

ICP-Optical Emission Spectroscopy

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Using Multicomponent Spectral Fitting to Resolve Difficult Interferences in Metallurgical Samples with the Avio 550 Max ICP-OES

Introduction

For the determination of trace elements in metallurgical matrices, ICP-OES is a commonly-used technique due to its ability to handle high levels

of dissolved solids without the need for special sample introduction components or matrix separation schemes. The significance is that sample preparation does not have to involve large dilution factors, meaning that analyte levels introduced to the instrument are not greatly affected by dilutions.

Despite this advantage, the analysis of trace metals in metallurgical matrices also presents a challenge for ICP-OES: spectral interferences. Many elements have a large number of emission lines (i.e. approximately 20,000 for iron), which increases the potential for spectral interferences. This effect is compounded in metallurgical samples, where the matrix element(s) are present at high levels due to the minimal dilutions used.

While several methodologies exist to deal with spectral interferences, PerkinElmer's exclusive Multicomponent Spectral Fitting (MSF) algorithm is one of the most robust and easiest to work with. MSF is described in detail elsewhere¹, but, briefly, the software builds a multiple least squares model from known blank, analyte, and interference spectra, which allows for the deconvolution of spectra, yielding interference-free peaks. The robustness of MSF lies in the fact that it does not rely on setting background points or on only a limited number of data points; instead, MSF incorporates all of the spectral information available.

This work describes the analysis of a challenging metallurgical sample with PerkinElmer's Avio® 550 Max fully simultaneous ICP optical emission spectrometer (ICP-OES) using MSF to obtain accurate results.

Experimental

Samples and Sample Preparation

The sample was composed of 7500 mg/L Fe, 1500 mg/L Cr, and 1000 mg/L Ni in 16% aqua regia (v/v) and analyzed without dilution. The total dissolved solids content entering the instrument was 1% (10,000 mg/L). Measurements were made against external matrix-matched calibration curves composed of 0.02, 0.05, 0.1 mg/L standards prepared in 16% aqua regia; yttrium (Y) was used as an internal standard.

The MSF model was created using 2% HNO₃ (v/v) as a blank, 0.1 mg/L analytes in 2% HNO₃, and replicating the matrix as the interference (i.e. making a solution of 7500 mg/L Fe + 1500 mg/L Cr + 1000 mg/L Ni in 16% aqua regia from single-element standards).

Instrumental Conditions

All analyses were performed on an Avio 550 Max ICP-OES with Syngistix™ for ICP software, which has the unique ability to run analyte(s) in high, normal or low resolution modes. Specific instrumental parameters are shown in Table 1; the analytes and wavelengths are listed in Table 2. The standard sample introduction system was used, incorporating a SeaSpray™ nebulizer for enhanced sensitivity and compatibility with high-matrix samples. All analyses were performed in axial mode.

Results and Discussion

Initially, all analyses were done in high-resolution mode to resolve the spectral interferences. However, although adequate spectral resolution was achieved, the associated reduction in sensitivity did not allow for accurate measurements at the low concentration levels for analytes present in the sample. As a result, normal resolution was used in conjunction with MSF to resolve spectral interferences where they existed.

Figure 1 shows spectra for lanthanum (La) at 408.672 nm – an example of a wavelength which is adequately resolved without the use of MSF. The La peak appears between two matrix peaks: Ni and Fe. The sample, shown with the green plot, displays a small peak for La, corresponding to about 9 µg/L.

To confirm the identity of the La peak, La was analyzed in 2% HNO₃ (pink), as well as in the calibration standards (the 20 µg/L spectrum is shown in blue). Since all peaks align, this is confirmation that the peak is La.

Table 1. Avio 550 Max ICP-OES Instrumental Parameters and Conditions.

