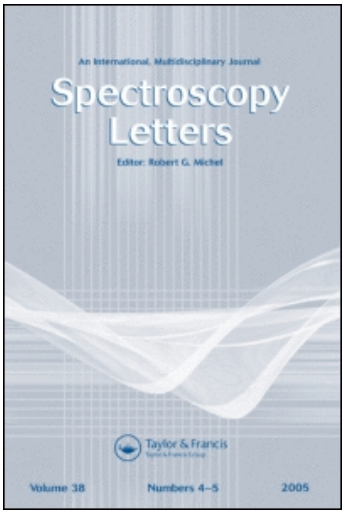


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# Emission Characteristics of the D.C., 100 kHz and 13.5 MHz Hollow Cathode Discharges

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# EMISSION CHARACTERISTICS OF THE D.C., 100 kHz AND 13.5 MHz HOLLOW CATHODE DISCHARGES

Key words : emission spectrometry, hollow cathode, plasma diagnostics, d.c. and r.f. discharges

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## ABSTRACT

Hollow cathode discharges in argon at various pressures and currents have been studied by optical emission spectroscopy. The cathodes were made of copper, bronze and brass. The discharges were supplied by direct, 100 kHz and 13.5 MHz currents. Atomic and ionic spectra of plasma gas and elements of cathode materials and molecular bands of ZnH and PN formed due chemical reactions between plasma components have been excited and measured. Relations between emission intensities, excitation temperatures and discharge conditions have been analysed and discussed.

## INTRODUCTION

Low pressure plasma discharges belong to well known and often used excitation and ionisation sources. Operating with a plane, pin-type or hollow cathodes, discharges have been widely applied for the direct solids elemental analysis by optical emission spectrometry (OES) and mass spectrometry (MS), in

quantitative surface analysis and in atomic absorption spectrometry [1-6]. In the very recent years, a meaningful progress has been performed in the field of application of glow discharges (GDOES and GDMS) to direct quantitative analysis of wide variety of solid materials and specimens. Improvements, modifications and developments of glow discharges (e.g. r.f.-GD sources both for mass and optical emission spectrometry) have enabled measurements of elements in solids with favourable precision and accuracy and relatively low limits of detection well sufficient for many analytical tasks [1].

In the last few years a number of papers devoted to emission spectroscopic characteristics and investigation of fundamental processes in glow discharges have been published [7-11]. Levy et al. [7] investigated emission of three copper lines in a low pressure, low current coaxial geometry glow discharge. Steers and Thorne [8] studied excitation of iron and chromium spectra in a microwave boosted discharge. Heintz et al. [9] investigated emission of magnetically enhanced Grimm-type discharge. Kuraica et al. [10] reported radial distributions of hydrogen and argon excitation temperatures and electron density in plasma of electrode plane glow discharge. Hoffman and Ehrlich [11] examined distribution of line intensities in plasma produced in a Grimm-type glow discharge.



In the present paper comparative studies of d.c., 100 kHz and 13.5 MHz hollow cathode discharges operating at various experimental conditions (pressure, current, material of the cathode) have been carried out. Variations of line and band intensities and ion to atom line intensity ratios with discharge parameters have been investigated and discussed taking into account analytical point of view.

## EXPERIMENTAL

A demountable hollow cathode lamp [12] cooled water was used here. The cathodes were made of copper and two its alloys, bronze and brass. All the cathodes were of the same size, 6 mm outer diameter, 35 mm total length, 4 mm axial hole and 20 mm hole depth. Adjustable power supplies of direct or high frequency currents were employed. Argon flowing continuously through the lamp under low pressure was used as the discharge support gas. Plasma spectrum was

observed through a quartz window. The spectrum was recorded by a Bentham sequential spectrometer and analysed using both Bentham and own software. Details of operating conditions and instrumentation are given in Table 1.

## RESULTS AND DISCUSSION

Atomic line and molecular band intensities, ion to atom line intensity ratios and excitation temperatures of atoms have been used here as the parameters for spectroscopic characteristics of the d.c., 100 kHz and 13.5 MHz discharges with hollow cathodes made of copper and copper alloys. When the brass cathode was employed the d.c. and 100 kHz discharges could operate with acceptable stability only at 30 and 50 mA. At higher currents the discharge in brass was unstable and not suitable for reliable quantitative measurements. Intensity measurements have been presented here using the same arbitrary units for all data.



