# application note

## Optimizing Analytical Performance in ICP-OES Applications

### Introduction

To obtain the best possible performance from an analytical instrument, it is necessary to optimize the operating parameters. This study discusses the parameters that affect the analytical performance of the GBC Integra range of ICP spectrometers and presents guidelines for determining the optimum parameter settings for a particular application.

In addition to selecting the appropriate elemental wavelengths, parameters that affect ICP-OES analytical performance include RF power, nebulizer gas flow rate, torch gas flow rate, viewing height and sample introduction rate. Of these RF power, viewing height and nebulizer gas flow rate are the most critical. The interaction of these parameters is complex and their effects vary depending on the elemental wavelength. To achieve the best performance, these parameters must be selected in the appropriate combinations. The remaining parameters have a less significant effect on performance and can be adjusted independently of these critical parameters.

### Wavelength Classification

When predicting the changes that will occur when a wavelength is selected it is necessary to understand its origin of emission, as this will affect the behaviour of each wavelength, even for the same element. The effect of the parameters on the line intensity relates to the wavelength origin, not the element.[1,2]

Elements in the plasma exist in equilibrium between ionic and atomic species. This makes it possible to group the wavelengths into transitions originating from the ***Atomic*** or ***Ionic*** state. The wavelengths are further characterised as ***Hard*** (first ionization potential >8 eV, second ionization potential >15 eV) and ***Soft*** (first ionization potential <8 eV, second ionization potential <15 eV).

- a ***Hard Atomic*** wavelength is one that has a high 1st ionization potential. (e.g., P I 177.495 nm; 10.49 eV).
- a ***Hard Ionic*** wavelength is one that has a high 2nd ionization potential. (e.g., Al II 167.081 nm; 18.83 eV).
- a ***Soft Atomic*** wavelength is one that has a low 1st ionization potential. (e.g., Na I 588.995 nm; 5.14 eV).
- a ***Soft Ionic*** wavelength is one that has a low 2nd ionization potential. (e.g., Ba II 455.404 nm; 10.00 eV).

The classification of wavelengths is necessary as the effect of different operating parameters on analytical performance depends on them. The significance of these groupings is that optimum conditions for a ***Hard Atomic*** wavelength (which typically requires higher energy for excitation) may be inappropriate for a ***Soft Ionic*** wavelength, and a different set of optimized parameters may be required.

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## Experimental

### Reagents

A single multi-element solution containing 10 ppm of Cu, Fe, K, Na, Pb and Zn was prepared from high-purity 1000 ppm stock standards (BDH Chemicals, Spectrosol grade) and acidified in 1% nitric acid (BDH Chemicals, AnalaR grade).

### Instrument

A GBC Integra XL sequential ICP was used. The Integra XL offers total computer control of all operating parameters, including all gas flow rates, power level, pump rate and viewing position. It also includes hardware features such as stable thermostatted optics, high precision mass flow gas control for all gas lines, and a robust, free running 40 MHz RF generator. Each of these features is designed to improve analytical performance.

### Analytical Lines

In order to investigate the dependence of the various operating parameters on wavelength, elemental wavelengths covering a wide range of ionization potentials were selected. These wavelengths and their corresponding ionization potentials are given in Table 1.

**Table 1. Selected elemental wavelengths and their respective ionization potentials**

| Element | Wavelength (nm) | Ionization Potential (eV) |
|---|---|---|
| Fe II | 259.940 | 16.18 |
| Pb II | 220.353 | 15.03 |
| Zn I | 213.856 | 9.39 |
| Cu I | 324.754 | 7.73 |
| Na I | 588.995 | 5.14 |
| K I | 766.490 | 4.34 |

## Results

### The Effect of Nebulizer Gas Flow Rate

Figure 1 shows the behaviour of the six selected wavelengths as a function of the nebulizer gas flow rate. The intensity of hard wavelengths (Fe and Pb) increases at lower flow rates. This is because the flow rate directly controls the sample transit time through the plasma, affecting the level of atomisation achieved. Lower nebulizer flow rates increase the residence time of the analyte in the plasma, giving it longer to acquire the energy for high energy transitions.

