SPECTRAL CHARACTERISTICS OF HIGH-FREQUENCY DISCHARGES IN HOLLOW-ELECTRODE LAMPS*

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In order to increase the emission intensity of metal resonance lines in hollow-cathode lamps, the possibility of supplying the lamps with a high-frequency current was investigated. It was established that, compared with direct current glow discharges, high-frequency discharges provide an intensity increase by two orders of magnitude at the same line self-absorption level. The reasons for this difference are discussed. A simplified high-frequency lamp design is outlined.

Introduction. Self-absorption of resonance lines is the most severe limitation of uncooled hollow-cathode lamps used in atomic absorption spectral analysis. This makes it necessary to restrict oneself to minimum discharge currents, at which the radiation intensity is frequently insufficient for precision measurements, or to compromise between line broadening and intensity and to use intense yet necessarily broadened lines. This situation is particularly typical of elements which sputter easily, such as cadmium, copper, magnesium, lead, and zinc. This effect is due to the intense cathode sputtering and the relatively low excitation efficiency of metal vapors in dc glow discharges.

Certain working gases are capable of decreasing the self-absorption, while preserving the same emission intensity. In particular, it was established in [1] that neon, compared with xenon, can reduce the self-absorption of nickel and magnesium resonance lines. But this remedy is not always efficient enough. Moreover, the sputtering intensity of the cathode material and the excitation efficiency of the resonance lines depend in a very specific way upon the type of gas used. General recommendations that would be applicable to all elements cannot therefore be made.

On the other hand, it is known [2] that the near-electrode regions of high-frequency glow discharges are much more similar to the cathode portion of dc glow discharges and, in both discharge types, sputtering of internal electrodes can be observed. It is therefore interesting to explore the possibility of employing high-frequency glow discharges for exciting metal spectra in hollow-electrode lamps and to compare their spectral characteristics with those of the same lamps supplied with direct current.

Experimental. In this work we studied mainly the sealed lamps with uncooled hollow cathodes described in [1, 8]. The characteristics of a magnesium hollow-cathode lamp filled with argon to a pressure of 1 mm Hg and of an aluminum hollow-cathode lamp filled with neon to a pressure of 4 mm Hg were investigated. These two metals were not chosen by chance. The magnesium cathode lamp reveals extremely strong self-absorption when supplied with direct current [1]. Among the other metals, aluminum is characterized by high stability with respect to sputtering in discharges. Therefore it appeared doubtful whether it would be possible to excite the metal spectrum in the lamp by means of a high-frequency current.

Preliminary experiments established that lamps with semiclosed cathodes guarantee a spectral intensity which is several times greater than that of lamps with open hollow cathodes and for this reason lamps of the first type were used in the subsequent experiments. The properties of the lamps with direct current and high-frequency current are most conveniently correlated by comparing the emission intensities of resonance lines at the same self-absorption level in the discharges. The measurements were made with an interferometer which permits the intensity and contour of spectral lines to be recorded [1]. The interference pattern was scanned relative to the diaphragm separating the center spot by varying the pressure in a pressure chamber in which a Fabry-Perot standard with an intermediate ring 5 mm thick was situated.

The width of the resonance lines in hollow-cathode lamps is determined by the Doppler effect and self-absorption. Temperature changes (between 400 and 600 °K for the case of uncooled hollow-cathodes) essentially do not affect the total line width. Thus the half-width of a line as a function of the operating conditions is determined solely by the extent of self-absorption. Whenever the lines have a hyperfine structure, the extent of self-absorption can be more easily evaluated from the observed intensity ratio of the hyperfine structure components. When the self-absorption increases, the ratio of the components must tend to unity [6].

The high-frequency discharges were fed from a generator operating at a frequency of about 60 MHz [2]. Direct current discharges were supplied from a universal UIP-1 source which delivers a stabilized constant voltage of up to 600 V.

Figure 1 shows the relation between the observed half-width of the Mg 2852 Å line and the total intensity for dc and high-frequency discharges. With dc, the current through the lamp was varied (from 10 to 40 ma); in the second case the

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input of the HF generator was varied between 10 and 50 W.

