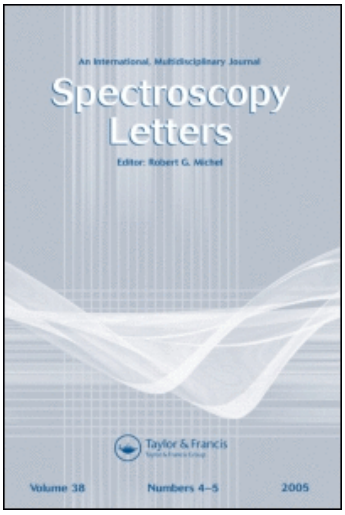

Spectroscopy Letters
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597299

A Power Interruption Technique for Determining the Difference Between Electron and Gas Temperatures in the Argon d.c. Arc Supplied with Aqueous Aerosol

Miroslav M. Kuzmanović[a]; Ankica Antić-Jovanović[a]; Milovan Stoiljković[b]; Mirjana S. Pavlović[b]; Momir Marinković[b]
[a] Faculty of Physical Chemistry, University of Belgrade, Belgrade, Yugoslavia [b] Laboratory of Physical Chemistry, The Vinča Institute, Belgrade, Yugoslavia

Online publication date: 09 August 2003

To cite this Article Kuzmanović, Miroslav M. , Antić-Jovanović, Ankica , Stoiljković, Milovan , Pavlović, Mirjana S. and Marinković, Momir(2003) 'A Power Interruption Technique for Determining the Difference Between Electron and Gas Temperatures in the Argon d.c. Arc Supplied with Aqueous Aerosol', Spectroscopy Letters, 36: 4, 303 — 312
To link to this Article: DOI: 10.1081/SL-120024580
URL: http://dx.doi.org/10.1081/SL-120024580

SPECTROSCOPY LETTERS
Vol. 36, No. 4, pp. 303–312, 2003

A Power Interruption Technique for Determining the Difference Between Electron and Gas Temperatures in the Argon d.c. Arc Supplied with Aqueous Aerosol

Miroslav M. Kuzmanović,[1,*] Ankica Antić-Jovanović,[1] Milovan Stoiljković,[2] Mirjana S. Pavlović,[2] and Momir Marinković[2]

[1]Faculty of Physical Chemistry,
University of Belgrade, Belgrade, Yugoslavia
[2]Laboratory of Physical Chemistry,
The Vinča Institute, Belgrade, Yugoslavia

ABSTRACT

The difference between electron and gas temperatures in a low current U-shaped d.c. arc with aqueous aerosol supply was studied using a power interruption technique. Monitoring of the temporal evolution of recombination continuum after power switch-off revealed that it was necessary to do a correction of the measured values due to a change in electron concentration. It was shown that the plasma studied was a two

*Correspondence: Miroslav M. Kuzmanović, Faculty of Physical Chemistry, University of Belgrade, P.O. Box 137, 11000 Belgrade, Yugoslavia; E-mail: miroslav@ffh.bg.ac.yu.

DOI: 10.1081/SL-120024580
0038-7010 (Print); 1532-2289 (Online)

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

temperature type and that the temperature difference ranges from 1850 K to 600 K for arc currents from 3 to 10.5 A, respectively. A comparison with literature results for pure argon arc plasma shows that aerosol introduction reduces the temperature difference.

Key Words: d.c. Plasma; Aerosol supply; Power interruption technique; Plasma diagnostics.

INTRODUCTION

The argon d.c. arc plasma has important applications in spectrochemical practice where it is used as an excitation source. Especially interesting are the arc plasmas with aqueous aerosol supply. A low-current stabilised U-shaped d.c. arc has a power of detection comparable with inductively coupled plasma devices.[1] The literature is scarce on the state of kinetic equilibrium, the difference between electron and gas temperatures, in aerosol supplied arc plasmas. On the other hand, knowledge about the state of kinetic disequilibria would contribute to a better understanding of the state of thermodynamical equilibrium and the analyte excitation mechanism in the plasma. The aim of the present paper is to study the thermal disequilibrium in an arc plasma supplied with aqueous aerosol, in the low-current regime, where the disequilibrium is maximal, and by applying the power interruption technique.

