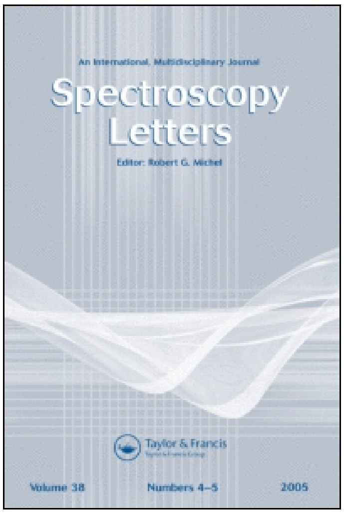

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

Influence of Lithium on the Axial Distribution of Thallium in Unipolar Arc

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To cite this Article Petrakiev, A. and Oreshkov, T.(1979) 'Influence of Lithium on the Axial Distribution of Thallium in Unipolar Arc', Spectroscopy Letters, 12: 3, 243 — 258
To link to this Article: DOI: 10.1080/00387017908069150
URL: http://dx.doi.org/10.1080/00387017908069150

SPECTROSCOPY LETTERS, 12(3), 243-258 (1979)

INFLUENCE OF LITHIUM ON THE AXIAL DISTRIBUTION OF THALLIUM IN UNIPOLAR ARC

Key words: Spectral analysis, axial distribution,
unipolar arc.

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ABSTRACT

An investigation is made of the axial distribution of thallium atoms in a unipolar arc dischrge depending on the interelectrode gap (of between 1 to 6 mm), the current intensity (of between 4 to 16 A), the lithium concentration (of between 0 to 8 per cent), and the position and polarity of the sample. With the aid of a time

extension of the spectrum, the space/time image of these dependences is obtained, as well as of the plasma parameters.

INTRODUCTION

Spectral line intensification in the area close to the electrodes of a d.c. arc was first observed by Mannkopff and Peters[1]. Subsequent investigations by a number of authors [2-6] have contributed to the clarification of the causes of near-electrode effects in the d.c. arc. When a sample is evaporated from the crater of a carbon electrode, depending on the sample's composition, the axial distribution shows an intensification of the spectral lines ih the near-cathode and the near-anode, or central part of the discharge. Similar effects have been observed also in a low-current unipolar discharge[7].

The high-current unipolar arc offers many advantages over the direct-current and the alternating-current arcs. The pauses between the individual arc pulses allow its use also as an intermittent arc.

In the present work an investigation is made of the axial distribution of the thallium atoms in a unipolar arc discharge depending on the place and polarity of the electrode containing the sample, on the distance between the electrodes, the intensity of the current, and the lithium concentration.A good knowledge of these effects is greatly useful for the optimization of the conditions of emission spectral analysis.Lithium is quite often used as a buffer in the spectral analysis.

EXPERIMENTAL

In conditions of a unipolar arc discharge in air medium the axial distribution of thallium was followed up in samples of powdered carbon with or without admixture of the easily ionized macrocomponent Li (Li_2CO_3).Seven series of samples, containing between 0 to 8 per cent Li,were prepared. Thallium concentration in all samples was kept at $5.10^{-3}\%$. Type RW III, 6 mm dia carbon electrodes were utilized, with sample craters of 4 mm dia and 3 mm depth on them. In order to obtain a detailed information about the axial distribution of the intensities of the spectral lines, the spectra were shot with the aid of a one-lens system, under precision focusing of the reduced image of the slit of a ISP-30 quartz spectrograph. With the aid of the flying cassette method the change in the axial distribution was investigated for one and the same discharge of the blackening, the temperature,the electron concentration, and the degree of ionization as a function of the time.For an exposure time t_e= 60 sec the distance between the electrodes was kept constant.

In order that the results thus obtained may be compared with the results of a.c. arc and d.c. arc discharges, exposure time and current intensity were accordingly rectified.The scheme utilized for the realization of a high-current unipolar arc discharge, allowing to operate with up to 20 A,is given in[8]. Type BLAU EXTRAHART WU-3 (ORWO) spectroscopic plates were utilized.

For the determination of the temperature T, the electron concentration n_e, and the degree of ionization α, into all samples tin and magnesium were introduced in the from of oxides.These two elements were selected, because a sufficient amount of reliable experimental and theoretical data[9-11] on the oscillator forces are available.