Conversely, the optimum intensity of soft wavelengths with low-energy ionization potentials (Na and K) is achieved at higher flow rates. These rates increase the sample flow through the plasma, providing low-energy conditions due to the reduced residence time of the analyte in the plasma.

In Figure 2 the background levels are shown as a function of nebulizer gas flow rate. The levels for the six analytical lines decreased with increasing flow rate, due to the low energy of the plasma at higher flow rates.

Figure 3 shows the effect of nebulizer gas flow rates on the signal-to-background ratio. The significant drop in intensity observed for hard wavelengths (Fe and Pb) indicates that the best sensitivity for these wavelengths is found at low nebulizer flow rates, even though background levels are low at higher gas flows. Conversely, the soft wavelengths (Na and K) show up to an order of magnitude better sensitivity at higher gas flows.

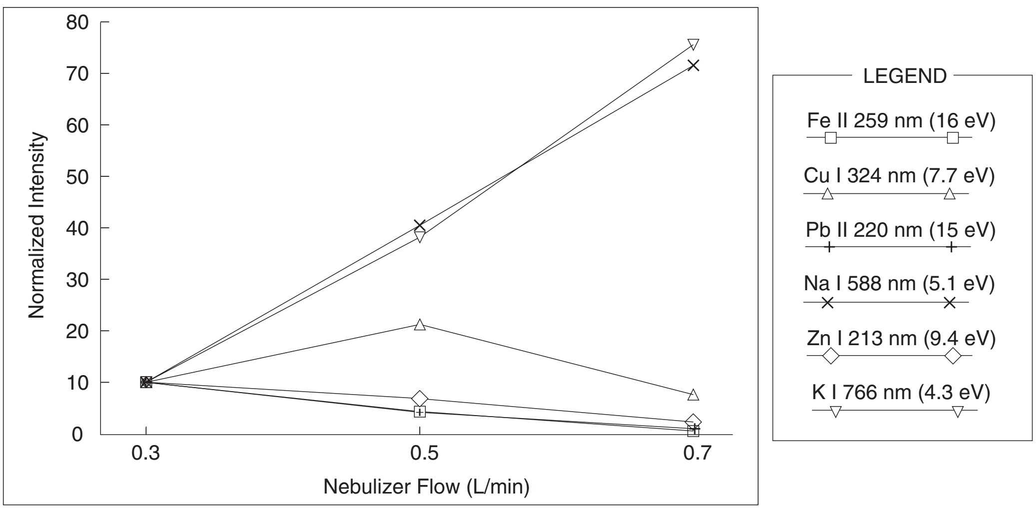


