Thermo Scientific Microanalysis Course

The world leader in serving science

Introduction

The SEM has 2 main functions:

1. Imaging
2. Analysis

Thermo Scientific provides the tools to add Analysis capabilities to the Imaging performance.

Three products are available:

1. Energy Dispersive X-ray Microanalysis (EDS)
2. Wavelength Dispersive X-ray Microanalysis (WDS)
3. Electron Backscatter Electron Diffraction (EBSD)

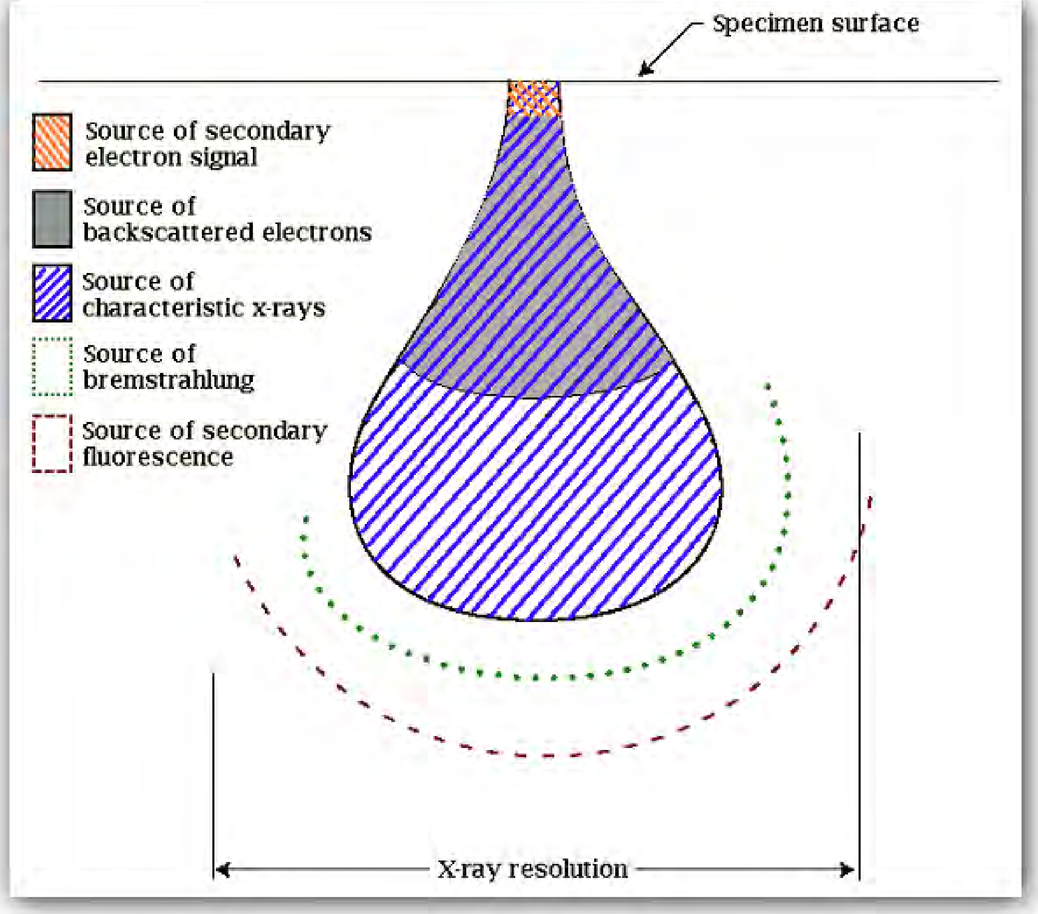
Interaction between the Electron Beam & the Sample

Electron Beam & Sample Interaction

Interaction Volume

- **The volume in which the primary electrons interact with a sample**

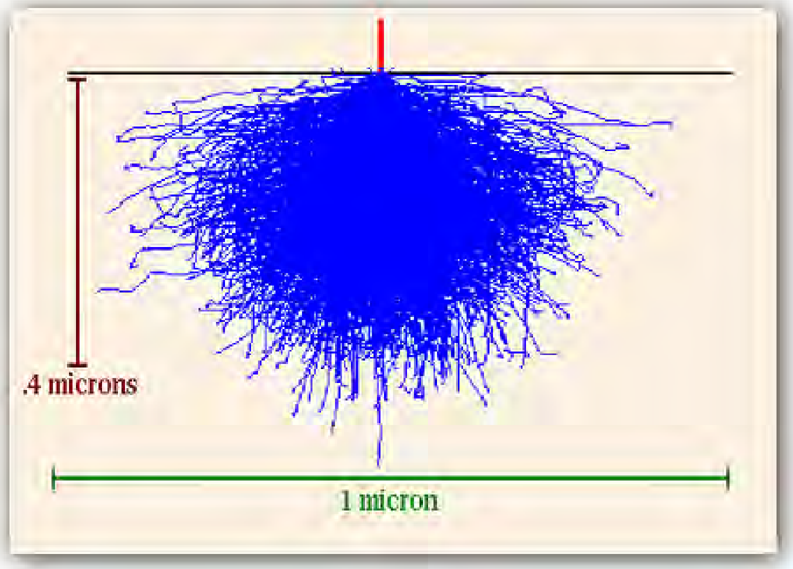
As electrons interact with the sample, they are scattered and spread.



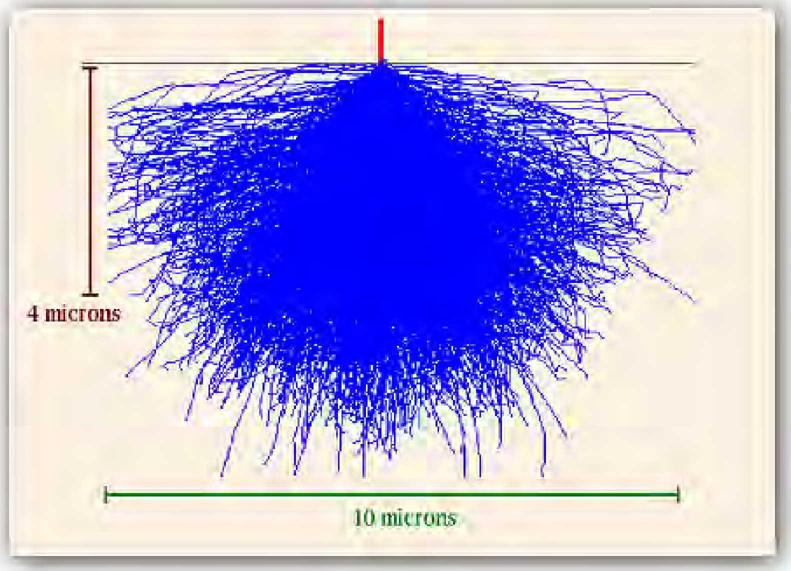
Electron Beam & Sample Interaction

Interaction Volume Simulation

Carbon Sample



Accelerating Voltage = 5KV

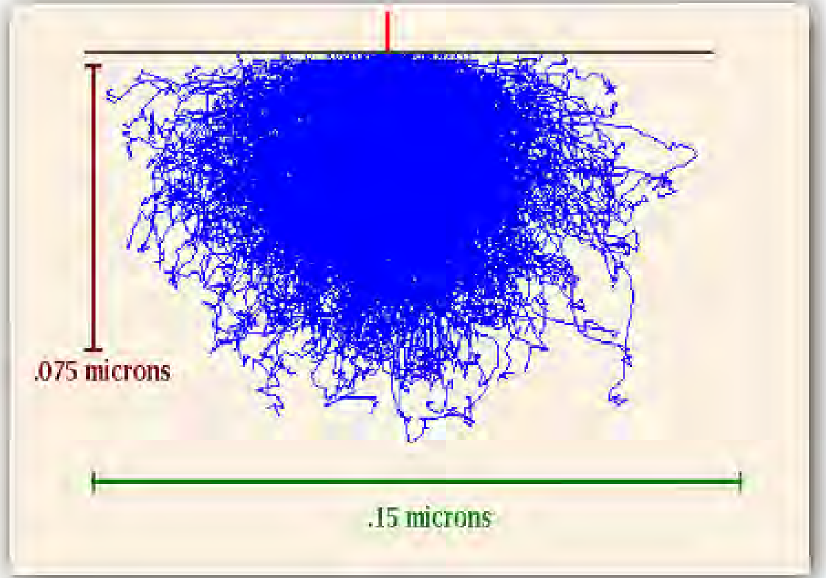


Accelerating Voltage = 25KV

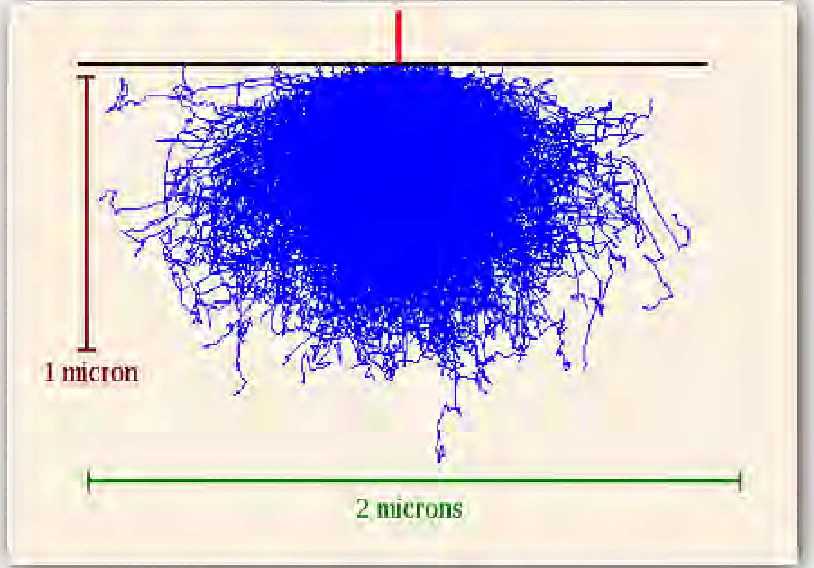
Electron Beam & Sample Interaction

Interaction Volume Simulation

Gold (Au) Sample



Accelerating Voltage = 5KV

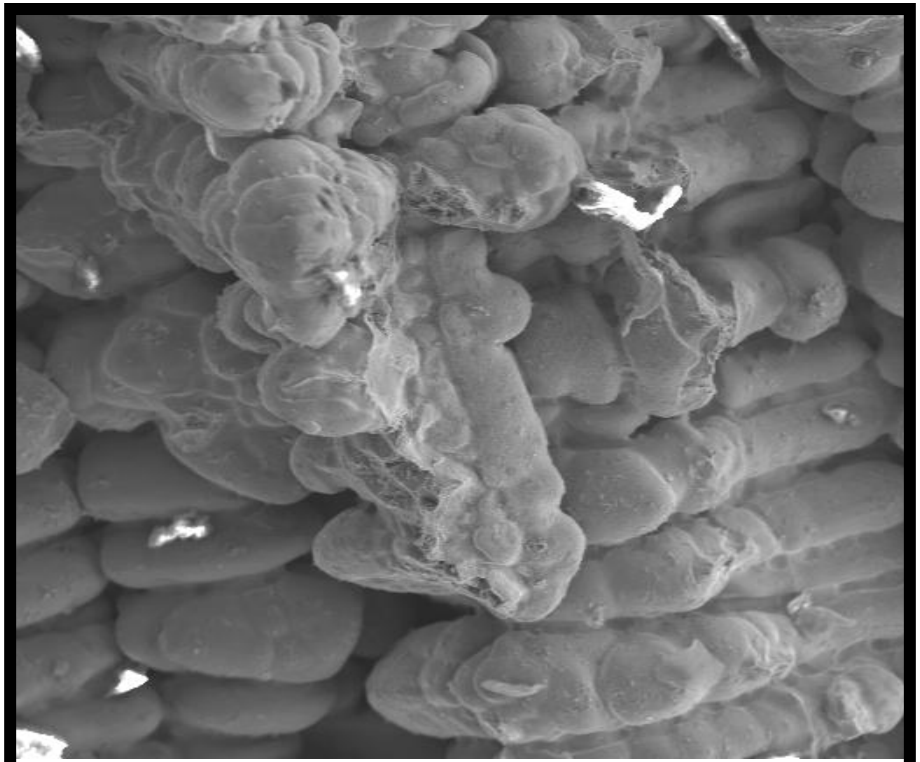


Accelerating Voltage = 25KV

Electron Beam & Sample Interaction

Secondary Electrons

- **Low energy (below 50eV) created near the surface of the specimen.**
- **Very little information about elemental composition of the sample.**
- **Topographic sensitivity and high spatial resolution make them the frequent choice for micrographic images.**

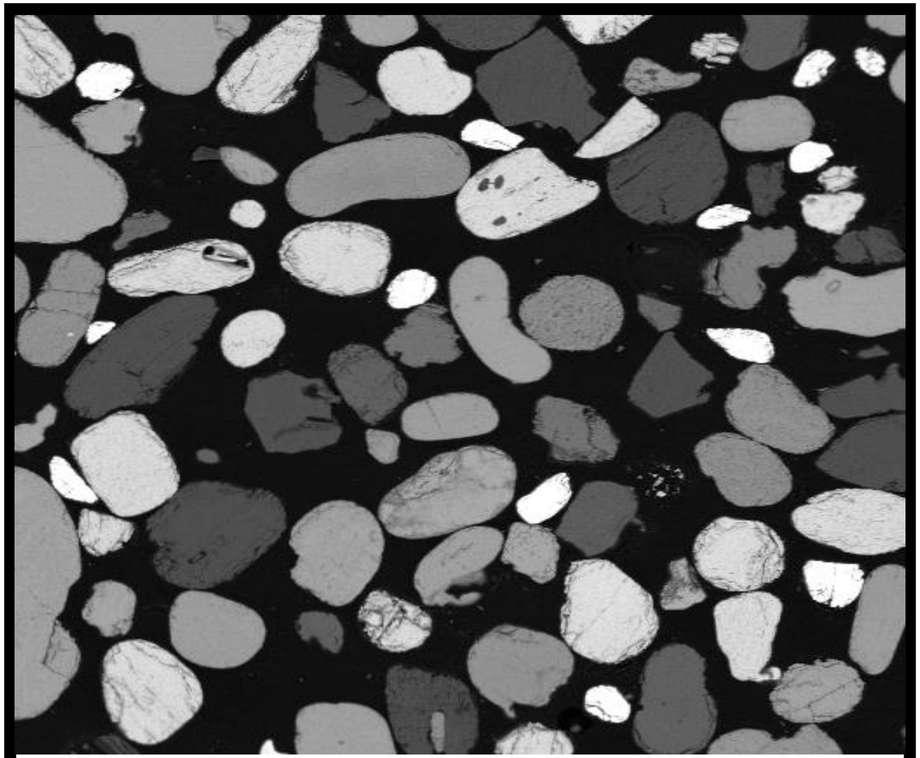


Secondary Electron Image

Electron Beam & Sample Interaction

Backscattered Electrons

- More energetic than secondary so they escape from deeper in the sample.
- Carries some information about the sample chemical composition.
- Not as much topography and lower spatial resolution compared to secondary electrons.



Backscattered Electron Image

Data sampling

How long are analytical SEMs on the market now? Around 50 years

In the last 50 years, how many SEMs have been made? Around 1500/yr so about 75.000

What is the effective lifetime of each SEM? Around 15 yrs, so 1.125.000 SEM-yrs

How many days is a SEM used per year? Around 200 days, so 225 million SEM-days

How many samples per day? Around 20 samples per day, so 4.500.000.000 samples

How many analyses on each sample? Maybe 20 analysis points, so 90.000.000.000 points

What is the volume of each analysis? One cubic micron

So what is total volume analysed in the last 50 years with all the SEMs in the world?

90.000.000.000 cubic micron, or 90 cubic millimeter

And how expensive was that?

75000 SEMS at 100.000 Euro per SEM means 7.500.000.000 Euro,
or over 80 million Euro per cubic millimeter

Where to find S.E.M.'s ??

The SEM has a lot in common with the famous German

Eierlegende Woll-Mich-Sau,

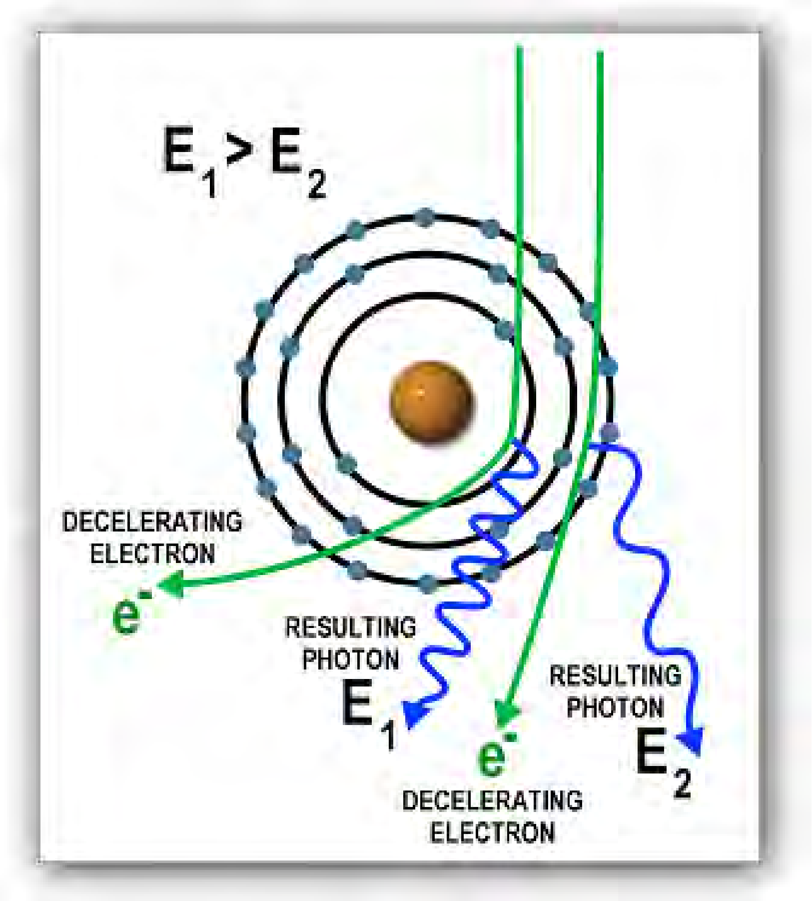
but there is one major difference: the SEM exists !!

