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EFFECTS OF CENTRAL ARGON FLOW RATE ON CHARACTERISTICS
OF INDUCTIVELY COUPLED PLASMA

KEY WORDS: emission, inductively coupled plasma, central
argon flow rate, excitation temperature,
interelement effect

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Introduction

In an inductively coupled plasma [ICP], the flow rate of carrier gas is one of the most significant parameters, while those of coolant and plasma less affect the analytical sensitivity. A sample solution nebulized and transported with the carrier gas passes through the hole, which possesses a lower temperature than the surrounding plasma doughnut^{1,2}. The increase of the nebulizing gas flow rate provides more sample introduction amounts, but the residence time of analyte

atoms in the plasma becomes short, which causes the decrease of the analytical sensitivity.

In this paper, the effects of the central (carrier) argon flow rate on the excitation temperature, emission intensity and interelement effect are investigated under the condition of constant introduction amounts of water mists and analyte atoms.

EXPERIMENTAL

An ICP source (Model ICAP-1 from Nippon Jarrell-Ash Co.) was used under the conditions of 1.4 kW RF power and 14.0 l min^{-1} and 1.0 l min^{-1} flow rates as coolant and plasma argon gases. Fig. 1 shows a cross-sectional view of the cross-flow nebulizer and the nebulization

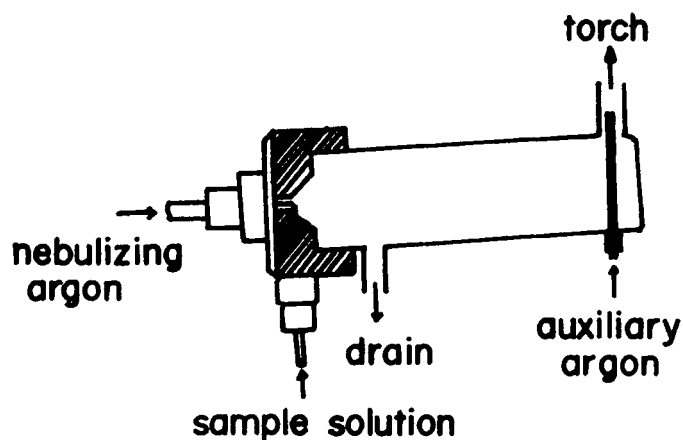


Fig. 1 Cross-sectional view of nebulizer and nebulization chamber

chamber. An auxiliary central argon inlet was set in order to observe the effect of the central argon, which passes through the plasma, without the influence of the sample nebulization. Sample aspirating rate was 0.43 ml min^{-1} at the nebulizing argon flow rate of 0.51 l min^{-1} .

A monochromator (Model JE-50 from Nippon Jarrell-Ash Co.) was an Ebert-type (focal length 0.5 m) with a grating ($1200 \text{ grooves mm}^{-1}$) blazed at 300 nm (linear dispersion 1.6 nm mm^{-1}). The slit widths of entrance and exit were both $10 \text{ }\mu\text{m}$. Observation height was 15 mm above the induction coil. Abel inversion was not carried out.

Iron $500 \text{ }\mu\text{g ml}^{-1}$ solution was used for the measurements of excitation temperature, and calcium $30 \text{ }\mu\text{g ml}^{-1}$ and zinc $100 \text{ }\mu\text{g ml}^{-1}$ solutions were of relative emission intensities of each atomic and ionic lines. The latter two solutions with and without the presence of 10 mg ml^{-1} of potassium were also used for the investigation of interelement effects.

RESULTS AND DISCUSSION

Iron excitation temperature

The excitation temperature is the most important property of plasma as an excitation source, and many measurements have been carried out to characterize the

ICP³⁻⁶. It is suitable to obtain the temperature from the analyte species for the discussions of the analytical sensitivity and interelement effect⁴⁻⁶. In this study, three line slope calculation^{5,6} was carried out using iron atomic lines, which are summarized in Table 1 together with excitation energies, statistical weights and relative transition probabilities.

Fig. 2 shows the effect of the central argon flow rate on the excitation temperature at 15.0 mm height above the induction coil. In this experiment, auxiliary argon gas was fed instead of the sample nebulizing gas to prevent the influence of water mists introduced to the plasma. The temperature remarkably decreases, when the flow rate is increased. Kalnicky et al⁶ reported that 5650 °K and 4200 °K of the excitation temperatures were obtained at carrier gas flow rates of 1.0 l min⁻¹ and 1.3 l min⁻¹, respectively, under the conditions of

Table 1
Wavelengths and Optical Data for Fe Lines

Wavelength (nm)	Excitation energy (cm ⁻¹)	g-value	Relative transition probability [*]
382.043	33096	9	4.02
382.444	26140	7	0.179
382.588	33507	7	3.74

* Relative transition probabilities normalized to the Fe I 371.994 nm line by Banfield and Huber [7].

