Quantification of Steels and Alloys using a dual source multidetector system

Part I: XRF-EDS and SEM-EDS analysis

Bruker Nano Analytics, Berlin, Germany

Webinar, March 23th, 2021

At. No.	Line S.	EDS Mass [%] Norm.	XRF Mass [%] Norm.	Comb. Mass [%] Norm.	Certified Val. /M%
8	K-Series	45.71	45.58	46.03	46.82
11	K-Series	10.54	10.32	10.61	10.68
12	K-Series	2.32	2.27	2.33	2.22
13	K-Series	1.34	0.89	0.89	0.95
14	K-Series	33.94	34.99	34.18	33.70
16	K-Series	0.16	0.12	0.12	0.11
19	K-Series	0.37	0.35	0.35	0.34
20	K-Series	5.30	5.34	5.34	5.08
22	K-Series	0.00	0.01	0.01	0.01
26	K-Series	0.28	0.03	0.03	0.03
33	K-Series	0.04	0.06	0.06	0.04
38	L-Series	0.00	0.04	0.04	–

Iron
Arsenic
Strontium
XRF: Oxygen quantification by stoichometry

Sn Ba Au Ni

MAG: 37x HV: 50kV

Presenters

Stephan Boehm

Product Manager XTrace / XSense
Bruker Nano Analytics, Berlin, Germany

Andrew Menzies, PhD

Sr. Applications Geology and Mining,
Bruker Nano Analytics, Berlin, Germany

Overview:
Motivation

Why using 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)

Overview:
Quantification of Steels and Alloys

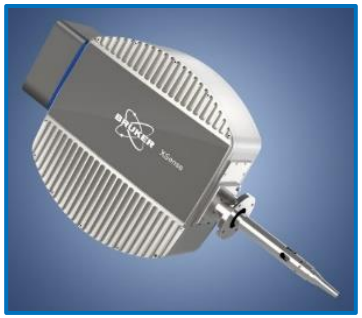
Part I of this webinar series will focus on the dual-beam sources (electron and X-ray source), and how they interact with the samples of interest to generate X-rays which are identified and quantified using EDS.

Part II will then compare these results with the measurements using the WDS collected on the same system.

- Terminology
- MicroXRF Introduction
- Quantification Methodologies
- Application to Steels and Alloys
- Summary and Conclusion

Introduction
Terminology

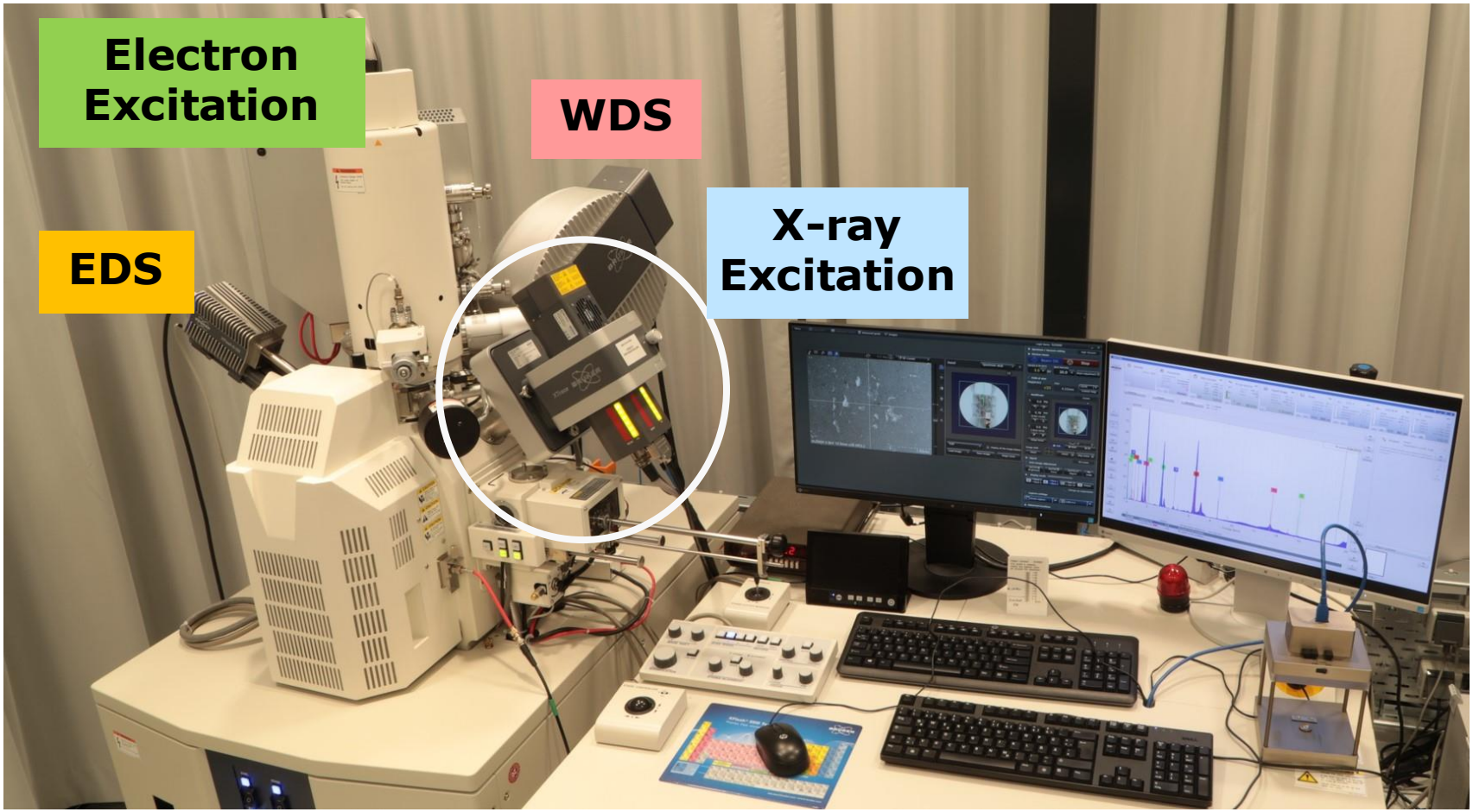
SEM-EDS: Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using an EDS (simultaneous element detection)



SEM-WDS: Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using a WDS (sequential element detection)

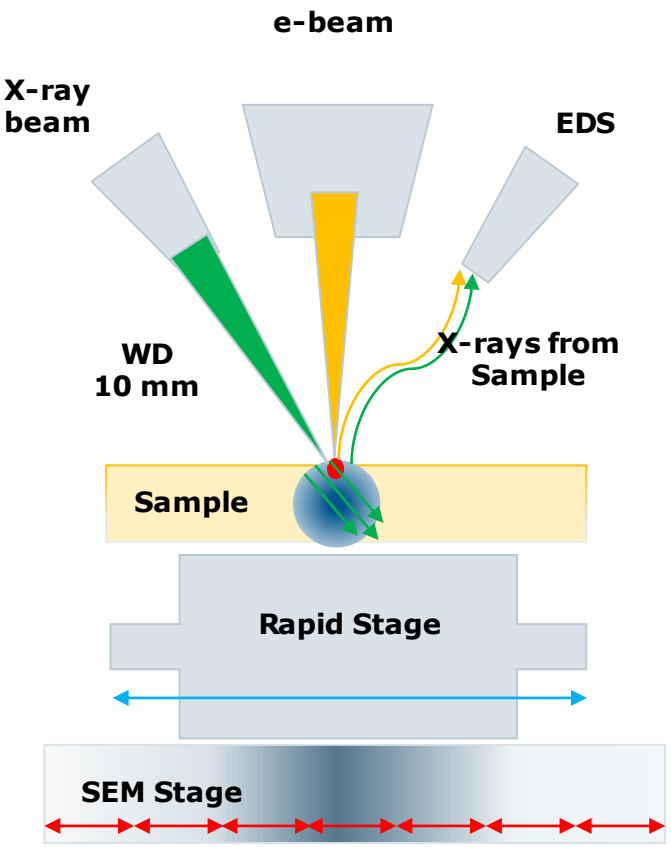
SEM-XRF-EDS: MicroXRF on SEM (XTrace): Analysis based on the sample interaction with an X-ray beam source from the Micro XRF attached to the SEM and the resultant X-rays that are detected using an EDS (simultaneous element detection)

Excitation: MicroXRF and Electron Detectors: EDS and WDS



Introduction
What is Micro-XRF on the SEM?

Enhanced SEM



2 Excitation Sources:

Electron Beam (e-beam)

Micro-XRF (X-ray beam)

1 Detector:

Energy Dispersive Spectrometer (EDS)

2 Stages:

SEM Stage

Rapid Stage

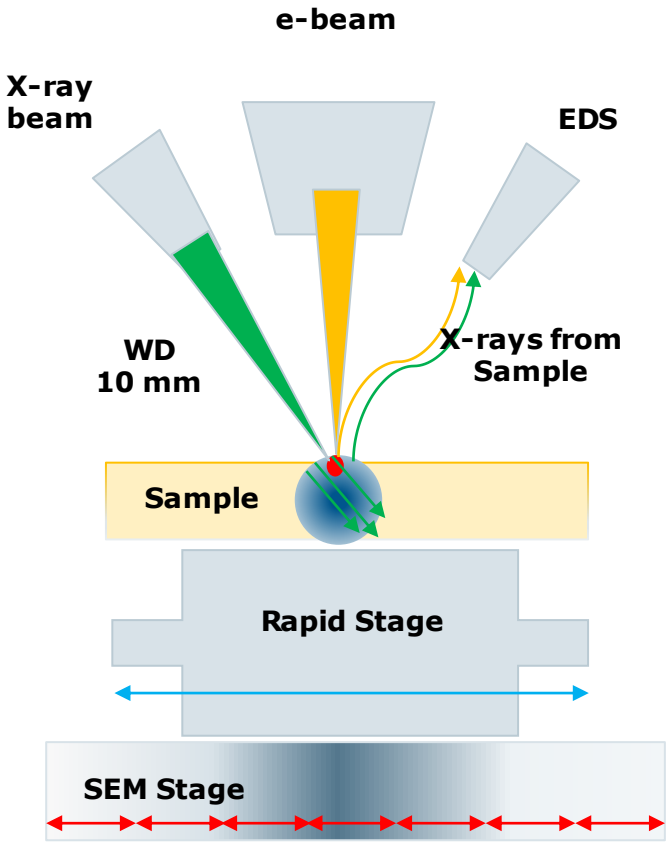
Micro-XRF and Electron Excitation Analysis

Excitation with either electrons or X-rays generate fluorescence radiation of the irradiated material.

Detection is normally performed with energy dispersive spectrometers (EDS), independent of the excitation source. Signal collection and spectral presentation is identical, but quantification is different.

Important differences:

- Spot Size
- Information depth
- Elemental Range
- Limits of detection
- Spectral Background
- Sample Handling

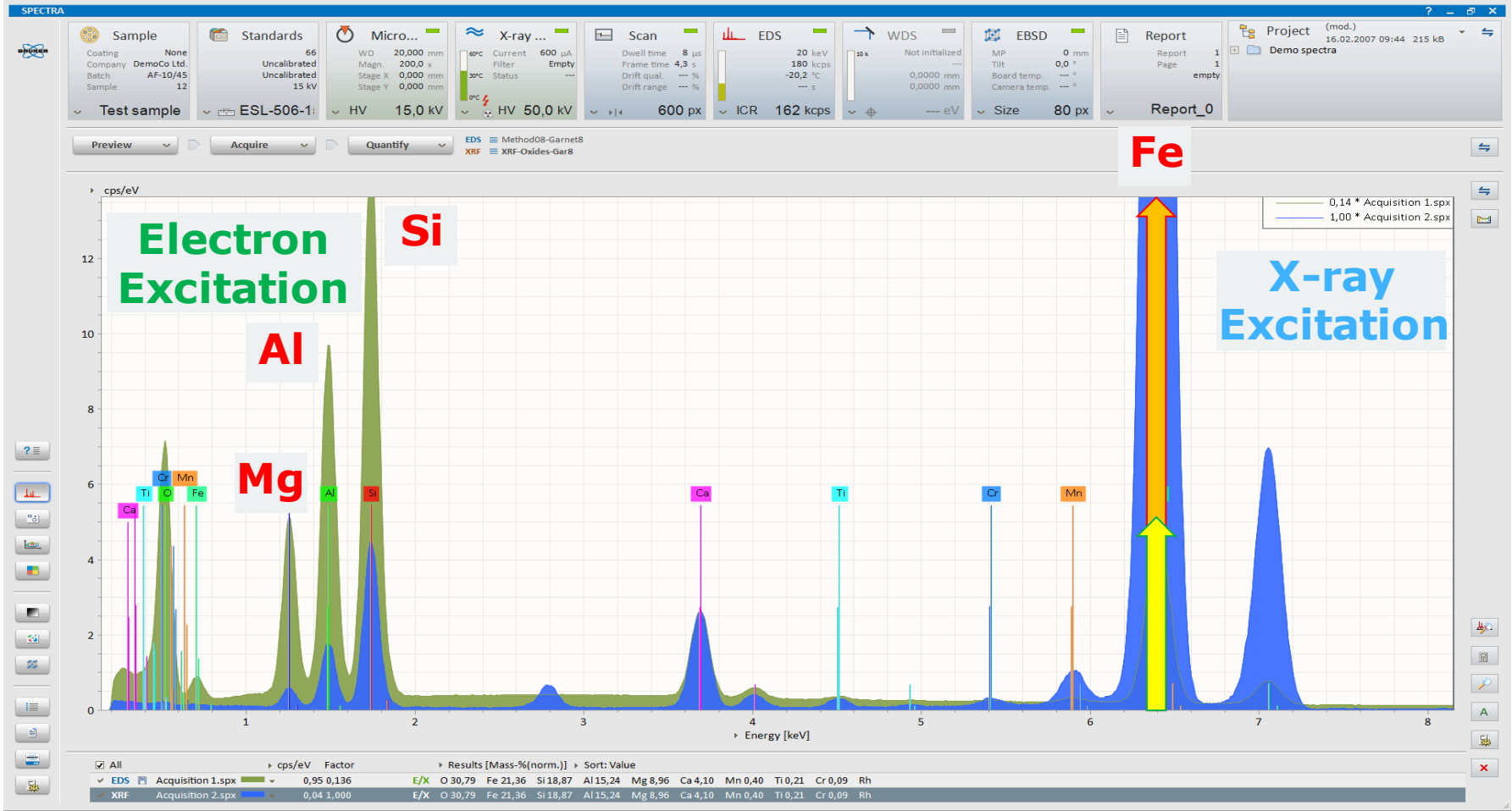


Analytical Parameters and Conditions
SEM-EDS vs SEM-WDS vs SEM-XRF

Parameter	EDS: E-beam (SEM-EDS)	WDS: E-beam (SEM-WDS)	EDS: Micro-XRF (SEM-XRF-EDS)
Analyzed Volume	Ø: few µm Information depth: µm; (depending primarily on electron energy)	Ø: few µm Information depth: µm; (depending primarily on electron energy)	Ø: 15-30 µm Information depth: µm to mm; (depending on analysed element and matrix)
Detectable Elements	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 6 (carbon)
Energy range	K- L –M – Lines (up to 20 keV)	70 eV – 3.6 keV (L- M- Lines)	K- L –M – Lines (up to 40 keV)
Concentration Range	Down to 1000 ppm	Down to 100 ppm	Down to 10 ppm
Quantification	Standard less and Standard based	Standard based	Standard less and standard based
Data collection	Simultaneously	Sequentially	Simultaneously
Sample Preparation	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Electrical Conductivity not required, samples doesn´t need to be polished
Sample Stress	Heating due to absorbed electrons	Heating due to absorbed electrons	Minimal
Typical SEM beam current	Variable	Variable > 10 nA	N/A

