

Back to the Roots – Part IV: An Introduction to micro-XRF on SEM

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SEM-XRF (XTrace): Introduction







Contraction SEM-XRF (XTrace) and Rapid Stage







SEM-XRF (XTrace): Introduction

SEM and Analytical Options: Electron and Photon Excitation for micro-XRF and EDS/WDS





Analytical Parameters and Conditions SEM-EDS vs SEM-XRF



Parameter	E-beam (SEM-EDS)	Micro-XRF (SEM-XRF-EDS)	e-beam
Spatial Resolution & Analyzed Volume	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)	X-ray beam EDS
Detectable Elements	Atomic number Z ≥ 4 (beryllium)	Atomic number Z ≥ 6 (carbon)	
Energy range	K-L–M–Lines (up to 20 keV)	K- L –M – Lines (up to 40 keV)	WD X-rays from
Concentration Range	Down to 1000 ppm	Down to 5 ppm	10 mm Sample
Quantification	Standard less and Standard based	Standard less and standard based	Sample
Data collection	Simultaneously	Simultaneously	
Sample Preparation	Sample needs to be electrically conductive (commonly carbon-coated), polishing required	Electrical Conductivity not required, samples doesn 't need to be polished	Rapid Stage
Sample stress	Heated due to absorbed electrons	minimal	
Spectroscopic resolution	Down to 121 eV for Mn Ka	Down to 121 eV for Mn Ka	SEM Stage
Distribution Measurements	By rastering e-beam	By continuously (Rapid) Stage movement since the X- ray optic is fixed in space	

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 fluoresced X-rays can still reach the detector





Information depths of selected element fluorescence lines in different matrices

SEM-XRF and Rapid Stage Integration in ESPRIT Software





Micro-XRF Installations: Adaptable to Various SEM models





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Introduction to Micro-XRF and Rapid Stage Differences to Electron Beam Excitation



Micro-XRF Benefits:

- Non-destructive analytical technique
- No charging effects
- Minimal Sample Preparation Required
- Lower detection limits (down to 5 ppm)
- Wide elemental range (from Z = 6 to
 - 92)
- High Energy Lines Detection (Full Spectrum Range up to 40 keV)
- Ideal for Low kV or Beam sensitive samples
- Fast Large Area Mapping
- Micrometer scale measurement over cm
- Versatility in Application









SEM-XRF : Application Fields



The following Application fields will have benefits from the enhanced functionality on the SEM:

- Materials Science
- Archaeology and Art Conservation
- Environmental Science
- Geology and Mineralogy
- Forensics
- Electronics and Semiconductor Industry



SEM-XRF (XTrace): Materials Science

Rare Earth Elements: X-ray Energies







SEM-XRF Analysis of Rare Earth Elements (REE's): Comparison with SEM-EDS



SEM-EDS is better for low energy lines

SEM-XRF is better for high energy lines



SEM-XRF Analysis of Rare Earth Elements (REE's): Applications – High Index Glass





SEM-XRF Analysis of Rare Earth Elements (REE's): Applications – High Index Glass





Analysis of Steels and Alloys Excitation: Micro-XRF; Detector: EDS

Analytical Conditions Point Analysis: 50 kV, 600 uA, No Filter, 130 kcps, under vacuum, Working Distance 12 mm, 120 seconds



All (wt%) Reconciliation





Analysis of Steels and Alloys Individual Elements



Micro-XRF Excitation. EDS Detector. SEM-XRF-EDS.



Analysis of Steels and Alloys Combined Analysis



Sample 32: AISI 422-205B

	Combined	SEM-EDS	MicroXRF	Certified	Element
SFM-				0.22	C
				0.05	N
				0.01	Al
Low-Z	0.33	0.34		0.37	Si
elements				0.01	Р
				0.00	S
	0.00		0.003	0.00	Ti
	0.26		0.279	0.26	V
	11.32	11.37	11.084	11.72	Cr
SEM-XRF	0.75	0.87	0.797	0.68	Mn
Lick 7	83.20	84.55	83.243	83.70	Fe
Figh-Z	0.02	0.49	0.024	0.03	Со
elements	0.67	0.54	0.692	0.70	Ni
	0.15		0.177	0.15	Cu
	0.01		0.012	0.02	Nb
	0.94	0.95	0.970	0.97	Mo

