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Analytical Application of Glow Discharge Atomic Absorption Spectroscopy (GD-AAS) Using Three Types of Jet Configurations Under Power Mode

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Abstract: Three anode configurations of six-jet, cone-jet and cylindrical-jet are tested for their analytical performance under power mode operation. The effect of pressure, power and gas flow rate on atomic absorption signals have been studied. The increase of atomic absorption signal of sample element is observed at a fixed pressure in all configurations as the gas flow rate increase up to 300-600 sccm, and as the power dissipated in the glow discharge cell increase. The lower the pressure is in the glow discharge cell at a fixed discharge power and argon flow rate, the greater the absorbance of sample element is. The optimum conditions are taken from these data and a calibration curve of Cu in low-alloy steel sample is obtained. In this calibration curve, six-jet configuration shows the best analytical results varies as the sample element.

Keywords: Atomic absorption, Glow discharge, Power, Pressure, Argon gas flow rate, Three types of jet configuration.

1. Introduction

The glow discharge spectroscopy has been widely studied because the use of gas jet in sputtering makes this direct sampling method promising in practical application for atomic absorption spectroscopy. Gough *et al.* [1] reported that the gas flow improved the absorption signal by increasing the transport of the sputtered atom in to the observation zone. Bernard [2] discovered that gas jets that strike the sputtering surface significantly increase the sampling rate as well as the absorption signal in a sputtering chamber. These ideas have been investigated and further developed. Recently they are applied in the commercial Atomsource (Analyte Corp., Medford, OR), and the Atomsource has stimulated wide applications of gas-jet-enhanced sputtering vice versa. Ohls [3] used the Atomsource for the analysis of metals and alloys by atomic absorption spectroscopy. Kim and Piepmeier [4] investigated the effects of gas flow rate on sputtering characteristics by measuring atomic absorption, emission, and sample loss rate. They reported an increase in the sample loss rate and atomic absorption signal with increase in gas flow rate. Fang and Marcus [5] studied the role of discharge voltage, current, and pressure in a planar, diode glow discharge. They revealed that the sample loss rate was dependent on the squared current and was proportional to the discharge power. Hutton *et al.* [6] investigated the effect of argon gas flow rate upon the atomic emission and atomic absorption signals at constant pressure with a constant power or voltage. Kim *et al.* [7] applied three types of jet configuration in the glow discharge spectroscopy system, because a six-jet configuration may not be appropriate to, for example, in-depth analysis for its typical pattern on sample surface.

2. Experimental

2.1. Equipment

The glow discharge atomic absorption spectroscopy system and three anode configurations which were used in this work had been described by Kim *et al.* [7] although some modification had been made for the absorption measurement and power supply. The modified glow discharge atomizer was installed in a commercial AAS (Varian Mode Spectra AA - 30, Techtron Pty, Victoria, Australia) in the place of a flame burner. Hamamatsu hollow cathode lamps were used as light sources. The power supply (PNCs 1500-400 ump, Heinzinger, Germany) used for the sputtering studied was capable of independent regulation of current , voltage, or power. The sputtering gas was passed through a mass flow controller (MKS, Andover, MA) which controlled the operating flow rate of argon between 0 to 2000 sccm. The pressure inside the sputtering cell was monitored on the outlet side using a Pirani gauge (Blazers TPG 300, Furstentum, Liechtenstein). The pressure was controlled by throttling the vacuum line using a Whitey needle valve installed between the cell and vacuum pump. A two stage vacuum pump of 450 L/min (Varian SD450, Lexington, MA) provided the vacuum inside of the discharge cell.

2.2. Experimental

The voltage-current characteristic curves of jet configurations with argon gas flow rate were obtained at 4.0 mbar and 6.0 mbar when KSS 101 low-alloy steel sample was sputtered at 80 W. The curves which showed the effect of discharge power, pressure, and argon gas flow rate on absorption signals with jet configurations were obtained by measuring the absorbance of copper which was introduced to the optical path by sputtering blocks of KSS 101. The calibration curves of Cu was obtained by sputtering blocks of KSS 101-106 at 4.0 mbar, 80 W, and 400 sccm. This discharge parameters were chosen from the experimental results.