Atomisation of a sample is the first step of elemental analysis. In glow discharges the atomisation is as a rule accomplished via cathodic sputtering. Under assumption that in our HCD the sputtering was dominating type of transport of metals to plasma zone sputtering rates for brass were 5800, 2300 and <10 μg/min in the d.c. (50 mA), 100 kHz (50 mA) and 13.5 MHz (200 mA) discharges, respectively. For copper and bronze sputtering rates were about two orders lower than for brass. Jin-Chun Woo et al. [13] found sputtering rates (at the same argon pressure) in r.f. Grimm-type GD 1300 and 2300 μg/min for copper and brass, respectively.

### Argon Spectrum

Atomic and ionic lines of argon were observed at all studied experimental conditions. In the d.c. and 100 kHz discharges ionic lines (Ar II) and atomic lines (Ar I) were strong and numerous. In the 13.5 MHz discharge atomic argon spectrum was dominating and the Ar II lines were less intensive.

A few argon lines (Ar I 419.07, 419.84, 420.07, 451.07, 452.23 and Ar II 405.29, 407.20) have been chosen for intensity measurements. The Ar I 419.84 nm line intensity versus pressure for one selected current is shown in Fig. 1a. The same relations between intensity and pressure were observed for the other argon lines.

TABLE 1
Experimental Conditions and Instrumentation

| | |
|---|---|
| Discharge operating parameters | |
| current | |
| d.c. | 30, 50, 70 mA |
| 100 kHz | 30, 50, 70 mA |
| 13.5 MHz | 120, 160, 200 mA |
| argon pressure | 0.27, 0.67, 1.07 kPa |
| Spectrometer | Bentham 300HR |
| entrance/exit slit | 25/50 μm |
| grating | holographic, 1800 lines/mm |
| spectral range | 190 - 800 nm |
| photomultiplier | DH3 Hammamatsu |



Rise of discharge current has led to an increase of argon emission whereas the line intensities have significantly decreased with pressure. Only for the brass cathode at d.c. and 100 kHz a different relation has been observed. Generally, variations of argon intensities with cathode material and current frequency were not significant.

Plasma electron density effects on both line profile and ion to atom line intensity ratio. Measurements of the ion to atom intensity ratio bring information on relation between electron densities and experimental conditions. The Ar II 405.29/ Ar I 419.84 intensity ratio versus pressure for different discharges and cathode materials is shown in Fig. 1b. As can be seen from this figure the ion to atom ratio has been very close in the d.c. and 100 kHz discharges for all cathode materials and almost independent on pressure. A very weak lowering of the intensity ratio with pressure was observed if argon ionic lines with higher excitation energies were used while a nonsignificant rise was found for the ionic lines with lower excitation energies. In the 13.5 MHz discharge the Ar II / Ar I ratio was a few times lower than in the d.c. and 100 kHz plasma and a dependence on cathode material was observed.

