RADIALLY RESOLVED MEASUREMENTS OF THE EMISSION INTENSITY IN THE PRESENCE OF MATRIX ELEMENTS IN INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRY

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Abstract

Radially resolved emission profiles of Sr, Mn and Zn analyte lines have been used to study the matrix effects in the presence of potassium chloride and phosphoric acid in inductively coupled plasma atomic emission spectrometry. The effects of these two matrices on the excitation temperature at a forward power of 1.3 kW and 1.6 kW is discussed. It is shown that both matrices influence the radially resolved excitation temperature and the analyte emission line profiles. At a higher operating power an increase in the excitation temperature of about 1000 K is observed for a potassium matrix. There are no simple relationships between the variations in the excitation temperature and changes in the analyte emission intensities. The differences in the radially resolved emission intensity profiles between Zn with a higher ionisation potential and Sr and Mn with lower and moderate ionisation potentials in the presence of potassium and phosphorous matrices at 1.3 kW are significant. However, in the vicinity of the central channel of the plasma, at 1.6 kW, these differences are lower indicating that the increase in excitation temperature plays a role in minimising matrix effects.

Introduction

In spite of intensive work in the field of inductively coupled plasma atomic emission spectrometry (ICP-AES) the ICP remains an important object of study (1, 2). The study of the processes occurring within the plasma, such as desolvation, vaporisation, atom/ion formation and excitation, is important particularly from the point of their control. So that any shortcomings which exist in atomic emission spectrometric analysis can be lowered or eliminated and existing methods for atomic spectrometric analysis optimised.

A study of spectral interferences and sample matrix effects were directed toward the effects on analyte emission by adding different matrices (3-11). The variation in experimental parameters such as the power supplied to the plasma and the carrier gas flow do not have an equal effect on the analytical emission lines, which differ in ionisation and excitation energy (12, 13). Certain authors classify analytical emission lines into two groups, “soft” and “hard” lines. Whereas the intensity of hard lines is relatively independent, soft lines are dependent on operating parameters (12). It has been shown that that the ionic lines are always hard, whereas atomic lines are either hard or soft, depending on the excitation energy of the analyte line and the observation position (14). However, the fundamental processes that control analyte emission intensity and spatial dependence are not fully understood (15). At this point a study of the spatial distribution of emission intensity and the parameters which characterise the ICP (e.g. temperature and electron number density) is essential for a better understanding of the ICP and for improving instrumental techniques that incorporate the ICP-AES.

The aim of this work is to investigate the effects of potassium chloride and phosphoric acid and operating power on the radial spatial distribution of emission from Sr, Mn and Zn ionic lines. Potassium and phosphorous matrices were chosen since they contain elements with low and high ionisation energy (E_i), respectively (E_i of potassium is 4.3 eV and of phosphorous 11.1 eV). The analytes studied differ in their ionisation and excitation energies. Spatially resolved measurements can provide an insight into the location of matrix effects. To this end, radially resolved emission intensities were considered along with a spatially resolved excitation temperature. Because the forward power significantly alters the plasma excitation conditions and will also influence the magnitude of the matrix effects (1-4). Experiments were made using two different power settings and the correlation between the radially resolved analyte ionic emission intensities and excitation temperatures obtained by measuring the intensity of the iron ionic emission lines is presented.

Experimental

Instrumentation

Applied Research Laboratories (ARL) 3520 OES sequential vacuum spectrometer equipped with an SAS 11 automation system for instrumental control, data acquisition, and data manipulation was used. Table 1 lists the instrumental facilities and operating parameters used in this study, while the analytes selected and the spectral data of the lines considered are listed in Table 2.

Table 1. Instrumental and operating conditions

Spectrometer	Monochromator with 1 m radius concave grating in Paschen-Runge mounting
Grating	1080 grooves/mm with reciprocal linear dispersion 0.926 nm/mm
Slit widths	Primary: 20 µm Secondary: 50 µm
RF Generator	Quartz-controlled, 27.12 MHz Operating power: 1.3 and 1.6 kW
Plasma Torch	Three concentric quartz tubes, Fassel type
Nebulizer	Glass concentric, Meinhard type
Argon flow	Carrier 0.95 1/min Plasma 0.80 1/min Coolant 12 1/min
Observation height	15 mm above the load coil

Procedures

By translating the ICP source in steps of 0.25 mm, lateral emission intensities were acquired. Laterally resolved emission intensities were converted into radially resolved emission intensity by using the Abel inversion procedure commonly used in optical emission spectrometry (16).