3. Results and Discussion

3.1. Dependence of the discharge voltage and current.

The changes of discharge voltage and current with various jet configurations at 80 W are shown in *Fig. 1* as the function of argon gas flow rate. At a fixed pressure (4.0 mbar or 6.0 mbar), the discharge voltage decreases as the argon gas flow rate increases in all jet configurations, and the discharge current increases because of a constant power. As the pressure changes from 4.0 mbar to 6.0 mbar, the discharge voltage decreases in all jet configurations. Kim and Piepmeier [4] have considered the reason for this decrease in discharge voltage with increasing argon gas flow rate as a local high pressure which a gas jet provide between the cathode and anode. As is evident in *Fig. 1*, higher pressure requires lower discharge voltage.

In the case of cylindrical-jet configuration, the discharge voltage decreases from 720 V to 597 V at 4.0 mbar, and from 587 V to 505 V at 6.0 mbar as argon gas flow rate increases. The difference of the voltage between 100 sccm and 1000 sccm are 123 V at 4.0 mbar and 82 V at 6.0 mbar. From these results, it is apparent that argon gas flow rate which causes a local pressure more efficiently influences on the discharge voltage in lower pressure. Cylindrical-jet configuration shows the highest voltage and the lowest current in maintaining glow discharge in all pressures and argon gas flow rates. From these results, it is thought that independently of the effect of argon gas flow rate on the discharge voltage, there is another factor which determines the voltage, and that the gas flow pattern which is dependent on the geometry of jet configuration may play as important role.

The voltage of cone-jet configuration decreases from 664 V to 584 V at 4.0 mbar and from 544 V and 497 V at 6.0 mbar as argon gas flow rate increases. The differences of the voltage between 100 sccm and 1000 sccm at 4.0 mbar and 6.0 mbar are 80 V and 47 V, respectively. When the values of the difference are compared with those of cylindrical-jet configuration, cone-jet configuration show less dependence of the discharge voltage on argon gas flow rate.

When the pressure in the discharge cell is 4.0 mbar, from 100 sccm to 300 sccm, cone-jet configuration has higher voltage and lower current than six-jet configuration, but there is a sharp drop in six-jet configuration. The discharge voltage of six-jet configuration is lower than that of con-jet configuration from 400 sccm. As the pressure changes to 6.0 mbar, the argon gas flow rate at which the

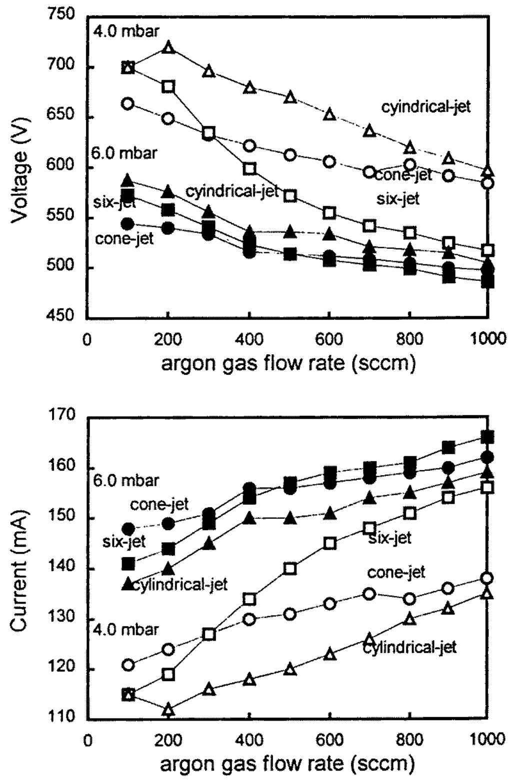

Fig. 1. Dependence of discharge voltage and current of three types of jet configurations on argon gas flow rate at a fixed power (80 W).

