Advanced Data Mining in Micro-XRF

Bruker Nano Analytics, Berlin, Germany
Webinar, September 4, 2018

Q&A

Are There Any Questions?

Please type in the questions you might have in the Q&A box and press *Send*.

M4 TORNADO Webinar
Presenters

Falk Reinhardt

Application Scientist,
Bruker Nano Analytics, Berlin, Germany

Dr. Roald Tagle

Sr. Application Scientist,
Bruker Nano Analytics, Berlin, Germany

M4 TORNADO Webinar
Outline

- Introduction
  - Presenters
  - The M4 instrument
  - Micro-XRF
  - Position Tagged Spectroscopy

- Homogeneous samples? – Cu- and Fe-alloys
- Heterogeneous in 1 dimension – drill core
- Heterogeneous – concrete
- Live part – data extraction and evaluation
- Summary

M4 TORNADO micro-XRF spectrometer
Standard configuration

30 W micro-focus Rh tube with polycapillary lens
for excitation spot sizes < 20 µm (for Mo-Kα)
Option: other target materials and second X-ray tube (collimated) for extended excitation conditions

30 mm² silicon drift detector (SDD)
with energy resolution < 145 eV (for Mn-Kα)
Option: second detector with second independent SPU for double pulse throughput
Option: 60 mm² detector(s)

Sealed sample chamber
with adjustable pressure between 1 mbar (for detecting light elements down to Na) and ambient pressure

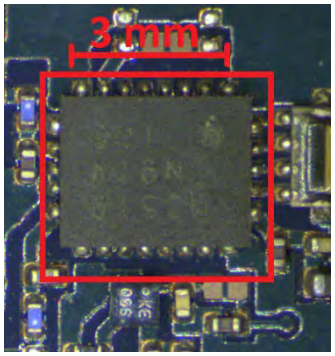
Sample stage with measureable area of 190 mm x 160 mm

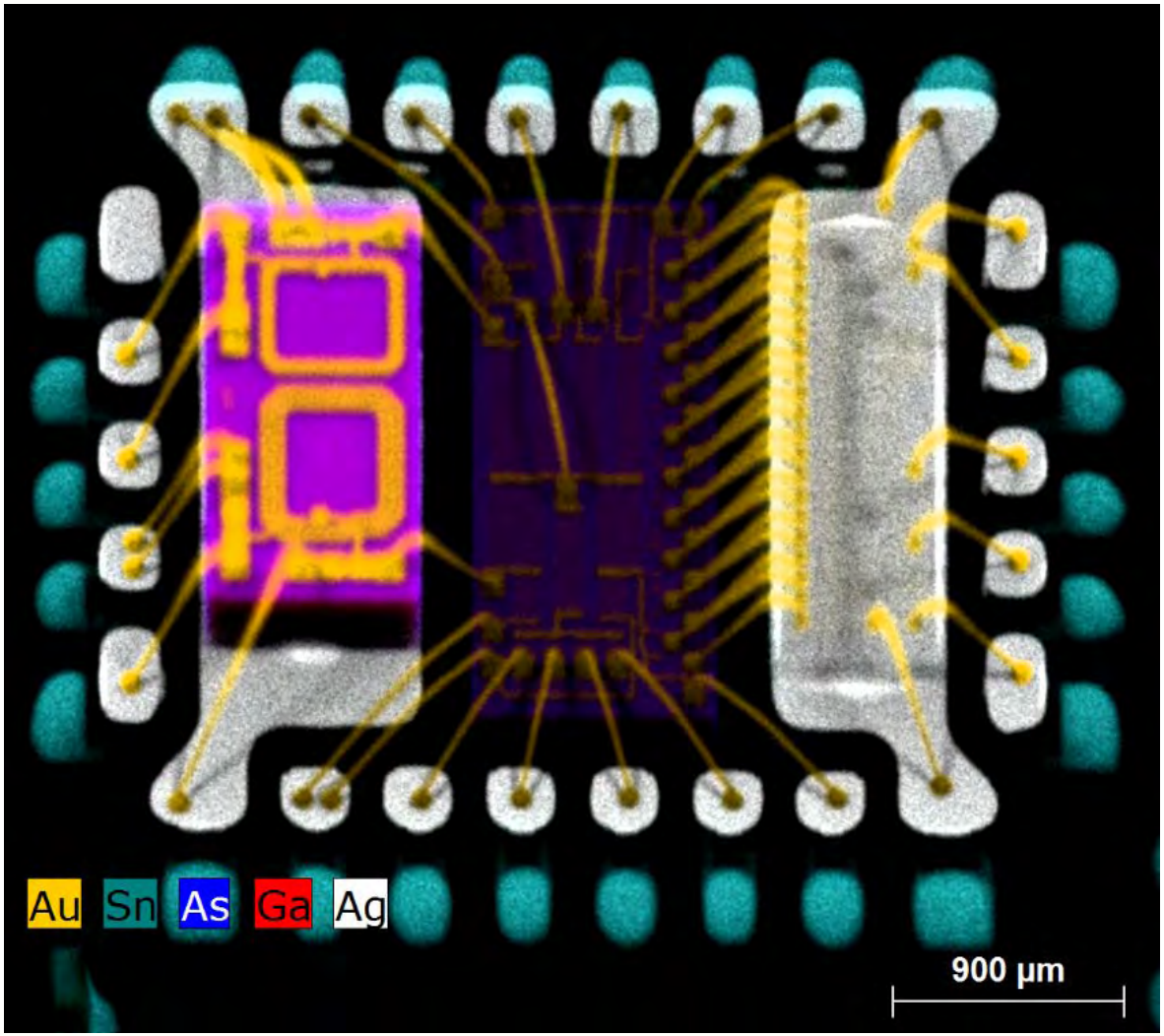
Maximum sample height 120 mm, maximum sample weight 5 kg

Sample stage speed up to 100 mm/s, minimum step size 4 µm

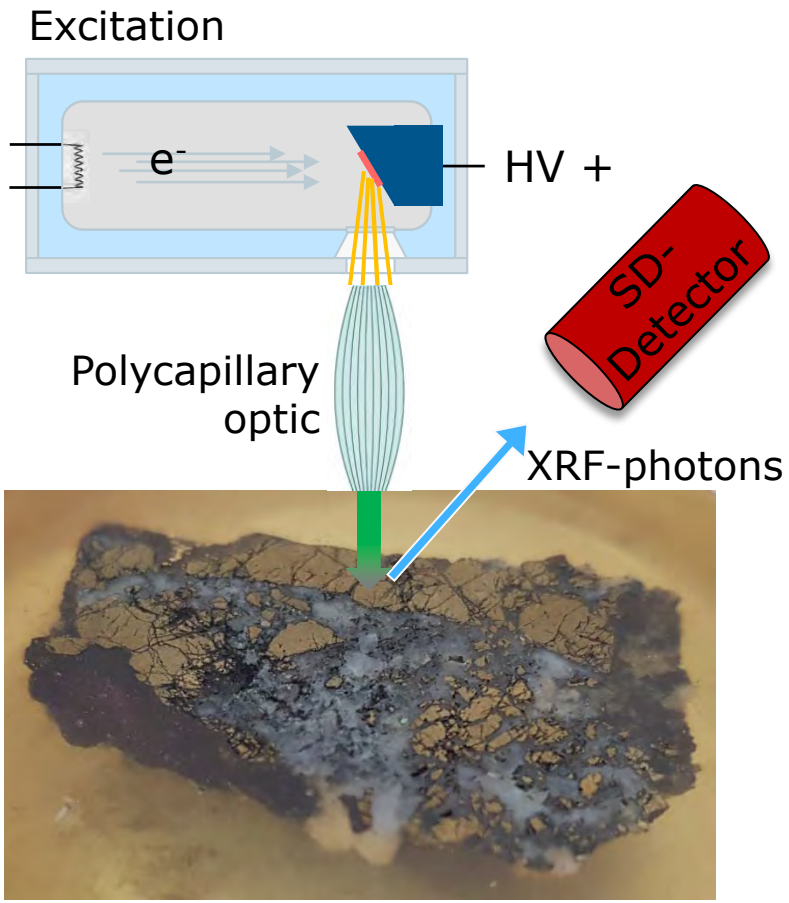
Micro-XRF features and benefits
At a glance

- Little to no sample preparation
- Non-destructive
- Elemental information
- Small spot analysis
- Information from within the sample
- Large-scale
- Quantification

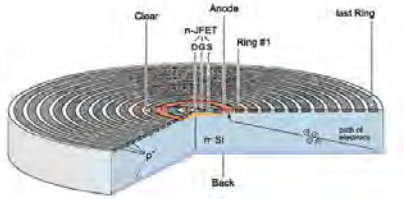




X-Ray Fluorescence
…elemental analysis



XRF Detection



Silicon **D**rift **D**etector
with XFlash® Technology

- X-rays can be guided onto a small spot
- Spatially resolved element-specific signal
- Intensity ratios of observed elemental lines can be used for quantification