Parameter	Value
Nebulizer	SeaSpray™
Spray Chamber	Baffled glass cyclonic
RF Power	1500 W
Injector	2.0 mm alumina
Plasma Gas Flow	14 L/min
Aux. Gas Flow	0.4 L/min
Nebulizer Gas Flow	0.62 L/min
Torch Position	-4
Plasma View	Axial
Resolution	Normal
Sample Uptake Rate	1.50 mL/min
Sample Uptake Tubing	Black/Black (0.76 mm id), Viton
Drain Tubing	Red/Red (1.14 mm id), SolvaFlex
Replicates	3
Read Time	5 sec (min and max)

Table 2. Elements and Wavelengths.

Element	Wavelength (nm)
B	208.957
Ce	456.236
La	408.672
Nb	313.079
Nd	430.358
Sn	189.927
Zr	343.823

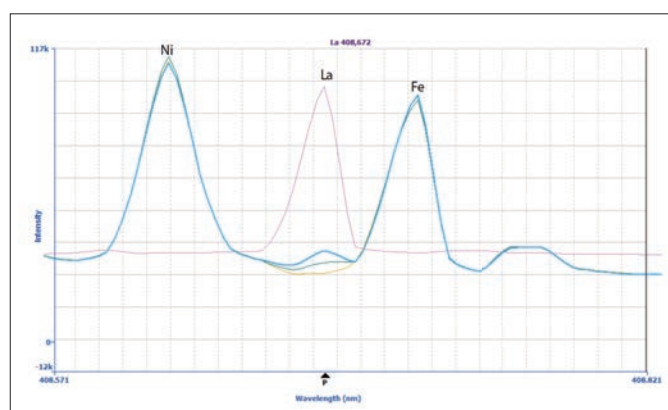


Figure 1. Spectra of La 408.672 nm in the sample (green), 20 µg/L La spike in the sample (blue), 100 µg/L La in 2% HNO₃ (pink), and a matrix blank (yellow).

The power of MSF in resolving interferences can clearly be seen when looking at zirconium (Zr) at 343.823 nm, as shown in Figures 2 and 3. In Figure 2, the spectra of the matrix blank (yellow), matrix blank plus 20 µg/L spike (blue), sample (green), and 100 µg/L Zr in 2% HNO₃ (pink) are shown. There is little difference in the spectra of matrix blank, 20 µg/L spike, and sample, both in peak shape and intensity. However, the peak shape of the Zr peak without the matrix (pink) differs from the peak shape of the other three spectra. This difference in peak shape indicates the presence of an interference originating from the matrix. Upon closer inspection, Fe has an emission line very close to Zr (Fe = 343.831 nm; Zr = 343.823 nm) which distorts the peak originating from the matrix.

From these spectra, in Figure 2, it appears that Zr cannot be accurately measured in the presence of Fe. However, by applying MSF, the interfering peaks are removed, and the Zr peak is clearly seen, shown in Figure 3. In Figure 3a, the blue spectrum is the sample without MSF applied, while the pink spectrum results from the application of MSF. To confirm that the peak in the pink spectrum in Figure 3a is really Zr, the sample was spiked with 100 µg/L of Zr and analyzed again with MSF applied. As seen in Figure 3b, the pink peak is larger, confirming the presence of additional Zr.

With the MSF model established and applied, the sample was analyzed along with a 100 µg/L analyte spike. The results (Table 3) show all spike recoveries are within 15% of the true values, indicating accurate results.

Conclusions

This work has demonstrated the ability of PerkinElmer's Avio 550 Max fully simultaneous ICP-OES to resolve challenging interferences in a metallurgical sample using Multicomponent Spectral Fitting (MSF). Taking advantage of MSF allows samples to be analyzed in normal resolution mode, thereby not losing intensity at the expense of resolution. With metallurgical samples, there are a limited number of matrix components, but they are present at high levels, which lead to numerous spectral interferences. By applying MSF, most interferences can be resolved, making MSF a valuable tool for the analysis of impurities in metals and alloys.

References

1. "Multicomponent Spectral Fitting", Technical Note, PerkinElmer Inc., 2016.

