Spatial Distribution of Excited Argon Species in an Inductively Coupled Plasma

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Spatial(radial and height) distributions of excited argon species are measured for an inductively coupled plasma under five operating conditions: 1) no carrier gas, 2) carrier gas without aerosol, 3) carrier gas with desolvated aerosol, 4) carrier gas with aerosol, 5) carrier gas with aerosol and excess lithium. A complete RF power mapping of argon excited states is obtained. The excited states of argon for a typical analytical torch rapidly diffuse towards the center in the higher region of the plasma. The presence of excess lithium makes no significant change in the excited states of argon. The increase in the RF power increases the intensity of argon excited states uniformly across the radial coordinate.

Introduction

The inductively coupled plasma (ICP) has become widely used as an excitation source for analytical atomic emission spectrometry. The advantages often cited are its apparent high sensitivity and relative freedom from interelement interferences. However, recent works have demonstrated that the interelement effect from easily ionizable elements (EIE) not only exists in the ICP, but also analyte emission intensity is a complex function of the operating parameters.[1-3]

To optimize the operating conditions of the ICP and to characterize the interference effect from EIE, the excitation mechanisms of the analyte were studied by many workers, and the brief description of the existing mechanisms related with electron number density and argon excited states were recently reviewed by DeGalan[4] and Vlcek.[5-6] In order to support the proposed analyte excitation mechanisms, quantitative data on the spatial distributions of plasma electron and argon excited states including matastable states should be fully characterized. Although there have been numerous papers in the literature that have treated electron number densities[7-10] in the ICP, only scattered data of excited argon species[11-13] were presented.

In the present work, using a commercial torch commonly used for analytical application, the radial distribution of two series of argon exited states at three plasma heights and three power levels under five operating conditions are measured in order for the analysts to be able to deduce the distribution of excited states argon when the operating conditions are varied. The five operating conditions are 1) no carrier gas, 2) carrier gas without aerosol, 3) carrier gas with partially desolvated aerosol, 4) carrier gas with aerosol (normal operating condition), and 5) carrier gas with aerosol and excess lithium. The observations were made 4-16mm above the induction coil to study the intial phase of analyte-exited argon species interactions. Two series of argon lines chosen are 4s←5p and 4p←nd. The lateral intensities are measured and inverted into the radial intensities by the Abel inversion method.[14-15]

Experimental

The Plasma system used was the Plasma Therm ICP-2500 (Plasma Therm Inc., Kressen, USA). The RF generator is of the crystal controlled type operating at the frequency of 27 MHz. The cross flow nebulizer, Scott type spray chamber and torch were supplied by the same manufacturer. The detector system centered around a Hilger-Engis model 1000 Czerny-Tuner grating spectrometer. The grating size is 102 mm by 102 mm with 1200 lines/mm. The one meter spectrometer has a dispersion of 0.83 nm/mm.

The plasma torch lies horizontal with respect to the vertical entrance slit of monochromator and the vertical movement of mask with a small opening allows the lateral scanning of the plasma at a given height. The height of the plasma being observed is changed by sliding the torch horizontally. A two fold image reduction lens was placed before the entrance slit, so that the mask opening of 0.1 mm and vertical derive in the steps of 0.1 mm provide spatial resolution of 0.2 mm at the center of plasma. With the above arrangement the detector response was observed to be fairly constant for lateral distance of 0.6 mm from lateral center.

For normal operation of ICP (carrier gas with aerosol), the amount of aerosol delivered to the torch was 0.045 mL/min. For desolvation studies, the aerosol of carrier gas was passed through the heater and condenser combination to trap the water, and it had been used by Dickinson[16] on an ultrasonic neulizer system. About 88% of water was removed[17] by the arrangement. The concentration of lithium added to the analyte solution was 1000 ppm. The experimental operating conditions chosen for this study was 15 L/min coolant flow, 0.9 L/min carrier flow and zero auxiliary flow. The RF power was maintained at 1.25 kW unless otherwise specified.

