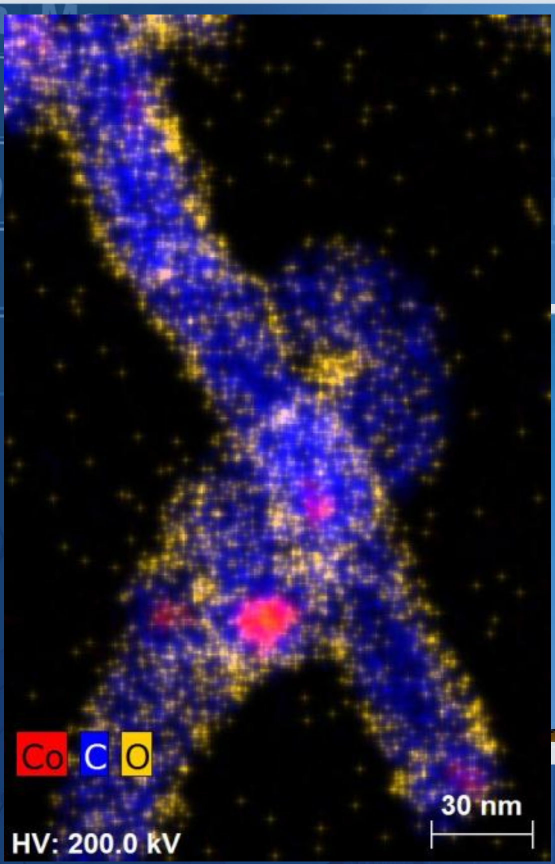
TEM, STEM and T-SEM EDS Quantification at its Best

Webinar, June 2019



TEM, STEM and T-SEM EDS Quantification at its Best

Speaker:

Meiken Falke,

Global Product Manager TEM-EDS,

Bruker Nano GmbH, Berlin

Host:

Max Patzschke

Application Scientist,

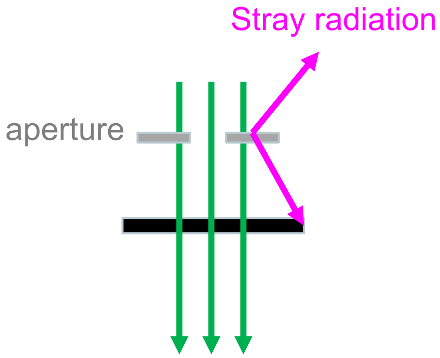
Bruker Nano GmbH, Berlin

Outline

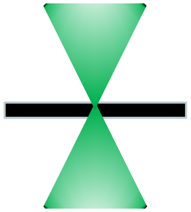
- Intro: TEM, STEM and T-SEM EDS
- Geometry Considerations
  - collection / take off angle
  - Sample position … tilt, mounting, shape
- TEM EDS Quantification
- TEM EDS Quantification and Display of Results:
  - ESPRIT implementation
  - ESPRIT SW use for TEM-EDS explained in simple steps
- Problems, Tricks and Tips

EDS from Electron Transparent Samples

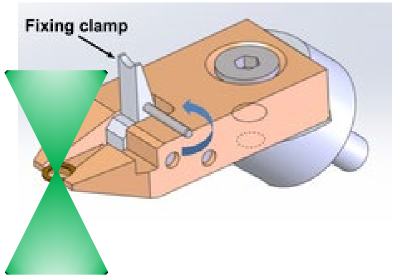
TEM



STEM
Scanning TEM

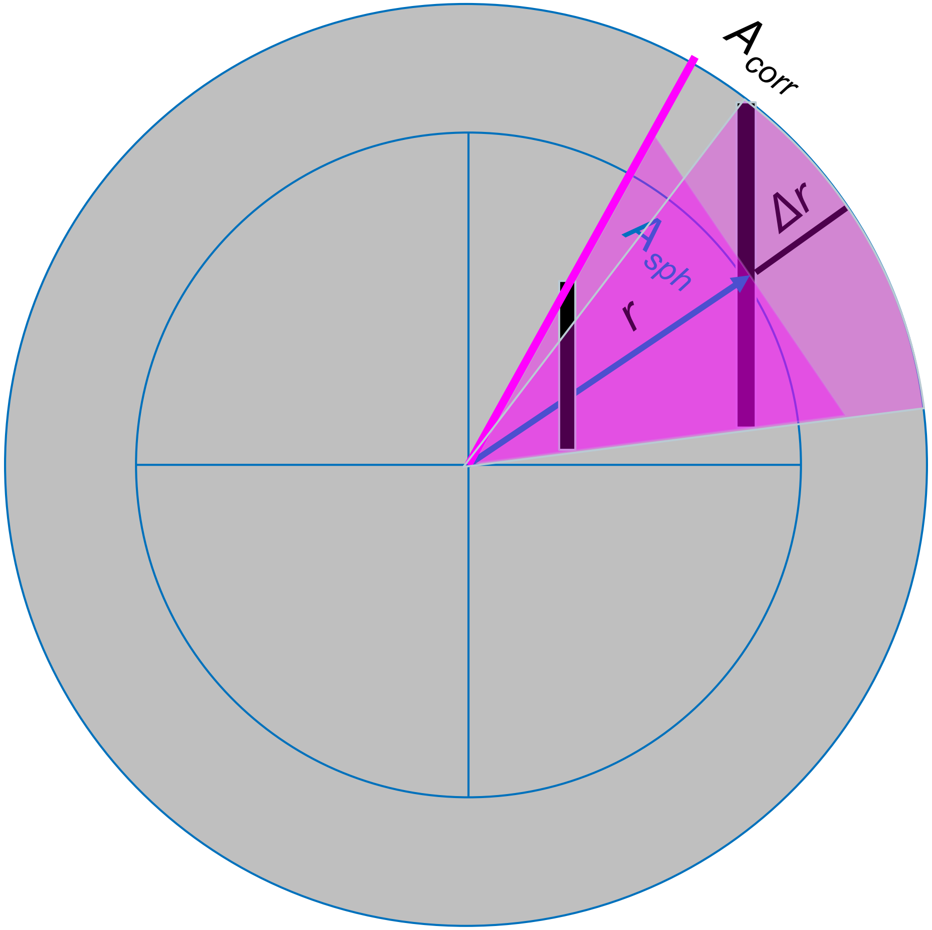


SEM: „T-SEM“



- TKD specimen holder
- Commercial STEM holders
- Home made versions

Solid Angle Correction for Flat SDD in 2D



The solid angle of $A_{D\_Flat\_vertical}$

$\Omega = A_{corr} / (r+\Delta r)^2$

Smaller detector closer to specimen enables

- Larger A_{corr}
- ➢ Larger solid angle

A large take-off angle above the sample is needed to avoid shadowing and stray radiation > use small area!

Small detector areas can be positioned higher above the sample due to geometric constraints in TEM.

References

How to calculate geometric solid angle:

N. Zaluzec, on solid angle Microsc. Microanal., 15 (2009) 93;

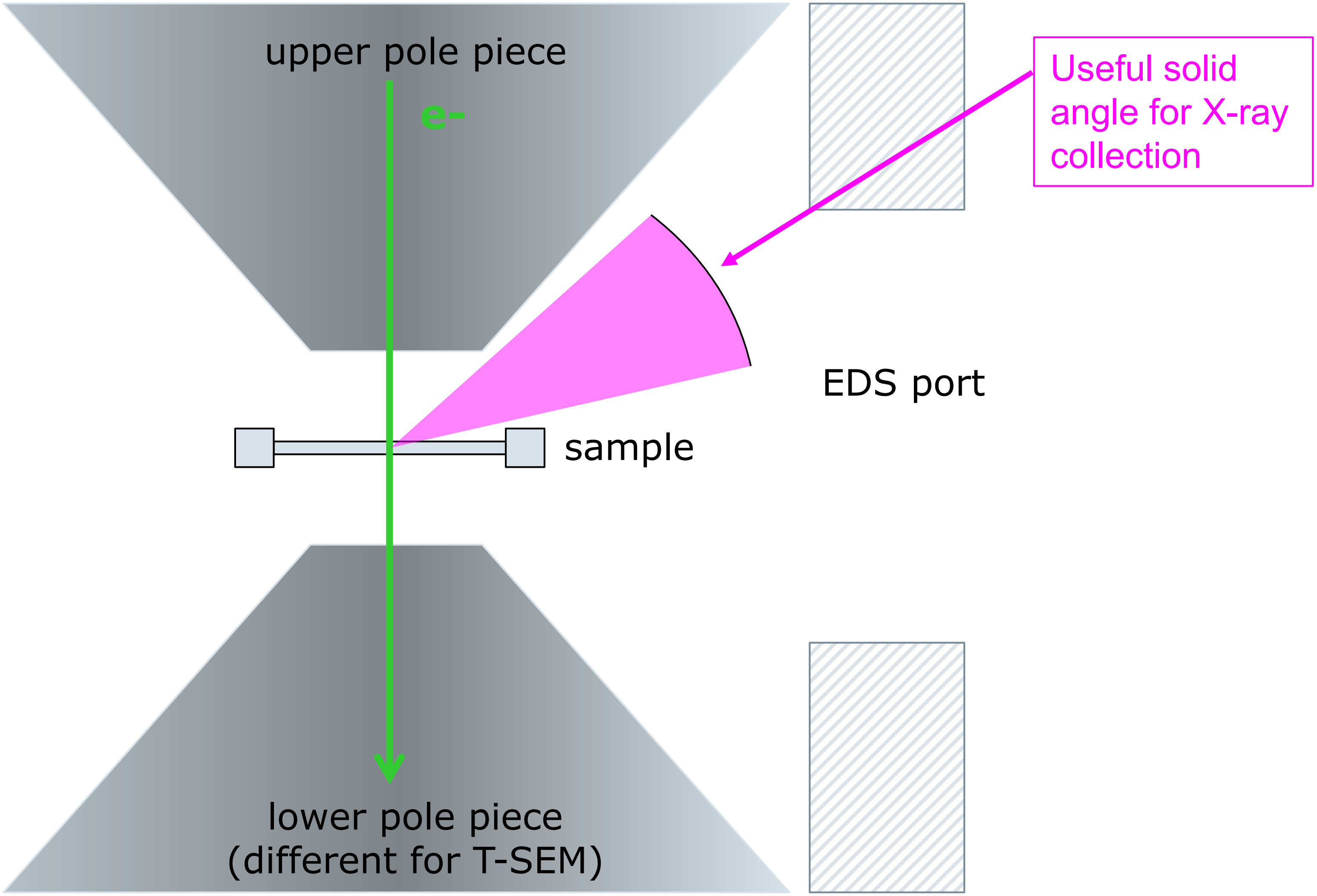
Also check Nestors web page!

How to measure solid angle using standard:

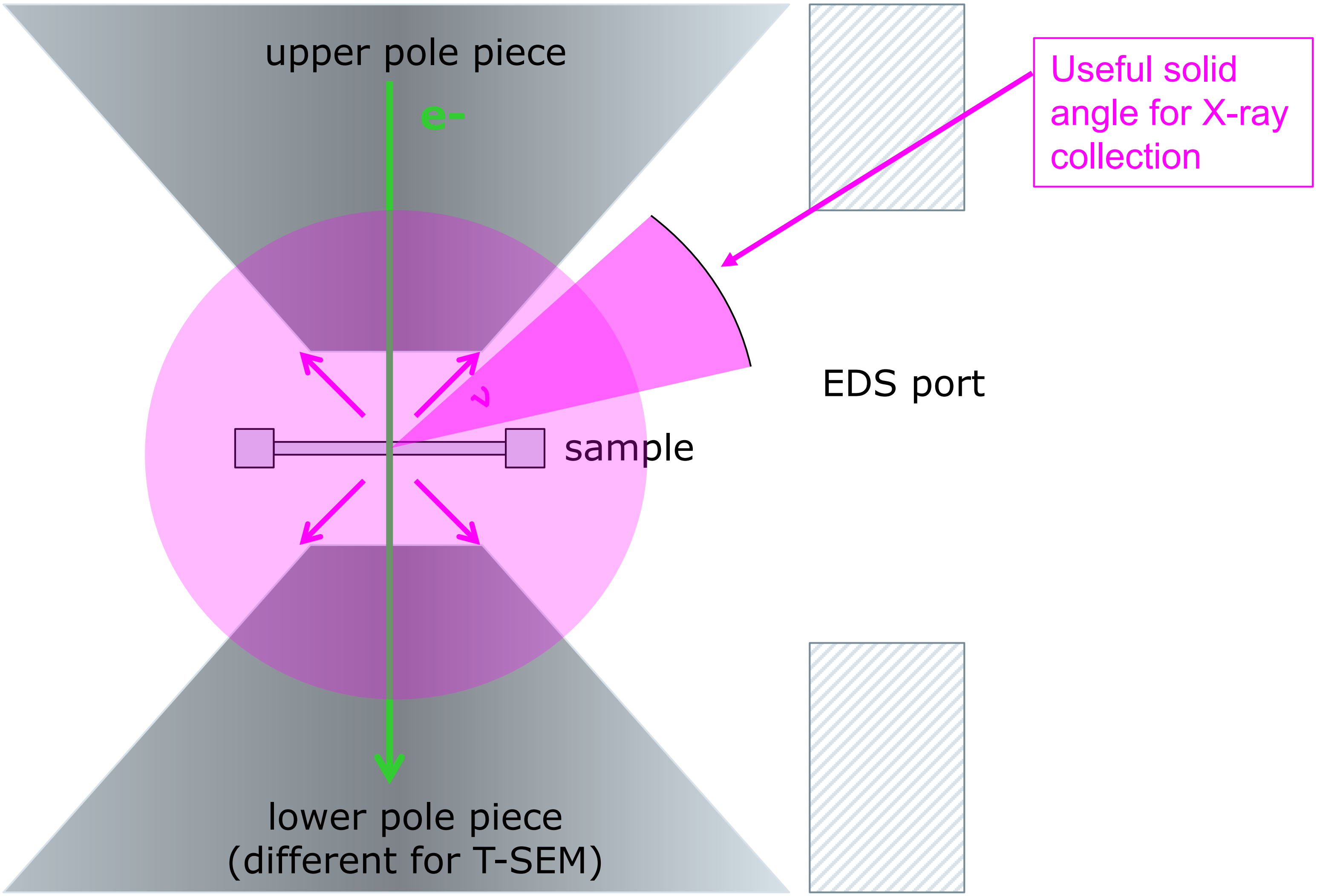
R. F. Egerton, S. C. Cheng, Ultramicroscopy 55 (1994) 43-54;

Also see formulas on later slides!