The power interruption technique[2] is a useful diagnostic method for studying thermal disequilibrium. Some important applications of the technique to several spectrochemical sources are: the argon arc,[3,4] the inductively coupled plasma[5,6] and the microwave plasma.[7] The method is based on comparing the population of excited atomic levels before and after the current switch-off. If the population of the observed level is predominantly controlled by the Saha balance, which is the balance of recombination and ionisation by collision with the electrons, and if there is a difference in plasma temperatures between electrons and heavy particles, power switch-off will produce an increase in excited state population, and a jump in the intensity of the spectral line will occur, Eq. 1:

$$\ln\left(\frac{I^*}{I}\right) = \frac{3}{2}\ln\gamma + (E_{ion} - E_p)\left(\frac{\gamma - 1}{kT_e}\right) \tag{1}$$

where I^* is the spectral line intensity after the switch-off, and I is the intensity before the switch-off, γ is the ratio of electron temperature before and after the switch-off, i.e. the ratio of the temperature of the electrons before the current switch-off and the temperature of heavy particles.[6] The ionisation energy is

denoted by E_{ion} and the excitation energy of the level observed is denoted by E_p. It is presumed that the current interruption does not change the temperature of the gas and the concentration of electrons, thus the only effect being that the temperature of the electrons falls down to the level of the gas temperature. In order for Eq. 1 to be valid it is necessary for the excited level observed to be in partial thermodynamic equilibrium, and that electron concentration does not vary during the time interval between the power switch-off and the appearance of the intensity maximum. If the electron concentration varies then Eq. 1 must be corrected to:[8,9]

$$\ln\left(\frac{I^*}{I}\right) + \ln\left(\frac{n_e^2}{n_e^{*2}}\right) = \frac{3}{2}\ln\gamma + (E_{ion} - E_p)\left(\frac{\gamma - 1}{kT_e}\right) \tag{2}$$

where n_e is the electron concentration before, and n_e^* after, the power switch-off. By measuring the ratio of the intensities before and after the power switch-off, it is possible, with known electron temperature, to calculate the gas temperature. It is assumed that demixing due to diffusion[10,11] is a considerably slower process then excitation and it was therefore disregarded in the present work.

EXPERIMENTAL

The Arc Device

The arc device (Figure 1) used in the present work is described in detail elsewhere.[1,12] Only a brief outline will be given here. The U-shaped arc column (G) is formed between a graphite anode (A) and a carbon cathode (B) in a channel of 16 mm diameter, formed by water-cooled brass segments (C, D, E). The metal segments are electrically insulated by insulation segments (F). A gas that carries aerosol particles was introduced into the cavity of the central segment, tangentially to the arc column, providing additional vortex stabilisation. The observed horizontal section of the arc column was 40 mm long, the axis of which was set parallel to the optical axis of the monochromator. Geometrical features of the plasma make possible ''end-on'' observation and the evaluation of the spatially resolved measurement without the use of Abel inversion. The intensity data were obtained when the arc axis region of the horizontal part of the arc column was imaged on the entrance slit of the monochromator, so the obtained results are related to the arc axis region. The aerosol stream of 2.7 L/min was fed through the central segment and only a small stream of pure argon into the region around the electrodes, in order to reduce their