***Figure 1** Normalized analyte intensity as a function of nebulizer gas flow rate*

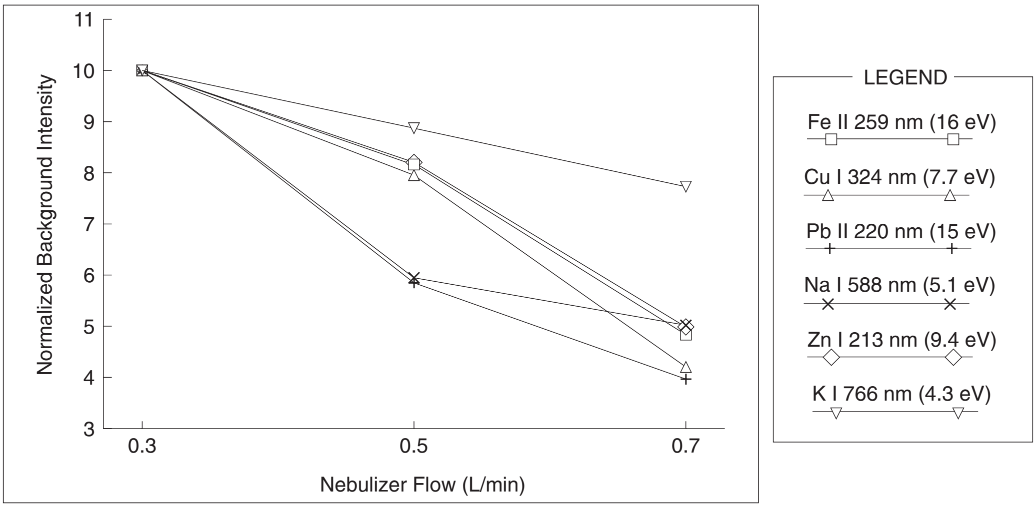


***Figure 2*** *Normalized background intensity as a function of nebulizer gas flow rate*

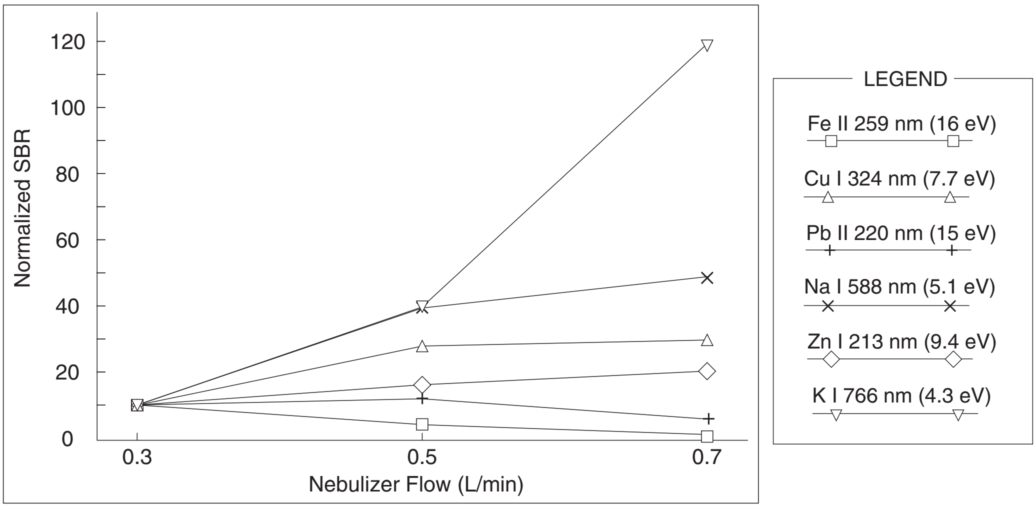


***Figure 3*** *Normalized signal-to-background ratio (SBR) as a function of nebulizer gas flow rate*

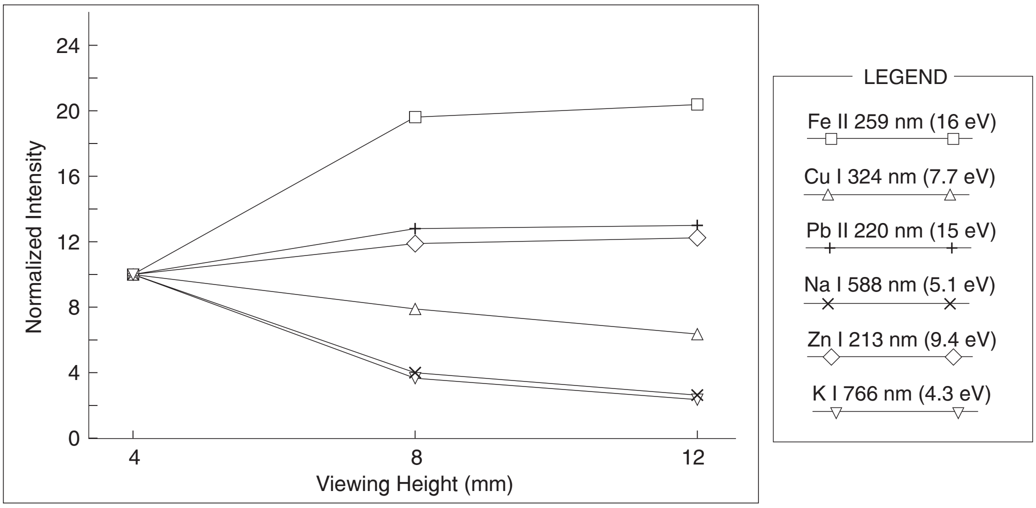


***Figure 4*** *Normalized analyte intensity as a function of viewing height*

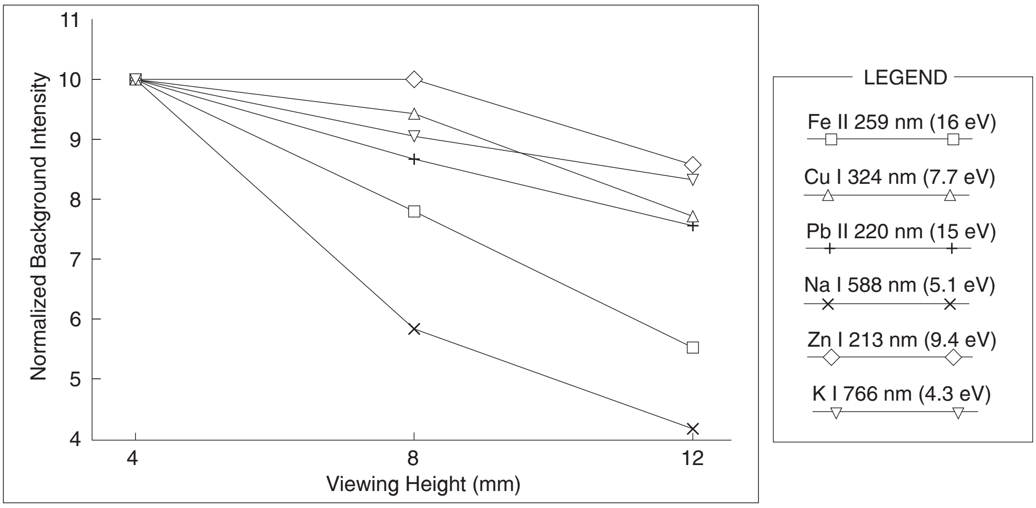