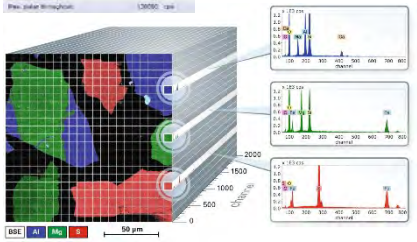
From question to results

Sample

Analytical Question

Measurement conditions

Data set

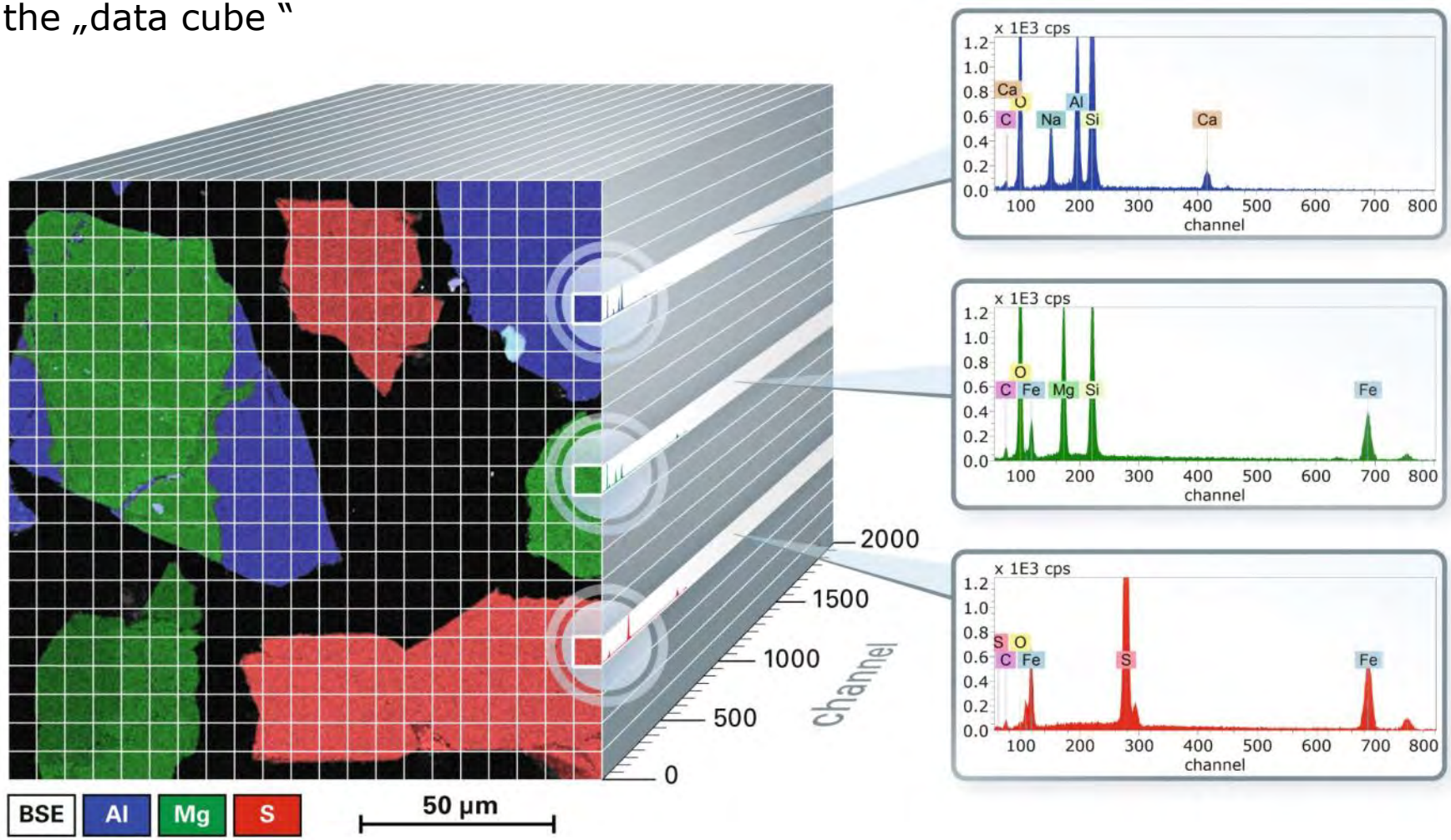


Data mining

Results

PTS – Position Tagged Spectroscopy
all map data at hand

the „data cube “



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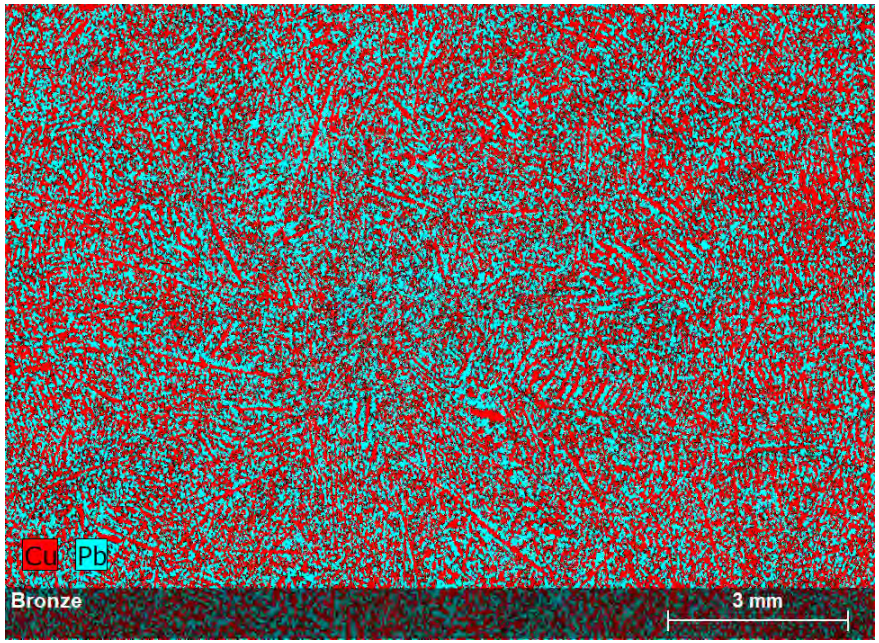
Analytical question:
homogeneity of a bronze slab



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Analytical question:
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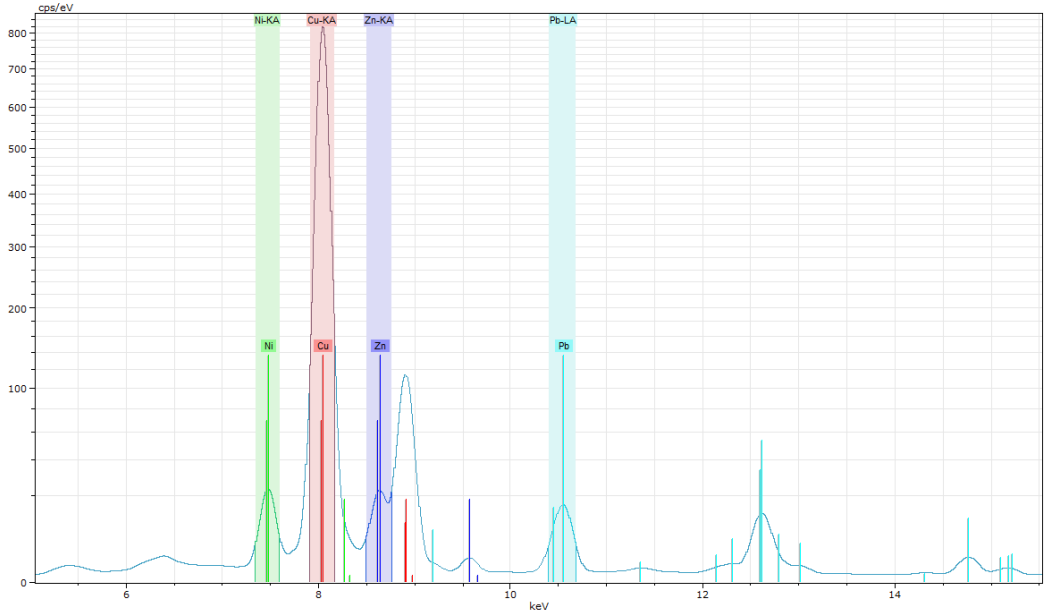
Situation before measurement:
All expected elements selected



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Situation before measurement:
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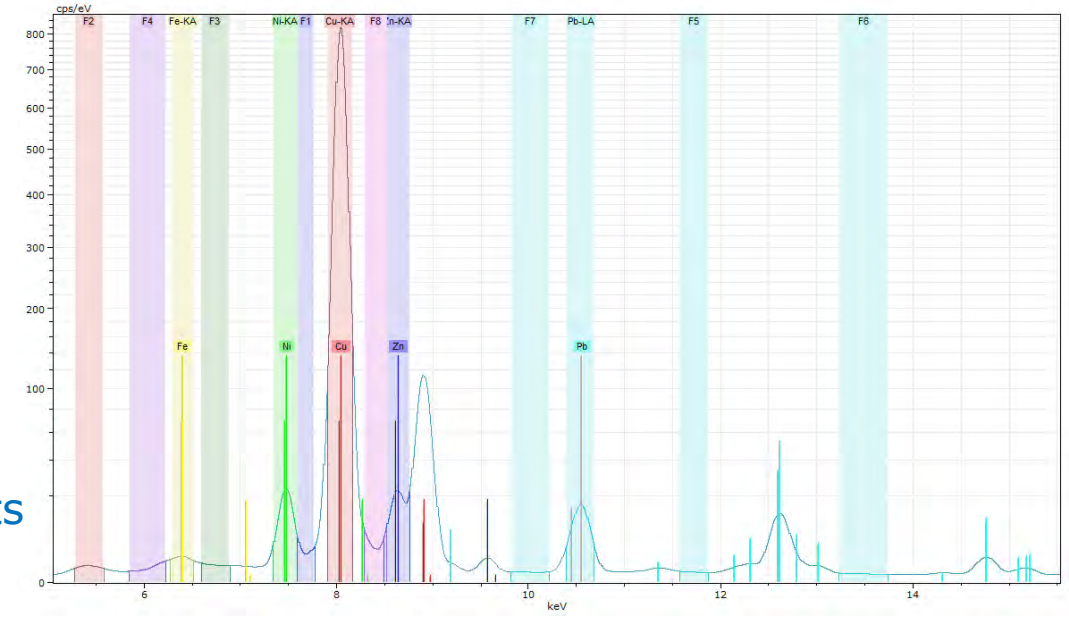
Post evaluation:
- Sum spectrum reveals additional peaks
- Identify unexpected elements
- Define ‘free regions’



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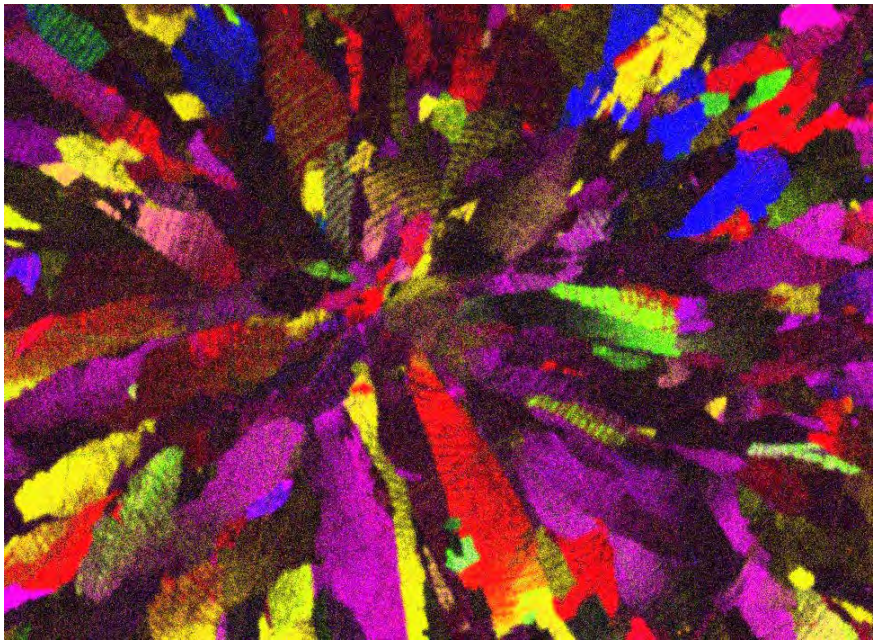
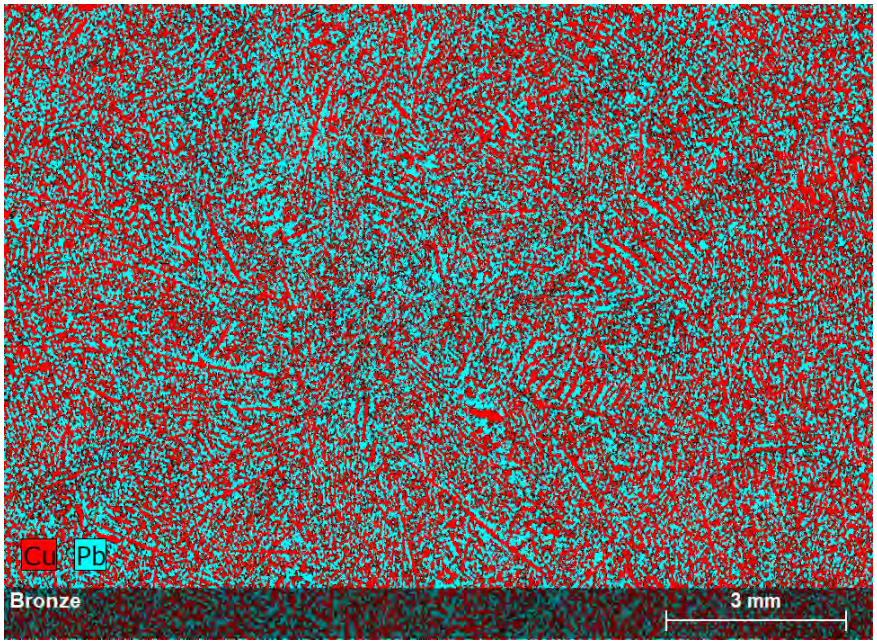
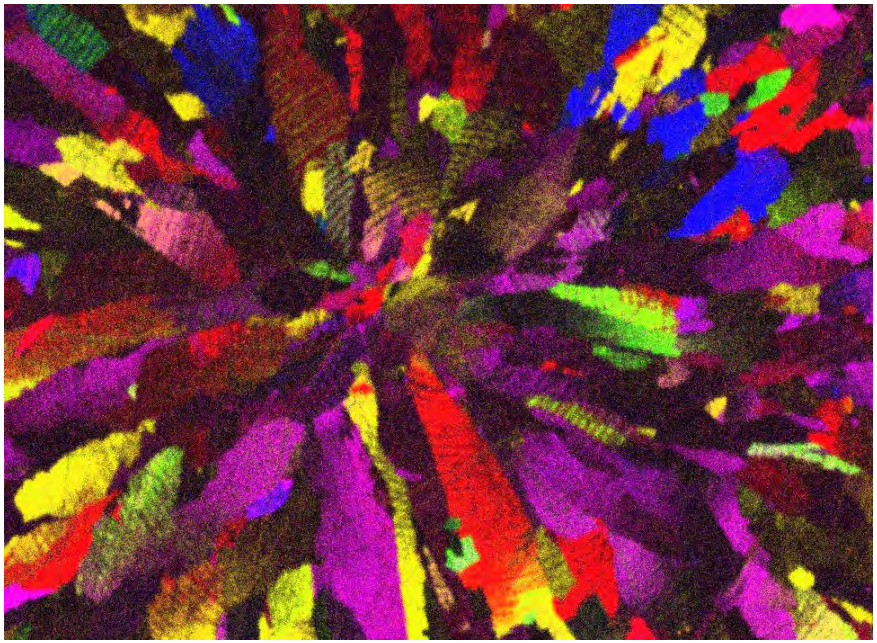


Here: the additional peaks are diffraction peaks, which reveal crystalline structure of the sample.