Energy Dispersive Spectra
Comparison: Electron vs X-ray Excitation

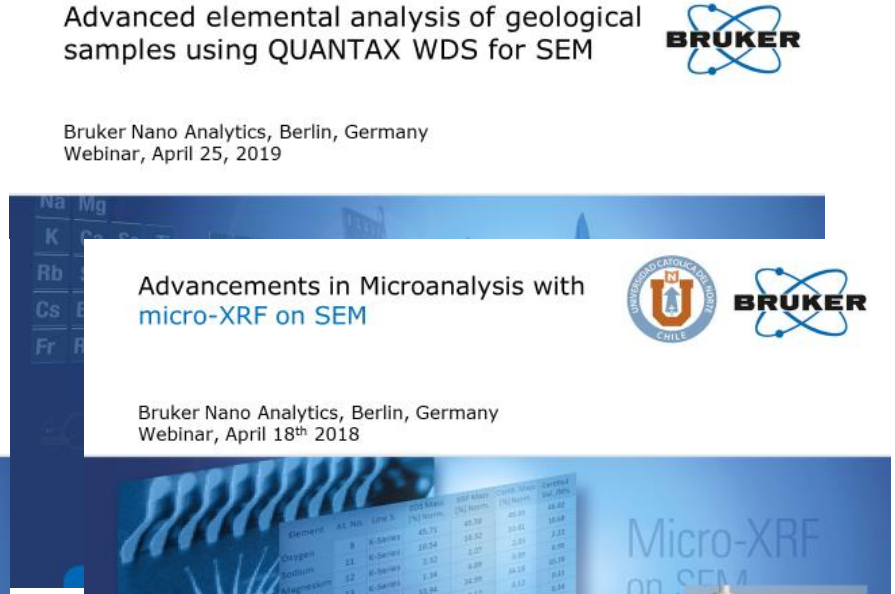
Garnet Spectra: Light element signal intensity higher for electron excitation.



Introduction
Historic and Current Webinars

www.bruker.com/events/webinars.html

Filter: EDS, WDS, EBSD, Micro-XRF on SEM



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.

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

Benefit of combined SEM-EDS and micro-XRF

Quantification of Cast Iron

Elem	Cert	EDS	XRF
C	2.51	2.84	
Al	0.013		0.023
Si	0.829	0.708	1.11
P	0.027		0.016
S	0.01	0.053	0.364
Ti	0.022		0.024
V	0.036		0.034
Cr	0.507	0.520	0.476
Mn	1.94	1.84	1.91
Fe	93.7	94.0	95.7
Ni	0.03		0.023
Cu	0.075		0.063
Zn	0.023		0.013
As	0.016		0.025
Nb	0.051		0.061
Mo	0.071		0.072
Sn	0.011		0.005
Sb	0.025		0.005
W	0.066		0.066
Pb	0.011		0.045
Bi	0.014		0.001

Problems when using a single method:

- Electron excitation is not good for trace concentrations
- Trace element concentrations possible with X-ray excitation but light elements are not idea.
- Thus the (normalized) quantification results for the main components could be wrong
- Deconvolution of overlapping peaks, e.g. S due to the overlap of S-K with Mo-L and Pb-M

Haschke, M, and Boehm, S, 2017, Micro-XRF in Scanning Electron Microscopes. In: Advances in Imaging and Electron Physics, Hawkes, P. W. (ed.), vol 199, Academic Press, pp. 1-60

Benefit of combined SEM-EDS and micro-XRF

Quantification of Cast Iron

Elem	Cert	EDS	XRF	Comb
C	2.51	2.84		2.84
Al	0.013		0.023	0.022
Si	0.829	0.708	1.11	0.910
P	0.027		0.016	0.044
S	0.01	0.053	0.364	0.036
Ti	0.022		0.024	0.025
V	0.036		0.034	0.033
Cr	0.507	0.520	0.476	0.495
Mn	1.94	1.84	1.91	1.84
Fe	93.7	94.0	95.7	93.0
Ni	0.03		0.023	0.02
Cu	0.075		0.063	0.058
Zn	0.023		0.013	0.013
As	0.016		0.025	0.023
Nb	0.051		0.061	0.057
Mo	0.071		0.072	0.067
Sn	0.011		0.005	0.005
Sb	0.025		0.005	0.005
W	0.066		0.066	0.077
Pb	0.011		0.045	0.042
Bi	0.014		0.001	0.002

Solution:

In the combined analysis the concentration of the heavy elements (Mo-K, Pb-L) determined with X-ray excitation can be used to calculate their peak intensity in the range of S-K radiation and then only the difference is caused by S

→ Combined analysis allows the determination of mass fraction of all elements with a better accuracy than the quant only from a single excitation.

Haschke, M, and Boehm, S, 2017, Micro-XRF in Scanning Electron Microscopes. In: Advances in Imaging and Electron Physics, Hawkes, P. W. (ed.), vol 199, Academic Press, pp. 1-60

Basics of FP Quantification
Sherman's Equation

Quantitative X-ray Fluorescence analysis is based on sample properties and the physical processes of known probability.

These are known as the **Fundamental Parameters (FP)**.

The Sherman Equation is the basis for all XRF FP quantification

$$I_{\mathrm{fl},i} = K_i \cdot \int_{E_{\mathrm{abs},i}}^{E_{\max}} \int_{x=0}^{D} I_0(E) \cdot e^{\frac{-\mu_S(E)\cdot\rho_S\cdot x}{\sin(\varphi_{\mathrm{in}})}} \cdot C_i \cdot \tau_{i,E} \cdot Q_i(E, E_{\mathrm{fl}}) \cdot e^{\frac{-\mu_S(E_{\mathrm{fl}})\cdot\rho_S\cdot x}{\sin(\varphi_{\mathrm{out}})}} \cdot \frac{\Omega}{4\pi} \cdot \varepsilon^{\mathrm{D}} \, \mathrm{d}x \, \mathrm{d}E$$

Excitation spectrum (as it reaches the sample)

Attenuation of excitation radiation when penetrating into the sample

Sample composition and interaction probabilities

Attenuation of fluorescence radiation when leaving the sample

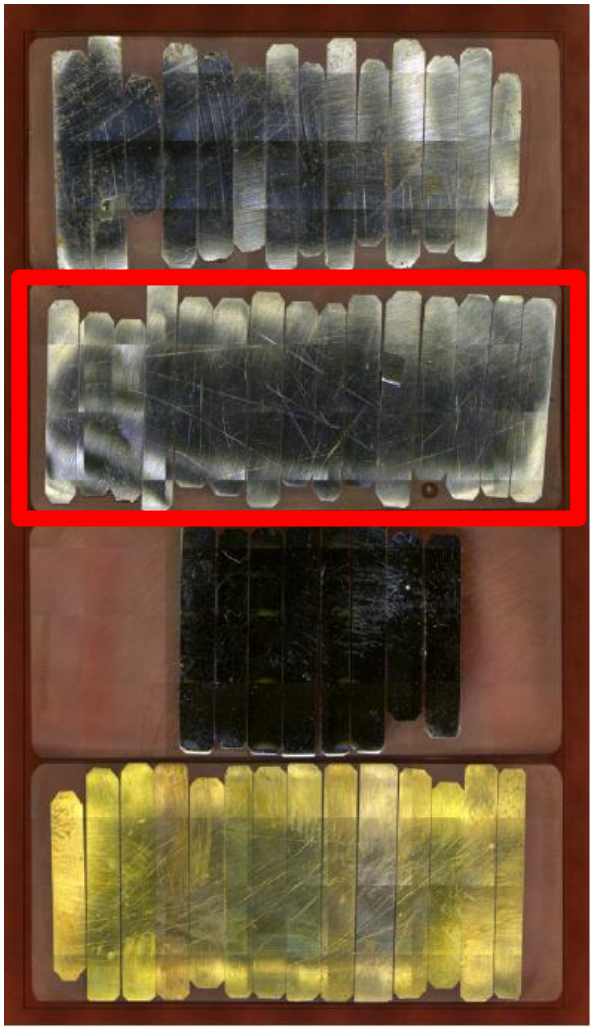
Solid angle of detection and detector sensitivity

Instrument sensitivity for the respective element

Analysis of Steels and Alloys
Example

- It is important for the manufacturers of components using steels, alloys or other metals to know the composition of the material to be sure that the end-product can fulfil demanded specifications.
- The addition of heavy metals is essential for the mechanical and thermal properties of alloy steels.
- If it does not meet these demands, it might cause damage to the component or equipment.
- SEM-EDS analysis is challenging due to the
  - insufficient detection limit
  - line overlapping in the low energy range
  - specimen inhomogeneity
- Understanding steels / alloys:
  - Overall composition: Point Analysis
  - Inclusions: Mapping

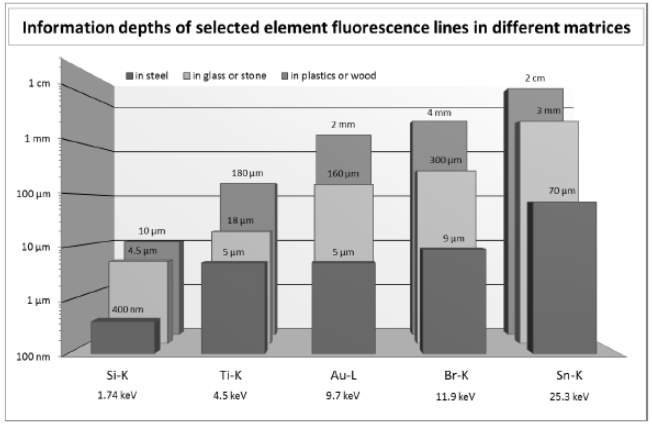
Analysis of Steels and Alloys
Case Study



- SAMPLES: Set of 51 ARMI steels with known (certified) compositions
- Cast in Epoxy Resin and Polished
- High-Fe, **Cr-Ni steels**, Cu-alloys

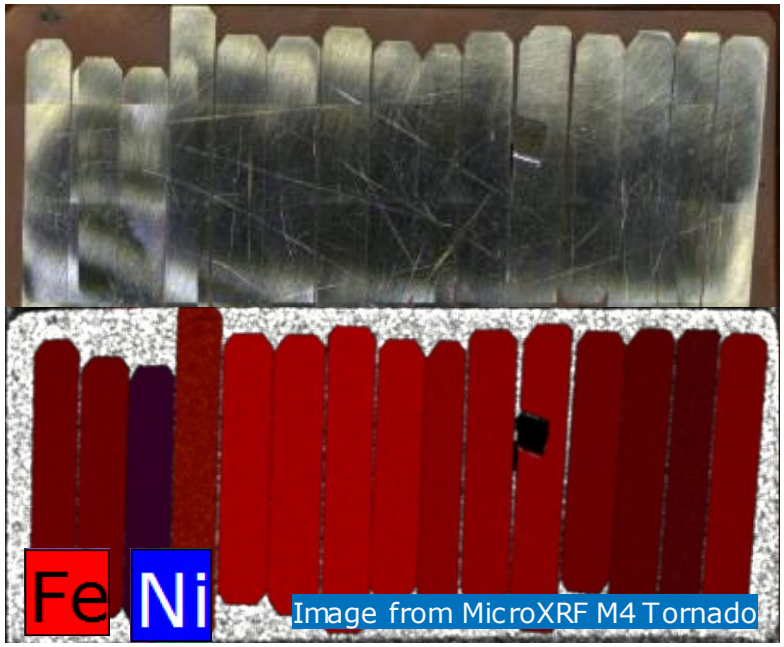
Steel samples have two main advantages:

- They are pretty homogeneous
- Even for the highest energy elements the information depth is restricted to below 100 µm (up to Zn even < 5 µm)



→ Even small chips/flakes of steel can be quantified for classification

Analysis of Steels and Alloys
Samples



- Major Elements:

Cr, Fe, Mn, Ni

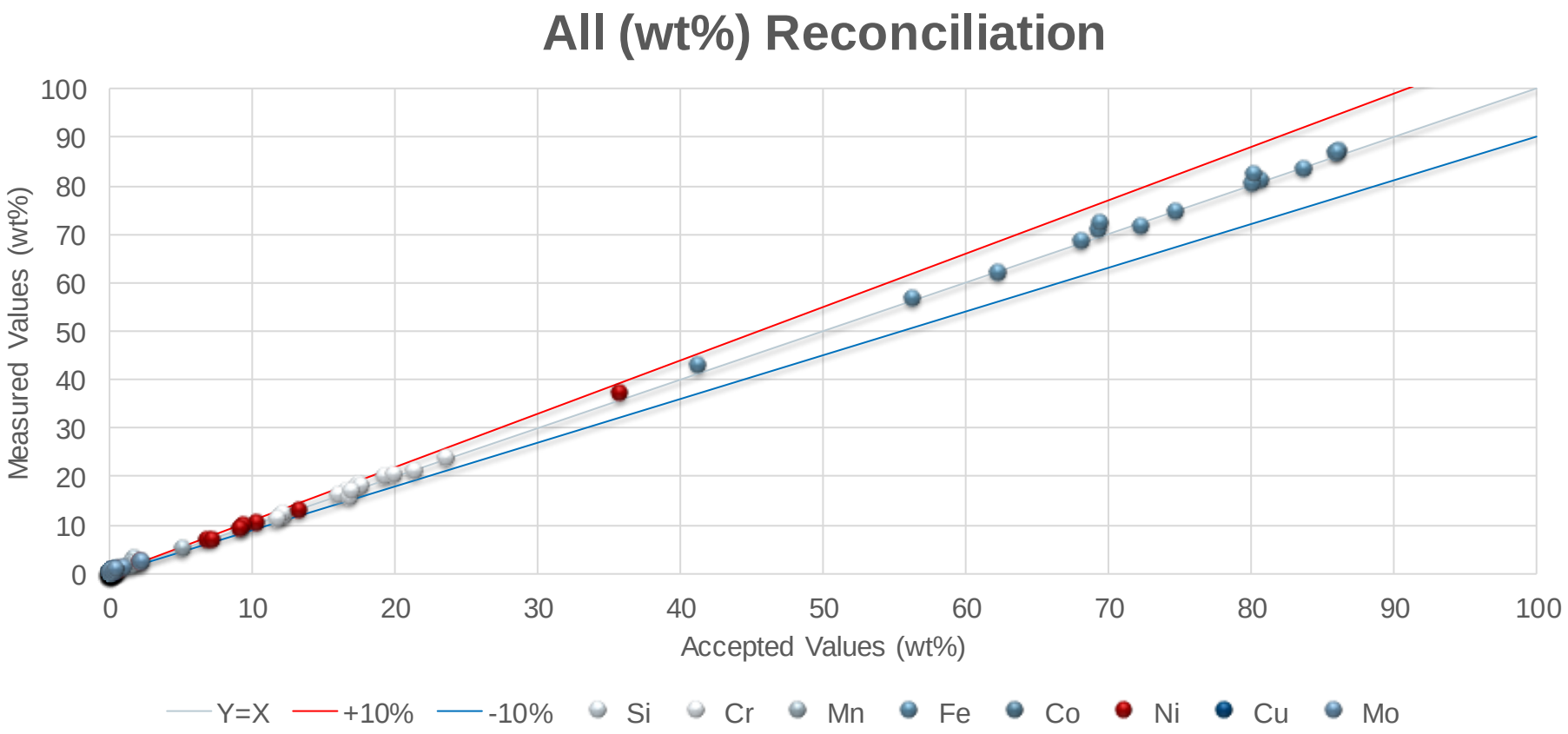
- Minor and Trace Elements:

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

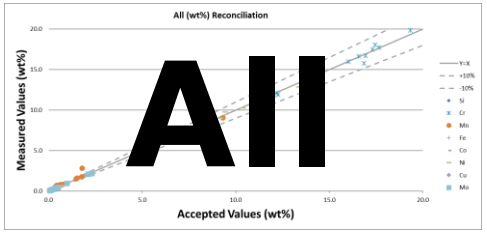
Analysis of Steels and Alloys
Excitation: Micro-XRF; Detector: EDS

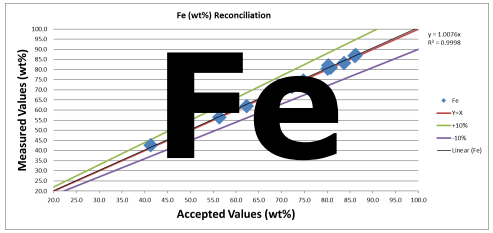
Analytical Conditions Point Analysis: 50 kV, 600 uA, No Filter, 130 kcps, under vacuum, Working Distance 12 mm, 120 seconds

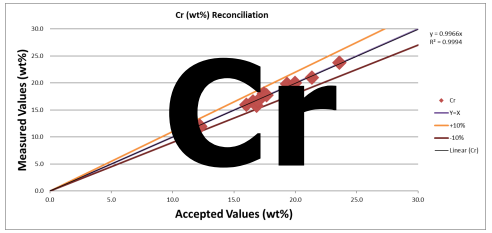


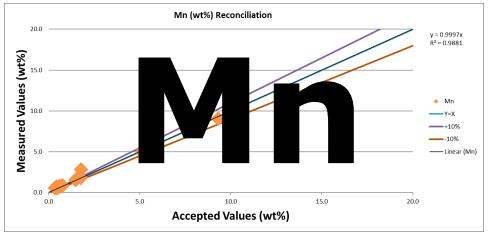
Analysis of Steels and Alloys
Individual Elements: Ti (Minor / Trace)

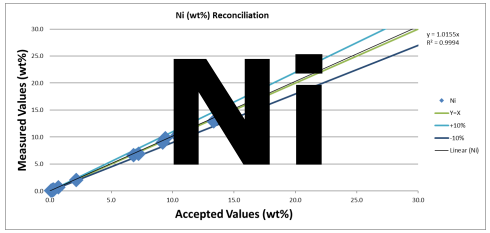
Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

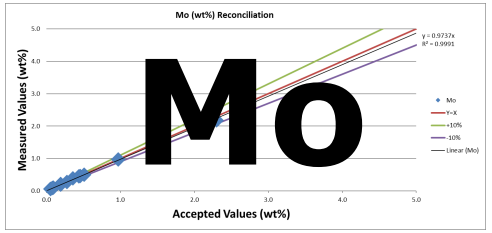


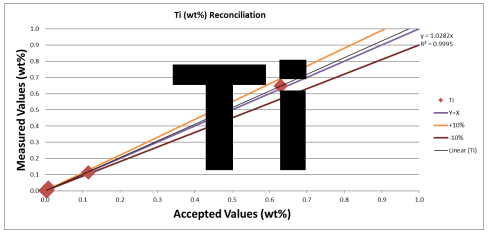


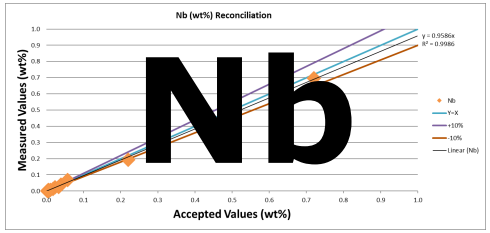


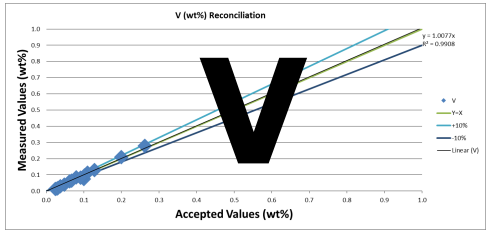




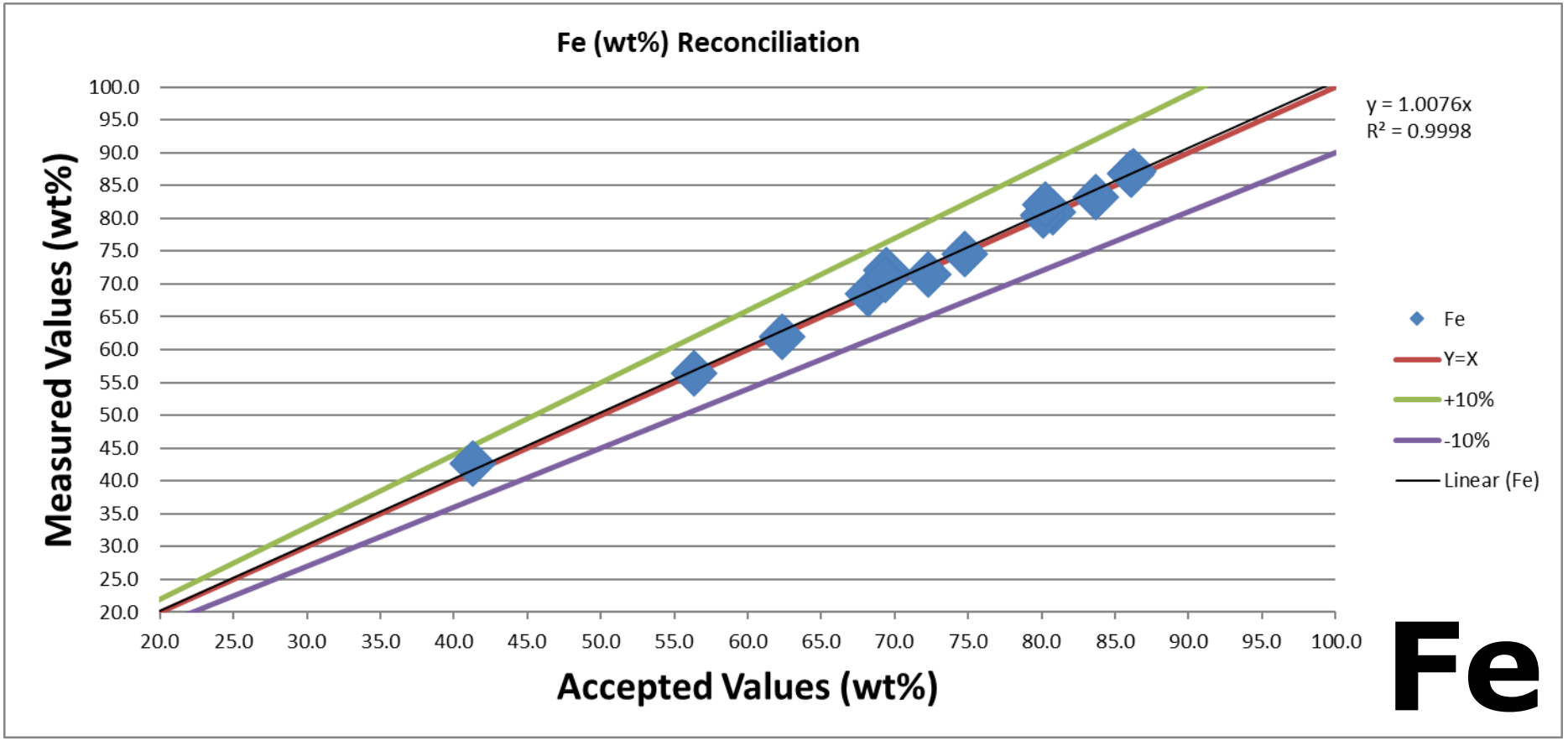






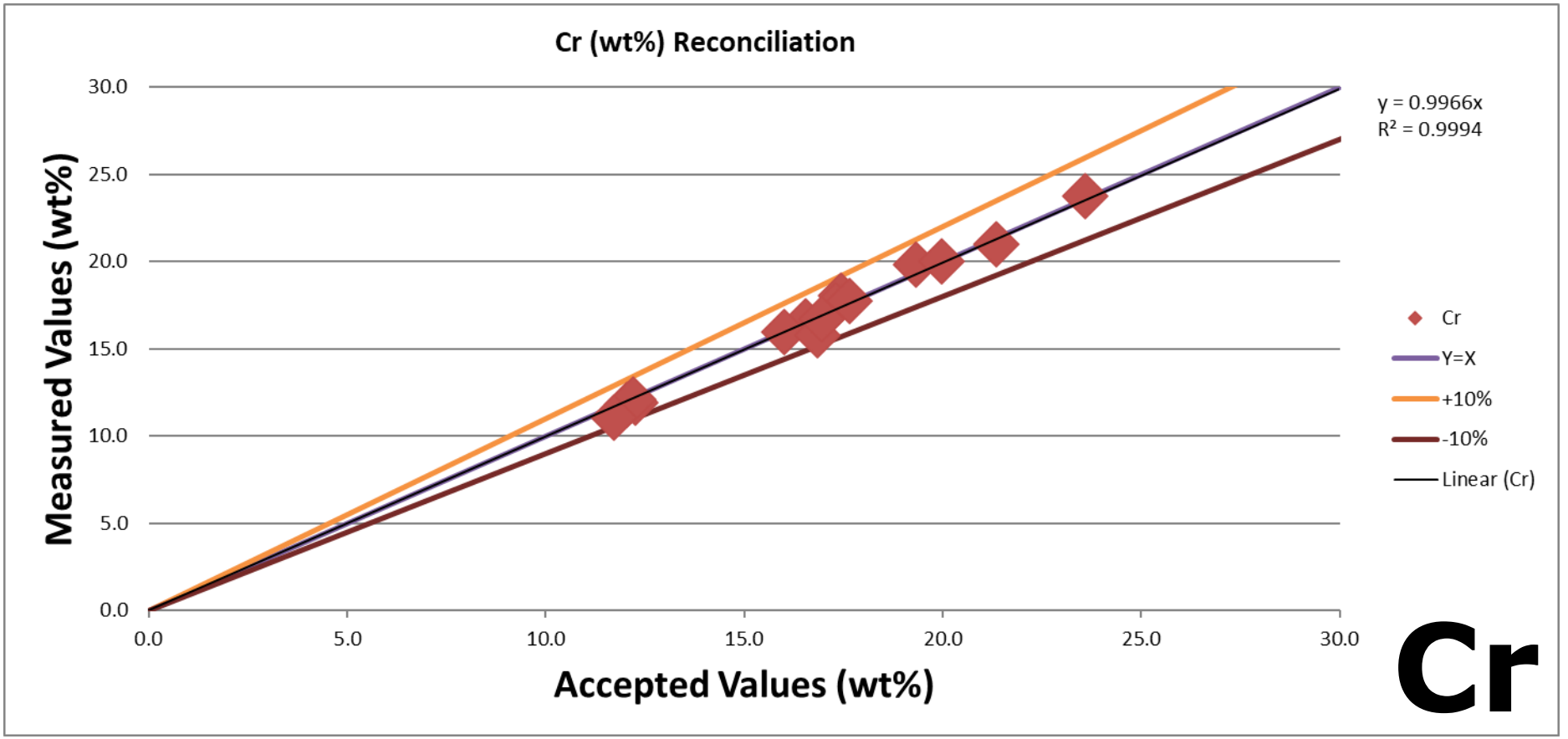


Analysis of Steels and Alloys
Individual Elements: Fe (Major)



