EDS

Comparison of standardless and standardbased quantification, using Cr-Ni-steel as an example

Application Note # EDS-01

Introduction

Precision and reliability of standardless and standard-based quantification are one of the most common issues in the evaluation of energy dispersive spectra.

The measurements discussed in this document relate to a Cr-Ni-steel sample, the composition of which was originally determined with XRF and S-OES. Steel analysis using EDS generally deals with calculating the content of elements in the intermediate atomic number range through evaluation of the K-lines of the X-ray spectrum. Two critical factors influence the accuracy of the quantification decisively:

1. Identification errors:
Apart from the main constituents iron, chromium and nickel Cr-Ni-steel may contain a number of elements, partially with a concentration of well below 1% – and therefore clearly close to the detection limits of an EDS analysis. Identification already may be problematic because of occurring peak overlaps (see next paragraph), and unidentified elements adversely influence quantification results.

2. Problems in peak deconvolution:
The intermediate atomic number range (24–28) exhibits overlaps of the Kß line of an element with the Kα line of the element with the next higher atomic number. In the case of steel this means Cr Kß overlaps with Mn Kα, Mn Kß with Fe Kα and so forth. Deconvolution errors therefore lead to calculation of an incorrect concentration of the elements in question.

Methods used

A Bruker QUANTAX system equipped with a 4th generation liquid nitrogen free XFlash® 4010 Detector (energy resolution 125 eV for manganese Kα) was used for spectra acquisition and evaluation. Spectra acquisition was performed under following conditions:

- Accelerating voltage: 20 kV
- Acquisition time: 500 s
- Input count rate: 3,000 cps

Acquired spectra were first evaluated standardless using the peak-to-background model (P/B) and subsequent ZAFcorrection. The results were used to select the appropriate standard from a range of available steel standards and quantitative evaluation through Φ(ρ,z)-correction was performed with it.

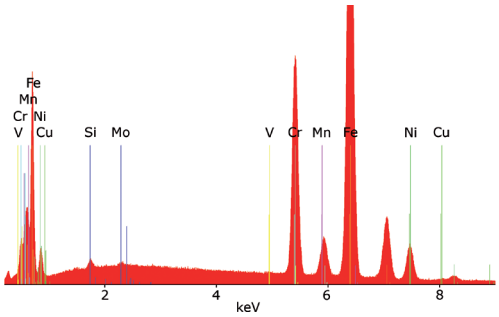

Figure 1
EDS spectrum at measurement point 4

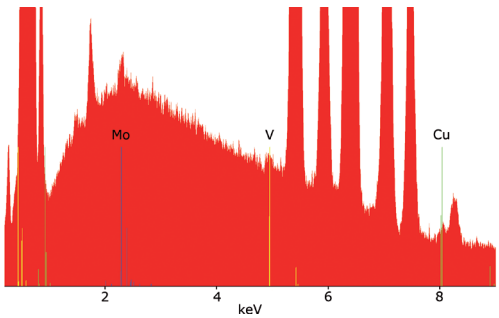

Figure 2
Enlarged representation of the spectrum in Figure 1

Results

Identification

An automatic peak identification could detect the following elements: Silicon, chromium, iron, nickel, manganese, copper, molybdenum and vanadium (Figure 1), the latter can only be seen in the enlarged spectrum (Figure 2).

Well separated peaks in a spectrum are detected during automatic identification if they exceed the detection limit, meaning they are significantly higher than the background. This is no longer possible in case of line overlaps. Here the type of peak overlap (superposition of different line series, Kß/Kα overlap) plays a decisive role in identification. In this case manganese was correctly identified as an additional element through the recognition of height deviation of the Cr Kα-peak in relation to Cr Kß from the theoreticallyexpected value. This method fails if the concentration of an element comes close to the detection limit. Additional elements can only be determined through evaluation of the results of a spectrum deconvolution. For this the acquired net count spectrum (black outline in Figure 3) is compared with the deconvolution results (colored peaks in Figure 3).