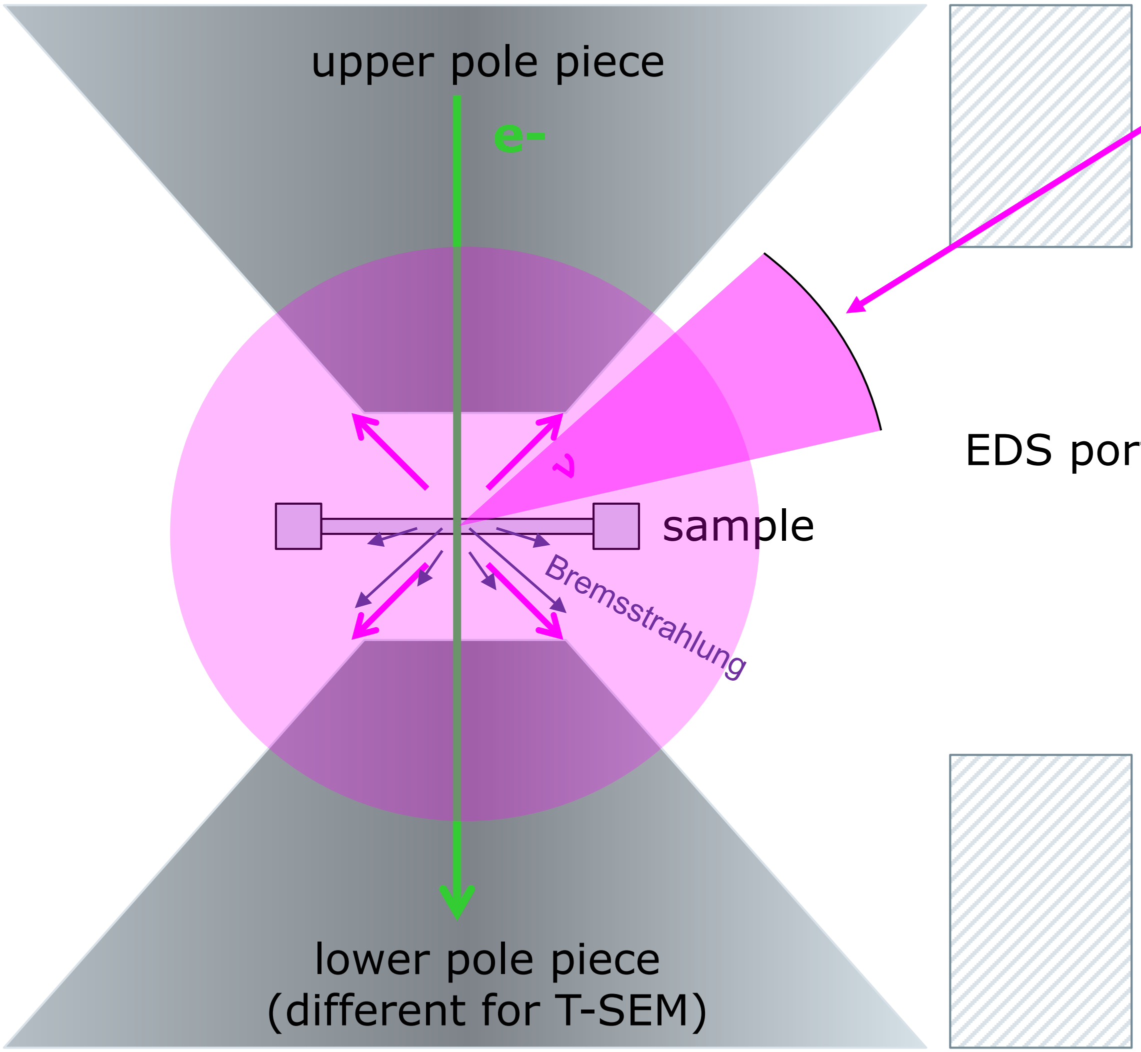
Geometric Limitations



Geometric Limitations

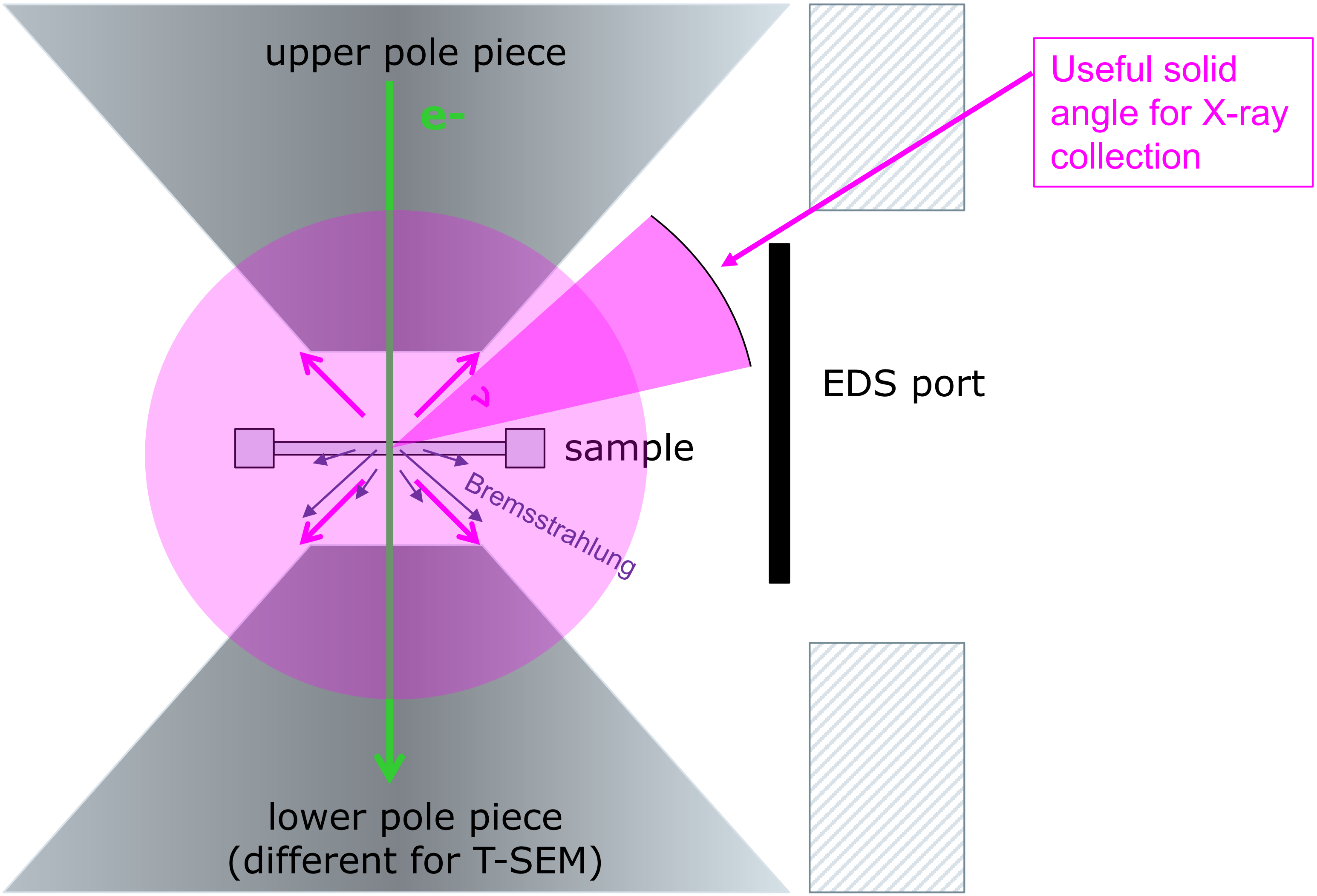


Geometric Limitations

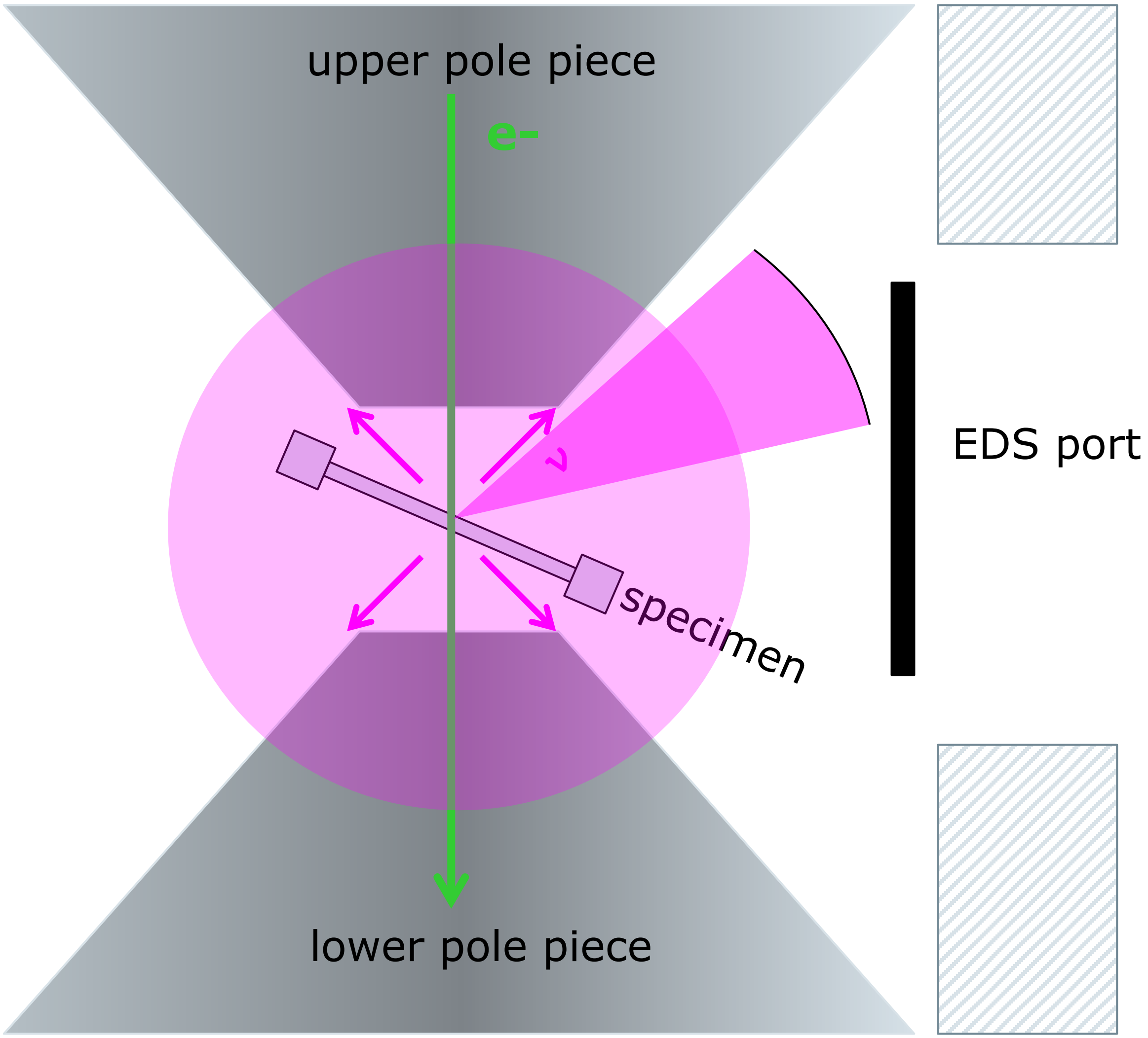


Useful solid angle for X-ray collection

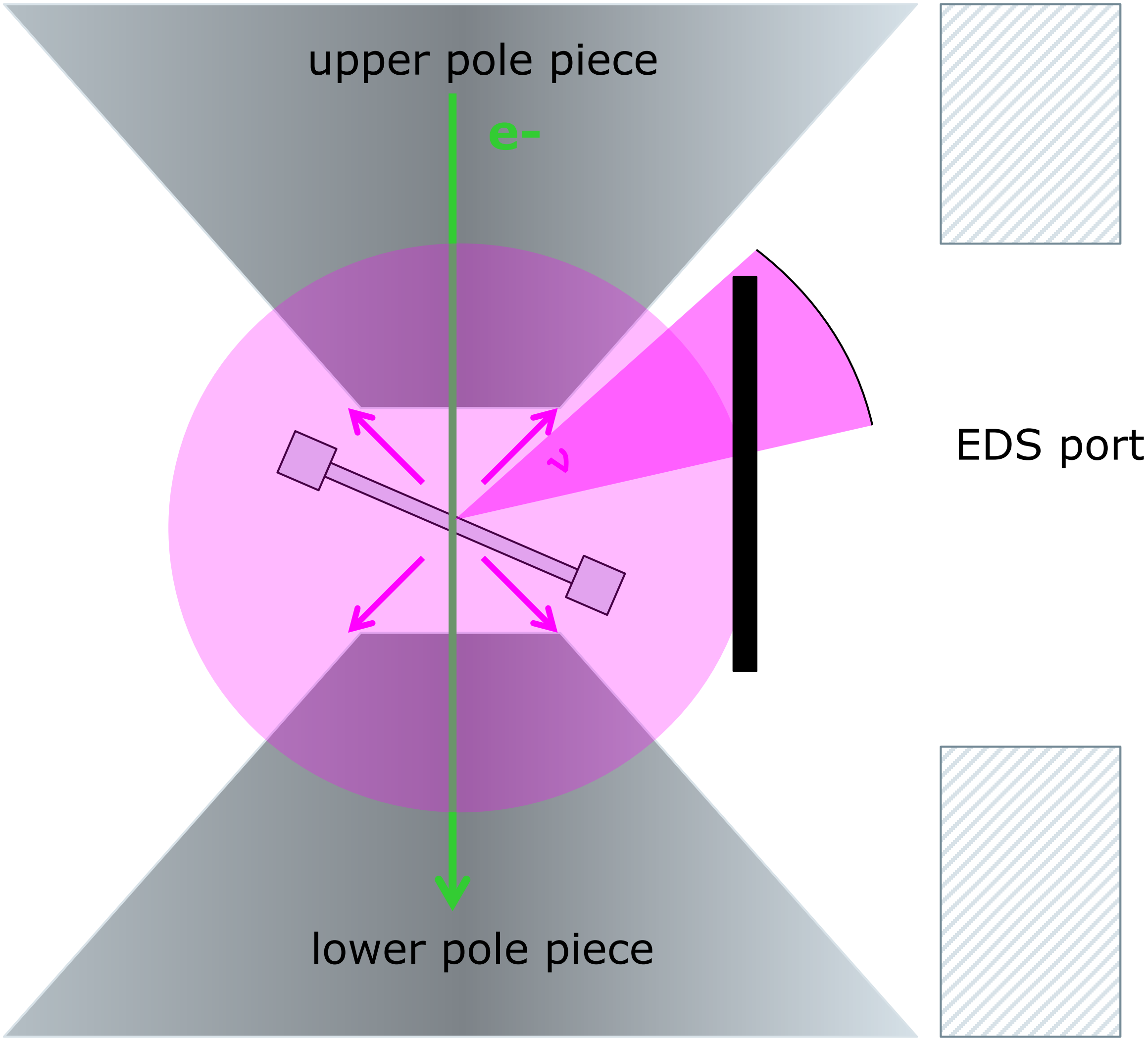
Geometric Limitations



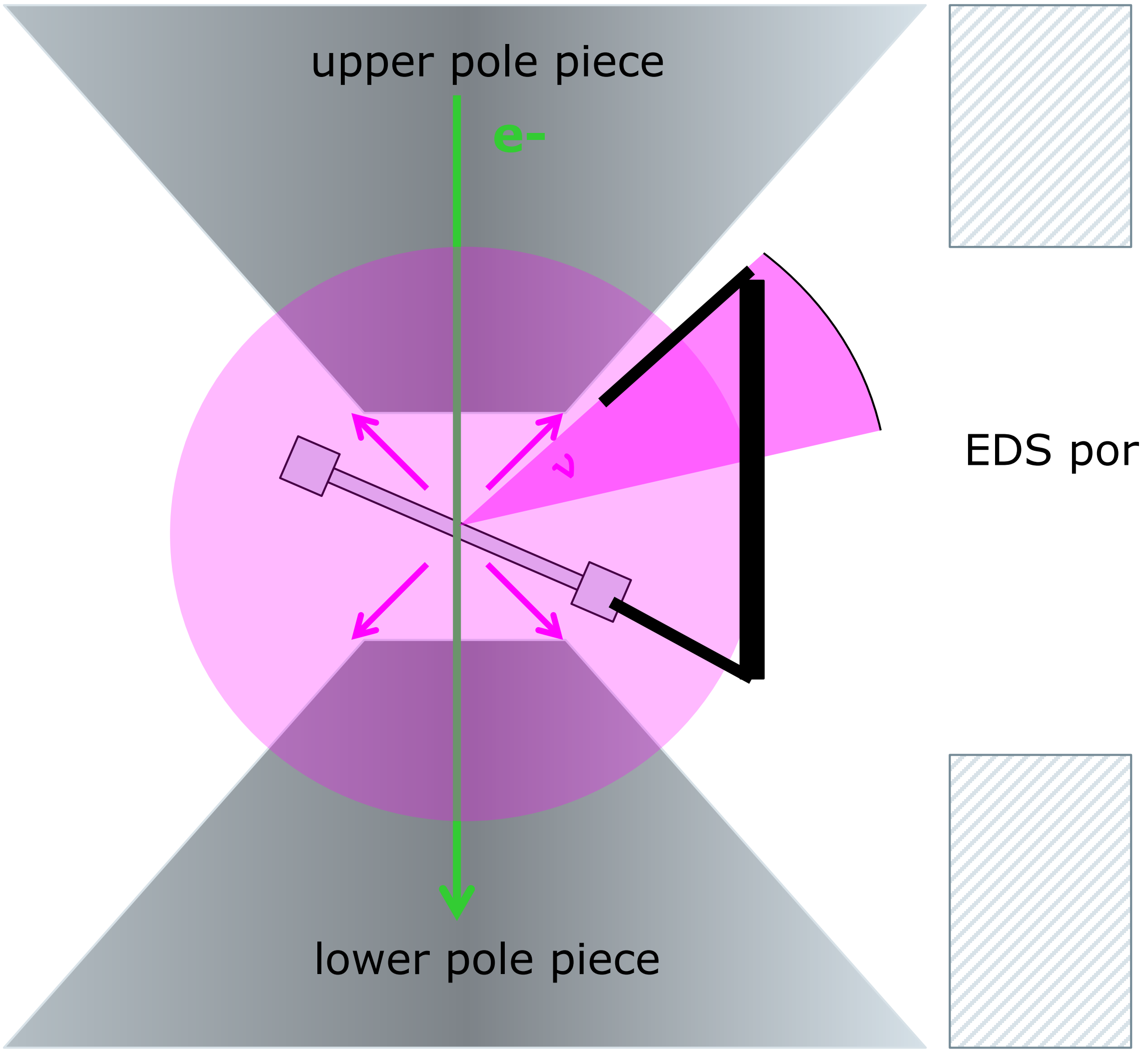
Geometric Limitations



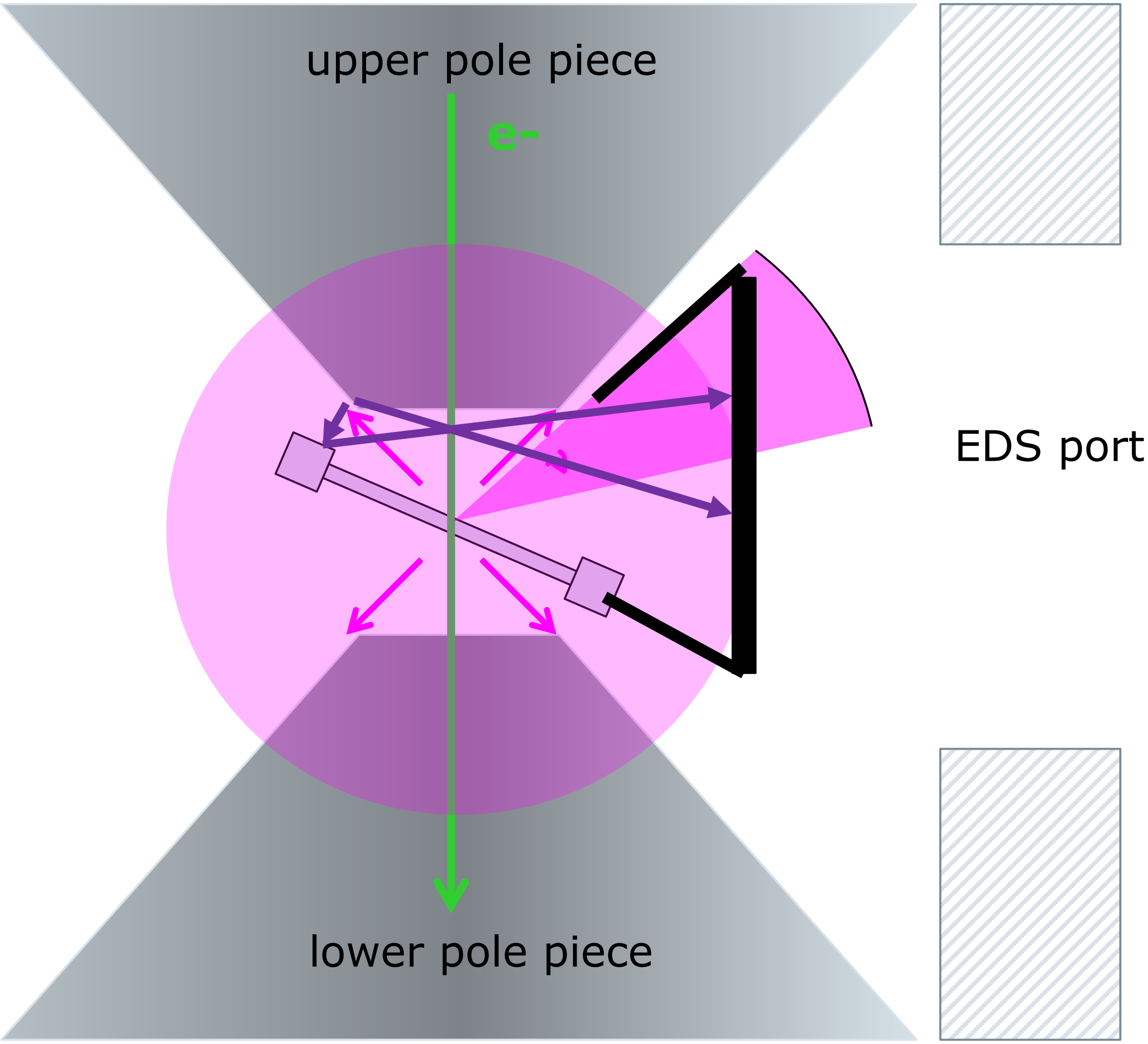
Geometric Limitations



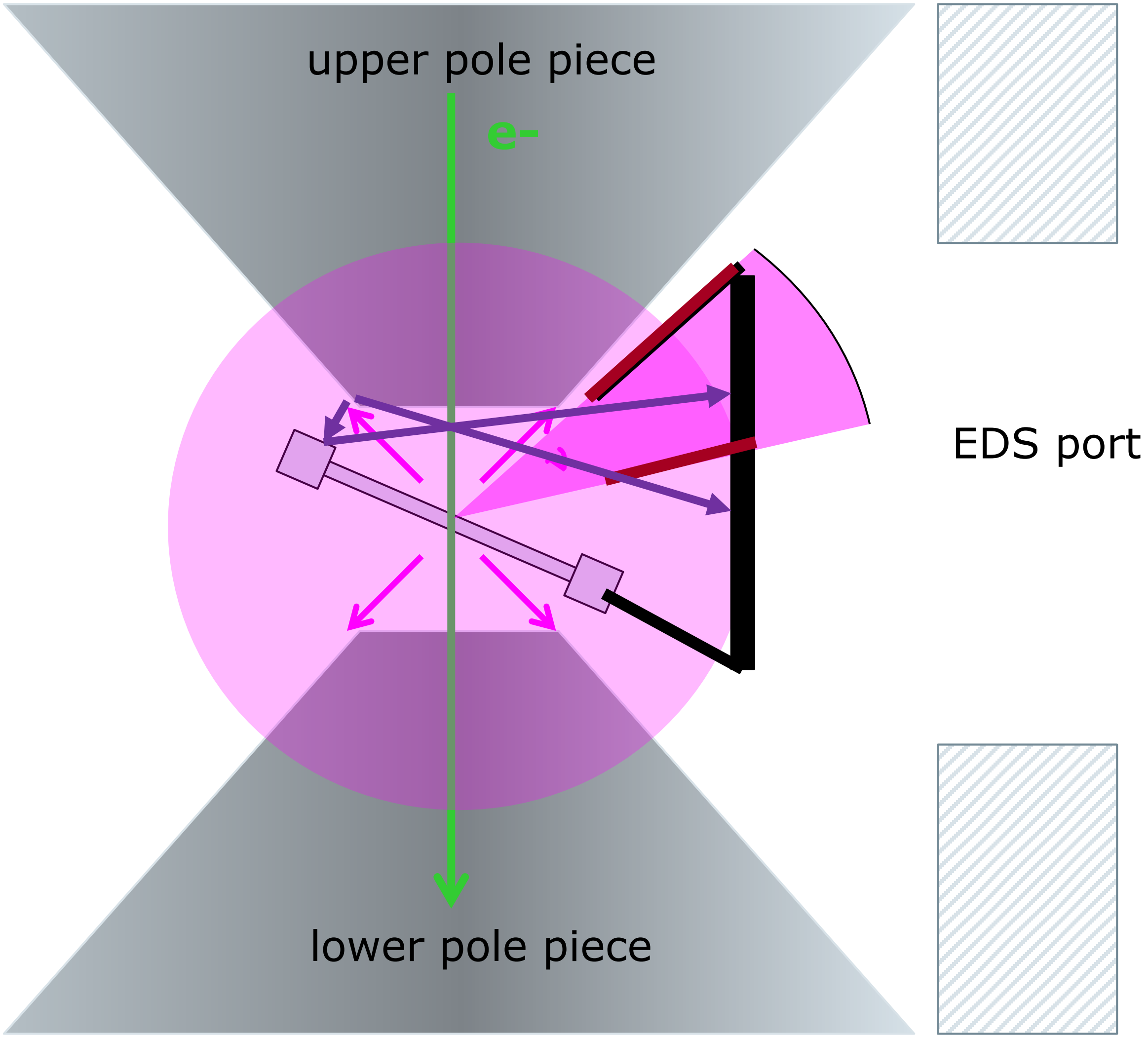
Geometric Limitations



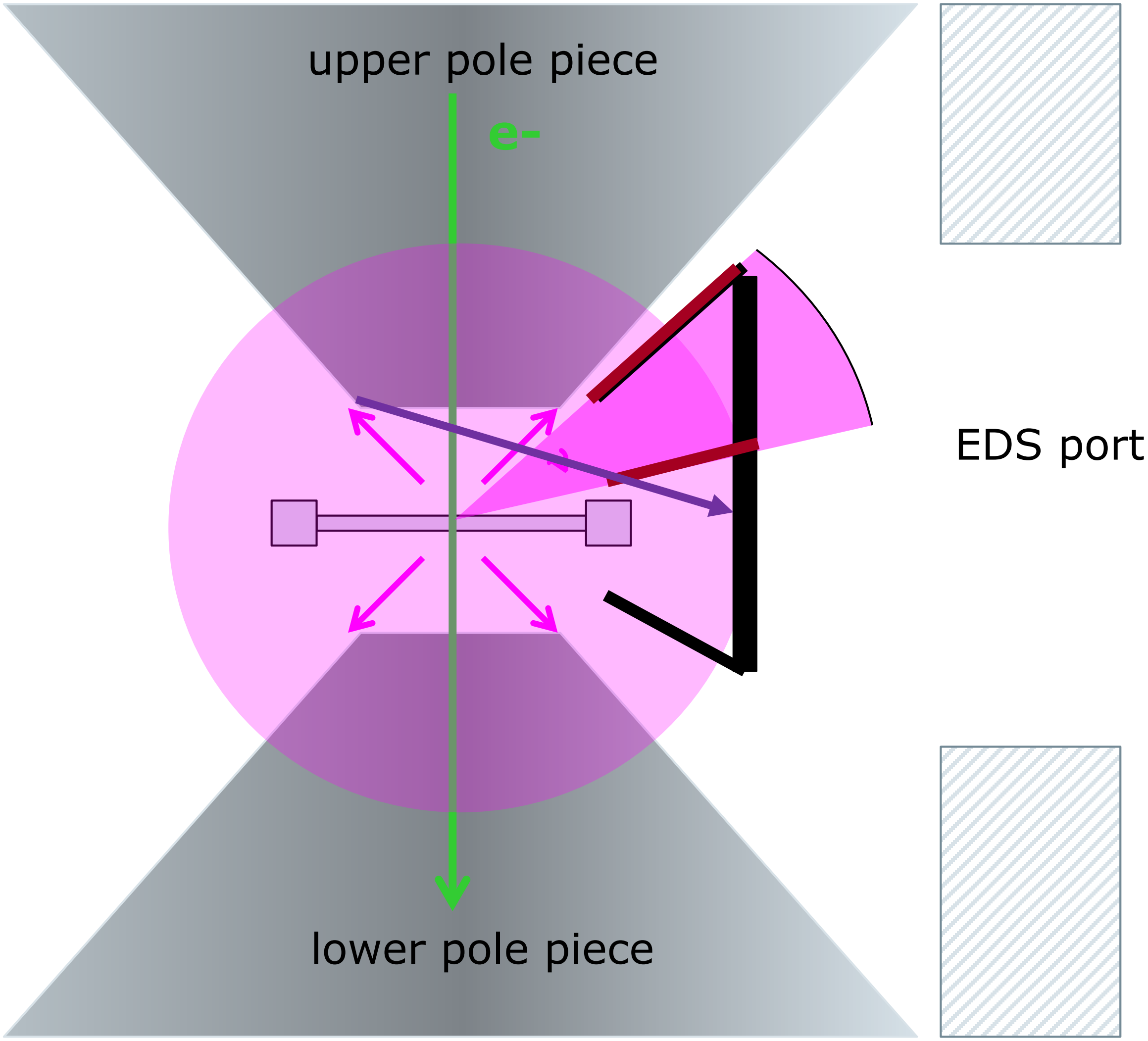
Geometric Limitations



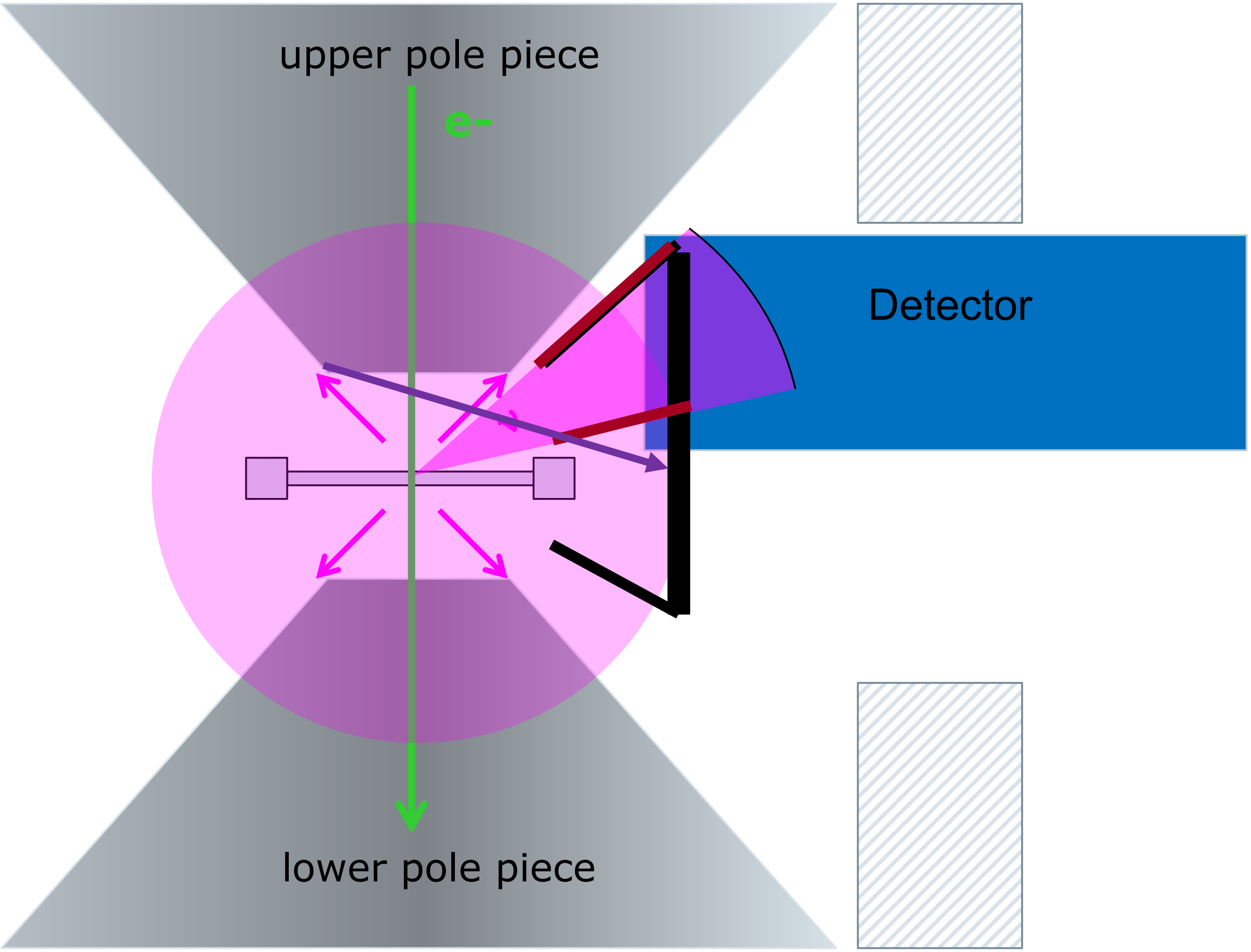
Geometric Limitations



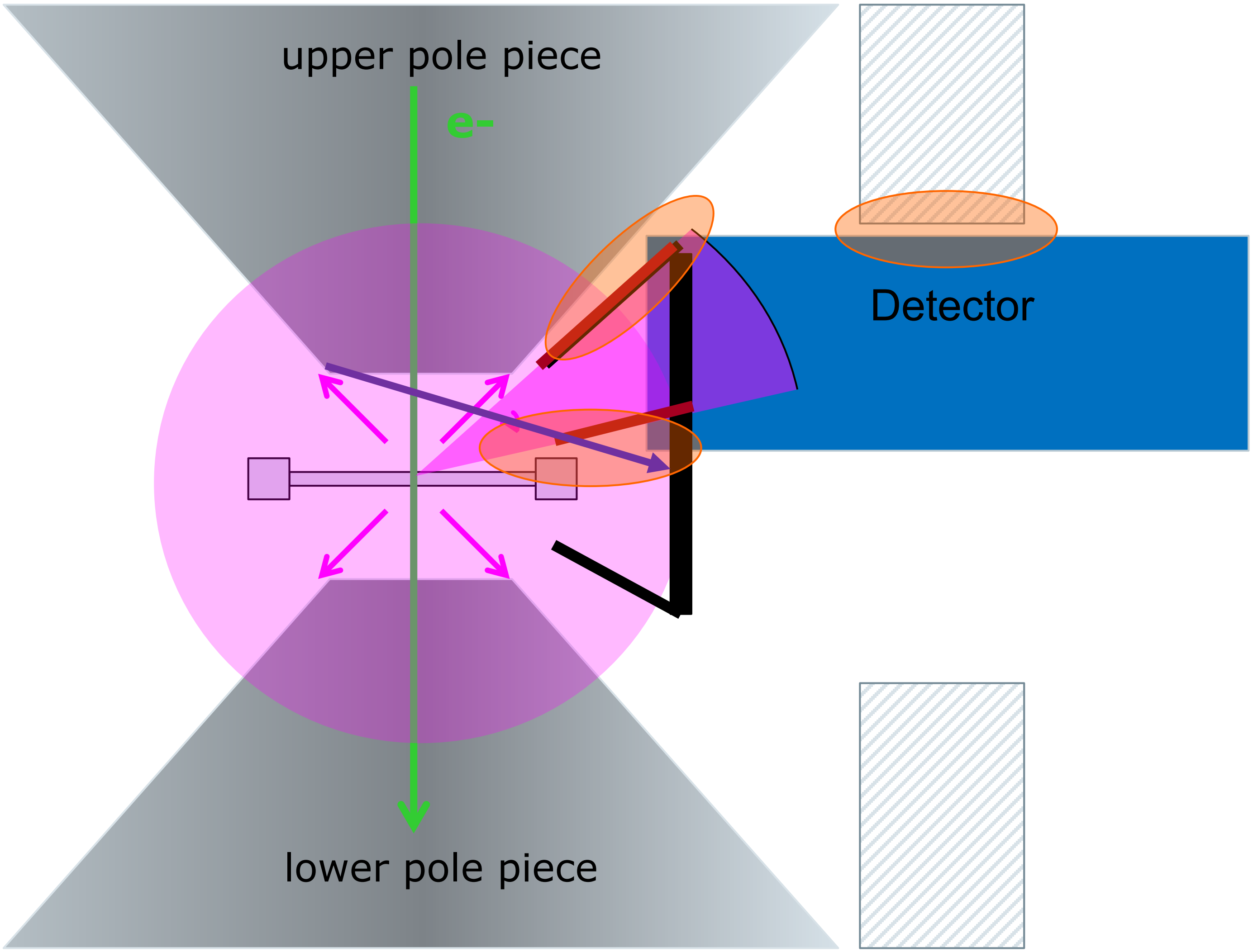
Geometric Limitations



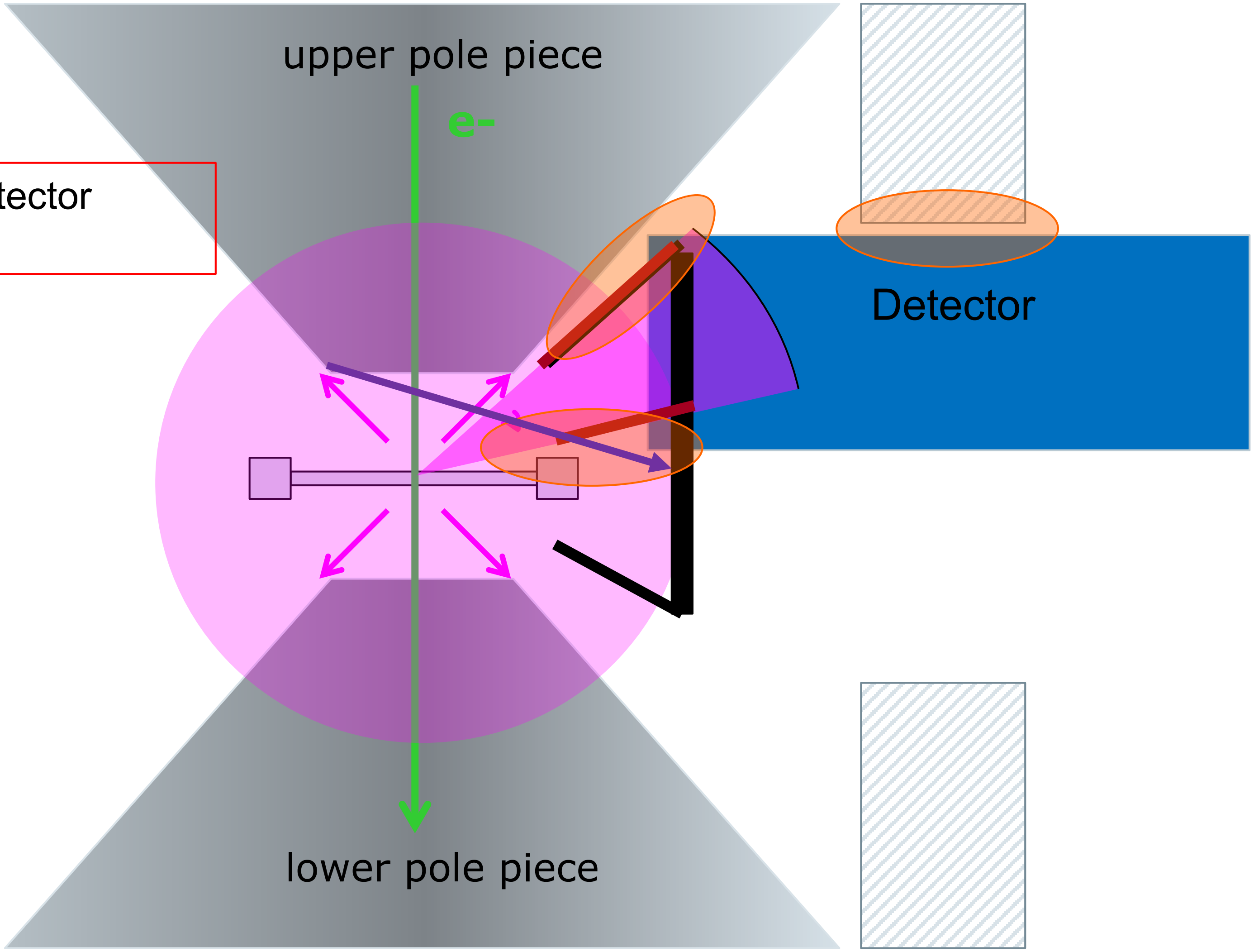
Geometric Limitations



Geometric Limitations

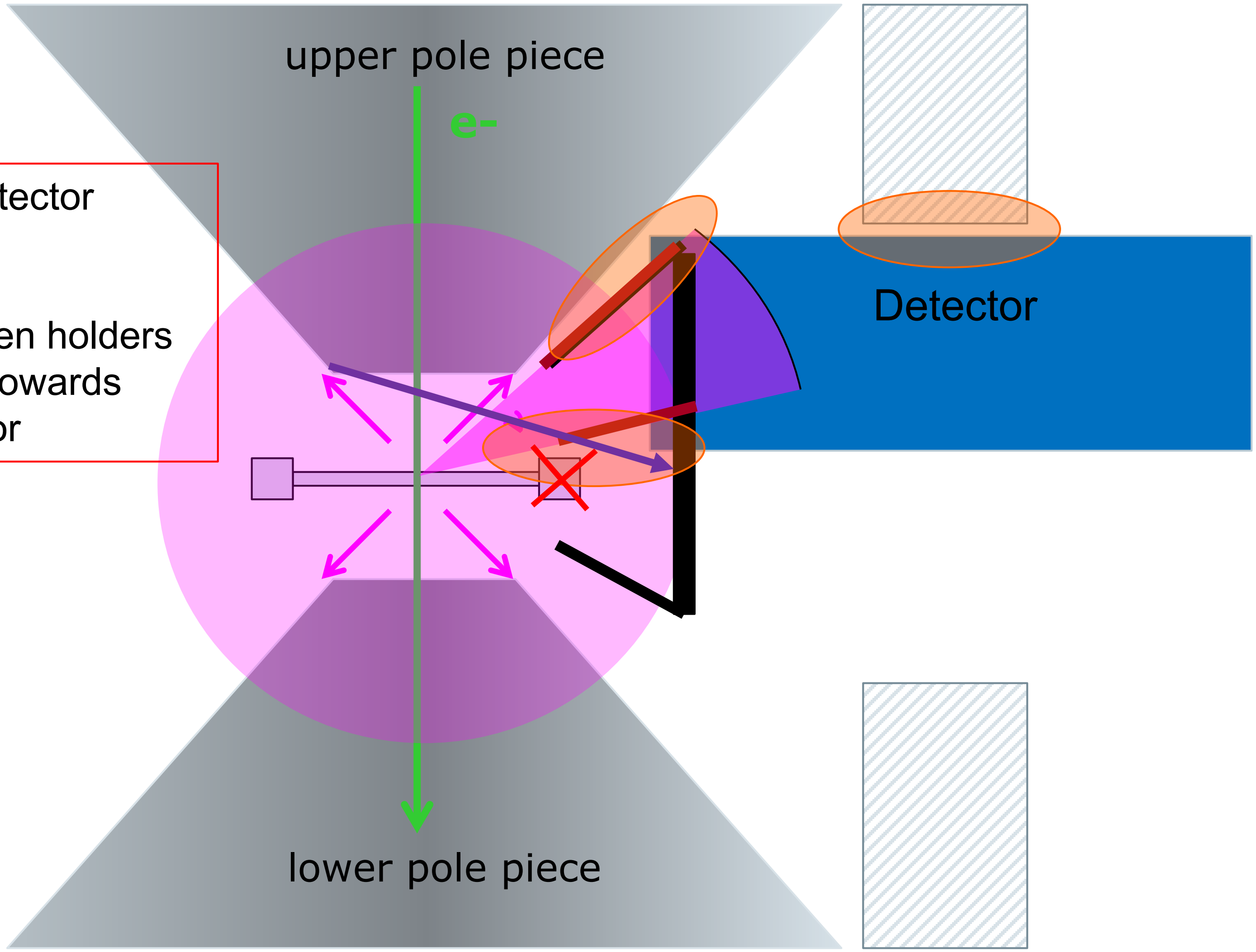


Geometric Limitations



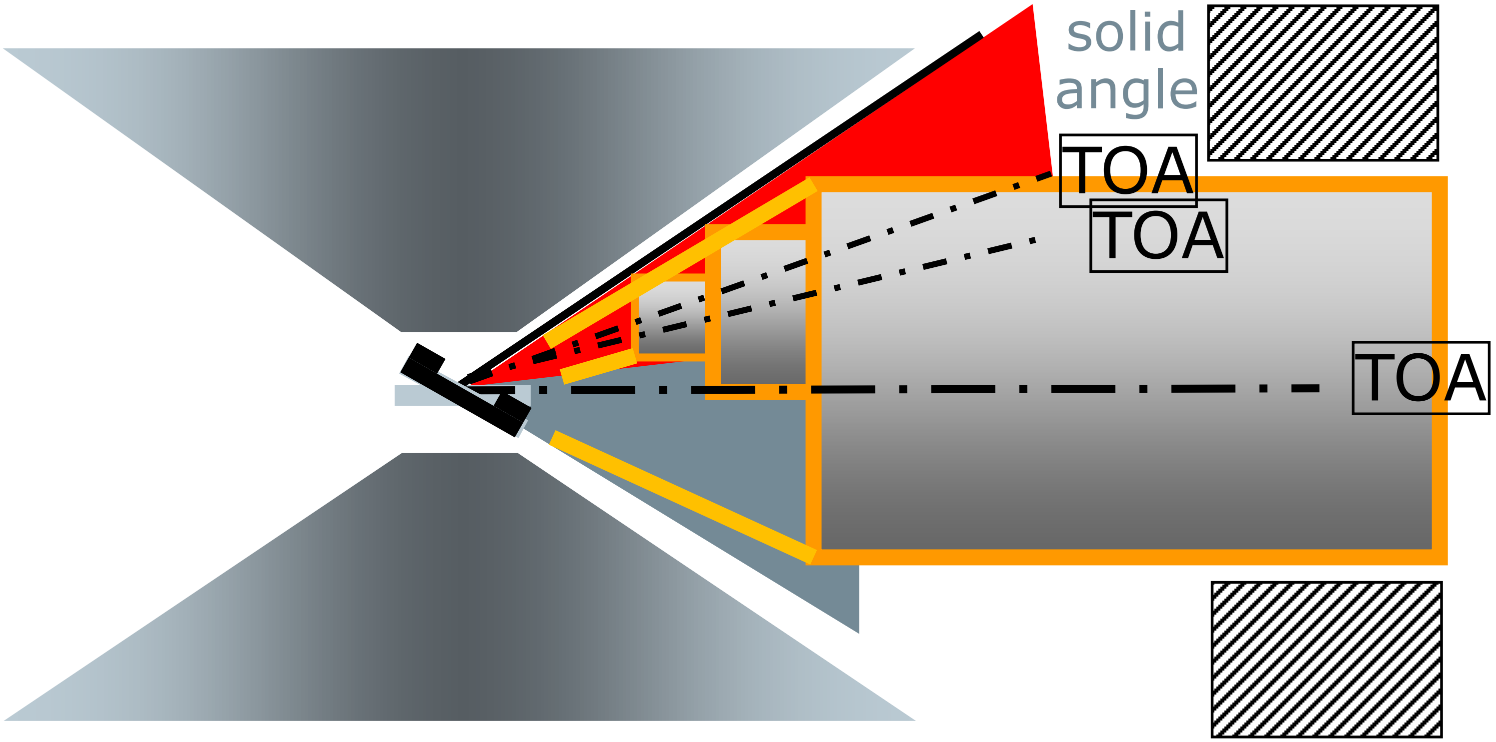
- Optimize detector position

Geometric Limitations

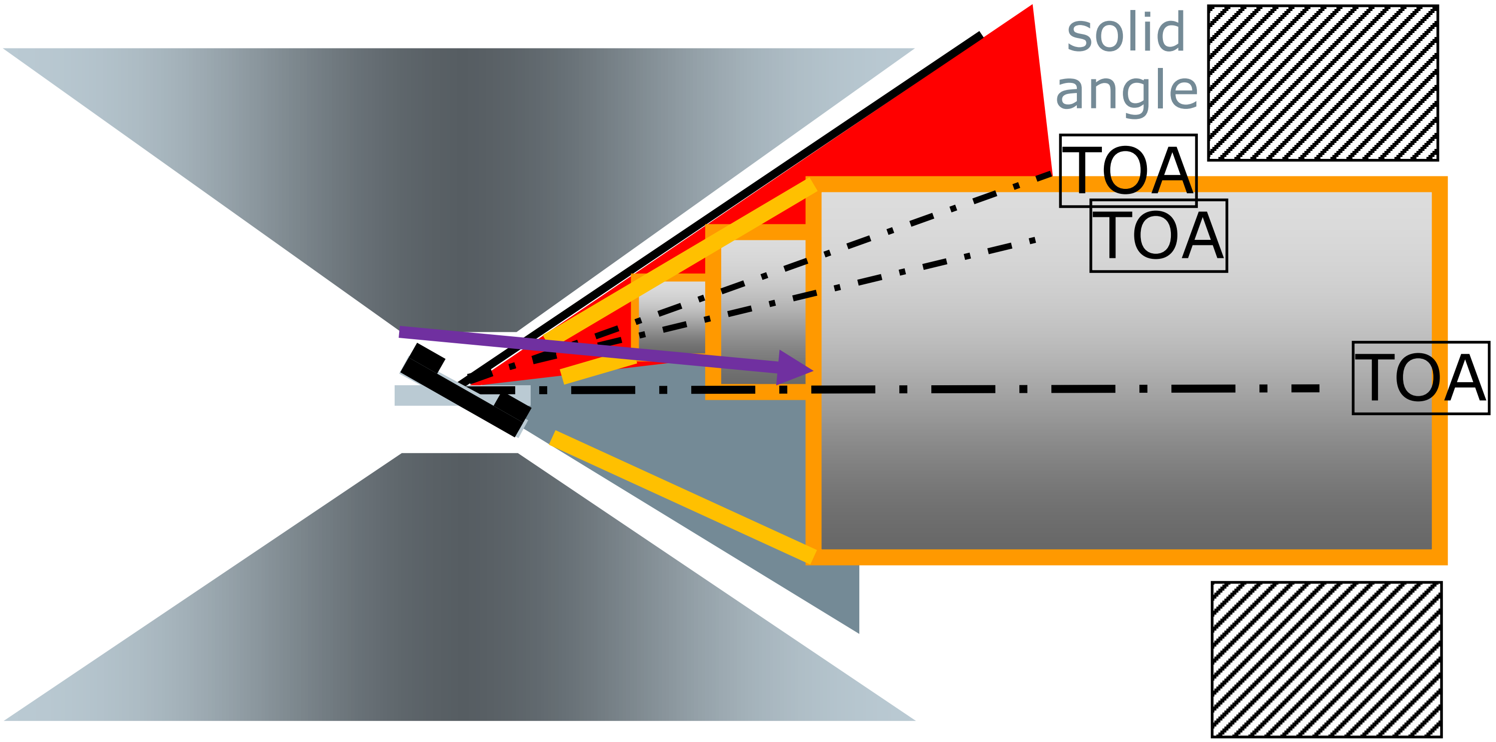


- Optimize detector position
- Use specimen holders with cutout towards EDS detector

Geometric Limitations (TEM): Solid and take-off angle!!