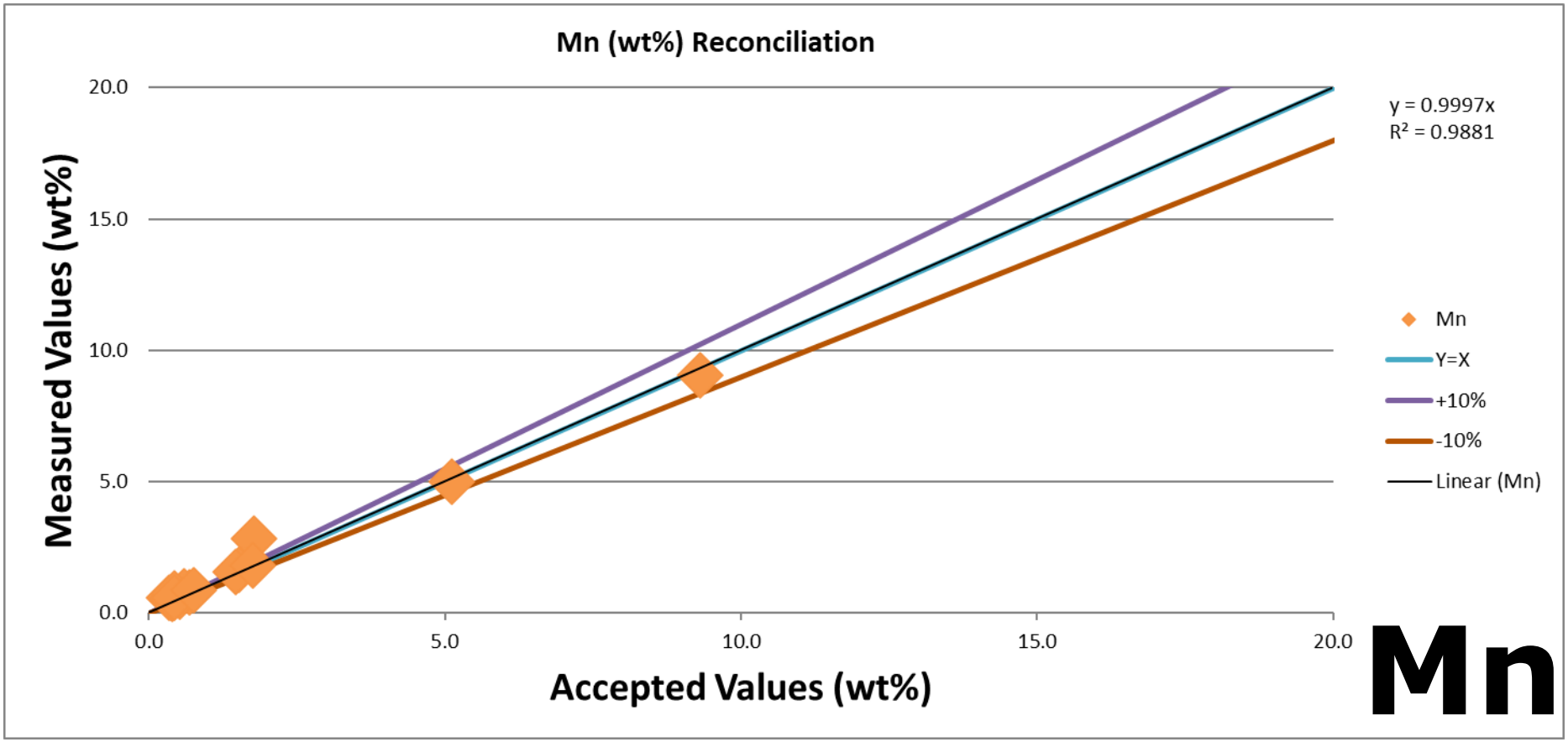
Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

Analysis of Steels and Alloys
Individual Elements: Cr (Major)



Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

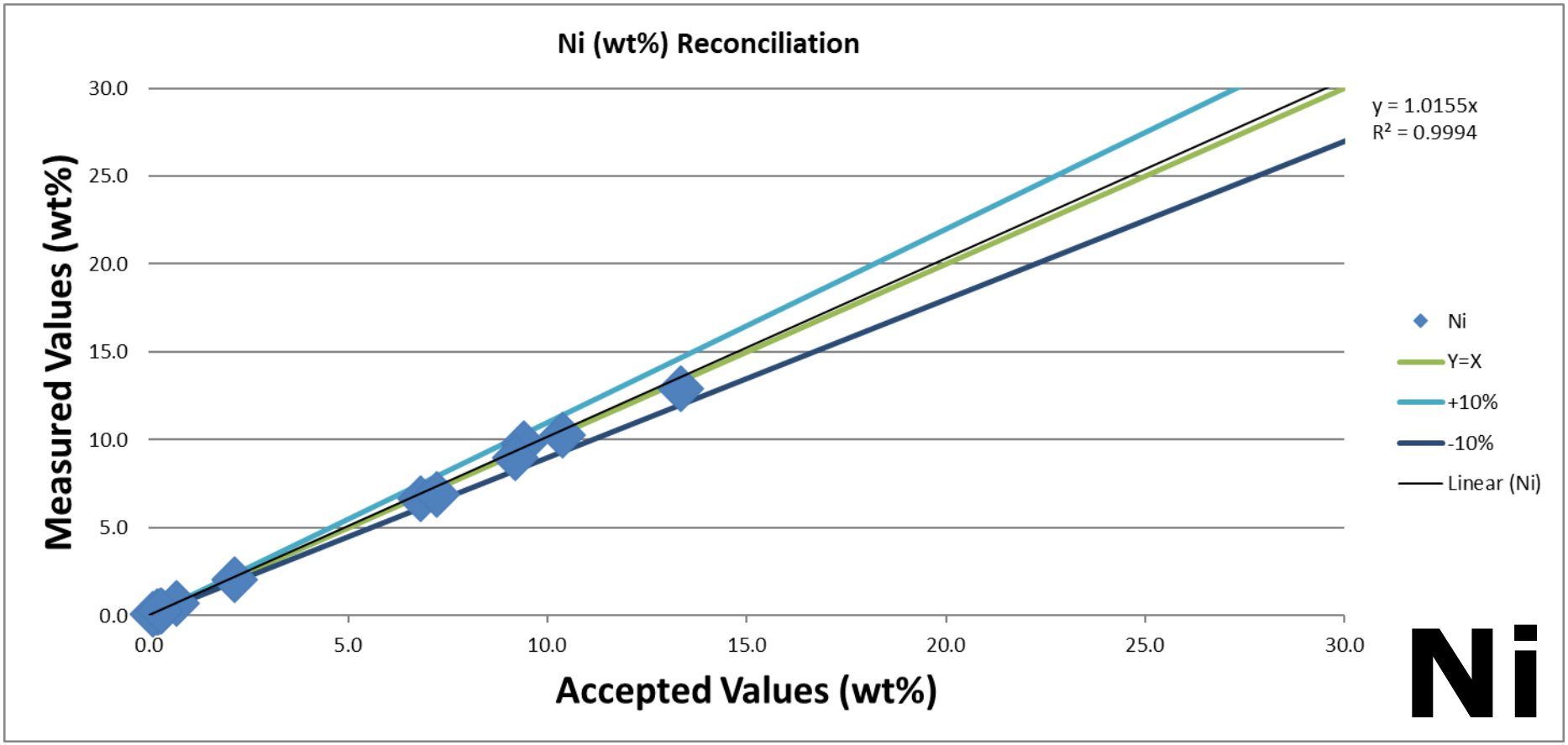
Analysis of Steels and Alloys
Individual Elements: Mn (Major / Minor)



Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

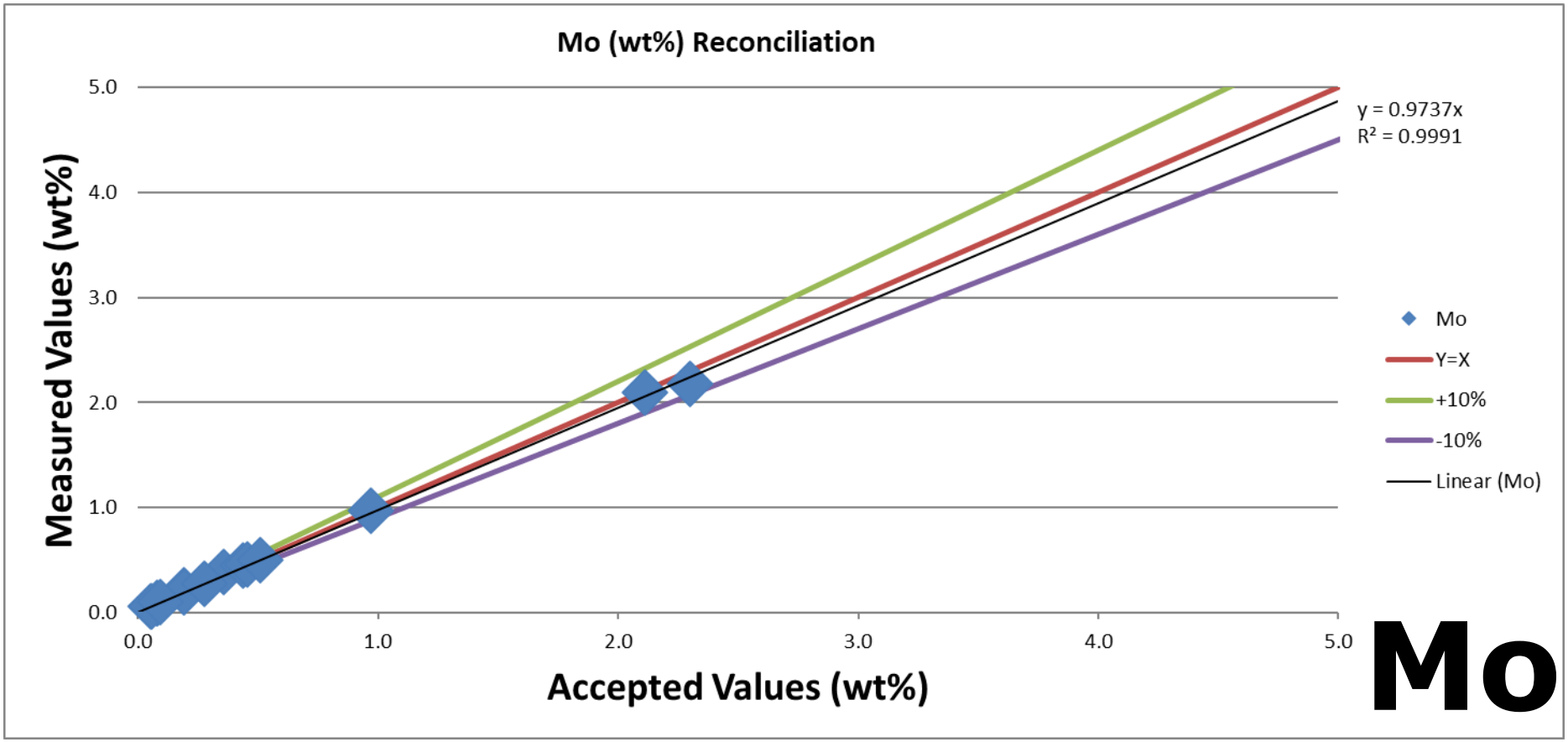
Analysis of Steels and Alloys

Individual Elements: Ni (Major / Minor / Trace)



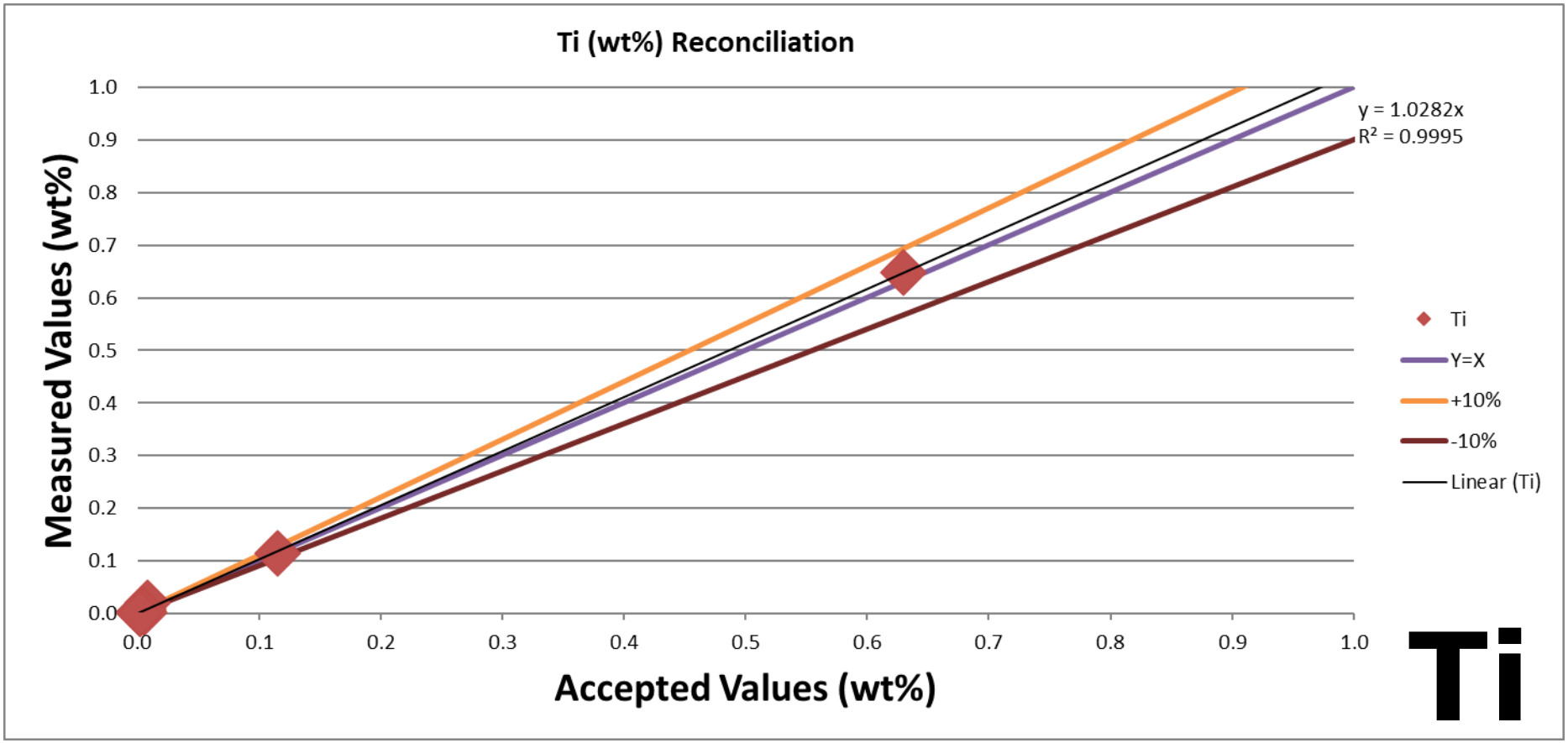
Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

