RESONANT-LIKE REABSORPTION FOR COPPER AND SILVER IN AN AC ARC PLASMA

V. I. Zhuravleva, M. L. Petukh, and A. A. Yankovskii

Resonant lines are usually employed in determining minor components, although they are subject to reabsorption. If there is strong reabsorption they may be self-reversal, which can increase the analysis error.

Reabsorption must be allowed for in determining elements such as copper and silver, for which there is a certain concentration range in which reabsorption occurs increasingly, while nonresonant lines either do not appear or have low intensities.

Element concentrations in a plasma are determined not only by those in the specimen but also by the evaporation rates, which are dependent on the discharge conditions and mode of injection. When a sample evaporates from the end of an electrode, the entry rate and concentration are initially higher than in the evaporation of the same amount from an electrode crater [1]. One expects that reabsorption on evaporation from the end of an electrode will be stronger than that for a crater. This must be borne in mind with laser or spark sampling, as well as in the evaporation of the dry residue from a drop of solution or other method of dispensing the sample on the end of the electrode.

In some cases, it is also necessary to check for reabsorption in plasma diagnosis from line intensities.

One can check for the effects of reabsorption on the intensities in various ways: by measuring the intensity ratios for multiplets, which should be constant in the absence of reabsorption, by using the growth curve, i.e., the dependence of the line intensity on element concentration [2], or by using the line shape [3, 4].

Clearly, only multiplet reabsorption can be checked from line-intensity ratios. The growth curve gives only an approximate indication of the element concentration at which reabsorption starts, since the change in slope is gradual. The line-shape method is more general, but it requires the use of high-resolution instruments.

Fig. 1. Line shapes for Ag I 328.0 nm (a) and Cu I 324.7 nm (b) obtained on evaporation in an arc arc (6 A) from the ends of carbon electrodes for material produced by the following numbers of laser pulses: 1 (1), 5 (2), and 30 (3).

Also, in the literature there is virtually no experimental evidence on the concentrations at which the effects of reabsorption on line intensities can be neglected.

Developments in analysis with laser sampling can involve evaporation from the ends of electrodes, i.e., under conditions fairly favorable to reabsorption, so we have estimated the silver and copper concentrations at which the reabsorption of the AgI 328.0 and CuI 324.7 nm lines can be neglected.

To measure the line shapes, we photographed the spectra with a PGS-2 spectrograph in the third order with single and double ray passage giving the reciprocal linear dispersions of 0.23 and 0.12 nm/mm correspondingly. We used plates type II. The slit width was 0.01 mm.

It is necessary to estimate the instrumental broadening in order to determine the widths reliably. We used a lamp with a copper hollow cathode, which gave narrow lines almost free from reabsorption.

The line width corresponds to the Doppler broadening if the lamp works at low currents (6-8 mA) [5-8]. The Doppler temperatures of various hollow-cathode lamps at such currents have been found to be 410-630°C [7].

The lamp spectrum was photographed in the 320-nm region in the second order with double ray passage giving a reciprocal linear dispersion of 0.18 nm/mm. The lamp current was 8 mA. The Doppler width was calculated from

$$\Delta \lambda_D = \frac{2\lambda}{c} \sqrt{2RT\ln2/M}$$

with $T = 630°C$, which corresponds [7] to a current of 8 mA. The instrumental width is given [8] by

$$\Delta \lambda_{\text{in}} = \sqrt{\Delta \lambda_{\text{exp}}^2 - \Delta \lambda_D^2 / \ln2}.$$ 

One of the narrowest lines is Cu I 314.8 nm, and the observed width is 0.0015 nm, Doppler width 0.0007, instrumental width 0.0012 nm. On the basis of the plate resolving power, one can resolve intervals of 0.003-0.0015 on photographing spectra in the third order with single and double ray pass correspondingly.

The line shapes were constructed from the photometric data, the photometry being performed with a slit width of 0.01 mm. We used a part of the spectrum recorded through the attenuator step with 100% transmission. The line width was determined as the distance between identical densities on the two sides of the maximum and equal to the maximum density obtained with a 50% transmission step.

We varied the concentration in the ac arc (6 A) by varying the amount of material deposited on the end of the carbon electrode, which was turned down to a truncated cone with a diameter for the flat of about 2.5 mm. In preliminary experiments, the material was transferred to the electrodes by laser sampling, where the number of pulses was varied. The amount of material deposited on the electrodes was estimated by the method described in [9].

1196