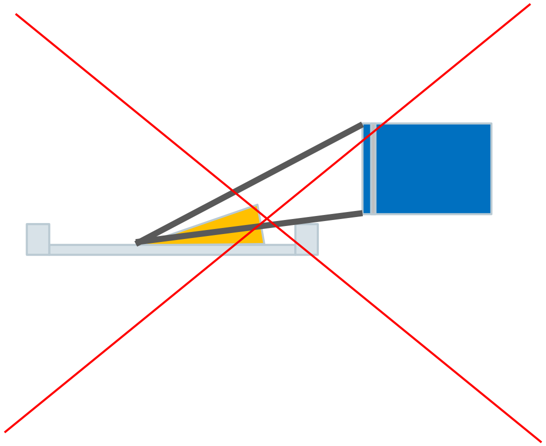


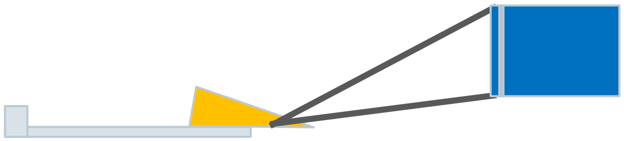
Geometric Limitations (TEM)



Inverse solid angle! … how much of the surroundings do we see?
A small collimator opening is better to avoid system peaks.

Specimen Mounting





- Thinnest part of specimen must point towards EDS detector
- The specimen holder must have a cut out towards EDS detector
- Make sure that the path for X-rays is not obstructed by sample or grid parts or holder
- Beware: most holders are turned 180° during insertion

Specimen Mounting;
View along column

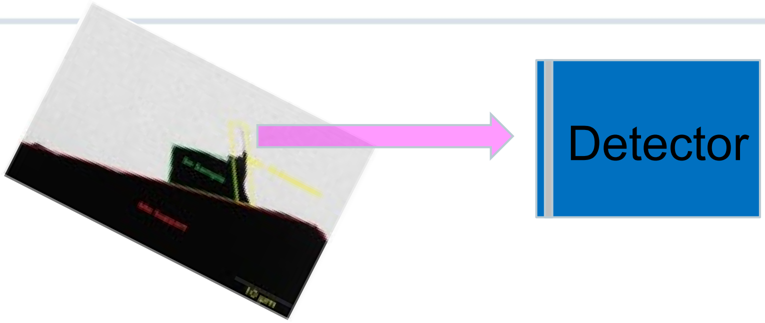
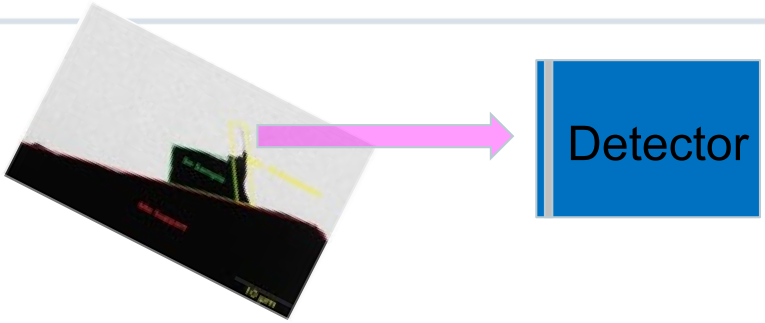
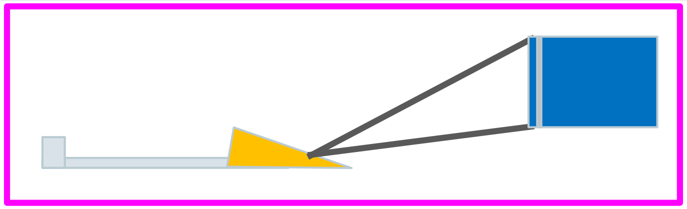
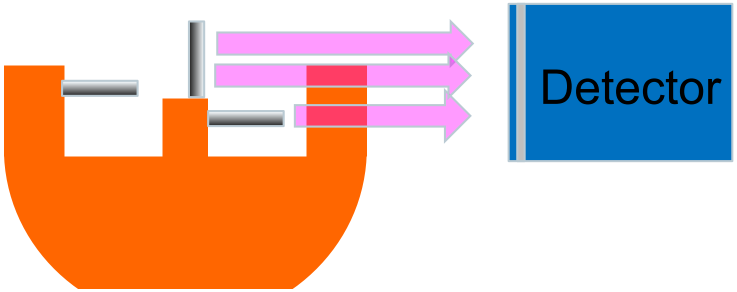


Image source: www

Specimen Mounting;
View along column







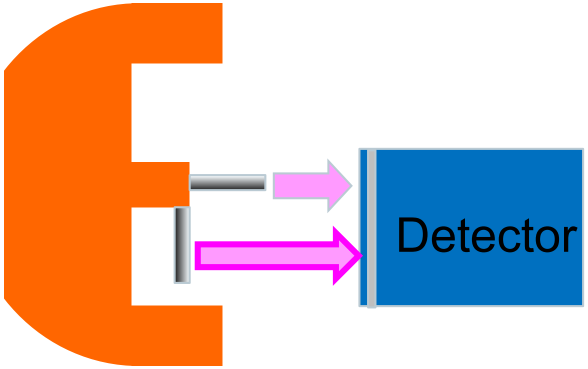


Image source: www

- Thinnest part of specimen must point towards EDS detector
- Make sure that the path for X-rays is not obstructed
- Consider tilt effects

TEM EDS Quantification; R. Egerton

1994, line intensity for a particular element line / transition

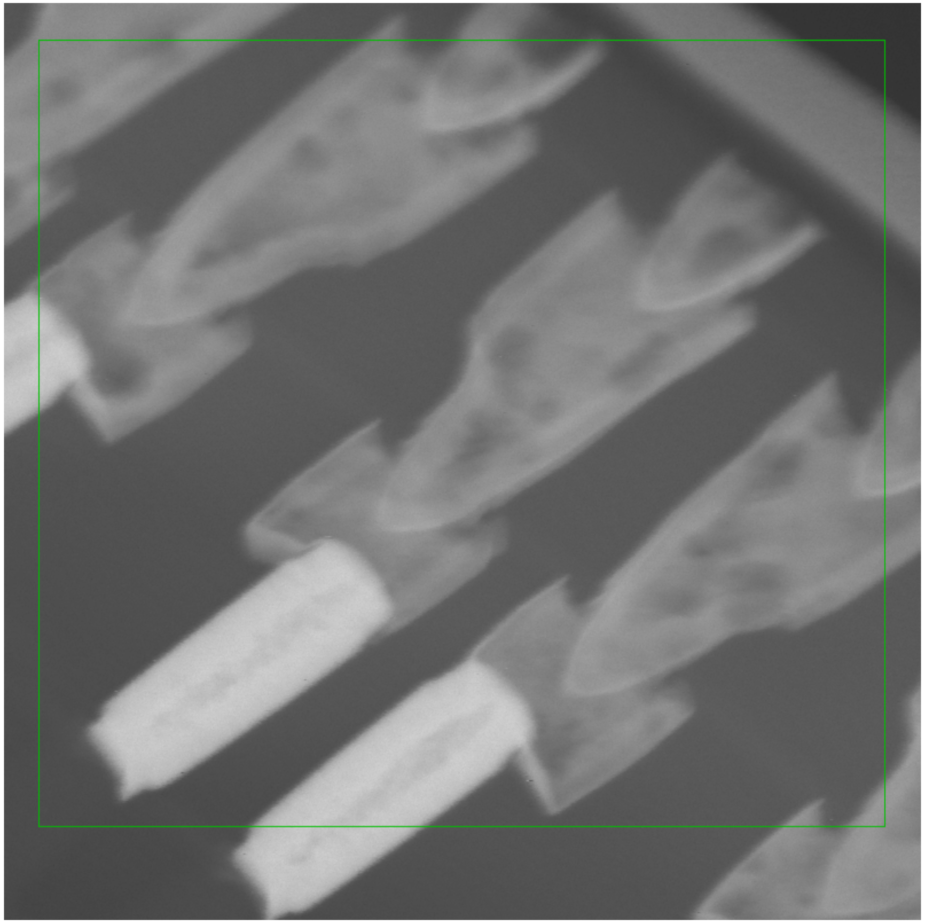
$$I_x = N_A\, \sigma_A\, \omega_A\, (\Omega/4\pi)\, \varepsilon\, N_e = n_A\, t\, \sigma_A\, \omega_A\, (\Omega/4\pi)\, \varepsilon\, N_e$$

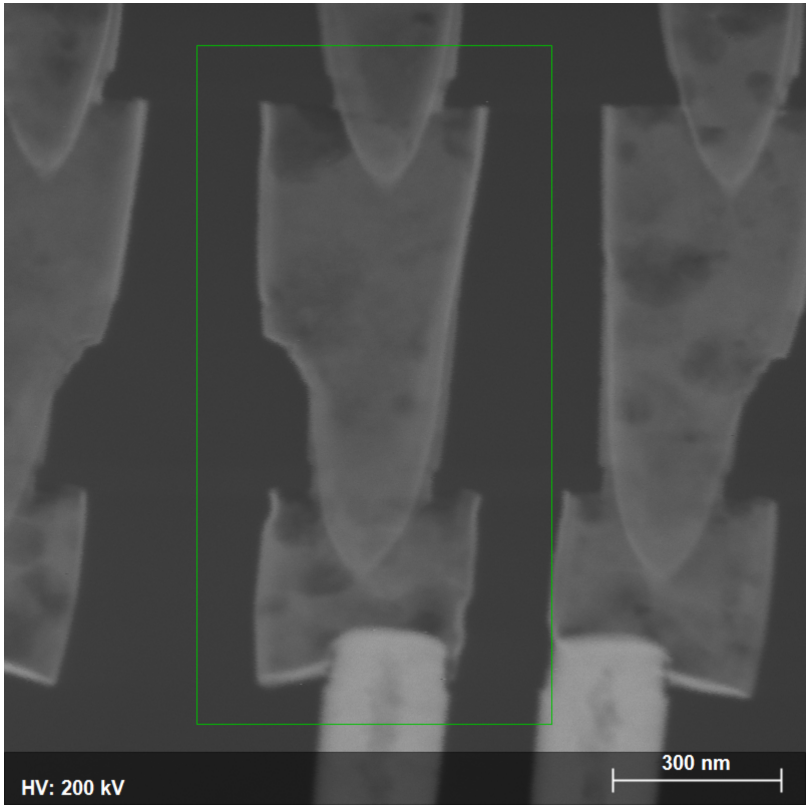
Cliff and Lorimer: $\frac{I_A}{I_B} = \frac{C_A}{k_{AB}\, C_B}$; k_{AB} can be determined experimentally **or theoretically**

I_x	number of X-ray photons in a characteristic peak of species A
N	number of atoms per unit volume
$n\ t$	number of atoms per unit area times thickness
σ	ionization cross section (Casnati et al., 1982, Bote et al., 2009)
ω	fluorescence yield (Hubbell et al., 1994, Krause, 1979)
$\Omega/4\pi$	solid angle / geometrical collection efficiency
ε	detection quantum efficiency
N_e	number of incident electrons

+ absorption

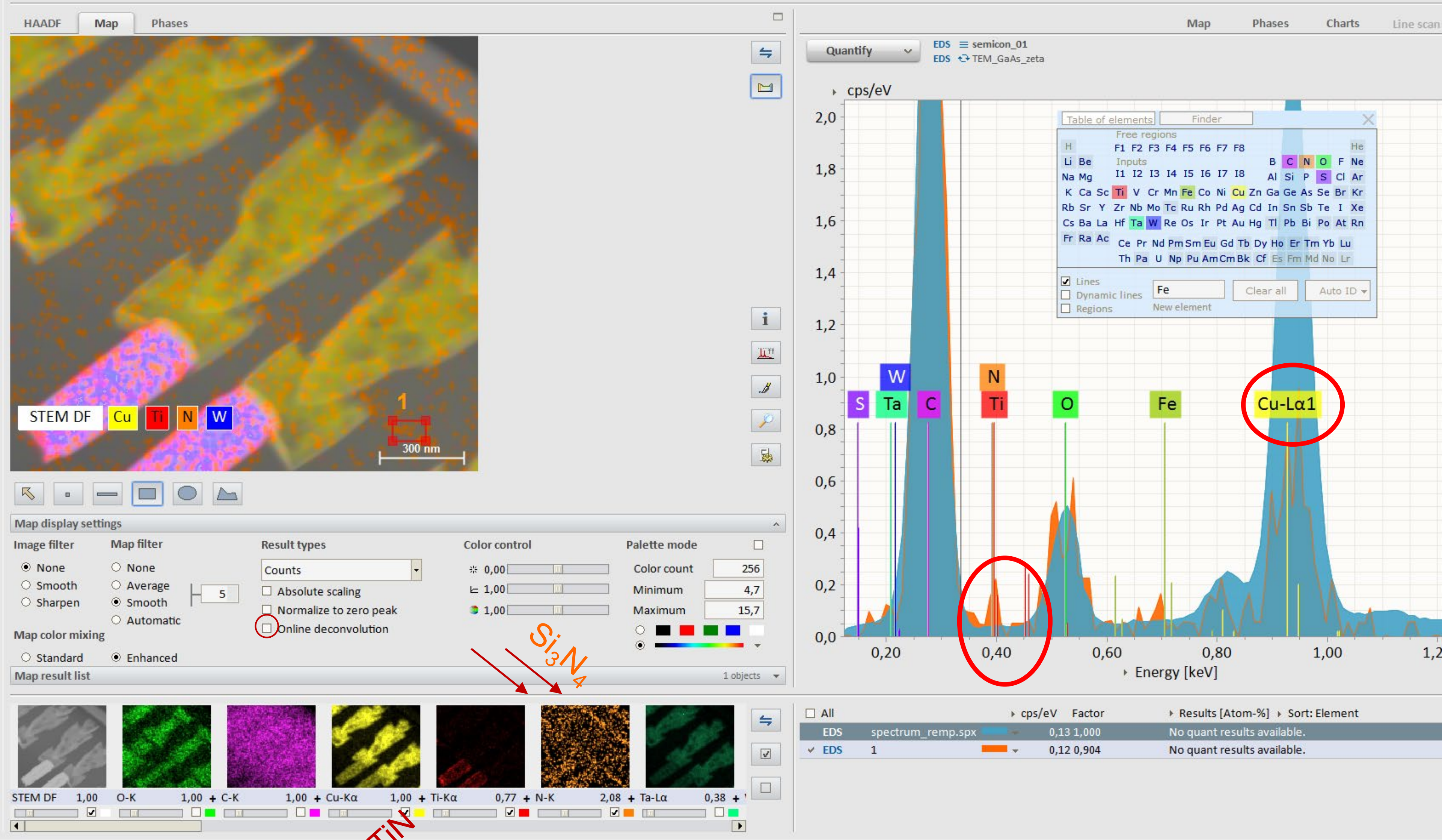
Semiconductor Structure;
Standard STEM, 30mm2 SDD, ~ 0.1sr





Semiconductor Structure; First View

Standard STEM, 30mm2 SDD, ~ 0.1sr



Lines ☑ Dynamic lines ☐ Regions ☐ Fe

Map display settings

Image filter: ● None ○ Smooth ○ Sharpen

Map filter: ○ None ○ Average ● Smooth ○ Automatic 5

Result types: Counts
☐ Absolute scaling
☐ Normalize to zero peak
☐ Online deconvolution

Color control: 0,00 1,00 1,00

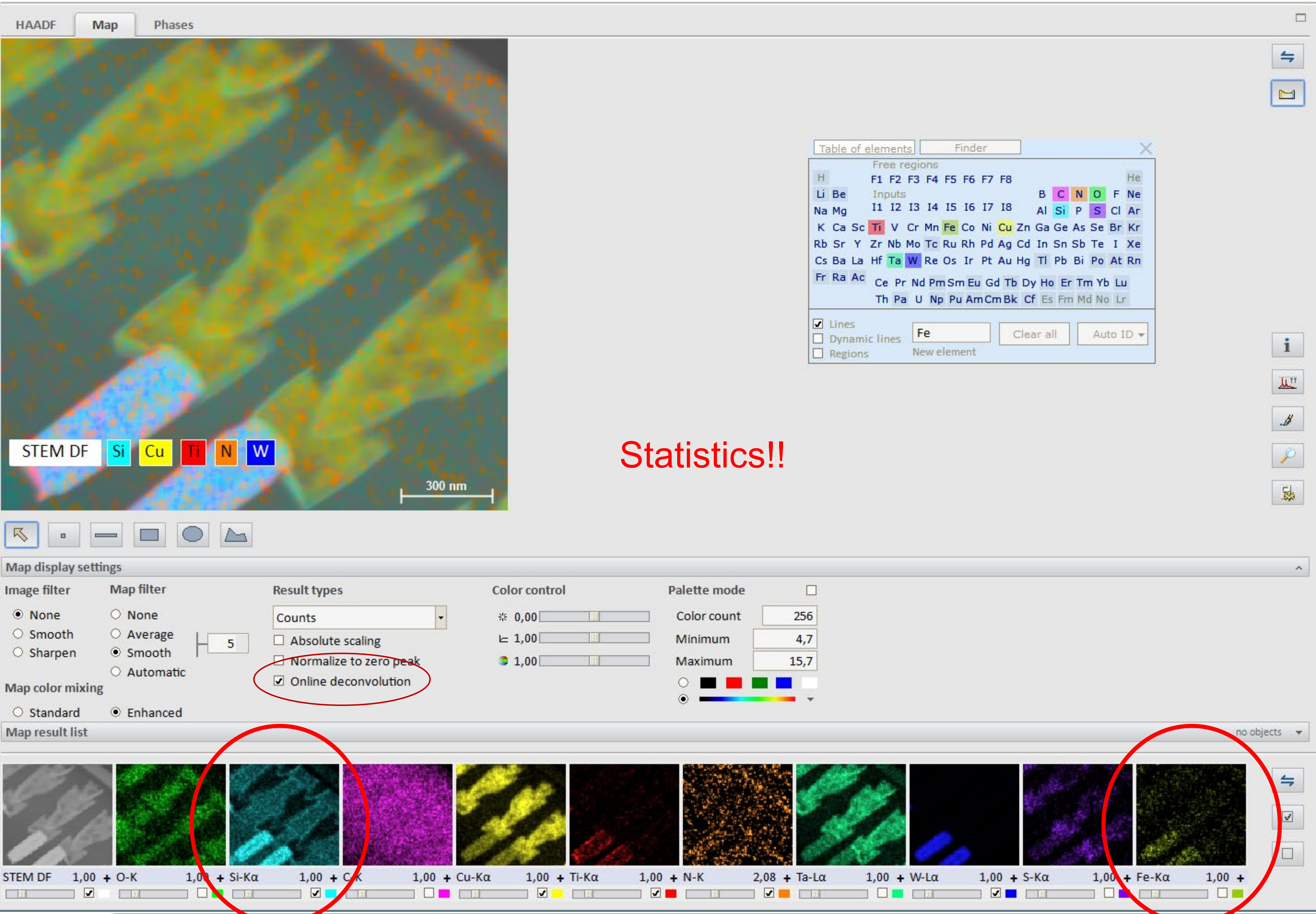
Palette mode ☐
Color count 256
Minimum 4,7
Maximum 15,7

Map color mixing: ○ Standard ● Enhanced

Map result list — 1 objects

STEM DF	O-K	C-K	Cu-Kα	Ti-Kα	N-K	Ta-Lα
1,00	1,00	1,00	1,00	0,77	2,08	0,38
☑	☐	☐	☑	☑	☑	☐

☐ All	cps/eV	Factor	Results [Atom-%] Sort: Element
EDS spectrum_remp.spx	0,13	1,000	No quant results available.
✓ EDS 1	0,12	0,904	No quant results available.



Statistics!!

☑ Lines
☐ Dynamic lines
☐ Regions
Fe

Image filter
● None
○ Smooth
○ Sharpen

Map filter
○ None
○ Average
● Smooth
○ Automatic
5

Map color mixing
○ Standard
● Enhanced

Result types
Counts
☐ Absolute scaling
☐ Normalize to zero peak
☑ Online deconvolution

Color control
0,00
1,00
1,00

Palette mode ☐
Color count 256
Minimum 4,7
Maximum 15,7

Map	Factor	Shown
STEM DF	1,00	☑
O-K	1,00	☐
Si-Kα	1,00	☑
C-K	1,00	☐
Cu-Kα	1,00	☑
Ti-Kα	1,00	☑
N-K	2,08	☑
Ta-Lα	1,00	☐
W-Lα	1,00	☑
S-Kα	1,00	☐
Fe-Kα	1,00	☐

Semiconductor Structure; First View: Specimen region of interest for quant.

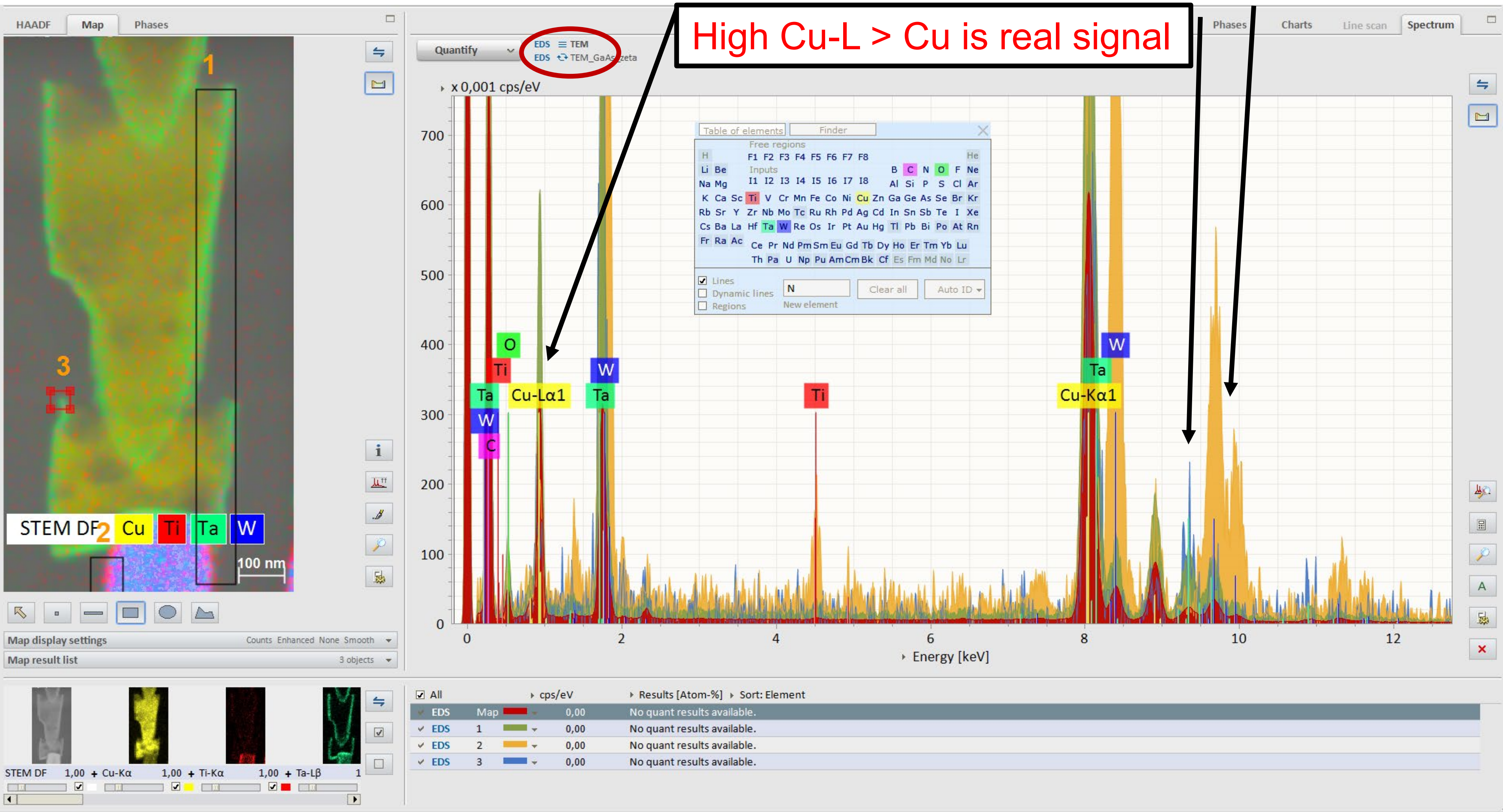
Check composition / condition variations

☑ All ‣ cps/eV ‣ Results [Atom-%] ‣ Sort: Element

EDS	Map	🟥	0,00	No quant results available.
EDS	1	🟩	0,00	No quant results available.
EDS	2	🟧	0,00	No quant results available.
EDS	3	🟦	0,00	No quant results available.

Semiconductor Structure; First View: Specimen region of interest;

Check composition / condition variations

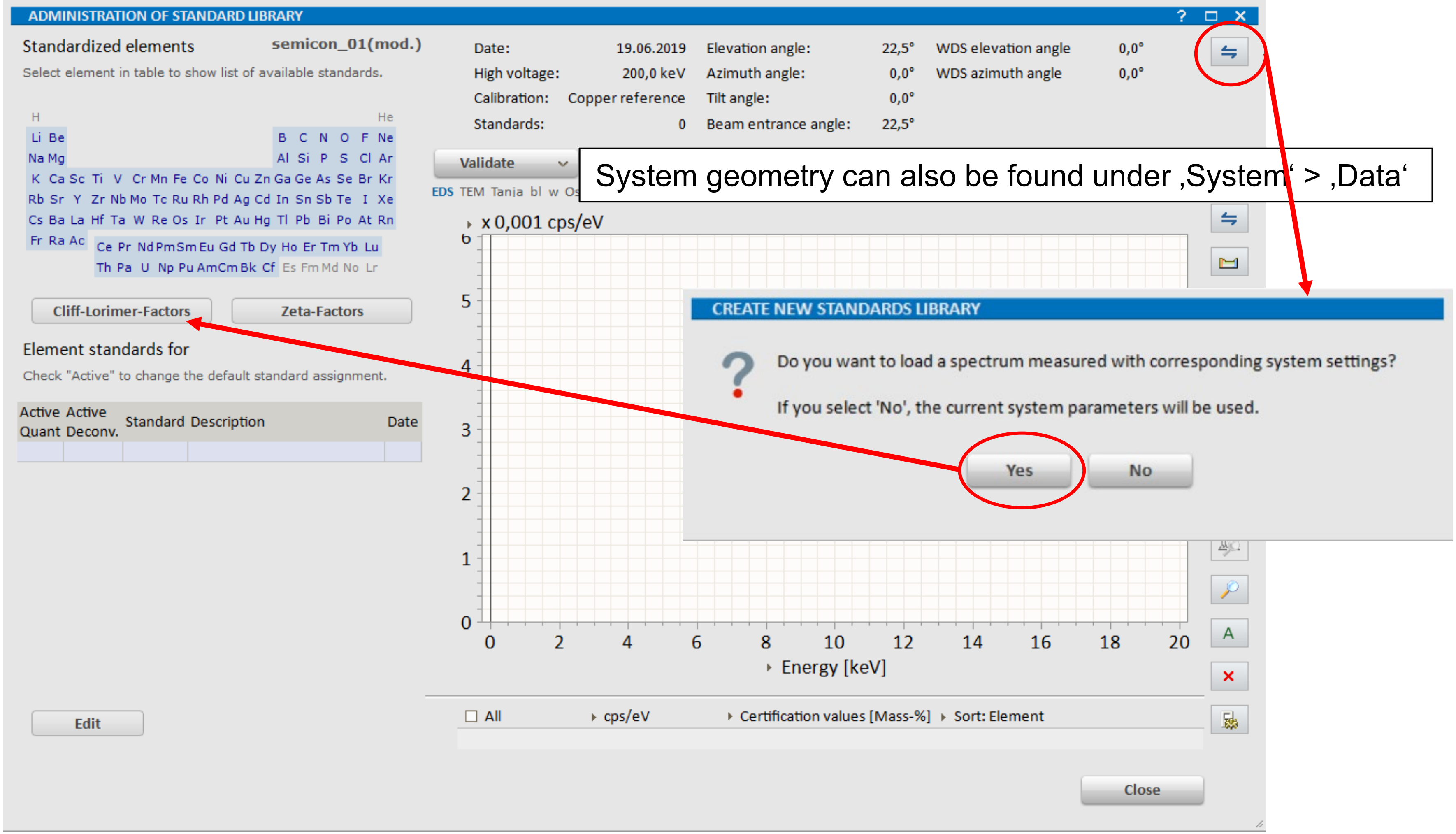


High Cu-L > Cu is real signal

☑ All			cps/eV	Results [Atom-%] Sort: Element
EDS	Map	🟥	0,00	No quant results available.
EDS	1	🟩	0,00	No quant results available.
EDS	2	🟧	0,00	No quant results available.
EDS	3	🟦	0,00	No quant results available.

For Cliff-Lorimer quantification: calculate theoretical Cliff-Lorimer factors for the specific geometry and conditions

‚Standards' menu:



ADMINISTRATION OF STANDARD LIBRARY

Standardized elements semicon_01(mod.)

Select element in table to show list of available standards.

Date: 19.06.2019
High voltage: 200,0 keV
Calibration: Copper reference
Standards: 0
Elevation angle: 22,5°
Azimuth angle: 0,0°
Tilt angle: 0,0°
Beam entrance angle: 22,5°
WDS elevation angle 0,0°
WDS azimuth angle 0,0°

Element standards for

Check "Active" to change the default standard assignment.

