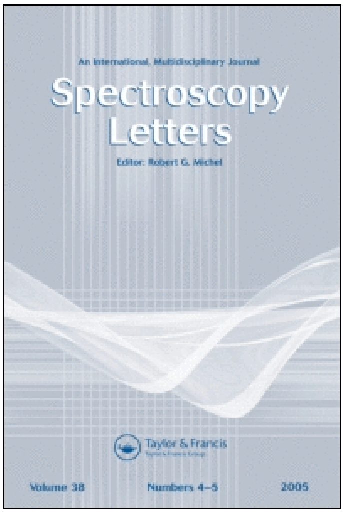


Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Modified Version of the Grimm's Glow Discharge Lamp for Use as a Demountable Hollow Cathode Emission Source. III. Blackening as a Function of Discharge Parameters

S. Caroli[a]; O. Senofonte[a]; A. Alimonti[a]; N. Violante[a]
[a] Laboratorio di Tossicologia, Istituto Superiore di Sanitá, Rome, Italy

To cite this Article Caroli, S. , Senofonte, O. , Alimonti, A. and Violante, N.(1980) 'A Modified Version of the Grimm's Glow Discharge Lamp for Use as a Demountable Hollow Cathode Emission Source. III. Blackening as a Function of Discharge Parameters', Spectroscopy Letters, 13: 12, 905 — 931

To link to this Article: DOI: 10.1080/00387018008064077

URL: http://dx.doi.org/10.1080/00387018008064077

SPECTROSCOPY LETTERS, 13(12), 905-931 (1980)

A MODIFIED VERSION OF THE GRIMM'S GLOW DISCHARGE LAMP FOR USE AS A DEMOUNTABLE HOLLOW CATHODE EMISSION SOURCE. III. BLACKENING* AS A FUNCTION OF DISCHARGE PARAMETERS

Key words: Hollow Cathode, Glow Discharge, Emission Spectroscopy, Aluminium, Copper, Graphite, Photographic Blackening.

S. Caroli, O. Senofonte, A. Alimonti, N. Violante
Laboratorio di Tossicologia, Istituto Superiore di Sanità, Viale Regina Elena, 299, 00161 - Rome, Italy

ABSTRACT: The influence of anode distance from hollow cathode on the blackening* of spectral lines excited by means of the modified Grimm's lamp was investigated for three representative cathodic materials, i.e. aluminium, copper and graphite using argon as the carrier gas. On the basis of the experimental results as well as voltage-current characteristic curves at distances of 7, 15, 20, 25 and 33 mm, it was possible to conclude that the optimal sets of discharge parameters for all the materials investigated are based on an electrode distance of 20-25 mm. In the case of copper a distance of 33 mm was also found to be highly suitable. An increase in the emission of copper lines at the largest anodic length with increasing pressure of the noble gas was also observed, in contrast with the behavior of the same element at shorter distances. A tentative interpretation of the phenomenon is given.

INTRODUCTION

In the two preceding parts[1,2] of this study, we discussed a modified form of the Grimm's glow discharge radiation source which proved to be a type of hollow cathode lamp with promising features. Voltage-current intensity characteristic curves

*Blackening = increase in intensity

were also deduced at the time by varying the distance between the electrodes without modifying the geometry of the other components of the lamp. To this purpose anodes of different lengths were mounted in the tube. On the basis of those preliminary results it was possible to establish the optimal parameters (gas pressure, current intensity, electrode distance) corresponding to ranges of high stability of the discharge process for three representative cathodic materials, i.e. aluminium, copper and graphite.

The aim of the present study is to elucidate the dependence of blackening of spectral lines emitted by the hollow cathode in the modified tube on electrode distance within the noble gas pressure and current intensity ranges previously selected for best discharge stability. We will further clarify the capabilities of this modified radiation source and provide a sufficiently sound basis for its analytical applications.

EXPERIMENTAL

The construction of the hollow cathode tube used for this research has already been reported in the preceding articles[1,2]. This paper is primarily concerned with the variations of blackening as a function of the distance of the tubular steel anode from the hollow cathode at various carrier gas pressures and current intensity values using demountable anodes of five different lengths. In this way the distances between the electrodes resulted in being 7, 15, 20, 25 and 33 mm respectively, which coincide with those already employed to deduce the voltage-current intensity characteristic curves in the preceding paper[2].

The sets of experimental conditions chosen to carry out blackening measurements comprise current intensities ranging from 25 to 400 mA and argon pressures between 90 and 1120 Pa. Obviously, for each cathodic material at a given electrode distance and working with a preselected gas pressure, the practicable current intensity range is not always the same; at times it must considerably be reduced to obtain a stable and reproducible discharge with homogeneous sputtering of the cathodic surface.

The instrumentation employed consisted of a SPV 1m/800 vacuum spectrograph equipped with a HVG 2 current-stabilized electric source (both by RSV, West Germany), a vacuum gauge Thermotron TM 14/2 (Leybold-Heraeus, West Germany), a digital voltmeter Hewlett-Packard 3476 A, and a micrometric needle valve to control and maintain constant flow of carrier gas. A Bausch & Lomb concave grating (Paschen-Runge mounting, 1 m radius, 1200 grooves mm^{-1}) was used. Further details on apparatus can be found in previous articles[3,4].

The materials employed for discharge as well as the carrier gas were of the highest purity degree commercially available.

Blackening values were read by a microdensitometer MD-100 (Jenoptik Jena, East Germany), which enables measurements of values as high as 3.2 blackening units with a relative error of less than 2 %. Background correction was always applied, although it proved to be negligible in all the cases under study. In fact, background blackening never exceeded 0.015 units in the whole spectral range utilized.

Spectra were photographed on Kodak Spectrum Analysis No. 1 (SA 1) films, which were developed for 4 min at 20 $\pm$ 0.1 °C in a Kodak D-19 solution. Films were processed with extreme care under strictly specified conditions, as already reported[3], since reliability of results depends on this step.

For each cathodic material three different spectral lines were chosen after preliminary exposures to select the most suitable for our investigation, i.e. those characterized by a sharp profile and not affected by self-absorption phenomena. Each set of spectral lines covers a wide spectral range and includes lines of both atomic and ionic origin in order to ascertain the role played by wavelength and origine of the lines. Table 1 below lists the spectral lines utilized, together with other relevant information.

The procedure adopted was the following: for each cathodic material and each electrode distance the flow of the carrier gas was carefully regulated at the lowest pressure value of the range mentioned above (90 Pa) and current intensity was applied stepwise starting from the minimum value compatible with a stable discharge. The whole series was then repeated for all the other gas pressures (170, 230, 440, 690 and 1120 Pa, respectively). Exposures were made in duplicate for each combination of the above parameters, and the averaged blackening values of each spectral line were finally plotted as a function of applied current intensity at constant gas pressure and electrode distance.

This representation was thought to be more expedient than that based on the dependence of blackening on gas pressure. In fact, in a sputtering source two of the three variables always depend on one another. Since most of the electric source units commercially available for the operation of sputtering lamps permit an accurate control of current intensity, whereas gas pressure is maintained at a predetermined value, the former can be considered the true independent variable. Under these conditions, the third parameter, voltage, assumes values univocally determined by the other two. In any case, the two representations are obviously converted one into the other without difficulty and are entirely equivalent. In this connection it is worth mentioning that it was not necessary to plot blackening against the power dissipated in the lamp since, in the adopted ranges of high stability of discharge, the voltage increased only slightly with applied current intensity and was practically independent of time. This means in practice that the overall behavior of the curves

TABLE 1

Spectral Lines and Exposure Parameters Adopted for Measuring Blackening Values (Entrance Slit of the Spectrograph: 30 μ m).