***Figure 5*** *Normalized background intensity as a function of viewing height*

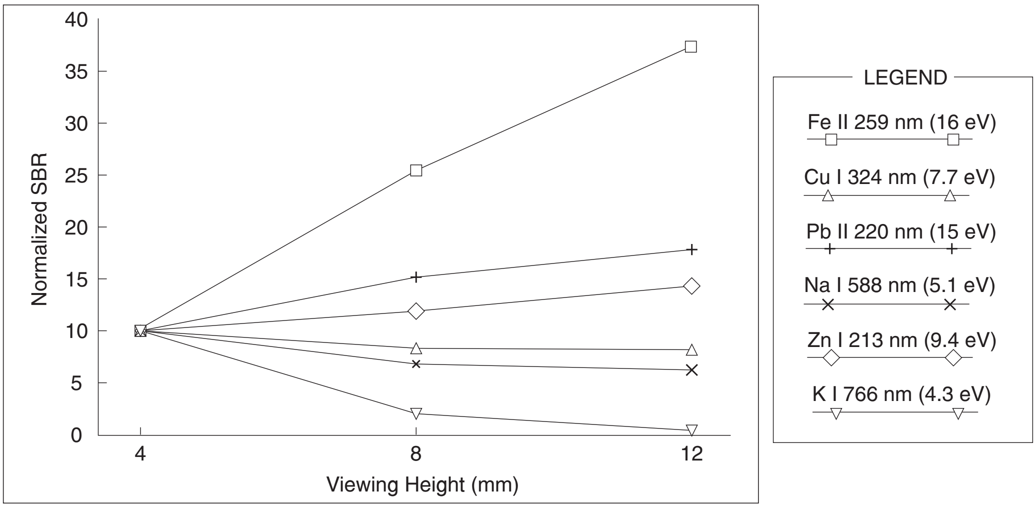


***Figure 6*** *Normalized signal-to-background ratio (SBR) as a function of viewing height*

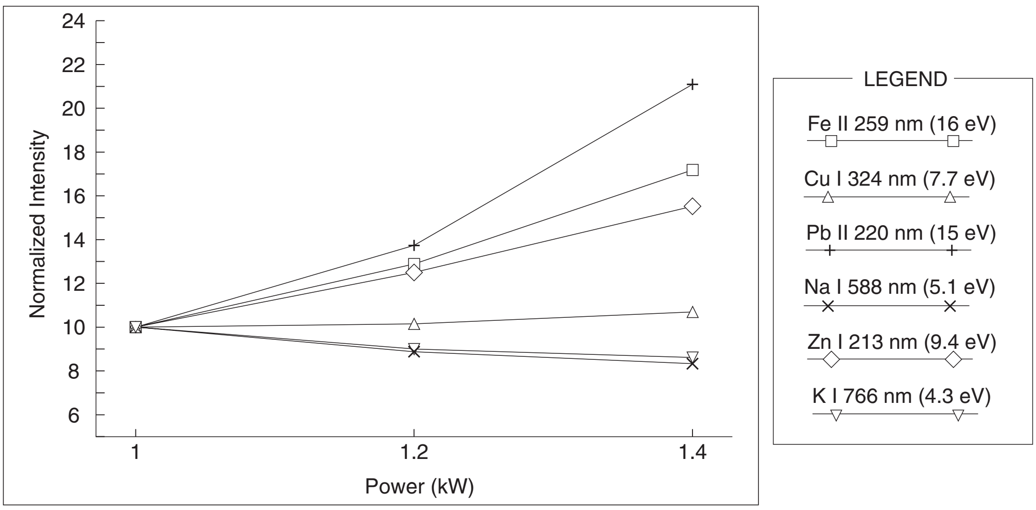


***Figure 7*** *Normalized analyte intensity as a function of RF power*

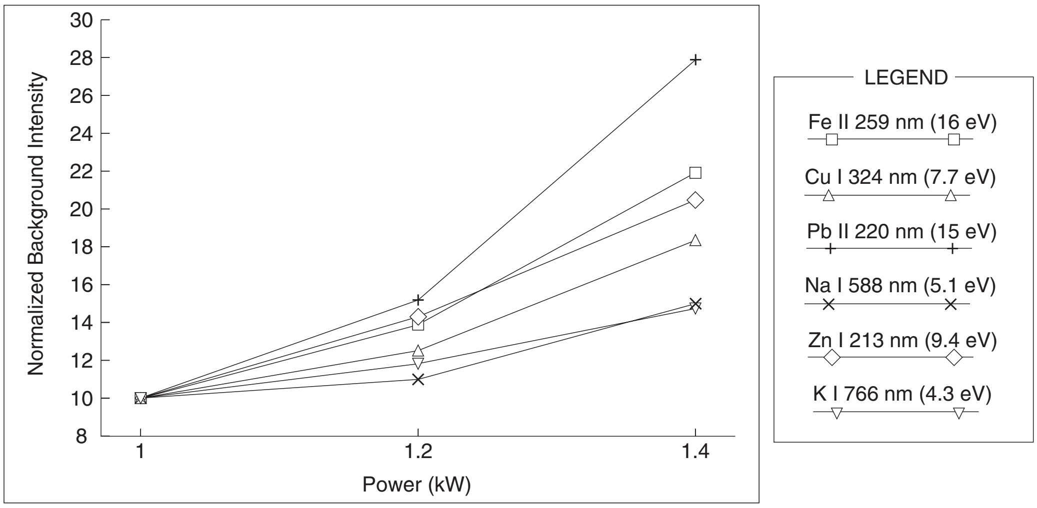


***Figure 8*** *Normalized background intensity as a function of RF power*

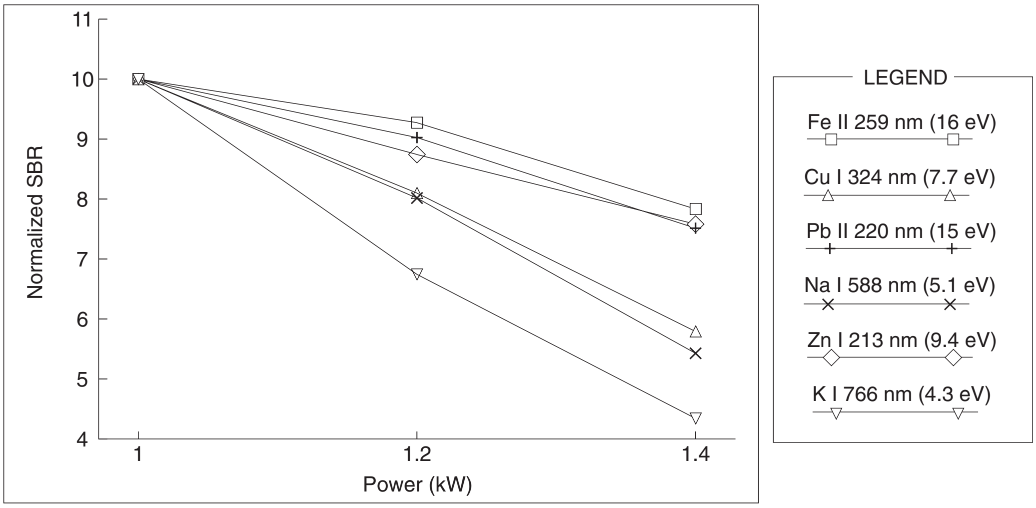