Results and Discussion

In order to characterize the excited states of argon in the ICP, two series of emission lines, 4s←5p and 4p←nd were chosen. The measured lateral argon intensity, $I(x)$ was inverted to form a radial profile, $I(r)$ by using the Abel inversion method described previously.[14] The observed lateral intensity data were fitted to a symmetric function (Eq. 1) by the least squares, and the function is then numerically inverted into a radial function by the Abel inversion method.

$$I(r) = [C_2 + C_3(x - C_1)^2 + C_4(x - C_1)^4] \exp[-C_5(x - C_1)^2] \quad (1)$$

where x is the lateral coordinate from radial center, and C_1-C_5

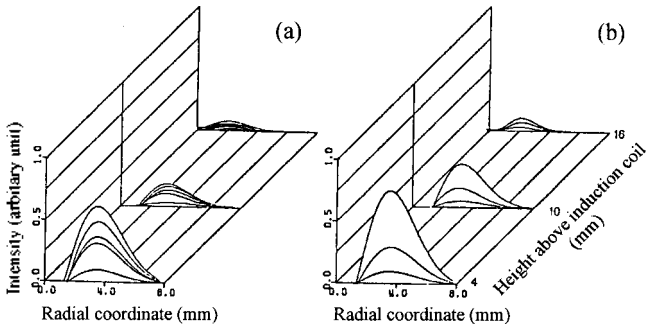

Figure 1. Radial argon emission profiles of the normal operating conditions at three plasma heights. (a) 4s←5p lines at 1.25 kW (from top 425.9, 433.3, 430.0, 426.6 and 425.1 nm), (b) 4p←nd lines at 1.25 kW (from top 549.6, 522.1 and 506.0 nm).

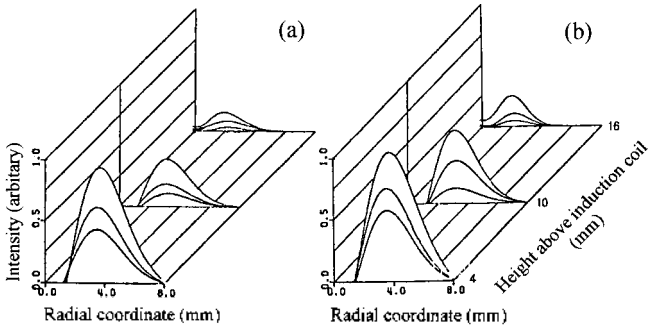

Figure 2. Radial argon emission profiles of three power levels at tree plasma heights. (a) 425.9 nm (from top 1.5 1.25 and 1.0 kW), (b) 549.6 nm (from top 1.5, 1.25 and 1.0 kW).

are the coefficients which are adjusted for best curve fitting. The most of the measured lateral intensities are quite symmetric (less than 5% asymmerty) and the use of symmetric function of $(x\text{-}c_1)$ has advantages over the polynomial fitting of the one-sided profile.[14]

Radially inverted profiles of the two series 4s←5p band (425.1, 425.9, 426.6, 430.0 and 433.3 nm) and 4p←nd band (506.0, 522.1 and 549.6 nm) for normal operating conditions at three plasma heights (4, 10 and 16 mm above induction coil) are shown in Figure 1(a) and Figure 1(b). In the present studies, the center of the observation height for quantitative analysis is roughly 15 mm above the induction coil. At the lower region of the plasma heights, significant background emissions in the lateral intensity were observed and they were corrected before Abel inversion. The estimated uncertainties are minimal (less than 5%) at the radial maxima and slowly increase as the radial intensities decrease towards radial center.[14]

The spatial emission intensity profiles of both 4s←5p and 4p←nd series are essentially alike. The spatial maps of argon emission intensities show that they resemble a hollow cylinder at the lower region of the plasma (4 mm and 10 mm) and excited argons diffuse towards the center in the higher region of the plasma (16 mm). At the low region of the plasma the excited argons are not observed in the central channel where analyte passes. In the present studies, the radius of the aerosol injection tube of the torch is 0.75 mm and the radius of central channel of the analyte pass is roughly less than 2.0 mm. It indicates that the excited argon species do not play a role for the excitation of analytes at the low region of the plasma. Figure 1(a) also shows that the 425.1 nm line which connects to metastable state (11.55 eV) of argon does not show any significant differences from the other emission lines. Therefore, the ionization of analyte by Penning ionization process[18] which enhances the emission intensities of analyte ionic lines by the collisions with metastable state argon seems to be not important.