PTS – Position Tagged Spectroscopy
all map data at hand





Here: the additional peaks are diffraction peaks, which reveal crystalline structure of the sample.

The data block contains all spectroscopic data and keeps it available for offline analysis.

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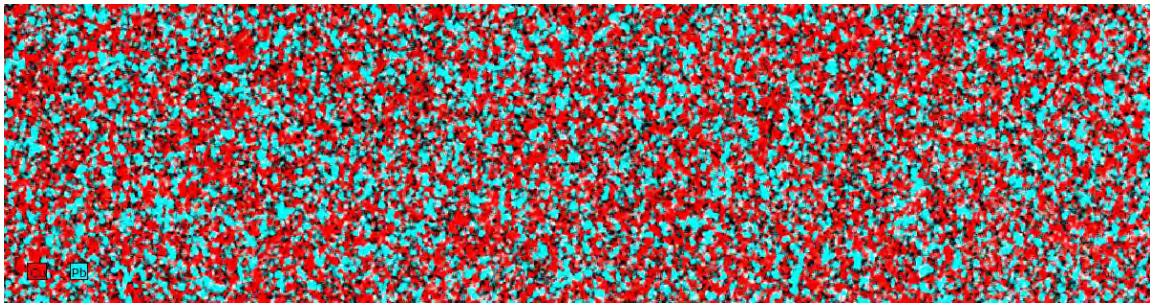
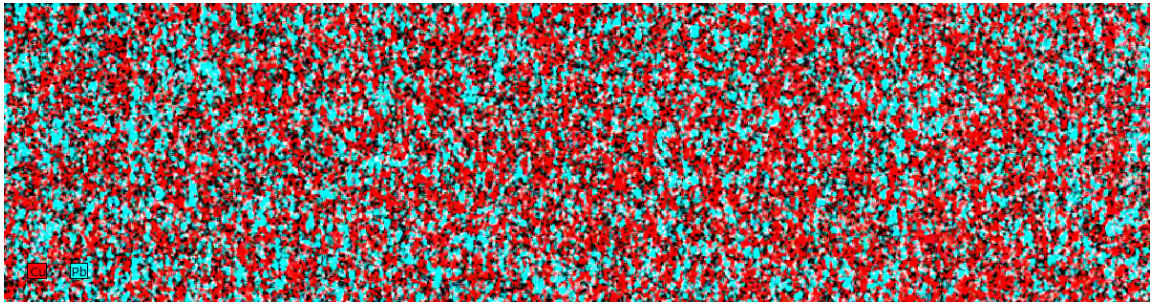
Bronze
Cu-Pb-distribution

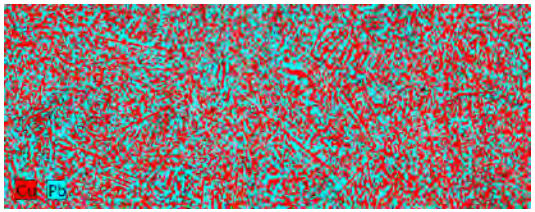


BAM
ERM-EB 375
Cu 58 %, Zn 39 % Pb 2.9 %

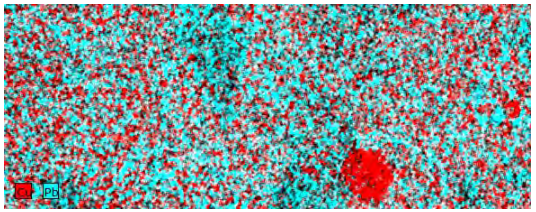


ARMI
CDA 360 73B
Cu 61.5 %, Zn 35.5 % Pb 1.9 %

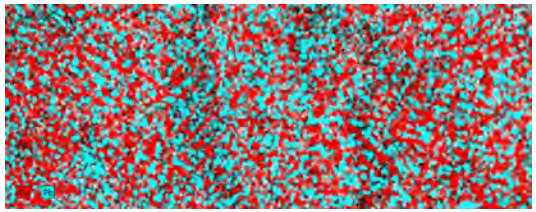
LGC Standards
SUS RC36
Cu 82.5 %, Zn 0.25 % Pb 9.6 %



ARMI
CDA 932
Cu 83.2 %, Zn 2.6 % Pb 6.8 %

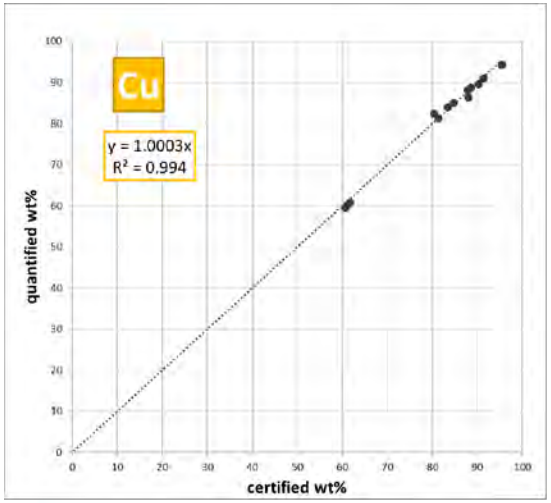


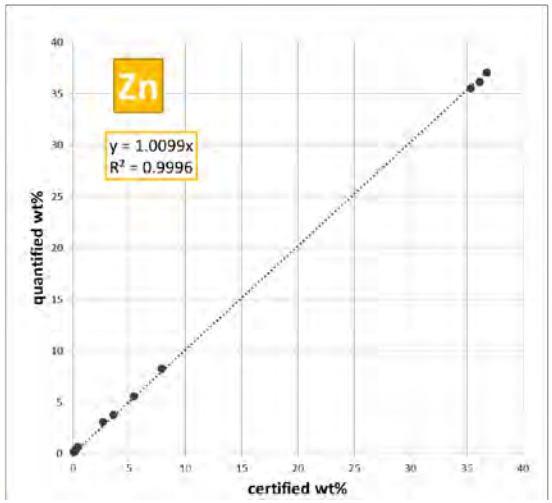
ARMI
CDA 397
Cu 80.2 %, Zn 0.04 % Pb 9.2 %

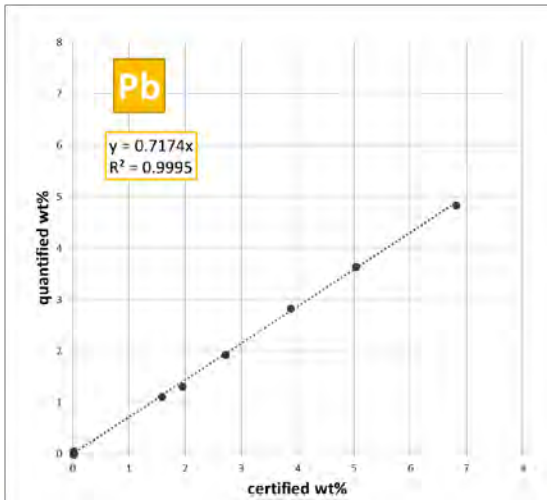


Bronze
FP-Quantification

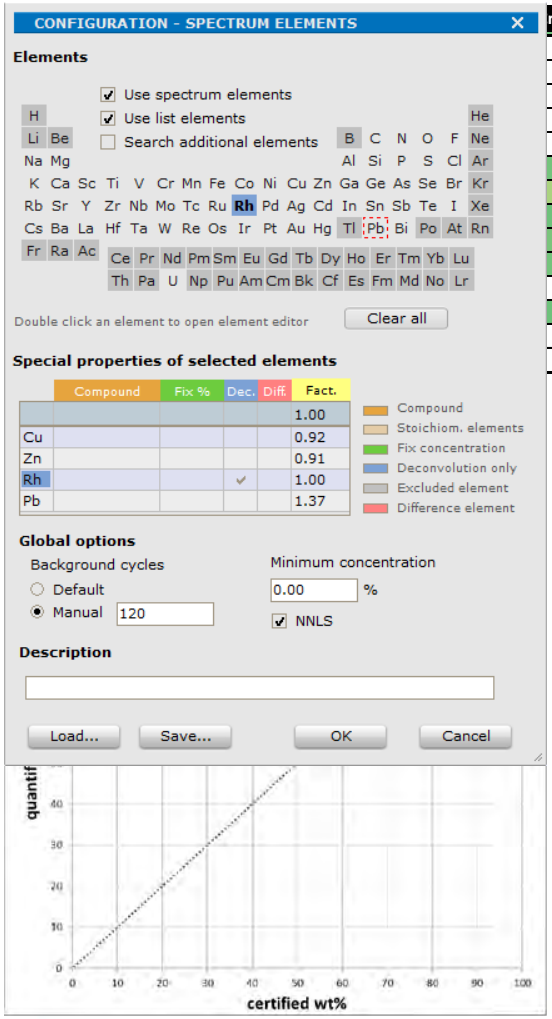
Grade-IARM	Al	Co	Cr	Cu	Fe	Mn	Mo	Nb	Ni	P	Pb	Si	Sn	Ti	V	W	Zn	Zr
CDA314-72B	T	T	T	90.1	0.0	T	T	T	0.0	0.0	2.0	0.0	0.0	T	T	T	7.8	T
CDA360-73B	0.0010	0.0	T	61.5	0.2	0.0	T	T	0.1	0.0	2.7	0.0	0.2	T	T	T	35.3	T
CDA485-76B	0.0050	0.0	T	60.5	0.1	0.0	T	T	0.0	0.0	1.9	T	0.7	T	T	T	36.7	T
CDA510-77B	0.0010	T	T	95.2	0.0	0.0	T	T	0.0	0.1	0.0	0.0	4.7	T	T	T	0.0	T
CDA544-78B	0.0020	T	T	87.7	0.0	0.0	T	T	0.1	0.2	3.9	T	4.7	T	T	T	3.6	T
CDA623-79B	9.1900	0.0	0.0	88.4	2.1	0.2	T	T	0.1	0.0	0.0	0.0	0.0	T	T	T	0.0	T
CDA630-80B	10.1900	0.0	0.0	81.2	3.3	0.5	T	T	4.7	0.0	0.0	0.0	0.0	T	T	T	0.1	T
CDA642-81B	6.7000	T	0.0	91.2	0.0	0.0	T	T	0.0	0.0	0.0	1.8	0.0	T	T	T	0.2	T
CDA655-82B	0.0020	T	0.0	95.3	0.1	1.0	T	T	0.0	0.0	0.0	3.2	0.0	T	T	T	0.4	T
CDA706-84B	0.0020	0.0	0.0	87.9	1.3	0.6	T	T	10.0	0.0	0.0	0.0	0.0	T	T	T	0.1	T
CDA836-86C	0.0020	T	T	84.6	0.2	0.0	T	T	0.3	0.0	5.0	0.0	4.4	T	T	T	5.4	T
CDA857-87B	0.2000	0.0	0.0	60.9	0.3	0.0	T	T	T	0.0	1.6	0.0	0.8	T	T	T	36.1	T
CDA932-91C	0.0020	T	T	83.2	0.0	0.0	T	T	0.5	0.1	6.8	0.0	6.8	T	T	T	2.6	T
CDA937-BS937B-1	T	T	T	80.2	0.0	T	T	T	0.4	0.0	9.2	T	9.7	T	T	T	0.0	T



