Fast, Accurate and Precise Quantification Results Using An Annular Silicon Drift Detector: Bruker's XFlash FlatQUAD



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Presenters





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- Introduction
- Microanalysis and the FlatQUAD: Technical Introduction
- Analytical Considerations
- Examples: Quantification
- Examples: Mapping and Mineralogy
- Summary and Conclusions

Bruker SEM Analyzers Our "evolving eyes"





Facts for the XFlash® FlatQUAD







- Annular design, 4x15 mm² = 60 mm²
- Placed between pole piece and sample (hole in the center for the primary beam)
- Energy resolution Mn K $\alpha \leq 129 \text{ eV}$
- Combination of high count rate capability and high solid angle ($\Omega \sim 1.1 \text{ sr}$)



Collection Efficiency: Solid Angle for X-ray collection





$$\Omega = \frac{A}{d^2}$$

Achieve higher solid angle by:

Chip <u>area A</u> but, smaller areas have advantages:

less cooling, less weight > higher stability, less pile up, better TOA > better P/B, better energy resolution, higher OCR/ICR = higher efficiency

Distance d: get as close as possible



 $\Omega_{\rm EDS-SEM} \sim 0.01$ – 0.1 sr are typical for side entry

 $\Omega_{\rm EDS-S/TEM} \sim 0.1$ – 0.4 sr are typical for side entry

Some 100 mm² in STEM ~ 0.5 sr

XFlash[®] FlatQUAD: Advantage of large solid angle

- Guaranteed energy resolution Mn-Ka 129 eV (other resolutions on request)
- 4 x 15 mm² = 60 mm²
- Annular design
- Central aperture for the primary beam
- Designed to be placed between pole piece and sample
- Segments very close to sample
- 4 x 600.000 cps = 2.400.000 cps

combination of

high count rate capability

large solid angle + high TOA max solid angle at d = 2.5 mm: $\Omega > 1.1$ sr





XFlash[®] FlatQUAD: Advantage of high take-off angle and annular design



Take-off angle comparison: XFlash[®] FQ vs. conventional SDDs:



Polymer compound XFlash[®] FlatQUAD vs. 30 mm² SDD



Polymer composite containing organic clays



XFlash[®] FlatQUAD

- 3 kV, 220 pA, **10 kcps**
- >12 times higher count rate
- No shadow effects



XFlash[®] 30 mm²

- 3 kV, 220 pA, **0.8 kcps**
- Shadow effects due to rough surface

Specimen Courtesy: Dalto et al., Universidade Federal do Rio de Janeiro

Polymer compound XFlash[®] FlatQUAD





- Using the zoom function in Esprit, smallest features and pores can be investigated due to annular design of the FlatQUAD
- Shadow effects are minimized.







- Shadow effects are minimized
- No sample preparation
- Acquired in 1min with 6 kV under high vacuum.
- The structure can resist heavy weights

• 51sec acquisition time, 6 kV, 4096pixel

Sea Urchin (Paracentrotus lividus) from the aegean sea





- The structure can resist heavy weights
- Influences researchers on new materials and also architecture











51sec acquisition time, 6 kV, 4096pixel

Sea Urchin (Paracentrotus lividus) from the aegean sea

- Shadow effects are minimized
- No sample preparation
- Acquired in 1min with 6 kV under high vacuum.







• 51sec acquisition time, 6 kV, 4096pixel

Sea Urchin (Paracentrotus lividus) from the aegean sea

- Small sandgrains and deposits of NaCl can be observed in detail
- Shadow effects are minimized
- No sample preparation
- Acquired in 1min with 6 kV under high vacuum.