Al Alloy Improved LOD comparison EDS - XRF



	Mg	AI	Si		V	Cr	Mn	Fe	Ni	Cu	Zn	Ga	Sr
EDS mean concentration value	1.20	85.09	11.43	n.d.	n.d.	b.d.	n.d.	0.36	0.91	0.91	0.10	n.d.	n.d.
Micro-XRF mean concen- tration value	0.85	83.87	12.83	0.03	0.01	0.06	0.03	0.36	0.93	0.93	0.10	0.01	0.03
Certificied values	1.1	84.52	12.00	0.011	0.0099	0.051	0.033	0.31	0.89	0.89	0.098	0.02	0.026



Fig. 1 Photograph of the analyzed specimen Alcoa Deltalloy® 4032



Large Area Maps Rapid Stage + SEM Stage: SEM-XRF





Large Samples:

Concrete Block: 61.8 mm x 74.4 mm

Such samples require a combination of the Specialised high speed stage + SEM Stage.

The sample is analysed in 4 maps which are mosaiced at the completion of the analysis.

Image Extension: SEM is 14 x 22



SEM-XRF (XTrace): Archaeology and Art Conservation

Analysis of Cu-bearing Ores Atacamite

Analysis of Atacamite: Use of Filters for Trace elements





Ca Cl Cu

MAG: 30x HV: 50 kV WD: 12 mm

5 mm





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Analysis of Ceramics: Large Area Maps

WEBINAR: SEM-XRF (XTRACE)

Third Row: Ca, Ti, Cr; Bottom Row: Mn, Fe, F1

Ceramic Samples from Northern Chile

d

Identify different mineral phases – probable different source material







SEM-XRF: Analysis of Roman Coins





Dominated by XRF Signal



Areas of Combined XRF and e-Beam analysis





SEM-XRF (XTrace): Environmental Science

WEBINAR: SEM-XRF (XTRACE) Analysis of Soil Samples: Large Area Maps





Analysis of Soil Samples: Large Area Maps





After Maximum Pixel Spectra determines presence of Trace elements.

Detailed investigation confirms presence of both Pb and As

Analysis of Soil Bedrock: Large Area Maps

Polished Sections:

Standard Size: 45 x 30 mm Such samples can be completely analysed using the Specialised high speed stage only. *Example: Soil Sample from Korea*

Analytical Parameters:

Tube Voltage: Rh at 50 kV Anode Current: 600 uA Pixel Spacing: 25 um Analytical Time: 755 mins





Top: Elemental Maps; Bottom Left: Mixed Elemental Map; Bottom, Right: X-Ray Intensity Map.





SEM-XRF (XTrace): Geology

SEM-XRF: Hypermap Results Analytical Parameters







SEM-XRF-EDS: Hypermap Results Analytical Parameters



Clinopyroxene

Garnet

Metasomatic Interaction

Quantitative Microanalysis with SEM-XRF Point Analysis - major elements



Comparison XRF-EDS spectra for the same point: analytical precision

Element	Unit	EPMA Values	XRF-EDS Values	Std. Dev.	Maximum	Minimum	Range
SiO2	(%)	39.28	39.22	0.18	39.48	38.89	0.58
TiO2	(%)	0.28	0.30	0.02	0.33	0.26	0.07
AI2O3	(%)	22.51	21.68	0.31	22.21	21.23	0.98
Cr2O3	(%)	0.12	0.11	0.01	0.11	0.09	0.02
FeO	(%)	21.00	21.41	0.20	21.85	21.18	0.67
MnO	(%)	0.47	0.47	0.01	0.50	0.46	0.04
MgO	(%)	11.44	12.22	0.32	12.62	11.57	1.05
CaO	(%)	4.57	4.36	0.05	4.45	4.29	0.16



Quantitative Microanalysis with SEM-XRF Point Analysis – major and trace elements



