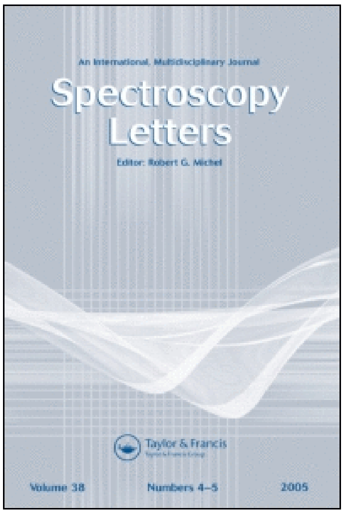

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Comparison of Spectra Excited in HF and DC Hollow Cathode Discharges

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To cite this Article Borkowska-burnecka, J. and Zyrnicki, W.(1987) 'Comparison of Spectra Excited in HF and DC Hollow Cathode Discharges', Spectroscopy Letters, 20: 10, 795 — 803
To link to this Article: DOI: 10.1080/00387018708081588
URL: http://dx.doi.org/10.1080/00387018708081588

SPECTROSCOPY LETTERS, 20(10), 795-804 (1987)

COMPARISON OF SPECTRA EXCITED IN HF AND DC HOLLOW CATHODE DISCHARGES

KEY WORDS: hollow cathode, high frequency discharge, direct current discharge, emission atomic spectra

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ABSTRACT

Spectra excited in hollow cathode discharges operating at high frequency (27.2 MHz) and direct currents have been compared. The cathodes made of copper, brass and steel and argon as a carrier gas were used. Line intensity ratios (I_{hf}/I_{dc}) for species excited at different pressures have been investigated and discussed.

INTRODUCTION

A hollow cathode discharge (HCD) has been extensively used as an excitation source in atomic and molecular spectroscopy. The discharge due to its stability and reproducibility, low background and production of narrow spectral lines has been widely employed in analytical atomic spectroscopy for different samples such as metalls, alloys, biological materials, ores, powders, liquids and gases. Hollow cathode lamps are used both in emission and absorption analysis. A comprehensive review of HCD applicability has been performed by Caroli[1].

A disadvantage of the hollow cathode lamps is that spectra excited in this source are of relatively low intensity, especially in comparison with ICP. Many studies have been devoted to various modifications of the hollow cathode discharge to increase intensity of the emitted spectra. Some studies have dealt with methods of power supply to the discharge, e.g. superposition of secondary discharge[2-4], application of a pulse supply[5,6] or a high frequency diascharge[7], coupling HCD with a magnetic field[8] and microwave-coupled HCD[9,10].

In this study spectra excited in HCD operating at high frequency current (27.2 MHz) and in HCD supplied by direct current have been compared and discussed.

EXPERIMENTAL

A demountable hollow cathode lamp[11,12] was used here for the experiments. The hollow cathode discharge was operated at direct current of 50 mA (300 V) or high frequency current of 27.2 MHz (10 W of nominal output power). Uncooled cathodes (4 or 2.5 mm in inner diameter, 25 mm of depth and 35 mm of length) were made of copper, brass (Mo-58)and steel (NW-2). Argon flowing continuously through the lamp at a pressure of 3, 6 and 10 Torr was a carrier gas. Spectra were photographed in the first order of a plane grating spectrograph at a reciprocal linear dispersion of 0.7 nm/mm on the Kodak No 3 plates. Exposure times were of 15, 30 and 90 s. Photographic blackening measurements were made with a recording microphotometer MD-100. Emulsion calibration curves performed with the aid of three-step filter of the spectrograph were used to convert line densities into line intensities.

RESULTS

Spectra of hf and dc discharges recorded at the same operating conditions (pressure, kind of cathode, exposure time) on the same plate have been compared. Very rich atomic and ionic spectra of elements from the cathode materials and the carrier gas were excited both in the hf and dc discharges. Species excited in the discharges are summarized in Table 1.

In dc HCD ion lines were more prominent than in hf HCD.

