QUANTAX WDS

In-situ light element determination using WDS for SEM

Bruker Nano Analytics, Berlin, Germany

11 May 2022

Presenters

Dr. Ralf Terborg
Sr. Scientist,
Bruker Nano Analytics, Berlin, Germany

Dr. Michael Abratis
Sr. Applications Scientist WDS,
Bruker Nano Analytics, Berlin, Germany

Outline

01 Challenges with light element analysis

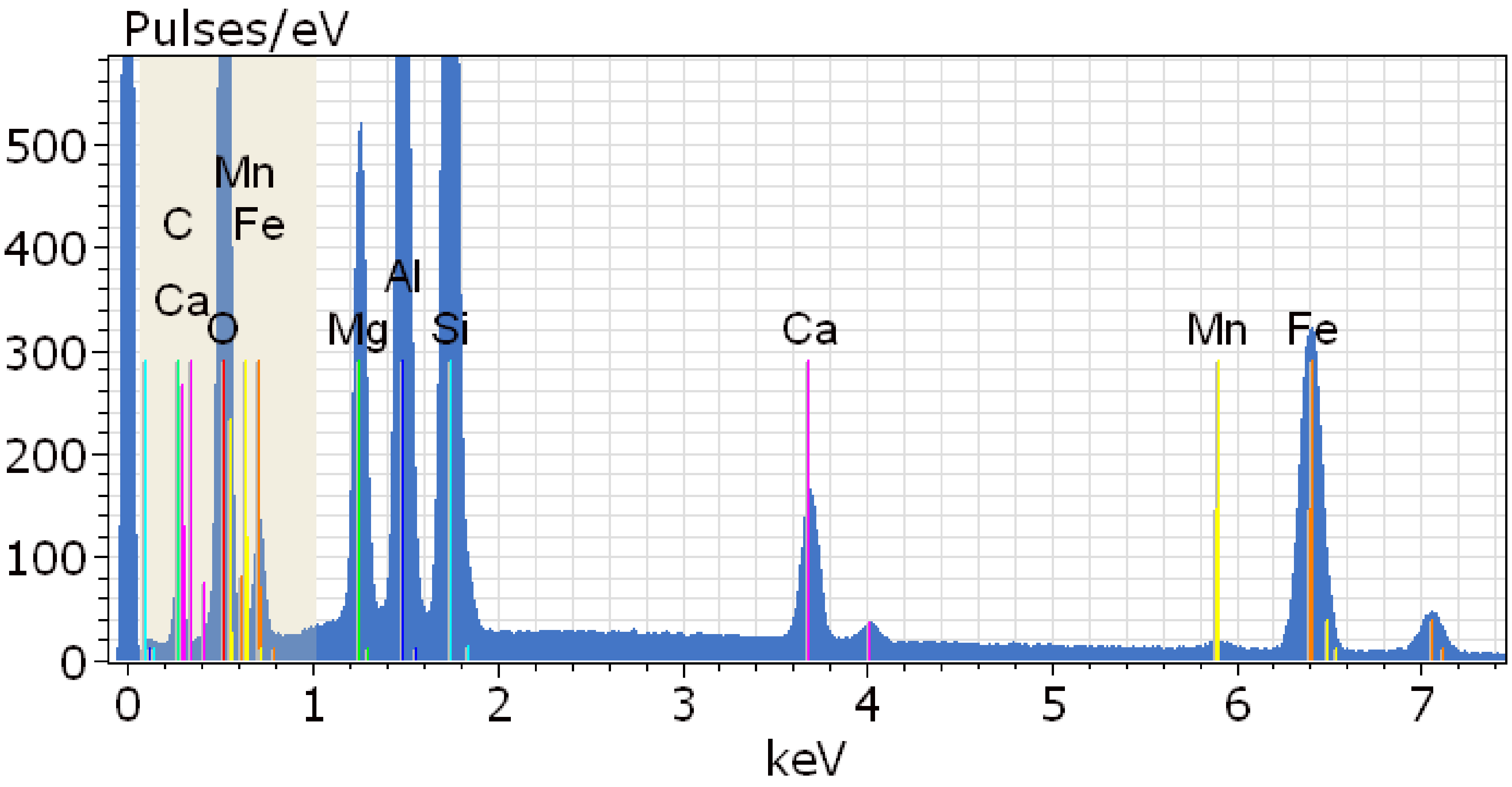
02 QUANTAX WDS solution for SEM

03 Applications examples on Be, B, C, N and O (incl. workflows)

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Challenges with light element analysis

Definition low energy range and light elements

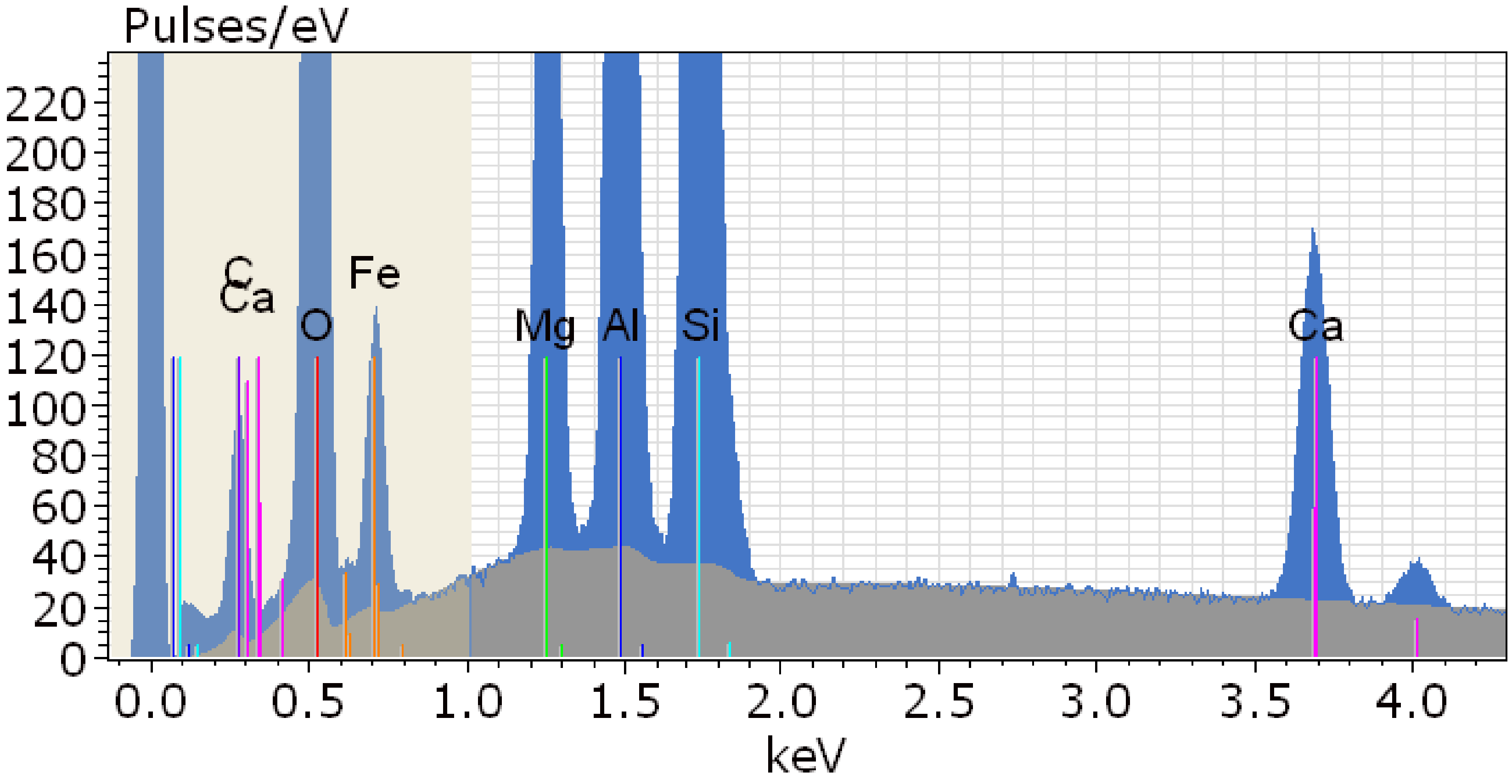


Almandine Garnet: $Fe_3Al_2Si_3O_{12}$ (+ Mg, Ca,…)

HV=20 kV

- Low energy range: E < 1keV
- Light elements Z<11: (Li, 54eV), Be (108eV), B, C, N, O, F (676eV)

Low energy range

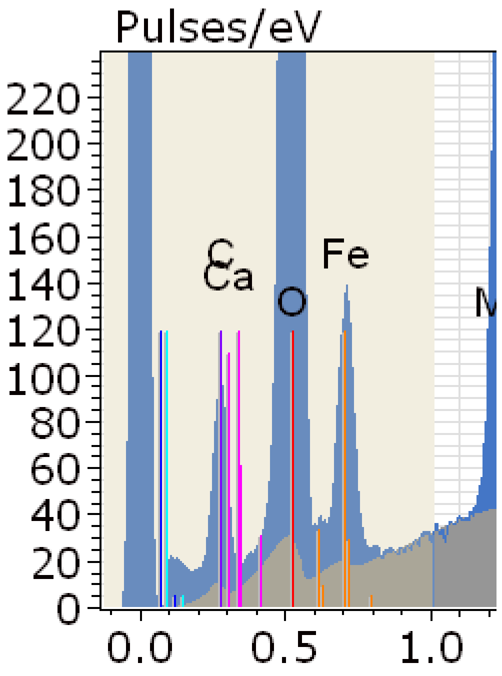


Almandine Garnet: $Fe_3Al_2Si_3O_{12}$ (+ Mg, Ca,…) HV=20 kV

- For E ≥ 1keV the background is clearly defined

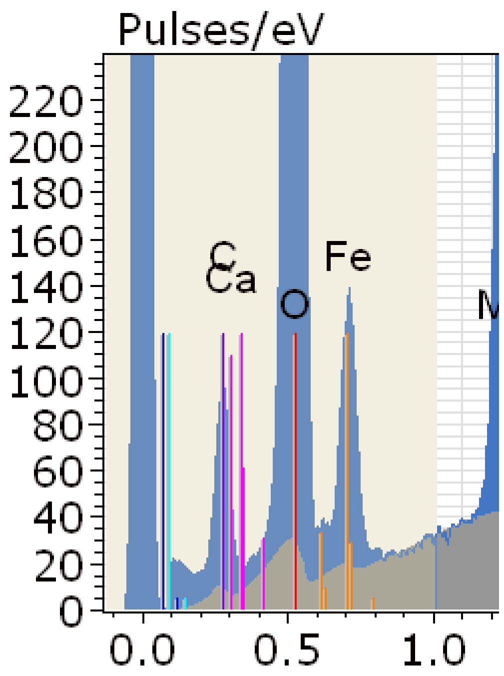
Low energy range

- for E ≥ 1keV the background is clearly defined
- for E < 1keV the background calculation is difficult:
  - BG is lower → errors due to statistical noise
  - high absorption edges, variations in TOA influence low energy BG shape
- high line density → overlap likely, determination of peak free areas difficult, especially for EDS



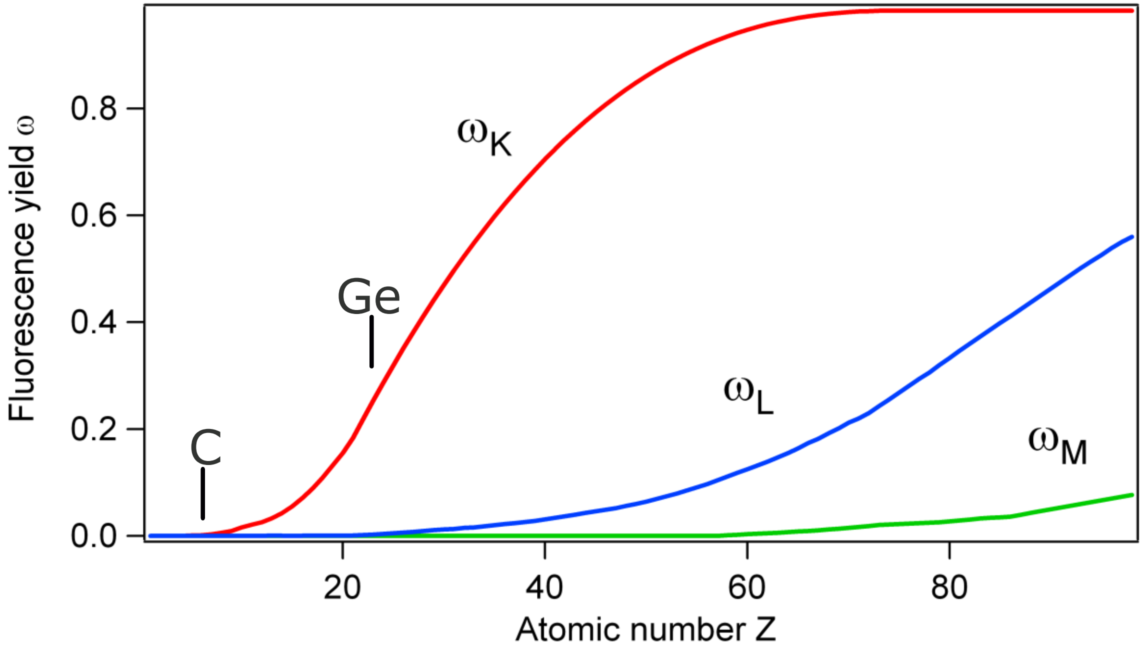
Parameters which are important for light element quantification

- Fluorescence yield of element
- Quantum efficiency ε of detector at the line energy
- Absorption of line



Fluorescence yield and quantum efficiency

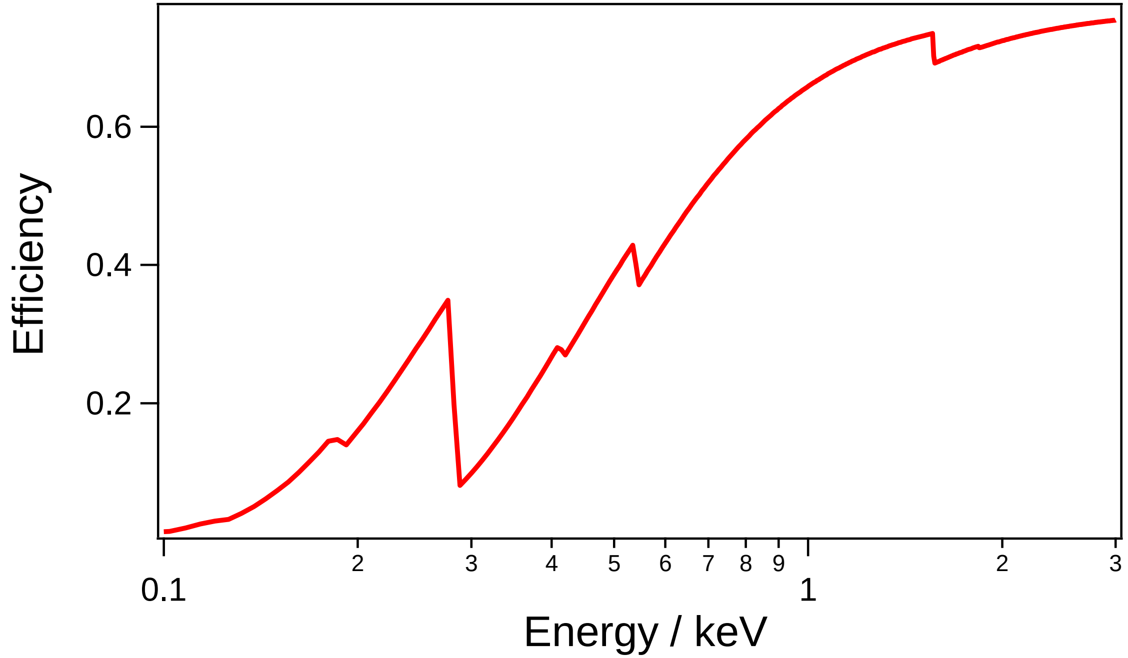
- Fluorescence yield (ω):



