Effects of Potassium Chloride on the Analytical Characteristics of the Capillary Arc Excitation Source

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In emission spectrometry using a capillary arc as an excitation source, the effects of potassium chloride in solutions on the spectrum and background intensities, analytical curves, precision, and sensitivity have been investigated. Sample solutions were sprayed with a pneumatic glass nebulizer, passed through a modified desolvation device, and the desolvated aerosols were introduced into the arc plasma to be excited. The capillary arc operated satisfactorily at a low argon flow rate of 1.15 l/min. The spectrum intensity of iron increased and the background emission decreased with increasing potassium chloride concentration. When spraying solutions with more than 0.5 M potassium chloride, potassium chloride deposited on the inside of the capillary, reducing the emission stability. The use of 0.1 M potassium chloride solutions resulted in the improvement in detection limits for all the elements tested but tungsten and zirconium without marked decrease in the slope of analytical curves and reduction in the precision of measurements.

1. Introduction

In recent years there has been an increasing interest in emission spectrometric methods to determine trace elements in solutions. One of the methods is low power dc arc plasma spectrometry. Characterization of the arc plasma and modifications of reported plasma jet or plasma arc devices were described by various authors.¹⁻⁶⁾ Most of the devices consume high flow rates of inert gas, generally ranging from 3 to 12 l/min, to maintain the

stable emission. A simple dc capillary arc plasma source, which was developed for the excitation of fine particles produced from the surface of a solid metal sample with an aerosol generator, proved the excellent emission stability at argon flow rates of less than 3 l/min.⁷⁾ Denton *et al.*⁸⁾ demonstrated the applicability of the capillary arc plasma as an excitation source for solution analysis. They used a tantalum heating-atomizer coil, onto which a 5- μ l aqueous solution was placed from a pipette. One of the authors of the present paper has

coupled a slightly modified capillary arc source to a nebulizer-desolvation system to permit continuous sample introduction. Electrical and emission characteristics of the capillary arc source, plasma temperatures, and detection limits for some elements have been described in the previous paper.⁹⁾ The capillary arc operated with an economical flow rate of argon, approximately 1.5 l/min, maintaining the high stability of emission suitable for use with instantaneous photoelectric read-out.

A problem experienced with the source is a relatively high level of background emission which is a characteristic of most arc devices. In plasma jet or wall-stabilized arc emission spectrometry, alkali elements have often been used for depressing background emission and for suppressing ionization,^{5, 6, 10, 11)} while no experimental study has been reported on the introduction of alkali elements into the capillary arc plasma. This paper describes the effects of potassium chloride on the spectral line intensity, background intensity, precision of measurements, calibration curves, and detection limits for many elements in the capillary arc spectrochemical analysis of solutions.

2. Experimental

2.1 Apparatus and procedure

A schematic drawing of the capillary arc source unit is given in Fig. 1. The unit consists of four parts; a copper anode body, boron nitride insulator with a 3.2-mm i.d. capillary, pointed 3-mm diameter thoriated tungsten cathode, and copper body with an exhaust

Fig. 1. Cross-section of the capillary arc excitation source.

1. Quartz window, 2. Teflon adaptor, 3. Copper anode body, 4. Boron nitride insulator, 5. Copper body with an exhaust opening.

Fig. 2. Analytical system consisting of sample desolvation, capillary arc source, and photoelectric recording units.

A, Capillary arc source unit; B, Filter pump; C, Argon cylinder 1; D, Flowmeter 1; E, Argon cylinder 2; F, Flowmeter 2; G, Nitrogen cylinder; H, Flowmeter 3; I, Sample solution; J, Nebulizer; K, Spray chamber; L, Heater; M, Water-cooled condenser 1; N, Water-cooled condenser 2.

opening. The arc plasma is confined in the capillary tube of the insulator to maintain the stability of the discharge.

The analytical system used is shown in Fig. 2. Argon (cylinder 1) was used as the plasma forming and sample carrier gas. Aqueous solutions were sprayed into a Pyrex glass chamber with a pneumatic nebulizer. The spray chamber is 100 cm long and has a 70-mm i.d. The gas stream containing sample droplets is passed through the desolvation device and the desolvated sample aerosol is introduced into the arc plasma through a 10-mm diameter opening near the observation window of the source unit. The arc works at argon flow rates between 0.5 and 2.5 l/min. Commercially available nebulizers generally operate at flow rates too high for the plasma. To permit the use of low gas flow rates consistent with optimal operation of the plasma, a concentric pneumatic nebulizer was made of Pyrex glass. It proved to operate satisfactorily at spray gas flow rates of 0.8 to 2 l/min, though the sample droplets were not so fine as those produced with a commercial Beckman type nebulizer.