Trace elements possible with Micro-XRF

Element	Unit	90 sec	120 sec	180 sec
SiO2	(%)	39.04	39.17	39.20
TiO2	(%)	0.28	0.28	0.29
AI2O3	(%)	22.23	21.97	21.87
Cr2O3	(%)	0.11	0.11	0.11
FeO	(%)	21.16	21.05	21.02
MnO	(%)	0.49	0.48	0.48
MgO	(%)	12.29	12.57	12.63
CaO	(%)	4.35	4.31	4.33
N 1 2				
NI	(ppm)	26	18	28
NI Cu	(ppm) (ppm)	26 3	18 5	28 4
Cu Zn	(ppm) (ppm) (ppm)	26 3 173	18 5 143	28 4 150
Cu Zn Ga	(ppm) (ppm) (ppm) (ppm)	26 3 173 7	18 5 143 0	28 4 150 28
Cu Zn Ga Ge	(ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17	18 5 143 0 22	28 4 150 28 17
Cu Zn Ga Ge As	(ppm) (ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17 28	18 5 143 0 22 28	28 4 150 28 17 28
Cu Zn Ga Ge As Rb	(ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17 28 41	18 5 143 0 22 28 69	28 4 150 28 17 28 59
Cu Zn Ga Ge As Rb Sr	(ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17 28 41 28	18 5 143 0 22 28 69 0	28 4 150 28 17 28 59 28
Cu Zn Ga Ge As Rb Sr Y	(ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17 28 41 28 28 2	18 5 143 0 22 28 69 0 28 28	28 4 150 28 17 28 59 28 28 3
Cu Zn Ga Ge As Rb Sr Y Zr	(ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm) (ppm)	26 3 173 7 17 28 41 28 41 28 2 2 157	18 5 143 0 22 28 69 0 28 143 143 143 157	28 4 150 28 17 28 59 28 59 28 3 171



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	KAISi308





SEM Micro-XRF Analysis: Epithermal Au Large Area Mapping





Epithermal Gold-bearing rock sample from Karangahake, New Zealand

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



SF2

SF1



1 cm

SF5

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









Single Field 6 Large Gold Grain; Associated with Silver

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

SEM-EDS (e-beam) and AMICS Area: SF6





















SEM-XRF (XTrace): Forensics

Micro-XRF on SEM NIST Standard Glasses

Analysis of NIST Standard Glasses with dopped concentrations in the approximate range of:

NIST 610:	500 ppm
NIST 612:	50 ppm
NIST 614:	5 ppm

Easily identify trace element concentrations

SE Image

Ce

La

Nd

Eu



Micro-XRF on SEM Applications: Trace Elements



Glass analysis: NIST 610





Forensics: Glass fragment analysis

Micro-XRF on SEM Applications: Analysis of Glass

Glasses mounted for analysis











SEM-XRF: Analysis of Beach Sands



Analysis of Beach Sand

Loose Grains Various Size Fractions Uncoated Large Area High Speed Stage Movement







SEM-XRF (XTrace): Electronics and Semiconductor Industry

MICRO-XRF ON SEM: XTRACE

Micro-XRF on SEM Applications: Electronics and Semiconductors (Layer Analysis)





Electronics: Failure analysis on PCB



Electronic & Semiconductors: Thin film analysis on various layer structures (solar cells, electronic contacts etc.)

SEM-XRF Analysis of Rare Earth Elements (REE's): Applications – Electronics







Image courtesy of Benjamin Monneron-Enaud, TU Bergakademie Freiberg, Germany.

SEM-XRF Analysis of Rare Earth Elements (REE's): Applications – Electronics





REEs Example: Applications – Electronics





6.5



SEM-XRF (XTrace): Summary and Conclusions

Summary and Conclusions: Micro-XRF on SEM

2 Excitation Sources: Electron Beam (e-beam) Micro-XRF (X-ray beam)

1 Detector: Energy Dispersive Spectrometer (EDS)

2 Stages: SEM Stage Rapid Stage



Micro-XRF Benefits:

- Non-destructive analytical technique
- No charging effects
- Minimal Sample Preparation Required
- Lower detection limits (down to 5 ppm)
- High Energy Lines Detection (Full

Spectrum Range up to 40 keV)

- Ideal for Low kV or Beam sensitive samples
- Fast Large Area Mapping
- Micrometer scale measurement over cm

Workflow: Correlating Micro-XRF / e-beam / EDS / WDS analysis





Micro-XRF (M6 JETSTREAM, M4 TORNADO, SEM-XRF (XTRACE))

- Fast analysis over large area
- Confirm presence of elements of interest
- Identify areas for further analysis
- Store stage positions of those areas

SEM-EDS

- High spatial resolution
- Fast analysis over small area
- Identify elemental and mineralogical relationships and associations on the micro- nano- scale.