Fluorescence yield (ω):

$$\omega_K = \frac{\#K\ photons\ produced}{\#K - shell\ ionizations}$$

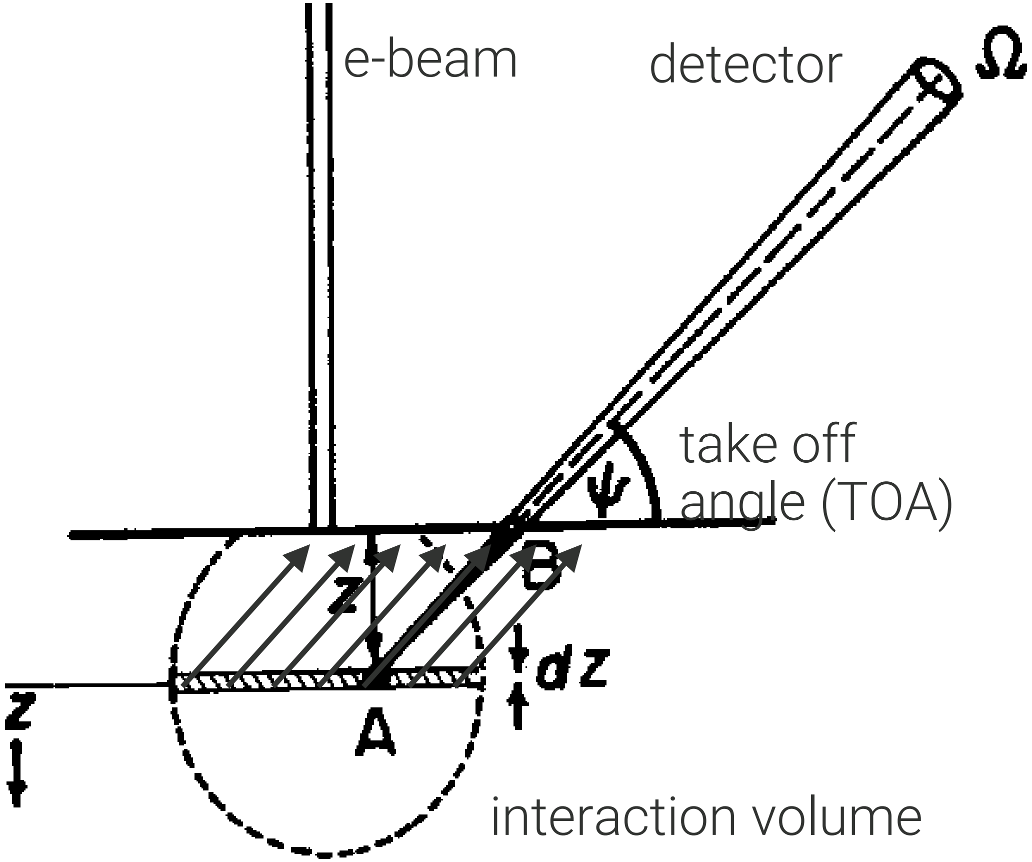
- Quantum efficiency of EDS



$$\varepsilon = \frac{\#\text{ detected x-rays}}{\#\text{ incoming x-rays}}$$

Absorption effect

- X-rays which are excited at a certain depth z will be partly absorbed on their way to sample surface



$$f_A = \frac{\#\text{ x-rays leaving sample}}{\#\text{ generated x-rays}}$$

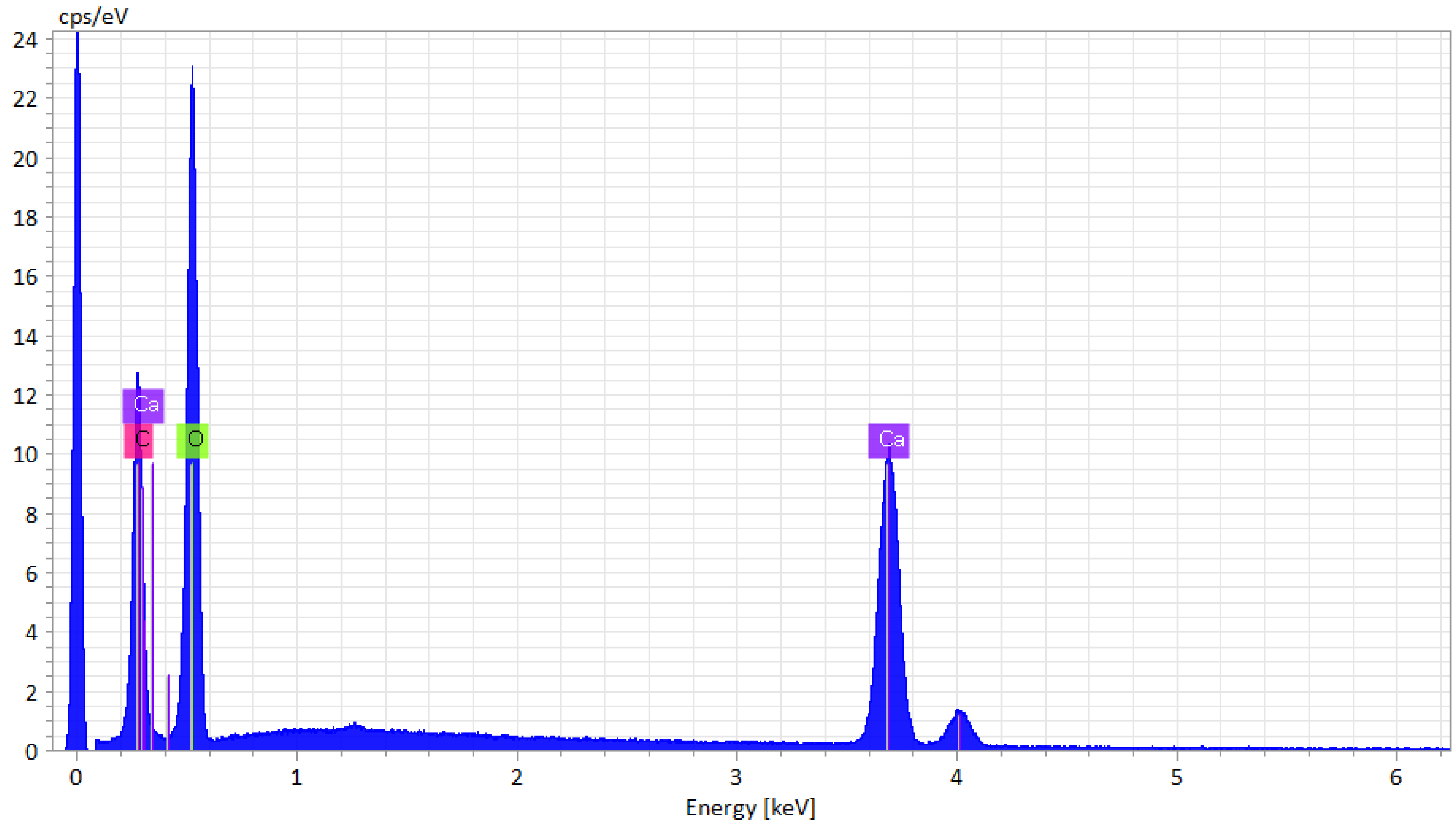
$f_A = 1$: no absorption

$f_A = 0.1$: 90% absorption

f_A depends on path length
→ TOA
→ HV (mean depth)

Absorption effect of Ca, C and O in $CaCO_3$

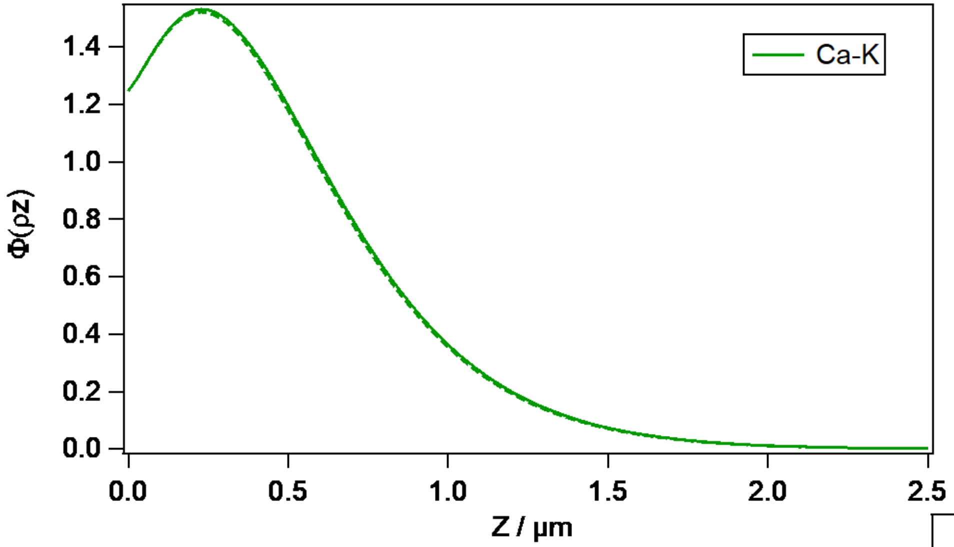
- $\Phi(\rho z)$ curves (generated/emitted) need to be used.



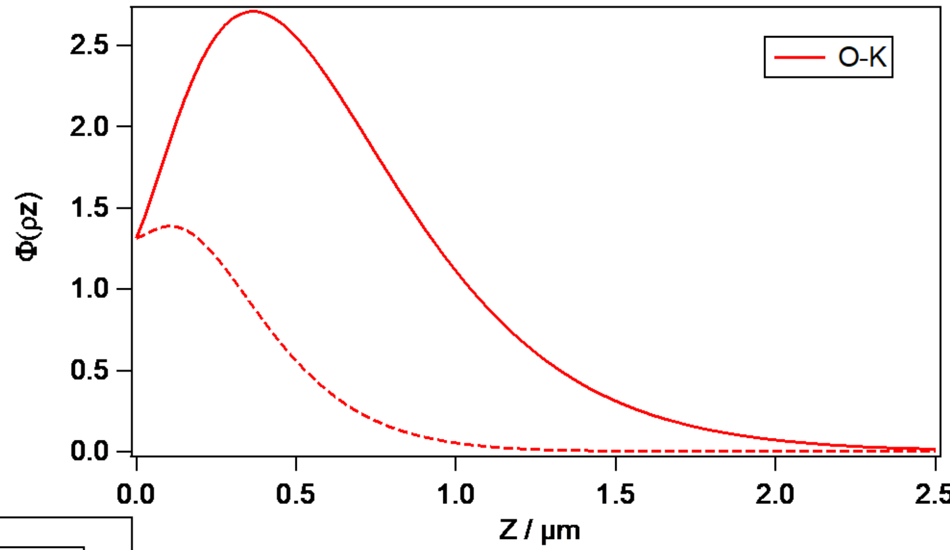
$CaCO_3$, 10kV

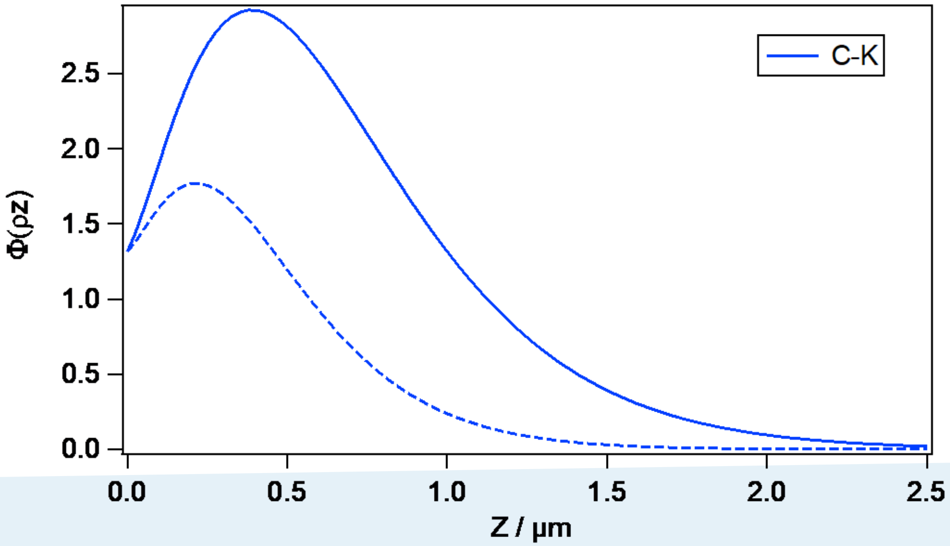
Absorption effect of Ca, C and O in $CaCO_3$

- Φ(ρz) curves (generated /emitted) need to be used.



Generated radiation
Emitted radiation





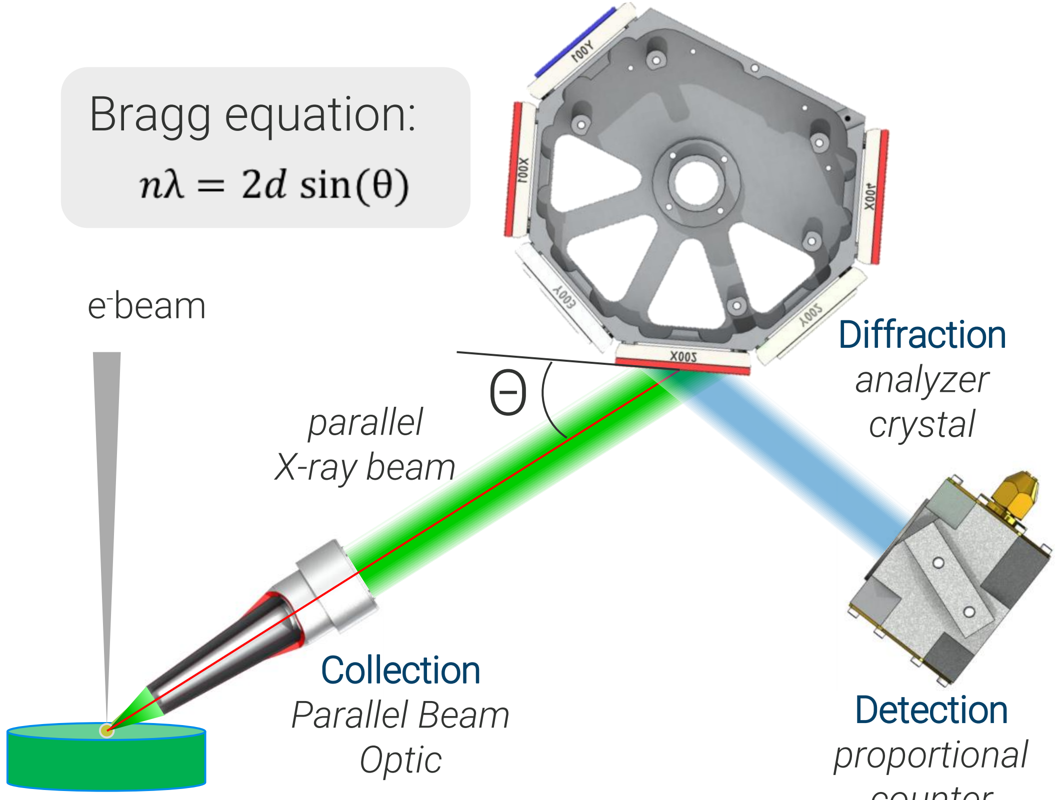
QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

