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)
Challenges with light element analysis
Definition low energy range and light elements

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

Almandine Garnet:
$\text{Fe}_3\text{Al}_2\text{Si}_3\text{O}_{12}$
(+ Mg, Ca,...)
HV=20 kV
Low energy range

- For $E \geq 1$ keV the background is clearly defined

Almandine Garnet:
$Fe_3Al_2Si_3O_{12}$
(+ Mg, Ca, ...)
HV=20 kV
Low energy range

- for $E \geq 1\text{keV}$ the background is clearly defined
- for $E < 1\text{keV}$ the background calculation is difficult:
  - $\text{BG is lower} \rightarrow \text{errors due to statistical noise}$
  - high absorption edges, variations in TOA influence low energy BG shape
- high line density $\rightarrow$ 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 $\varepsilon$ of detector at the line energy
- Absorption of line

![Graph showing pulses per electron volt (eV) for various elements: Ca, O, Fe, and N.](image)
Fluorescence yield and quantum efficiency

- **Fluorescence yield ($\omega$):**

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

- **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
  - \( \rightarrow \) TOA
  - \( \rightarrow \) 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 CaCO₃

- $\Phi(\rho z)$ curves (generated / emitted) need to be used.
Working principle of QUANTAX WDS

Bragg equation:

\[ n\lambda = 2d \sin(\theta) \]

QUANTAX WDS uses Bragg spectrometer and Parallel Beam Optic (PBO)
Working principle of QUANTAX WDS

Bragg equation:

\[ n\lambda = 2d \sin(\theta) \]

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

**Typical parameters**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>High voltage</td>
<td>5 kV</td>
</tr>
<tr>
<td>Beam current</td>
<td>5 nA</td>
</tr>
<tr>
<td>Monochromators</td>
<td>Multilayer 200, 80, 60</td>
</tr>
<tr>
<td>Standards</td>
<td>close to sample composition</td>
</tr>
<tr>
<td>Acquisition time Range</td>
<td>1 s (per step)</td>
</tr>
<tr>
<td>Acquisition time P/B</td>
<td>60 s (peak time)</td>
</tr>
<tr>
<td>Acquisition time Map</td>
<td>300 s (per element)</td>
</tr>
</tbody>
</table>

**Optimum peak intensity (B-Kα)**

- ionizations
- absorption factor

**Bragg equation:**

\[ n\lambda = 2d \sin(\theta) \]
Light element spectra acquired by EDS and WDS

Conditions:
5 kV, 5 nA

Multilayers:
200 Å, 80 Å, 60 Å

Samples:
Pure elements: Be, C and compounds: BN, SiO₂, CaF₂

WDS shows higher sensitivity, higher peak/background ratios and better spectral resolution
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.
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
Boron
Boron in glasses

- Low-vacuum analyses of uncoated glasses

**WDS energy range scan**

- **B-Kα**
  - High Boron glass: 3.8 wt% B
  - Medium Boron glass: 2.0 wt% B
  - Low Boron glass: 0.2 wt% B

**EDS spectrum of borosilicate glass**

- 30 Pa
- 3 kV
- 11 nA
- 30 Pa
- 5 kV
- 5 nA

**WDS can successfully quantify low B contents in glass**
Boron in layered samples

- Detection of Boron in thin $B_4C$ layers

Evidence for Boron down to the thinnest layer

- $3...5\text{ nm SiO}_2$
- $1\text{ nm}$
- $3\text{ nm}$
- $10\text{ nm}$ $B_4C$
- $20\text{ nm}$
- $50\text{ nm}$

5 kV, 3.5 nA, 5 s/eV

BRML80 ($2d = 80\text{Å}$)

BRML200

BRML80

50 nm

20 nm

10 nm

3 nm

1 nm
Boron in steel

- Combined WDS – EDS mapping of a Boron steel

Cementite (Fe₃C): 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
Carbon
Mapping carbon distribution in steel

- Carbide bearing steel

  **AISI 440C-13C**

  
  5 min mapping

  **Cr$_{23}$C$_6$$^\text{5.7 wt.\% C}$$^\text{Ch 1, WX C, KA1, WX Fe, LA1}$$^\text{MAG: 10.00x, HV: 4 kV, WD: 14.9 mm, Px: 43 nm}$$^\text{2 \mu m}$$^\text{Sample: TU Eindhoven – 5 min}

- Dual phase steel

  **DP 600**

  
  **Martensite (0.3 % C)$$^\text{SE, WX C, KA1, Fe}$$^\text{MAG: 6000x, HV: 20 kV, WD: 12.7 mm, Px: 20.7 nm}$$^\text{7 \mu m}$$^\text{Sample: TU Eindhoven – 5 min}

  **Ferrite (0.01 % C)**

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
Nitrogen
Nitrogen in minerals

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

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

WDS range scans

- **Nitratine** (NaNO₃)
- **Halite** (NaCl)
- **Niter** (KNO₃)

Distinct nitrogen contents in different mineral phases

Sample: A. Menzies

600 x 450 px / 1.3 x 1 mm, 18 min
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
Oxygen
Oxygen in cast iron and stainless steel

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

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

10 kV, 28 nA, 10 s/2eV
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