The desolvation device consists of a heated quartz tube and water-cooled condensers. A

portion of the 70-cm length of 24-mm i.d. quartz tube is heated with an electric heater. The maximum power of the heater is 800 W. The excess introduction of water vapor into the plasma not only produces intense emission of OH band spectra but causes consumption of the boron nitride wall and of the cathode tip. In order to overcome these problems, the two connecting condensers replaced a commercial Liebig condenser used in the previous work. The condenser 1 is the remaining portion (18 cm long) of the quartz tube and is water-cooled. The condenser 2 is constructed of a three-turns spiral glass tube (12-mm i.d., 70 cm long) passing through a water-circulating glass bottle. The performance of the improved desolvation device resulted in less consumption of the insulator and electrode, and the OH band emission was reduced approximately one-half. The overall efficiency of this sample introduction system was estimated by measuring the drain from the spray chamber and the condensate from the condensers for 50-ml quantities of solution uptake. The average efficiency was 3 per cent for a constant argon flow of 1.15 l/min. The solution uptake rate was 4.4 ml/min at the same argon flow rate.

A separate stream of argon was supplied through the flowmeter 2 around the cathode to reduce electrode consumption. When nitrogen was used as an additive gas, it was introduced into the plasma through a tangential

opening near the anode. The dc power supply, photomultiplier power supply, spectrometer, and detector have been previously described.⁹⁾ An image of the plasma was focussed with the first quartz lens on to an aperture positioned directly in front of the second quartz lens. In this study, to screen the intense argon emission from the central portion (2-mm diameter core) of the plasma, a mask of a 5-mm diameter disk was positioned at the aperture. The mask enabled selection of a region of high signal-to-background ratio in the plasma. The image selected was projected on to the entrance slit of the spectrometer through the second lens.

Table I gives the typical operating conditions used in this study.

2.2 Reagents

All solutions were prepared from stock solutions with deionized water and acidified (0.01–0.1 N) with hydrochloric acid just before use. Hydrochloric acid and potassium chloride used were reagent grade.

3. Results and discussion

3.1 Emission intensities of line and background

The emission intensity of an iron ionic line and the background intensity at the wavelength of the line were measured as a function of potassium chloride concentration. The measurements were made with solutions containing 10 $\mu\text{g/ml}$ of iron and potassium chloride in the concentration range 0 to 0.5 M. As shown in Fig. 3, an enhancement effect of potassium chloride on the spectral emission as well as a

Table I. Typical operating conditions.

DC capillary arc plasma	
Operating current	6A
Operating voltage	35V
Spray gas	Argon at 1.15 l/min
Cathode gas	Argon at 0.10 l/min
Spectrometer	
Reciprocal linear dispersion	0.62 nm/mm at 300 nm in the first order
Entrance slit width	7 μm
Exit slit width	50 μm
Exit slit height	6 mm
RC circuit	
Time constant	0.1 s
Amplifier	DC picoammeter
Recorder	1-V strip chart recorder

Fig. 3. Effects of increasing potassium chloride concentration on the emission intensity of Fe (II) 259.94 nm line and background intensity.

depression effect on the background intensity is observed. However, it is not recommended to use higher concentrations of KCl solutions, because potassium chloride deposits on the capillary wall of boron nitride and also detection limits for some elements are limited by impurities contained in potassium chloride. The presence of potassium chloride in excess of 0.5 M resulted in the deposition and emission fluctuation.

Fig. 4. Effects of potassium chloride and added nitrogen on the apparent background intensity over the wavelength range from 250 to 600 nm.

Variations in the apparent background intensity over the wavelength range 250 to 600 nm are shown in Fig. 4. When nitrogen is introduced at a flow rate of 20 ml/min to the plasma as the additive gas, the background intensity decreases over all the measured wavelength range but a region in the vicinity of 350 nm. Larger reduction in the background intensity, however, is observed when spraying a 0.1 M KCl solution. In order to achieve the background level as low as that for the KCl solution, it was necessary to add nitrogen to the plasma at a high flow rate of 500 ml/min. The high flow rate of nitrogen, however, decreased the emission stability.

