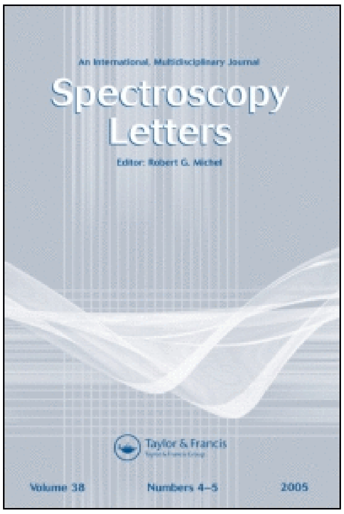

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Spectroscopic Study of a Hollow Cathode Discharge Operating at Direct and High Frequency Currents - Temperature Measurements

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SPECTROSCOPIC STUDY OF A HOLLOW CATHODE DISCHARGE OPERATING AT DIRECT AND HIGH FREQUENCY CURRENTS - TEMPERATURE MEASUREMENTS

Key words: Hollow Cathode, Direct Current Discharge, High Frequency Discharge, Atoms, Ions, Excitation Temperatures

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ABSTRACT

Spectra excited in a hollow cathode discharge operating at high frequency and direct currents have been studied. Samples (La_2O_3 and Y_2O_3) were placed in the copper hollow cathodes and argon was a carrier gas. The excitation temperatures of Ar I, Ar II, Cu I, Y I, Y II and La II in high frequency and direct current hollow cathode discharges have been determined and compared.

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INTRODUCTION

A hollow cathode discharge has been widely used for years in absorption and emission spectroscopy. An exhaustive review study on the hollow cathode discharge, its theory and application, mainly in the area of analytical emission spectroscopy, has been recently published by Caroli[1]. Such advantages as stability of the discharge, high signal-to-background intensity ratios and narrow lines have made the hollow cathode useful for analytical purposes. Relatively low intensity of the spectra excited in this discharge is a disadvantage of the hollow cathode. Thus, especially in the last years, studies aiming to increase the radiation emitted by the hollow cathode discharge have been undertaken. Some authors have proposed new types (shapes) of the cathodes (e.g. a microcavity hollow cathode[2], a conical bottom hollow cathode[3,4], double hollow cathodes[5]) while other studies have investigated cooling of the cathodes[6]. Some papers have dealt with additional energy sources, such as microwave discharge[7], magnetic field[8] or a secondary discharge boosted lamp[9] and application of these modified excitation sources in spectrochemical analysis. Promising results showing increase of the intensity by one order or more have been obtained.

Plasma temperature is one of the most important parameters characterizing plasma and discharge. Excitation temperatures of plasma produced by the direct current (dc) hollow cathode discharge have been the subject of many studies[10-14]. In the present study measurements of excitation temperatures for plasma generated in the high frequency (hf) hollow cathode discharge have been undertaken. The temperatures of Ar I, Cu I, Y I, Ar II, Y II and La II have been measured in the hf and dc hollow cathodes under the same conditions (pressure, plasma composition, type and dimensions of cathode, electrode arrangement) and compared.

EXPERIMENTAL

A demountable hollow cathode lamp[10,13] was used. Conventional copper hollow cathodes (empty and containing small amount of La_2O_3 or Y_2O_3) operated at high frequency current of 27.2 MHz (excit power of about 30 W) and at direct current of 75 mA (250-300 V). At the high frequency discharge the cathode and the anode were directly connected with the high frequency power supply and direct current power supply was at that time off. Argon flowing continuously through the lamp at pressure of 5 Tr was a carrier gas. The hollow cathodes were of 40 mm in total length, 28 mm in depth, 4 mm in inner diameter and 6 mm in outer diameter. Spectra excited in the hollow cathode were recorded in the first order of a plane grating spectrograph PGS-2 on ORWO WU-2 plates. The line blackening was measured on microphotometer MD-100 (Zeiss - Jena) and then reduced in the same way as that described in Refs. 10 and 13.

EXCITATION TEMPERATURE MEASUREMENTS

Under the assumption of partial LTE in plasmas studied the excitation temperatures have been determined by plotting values of $\ln I_m \lambda_m g_m^{-1} A_m^{-1}$ against E_m, where m - the line number, I - the line intensity, λ - the line wavelength, A - the transition probability and g and E - the statistical weight and electronic energy of the upper state of atom or ion. On the basis of this relation the temperatures and their standard deviation uncertainties have been calculated using the least squares procedure.