***Figure 9*** *Normalized signal-to-background ratio (SBR) as a function of RF power*

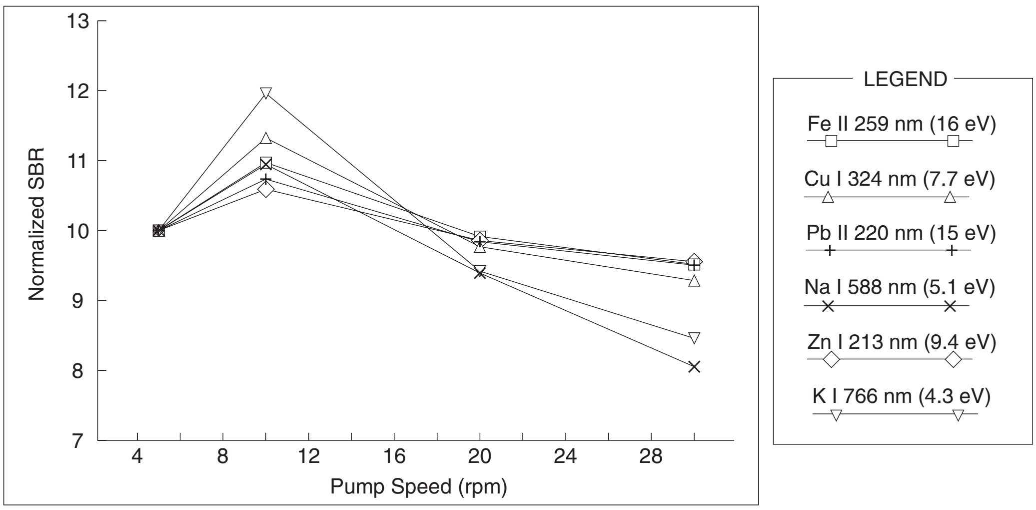


***Figure 10*** *Normalized signal-to-background ratio as a function of pump speed*

## The Effect of Plasma Viewing Height

The behaviour of hard and soft wavelengths as a function of the nebulizer gas flow rate has been shown to be dependent on the energy of the plasma. Since the plasma has a temperature gradient, a similar trend could be expected as a function of viewing height.