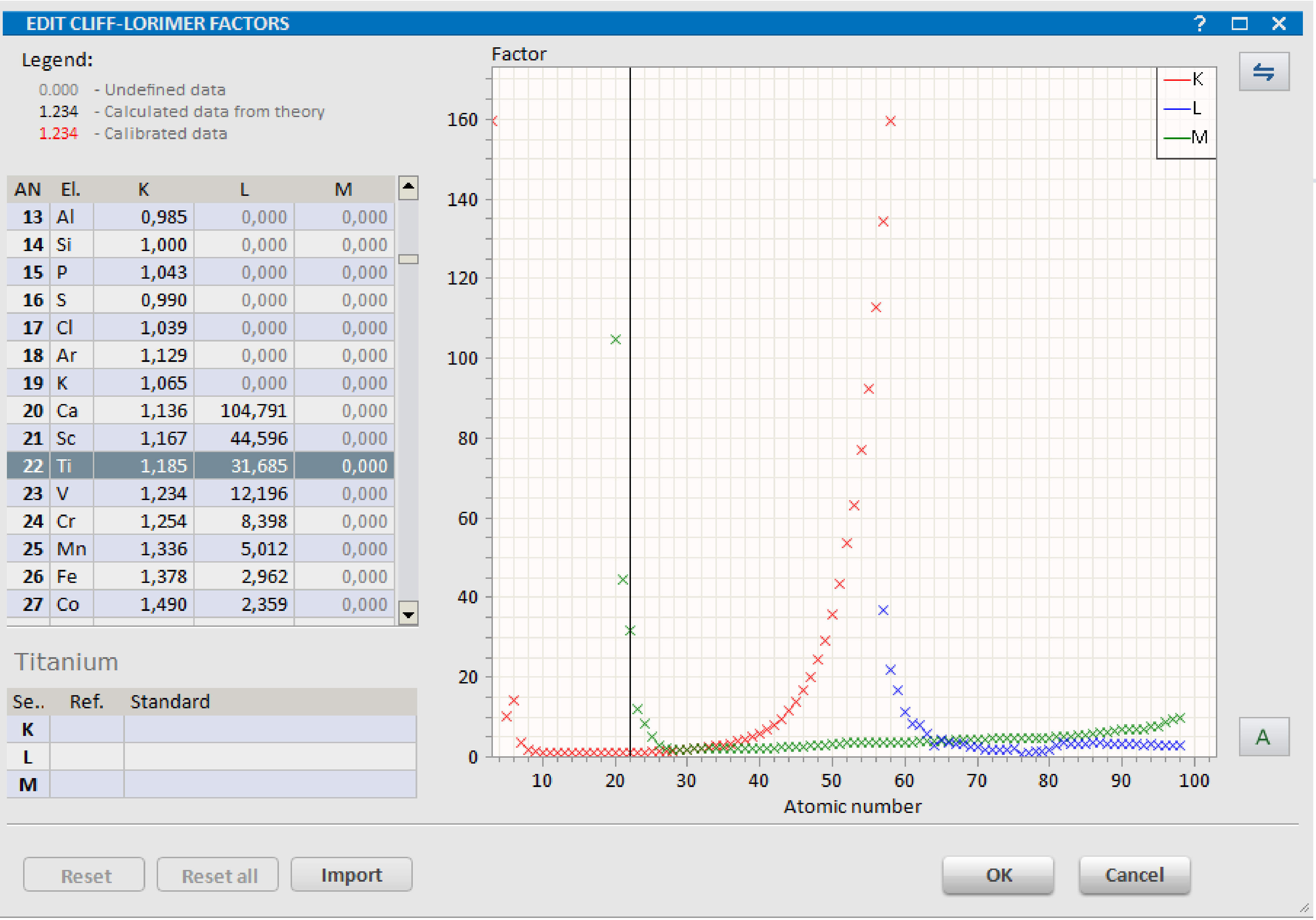
Active Quant	Active Deconv.	Standard	Description	Date

CREATE NEW STANDARDS LIBRARY

Do you want to load a spectrum measured with corresponding system settings?

If you select 'No', the current system parameters will be used.

System geometry can also be found under ‚System' > ‚Data'



Legend:

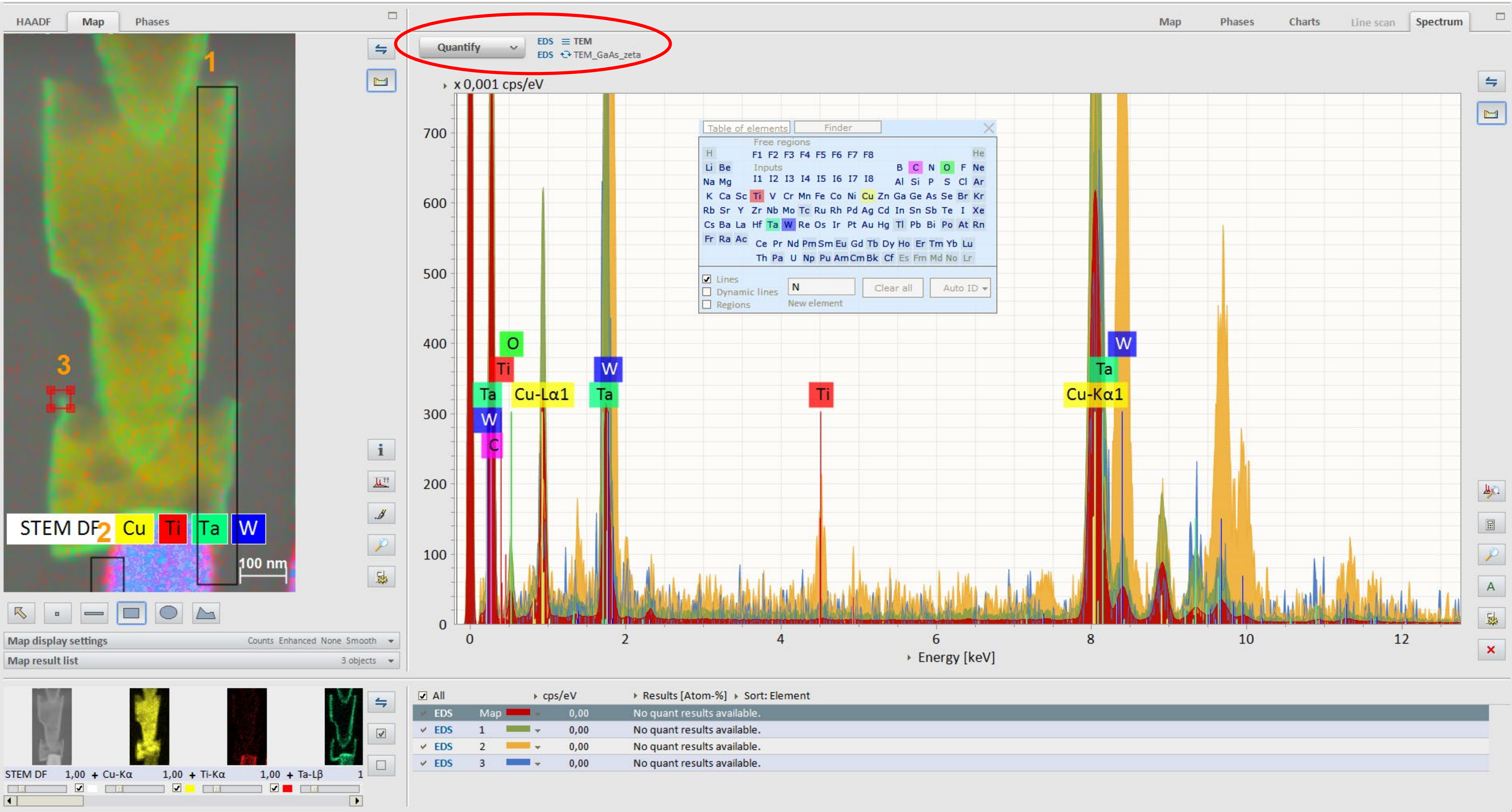
0.000	- Undefined data
1.234	- Calculated data from theory
1.234	- Calibrated data

AN	El.	K	L	M
13	Al	0,985	0,000	0,000
14	Si	1,000	0,000	0,000
15	P	1,043	0,000	0,000
16	S	0,990	0,000	0,000
17	Cl	1,039	0,000	0,000
18	Ar	1,129	0,000	0,000
19	K	1,065	0,000	0,000
20	Ca	1,136	104,791	0,000
21	Sc	1,167	44,596	0,000
22	Ti	1,185	31,685	0,000
23	V	1,234	12,196	0,000
24	Cr	1,254	8,398	0,000
25	Mn	1,336	5,012	0,000
26	Fe	1,378	2,962	0,000
27	Co	1,490	2,359	0,000

Titanium

Se..	Ref.	Standard
K		
L		
M		

Semiconductor Structure; First View

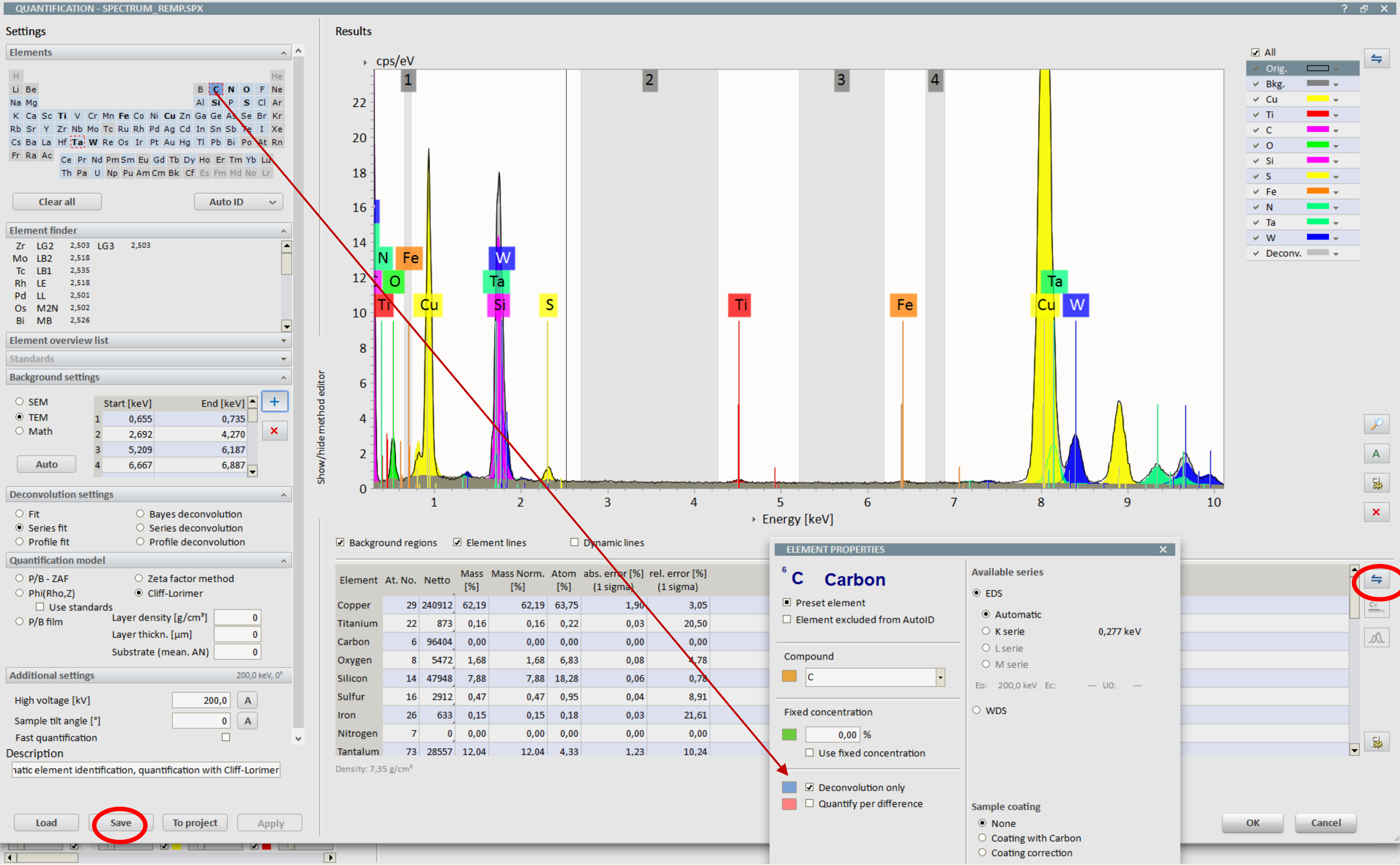


Quantify
EDS ≡ TEM
EDS TEM_GaAs_zeta

☑ All | cps/eV | Results [Atom-%] | Sort: Element

EDS	Map	0,00	No quant results available.
EDS	1	0,00	No quant results available.
EDS	2	0,00	No quant results available.
EDS	3	0,00	No quant results available.

Quantification setup



Element finder

Zr	LG2	2,503	LG3	2,503
Mo	LB2	2,518		
Tc	LB1	2,535		
Rh	LE	2,518		
Pd	LL	2,501		
Os	M2N	2,502		
Bi	MB	2,526		

Background settings

○ SEM
● TEM
○ Math

	Start [keV]	End [keV]
1	0,655	0,735
2	2,692	4,270
3	5,209	6,187
4	6,667	6,887

Auto

Deconvolution settings

○ Fit
● Series fit
○ Profile fit
○ Bayes deconvolution
○ Series deconvolution
○ Profile deconvolution

Quantification model

○ P/B - ZAF
○ Phi(Rho,Z)
☐ Use standards
○ P/B film
○ Zeta factor method
● Cliff-Lorimer

Layer density [g/cm³]: 0
Layer thickn. [µm]: 0
Substrate (mean. AN): 0

Additional settings 200,0 keV, 0°

High voltage [kV]: 200,0
Sample tilt angle [°]: 0
Fast quantification ☐

Description
natic element identification, quantification with Cliff-Lorimer

☑ Background regions ☑ Element lines ☐ Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Copper	29	240912	62,19	62,19	63,75	1,90	3,05
Titanium	22	873	0,16	0,16	0,22	0,03	20,50
Carbon	6	96404	0,00	0,00	0,00	0,00	0,00
Oxygen	8	5472	1,68	1,68	6,83	0,08	4,78
Silicon	14	47948	7,88	7,88	18,28	0,06	0,78
Sulfur	16	2912	0,47	0,47	0,95	0,04	8,91
Iron	26	633	0,15	0,15	0,18	0,03	21,61
Nitrogen	7	0	0,00	0,00	0,00	0,00	0,00
Tantalum	73	28557	12,04	12,04	4,33	1,23	10,24

Density: 7,35 g/cm³

ELEMENT PROPERTIES

^{6}C Carbon

☒ Preset element
☐ Element excluded from AutoID

Compound: C

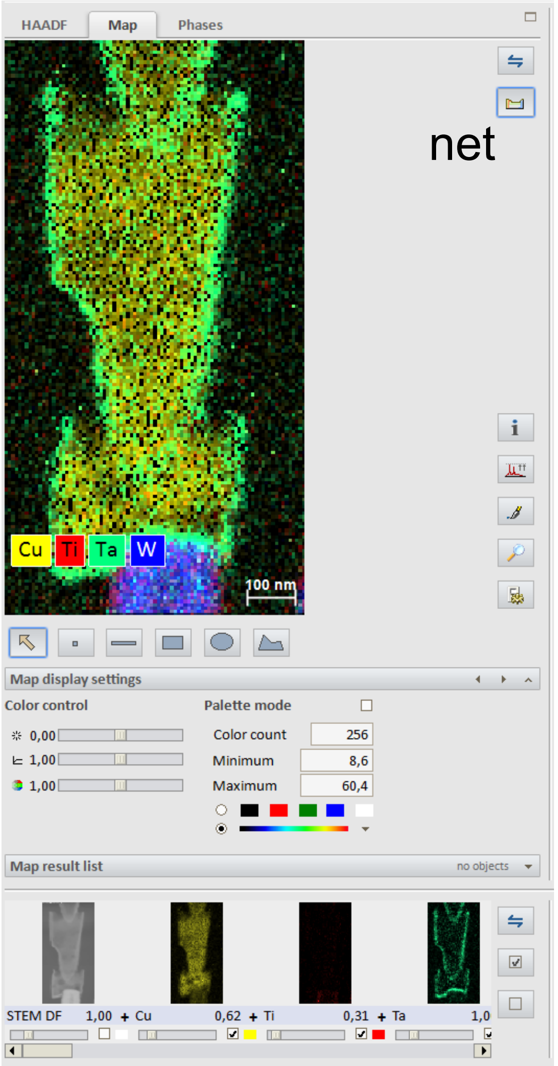
Fixed concentration: 0,00 %
☐ Use fixed concentration

☑ Deconvolution only
☐ Quantify per difference

Available series
● EDS
● Automatic
○ K serie 0,277 keV
○ L serie
○ M serie
Eo: 200,0 keV Ec: --- U0: ---
○ WDS

Sample coating
● None
○ Coating with Carbon
○ Coating correction

Element Mapping Results; theoretical C-L factors



Map display settings

Color control: 0,00 · 1,00 · 1,00

Palette mode ☐

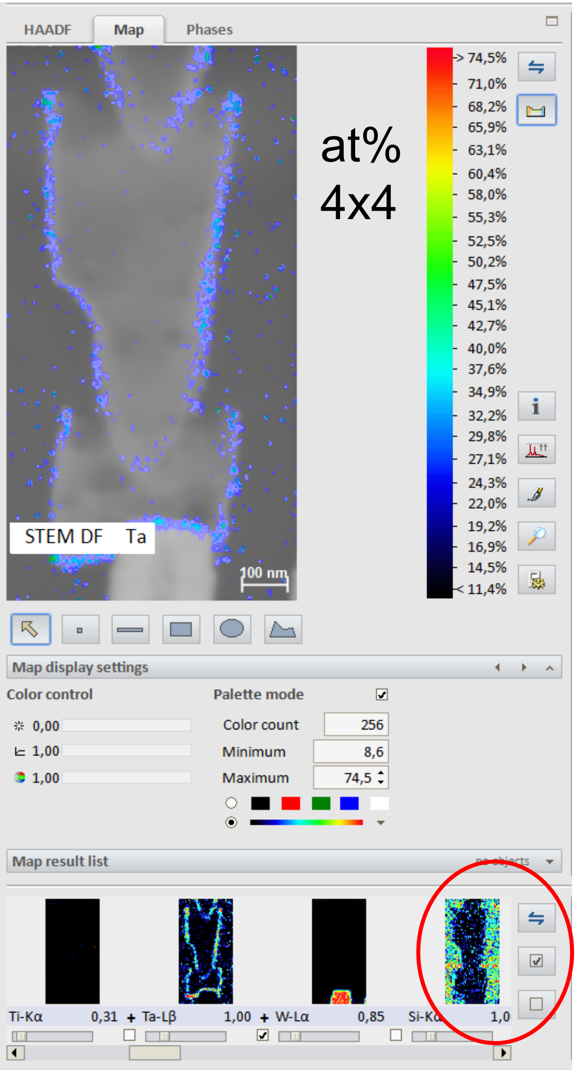
Color count 256

Minimum 8,6

Maximum 60,4

Map result list — no objects

STEM DF 1,00 + Cu 0,62 + Ti 0,31 + Ta 1,0



Map display settings

Color control: 0,00 · 1,00 · 1,00

Palette mode ☑

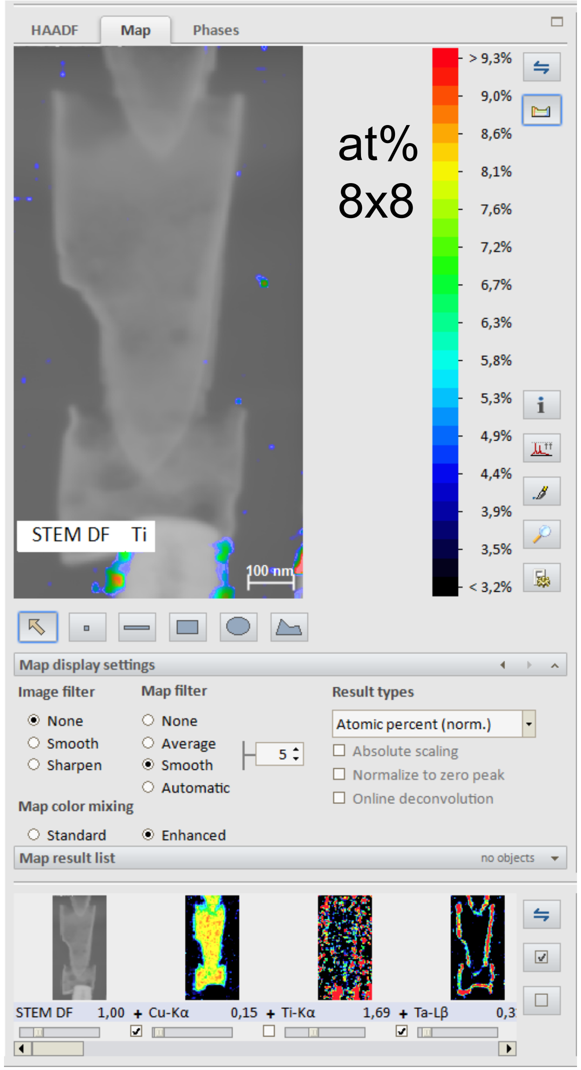
Color count 256

Minimum 8,6

Maximum 74,5

Map result list — no objects

Ti-Kα 0,31 + Ta-Lβ 1,00 + W-Lα 0,85 Si-Kα 1,0



Map display settings

Image filter: ● None ○ Smooth ○ Sharpen

Map filter: ○ None ○ Average ● Smooth ○ Automatic — 5

Result types: Atomic percent (norm.)

☐ Absolute scaling

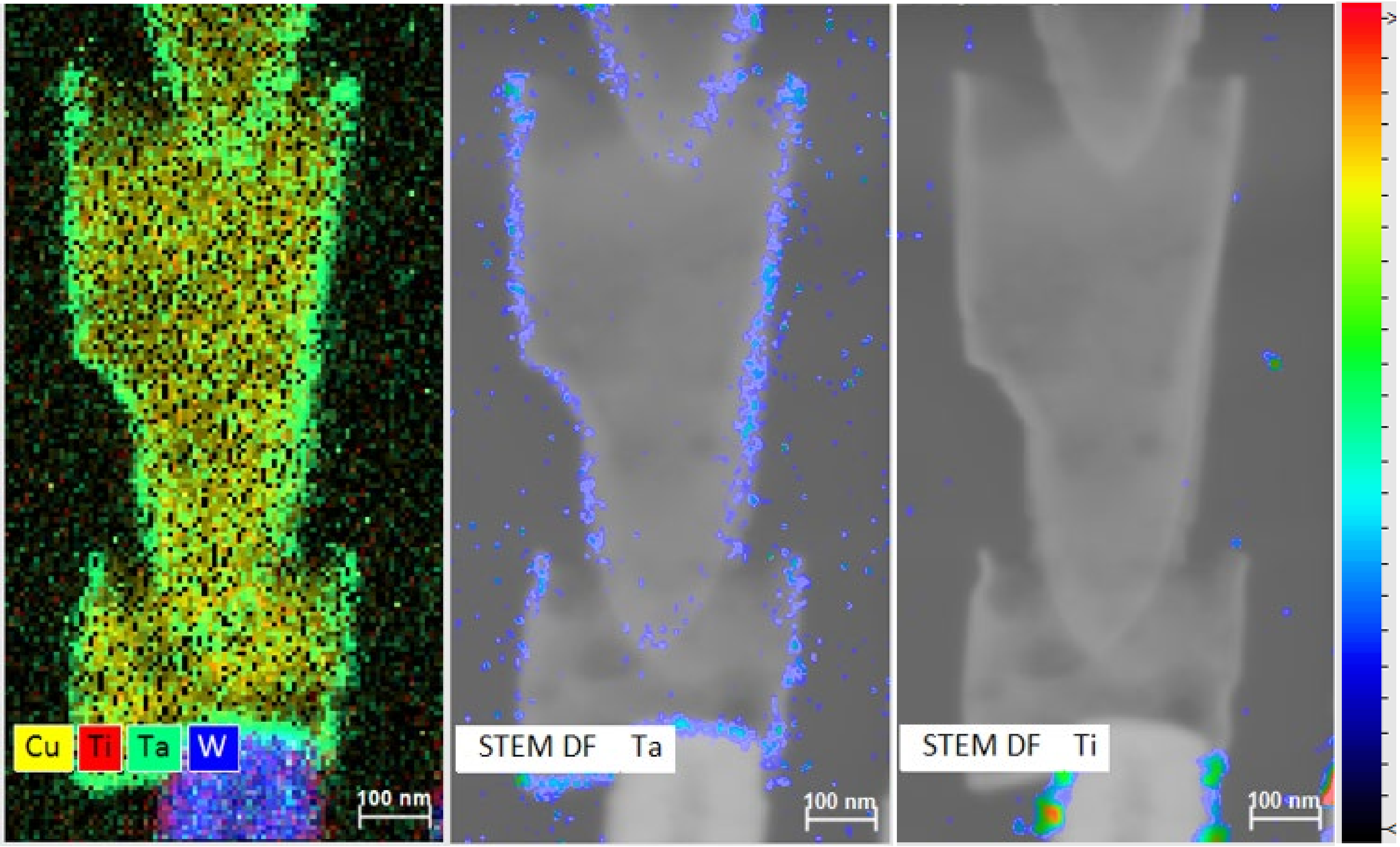
☐ Normalize to zero peak

☐ Online deconvolution

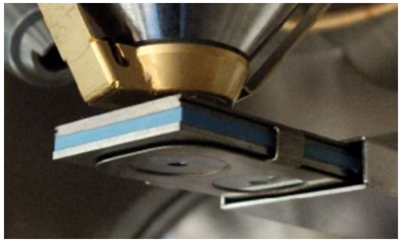
Map color mixing: ○ Standard ● Enhanced

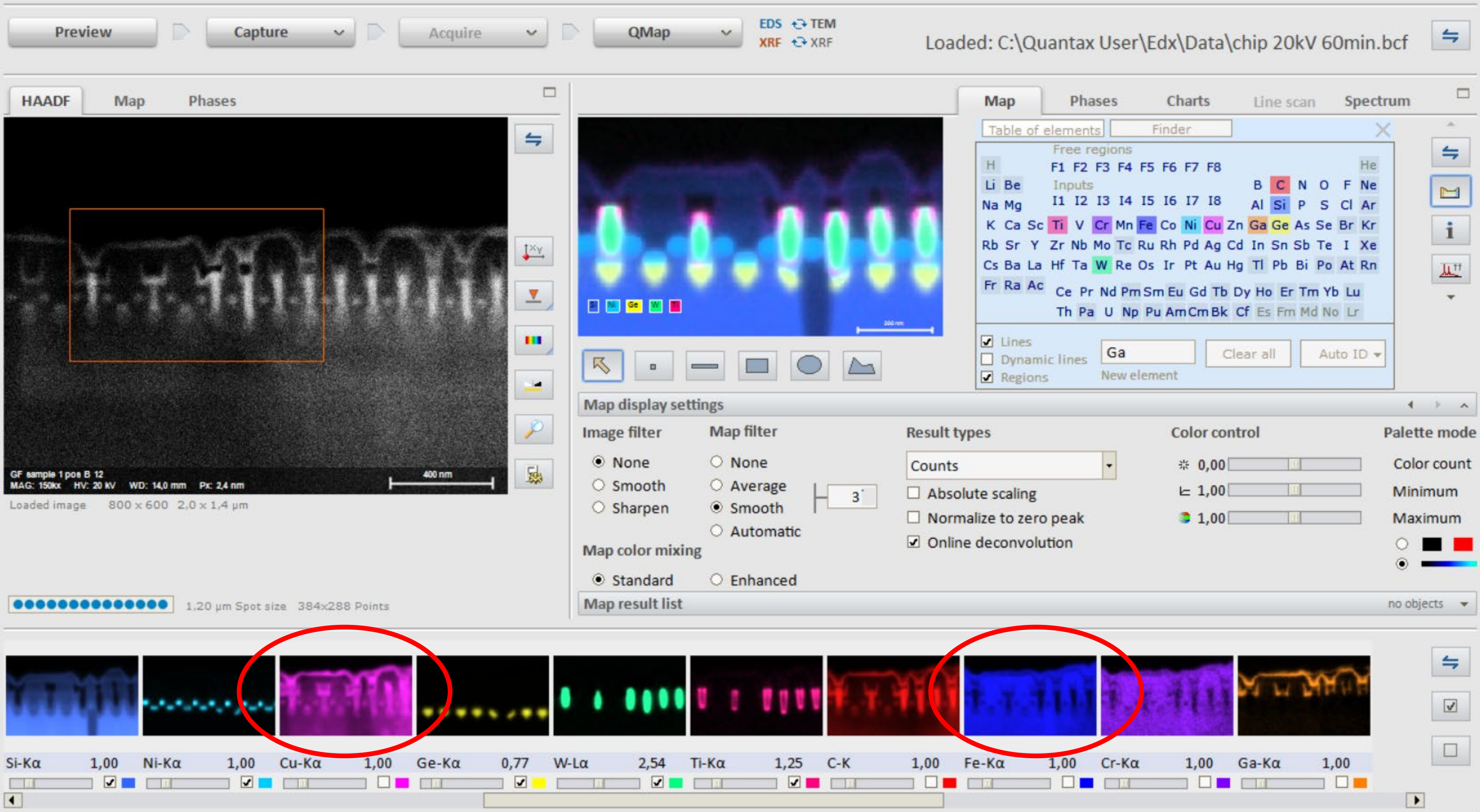
Map result list — no objects

STEM DF 1,00 + Cu-Kα 0,15 + Ti-Kα 1,69 + Ta-Lβ 0,3


Cu
Ti
Ta
W
100 nm
STEM DF Ta
100 nm
STEM DF Ti
100 nm

T-SEM
with radially symmetric EDS;
fluorescence





Loaded: C:\Quantax User\Edx\Data\chip 20kV 60min.bcf

Loaded image 800 x 600 2,0 x 1,4 µm

1,20 µm Spot size 384x288 Points

☑ Lines
☐ Dynamic lines
☑ Regions

New element: Ga

Map display settings

Image filter
● None
○ Smooth
○ Sharpen

Map filter
○ None
○ Average
● Smooth
○ Automatic
3

Map color mixing
● Standard
○ Enhanced

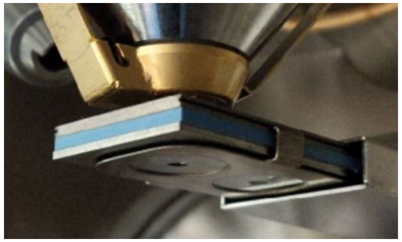
Result types
Counts
☐ Absolute scaling
☐ Normalize to zero peak
☑ Online deconvolution

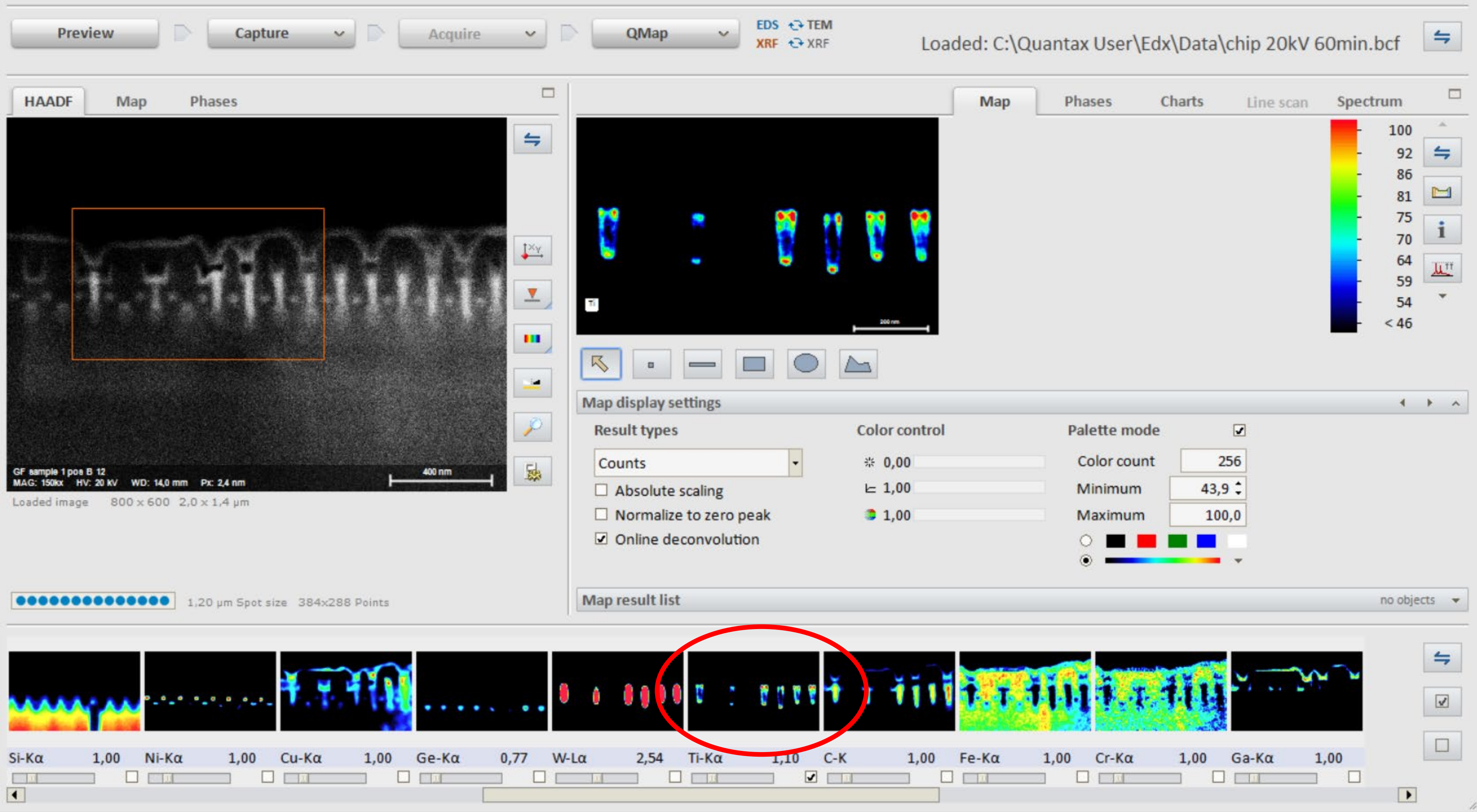
Color control
0,00
1,00
1,00

Palette mode
Color count
Minimum
Maximum

Si-Kα 1,00 ☑	Ni-Kα 1,00 ☑	Cu-Kα 1,00 ☐	Ge-Kα 0,77 ☑	W-Lα 2,54 ☑	Ti-Kα 1,25 ☑	C-K 1,00 ☐	Fe-Kα 1,00 ☐	Cr-Kα 1,00 ☐	Ga-Kα 1,00 ☐