Reagents

Potassium and phosphorous matrix solutions were prepared from KCl and H_3PO_4, respectively. The molar concentration of potassium and phosphorous was 0.25 and the analytes were present at a concentration of 50 µg ml^{-1}. For the excitation temperature measurements, Fe was added in a concentration of 100 µg ml^{-1}. Mili-Q water and analytical-reagent grade salts were used to prepare all the solutions. Measurements were made in triplicate.

Excitation temperature measurements

For T_{exc} determination the “relative method” was applied, which can be written as (17, 18):

$$T_{exc} = \frac{T_{ref}\ E^*_{ij}}{\Delta\ E^*_{ij} - k\ T_{ref} \ln R}$$

where $R = (I_i/I_j)/(I_i/I_j)_{ref}$ and (I_i/I_j) is the ratio of the line intensities at some position other than for reference point, $(I_i/I_j)_{ref}$ is the ratio of line intensities at the reference point, T_{ref} is the reference value of the excitation temperature, E^*_{ij} is the excitation energy of state i (j) of the line involved, $\Delta E^*_{ij} = E^*_i - E^*_j$ and k is the Boltzmann constant.

Table 2. Wavelengths (λ), excitation energies (E_q) and ionisation energies (E_i) for Sr, Mn, Zn and Fe

Element	λ (nm)	E_q (eV)	E_i (eV)
Sr II	407.77	3.04	6.09
Mn II	279.55	4.81	7.43
Zn II	202.55	6.12	9.28
Fe II	256.69	5.91	7.90
Fe II	275.33	7.77	7.90

Results and discussion

Excitation temperatures. Matrix effects in ICP-AES are usually studied by measuring spatially integrated emission intensities. However, because of the inhomogeneity of the ICP more information can be obtained when the emission intensity and the characteristic parameters, such as excitation temperature, are mapped spatially.

Excitation temperature (T_{exc}) is an important parameter for characterising an emission source since it determines the fraction of atomic species in a particular excited electronic state. Because of the lack of a local thermodynamic equilibrium in an argon ICP, the level population deviates from a Boltzmann distribution. Therefore, T_{exc} must be considered qualitatively in conjunction with the observed changes in emission intensities for all the lines, with the exception of that from which T_{exc} was calculated (3). Another problem is determining T_{exc} using the line reversal method, which is often used in ICP because it causes large uncertainties (±500 K at normal observation height). To avoid these we applied the so called "relative method", described by Houk (17), which requires only the relative intensities of at least two spectral lines with different excitation energies. The experiments were made at two power settings, at 1.3 and 1.6 kW, respectively. For comparison, the excitation temperature was measured in the absence of matrix elements.

For T_{ref} values of 5500 and 6000 K, based on previous studies (18) were chosen. These values correspond to the forward power settings 1.3 and 1.6 kW, respectively. For the reference temperature values (T_{ref}) the intensity ratio $(I_i/I_j)_{ref}$ was chosen at the central position (r = 0 mm). In experiments ionic iron lines were used. As it was shown by Houk (17) moving the reference position simply displaces the T_{exc} distributions while the basic shape is essentially independent of the reference position chosen.

In Fig. 1, the arbitrary T_{exc} profiles with and without matrix for operating power settings of 1.3 (Fig. 1a) and 1.6 kW (Fig. 1b) are shown. Under experimental conditions, changes in T_{exc} can be measured to ± 100 K when the uncertainty in the measured relative intensities is lower than 10%. This is true up to approximately 4 mm from the centre of the plasma. At greater distances from the plasma centre, because of the lowering of the measured emission intensity of spectral lines, the uncertainty can exceed ± 100 K. However, the experimentally determined uncertainty in T_{exc} on the basis of three replicate measurements of the analyte line emission intensity is below ± 200 within the observation range.

