

EXCITATION OF SPECTRA OF METALS
DURING DISCHARGE IN ELECTROLYTER. N. Medvedev¹, I. A. Zarubin², and A. D. Shokolov³

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Temperatures of electrolyte discharge on a metal current concentrator (with different polarity) at voltages of up to 1 kV were measured by spectral pyrometry. It is shown that for metal current concentrators, the temperature is higher than for diaphragm concentrators at the same applied voltage and reaches 4000 K which is sufficient to excite the atoms of most metals. Spectra of solutions of NaCl, K₂CO₃, CuSO₄, CaCl₂, MgSO₄, and FeCl₃ were obtained using a Kolibri-2 spectrometer (VMK-Optoelectronic, Novosibirsk, Russia). Calibration curves of the relative line intensities of potassium and magnesium vs. mass concentration were constructed.

Keywords: liquid discharge; emission spectral analysis

1 Introduction

A method for quantitative determination of metals in conductive liquids using a diaphragm discharge was tested in [1]. The obtained detection limits for copper and potassium (~ 50 mg/l) are insufficient for a quantitative determination of these elements in water bodies because of the maximum permissible concentrations. The temperature of 2200 K measured by the spectral pyrometry method [2] is sufficient only for dissociation of alkaline and alkaline earth metals [3].

To reduce the detection limit of metals in conductive liquids and to increase the plasma temperature, the studies of a discharge on a metal current concentrator in electrolyte solutions have been performed.

A zone with high electric field strength is formed near a metal sharpener, thus making it possible to ionize and excite the atoms of the medium at a voltage between the electrodes several times lower than the breakdown voltage. Placing the sharpener in electrolyte, the excitation voltage of the atoms was further reduced due to the fact that the opposite electrode is the wall of the bubble surrounding the sharpener and in this case, the electrode gap is minimal. Next, in the presence of plasma in the bubble, it increases in size due to evaporation from the walls and can reach the opposite metal electrode. This leads to closure of the electrode gap and reach-through breakdown between the sharpener and the opposite electrode [4].

2 Experimental

The experiments were conducted at atmospheric pressure and room temperature. The experimental setup used is shown in Fig. 1. Round cell 1 was filled with electrolyte; at the bottom was an epoxy resin wall 2 with a glued-in ring of tungsten foil 3. The upper end of the foil was aligned with the upper edge of the wall. The foil thickness was 0.07 mm

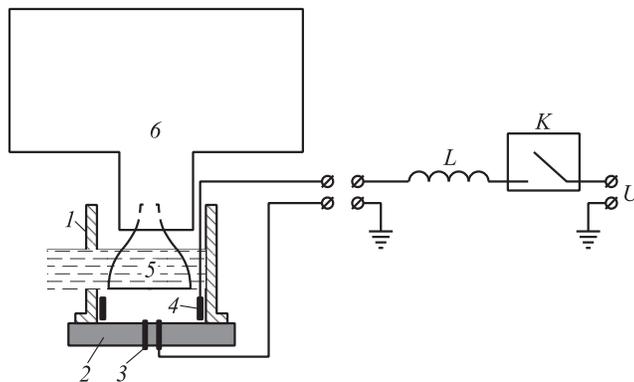


Figure 1 Schematic of the experimental setup for recording discharge spectra on metal current concentrators

and the diameter of the ring was 2 mm. The opposite ring-shaped electrode 4 was located on the wall of the cell. Focon 5 was used to focus the light onto the entrance slit of spectrometer 6 (Kolibri-2, VMK-Optoelectronic) with a spectral wavelength range $\lambda = 190\text{--}1100$ nm.

The experiments were performed with both positive and negative polarities of the metal concentrator which was the ring of tungsten foil.

The opposite electrode was made of stainless steel.

In the experiments, the $5 \cdot 10^{-6} \dots 1\%$ (wt.) solutions of K_2CO_3 , CuSO_4 , CaCl_2 , MgSO_4 , and FeCl_3 in distilled water were used.

The salt NaCl at a fixed concentration was added to the solutions to provide conductivity and normalization of the spectra.

The discharge circuit consisted of an inductor $L = 18$ mH and an electron switch K which was triggered simultaneously with the start of spectrum recording. The setup was connected to a constant-voltage source $U = 500\text{--}1200$ V.

The discharge time and the exposure in spectrum recording were 0.5–1 s.

3 Experimental Results

Figure 2 shows the spectra of solutions of 0.1%(wt.) NaCl and 1%(wt.) MgSO_4 with positive (Fig. 2a) and negative (Fig. 2b) polarity of the metal current concentrator.