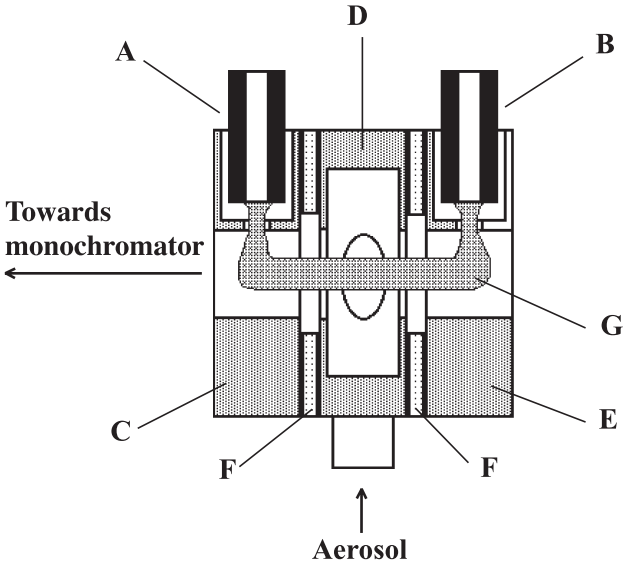

Figure 1. A schematic representation of the U-shaped d.c. arc device. A and B-electrodes, C, D and E-metal segments, F-insulator segments and G-arc column.

consumption. Distilled water was sprayed by a concentric glass nebulizer in conjunction with a double-pass spray chamber.

Monochromator

The 2m monochromator was equipped with a diffraction grating (651 grooves per mm, blazed at 550 nm). Based on preliminary measurements of the line widths, to ensure integral line intensity measurements, the entrance and exit slits were selected to give a larger monochromator spectral band pass than the width of the spectral line used. The horizontal section of the arc column was projected onto an entrance slit in a 1:1 ratio by an achromatic lens.

Power Interruption

Power interruption was realised by an electronic switch based on fast MOSFET transistors connected in parallel with the arc gap. The arc current range was from 3 A to 10.5 A, and the switched-off state can last up to 200 μs. The arc discharge extinguishes at longer durations of the switched-off state. The time constant of the current variation is better than 1 μs.

Detection of Time Resolved Signal

The photomultiplier current was amplified by a factor of 50 with a fast pre-amplifier, and fed into a digital storage oscilloscope. The oscilloscope is PC controlled via a GPIB interface. The oscilloscope traces are averaged 32 times, and subsequently transferred to the PC.

RESULTS AND DISCUSSION

Temporal Responses of Ar Lines

A typical instantaneous response of argon lines is presented in Figure 2, the example being the Ar I 415.86 nm line and an interruption of a 4 A current. The time needed for the spectral line intensity to reach the maximum is around 5 μs. As observable from Figure 2, it was necessary for weaker lines to take into account the evolution of the continuum beside the line, so that the intensity jump after the power switch-off could be accurately determined. Figure 3 illustrates the intensity jump after the power switch-off as a function of excitation energy of the argon line observed, at a current of 6 A. The

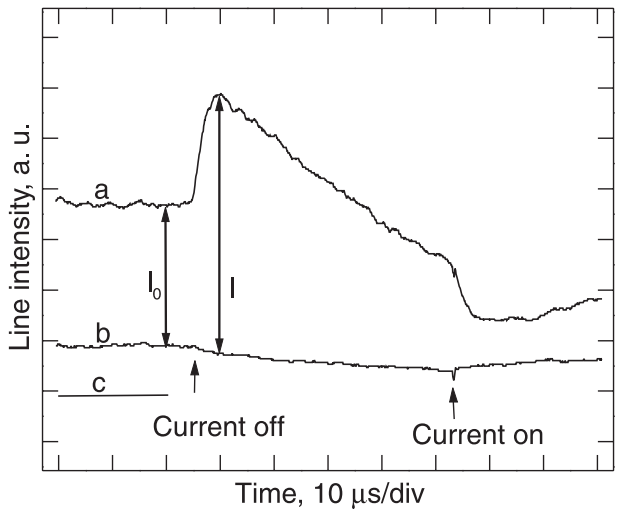

Figure 2. Response of Ar I 415.86 nm line intensity to current interruption, trace a. Trace b represents the evolution of the background at the side of the line, recorded at the same sensitivity of the detector. The level of dark current is denoted by c. The stationary state arc current is 4 A.