T-SEM
with radially symmetric EDS;
fluorescence, pseudo color





Loaded: C:\Quantax User\Edx\Data\chip 20kV 60min.bcf

GF sample 1 pos B 12
MAG: 150kx HV: 20 kV WD: 14,0 mm Px: 2,4 nm

Loaded image 800 x 600 2,0 x 1,4 µm

1,20 µm Spot size 384x288 Points

Result types

Counts

☐ Absolute scaling
☐ Normalize to zero peak
☑ Online deconvolution

Color control

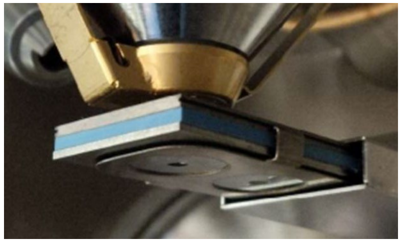
0,00
1,00
1,00

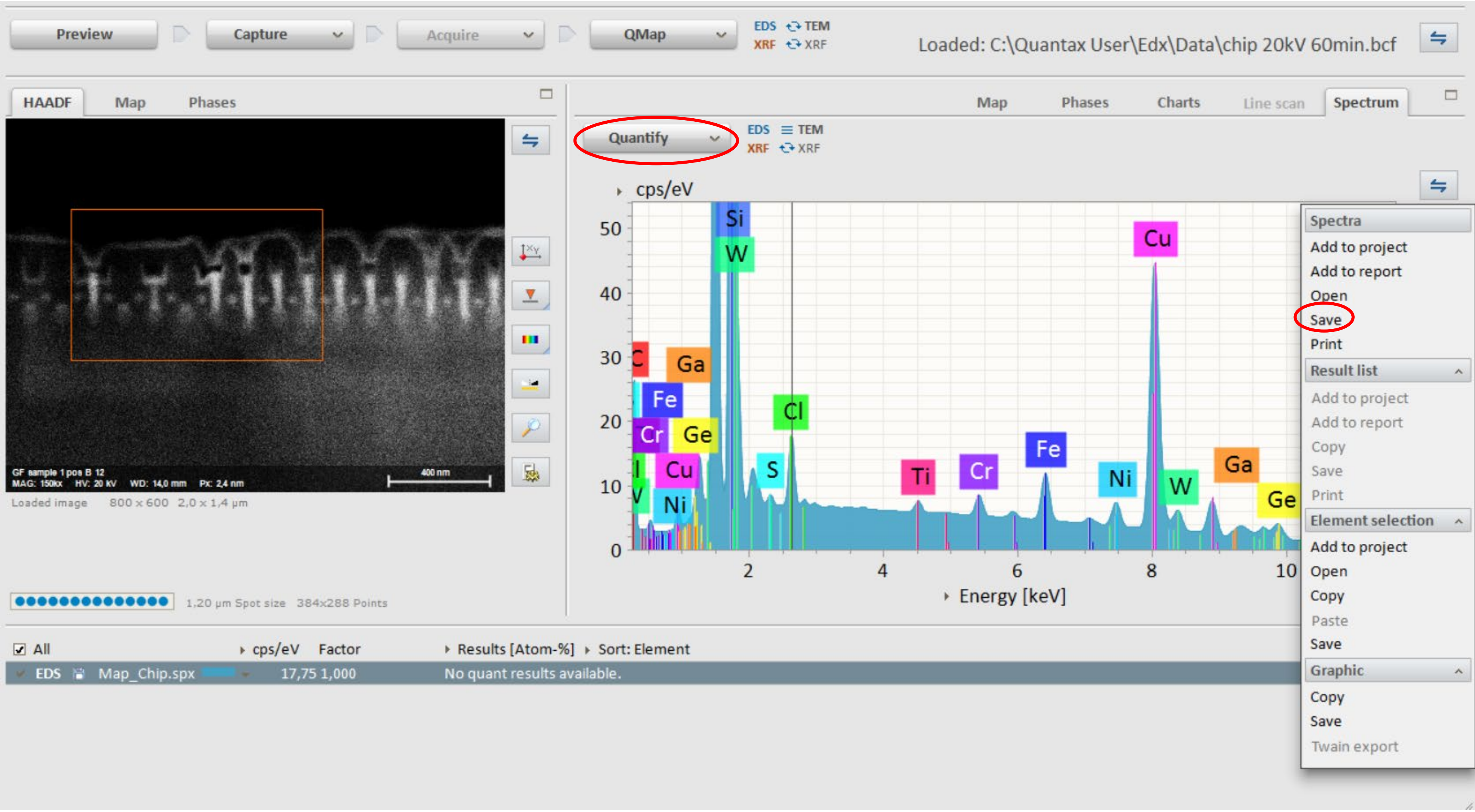
Palette mode ☑

Color count 256
Minimum 43,9
Maximum 100,0

Si-Kα	Ni-Kα	Cu-Kα	Ge-Kα	W-Lα	Ti-Kα	C-K	Fe-Kα	Cr-Kα	Ga-Kα
1,00	1,00	1,00	0,77	2,54	1,10	1,00	1,00	1,00	1,00
☐	☐	☐	☐	☐	☑	☐	☐	☐	☐

T-SEM
with radially symmetric EDS;
fluorescence >system peaks





Loaded: C:\Quantax User\Edx\Data\chip 20kV 60min.bcf

GF sample 1 pos B 12
MAG: 150kx HV: 20 kV WD: 14,0 mm Px: 2,4 nm

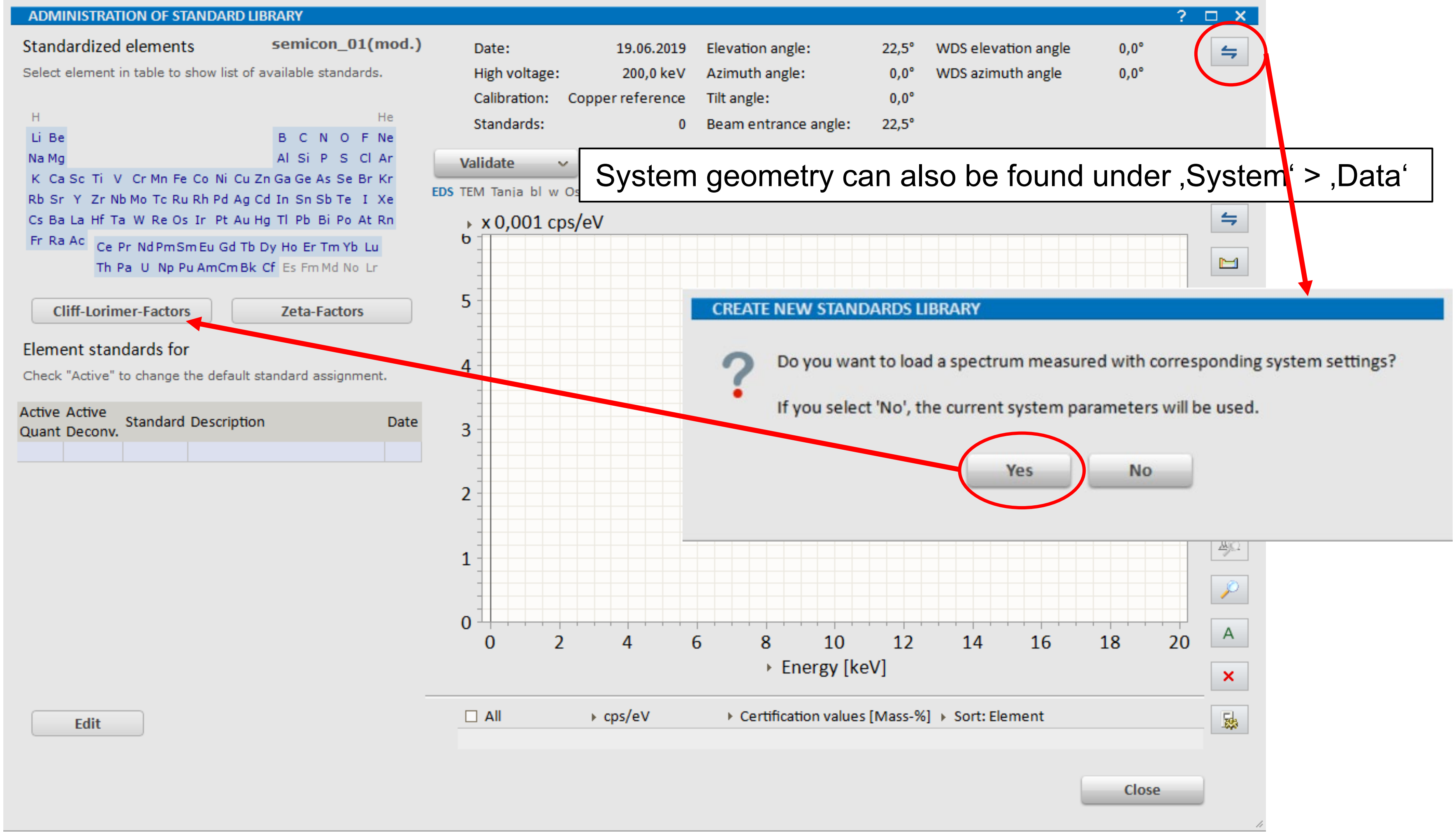
Loaded image 800 x 600 2,0 x 1,4 µm

1,20 µm Spot size 384x288 Points

EDS Map_Chip.spx 17,75 1,000 No quant results available.

For Cliff-Lorimer quantification: calculate theoretical Cliff-Lorimer factors for the specific geometry and conditions

‚Standards‘ menu:



ADMINISTRATION OF STANDARD LIBRARY

Standardized elements semicon_01(mod.)

Select element in table to show list of available standards.

Date: 19.06.2019
High voltage: 200,0 keV
Calibration: Copper reference
Standards: 0
Elevation angle: 22,5°
Azimuth angle: 0,0°
Tilt angle: 0,0°
Beam entrance angle: 22,5°
WDS elevation angle 0,0°
WDS azimuth angle 0,0°

System geometry can also be found under ‚System‘ > ‚Data‘

Element standards for

Check "Active" to change the default standard assignment.

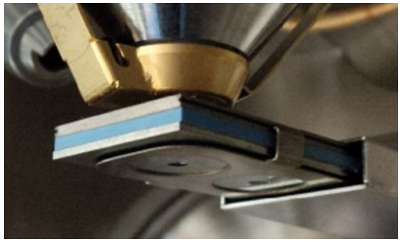
Active Quant	Active Deconv.	Standard	Description	Date

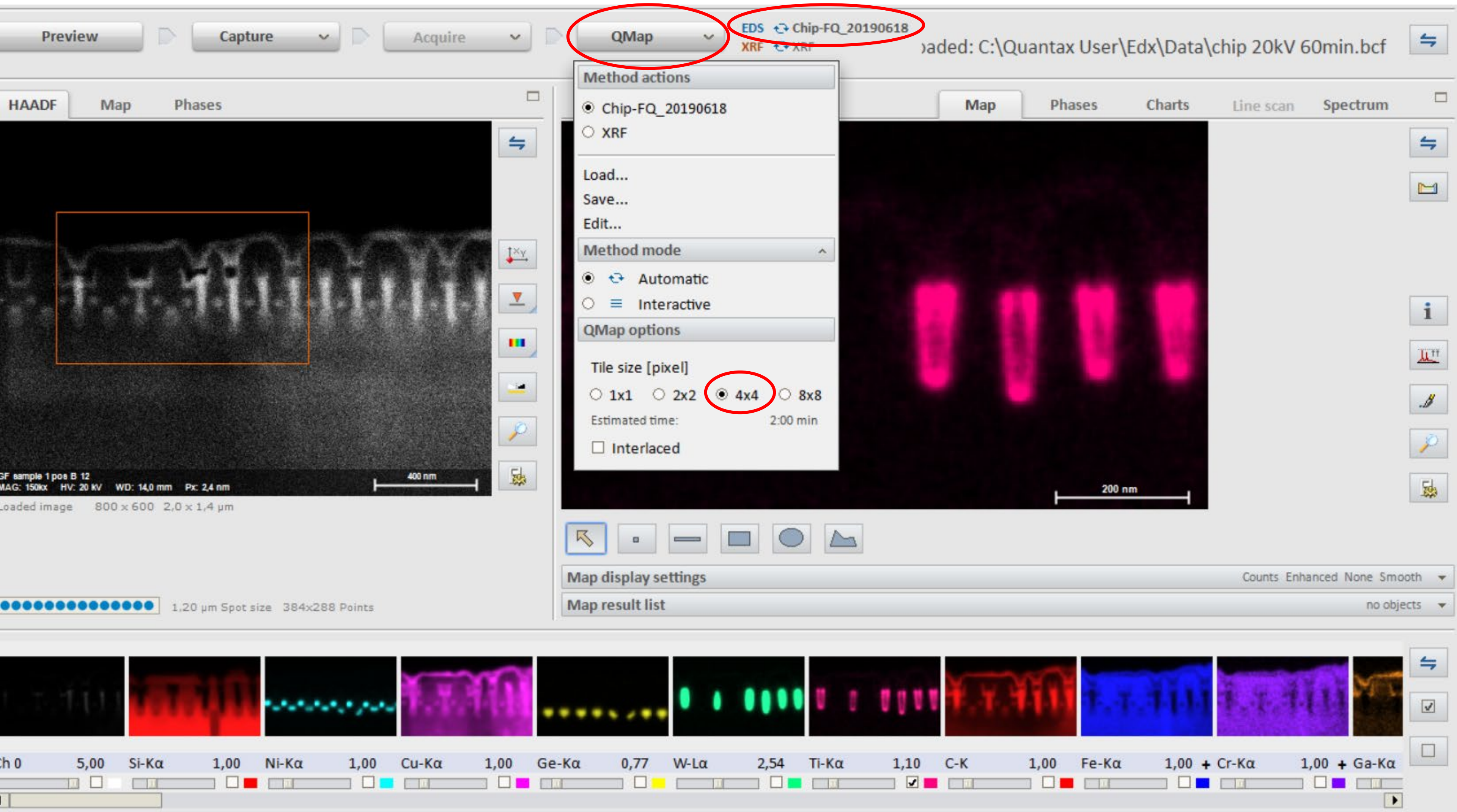
CREATE NEW STANDARDS LIBRARY

Do you want to load a spectrum measured with corresponding system settings?

If you select 'No', the current system parameters will be used.

Qmap setup





…aded: C:\Quantax User\Edx\Data\chip 20kV 60min.bcf

Method actions

● Chip-FQ_20190618
○ XRF

Load...
Save...
Edit...

Method mode

● Automatic
○ Interactive

QMap options

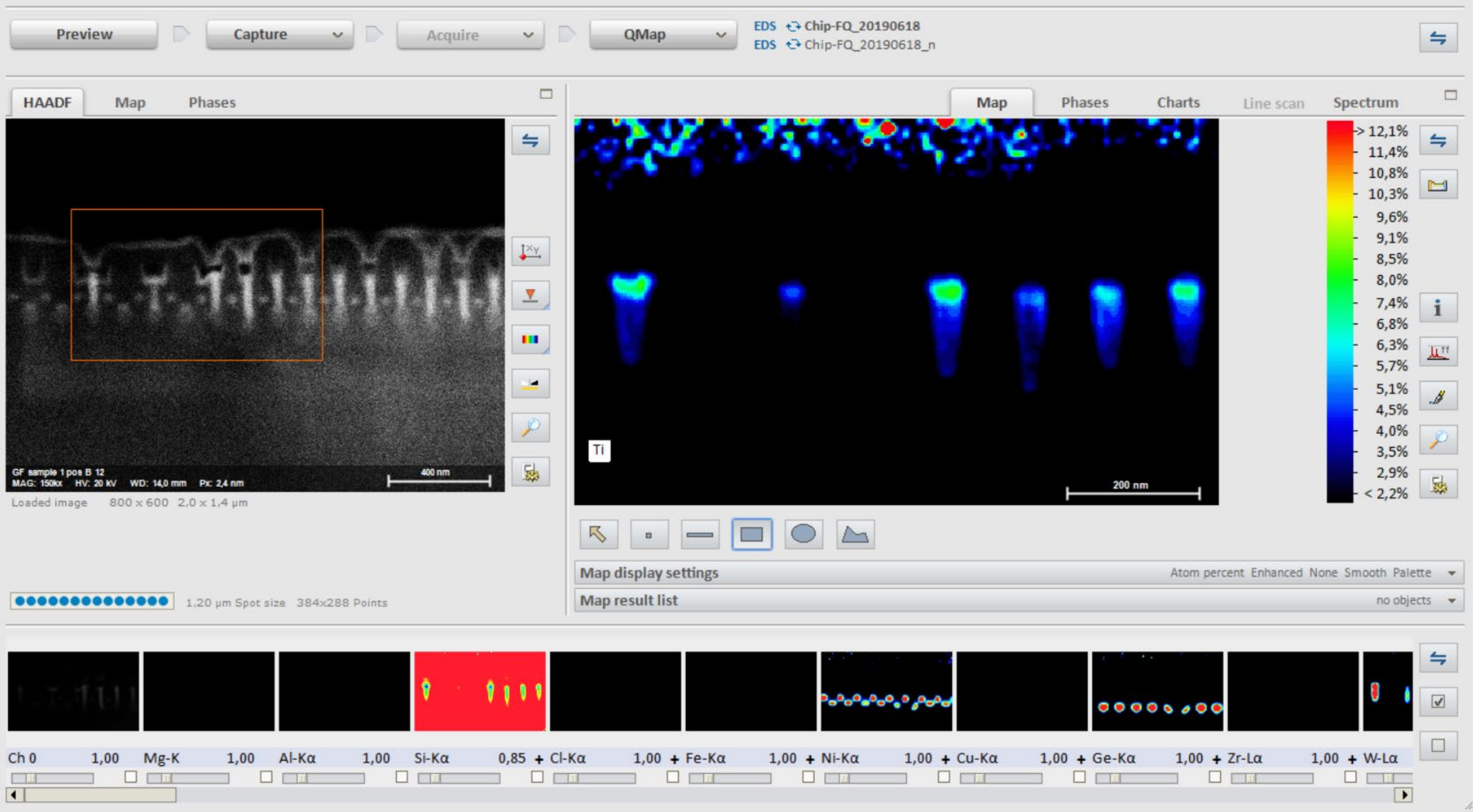
Tile size [pixel]

○ 1x1 ○ 2x2 ● 4x4 ○ 8x8

Estimated time: 2:00 min

☐ Interlaced

Display quant result in at% for Ti



EDS Chip-FQ_20190618
EDS Chip-FQ_20190618_n

GF sample 1 pos B 12
MAG: 150kx HV: 20 kV WD: 14,0 mm Px: 2,4 nm

Loaded image 800 x 600 2,0 x 1,4 µm

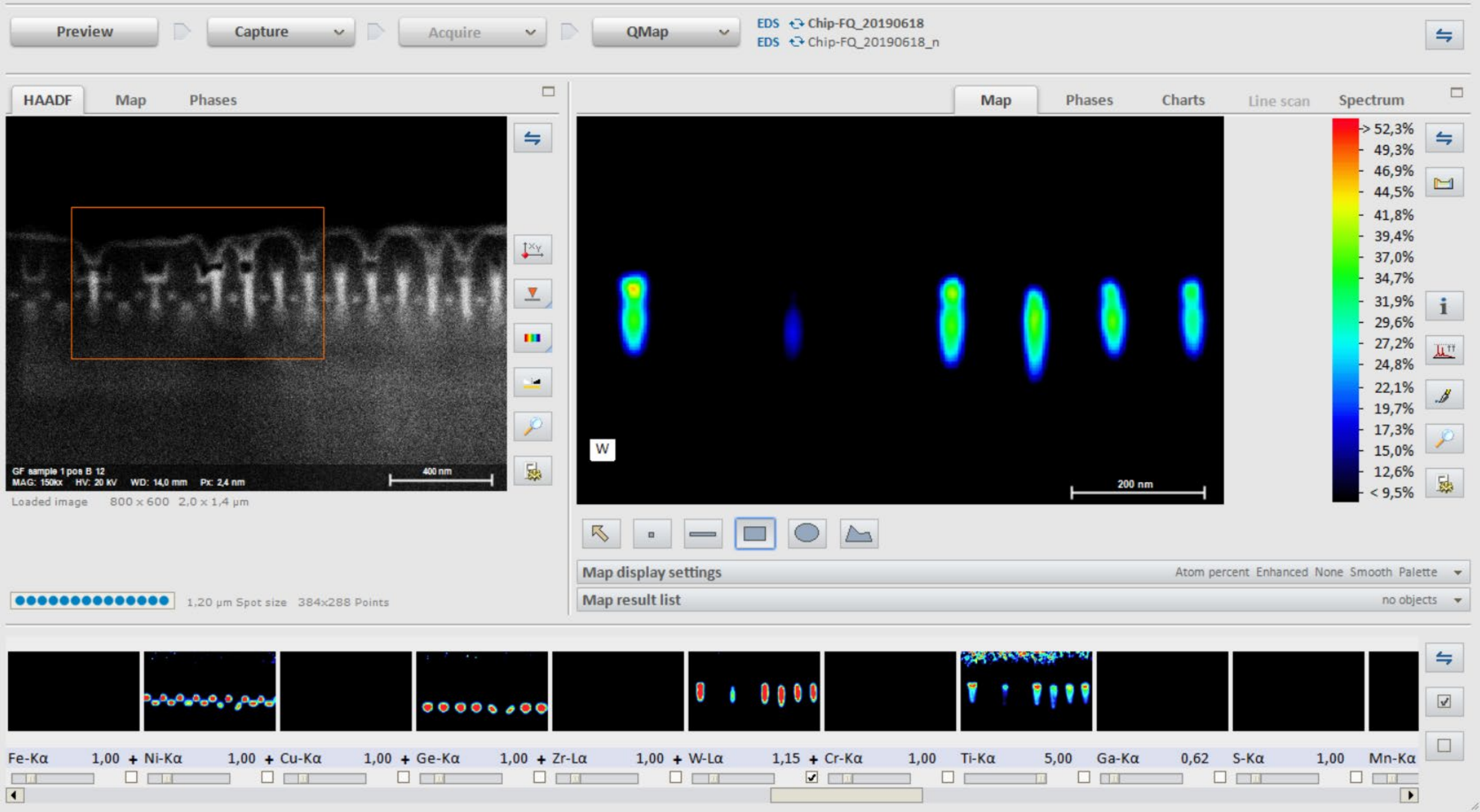
1,20 µm Spot size 384x288 Points

Map display settings: Atom percent Enhanced None Smooth Palette

Map result list: no objects

Ch 0 1,00
Mg-K 1,00
Al-Kα 1,00
Si-Kα 0,85
Cl-Kα 1,00
Fe-Kα 1,00
Ni-Kα 1,00
Cu-Kα 1,00
Ge-Kα 1,00
Zr-Lα 1,00
W-Lα

Display quant result in at% for W



GF sample 1 pos B 12
MAG: 150kx HV: 20 kV WD: 14,0 mm Px: 2,4 nm

Loaded image 800 x 600 2,0 x 1,4 µm

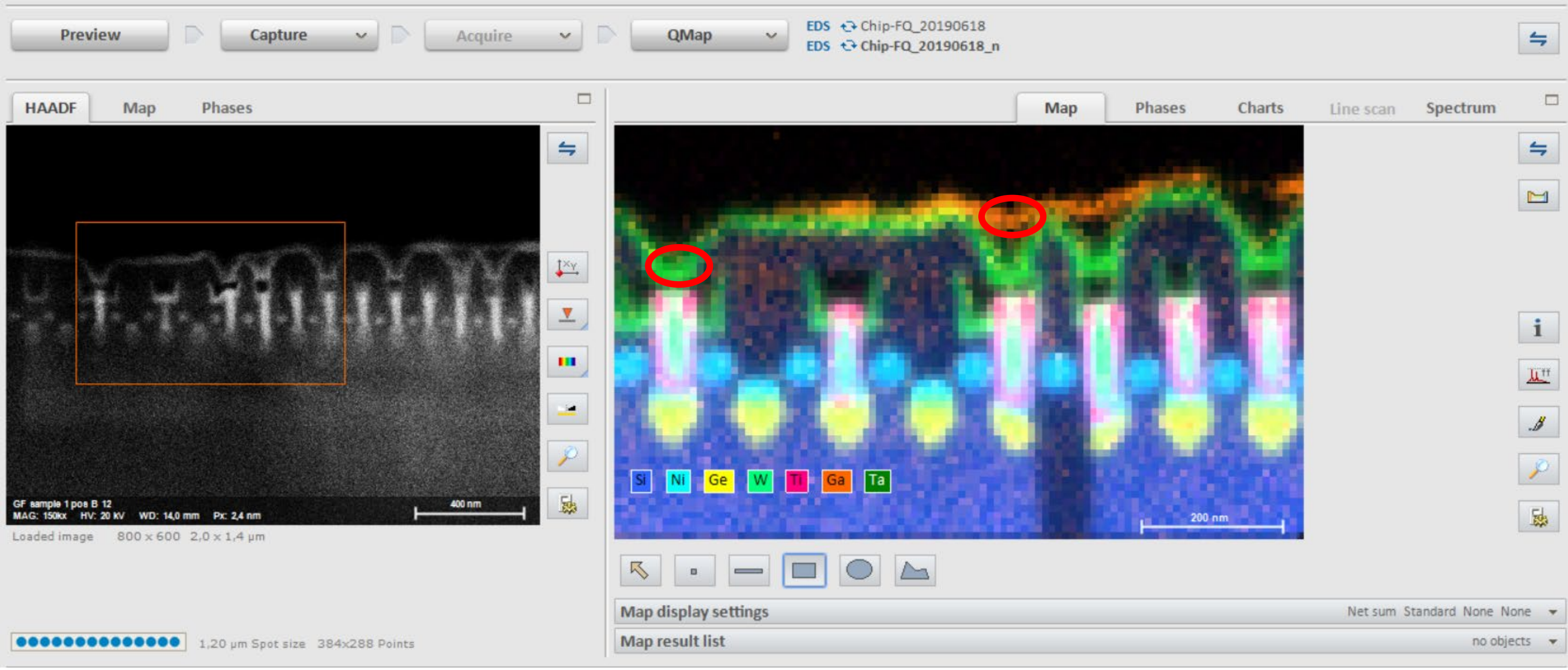
1,20 µm Spot size 384x288 Points

Map display settings: Atom percent Enhanced None Smooth Palette

Map result list: no objects

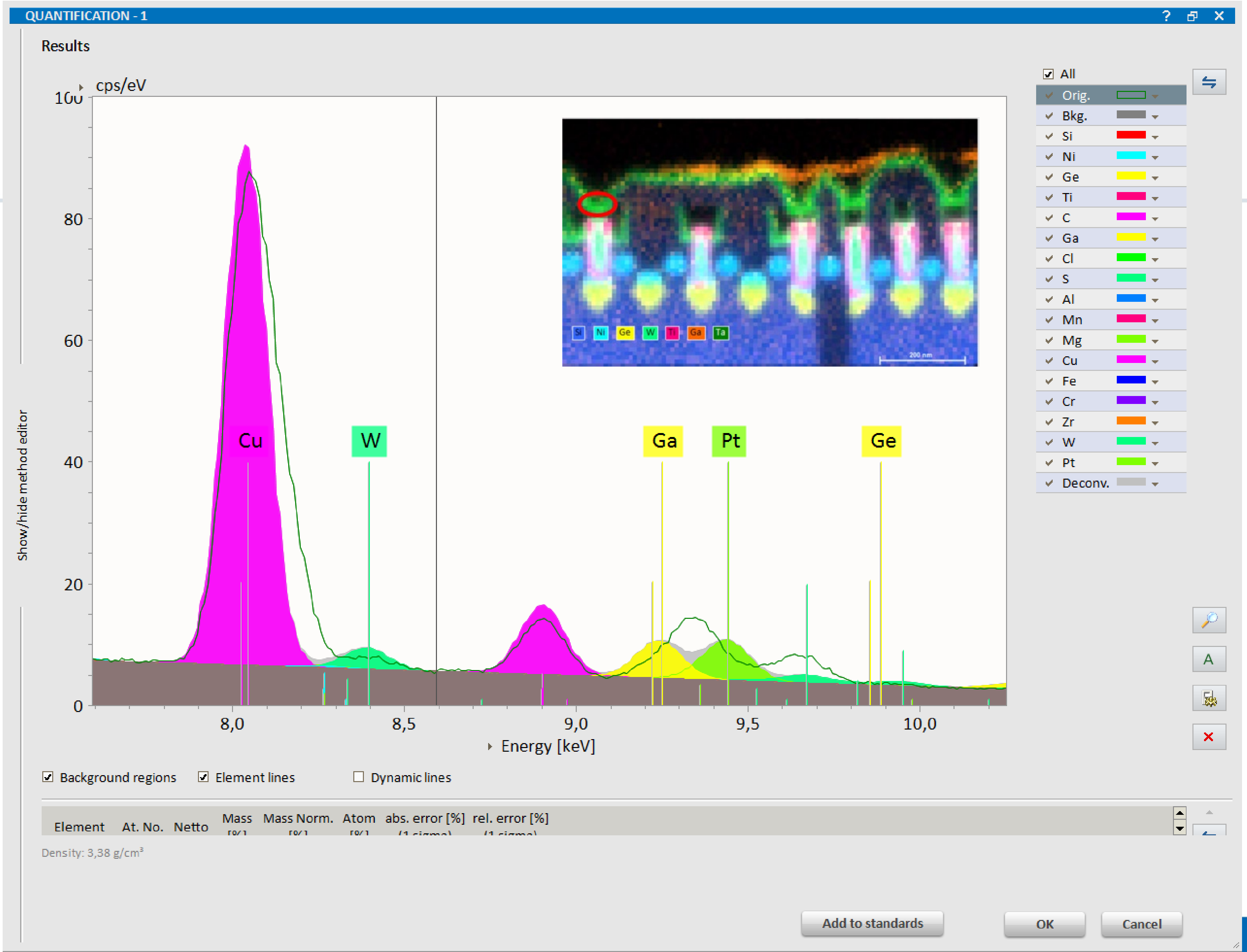
Fe-Kα 1,00 + ☐
Ni-Kα 1,00 + ☐
Cu-Kα 1,00 + ☐
Ge-Kα 1,00 + ☐
Zr-Lα 1,00 + ☐
W-Lα 1,15 + ☑
Cr-Kα 1,00 ☐
Ti-Kα 5,00 ☐
Ga-Kα 0,62 ☐
S-Kα 1,00 ☐
Mn-Kα