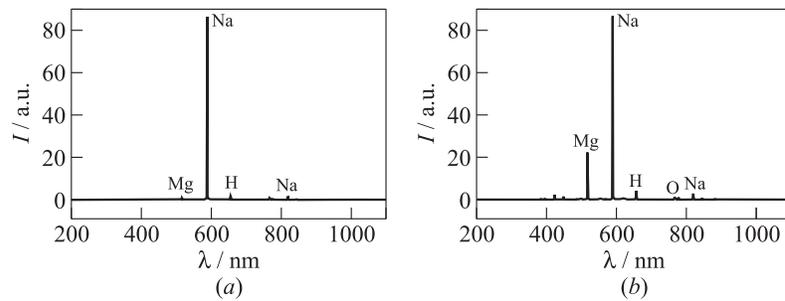


Figure 2 Spectrum of an aqueous solution of 1%(wt.) MgSO_4 and 0.1%(wt.) NaCl : (a) positive polarity, $U = 900$ V; and (b) negative polarity, $U = 500$ V

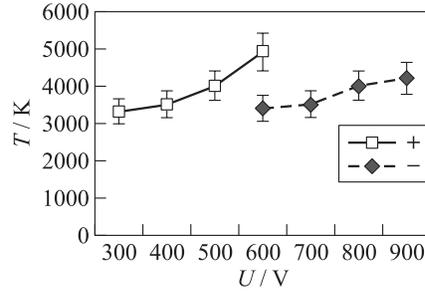


Figure 3 Temperature of the discharge plasma vs. voltage: 1 — positive polarity; and 2 — negative polarity

Comparison of the spectra in Figs. 2a and 2b shows that in the case of negative polarity, the lines of the metals are much more intense than those in the case of positive one.

Using the spectral pyrometry method [2], one can determine the plasma temperature using the characteristics of the resulting spectrum. The temperature is equal to the slope of the line obtained in the construction of the thermal radiation spectrum in the coordinates:

$$x = \ln \left(\frac{I\lambda^5}{C_1} \right) ; \quad y = \frac{C_2}{\lambda}$$

(I is the radiation intensity at wavelength λ ; $C_1 = 37418 \text{ W}\cdot\mu\text{m}^4/\text{cm}^2$, and $C_2 = 14388 \mu\text{m}\cdot\text{K}$).

Figure 3 shows the curves of plasma temperature vs. voltage for discharges on the metal concentrator with positive and negative polarity. The liquid was a solution of 0.5% (wt.) CaCl_2 + 0.5% (wt.) NaCl in distilled water. The lower voltage limit corresponds to the threshold of occurrence of the calcium lines (422.67 nm), and upper voltage limit to the reach-through breakdown between the metal electrodes.

As can be seen from Fig. 3, the discharge plasma temperature for the metal concentrator far exceeds that for diaphragm concentrators at the same voltage [1]. Furthermore, at negative polarity of the metal concentrator, the required temperature is reached at a lower voltage and a reach-through breakdown between the electrodes occurs already at a voltage of 600 V.

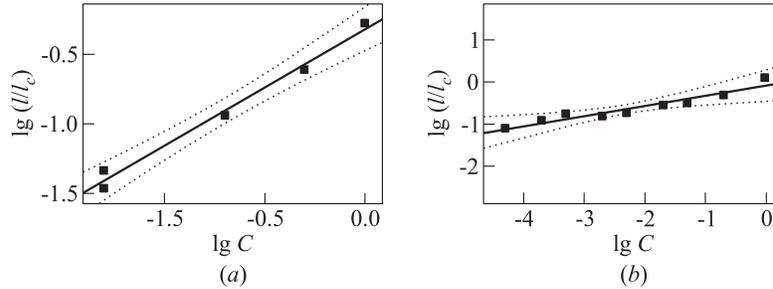


Figure 4 Calibration curve for determining calcium (422.67 nm) (a) and magnesium (518.36 nm) (b)

This is explained by differences in the mechanisms of excitation and ionization of matter, similarly to the corona discharge [5], which provides a flow of positive metal ions to the discharge zone at negative polarity of the metal sharpener due to electron emission.

The replacement of diaphragm current concentrator by metal concentrators provided a reduction in the detection limit of metals by several orders of magnitude (from ~ 50 mg/l to ~ 50 μ g/l for potassium hydroxide). For magnesium, the detection limit was ~ 50 μ g/l; for calcium, ~ 200 μ g/l; and for copper, ~ 2 mg/l, which is comparable with those of flame photometry methods [3] and is sufficient for the analysis of maximum permissible concentrations of metals in water infrastructure facilities.

Figure 4 shows the calibration curves of the relative line intensity I/I_c for calcium at a wavelength of 422.67 nm (Fig. 5a) and for magnesium (Fig. 5b) at a wavelength of 518.36 nm vs. mass concentration C in a logarithmic scale. The Na line at 588.99 nm was used as the reference line.

The calibration curve is described by the equation [6]:

$$\lg\left(\frac{I}{I_c}\right) = c_0 + c_1 \lg(C) .$$

Thus, this study shows the possibility of using discharge on a metal current concentrator in electrolyte solutions for a quantitative determination of metals in liquids.

4 Concluding Remarks

This study shows the possibility of a quantitative spectral analysis of metals in conductive liquids during discharge on metal current concentrators. The detection limits for metals are determined: K ($50 \mu\text{g/l}$), Cu (2 mg/l), Mg ($50 \mu\text{g/l}$), and Ca ($200 \mu\text{g/l}$). These limits are comparable with those of existing methods of flame photometry [3] and allow the analysis of metals in water infrastructure facilities without using bulky equipment.

Acknowledgments

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