X-Ray Excitation

X-ray excitation

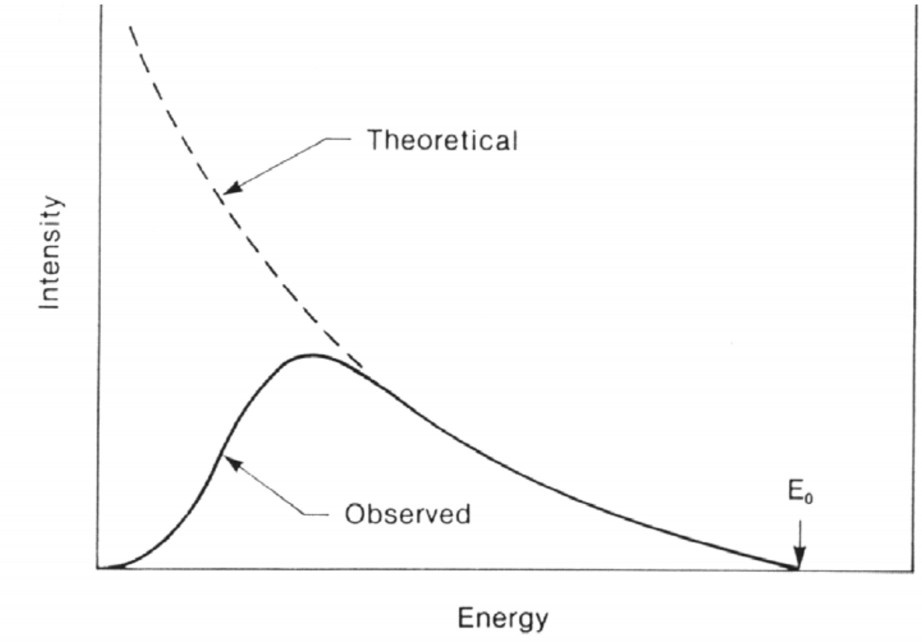
Elastic scattering

- Primary electron beam is elastically scattered by the nucleus.
- The interaction causes the primary electron to lose some or all of its energy. (So it is not really fully elastic….)
- Produces a continuous spectrum of radiation, which we see as the spectrum background.
- It is also known as Bremsstrahlung, or braking radiation, or continuum radiation.



X-ray excitation

- Continuum radiation due to elastic scattering
- Observed fall out at low energies due to X-ray absorption en route to the detector
- Background needs to be removed for quantification

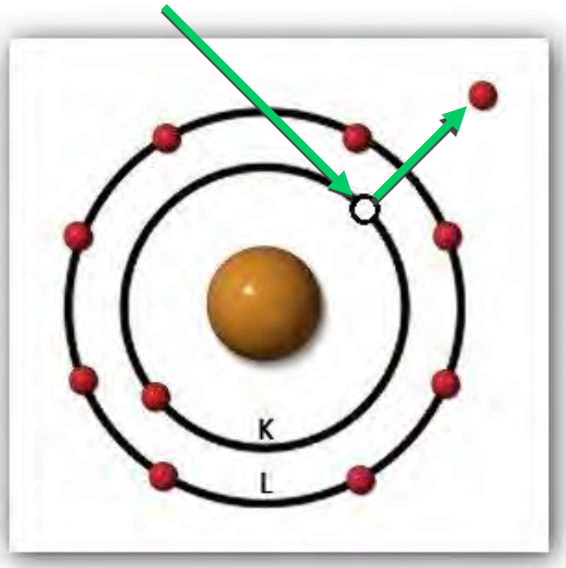


X-ray excitation

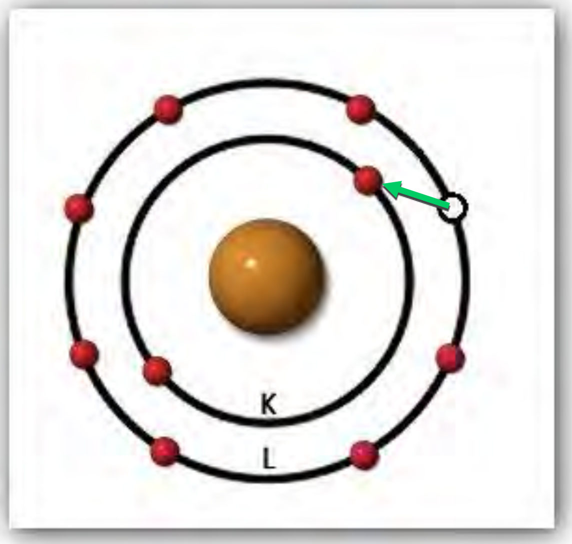
Inelastic scattering

- **Based on inner electron transitions between inner atomic shells.**

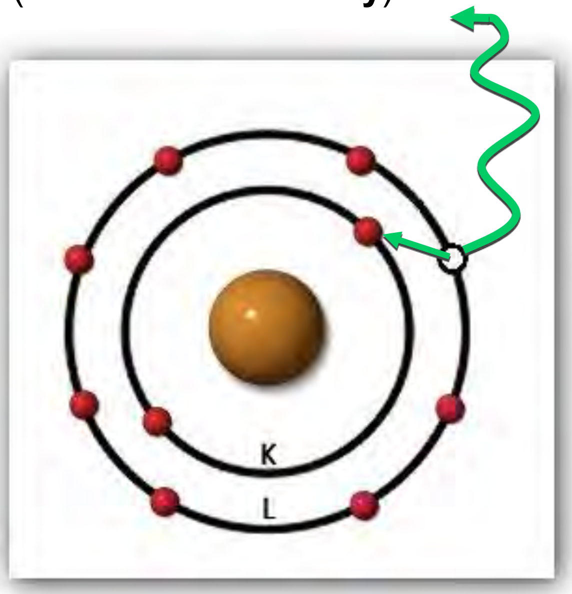
Energetic electron from an electron column dislodges an orbital electron.



Electron from a higher energy shell fills the vacancy, losing energy in the process.



The lost energy appears as emitted radiation of energy (**characteristic X-Ray**).



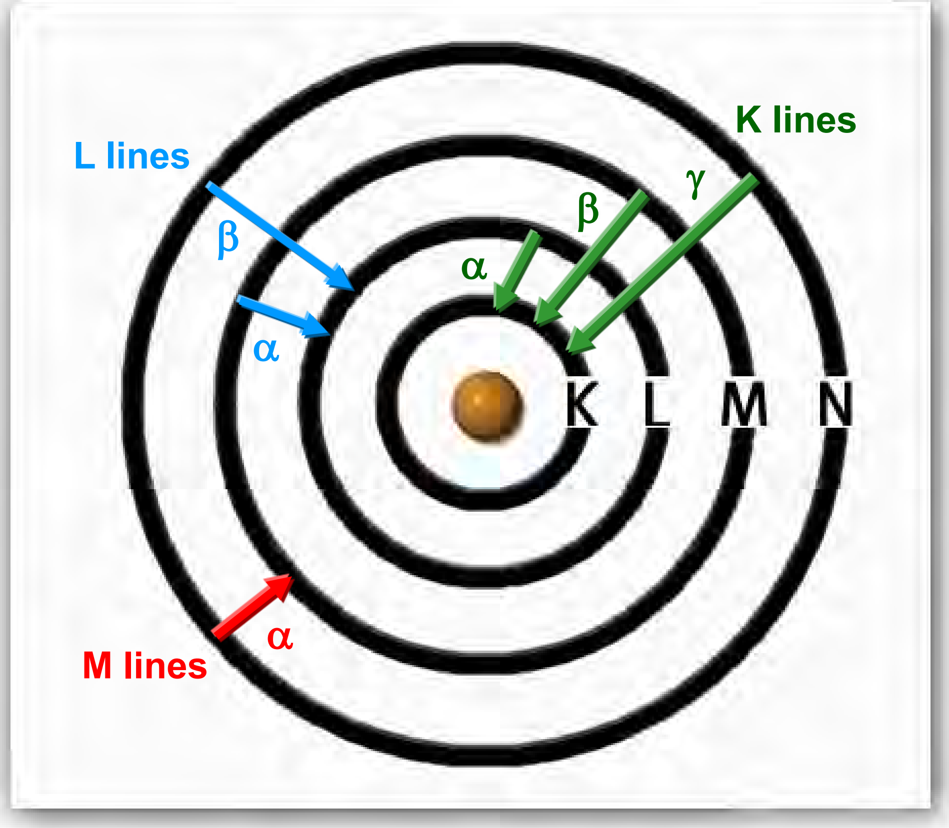
X-Ray names

The names of the X-Ray lines have two components

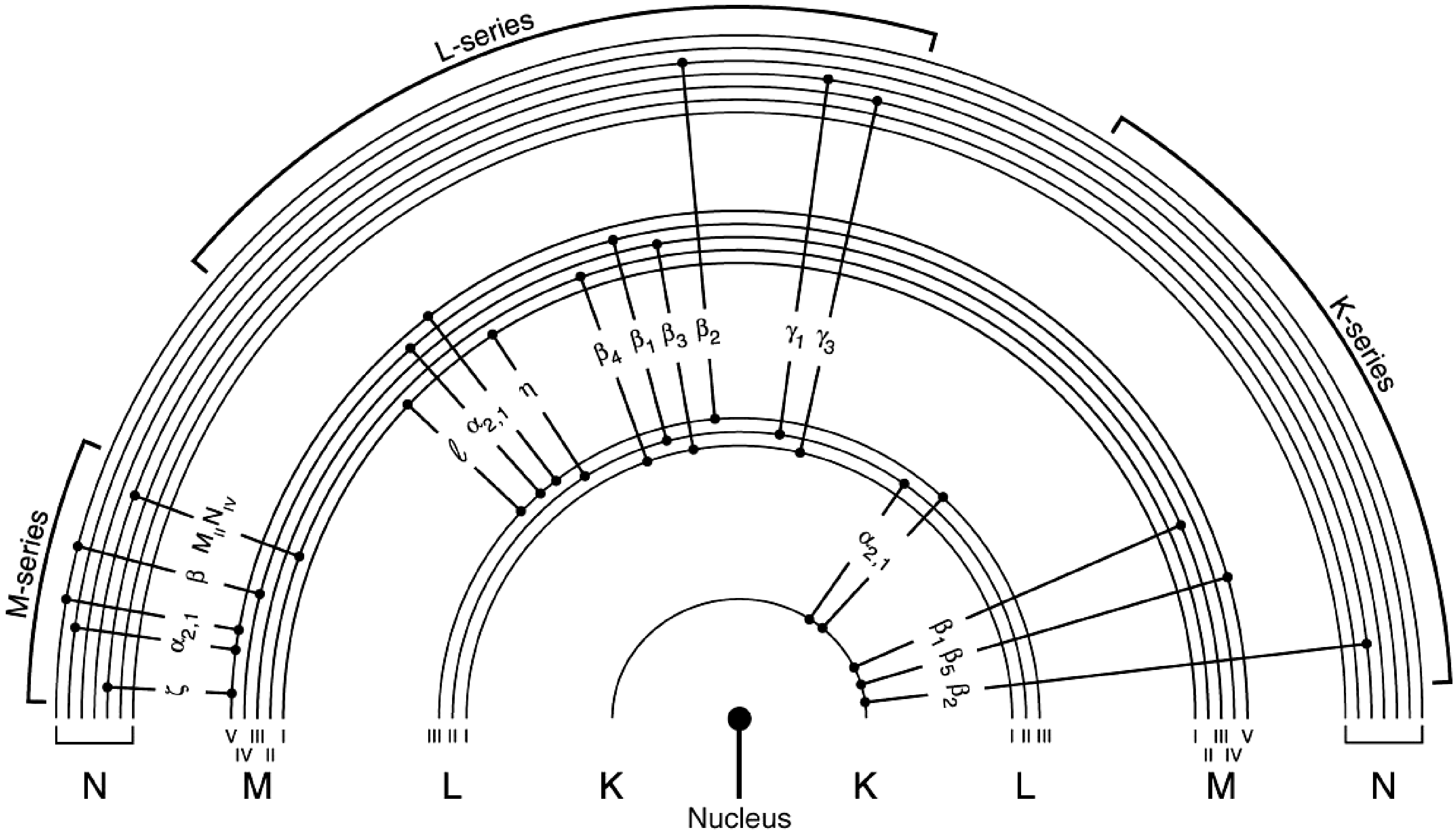
First: The energy level in which the vacancy occurs: **K, L, or M**

Secondly: The energy level in which the filling electron originates:

α → **1 level removed**
β → **2 levels removed**



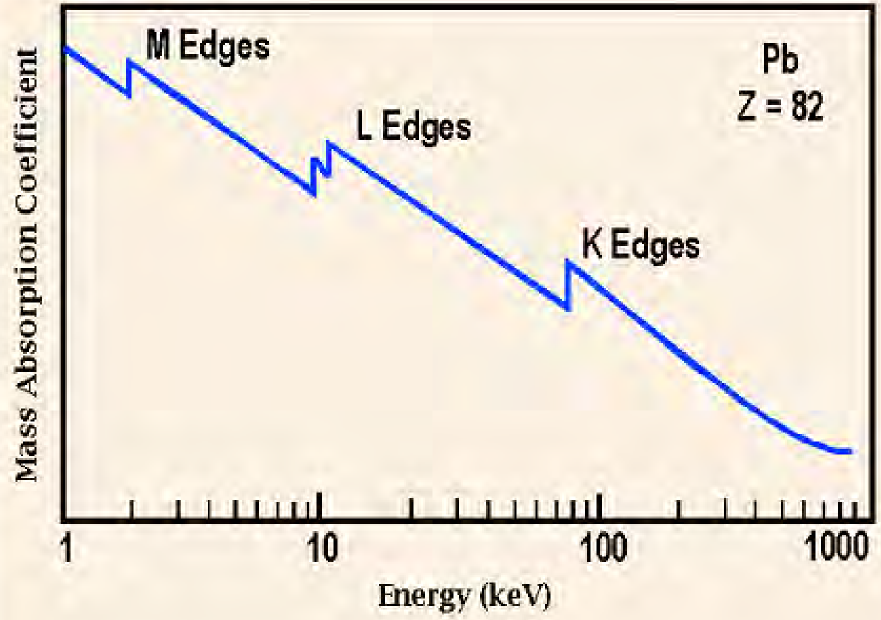
X-Ray Excitation



X-Ray Nomenclature & Excitation

Efficiency for X-Ray excitation

- Maximum efficiency is when kinetic energy (KV) is greater than the absorption edge.
- General rule is 1.5 to 2 times *over voltage* to ensure adequate excitation



Shells binding energies are also known as absorption edges.

X-Ray Nomenclature & Excitation

The number of X-Ray line series that an element can emit is dependent on the atomic number (Z).

- 04 - 19 (Be - K) we only use the K lines
- 20 - 56 (Ca - Ba) use the K & L lines
- 57 - 99 (La - Es) use the K, L & M lines

Most SEM voltages (max 35 kV) limit the number of a visible lines in a spectrum to a maximum of 2 lines:

(K & L) or (L&M)

Photon – Sample Interactions

Photon - Sample Interactions

Definitions of relevant terms

Absorption

As an X-Ray travels through the sample, it may be absorbed, giving up its energy entirely to an electron.

Energy of the X-Ray and density of the sample effect the X-Ray escape depth

Secondary Fluorescence

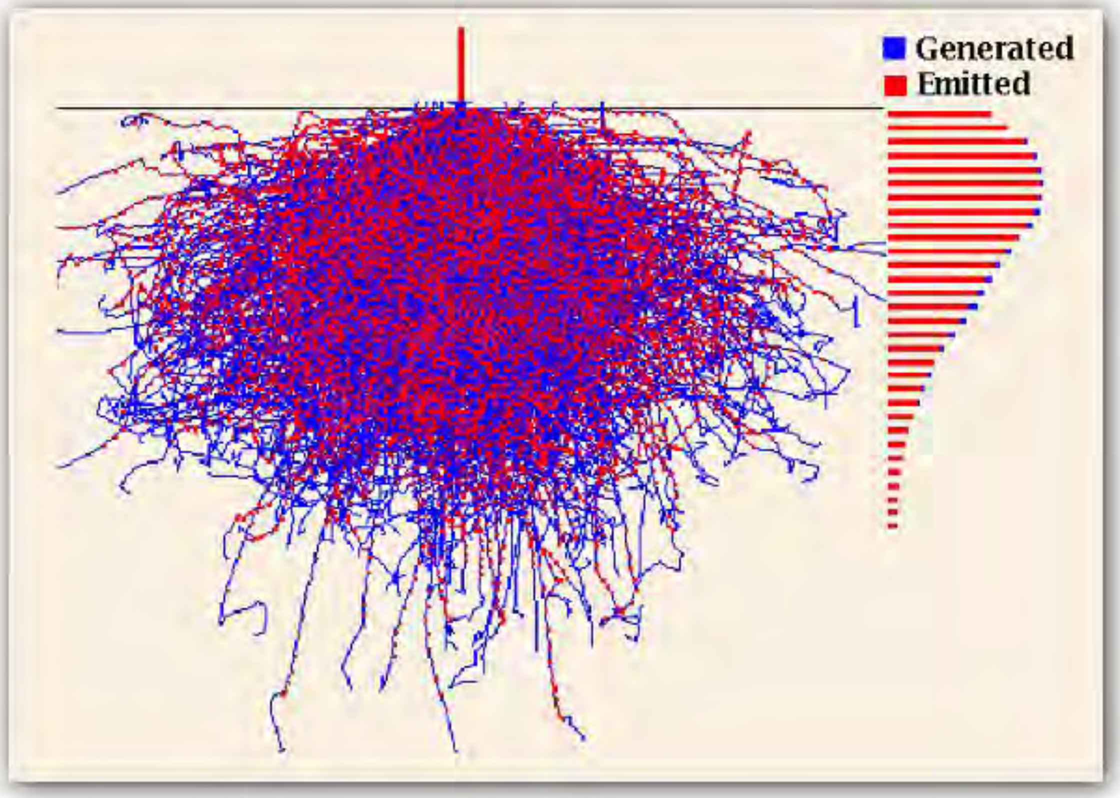
An X-Ray is absorbed by an atom in the sample, the absorbing atom is left in an excited state.

It relaxes and emits its own characteristic Fluorescence X-Ray.

Photon - Sample Interactions

Absorption example

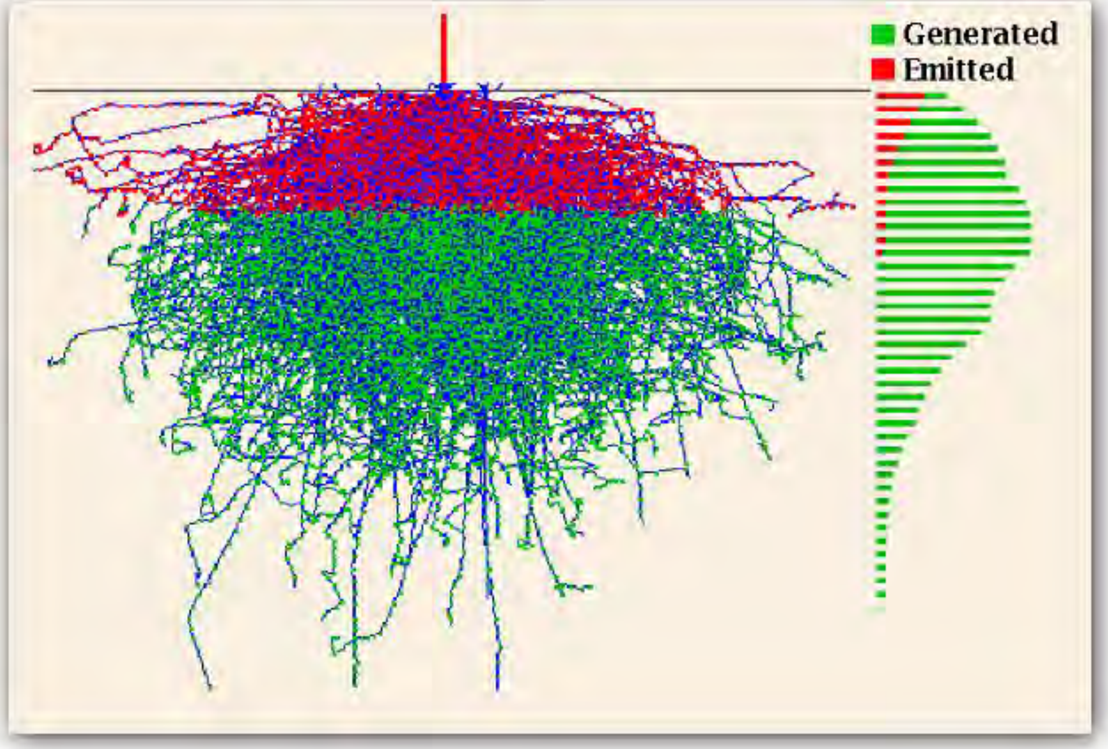
- Fe Kα X-Ray emission from an FeC sample



Photon - Sample Interactions

Absorption example

- C Kα X-Ray emission from an FeC sample



X-Ray Detectors

Si(Li) detectors

Si(Li) X-Ray detectors

- Liquid Nitrogen is used to cool the detector crystal to reduce dark-current and reduce thermal noise
- LN cooling method provides good resolution and analytical performance

Traditional Si(Li)

LN2 detector

UltraDry Silicon Drift Detector

The alternative to Liquid Nitrogen cooling

- Peltier cooled
- Performance equal to LN detector at low countrates
- Superior performance at high countrates
- Maximum throughput much higher than LN detectors
- For SEM and TEM these days!

