



## Application Note # Combined SEM techniques 01

# Quantification of steels and alloys using a dual source multidetector system on SEM

The accurate and precise analysis of steels and alloys is essential for understanding their mechanical and thermal properties. Such materials often have a wide range of elements at various concentrations down to trace ppm levels. Accordingly, it is not possible to determine the concentrations of all elements with a standard scanning electron microscope (SEM) and an energy dispersive spectrometer (EDS).

Specifically, the analysis of steels and alloys is challenging due to:

- The presence of low and high atomic number elements
- Concentration ranges from major elements (wt%) to trace elements (ppm)
- Elemental X-ray lines that overlap, especially in the low energy range
- Elements with high energy X-ray lines.

Therefore, the addition of a micro X-ray (micro-XRF) source and a wavelength dispersive spectrometer (WDS) will enhance the analytical capability of the SEM to use the advantages of each component.

In this application note the use of two excitation sources (electrons and X-rays) utilized in combination with two possible detectors (EDS or WDS) will be discussed.

### Sample

This application note presents the results for combined SEM-based EDS, WDS, and micro-XRF on SEM analyses of a range of standard steel samples with varying elemental concentrations, specifically 15 ARMI (Analytical Reference Materials International) steels with known certified compositions (see Fig. 1).

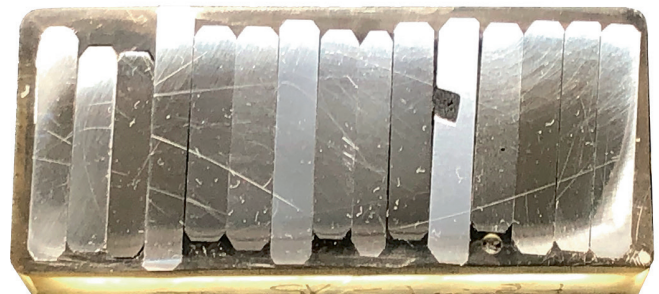


Fig. 1 15 ARMI steel samples with known certified compositions used in this study.

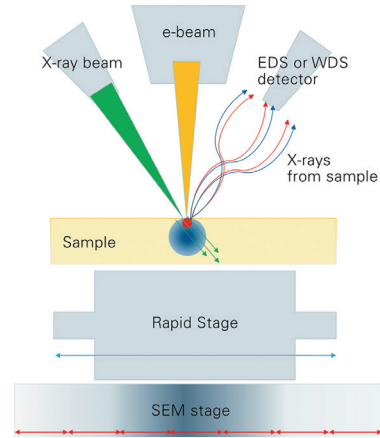
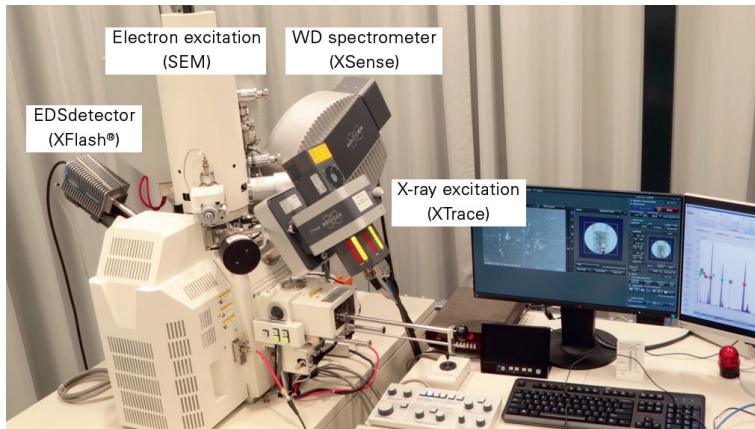


Fig. 2 Left: SEM with an X-ray source and a WD spectrometer attached in addition to the EDS detector. Right: Schematic of the analytical sources and detectors. Both excitation modes generate different excitation volumes, the resultant X-rays are detected with an EDS or WDS detector (red from e-beam excitation and blue from X-ray excitation).

### Measurement conditions

All results were obtained using the following setup (Fig. 2):

- EDS: QUANTAX EDS system with XFlash® 6 I 60, a 60 mm<sup>2</sup> active area silicon drift detector (SDD) with an energy resolution of 126 eV for Mn K $\alpha$ , mounted on SEM.
- Micro-XRF on SEM: QUANTAX Micro-XRF system equipped with XTrace (mounted on the same SEM), the focused X-ray photon source with a Rh anode, and the above described XFlash® EDS detector.
- WDS: QUANTAX WDS system equipped with XSense (mounted on the same SEM), the parallel beam spectrometer with up to six analyzer crystals and a pressure-controlled FPC dedicated to high efficiency in the low X-ray energy range.

### The strength of each system

Table 1 shows the different capabilities for each of the various components and the benefits they bring to an analysis, in this case specifically related to quantification. It should be noted that the analysed volume is different for the electron and X-ray source excitation (see Fig. 2 right), and this must be considered when doing a combined quantification. That is, the sample is assumed to be homogeneous over the interaction volume of both excitation sources. In the case of steel analysis this may be problematic when trying to quantify small micrometer sized inclusions.