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

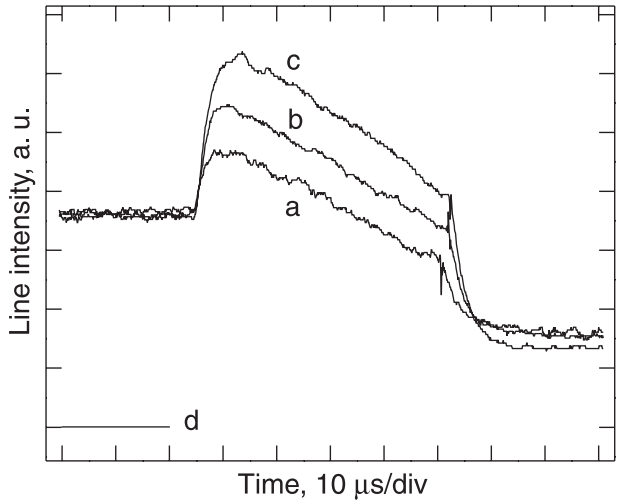

Figure 3. Dependence of the temporal responses of argon spectral lines on the excitation energy. Trace a—E_{exc} = 15.3 eV, Ar I 518.78 nm, trace b—E_{exc} = 14.53 eV, Ar I 415.86 nm and trace c—E_{exc} = 13.33 eV, Ar I 727.29 nm. The level of dark current is denoted by d.

intensities were normalised to the stationary state value. Higher excitation energy lines give smaller intensity jumps and vice versa. A decrease in arc current increases the disequilibrium and the intensity jump, Figure 4.

Temporal Evolution of the Continuum

In order to check whether the electron concentration varies during the rise of the spectral line intensities, we checked the temporal evolution of the recombination continuum at 430 nm, for several currents, Figure 5. The recombination continuum is directly proportional to n_e^2 and inversely proportional to $T_e^{1/2}$. The effect of T_e on the evolution of continuum is only manifested in an interval of a few μs after the power switch-off, when the electron temperature falls to the level of gas temperature. This is why the assessment of the decrease of the square of electron concentration in the risetime of spectral line intensity, was not carried out in that interval, but after it had ended. The rate of electron concentration decrease does not vary significantly in the time interval observed (15 μs). It was found that, after the power interruption, during an interval of 6 μs, the squares of electron concentrations for currents of 8 A and 6 A fall by 8%, whereas for a current

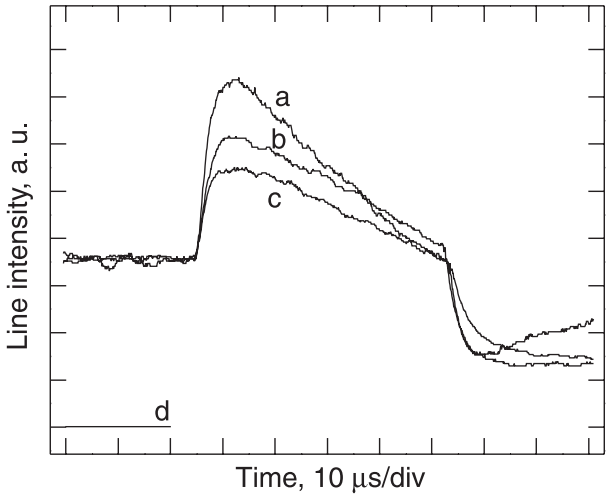

Figure 4. Dependence of the temporal responses of Ar I 727.29 nm line on the arc current intensity. Trace a—4 A, trace b—6 A, and trace c—8 A. The level of dark current is denoted by d.