Figure 2(a) and Figure 2(b) show the radial intensities of 425.9 and 549.6 nm at three power levels (1.0, 1.25 and 1.5 kW). The increases in the power level increase the argon emission intensities uniformly at all heights. Excited argons are not observed in the central channel at the lower region of the plasma (4 mm and 10 mm) even at 1.5 kW. They are gradually increased at 15 mm above induction coil at 1.25 and 1.5 kW power levels.

The radial emission profiles of the 425.9 nm line at 1.25

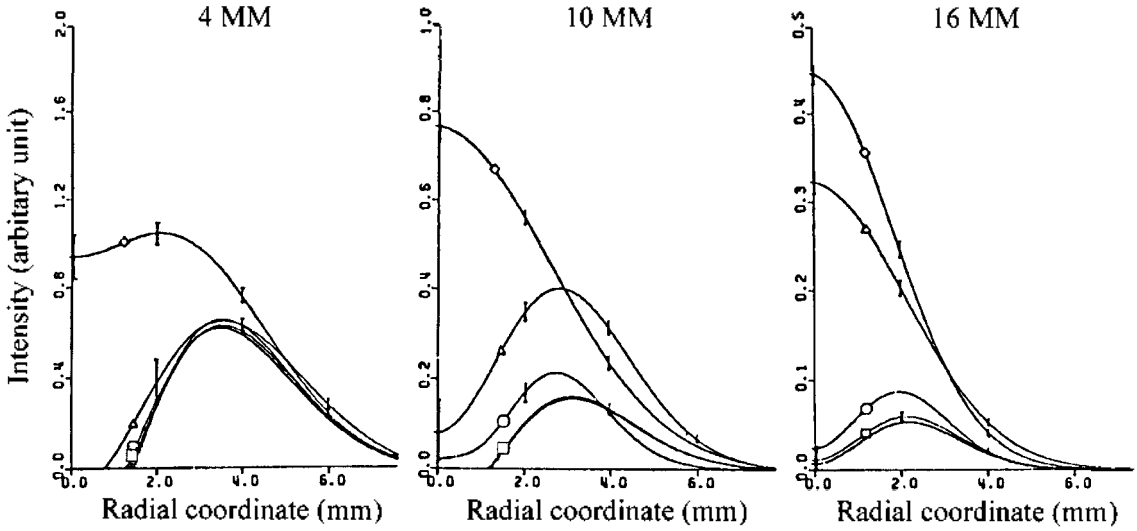

Figure 3. 425.9 nm argon emission profiles for five operational conditions at three plasma heights. no carrier gas (◇), carrier gas without aerosol (△), carrier gas with desolvated aerosol (○), carrier gas with aerosol (□), and carrier gas with aerosol and 1000 ppm Li (unmarked).

kW for the five plasma operation conditions including the presence of excess lithium are shown in Figure 3. Argon emission profiles show fairly smooth distribution when the carrier gas is turned off. The strong argon emission intensities are observed at the radial center at all heights. However, even only with a carrier gas there appears a sharp depression at the radial center at 4 mm above the induction coil, forming a toroidal plasma. As one observes the emission structure along the plasma heights at radial center, emission intensities are slowly recovered at 10 mm above the induction coil. The core depression is steepest at 4 mm, and is recovered slowly to have the emission maxima at the radial center at 16 mm. The presence of aerosol further suppresses the emission intensities at the radial center and the maximum intensity was observed at about 2 mm off-axis from radial center at 16mm above the induction coil.

Figure 3 also shows that emission intensities of the carrier gas with aerosol (normal operating condition) and carrier gas with aerosol and excess lithium (EIE) do not show significant differences. The excess lithium (1000 ppm) only slightly suppressed the emission intensities at 16 mm above the induction coil, but the differences are within the error ranges. Recently, Hieftje *et al.*[3] reported radial intensities of CaI (422.7 nm) and CaII (393.3 nm) when the lithium concentrations were varied from 0 to 1000 ppm. Both the atomic and ionic intensities of calcium showed the same trends of interference effects with EIE. At low regions of plasma, maximum intensities were observed at about 1.5 mm off-axis from center, and they showed enhanced interference effect. The interference effects were gradually increased as the concentrations of lithium were increased. At higher regions, maximum intensities were observed at the radial center and added lithium suppressed the intensity. No observable changes in argon emission intensities with and without lithium in Figure 3 suggest that excited argons do not significantly influence the interelement effects by EIE in the ICP.

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