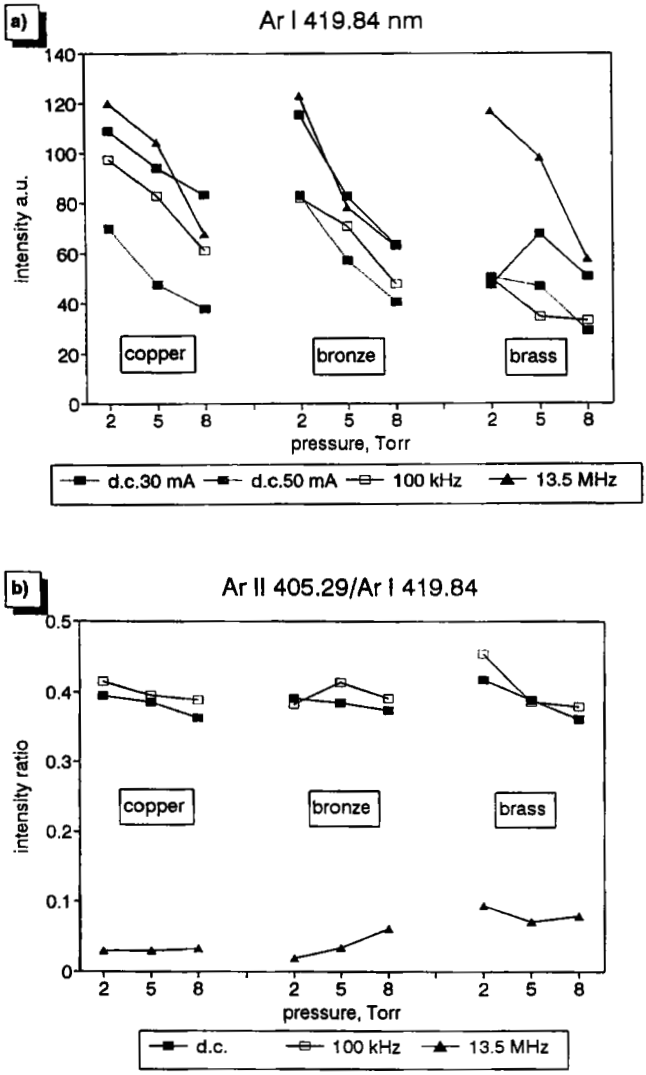


FIG. 1. Argon spectrum measurements in various hollow cathode discharges
a) the Ar I 419.84 nm line intensity
b) the Ar II 405.29/ Ar I 419.84 intensity ratio

## Spectra of Cathode Material Elements

### *Copper*

Strong copper atomic lines were observed for all studied discharges. Copper ionic lines were quite easily excited using copper and bronze cathodes at direct and 100 kHz currents. For the brass cathode at 13.5 MHz, ionic copper lines were in practice not observed. The Cu I 324.7 nm line intensity measured at various operating conditions is presented in Fig. 2a. Intensity - pressure relations for the other atomic copper lines were consistent with that for the Cu I 324.7 nm line. The Cu I line intensities decreased with pressure significantly in d.c. and 100 kHz discharges for copper and bronze cathodes. In the 13.5 MHz discharge for each cathode material the copper line intensities were considerably lower than observed at d.c. and 100 kHz.. In brass hollow cathode discharges the Cu I line intensities were practically independent on current frequency (see Fig. 2a).

### *Lead*

Lead was the component of all the cathode materials. The lead concentrations were as follows: copper - 0.0005%, bronze - 2% and brass - 1%. Only atomic lines were excited here. The intensity - pressure dependence for the Pb I 405.8 nm line in various discharges is shown in Fig. 2b. The Pb I intensities in the d.c. and 100 kHz discharges were similar and higher than at 13.5 MHz. At d.c. and 100 kHz discharges, lead intensity decreased rapidly with pressure in brass cathode and increased in copper and bronze cathodes. It indicates an influence of the cathode material on spectral characteristics of HCD.

### *Tin*

Tin spectrum was well developed in bronze (10% Sn) and weak in brass (<1% Sn) HCD. Atomic spectrum was more intensive than ionic. Relations between atomic tin line intensities and pressure were dependent on cathode material and kind of discharge (see Fig. 3a). In the 13.5 MHz discharge the Sn I intensity grew up with pressure both for bronze and brass cathode. The line intensities of tin from bronze decreased with pressure in the d.c. and 100 kHz discharges, while for tin from brass a rise was observed.