Analysis of Steels and Alloys
Individual Elements: Mo (Minor / Trace)



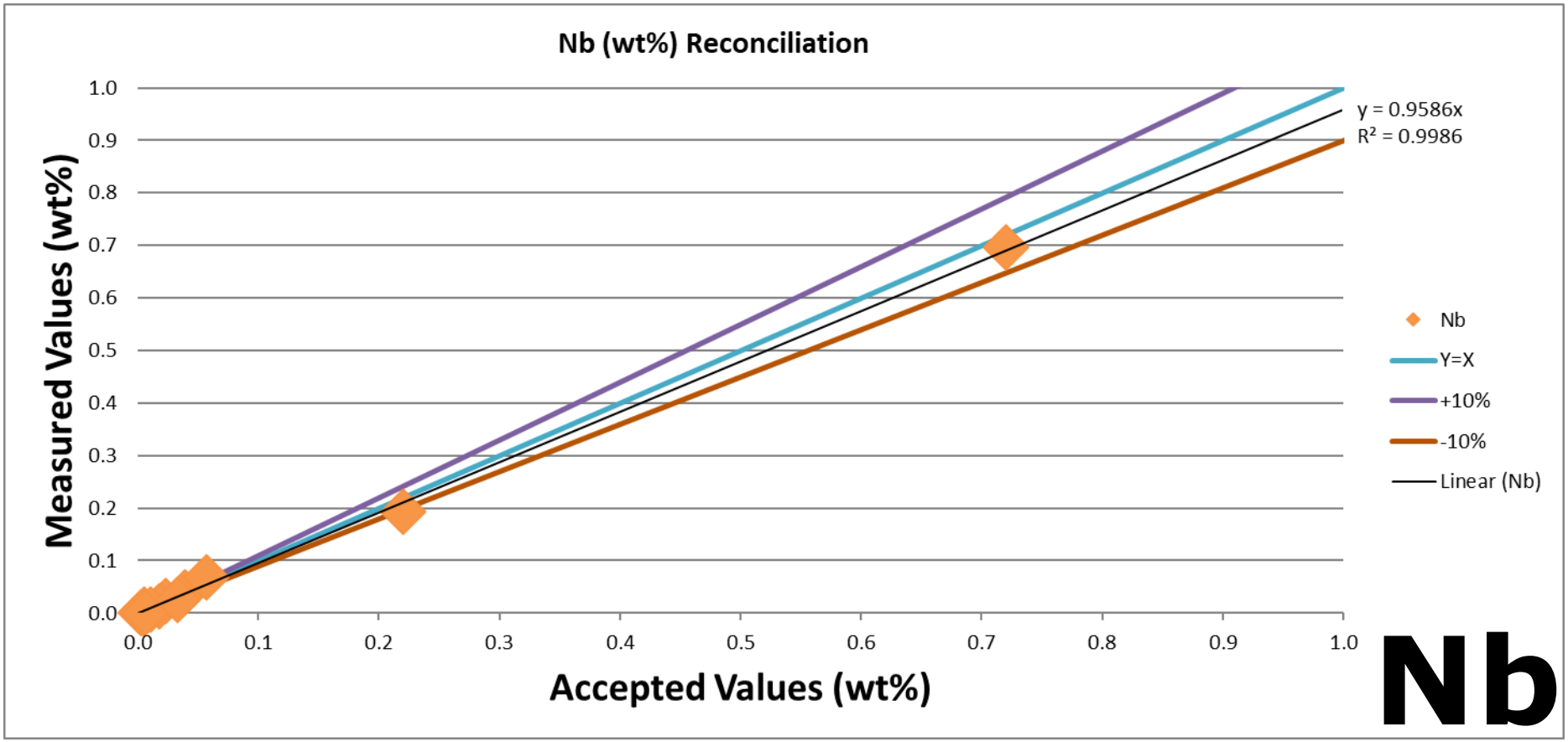
Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

Analysis of Steels and Alloys
Individual Elements: Ti (Minor / Trace)



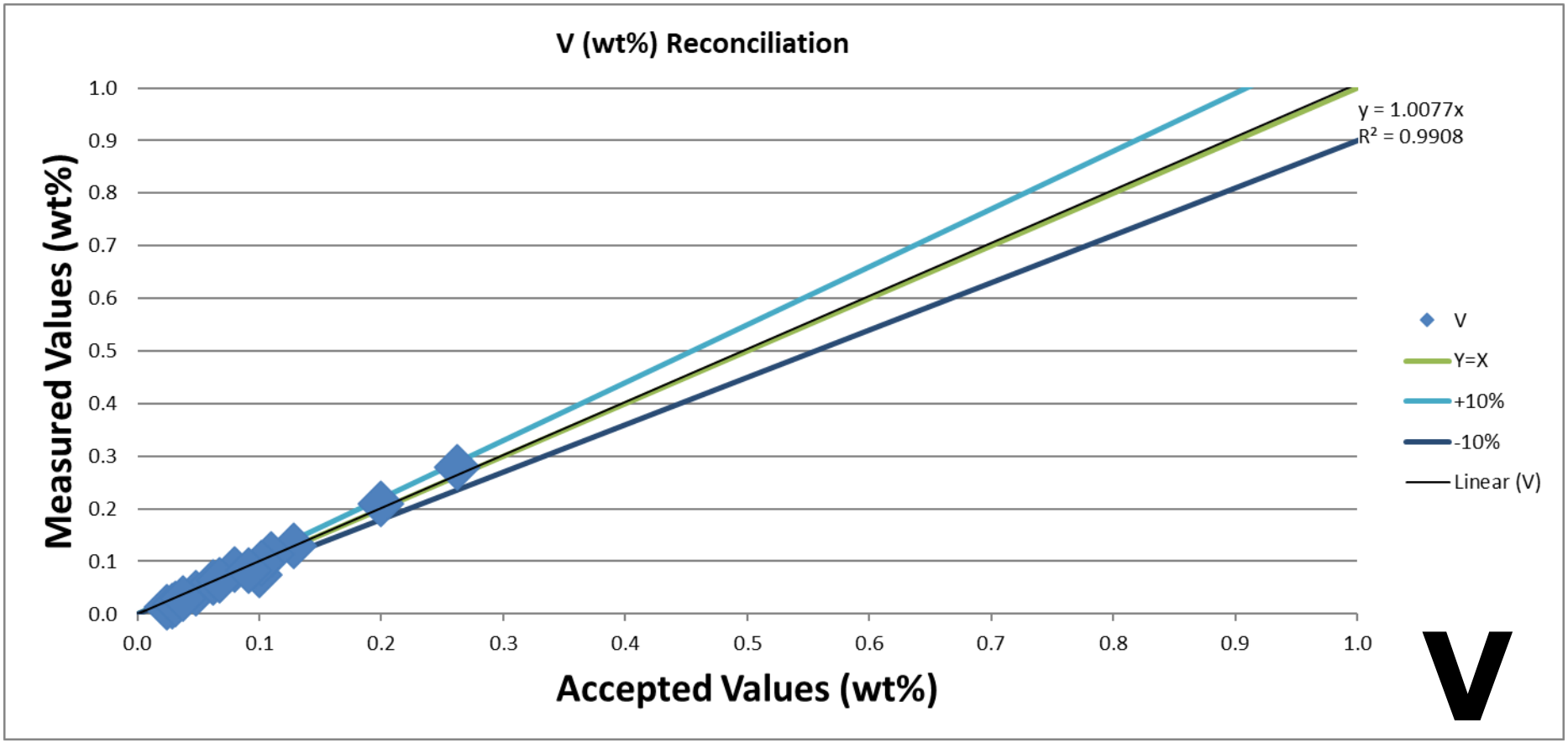
Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

Analysis of Steels and Alloys
Individual Elements: Nb (Minor / Trace)



Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

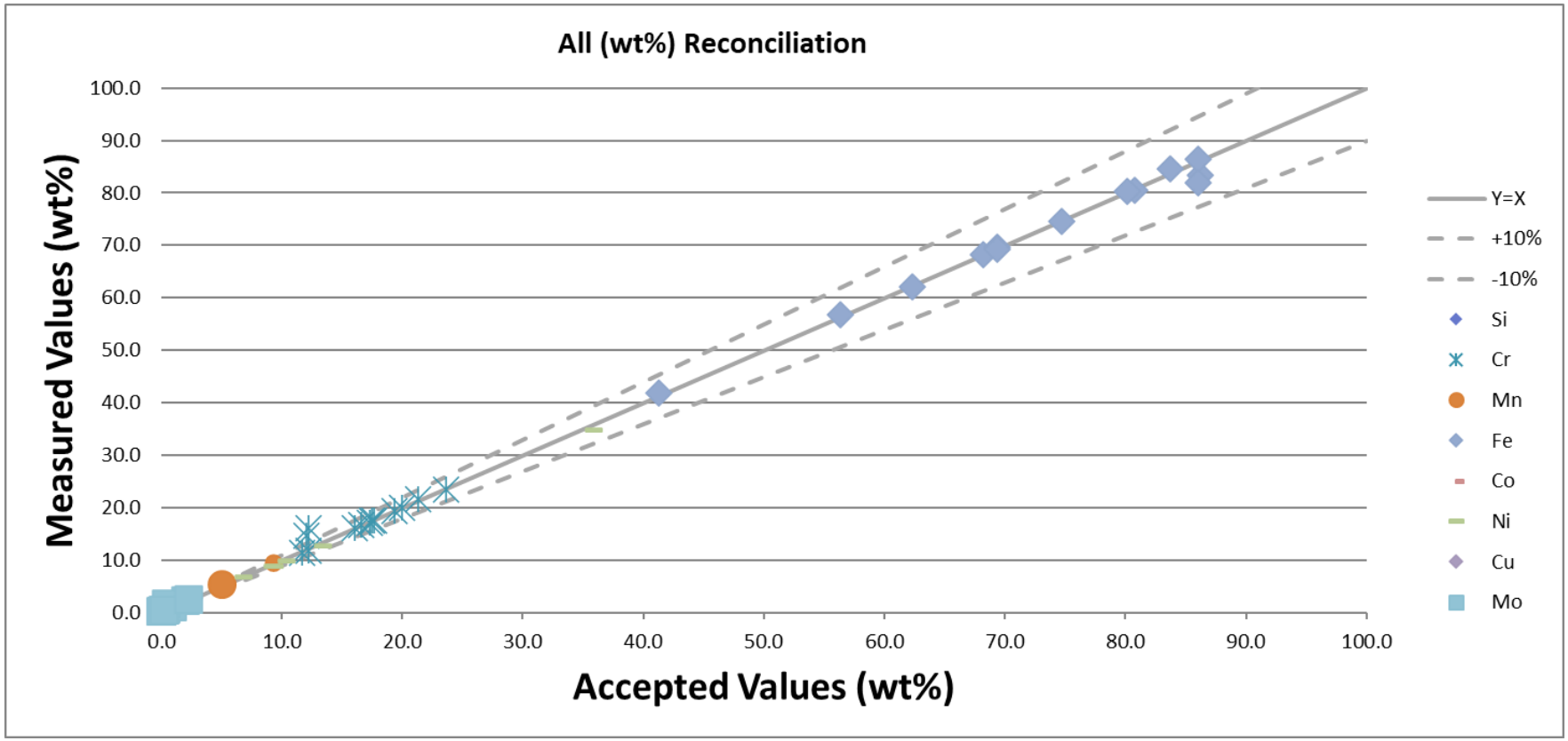
Analysis of Steels and Alloys
Individual Elements: V (Minor / Trace)



Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.