Quantification of MoS₂ at 5kV Sample with Topography





Quantification of MoS_2 at 5kVDeconvolution and Quantification Results





Quantification of MoS₂ at 5kV Deconvolution and Quantification Results





Presentation Example Overview



Point Analysis:

- Mineral Grains: Mantle and Volcanic
 - Mounted, Polished and Carbon Coated
 - Standard-based and Standardless Quantification
 - Different accelerating voltage (kV)

Hypermap Analysis:

- Mineral Grains: Mantle and Volcanic
- Mantle Peridotite
 - Feature / Phase Analysis
 - AMICS Automated Mineralogy

SEM-EDS: FlatQUAD Point Analysis: Quantification



Esprit Software: Analytical Parameters

Seperative Sample Standards Micro > × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × × <t< th=""><th>Acquire 🗸</th><th>Quantify</th><th>~</th></t<>	Acquire 🗸	Quantify	~
<pre>Preview Cognie Control Co</pre>	 Acquisition paramete Automatic Pre Manual Real time [s] Live time [s] Live time [s] Counts Region start [keV] Region end [keV] 	ecise	

	Exhaustive	Precise	Fast
Counts	1 000 000	250 000	50 000

SEM-EDS: FlatQUAD Point Analysis: Spectrum Acquisition



Hardware considerations:

- **20 kV:** 1 + 6 µm mylar window
- **12 kV:** 1 +2 µm mylar window
- **6 kV:** 1 μm mylar window



Require different windows to filter this increased signal

Thus there is a different transmission of X-ray signal intensities depending on kV / window combination selected

However, this is accounted for in the quantification procedures

Quantitative Microanalysis Smithsonian Standards



SEM-BSE Image

Combined Elemental Maps (Si, P, and Fe)



SEM-EDS: FlatQUAD Point Analysis: Quantification



Smithsonian Standards Reference:

Jarosewich, E., Nelen, J. A., and Norberg, J.A., 1980. Reference samples for electron microprobe analyses, Geostandards Newsletter, Vol. 4, p.43-47.

Element	Clinopyroxene: Standards Used	Garnet: Standards Used
Si	Augite	Garnet (Almandine-Grossular)
Ti	Ilmenite	Ilmenite
AI	Augite	Garnet (Almandine-Grossular)
Cr	Chromite	Chromite
Fe	Ilmenite	Garnet
Mn	Ilmenite	Ilmenite
Mg	Diopside	Garnet (Pyrope)
Ca	Diopside	Garnet (Almandine-Grossular)
Na	Augite	
Κ	Microcline	
0	Augite	Garnet

Geological Applications: Mantle Minerals



Mantle Minerals



Kimberlite Indicator Minerals (KIM´s)



Geological Applications: Mantle Minerals - Composition



Garnet	 (Ca,Mg,Fe)₃(AI,Cr,Fe³⁺)₂(SiO₄)₃ Minor: Mn y Ti, y Trace: Ni
Olivine	 (Mg,Fe)₂SiO₄ Minor: Ca, Mn, y Trace: Ni
Clinopyroxene	 (Ca,Na)(Mg,Fe,AI)(Si,AI)₂O₆ Minor: Cr
Orthopyroxene	 (Mg,Fe)SiO₃ Minor: AI
Spinel	 (Mg,Fe)(Al,Cr,Fe³⁺)₂O₄ Minor: Ti

FlatQUAD: Standard Based Point Analysis Volcanic Grain Mounts



Carbon Coated High Quality Polish



FlatQUAD: Standard Based Analysis Voltage: 12 kV Garnet: 20 Grains



Quickly quantify different mineral phases Analysis of 20 Grains

Voltage: 12 kV Analytical Time: Exhaustive (1,000,000 counts)



Solid Line is 1:1

FlatQUAD: Standard Based Analysis Voltage: 12 kV Garnet: 20 Grains





FlatQUAD: Standard Based Analysis Voltage: 12 kV Clinopyroxene: 50 Grains



Voltage: 12 kV Analytical Time: Exhaustive

Quickly quantify different mineral phases Analysis of 50 Grains



Graphic Solid Line is 1:1

FlatQUAD: Standard Based Analysis Voltage: 12 kV Clinopyroxene: 50 Grains





FlatQUAD: Standardless Normalised Voltage: 12 kV Clinopyroxene: 50 Grains



Quickly quantify different mineral phases Analysis of 50 Grains

Voltage: 12 kV Analytical Time: Exhaustive (1,000,000 counts)