Cathodic Material	Spectral Line (nm)	Excitation Potential (eV)	Gas Pressure (Pa)	Exposure Time (s)	Electrode Distance (mm)
	(I) 396.153	3.13			
Al	305.715	7.66	90-1120	30	7-25
	(II) 281.618	11.82			
	(I) 345.785	4.97			
Cu	(I) 301.084	5.50	90-1120	30	7-33
	(II) 227.625	5.70			
	(II) 283.760	16.34			
C	(II) 283.671	16.34	90-1120	30	7-33
	(I) 247.857	7.69			

is not affected by reporting current intensity on the abscissas instead of power. The former method was preferred for the same reasons discussed above, as electric source units allow regulation of current intensity and not of power, even though the latter would be more logical and appropriate.

The variations in blackening with working parameters were also investigated for several argon lines, respectively at 228.264, 275.392, 285.533 and 303.352 nm. Results showed that the dependence of their blackening on anodic length is much less pronounced than that of lines emitted by the cathodic material. Moreover, increasing current intensity and gas pressure only slightly affect their emission, so that plots of blackening differences calculated by pairing one line emitted by the cathode with one emitted by the rare gas do not substantially deviate from the general pattern of the curves.

All measurements were carried out in flowing argon. It could be ascertained that the pressure inside the hollow cathode was the same as that measured at the outlet of the lamp by removing the cathode and inserting in its place a second gauge tube connected to the vacuum gauge as the first one placed at the outlet of the lamp. No difference could be noted between the indications given simultaneously by the two gauge tubes, whatever the gas pressure or the electrode distance applied.

Analogously, blackening curves obtained with steady carrier gas resulted as completely superimposed to those referring to spectra obtained in flowing argon. In this case it must be stressed that exposures were limited to the first 2 - 3 minutes of operation owing to the fact that impurities forming in the discharge process could not be removed as with flowing argon. Both procedures confirm that pressure values read on the scale of the vacuum gauge (preliminarly calibrated by means of an absolute Kammerer) correspond to those inside the hollow cathode.

RESULTS

The blackening-current intensity curves obtained following the procedure described above by the modified radiation source are reported in Figs. 1 through to 11 for the three materials under investigation. It must be emphasized that all the curves are plotted only in those current intensity intervals in which the discharge showed very high stability. It does not mean, in other words, that the discharge ensues only within these ranges, but simply that blackening values obtained outside these limits cannot be considered fully reliable in consequence of some instability in the resulting voltage as well as in discharge process.

Aluminium Cathodes

The graphs relative to this metal are reported in Figs. 1 to 3. From them the following conclusions can be easily drawn: i) at short electrode distances (up to 15 mm) stable discharges are obtained only at current intensities no higher than 100 mA, this being valid for all three Al lines; ii) at short electrode distances the dependence of blackening on current intensity is greatly different from line to line as far as the slope of the curves is concerned; iii) at a distance of 20 mm the interval pertaining to stable discharges appears to be greatly increased, current intensities as high as 400 mA being still attainable; iv) blackenings measured at lower gas pressures are generally more intense than those pertaining to higher pressures.

Furthermore, it must be noted that in no case the distance of 33 mm gave suitable discharge. No graphs are therefore plotted for the fifth anodic length. All in all, the most advantageous situation for the blackening of Al lines seems to be that occurring at a distance of 20 mm, independent of wavelength or origin of the spectral lines.

Copper Cathodes

The plots referring to this second material (Figs. 4 to 6) show clearly that in comparison with aluminium, copper gives a wider interval of current intensities within which

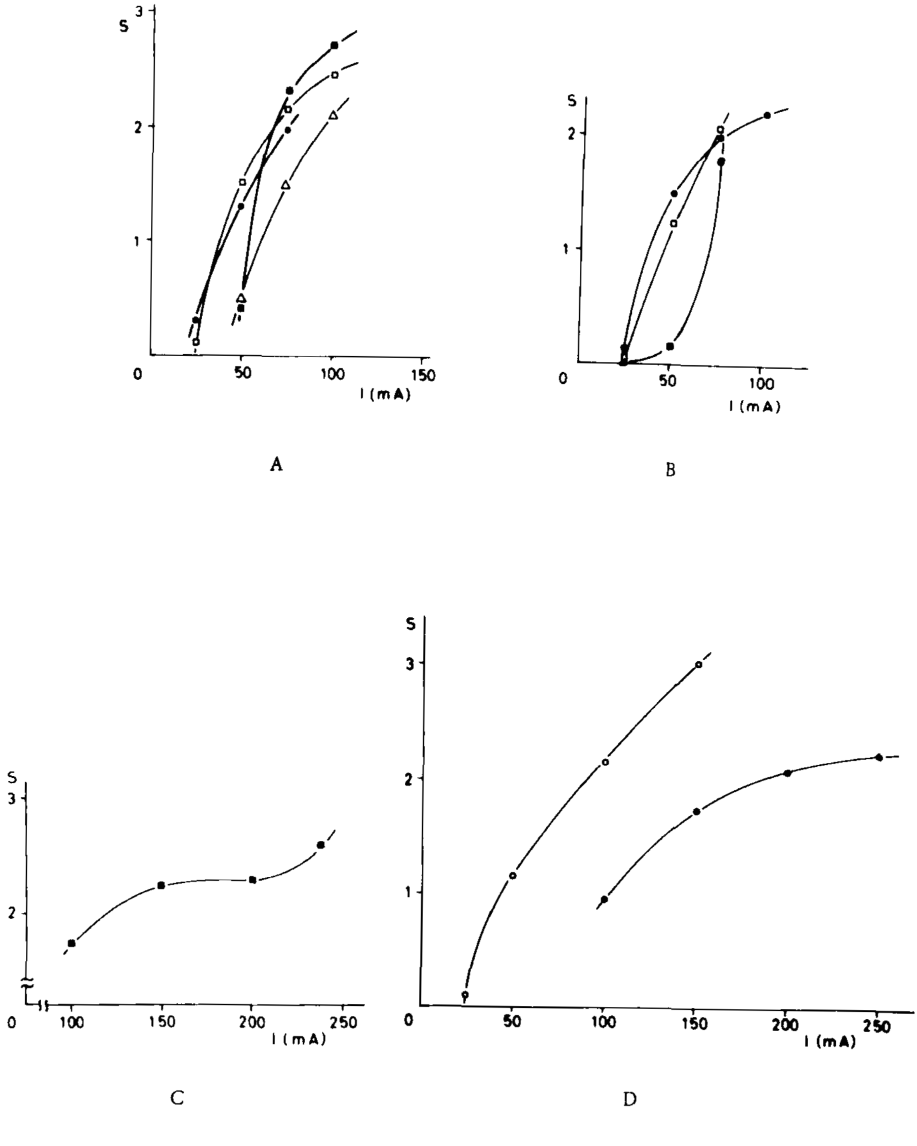


FIG. 1 - Blackening-Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line Al(I) 396.153 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25. Gas Pressure (Pa): o = 90; ▲ = 170; ● = 230; □ = 440; ■ = 690; Δ = 1120.