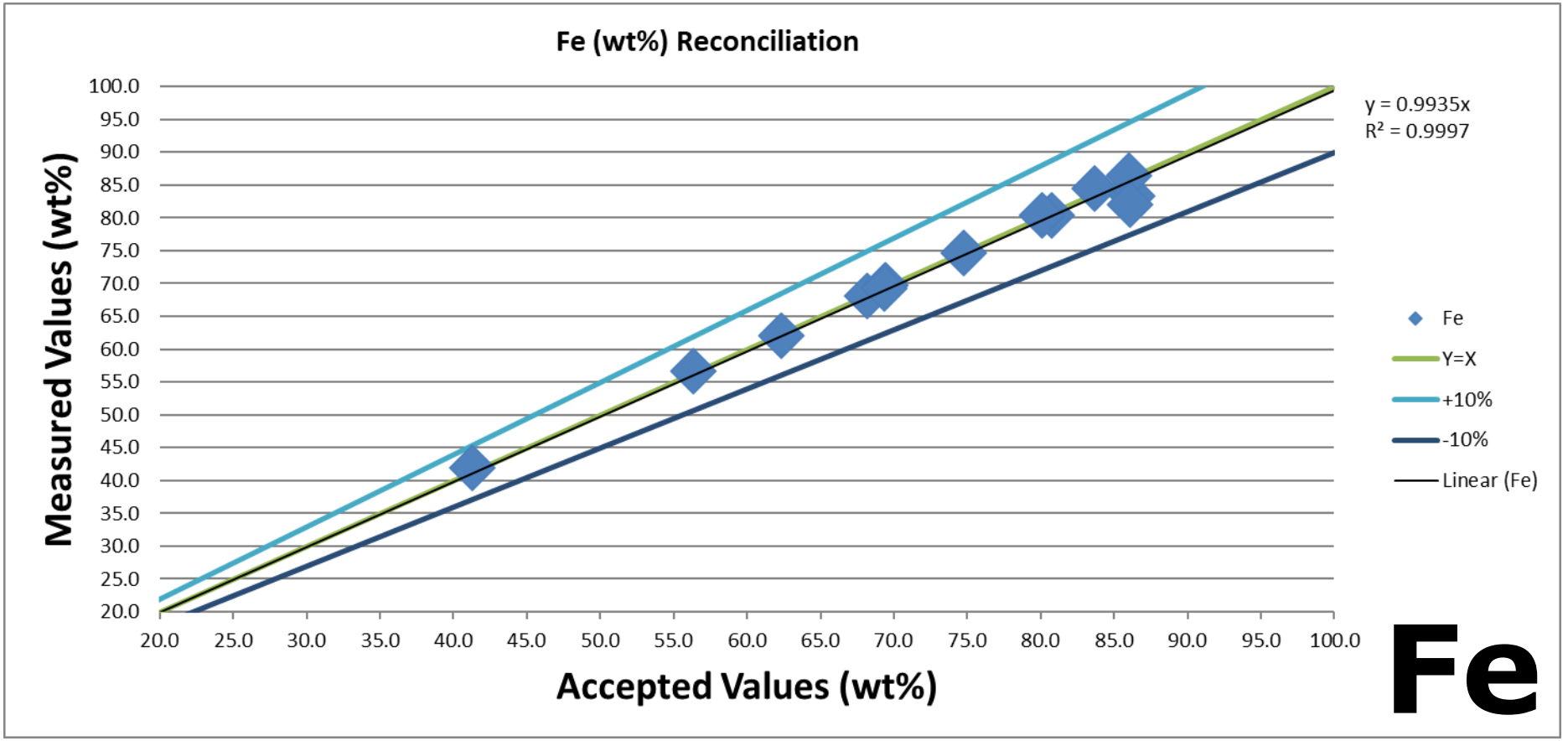
Analysis of Steels and Alloys
Excitation: Electron; Detector: EDS

Analytical Conditions Point Analysis: 20 kV, 10 mA, 275 kcps, under vacuum, Working Distance 12 mm, 120 seconds



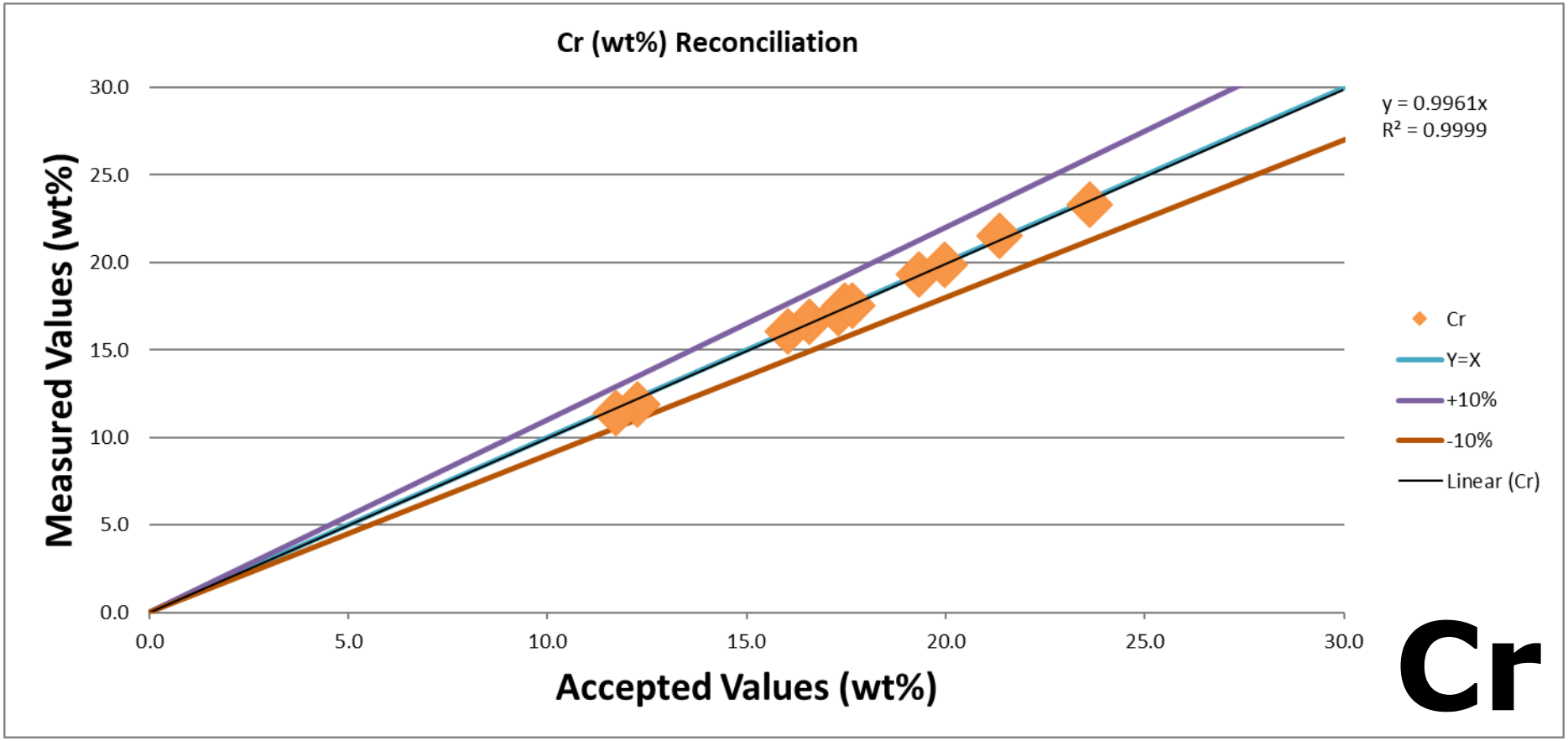
Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Individual Elements: Fe (Major)



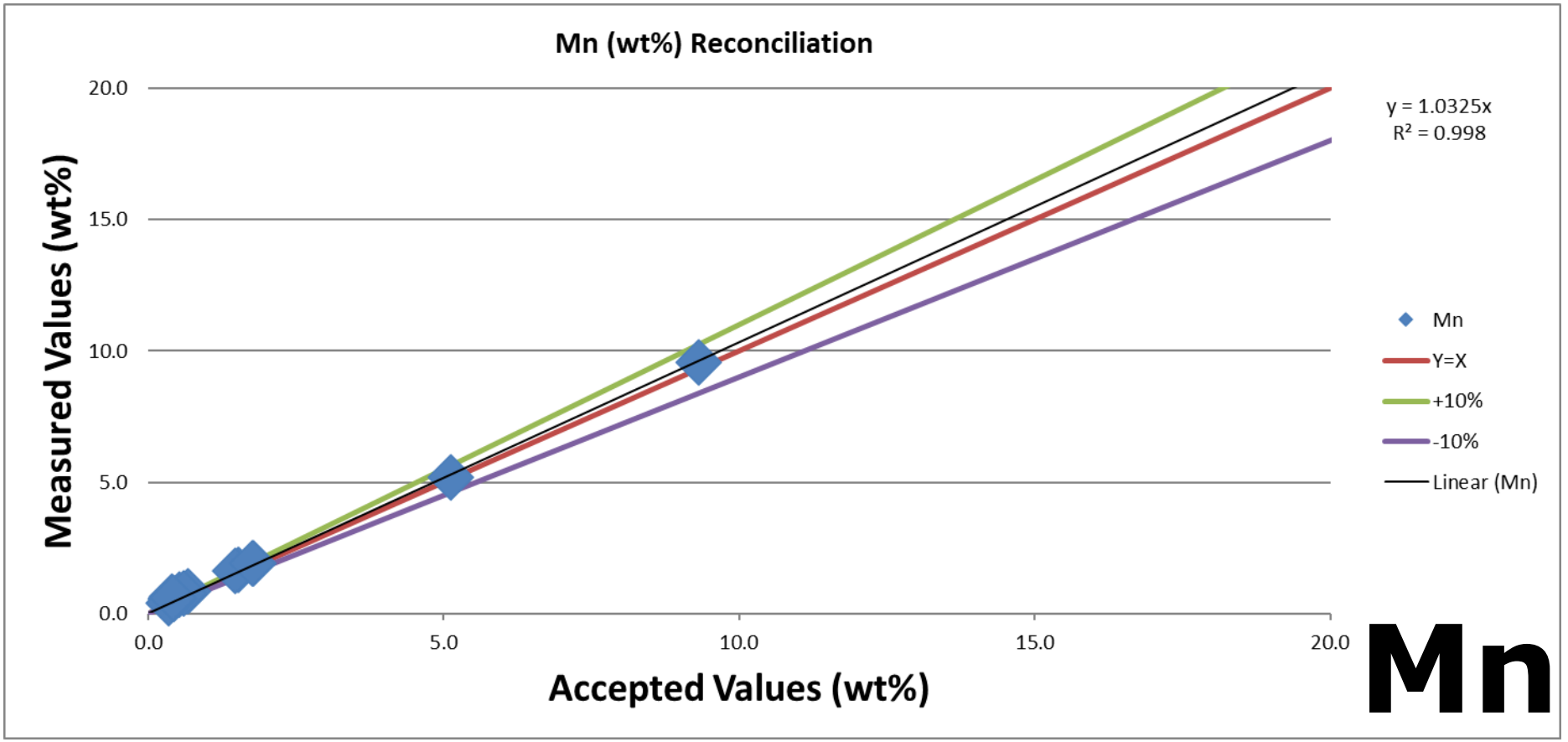
Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Individual Elements: Cr (Major)



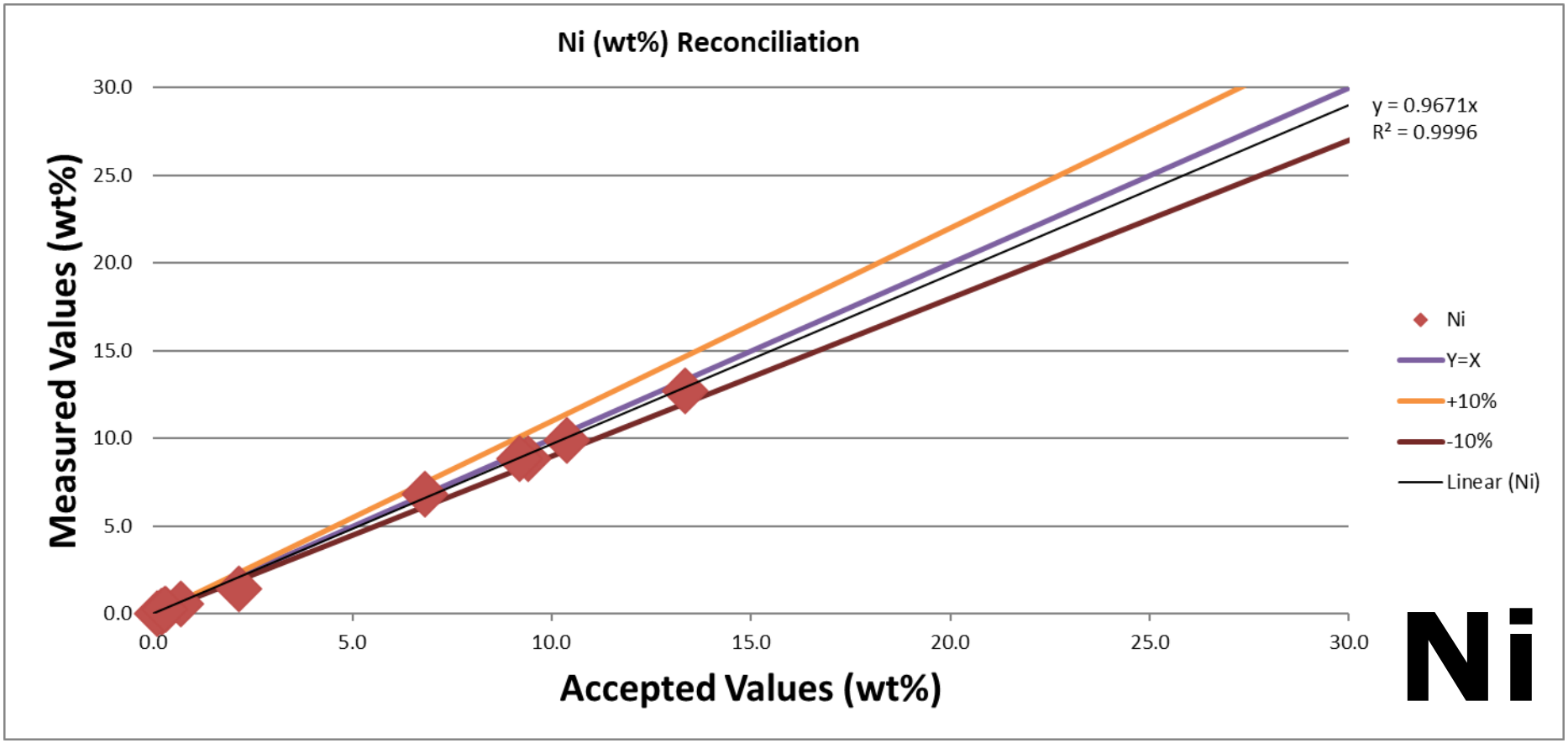
Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Individual Elements: Mn (Major / Minor)