Micro-XRF on SEM can detect higher energy lines, thus improving accuracy for high-Z elements. On the other hand, WDS is especially sensitive for the light elements and low

Table 1 Comparison of various relevant parameters when using the EDS, WDS or Micro-XRF on SEM setup.

Parameter	EDS: e-beam excitation (QUANTAX EDS system)	WDS: e-beam excitation (QUANTAX WDS system)	Micro-XRF: X-ray beam excitation (QUANTAX Micro-XRF system)
Analyzed volume	Ø few µm Information depth: µm (primarily depending on electron energy)		Ø 15 - 30 µm Information depth: µm to mm (depending on analyzed element and matrix)
Detectable elements	Z ≥ 4 (beryllium)		Z ≥ 6 (carbon)
Energy range	K-L-M lines (up to 40 keV)	K-L-M lines (70 eV - 3.6 keV)	K-L-M lines (up to 40 keV)
Concentration range	down to 1000 ppm	down to 100 ppm	down to 10 ppm
Quantification	standardless + standard-based	standard-based	standardless + standard-based
Data collection	simultaneously	sequentially	simultaneously
Sample preparation	electrical conductivity (commonly carbon coating) and sample polishing required		electrical conductivity and sample polishing not required
Sample stress	heating due to absorbed electrons		minimal
Typical SEM beam current	variable	variable, > 10 nA	-

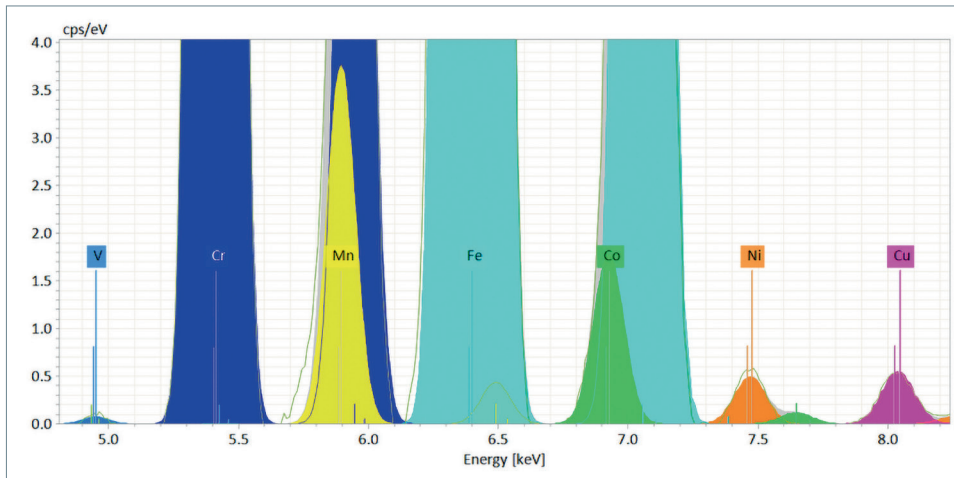


Fig. 3 Deconvolution of an EDS spectrum generated by micro-XRF showing the capability to correctly identify elements at low concentrations and with peak overlaps.

energy X-ray lines. Both the WDS and micro-XRF on SEM analysis have significantly lower detection limits when compared to standard EDS analysis, which generally has a lower limit of approximately 1000 ppm.

An important advantage of using EDS is that the measurement is simultaneous for all elements, whilst for the WDS the elements are collected sequentially. Accordingly, a quantified analysis will be improved when combining the benefits of all the aforementioned systems.

### EDS quantification

The major elements can be clearly identified, as well as some minor elements. These elements can be quantified using standardless or standard-based quantification routines. For the present study, standardless quantification with the PhiRhoZ matrix correction was used for all the major elements.

### Micro-XRF on SEM + EDS quantification

Quantification of micro-XRF results is using the standardless fundamental parameter (FP) method which is theoretically well understood and applicable to a wide range of matrices as described by Hascke and Boehm (2017). The accuracy of these results is increased when using a correction factor for each element based on the analysis of standards.

Fig. 3 shows the ability of the micro-XRF on SEM + EDS to correctly detect and deconvolute minor and trace elements in steel, and it is evident that the trace concentrations for high energy elements are detectable.

### WDS quantification

WDS quantification is standard-based. Concentration data is derived by comparison of net counts between the unknown (sample) and reference material (standards). As for any standard-based method, it is important to maintain identical conditions during measurement on sample and standard, including acceleration voltage (kV) and (source-specimen-detector) geometry. The latter is also the reason for the requirement of a flat and well-polished sample surface.

Since the beam current directly influences the generated X-ray intensity, it is important to record this factor during measurements. Matrix correction was done using the PhiRhoZ method. Standards for trace element quantification were pure metals (Si, Cu, Mo, W) or simple compounds ( $\text{Al}_2\text{O}_3$ , InP,  $\text{FeS}_2$ ).