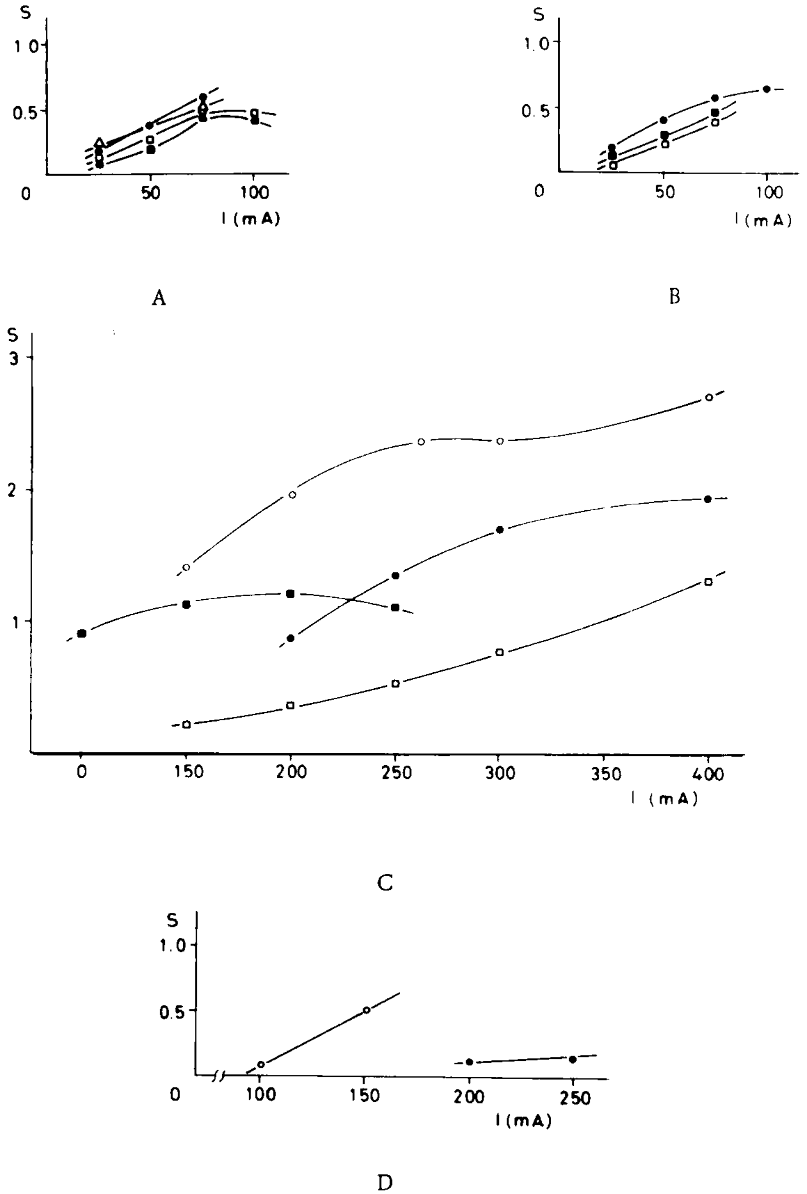


FIG. 2 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line 305.715 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25. Gas Pressure (Pa): o = 90; ▲ ◘ 170; ● = 230; □ = 440; ■ = 690; Δ = 1120.

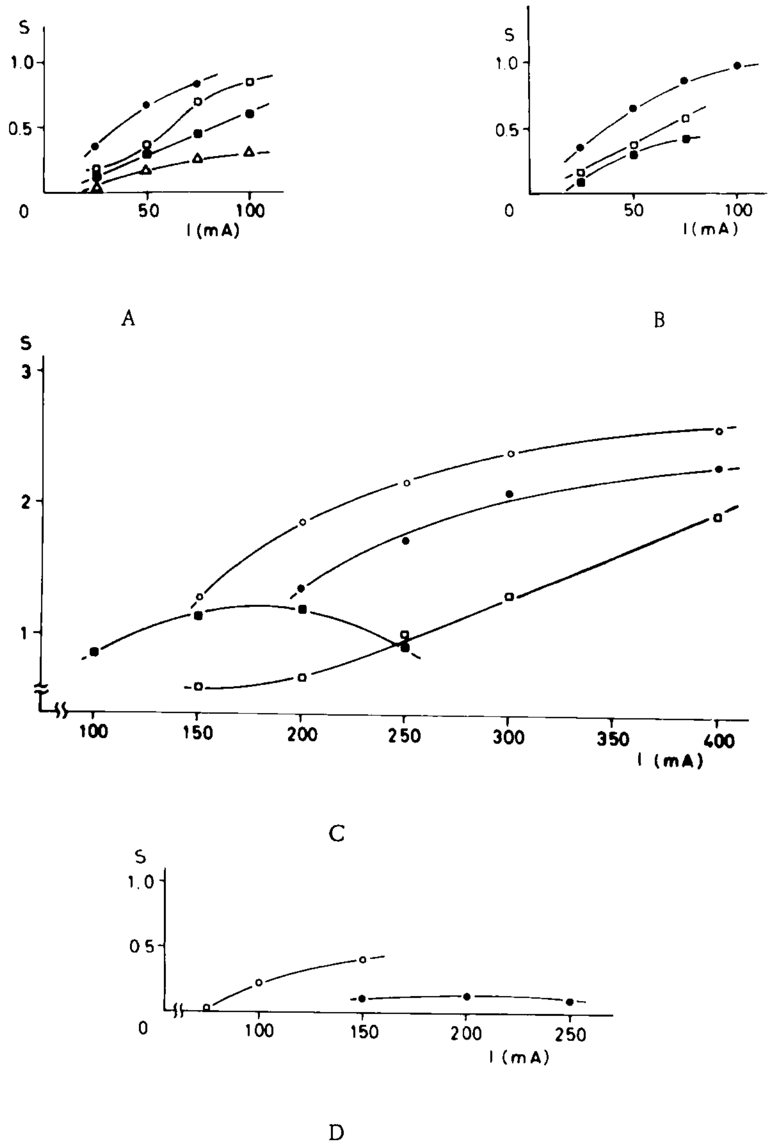


FIG. 3 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line Al(II) 281.618 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25. Gas Pressure (Pa): o = 90; ▲ = 170; ● = 230; □ = 440; ■ = 690; △ = 1120.

stability of the discharge is highly satisfactory and blackening reaches suitable values. As a rule each electrode distance corresponds to a set of curves with rather regular behavior. At distances of 20 and 33 mm however the behavior of the blackening curves appears to be even better than in the remaining cases, albeit the difference is really not so remarkable.