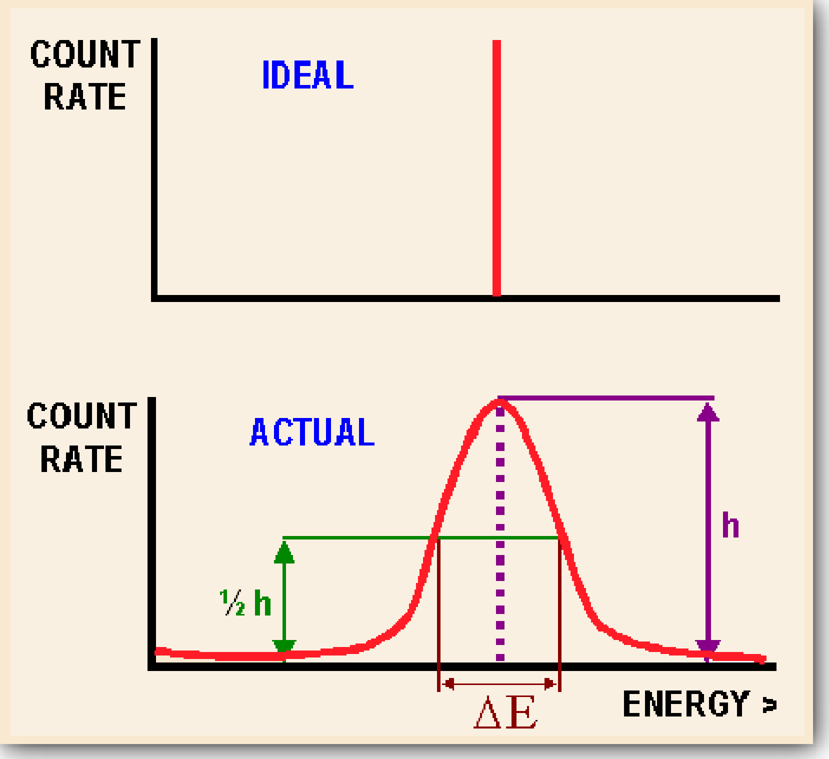
X-Ray Instrumentation

Detector specifications: resolution

- Evaluated based on spectral resolution
- Full Width Half Maximum (FWHM) measurements determines resolution

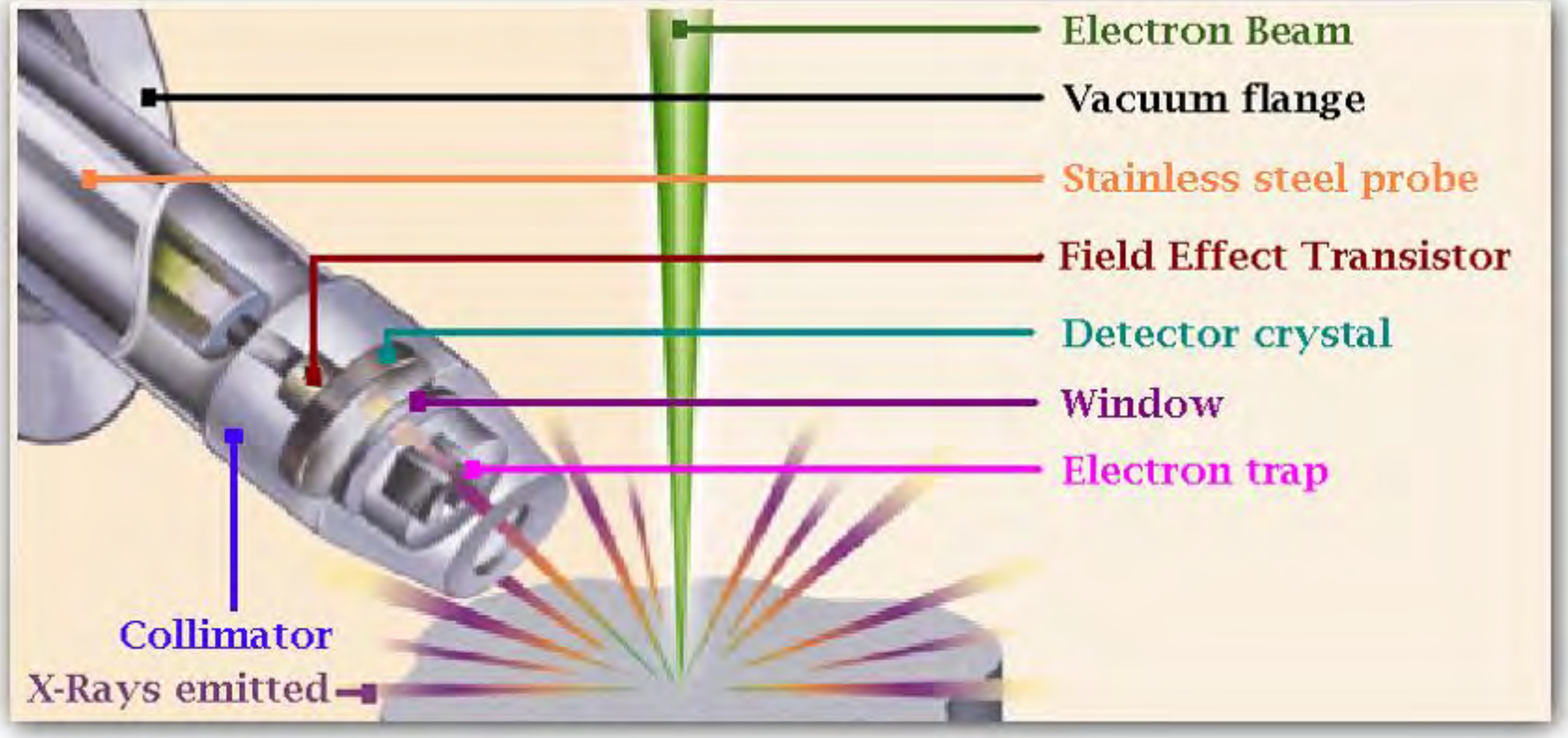
FWHM measurement at Mn Ka is the industry standard

FWHM @ F Ka is used to check light element performance



X-Ray Instrumentation

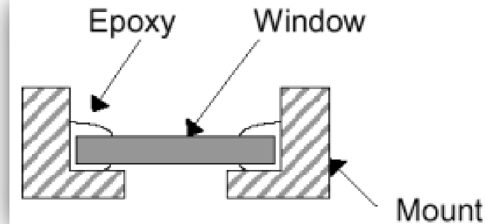
X-Ray detector components (Si(Li) detector)

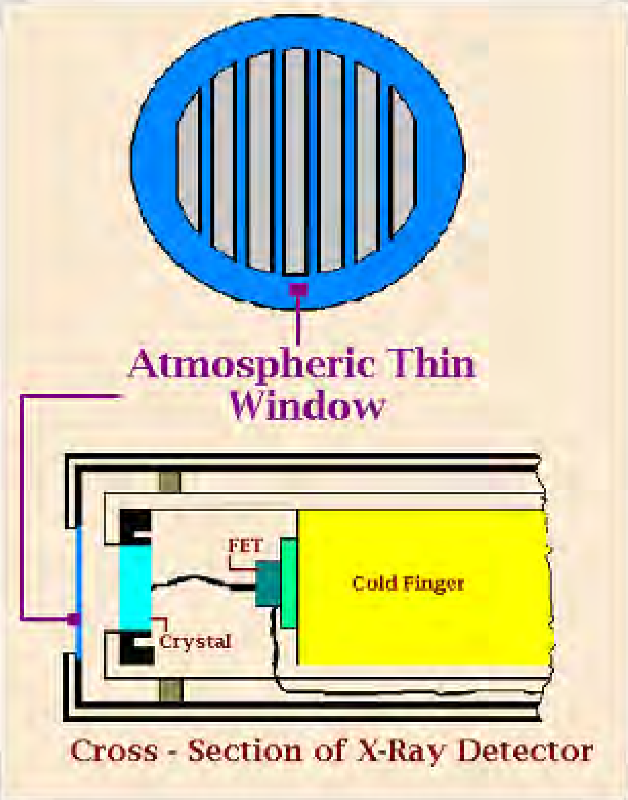


X-Ray Instrumentation

Detector components: Polymer Window

- Provides a barrier to maintain vacuum and protects the detector electronics
- Impermeable to gas and water
- Allows low energy X-Ray transmission





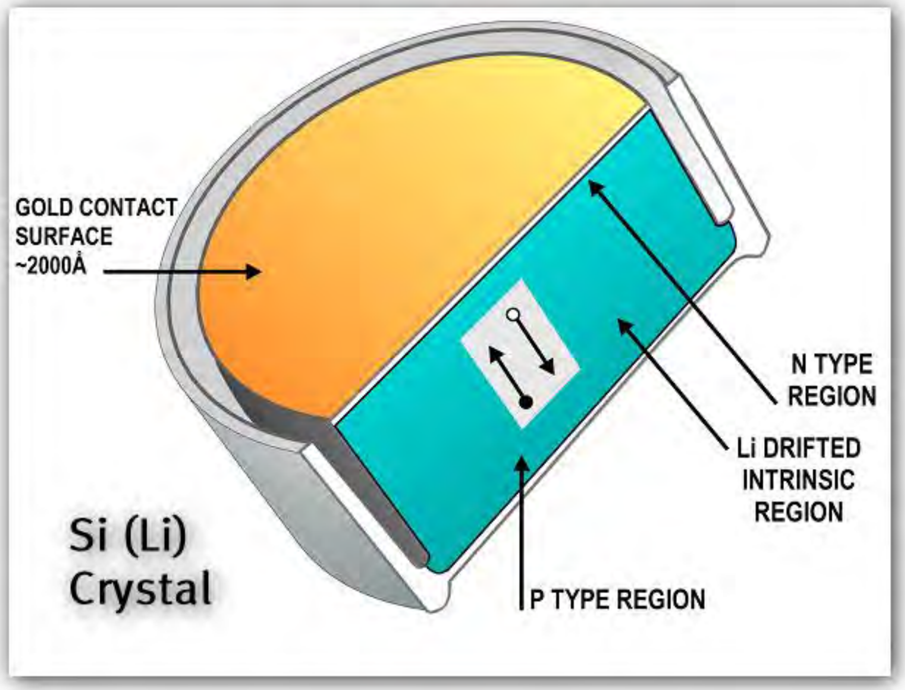
X-Ray Detection Process: Si(Li)

X-Ray Instrumentation

Detector components: Si(Li) Crystal

- Pell (1960) added Lithium at elevated temperatures at reverse bias and created the Si(Li) Crystal

Intrinsic semiconductors will not conduct current in an applied electric field unless it absorbs energy causing electrons to be promoted to the conductance band.

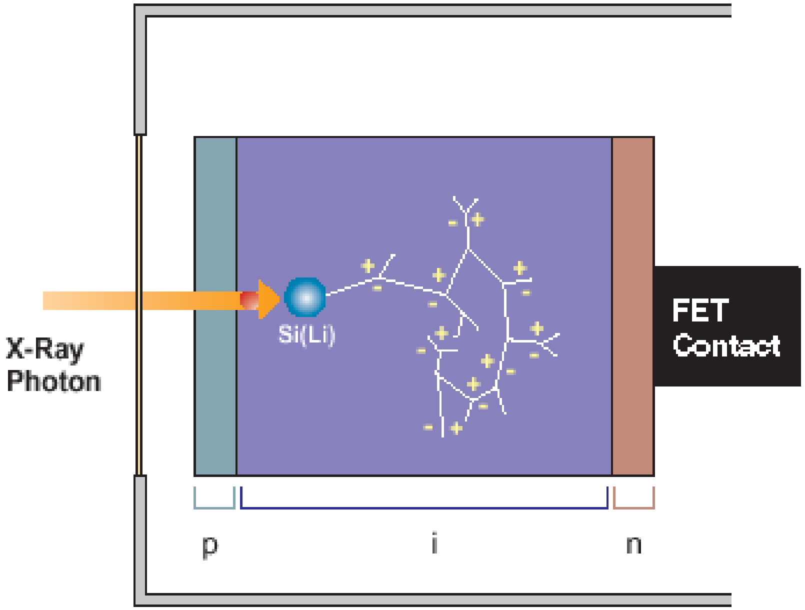


X-Ray Detection Process

X-Ray conversion

- An energetic photon (X-Ray or light) enters the crystal and is captured
- The energy is absorbed by a series of ionizations and creates a number of electron-hole pairs
- The positive holes and negative electrons are drawn to opposite ends of the crystal by the bias voltage, producing a charge signal

The charge signal is proportional to the energy of the original X-Ray photon

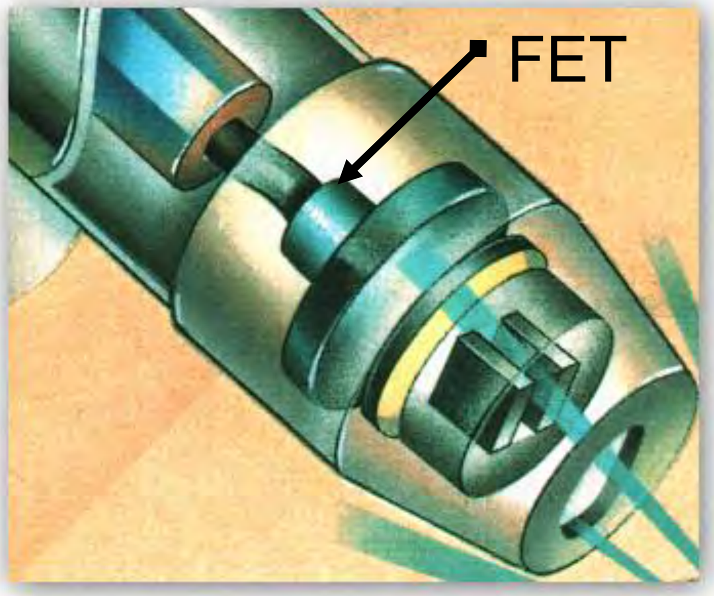


X-Ray Instrumentation

Detector components: Field Effect Transistor

- A field-effect transistor (FET) is a type of transistor commonly used for weak-signal amplification and is attached to the crystal

Provides voltage ramp where X-Ray voltage step appears and is the first stage of the amplification process.



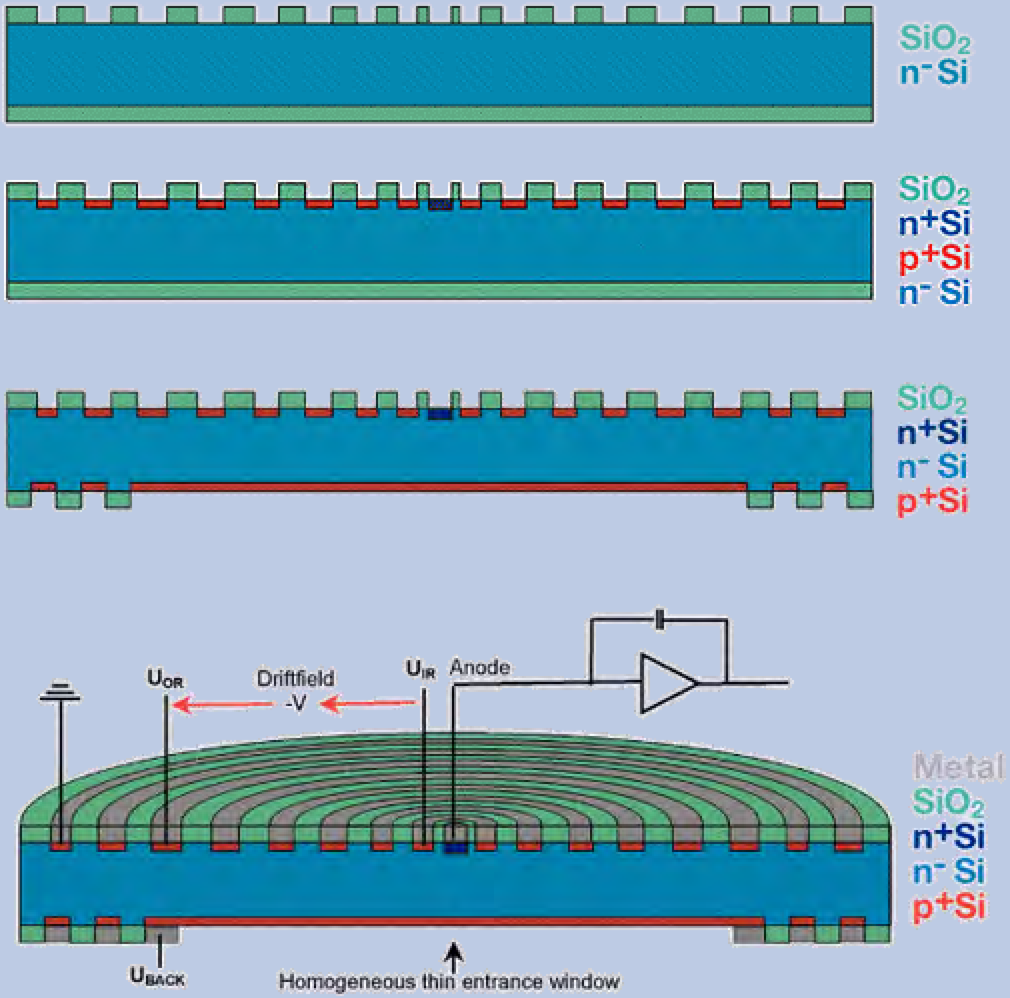
X-Ray Detection Process:
Silicon-Drift detectors