Fig. 1a shows that T_{exc} at a forward power of 1.3 kW in the absence of matrix increases by about 500 K at the centre of the plasma in comparison to the radial distance of 2 mm from the centre of the channel. This effect disappears for a aqueous solution at 1.6 kW and differs when the matrix solution is aspirated. At a power setting of 1.3 kW the excitation temperature in the presence of phosphorous remains practically constant (Fig. 1a), whereas at 1.6 kW (Fig. 1b) it is enhanced at the centre of the plasma for 500 K. For the potassium matrix a relative enhancement in T_{exc} at a distance of 1.5 mm from the central channel is observed at 1.3 kW. This maximum in T_{exc} may result from

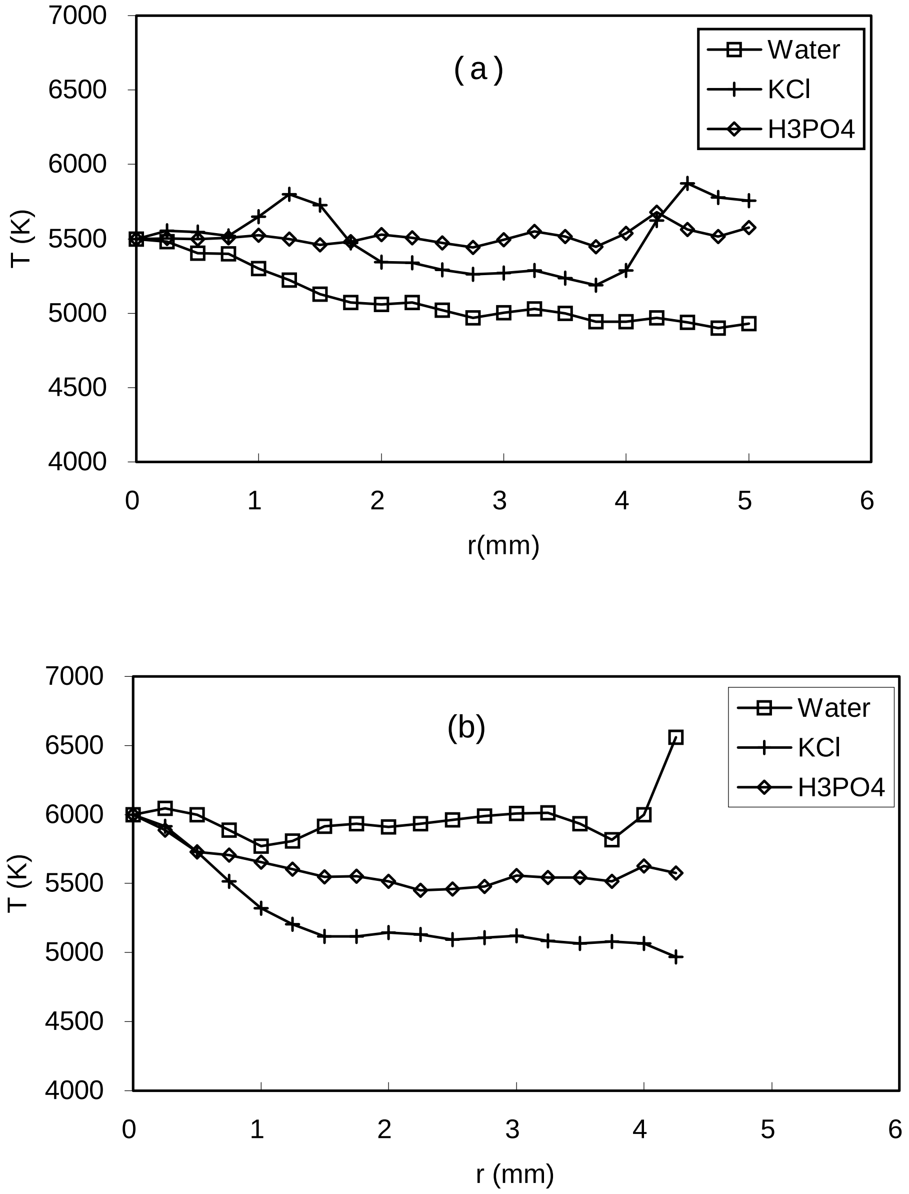


Figure 1. Arbitrary radially resolved Texc profiles for Fe II. Reference position is chosen on axis of the plasma. Forward power: 1.3 kW (a); 1.6 kW (b).