Quant result with 4x4 pixel binning: net counts, now check of 2 ROI



Map display settings: Net sum Standard None None

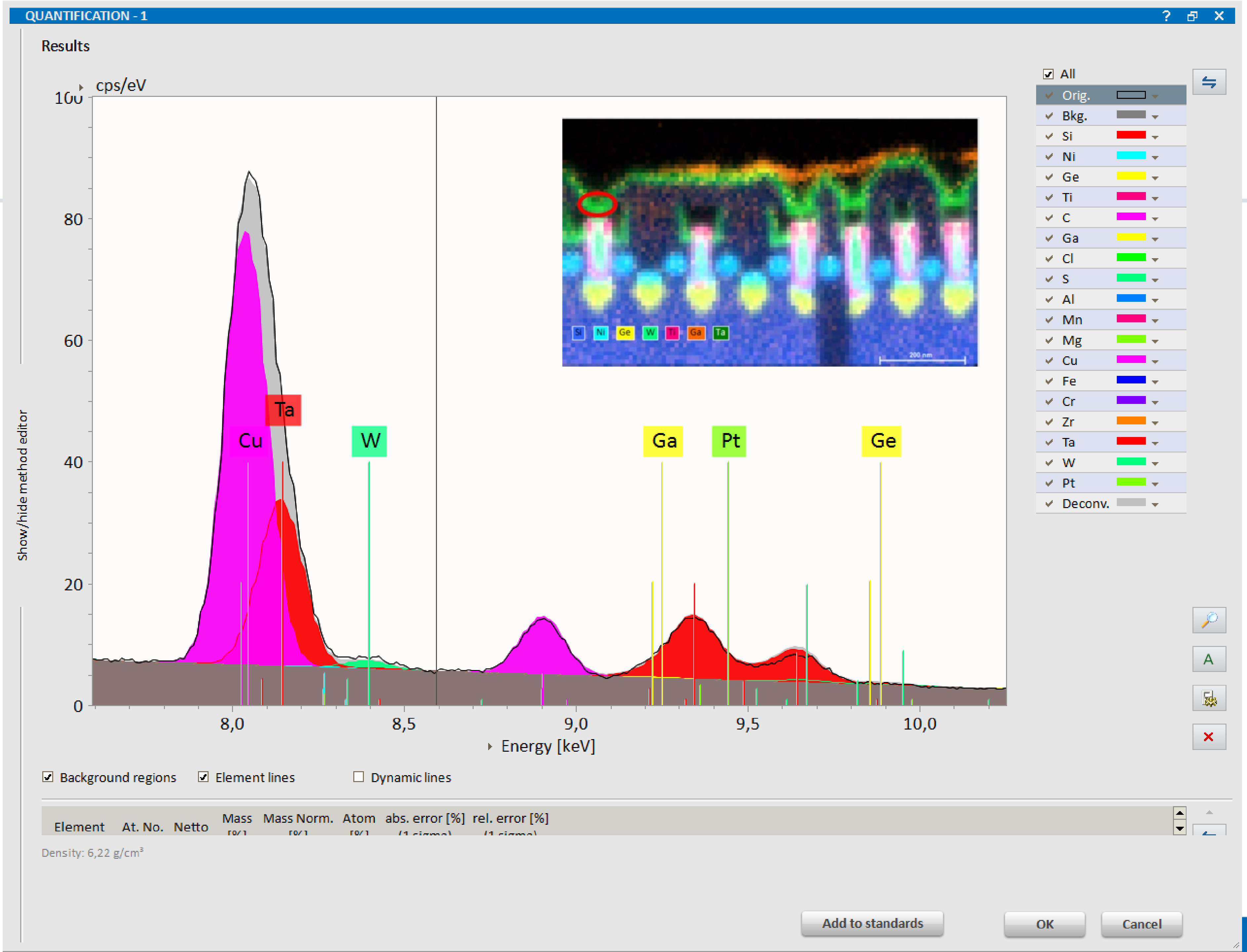
Map result list: no objects



☑ Background regions ☑ Element lines ☐ Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)

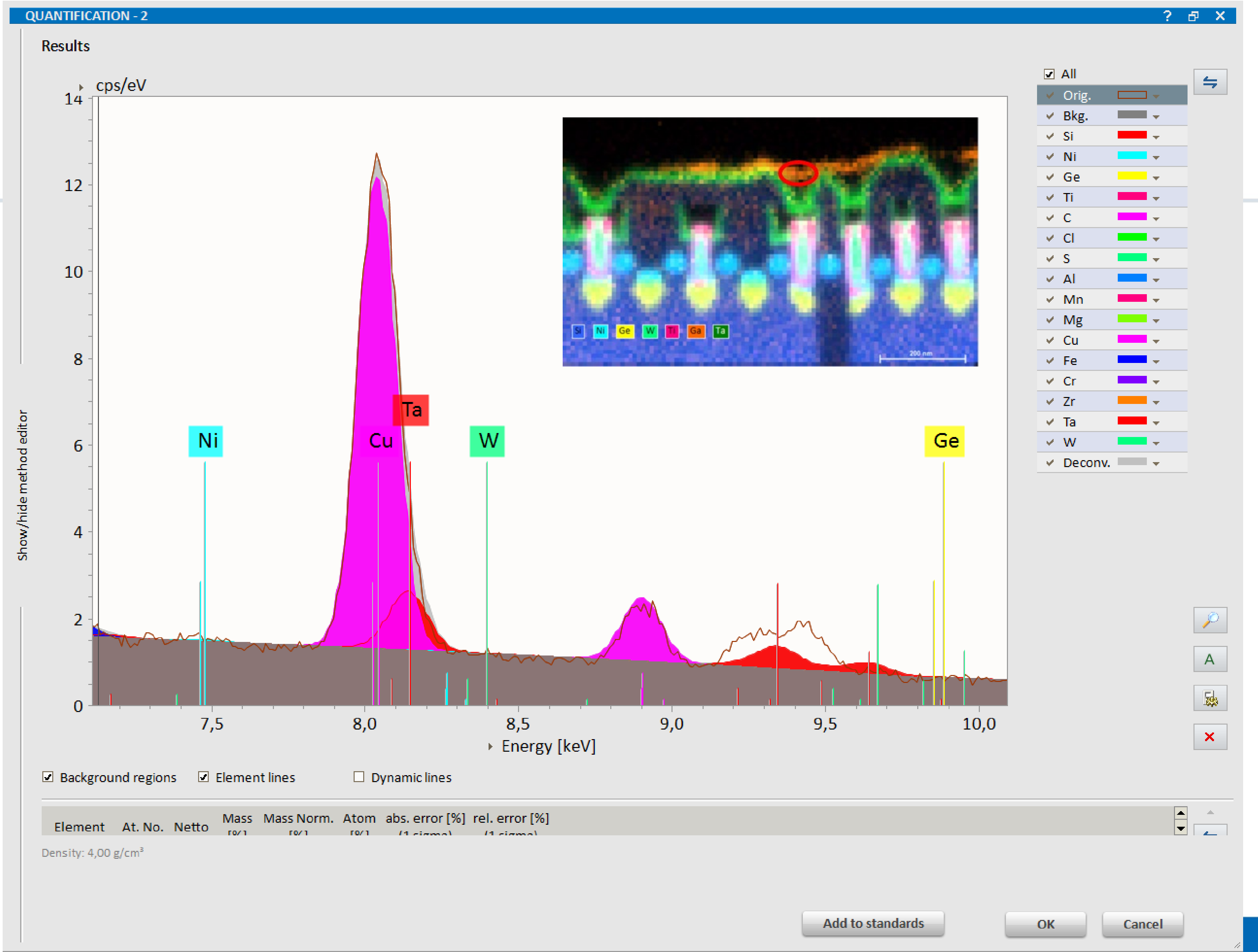
Density: 3,38 g/cm³



☑ Background regions ☑ Element lines ☐ Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)

Density: 6,22 g/cm³

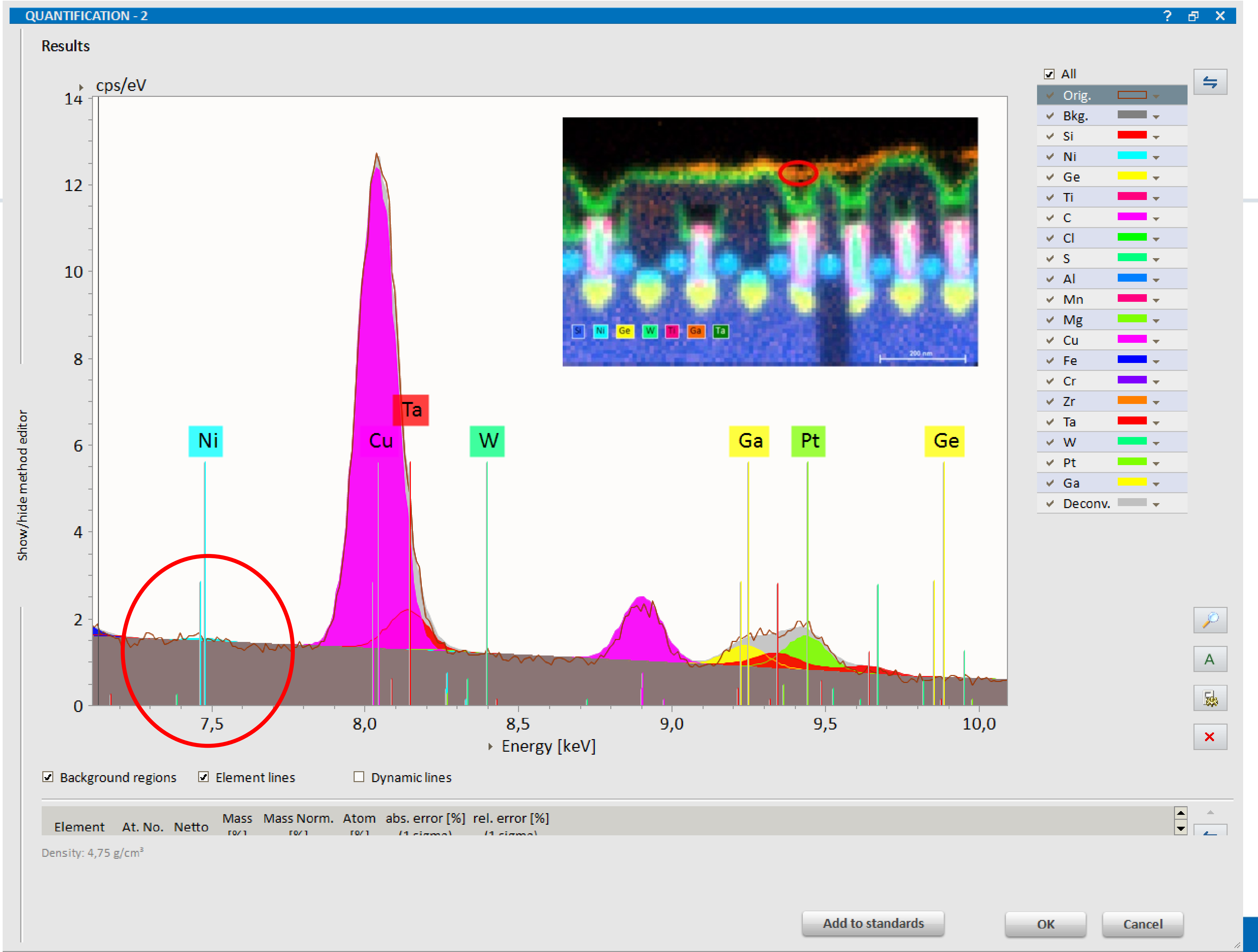


Results

☑ Background regions ☑ Element lines ☐ Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)

Density: 4,00 g/cm^3



☑ Background regions ☑ Element lines ☐ Dynamic lines

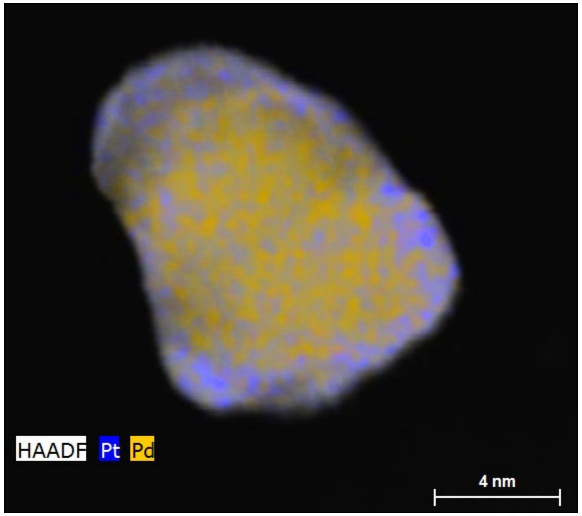
Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)

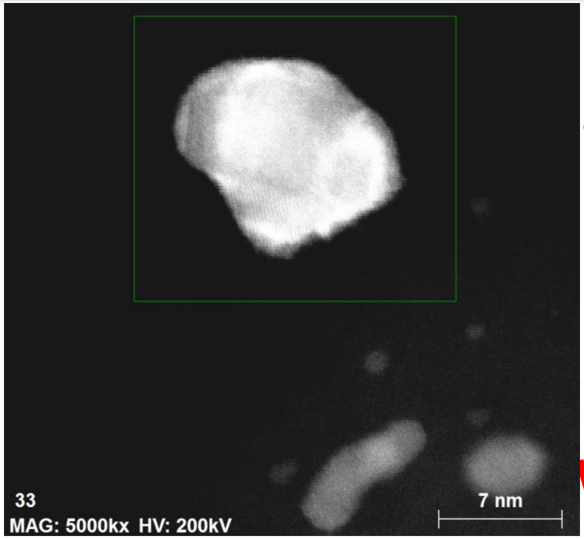
Density: 4,75 g/cm³

EDS for Catalysis, Quantification

Pt-Pd Core Shell Particles

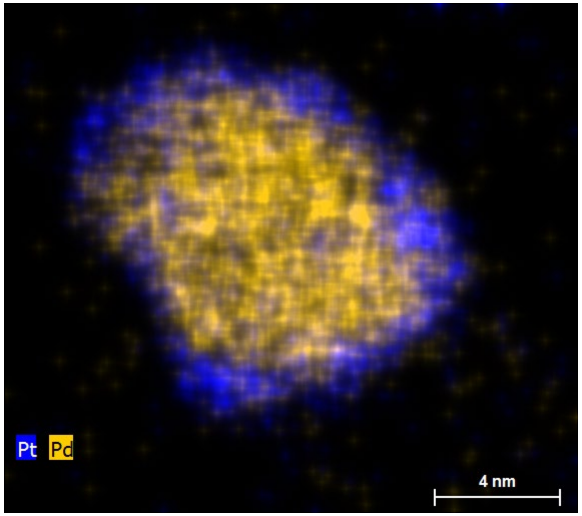
mass%, 30 mm², 0.12 sr (Standard EDS); Cs-corr. STEM

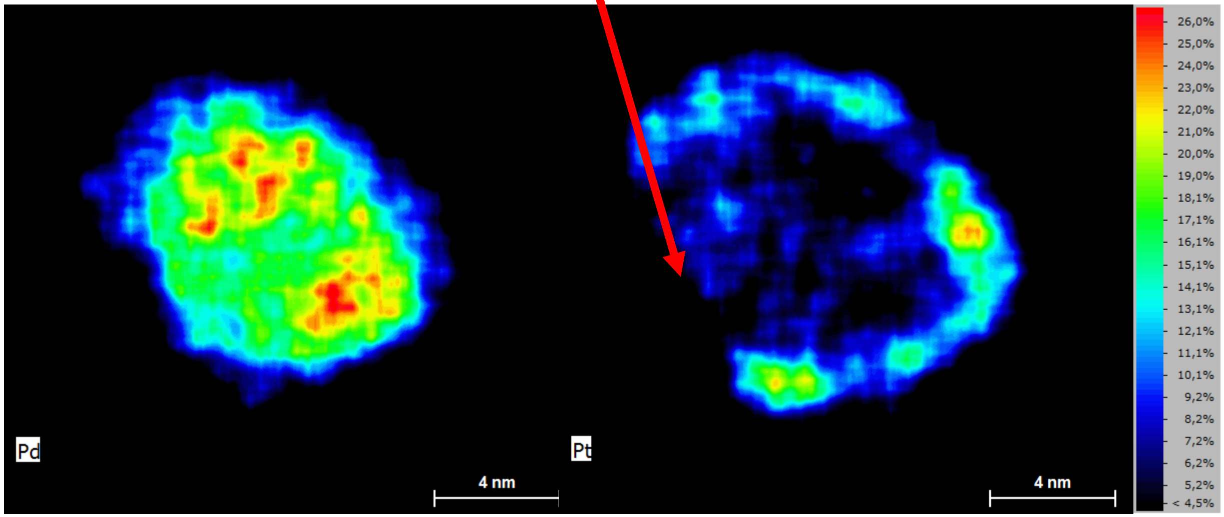




Data courtesy:Dogan Ozkaya,
Johnson Matthey
Technology Center

Pt shell not closed
due to fabrication procedure

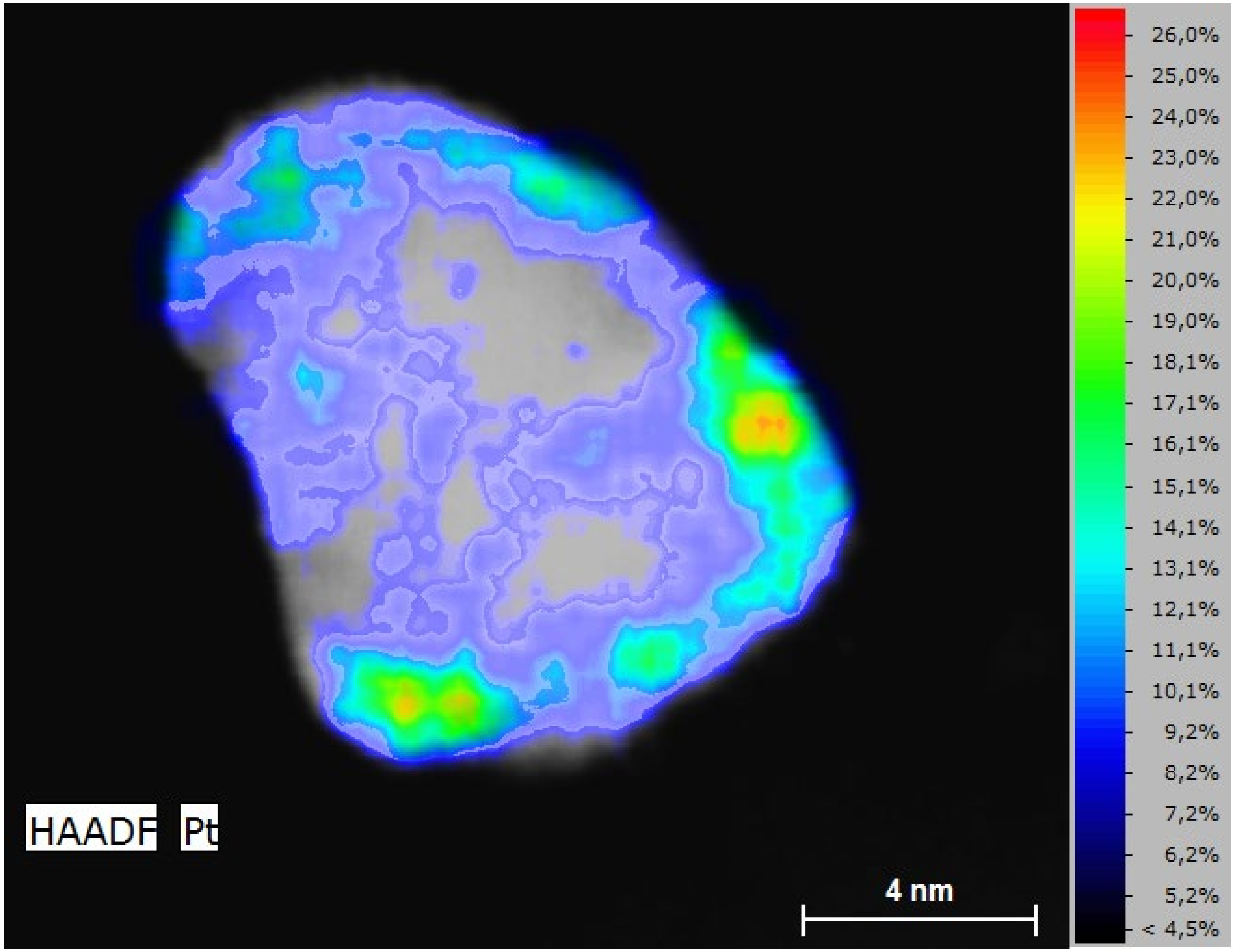




EDS for Catalysis, Quantification

Pt-Pd Core Shell Particles

mass%, 30 mm^2, 0.12 sr (Standard EDS); Cs-corr. STEM



Data courtesy:
Dogan Ozkaya,
Johnson Matthey
Technology Center

EDS for Life Science at 0.1sr
Malaria Parasite: *Plasmodium* in erythrocyte treated with Chloroquine


science.nationalgoegraphic.com

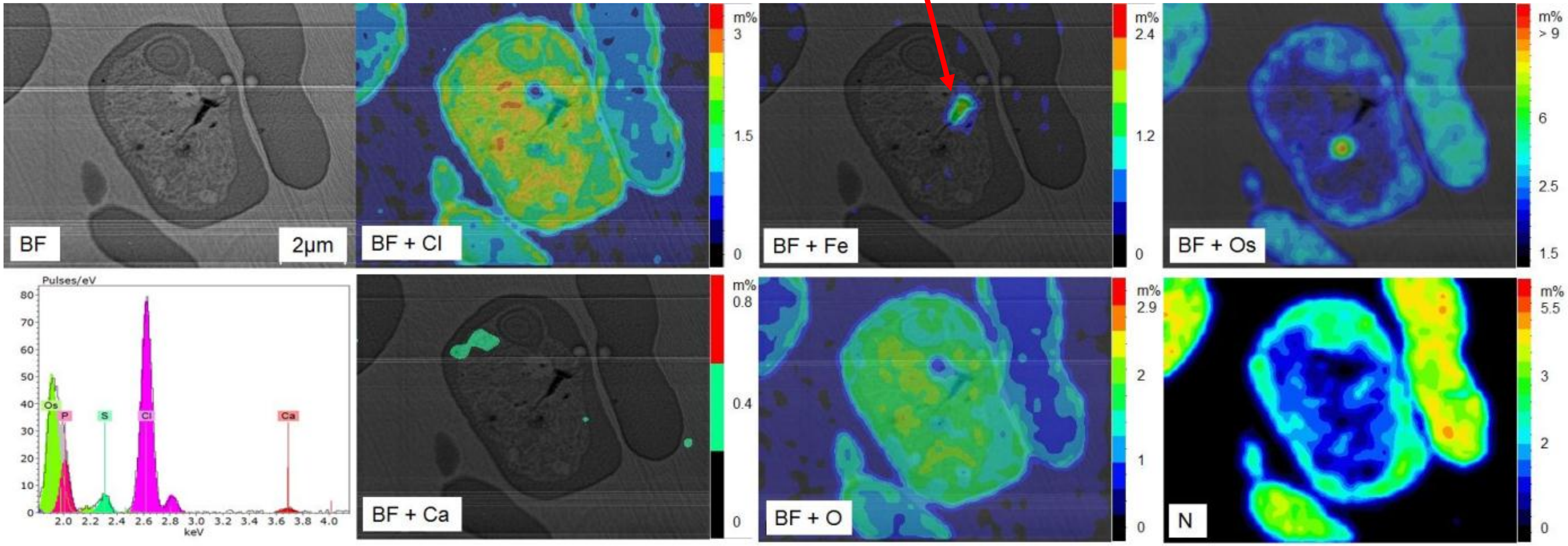
The parasite multiplies by destroying red blood cells.

Iron intake in food vacuole, since the parasite is digesting hemoglobin

Malaria can be treated e.g.by Chloroquine


Anopheles mosquito

science.nationalgoegraphic.com



Data courtesy: C. Biot and C. Slomianny, Laboratory of Cell Physiology, University of Lille, France

TEM EDS Quantification; R. Egerton

1994, line intensity for a particular element line / transition

$$I_x = N_A\, \sigma_A\, \omega_A\, (\Omega/4\pi)\, \varepsilon\, N_e = \boxed{n_A\, t}\, \sigma_A\, \omega_A\, (\Omega/4\pi)\, \varepsilon\, N_e$$

Standard for Zeta-Factor Bulk, thick

$$\rho\, t = \zeta_A \frac{I_A A_A}{C_A D_e} \ldots$$

Cliff and Lorimer:

$$\frac{I_A}{I_B} = \frac{C_A}{k_{AB}\, C_B}$$

; k_{AB} can be determined experimentally **or theoretically**

I_x	number of X-ray photons in a characteristic peak of species A
N	number of atoms per unit volume
$n\, t$	number of atoms per unit area times thickness
σ	ionization cross section (Casnati et al., 1982, Bote et al., 2009)
ω	fluorescence yield (Hubbell et al., 1994, Krause, 1979)
$\Omega/4\pi$	solid angle / geometrical collection efficiency
ε	detection quantum efficiency
N_e	number of incident electrons

+ absorption

TEM EDS Quantification; R. Egerton

1994, line intensity for a particular element line / transition

Standard for Zeta-Factor Bulk, thick …

$$I_x = N_A \, \sigma_A \, \omega_A \, (\Omega/4\pi) \, \varepsilon \, N_e = \boxed{n_A \, t} \, \sigma_A \, \omega_A \, (\Omega/4\pi) \, \varepsilon \, N_e$$

$$\rho \, t = \zeta_A \frac{I_A A_A}{C_A D_e} \ldots$$

With few ζ data points all ζx can be calculated from existing ***k***-factors!

Cliff and Lorimer:

$$\frac{I_A}{I_B} = \frac{C_A}{k_{AB} \, C_B}$$

; k_{AB} can be determined experimentally **or theoretically**

I_x	number of X-ray photons in a characteristic peak of species A
N	number of atoms per unit volume
$n\ t$	number of atoms per unit area times thickness
σ	ionization cross section (Casnati et al., 1982, Bote et al., 2009)
ω	fluorescence yield (Hubbell et al., 1994, Krause, 1979)
$\Omega/4\pi$	solid angle / geometrical collection efficiency
ε	detection quantum efficiency
N_e	number of incident electrons

+ absorption

TEM EDS Quantification
Cliff Lorimer / Zeta-factor … + EELS!

The CL-method is a ratio method by Graham Cliff and Gordon Lorimer:

$$\frac{C_A}{C_B} = k_{AB} \frac{I_A}{I_B}$$

G. Kothleitner, Micr. Microanal. 2014
M. Watanabe, J. of Micr. 2005:
For a **standard with known density *ρ* and known thickness *t* *ζ*** can be determined: ***D_e* (total electron dose) must be known for all measurements.**

EELS: $t/\lambda = \log_e (I^E_{total} / I^E_0)$

$$\boxed{\rho\, t} = \zeta_A \frac{I_A A_A}{C_A D_e} \ldots = \frac{I^E_{core}}{I^E_{0\_low}\, \sigma} \, \frac{\text{AtWeight}}{N_{Avog}}$$

Then, for a sample C_A, C_B … and ρt are unknown with:

$$C_A + C_B = 1$$

$$(C_1 + C_2 + \ldots = 1)$$

$$\rho\, t = \frac{\zeta_A I_A + \zeta_B I_B}{D_e}$$

A_A

A_B

absorption coefficients

$$C_A = \frac{\zeta_A I_A}{\zeta_A I_A + \zeta_B I_B}$$

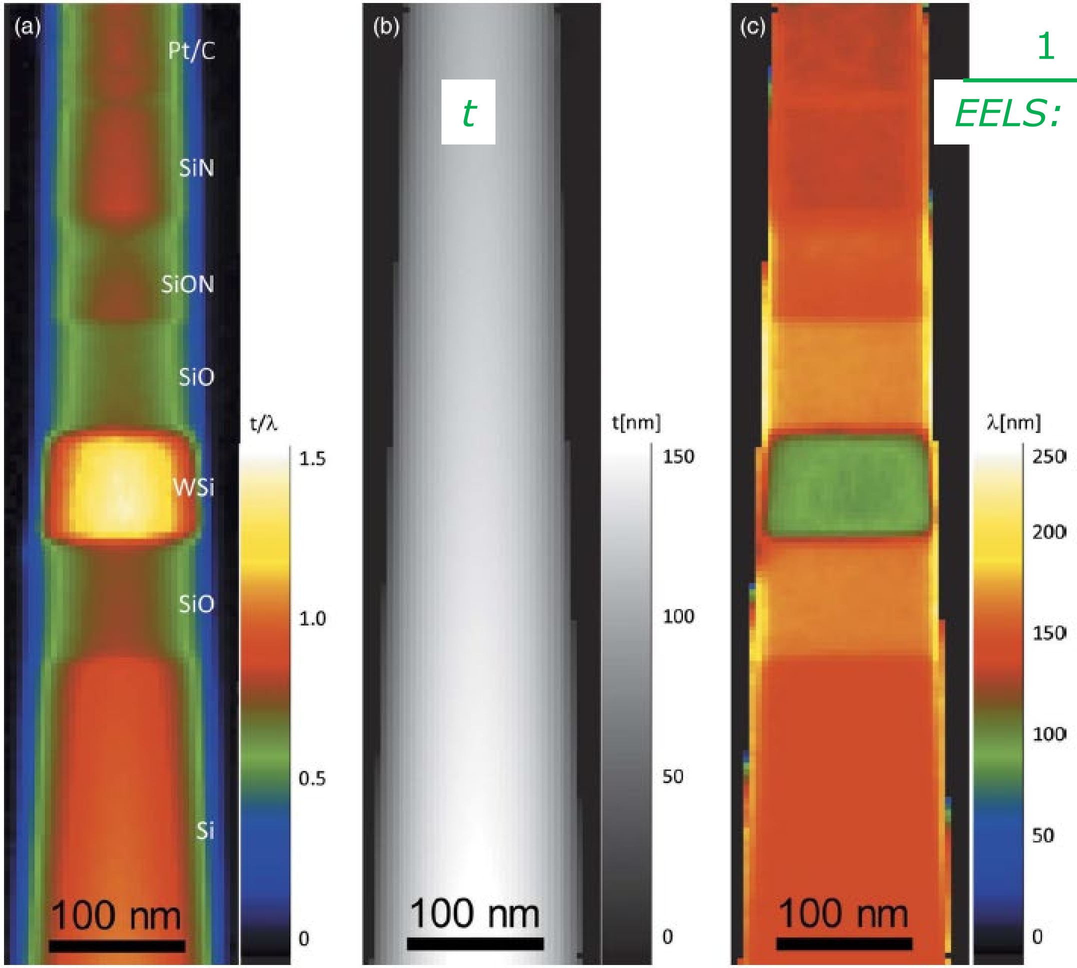
$$C_B = \ldots$$

G. Kothleitner, Micr. Microanal. 20 (2014) 678, on assumption-less analysis

G. Kothleitner et al., Microsc. Microanal. **20** (2014) 678
Towards assumptionless analysis …

682 Gerald Kothleitner et al.

EELS: t/λ



$$\frac{1}{\text{EELS: } t/\lambda} \times t = \lambda$$

Figure 3. Relative thickness map (t/λ) (**a**), and model of the thickness of the focused ion beam milled cone (**b**). The inverse of (**a**) multiplied by (**b**) yields a map displaying the inelastic mean free paths λ of the sample, used for further thickness calibrations (**c**).

