Some modifications of hollow cathode discharge tubes and their application*

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1. Introduction

The wide range of research, scientific and applied tasks solved through the hollow cathode discharge (HCD) leads to different requirements with respect to the HCD. These demands may be met by using constructive modified cathodes, different from the conventional hollow cathodes in the quality of the discharge.

Most generally, we consider three modifications of hollow cathode discharge tubes, used in atomic absorption spectroscopy and in experiments of coherent excitation (type of alignment) of the levels in HCD (a new addition to the physics and the possibilities of this discharge [1]).

2. Transparent hollow cathode

In some cases spectroscopic investigations of the by-electrode phenomena in plasma, as well as of the plasma itself, are hampered by the opacity of the metallic electrodes. An analogical problem arises in the spectroscopic investigation of the HCD. One particular solution, e.g., the perforation of the electrode or whatever can break its totality, is not always acceptable due to local inhomogeneities that may appear in the plasma layer. We took advantage of solution valid for the cases, when the chemical content and properties of the electrode are of no interest. We have, namely, deposited a transparent conducting layer on a glass substrate of an arbitrary geometry, which acts as a transparent electrode. The deposited thin SnO_2 -layer is sufficiently transparent in the visible and higher wavelength ranges and is strongly adhesive due to strong bond Si-O-Sn. The remaining details are described in [2].

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Some investigations on the spectral intensities of helium lines in discharge tubes with cathode-anode systems of transparent conducting layer are shown in Fig. 1. By combining the polarities of the power supply on the electrodes 1 and 2 the spectral intensities in the HCD and in the positive column of the discharge were compared (Fig. 1a).



Fig. 1. Discharge tube with transparent anode and hollow cathode: a - flat electrodes b - cylindrical electrodes (1, 2 - transparent electrodes)

Obviously, the treatment of the transparent conducting layers as an electrode allows us to shape the glow and to experiment with hollow cathodes of arbitrary form and structure, satisfying the criterion [3] for the HCD. The transparence of the cathode allows also spectral investigations made along different axes of symmetry of the HCD, which is of particular importance in the experiments of coherent excitation in HCD [2, 4].

The glass-conducting layer system can be used as a suitable substrate-electrode for the following electro-chemical technologies on a glass substrate. Our experiments in this aspect showed the importance of the problem for homogenization of the local layer resistivity.

3. Spiral hollow cathode

Recently the investigations on a laser system of metal vapours have been performed with a hollow cathode in the form of a spiral [5, 6]. This cathode, besides some functional advantages (e.g., simplified diffusion of the metal vapours toward the active region, easily increasing working voltage, etc.), possesses also typical electrical and spectral characteristics. The results obtained in a generation regime (and close to it) and their probable physical nature (the hampered discharge character) draw our attention toward some characteristics of the spiral hollow cathode discharge (SHCD) at low pressure of the working gas and not high discharge current — including the working regions for the lamps with a hollow cathode for atomic-absorption analysis (AAA) and for Hanle experiments in HCD.

Experiments were carried out with spiral cathodes of Mo, Cu, Ni, characterized by the following parameters: length L = 17 mm, inner diameter 2R = 4 mm, step of the spiral — up to 2.5 mm, wire thickness 1 mm. The spectral intensities and the polarization characteristics are measured for the lines Ne I 626.6 nm, Ne I 352.0 nm, Ni I 341.5 nm, Mo I 379.8 nm and Mo I 390.3 nm. Structures are shown in Fig. 2. The conditions and the geometry of the calssical hollow cathode discharge used in the lamps for AAA are realized in a spiral cathode.



Fig. 2. Discharge tube with a spiral hollow cathode: 1 - anode, 2 - hollow cathode

1. Some data are compared to analogical ones obtained in an ordinary hollow cathode of the same dimensions: 2R = 4 mm, lenght L = 17 mm. For neon pressure ranging within 0.35-4.70 Torr, discharge current of 5-25 mA and at equal current densities, the intensities of the last three spectral lines in the two cathodes differ insignificantly while for Ne I 626.6 nm a decrease is recorded in a spiral cathode. The latter, however, allows the discharge under gas pressures even lower than those admissible in the conventional cylindrical cathode.

For the investigated lines the polarization degree $P = (I_{||} - I_{|}) (I_{||} + I_{|})^{-1}$, $(I_{||} \text{ and } I_{|} \text{ being two orthogonal polarizations of the spectral intensity) in the spiral cathode proved to be essentially higher. This result allows us to expect a higher extent of coherence of the excited levels in the SHCF than in the usual cylindrical cathode. We can also state that under equal conditions the value <math>P$ depends on the step D of the spiral, as illustrated in Fig. 3. Apparently, an optimization along D is necessary to achieve P_{\max} . The correlation between P and the pressure of the working gas P_{Ne} in the tube is shown in Fig. 4 — two contrary tendencies are available in the dependence $P(P_{\text{Ne}})$, where at a discharge current over 20 mA only the branch $P \sim P_{\text{Ne}}^{-1}$ is registered, the character of which may be ascribed to the depolarization effect of the interatomic collisions.

