



Bruker Nano Analytics, Berlin, Germany Webinar



Presenters





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Overview: Trace Elements and Mineralization



- The motivation and analytical challenge
- Short introduction to the analytical techniques applied in this work
- Advantages of combining analytical techniques
 - Case Study 1: Au (Gold)
 - Case Study 2: Co (Cobalt)
 - Sample size and analytical solution
 - Spectroscopical overlaps and analytical considerations
- Summary and Conclusion



The motivation and analytical challenge:

- In many economic deposits the element or mineral of interest is a trace component.
- The ability to identify or even extract these elements and minerals depends on how they
 occur.
- Such information is important to understand the genesis of the deposit as well as the mineral and metallurgical processes to yield the maximum recovery.
- The analytical questions and samples to be studied cover a wide range in terms of sample and relevant mineral sizes; in addition, occasional spectroscopical challenges such as element overlaps might hinder the evaluation.

The examples shown will highlight the difference between a trace element and trace mineral characterization as well as the multiple analytical tools for the ultimate project goal.

Overview: Analytical techniques

Benchtop micro-XRF:

Micro-XRF is spatially resolved X-ray fluorescence analysis. The high spatial resolution is achieved by using a focusing polycapillary x-ray optic. Generated fluorescent signal is analyzed using one or two SDDs.

Scanning electron microscope (SEM) and analytical add-on options

The SEM is a well-known analytical technique based on electron beam spatially resolved imaging and elemental composition analysis using Energy Dispersive Spectrometers (EDS). Additional options such as wavelength dispersive spectrometers (WDS) as well as focused X-ray beam sources have been added to complement the analytical capabilities.

Micro-XRF M4 TORNADO PLUS

SEM-EDS: QUANTAX Micro-XRF: XTrace SEM-WDS: XSense









Overview: Micro-XRF as an analytical technique





No sample preparation

Aus Br. Sn. recipe Aller 4 (refs. of 1400 µm

Information from the Tr depth of the sample se



Main analytical advantages of micro-XRF



Reference samples free and standard supported quantify-cation options

Micro-XRF M4 TORNADO PLUS



Micro-XRF: XTrace



Analytical differences:

- M4 TORNADO PLUS as a benchtop instrument allows faster scan of lager samples and heavier sample (up to 30 cm and 7 kg) at higher resolution
- XTrace as and ad-on techniques allows to combine the advantages of micro-XRF with the associated SEM options (high spatial resolution of the E-Beam and resolution of the WDS)

Overview: Scanning Electron Microscopy (SEM) and analytical options

Analytical advantages of SEM-EDS and SEM-WDS relevant for this work



SEM-EDS-WDS: Analysis based on the sample interaction with an electron beam source from the SEM and the resultant X-rays that are detected using either and SDD or and WDS.

* For 121 eV for Mn Ka (equivalent to 73 eV for a Si Ka), ** for Si Ka

SEM-EDX: QUANTAX





SEM and analytical options: Electron and Photon Excitation for micro-XRF and EDS/WDS





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



| Parameter | EDS: E-beam | WDS: E-beam | Micro-XRF | | |
|--------------------------|---|---|---|--|--|
| | (SEM-EDS) | (SEM-WDS) | (SEM-XRF-EDS or benchtop) | | |
| Analyzed Volume | Ø: few µm Information depth: µm; (depending primarily on electron energy) | Ø: few µm Information depth: µm; (depending primarily on electron energy) | Ø: 15-30 µm Information depth: µm to mm; (depending on analysed element and matrix) | | |
| Detectable Elements | Atomic number $Z \ge 4$ (beryllium) | Atomic number $Z \ge 4$ (beryllium) | Atomic number $Z \ge 6$ (carbon) | | |
| Energy range | K- L –M – Lines (up to 20 keV) | 70 eV – 3.6 keV (L- M- Lines) | K- L –M – Lines (up to 40 keV) | | |
| Concentration Range | Down to 1000 ppm | Down to 100 ppm | Down to 5 ppm | | |
| Quantification | Standard less and Standard based | Standard based | Standard less and standard based | | |
| Data collection | Simultaneously | Sequentially | Simultaneously | | |
| Sample Preparation | Sample needs to be electrically conductive (commonly carbon-coated), polishing required | Sample needs to be electrically conductive (commonly carbon-coated), polishing required | Electrical Conductivity not required, samples doesn 't need to be polished | | |
| Sample size / weight | Usually 5 to 10 cm (depends on SEM) | Usually 5 to 10 cm (depends on SEM) | 5 to 10 cm (depends on SEM) up to 30 cm and 7 kg for benchtop instrument | | |
| Spectroscopic resolution | Down to 121 eV for Mn Ka | ~ 4 eV for Si Ka | better than 145 eV for Mn Ka (depending of detector even down to 121 eV) | | |