In our experiments, the error of the line half-width measurements was evaluated from the reproducibility of the results and did not exceed 0.004 cm\(^{-1}\); that of the intensity measurements amounted to less than 3%. It must be mentioned that the true line half-width is smaller than the figures indicated in Fig. 1, since the apparatus-induced line broadening was not taken into account. But since the apparatus-induced broadening remained constant during the experiment, the observed change of the width was practically due solely to variations of the self-absorption.

It follows from Fig. 2 that, at equal linelengths, high-frequency discharges provide at least 100-fold higher intensities relative to dc discharges. Even with minimum measurable intensity levels in dc discharges, the Mg 2852 Å resonance line was broader than that of the high-frequency discharge, i.e., the self-absorption in a dc discharge cannot be removed by making the lamp current as small as possible.

Further experiments revealed that not only are the spectra of the other easily evaporated metals (In, Sn, Pb, Cu, etc.) strongly excited in high-frequency discharges, but so also are the spectra of the least sputterable metals, iron and aluminum. Fig. 2 shows the results of width measurements and the component ratio of the hyperfine splitting of the Al 3092 Å line as a function of the total emission intensity. The current was varied from 10 to 120 mA, the input from the HF generator from 16 to 60 W.

The line Al 3092 Å \((3^2 P_{01}^0 - 3^2 D_{13/2}, \nu_i)\) consists of two components corresponding to transitions from the upper levels \(3^2 D_{13/2}\) and \(3^2 D_{1/2}\) to the lower level \(3^2 P_{01}^0\).

The distance between the components of the line amounted to 1.34 cm\(^{-1}\) (with a constant 1.0 cm\(^{-1}\) standard, these components are separated on the interferograms at a distance of 0.34 cm\(^{-1}\)).

The curves of Fig. 2 reveal that at arbitrary currents the ratio of the Al 3092 Å components in a dc discharge is smaller than that in a high-frequency discharge. This indicates that self-absorption occurs in a dc discharge even of an element as different to sputter as aluminum.

The maximum intensity increase for the same self-absorption level amounts to a factor of approximately 25. We developed and tested the simplified lamp design based on these investigations and shown in Fig. 3. Compared with conventional designs, it has smaller dimensions and no second electrode. As a matter of fact, the relatively large dimensions of conventional sealed hollow-cathode lamps [1, 3] are, to a large extent, due to the adsorption of the working gas by a metal layer deposited upon the lamp walls; in its turn, this adsorption determines the lifetime of the lamp. The absence of such an intense metal sputtering in a high-frequency discharge made it possible to reduce the lamp dimensions substantially without any restrictions on its operational life.

We believe the construction of a high-frequency lamp with an electrode sealed in the lamp bulb (Fig. 3b) should be of particular interest. In this type of high-frequency lamp, the electrode can be rapidly cooled, and thus the Doppler broadening of the line can be reduced.

Interferometer measurements of the contour of the NeI 3369 Å line excited in a lamp of similar design revealed that at an HF input of 32 W the half-width is 0.036 cm\(^{-1}\) smaller upon cooling with liquid nitrogen than without such cooling. With the uncooled electrode at a temperature of 400°K, this difference is equivalent to a temperature change to 250°K. Therefore the temperature inside the electrode cooled with liquid nitrogen \((bp = 77°K)\) amounts to 150°K, i.e., it differs from the temperature of the cathode walls by only 70°.

Discussion of the results. The most important result of the above investigation is the fact that at equal emission intensities in the metal spectrum the sputtering is less extensive in a high-frequency discharge than in a dc discharge. Let us consider this property of a high-frequency discharge in the light of modern ideas regarding the mechanism of electrode sputtering and spectrum excitation.

The sputtering of cathode material in a high-frequency discharge, as well as in a dc discharge, originates from collisions of positive ions at the cathode walls and depends upon the number and energy of the ions bombarding the electrode [4]. The energy of the ions in a dc glow discharge is determined by the cathode voltage drop, which usually amounts to several hundred volts and remains approximately constant when the discharge power changes.