QUANTAX WDS – technique and applications

Working principle of QUANTAX WDS

Bragg equation:

$$n\lambda = 2d\,\sin(\theta)$$



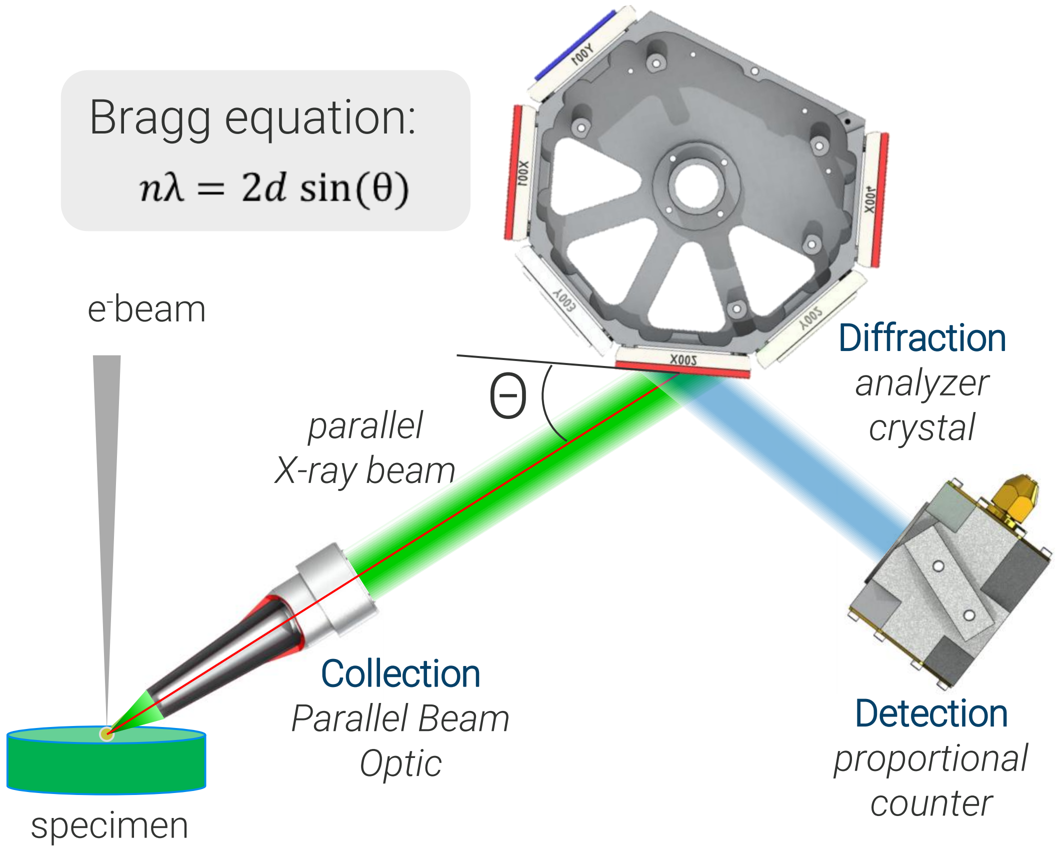
QUANTAX WDS

➡ QUANTAX WDS uses Bragg spectrometer and Parallel Beam Optic (PBO)

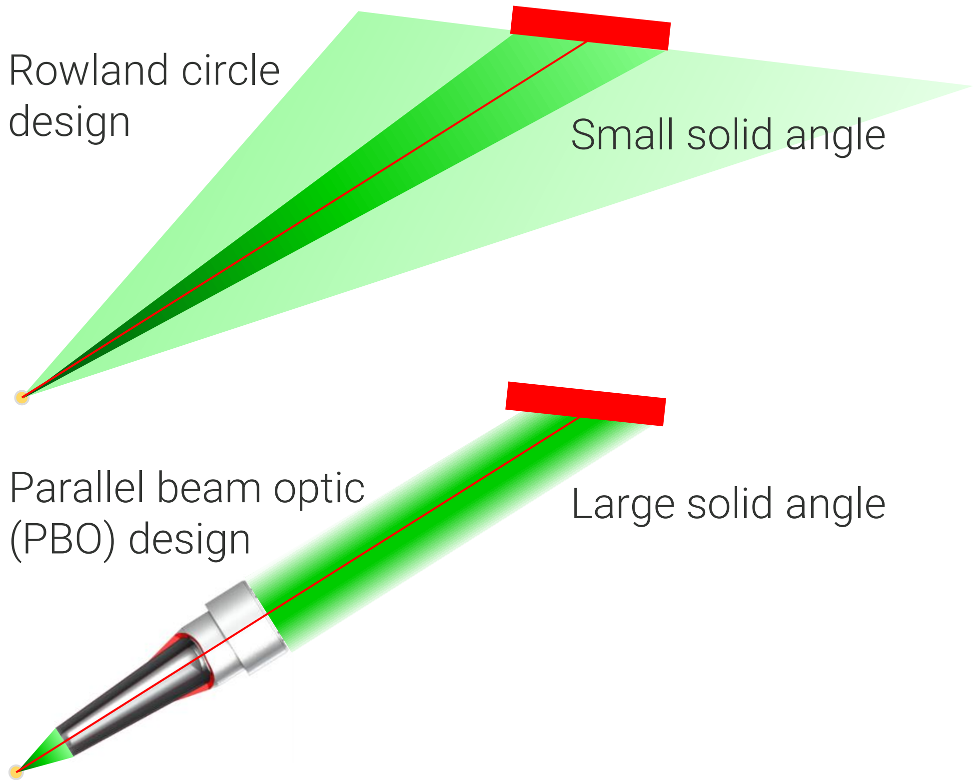
Working principle of QUANTAX WDS

Bragg equation:

$$n\lambda = 2d\sin(\theta)$$



Different WDS configurations

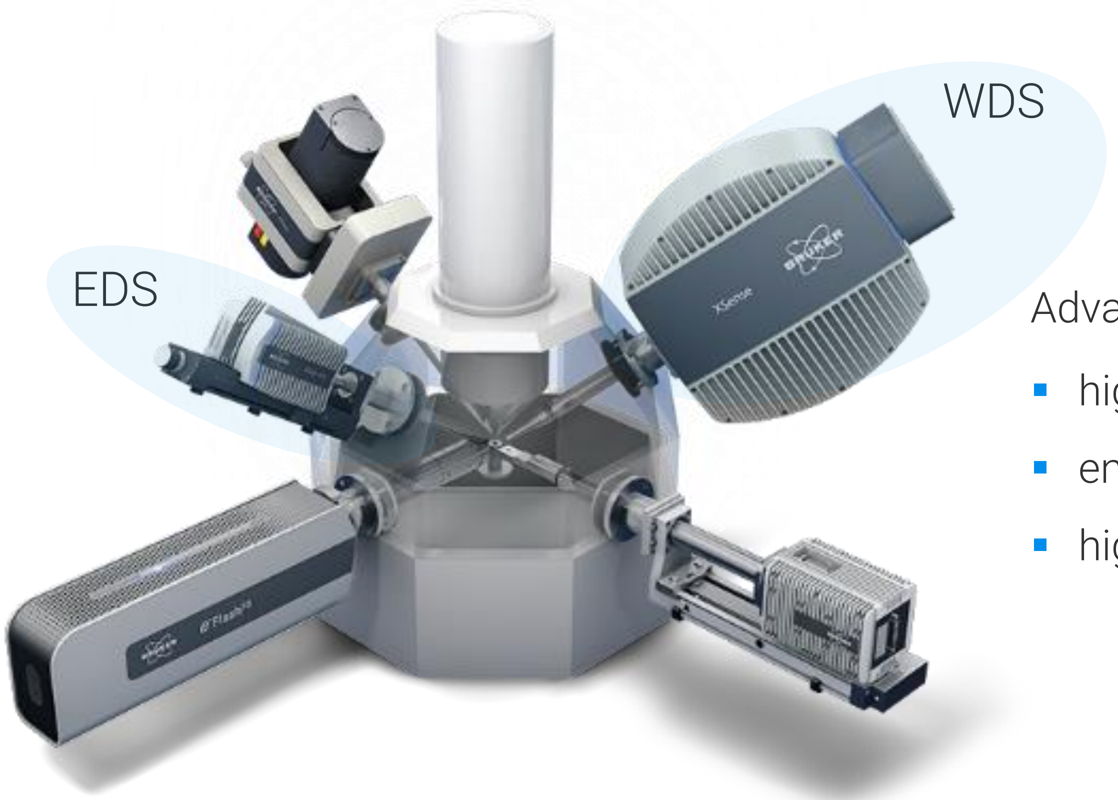


Large solid angle with PBO results in high sensitivity for low X-ray energies

Advantages of combining QUANTAX WDS and QUANTAX EDS

Advantages of EDS:

- fast results
- simultaneous detection
- low beam currents

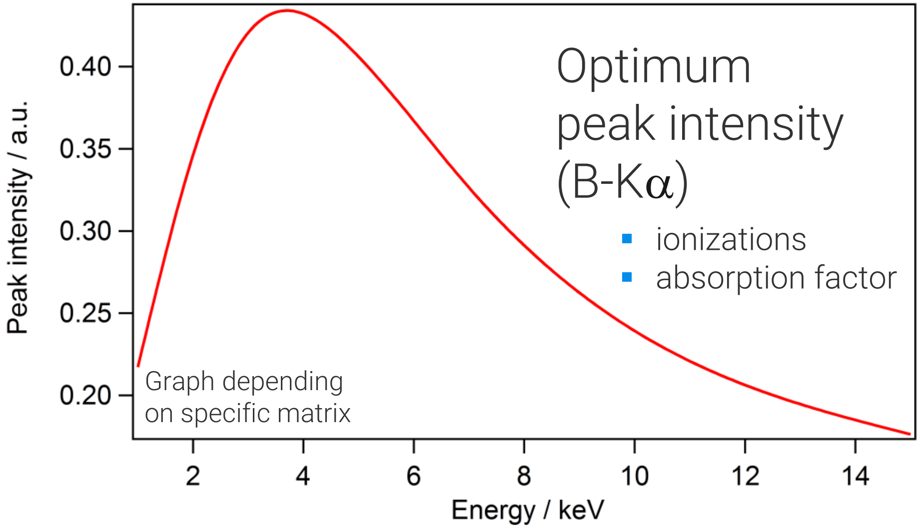


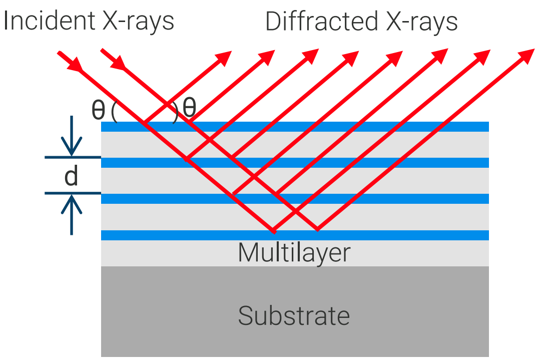
Advantages of WDS:

- higher spectral resolution
- enhanced P/B-ratios, i.e. lower LOD
- higher sensitivity for light elements

→ WDS is an ideal technique to complement EDS in challenging applications

Analytical conditions for light elements



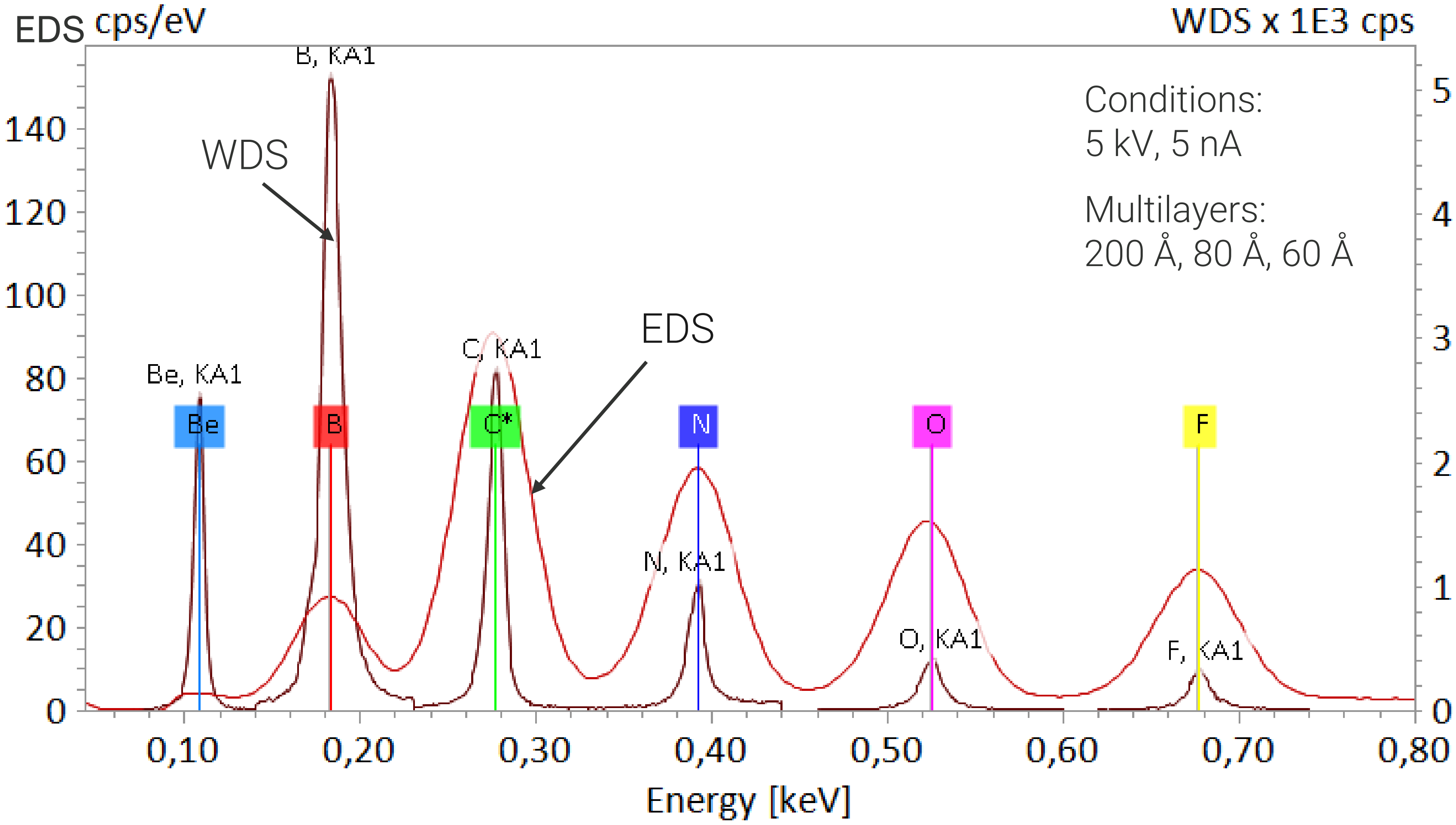


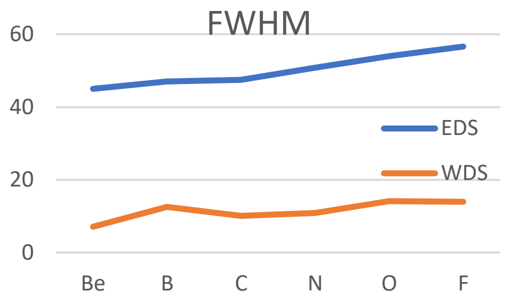
Multilayer mirror

Bragg equation:
$n\lambda = 2d\,\sin(\theta)$

Typical parameters	
High voltage	5 kV
Beam current	5 nA
Monochromators	Multilayer 200, 80, 60
Standards	close to sample composition
Acquisition time Range	1 s (per step)
Acquisition time P/B	60 s (peak time)
Acquisition time Map	300 s (per element)

Light element spectra acquired by EDS and WDS





Samples:

Pure elements: Be, C and compounds: BN, SiO_2 CaF_2

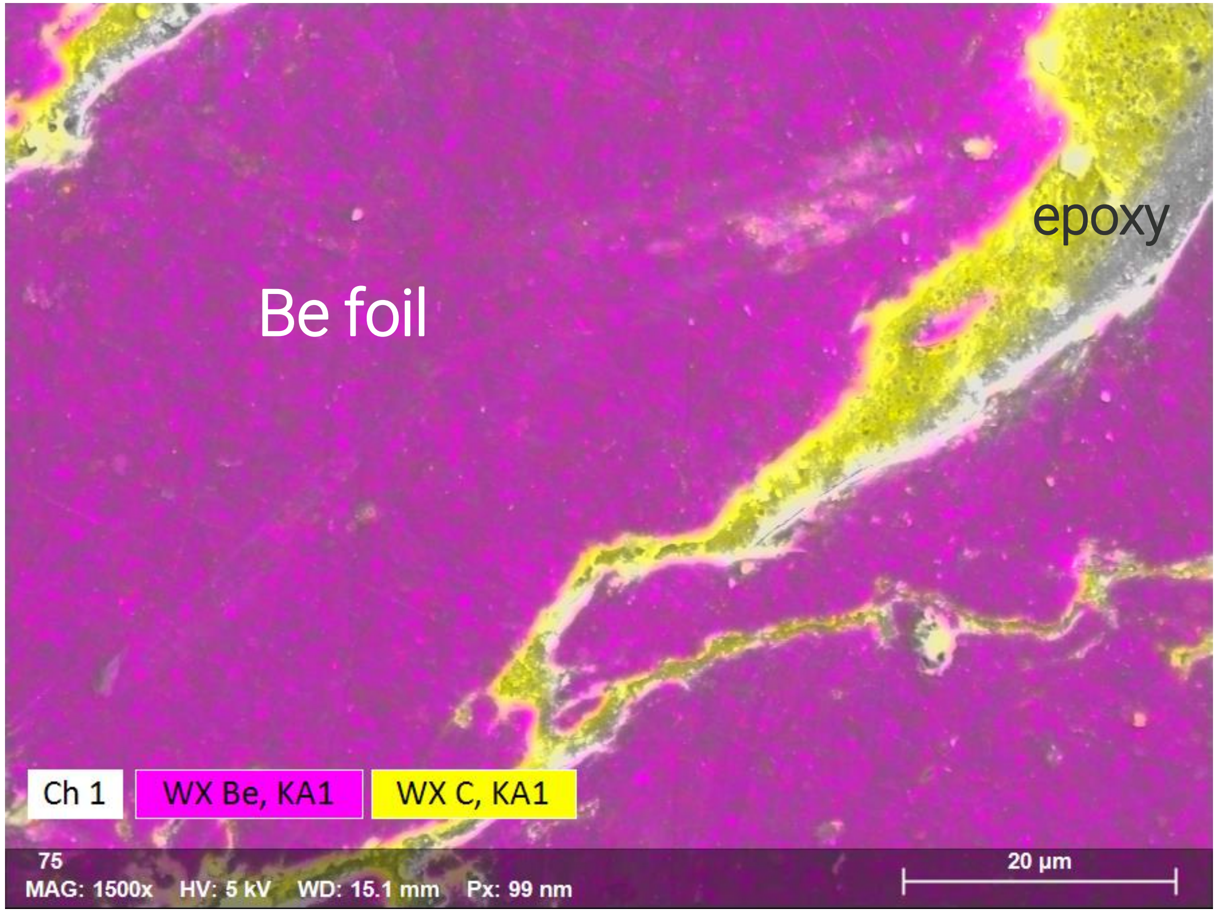
WDS shows higher sensitivity, higher peak/background ratios and better spectral resolution

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Beryllium

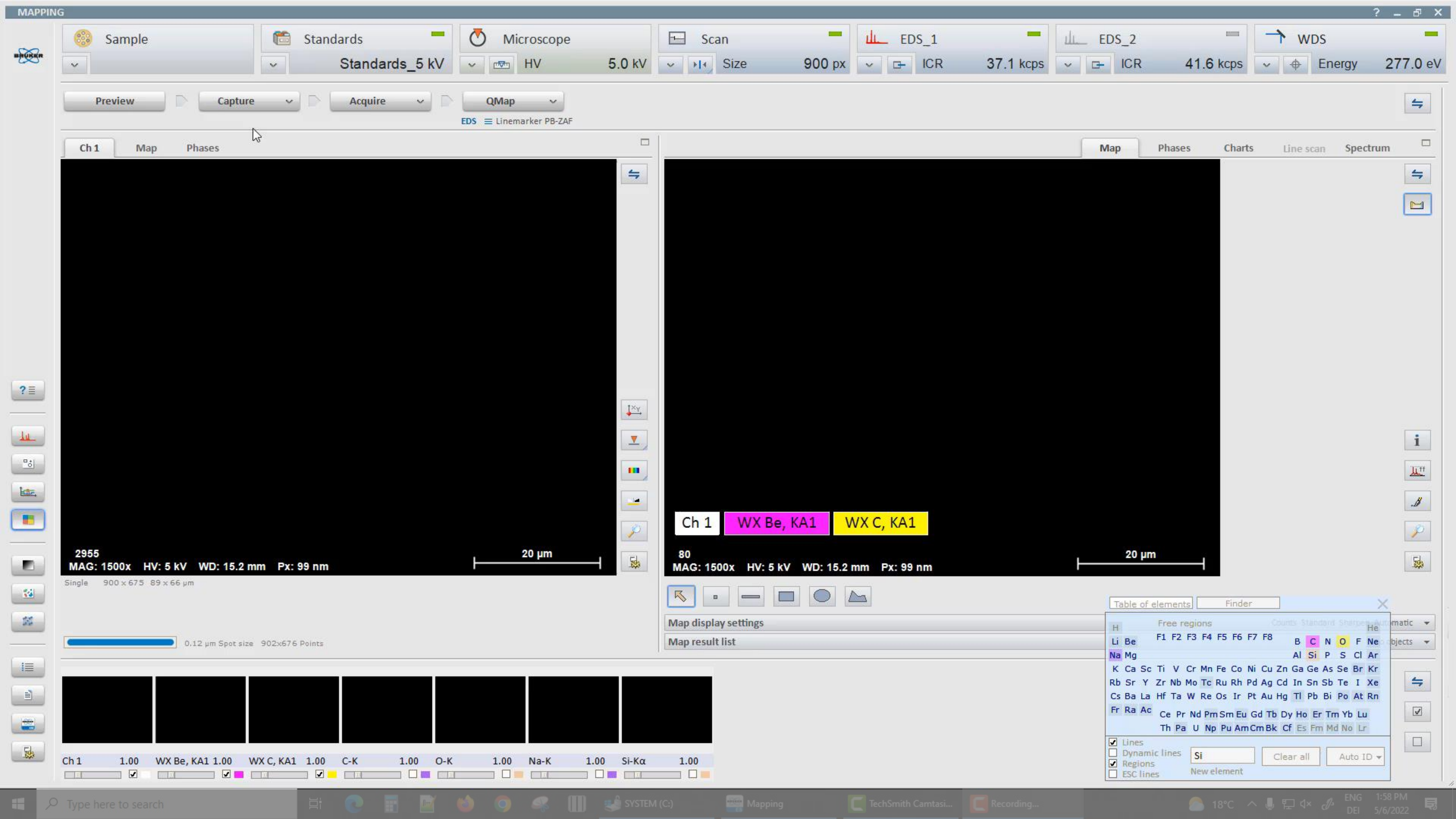
WDS mapping of Beryllium

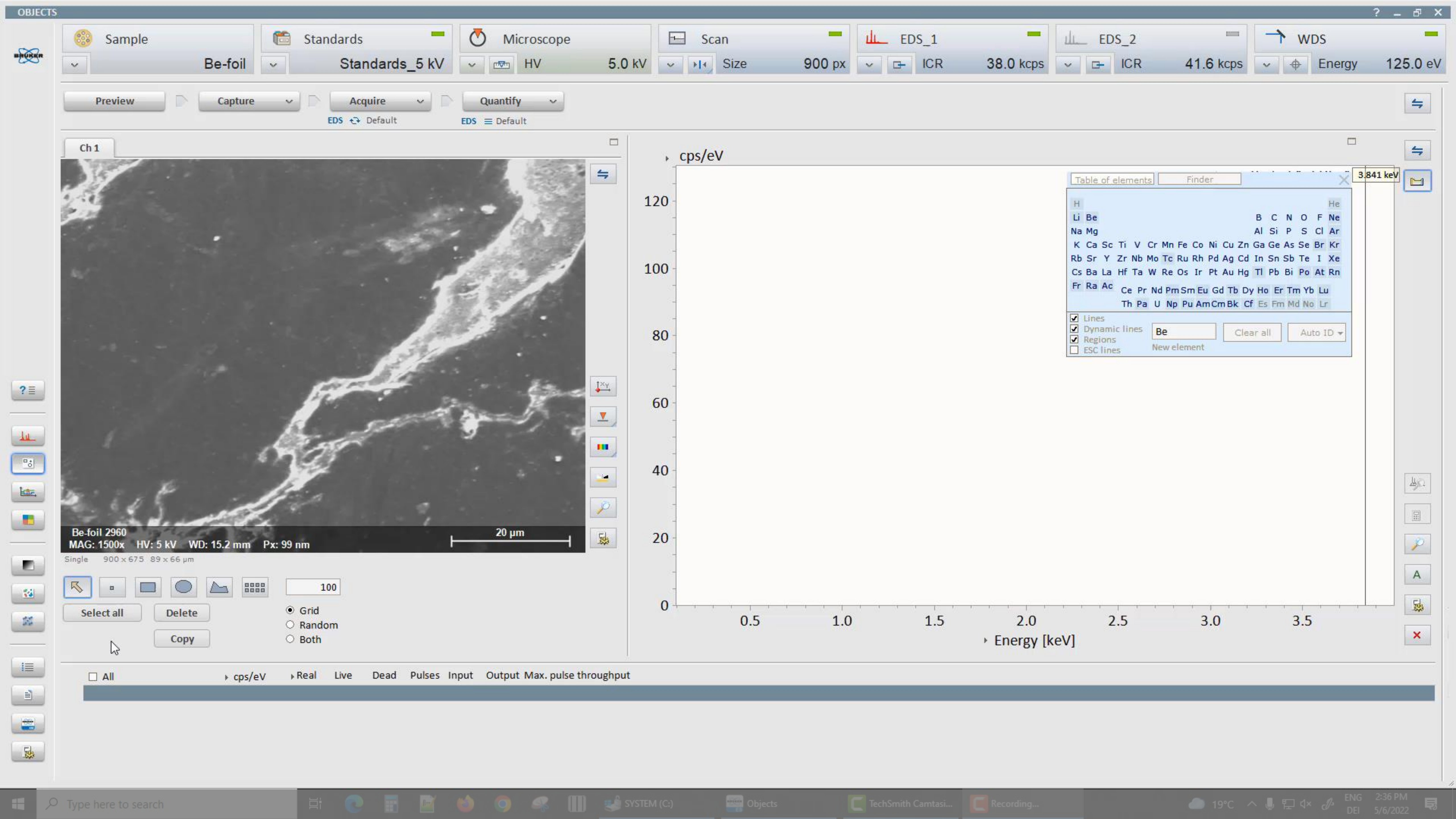
- Mapping a C-coated Be foil on epoxy resin



Analytical conditions	
FOV [µm]	89 x 66
Pixel	900 x 675
WD	15 mm
High voltage	5 kV
Beam current	8 nA
Acquisition time	Be-Kα: 1 min C-Kα: 1 min

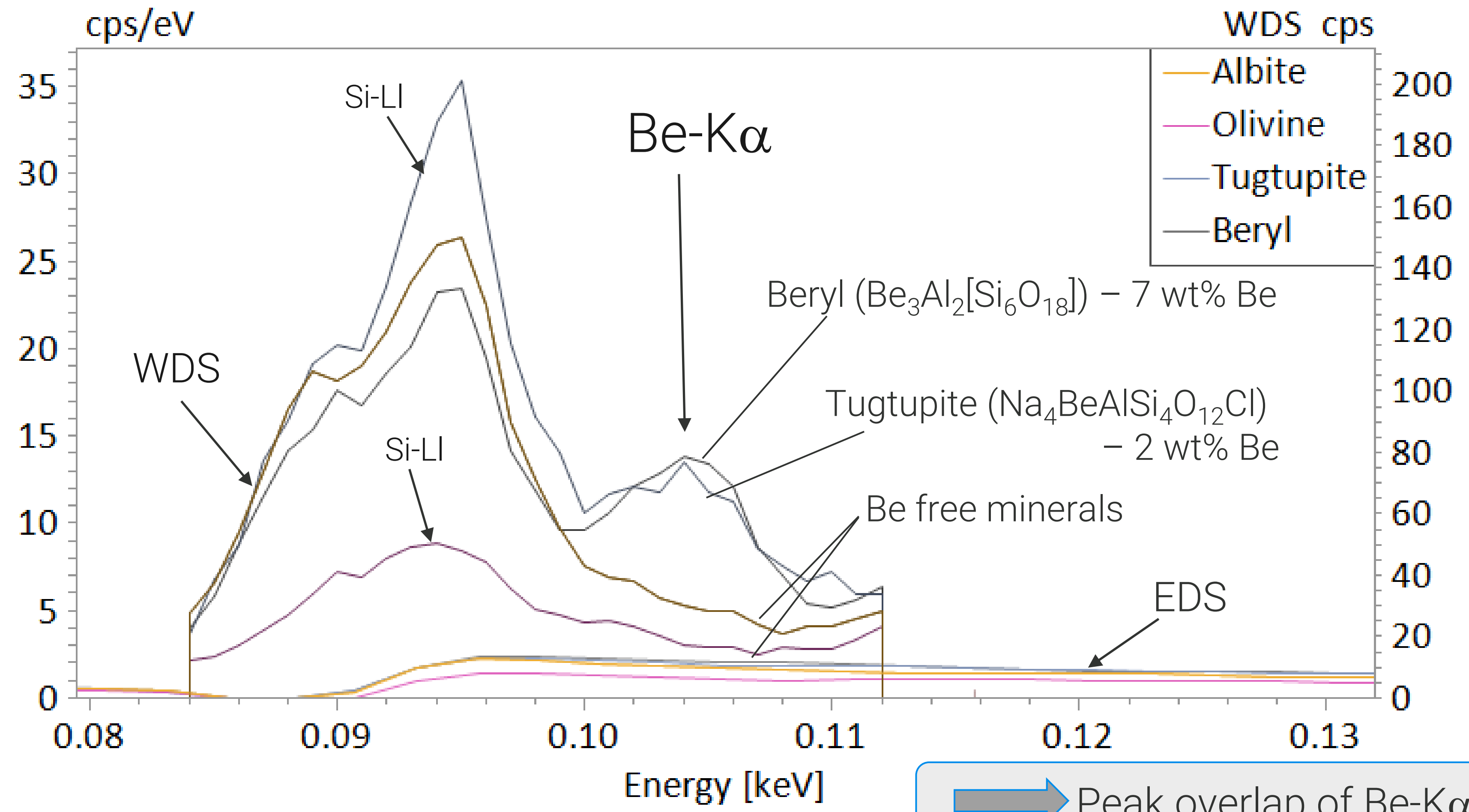
→ Light element mapping can be extremely fast


MAPPING
Sample
Standards
Standards_5 kV
Microscope
HV 5.0 kV
Scan
Size 900 px
EDS_1
ICR 37.1 kcps
EDS_2
ICR 41.6 kcps
WDS
Energy 277.0 eV
Preview
Capture
Acquire
QMap
EDS Linemarker PB-ZAF
Ch 1
Map
Phases
2955
MAG: 1500x HV: 5 kV WD: 15.2 mm Px: 99 nm
20 µm
Single 900 x 675 89 x 66 µm
0.12 µm Spot size 902x676 Points
Map
Phases
Charts
Line scan
Spectrum
Ch 1
WX Be, KA1
WX C, KA1
80
MAG: 1500x HV: 5 kV WD: 15.2 mm Px: 99 nm
20 µm
Map display settings
Map result list
Table of elements
Finder
Free regions
F1 F2 F3 F4 F5 F6 F7 F8
Lines
Dynamic lines
Regions
ESC lines
Si
New element
Clear all
Auto ID
Ch 1 1.00
WX Be, KA1 1.00
WX C, KA1 1.00
C-K 1.00
O-K 1.00
Na-K 1.00
Si-Kα 1.00
Type here to search
SYSTEM (C:)
Mapping
TechSmith Camtasi...
Recording...
18°C
ENG
DEI
1:58 PM
5/6/2022


OBJECTS
Sample
Be-foil
Standards
Standards_5 kV
Microscope
HV 5.0 kV
Scan
Size 900 px
EDS_1
ICR 38.0 kcps
EDS_2
ICR 41.6 kcps
WDS
Energy 125.0 eV
Preview
Capture
Acquire
Quantify
EDS Default
EDS Default
Ch 1
Be-foil 2960
MAG: 1500x HV: 5 kV WD: 15.2 mm Px: 99 nm
20 µm
Single 900 x 675 89 x 66 µm
100
Select all
Delete
Copy
Grid
Random
Both
cps/eV
120
100
80
60
40
20
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Energy [keV]
3.841 keV
Table of elements
Finder
H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl Ar
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Nb Mo Tc Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po At Rn
Fr Ra Ac
Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lr
Lines
Dynamic lines
Regions
ESC lines
Be
New element
Clear all
Auto ID
All
cps/eV
Real Live Dead Pulses Input Output Max. pulse throughput
Type here to search
SYSTEM (C:)
Objects
TechSmith Camtasi...
Recording...
19°C
ENG
2:36 PM
5/6/2022