Overview: Characterization Workflow of a multiscale approach





Micro-XRF M4 TORNADO PLUS



SEM-EDS-Micro-XRF-WDS



Butcher AR (2020) Upscaling of 2D mineralogical information to 3D volumes for geoscience applications using a multi-scale, multi-modal and multi-dimensional approach. *EMAS 2019*, *Conference Proceedings Volume, Trondheim*, 19-23 May 2019.

Trace Elements and Mineralization: Case Study 1 – Gold (Au)



Analyzing Large Samples: Drill Core (Micro-XRF)

Overview: Analysis for Gold

Gold can occur as a native element (mineral) or as high concentrations in a mineral (electrum, calaverite). Gold can also occur as a trace element in the structure of other minerals, for example **arsenopyrite**.

Electrum: Au = 70 to 95 wt%

Arsenopyrite: Au = 50 ppm (0.005 wt%)

For example: if a sample has 58 ppm

If the gold is in the form of Native Gold or Au-bearing mineral, then then elemental or mineralogical hyper-mapping (microXRF or SEM-EDS or AMICS) will detect the gold.

If the gold is included in arsenopyrite then it is unlikely that the gold will be detected.

Note: The arsenopyrite will be detected, however, point analysis with the microXRF would be required to determine if the arsenopyrite contains any gold.







Case Study: Gold (Au) Drill Core/Rock Samples: Hyperspectral Datasets



In the following examples for different Au deposits we will show the ability to identify Gold-bearing minerals and to focus on obtaining the most information possible.



Micro-XRF images:

Top: optical mosaic, red box is the area of analysis (18 cm x 4 cm); Middle: combined elemental map of K (blue) and Au (orange) Bottom: AMICS mineralogy map



Case Study 1: Gold (Au) Analysis of Drill Core: Elemental Maps





Case Study 1: Gold (Au) Analysis of Drill Core: Elemental Maps





Case Study 1: Gold (Au) Analysis of Drill Core: Gold Identification





Case Study 1: Gold (Au) Analysis of Drill Core: Gold Grains Identification





Case Study 1: Gold (Au) Analysis of Drill Core: Gold Grains Analysis



Identified Elements in the "large" gold grain from Map 02

Grain Size: 300-400 µm

Showing the Au and Ag peaks.