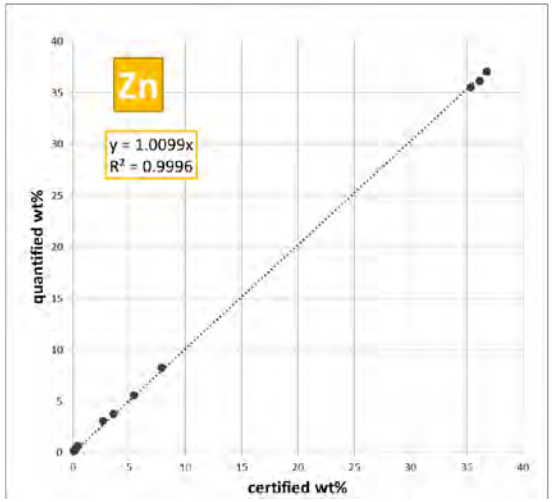


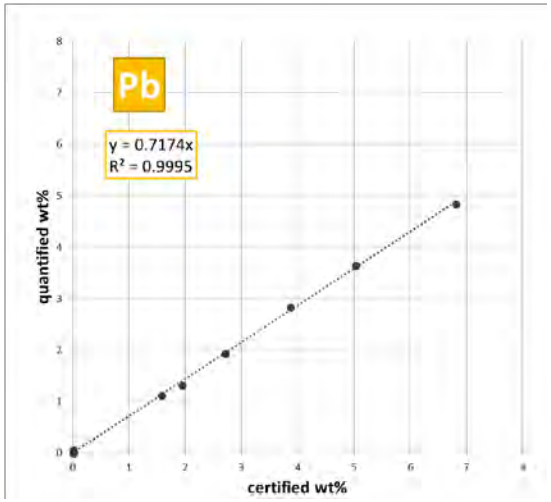


Bronze
FP-Quantification – Type calibration

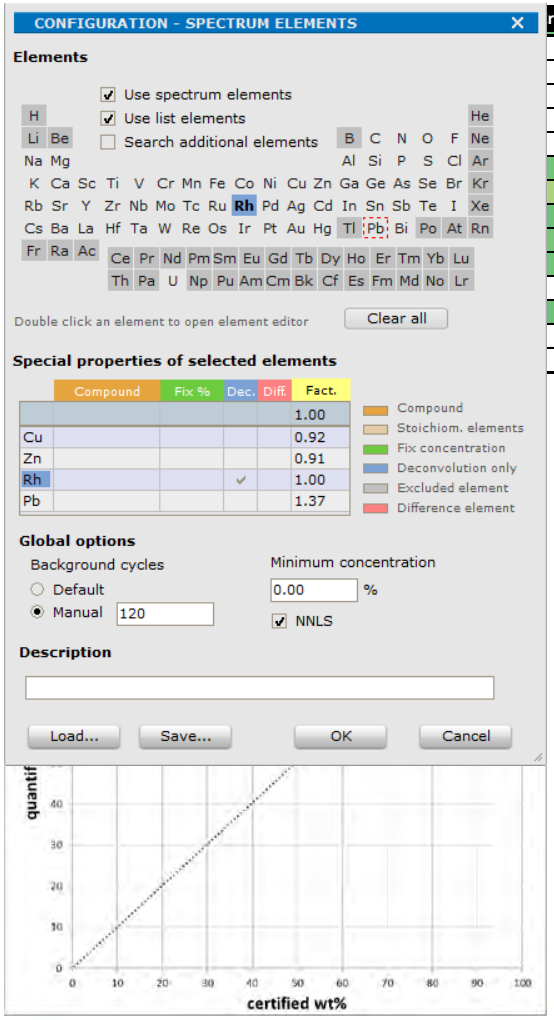


r	Cu	Fe	Mn	Mo	Nb	Ni	P	Pb	Si	Sn	Ti	V	W	Zn	Zr
T	90.1	0.0	T	T	T	0.0	0.0	2.0	0.0	0.0	T	T	T	7.8	T
T	61.5	0.2	0.0	T	T	0.1	0.0	2.7	0.0	0.2	T	T	T	35.3	T
T	60.5	0.1	0.0	T	T	0.0	0.0	1.9	T	0.7	T	T	T	36.7	T
T	95.2	0.0	0.0	T	T	0.0	0.1	0.0	0.0	4.7	T	T	T	0.0	T
T	87.7	0.0	0.0	T	T	0.1	0.2	3.9	T	4.7	T	T	T	3.6	T
0.0	88.4	2.1	0.2	T	T	0.1	0.0	0.0	0.0	0.0	T	T	T	0.0	T
0.0	81.2	3.3	0.5	T	T	4.7	0.0	0.0	0.0	0.0	T	T	T	0.1	T
0.0	91.2	0.0	0.0	T	T	0.0	0.0	0.0	1.8	0.0	T	T	T	0.2	T
0.0	95.3	0.1	1.0	T	T	0.0	0.0	0.0	3.2	0.0	T	T	T	0.4	T
0.0	87.9	1.3	0.6	T	T	10.0	0.0	0.0	0.0	0.0	T	T	T	0.1	T
T	84.6	0.2	0.0	T	T	0.3	0.0	5.0	0.0	4.4	T	T	T	5.4	T
0.0	60.9	0.3	0.0	T	T	T	0.0	1.6	0.0	0.8	T	T	T	36.1	T
T	83.2	0.0	0.0	T	T	0.5	0.1	6.8	0.0	6.8	T	T	T	2.6	T
T	80.2	0.0	T	T	T	0.4	0.0	9.2	T	9.7	T	T	T	0.0	T





Bronze
FP-Quantification – Type calibration



r	Cu	Fe	Mn	Mo	Nb	Ni	P	Pb	Si	Sn	Ti	V	W	Zn	Zr
T	90.1	0.0	T	T	T	0.0	0.0	2.0	0.0	0.0	T	T	T	7.8	T
T	61.5	0.2	0.0	T	T	0.1	0.0	2.7	0.0	0.2	T	T	T	35.3	T
T	60.5	0.1	0.0	T	T	0.0	0.0	1.9	T	0.7	T	T	T	36.7	T
T	95.2	0.0	0.0	T	T	0.0	0.1	0.0	0.0	4.7	T	T	T	0.0	T
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0.0	81.2	3.3	0.5	T	T	4.7	0.0	0.0	0.0	0.0	T	T	T	0.1	T
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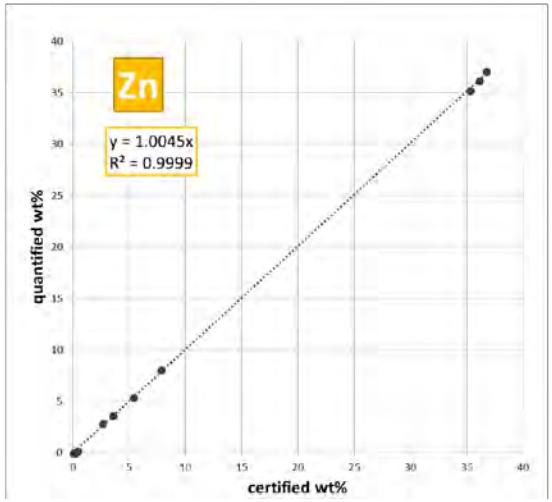
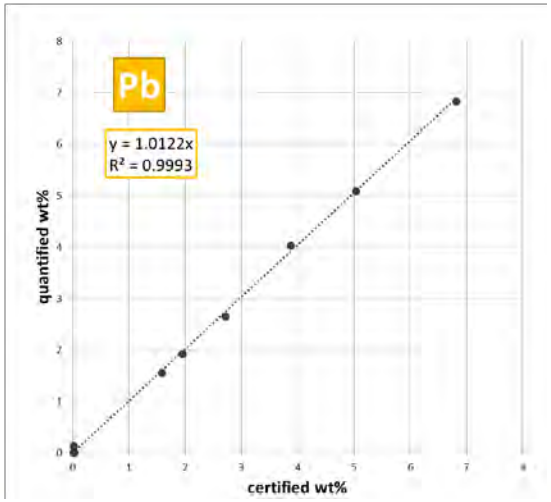
T	83.2	0.0	0.0	T	T	0.5	0.1	6.8	0.0	6.8	T	T	T	2.6	T
T	80.2	0.0	T	T	T	0.4	0.0	9.2	T	9.7	T	T	T	0.0	T





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CDA510-77B	0.0010	T	T	95.2	0.0	0.0	T	T	0.0	0.1	0.0	0.0	4.7	T	T	T	0.0	T
CDA544-78B	0.0020	T	T	87.7	0.0	0.0	T	T	0.1	0.2	3.9	T	4.7	T	T	T	3.6	T
CDA623-79B	9.1900	0.0	0.0	88.4	2.1	0.2	T	T	0.1	0.0	0.0	0.0	0.0	T	T	T	0.0	T
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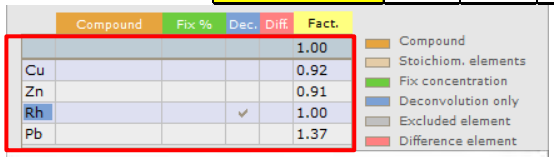
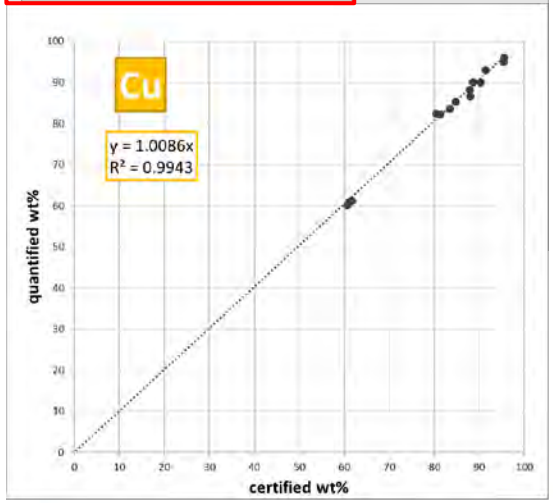
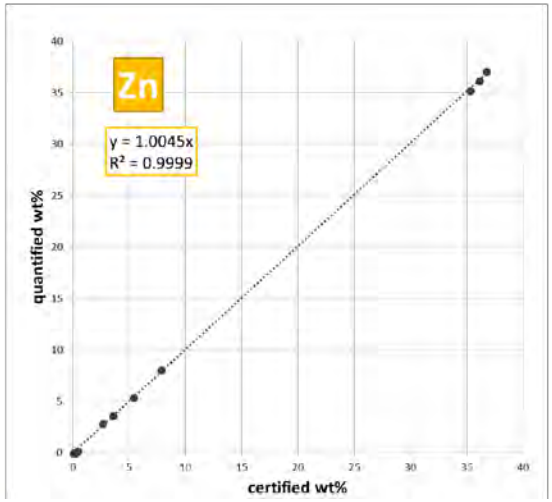
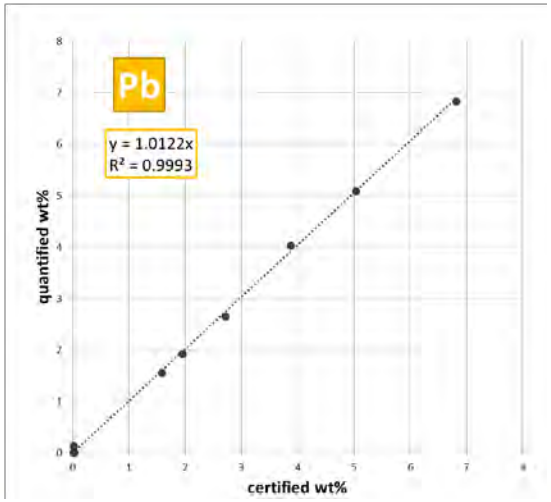
CDA857-87B	0.2000	0.0	0.0	60.9	0.3	0.0	T	T	T	0.0	1.6	0.0	0.8	T	T	T	36.1	T
CDA932-91C	0.0020	T	T	83.2	0.0	0.0	T	T	0.5	0.1	6.8	0.0	6.8	T	T	T	2.6	T
CDA937-BS937B-1	T	T	T	80.2	0.0	T	T	T	0.4	0.0	9.2	T	9.7	T	T	T	0.0	T