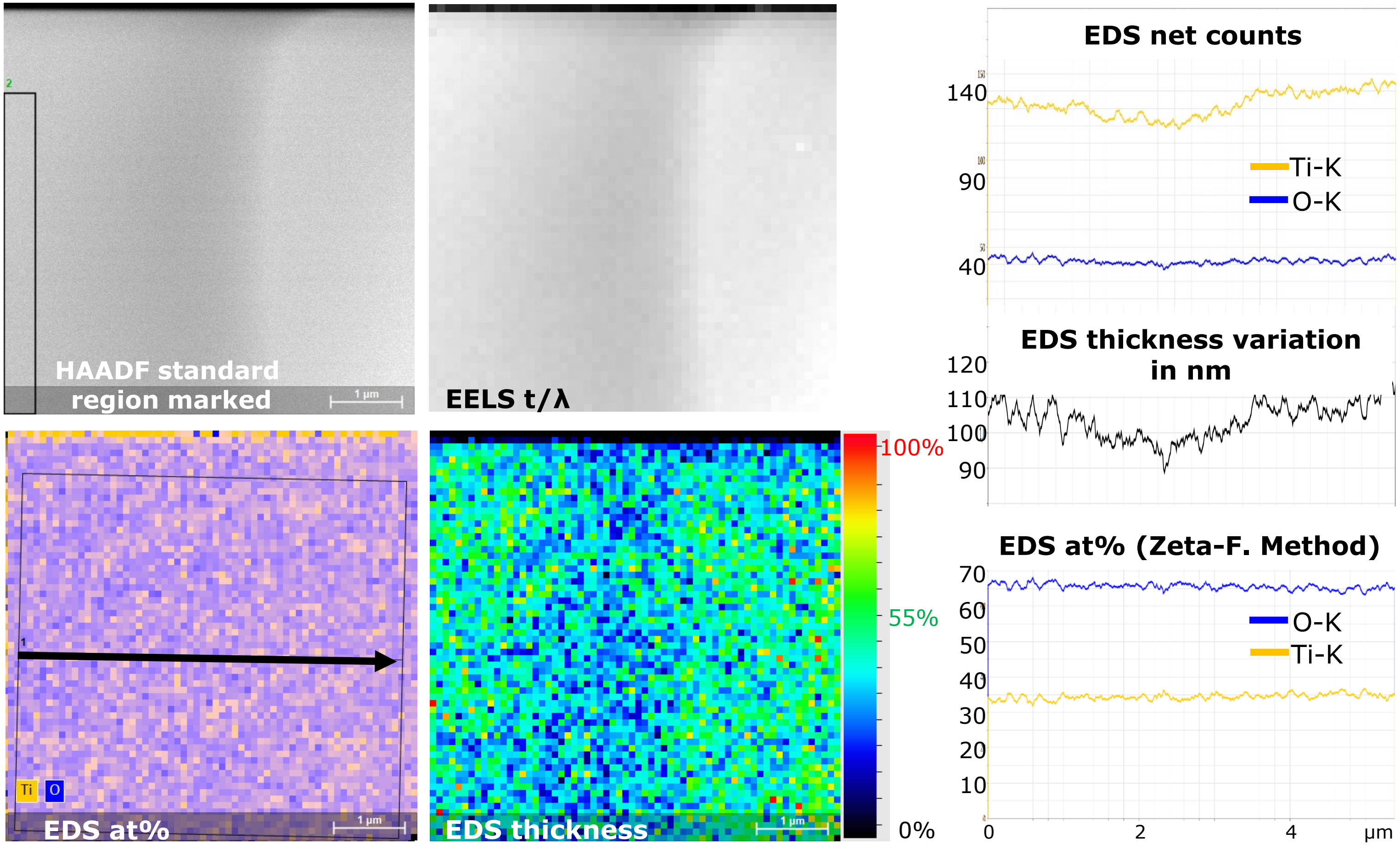
G. Kothleitner, Micr. Microanal. 2014

TEM Quantification in Esprit

Zeta Factor Method to Retrieve Thickness and Composition,

EELS used here only as Reference

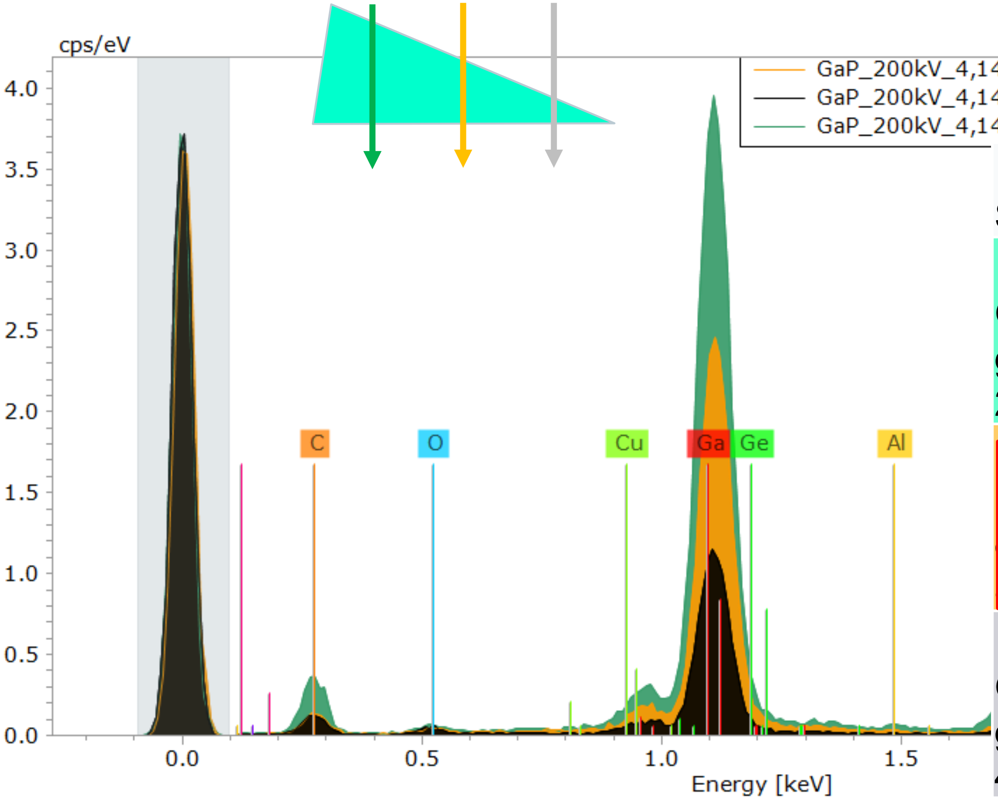
TiO_2



+ G. Kothleitner, Micr. Microanal. 2014

TEM Quantification in Esprit 2.1

Zeta Method: GaP wedge

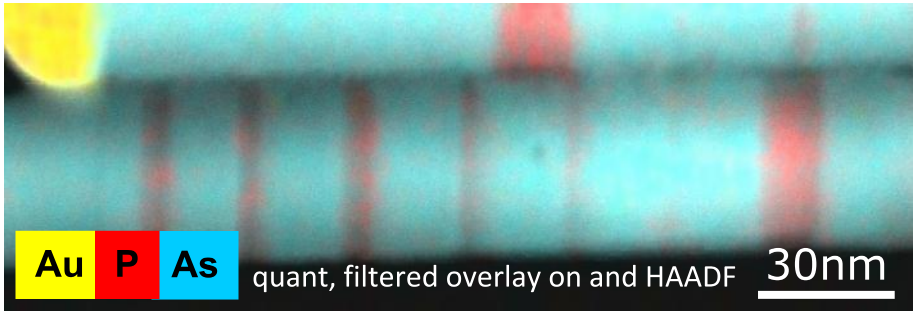


Spectrum	P in at%	Ga in at%	d_nom nm	d_zeta nm
GaP_200kV_4,14g_cm3_Q_145_120nm_104pA.spx	49.24	50.76	120	145
GaP_200kV_4,14g_cm3_St_080_080nm_104pA.spx	50.04	49.96	standard 80	80
GaP_200kV_4,14g_cm3_Q_034_040nm_104pA.spx	46.69	53.31	40	34
Mean	48.66	51.34		
Sigma 3	1.75	1.75		

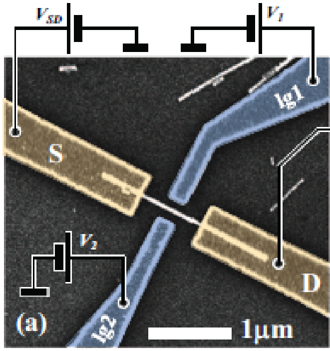
Probe current and thickness variations in standard and sample cause deviations. Product *pt* can't be well disentangled. Kothleitner et al. on assumptionless quantification !

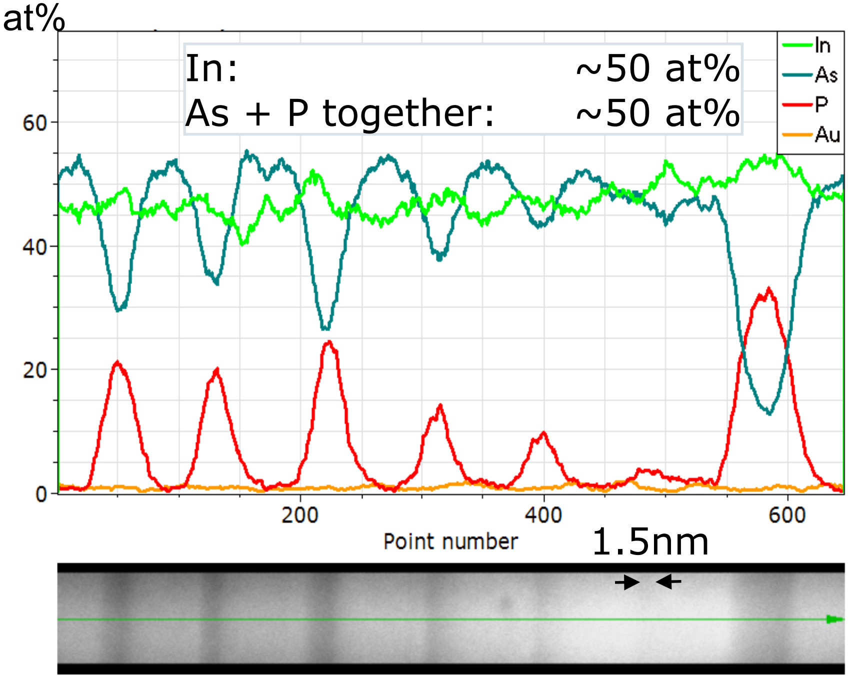
Experimental C-L or Zeta factors:

InAs Nanorods with P-rich layers:
Quantified Linescan,
30mm² SDD, SLE window, 0.12sr

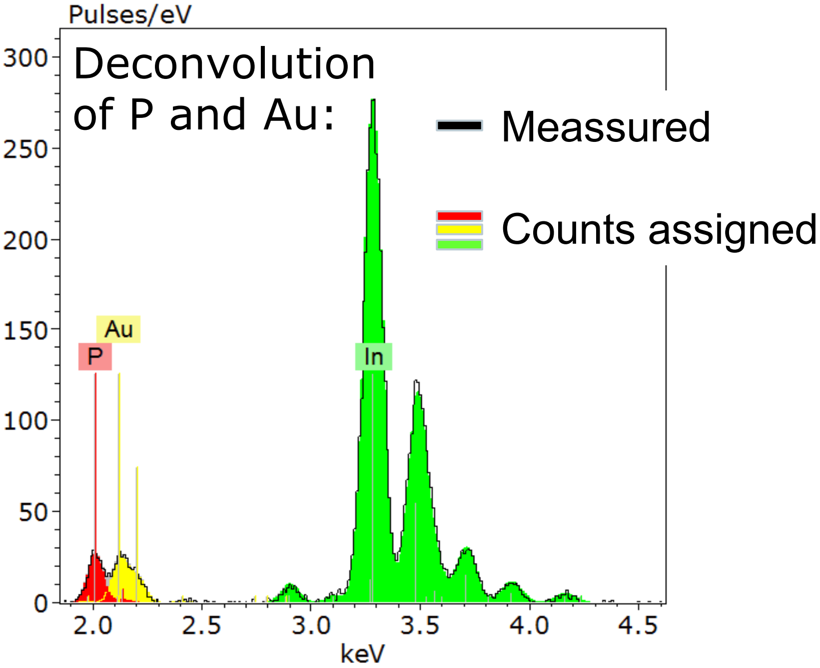


Single
e^- transistor:





In: ~50 at%
As + P together: ~50 at%

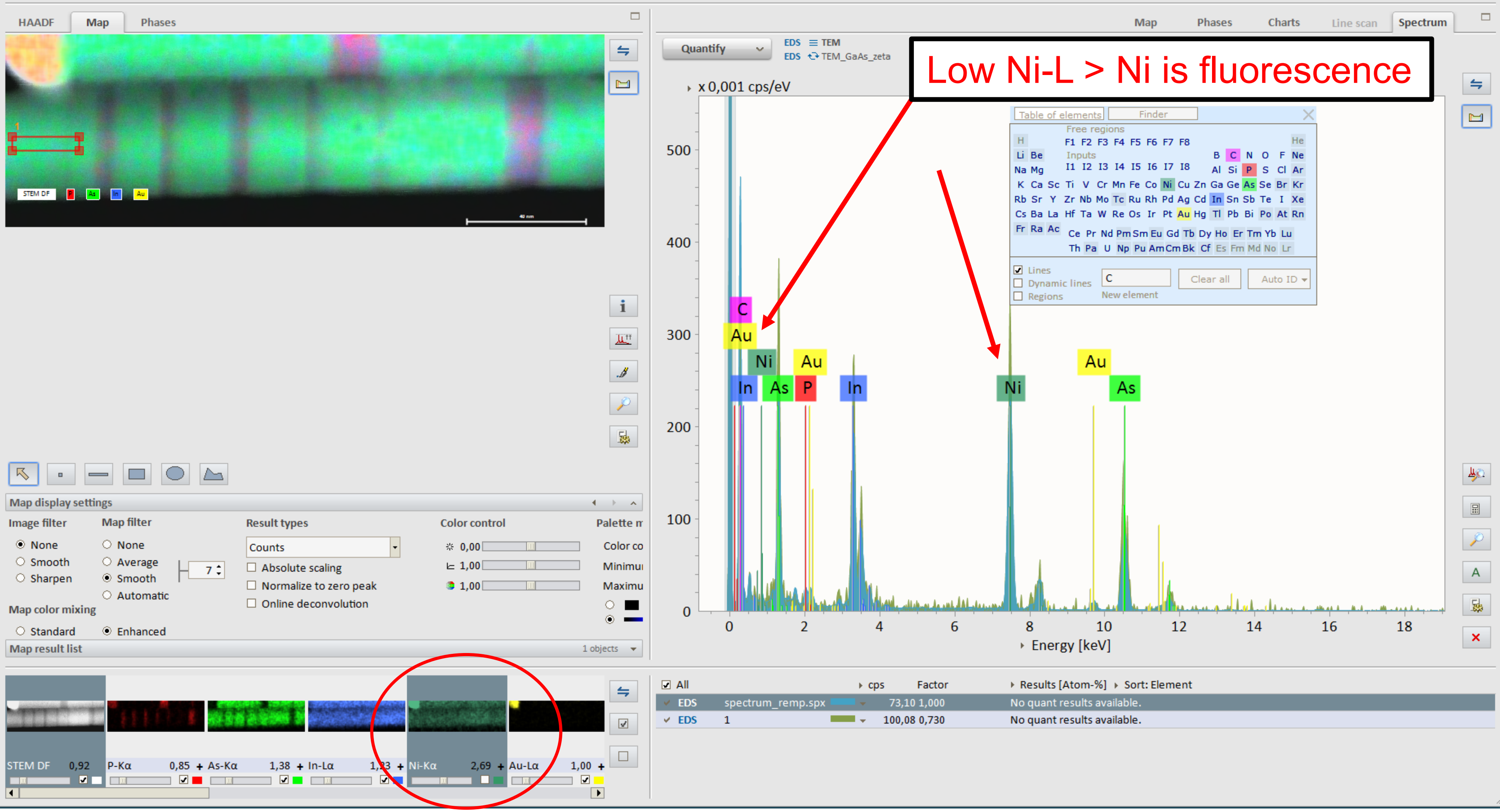


Deconvolution of P and Au:

▬ Meassured

🟥🟨🟩 Counts assigned

Respective data set view; see Ni-stray radiation from Ni grid: no/low Ni-L line!



Low Ni-L > Ni is fluorescence

Image filter
● None
○ Smooth
○ Sharpen

Map filter
○ None
○ Average
● Smooth
○ Automatic
7

Result types
Counts
☐ Absolute scaling
☐ Normalize to zero peak
☐ Online deconvolution

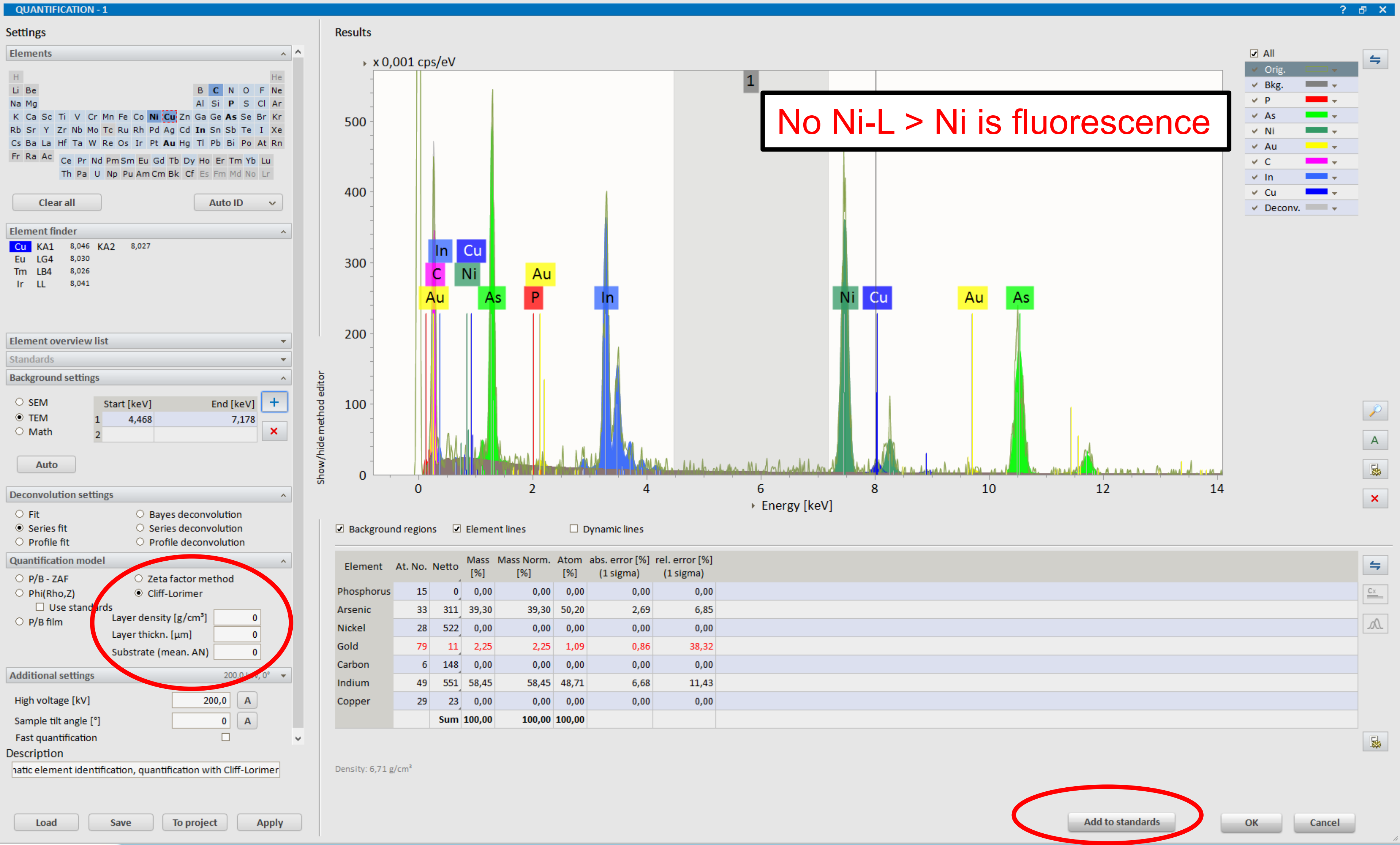
Color control
0,00
1,00
1,00

Map color mixing
○ Standard
● Enhanced

☑ All		cps	Factor	Results [Atom-%]
EDS	spectrum_remp.spx	73,10	1,000	No quant results available.
EDS	1	100,08	0,730	No quant results available.

Sort: Element

Quantification: exp. Cliff-Lorimer factors



No Ni-L > Ni is fluorescence

Element finder

Cu	KA1	8,046	KA2	8,027
Eu	LG4	8,030		
Tm	LB4	8,026		
Ir	LL	8,041		

Element overview list

Standards

Background settings

○ SEM
● TEM
○ Math

	Start [keV]	End [keV]
1	4,468	7,178
2		

Auto

Deconvolution settings

○ Fit
● Series fit
○ Profile fit
○ Bayes deconvolution
○ Series deconvolution
○ Profile deconvolution

Quantification model

○ P/B - ZAF
○ Phi(Rho,Z)
☐ Use standards
○ P/B film
○ Zeta factor method
● Cliff-Lorimer

Layer density [g/cm³] 0
Layer thickn. [µm] 0
Substrate (mean. AN) 0

Additional settings 200,0 kV, 0°

High voltage [kV] 200,0
Sample tilt angle [°] 0
Fast quantification ☐

Description

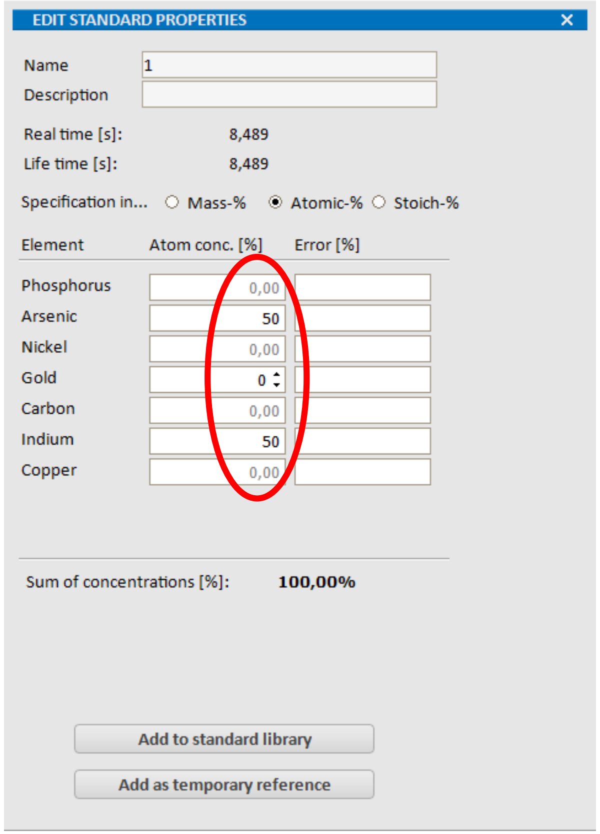
hatic element identification, quantification with Cliff-Lorimer

☑ Background regions ☑ Element lines ☐ Dynamic lines

Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
Phosphorus	15	0	0,00	0,00	0,00	0,00	0,00
Arsenic	33	311	39,30	39,30	50,20	2,69	6,85
Nickel	28	522	0,00	0,00	0,00	0,00	0,00
Gold	79	11	2,25	2,25	1,09	0,86	38,32
Carbon	6	148	0,00	0,00	0,00	0,00	0,00
Indium	49	551	58,45	58,45	48,71	6,68	11,43
Copper	29	23	0,00	0,00	0,00	0,00	0,00
		Sum	100,00	100,00	100,00		

Density: 6,71 g/cm³

Quantification: exp. Cliff-Lorimer factors, Change the less well known factors: (if overlapps, low energy, L-lines)



EDIT STANDARD PROPERTIES

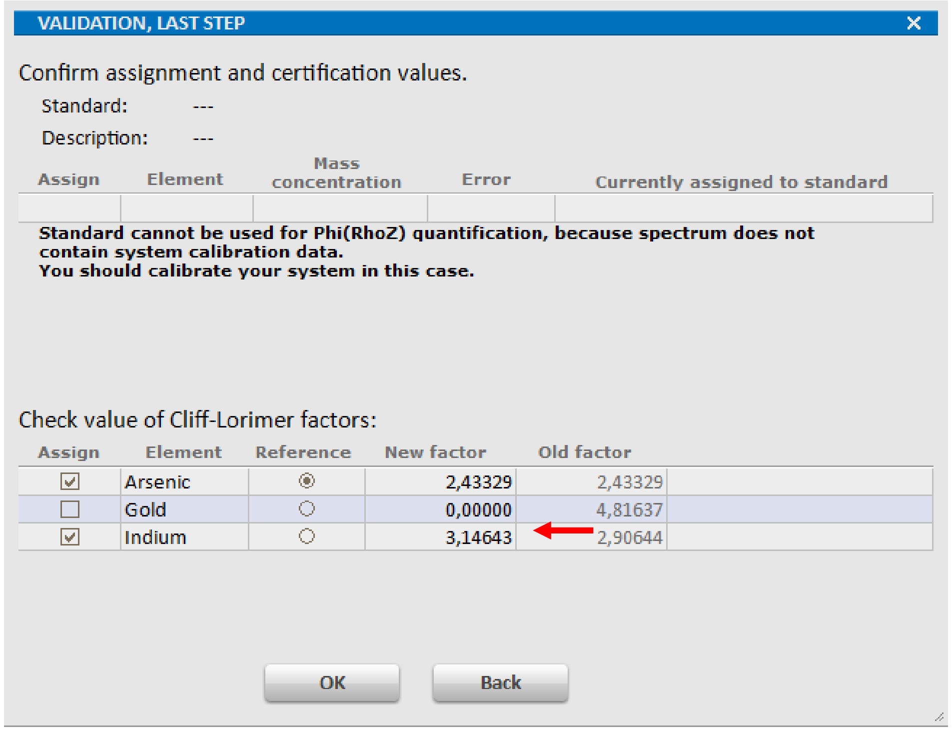
Name: 1
Description:

Real time [s]: 8,489
Life time [s]: 8,489

Specification in... ○ Mass-% ● Atomic-% ○ Stoich-%

Element	Atom conc. [%]	Error [%]
Phosphorus	0,00	
Arsenic	50	
Nickel	0,00	
Gold	0	
Carbon	0,00	
Indium	50	
Copper	0,00	

Sum of concentrations [%]: **100,00%**



VALIDATION, LAST STEP

Confirm assignment and certification values.

Standard: ---
Description: ---

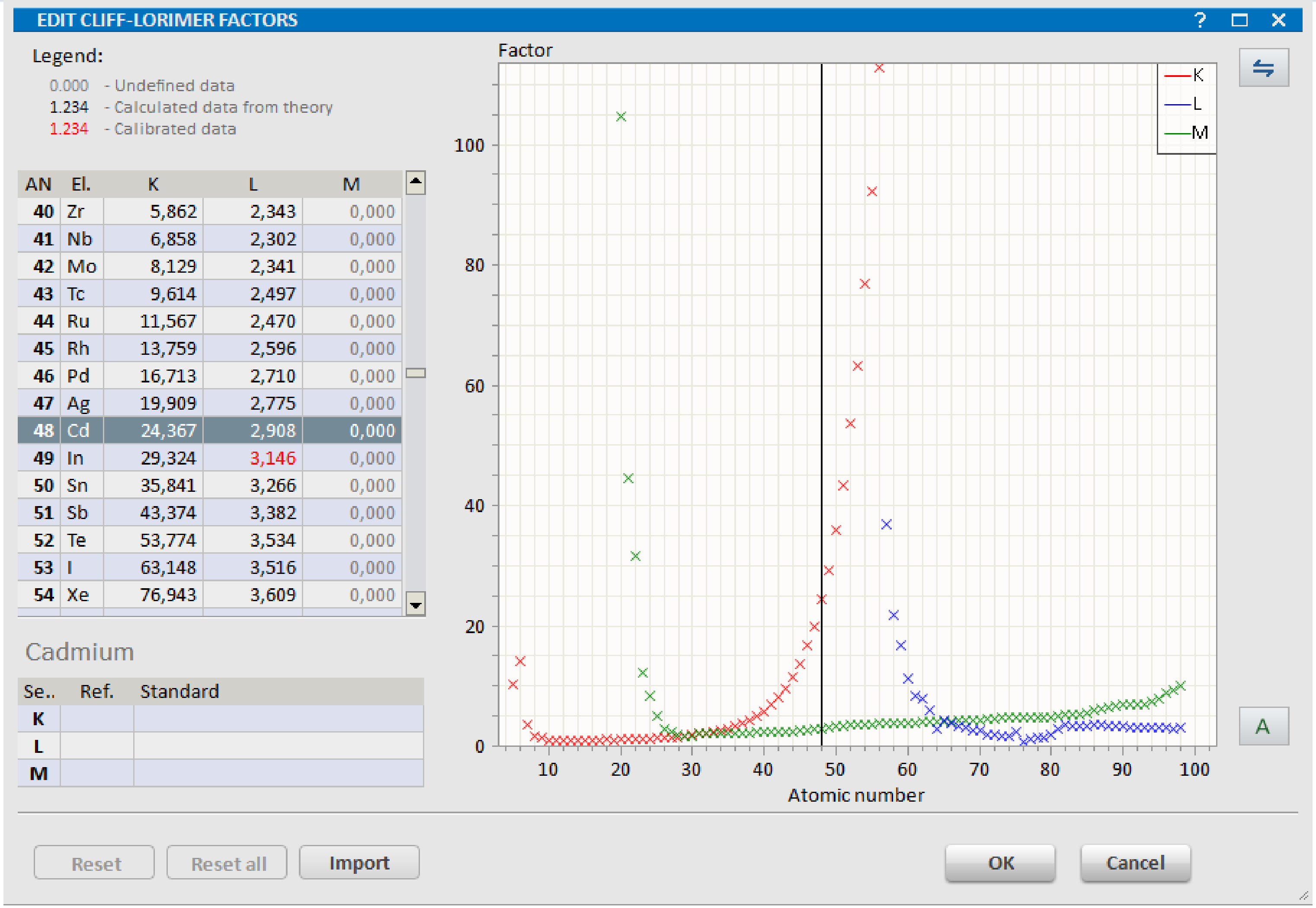
Assign	Element	Mass concentration	Error	Currently assigned to standard

Standard cannot be used for Phi(RhoZ) quantification, because spectrum does not contain system calibration data.
You should calibrate your system in this case.

Check value of Cliff-Lorimer factors:

Assign	Element	Reference	New factor	Old factor
☑	Arsenic	●	2,43329	2,43329
☐	Gold	○	0,00000	4,81637
☑	Indium	○	3,14643	2,90644

Quantification: Cliff-Lorimer factors, Experimentally determined factor in red



Legend:

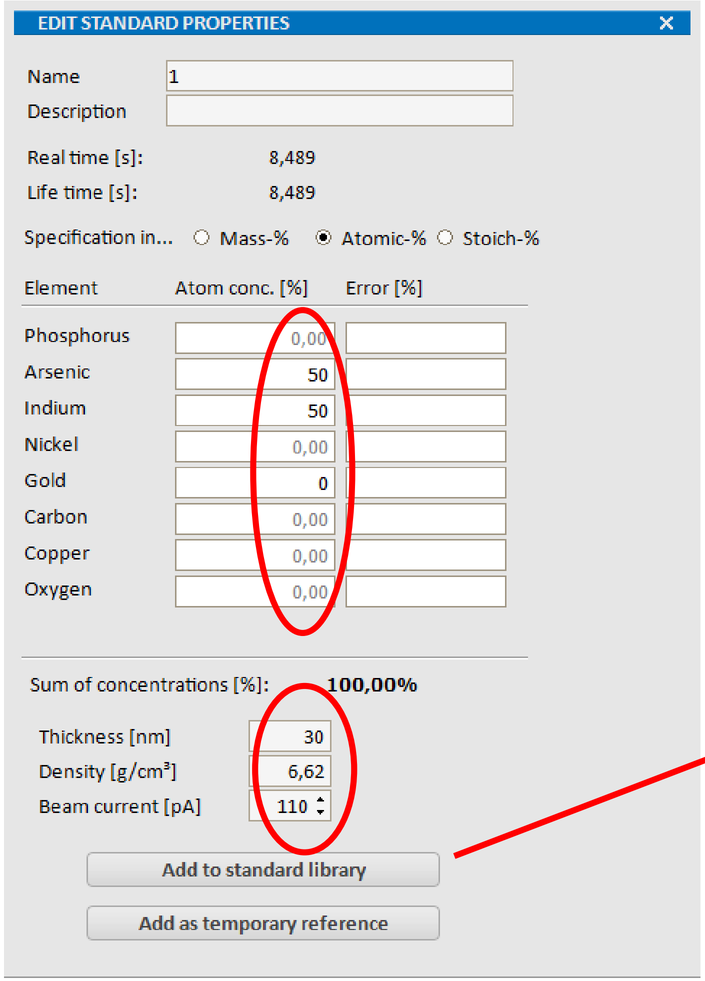
0.000	- Undefined data
1.234	- Calculated data from theory
1.234	- Calibrated data

AN	El.	K	L	M
40	Zr	5,862	2,343	0,000
41	Nb	6,858	2,302	0,000
42	Mo	8,129	2,341	0,000
43	Tc	9,614	2,497	0,000
44	Ru	11,567	2,470	0,000
45	Rh	13,759	2,596	0,000
46	Pd	16,713	2,710	0,000
47	Ag	19,909	2,775	0,000
48	Cd	24,367	2,908	0,000
49	In	29,324	3,146	0,000
50	Sn	35,841	3,266	0,000
51	Sb	43,374	3,382	0,000
52	Te	53,774	3,534	0,000
53	I	63,148	3,516	0,000
54	Xe	76,943	3,609	0,000

Cadmium

Se..	Ref.	Standard
K		
L		
M		

Zeta-factor method: Need beam current and Standard with known c, t, ρ can be calculated or known



EDIT STANDARD PROPERTIES

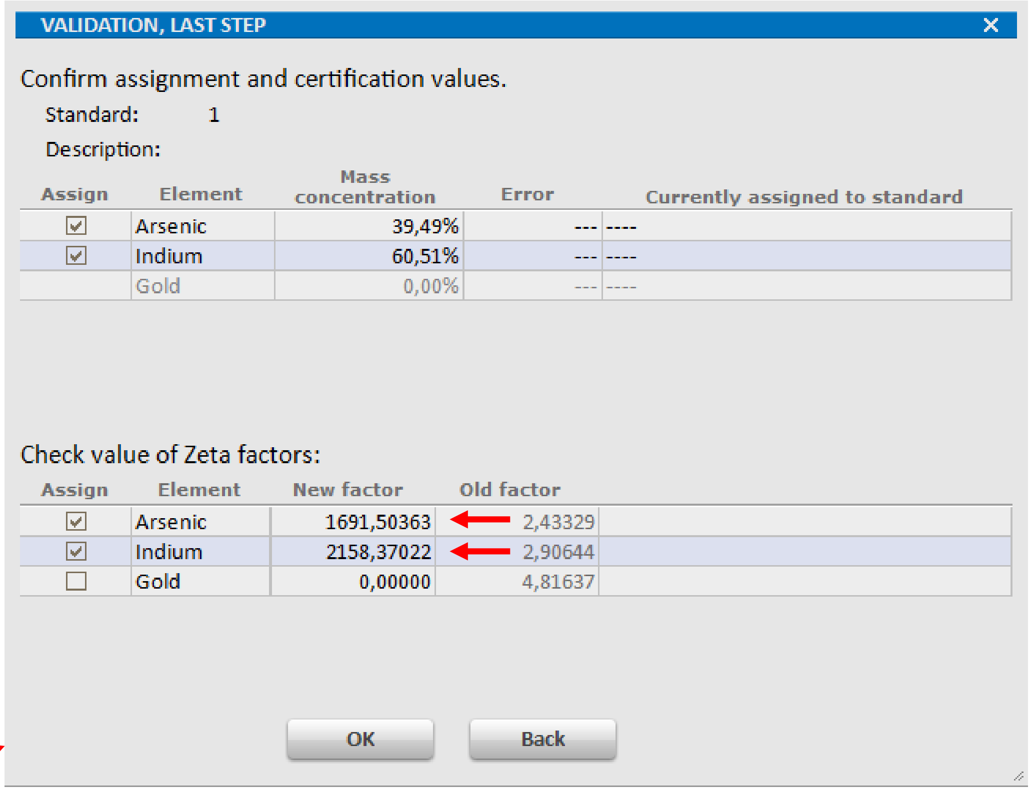
Name	1
Description	
Real time [s]:	8,489
Life time [s]:	8,489

Specification in... ○ Mass-% ● Atomic-% ○ Stoich-%

Element	Atom conc. [%]	Error [%]
Phosphorus	0,00	
Arsenic	50	
Indium	50	
Nickel	0,00	
Gold	0	
Carbon	0,00	
Copper	0,00	
Oxygen	0,00	

Sum of concentrations [%]: **100,00%**

Thickness [nm]	30
Density [g/cm^3]	6,62
Beam current [pA]	110



VALIDATION, LAST STEP

Confirm assignment and certification values.