Time and pressure have been used as variable parameters at comparison of lines emitted by the dc and hf hollow cathode discharges.

Line densities versus time for elements of the cathode materials have been investigated. Vaporization curves for the elements in dc HCD were such as those reported previously (e.g. in Ref. 13). Comparison in the form of differences in the line densities ($\Delta S = S_{hf} - S_{dc}$) for major and minor elements of the copper, brass and steel cathodes is presented in Fig. 1. The preburn time for all the cathodes used here was 30 s. Results presenting in Fig. 1 indicate that for Zn, Fe and Cr, volatilisation processes are very similar

Table 1

Species excited in the dc and hf discharges

copper
Ar I, Ar II, Cu I, Cu II, Ag I, Pb I
brass
Ar I, Ar II, Cu I, Zn I, Zn II, Pb I, Pb II, Sn I, Cd I, ZnH (only in the hf discharge)
steel
Ar I, Ar II, Fe I, Fe II, Mn I, Mn II, Cr I, W I

in the hf and dc discharges. For Cu relatively small differences are observed both for the copper and brass cathodes. Significant differences in the volatilisation processes are found for Pb, Mn and W. This is suprising because these elements have quite different physical properties.

Intensities of lines excited in the dc and hf discharges under the pressures of 3, 6 and 10 Torr have been compared. Intensity ratios of chosen lines of argon and elements being major and minor components of the cathode materials (I_{hf}/I_{dc}) versus pressure for the cathodes made of copper, brass and steel are presented in Figs. 2-6, respectively. Atomic and ionic lines have been used for the comparison. For some species (Ar II, Cu I) lines with different energies of the upper electronic states have been chosen to compare electronic energy distributions in the dc and hf discharges.

The intensity ratios for Ar II lines have been mostly close to unity and independent or weekly