Rh

Mineral → Electrum



Case Study 1: Gold (Au) Gold Grains Analysis: Elemental Composition





| Spectrum | Ag | Au |
|-------------------------|------|------|
| Au-Map02-Grain01- 1.spx | 4.3 | 95.7 |
| Au-Map02-Grain01- 2.spx | 4.2 | 95.8 |
| Au-Map05-Grain01- 1.spx | 3.3 | 96.7 |
| Au-Map05-Grain01- 2.spx | 2.2 | 97.8 |
| Au-Map05-Grain02- 1.spx | 3.8 | 96.2 |
| Au-Map06-Grain01- 1.spx | 4.3 | 95.7 |
| Au-Map06-Grain01- 2.spx | 4.7 | 95.3 |
| Au-Map06-Grain02- 1.spx | 3.8 | 96.2 |
| Au-Map07-Grain01- 1.spx | 4.9 | 95.1 |
| Au-Map08-Grain01- 1.spx | 4.7 | 95.3 |
| Au-Map10-Grain01- 1.spx | 4.6 | 95.4 |
| Au-Map10-Grain02- 1.spx | 4.7 | 95.3 |
| Au-Map10-Grain03- 1.spx | 4.3 | 95.7 |
| Au-Map10-Grain04- 1.spx | 4.5 | 95.5 |
| Au-Map12-Grain01- 1.spx | 4.1 | 95.9 |
| | | |
| Mean value: | 4.2 | 95.8 |
| Std. Abw.: | 0.7 | 0.7 |
| Std. Abw. rel. [%]: | 16.5 | 0.7 |
| Conf. interval: | 0.2 | 0.2 |

Case Study 1: Gold (Au) Micro-XRF: High Resolution Map Area 02





Selected areas mapped at 5 micrometers pixel spacing



Automated Mineralogy (AMICS) Analysis of Drill Core











Trace Elements and Mineralization: Case Study 1 – Gold (Au)



Analyzing Large Samples: Rock Sample (Micro-XRF and SEM)

Case Study 1: Gold (Au) Epithermal Gold



| Mineral | Formula | | |
|-------------------|-----------------------------------|--|--|
| Native Gold | Au | | |
| Native Silver | Ag | | |
| <u>Sulphides</u> | | | |
| Pyrite | FeS ₂ | | |
| Chalcopyrite | CuFeS ₂ | | |
| Galena | PbS | | |
| Sphalerite | ZnS | | |
| Gangue Mineralogy | | | |
| Quartz | SiO ₂ | | |
| Adularia | KAISi ₃ O ₈ | | |





SEM Micro-XRF Analysis: Epithermal Au Large Area Mapping



| | a a sh | Se antes a | | Soft and the | Beam: | X-ray |
|--|-----------------------|------------|---------|-----------------------|------------------------|-------------------------|
| | | | ofar | the state | High Voltage: | 50 kV |
| section of | -had | | | - Mary | Anode Current: | 600 μΑ |
| | and the second second | s | | and the second second | Analytical Spacing: | 100 µm |
| and the second second | Erst st | | | | Dwell Time: | 64000 µs (64 ms) |
| | | 1 da | ta l | | Analytical Area: | 4.5 x 4.5 cm |
| real for the second | C. M. | and the | | | Total Analytical Time: | 188 minutes |
| | | | Carls . | | Spot Size: | 25 μm |
| and the second | |) June | | | Interaction Depth: | 10 – 100 µm |
| and a set of | Al | Si | S | K | Host Rock Fler | ments: Al, Si, K |
| 165 199 | | | Ŭ | | HOST NOCK LICI | nents. Al, SI, K |
| man to the | Fe | Cu | Zn | As | Mineralization: | S, Fe, Cu, Zn, As |
| | Se | Pb | Ag | Au | Economic Mine | eralization: Au, Ag, Se |

Epithermal Gold-bearing rock sample from Karangahake, New Zealand

Micro-XRF on SEM Identifying Gold (Au) in the Sample





Distinct and clear Au: Au-L_β X-ray energy Lines.

Presence of Au in the sample is confirmed. But is it identified correctly?

Micro-XRF on SEM Identifying Gold (Au) in the Sample







Distinct and clear Au-La and Au-L β X-ray energy Lines. Presence of Au in the sample confirmed.



Micro-XRF on SEM (X-ray Beam) Identifying Gold (Au) in the Sample





Summed points within Grain – High Counts, clear and confirmed elemental peaks

Mining and Exploration Applications: Epithermal Gold



Micro-XRF hypermaps successfully identify the presence and location of Au Grains within the sample.

The sample can be analyzed with no carbon coat and at low vacuum.