Fe-alloy
Overview and Measurement Conditions

Mapped area: 78.5 mm x 36.8 mm

Pixel size: 25 µm

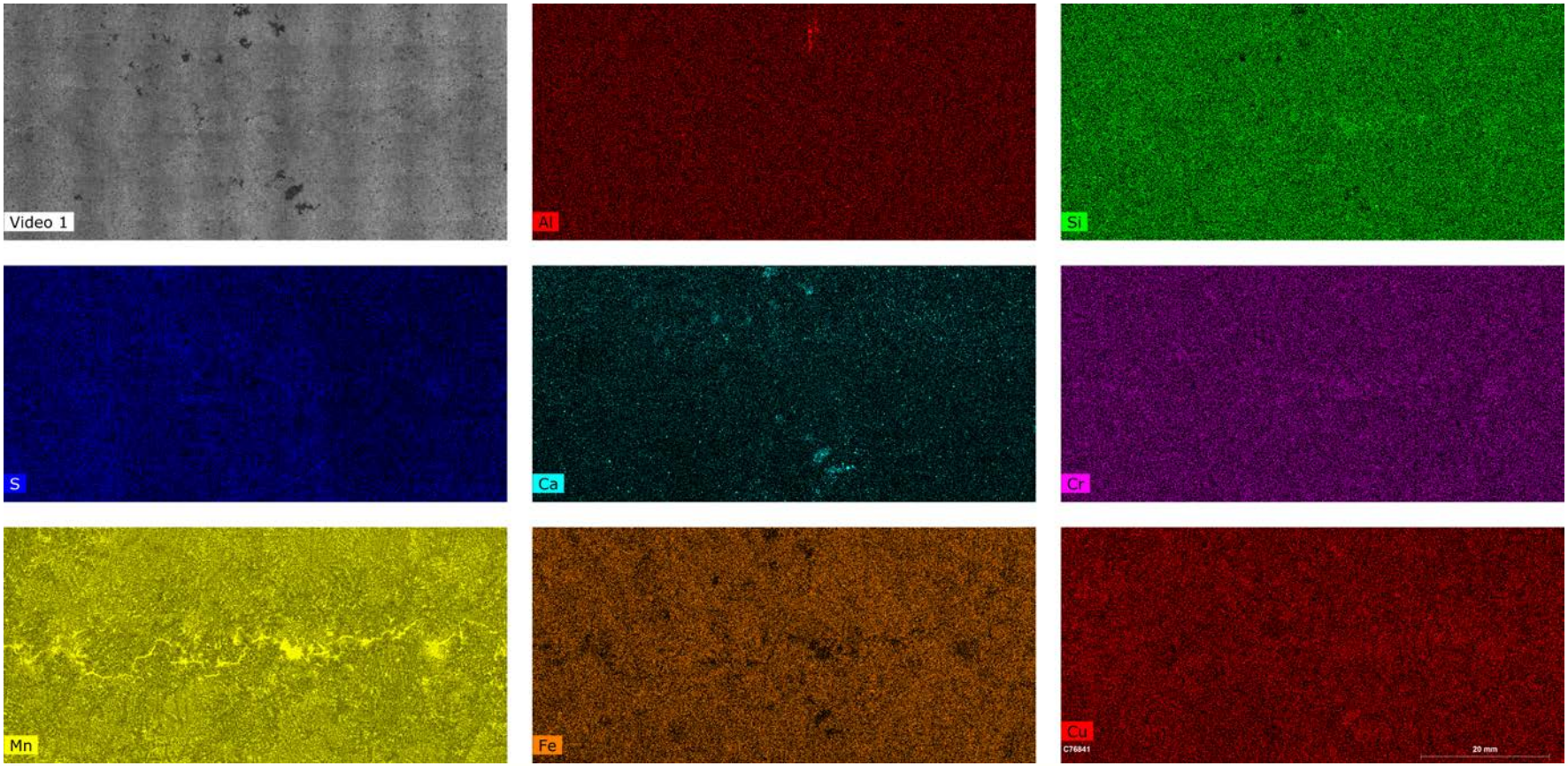
Dwell time: 3 ms/pixel

Overall: 4.6 Mpixel, 6:20 h.

Mapping parameters		
Width:	3139	pixel
	78.48	mm
Height:	1473	pixel
	36.825	mm
Pixel Size:	25	µm
Total number of pixel:	4623747	pixel
Acquisition parameters		
Frame count:	1	
Pixel time:	3	ms/pixel
Measure time:	1:56 h	
Overall time:	6:20 h	
Stage speed:	8.3	mm/s
Stage position (X,Y,Z):		
Tube parameter		
High voltage:	50	kV
Anode current:	198	µA
Filter:	Empty	
Optic:	Lens	
SpotSize:	25	
Chamber at:	Air 20	mbar
Anode:	Rh	
Detector parameters		
Selected detectors:		
Max. pulse throughput:	130000	cps

Fe-alloy
Element Distributions

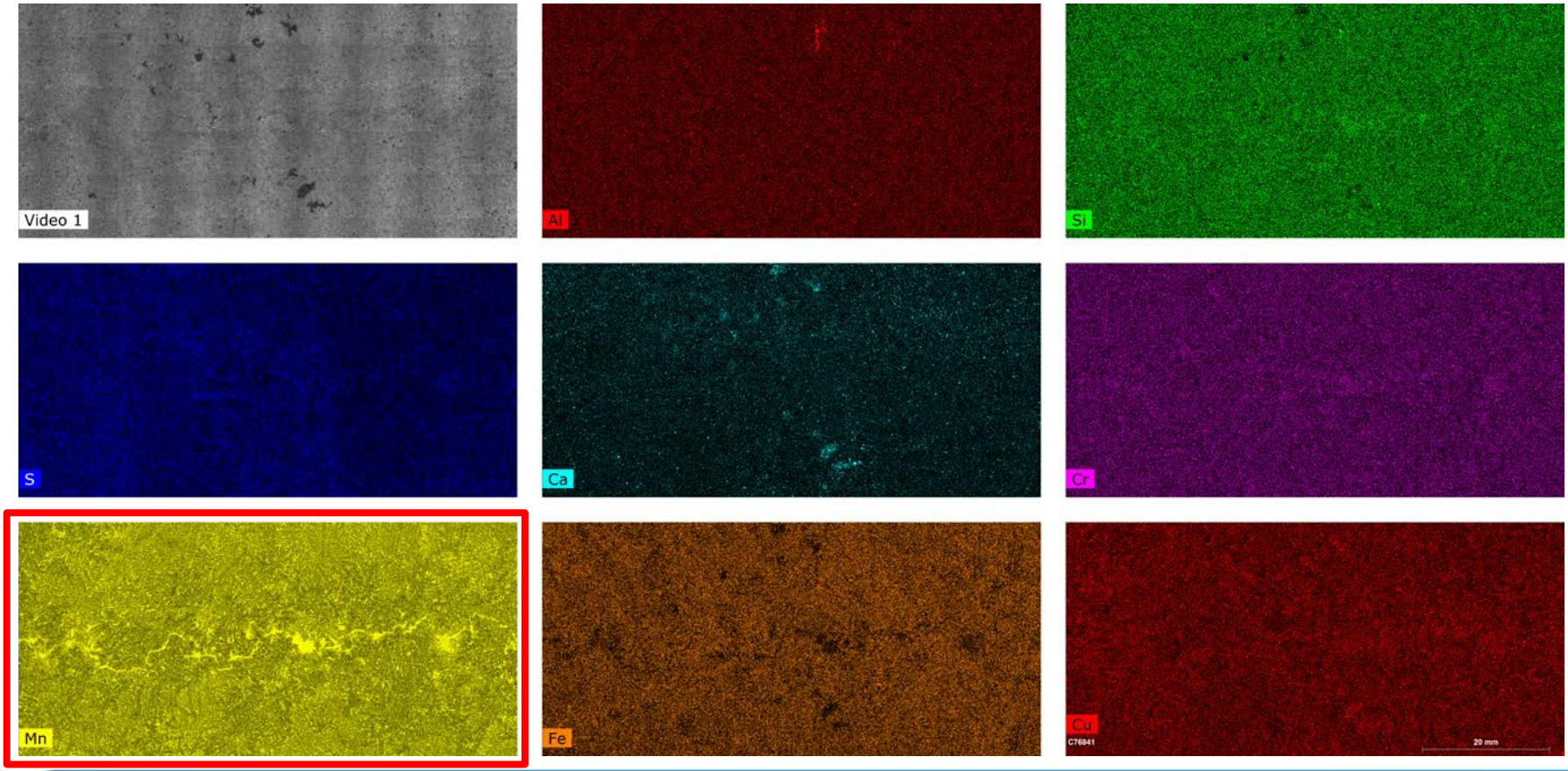
Net intensity distributions for the identified elements.



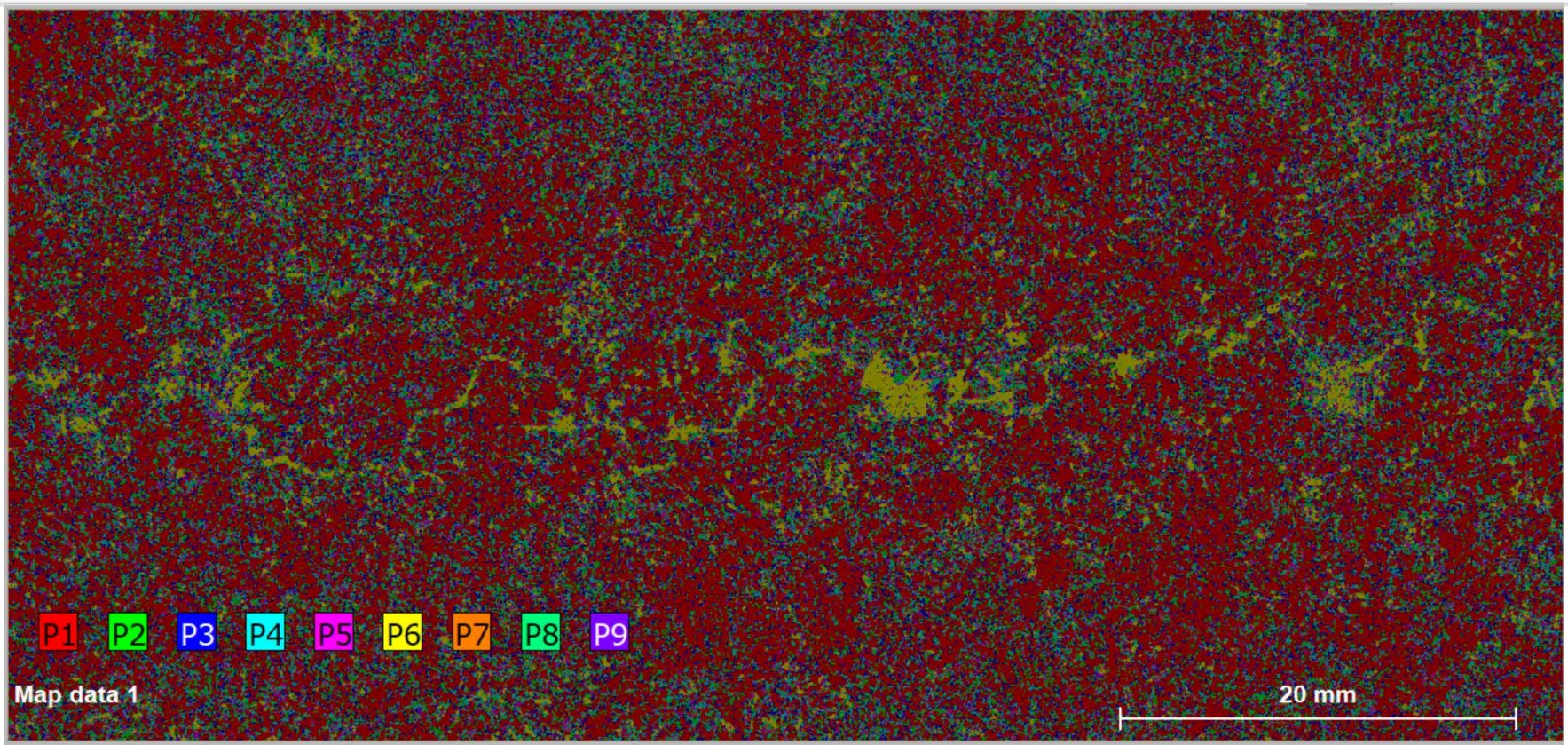
Fe-alloy
Element Distributions

Net intensity distributions for the identified elements.

Mn shows an interesting ‘horizon’.