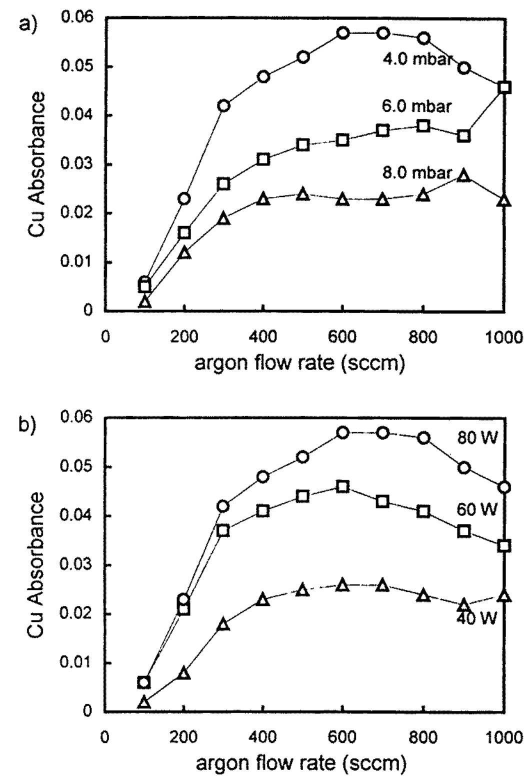

Fig. 2. The change in the absorbance of copper for cone-jet configuration a) at a constant power (80 W) and b) at a constant pressure (4.0 mbar).

voltages of cone-jet and six-jet have the same value is changed to 500 sccm. As discussed before, argon gas flow rate influences more efficiently on the discharge voltage in lower pressure. Therefore, at 4.0 mbar, the point which shows same value of the discharge voltage of six-jet and cone-jet appears earlier.

The range of discharge voltage of six-jet configuration covers from 700 V to 517 V at 4.0 mbar, and from 573 V to 486 V at 6.0 mbar. The differences are 183 V at 4.0 mbar and 87 V at 6.0 mbar. These values more obviously support the conclusion of the dependence of the discharge voltage on argon gas flow rate and the pressure, and the difference of the geometry of jet configuration is thought to determine the degree of this dependence.

3.2. Effect of power, pressure, and argon gas flow rate on the absorption signal.

The change in the absorbance of copper at various pressures and powers with variation in argon gas flow rate for the cone-jet configuration are shown in *Fig. 2*.

In *Fig. 2*a, the absorbance of copper is plotted as a function of argon gas flow rate in various pressures when the discharge power is 80W. In the case of the pressure for 4.0 mbar, the absorbance of copper steeply increase with argon gas flow rate up to 300 sccm. After this point, the increasing rate is reduced and the maximum absorbance appears at 600 sccm, then the absorption signal decrease. At 6.0 mbar and 8.0 mbar, the absorption signal shows a plateau from 400 sccm, and it does not decrease with increasing argon gas flow rate. For a given power (or current) and pressure, an increase of argon gas flow means an increase of transport efficiency and a decrease of re-deposition of sputtered atom. But because of a constant pressure, as argon gas flow rate increase the residence time of sputtered atom in analysis volume decrease [8]. Therefore there may be an optimum argon gas flow rate that will provide the best analytical signal. In cone-jet configuration, the optimum argon gas flow rate is 500-600 sccm and is

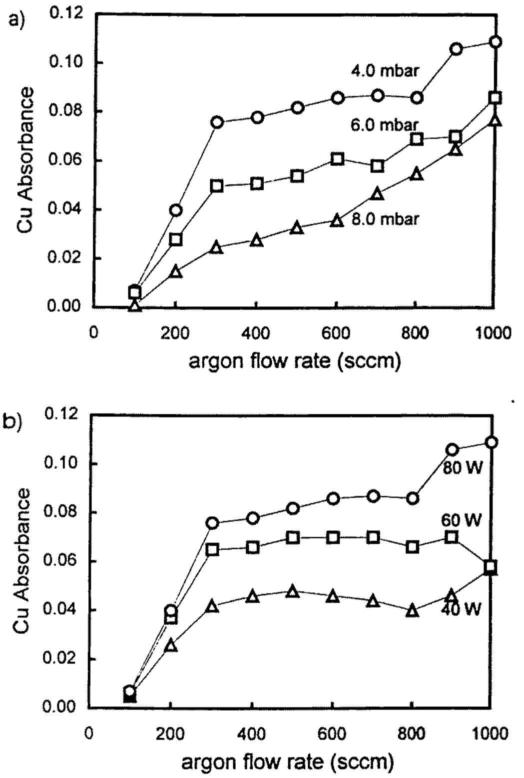

Fig. 3. The change in the absorbance of copper for six-jet configuration a) at a constant power (80 W) and b) at a constant pressure (4.0 mbar).

