

# Laboratory Products Focus

## Use of Innovative Software for Line Selection in Steel Analysis Using High Resolution ICP-AES

*The analysis of complex matrices, containing many elements and possibly line-rich elements, often requires high resolution because of the increased risk of spectral interferences. ICP-AES using a monochromator and photomultiplier tube based detection are the most suitable systems for such analysis because they offer the highest resolution achievable, allowing the analysis of many elements, even in complex matrices, using the primary most sensitive lines for an element.*

*However, line selection remains a crucial step as it can greatly affect the accuracy of the results. The analyst should conduct this step with great care, even if it is long and time-consuming. To assist the analyst in completing this step, HORIBA Scientific developed CLIP, Collection of Line Intensity Profiles, which will suggest the most appropriate lines for a given analysis, which provide adequate sensitivity and freedom from spectral interferences.*

*CLIP is a versatile tool that can be used with all of HORIBA Scientific high resolution ICP-AES to greatly shorten the line selection step, saving time for the laboratory and the analyst.*



Figure 1. ULTIMA 2 Spectrometer

### Author Details:

Matthieu Chausseau,  
Odile Hirsch and George Thomas  
Horiba Jobin Yvon  
Email: matthieu.chausseau@horiba.com

### CLIP: LINE SELECTION TOOL

The development of CLIP was possible thanks to the unique and proprietary ICP-dedicated database  $S^3$ -base. This database, initially built using the CCD based detection HORIBA Scientific model ACTIVA-M ICP-AES, contains more than 50,000 lines identified through real ICP experiments and assigned with the corresponding spectroscopic data (wavelength, ionization state, limit of detection...). This database, already described in the literature, is widely used on ACTIVA-M ICP-AES instruments.

To extend the use of the information contained in the  $S^3$ -base with high resolution ICP-AES, the detection limits have been updated and a mathematical algorithm has been developed to perform the profile calculation for each line. This algorithm considers the Doppler effect on line broadening based on the plasma temperature and the effect on line width of the focal length, the grating, measurement order and the entrance and exit slits of the spectrometer.

Calculations of theoretical profiles are made according to the expected elements and their concentration range as provided by the analyst. This information may already be known by the analyst or it may be determined by a semi-quantitative analysis. Semi-quantitative analysis can be performed on Horiba Scientific high resolution ICP-AES through a full spectrum acquisition thanks to the patented High Dynamic Detection feature.

Once the list of elements and concentration ranges are provided, CLIP starts the calculations and displays the profiles for each analyte. For a given analyte line, the lowest expected concentration is displayed along with the highest concentration expected for the other elements. The most pessimistic conditions are thus displayed and the analyst can validate or reject analyte lines. As the spectra can be displayed for each slit combination, validation can also be performed for the most appropriate combination.

### APPLICATION

An ULTIMA 2, (Figure 1), one meter focal length ICP-AES equipped with a 2400 g/mm grating optimised for first and second order measurements was used. The resolution achieved was less than 5pm for wavelengths in the 160-320nm second order range and less than 10pm for wavelengths higher than 320nm using the first order. This instrument is particularly well suited for the determination of trace elements in steels. Because of the high amounts of line-rich elements such as Iron, Chromium and Nickel over the wavelength range used with ICP-AES, the risk of spectral overlap is greatly increased. Using the high resolution ULTIMA 2 ICP-AES was very beneficial to minimise spectral interferences.

As the composition of steel is quite well known, the expected concentration range can be easily provided by the analyst. CLIP was used to determine the adequate wavelengths according to this information.

The expected elements, both analytes and major elements that may induce spectral interferences, as well as their expected concentration ranges were those specified in Table 1. Figures 2, 3 and 4 illustrate the benefits of the interactive display, thanks to the information of the  $S^3$ -base.