The silicon-drift detector

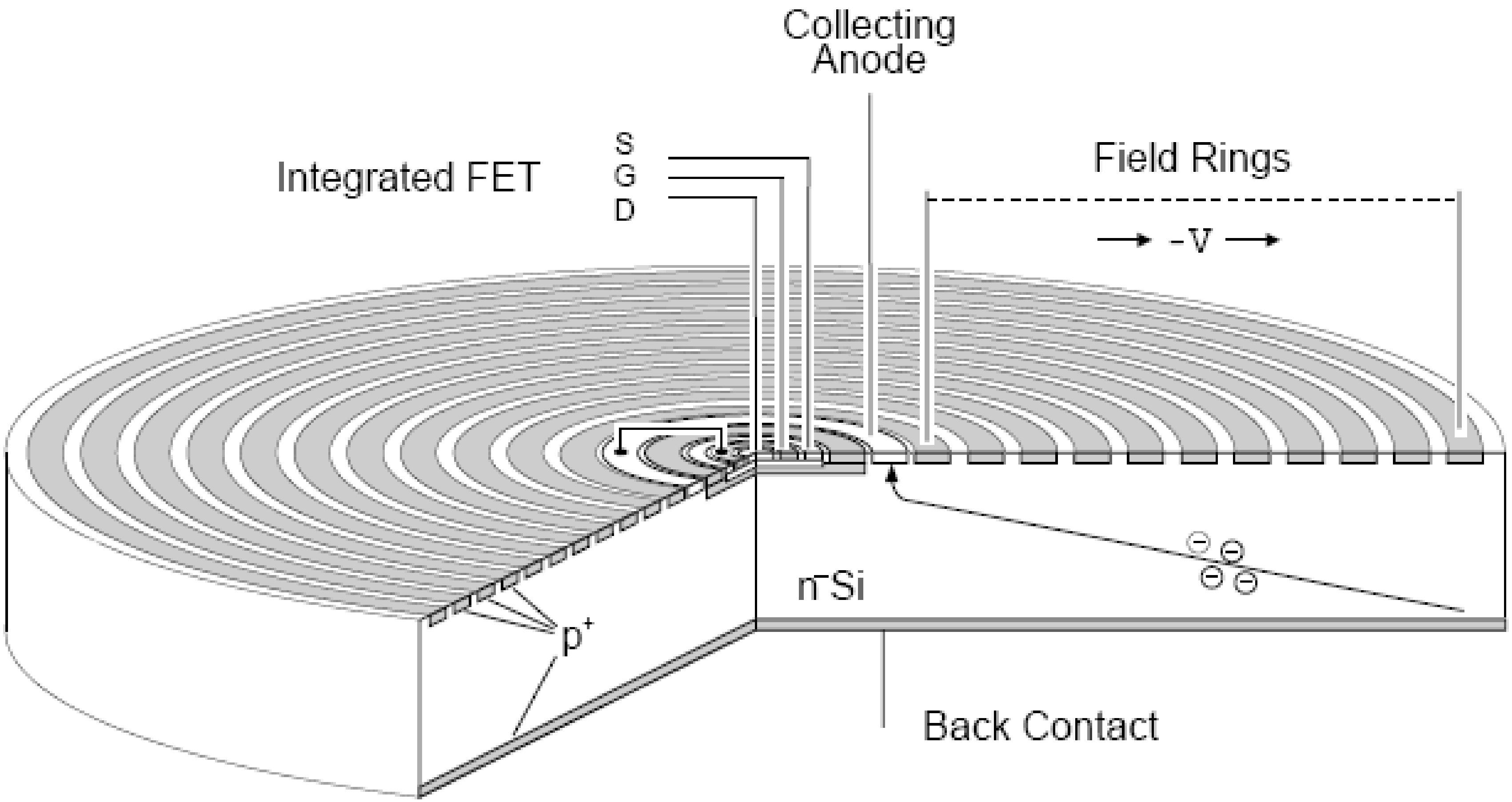
Silicon-drift technology was already discussed in 1985, so nearly 30 years ago.

But from a first experiment to a routine detector for EDS took nearly 20 years.

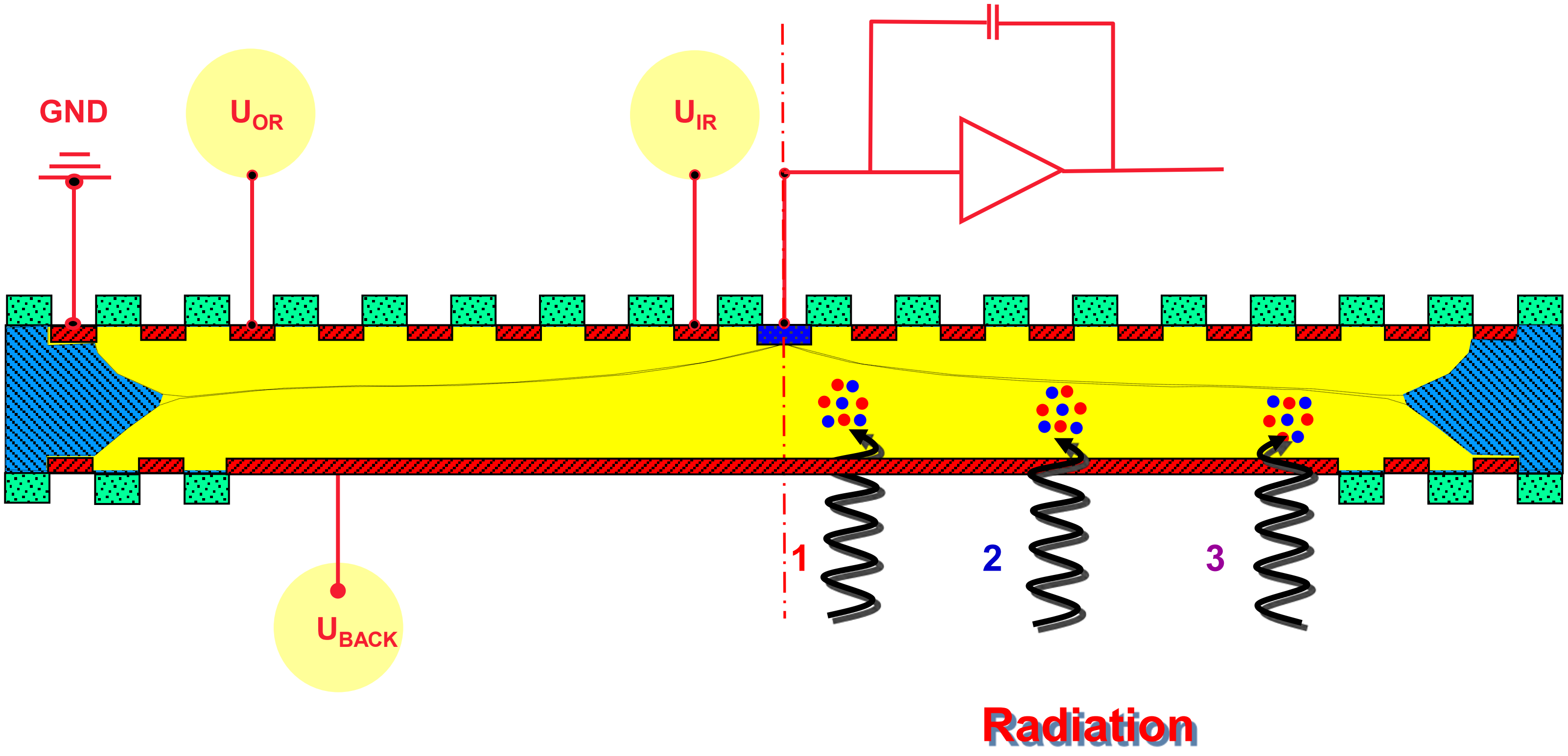
How to make a SDD sensor



SDD sensor

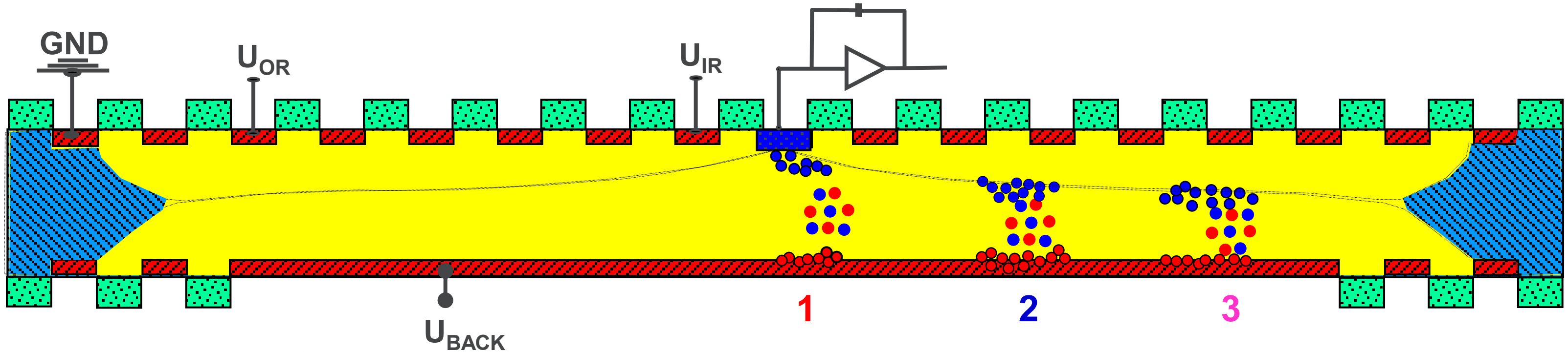

Collecting Anode
Integrated FET
S
G
D
Field Rings
-V
n⁻Si
p⁺
Back Contact

Function of Silicon Drift Detector



Absorption of x-rays

Function of Silicon Drift Detector

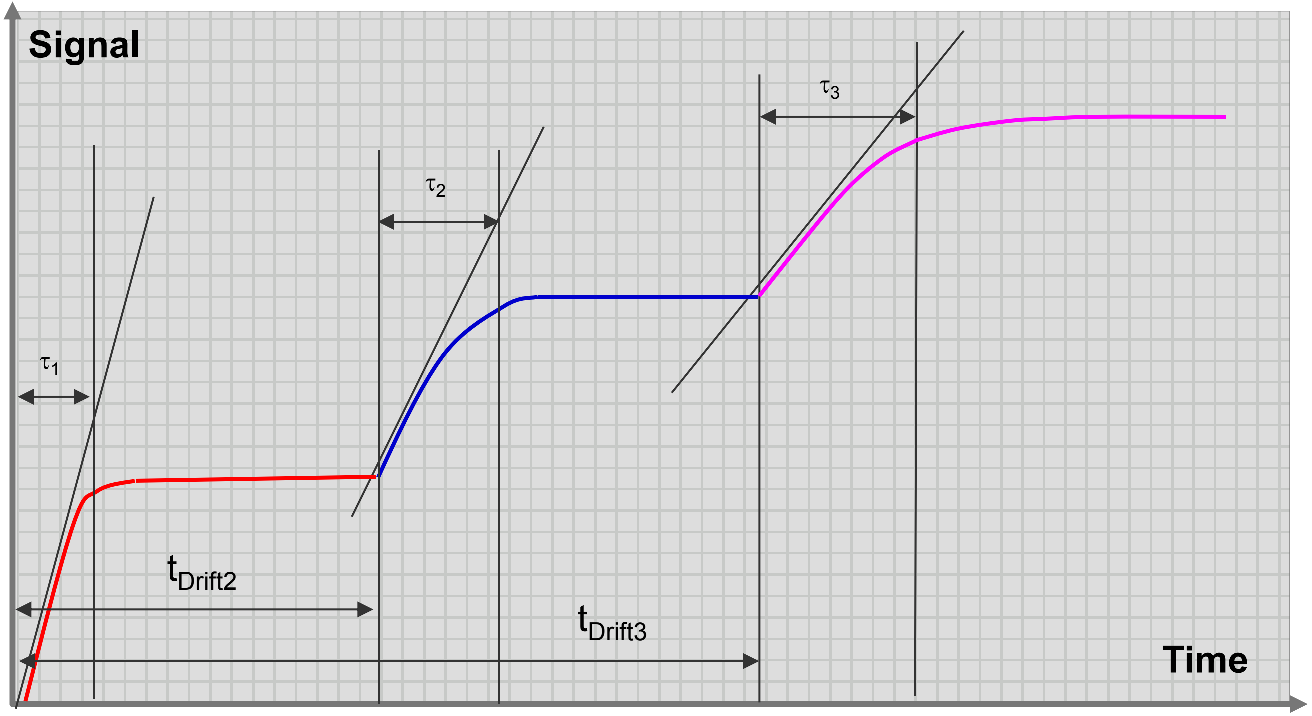


Charge Collection:

Event 1 signal 1

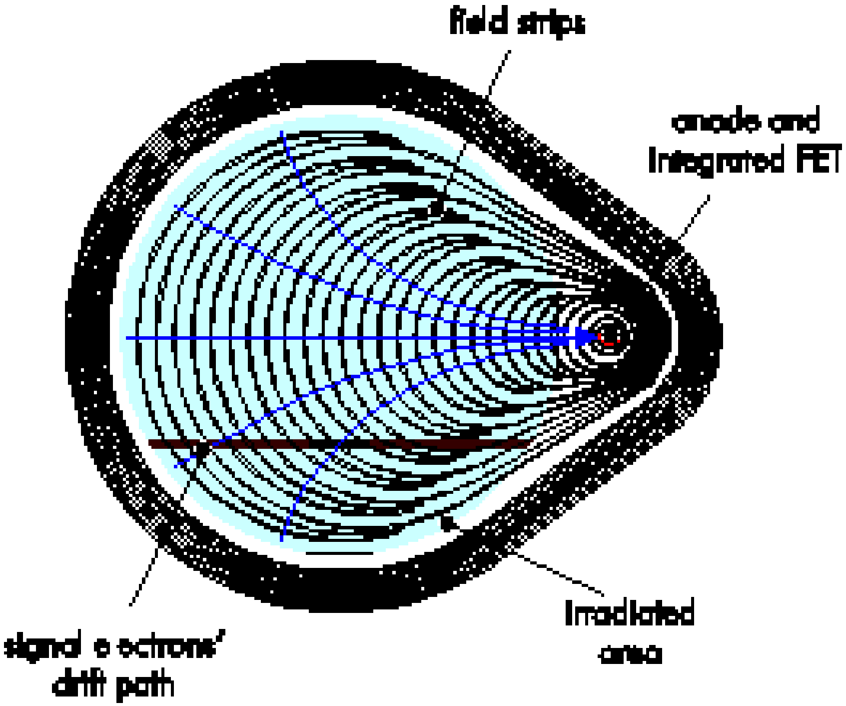
Event 2 signal 2

Event 3 signal 3



4th Generation SDD detectors

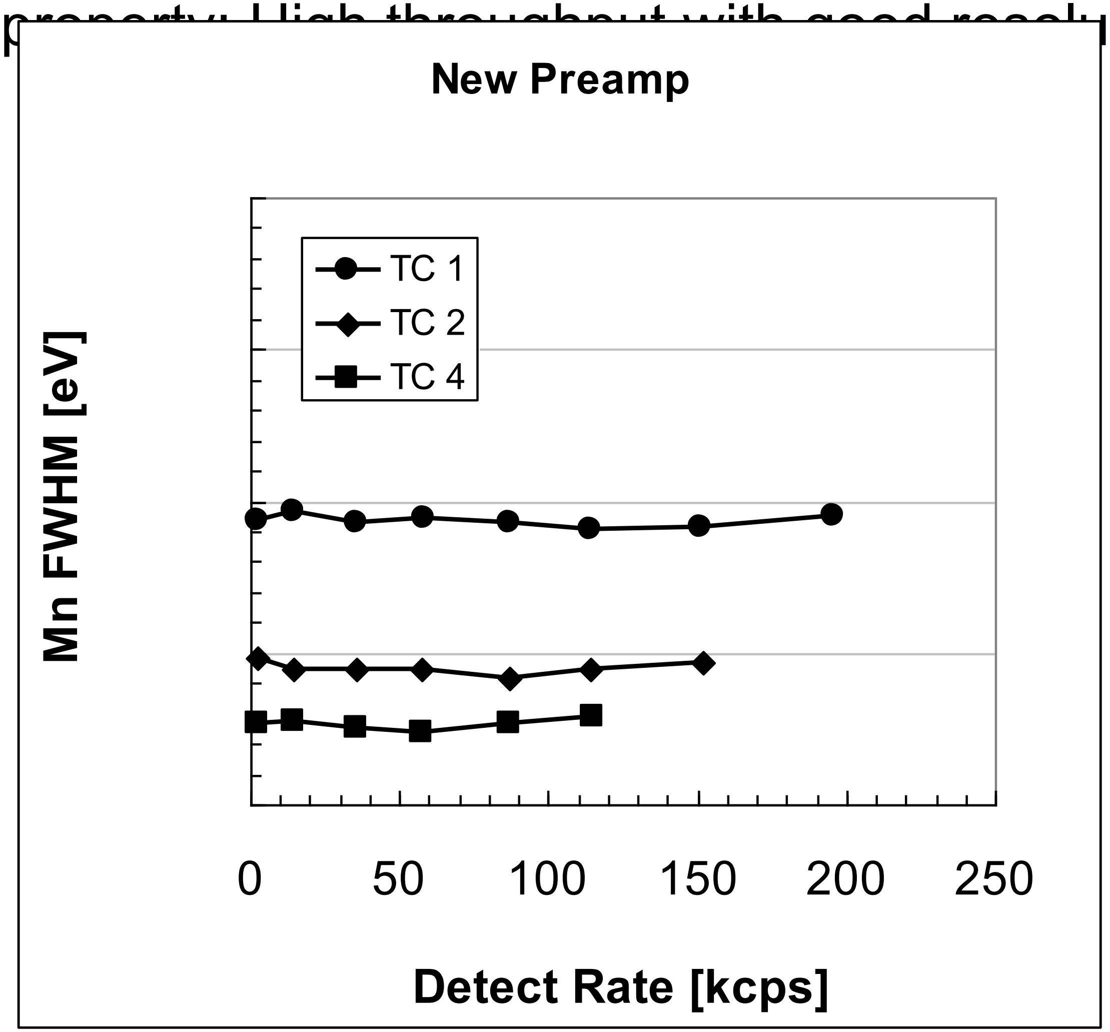
Droplet shape moves anode to area shielded from incoming X-rays



Anode FET mounted on device to minimize capacitance and maximize throughput.