WDS quantification can be combined with either standard-based or standardless EDS quantification. Fig. 4 shows certified nitrogen contents for 14 stainless-steel samples compared to quantification results determined by WDS.

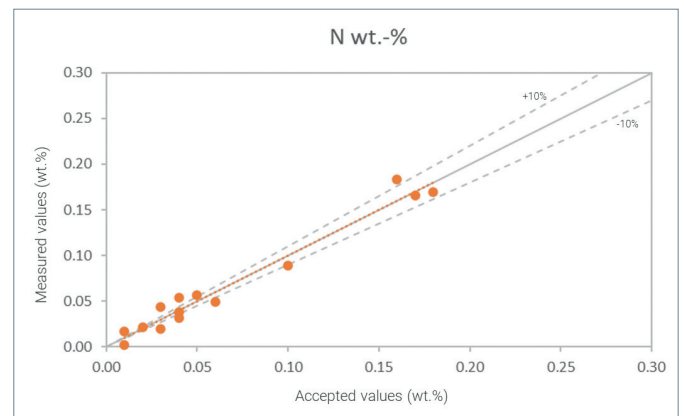


Fig. 4 Reconciliation data between measured WDS value and certified values for nitrogen in steels.

Table 2 Example of the combined quantification process for a steel sample. Color code: green = suitable data, light green = may be suitable when above trace element level, light grey = not determined (n.d.), light orange = reference values.

Step 1		Step 2		Step 3		Step 4		Reference	
Element	EDS	Element	Micro-XRF	Element	WDS	Element	Final	Certified	Element
C	n.d.	C	n.d.	C	≤ 0.36	C	≤ 0.36	0.05	C
N	n.d.	N	n.d.	N	0.02	N	0.02	0.02	N
Al	n.d.	Al	n.d.	Al	0.00	Al	0.00	0.00	Al
Si	0.36	Si	n.d.	Si	0.328	Si	0.35	0.36	Si
P	n.d.	P	n.d.	P	0.029	P	0.03	0.03	P
S	n.d.	S	n.d.	S	0.013	S	0.01	0.03	S
Ti	n.d.	Ti	0.002	Ti	n.d.	Ti	0.002	0.00	Ti
V	n.d.	V	0.059	V	n.d.	V	0.059	0.06	V
Cr	17.09	Cr	17.496	Cr	n.d.	Cr	17.41	17.30	Cr
Mn	1.92	Mn	1.788	Mn	n.d.	Mn	1.79	1.76	Mn
Fe	69.33	Fe	70.713	Fe	n.d.	Fe	69.40	69.33	Fe
Co	0.60	Co	0.154	Co	n.d.	Co	0.15	0.14	Co
Ni	8.86	Ni	9.012	Ni	n.d.	Ni	9.00	9.19	Ni
Cu	0.50	Cu	0.501	Cu	0.458	Cu	0.49	0.47	Cu
Nb	0.74	Nb	0.695	Nb	n.d.	Nb	0.70	0.72	Nb
Mo	0.44	Mo	0.448	Mo	0.393	Mo	0.45	0.44	Mo

## Combined Quantification

Combining the strengths of each of the three techniques provides the most robust quantification results for steel analyses. EDS is a fast and versatile method to determine all the major elements in the samples. The combination of micro-XRF and EDS, however, provides more precise data on transition metals and heavy elements due to its lower background and a quantification based on the high-energy X-ray lines. This is especially relevant for low concentration levels (trace elements). WDS contributes best data on light (C, N), relatively light (Al, Si, P) and overlapping elements (S).

Iterative steps towards a combined analysis approach are as follows: Quantification starts with primary EDS results (Step 1). Results for the high-Z elements generated by micro-XRF on SEM are determined in an iterative process on basis of the EDS data (Step 2). WDS quantification for selected elements is combined with one of the other techniques to cover the element inventory of the sample which is required for matrix correction calculations (Step 3). In a subsequent combination of the three data sets, most robust results are selected, and the matrix correction is recalculated to deliver the final quantification results (Step 4). All quantification results are shown in Table 2.

## Conclusion

Steel is a complex material with a wide range of elements and concentrations that cannot be characterized satisfactorily with a single analytical method only. Combining EDS, WDS and micro-XRF on SEM provide the unique possibility to quantify all the relevant element inventory with the best possible accuracy and precision. Only Bruker equipment facilitates the usage of EDS, WDS and micro-XRF systems on a single scanning electron microscope (SEM) for best possible microanalysis of single sample spots.

## References

Haschke, M. and Boehm, S.: Chapter One – Micro-XRF in Scanning Electron Microscopes, *Advances in Imaging and Electron Physics*, Elsevier (Editor P. Hawkes), Vol. 199, 2017, pages 1- 60, <https://doi.org/10.1016/bs.aiep.2017.01.001>

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