According to the profiles of Aluminum lines shown in Figure 2, it is obvious that Al 167.020 nm, Al 396.152 nm and Al 394.401 nm lines cannot be used due to spectral interferences from the concomitant elements Iron, Vanadium, Chromium, Molybdenum and Manganese. According to the profile at 237.312 nm (Figure 3), this line can be validated thanks to the high resolution of the system.

The same procedure can be followed for the selection of Phosphorus lines. According to the profiles of Figure 4, the two most sensitive lines (P 177.440 nm and P 213.618 nm) are not suitable for the analysis due to spectral interferences and the line at 178.221 nm has to be used. The spectral interference of Copper on Phosphorus is well known in ICP-AES but CLIP is not only displaying the spectral interference but truly helping the analyst in finding an adequate line for the Phosphorus determination, free from spectral interference and with adequate sensitivity.

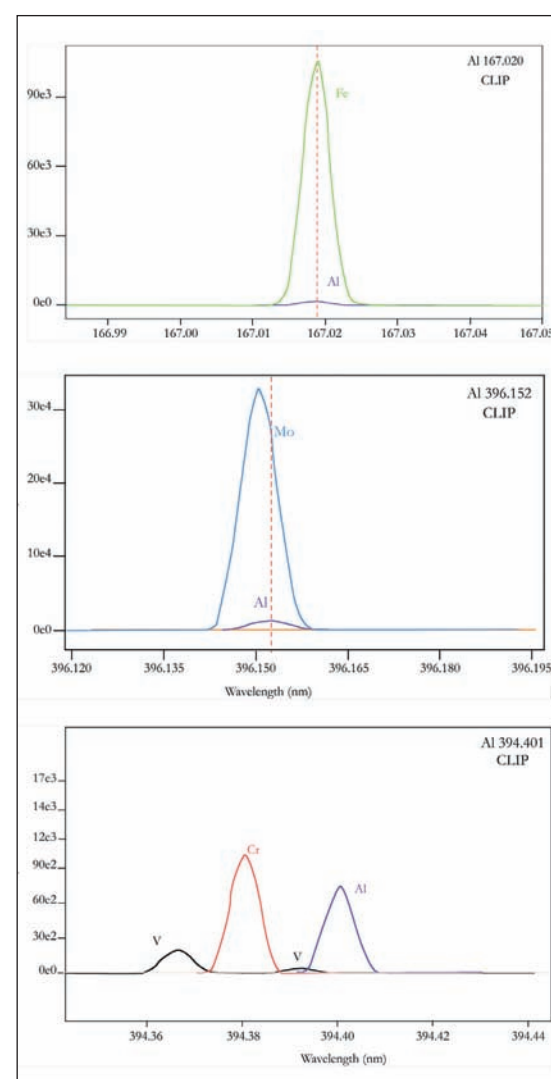


Figure 2. CLIP Profiles for Aluminum lines

The spectral interferences on P 177.440 and P 213.618 nm do not occur exactly at the wavelength of the emission line but lines of the interfering elements are very close to them. As CLIP calculates profiles with the assumption of a Gaussian peak shape, experimental profiles will exhibit an increased magnitude for the line wings. The most sensitive lines of Phosphorus will then suffer from spectral interference due to the line wings of the interfering elements.

Line selection was performed on several elements in the same way. Lines were then selected according to the profiles displayed with CLIP for the following elements: Cobalt, Manganese, Iron, Copper, Chromium, Molybdenum, Niobium, Nickel, Silicon, Tin and Vanadium. The lines selected are given in Table 2. To achieve the best compromise between sensitivity and resolution, an entrance slit of 20  $\mu\text{m}$  was used along with an exit slit of 15  $\mu\text{m}$ .