Spectroscopic measurements of temperatures have been carried out on lines of argon Ar I and Ar II, copper Cu I, lanthanum La II and yttrium Y I and Y II. The atomic and ionic lines used for the measurements have been listed in Tables 1 and 2. The lines selected for the measurements were recorded as free from overlapping both in hf and dc discharges. The upper state energies of lines of La I excited here did not differ very much (less than 0.3 eV). Therefore, the La I temperature could not be determined. Nevertheless, no significant differences were observed in plots of $\ln I_m \lambda_m g_m^{-1} A_m^{-1}$ versus E_m for the hf and dc discharges. Values of transition probabilities for argon lines were taken from Refs. 15 and 16 and for lines of other elements from Ref. 17. The excitation temperatures derived from atomic and ionic lines in the hf and dc discharges are presented in Tables 3 and 4, respectively. Boltzmann plots for the Cu I and Y I lines are shown in Figs. 1 and 2. The Y II temperatures obtained here are surprisingly low. The relation $T_{ex}(\text{ions}) > T_{ex}(\text{atoms})$ is commonly observed[13,14]. Poor knowledge of transition probabilities for yttrium lines can explain the relation $T_{Y\ I} > T_{Y\ II}$ observed here.

TABLE 1
Lines of Atoms Used for Measurements,
Wavelengths in nm

Lines of Cu I (E_m from 5.42 to 6.12 eV)					
261.837	276.637	282.437	288.293	296.117	299.736
301.084	303.610	320.823	327.982		
Lines of Y I (E_m from 2.67 to 4.13 eV)					
359.201	404.763	417.413	423.594	450.595	464.370
476.097					
Lines of Ar I (E_m from 14.46 to 15.06 eV)					
360.652	363.446	383.468	404.442	416.418	418.188
425.118	425.936	433.534	434.517	451.073	452.232
459.610					

TABLE 2
Lines of Ions Used for Measurements,
Wavelengths in nm

Lines of La II (E_m from 3.04 to 4.88 eV)					
398.852	404.291	409.954	414.174	415.197	415.278
419.236	419.655	423.095	423.838	428.697	429.605
Lines of Y II (E_m from 2.95 to 4.01 eV)					
321.668	324.228	349.608	354.901	360.073	360.192
363.312	366.461	377.433	378.870	395.036	398.260
417.752	435.873	439.801			
Lines of Ar II (E_m from 19.22 to 24.82 eV)					
371.821	372.931	373.789	380.946	394.610	396.836
397.936	401.387	410.391	434.806	435.220	440.099
457.935	460.959	463.725	465.789		

TABLE 3

Excitation Temperatures of Atoms along with their Standard Deviation Uncertainties, in K

The Atom Temperature	Discharge hf	dc	Plasma
$T_{Cu\ I}$	2260±220	2220±160	$Cu+La_2O_3$
	1970±150	1950±130	$Cu+Y_2O_3+Ar$
$T_{Y\ I}$	5530±650	5880±520	$Cu+Y_2O_3+Ar$
$T_{Ar\ I}$	4000±300	3200±300	Cu+Ar
	4500±400	3300±300	$Cu+La_2O_3+Ar$
	4400±300	3400±300	$Cu+Y_2O_3+Ar$

TABLE 4

Excitation Temperatures of Ions along with their Standard Deviation Uncertainties, in K

The Ion Temperature	Discharge hf	dc	Plasma
$T_{La\ II}$	5460±170	5520±150	$Cu+La_2O_3+Ar$
$T_{Y\ II}$	3740±120	3640±90	$Cu+Y_2O_3+Ar$
$T_{Ar\ II}$	19400±600	19600±600	Cu+Ar
	18800±600	18700±600	$Cu+La_2O_3+Ar$
	20400±700	17200±500	$Cu+Y_2O_3+Ar$