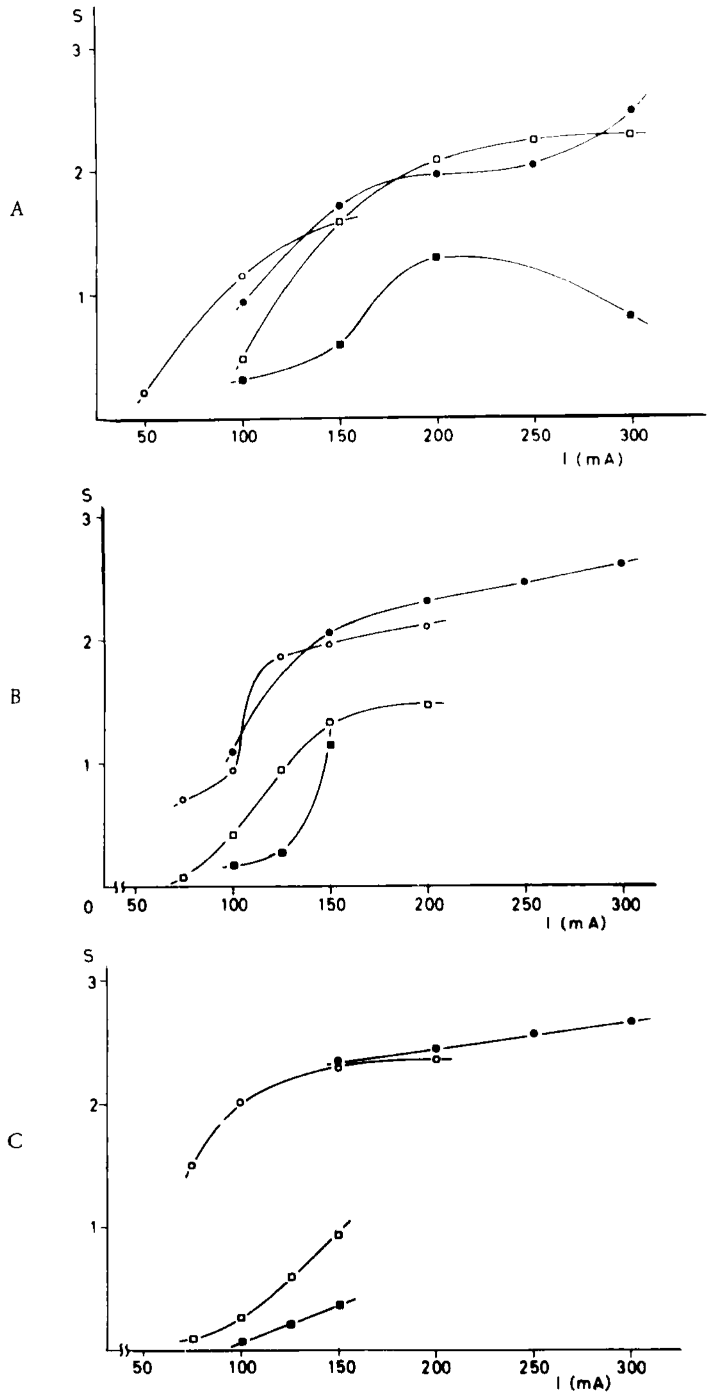
An interesting phenomenon must be also outlined. At a distance of 33 mm, curves at higher pressures show a tendency to be characterized by higher blackening values, in contrast to the general pattern observed at shorter distances. Moreover, discharge at the longest distance was accompanied by the presence of a luminescent cone which, starting from the inner part of the cathode, reached the anode with its base while its intensity increased notably.

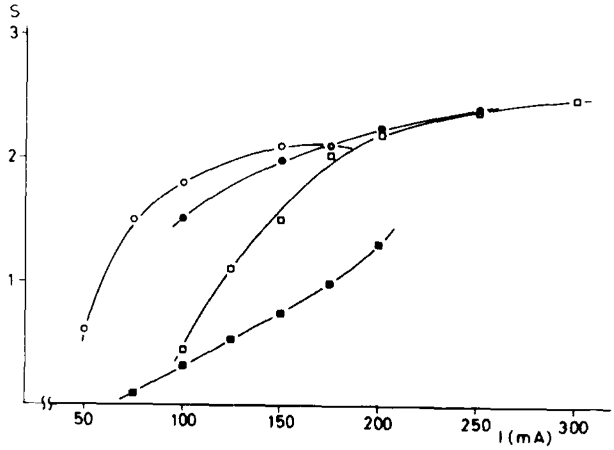
Overall behavior for the three copper lines was the same, regardless of wavelength and line origin. This is shown more explicitly by plotting the blackenings either against current intensity at constant gas pressure and varying anodic length or against electrode distance at constant gas pressure and varying current intensity (see Figs. 7 and 8, respectively). Data reported therein coincide obviously with those of the preceding plots for the same spectral line; they are simply distributed in a different manner to demonstrate the inversion mentioned above.

From comparative inspection of the graphs plotted in Figs. 6, 7 and 8 it can be concluded that at a filler gas pressure of between 230 and 440 Pa (most likely at ca. 330 Pa) there is an inversion point below which blackening reaches a maximum at an electrode distance of ca. 20 mm. On the other hand, this distance corresponds to a minimum when pressure values are above this inversion point. In the latter case, a further increase in electrode distance is responsible for a very steep increase in blackening; it can also be said that the influence of current intensity becomes progressively less pronounced.

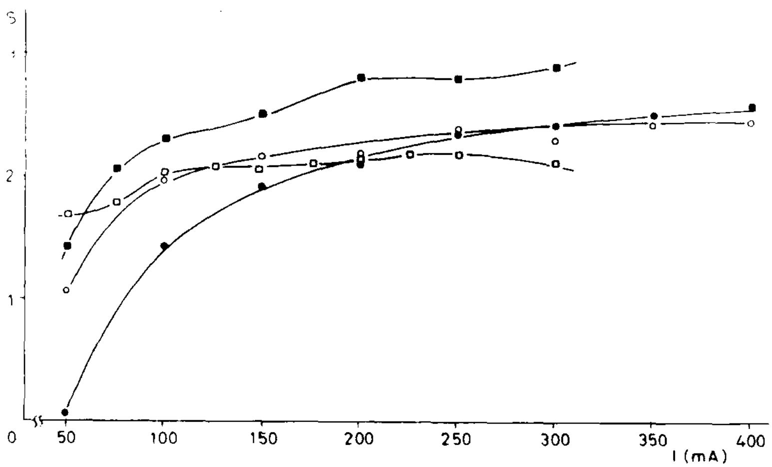
<u>Graphite Cathodes</u>

For this last material, the plots reported in Figs. 9 to 11 clearly testify a very reduced dependence of blackening on current intensity, gas pressure and anodic length. In fact, the curves present almost negligible slopes (with the exception of the line at 247.857 nm as far as the part of the curve below 100 mA is concerned), are virtually linear and tend to merge into one another. Owing to the fact that the curves plotted at different gas pressures have such similar behavior, occasionally overlapping, no meaningful trend of the dependence of the curves on the electrode distance could be deduced. Consequently, it can be said that in the case of graphite cathodes all the distances tested in this research are suitable for obtaining blackening values of practical use. On the other hand, if the


A
B
C
S
3
2
1
0
50
100
150
200
250
300
I (mA)