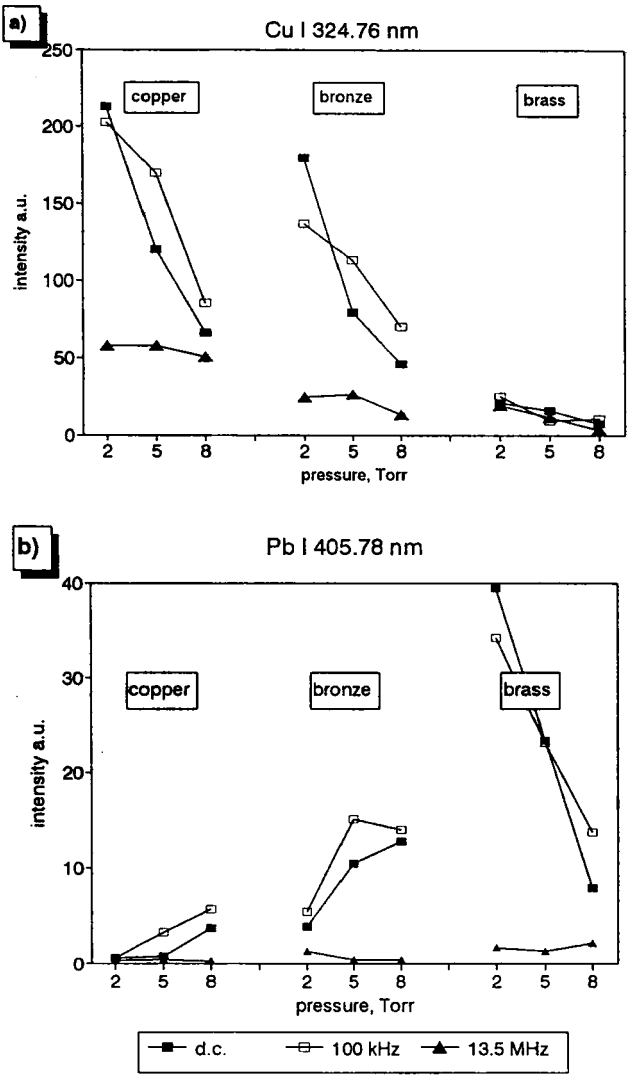


FIG. 2. The Cu I 324.75 nm (a) and Pb I 405.78 nm (b) line intensities versus pressure in various hollow cathode discharges

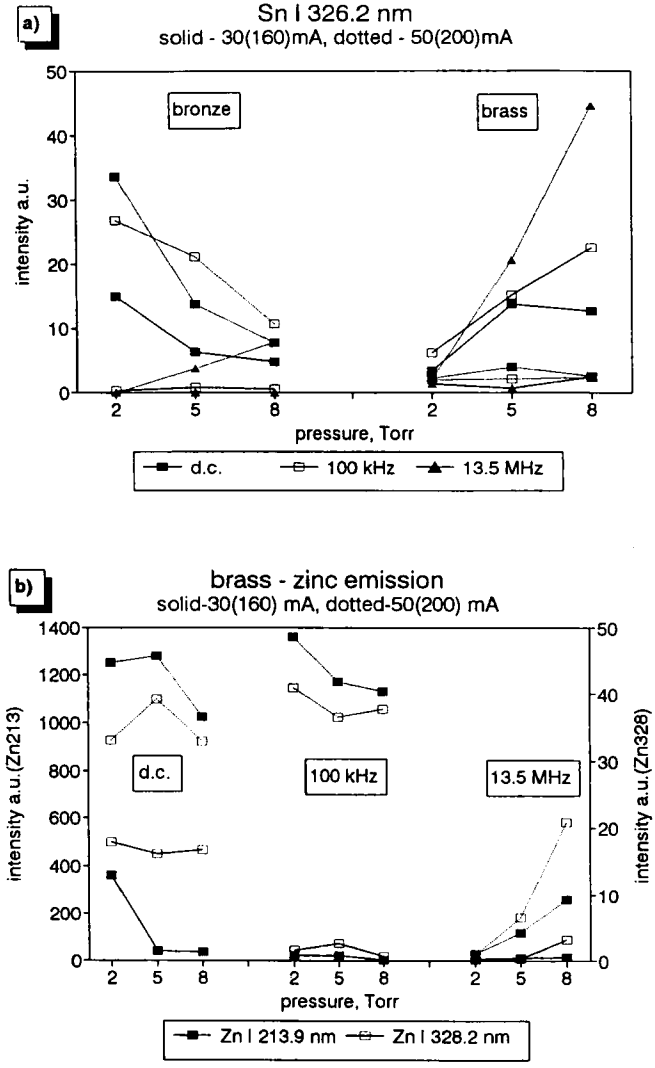


FIG. 3. Emission line intensities of tin (a) and zinc (b) versus pressure in various hollow cathode discharges

*Zinc*

A strong spectrum of atomic and ionic zinc was excited using brass cathode. The Zn I 213.9 nm line was of outstanding intensity. Atomic and ionic line intensities in d.c. and 100 kHz discharges were comparable and much more higher than those observed at 13.5 MHz. Atomic emission of zinc in various discharges is shown in Fig. 3b. In the 13.5 MHz discharge the Zn I and Zn II line intensities increased significantly with pressure as it was observed for the tin lines.