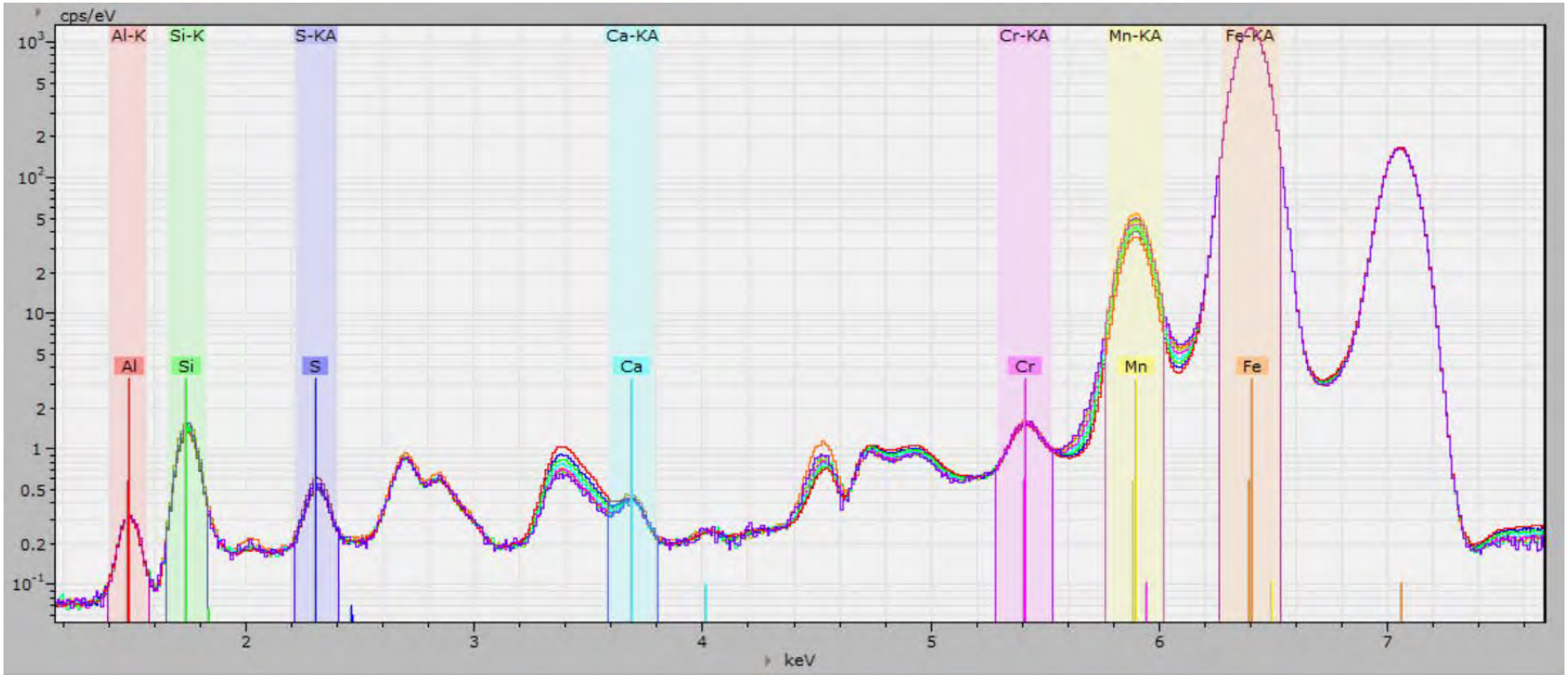
Fe-alloy
Mn distribution – phase analysis



0.00 0.27 1.00

Counts	Area	Video 1	Al-K	Si-K	S-KA	Ca-KA	Cr-KA	Mn-KA	Fe-KA
P1	50.0 %	--	--	--	--	--	--	16.43	--
P2	12.5 %	--	--	--	--	--	--	19.04	--
P3	11.2 %	--	--	--	--	--	--	18.13	--
P4	9.7 %	--	--	--	--	--	--	19.96	--
P5	6.5 %	--	--	--	--	--	--	20.92	--
P6	4.2 %	--	--	--	--	--	--	25.00	--
P7	2.8 %	--	--	--	--	--	--	21.82	--
P8	2.2 %	--	--	--	--	--	--	22.65	--
P9	0.9 %	--	--	--	--	--	--	23.51	--

Fe-alloy
Mn distribution – phase spectra



All		cps/eV	Results [Mass-% (norm.)]							Sort: Value
P1		0.27	Fe 96.07	Mn 2.21	Si 1.05	Al 0.54	S 0.07	Cr 0.03	Ca 0.03	Rh
P2		0.24	Fe 95.67	Mn 2.59	Si 1.08	Al 0.53	S 0.07	Cr 0.03	Ca 0.03	Rh
P3		0.26	Fe 95.83	Mn 2.46	Si 1.06	Al 0.53	S 0.07	Cr 0.03	Ca 0.03	Rh
P4		0.24	Fe 95.54	Mn 2.73	Si 1.09	Al 0.52	S 0.07	Cr 0.03	Ca 0.03	Rh
P5		0.23	Fe 95.37	Mn 2.87	Si 1.10	Al 0.53	S 0.07	Cr 0.03	Ca 0.03	Rh
P6		0.22	Fe 94.57	Mn 3.50	Si 1.28	Al 0.50	S 0.10	Cr 0.03	Ca 0.03	Rh
P7		0.23	Fe 95.25	Mn 3.00	Si 1.11	Al 0.51	S 0.08	Ca 0.03	Cr 0.03	Rh
P8		0.22	Fe 95.09	Mn 3.12	Si 1.15	Al 0.51	S 0.08	Cr 0.03	Ca 0.03	Rh
P9		0.19	Fe 94.95	Mn 3.25	Si 1.16	Al 0.50	S 0.08	Cr 0.03	Ca 0.02	Rh

M4 TORNADO Webinar
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  - The M4 instrument
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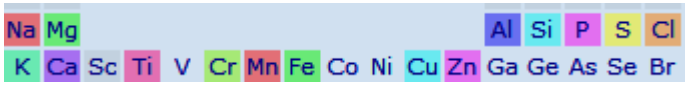
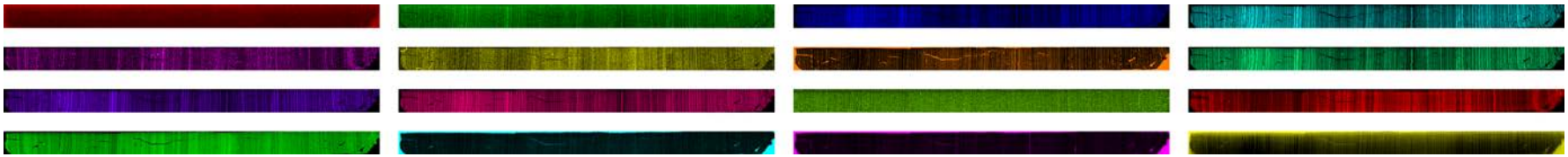
- Heterogeneous in 1 dimension – drill core
- Heterogeneous – concrete
- Live part – data extraction and evaluation
- Summary

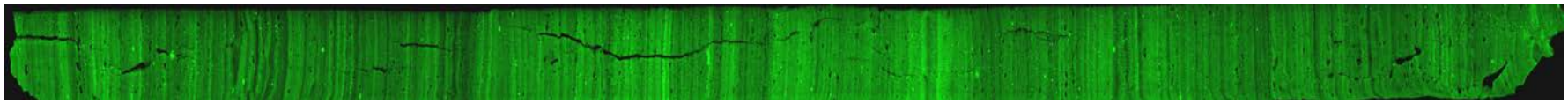
Drill core
Lake sediment





Fe

Intensity map

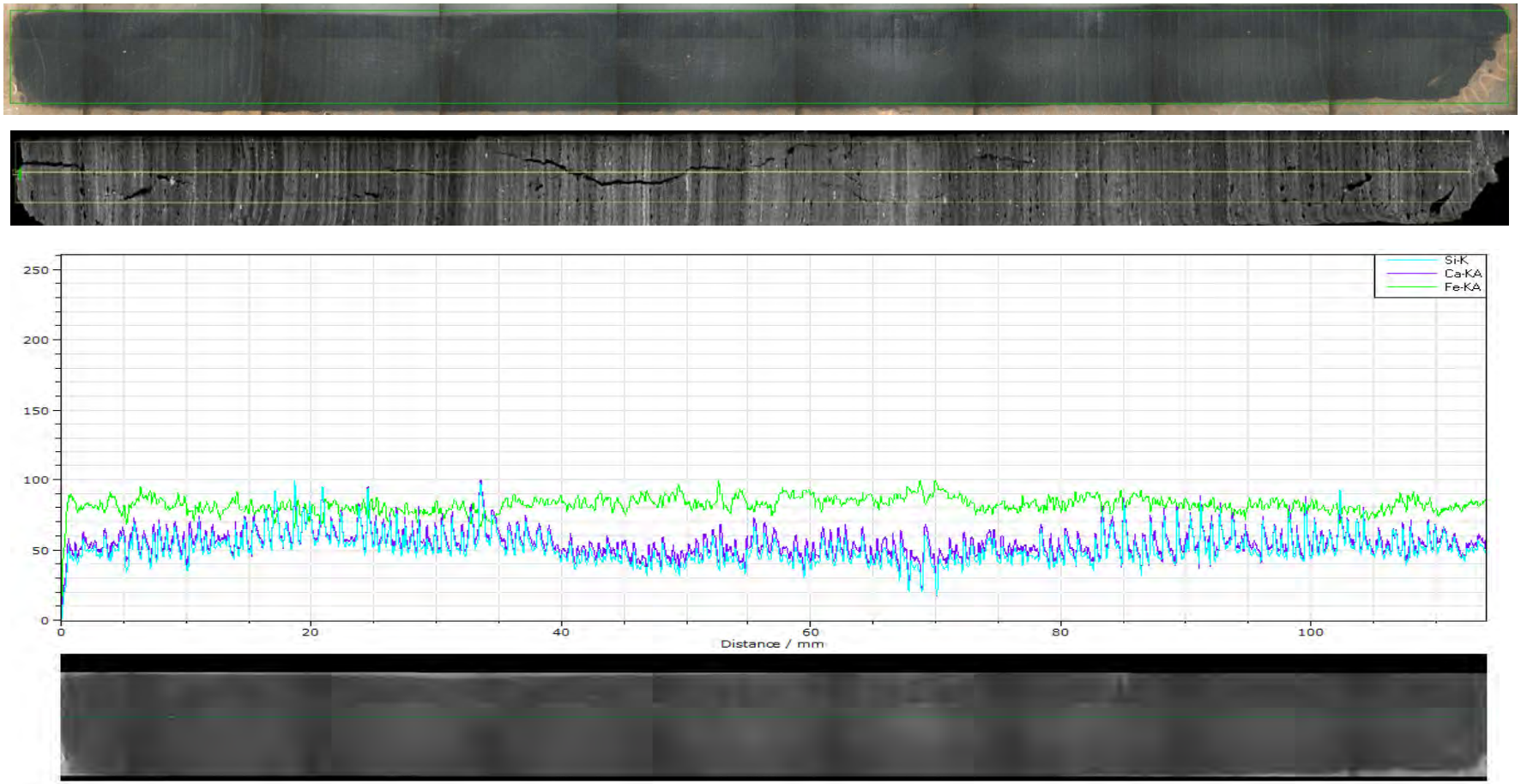


Si

K

Ca

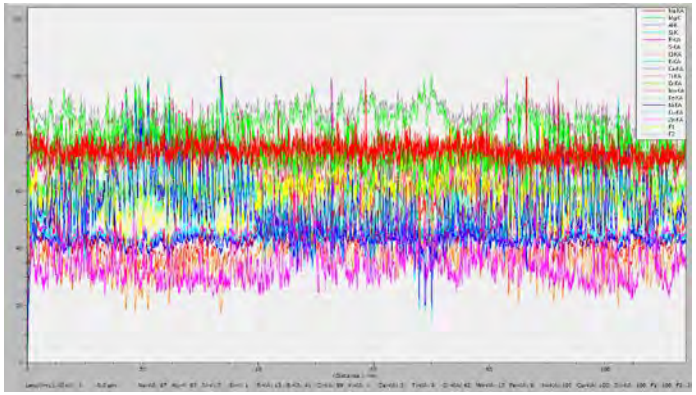
Drill core
Line object



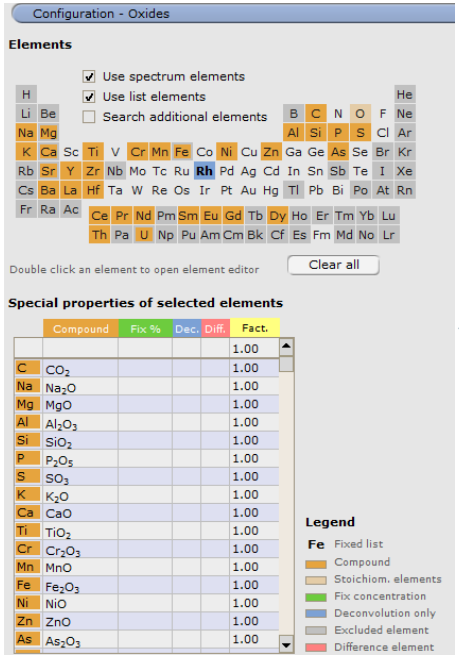
A line can be drawn over the map and the line can be widened to improve statistics. Selected elements can then be plotted directly in the software. For additional plot options the data can be extracted to make it accessible for other plot software.