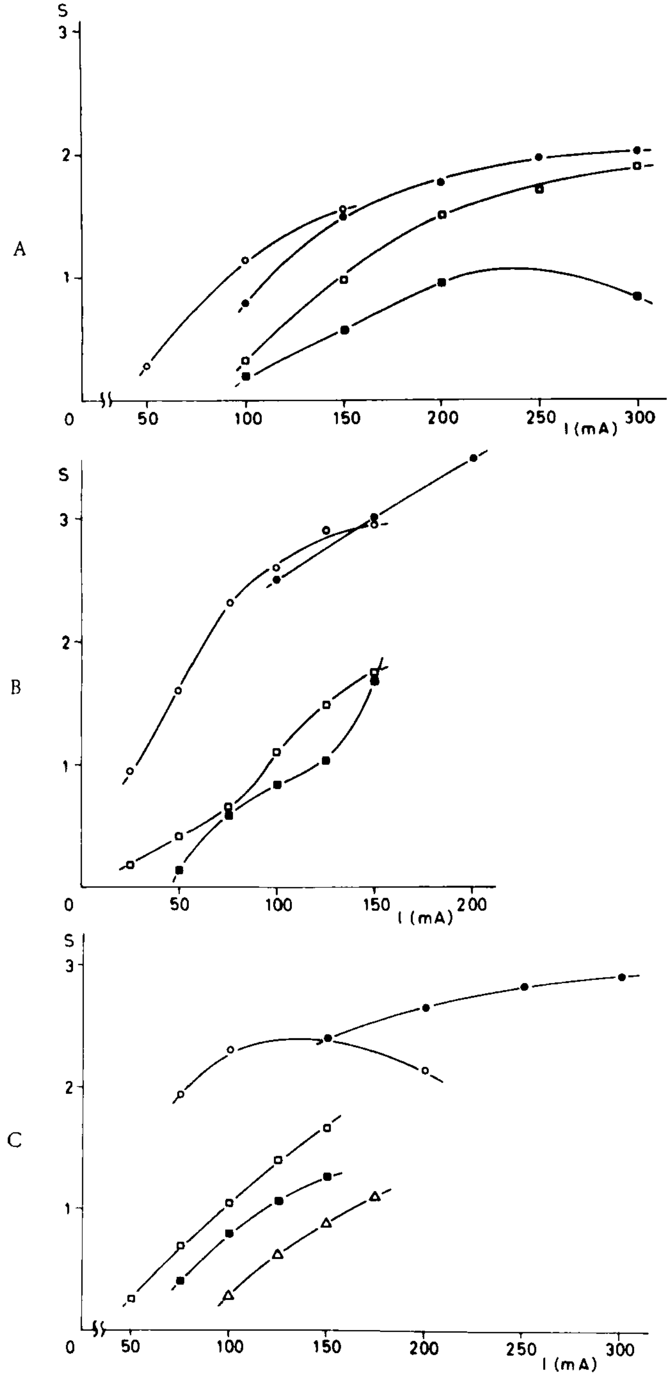


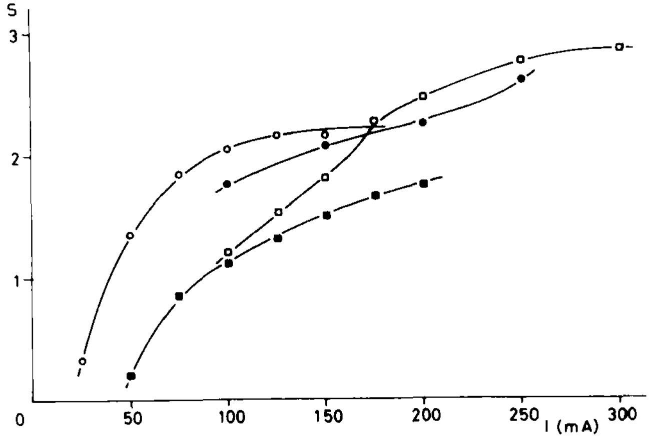
D



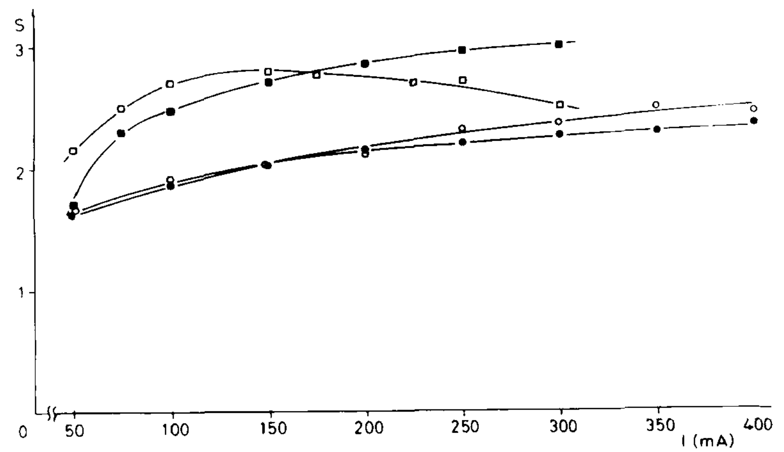
E

FIG. 4 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line Cu(I) 345.785 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; ▲ = 170; ● = 230; □ = 440; ■ = 690; △ = 1120.


A
S
3
2
1
0
50
100
150
200
250
300
I (mA)
B
S
3
2
1
0
50
100
150
200
I (mA)
C
S
3
2
1
0
50
100
150
200
250
300
I (mA)

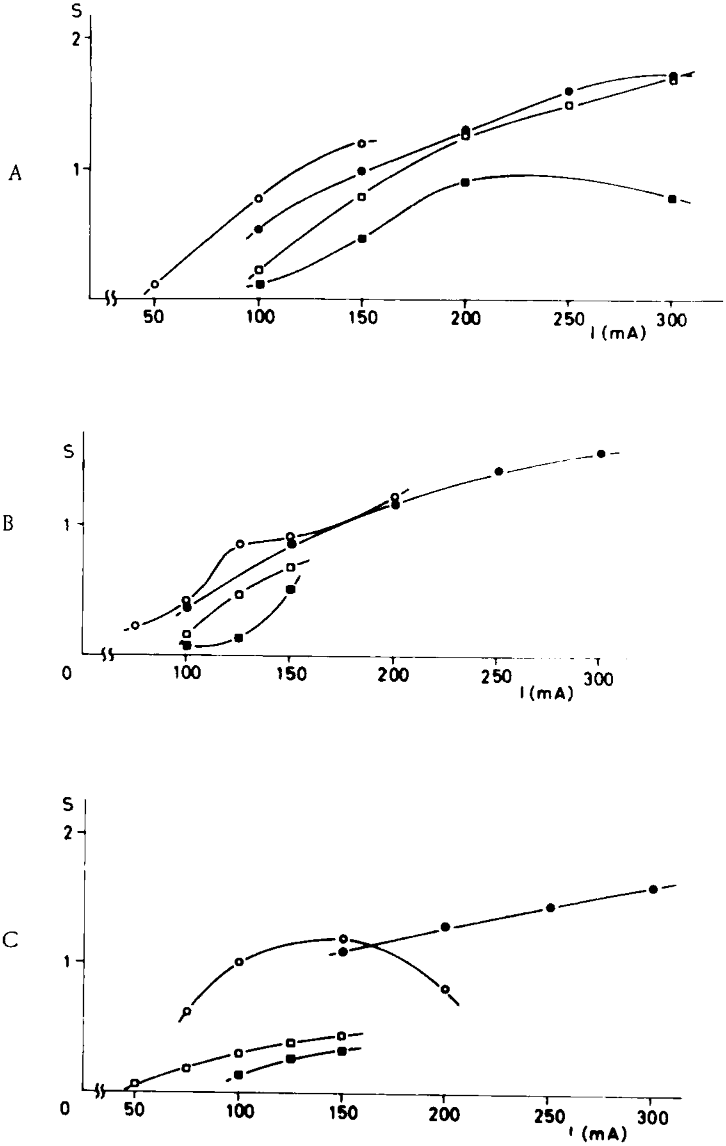


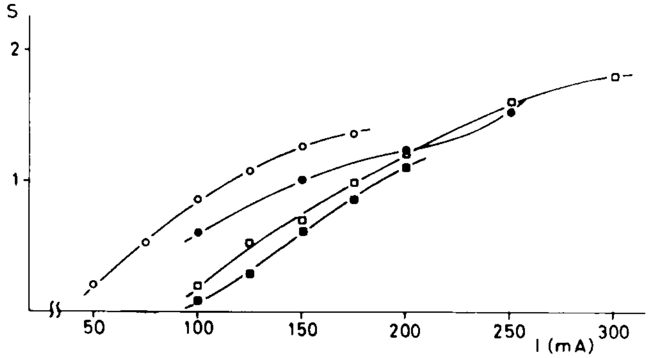
D



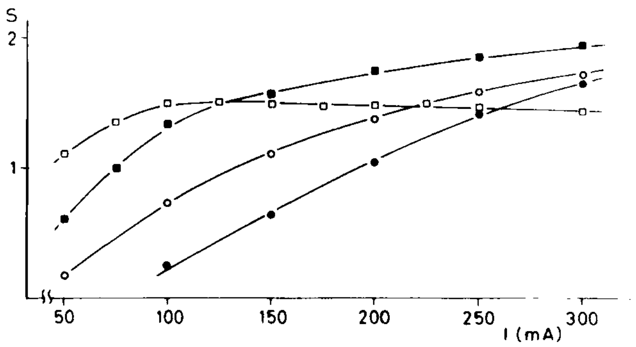
E

FIG. 5 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line Cu(I) 301.084 nm. Electrode Distance (mm): A, 7; B, 15: C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; ▲ = 170; ● = 230; ◻ = 440; ■ = 690; △ = 1120.