Beryllium-minerals vs. Be-free minerals

- WDS energy range scan for Be-Kα



5 kV, 17 nA
Dwell time:
10 s / step

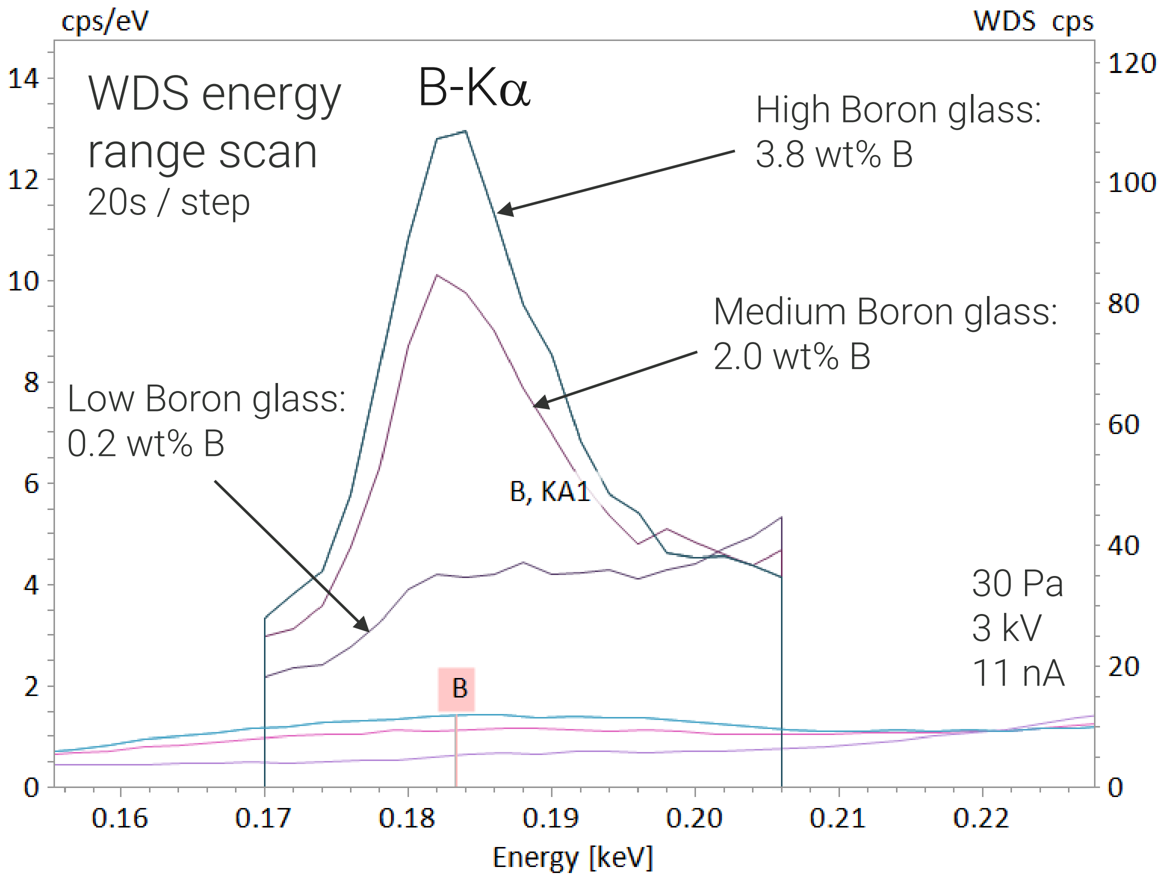
Peak overlap of Be-Kα and Si-L is resolved

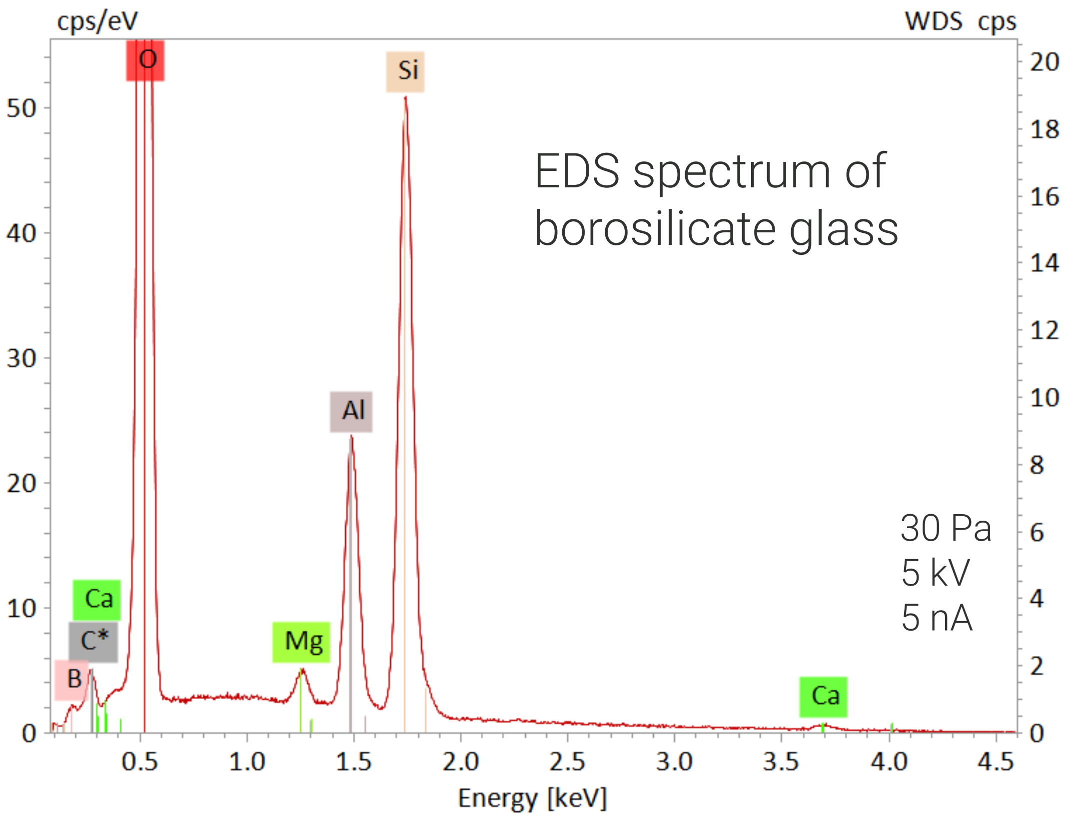
QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Boron

Boron in glasses

- Low-vacuum analyses of uncoated glasses

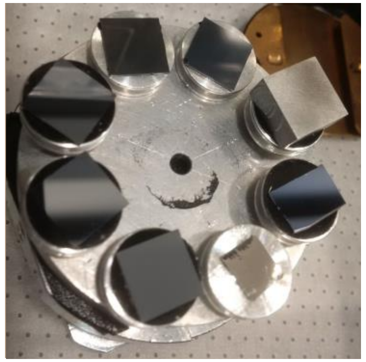


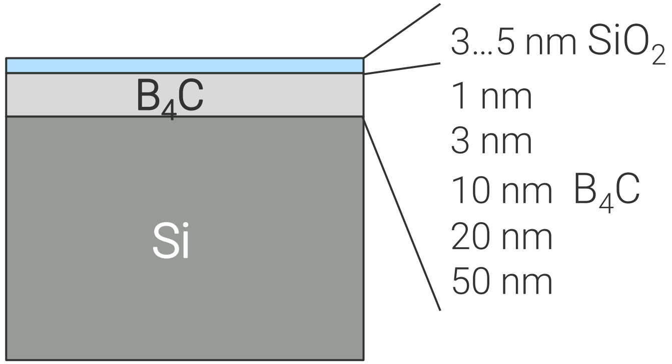


WDS can successfully quantify low B contents in glass

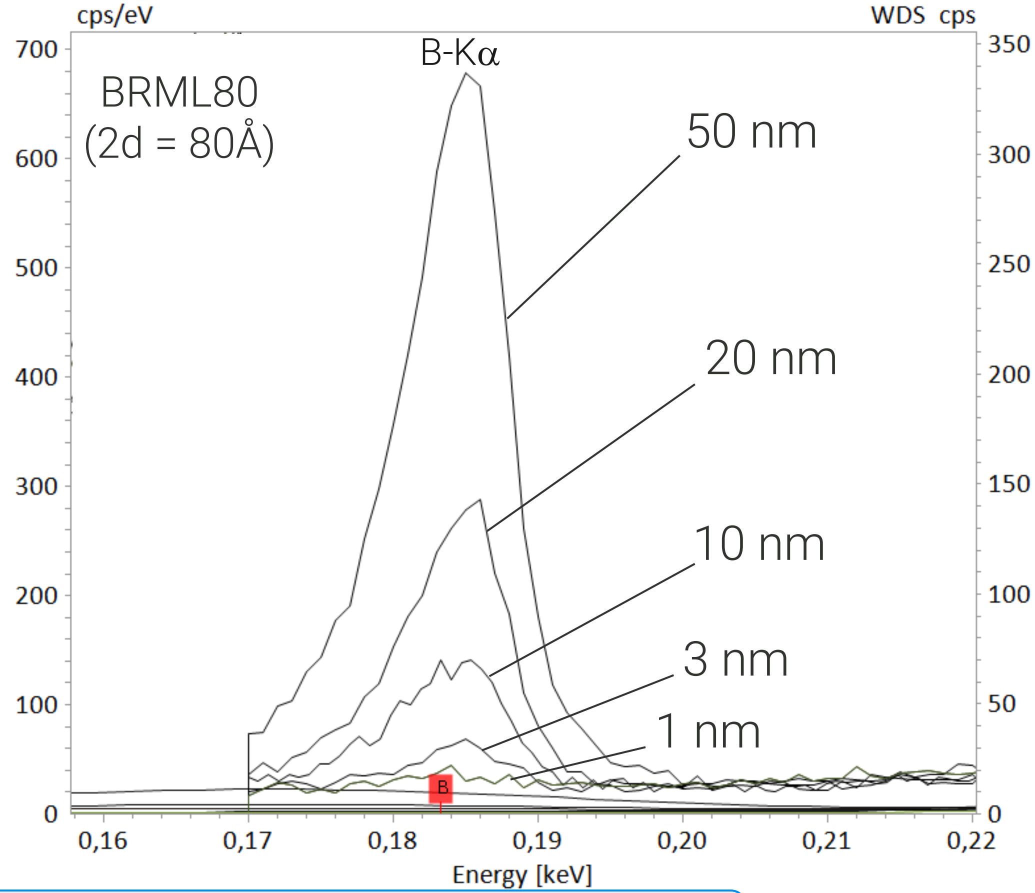
Boron in layered samples

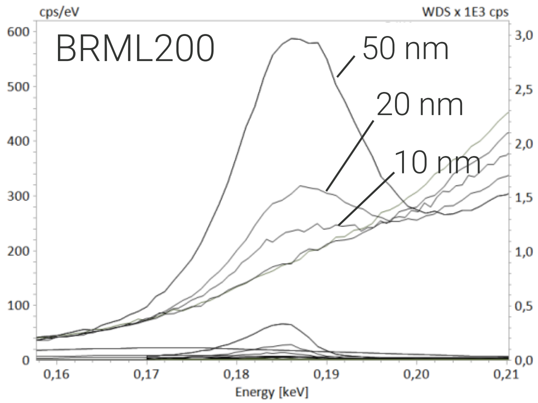
- Detection of Boron in thin B_4C layers