 Follow-up analyses can be achieved by switching to e-beam SEM analyses (requires sample coating and high vacuum)

Or

• Selecting specific areas in the sample for further sample preparation prior to analyze

Micro-XRF on SEM (X-ray Beam) Identifying Gold (Au) in the Sample





SEM-EDS (e-beam) Identifying Gold (Au) in the Sample









Single Field 6 Large Gold Grain; Associated with Silver Other mineralization:

Other mineralization: Pyrite (FeS2), Chalcopyrite (CuFeS2), Galena (PbS), Sphalerite (ZnS)

SEM-EDS (e-beam) Identifying Gold (Au) in the Sample





Micro-XRF: Large Area Map





SEM-EDS: Detailed Small Area Maps

Single Field 5, 6 and 7 Large Gold (Au) Grains;

Associated with Silver – Mineralogy Electrum

Other mineralization: Pyrite (FeS2), Chalcopyrite (CuFeS2), Galena (PbS), Sphalerite (ZnS)





Trace Elements and Mineralization: Case Study 1 – Cobalt (Co)



Analyzing Large Samples: Drill Core (Micro-XRF)

Case Study 2: Cobalt (Co) Battery Elements



In-situ non-destructive analysis Drill Core – 1 meter section



Centimeter-scale elemental mapping of cobalt mineralisation in drill hole PAL0163 by micro-XRF (directly onto a cut surface of a drill core), to reveal the spatial distribution of mineral species and their relationship to the micro-structural fabric.

Case Study 2: Cobalt (Co) Battery Relevant Elements



Ore mineralogy, petrogenesis and metallurgy

Centimeter-scale elemental mapping of cobalt mineralisation in drill hole PAL0163 by micro-XRF (directly onto a cut surface of a drill core), to reveal the spatial distribution of mineral species and their relationship to the microstructural fabric.



Case Study 2: Cobalt (Co) Battery Elements



Identification of key elements of interest

Overlayed Mixed Element images can lead to mineral identification

High resolution scans can identify textures and associations



Case Study 2: Cobalt (Co) Battery Elements



Identification of key elements of interest

Overlayed Mixed Element images can lead to mineral identification

High resolution scans can identify textures and associations


Case Study 2: Cobalt (Co) Automated Mineralogy (AMICS)





Linnaeite (Co⁺²Co⁺³₂S₄) Cobaltite (CoAsS)

Case Study 2: Cobalt (Co) Automated Mineralogy (AMICS)





Case Study 2: Cobalt (Co) Grain Size Distribution - Linnaeite (Co₃S₄)





Cobaltite (CoAsS)



AMICS Mineralogy

Case Study 2: Cobalt (Co) Grain Size Distribution - Linnaeite (Co₃S₄)





AMICS Mineralogy

Case Study 2: Cobalt (Co) Co Concentration





Total Spectrum (Whole Rock)

Co concentration \rightarrow 10400 ppm

Cobalt content at the depths of 417.6 - 418.6 m:

Chemical assay

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Co concentration \rightarrow 9769.3 ppm
(reported by Mawson Oy)
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Total Spectrum (Whole Rock) Micro XRF: Co 1.04 wt. %

Case Study 2: Cobalt (Co) Identification of Co-in-pyrite











Automated Mineralogy (AMICS): Micro-XRF vs SEM



PAL0163 – 418.29m

418.29m 417.55m 418.05m Thin Section of Co-Ore showing Optical SEM **Micro-XRF** the Sulphide phases. Automated Mineralogy (AMICS) possible with both Micro-XRF and SEM. Principally Pyrrhotite and Cobaltite

Automated Mineralogy (AMICS): Micro-XRF vs SEM





SEM-EDS Analysis: Co-in-Pyrite



Analysis of small (<100 μm) Co-bearing pyrite grain. Left: Individual Element intensity maps (BSE, Fe, S, and Co);



SEM-EDS Analysis: Co-in-Pyrite



Analysis of small (<100 μ m) Co-bearing pyrite grain.