the electron enhanced collisional excitation at these distances (at a power of 1.2 kW) in the presence of potassium as it was found by Jian and coworkers (**7**). At 1.6 kW there is a higher change in T_{exc} (about 1000 K) between ± 2 mm radial distance from the central channel. Excitation temperature profiles show no remarkable variation at radial distances between 2 and 4 mm.

Matrix effects. The matrix effect, M, is defined as the percentage difference in the net line signals between solutions of the analyte with and without the matrix. At a forward power of 1.3 kW (Fig. 2) radially resolved matrix effects show a difference in behaviour between matrices and the analytes. In the presence of a potassium matrix (Fig. 2a) a depressant effect occurs for Sr and Mn until 3.5 mm from the centre of the plasma at which the depressant effect turns into an enhancement ("crossover point"). In contrast, no crossover point is observed for Mn and Sr in the presence of phosphorous (Fig. 2b). For Zn a depression of about 40% occurs for both matrices at 1.3 kW near the centre of the plasma and the crossover point is closer to the centre of the plasma. Further, the magnitude of the matrix effects for Zn is greater than for Mn and Sr. This difference might be due to the higher ionisation potential for Zn which requires a greater amount of energy for excitation.

When forward power is increased to 1.6 kW (Fig. 3) the differences in the matrix effects between the elements studied are minor near the axis. At this power setting in the presence of potassium an enhancement effect for Mn and Sr emission intensity at a distance greater than 2 mm of axis is observed. In the presence of phosphorous (Fig. 3b) the radial profiles for Zn, Mn and Sr are similar up to a distance of 2 mm from the axis. At greater radial distances the Mn line intensity is increased, whereas Mn ad Sr radial profiles remain unchanged.

The overall decrease in the analyte line emission intensity near the central channel at both power settings suggests that the presence of a matrix reduces the excitation ability. This is due to a transfer of the discharge energy to the matrix, especially near the centre of the plasma. Since at a higher operating power the T_{exc} are higher near the axis of the plasma, it is supposed that the dissimilarity caused by the addition of matrix elements can be minimised by carefully adjusting the operating power. Recent investigations concerning the analysis of samples with complex matrices supports this hypothesis (2, 19). However, other processes in the plasma like the shift in ionisation equilibrium and vaporisation processes may also play an important role in the magnitude of the matrix effects.