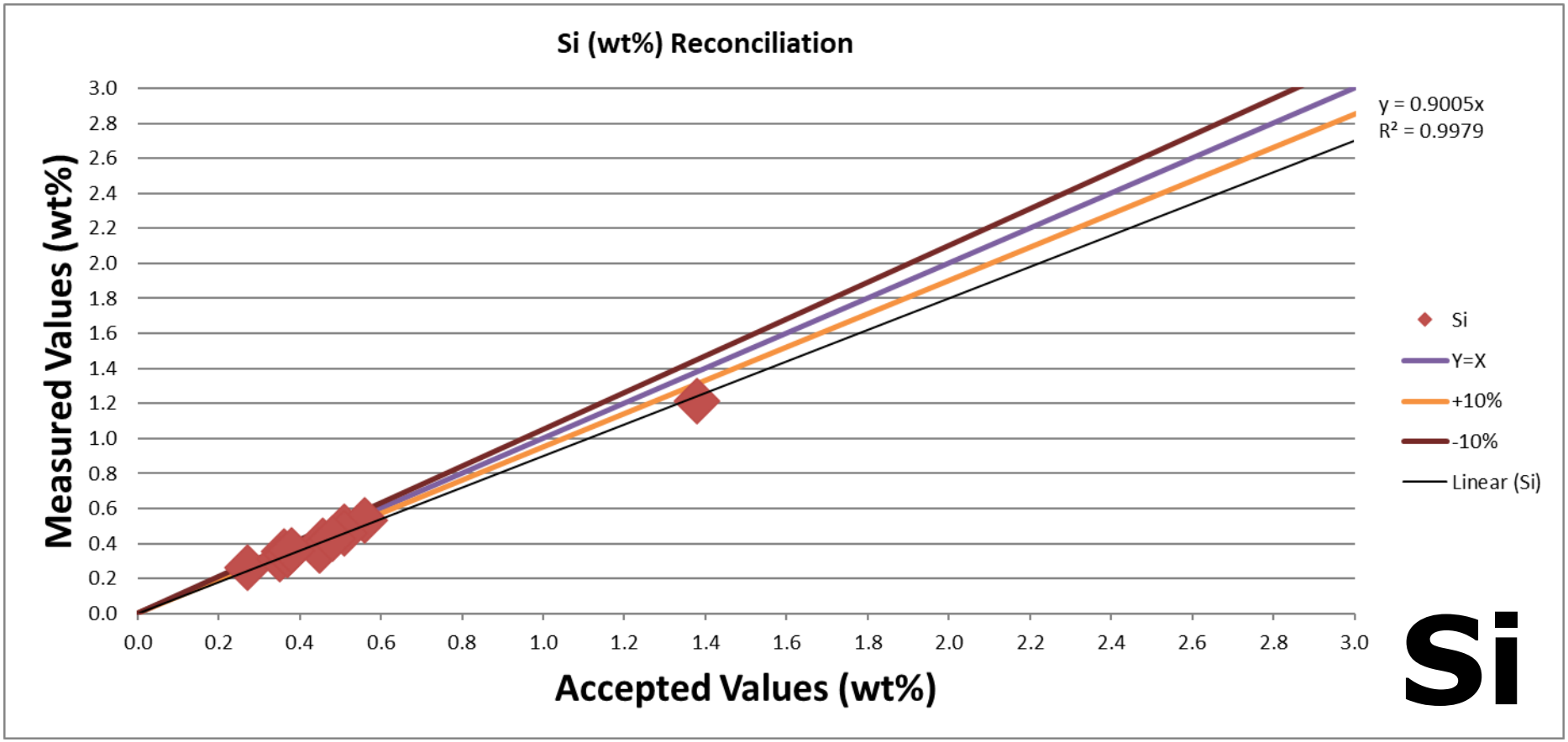
Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Individual Elements: Ni (Major / Minor)



Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Individual Elements: Si (Minor)

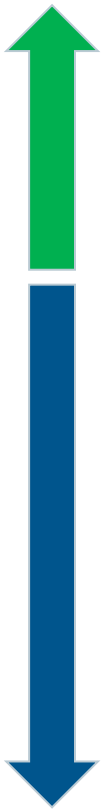


Electron Excitation. EDS Detector. SEM-EDS.

Analysis of Steels and Alloys
Combined Analysis

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

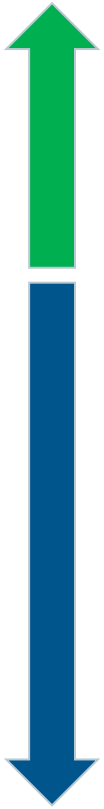
SEM-XRF

High-Z elements

Analysis of Steels and Alloys
Combined Analysis

Sample 28: AISI 347-8D

Element	Certified	MicroXRF	SEM-EDS	Combined
C	0.05			
N	0.02			
Al	0.00			
Si	0.36		0.36	0.35
P	0.03			
S	0.03			
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	0.501	0.50	0.49
Nb	0.72	0.695	0.74	0.67
Mo	0.44	0.448	0.44	0.42



SEM-EDS/WDS

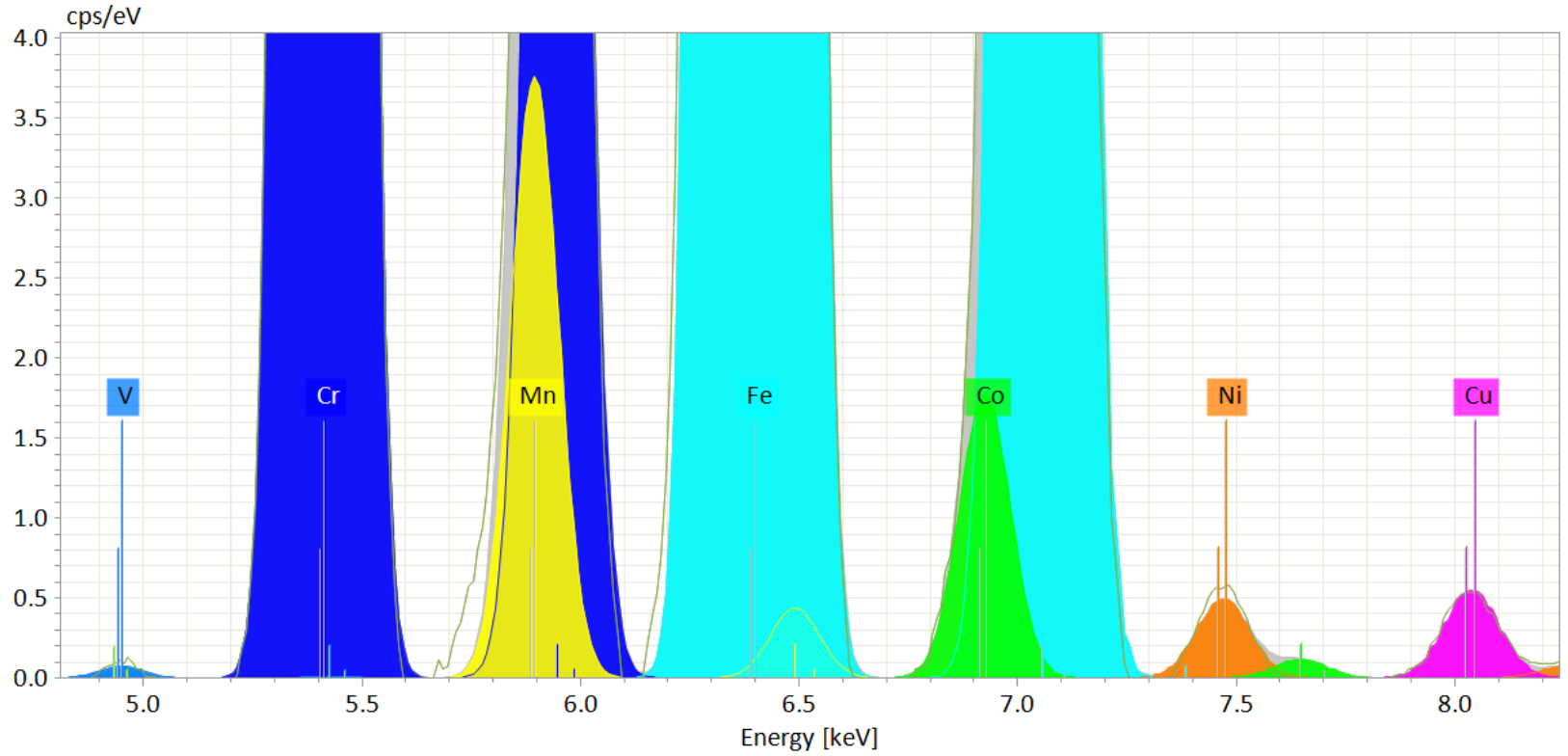
Low-Z elements

SEM-XRF

High-Z elements

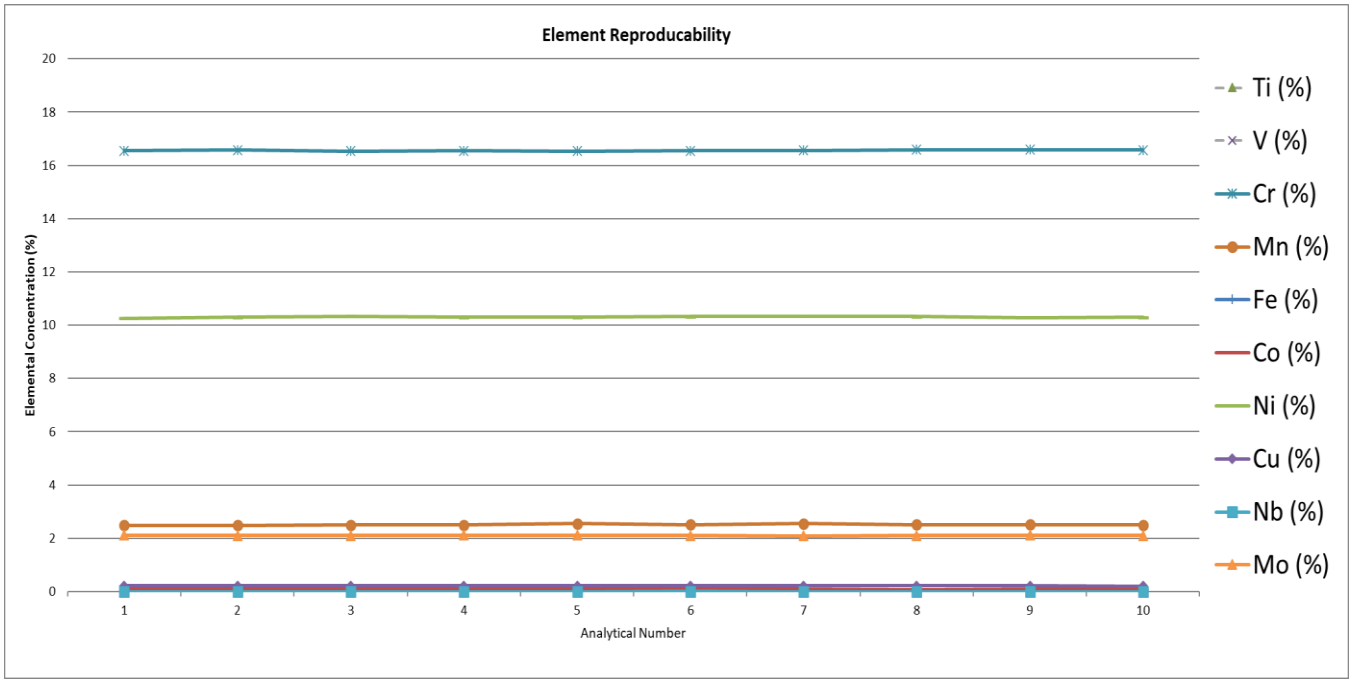
Analysis of Steels and Alloys
Deconvolution

- Deconvolution, Peak Overlaps, and Background



Analysis of Steels and Alloys
Repeat Analysis: Same Spot

- Reproducible analytical results when analysing the same spot
- Small Standard Deviation

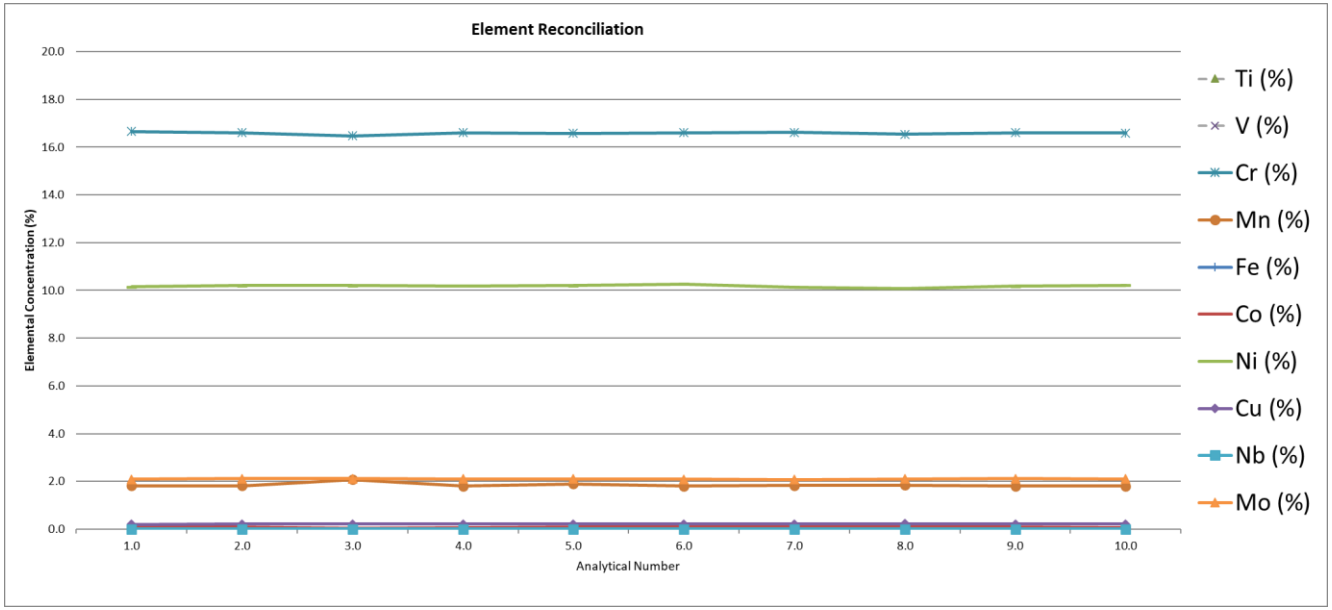


Element	Accepted Values	Average
Ti	0.01	0.01
V	**0.03**	**0.01**
Cr	16.56	16.59
Mn	**1.78**	**1.85**
Fe	68.19	69.00
Co	**0.14**	**0.09**
Ni	10.38	10.18
Cu	**0.17**	**0.21**
Nb	0.00	0.00
Mo	**2.11**	**2.10**

- Sample 25: AISI 316-5D

Analysis of Steels and Alloys
Repeat Analysis: Same Sample

- Reproducible analytical results when analysing the same sample in different positions
- Small Standard Deviation, indicates homogeneous sample



