Quantification of Steels and Alloys using a dual source multidetector system. Part II: SEM-WDS adding to XRF-EDS and SEM-EDS analysis

Bruker Nano Analytics, Berlin, Germany

Webinar, April 29, 2021

Presenters

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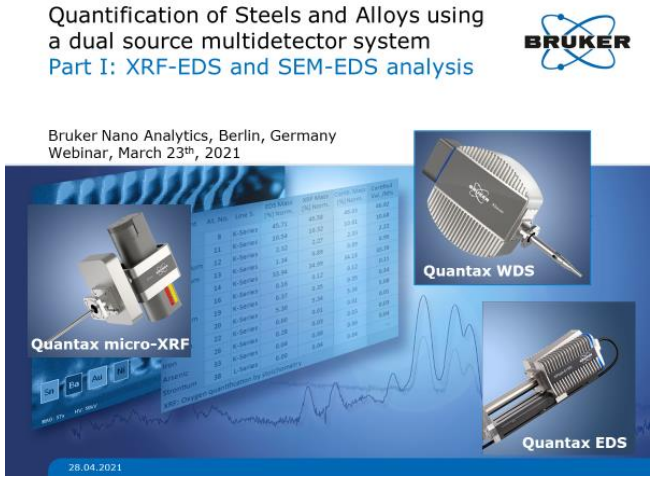
Overview
Quantification of Steels and Alloys

Webinar structure

- **Part I** of the webinar series focused on the dual-beam sources (electron and X-ray source), and how they interact with the samples of interest to generate X-rays which are identified and quantified using EDS.
- **Part II** will now compare the earlier results with the measurements using the WDS collected on the same system.

- Multi method approach
- SEM WDS Introduction
- Samples and Methods
- Application to Steels and Alloys
- Summary and Conclusion



Webinar: Part I – available at:
https://www.bruker.com/en/news-and-events/webinars/2021/XRF-EDS-and-SEM-EDS-Analysis.html

Overview
Motivation for multi-method approach

- Why use different analytical techniques for steel analysis?

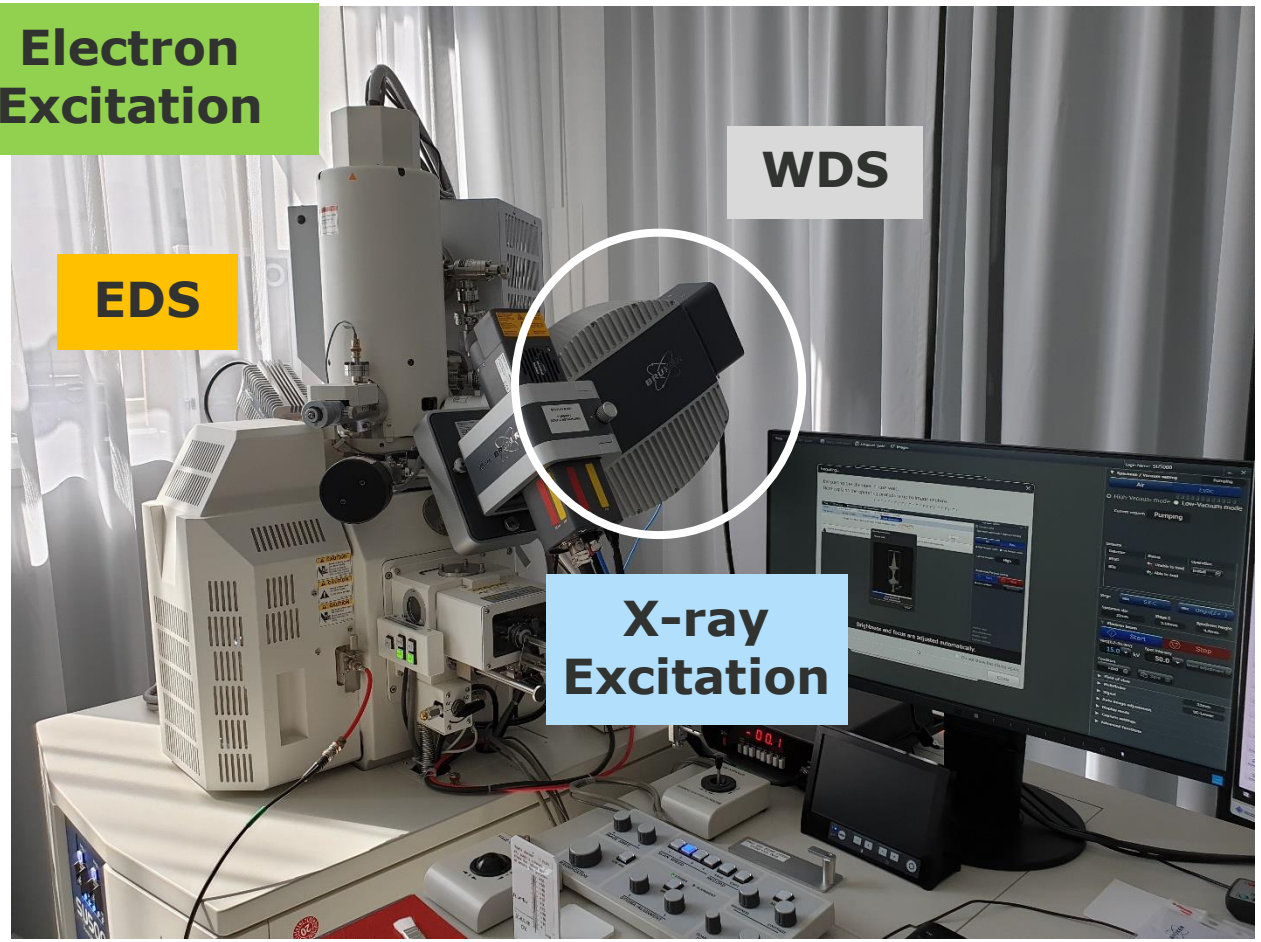
- Quantification of Steels and Alloys can be problematic due to the various elements of interest ranging from very low Z-numbers up to high Z-elements and the range of concentrations present from majors through to traces.
- **E-beam excitation / EDS detection:**
  - Very good low Z-element sensitivity / spatial resolution
  - Relatively high spectral background / limiting in sensitivity
- **X-ray excitation / EDS detection:**
  - Low spectral background / high sensitivity for higher Z-elements
  - Limitation in spatial resolution/ light element detection
- **E-beam excitation / WDS detection:**
  - High spectral resolution; improved P/B ratio compared to e-beam / EDS
  - Sequential analysis (one element at a time)

Excitation: X-ray and electron beam
Detectors: EDS and WDS

FEG SEM

Dual source excitation:
e-beam
X-ray beam

Dual Detectors:
EDS
WDS



What have we learned from Part I ?
Combined Analysis of Steel

Sample 32: AISI 422-205B

Element	Certified	MicroXRF	SEM-EDS	Combined
C	**0.22**			
N	**0.05**			
Al	**0.01**			
Si	**0.37**		0.34	**0.33**
P	**0.01**			
S	**0.00**			
Ti	**0.00**	0.003		**0.00**
V	**0.26**	0.279		**0.26**
Cr	**11.72**	11.084	11.37	**11.32**
Mn	**0.68**	0.797	0.87	**0.75**
Fe	**83.70**	83.243	84.55	**83.20**
Co	**0.03**	0.024	0.49	**0.02**
Ni	**0.70**	0.692	0.54	**0.67**
Cu	**0.15**	0.177		**0.15**
Nb	**0.02**	0.012		**0.01**
Mo	**0.97**	0.970	0.95	**0.94**

SEM-EDS/WDS

Low-Z elements

SEM-XRF

High-Z elements

Analysis of Steels and Alloys: Combined Quantification

➢ If both electron and X-ray excitation are available, the benefits of both methods can be combined.

That is:

1. better light element sensitivity of electron excitation, e.g., from C to Si typically have smaller statistical error and better sensitivity,
2. better trace element sensitivity for heavy elements of X-ray excitation

- *Thus, the results for each quantification method can be calculated seperately, and then the results for the elements with better sensitivity and accuracy are used to calculate an improved combined quantification.*

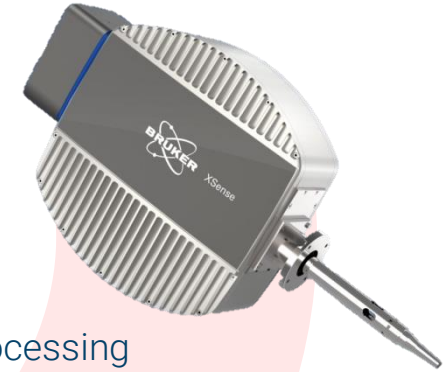
- However, it is still possible to improve the results with the addition of SEM-WDS

- Note: the sample has to fulfil the requirements for both excitation types, i.e., the sample needs to be conductive and polished and has to be homogeneous

QUANTAX WDS
System Components

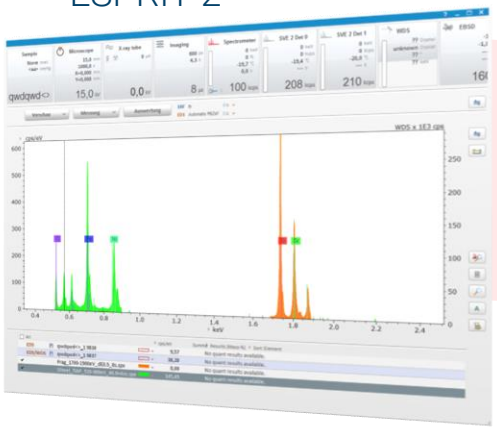
QUANTAX WDS: integral part of the QUANTAX family

XSense™ WD spectrometer



Signal processing unit SVE 6

ESPRIT 2



- Spectrum, P/B-acquisition in ‘Spectrum’ and ‘Objects’ mode
- Mapping and LineScan
- Quantification (SB, coupled quant possible)
- Device control

… all integrated in the Esprit GUI

Introduction
Motivation for WDS application in steel analysis

01 Determine traces of low-Z elements in steel
- Contents of Al, Si, P, S

02 Determine light elements in steel
- Contents of N, C

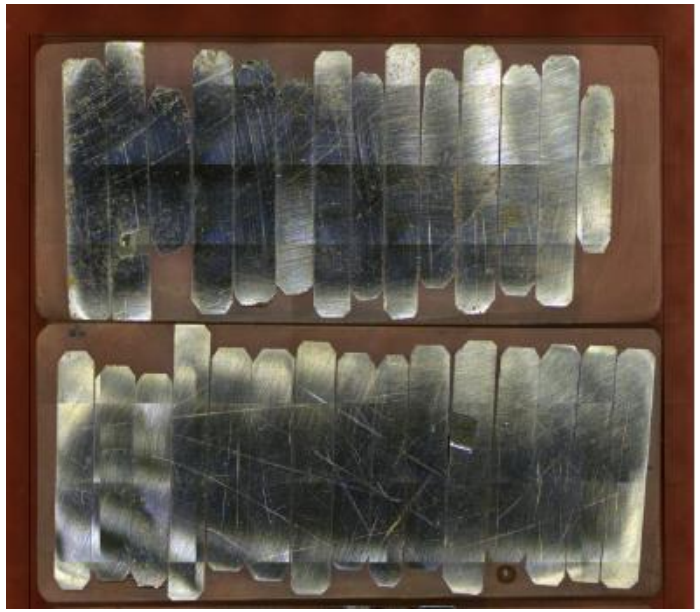
03 Resolve spectral overlaps in steel
- Peak overlaps of W-M with Si-K; Mo-L with S-K

04 Resolve spatial sample heterogeneities
- Small-scale elemental variations, e.g. C

Analysis of Steels
Samples

Steel & iron set I (ARMI)

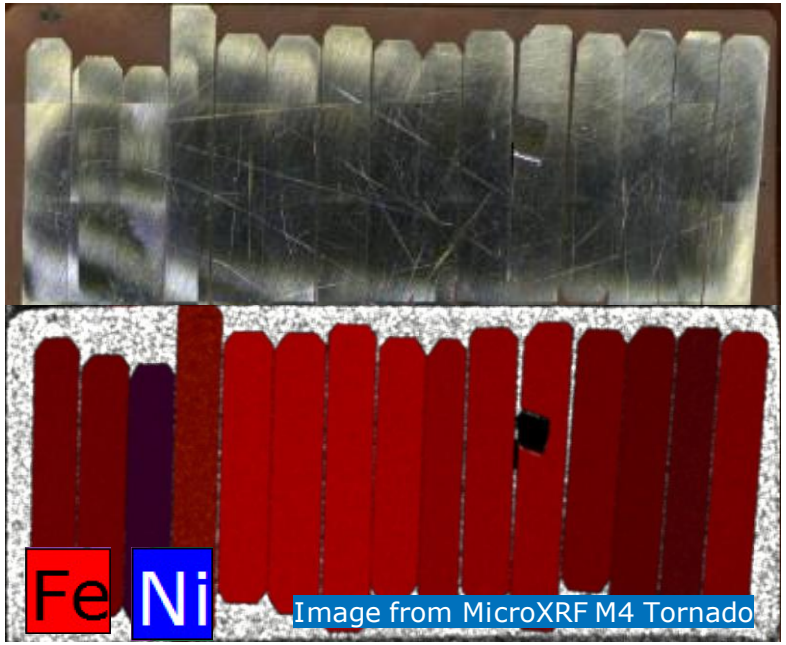
- 15 Cr-Ni steels, 14 irons
- Variable major and trace element contents
- Certified compositions



Steel set II (ACX)

- 15 Cr-Ni steels
- Variable major and trace element contents
- Certified compositions

Analysis of Steels
Samples



- Major Elements:

Cr, Fe, Mn, Ni

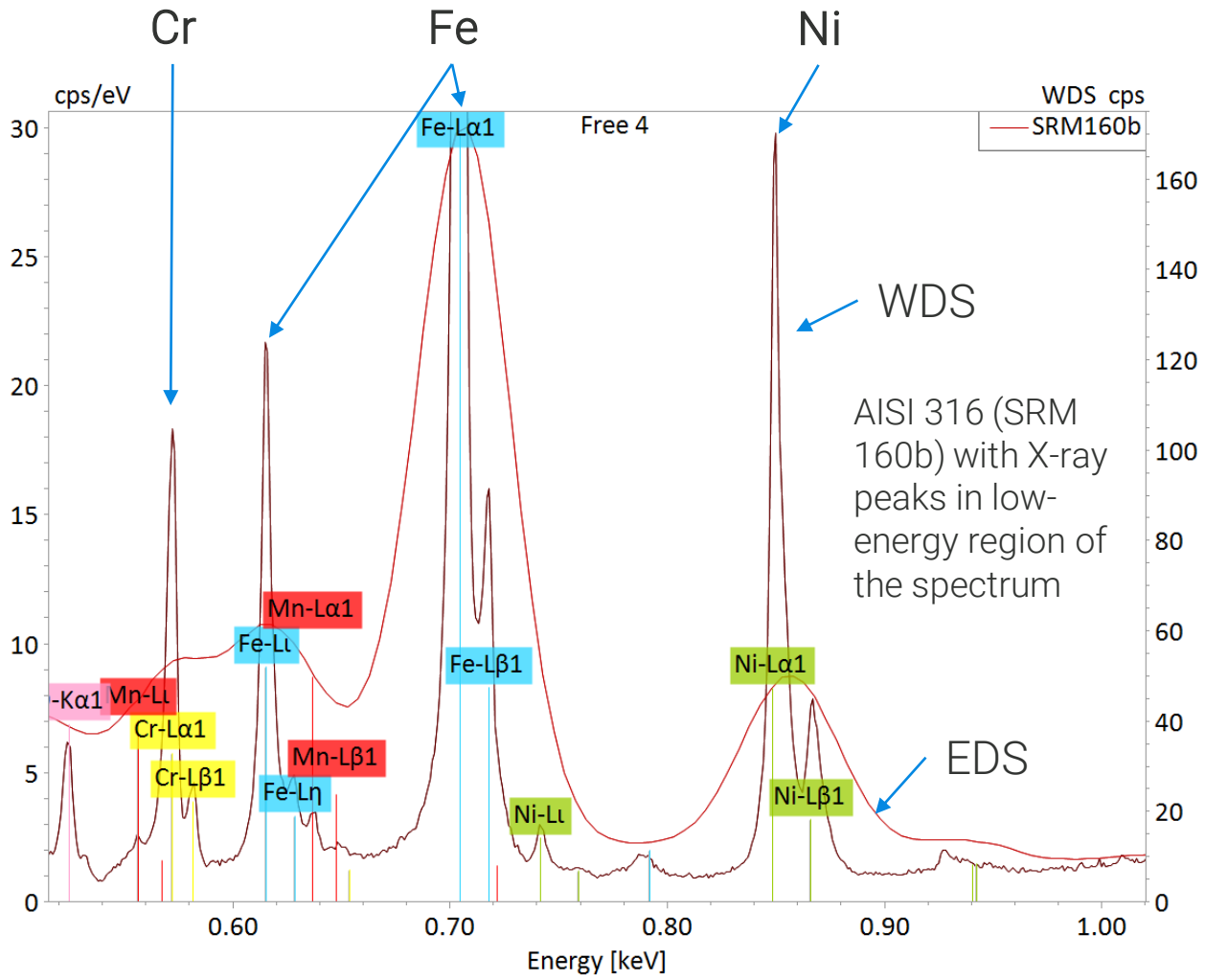
- Minor and Trace Elements:

C, N, Al, Si, P, S, Ti, V, Co, Cu, Nb, Mo, Sn, W

Element	Minimum (%)	Maximum (%)	Range (%)
C	0.02	1.02	1.00
N	0.01	0.33	0.32
Al	0.00	1.16	1.16
Si	0.27	1.38	1.11
P	0.01	0.04	0.03
S	0.00	0.29	0.29
Ti	0.00	0.63	0.63
V	0.02	0.26	0.24
Cr	11.72	23.60	11.88
Mn	0.35	9.31	8.96
Fe	41.29	86.23	44.95
Co	0.02	0.18	0.17
Ni	0.11	35.84	35.73
Cu	0.03	0.47	0.44
Nb	0.00	0.72	0.72
Mo	0.06	2.30	2.25
Sn	0.00	0.01	0.01
W	0.01	1.10	1.09
Total	100.00	100.00	0.00

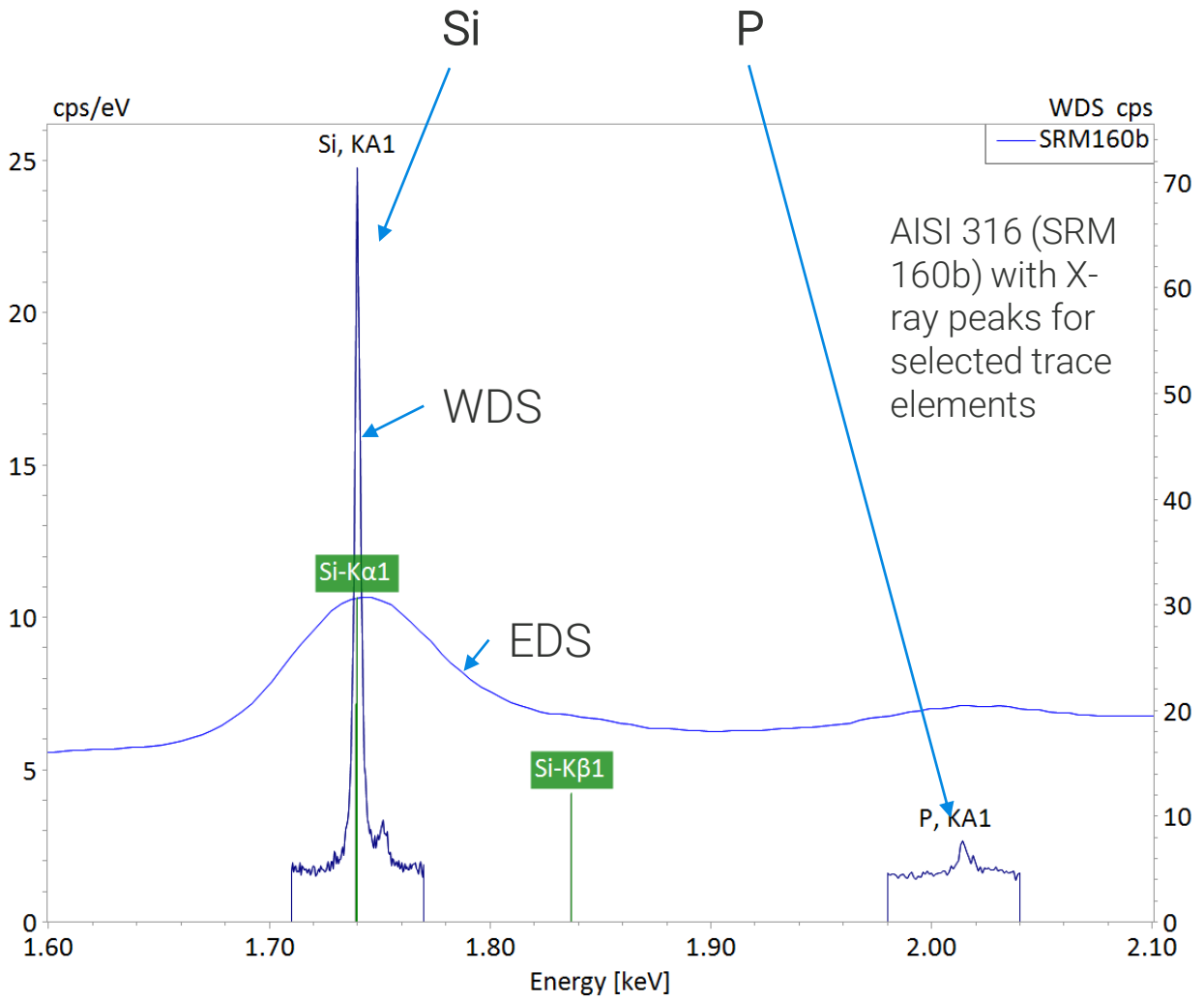
WDS methodology
Major elements in steel

- WDS designed for highest efficiency in low X-ray energy region
- Fe, Cr, Ni determination on L-lines
- Energy selective technique → sequential acquisitions
- Acquisitions on reference material necessary
- Major elements equally covered by EDS, micro-XRF
- Possible but not required by WDS



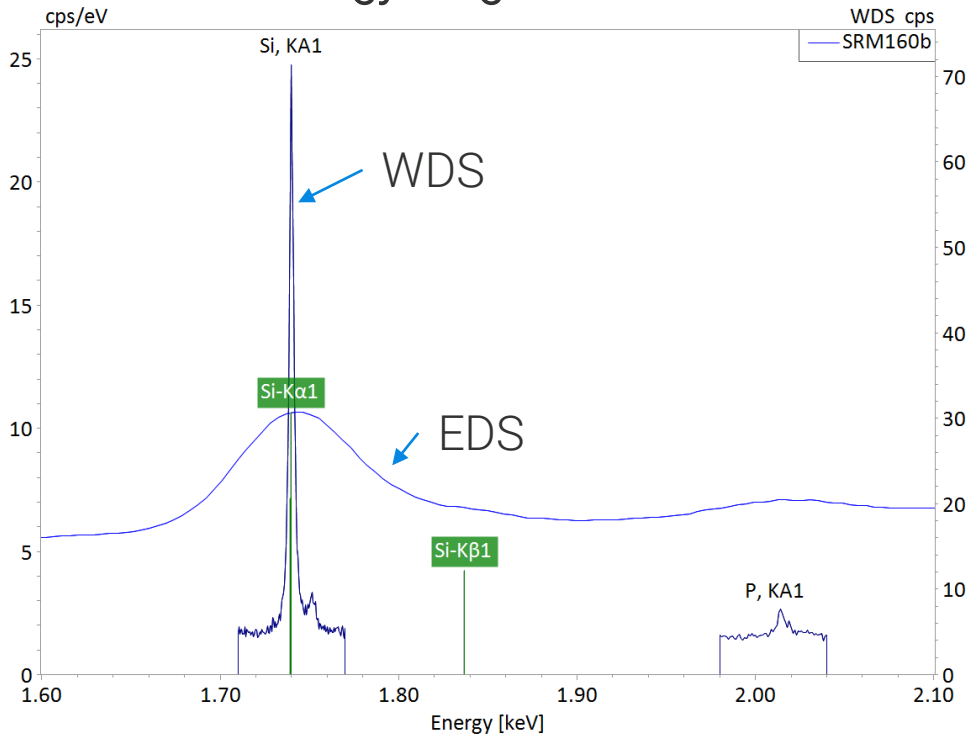
WDS methodology
Trace elements in steel

- Better peak resolution
- High peak to background ratios
- Low detection limits
- Especially for lines < ~2 keV (complements µXRF)
- Time effort rewarded by high precision and accurracy



WDS methodology
Two different acquisition modes

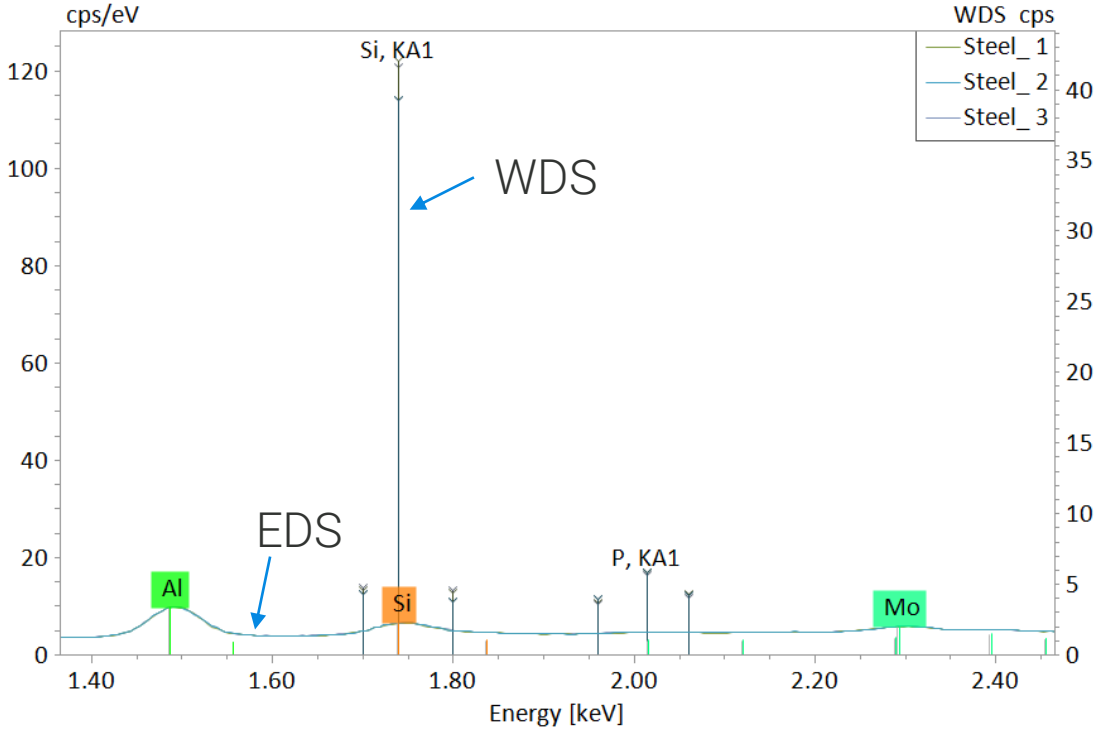
Energy range scans



Suitable for qualitative determination

= intuitive, convincing presentation

Peak to background measurements



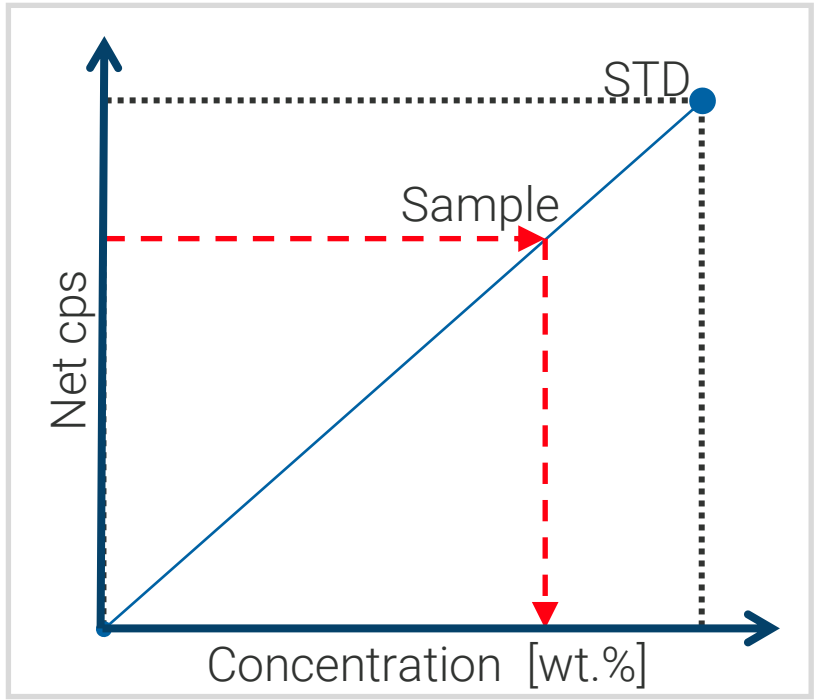
Suitable for quantification

= faster acquisition, better statistics

Methodology
Standard-based quantification

- Determine net peak intensities of „unknown“ sample
- Compare to reference (standard) net peak intensities
- Acquire at identical conditions (geometry, acceleration voltage)
- Record beam current value
- Correct for matrix effects (ZAF)