SEM-WDS

- High spatial resolution (similar to EDS)
- Resolution of peak overlaps
- Low detection limits
- High sensitivity for low X-ray energy range

Micro-XRF on SEM (XTrace): **Further Information**



QUANTAX Micro-XRF

Trace Element Sensitivity with Minimal Sample Preparation

High-Speed Elemental X-ray Mapping even over Large Areas Film Thickness Analysis

ELECTRON MICROSCOPE ANALYZERS

BRUKER





Large Area Mapping of Mineralogical Samples

The new Rapid Stage is specifically designed for SEMs to enable large area mapping over millimeter (mm) to centimeter (cm) scales. This will eliminate potential SEM X-ray intensity variation artifacts associated with low magnification mapping and thus enhance elemental and mineralogical information in a timeous manor that was previously not possible.

→ READ MORE





Elemental and Mineral distribution in **Dual Source Applications for Exploration**

The ability to observe elemental changes within samples is important to understand geological processes and ore deposit genesis. The dual source system which incorporates a micro-XRF on a SEM enables elemental X-ray mapping over large areas, which shows major, minor and also trace elements on the ppm scale.

Exotic-Cu Deposits

and Mining: Au-bearing Epithermal Samples

The combination of micro-XRF with SEM enables the potential to analyze samples at multiple scales, from centimeters (cm) to millimeters (mm) to micrometers (µm) and below within a solitary system. Thus, by adding the micro-XRF to an SEM you convert your SEM to a dual source system, meaning that there are 2 excitations sources, the e-beam and photon beam. Either source can be used individually, or simultaneously, to generate sample X-rays that will be measured using the same EDS detector.

→ READ MORE



Search for: **QUANTAX Micro-XRF**



Mantle Petrology and the Source of Diamonds

We present a SEM-XRF element map of a mantle garnet-spinel peridotite from the diamond-bearing Newlands kimberlite (South Africa, Kaapvaal Craton). The intensity of the various elements indicates certain minerals that are present in the sample.

→ READ MORE



Identification of Contaminants and Toxins in Soils

Large Area Mapping (Hypermaps) using SEM-XRF can be performed on samples with topography. That is, minimal sample preparation is required and the sample can be analyzed directly without any degredation. This is particularly relevant in the analysis of soils, where any form of sample preparation, such as mounting and polishing or carbon coating, may alter the specimen.



Thin Film Analysis with SEM micro-XRF

As X-rays may pass through matter, X-ray Fluorescence (XRF) allows the determination of layer thickness. Using micro-XRF on SEM, the layer analysis (thickness and composition) is rendered feasible with spatial resolution at the micrometer scale. Layer analysis is strongly based on quantification using atomic fundamental parameter (FP).

→ READ MORE







Micro-XRF General Information Further Information



https://www.bruker.com/

Search for: QUANTAX Micro-XRF

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QUANTAX N	licro-XRF						
Trace Element Sensitivity v	vith Minimal Sample Prep	aration					
High-Speed Elemental X-ray Mapping even ove Large Areas Film Thickness Analysis		R.					

Upcoming Webinars:

Back To The Roots, Part V:

Advantages of standard-supported micro-XRF quantification: Where are we today in terms of performance of FP quantification?

Date: 02.05.2023 (10 am, 5 pm)

And a new SEM-XRF webinar in June



LinkedIn Posts: #BrukerXTrace





More Information

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Innovation with Integrity



X-ray Fluorescence and Electron Excitation Analysis

- Excitation with either electrons or X-rays generate fluorescence radiation of the irradiated material.
- Detection is normally performed with energy dispersive spectrometers (EDS), independent of the excitation source. Signal collection and spectral presentation is identical, but quantification is different.
- Main differences:
 - > Spot Size
 - Information depth
 - Elemental Range (Energy)
 - Limits of detection (Concentration)
 - Spectral Background
 - Sample Handling



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 e-beam 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.





Overview: Characterization Workflow of a multiscale approach



a multi-scale, multi-modal and multi-dimensional approach. EMAS 2019, Conference Proceedings Volume, Trondheim, 19-23 May 2019.



Micro-XRF M4 Tornado Plus

GTK



SEM-EDS-Micro-XRF-WDS



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Innovation with Integrity Webinar 2023

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Micro-XRF Possibilities



No sample preparation



Information from the depth of the sample



Trace element sensitive



Reference samples and standard supported quantification options

Micro-XRF: XTrace



Rapid Stage



- **XTrace** 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)
- X-ray beam is fixed in space and cannot raster as a e-beam can do, element distribution measurements will be performed via stage movement (either SEM stage or Rapid Stage)