### VALUE OF CLIP

The time spent on the acquisition of the profiles for line selection is significantly reduced thanks to CLIP. The analyst can select and validate lines that are sensitive enough and free from spectral interferences without any experiment and sample preparation. The same procedure without CLIP requires the preparation of many synthetic standards and the acquisition of many profiles for all the analyte wavelengths to check for spectral interferences. For the determination of 10 elements in steel, the analyst has to prepare at least 10 standards and to perform at least 10 profiles for each analyte wavelength leading to an extended analysis time on the ICP-AES whereas CLIP gives the answer in a few minutes. A filtering algorithm can also be applied to automatically eliminate the lines suffering from spectral interference so only the relevant lines are displayed on the main screen, reducing the time needed to validate the lines.

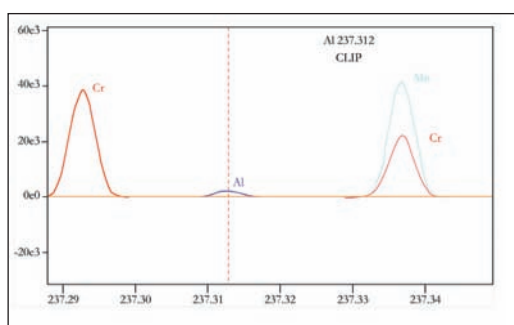


Figure 3. CLIP Profile for Al 237.312 nm line

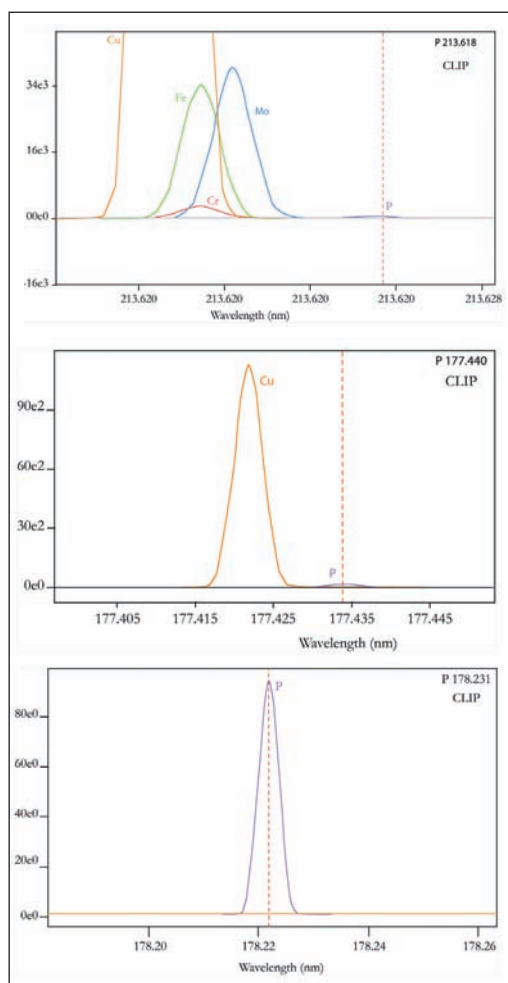


Figure 4. CLIP Profiles for Phosphorus lines

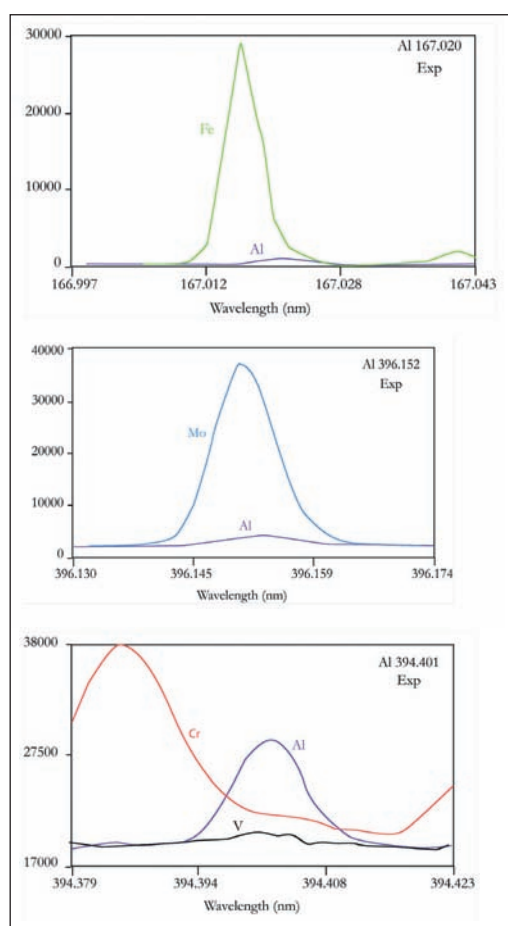


Figure 5. Experimental profiles for Aluminum lines

At any time, the analyst is able to visualise the profiles for all the lines available in the S<sup>3</sup>-base for each element, making it possible to understand why some lines have been rejected. It is also possible to validate a line that was not initially suggested by CLIP.

## LINE PROFILES: THEORY AND EXPERIMENT

Experimental profiles were acquired and compared to theoretical profiles for Aluminum and Phosphorus for many interfered wavelengths and are displayed in Figures 5 and 6, respectively.