Why SDD detectors

Key property: High throughput with good resolution

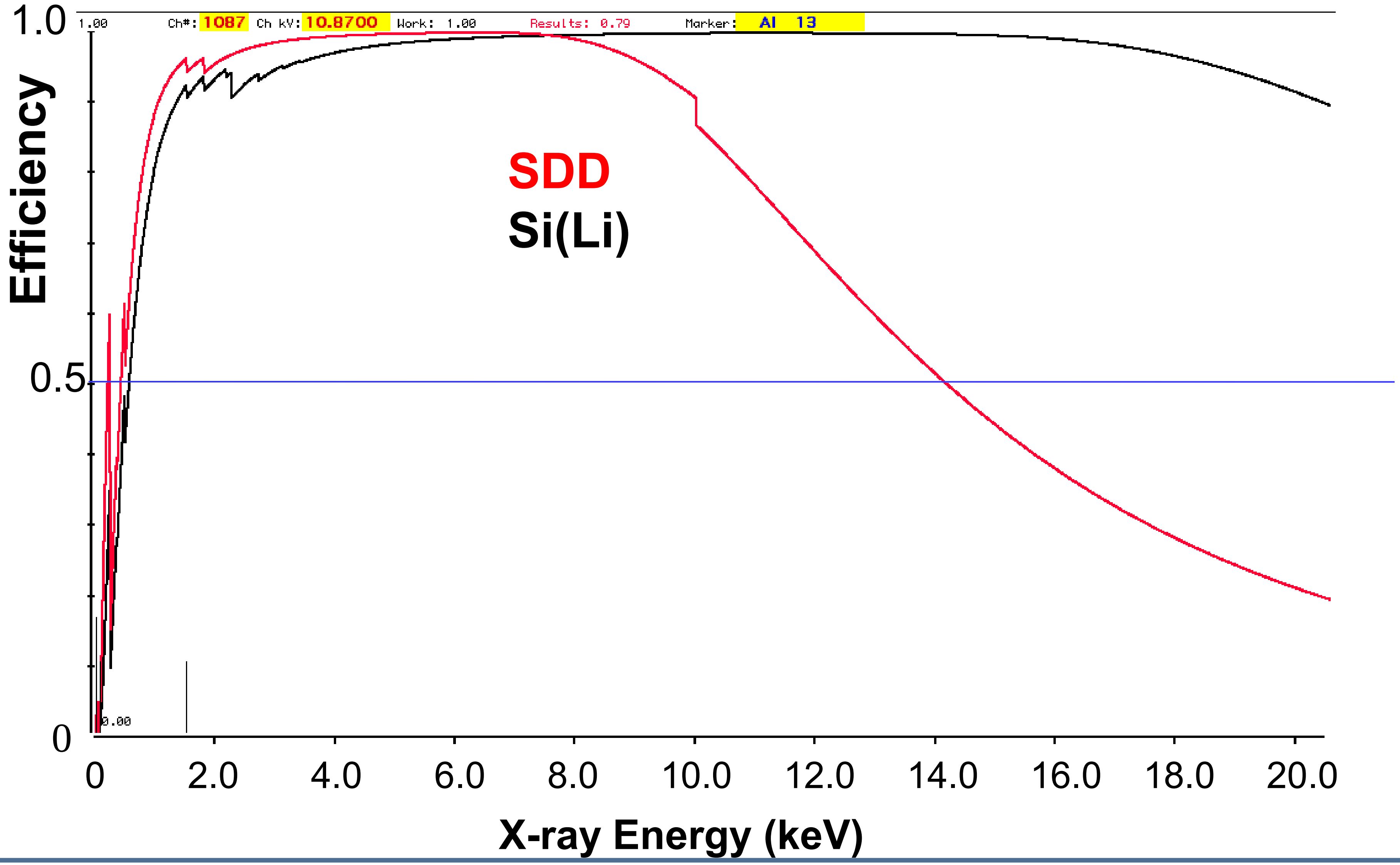


Detector efficiency SDD vs. Si(Li)

The SDD sensor is only 450 micron thick. This means:

- High energy X-rays will travel through the sensor
- Very high energy X-rays will fluorescent other X-rays, creating artifacts (e.g. in TEM)
- Quantification routines need to be adjusted to compensate for this effect
  - Filter-fit method: new reference spectra
  - Gaussian fit method: calculate detector efficiency for each X-ray (from calibration curve or theoretical calculations)
- Reduced intensity of all peaks > 10 keV
- Around 50% reduction in peak intensity at 16 keV (Mo-Kα)
- When this effect is properly accounted for, quantification is equally accurate with SDD as with Si(Li)

Detector efficiency SDD vs. Si(Li)



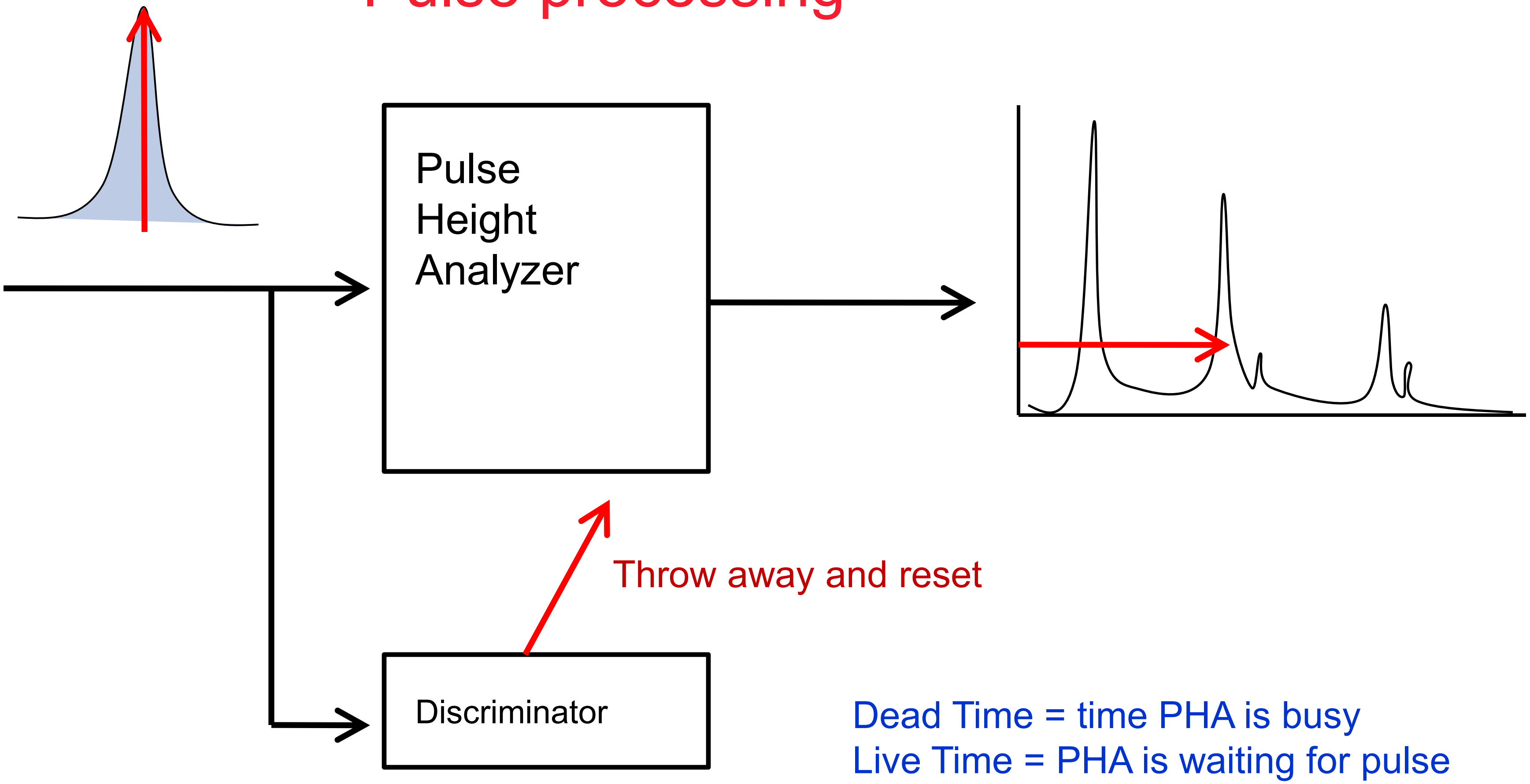
UltraDry SDD detector

- Introduced in 2014: 6th Generation SDD sensor
- Peltier cooled with vibration free passive convection cooling
- Resolution <123 eV (10 mm^2 sensor)
- Range of active areas: 10, 30, 60, and 100 mm^2
- Detection from Be upwards

Electronics

X-Ray Detection Process

Pulse processing



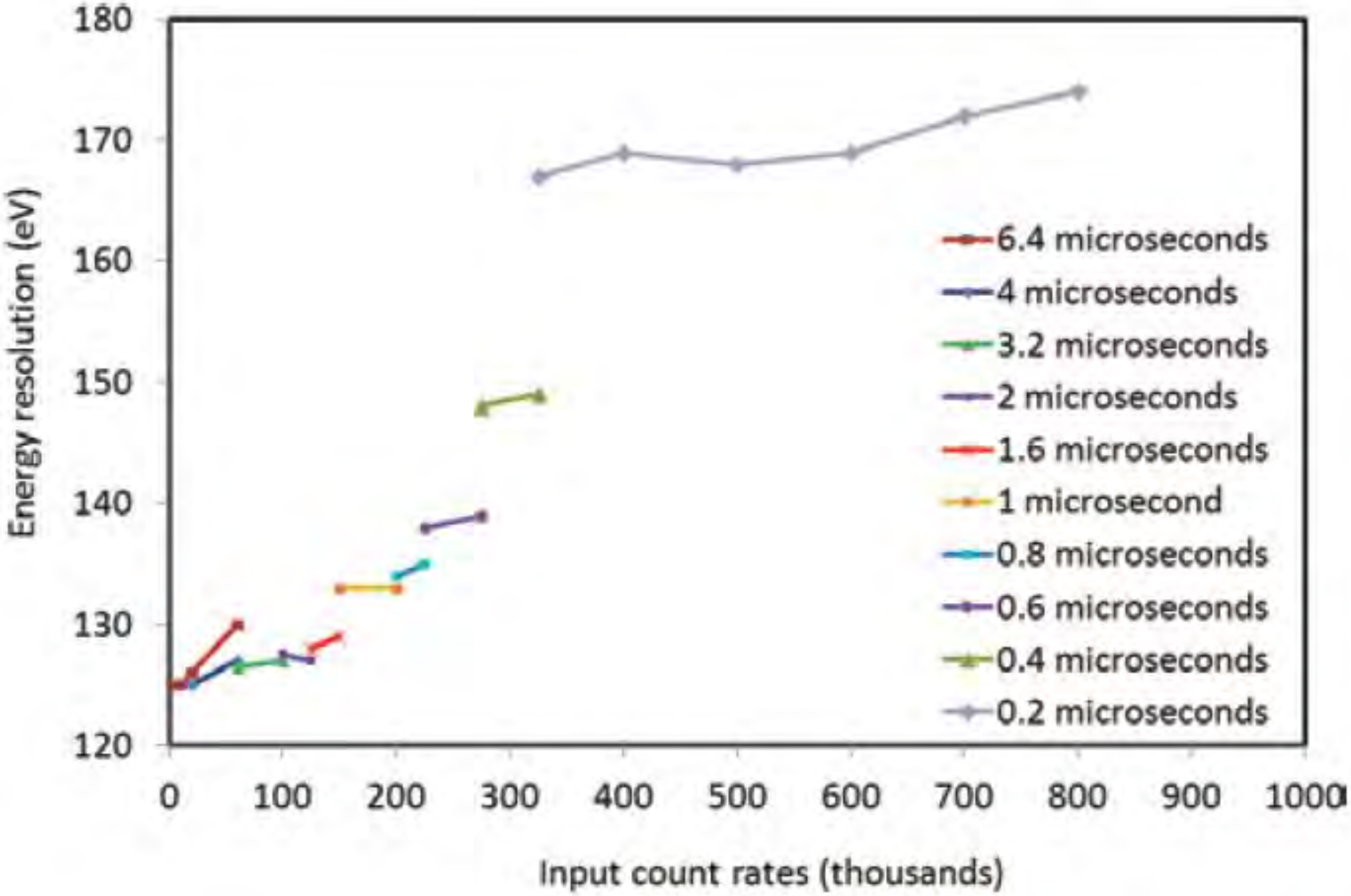
Pulse Height Analyzer

Discriminator

Throw away and reset

Dead Time = time PHA is busy
Live Time = PHA is waiting for pulse

Recommendation: 20% < DT% < 50%

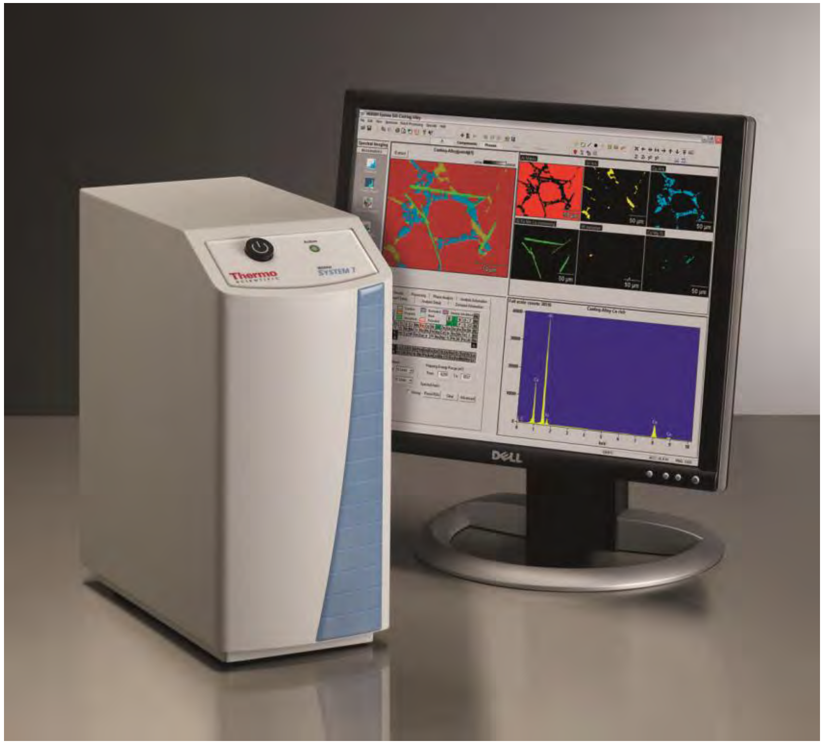


Longer integration times result in superior energy resolution
Shorter integration times are required for high count rates

X-Ray Instrumentation Thermo

Intelligent Digital Acquisition Electronics

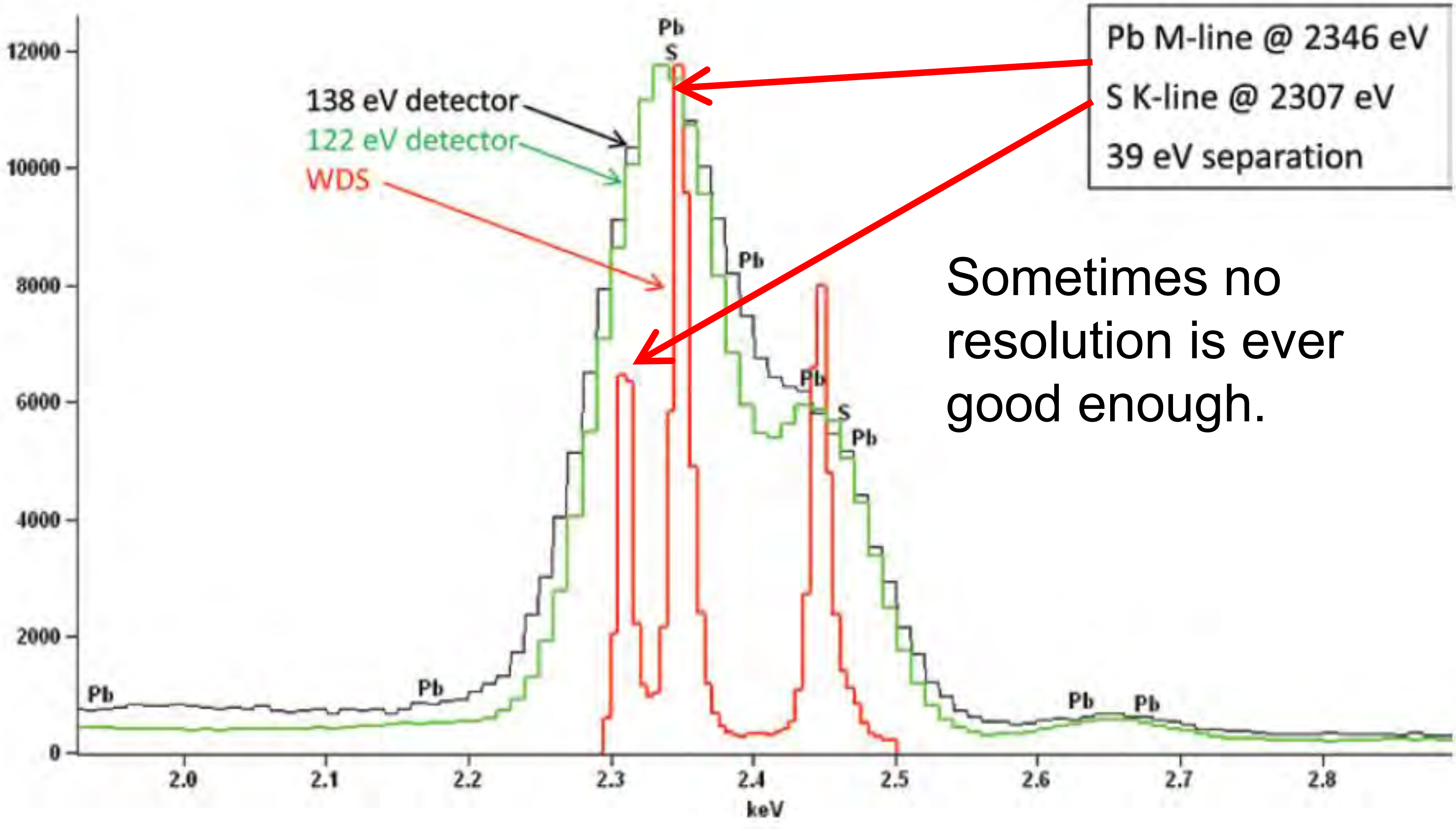
- Dedicated 32 bit microprocessor
- High speed, bi-directional data transfer link
- True digital pulse processor electronics using Digital signal processors (DSPs) for improved resolution



Detector Resolution Discussion

- How important is resolution?
- How does resolution affect performance?

What does high count rate resolution look like?