Graphic Solid Line is 1:1

FlatQUAD: Standardless Normalised Voltage: 12 kV Clinopyroxene: 50 Grains



Quickly quantify different mineral phases Analysis of 50 Grains

Voltage: 12 kV Analytical Time: Exhaustive (1,000,000 counts)



. Solid Line is 1:1

FlatQUAD: Standard Based Analysis Voltage: 6 kV Clinopyroxene: 30 Grains



Quickly quantify different mineral phases Analysis of 30 Grains

Voltage: 6 kV Analytical Time: Exhaustive (1,000,000 counts)



Graphics Solid Line is 1:1

FlatQUAD: Standard Based Analysis Voltage: 6 kV Clinopyroxene: 30 Grains





FlatQUAD: Standard Based Analysis Voltage: 6 kV and 12 kV Clinopyroxene



Element	Acclerating Voltage: 6 kV	Acclerating Voltage: 12 kV
Mg	Mg K – 1.254	Mg K – 1.254
Si	Si K – 1.740	Si K – 1.740
Ca	Ca K – 3.691	Ca K – 3.691
Fe	Fe L – 0.705	Fe K – 6.401

Voltage: 6 kV Analytical Time: Exhaustive



Solid Line is 1:1 Dashed Lines are +/- 10%

Voltage: 12 kV Analytical Time: Exhaustive





20 Repeat Analyses Clinopyroxene



	SiO2 (%)	TiO2 (%)	AI2O3 (%)	Cr2O3 (%)	FeO (%)	MnO (%)	MgO (%)	CaO (%)
Spectra_CVO-CPX-42 61	55.98	0.19	2.13	0.50	9.90	0.26	30.99	1.23
Spectra_CVO-CPX-42 62	55.94	0.17	2.19	0.56	9.76	0.19	30.83	1.32
Spectra_CVO-CPX-4263	55.78	0.18	2.19	0.61	9.53	0.22	30.96	1.18
Spectra_CVO-CPX-42 64	55.94	0.12	1.90	0.50	9.88	0.28	30.79	1.31
Spectra_CVO-CPX-4265	55.81	0.19	2.18	0.55	9.80	0.19	30.97	1.26
Spectra_CVO-CPX-4266	55.71	0.16	2.15	0.53	9.80	0.17	31.02	1.24
Spectra_CVO-CPX-4267	56.03	0.18	2.00	0.55	9.52	0.24	30.93	1.15
Spectra_CVO-CPX-4268	55.36	0.18	2.09	0.49	10.41	0.29	30.13	1.32
Spectra_CVO-CPX-42 69	55.53	0.15	2.10	0.59	9.97	0.25	30.54	1.18
Spectra CVO-CPX-4270	55.35	0.20	2.10	0.55	9.71	0.25	30.81	1.23
Spectra_CVO-CPX-4271	55.98	0.13	2.02	0.52	9.89	0.27	30.98	1.28
Spectra_CVO-CPX-4272	55.06	0.23	2.53	0.52	10.97	0.27	29.49	1.33
Spectra CVO-CPX-4273	55.61	0.23	2.09	0.56	10.27	0.26	30.63	1.28
Spectra CVO-CPX-4274	55.84	0.18	2.12	0.57	9.76	0.16	30.89	1.27
Spectra_CVO-CPX-4275	55.62	0.16	2.12	0.56	10.27	0.25	30.13	1.38
Spectra CVO-CPX-4276	55.16	0.19	2.20	0.33	11.69	0.26	29.58	1.34
Spectra CVO-CPX-4277	55.61	0.14	2.08	0.59	10.82	0.22	30.26	1.23
Spectra CVO-CPX-4278	56.05	0.20	1.87	0.48	9.97	0.20	30.89	1.22
Spectra CVO-CPX-4279	55.31	0.21	2.46	0.47	10.83	0.21	29.99	1.46
Spectra CVO-CPX-4280	55.39	0.14	2.13	0.41	11.44	0.29	29.64	1.16