Standard: 1

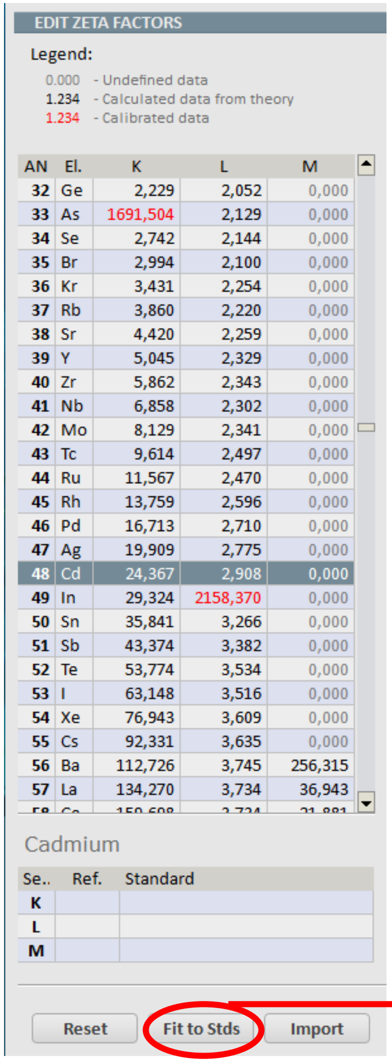
Description:

Assign	Element	Mass concentration	Error	Currently assigned to standard
☑	Arsenic	39,49%	---	----
☑	Indium	60,51%	---	----
	Gold	0,00%	---	----

Check value of Zeta factors:

Assign	Element	New factor	Old factor
☑	Arsenic	1691,50363	2,43329
☑	Indium	2158,37022	2,90644
☐	Gold	0,00000	4,81637

Get all Zeta-factors from the C-L factors

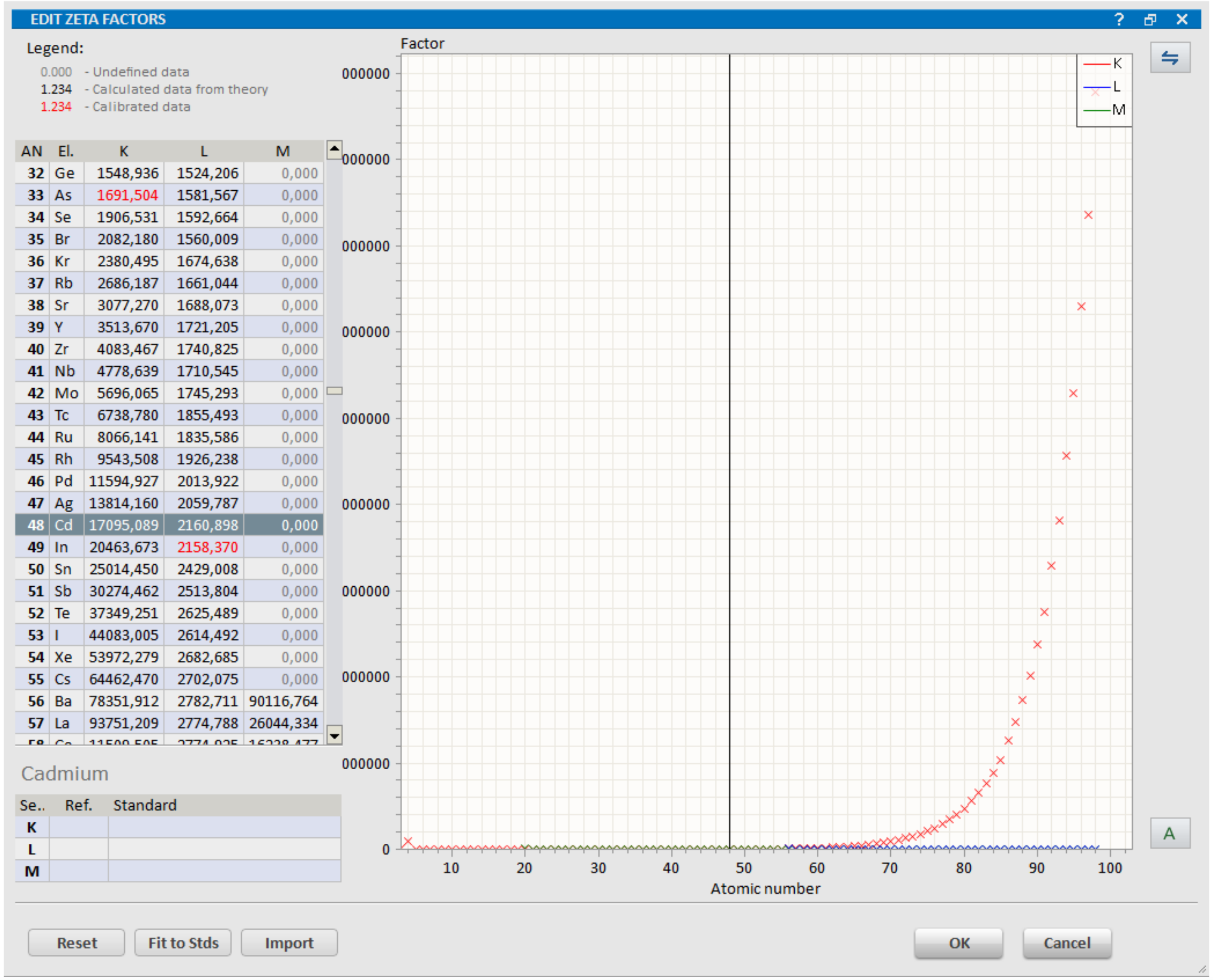


Legend:
0.000 - Undefined data
1.234 - Calculated data from theory
1.234 - Calibrated data

AN	El.	K	L	M
32	Ge	2,229	2,052	0,000
33	As	1691,504	2,129	0,000
34	Se	2,742	2,144	0,000
35	Br	2,994	2,100	0,000
36	Kr	3,431	2,254	0,000
37	Rb	3,860	2,220	0,000
38	Sr	4,420	2,259	0,000
39	Y	5,045	2,329	0,000
40	Zr	5,862	2,343	0,000
41	Nb	6,858	2,302	0,000
42	Mo	8,129	2,341	0,000
43	Tc	9,614	2,497	0,000
44	Ru	11,567	2,470	0,000
45	Rh	13,759	2,596	0,000
46	Pd	16,713	2,710	0,000
47	Ag	19,909	2,775	0,000
48	Cd	24,367	2,908	0,000
49	In	29,324	2158,370	0,000
50	Sn	35,841	3,266	0,000
51	Sb	43,374	3,382	0,000
52	Te	53,774	3,534	0,000
53	I	63,148	3,516	0,000
54	Xe	76,943	3,609	0,000
55	Cs	92,331	3,635	0,000
56	Ba	112,726	3,745	256,315
57	La	134,270	3,734	36,943

Cadmium

Se..	Ref.	Standard
K		
L		
M		



Legend:
0.000 - Undefined data
1.234 - Calculated data from theory
1.234 - Calibrated data

AN	El.	K	L	M
32	Ge	1548,936	1524,206	0,000
33	As	1691,504	1581,567	0,000
34	Se	1906,531	1592,664	0,000
35	Br	2082,180	1560,009	0,000
36	Kr	2380,495	1674,638	0,000
37	Rb	2686,187	1661,044	0,000
38	Sr	3077,270	1688,073	0,000
39	Y	3513,670	1721,205	0,000
40	Zr	4083,467	1740,825	0,000
41	Nb	4778,639	1710,545	0,000
42	Mo	5696,065	1745,293	0,000
43	Tc	6738,780	1855,493	0,000
44	Ru	8066,141	1835,586	0,000
45	Rh	9543,508	1926,238	0,000
46	Pd	11594,927	2013,922	0,000
47	Ag	13814,160	2059,787	0,000
48	Cd	17095,089	2160,898	0,000
49	In	20463,673	2158,370	0,000
50	Sn	25014,450	2429,008	0,000
51	Sb	30274,462	2513,804	0,000
52	Te	37349,251	2625,489	0,000
53	I	44083,005	2614,492	0,000
54	Xe	53972,279	2682,685	0,000
55	Cs	64462,470	2702,075	0,000
56	Ba	78351,912	2782,711	90116,764
57	La	93751,209	2774,788	26044,334

Cadmium

Se..	Ref.	Standard
K		
L		
M		

Left counts, right quantified;
Line Scan > Line Profile

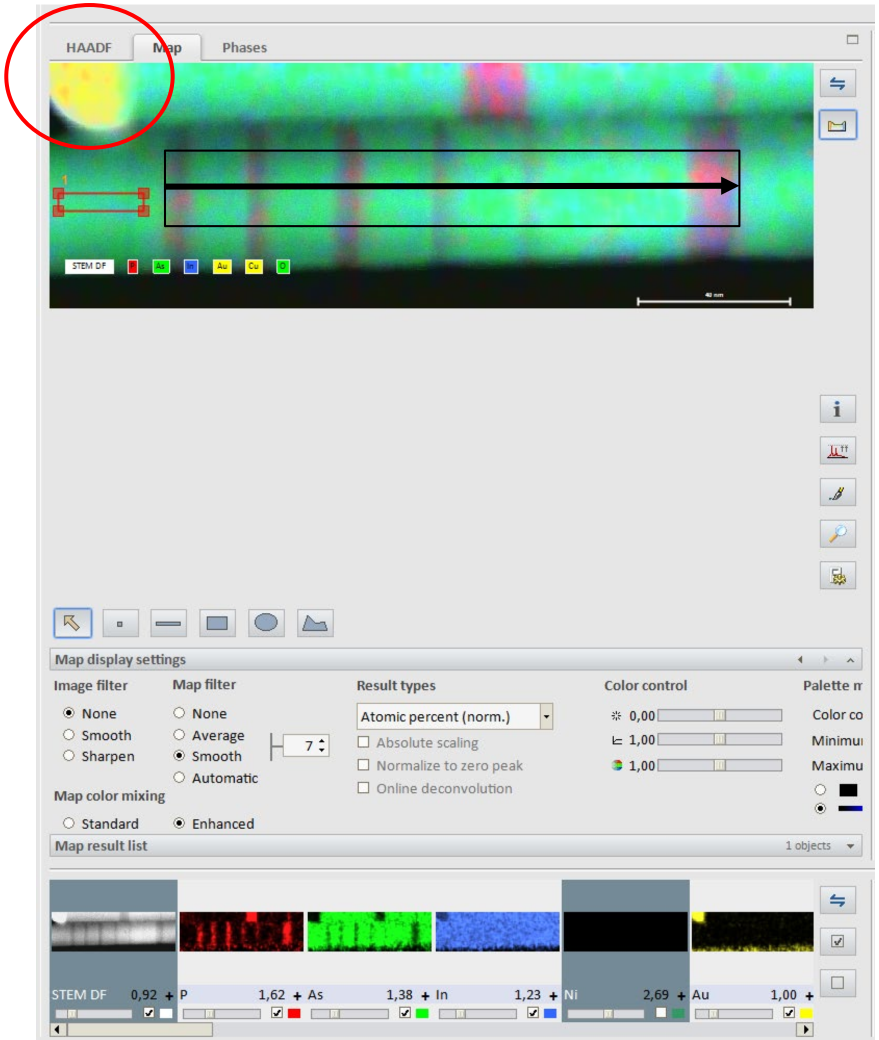
Widen the line scan + moving average along line scan

Map display settings

- Image filter: ● None ○ Smooth ○ Sharpen
- Map filter: ○ None ○ Average ● Smooth ○ Automatic; 7
- Result types: Counts
  - ☐ Absolute scaling
  - ☐ Normalize to zero peak
  - ☐ Online deconvolution
- Color control: 0,00; 1,00; 1,00
- Map color mixing: ○ Standard ● Enhanced

Map result list — 1 objects

STEM DF	P-Kα	As-Kα	In-Lα	Ni-Kα	Au-Lα
0,92	0,85	1,38	1,23	2,69	1,00



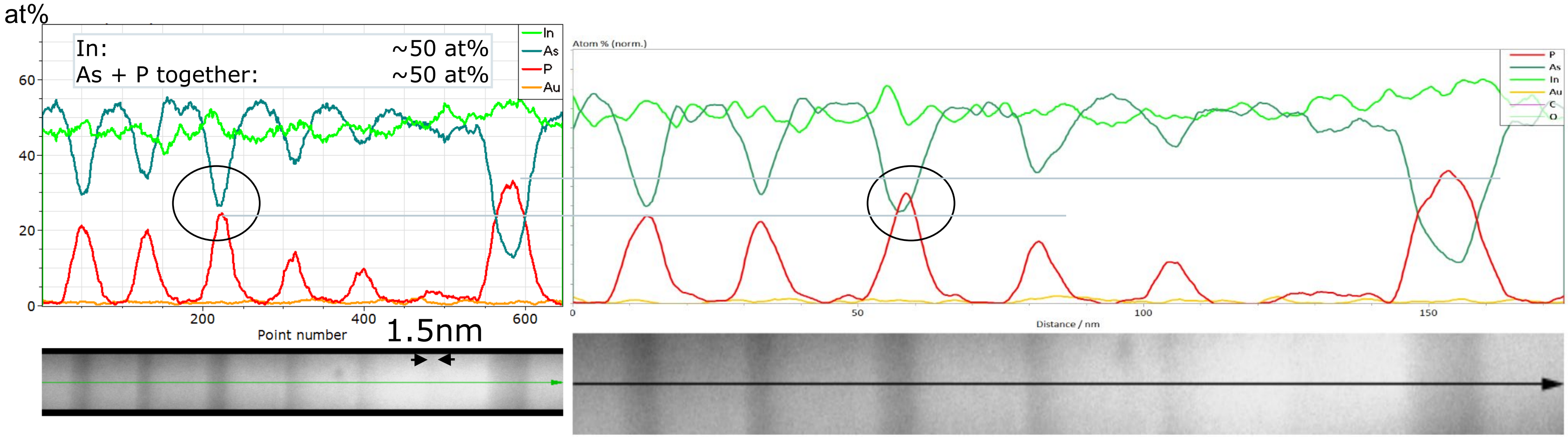
Map display settings

- Image filter: ● None ○ Smooth ○ Sharpen
- Map filter: ○ None ○ Average ● Smooth ○ Automatic; 7
- Result types: Atomic percent (norm.)
  - ☐ Absolute scaling
  - ☐ Normalize to zero peak
  - ☐ Online deconvolution
- Color control: 0,00; 1,00; 1,00
- Map color mixing: ○ Standard ● Enhanced

Map result list — 1 objects

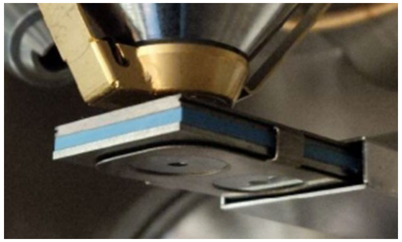
STEM DF	P	As	In	Ni	Au
0,92	1,62	1,38	1,23	2,69	1,00

Left C-L, right Zeta-factor method:
C-L underestimates P content

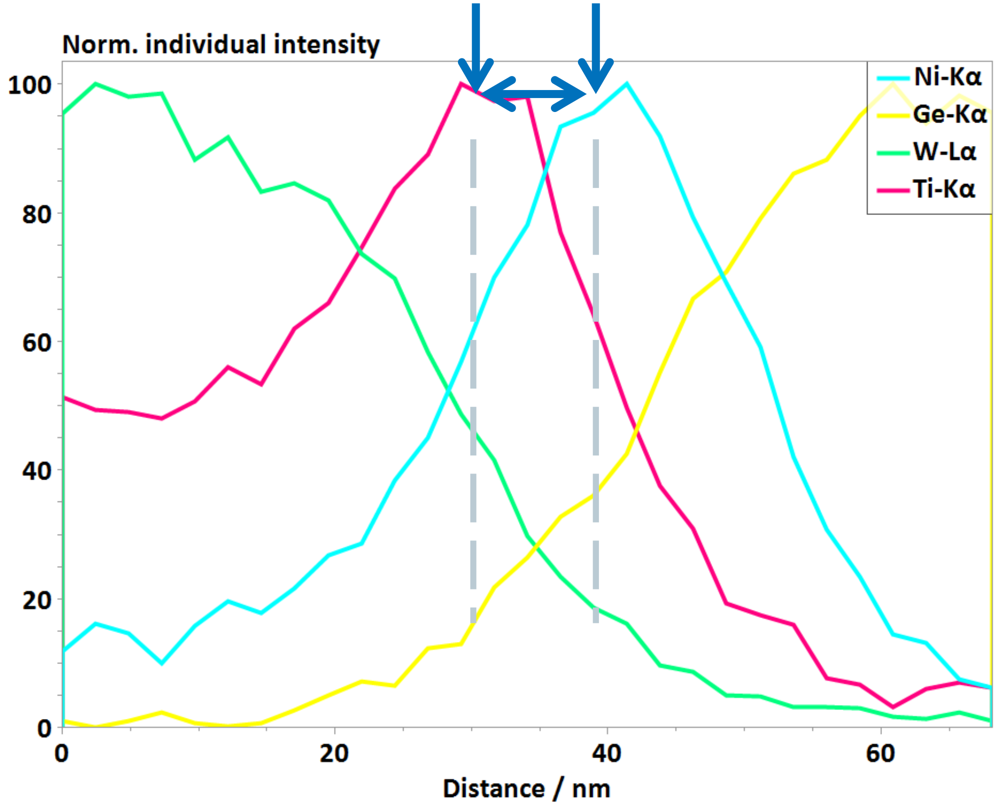


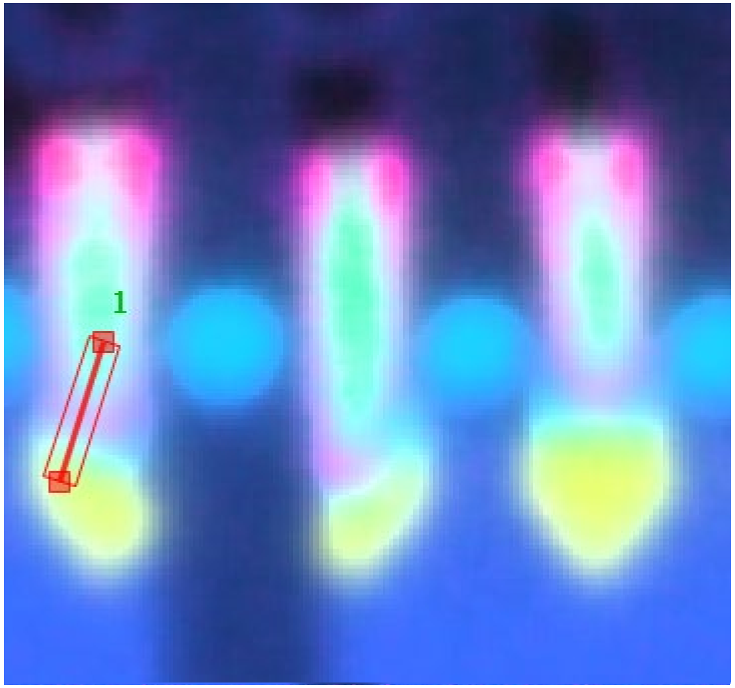
- The Zeta-factor method is particularly helpful in case of light/heavy element mixtures
- Cliff-Lorimer also offers some absorption correction suitable for K-lines
- Both are precise within few at% depending on materials
  - C-L measures relative within one sample series under same conditions
  - Zeta measures absolute values, beam current must be stable and standard well known

T-SEM EDS;
Semiconductor Structure:
Line Scan as well



10 nm lateral resolution of Ni and Ti distribution maxima





Extracted linescan from the map data
Effective measurement time of lineprofile: 8 s

SDD (30mm^2, ~0.1sr) on Cs-corrected JEOL 2100 STEM

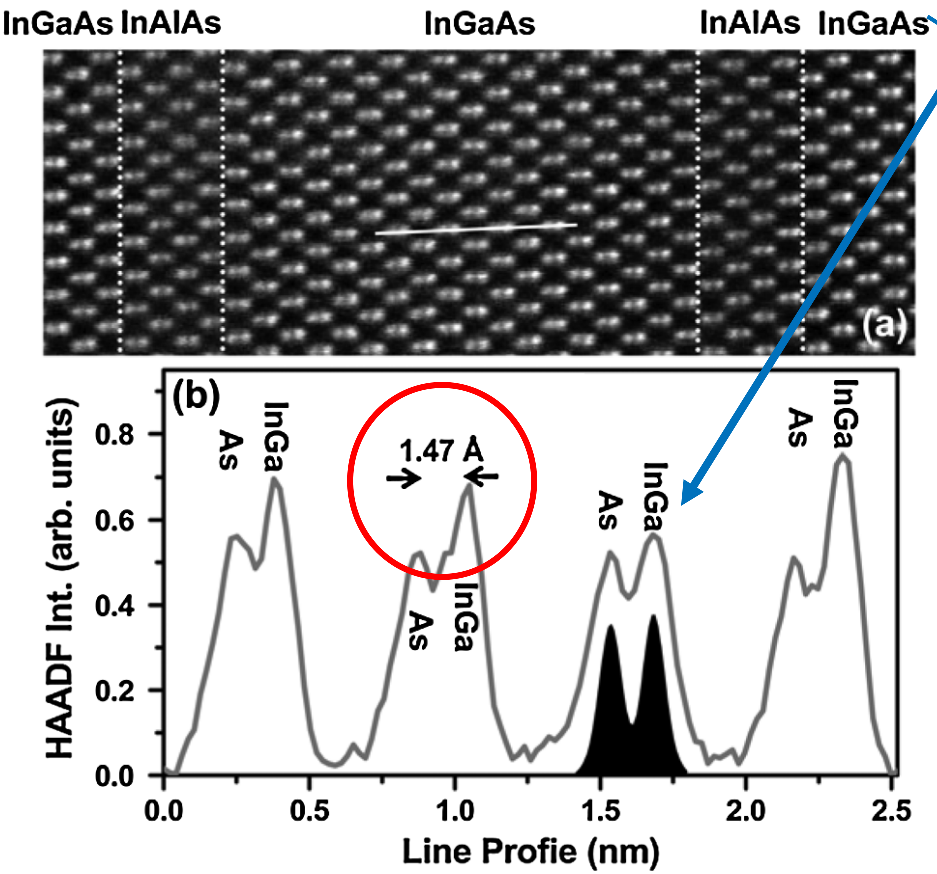
First Atom Column Mapping with SDD

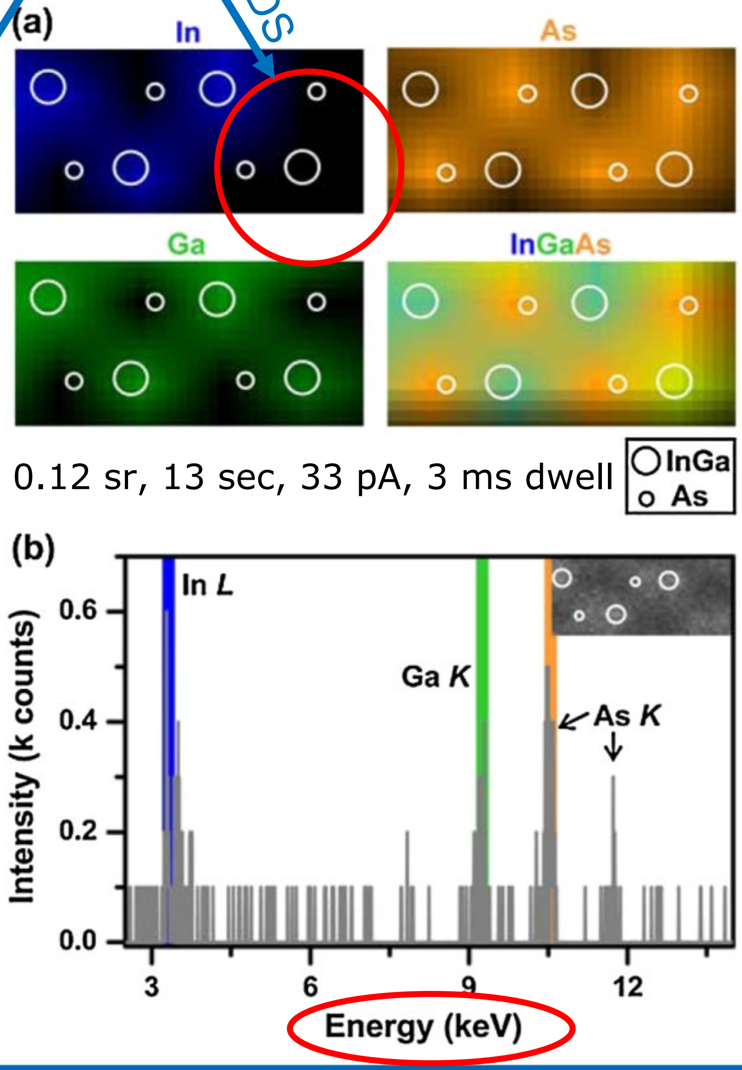
Indium missing in one atomic column

Forbes, … Mc Comb et al.: Simulation needed, to correctly interpret atom column EDS!

HAADF signal

EDS

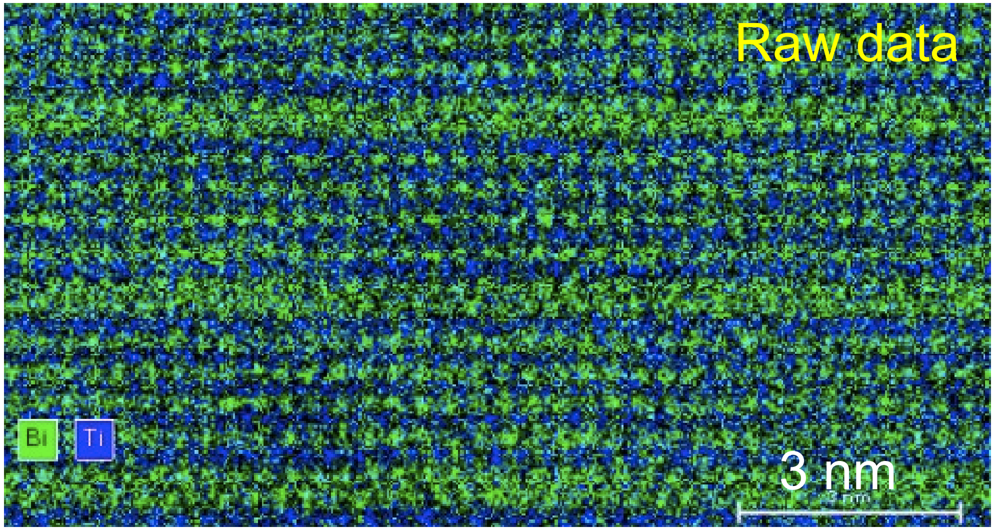


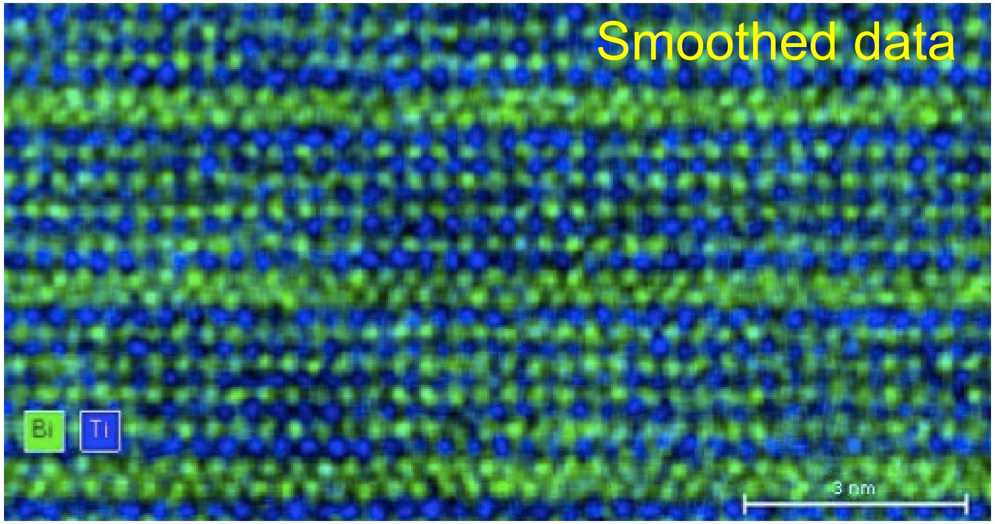


0.12 sr, 13 sec, 33 pA, 3 ms dwell

M. W. Chu et al., Phys. Rev. Lett. 104, 196101 (2010)

Columns: easier than single atom ID: EDXS Mapping of $Bi_6Ti_xFe_yMn_zO_{18}$





TCD (Trinity College Dublin) Nion UltraSTEM200XE 200 kV with Bruker 100 mm^2 X-Flash SD detector, 100 mm^2 windowless SDD; 0.7 sr collection angle.

432x225 pixels, 4.1 msec/pix => 400 sec for map.

No drift correction.
Bi = green, Ti = blue.

courtesy Lynette Keeney, Clive Downing and Valeria Nicolosi. TCD, Ireland.

Atom column EDS needs simulation for correct interpretation
B. D. Forbes et al., PHYSICAL REVIEW B **86**, 024108 (2012)

L. Keeney et al., Scientific Reports 7, Article number: 1737 (2017)

Summary;
EDS for electron transparent samples

- Electron transparent samples can be analysed in TEM and SEM.
- Geometry must be determined completely to understand or avoid, if possible, systematic errors.
- Careful analysis allows to determine most systematic errors.
- The Zeta-factor method delivers absorption correction and thickness determination, density and thickness are still difficult to disentangle > combine with EELS.
- Atom column EDS needs theory support to account for channeling and cross talk between columns.
- **Use EDS to it‘s full potential**, just element ID is not satisfactory!

EDS Quantification of electron transparent samples in TEM, STEM and T-SEM

Q & A

BRUKER

Innovation with Integrity