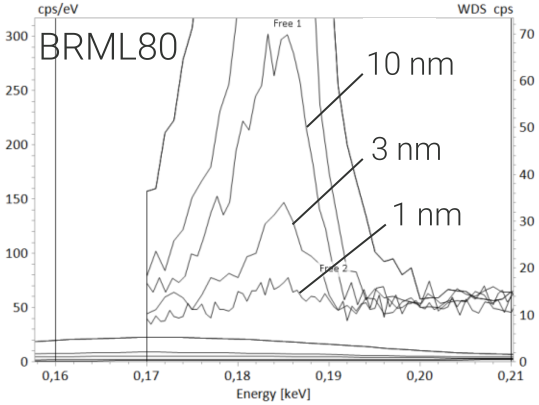




5 kV, 3.5 nA, 5 s/eV



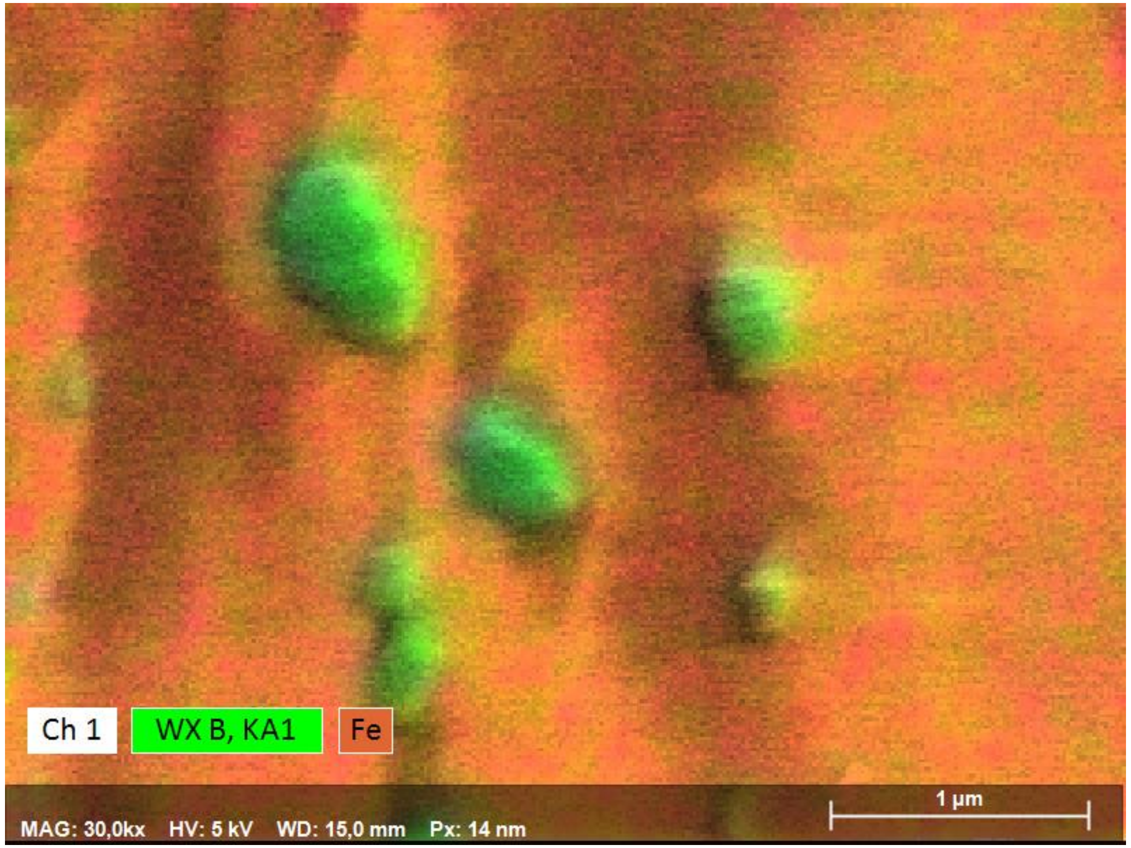


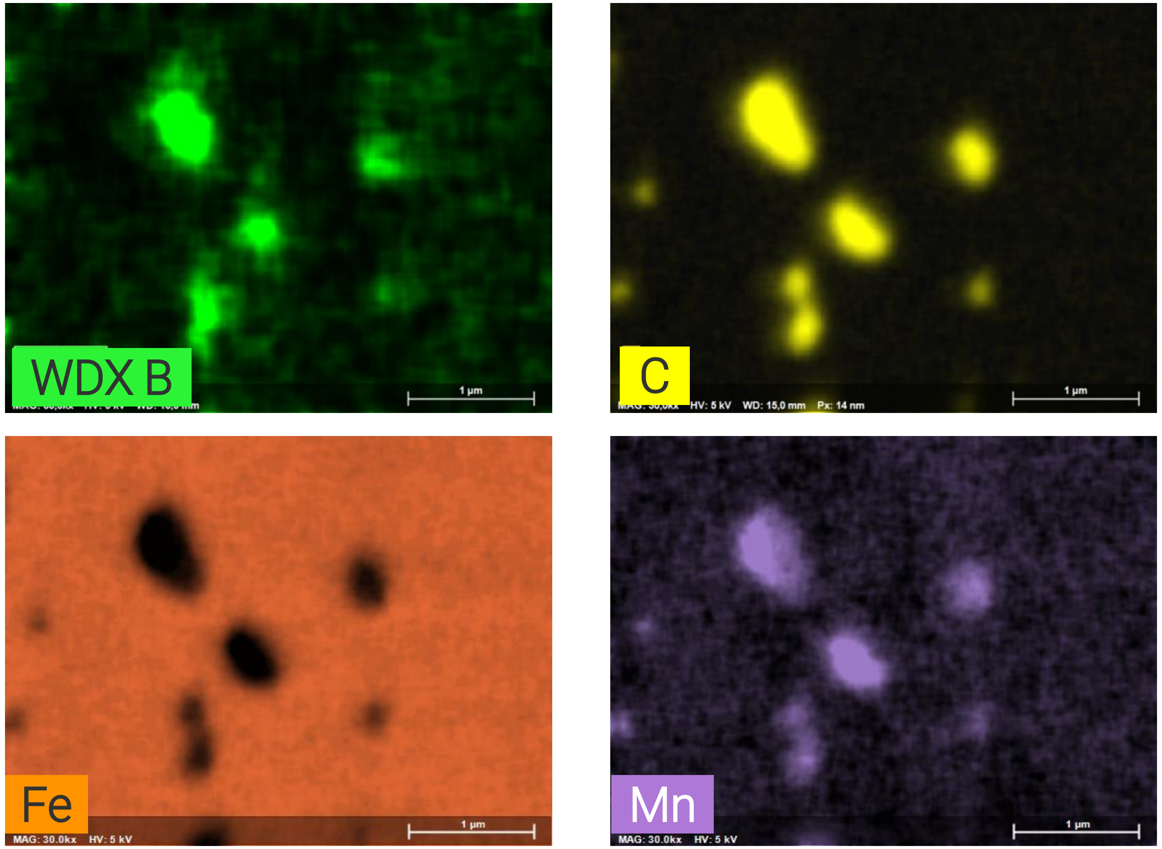


Evidence for Boron down to the thinnest layer

Boron in steel

- Combined WDS – EDS mapping of a Boron steel





Sample: Dr. Murugaiyan Amirthalingam, IIT Madras

Cementite (Fe_3C): 0.4 wt% B, matrix steel: 0.2 wt% B

300 x 225 px, 225 µs/px, 120 min/map

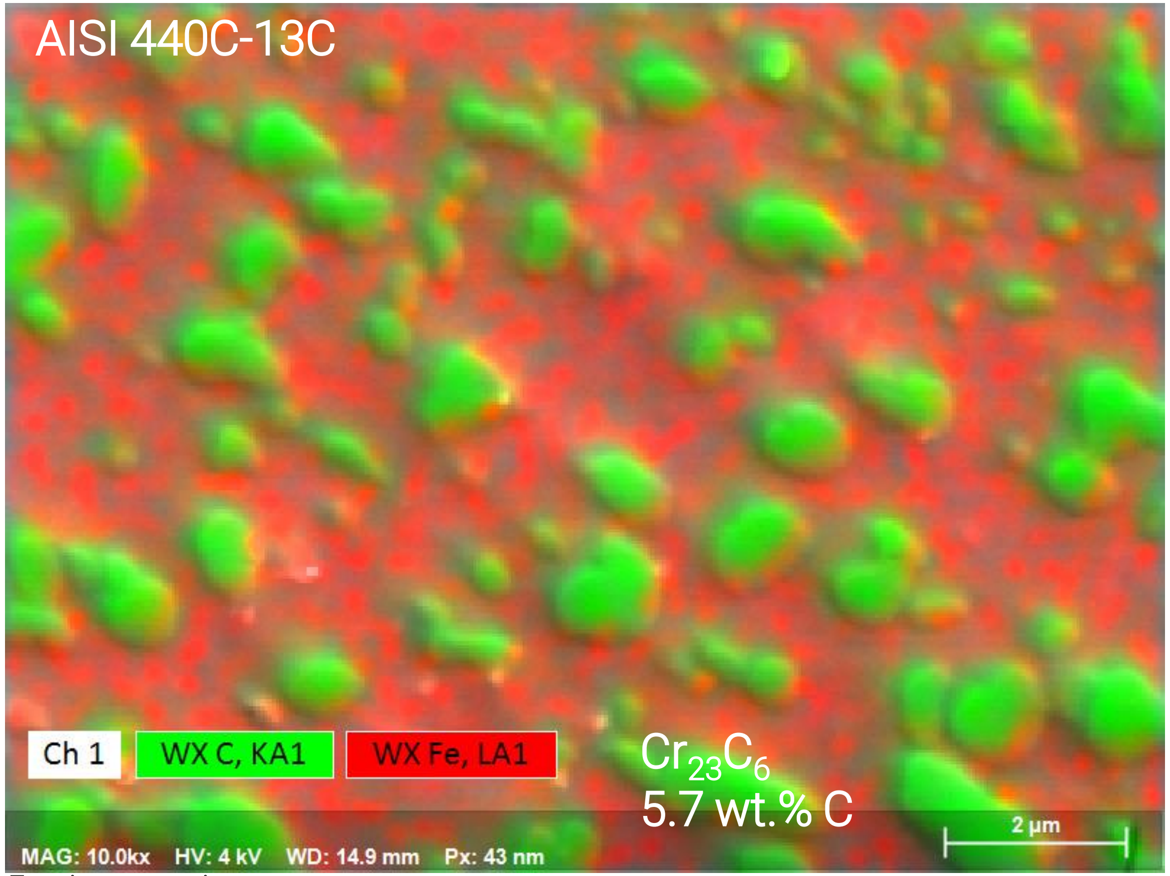
→ Heterogeneous Boron distribution on sub-micron scale

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Carbon

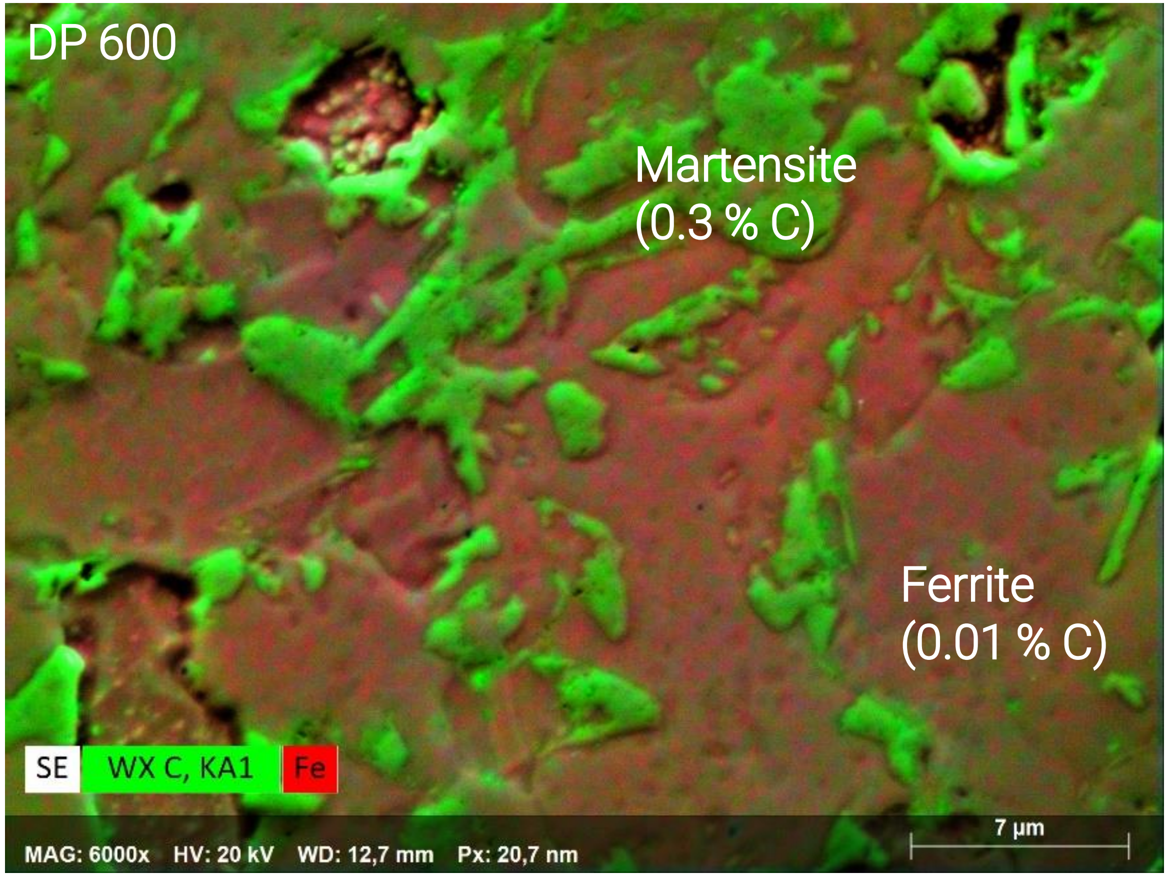
Mapping carbon distribution in steel

- Carbide bearing steel



5 min mapping

- Dual phase steel

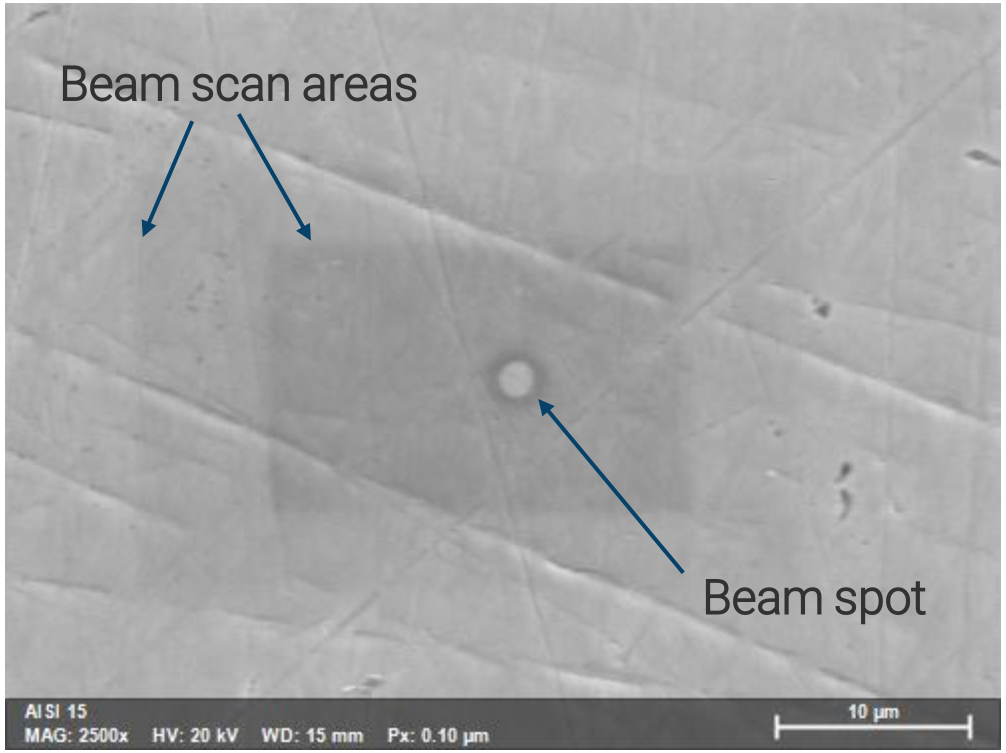


Sample: TU Eindhoven – 5 min

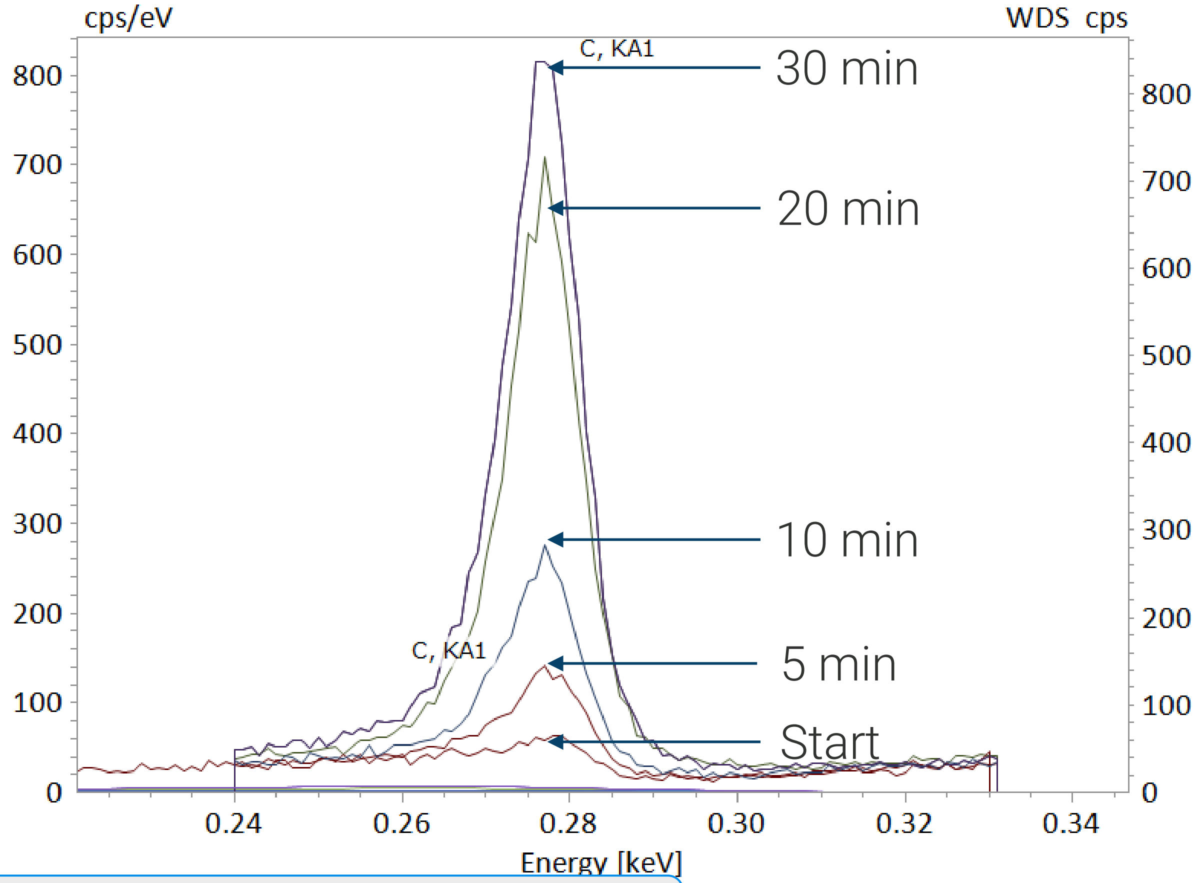
➡ Fast mapping is possible and preferred to minimize contamination