The acquired iron Kß-peak in Figure 3 shows a significant deficit on the low energy side compared to the deconvoluted peak (red), as

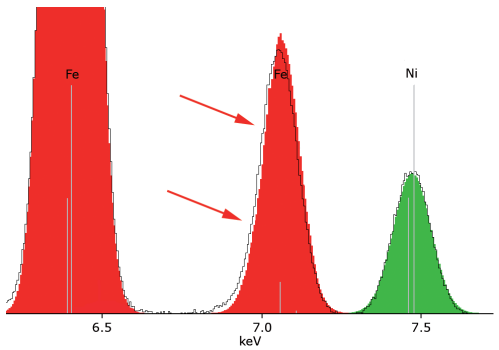

Figure 3
Deconvolution results without consideration of the element cobalt

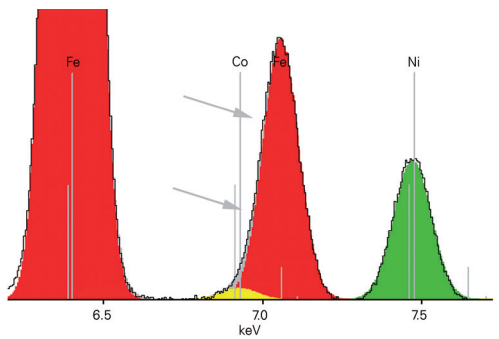

Figure 4
Deconvolution result under consideration of cobalt

well as a shift of the energetic peak position towards higher energies. The reason for this can only lie in the presence of an additional element, in this case cobalt. Inclusion of cobalt (yellow) as shown in Figure 4 leads to a perfect match of acquired spectrum and deconvolution result (the grey peak in the background is the sum of Fe Kß and Co Kα-peak deconvolution).

Quantitative Evaluation

An adequate standard for the standard-based analysis using Φ(ρ,z)-correction was selected according to the results of the standardless quantification (Table 1).

In case of the sample measured here the ideal condition of an available standard containing all relevant elements, with the exception of vanadium, existed. As can be seen in Table 2, the composition of this standard is very close to the standardless calculated values of the specimen. The lack of vanadium in this standard was considered in the subsequent standard-based evaluation through standardless quantification of this element.

The results of standardless and standard-based quantification (Table 1 and Table 3) are identical within the expected error limits, with the exception of cobalt. Therefore an additional standardless analysis was performed, calculating the cobalt content with a reference sample (Table 4).

Table 1
Standardless (P/B-ZAF) quantification

Spectra	Si	V	Cr	Mn	Fe	Co	Ni	Cu	Mo
Point 1	0.26	0.13	17.81	1.55	71.26	0.51	7.78	0.42	0.27
Point 2	0.26	0.11	17.36	1.58	71.31	0.71	8.09	0.31	0.27
Point 3	0.26	0.13	17.80	1.53	71.39	0.56	7.59	0.48	0.26
Point 4	0.28	0.12	18.00	1.55	71.22	0.47	7.48	0.57	0.31
Point 5	0.27	0.14	17.78	1.46	71.50	0.63	7.51	0.42	0.28
Point 6	0.26	0.13	17.97	1.55	71.25	0.56	7.61	0.39	0.29
Point 7	0.25	0.14	17.81	1.52	71.41	0.52	7.57	0.47	0.31
Point 8	0.29	0.15	17.41	1.56	71.26	0.62	8.04	0.38	0.29
Point 9	0.28	0.14	17.71	1.56	71.45	0.59	7.70	0.26	0.32
Point 10	0.27	0.12	17.91	1.54	71.15	0.50	7.64	0.54	0.33
Average	**0.27**	**0.13**	**17.75**	**1.54**	**71.32**	**0.57**	**7.70**	**0.42**	**0.29**
σ (±wt.%)	0.01	0.01	0.22	0.03	0.11	0.07	0.21	0.10	0.02

Table 2
Composition of the standard ACX-P07/97

Standard	N	Si	Cr	Mn	Fe	Co	Ni	Cu	Mo
AXC-P07/97	0.06	0.32	18.35	1.38	70.61	0.21	8.13	0.43	0.29

Table 3
Standard-based quantification (Φ(ρ,z)-correction)