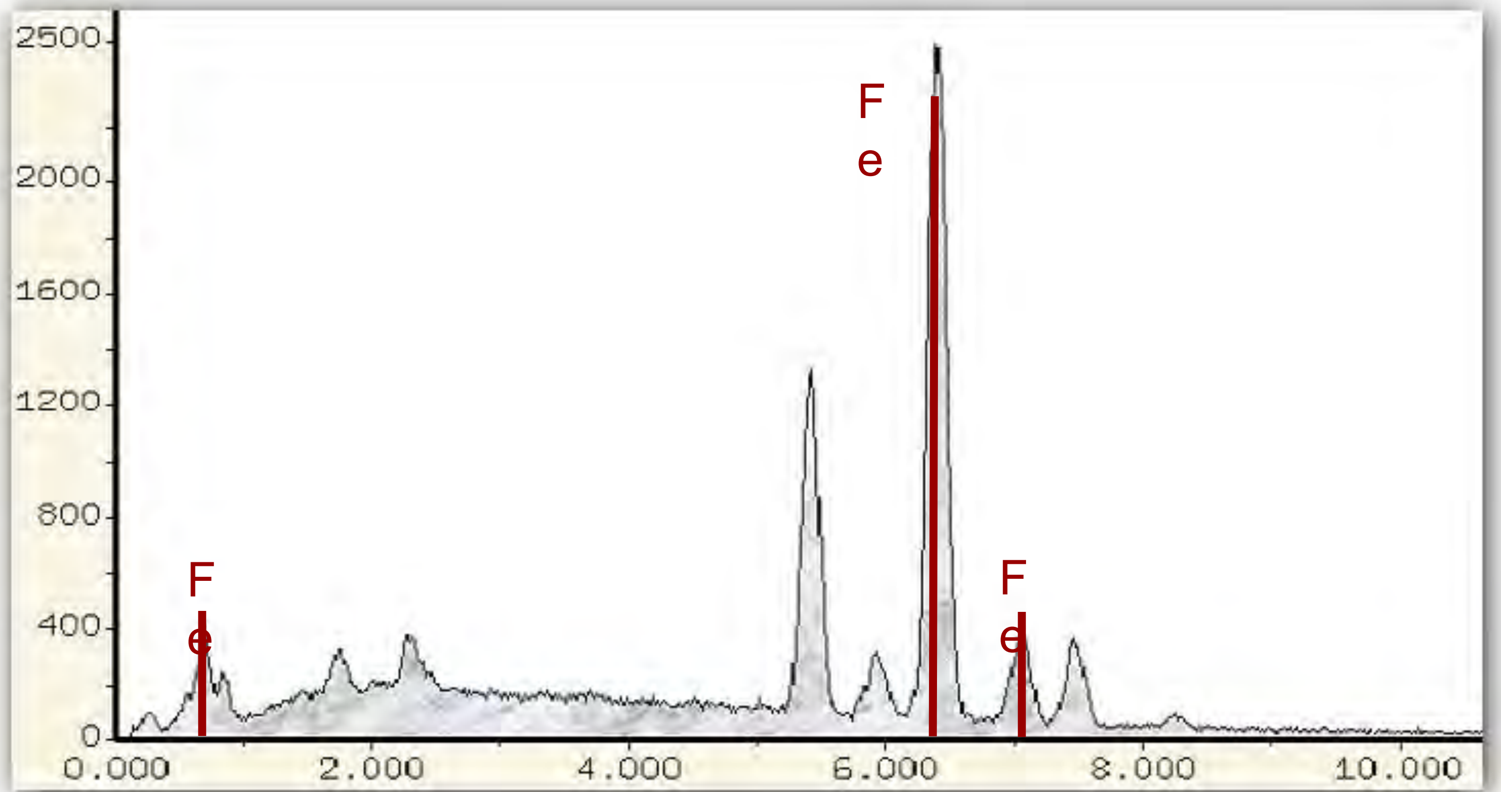
Pb M-line @ 2346 eV
S K-line @ 2307 eV
39 eV separation

Sometimes no resolution is ever good enough.

Qualitative Concepts

Qualitative Concepts

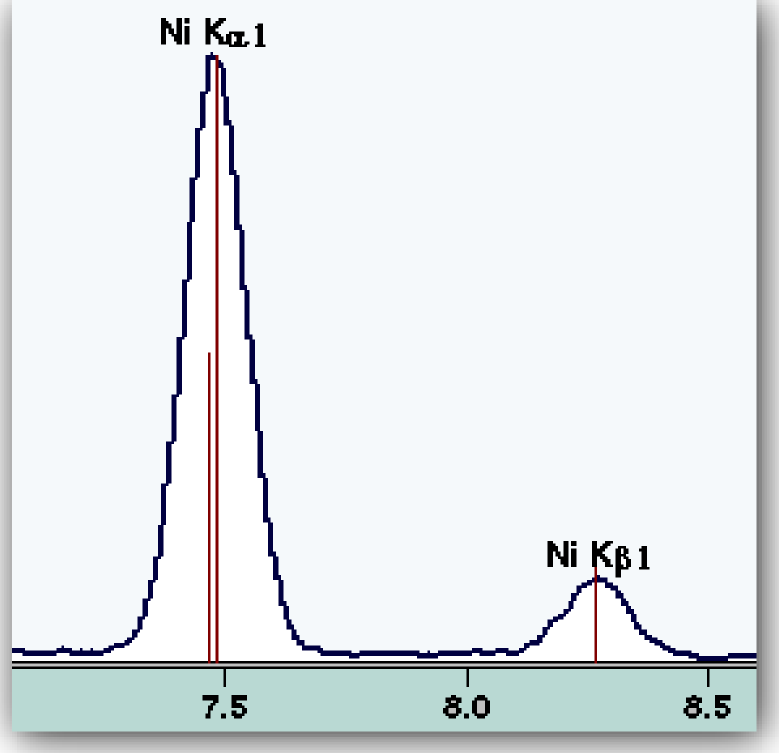
Process of element identification



Qualitative Concepts

K line series: relationships

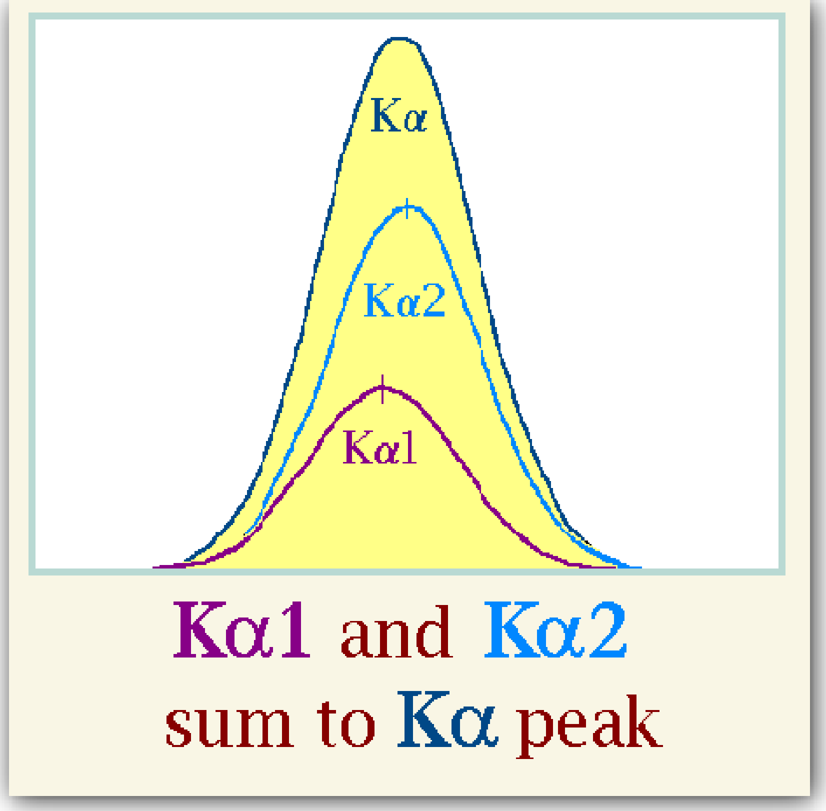
- **Peak shape is generally gaussian except in an overlap situation**
- **Kβ is usually 20% the size of the Kα peak**
- **Kα and Kβ peaks separate with increasing atomic number**
- **Kα peak is comprised of Kα1 and Kα2 peaks**



Qualitative Concepts

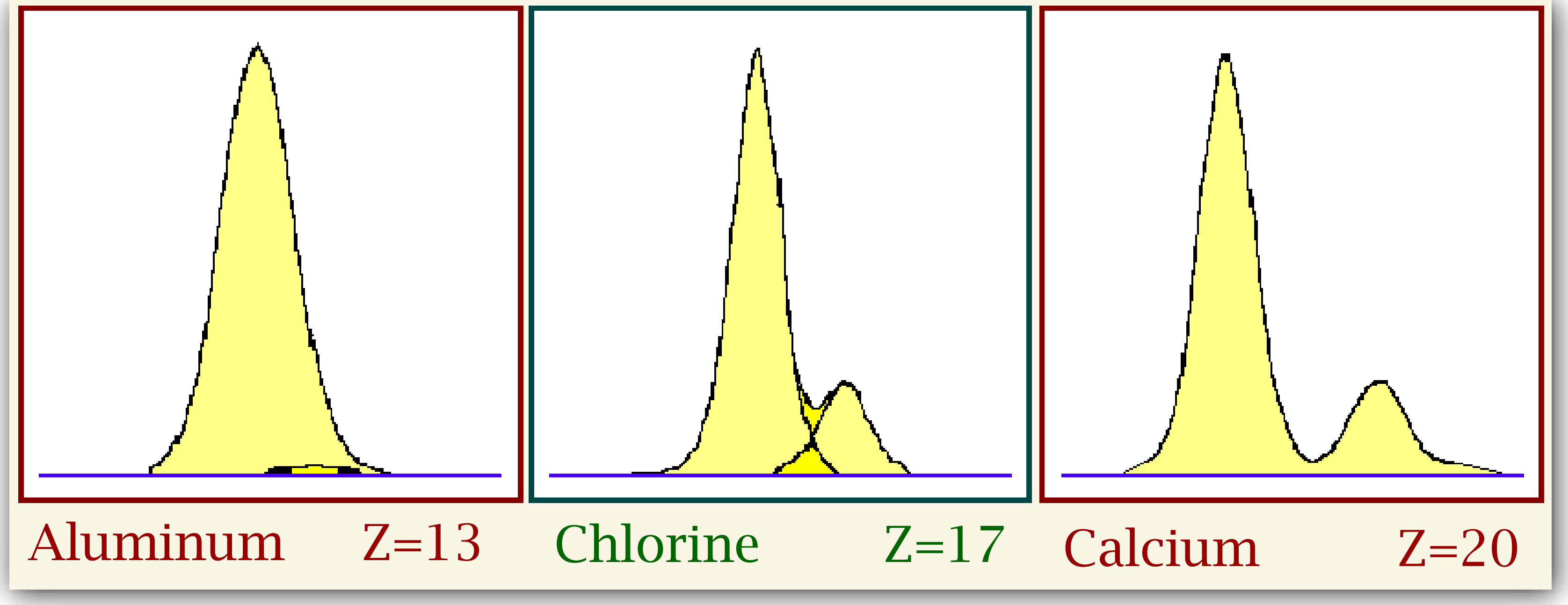
K line series: Ka peak

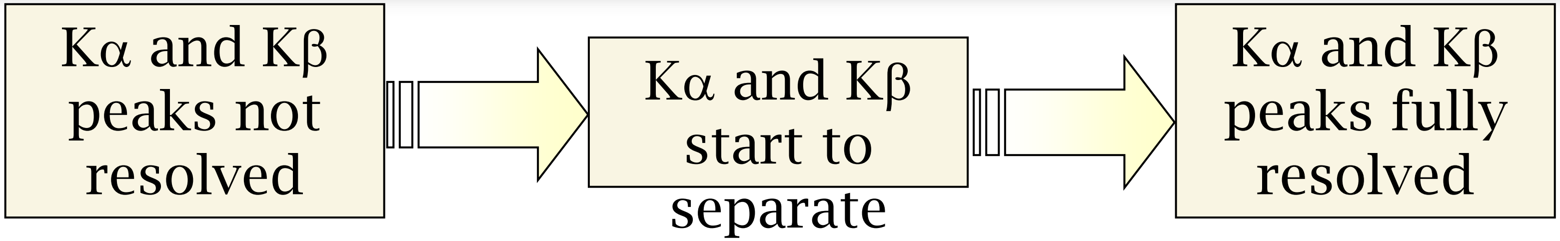
- Kα peak is the summation of the Kα1 and Kα2 peaks
- EDS detectors do not have sufficient resolution to show the individual peaks
- Kα1 and Kα2 will separate with atomic number, which explains peak broadening
- Use the weighted Kα energy



Qualitative Concepts

K line series: Kα & Kβ separation example





Kα and Kβ peaks not resolved

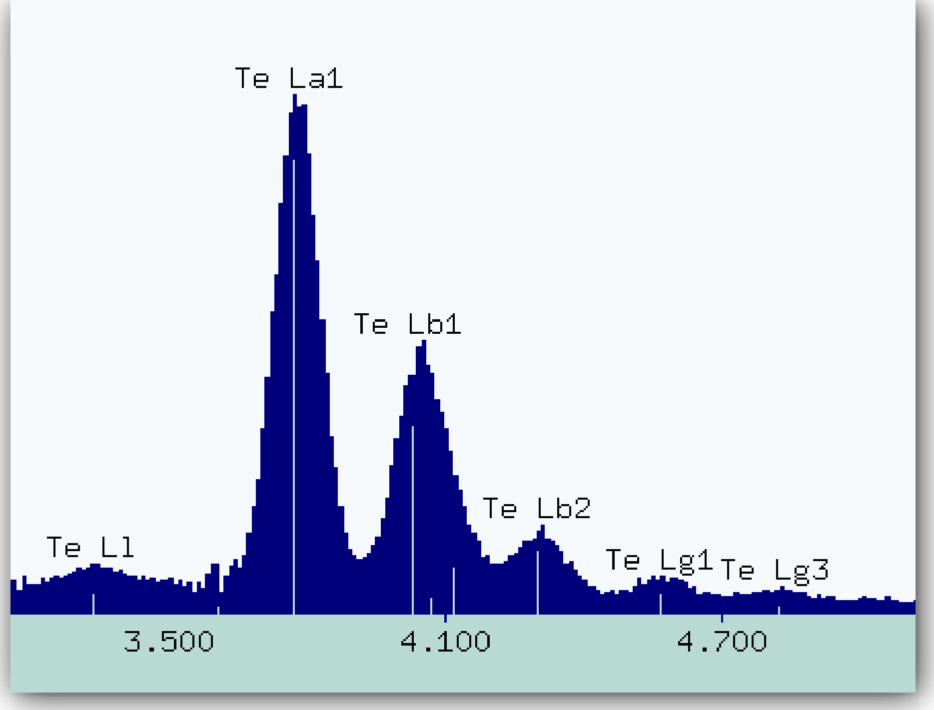
Kα and Kβ start to separate

Kα and Kβ peaks fully resolved

Qualitative Concepts

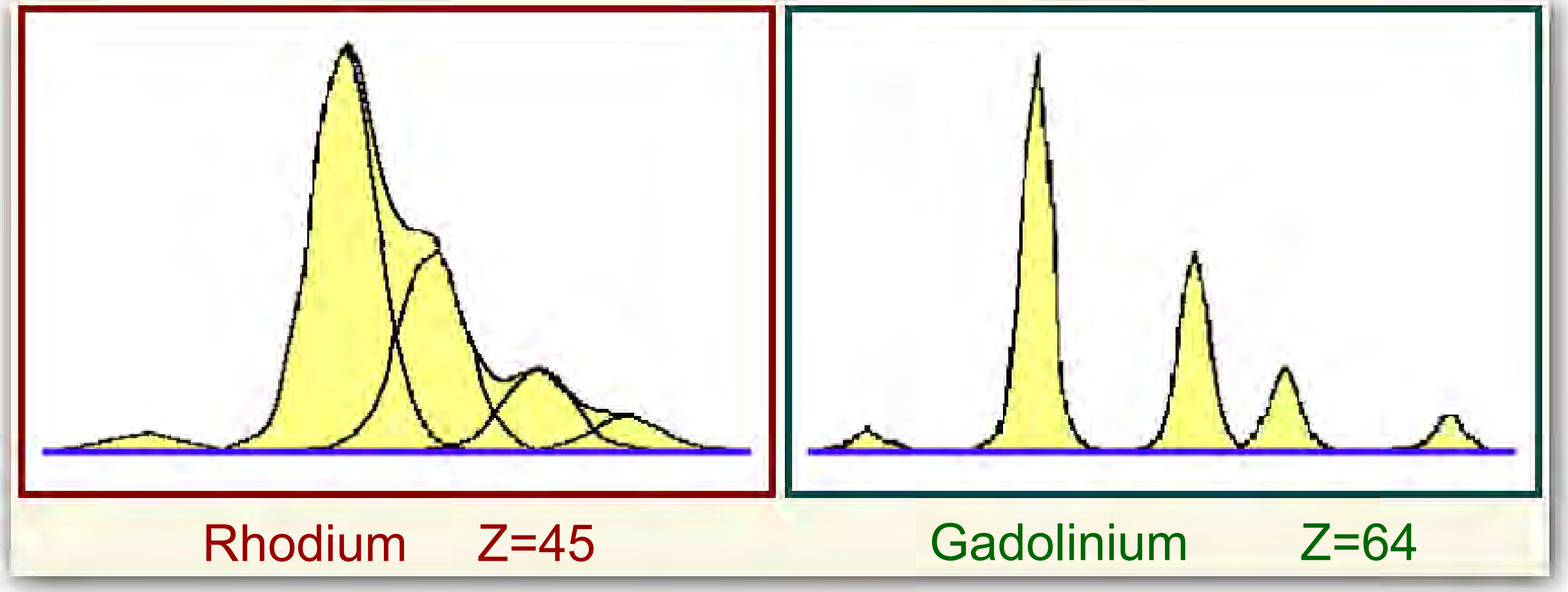
L line series: relationships

- **Distinct peak structure, especially evident at higher energies**
- **Severely overlapped at lower energies**
- **Generally not useful for elements lower than Calcium**
- **Lines do not exist below Sodium**



Qualitative Concepts

L line series: separation example



Rhodium Z=45

Gadolinium Z=64

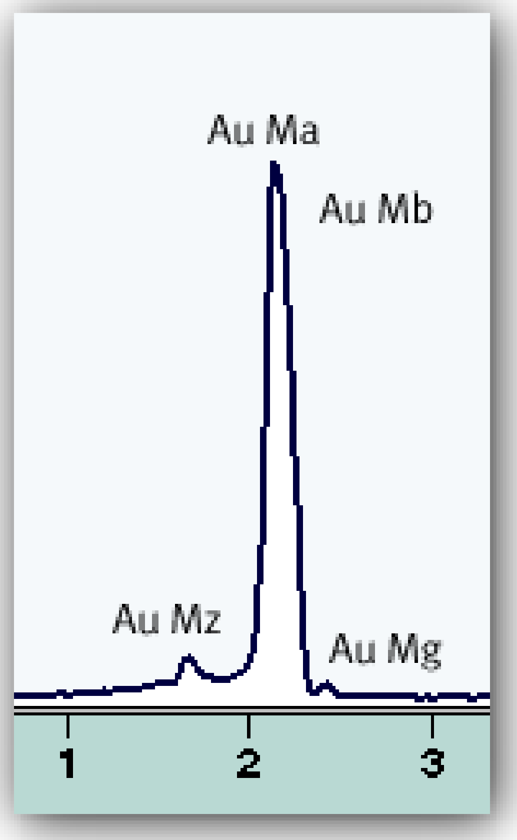
L line series not fully resolved

L line series fully resolved

Qualitative Concepts

M line series: relationships

- Distinct peak structure, but most M lines are not separated
- Severely overlapped peaks will present a non-gaussian shape
- Generally not useful until atomic number is greater than Lanthanum
- Do not exist below Potassium

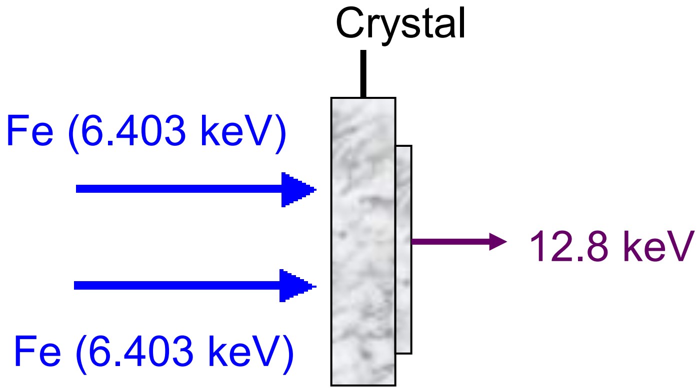


Qualitative Concepts

Spectral artifacts: sum peaks

- Created when 2 or more X-Rays enter the detector crystal at exactly the same time
- Normally made up of integer multiples of the parent peak
- Can be reduced by keeping count rates low, generally low enough to keep the deadtime below 30%

Iron sum peak example:



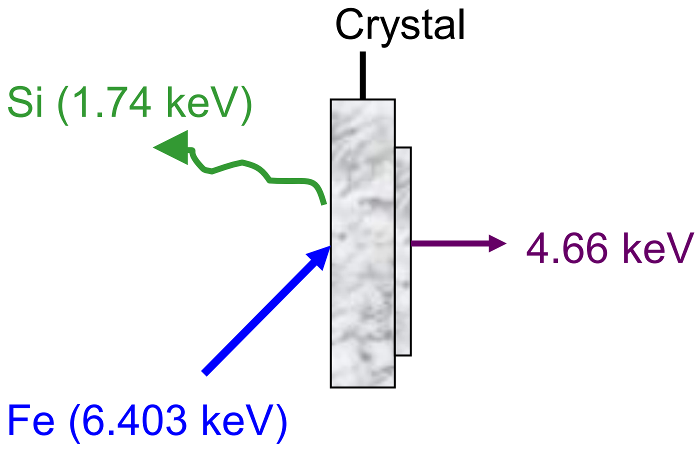
Sum Peak = Fe + Fe

Qualitative Concepts

Spectral artifacts: escape peaks

- **Created when the detector crystal emits a Silicon X-Ray that results in the loss of electron flow proportional to the Silicon photon energy**
- **Function of incoming X-Ray energy and the detector to sample geometry**
- **Can be modeled and accounted for in an analysis**

Iron escape peak example:



Escape Peak = Fe - Si

Quantitative Concepts

Quantitative Concepts

Definition and overview

- **The quantitative application software calculates the relative concentrations of chemical elements in a sample.**
- **It is assumed that the number of counts in spectral peaks will reflect the concentrations of the elements**

This relationship between net peak counts & concentration is complicated by 3 main factors:

1) The effects of atomic number
2) Absorption within the sample
3) Fluorescence within the sample

Warning:

Peak heights are very loosely correlated to actual concentration!!!