3.2 Precision

An example of repetitive measurements of a spectrum is shown in Fig. 5. The measurements were made for the emission of Zr (II) 339.20 nm line from a standard solution containing 1 $\mu\text{g/ml}$ of zirconium and for the emission

Fig. 5. Typical precision of eight repetitive measurements for a 1 $\mu\text{g/ml}$ of zirconium solution and blank solution.

at the same wavelength from a reagent blank solution. Generally, it is difficult to determine low concentrations of zirconium by conventional flame emission or absorption spectrometry because zirconium forms a refractory oxide in the flame. Also OH band spectra interfere with the zirconium line which is sensitive in plasma emission spectrometry. The result shows that the capillary arc provides not only satisfactory emission reproducibility but high sensitivity in the signal intensity.

Relative standard deviations for various elements in aqueous solutions with and without potassium chloride were calculated from the average of ten consecutive measurements. In Fig. 6, the relative standard deviation obtained

Fig. 6. Relative standard deviations plotted vs. concentration of analytes divided by detection limits.

×, Al (I) 396.15 nm; ○, Ba (II) 455.40 nm; □, Ca (II) 393.37 nm; ▤, Cd (I) 228.80 nm; ▽, Fe (II) 259.94 nm; ⊙, Ga (I) 417.21 nm; △, Mg(II) 279.55 nm; ●, Mo (I) 379.83 nm; △, Te(I) 214.28 nm; ■, Zr (II) 339.20 nm.

is plotted against the ratio of the concentration of the test element to the detection limit of the element given later in this paper (Table II). The ratio, that is, the number in abscissa is considered to be proportional to the magnitude of the signal observed. Clearly the relative standard deviation is independent of the kind of the element, but dependent on the magnitude of the signal. In the concentration range above 100 times the detection limit, determinations can be made with high precisions of less than 2 per cent by the proposed method. No marked reduction in the precision is caused by the introduction of potassium chloride.

3.3 Calibration curves and detection limits

Typical analytical curves are shown in Fig. 7. Three repetitive measurements were made for each solution and the average value was calculated. Recording time required for each solution was within a minute. The result indicates that linear plots are obtained over three orders of magnitude. Very slight decrease in the slopes is occasioned by the presence of potassium chloride; the slopes were 1.03 and 1.01 for barium and vanadium, respectively, and 0.993 for both the elements in 0.1 M KCl solutions. The calibration curve of barium shifted upward in the presence of potassium chloride, whereas the shifting was scarcely observed for the curve of vanadium. Most of the elements tested (given in Table II), with the exception of such refractory elements as

Fig. 7. Calibration curves for barium and vanadium with and without potassium chloride. Ba (II) 455.40 nm line: ○, aqueous solution; ●, 0.1 M KCl solution. V (I) 437.92 nm line: △, aqueous solution; ▲, 0.1 M KCl solution.

Table II. Detection limits, $\mu\text{g/ml}$.

Element	Wavelength nm	Aqueous soln	0.1 M KCl soln
Al (I)	396.15	0.3	0.04
Ba (II)	455.40	0.015	0.005
Ca (II)	393.37	0.004	0.004*
Cd (I)	228.80	0.09	0.04
Cs (I)	455.53	20	8
Fe (II)	259.94	0.1	0.02*
Ga (I)	417.21	0.1	0.03
La (II)	408.67	1	0.5
Mg (II)	279.55	0.004	0.002*
Mo (I)	379.83	0.05	0.04
Ni (I)	341.47	0.65	0.05
Sb (I)	259.81	0.3	0.16
Se (I)	203.99	3	1
Sn (I)	270.65	0.2	0.1
Te (I)	214.28	0.8	0.25
V (I)	437.92	0.15	0.09
W (I)	400.88	0.6	0.9
Zn (I)	213.86	0.2	0.04
Zr (II)	339.20	0.06	0.1

* Limited by blank from potassium chloride.

vanadium, zirconium, and tungsten, were similar in the tendency to barium.