The determination of the temperature is done by the bilinear method of Ornstein and Brinkman, on the spectral lines Sn I 249.6 nm and Sn I 254.7 nm, with the aid of the formula:

$$T = \frac{5040\,(E_1 - E_2)}{\lg \dfrac{(gA)_1}{(gA)_2} - \lg \dfrac{\lambda_1}{\lambda_2} - \lg \dfrac{I_1}{I_2}} \qquad (1)$$

where: E_1 and E_2 - the excitation potentials of the lines λ_1 and λ_2; $(gA)_1$ and $(gA)_2$- the probabilities of the radiation transitions; and I_1 and I_2 - the intensities of the respective spectral lines.

The determination of the electron concentration is done with the aid of the lines Mg II 279.5 nm and Mg I 285.2 nm, by the formula [10]:

$$\lg n_e = -\lg \frac{I_{279.5}}{I_{285.2}} - 7.72 \frac{5040}{T} + \frac{3}{2} \lg T + 15.684 \qquad (2)$$

The degree of ionization of the thallium atoms is determined in accordance with the formula:

$$\lg \frac{\alpha_{Tl}}{1-\alpha_{Tl}} = \lg \frac{\alpha_{Mg}}{1-\alpha_{Mg}} - \frac{5040}{T}(\bar{V}_{Tl} - \bar{V}_{Mg}) \qquad (3)$$

where: $\bar{V}_{Tl}$ and $\bar{V}_{Mg}$ - rectified potentials of ionization of thallium and magnesium [10].

RESULTS AND DISCUSSION

Thallium spectral line intensity in the individual sectors of the analytical gap gives information on the distribution of thallium atoms. We expected not very pronounced near-electrode effects, but our experimental results have shown such effects to be rather strong.

An investigation of the distribution of the lines in the interelectrode gap depending on the size of the discharge clearance for samples without lithium content, has shown an intensification of their blackening in the area closer to the cathode and a decline near the anode, regardless of the position of the electrode which contains the sample. The introduction of lithium leads to a redistribution of the intensity in some cases. On Fig. 1 the change in the blackening of the spectral line Tl I 276.8 nm is shown depending on the distance of the electrodes for a current intensity of 8 A, and a different position and polarity of the electrode for a sample containing 2 per cent Li.

It is seen that when the sample is an anode and when it is in the lower electrode (Fig.1a), an intensification is observed in the near-anode part of the

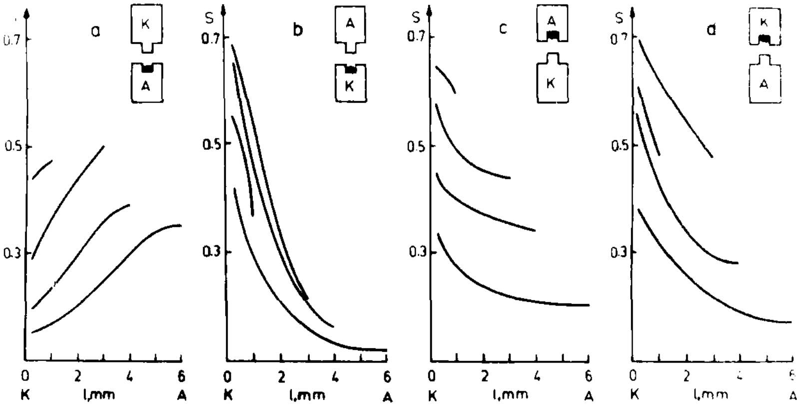

FIG. 1

Axial distribution of the glow of the spectral line of Tl I 276.8 nm, depending on the distance between the electrodes their position and their polarity in persence of 2 per cent Li.

discharge, i.e. close to the electrode with the sample. In all other cases (Fig.1b,c and d) there is a cathode intensification, and with the increase in the interelectrode gap, a more even glow of the spectral lines intervenes, which is probably to be attributed to the joint action of the pulsed axial electric field, and the different intensity and speed of the convection and diffusion processes, which can be coincident or not in respect of direction.

We carried out our further investigation using a fixed discharge gap and a varying current intensity. The interelectrode distribution of the thallium was investigated for samples with or without a 2 per cent lithium admixture, a current intensity of 4, 8, 12 or 16 A, and a 3 mm discharge gap. Some of the results are shown on Fig. 2 and Fig. 3.