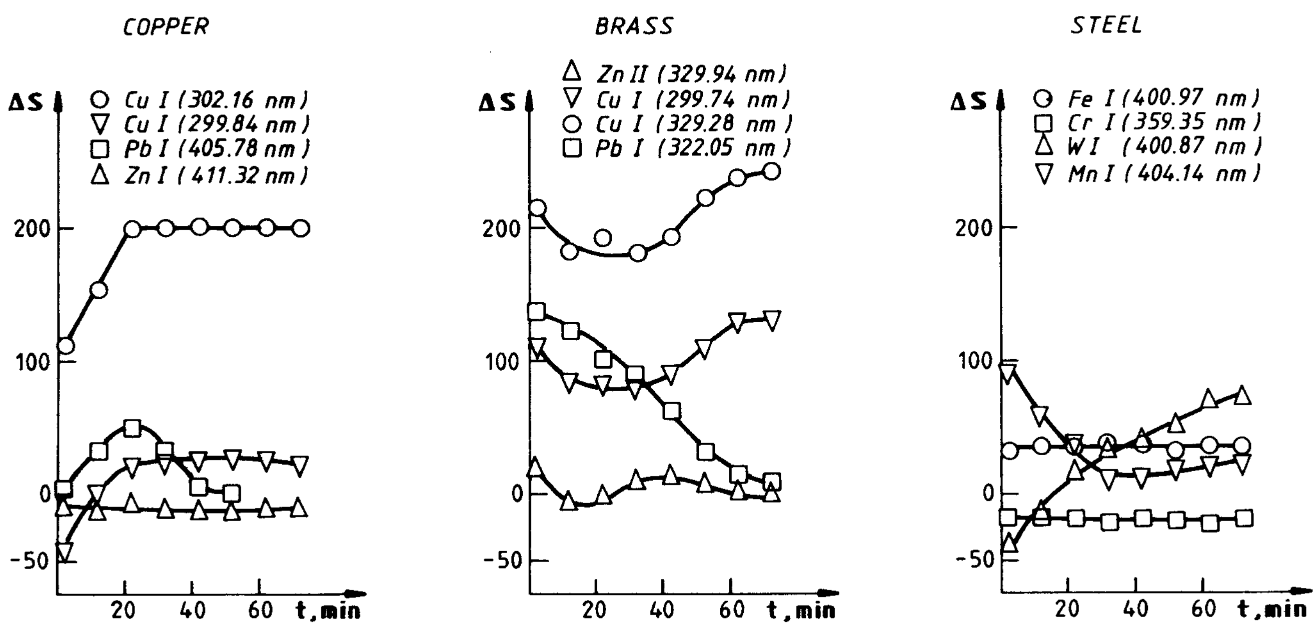

Fig. 1. Density versus time curves for chosen elements of the cathode materials (p = 6 Torr, $\Delta S = S_{hf} - S_{dc}$).

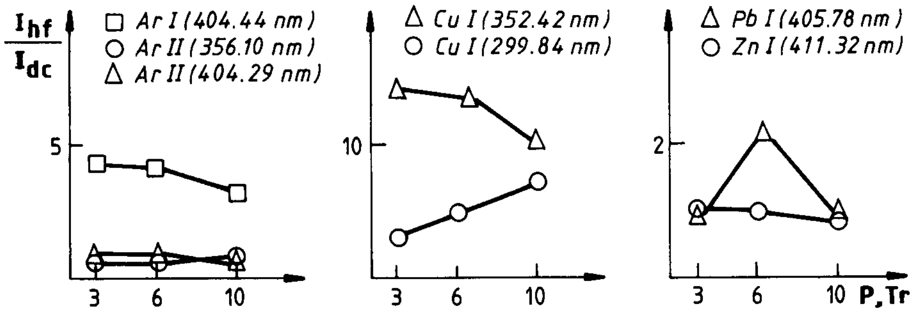

Fig. 2. Intensity ratios (I_{hf}/I_{dc}) of species excited in the copper cathodes (4 mm in inner diameter).

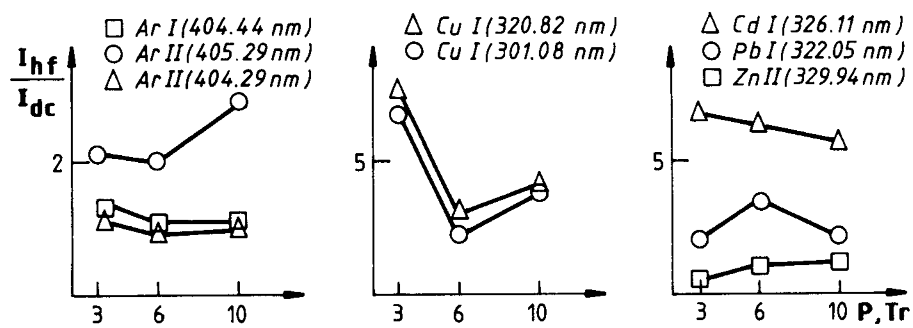

Fig. 3. Intensity ratios (I_{hf}/I_{dc}) of species excited in the brass cathodes (4 mm in inner diameter).

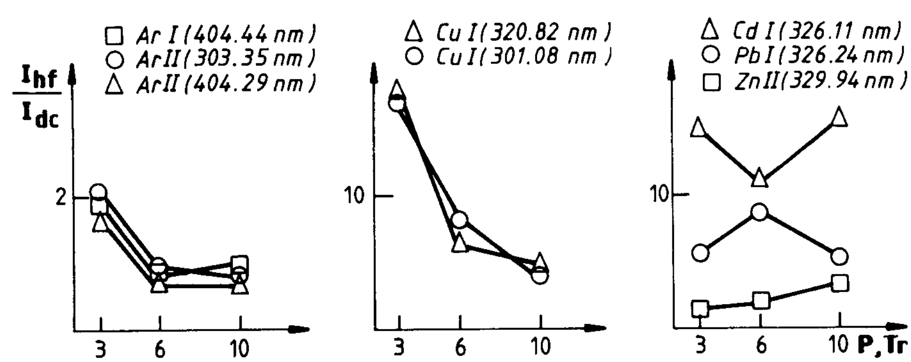

Fig. 4. Intensity ratios (I_{hf}/I_{dc}) of species excited in the brass cathodes (2.5 mm in inner diameter).