Element	Accepted Values	Average
Ti	0.01	0.01
V	**0.03**	**0.01**
Cr	16.56	16.56
Mn	**1.78**	**2.51**
Fe	68.19	68.68
Co	**0.14**	**0.08**
Ni	10.38	10.31
Cu	**0.17**	**0.21**
Nb	0.00	0.00
Mo	**2.11**	**2.11**

- Sample 25: AISI 316-5D

Analysis of Steels and Alloys
Repeat Analysis: Same Sample

- Reproducible analytical results when analysing the same spot
- Small Standard Deviation

	Ti (%)	V (%)	Cr (%)	Mn (%)	Fe (%)	Co (%)	Ni (%)	Cu (%)	Nb (%)	Mo (%)
1.spx	0.01	0.01	16.55	2.48	68.59	0.09	10.26	0.21	0.00	2.12
2.spx	0.01	0.02	16.57	2.48	68.70	0.09	10.30	0.21	0.00	2.11
3.spx	0.01	0.01	16.53	2.50	68.72	0.08	10.34	0.22	0.00	2.11
4.spx	0.01	0.02	16.55	2.50	68.67	0.08	10.30	0.21	0.00	2.12
5.spx	0.01	0.01	16.53	2.55	68.64	0.08	10.30	0.22	0.00	2.12
6.spx	0.01	0.01	16.55	2.52	68.67	0.08	10.32	0.22	0.00	2.11
7.spx	0.01	0.02	16.56	2.55	68.68	0.09	10.34	0.21	0.00	2.09
8.spx	0.01	0.01	16.59	2.51	68.70	0.08	10.32	0.22	0.00	2.11
9.spx	0.01	0.02	16.59	2.51	68.73	0.09	10.28	0.21	0.00	2.12
10.spx	0.01	0.01	16.57	2.49	68.70	0.08	10.29	0.21	0.00	2.11

Analysis of Steels and Alloys
Considerations

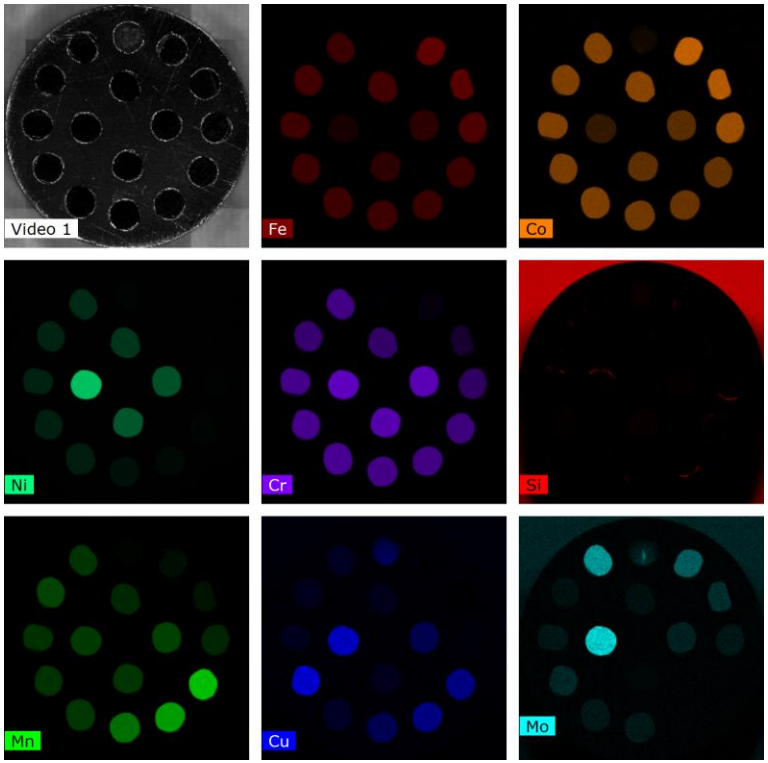
- As with all microanalysis, it is important to understand the analytical goal prior to analysis. This often requires an understanding of the sample.
- Steels are often homogenous on a micrometer scale.
- Thus the difference in analytical volume between electron and X-ray excitation will not influence the quantification and interpretation off results.

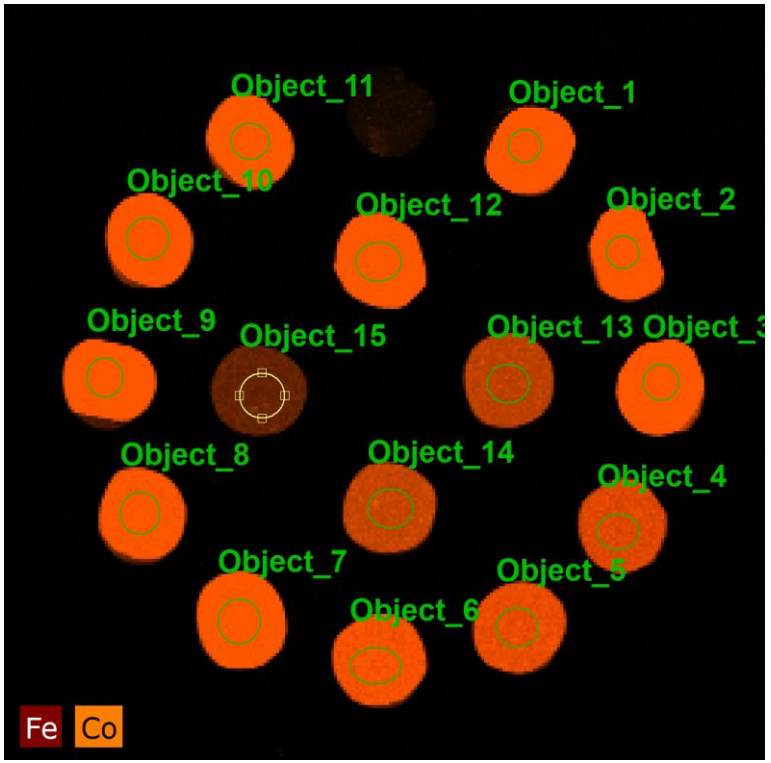
However, sometimes, steels are segregated and may contain small impurities. If so, then there could be a difference between the two techniques due to the excitation volume. That is the higher resolution of electron excitation and the greater penetration depth of the X-ray excitation may generate a combined result that is inconsistent for interpretation.

To resolve this, an area map could be done.

Large Area Maps:
Micro-XRF and Electron excitation

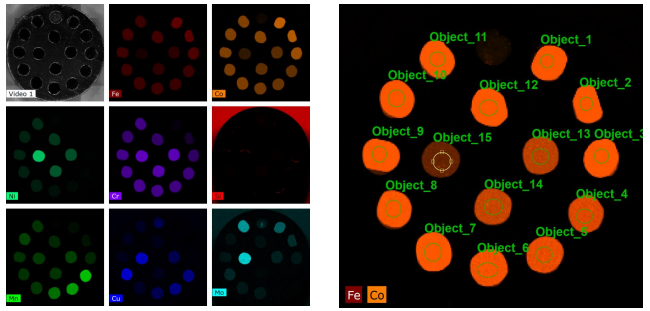
- Both micro-XRF and electron excitation are capable of both point analysis and mapping.
- Difference in Beam Size and Area of excitation

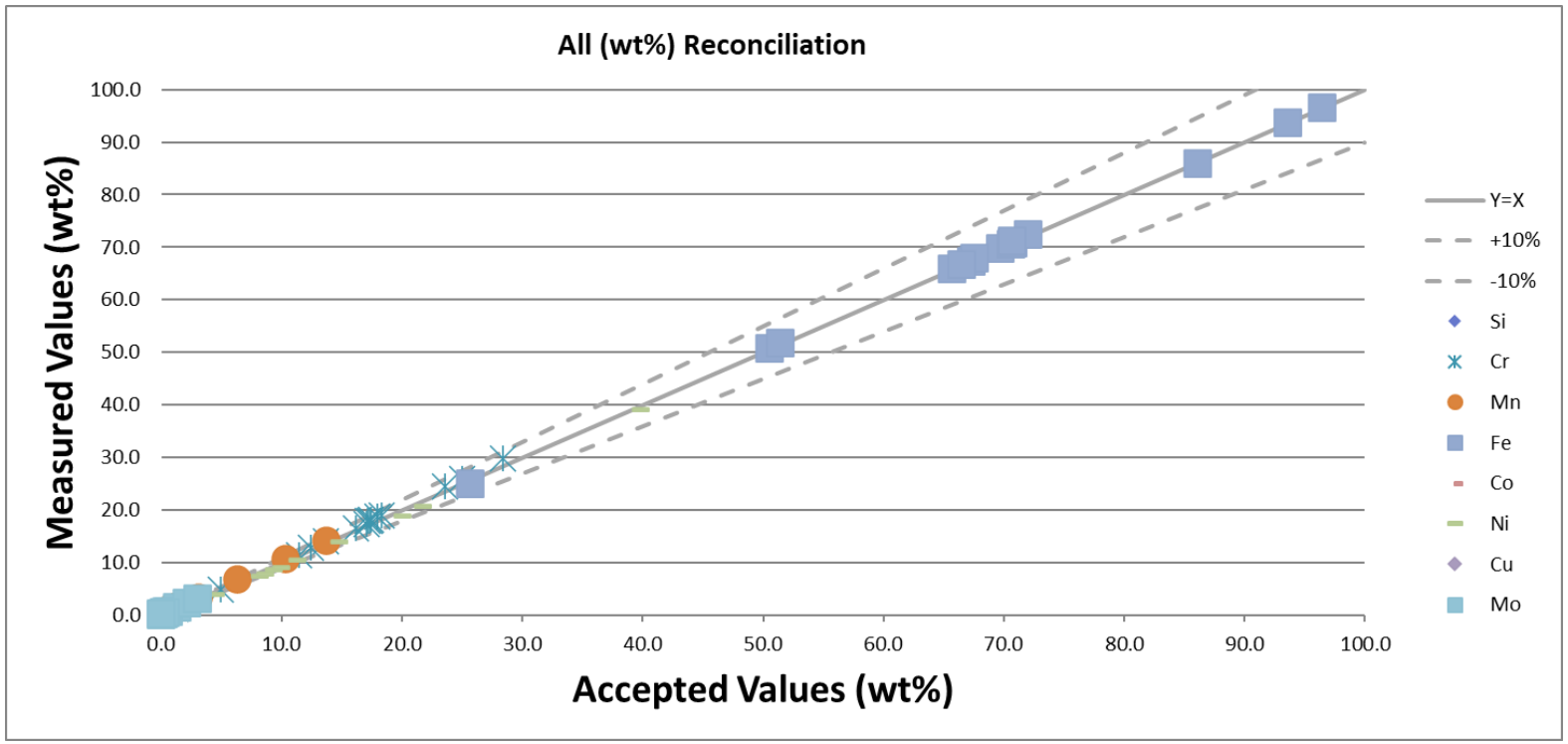




Large Area Maps:
Micro-XRF and Electron excitation

Quantification of selected areas from within a mapped area





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

More Information

For more information, please contact us:

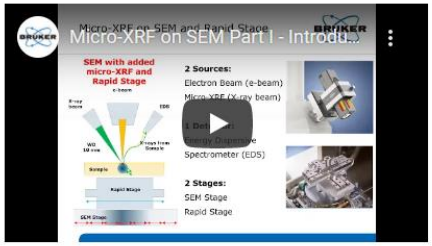
Bruker Nano GmbH

info.bna@bruker.com

and

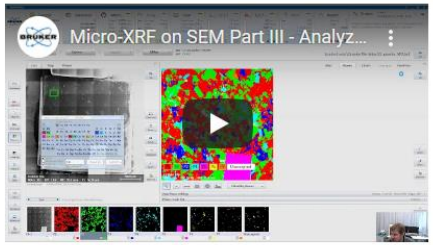
If you want to learn more about practical micro-XRF analysis including sample, measurement setup, and evaluation, our latest video series is available via the Bruker website and youtube

Product Videos



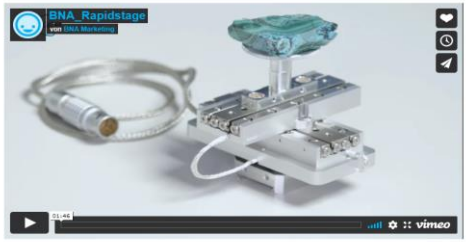
Part I - Introduction to micro-XRF and the Rapid Stage on a SEM

Part II - Loading a sample and performing a measurement



Part III - Analyzing a measured dataset

Rapid Stage

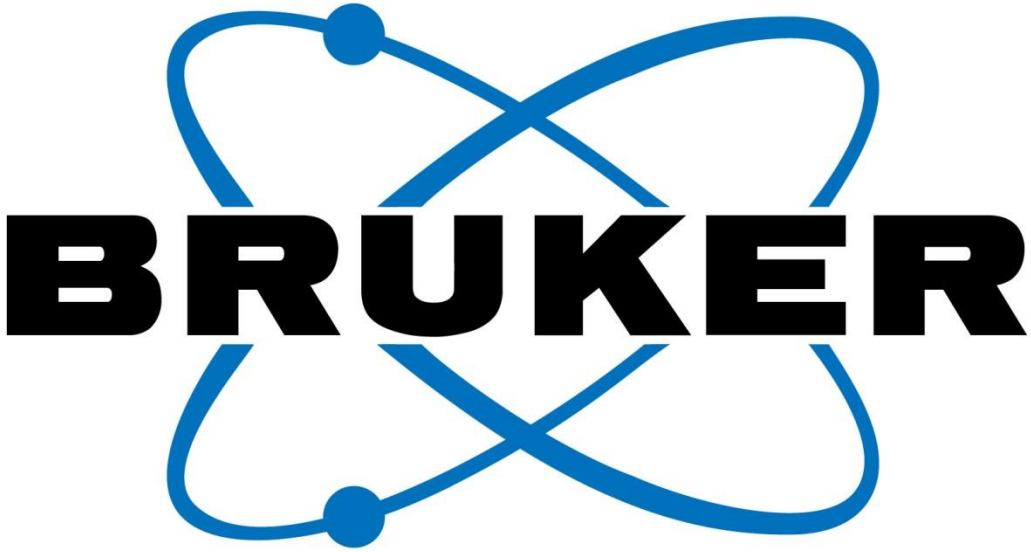


The Rapid Stage can be mounted on top of the SEM stage for fast mapping over large sample areas.

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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