Carbon contamination during analysis

- Carbon contamination on sample surface



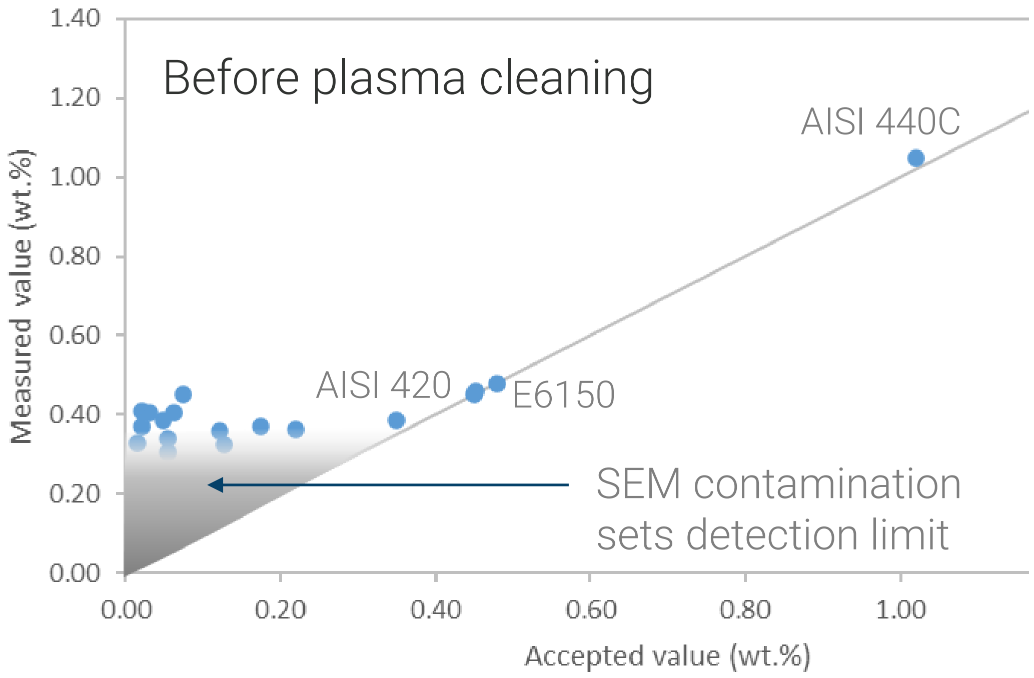
- Increasing carbon deposition over time

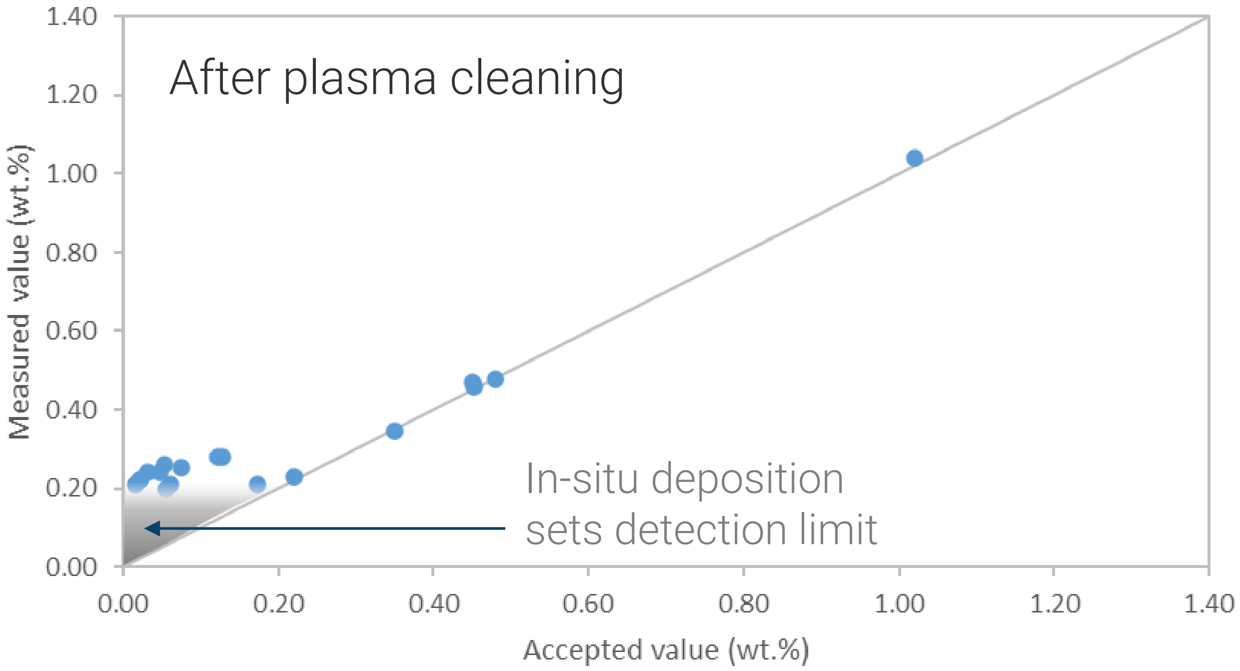


Carbon is instantaneously deposited on the area of analysis

Carbon contents in steel

- Carbon quantification is a challenge for analysis on SEM





Note: Further improvement possible with air jet and cold finger

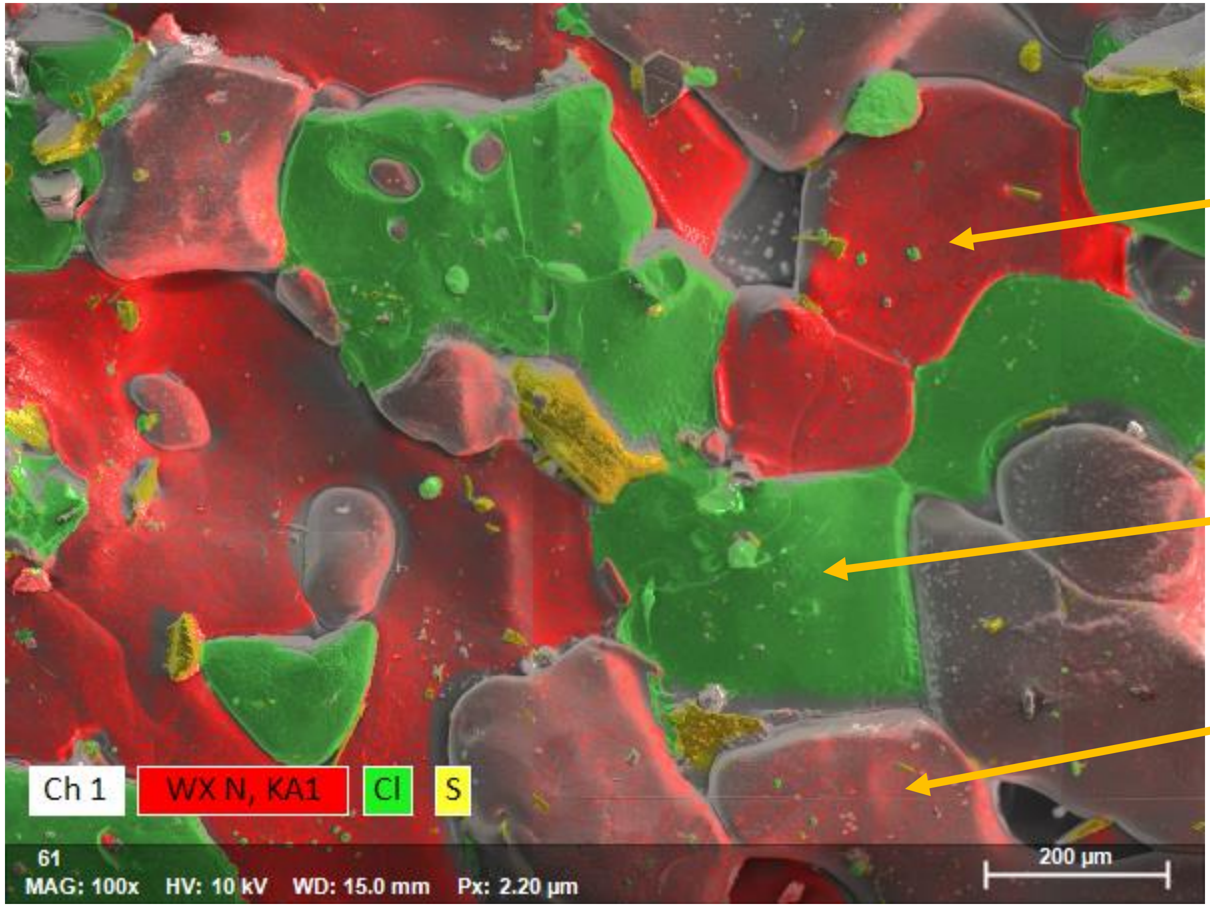
➡ The LOD for Carbon depends on technical measures to lower contamination