Simultaneously with the spectral measurements, the value of the cathode potential drop U is also fixed. The latter appears to be higher in the SHCD, at that $U \sim D$.

2. Physical and technological considerations encourage to examine the possibilities of the spiral cathode offered when modifying the hollow cathode in lamps for AAA [7]. We took account of the following advantages of the SHCD:

- More efficient cooling of the emitting plasma, which is a precondition for increasing the intensity to width ratio of the spectral lines, therefore, the slope of the graduated graph (dependence of the magnitude of atomic absorption (AA) signal on the concentration (c, in ppm) for the investigated elements) and of the concentration sensitivity of the analysis.







Fig. 4. Polarization Pdegree of the line Ni I 341.5 nm in spiral hollow cathode as a function of the gas pressure $P_{\rm Ne}$ (discharge current - 20 m A)

- Facilitated and simplified technology for preparation of the cathode, especially for metals and alloys highly resistent to mechanical treatment which, on the other hand, are widely spread in the form of thin wires.

- Reduced consumption of metals and alloys necessary for preparation of the cathode, especially important for rare and expensive elements.

The prepared lamps with a spiral cathode for AAA of Mo, Ni, Cu and Ag are tested on a Carl-Zeiss spectrophotometer. An increase of the concentration sensitivity of the analysis is observed for these elements in comparison to the lamps with a cylindrical cathode. The graduated curves for Ni built along the resonance line Ni I 232.0 nm are shown in Fig. 5. The optimal discharge current for the lamp with a spiral cathode was 12 mA, while for that with a cylindrical



Fig. 5. Calibration graphs for AAA of Ni at the analytical line Ni I 232.0 nm: 1 - spiral hollow cathode, 2 - cylindrical hollow cathode

one -15 mA; the slope of graph (1) is better than that for the ordinary one (2), respectively the calculated concentration sensitivity is increased with $75^{\circ}/_{0}$. Since the slope of the graph reflects complexly the correlation intensity with width of the analytical line, the increased slope in the spiral cathodes confirms our initial consideration for a more efficient cooling of the emitting plasma in the spiral cathode. We have taken into account the fact that the Doppler effect is the factor deciding upon the width of the atomic lines emitted from the HCD, under the described conditions of experiment.

The tests of the lamps with a SHCD for AAA are continued.

In spite of the preliminary and, in a certain sense, phenomenological character of our investigations on spiral hollow cathodes, the results obtained give some new possibilities of their application in spectroscopic tasks of different types, apart from those in [5, 6].

4. Hollow cathode discharge tube with a cone bottom

In this cathode the flat bottom of the classical hollow cathode is replaced by a cone one (Fig. 6) [8]. Preserving all the remaining geometrical dimensions of the cylindrical cathode and the parameters of the discharge (discharge current and pressure of the filling gas) we have stated that the intensity of the spectral



Fig. 6. Discharge tube with a cone bottom hollow cathode: 1 - cathode, 2 - anode

lines in the new cathode increases with the increasing emitting surface. For the lines of the atomized metal of the cathode or of the inserted sample, the intensity increases maximally by an order, while for those of the inert gas its change is negligible. Figure 7 illustrates this effect for the line Al I 309.3 nm. In [9] the observed spectroscopical effect is experimentally optimized in a cathode with a cone bottom. The analysis of the Hanle signals showed that in this cathode the discharge flows at an increased concentration of the atomized substance [10].

The results obtained due to this modification of the hollow cathode allowed us to prepare lamps for AAA of Fe, Ni, Al, Mo, Mg, Cu and Zn. The qualities of these lamps are evaluated by comparing their calibration graphs with the graphs of lamps with a flat-bottomed hollow cathode. Different trade marks of spectrophotometers have been used for the comparative measurements. The calibrated graphs for analysis of Ni along the resonance line Ni I 232.0 nm (spectrophotometer Perkin Elmer) are shown in Fig. 8. The new lamp has a twice steeper graph (1) than that of the lamp with a flat-bottomed cathode (2) at four times lower value of the optimal discharge current, and correspondingly, the concentration sensitivity and the limit of discovery are three times better.



Fig. 7. Intensity of the spectral line Al I 309.3 nm in a flat bottom (I) and cone bottom (II) hollow cathodes as a function of gas pressure



Fig. 8. Calibration graphs for AAA of Ni at the analytical line Ni I 232.0 nm: 1 - cone bottom cathode, 2 - flat bottom cathode

Our results for the investigated elements show that in a cathode with a cone bottom the optimal discharge current is lower at equal and even better concentration sensitivity, in comparison with the ordinary cathode. At the same time increased stability in the working regime of the lamp is observed.

Except for the considered analytical application, the spectral lamps with the new cathode are more suitable than a standard light source having also in mind the listed spectroscopic advantages.

According to our opinion the investigated modification of the HCD is also promising for other applications of this source.

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