Left: Individual Element intensity maps (BSE, Fe, S, and Co)



Middle: Combined elemental maps: Fe, S, and Co



Right: Quantified Co Map



SEM-EDS Analysis: Co-in-Pyrite



Left: Position of Line Scan on combined elemental maps: Fe, S, and Co





Benefits: Understanding crystal growth and compositional changes and thus petrological implications and mineralization.

Bottom Right: Zoom of Line Scan of Fe and Co

SEM-EDS Analysis: Automated Mineralogy (AMICS)



Left: BSE Image



| Pyrite-HighCo | |
|---------------|--|
| Pyrite-MedCo | |
| Pyrite-LowCo | |
| Pyrrhotite | |
| Other | |

Middle: AMICS mineralogical map showing the different pyrite classifications based on Co concentrations





Benefits: Ability to add accurate Co deportment to metallurgical calculations

Right: Individual zones of pyrite grain based on Co-concentrations.

SEM-EDS Analysis: Automated Mineralogy (AMICS)



Left: AMICS mineralogical map showing general mineral classifications. Note that Pyrite has a single classification.

Linnaeite Cobaltite Quartz Albite Orthoclase Biotite Chlorite Tremolite Pyrrhotite Pyrite Titanite Apatite Calcite Zircon Others Epoxy-Resin Rutile Pyrite-HighCo Pyrite-MedCo Pyrite-LowCo Pyrrhotite Other

Right: AMICS mineralogical map showing the different pyrite classifications based on Co concentrations.

Benefits: Ability to add accurate Co deportment to metallurgical calculations

SEM-WDS Analysis: Trace Element Distribution in Pyrite





WDS allows to improve EDS Co identification, especially in Fe-bearing Better assessment of Co contained in



Energy Dispersive Spectra Comparison: Electron vs. X-ray Excitation





The garnet has: 40 wt% SiO2 and 20 wt% FeO.

The different spectrum profiles are obvious. For example, the ebeam spectra (in green) the lighter elements are more intense.

Whereas for the heavier elements the X-ray spectrum (in blue) has a significantly more intense signal.

Introduction Terminology











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

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

Exiting with electrons



Spatial Resolution and Analyzed Volume: Transmission and Attenuation



The transmission of X-rays is important for excitation of samples as well as for the fluorescence radiation.

Penetration depth: the depth that can still be excited

Information depth: the depth from which fluorescence X-rays can still reach the detector



+ ray tube



In-situ non-destructive Micro-XRF analysis: **Analytical Conditions**





50 micron pixel scan

Less than 9 hours total measurement

> **Demonstration of** variable resolution

In-situ non-destructive Micro-XRF analysis: **Analytical Conditions: Pixel Spacing**







55

Summary and Conclusions: Analytical Benefits



Micro-XRF Benefits:

- Lower detection limits (down to 10 ppm)
- Detection of High Energy X-ray Lines (Full Spectrum Range up to 40 kV)
- Micrometer scale measurement over large area
- Ideal for Low kV or Beam Sensitive samples
- Minimal Sample Preparation Required, No charging effects
- Fast elemental X-ray mapping over large areas

SEM-EDS-WDS Benefits:

- Higher Beam Resolution
- Smaller sample interaction area
- Improved element resolution when using WDS

Summary and Conclusions: Applications



- In many applications, e.g., geology and mining, the element or mineral of interest is a trace component. Thus, the ability to analytically identify them can be important but challenging.
- Combining micro-XRF and SEM analytical information (either as two sperate systems or as one combined system) greatly enhances the sample information, specifically in relation to sample size, analytical resolution, element detection, and sample preparation.
- Accordingly, the benefits of each system can be applied to relevant samples, improving analytical and project workflows.
- This includes both elemental and mineralogical information through the relevant software (ESPRIT, M4, or AMICS).

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Questions and Answers



Are There Any Questions?

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



Innovation with Integrity