Spectra	Si	V	Cr	Mn	Fe	Co	Ni	Cu	Mo
Point 1	0.32	0.12	18.22	1.52	70.78	0.11	8.26	0.38	0.29
Point 2	0.33	0.11	18.29	1.56	70.73	0.15	8.24	0.29	0.30
Point 3	0.31	0.13	18.24	1.50	71.02	0.12	7.99	0.42	0.27
Point 4	0.33	0.11	18.18	1.51	70.92	0.10	8.05	0.48	0.31
Point 5	0.33	0.13	18.27	1.44	71.12	0.14	7.90	0.37	0.30
Point 6	0.31	0.13	18.34	1.52	70.93	0.12	8.01	0.34	0.30
Point 7	0.30	0.14	18.25	1.49	71.04	0.11	7.95	0.40	0.32
Point 8	0.36	0.14	18.19	1.54	70.68	0.13	8.27	0.36	0.32
Point 9	0.34	0.13	18.33	1.54	70.97	0.13	7.99	0.25	0.34
Point 10	0.33	0.11	18.36	1.51	70.80	0.11	7.99	0.46	0.34
Average	**0.33**	**0.11**	**18.27**	**1.51**	**70.90**	**0.12**	**8.07**	**0.37**	**0.31**
σ (±wt.%)	0.02	0.01	0.06	0.03	0.15	0.01	0.14	0.07	0.02

Spectra	Si	V	Cr	Mn	Fe	Co	Ni	Cu	Mo
Point 1	0.27	0.13	17.88	1.56	71.55	0.11	7.82	0.42	0.27
Point 2	0.26	0.11	17.45	1.59	71.71	0.15	8.14	0.31	0.28
Point 3	0.26	0.13	17.88	1.54	71.70	0.12	7.63	0.49	0.26
Point 4	0.28	0.12	18.06	1.56	71.49	0.10	7.51	0.58	0.31
Point 5	0.27	0.14	17.87	1.48	71.85	0.14	7.55	0.42	0.28
Point 6	0.26	0.13	18.05	1.56	71.56	0.12	7.64	0.39	0.29
Point 7	0.25	0.14	17.88	1.53	71.70	0.11	7.60	0.47	0.31
Point 8	0.29	0.15	17.50	1.57	71.60	0.13	8.08	0.38	0.29
Point 9	0.28	0.14	17.79	1.57	71.78	0.13	7.74	0.26	0.32
Point 10	0.27	0.12	17.97	1.55	71.43	0.11	7.68	0.54	0.33
Average	**0.27**	**0.13**	**17.83**	**1.55**	**71.64**	**0.12**	**7.74**	**0.43**	**0.29**
σ (±wt.%)	0.01	0.01	0.21	0.03	0.13	0.02	0.21	0.10	0.02

Table 4
Standardless (P/B-ZAF) quantification with reference for cobalt

Method	Si	V	Cr	Mn	Fe	Co	Ni	Cu	Mo
P/U-ZAF, reference for cobalt	0.27	0.13	17.83	1.55	71.64	0.12	7.74	0.43	0.29
Φ(ρ,z) standardbased	0.33	0.13	18.27	1.51	70.90	0.12	8.07	0.37	0.31
Comparison S-OES, XRF	0.33	0.09	18.30	1.61	70.56	0.14	8.13	0.37	0.29

Table 5
Comparison of standardless (Co-reference) and standard-based analysis with composition obtained through S-OES and XRF

Conclusions

1. In many cases automatic element ID is insufficient, especially when peak overlaps with elements of low concentration exist. In this case a powerful spectra deconvolution tool in combination with a detector of excellent resolution is an absolute necessity to produce reliable results.

2. The procedure discussed in this paper proves a practical approach to quantitative analysis:

a) Initial standardless quantification

b) Use of the results for selection of an appropriate standard

c) Standard-based quantification for highest accuracy. If necessary, the hybrid method – as offered by QUANTAX – can be used in case of missing standards for specific elements, these elements can then be quantified standardless.

3. Standardless P/B-ZAF analysis can be further optimized through references for critical elements. This is also useful for the analysis of rough surfaces.

Acknowledgement
Sample courtesy of ACERINOX S.A., Los Barrios (CADIZ), Spain.

All configurations and specifications are subject to change without notice.
Order No. DOC-A82-EXS001, Rev. 2.1 © 2015 – 2025 Bruker Nano GmbH, Am Studio 2D, 12489 Berlin, Germany.

Electron Microscope Analyzers
Bruker Nano GmbH
Berlin · Germany
info.ema@bruker.com

www.bruker.com/quantax-eds-for-sem