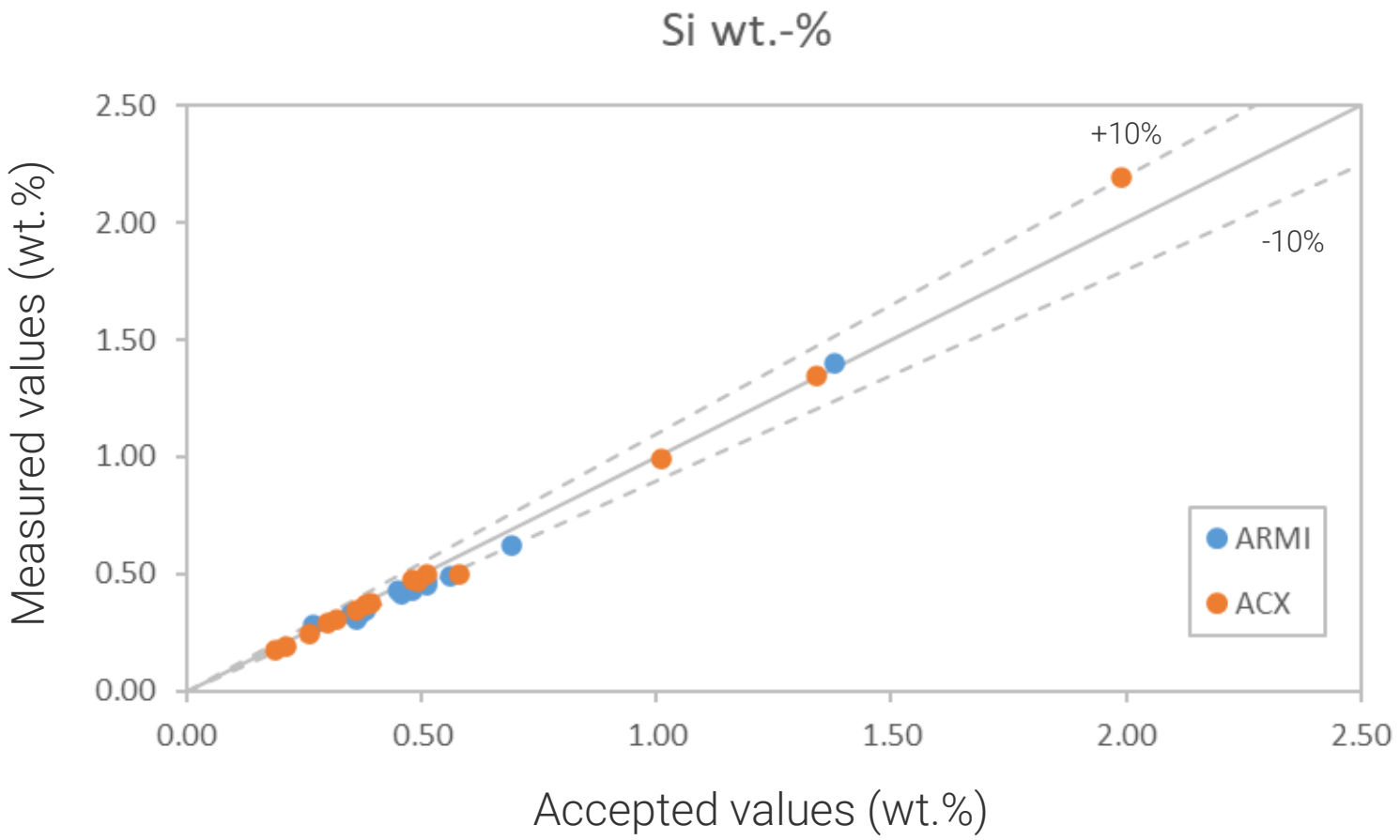
$$\frac{C_i^S}{C_i^{Std}} \propto \frac{N_i^S}{N_i^{Std}} \frac{(k_Z k_A k_F)_{i,S}}{(k_Z k_A k_F)_{i,Std}}$$



Trace element determination by WDS
Silicon (Si-Kα)

Analytical Conditions Point Analysis:

20 kV, 70 nA,, under vacuum, WD 15 mm, 300 seconds



Si Range:

0.19 – 1.99 wt.%
83% < 0.6 wt.%

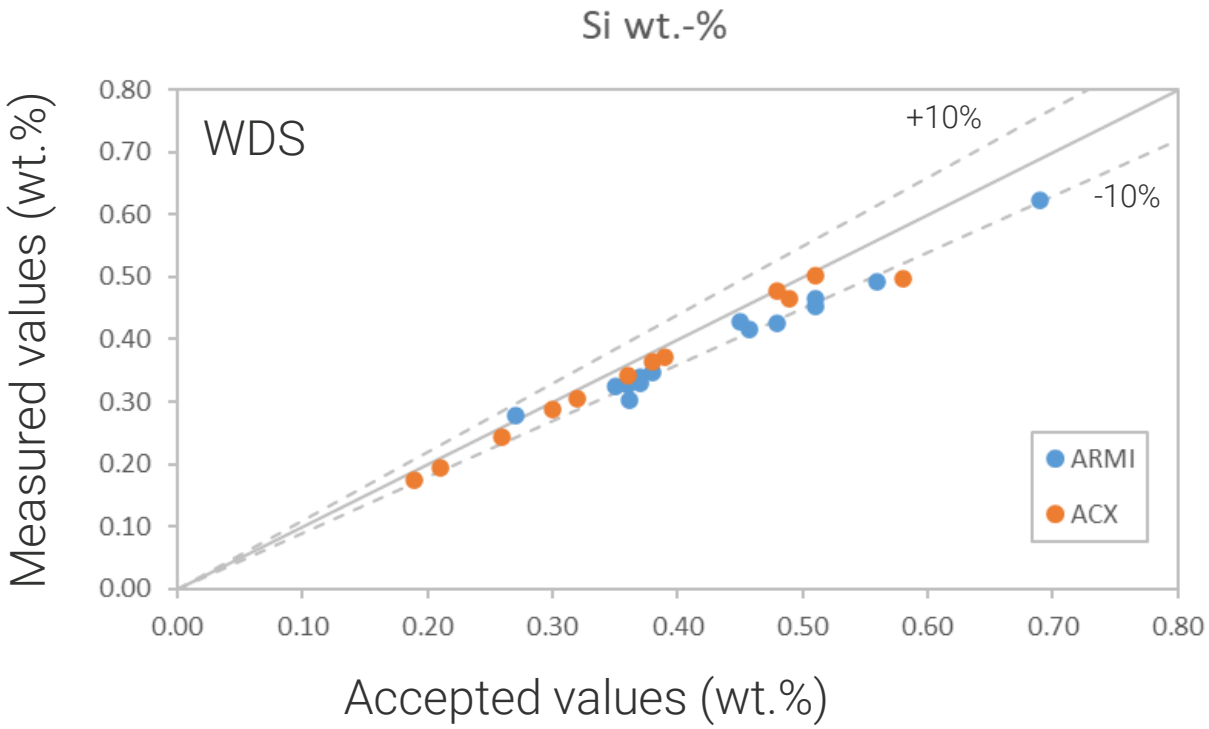
WDS Results:

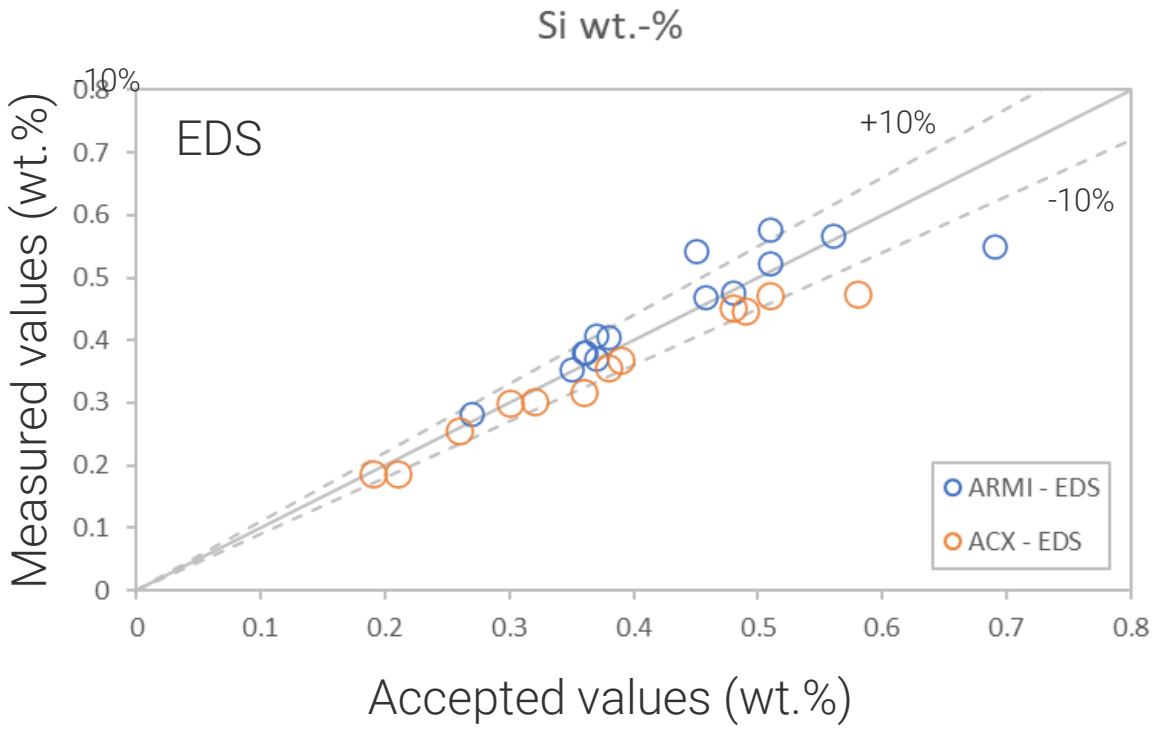
Minor to trace element concentrations

Accurate and precise

Trace element determination by WDS
Silicon (Si-Kα)

Focus on lowest concentrations (0.2 – 0.7 wt.%)





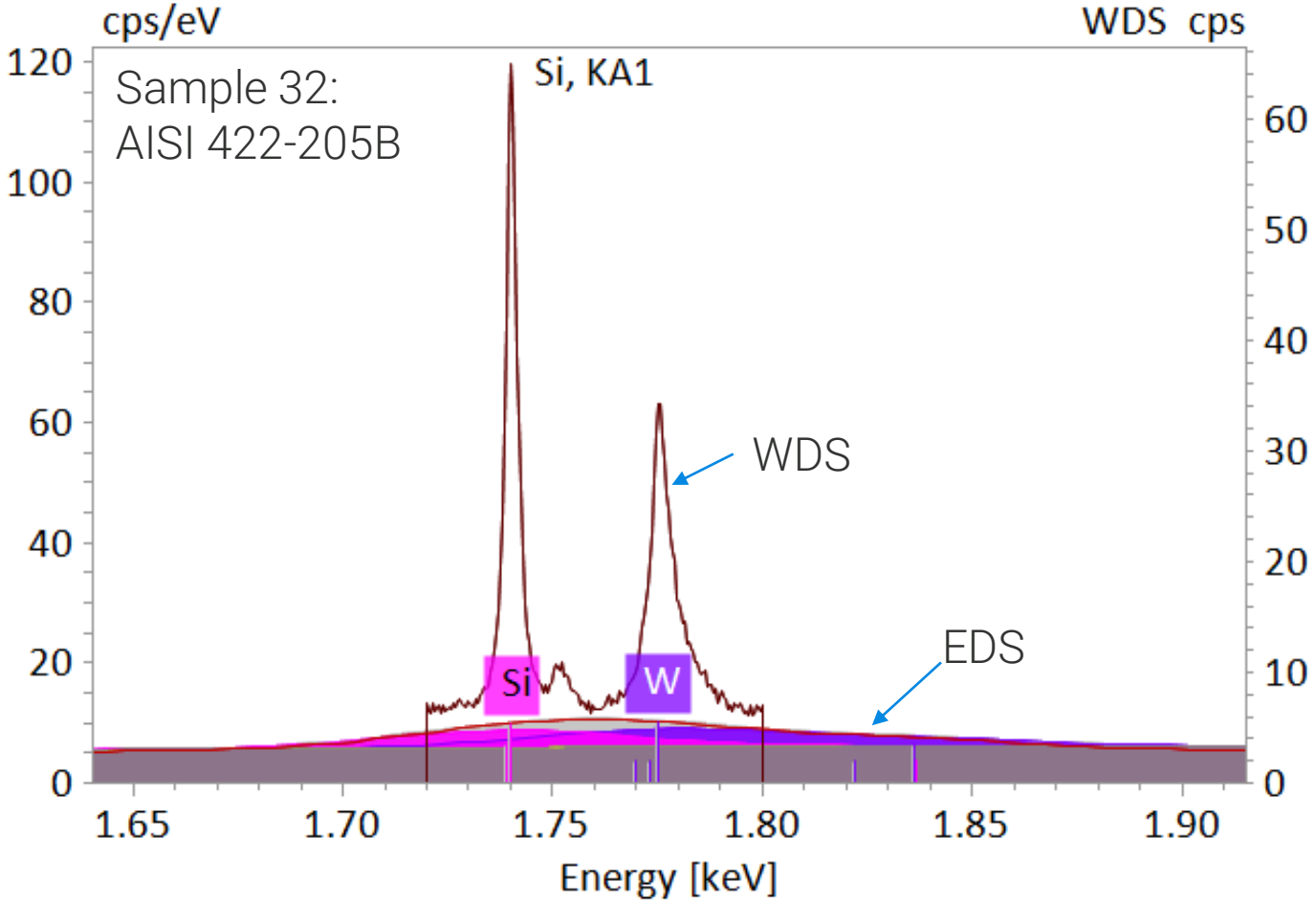
Peak resolution by WDS
Tungsten (W-Mα) and Silicon (Si-Kα)

WDS Results:

Determination of Si and W

Comparing WDS and EDS

Peak resolution vs. peak deconvolution



Si: 0.37 wt.%

W: 1.1 wt.%

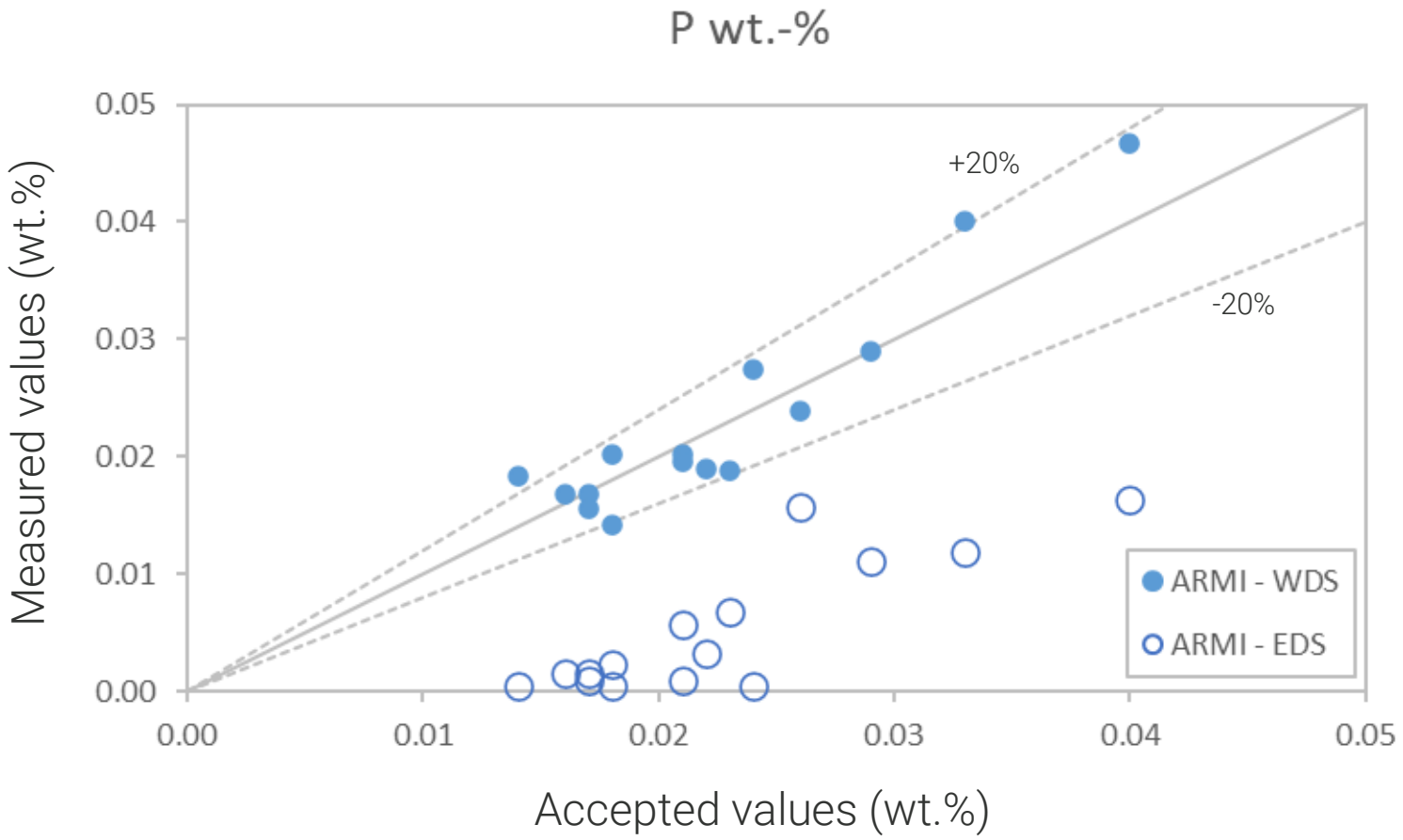
Δ Si-Kα – W-Mα: 35 eV

Trace element determination by WDS
Phosphorous (P-Kα)

WDS Results:

Trace element concentrations

Still well matching accepted concentration values



Range:

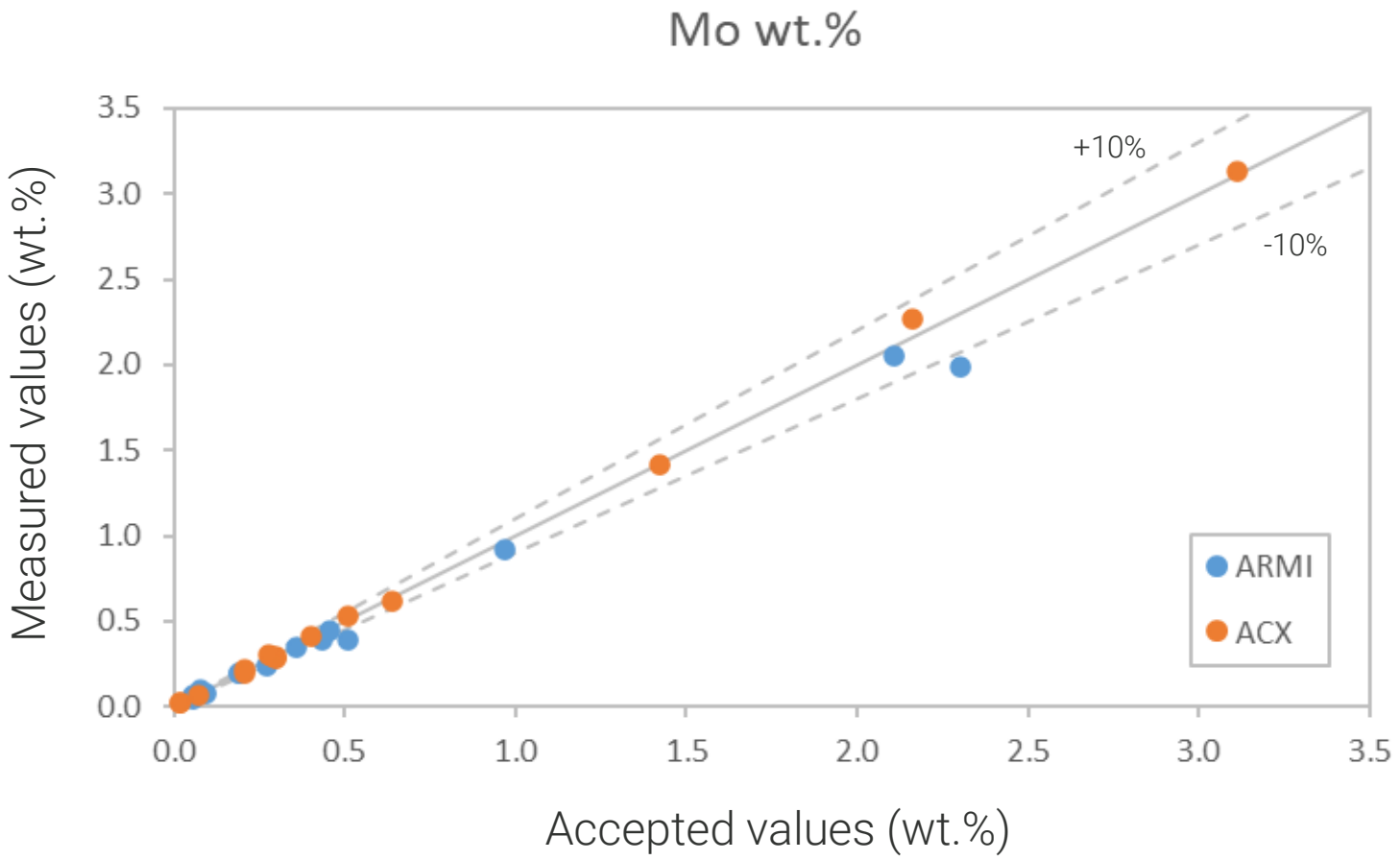
P: 140 – 400 ppm

Trace element determination by WDS
Molybdenum (Mo-Lα)

WDS Results:

Precise and accurate

Wide range of concentrations



Range:

Mo: 0.02 – 3.11 wt.%

77% < 0.52 wt.%

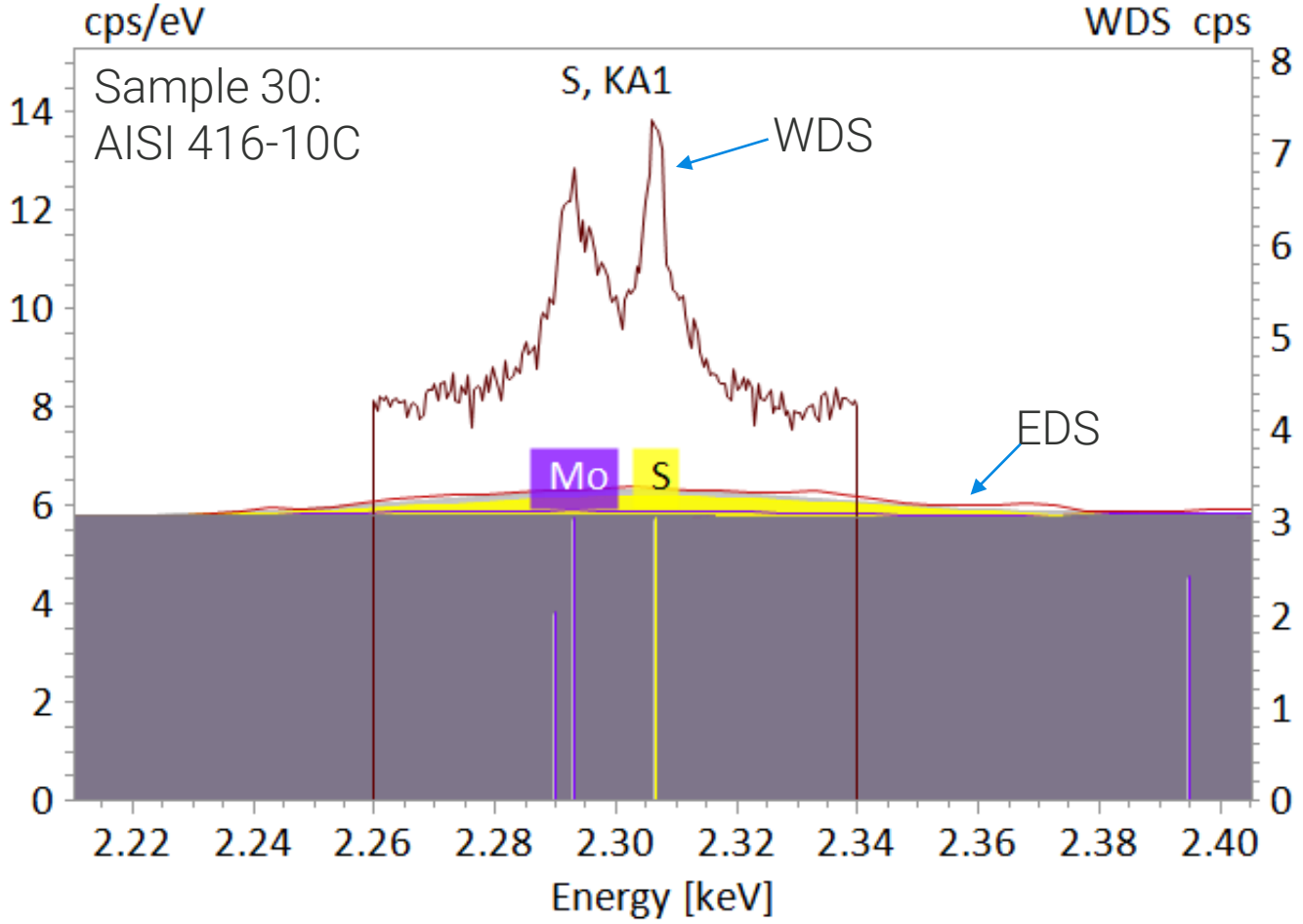
Peak resolution by WDS
Molybdenum (Mo-Lα) and Sulfur (S-Kα)

WDS Results:

Determination of Mo and S

Comparing WDS and EDS

Peak resolution vs. peak deconvolution



Mo: 0.08 wt.%

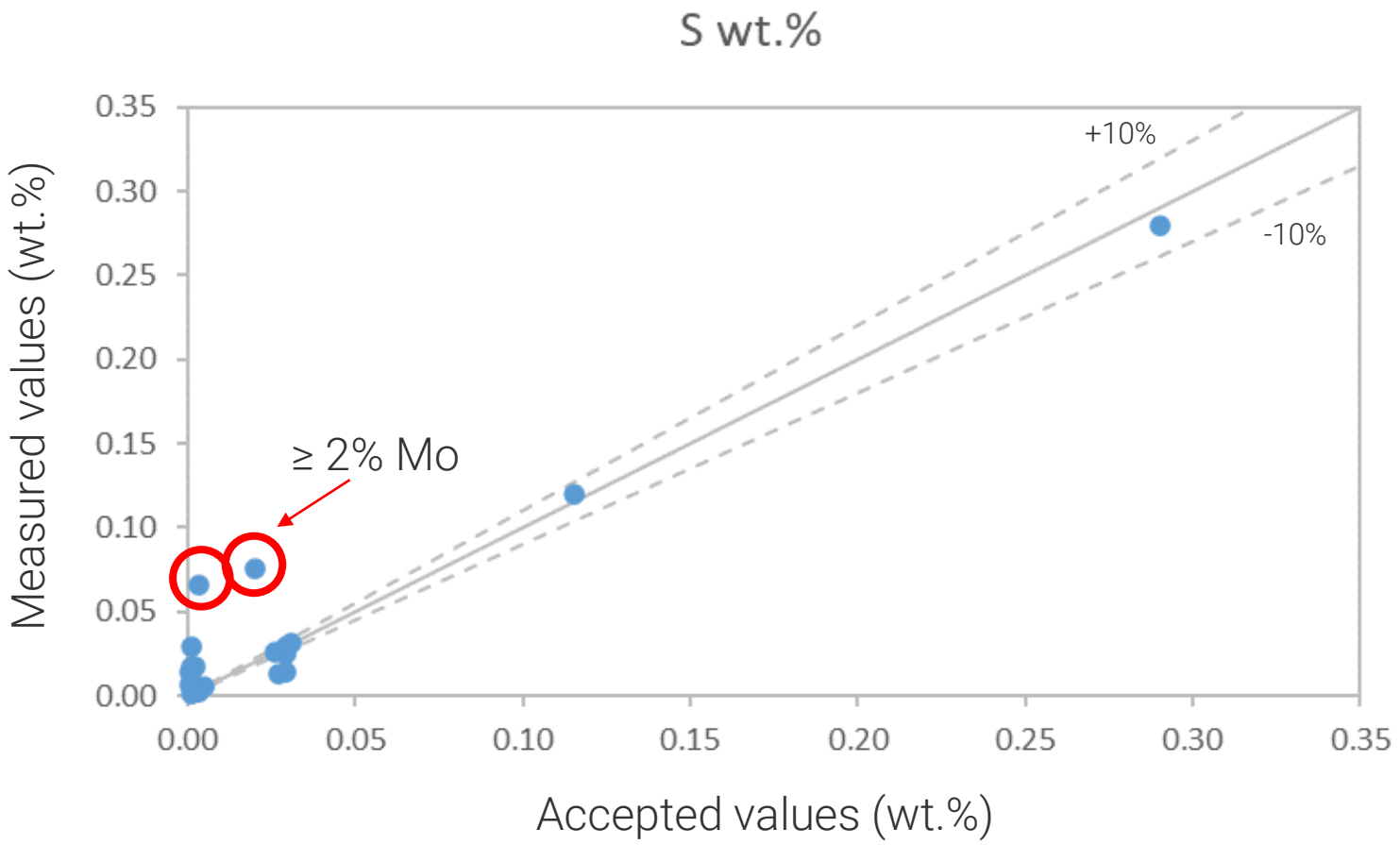
S: 0.29 wt.%

Δ S-Kα – Mo-Lα: 14 eV

Trace element determination by WDS
Sulfur (S-Kα)