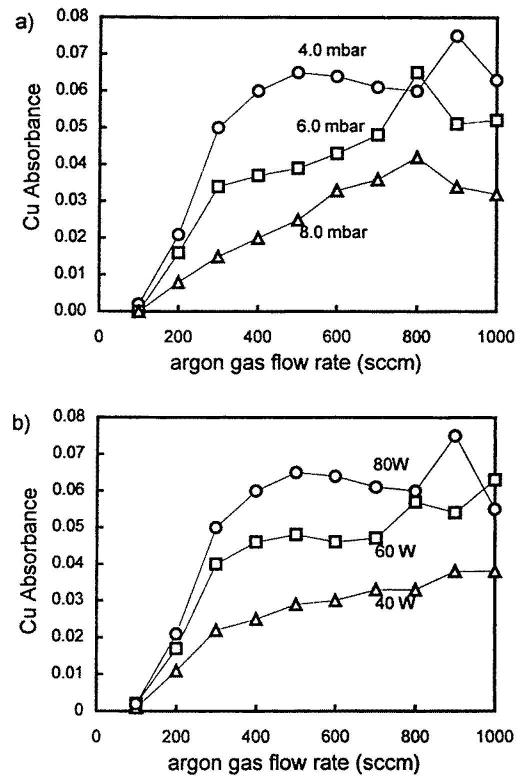

Fig. 4. The change in the absorbance of copper for cylindrical-jet configuration a) at a constant power (80 W) and b) at a constant pressure (4.0 mbar).

dependent on the pressure. A similar study of effects of the argon gas flow rate upon the absorption signal of copper was performed by two groups, Hutton *et al.* [6] and Kim *et al.* [7]. Hutton *et al.* [6] showed that the absorbance signal increased with increasing gas flow rate up to 500 sccm, after which all curves leveled off, then concluded that the transport efficiency of atom was at maximum at a flow rate 500 sccm for a pressure of 10 Torr. Kim *et al.* [7], while, showed that the maximum absorbance of copper was obtained when the gas flow rate was between 100 -200 sccm. These results indicate that the operation mode as well as the discharge cell dimension [7] and the pressure may influence on the optimum condition of argon gas flow rate.

The absorbance of copper increase, as the pressure in the glow discharge cell decrease. For a given power (or current) and argon gas flow rate, a decrease of pressure increases sputtering because the sputtering ions attain a higher kinetic energy due to the increase in their mean free path. In other hand, the decrease of pressure increases losses of sputtered atom by diffusion [8]. Bank and Blade [9] discovered that the plume is less restricted at the lower pressure and higher gas flow rate. In measuring of absorbance, the signal is proportion to the light path length, and the light pass length is longer as the plume is larger. Therefore if the pressure reduced, losses of sputtered atom by diffusion increase, and light path length increases. The former has a negative effect, and the latter has a positive effect on the absorption signal. Considering this aspects, there may be an optimum pressure that will provide the best analytical signal but may be very low. In the pressure range we worked, the lower the pressure is, the greater the absorbance of copper is.

As shown in *Fig. 2*b, the absorbance of copper was plotted in various power when the pressure in the discharge cell is 4.0 mabr. The absorbance of copper steeply increase with argon gas flow rate up to 300 sccm in all discharge powers. The absorbance reaches the maximum at 600 sccm and then decreases with increasing argon gas flow rate. The absorbance of copper increases with increasing discharge power.

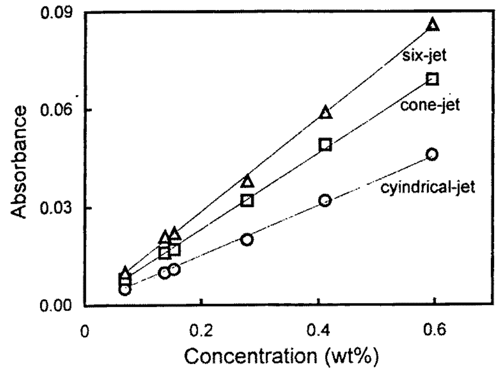

Fig. 5. Analytical calibration curve for Cu (324.8 nm).

Fang and Marcus [5] have discovered that the sample loss rate for a flat cathode is proportional to the electrical power dissipated in the glow discharge cell. If argon gas flow rate is constant, which means the transport efficiency is constant, the increase of absorbance of copper is due to the increase of sample loss rate with increasing the discharge power.

Fig. 3 shows the change in the absorption signal of copper at various pressures and powers with variation in argon gas flow for the six-jet configuration.