Quantitative Concepts

ZAF definitions

Z Atomic number correction

Accounts for the effects of atomic number on excitation efficiency, fluorescent yield, and detector efficiency. A measure of the electron range in the sample, the backscatter coefficient and the energy spectrum of the backscatter signal.

A Absorption correction

Reflects the likelihood that once created within the sample, an X-Ray will be absorbed before being detected. The mass attenuation coefficient and the path the X-Rays take out of the sample describe the A factor.

F Fluorescence correction

X-rays generated in the sample that have sufficient energy to excite other atoms in the sample may generate X-Ray signal that is detected along with the primary spectrum. This is the F term.

Quantitative Concepts

Correction methods

ZAF

Adjusts theoretical reference spectrum for atomic number (Z), absorption (A), and fluorescence (F) factors.

*Used in metallurgical SEM applications.

Proza

Adjusts theoretical reference spectrum for atomic number (Z), absorption (A), and fluorescence (F) factors.

*Used for light element in a heavy matrix SEM applications

Quantitative Concepts

K-ratio

- The Z, A, and F corrections are applied to *K-Ratios*

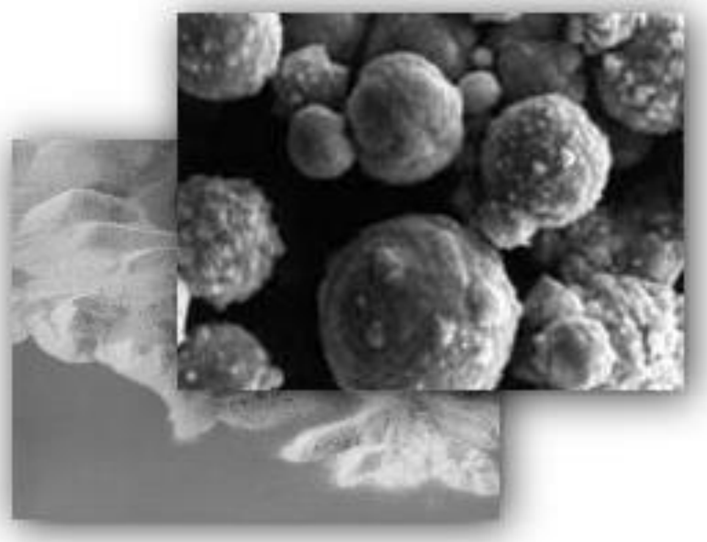
$$\text{k-ratio} = \frac{\text{net peak counts}}{\text{std counts}}$$

- The ratio between the number of X-Rays counted in the peak for an element and number of X-Rays counted for the same element, under the same conditions, in a sample of known concentration.

Quantitative Concepts

Notes:

- **Particles:** Accurate quantitative analysis is only possible if the particle is bigger than the interaction volume and the particle has a flat smooth surface.
- **Thin film measurements** can only be done accurately if the interaction volume is contained within one layer
- **Powders** can not be quantified accurately



Spectral Imaging

Outline

- X-ray Mapping
- Artifacts in X-ray Mapping
- Quantitative X-ray Mapping
- Phase Mapping
- Conclusions

X-ray Mapping

The purpose of X-ray mapping is to show the elemental distribution of elements in a inhomogeneous sample.

To do this the electron microscope (SEM or TEM) needs to allow external control of the electron beam. The EDS system then needs to be equipped with a scangenerator to move the electron beam over the sample.

The EDS system will acquire an EDS spectrum at regular intervals, and will process each spectrum to obtain elemental information: peak intensities.

X-ray Mapping: Speed

The main issue with X-ray mapping is speed.

A decent X-ray map might be 250 x 250 datapoints (pixels), or 62.500 spectra.

A good spectrum should contain at least 10.000 X-ray counts, even more if trace elements are involved.

At a countrate of 20.000 cps (input) or 10.000 cps (stored) this means the acquisition time is 62.500 seconds, or 18 hours or so. This is generally not acceptable.

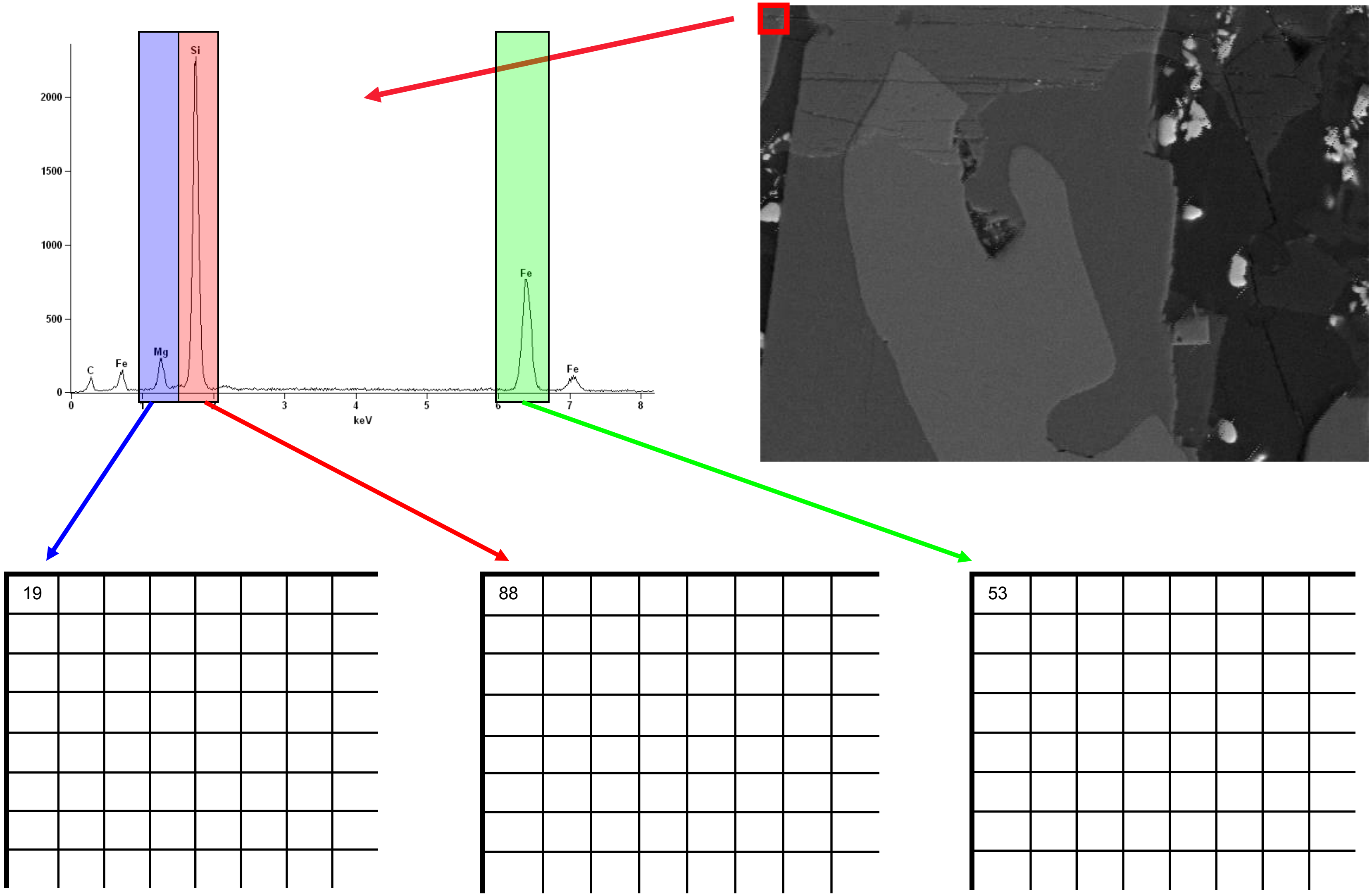
So you either have to increase the countrate, at the expense of spectral resolution, or decrease the number of counts needed for a spectrum.

Generally, one tries to get away with 100 to 200 counts in a spectrum, which reduces the time for one pixel to 10 to 20 milliseconds, and limits the total acquisition time to less than 1000 seconds, or 20 minutes.

But spectra with so little counts are very noisy. To get sensible data from it, the Region-Of-Interest (ROI) technique has been developed.

An energy window is set over each peak in the spectrum, and the gross count in each window is measured.

X-ray mapping: ROI mapping



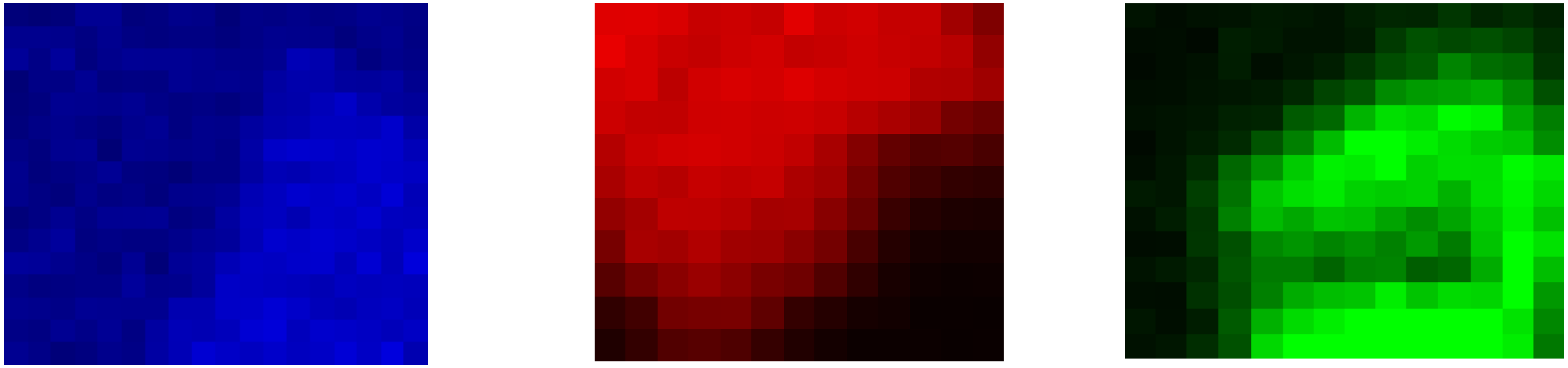
X-ray mapping: ROI mapping

19	x	x	x	x	x	x	X
x	x	x	x	x	X	x	X
X	x	x	x	x	x	x	X
X	x	X	x	X	x	X	x
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
x	X	x	X	x	X	x	X

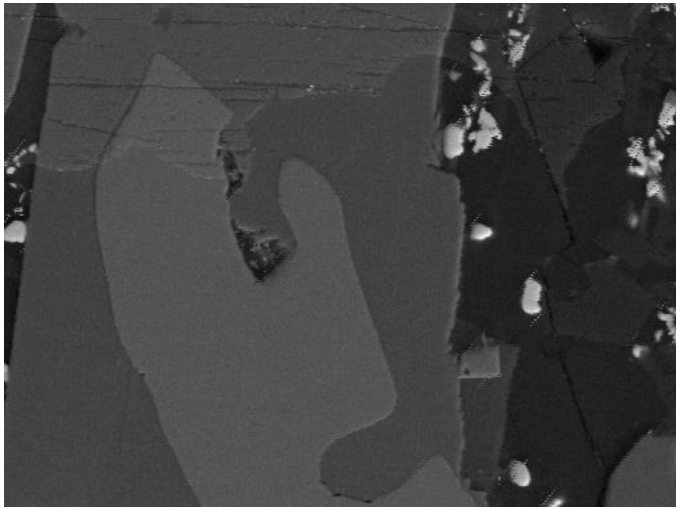
88	X	X	x	X	x	X	x
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
x	X	x	X	x	X	x	X

53	x	X	x	X	x	X	x
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
X	X	X	X	X	X	X	X
x	X	x	X	x	X	X	X

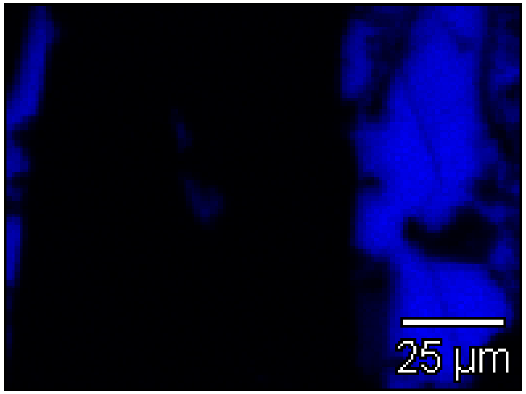
But an Excel sheet with 62.500 numbers is not very informative. So we convert them to color images. We search for the maximum value is each cell, and give that a bright color (100% of maximum intensity). All the other pixels are then scaled in brightness according to the percentage of the maximum intensity.

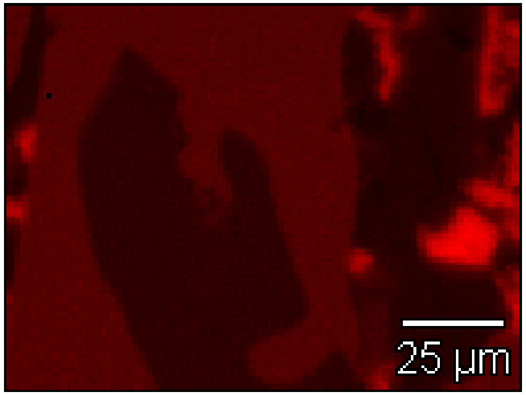


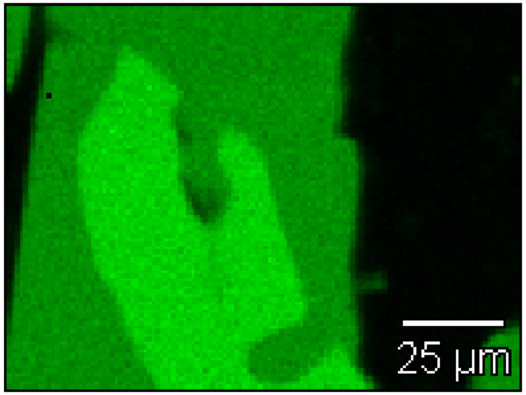
X-ray mapping: ROI mapping



The human brain can do the low-pass filtering to create images that are easily interpreted


Mg-K


Si-K


Fe-K

ROI X-ray mapping: Artifacts

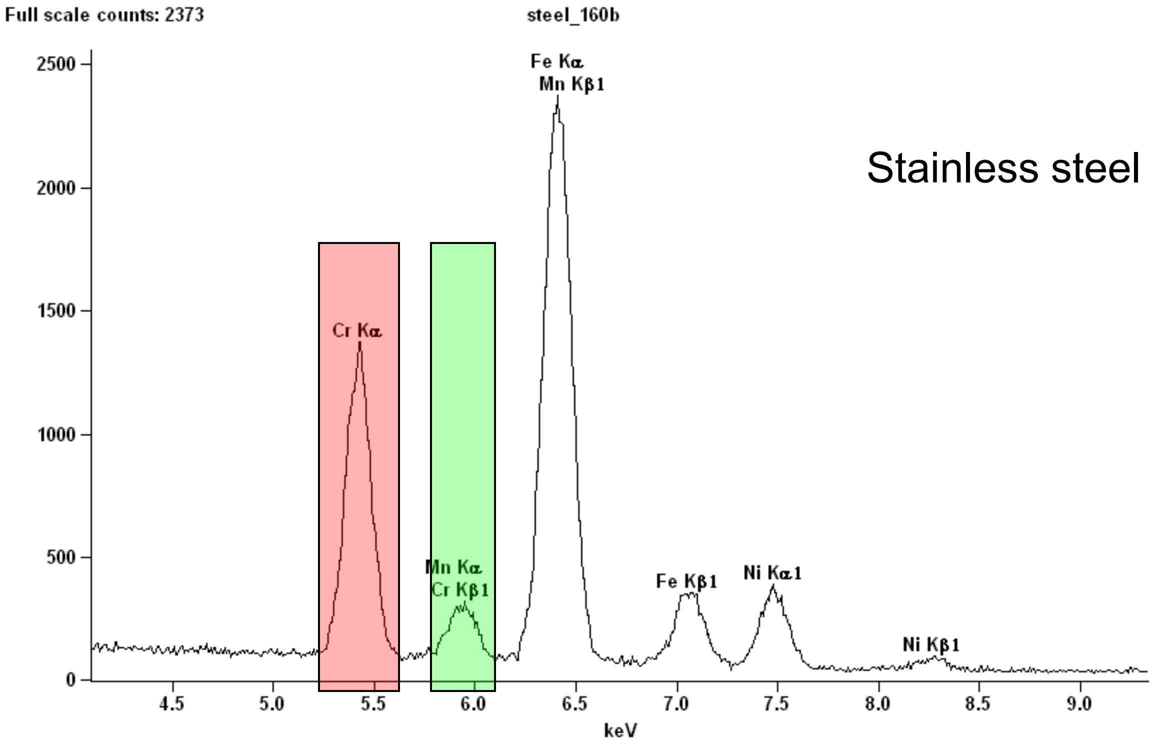
This standard technique for creating X-ray maps is notorious for its artifacts, that can even trick experienced operators to misinterpret these maps. The most common artifacts are:

-Peak overlaps

-Atomic number variations

-Geometry effects

ROI X-ray mapping: 1. Peak overlap artifact



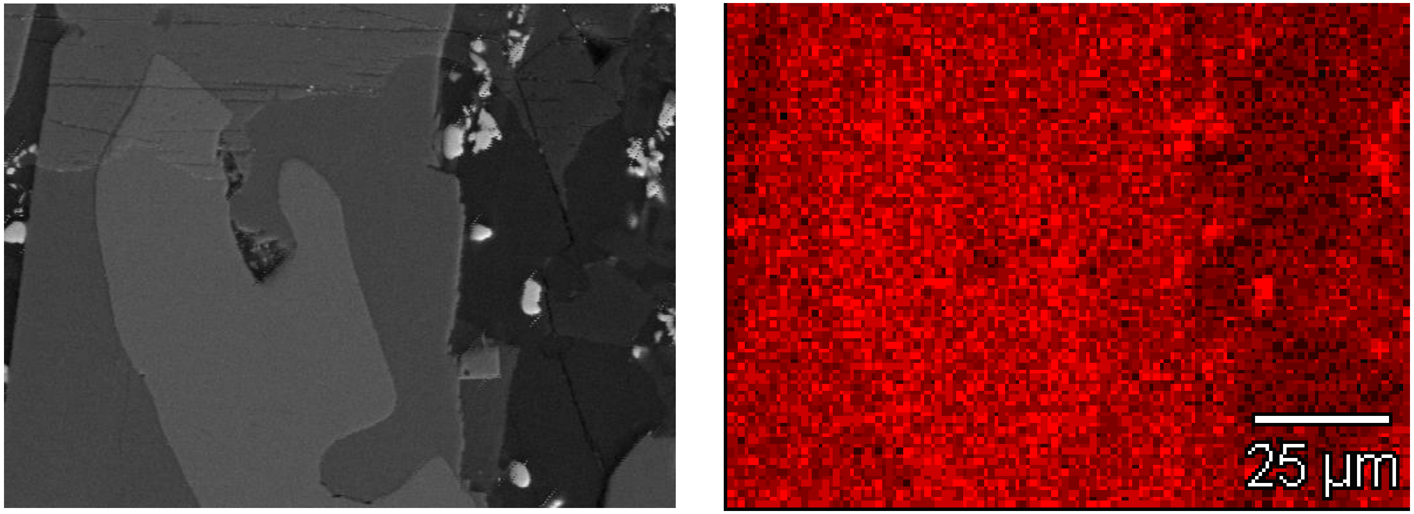
Stainless steel

The ROI map of Mn-Kα contains also information on the Cr-Kβ peak, so if the Cr intensity varies from one area to another, the Mn map will display the same variations, even if the Mn level itself is constant.