A good agreement was found between theory and experiment. As mentioned above, it may be seen that the magnitude of the wings is slightly increased on experimental profiles compared to theoretical profiles (Figures 2 and 4). This difference between experiment and theory is due to the fact that only a Gaussian shape of the lines was assumed for the profiles calculation, while the Lorentzian shape (predominant on the line wings) was not applied because it differs for each line. During line validation, the analyst has to keep in mind that the lines may not be fully separated due to their wings.

Table 1. Elements and expected concentration range

Set Elements concentration limits

Element	LCL	UCL	Unit
Al	0.1	2.5	mg/l
Co	0.2	5	mg/l
Cr	2	250	mg/l
Cu	0.2	25	mg/l
Fe	400	1000	mg/l
Mn	4	25	mg/l
Mo	0.05	50	mg/l
Nb	0.03	5	mg/l
Ni	1	400	mg/l
P	0.05	1	mg/l
Si	2	30	mg/l
Sn	0.01	1	mg/l
V	0.2	5	mg/l

Table 2. Selected lines

Element	Wavelength (nm)
Al	237.312
Co	231.160
Cr	267.716
Cu	221.458
Fe	259.940
Mn	257.610
Mo	202.030 and 204.598
Ni	231.604
P	178.229
Si	288.158
Sn	189.930
V	292.402

Table 3: Operating conditions

Parameter	Specification
Power	1200W
Plasma gas	12 L/min
Auxiliary gas	0 L/min
Sheath gas	0.2 L/min
Nebulizer gas	0.7 L/min (2.9 bars)
Sample uptake	1 mL/min
Sample introduction system	Parallel flow nebulizer in Teflon
Torch	Cyclonic spray chamber Fully demountable torch with 3 mm i.d. alumina injector
Plasma view	Radial with Total Plasma View

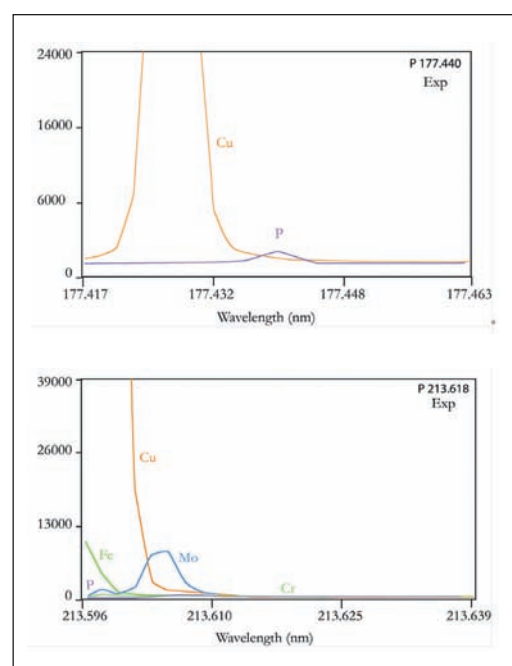


Figure 6. Experimental profiles for Phosphorus lines.