20 Repeat Analyses: Clinopyroxene All major and minor elements within error



Element	Accepted Values	FlatQUAD Average	FlatQUAD Std Dev	FlatQUAD Maximum	FlatQUAD Minimum	FlatQUAD Range
SiO ₂	55.60	55.65	0.30	56.05	55.06	0.99
TiO ₂	0.20	0.18	0.03	0.23	0.12	0.11
Al ₂ O ₃	2.00	2.13	0.15	2.53	1.87	0.66
Cr ₂ O ₃	0.60	0.52	0.07	0.61	0.33	0.28
FeO	9.60	10.21	0.63	11.69	9.52	2.17
MnO	0.20	0.24	0.04	0.29	0.16	0.13
MgO	30.40	30.52	0.52	31.02	29.49	1.53
CaO	1.20	1.27	0.08	1.46	1.15	0.30









FlatQUAD: Hypermapping Volcanic Grain Mounts



2048 µS

Pixel Dwell Time:

Quickly identify various mineral phases: Different Clinopyroxene Compositions

Project (mod.) 18/09/2019 14:00 3 kB 🛅 Stan... O \approx -回 Report Sam... III Map result table 80 px v Report_0 Test sam ~ m ESL-5 ~ HV ~ +I+ 1000 0.0 60 kcps v EDS + Linemarker + PB-ZA QMap 4 JS Map CVZ-Cpx Map01 100pxl 2048uS Mag200x 3500kcps 08x12.bcf XRF + XRF Ch1 Map Phases Phases Charts Line scan Spectrum 4 ≒ MAD Mapping parameter 4 Width: 600 pixel 9246 µm ?≣ 825 pixel Height 12588 µm 15 µm Pixel size: 14 i Acquisition paramete <u>"</u> Pixel time: 2.0 ms Overall time: 16 min Kaz. 1 Microscope parameter . High voltage: 15 kV Working distance: 13 mm Magnification: 200 x 1 • lear all Auto ID 🔻 Sample information CVZ Cpx - 53 Name: Description: the second Map display settings nts Standard None Mean Close 000000000000 0.75 µm Spot size 750x563 Points Map result list 12 1 -Са-Ка Cr-Ka 1.00 Si-K 1.00 Al-K 1.00 Κ-Κα 1.00 Mn-Ka 1.00 Ti-Ka 1.00 Na-Ka Fe-Ka H ଜ 🕩 🗰 ENG

FlatQUAD: Hypermapping Volcanic Grain Mounts



Quickly identify various mineral phases: Different Clinopyroxene Compositions Pixel Dwell Time: 2048 µS Input Count Rate (ICR): 2,100,000 cps



nt Mixed Element Intensity Maps

Optical Image

Individual Element Intensity Maps

FlatQUAD: Hypermapping Volcanic Grain Mounts

Quickly identify different clinopyroxene compositions



Input Count Rate (ICR): 2,100,000 cps



Total Analytical Time: Decreasing

16 minutes

126 seconds

15 seconds

2 seconds

FlatQUAD: Hypermapping Volcanic Grains

Titanomagnetite symplectic textures in volcanic grains





FlatQUAD: Hypermapping Volcanic Grains

Titanomagnetite symplectic textures in volcanic grains



Fe Quant Map



SEM-EDS: Hypermapping Volcanic Grains

Titanomagnetite symplectic textures in volcanic grains





FlatQUAD: Hypermapping Volcanic Grains

Zonation in clinopyroxene grain









Intensity Maps

Measurement Conditions

High Voltage:	15 kV
Pixels:	800 x 1050
Measurment Time:	28 min
SDD:	4 x 60 mm ²
Dwell time:	2048 µs
FOV:	16 mm
Pixel size:	15 µm
Fields:	8 x 14 (112)
Magnification:	200x
ICR:	2,200,000 cps