*Molecular Spectra*

Molecular spectra of species originated from plasma working gas have been observed in glow discharges quite often. In the present study the PN and ZnH molecules have been formed as a result of chemical reactions of cathode material components (P from bronze and Zn from brass) and easily excited. The PN bands belonging to the $^1\Pi$ - $^1\Sigma$ system [14] have been degraded to red and close double headed. The ZnH bands assigned as the $^2\Pi$ - $^2\Sigma$ 0-0 and 1-1 transitions [14] recorded at partially resolved rotational structure were of relatively high intensity. The ZnH bands with P and Q heads were degraded to the violet. The relations between the PN and ZnH band intensities and operating conditions are shown in Fig. 4. The strongest ZnH emission was recorded in the 13.5 MHz discharge, while the PN emission could not be observed for this current frequency.

In application of HCD and GD plasma to quantitative elemental analysis an assumption is made that chemical reactions involving atomic and molecular species released from analysed materials do not affect the plasma. This problem in point of view of quantitative depth profile analysis by glow discharge was discussed by Bengtson [15]. Observation of strong bands of the PN and ZnH molecules at various excitation conditions in HCD indicates that a significant fraction of materials transported to plasma forms molecular species. It leads to a loss of signal intensity for phosphorus and zinc. It is very likely to appear in some other elemental analysis by glow discharges, including the quantitative depth profile analyses by GD.

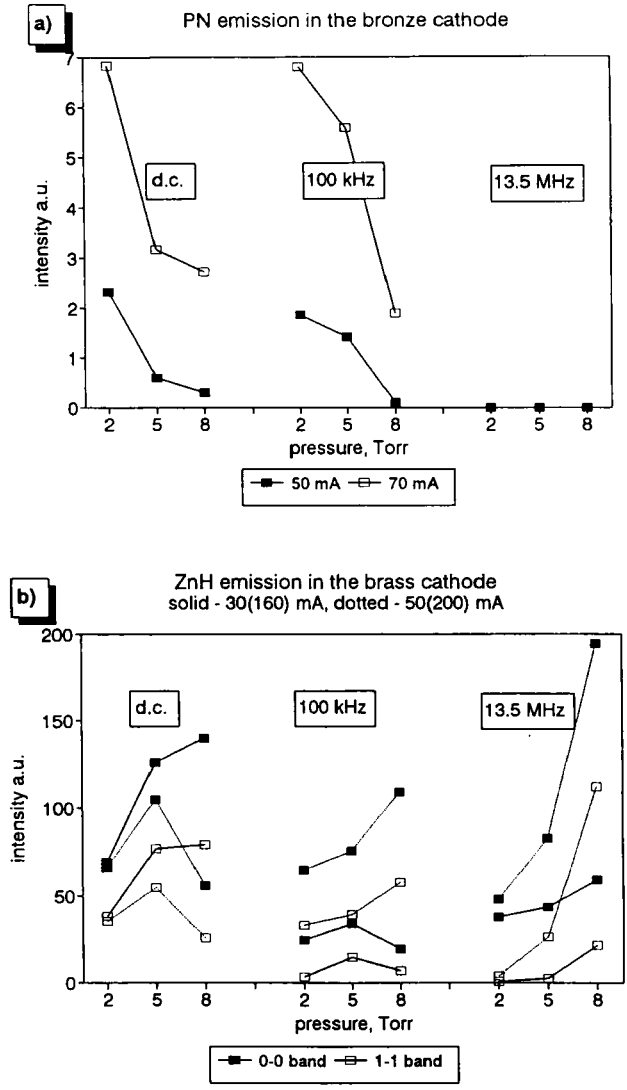


FIG. 4. The molecular band intensities observed in hollow cathode discharges
a) the PN band emission in bronze cathode
b) the ZnH band emission in brass cathode