WDS Results:

Most match accepted values
Some deviate due to high Mo



Range:

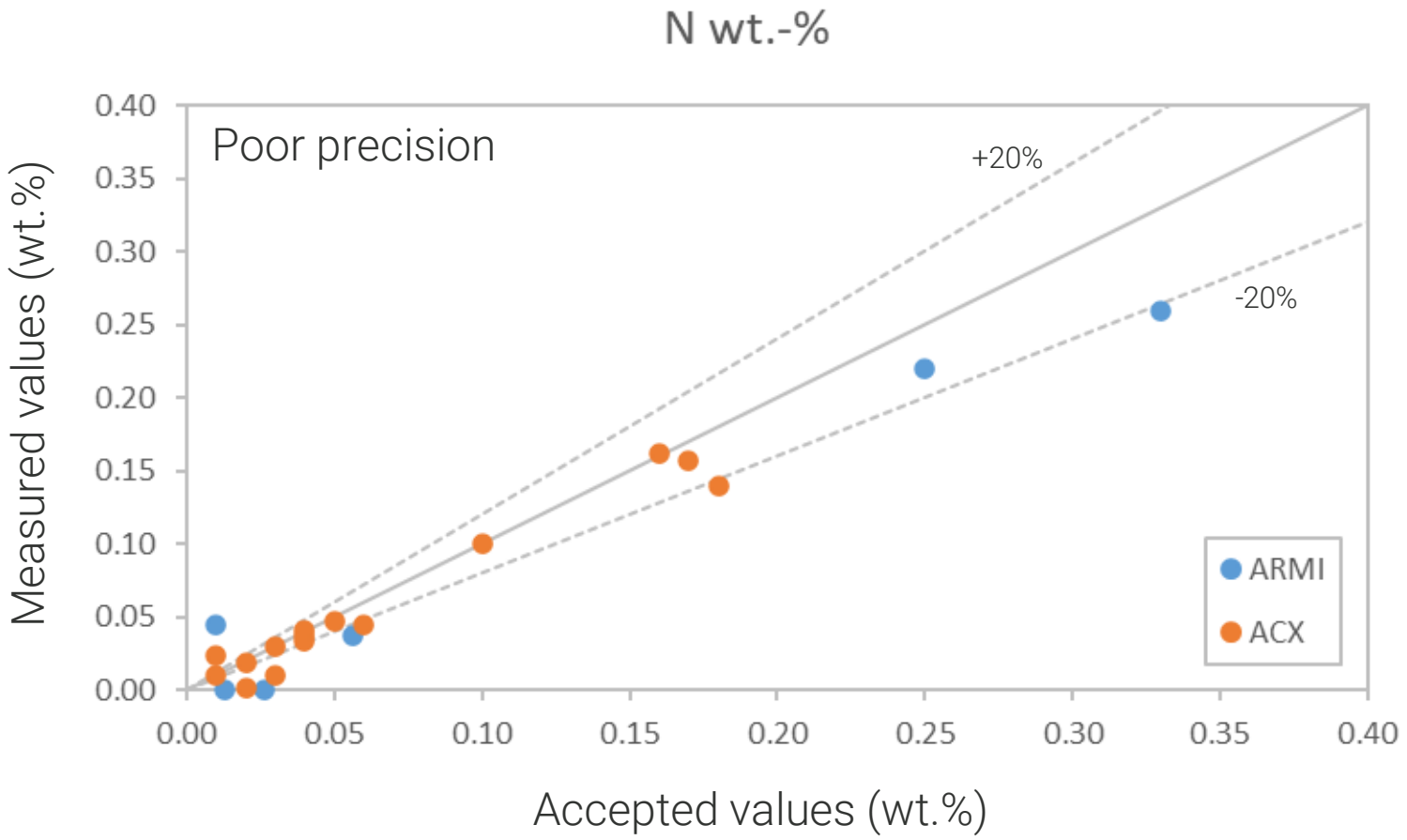
S: 4 – 2900 ppm

86% < 300 ppm

Light element determination by WDS
Nitrogen (N-Kα) with BRML60

Analytical Conditions Point Analysis:

4 kV, 20 nA,, under vacuum, WD 15 mm, 60 seconds



Range:

N: 0.01 – 0.33 wt.%
80% < 600 ppm

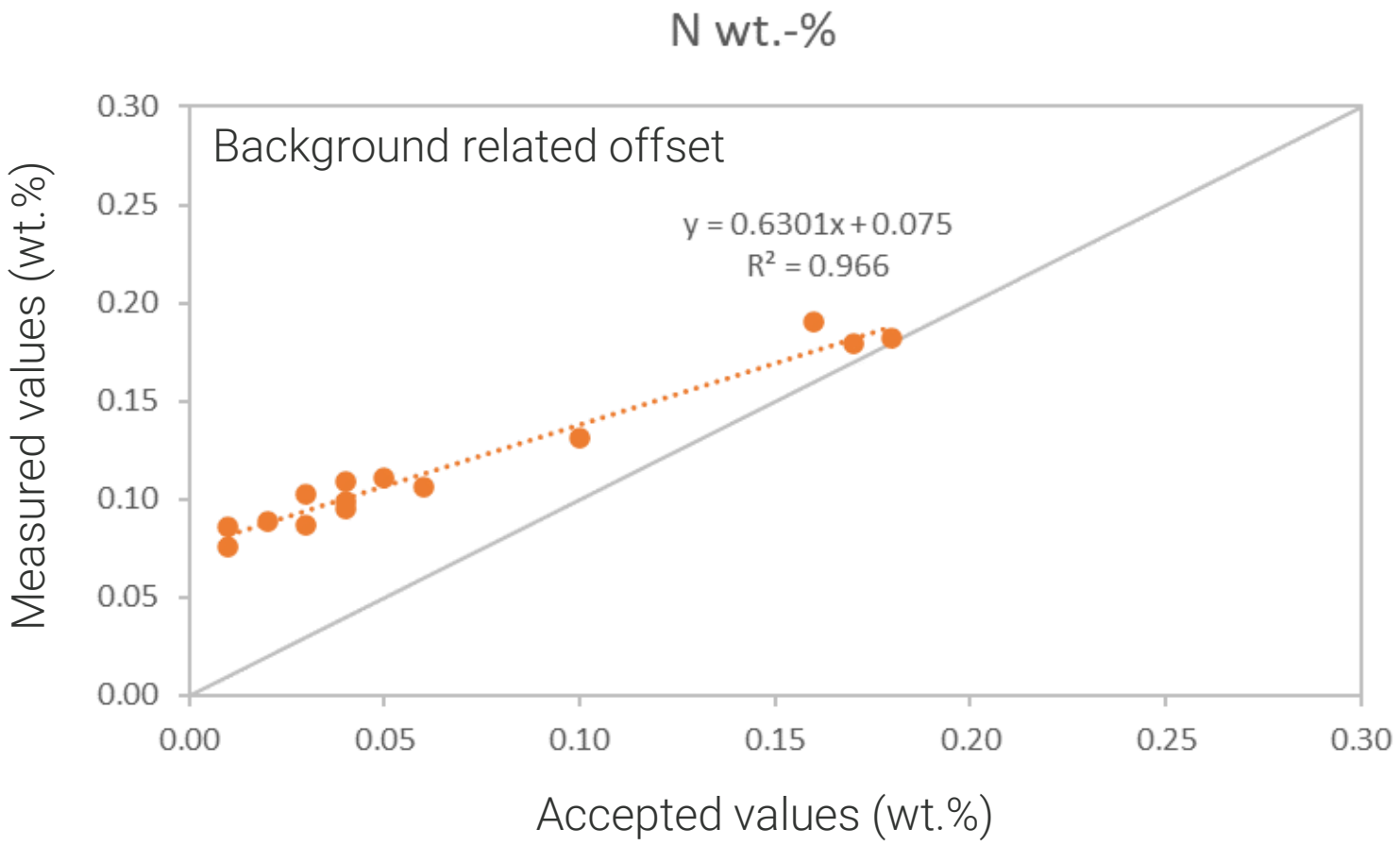
BRML60
low sensitivity

25 cps/nA
P/B: 36
@N-Kα, 10kV, BN

Light element determination by WDS
Nitrogen (N-Kα) with BRML80

WDS Results:

BRML80 option
high sensitivity
precise
but offset
background



Range:

N: 0.01 – 0.33 wt.%

80% < 600 ppm

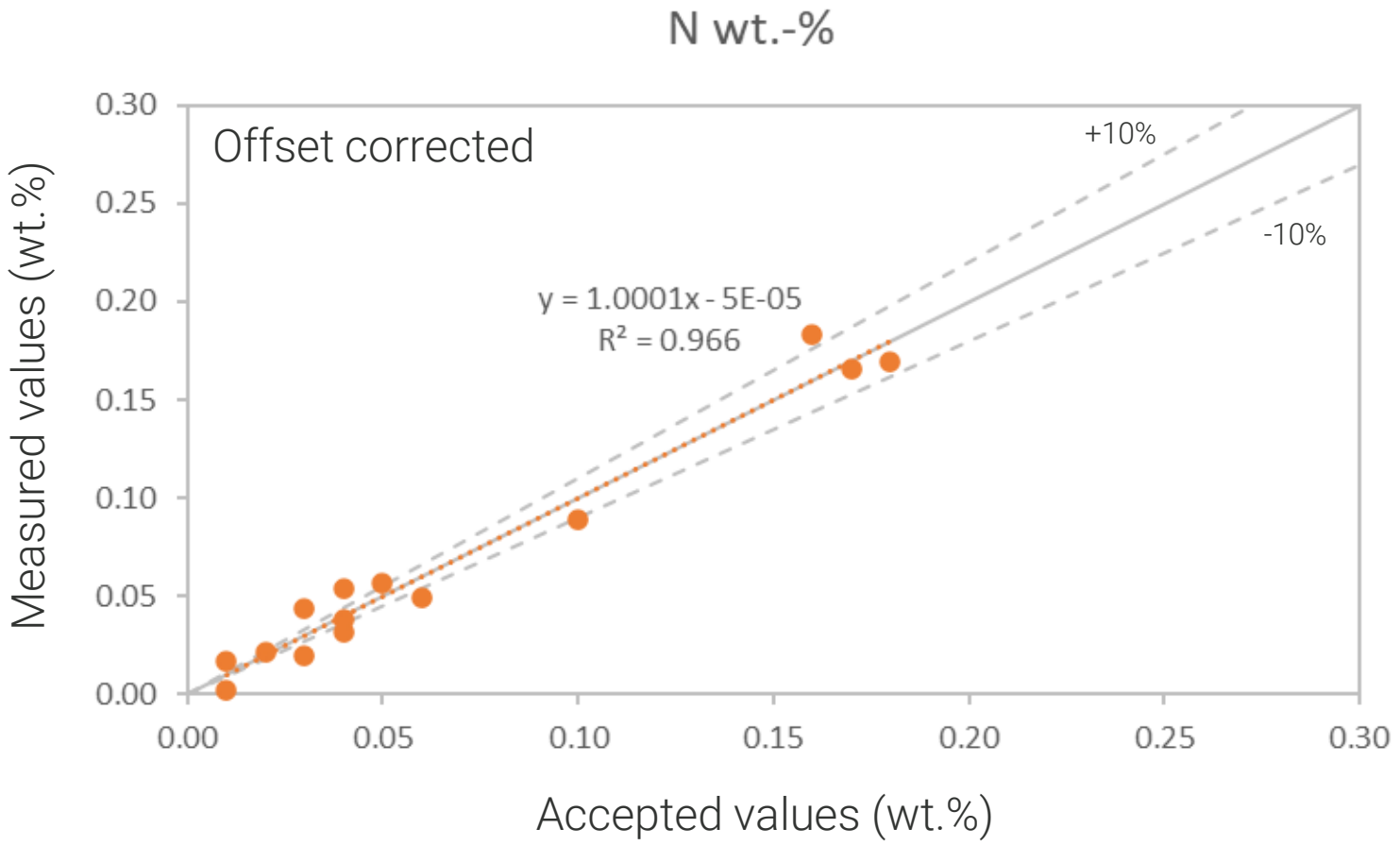
BRML80
250 cps/nA
P/B: 39
@N-Kα, 10kV, BN

Background:
Sc-Lα @ 395 eV

Light element determination by WDS
Nitrogen (N-Kα) with BRML80

WDS Results:

BRML80 corrected accurate and precise



Range:

N: 0.01 – 0.33 wt.%

80% < 600 ppm

BRML80
250 cps/nA
P/B: 39
@N-Kα, 10kV, BN

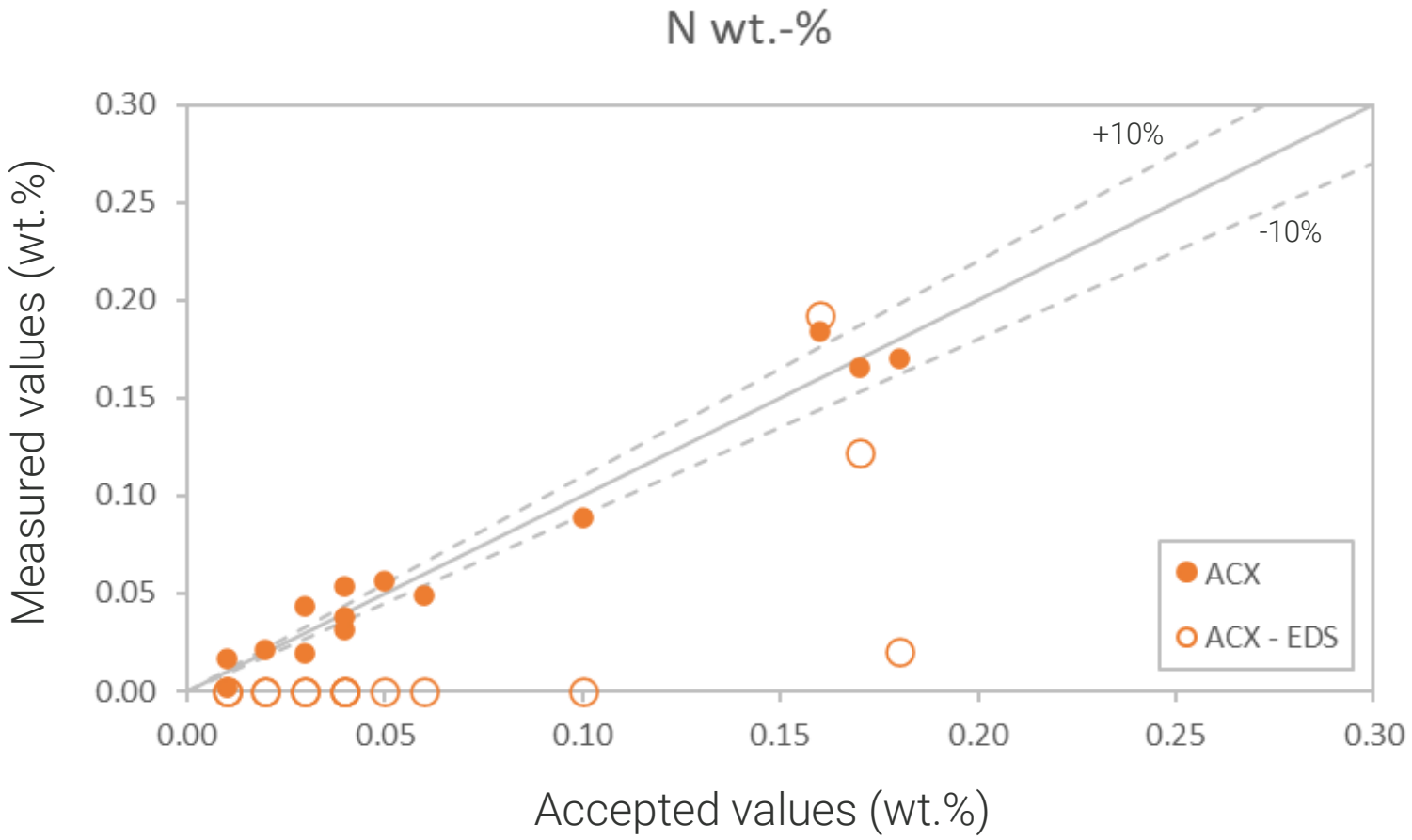
Background corrected

Light element determination by WDS
Nitrogen (N-Kα) with BRML80

WDS Results:

High sensitivity for light elements

Precise and accurate down to 100 ppm



Range:

N: 0.01 – 0.33 wt.%

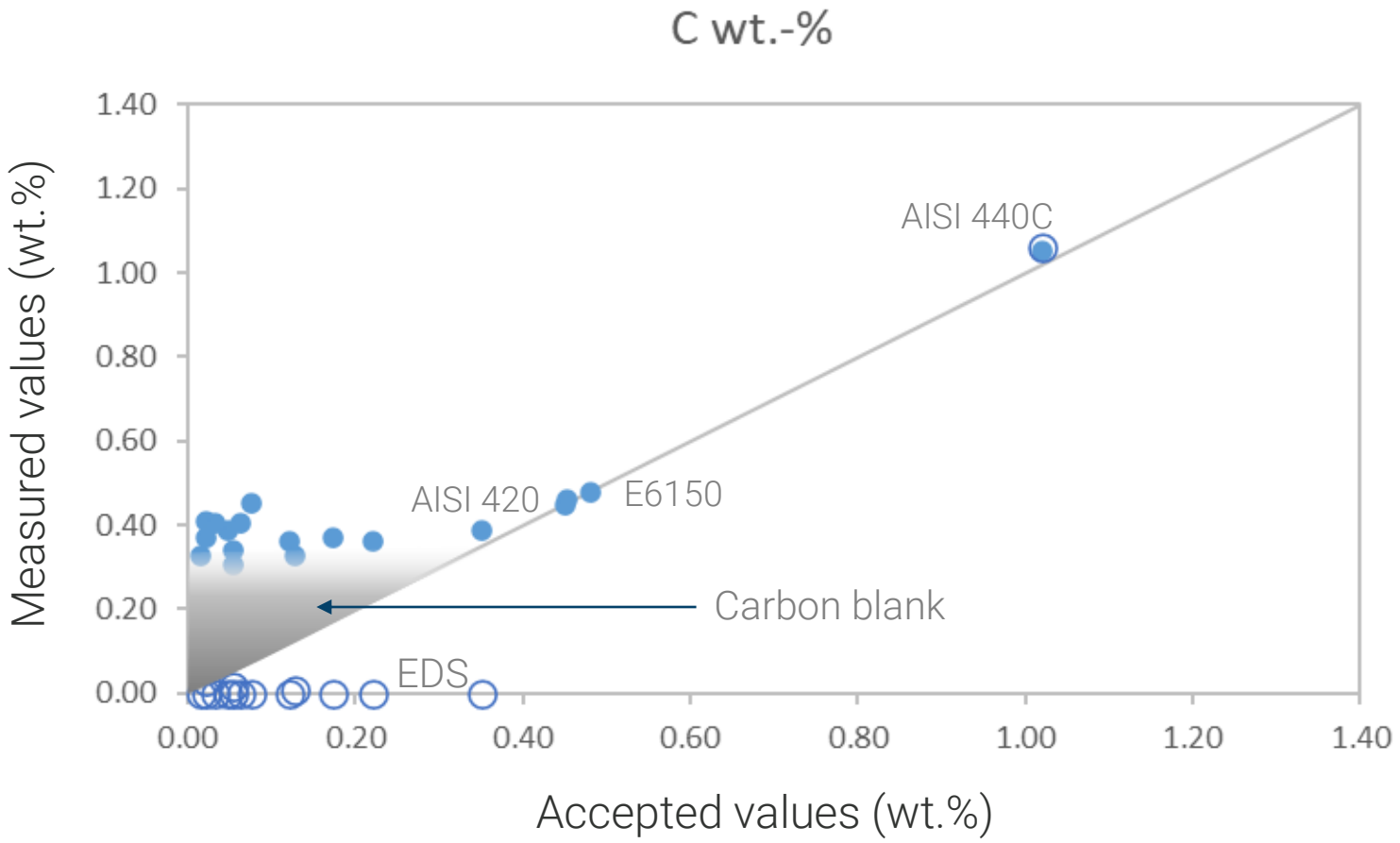
80% < 600 ppm

BRML80
Offset corrected

Light element determination by WDS
Carbon (C-Kα)

WDS Results:

High C samples match lower limit currently at 0.3 wt.%



Range:

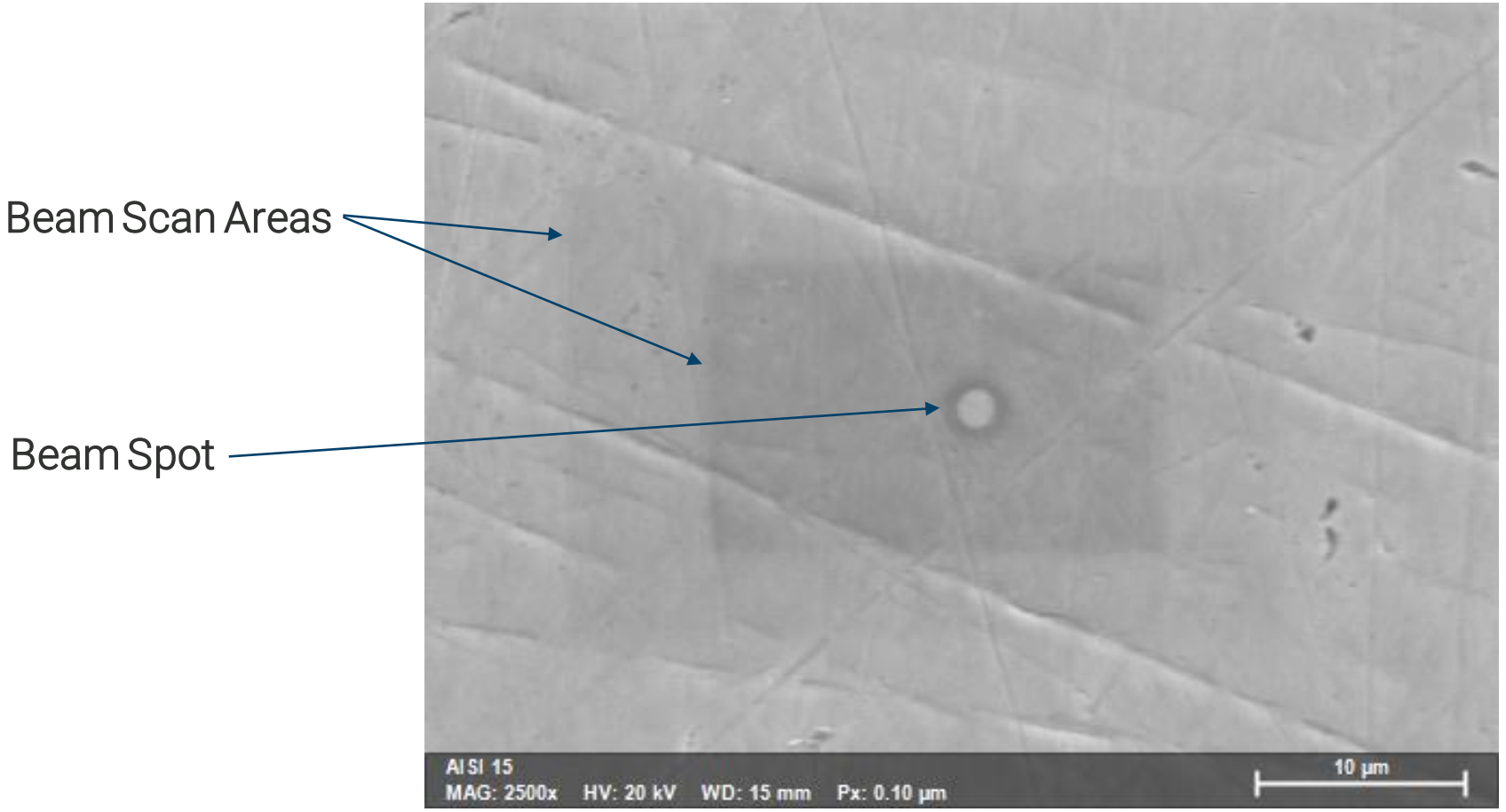
C: 0.002 – 1.04 wt.%
69% < 0.3 wt.%

Limitation for carbon determination

Not due to WDS sensitivity

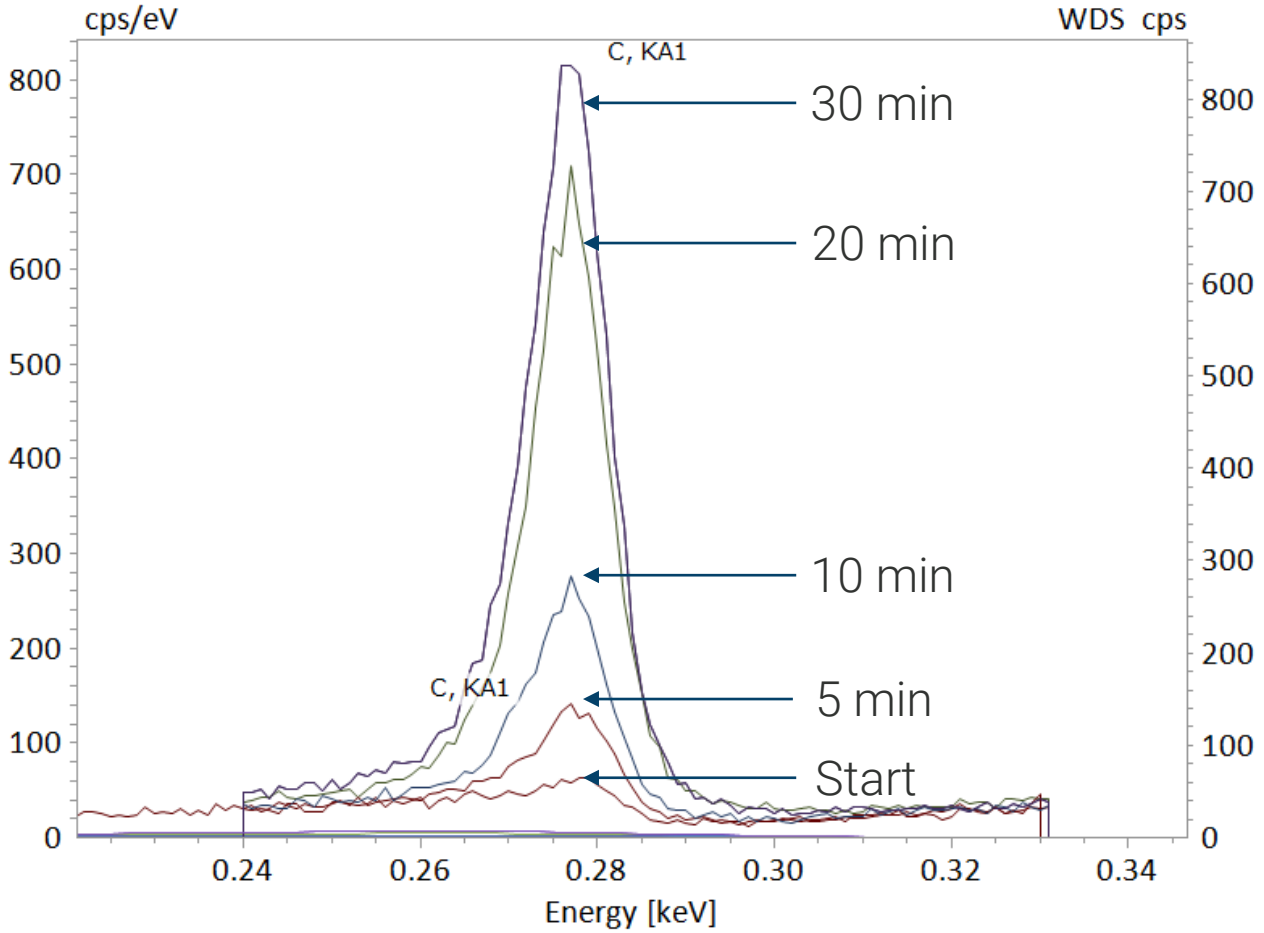
But due to system blank

Light element determination by WDS
Carbon contamination during sample analysis

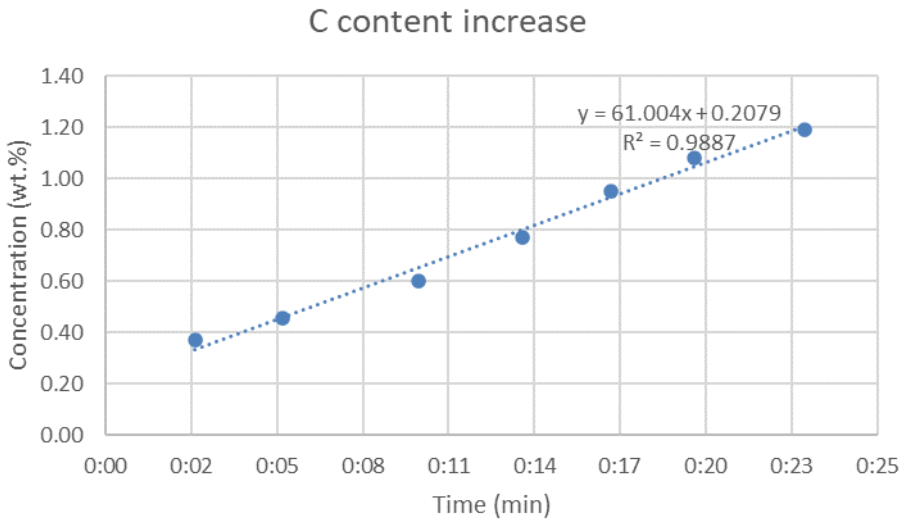


Carbon contamination on a steel sample surface

Light element determination by WDS
Carbon contamination over time

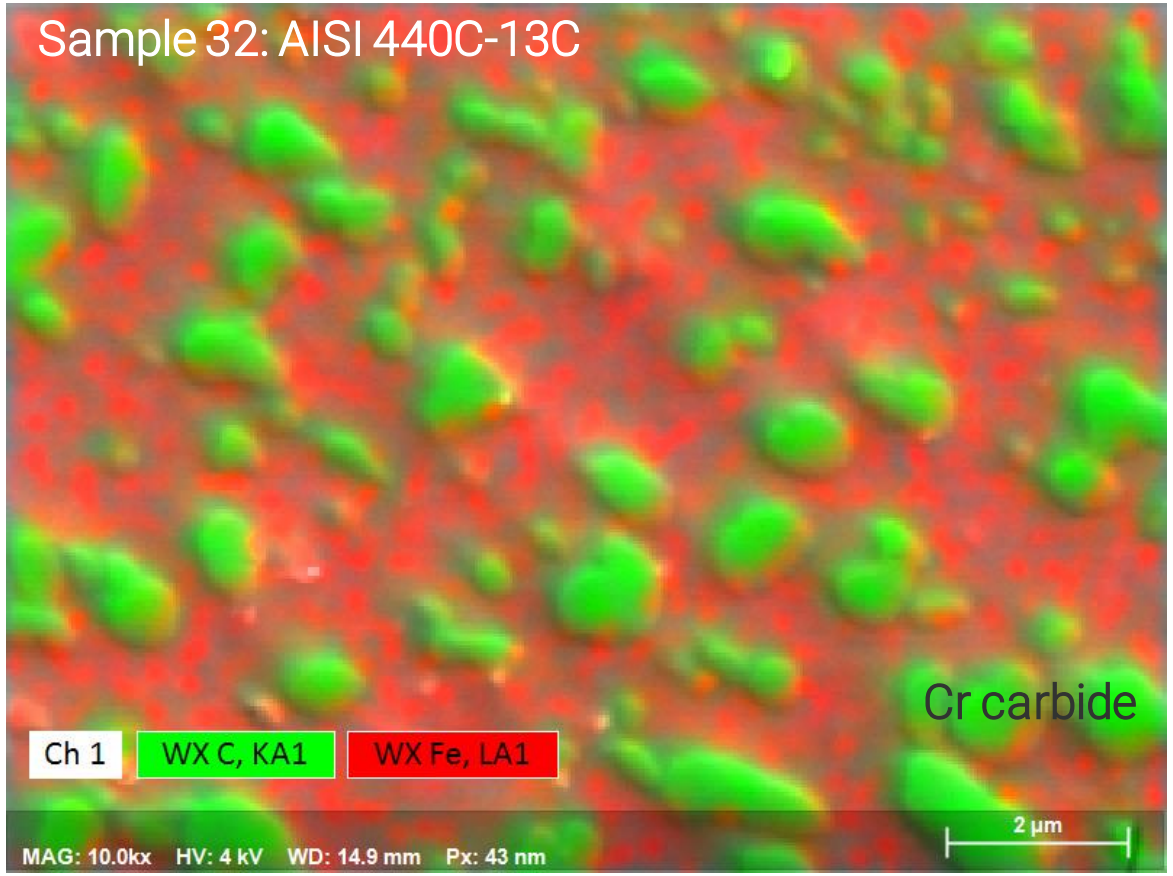


Increasing carbon deposition on sample surface during measurement

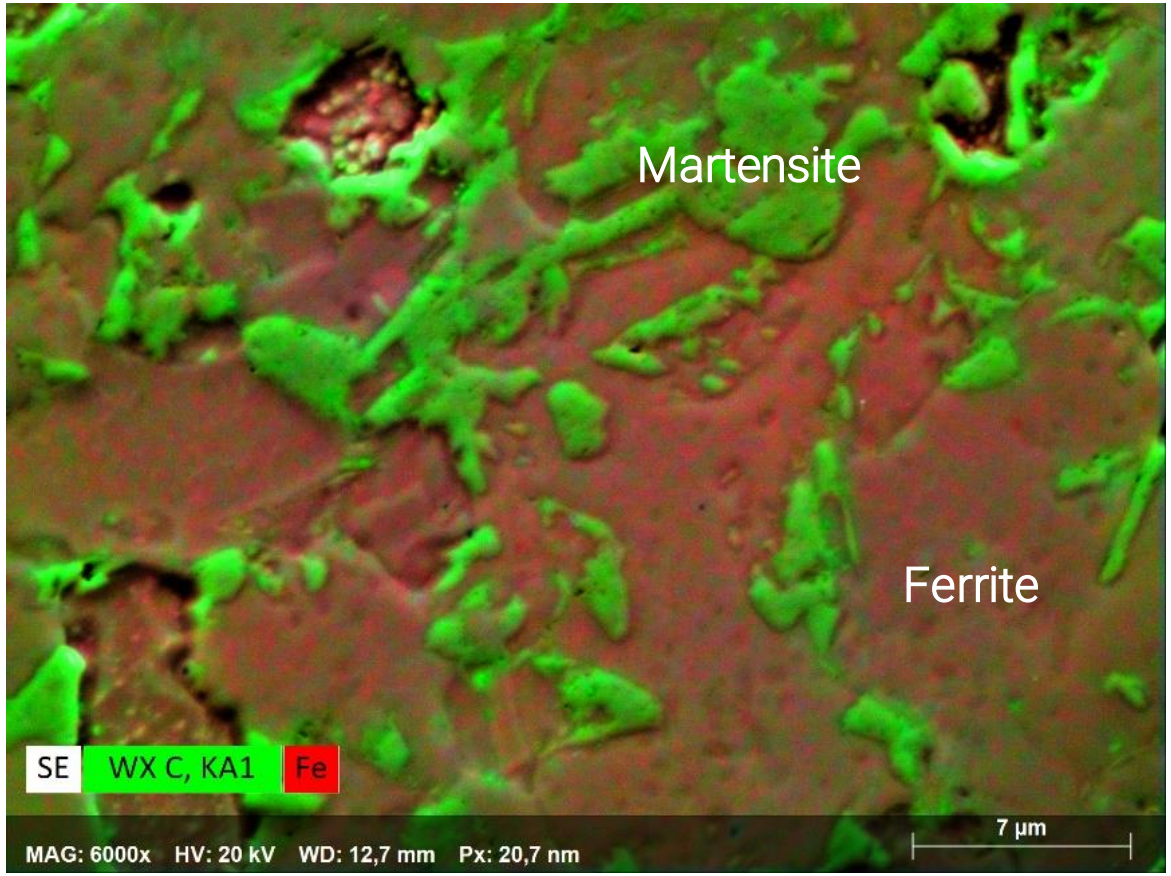


Light element determination by WDS
Heterogeneous carbon distribution

Carbide bearing steel



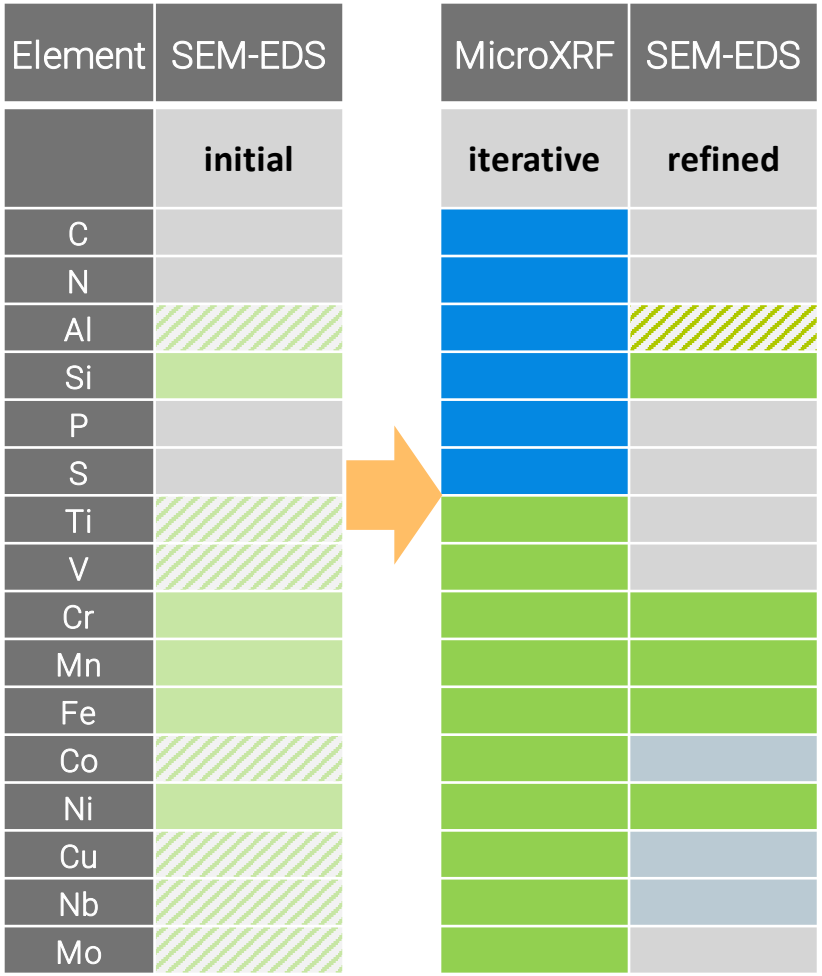
Dual phase steel



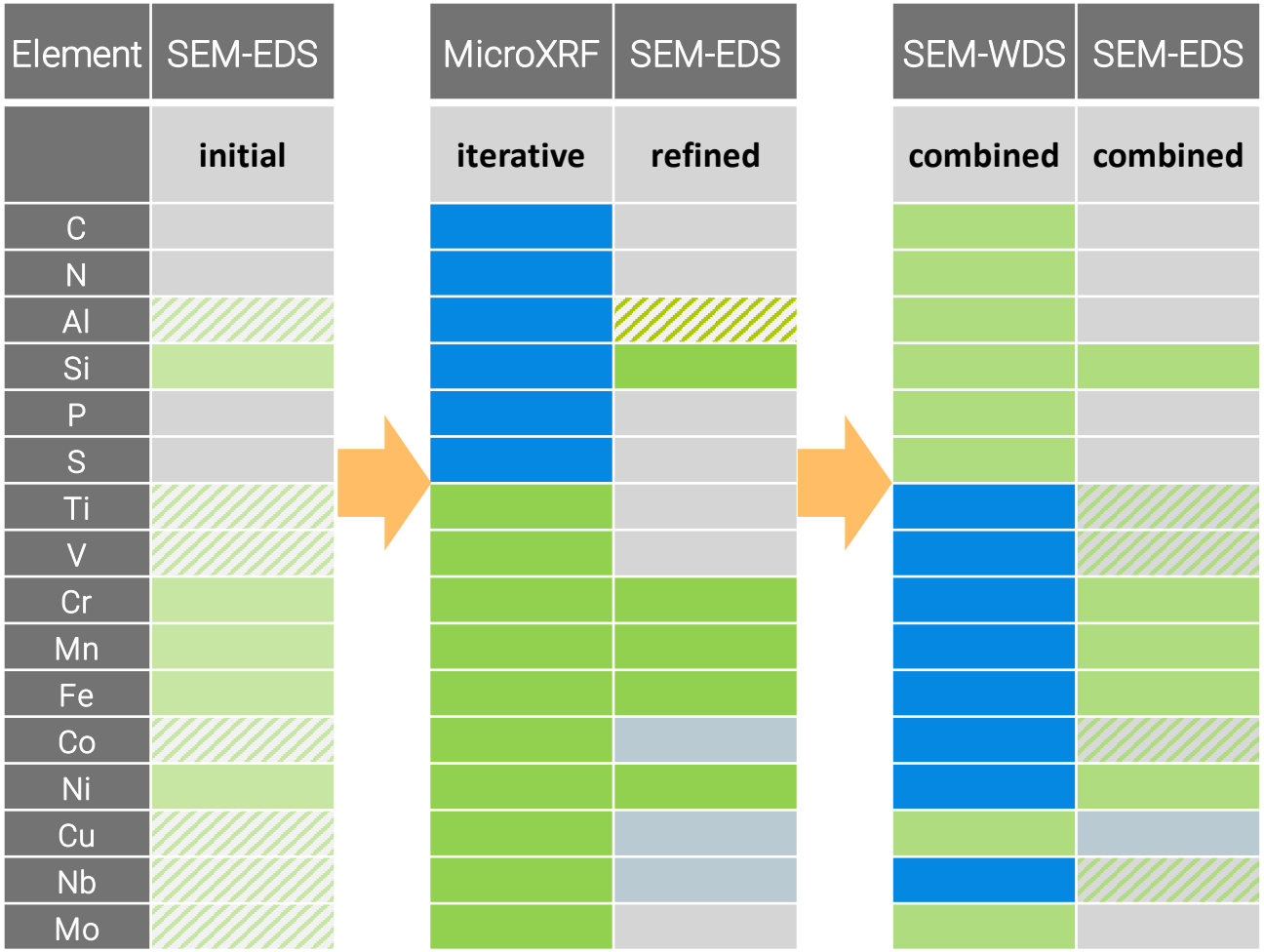
Methodology
Combined analysis process

Element	SEM-EDS
	initial
C	
N	
Al	
Si	
P	
S	
Ti	
V	
Cr	
Mn	
Fe	
Co	
Ni	
Cu	
Nb	
Mo	