Figure 4 shows the intensity of the different wavelengths as a function of viewing height. The maximum intensity of soft lines (Na and K) occurs at low heights, corresponding to the low-energy part of the plasma. The maximum intensity for hard wavelengths (Fe and Pb) occurs at higher viewing heights, corresponding to the high-energy part of the plasma. Figure 5 shows the background levels as a function of viewing height. The background intensity at low heights results from continuous emission from the annulus, which decreases with increased height.

The signal-to-background ratio as a function of the viewing height is shown in Figure 6. Although the background levels are higher at lower heights, the significant increase in intensity for soft wavelengths (Na and K) at lower heights produces the best signal-to-background ratios low in the plasma. Conversely, hard wavelengths show better ratios in the high-energy part of the plasma.

## The Effect of Power Level

Power levels are critical when establishing optimum operating conditions. Higher power generates high temperature plasma conditions and with increased power levels, should lead to increases in intensity for hard wavelengths (Fe and Pb). At lower power, with lower energy conditions, soft wavelengths (Na and K) would be expected to be more intense. Figure 7 shows the intensity measurements as a function of the RF power level for the six lines studied and confirms this expectation.

Background measurements as a function of power levels are shown in Figure 8. The background intensity rises with increased power levels due to the high energy of the plasma at higher power levels. This rise indicates that the monitoring of background signal is important. Depending on the wavelength, an increase in the total signal with higher power may be due only to an increase in the background levels, rather than an increase in analyte signal.

Figure 9 shows that the effect on the signal-to-background ratio is the same for both soft and hard wavelengths as a result of the higher background levels found at higher powers.

As the background level increases more rapidly with power than the analyte intensity, the best signal-to-background ratio is found at lower power for all wavelengths. However, there is a lower practical limit, dictated by the plasma stability. For aqueous solutions, the Integra XL is typically run at 1 kW, whereas for organic solvents 1.3 kW is typical.

### The Effect of Pump Speed

Nebulizer efficiency is critical to sensitivity and precision of analysis. The pump speed affects the volume of the aerosol and the efficiency of nebulization. If the sample delivery rate is too high, this may increase the formation of large droplets in the spray chamber, resulting in an increase in background level. Therefore, it is important to optimize the pump speed on signal-to-background ratio.

Figure 10 shows the behaviour of the signal-to-background ratio for the six analytical lines, as a function of pump speed. This figure shows that optimum pump speed is dependent on the nebulizer and sample matrix and independent of the wavelength. Once the optimum pump speed has been determined for a particular nebulizer and sample matrix, it does not have to be varied on an element-by-element basis. However, the optimum pump rate should be verified when the nebulizer or sample matrix has changed.

## Summary

Optimizing on signal intensity is sufficient for analysing high concentrations as the background signal is insignificant compared to the very high analyte signal. However, for analysis of low concentrations where the background signal contributes significantly to the total signal, optimization should be based on the maximum signal-to-background ratio.

When establishing optimum operating conditions for a particular application, it is important to note that both soft and hard wavelengths require a minimum of two different sets of operating conditions.

A low-energy plasma provides optimum operating conditions for soft wavelengths. Setting high nebulizer gas flows and measuring the emission low in the plasma at low power will achieve the low-energy conditions appropriate for soft wavelengths. Low power also suits the hard wavelengths. However, to generate the high-energy plasma conditions that are optimum for the hard wavelengths, a low nebulizer gas flow and a high viewing height are also necessary.