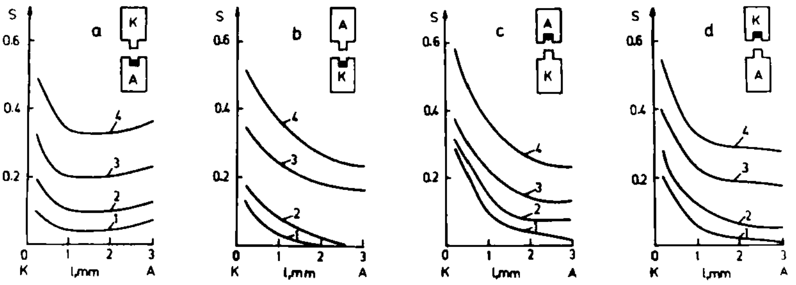

FIG. 2

Axial distribution of the glow of the spectral line of Tl I 276.8 nm, for a current intensity of 4, 8, 12 and 16 **A** (curves 1, 2, 3, 4, respectively) in a sample without Li content.

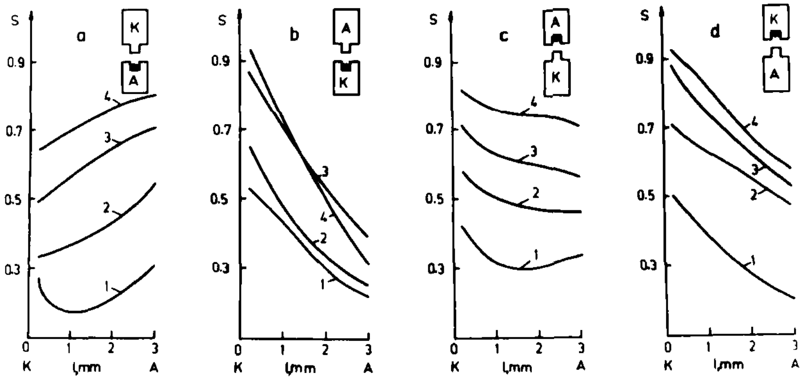

FIG. 3

Axial distribution of the glow of the spectral line Tl I 276.8 nm for a current intensity of 4, 8, 12, and 16 A (curves 1, 2, 3, 4, respectively) in a sample with 2 per cent Li content.

When the sample does not contain lithium, the axial distribution is essentially different, and with the increase in current intensity, the curves shift and become almost parallel to one another near the higher blackening values. The intensification of the line is in the near-cathode area, and when the sample is in the electrode with a positive polarity and which is below (Fig. 2a), a slight intensification is observed also in the near-anode area.

When 2 per cent Li is introduced into the sample (Fig. 3),with the increase in the intensity of the current a redistribution intervenes along the axis of the discharge. When the sample is in the lower electrode and when the latter is an anode (Fig.3 a), the intensification shifts towards the anode, but when it is in the upper electrode (Fig.3 c), the glow if the line is more even in the direction of the length of the discharge. When the polarity of the electrode with the sample in it is negative, the near-electrode effects are more pronounced in the area around the cathode, while in all casses the blackening of the line shows higher values compared with the samples without Li.

It is interesting to retrace the development of the axial distribution, again depending on the concentration of the lithium (Fig. 4).

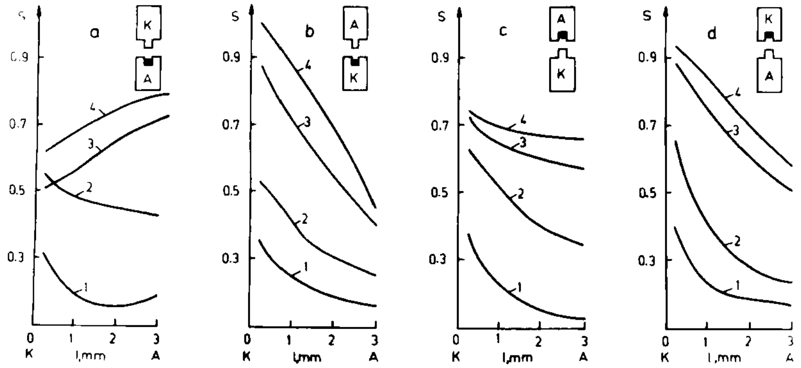

FIG. 4

Axial distribution of the glow of the spectral line Tl I 276.8 nm in a sample without Li content, or with 0.5, 2 or 8 per cent Li content (curves 1, 2, 3, 4, respectively), for a current of 12 A.