**Excitation Temperature Measurements**

A controversy exists about excitation temperature measurements for low pressure plasma sources, nevertheless it has seemed to be interesting to compare the excitation temperatures measured for various discharge conditions and cathode materials. Boltzmann plot exploiting a number of lines with a possibly wide range of upper state excitation energies enables determination of the excitation temperature if LTE or at least pLTE conditions may be assumed. For investigation of the excitation temperature variations the two line method [16] can be used quite well providing a proper selection of lines for which the difference between the energies of the upper electronic states must be at least 1 to 2 eV. The temperature (T) in the two line method is expressed by

$$T = (E_2-E_1)\,(k \ln (I_1 \lambda_1 g_2 A_2 I_2^{-1} \lambda_2^{-1} g_1^{-1} A_1^{-1}))^{-1} \qquad (1)$$

where k - the Boltzmann constant, E and g - the excitation energy and statistical weight of the upper electronic state, $\lambda$ and I - the line wavelength and intensity, A - the transition probability

Only Cu I and Zn I lines were suitable here for the excitation temperature measurements. Spectroscopic parameters of the lines selected for the temperature determination are given in Table 2. The Cu I and Zn I temperatures have been determined using the expression (1). Variations of sensitivity of the photomultiplier versus wavelength were taken into account. Excitation temperatures obtained here have been found to be practically independent on pressure and kind of discharge as it is presented in Table 3. The Cu I temperatures measured in the cathodes made of different materials have been consistent as it is shown in Table 4. The temperatures in Table 4 are arithmetic means of values measured at various pressures. The values obtained for copper and zinc are very similar.

The electrode material has shown to have negligible influence on the excitation temperatures. The values of the excitation temperatures obtained in the d.c. and 100 kHz discharges were very similar and only slightly different than those

TABLE 2
Spectroscopic Data of Lines Used for the Temperature Determination

| Element | λ, in nm | E, in eV | gA in $10^8 s^{-1}$ [17] |
|---|---|---|---|
| Cu I | 217.894 | 5.69 | 0.31 |
| | 324.754 | 3.82 | 4.1 |
| Zn I | 213.856 | 5.80 | 19.0 |
| | 275.645 | 8.50 | 0.69 |



TABLE 3
The Zn I Excitation Temperatures Measured in the Bronze HCD, in K

| discharge | pressure, kPa | | |
|---|---|---|---|
| | 0.27 | 0.67 | 1.07 |
| d.c. (50 mA) | 3850 | 3850 | 3770 |
| 100 kHz (50 mA) | 3930 | 3900 | 3870 |
| 13.5 MHz (200 mA) | 4250 | 4180 | 4240 |

TABLE 4
The Cu I Excitation Temperatures Measured in Various HCDs, in K

| discharge | cathode material | | |
|---|---|---|---|
| | copper | bronze | brass |
| d.c. (50 mA) | 4250 | 4160 | 3950 |
| 100 kHz (50 mA) | 4240 | 4250 | 4040 |
| 13.5 MHz (200 mA) | 3980 | 3900 | 3860 |

measured at 13.5 MHz. However these differences are lower than the expected error of measurements.

***The Ion/Atom Line Intensity Ratios***

Likely as for argon, ion to atom intensity ratios for metals have been investigated for various operating conditions. The results for selected lines of copper, zinc and tin are presented in Tables 5 and 6. In the brass cathode due to excitation of very rich zinc spectrum we were not able to measure ionic copper lines free from spectral interferences and the ion to atom ratio for copper could not be determined.

The ion to atom intensity ratio for metals showed a growth with pressure, with the exclusion of zinc. The Zn II/Zn I ratio in the d.c. and 100 kHz discharges did not exhibit any clear tendency and was practically independent on pressure. For copper the ion to atom intensity ratios were the lowest in the 13.5 MHz discharge. The ionisation degree, $\alpha$ for the process of a single ionisation is

$$\alpha = n_i \, (n_i + n_a)^{-1} \qquad (2)$$

where $n_i$ and $n_a$ are numbers of atoms or ions, respectively. The degree of ionisation can be obtained from the ion to atom line intensity ratio, provided that plasma is in LTE or nearly in this state [17]. Taking expressions for ionic and atomic line intensities and rearranging one can obtain

$$\alpha \, (1-\alpha)^{-1} = I_i \, I_a^{-1} \, g_a A_a \lambda_i (g_i A_i \lambda_a)^{-1} \, Z_i \, Z_a^{-1} \exp [(E_i - E_a)(kT)^{-1}] \qquad (3)$$