A
S
2
1
50
100
150
200
250
300
I (mA)
B
S
1
0
100
150
200
250
300
I (mA)
C
S
2
1
0
50
100
150
200
250
300
I (mA)

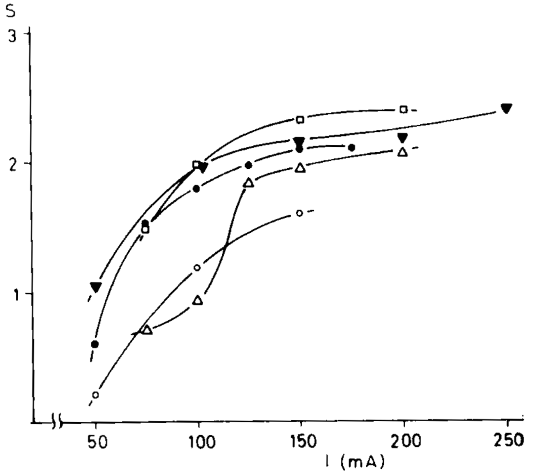


D

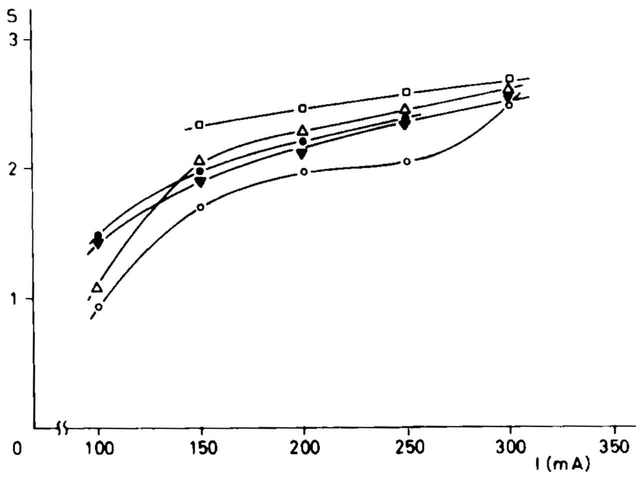


E

FIG. 6 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line Cu(II) 227.625 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; ▲ = 170; ● = 230; □ = 440; ■ = 690; Δ = 1120.



A



B

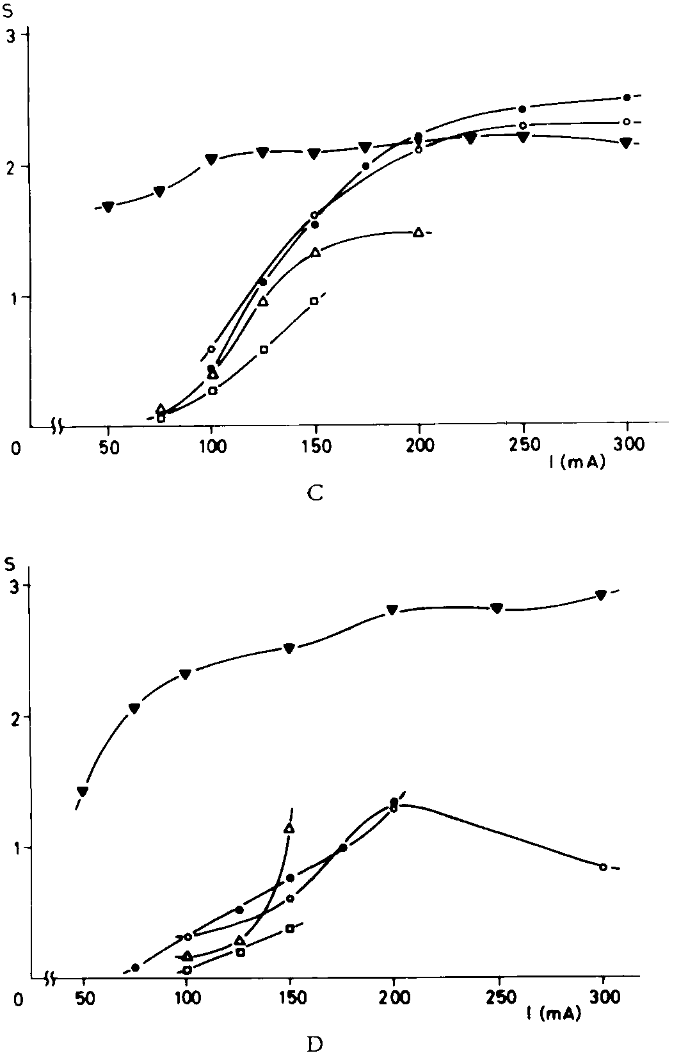


FIG. 7 - Blackening - Current Intensity Curves at Varying Electrode Distances with Constant Gas Pressure for Spectral Line Cu(I) 345.785 nm. Gas Pressure (Pa): A, 90; B, 230; C, 440; D, 690. Electrode Distance (mm): o = 7; Δ = 15; □ = 20; ● = 25; ▲ = 33.

voltage - current intensity curves described in Part II of this study[2] are taken into account, it is preferable to adopt a distance of 20 - 25 mm, corresponding to the highest discharge stability for this material.

DISCUSSION AND CONCLUSIONS

The data reported in this work demonstrate that at certain distances of the anode from the hollow cathode the behavior of the blackening values can be considered optimal. By combining the present results with those reported previously on the voltage - current intensity curves[2], it is possible to define sets of experimental parameters which are a reasonable compromise of contrasting requirements and can be considered as the ranges of the highest stability of the discharge process giving the most convenient blackening values. The whole situation is summarized in Table 2.

As a rule, the most widely applicable distance appears to be 20 mm, irrespective of the cathodic material used.

Our results also agree with the general mechanism accepted for the hollow cathode discharge. It is well known in fact, from relevant literature in this field[5-11], that an increase in gas pressure causes initially an increase in the amount of material sputtered from the cathodic surface owing to the higher number of carrier gas ions impacting the cathode. The emission intensity then reaches a maximum and a further increase of gas pressure causes a decrease in emission intensity since the redeposition process becomes concurrent with that of sputtering as a consequence of the shorter mean free path of gas ions. The position of the maximum depends, among other things, on the excitation energy of the line and applied current intensity.