An increased lithium concentration leads to the creation of more favourable radiation temperatures of the thallium spectral line, whose ionization potential is relatively low (6.11 eV). Because of this, thallium line intensity increases with an increased lithium concentration.

It is particularly interesting to retrave the space/time picture of the change in the blackening for the various positions and polarities of the electrode which contains the sample. On Fig. 5 four families of

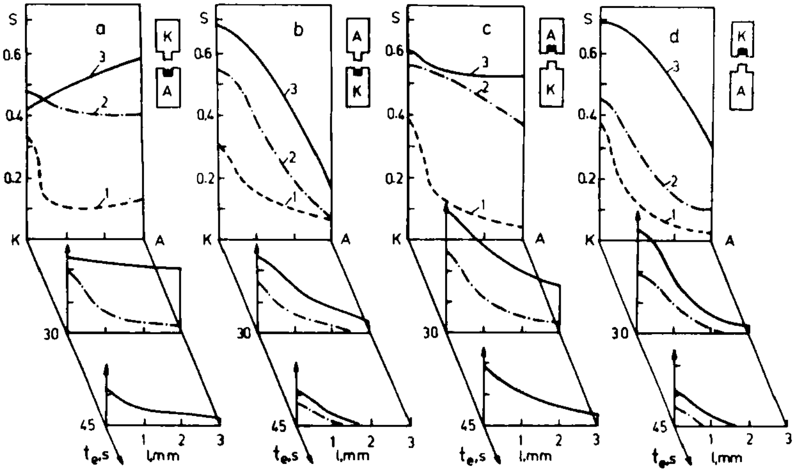

FIG. 5

The space/time axial distribution of the glow of the spectral line Tl I 276.8 nm in a sample without Li content, or with 0.5 or 2 per cent Li content (curves 1, 2, 3, respectively) for a current intensity of 12 A in the unipolar arc.

such curves are represented, which reflect both the case without lithium admixture, and the cases with a 0.5 to 2.0 per cent lithium content. The spectrograms were obtained by rapidly shifting the cassette (every 15 sec precisely), until a complete evaporation,without interrupting the discharge,was obtained.

When the sample is an anode and is below (Fig.5a) a redistribution of the blackening intervenes during the evaporation process. With samples which contain a 2 per cent lithium admixture, the intensification in the initial 15 sec is observed in the near-anode area, while during the subsequent exposures it passes through an intermediary position and shifts to the area around the cathode. In the other cases (Fig. 5 b, c, d) the intensification is in the near cathode area. In samples without any lithium content, the thallium is evaporated during the first 15 sec, and in all cases there is a pronounced near-cathode intensification. Samples with 0.5 per cent lithium content occupy an intermediary position, but the radiation is in the cathode area. In a general way, when the thallium and lithium concentration during the exposure is reduced, the near-cathode intensification in the blackening is more pronouced than the near-anode blackening. The time distribution thus obtained explains the various above-mentioned instances of simultaneous near-anode and near-cathode intensification (Fig. 1-4). In such cases we withness an integration throughout the exposure time, i.e. a summation of all the curves in one. A similar experiment allows to obtain a more detailed information on the kinetics of the processes of evaporation and excitation in the exposures individual moments. As far as we know, such a method has not been until now applied by other authors.

The axial space/time distribution of the blackening of the Tl I 276.8 nm atom spectral line and of the plasma parameters T, n_e and α for one and the same discharge, was simultaneously monitored, as is shown on Fig. 6 and Fig. 7.