Bogaerts et al. [18] combined the equation (3) and Saha formula to determine the ionisation temperature in a Grimm-type glow discharge and found the excitation and the ionisation temperatures were comparable. In this study the ionisation degree of zinc was evaluated assuming the Zn I and Zn II excitation temperatures are practically the same and using the equation (3). The Zn I 213.85 and Zn II 206.19 lines were used. The upper state energies of these lines (5.80 and 6.01 eV for the Zn I and Zn II, respectively) are very close. It should lower of error

TABLE 5
The Cu II 213.6/Cu I 217.9 Line Intensity Ratio

| Cathode | Discharge | Pressure, kPa | | |
|---|---|---|---|---|
| | | 0.27 | 0.67 | 1.07 |
| copper | d.c. | 0.161 | 0.196 | 0.212 |
| | 100 kHz | 0.144 | 0.169 | 0.217 |
| | 13.5 MHz | 0.024 | 0.033 | 0.054 |
| bronze* | dc | 0.17 | 0.30 | 0.53 |
| | 100 kHz | 0.22 | 0.34 | 0.41 |

* Copper ionic lines could not be measured with a reliable accuracy at 13.5 MHz



TABLE 6
The Zn II 206.2/Zn I 213.8 and Sn II 236.8/Sn I 276.2 Line Intensity Ratios

| Element | Discharge | Pressure, kPa | | |
|---|---|---|---|---|
| | | 0.27 | 0.67 | 1.07 |
| Zn (in brass) | dc | 0.051 | 0.057 | 0.050 |
| | 100 kHz | 0.054 | 0.047 | 0.040 |
| | 13.5 MHz | 0.021 | 0.041 | 0.079 |
| Sn (in bronze)* | dc | 0.075 | 0.089 | 0.28 |
| | 100 kHz | 0.068 | 0.087 | 0.11 |

* - Tin ionic lines were not observed at 13.5 MHz

introduced by temperature values. The ionisation degree for zinc was determined to be here from 1.4 % to 5.6 %.

## CONCLUSIONS

Various relations between line intensities and pressure have been found here for some elements in the d.c., 100 kHz and 13.5 MHz discharges in hollow cathodes made of different materials. Lowering copper emission intensity with pressure was observed for all kind of cathode material and discharge current. In the pressure range examined here, similar dependences were observed for other GD

and HCD sources [13,19,20]. Relations found in this work for tin and zinc when bronze or brass were used as the cathode materials, were comparable with those observed by Heintz et al. [9]. Rapid changes of lead and tin intensities versus pressure (see Figs. 2 and 3) indicate that plasma composition has significant effect on the emission intensity and it confirms importance of optimisation of excitation conditions in analytical performance by HCD-AES.

The excitation temperatures obtained from copper and zinc lines in our HCDs are comparable with those derived by Bogaerts et al. [18] for Fe and Ni. Both here and in study [18] excitation temperatures have been found to be insignificantly dependent on discharge conditions.

Absolute line intensities (absolute populations of excited states) measured in low pressure plasma have been strongly affected by pressure, current and cathode material. Collisions of metal atoms with electrons and noble gas atoms (in metastable states) are responsible for absolute populations in excited states of metal atoms. If one considers that relative and absolute populations of the excited atoms are in different way related with operating parameters a conclusion may be drawn that collisions between excited atoms in HCD plasma can not be neglected.

Chemical reactions between species from analysed samples including such „specific" conductive materials as alloys affect plasma in glow discharges and may change results of quantitative analysis. It has been proved here by observation of strong spectra of such molecules as ZnH and PN in plasma. Other molecules as e.g. $Cu_2$ , CuSn, SnH are also possible to be relatively easily formed if one takes into account their dissociation energies. It means that under some conditions a significant fraction of analysed element may be due to a chemical reaction in a form of molecular species and analytical signal of the element may be considerably decreased. It creates a potential danger for quantitative elemental analysis by low pressure plasma sources.

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