TABLE 2

Sets of Parameters Corresponding to Optimal Operative Conditions of the Modified Lamp

Cathodic Material	Current Intensity (mA)	Gas Pressure (Pa)	Electrode Distance (mm)
Al	100 - 400	230 - 690	20
Cu	150 - 300	230 - 330	20
	100 - 300	330 - 440	33
C	100 - 300	230 - 690	20

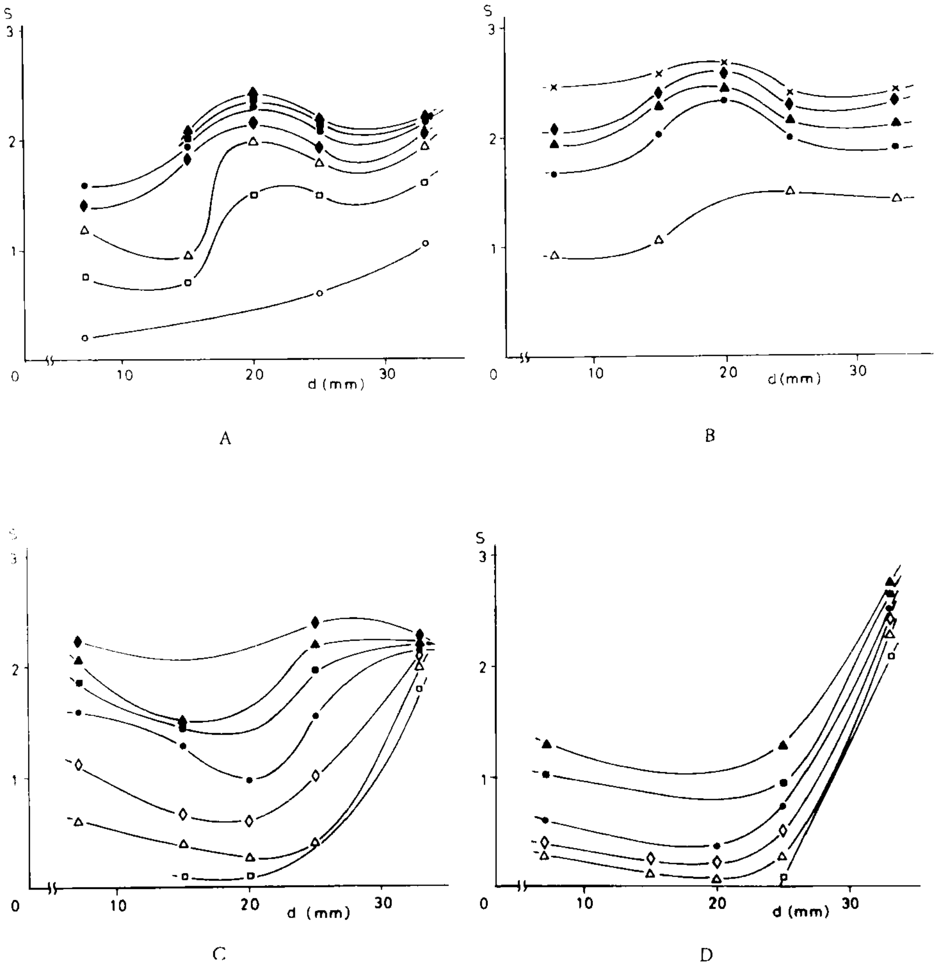
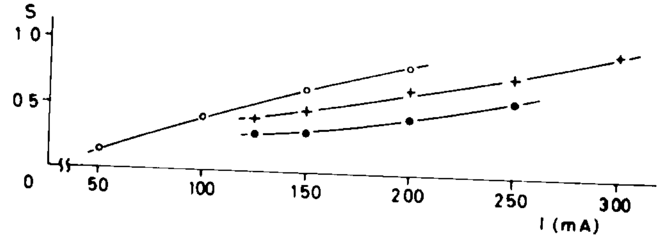
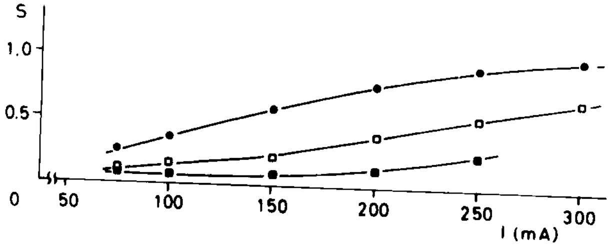


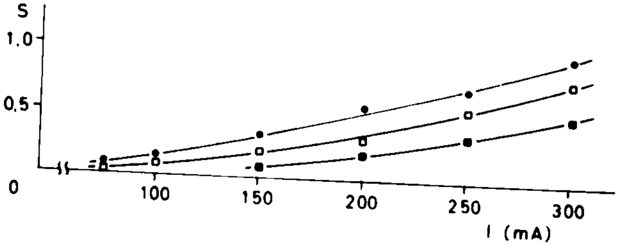
FIG. 8 - Blackening-Electrode Distance Curves at Varying Current Intensity with Constant Gas Pressure for Spectral Line Cu(I) 345.785 nm. Gas Pressure (Pa): A, 90; B, 230; C, 440; D, 690. Current Intensity (mA): o ◘ 50; □ = 75; △ = 100; ◇ = 125; ● = 150; ■ = 175; ▲ = 200; ◆ = 250; x = 300.


S
1.0
0.5
0
50
100
150
200
250
300
I (mA)

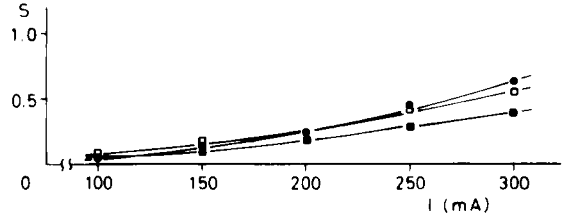
A


S
1.0
0.5
0
50
100
150
200
250
300
I (mA)

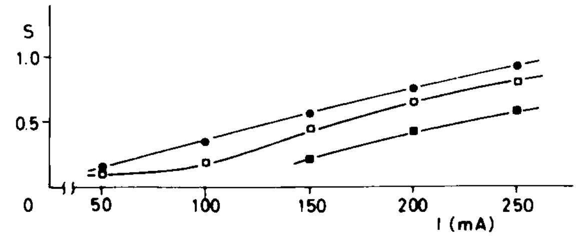
B


S
1.0
0.5
0
100
150
200
250
300
I (mA)

C

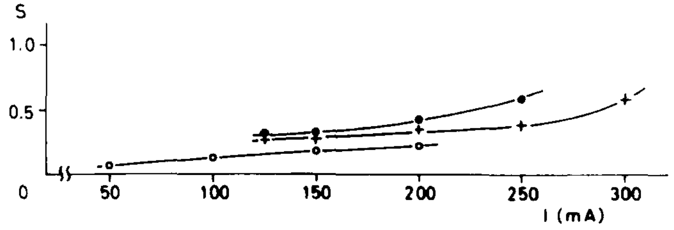


D

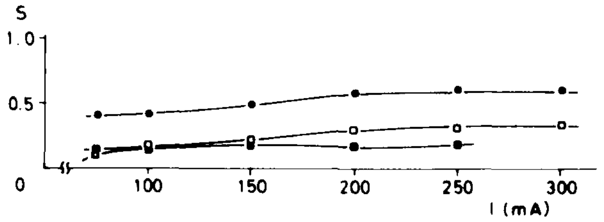


E

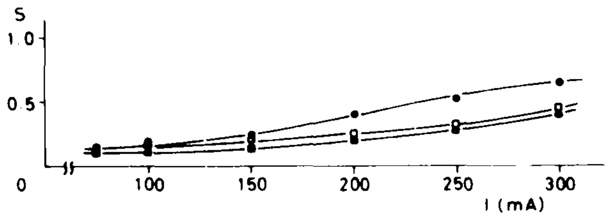
FIG. 9 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line C(II) 283.760 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; + = 170; ● = 230; □ = 440; ■ = 690.