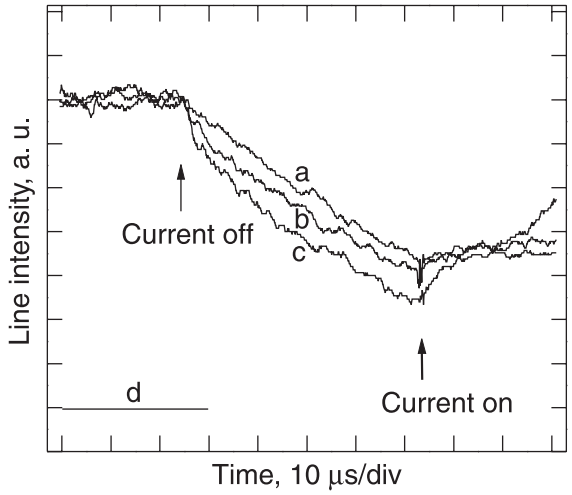

Figure 5. Dependence of temporal evolution of the continuum near 430 nm on the arc current. Trace a—8A, trace b—6A, and trace c—4A. The level of dark current is denoted by d.

of 4 A, it falls by 12%. After the power is switched on, the continuum signals increase again and reach the same level as before interruption after 1 ms.

Temperature Measurement

Eqs. 1 and 2 contain electron temperatures, which are hard to measure, especially in plasma that is not a pure argon plasma. In pure argon arc plasma, at currents below 10 A, the electron temperature could be higher than the excitation temperature by more than 1000 K,[4,13,14] depending on the current. In aqueous aerosol supplied plasma, we expect significantly smaller differences, especially if excitation temperatures of the lowest excited levels of argon are not measured. The excitation temperature was determined from absolute integral emissivities of the argon line at 430.01 nm, taking into account the plasma composition (89.5 mole % of Ar, 3.5 mole % of O, and 7 mole % of H). Absolute emissivities of the argon line were determined with a carbon arc anode as a radiation standard. A value of 0.00394×10^8 s^{-1} was taken as the probability of the transition of this line.

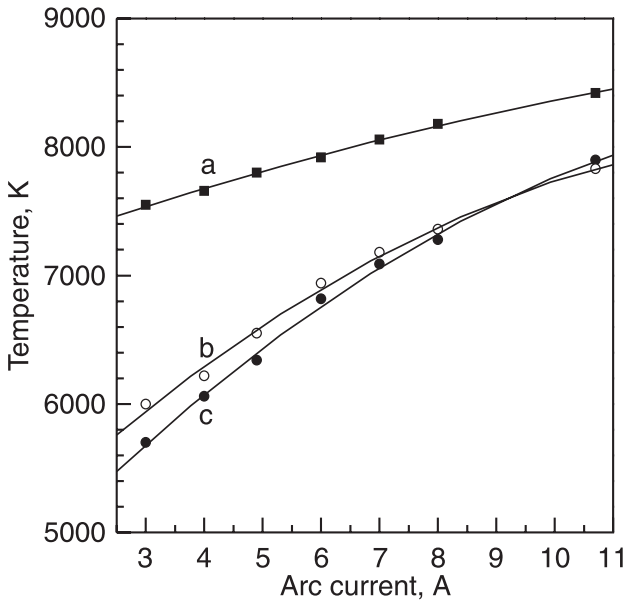

Figure 6. Dependence of excitation and gas temperature on the arc current. Trace a—excitation temperature, trace b—gas temperature evaluated from Ar I 549.59 nm line and trace c—gas temperature evaluated from Ar I 415.86 nm line.

Gas temperatures were calculated using Eq. 2, on the basis of a previously determined intensity jump, excitation temperature and correction for electron concentration decrease. In order for the results to be accurate, it is necessary that the lines, whose intensity jump is used, be in partial local thermodynamical equilibrium. It is therefore necessary to work with high excitation energy lines. On the other hand, for higher arc currents the intensity jump of such lines is small, so the measurement error is higher, but departure from equilibrium is smaller. Having all this in mind we determined gas temperatures for several currents using two spectral lines: Ar I 549.59 nm with an excitation energy of 15.33 eV, and Ar I 415.86 nm with an excitation energy of 14.53 eV, which shows higher intensity jumps.