Mixed Element Intensity Maps











Phase	Area %
P1	12.3
P2	9.5
P3	7.7
P4	34.4
P5	3.2
P6	0.2
Unassigned	32.8







Spectrum	Oxygen	MgO	CaO	Cr2O3	FeO	SiO2	Al2O3	K2O	MnO	TiO2	
P1	0.00	20.67	4.63	4.95	6.38	40.09	20.35	0.21	0.37	0.00	
P2	0.00	14.62	0.08	54.93	14.20	1.34	10.70	0.02	0.58	0.00	
Р3	0.00	33.46	1.38	1.07	6.78	49.09	3.39	0.88	0.19	0.19	
P4	0.00	16.89	18.38	3.87	1.73	50.41	3.48	0.46	0.00	0.00	
P5	0.00	25.24	2.34	3.30	4.40	41.25	15.39	4.91	0.10	0.20	





Phase	Area %	Mineral
P1	12.3	Garnet
P2	9.5	Chromite
P3	7.7	Olivine
P4	34.4	Clinopyroxene
P5	3.2	Metasomatism
P6	0.2	Sulphide
Unassigned	32.8	Glass Slide

FlatQUAD: Hypermap Results AMICS: Automated Mineralogy





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FlatQUAD: Hypermap Results AMICS: Chromite





Mineralogical Map: All phases shown

Modal Mineralogy: Quantification

Wt%

FlatQUAD: Hypermap Results AMICS: Chromite





Mineralogical Map: All phases shown Mineralogical Map: Chromite Mineral enhanced Other Minerals faded Chromite Mineral Map: Relative Positions

FlatQUAD: Hypermap Results AMICS: Chromite





Mineral Size Distribution - [Grain Laver]:[Chromite]:[Equivalent Circle]:[Coarse Sizes] **Chromite Mineral** Grains: Sorted by Size Sieve Size (µm) **Chromite Mineral**

Grains Size Distribution

Chromite Mineral Map: Relative Positions



Modal Mineralogy: How much of each mineral is present.

Elemental Assay: How much of each element is present (Whole Rock).

Elemental Distribution: How is the element of interest (EOI) distributed in each mineral? E.g. Cr in Chromite vs Pyrope Garnet.

Mineral Association: Identify how the minerals are associated with eachother, e.g. Chromite and Garnet and Clinopyroxene etc.

Grain Shape Factor: The shape of the grain, i.e. euhedral, elongated.

Mineral Density Distribution: Classify densities of minerals. Identify how the minerals are distributed among the densities.

Grade Recovery Curves: What % of minerals of interest (MOI) or element of interest (EOI) is recovered at what grade?

FlatQUAD: Hypermap Results Analytical Time





Analytical Time: Decreases

Note: Does not include stage movement time

FlatQUAD: Hypermap Results High count map vs. low count map





Major element distribution is visible in both maps

Due to background noise, minor elements are identified better in the high count map

High Count Map, (28 min), 8x14 fields (112) Low Count Map (3 sec), 8x14 fields (112)

Mapping of nano structures -Semiconductor



EDS Measurement parameters

Map size	400 x 240 px
Measurement time	60 minutes
HV	20 kV
Input count rate	380 kcps
WD	14 mm
Dead time	20%



Mapping of nano structures – Semiconductor Peak overlaps – online deconvolution





Mapping of nano structures – Semiconductor Lateral resolution of 10 nm





Extracted linescan from the map data

Mapping of nano structures – Au NP Lateral resolution of under 10 nm





Au-NP on TiO₂ Sponge-like coating for implants T. Yang et al., Colloids and Surfaces B: 145, 597 (2016). Ralf Terborg et al., Microscopy Today, 2017, 3: 35



- Au-nano particles (NP) to avoid implant inflamation
- NP change surface potential
- Settling bacteria get "electricuted".
- For successful tissue growth it is very important to judge the distribution of the NP and compare it to fluorescence light microscopy.



- The FlatQUAD gives fast, accurate and precise quantification results. This can be standard-based or standardless.
- Ideally suited for beam sensitive samples and/or samples were sample preparation like coating is impractical.
- Avoids shadow effects.
- Ultra high speed mapping over entire thin sections (40 x 30 mm) in less then 3 minutes are possible with stage movment.
- Smallest particles can be observed and analyzed with low beam currents.
- Superior to standard SDD in speed and count-rate.

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Are There Any Questions?

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



For more information, please contact us:

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Innovation with Integrity