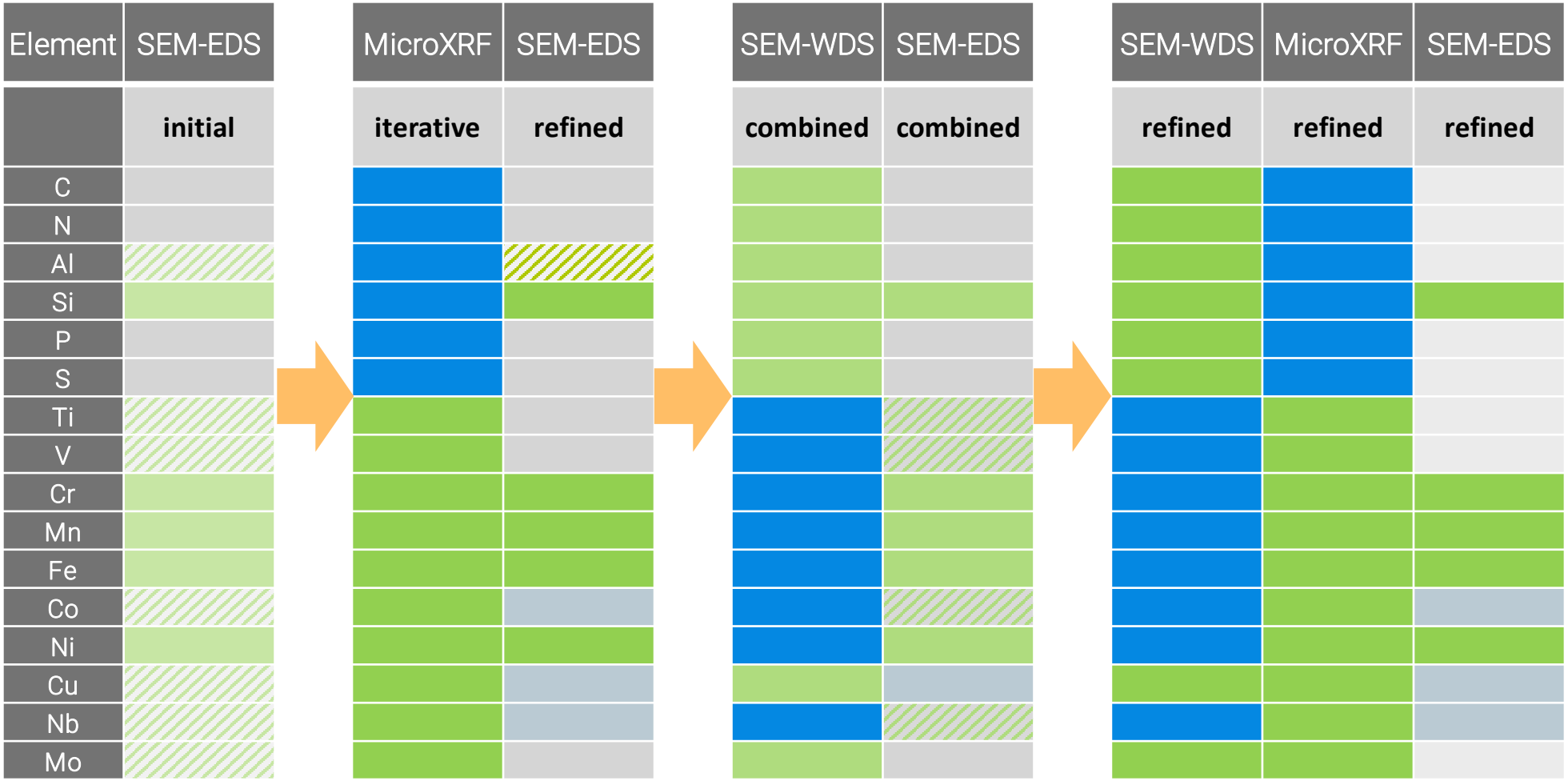
Methodology
Combined analysis process



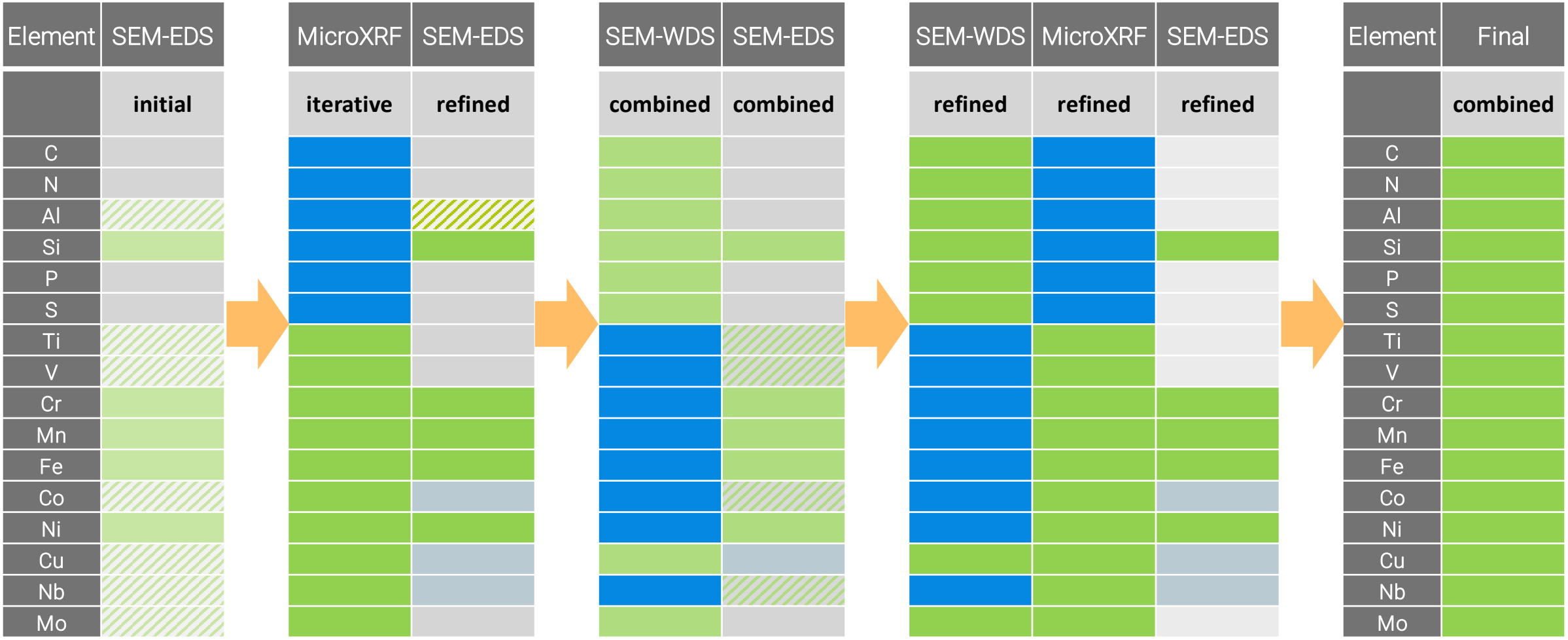
Methodology
Combined analysis process



Methodology
Combined analysis process



Methodology
Combined analysis process



Methodologies
Combined analysis process

Element	SEM-EDS	MicroXRF	SEM-EDS	SEM-WDS	SEM-EDS	SEM-WDS	MicroXRF	SEM-EDS	Element	Final
	initial	iterative	refined	combined	combined	refined	refined	refined		combined
C				≤ 0.36		≤ 0.36			C	≤ 0.36
N				0.02		0.02			N	0.02
Al				0.00		0.00			Al	0.00
Si	0.36		0.36	0.328	0.36	0.328		0.36	Si	0.35
P				0.029		0.029			P	0.03
S				0.013		0.013			S	0.01
Ti		0.002					0.002		Ti	0.002
V		0.059					0.059		V	0.058
Cr	17.09	17.496	17.09		17.09		17.496	17.09	Cr	17.41
Mn	1.92	1.788	1.92		1.92		1.788	1.92	Mn	1.74
Fe	69.33	70.713	69.33		69.33		70.713	69.33	Fe	70.11
Co	0.60	0.154	0.60		0.60		0.154	0.60	Co	0.14
Ni	8.86	9.012	8.86		8.86		9.012	8.86	Ni	9.00
Cu	0.50	0.501	0.50	0.458	0.50	0.458	0.501	0.50	Cu	0.49
Nb	0.74	0.695	0.74		0.74		0.695	0.74	Nb	0.67
Mo	0.44	0.448	0.44	0.393	0.44	0.393	0.448	0.44	Mo	0.42

Analysis of Steels and Alloys
Combined Analysis

Sample 32: AISI 422-205B

Element	Certified	SEM-WDS	MicroXRF	SEM-EDS	Combined
C	**0.22**	≤ 0.34			**≤ 0.34**
N	**0.05**	0.05			**0.05**
Al	**0.01**	0.004			**0.00**
Si	**0.37**	0.339		0.34	**0.34**
P	**0.01**	0.018			**0.02**
S	**0.00**	0.029			**0.00**
Ti	**0.00**		0.003		**0.00**
V	**0.26**		0.279		**0.26**
Cr	**11.72**		11.084	11.37	**11.32**
Mn	**0.68**		0.797	0.87	**0.75**
Fe	**83.70**		83.243	84.55	**83.20**
Co	**0.03**		0.024	0.49	**0.02**
Ni	**0.70**		0.692	0.54	**0.67**
Cu	**0.15**	0.162	0.177		**0.17**
Nb	**0.02**		0.012		**0.01**
Mo	**0.97**	0.919	0.970	0.95	**0.97**

SEM-WDS

Low-Z elements

SEM-XRF

High-Z elements

SEM-EDS detection

Analysis of Steels and Alloys
Combined Analysis

Sample 28: AISI 347-8D

Element	Certified	SEM-WDS	MicroXRF	SEM-EDS	Combined
C	**0.05**	≤ 0.36			**≤ 0.36**
N	**0.02**	0.02			**0.02**
Al	**0.00**	0.00			**0.00**
Si	**0.36**	0.328		0.36	**0.35**
P	**0.03**	0.029			**0.03**
S	**0.03**	0.013			**0.01**
Ti	**0.00**		0.002		**0.002**
V	**0.06**		0.059		**0.058**
Cr	**17.30**		17.496	17.09	**17.41**
Mn	**1.76**		1.788	1.92	**1.74**
Fe	**69.33**		70.713	69.33	**70.11**
Co	**0.14**		0.154	0.60	**0.14**
Ni	**9.19**		9.012	8.86	**9.00**
Cu	**0.47**	0.458	0.501	0.50	**0.49**
Nb	**0.72**		0.695	0.74	**0.67**
Mo	**0.44**	0.393	0.448	0.44	**0.42**

SEM-WDS

Low-Z elements

SEM-XRF

High-Z elements

SEM-EDS detection

Summary and Conclusions
QUANTAX WDS Benefits

High spectral resolution

- Pathological EDS peak overlaps can be resolved (e.g. Si-W, Mo-S)
- High peak to background ratio leads to low detection limits (e.g., Al, Si, P)

High perfomance for low X-ray energies

- Analysis of light elements (e.g. C, N)
- Trace contents for low-Z elements (e.g., Al, Si, P)

High spatial resolution

- Allows analysis of sub-µm structures (e.g., carbides)
- Full performance also at low kV (e.g., 2-10 kV)

Summary and Conclusions: Analysis of Steels and Alloys

X-ray and Electron Excitation can work in combination to provide improved quantitative results, using the benefits of each. Specifically:

- Electron excitation is preferable for light elements, e.g. C to Si
- X-ray excitation is preferable for heavy elements and trace concentrations

Samples can be analysed and quantified either as spot (point) analyses or from hypermaps.

Benefits of each analytical method can be utilised. For example:

- ***Micro-XRF:*** Sample Preparation is minimal for micro-XRF
  - No carbon-coating, No polishing
- ***Electron Beam***: High resolution for detecting small inclusions
- ***WDS:*** High spectral and spatial resolution, high perfomance for low X-ray energies

Thank you!

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More Information

For more information, please contact us:

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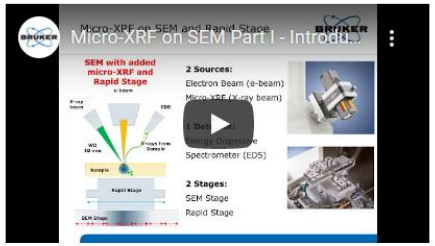
and

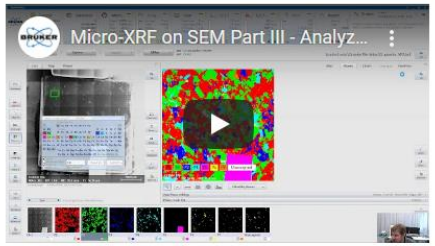
If you want to learn more about practical micro-XRF or SEM-EDS / WDS analysis including sample, measurement setup, and evaluation, our latest video series is available via the Bruker website and youtube

Product Videos



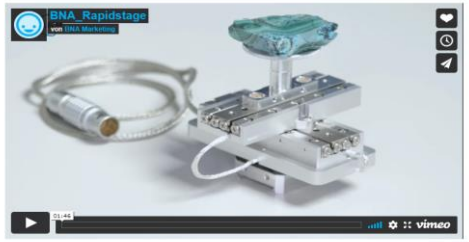
Part I - Introduction to micro-XRF and the Rapid Stage on a SEM

Part II - Loading a sample and performing a measurement



Part III - Analyzing a measured dataset

Rapid Stage



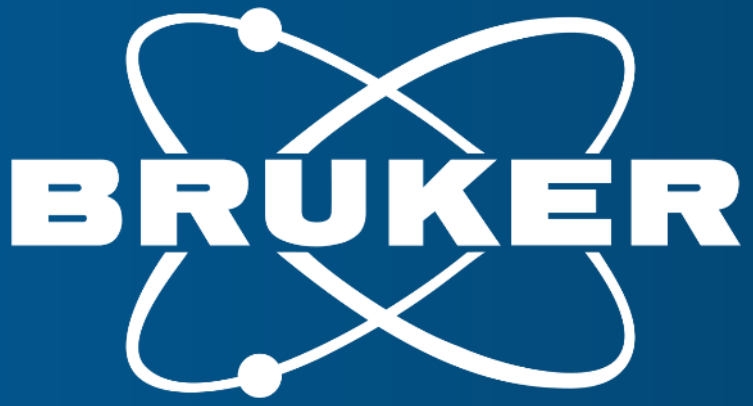
The Rapid Stage can be mounted on top of the SEM stage for fast mapping over large sample areas.

Questions and Answers

Are There Any Questions?

Please type in the questions you might have

in the Q&A box and press *Send*.



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