The intensification of the blackening in the near-cathode area (Fig. 6) when the substance transfer under the action of the electric field and the convection is of a contrary character, is probably related to the fact that in such a case the field and the plasma parameters exert an intensifying influence on the above effect. When the transfer of substance under the action of the electric field and the convection is in one and the same direction, the axial change in the blackening on the time is difficult to explain (Fig. 7). It is likely that in the first few seconds a predominant role is played by the processes of sample evaporation and

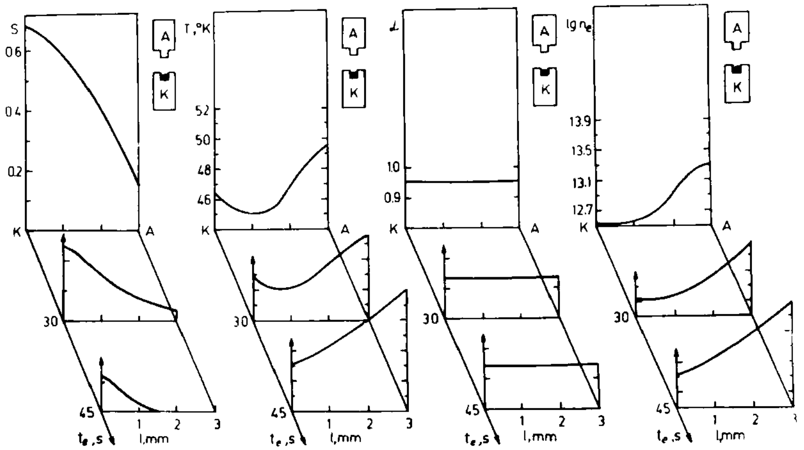

FIG. 6

Space/time axial distribution of:
(a) the blackening of the spectral line TlI 276.8;
(b) the plasma temperature T;
(c) the degree of ionization α ;
(d) the electron concentration n_e,
for an cathode sample, containing 2 per cent Li and an intensity of the unipolar current of 12 A.

the related plasma parameters, while with the decline in the thallium and lithium content during the exposure, the role of the electric field increases, as a result of which the redistribution takes place which observed in the glow of the spectral line of thallium.

CONCLUSION

From the experimental results regarding the axial distribution, the following conclusions can be drawn:

1. The concrete peculiarities of the axial distribution of thallium depend on the composition of the

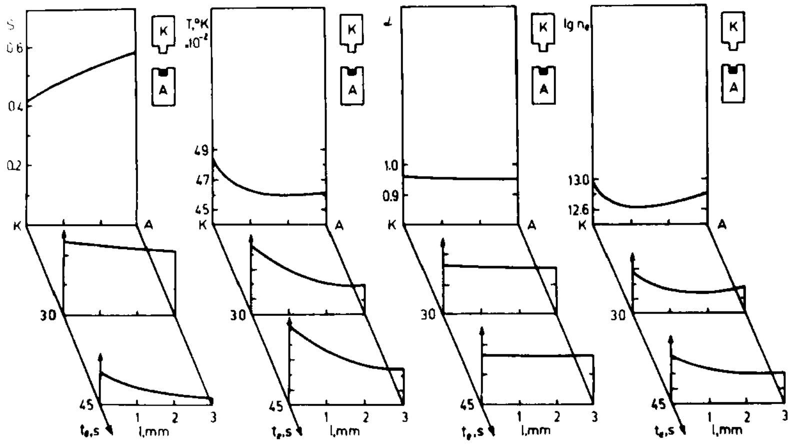

FIG. 7

Space/time axial distribution of:
(a) the blackening of the spectral line TlI 276.8;
(b) the plasma temperature T;
(c) the degree of ionization α ;
(d) the electron concentration n_e,
for an anode sample, containing 2 per cent Li and an intensity of the unipolar current of 12 A.

sample, the speed of its introduction into the discharge, the polarity and position of the electrodes, the intensity of the current, and the size of the discharge gap.

2. A lithium admixture causes changes in the conditions of entry of the sample and excitation of the spectral lines, as a result of which a redistribution of the blackening along the discharge axis intervenes. The introduction of considerable (2-8 per cent) amounts of lithium leads to an intensification in the near-

anode area when the sample is in the anode and is below. Total blackening increases an increased lithium content.

3. The space/time picture of the axial distribution shows that, depending on the lithium concentration and the time of exposure, a redistribution of the thallium atoms intervenes along the discharge axis, allows to obtain a more detailed information on the kinetics of the evaporation and excitation processes at the various moments of the exposure.

These results can serve as a basis for the optimization of the conditions of spectral analysis of powdered samples in a unipolar arc discharge. Besides that, they can be used for the realization of new experiments clarifying the evaporation and transport processes, as well as the processes of excitation in a unipolar discharge with the above parameters.

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Received 2-19-79

Accepted 3-01-79