### The Effect of Compromised Operating Conditions

The six analytical wavelengths were analyzed using two sets of operating conditions, one set optimized for the soft wavelengths (low-energy conditions) and the other optimized for the hard wavelengths (high-energy conditions). The two sets of conditions were achieved by changing the nebulizer gas flow rate and the viewing height. All other parameters were identical (see Table 2).

**Table 2. Operating conditions for low-energy and high-energy plasmas**

| | Low Energy | High Energy |
|---|---|---|
| Nebulizer Gas (L/min) | 0.8 | 0.5 |
| Viewing Height (mm) | 4 | 10 |
| Power (kW) | 1.0 | 1.0 |
| Plasma Gas (L/min) | 10 | 10 |
| Auxiliary Gas (L/min) | 0.4 | 0.4 |
| Pump Rate (rpm) | 15 | 15 |
| PMT (V) | 550 | 550 |

The results of these replicate analyses for the Pb 220.353 nm line, the Zn 213.856 nm line and K 766.490 nm line, for the two sets of conditions, are shown in Table 3.

**Table 3. Precision and accuracy at low-energy and high-energy conditions for three representative lines**

| | Typical Accuracy (Relative % ± 2SD | | Typical Precision %RSD ± 2SD | |
|---|---|---|---|---|
| | Low Energy | High Energy | Low Energy | High Energy |
| PbII 220 nm (15 eV) | 100 ± 3 | 100 ± 1 | 1.5 ± 0.4 | 0.6 ± 0.2 |
| ZnI 213 nm (9.4 eV) | 100 ± 1 | 100 ± 1 | 0.8 ± 0.2 | 0.4 ± 0.3 |
| KI 766 nm (4.3 eV) | 100 ± 2 | 100 ± 10 | 0.4 ± 0.2 | 1.1 ± 0.6 |

The accuracy of the analysis of the hard Pb wavelength was better under high-energy conditions. By contrast, the accuracy of the analysis of the soft K wavelength was better under low-energy conditions. In both cases, the results were the same for precision.

Interestingly, the Zn atomic wavelength, with an intermediate ionization potential (9.4 eV compared to 15 eV for Pb and 4.3 eV for K) shows similar accuracy when measured under both low- and high-energy conditions. This suggests that the Zn 213.856 nm line, unlike the Pb 220.353 nm line and the K 766.490 nm line, is not as sensitive to plasma conditions.

## Conclusion

In conclusion, the best accuracy and precision for most wavelengths can only be achieved under operating conditions optimized for individual wavelengths. The choice of operating conditions for a particular analysis will depend largely on which aspect of the analysis is most critical.

If all the elements in the analysis are critical, determining the optimum conditions for each elemental wavelength will be necessary. This is a time consuming exercise for method development and will affect the speed of analysis, as additional time will be required to change the operating conditions and allow them to stabilize for each wavelength.

One alternative is to optimize the critical element in the sample and analyze the remaining elements under the same conditions. This may lead to compromises, but these compromises will be on the less critical elements. Another alternative is to select operating conditions optimized for the element present in the lowest concentration. These conditions will allow that element to be analyzed with the best accuracy and precision, with compromises being made on elements present in higher concentrations.

Finally, if the sample workload permits, the wavelengths can be grouped into hard and soft wavelengths and set up in separate applications, one optimized for low-energy plasma conditions and the other optimized for high-energy plasma conditions.

As the Integra XL ICP-OES offers total computer control of all operating parameters, the optimization of analytical performance is simple and rapid. Combined with the ability to save and recall individual sets of operating parameters optimized for individual applications, this ensures reproducibility when changing operating conditions.

***References***

1. Montaser, A. and Golightly, D.W., Eds. Inductively Coupled Plasmas in Analytical Atomic Spectrometry, VCH Inc., New York (1987).
2. Boumans, P.W.J.M., Ed. Inductively Coupled Plasma Emission Spectroscopy, Part I, Methodology, Instrumentation and Performance. John Wiley and Sons, Inc., New York (1987).

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