Drill core
Exporting data

The line extracted from the map can be quantify to obtain the net intensity in the line work space

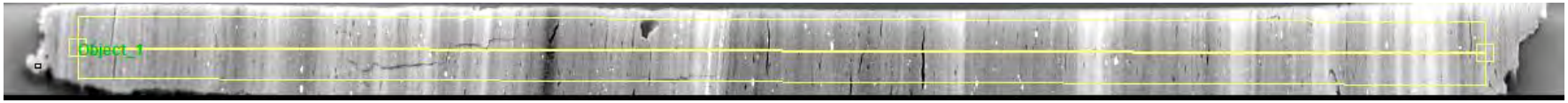


Quantification can be done using the Oxide method



Quantification results (wt.-%, net intensities) can be can be exported to excel

Drill core
Plot vs. Image



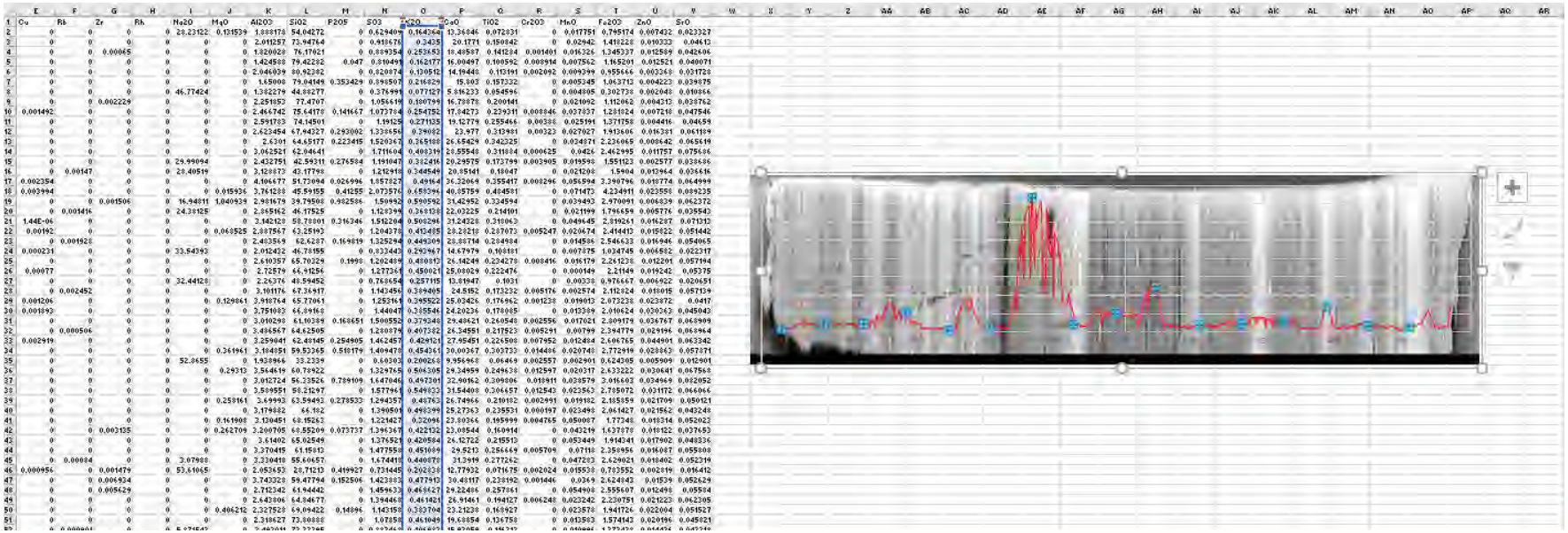
Line scan data
Add to project
Save...
Print...
Add to report
Graphic
Copy
Save...
Twain export

CONFIRM
Do you want to save point spectra too?
Yes
No

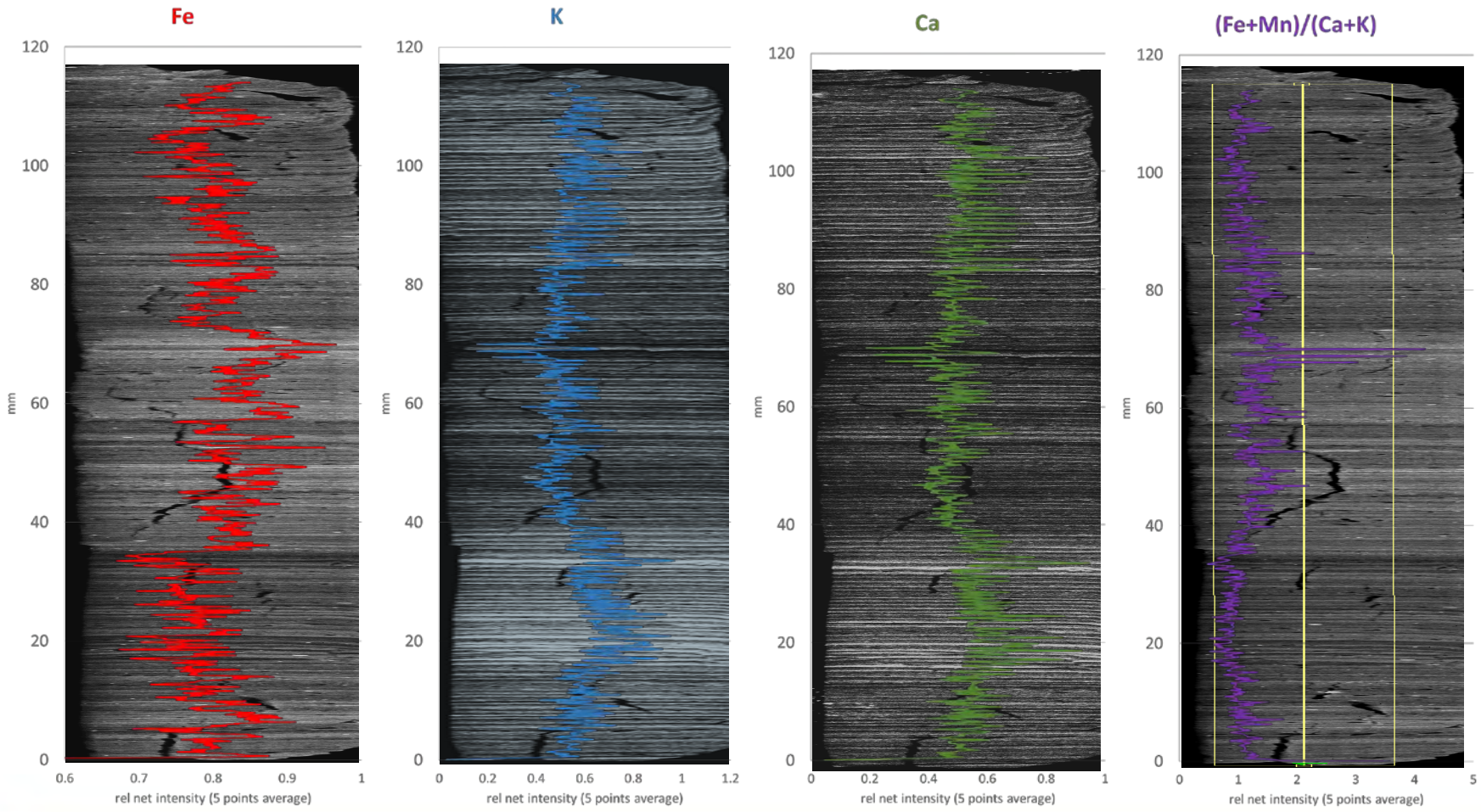
Quantify
Oxides

Results | Profiles | Spectrum

Add to project
Copy
Save...
Print...
Add to report
Twain export



Drill core
Plot vs. Image



M4 TORNADO Webinar
Outline

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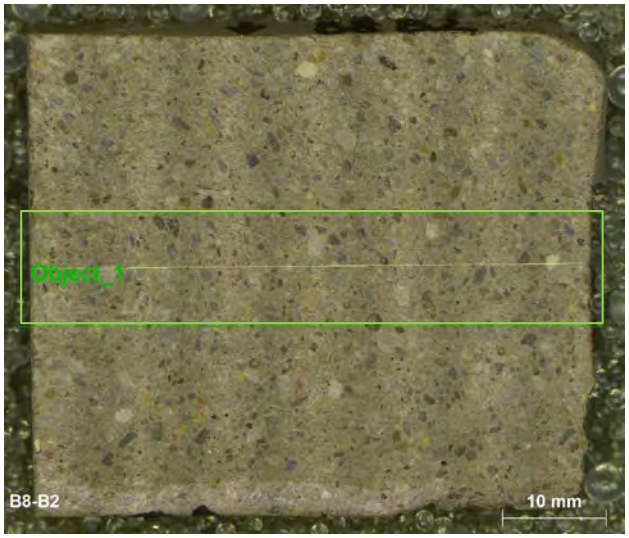
Concrete
A heterogeneous sample

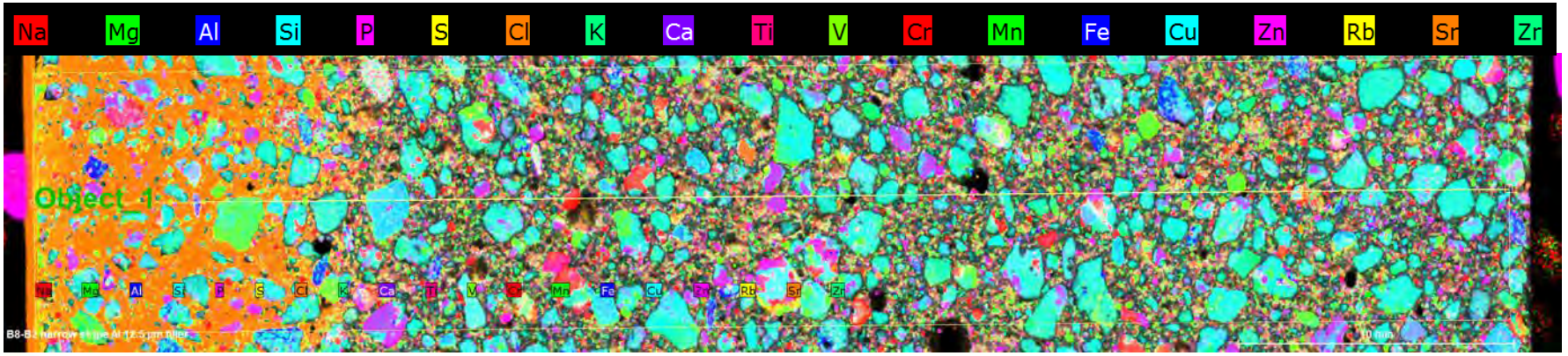


- 4 h scan on a region from left to right (thin green frame)
- gradient in Cl distribution (orange) clearly visible

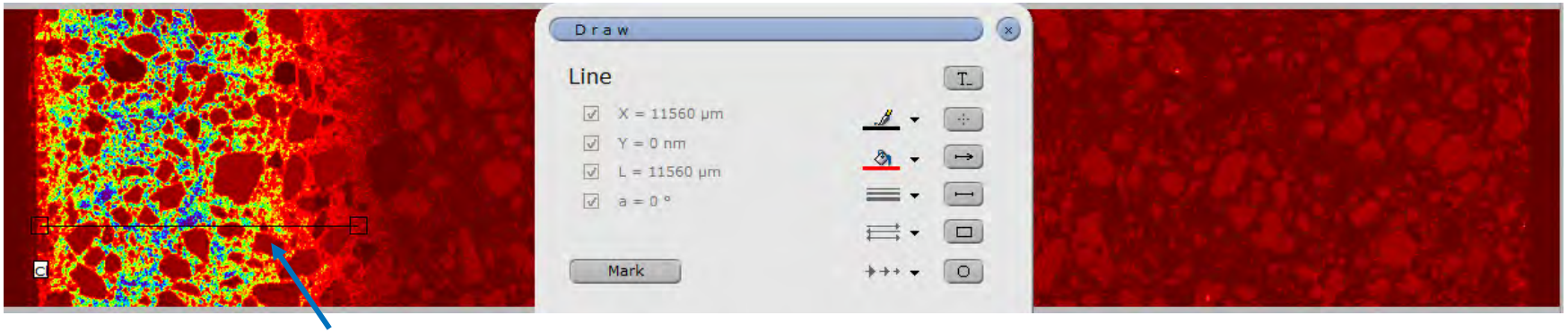
Map information

Mapping parameter		
Width:	2820	pixel
	56,4	mm
Height:	540	pixel
	10,8	mm
Pixel Size:	20	µm
Total number of pixel:	1522800	pixel
Acquisition parameter		
Frame count:	1	
Pixel time:	10	ms/pixel
Measure time:	4:13 h	
Overall time:	4:48 h	
Tube parameter		
High voltage:	50	kV
Anode current:	600	µA
Filter:	Empty	
Optic:	Lens	
Chamber at:	Vacuum 20,1	mbar
Anode:	Rh	
Detector parameter		
Selected detectors:	1,2	