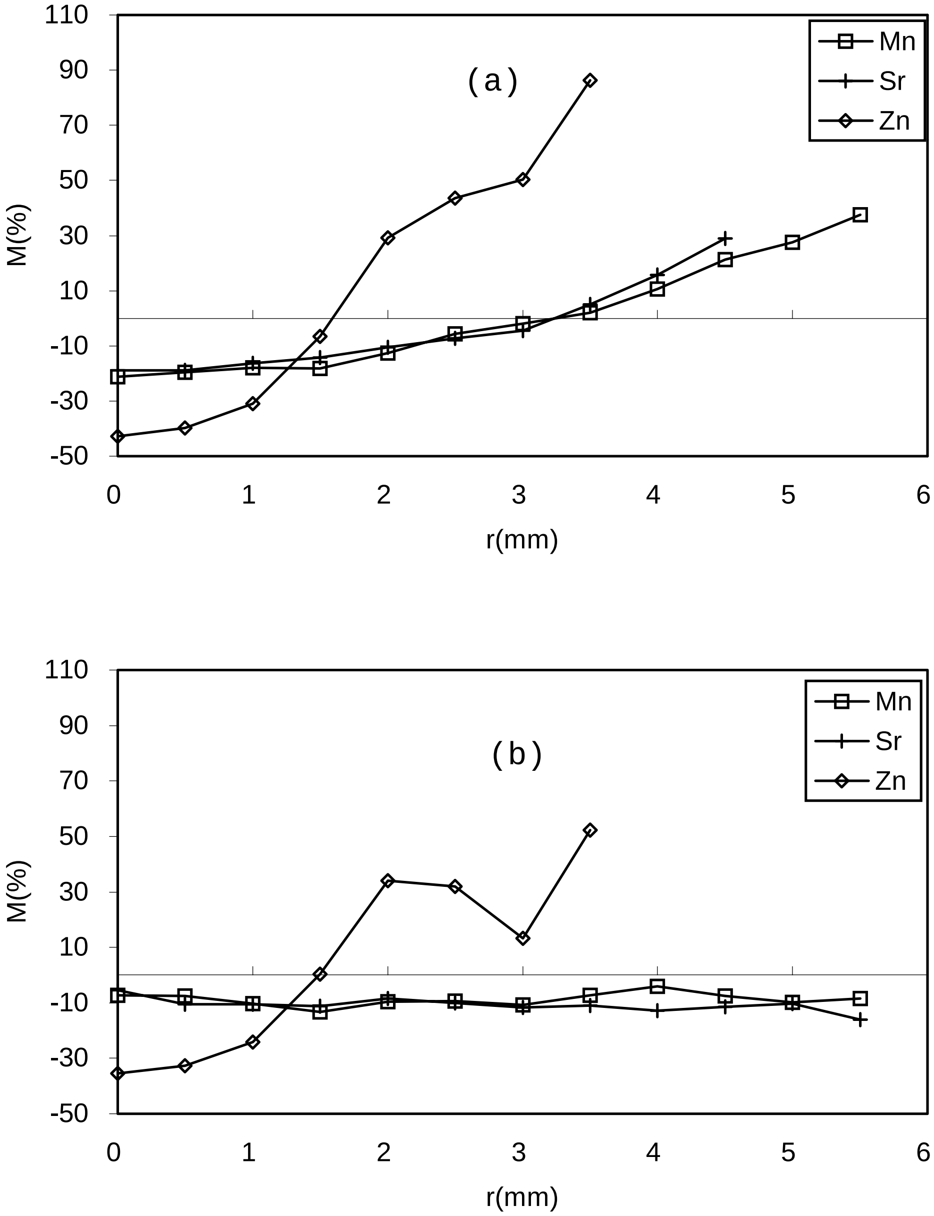
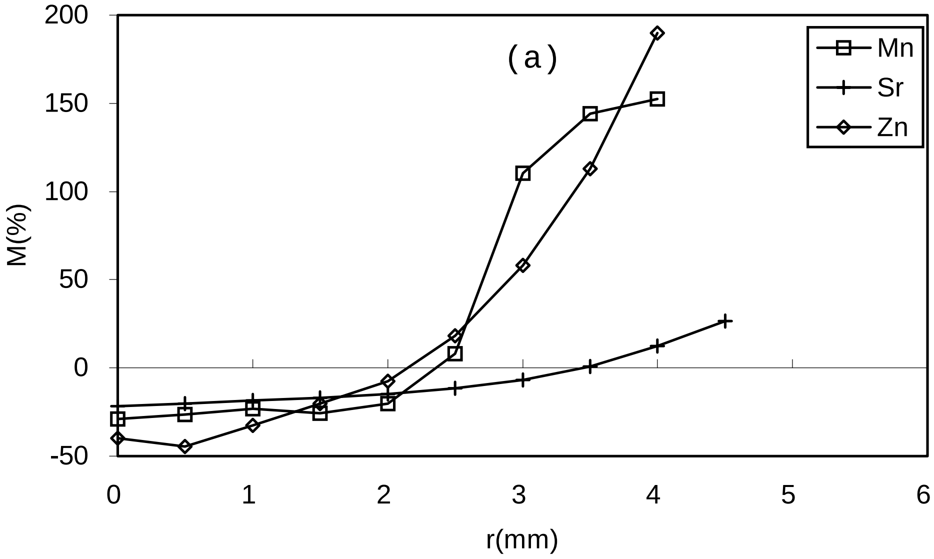


Figure 2. Radially resolved matrix effects (M) in the presence of potassium (a) and phosphorous (b) for Mn, Sr and Zn; Forward power: 1.3 kW.