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Nitrogen

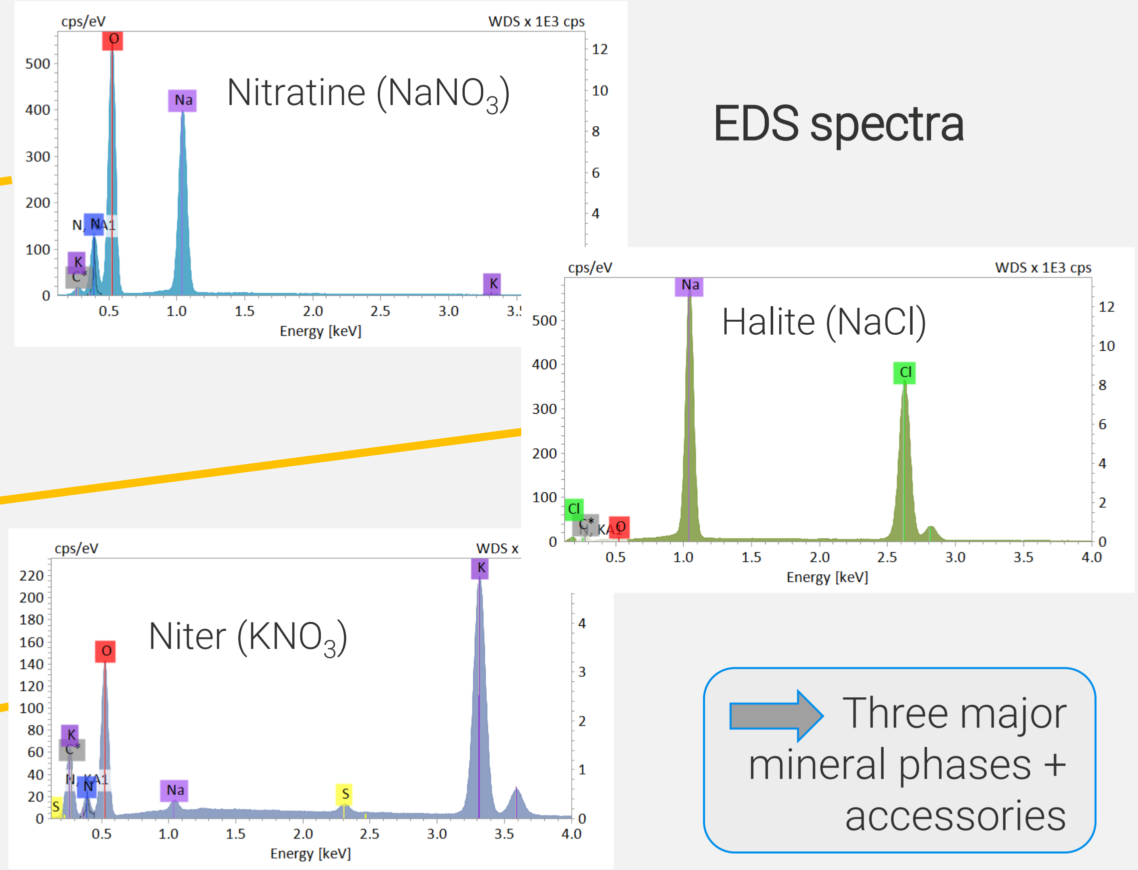
Nitrogen in minerals

- Combined WDS – EDS mapping of caliche ore from Atacama, Chile



Sample: A. Menzies

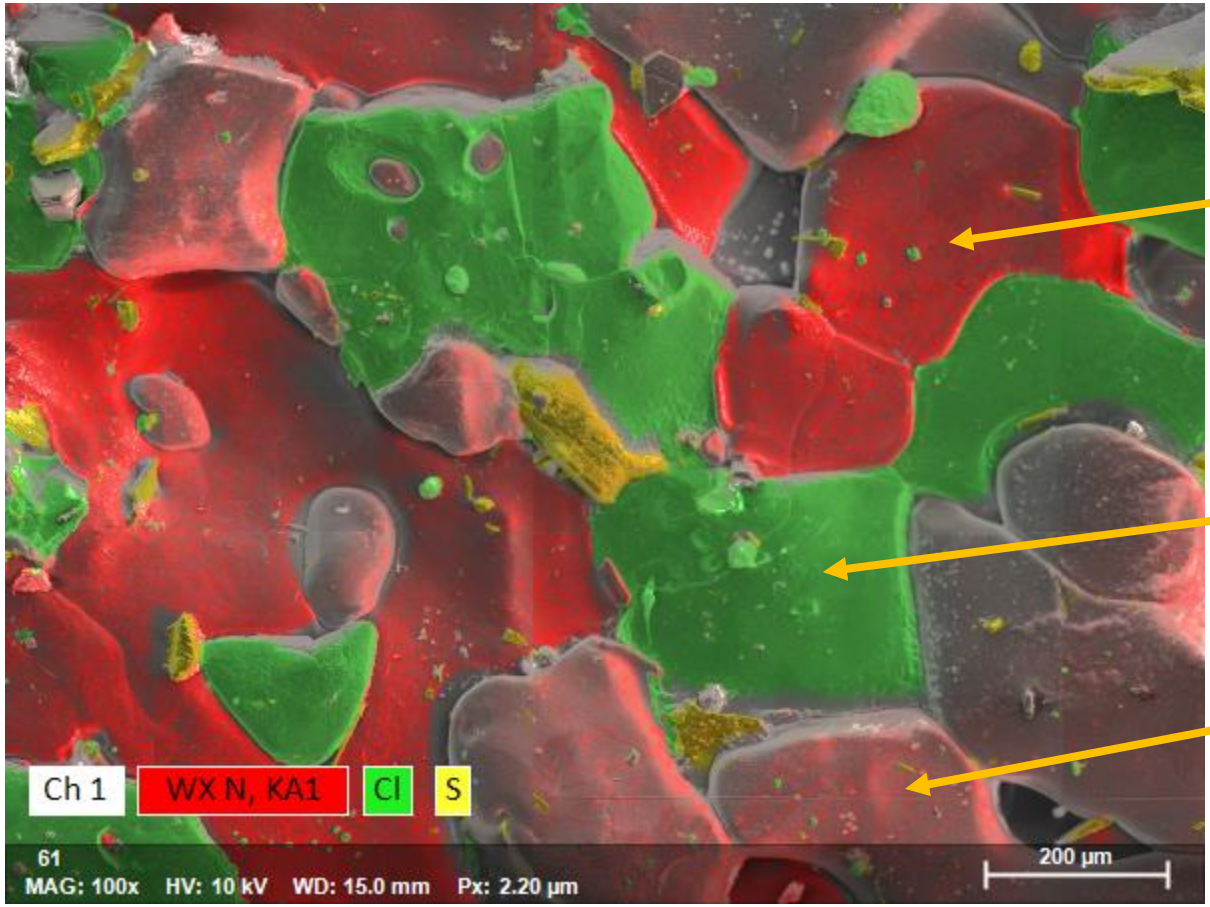
600 x 450 px / 1.3 x 1 mm, 18 min



Three major mineral phases + accessories

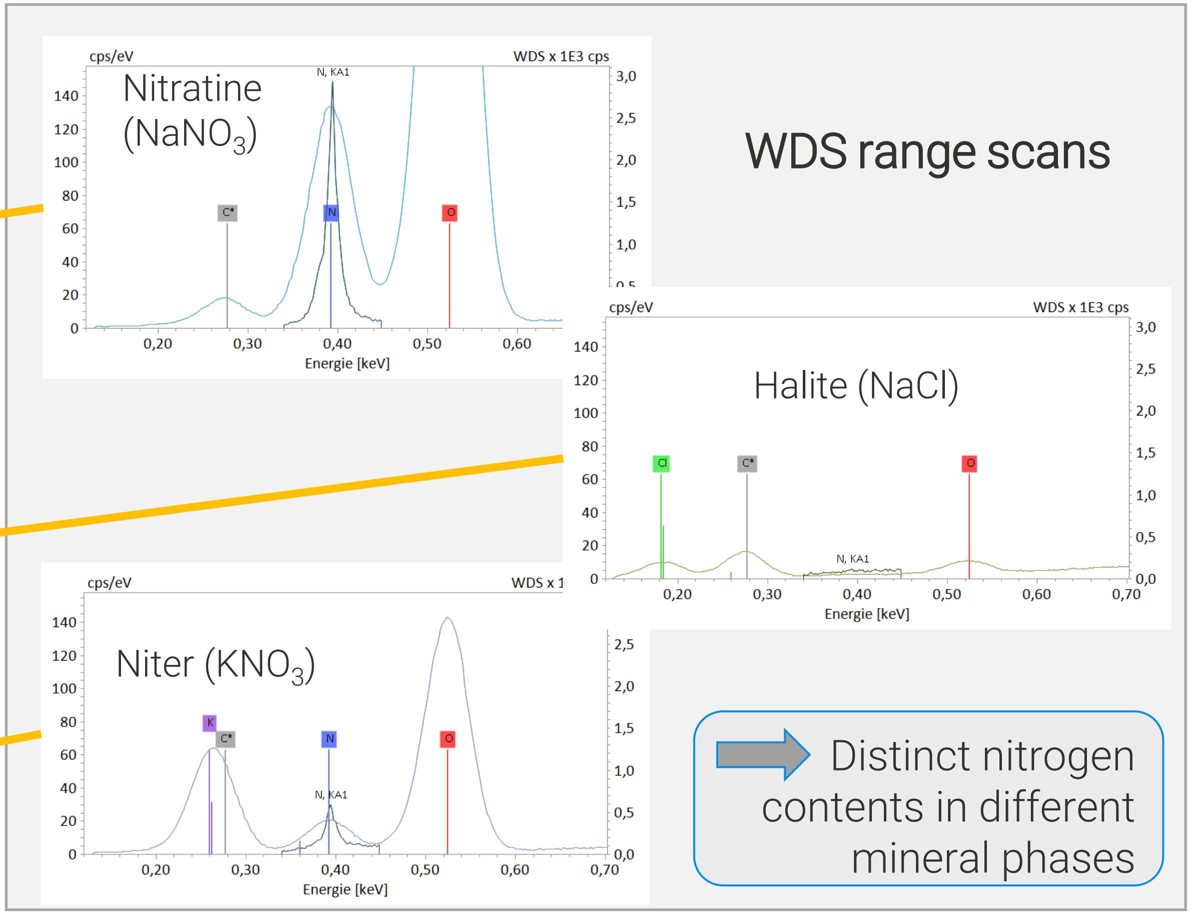
Nitrogen in minerals

- Combined WDS – EDS mapping of caliche ore from Atacama, Chile



Sample: A. Menzies

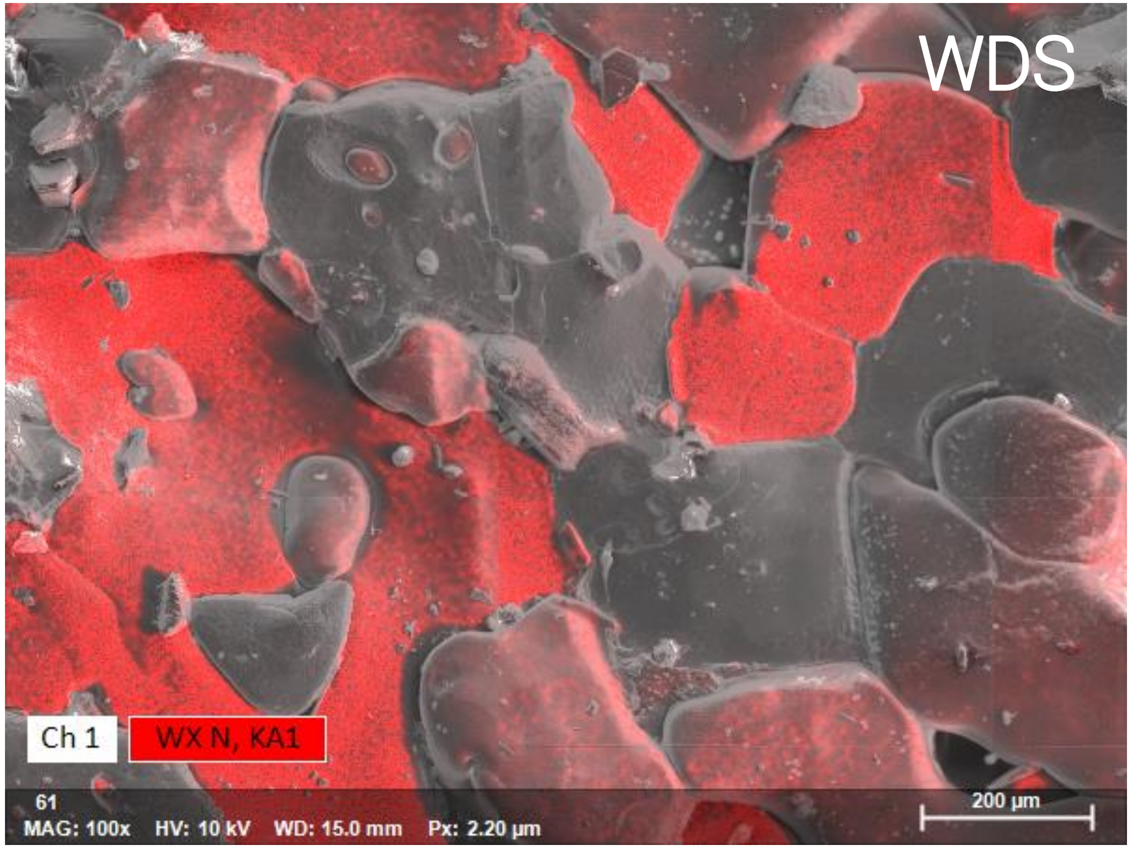
600 x 450 px / 1.3 x 1 mm, 18 min

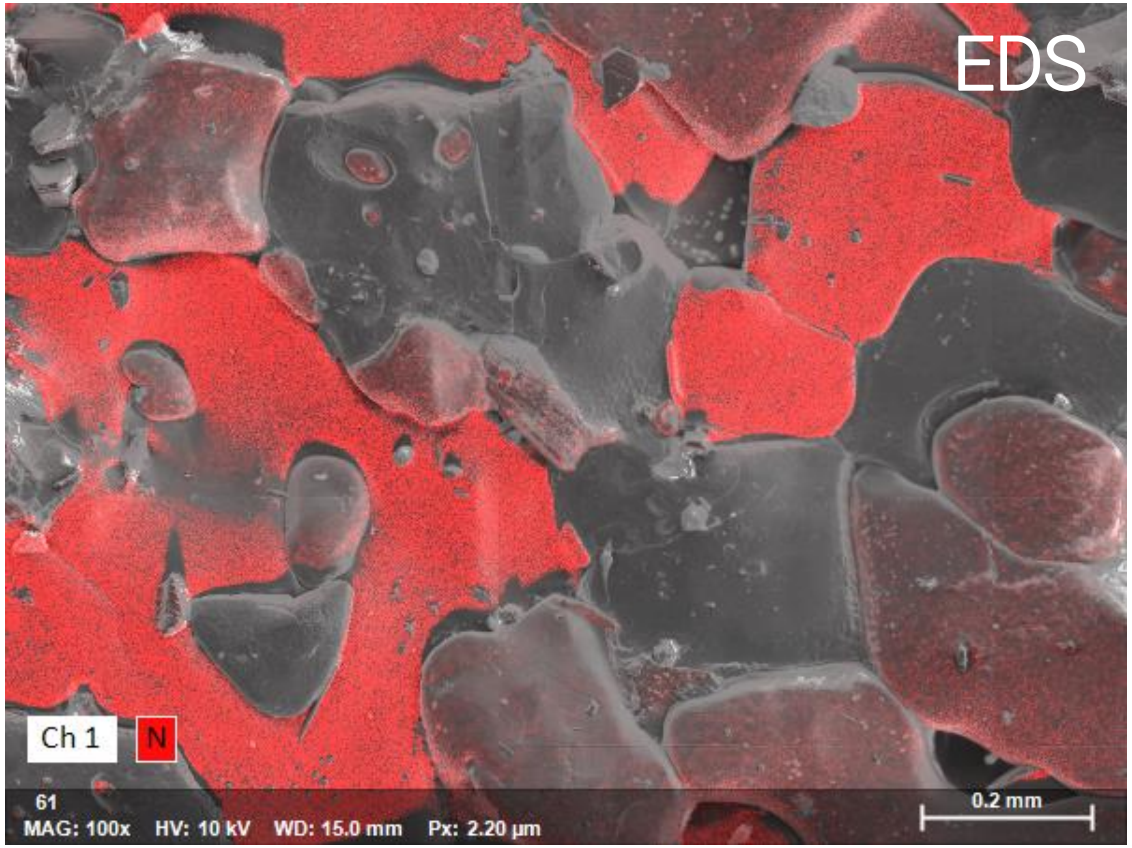


Distinct nitrogen contents in different mineral phases

Nitrogen in minerals

- WDS and EDS acquire X-rays simultaneously

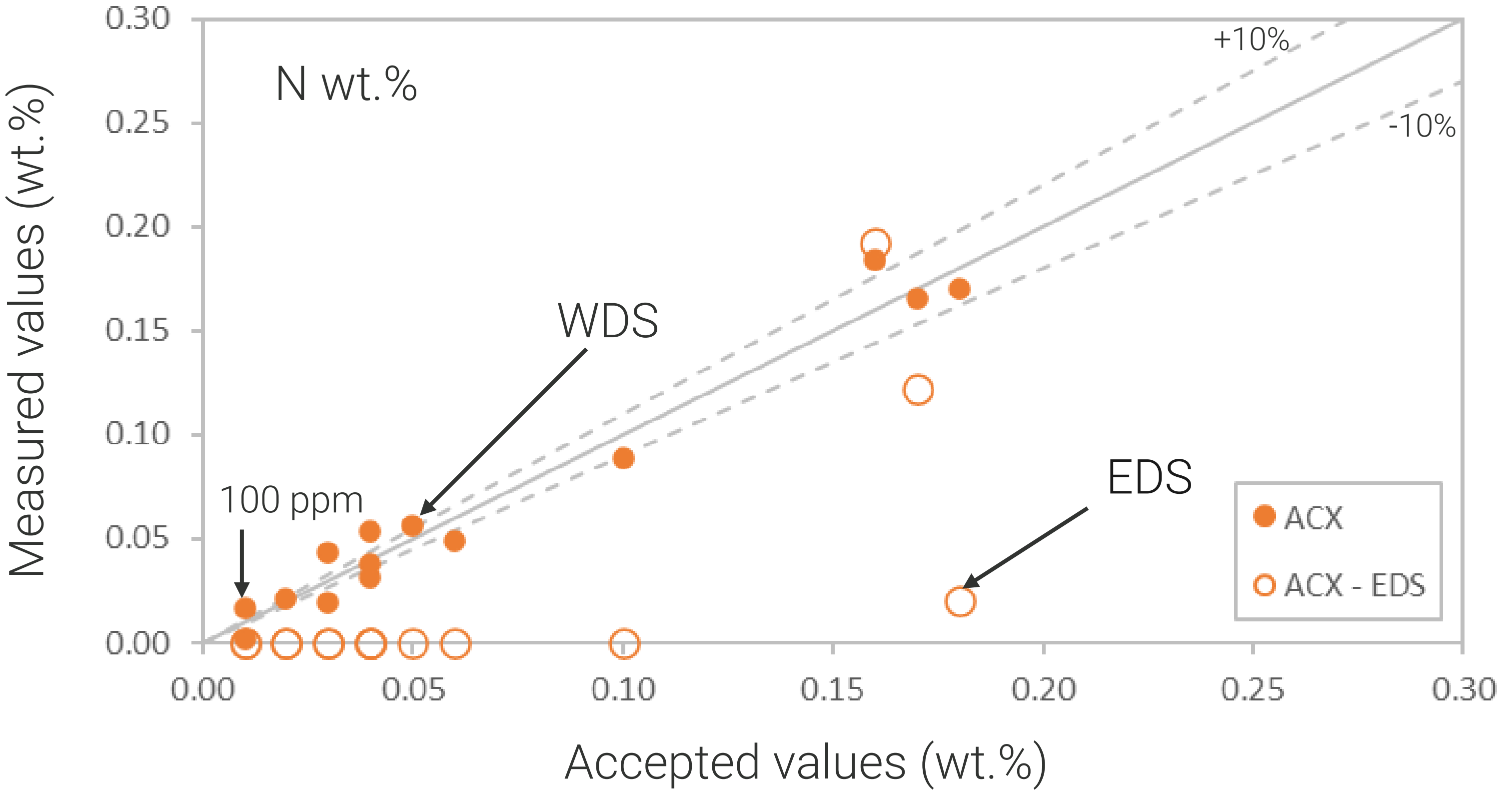




→ No large differences for major elements – WDS advantages for peak overlaps and trace elements

Nitrogen in steel

- Trace element quantification on certified reference steel samples



Samples:

15 certified steels (Acerinox) with nitrogen 100 – 1800 ppm

Parameter:

5kV, 10nA, 60s on peak

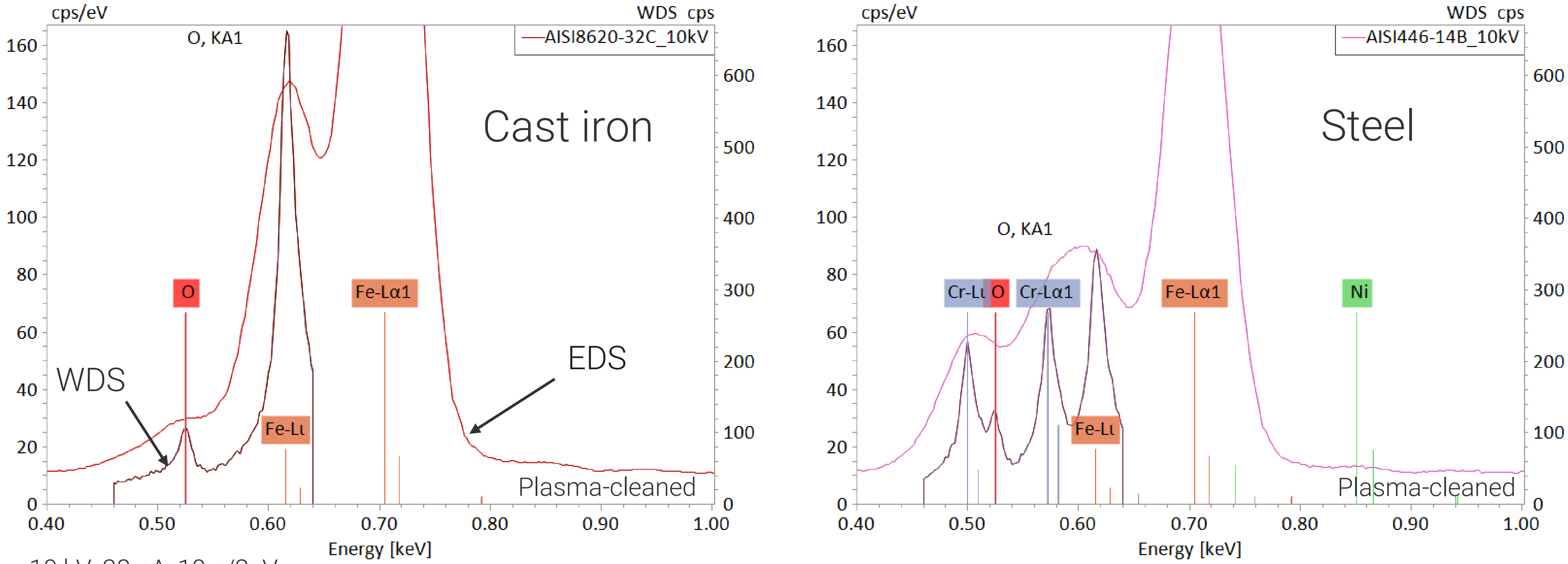
WDS has lower limit of detection (LOD) than EDS

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Oxygen

Oxygen in cast iron and stainless steel

- Scan for O-Kα in samples with and without Cr



10 kV, 28 nA, 10 s/2eV

→ WDS resolves peak overlap of O-Kα and Cr-L lines

QUANTAX WDS – LIGHT ELEMENT APPLICATIONS

Concluding remarks

Advantages of QUANTAX WDS

- Designed for low X-ray energies
- High solid angle with state-of-the-art mirror optic
- High sensitivity for the light elements
- High count rates also with low beam currents
- High peak to background ratios
- High spectral resolution

PLEASE TYPE IN THE QUESTIONS YOU MIGHT HAVE IN THE Q&A BOX AND PRESS *SEND*.

Any questions?

Innovation with Integrity