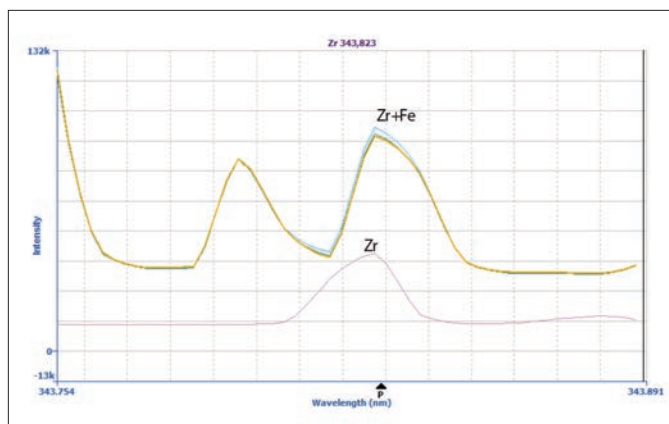


Figure 2. Spectra of Zr 343.823 nm in the sample (green), 20 µg/L Zr spike in the sample (blue), matrix blank (yellow), and 100 µg/L Zr in 2% HNO₃ (pink).

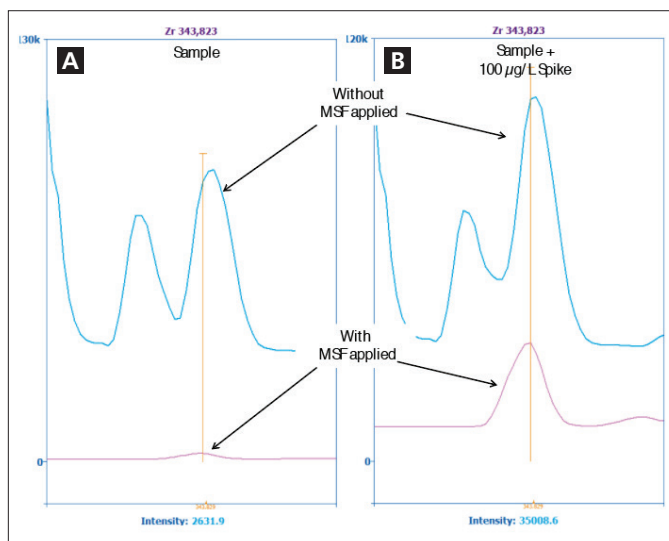


Figure 3. Spectra of Zr 343.823 nm in the sample (A) and in the sample spiked with 100 µg/L Zr (B) without MSF applied (blue) and with MSF applied (pink).

Table 3. Spike Recovery Results.

Element	Sample (µg/L)	Sample + Spike (µg/L)	% Recovery
B	4.34	101	97
Ce	9.78	112	102
La	9.82	113	103
Nb	5.07	110	105
Nd	6.69	111	104
Sn	0.9	109	108
Zr	11.3	111	100

Consumables Used

Component	Part Number
Sample Uptake Tubing, Black/Black (0.76 mm id), PVC	N0777043 (flared) 09908587 (non-flared)
Drain Tubing, Red/Red (1.14 mm id), PVC	09908585
SeaSpray™ Nebulizer	N0775345
Boron Standard, 1000 mg/L	N9300106 (125 mL) N9303760 (500 mL)
Cerium Standard, 1000 mg/L	N9303765 (125 mL) N9300110 (500 mL)
Chromium Standard, 10000 mg/L	N9304309 (125 mL) N9304311 (500 mL)
Iron Standard, 10000 mg/L	N9304113 (125 mL) N93007117 (500 mL)
Lanthanum Standard, 1000 mg/L	N9303780 (125 mL) N9300127 (500 mL)

Component	Part Number
Neodymium Standard, 1000 mg/L	N9303787 (125 mL) N9300135 (500 mL)
Nickel Standard, 10000 mg/L	N9304117 (125 mL) N9304116 (500 mL)
Niobium Standard, 1000 mg/L	N9303786 (125 mL) N9300137 (500 mL)
Tin Standard, 1000 mg/L	N9303801 (125 mL) N9300161 (500 mL)
Zirconium Standard, 1000 mg/L	N9303812 (125 mL) N9300169 (500 mL)
Autosampler Tubes	B0193233 (15 mL) B0193234 (50 mL)