Close



Concrete
Cl gradient in cement

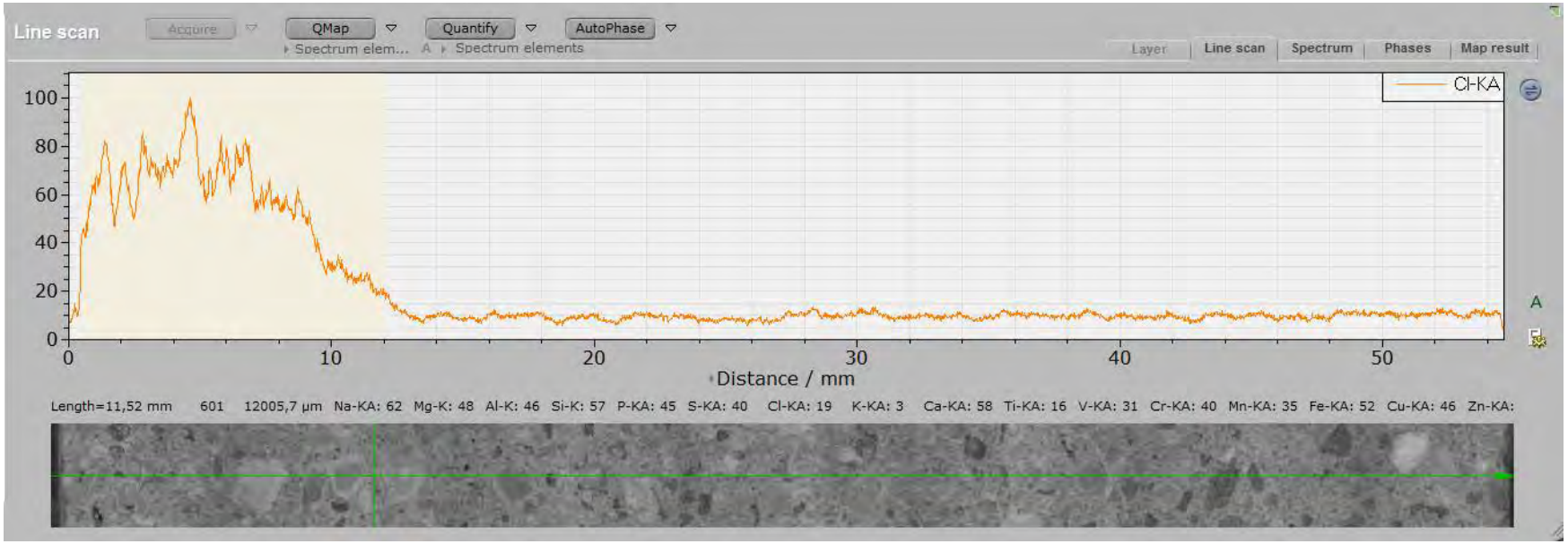


False color representation of the chlorine concentration

Obvious gradient

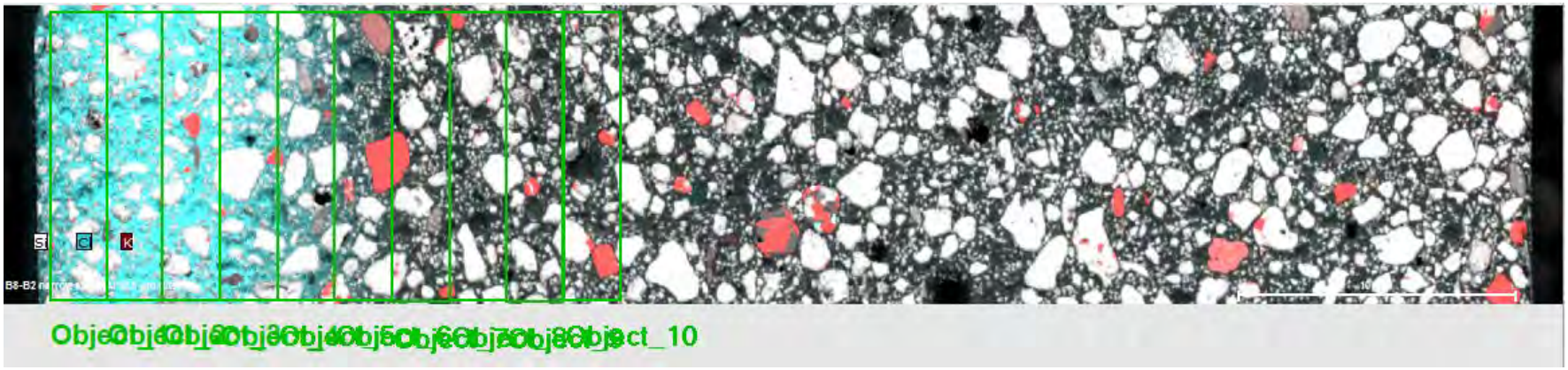
With the drawing tool a line has been drawn which is shown to be 11.5 mm long which gives an indication of the depth of Cl diffusion

Concrete
Cl depth from line scan

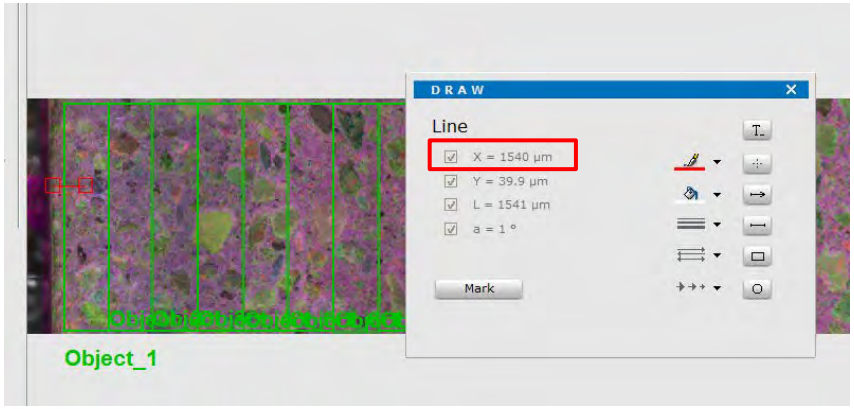


A line object can be drawn into the the Hypermap data. Therewith a line profile along the sample can be generated.
The Cl signal is increased in an area of which again is found to be ~ 11.5 cm in length

Concrete
… a more quantitative approach: objects

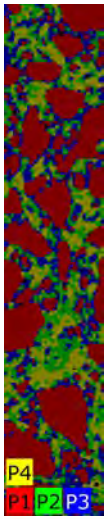


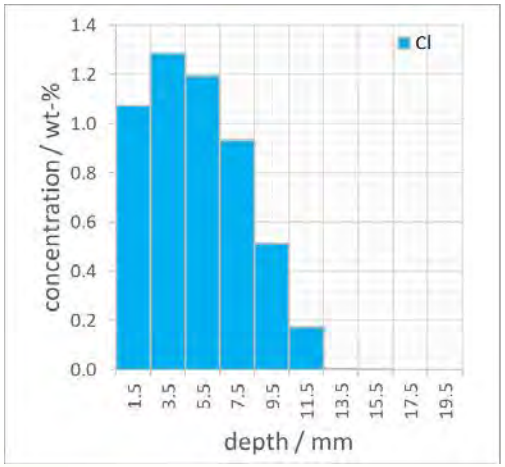
Draw objects into data cube and get their dimensions using the “draw tools”

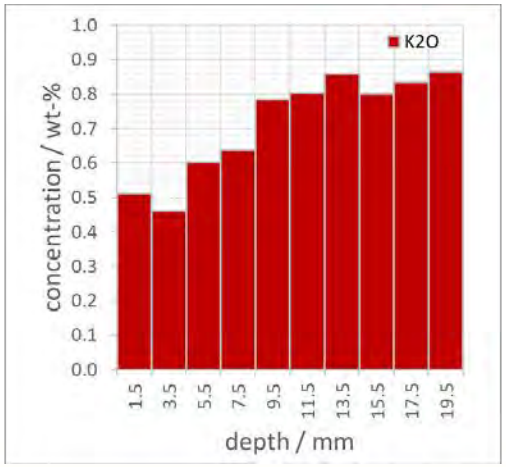


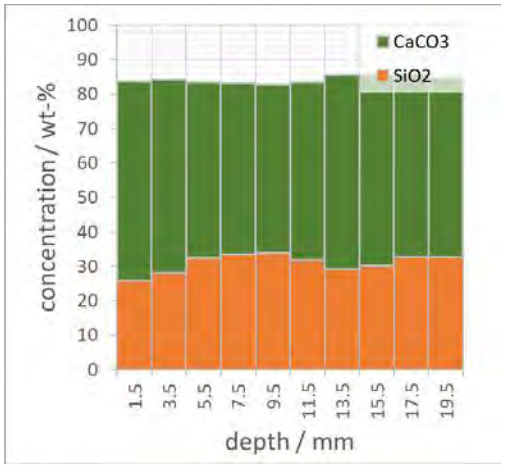
Concrete
phase analysis and concentrations

- Load each object
- Select only a signature element of the cement (here P)
- Press auto phase
- Select the cement phase
- Create sum spectrum
- Move the sum spectrum to the project (or save to disk)
- Repeat for all objects
- Import all phase sum spectra into point mode
- Quantify with appropriate method
- Export results table to Excel → plot









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Some data mining
Live

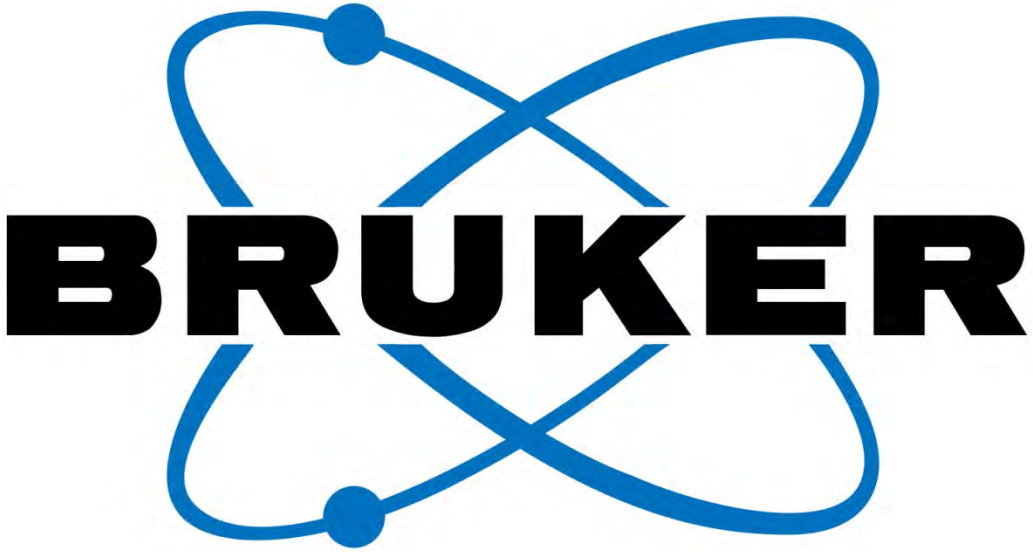
Summary

- Micro-XRF helps you understand (the inhomogeneity of) your sample
- The position tagged spectroscopy (HyperMap) allows to access all spectral information at a later time
- Any spectrum in the software can be quantified (but often shouldn‘t)
- To get a results, at first clarify the actual analytical question
- Find the correct measurement conditions
- Multiple approaches to useful results are possible for inhomogeneous samples
  - Use net peak areas as their significance is less affected by matrix effects
  - Use phase analysis to identify „homogeneous“ parts of a sample
  - Use data export for advanced results arithmetics
  - For quantification a type calibration usually corrects for sample effects
- Find an adequate results visualization (ideally suported by numbers)

Q&A

Are There Any Questions?

Please type in the questions you might have in the Q&A box and press *Send*.



Innovation with Integrity