Detection limits were measured for 19 elements in aqueous solutions and in 0.1 M KCl solutions. Data obtained are given in Table II. The spectral lines used are the most sensitive ones for each element studied. The detection limits represent the concentration of the analyte required to give two times the standard deviation of background fluctuation. As the fixed set of conditions shown in Table I were employed for the measurements, the values reported here should not be regarded as the best obtainable using the proposed method. As has been indicated in the previous paper, the detection capabilities of the proposed method are comparable to those obtainable by flame and plasma jet emission spectrometric techniques. The present results indicated that the detection limits for all the measured elements but tungsten and zirconium are improved by using the KCl solutions. In particular, the detection limits for Al, Fe, Ga, Ni, and Zn in the presence of potassium chloride were approximately one

order of magnitude lower than those obtained for the aqueous solutions without potassium chloride.

3.4 Excitation temperature and degree of ionization

Excitation temperatures of the arc plasma and ionization degree of iron in the plasma were measured while spraying a 1000 $\mu\text{g/ml}$ iron solution with and without potassium chloride. The excitation temperature was calculated from the observed relative intensities of two iron lines Fe (I) 370.56 nm and Fe (I) 370.93 nm using the following equation.

$$T = 5040(E_2 - E_1) / \{ \log (Ag)_2 \lambda_1 / (Ag)_1 \lambda_2 - \log I_2 / I_1 \} \quad (1)$$

where T is the excitation temperature (K), E the excitation energy (eV), A the transition probability, g the statistical weight, λ the wavelength, and I the relative intensity; the subscripts 1 and 2 refer to the lines Fe (I) 370.56 nm and Fe (I) 370.93 nm, respectively. The Ag -values of the two lines were taken from the American Institute Physics Handbook (second edition)¹²⁾ according to our previous study¹³⁾ concerning the selection of spectral lines and published Ag -values. Substituting the numerical values for the constants into the equation (1), we obtain

$$T = 4333 / (\log I_1 / I_2 + 0.842) \quad (2)$$

The degree of ionization α can be computed from the measured values of atom line and ion line intensities and the excitation temperature, viz.

$$\alpha = 1 / [1 + (I_a \lambda_a Z_a A_{ig} / I_i \lambda_i Z_i A_{ga}) \times \exp \{-11605(E_i - E_a) / T\}] \quad (3)$$

where Z is the partition function; the subscripts a and i refer to the atom line and ion line, respectively. In this study, Fe (I) 272.09 nm and Fe (II) 272.75 nm lines were chosen for the measurements, so

$$\alpha = 1 / \{1 + 11.336(I_a Z_a / I_i Z_i) \exp(-11350/T)\} \quad (4)$$

where the Ag -values were taken from the NBS Tables.¹⁴⁾ The partition functions at the measured temperatures were computed by

using the equations given by Galan *et al.*¹⁵⁾ The relative intensities were calculated from the average of ten consecutive measurements. The results obtained are

$$T = 4220 \text{ K}, \alpha = 0.536$$

for the aqueous solution without potassium chloride, and

$$T = 4260 \text{ K}, \alpha = 0.518$$

for the 0.1 M KCl solution, thus indicating that the introduction of potassium chloride into the capillary arc results in a slight rise in the temperature. The values of α exhibit the suppression of ionization caused by potassium chloride, as might have been expected.

The lower detection limits for many elements in the presence of potassium chloride seems to be mainly the result of the increase in the spectral line intensities due to the slightly higher temperature and simultaneous decrease in the background.[†] Presumably the latter effect is ascribed to the decreased concentration of the charged particles in the arc plasma.

4. Conclusion

When the potassium chloride concentration in solutions was lower than 0.5 M, the deposition of potassium chloride upon the inside of the capillary was negligibly small and the reduction in the emission stability of the discharge was scarcely observed. The use of 0.1 M KCl solutions improved the line-to-background ratios, thus lowering the detection limits for most of the elements examined. The proposed analytical system, which is relatively inexpensive, can be operated in an easy manner similar to that with chemical flames. There are reasonable possibilities for the use of the

[†] The rise in the lines intensities of some elements, e.g. Ni, Mg, Ga, was higher than that expected from the increase in the dissociation and excitation degrees due to the slight rise in the temperature. Although the present study is primarily directed to the measurement of analytical properties of the capillary arc plasma, further investigation will be necessary on the introduction efficiency of aerosols to the plasma, evaporation process of salts, and excitation process in the presence of potassium chloride.

capillary arc excitation method in the field of analytical emission spectrometry to determine trace elements in solutions.

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