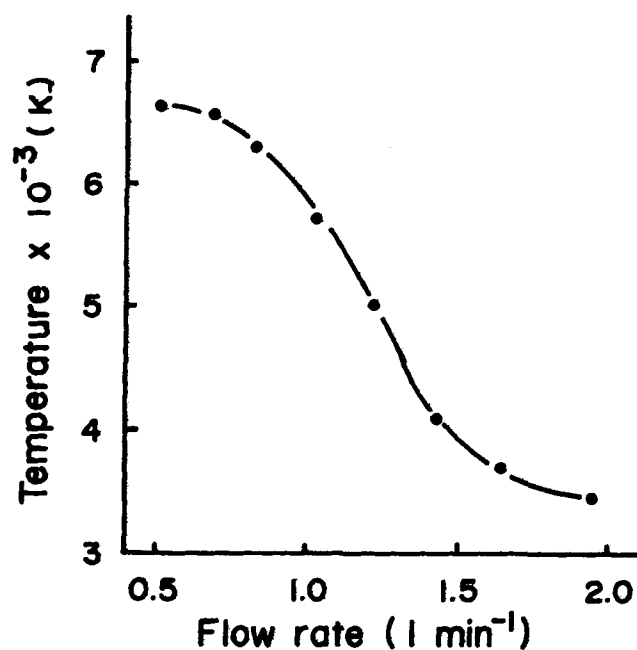


Fig. 2 Effect of the central argon flow rate on the excitation temperature

1.0 kW RF power and 15 mm observation height. Taking account of the difference in the power, the found values are reasonable. About 3000 °K decrease indicates that some changes might occur in the plasma characteristics.

Relative emission intensities of calcium and zinc

The effect of the flow rate on relative emission intensities at Ca I 422.7 nm, Ca II 393.3 nm, Zn I 213.9 nm and Zn II 206.2 nm are shown in Fig. 3. The amount of calcium and zinc introduced to the plasma were kept

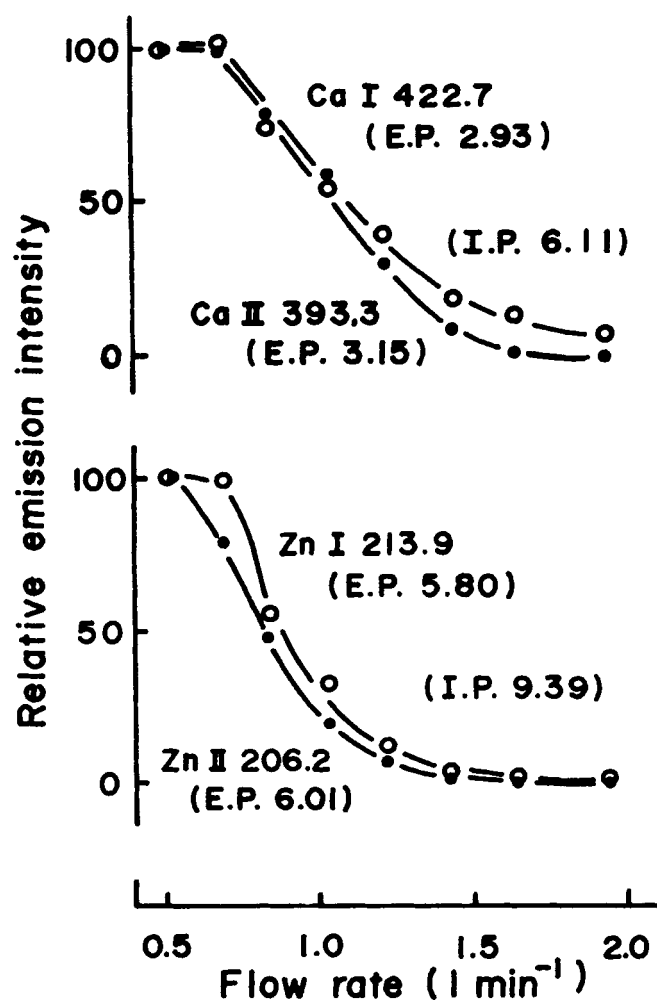


Fig. 3 Effects of the central argon flow rate on the emission intensities of atomic and ionic lines

E.P. : excitation potential (eV)

I.P. : ionization potential (eV)

constant when the auxiliary argon flow rate was increased up to 1.43 l min^{-1} . Emission intensities of every lines were decreased with the increase of the central argon flow rate, which seems to be due to the decrease of energy transfer from hot argon to the analyte. The lowering of the intensity slightly depends on the kinds of lines (atomic and ionic) and the values of ionization and excitation potentials. For example, the emission intensity at Zn II 206.2 nm decreases at the flow rate of 0.7 l min^{-1} , while those of other lines are almost constant. Further, the intensity at Ca I 422.7 nm tends to less decrease than the others. These phenomena show that the ionization equilibrium might be a little shifted to the atomic state when the flow rate is increased.