S
1.0
0.5
0
50
100
150
200
250
300
I (mA)

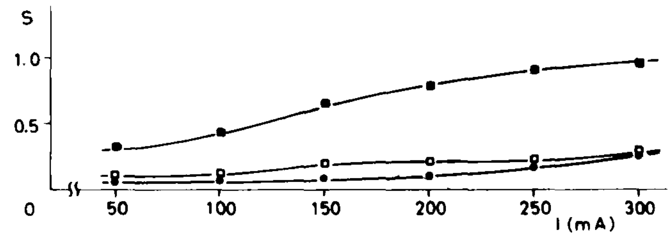
A


S
1.0
0.5
0
100
150
200
250
300
I (mA)

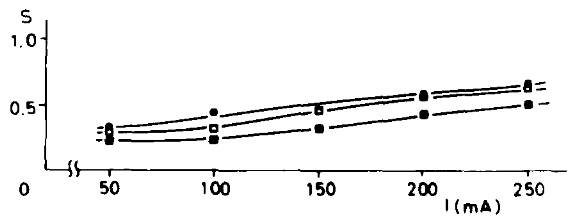
B


S
1.0
0.5
0
100
150
200
250
300
I (mA)

C

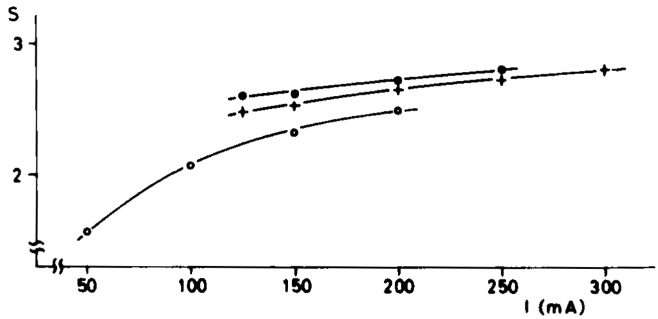


D

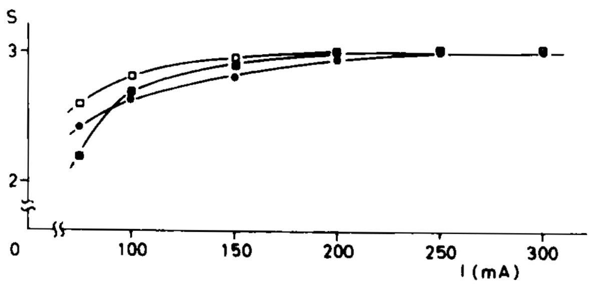


E

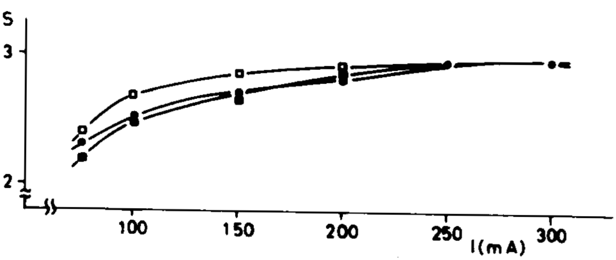
FIG. 10 - Blackening - Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line C(II) 283.671 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; + = 170; ● = 230; □ = 440; ■ = 690.


S
3
2
50
100
150
200
250
300
I (mA)

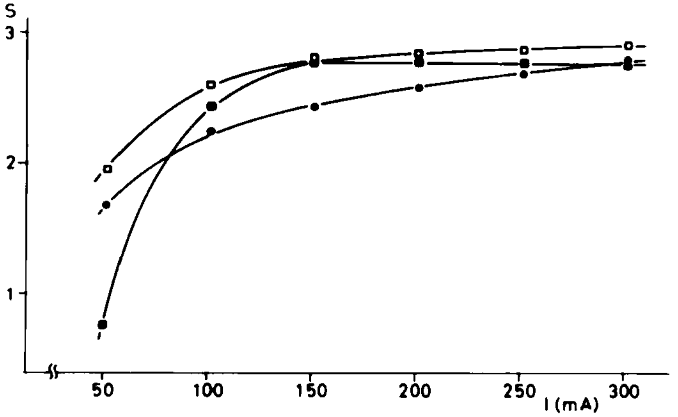
A


S
3
2
0
100
150
200
250
300
I (mA)

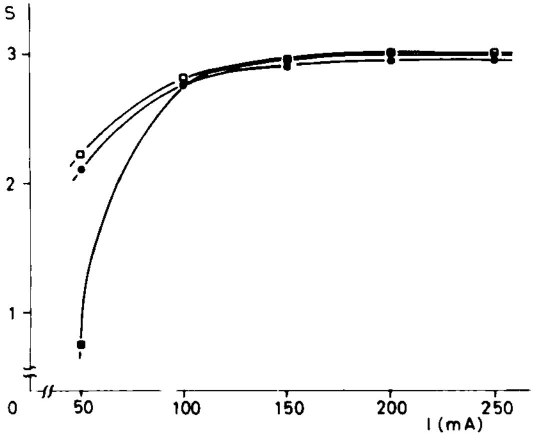
B


S
3
2
100
150
200
250
300
I(mA)

C



D



E

FIG. 11 - Blackening-Current Intensity Curves at Varying Pressures with Constant Electrode Distance for Spectral Line C(I) 247.857 nm. Electrode Distance (mm): A, 7; B, 15; C, 20; D, 25; E, 33. Gas Pressure (Pa): o = 90; + = 170; ● = 230; □ = 440; ■ = 690.

In the case of copper the behavior of blackening observed at an electrode distance of 33 mm is in partial contrast with these assumptions. On the other hand it should be borne in mind that aluminium and graphite are sputtered to a much lower extent than copper. For example, the extraction constant for copper using argon as the carrier gas is 0.85 and that of aluminium only 0.05, as reported by G. Knerr et al.[12]. The appearance of the luminescent cone described above as well as the thicker layer of material deposited on the glass shield of the anode in comparison with that observed at shorter electrode distances are clearly connected with the more intense attack on the cathodic surface of copper.

Further studies are underway in order to obtain a satisfactory explanation of the phenomenon also in the light of other important factors such as the role played by the positive column and the solid angle of sputtering in dependence of gas pressure and electrode distance.

Wavelength and atomic or ionic origin of the spectral lines do not seem to have any particular correlation with gas pressure or anodic length, although the findings of other researchers[9] reveal that an increase in the former parameter should lead to a more intense emission of ionic lines. A reliable interpretation of this matter will be possible, however, only after a systematic study based on a large (and therefore statistically significant) number of spectral lines of both types.

The possibility of use and general applicability of the hollow cathode tube, object of this study, can be fully exploited only when the operating parameters are selected in such a way that a sufficiently strong, stable and reproducible analytical signal is obtained. The sets of optimal electrode distances, gas pressures and current intensities provided in this investigation can be considered conclusive from this point of view.

Finally, the capabilities of this hollow cathode radiation source for the solution of analytical problems will be tested in the near future.

REFERENCES

1. A. Alimonti, S. Caroli, O. Senofonte, Spectrosc. Lett., 13 (1980), 307.
2. S. Caroli, A. Alimonti, O. Senofonte, Spectrosc. Lett., 13 (1980), (in press).
3. S. Caroli, O. Senofonte, Can. J. Spectrosc., 25 (1980), 73.
4. S. Caroli, P. Delle Femmine, Spectrosc. Lett., 11 (1978), 299.
5. W. Grimm, Spectrochim. Acta, 23 B (1968), 443.
6. M. Dogan, K. Laqua, H. Massmann, Spectrochim. Acta, 26 B (1971), 631.
7. C. G. Bruhn, W. W. Harrison, Anal. Chem., 50 (1978), 16.

8. Cen-Ghi-Thek, Vestn. Leningr. Univ., Ser. Fiz. Khim., 1958, 18.

9. P. P. Ostrumenko, Zh. Prikl. Khim., 5 (1966), 581.

10. A. N. Steinberg, Zh. Prikl. Khim., 2 (1965), 385.

11. G. H. C. Freeman, W. H. King, J. Phys. E, 10 (1977), 894.

12. G. Knerr, J. Maierhofer, A. Reis, Fresenius' Z. Anal. Chem., 299 (1967), 241.

Received: October 3, 1980
Accepted: November 4, 1980