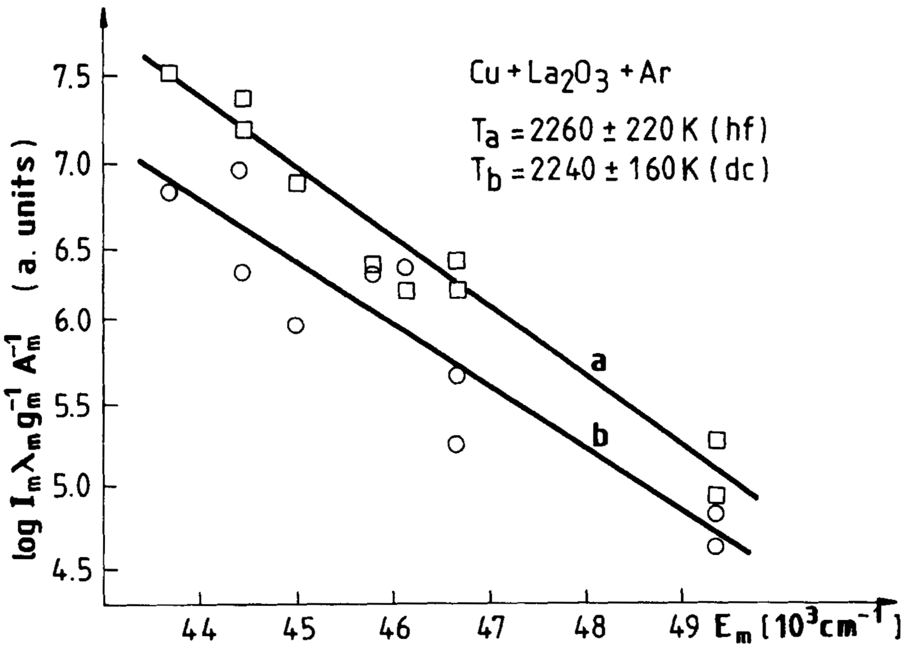

Fig. 1. Determination of the Cu I temperature

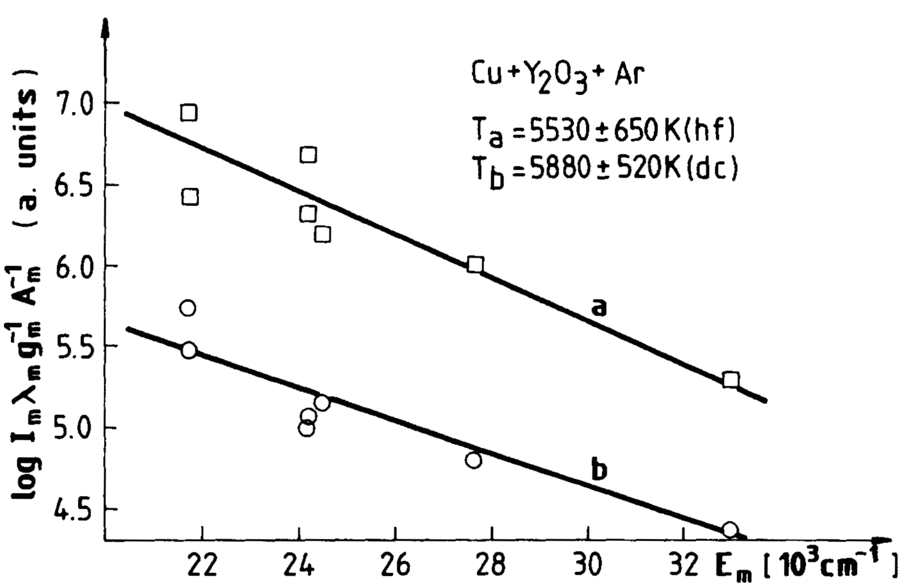

Fig. 2. Determination of the Y I temperature

DISCUSSION

Comparison of the excitation temperatures measured here in hf and dc discharges has shown that these temperatures are of the same order, often very close as those derived from the Y I and La II lines.

The Ar I temperatures for hf plasma are higher than these temperatures obtained for dc plasma but the differences are of the same order as the sum of standard deviation uncertainties of $T_{Ar\ I}$. It should be also mentioned that the Ar I temperature could not be determined here too exactly due to relatively small differences between maximum and minimum upper state energies of Ar I.

The differences between the present values of $T_{Ar\ I}$ and those obtained previously[10] are mainly caused by the fact that various lines have been used in the measurements. The ionization degree of lanthanum in plasma excited in the hollow cathode has been high due to a low ionization potential of lanthanum (5.58 eV). However, the presence of lanthanum, practically, has not influenced the excitation temperatures of other atoms (Ar I, Cu I) or ions (Ar II) present in plasma.

Comparison of intensities of lines emitted by the hf and dc hollow cathode discharges with respect to spectrochemical analysis of elements has been undertaken and will be subject of a separate study.

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