.: Conf. Ser. 1058 012034
[12] Sirotkin N A, Titov V A. 2017 J. Phys.: Conf. Ser. 789 012054
[13] Titov V A, Rybkin V V, Smirnov S A, Kulentsan A I, Choi H-S. 2006 Plasma Chem. Plasma Process. 26 543