It is observable from Figure 6 that the difference in electron and gas temperatures ranges between 1850 K (for the arc current of 3 A) to 600 K (for the arc current of 10.5 A). At lower arc currents, the lower excitation energy line shows lower gas temperatures compared to the higher excitation energy line. This probably means that its population departs from the partial local thermodynamic equilibrium more than the population of the higher energy line. Comparing the temperature differences obtained presently with the results for an arc burning in pure argon,[3,4] we see that noticeably smaller differences are obtained. This means that introduction of an aqueous aerosol into an arc plasma decreases the temperature difference, presumably due to more efficient energy transfer from electrons to hydrogen and oxygen atoms as heavy particles.

REFERENCES

1. Kuzmanović, M.M.; Pavlović, M.S.; Marinković, M. Emission spectrometric analysis of fresh waters with U-shaped d.c. arc with aerosol supply. Spectrosc. Lett. **1996**, *29* (2), 205–215.
2. Gurevich, D.B.; Podmoshenskii, I.V. Opt. Spectrosc. **1963**, *15*, 319.
3. Gleizes, A.; Kafrouni, H.; Dang Duc, H.; Maury, C. The difference between the electron temperature and the gas temperature in a stationary arc plasma at atmospheric pressure. J. Phys. D: Appl. Phys. **1982**, *15*, 1031–1045.
4. Nick, K.P.; Richter, J.; Helbig, V. Non-LTE diagnostic of an argon arc plasma. J. Quant. Spectrosc. Radiat. Transfer **1984**, *32*, 1–8.
5. Bydder, E.L.; Miller, G.P. A relaxation method for determining state of equilibrium and temperature ratio Te/Th in an argon ICPT. Spectrochim. Acta **1988**, *43B*, 819–829.
6. Fey, F.H.A.G.; Stoffels, W.W.; van der Mullen, J.A.M.; van der Sijde, B.; Schram, D.C. Instantaneous and delayed responses of line intensities

MARCEL DEKKER, INC.
270 Madison Avenue, New York, New York 10016

to interruption of the RF power in an argon inductively coupled plasma. Spectrochim. Acta **1991**, *46B*, 885–899.
7. Timmermans, E.A.H.; Tomas, I.A.J.; Jonkers, J.; Hartgers, E.; van der Mullen, J.A.M.; Schram, D.C. The influence of molecular gases and analytes on excitation mechanism in atmospheric microwave sustained argon plasma. Fresenius J. Anal. Chem. **1998**, *362*, 440–446.
8. Shindo, H.; Imazu, S.; Inaba, T. A theoretical treatment of the line-intensity jump in a decaying argon-arc plasma. J. Quant. Spectrosc. Radiat. Transfer **1980**, *25*, 77–81.
9. Miller, G.P. A theoretical evaluation of the relaxation method in determining the temperature ratio Te/Th in an ICP. Spectrochim. Acta **1990**, *45B*, 329–331.
10. Murphy, A.B. Demixing due to frictional forces in electric arc. Phys. Rev. Lett. **1994**, *73* (13), 1797–1800.
11. Murphy, A.B. Cataphoresis in electric arcs. J. Phys. D: Appl. Phys. **1998**, *31* (23), 3383–3390.
12. Marinković, M.; Antonijević, V.G. Evaluation of the detection capability of a U-shaped dc arc for spectrometric analysis of solutions. Spectrochim. Acta **1980**, *35B*, 129–138.
13. Eddy, T.L. Electron temperature detetrmination in LTE and non-LTE plasmas. J. Quant. Spectrosc. Radiat. Transfer **1985**, *33*, 197–211.
14. Benilov, M.S. Modeling of a non-equilibrium cylindrical column of a low-current arc discharge. IEEE Trans. Plasma Sci. **1999**, *27* (5), 1458.

Received September 30, 2002
Accepted May 21, 2003