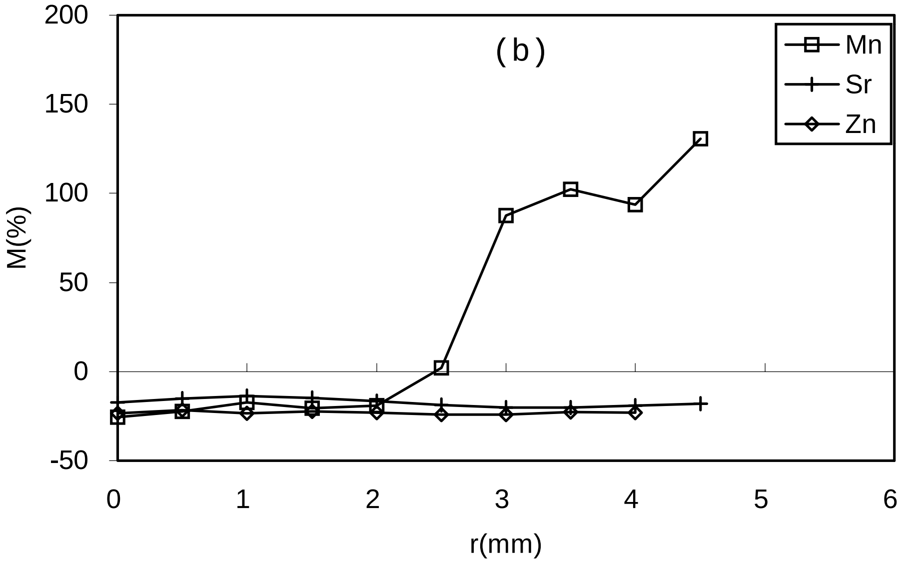


Figure 3. Radially resolved matrix effects (M) in the presence of potassium (a) and phosphorous (b) for Mn, Sr and Mn; Forward power: 1.6 kW.

Conclusions

The increase in operating power in inductively coupled plasma atomic emission spectrometry changes the radial distribution of the excitation temperature. At higher operating powers it is enhanced in the central channel of the plasma and this enhancement effect is greater for the matrix containing potassium than phosphorous. The investigation shows that the variations in the radially resolved line emission intensity profiles do not follow the changes in excitation temperature profiles. Therefore, matrix effects originating from the changes in the excitation conditions can not be eliminated completely by adjusting the operating parameters that result in changes in the excitation temperature, such as carrier gas flow rate and operating power. At an operating power of 1.6 kW the dissimilarities in the magnitudes of the matrix effects at a distance of less than 2 mm from the plasma centre are lower than at a power of 1.3 kW. This indicates that the operating power can be optimised to minimise the matrix effects during the analysis of sample solutions containing higher amounts of matrix elements.

Acknowledgements

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Povzetek

Preučevali smo vpliv kalijevega klorida in fosforjeve kisline na prostorsko porazdelitev temperature vzbujanja in intenzitete ionskih spektralnih črt Sr, Mn in Zn pri vzbujanju v emisijski spektrometriji z induktivno sklopljeno plazmo pri moči generatorja 1,3 in 1,6 kW. Izkazalo se je, da obe osnovi vplivata na prostorsko porazdelitev temperature vzbujanja in intenzitete preiskovanih emisijskih spektralnih črt. Največja sprememba temperature vzbujanja poteka pri višji moči generatorja (1,6 kW), kjer se v razdalji do 2 mm od središča plazme zmanjpa za približno 1000 K. V splošnem pa velja, da pri danih eksperimentalnih razmerah sprememba prostorske porazdelitve intenzitete spektralnih črt ne sledi spremembam temperature vzbujanja. Kljub temu pa je opaziti pri višji moči generatorja v bližini središča plazme manjše spremembe emisijske intenzitete za preučevane spektralne črte kot pri moči 1,3 kW. Ti rezultati kažejo, da s spreminjanjem napajalne moči generatorja in s tem posredno temperature vzbujanja lahko vplivamo na zmanjšanje matričnih vplivov.