The variation of the absorbance of copper with pressure and argon gas flow rate at 80 W is provided in *Fig. 3*a. When the pressure in the cell is 4.0 mbar, the absorbance of copper increases with argon gas flow rate up to 300 sccm, after which the curve shows a plateau up to 800 sccm, and then illogically increase. This sudden increase of absorption signal seems to be due to the change of discharge property. Howatson [10] classified discharge as a function of their voltage-current characteristics. As the current increased further by the increase of argon gas flow rate in the glow discharge, the current density becomes so high that intensive heating of the cathode causes thermal vaporization of the cathode. The sudden increase happens at this transition point, and because of the transition of the plasma, the absorbance of copper dose not obey the trend. In the case of 6.0 mbar, the curve is similar to the curve which is obtained in 4.0 mbar, but begins to increase at 700 sccm. The absorption signal of 8.0 mbar continuously increases, especially from 600 sccm. The increase of signals are explained by the same way we used in the case of 4.0 mbar. The current increases as the pressure increases. Therefore, it is reasonable to conclude that a sudden increase which is caused by the transition of the plasma appears earlier.

*Fig. 3*b illustrates the change of the absorbance of copper at 4.0 mbar. The absorbance of copper steeply increases up to 300 sccm, after which the all curves level off. As the discharge power is reduced, the change of plasma property does not happen.

Fig. 4 represents the absorption signal of copper at various pressures and powers for the cylindrical-jet configuration.

These curves are obtained at a constant power (80W) and a constant pressure (4.0 mbar), respectively. and are similar to the curves in Fig. 3, except for the unreasonable increase of absorbance at 800 - 900 sccm. This result is caused by the change of plasma property as we have discussed before.

	configuration type	the slop (abs/wt %)	r^2
	cone	0.118	0.999
Cu	six	0.144	0.999
	cylindrical	0.079	0.999

Table I The slopes of calibration curves and the value of r^2

3.3. Analytical Calibration Curves of sample element.

The calibration curves of Cu (324.8 nm) shown in *Fig. 5* are obtained for three types of jet configurations. The pressure in the cell is 4.0 mbar and the discharge power is 80 W. The curves show a good linearity in all configurations. Six-jet configuration shows the best analytical performance.

The slope of calibration curves and the value of r^2 is presented in *Table I*.

The values of r^2 display the good linearity of curves in all jet configuration.

Conclusions

The dependence of the discharge voltage and current on argon gas flow rate is investigated with three types of jet configuration. As argon gas flow rate and the pressure in the cell increase at fixed power, the discharge voltage decreases. Argon gas flow rate influences more efficiently on the discharge voltage in lower pressure, and the geometry of jet configuration is thought to be another factor which determines the discharge voltage.

The effect of pressure, power, and argon gas flow rate on atomic absorption signals have been studied. The increase of atomic absorption signal of sample element is observed at fixed pressure in all jet configurations as argon gas flow rate increases up to 300 - 600 sccm, and as the power dissipated in the glow discharge cell increase. After the point which shows the maximum absorbance, the curves decay or level off, which is dependent on the pressure and jet configuration. The absorbance of sample increases as the pressure decreases at a fixed power and argon gas flow rate.

To obtain the calibration curves of some elements, standard sample is used. The curve shows a good linearity up to 2% by weight.

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References

1. D. S. Gough, *Anal. Chem.*, **48**, 1926 (1976).
2. A. E. Bernard, *Spectroscopy* **2**, 24 (1987).
3. K. Ohls, *Z. Anal. Chem.*, **327**, 118 (1987).
4. H. J. Kim, and E. H. Piepmeier, *Anal. Chem.*, **60**, 2040 (1988).
5. D. Fang and R. K. Marcus, *Spectrochim. Acta*, **43B**, 1451 (1988).
6. J. C. Hutton, C. L. Charkrabarti, P. C. Bertels and M. H. Back, *Spectrochim. Acta*, **46B**, 193 (1991).
7. H. J. Kim, Y. S. Park, J. H. Cho, G. H. Lee, K. H. Cho, K. B. Lee and H. Kim, *J. Anal. At. Spectrom.* **10**, 335 (1995)
8. R. K. Marcus, *Glow Discharge Spectroscopies*, Plenum Press, N. Y. 1993
9. P. R. Banks and M. W. Blades, *Specrtochim. Acta*, **46B**, 501 (1991).
10. A. M. Howatson, *An Introduction to Gas Discharges*, Pergamon Press, Elmsford, N.Y., 1976.