Interelement effect with the presence of potassium

Fig. 4 also indicates the effects on the ratios of emission intensities of the lines of interest with and without 10 mg ml^{-1} potassium. The ratios for every lines are almost kept constant up to 0.93 l min^{-1} of central argon flow rate, and its value of 0.87 means the decrease of introduction amounts of calcium or zinc caused by the presence of large amounts of potassium. All the line intensities are enhanced in the presence of potassium above 1.0 l min^{-1} of the central flow rate. Kalnicky et al⁶ also reported that the intensity at Fe I 382.043 nm was fairly enhanced in the presence of 6.9 mg ml^{-1} of sodium at the carrier gas flow rate of

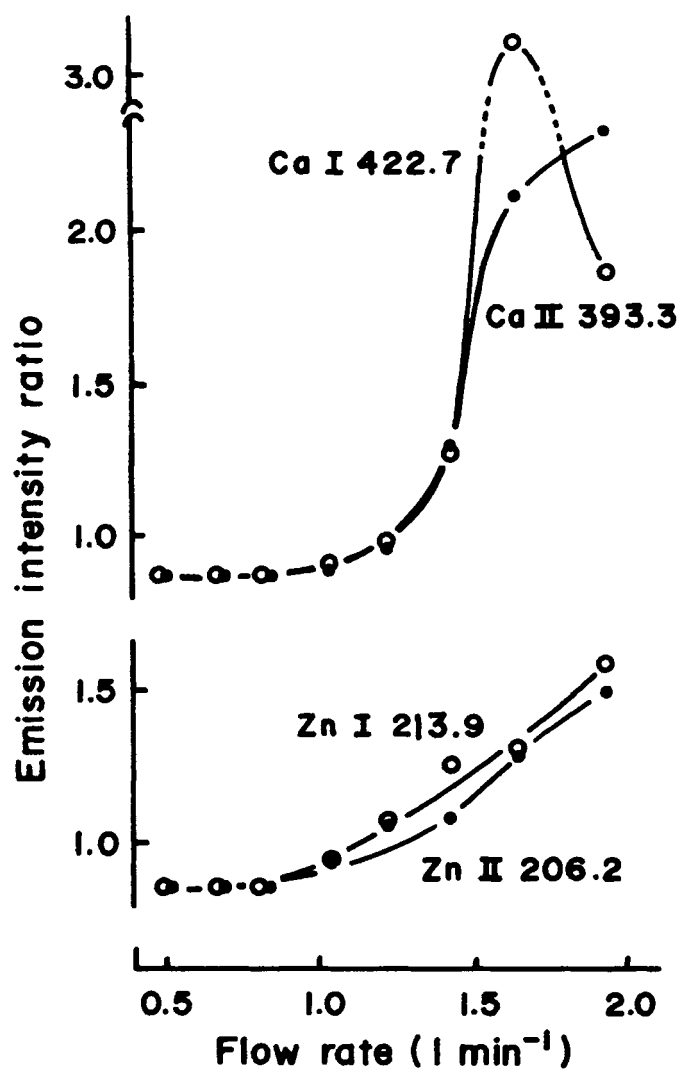


Fig. 4 Effects of the central argon flow rate on the ratios of the emission intensities observed with and without the presence of potassium

1.3 l min⁻¹. These enhancement effect are not due to the ionization interference, because ionic lines are enhanced. Both the atomic and the ionic lines of calcium were more enhanced than those of zinc. A maximum intensity ratio is observed at 1.63 l min⁻¹ flow rate in the case of calcium atomic line, for which the reasons are not elucidated at present. These enhancements in the presence of potassium under high flow rate is similar to the interelement effect observed in capacitively coupled microwave plasma [CMP] operated at 2450 MHz.

Conclusion and further discussion

Less than 1.0 l min⁻¹ carrier gas flow rate is recommended for practical analyses, where high analytical sensitivities can be obtained without the interelement effect in the presence of potassium.

Recently, the ICP has not been considered to be a local thermodynamic equilibrium [LTE] plasma by various authors. Boumans and de Boer suggested that departures from LTE resulted from the injection of carrier gas⁸. Investigations using this auxiliary argon flow method seem to be useful for the discussions of plasma diagnostics, which are now in progress.

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