Table 4. Measured concentrations, Certified Values and Recoveries

Certified Reference Material 295-1			
Line	Conc (%)	Certified Value (%)	Recovery (%)
Al 237.312	0.0213	0.0203	105
Co 231.160	0.043	0.045	95
Cr 267.716	19.89	19.51	102
Cu 221.458	1.485	1.481	100
Fe 259.940	47.23	48.36	98
Mn 257.610	1.712	1.758	97
Mo 202.030	3.952	3.996	99
Mo 204.598	3.907	3.996	98
Ni 231.604	24.1	24.4	99
P 178.229	0.0154	0.0157	98
Si 288.158	0.423	0.418	101
Sn 189.930	0.0025	0.0025	99
V 292.402	0.0430	0.0456	94

Certified Reference Material 184-1			
Line	Conc (%)	Certified Value (%)	Recovery (%)
Al 237.312	0.0053	0.0052	102
Co 231.160	0.055	0.056	98
Cr 267.716	1.339	1.287	104
Cu 221.458	0.06	0.06	97
Mn 257.610	0.525	0.528	100
Mo 202.030	0.475	0.457	104
Mo 204.598	0.468	0.457	102
Ni 231.604	3.360	3.318	101
P 178.229	0.0054	0.0056	97
Si 288.158	0.221	0.218	102
Sn 189.930	0.0044	0.0044	100
V 292.402	0.112	0.108	103

Certified Reference Material 182-1			
Line	Conc (%)	Certified Value (%)	Recovery (%)
Al 237.312	0.00194	0.0203	96
Cr 267.716	0.6100	0.5910	103
Cu 221.458	0.1470	0.1410	104
Mn 257.610	0.3820	0.3890	98
Ni 231.604	0.1511	0.1522	99
P 178.229	0.0088	0.0090	98
Si 288.158	0.3803	0.3680	103
Sn 189.930	0.0132	0.0135	98
V 292.402	0.1827	0.1770	103

## ANALYTICAL RESULTS

The accuracy of the method developed was checked using Certified Reference Materials, B295-1, B184-1 and B182-1 from the European Committee for Iron and Steel Standardisation. These materials were digested by weighing approximately 0.5 g of sample and using HCl, HNO<sub>3</sub> and HF with final concentrations of 2%, 0.4% and 0.4%, respectively. The final volume of sample was 500mL. The resulting samples were analysed on the ULTIMA 2 using the validated lines. The calibration was done using synthetic standards and a matrix matching technique.

The plasma parameters were optimised to obtain a good sensitivity along with good robustness of the plasma. All these parameters are given in Table 3. The results obtained are given in Table 4 as well as the certified concentrations and the recoveries obtained. Excellent recoveries were obtained for all the elements determined, proving the reliability of the information provided by the S<sup>3</sup>-base. The unmatched sensitivity of the ULTIMA 2 with its unique vertical torch and the Total Plasma View concept allow the determination of both major and trace elements on a single run using primary lines for most of the elements and ensuring perfect stability, even for a matrix as complex as a steel.

## CONCLUSION

The use of CLIP reduces the time needed for method development by displaying theoretical profiles for each analyte wavelength. The reliability of the display is ensured thanks to the information provided by the ICP-based spectral database, S<sup>3</sup>-base. A good agreement was found between theoretical and experimental profiles for the complex steel matrix, proving the reliability of the information provided. The experimental profiles and the results obtained on the Certified Reference Material using the wavelengths selected with CLIP show the reliability in the wavelength choice as well as the performance offered by the ULTIMA 2, even for complex matrices such as steels.