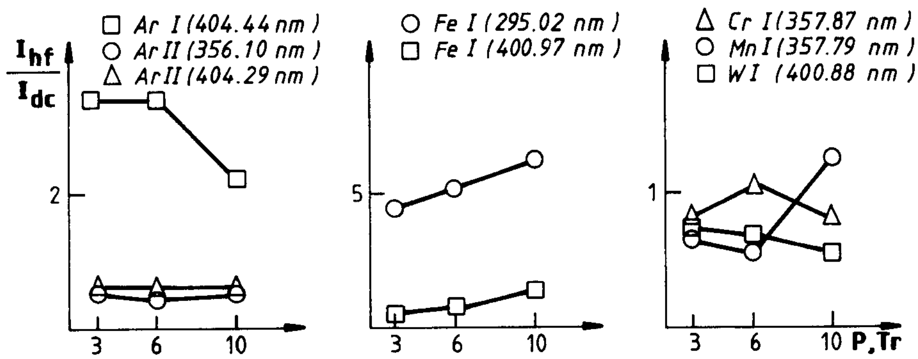

Fig. 5. Intensity ratios (I_{hf}/I_{dc}) of species excited in the steel cathodes (4 mm in inner diameter).

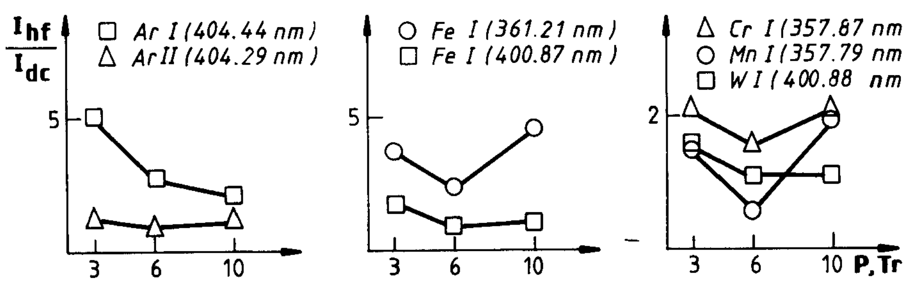

Fig. 6. Intensity ratios (I_{hf}/I_{dc}) of species excited in the steel cathodes (2.5 mm in inner diameter).

dependent on pressure and the cathode material. These ratios have been practically the same for lines with energies of the upper electronic states different by about 3 eV. For Ar I lines, the I_{hf}/I_{dc} values have clearly depended on the cathode material and not very strongly on pressure.

As can be seen in Figs. 2-6 the ratios I_{hf}/I_{dc} for particular elements have been in various way related to the material and inner diameter of the cathode and plasma pressure. The highest values of the ratios have been observed for lines of copper (up to 20) and cadmium (up to 15) and zinc (up to 10). In the case of Cu I lines (see Fig. 2), the I_{hf}/I_{dc} values have been significantly greater for the lines with higher energies of the upper electronic states. For Pb I lines emitted by the brass cathode the ratio I_{hf}/I_{dc} has been sensitive for the inner diameter size. For Fe I lines excited in the steel cathodes the intensity ratios, diiferent for particular lines, have changed weakly with pressure. Lines of Mn I, Cr I and W I have usually been of similar intensity $(0.5 < I_{hf} < I_{dc} < 2)$

Some conclusions can be drawn from the spectra compared here:

- the electronic energy distributions are very similar for the Ar II ions (the carrier gas) and different for some atoms from the cathode material (e.g. Cu I)
- the electron densities are various in hf HCD and dc HCD
- for some elements line intensities higher more than by one order are obtained using hf supply instead of dc supply.
- matrix effects in dc HCD are different from those observed in hf HCD.

ACKNOWLEDGMENTS

The support from Warsaw University under the Research Project 01.17 is gratefully acknowledged.

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Date Received: 07/13/87
Date Accepted: 08/14/87