ROI X-ray mapping: 2. Atomic number variation artifact

The ROI maps use both the peak and the background intensity in the energy window. But the background intensity varies with the local atomic number of the sample.

From the previous example: Potassium is not present. But if we ask the software to create a K-Kα X-ray map this map still shows intensity variations:



Electron image

K-Kα map

ROI X-ray mapping: 3. Geometry artifact

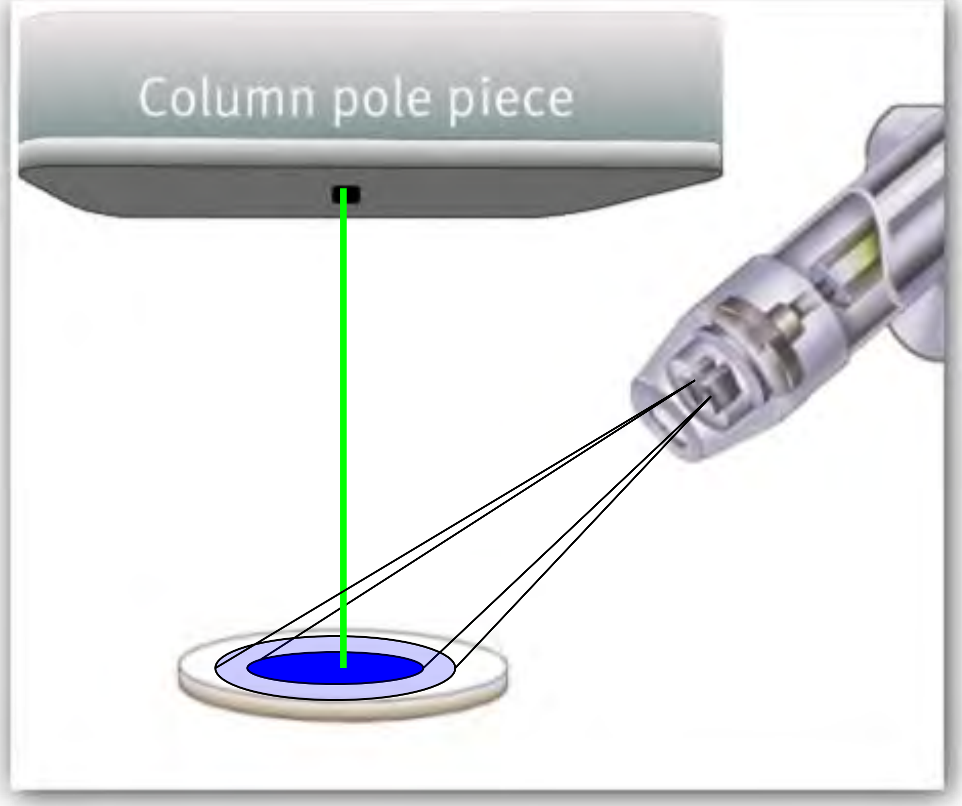
If X-ray mapping is done at a very low magnification then the maps will all seem a bit darker at the edge of the maps.

From within the dark blue disc the X-rays can ‘see’ the full crystal area.

But from the light-blue disk they can see only a smaller part of the crystal, so the probability for such an X-ray to get into the detector decreases.

The user can reduce this effect by retracting the detector a few centimeters.

If that is not possible, then one could increase the magnification, and acquire several X-ray maps in a mosaic pattern, and then ‘stitch’ the images together into one large map.



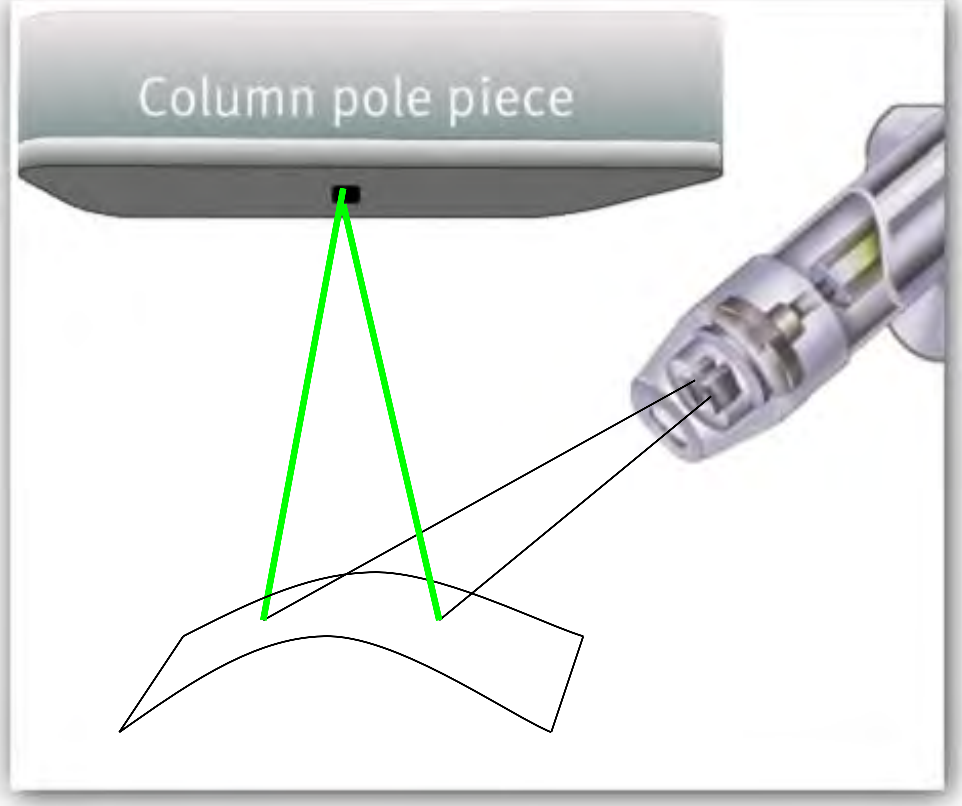
ROI X-ray mapping: 3. Geometry artifact

Artificial intensity variations can also occur if the sample is not completely flat

From the area that is tilted towards the detector X-rays can easily escape the sample.

From the area that is tilted away from the detector X-rays need to travel an extra distance through the sample, are therefore more strongly absorbed, and are thus reduced in intensity.

This effect varies from one element to another, depending on how strong the X-rays are absorbed.



Outline

- X-ray Mapping
- Artifacts in X-ray Mapping
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- Phase Mapping
- Conclusions

Quantitative X-ray mapping

So what can we do about these artifacts in ROI mapping?

- Peak overlaps
  - Do a proper peak deconvolution to separate peaks
- Atomic number variations
  - Remove the background before measuring peak intensities
- Geometry effects
  - Polish the sample until it is flat
  - Retract the detector

Solution: Quantify each spectrum the usual way

Quantitative X-ray mapping

So we need to quantify 62.500 spectra?

Yes, modern PCs can quantify easily 10.000 spectra per second

But you then need better quality spectra: 10.000 counts per spectrum

This can be achieved in a reasonable time in several ways:

1) Very high count rate
2) Lower the pixel resolution
3) Binning: add spectra from N x N matrix together

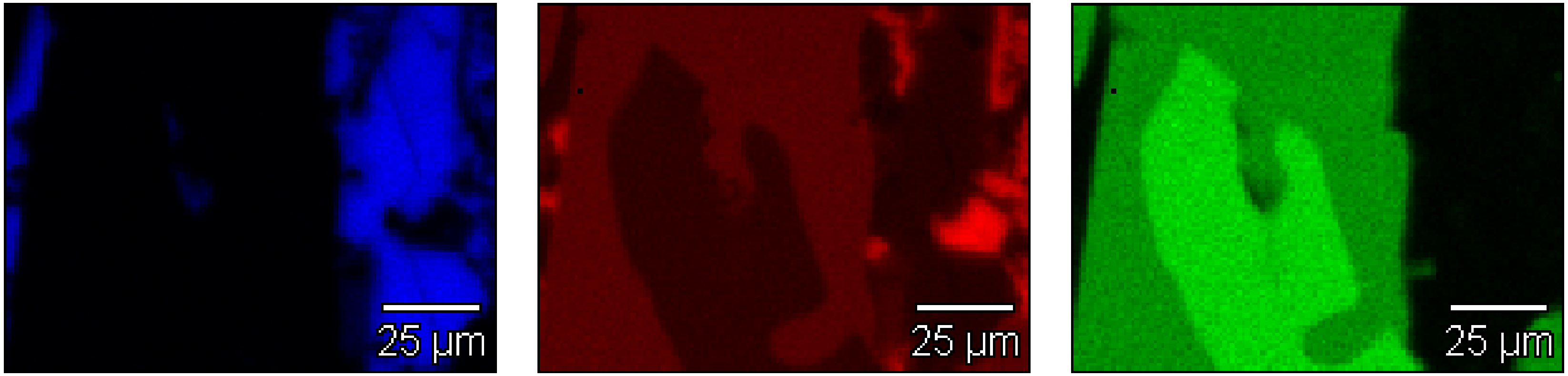
Quantitative X-ray mapping

1) Very high count rate? How high can you go?

- Use silicon-drift detector: can generate up to 1 million cps
- Use large area detector: 30 mm^2 crystal/sensor
- Use high-speed electronics: over 300.000 cps stored
- Make sure your SEM is set to a very high beam current
- Hope your sample doesn't disintegrate …….

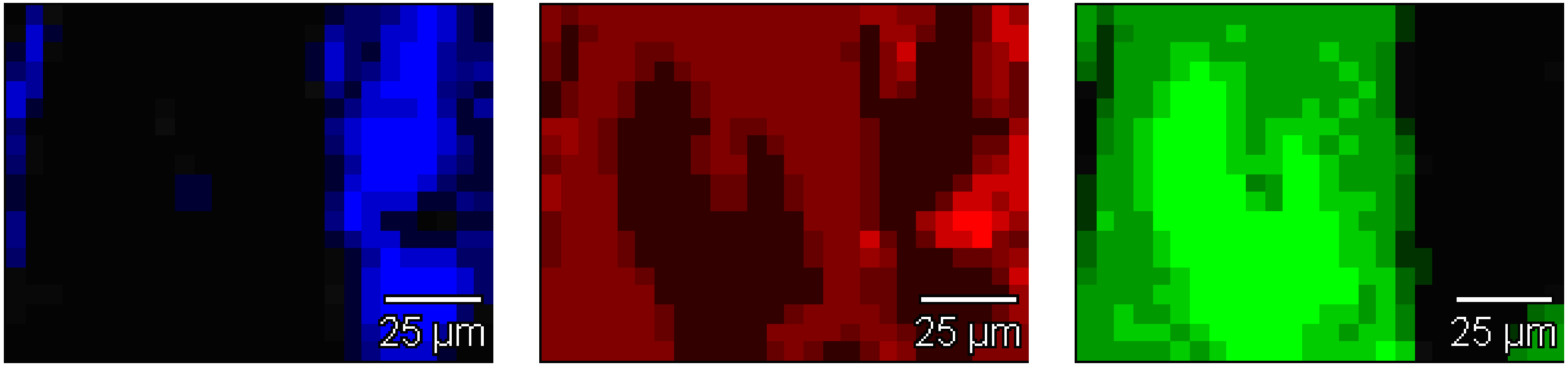
Quantitative X-ray mapping

2) Lower the pixel resolution? What images will that produce?



Mg-K Si-K Fe-K

Lowering the resolution to 50 x 40 pixels: 2000 pixels, so at 10.000 cps and 1 second per pixel this takes 2000 seconds or 35 minutes.



Quantitative X-ray mapping

3) Binning? Binning means you add pixels together and then process them. For that you need the original data from each point: the raw spectra.

So what you need is a Spectral Image: like an X-ray map but from each pixel the complete spectrum is stored. A 250 x 250 Spectral Image therefore contains 62.500 spectra.

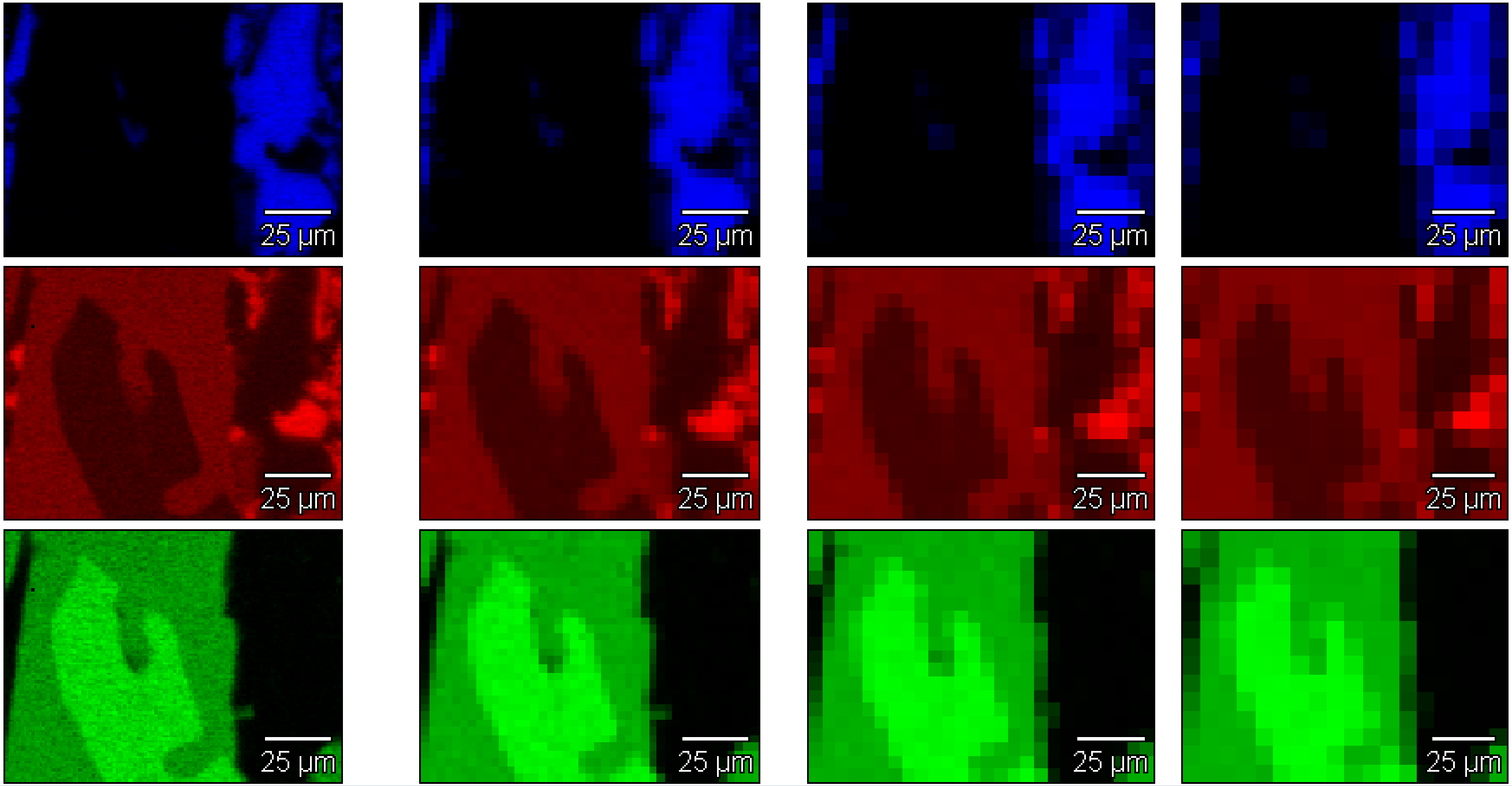
From such a dataset the user can extract information:

- Spectra from individual points or areas
- Linescans with variable number of points and line widths
- X-ray maps: both ROI maps and QuantMaps
- The QuantMaps can be extracted with kernel binning

Quantitative X-ray mapping

Quantmaps with variable binning levels

1 x1 3 x 3 5 x 5 7 x 7

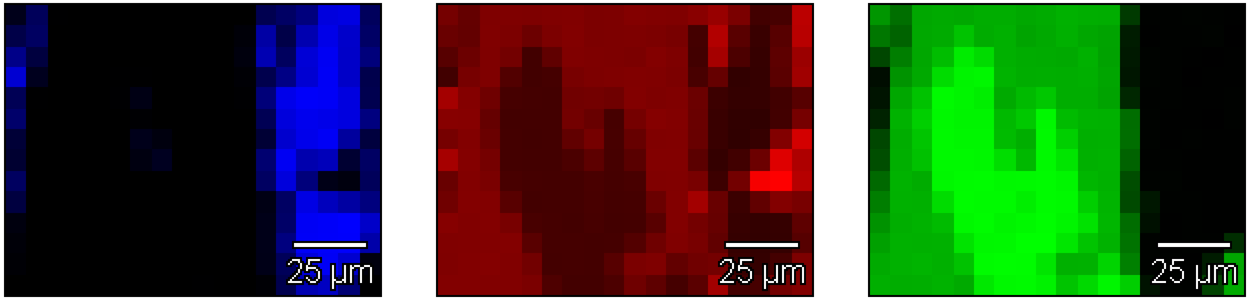


Quantitative X-ray mapping

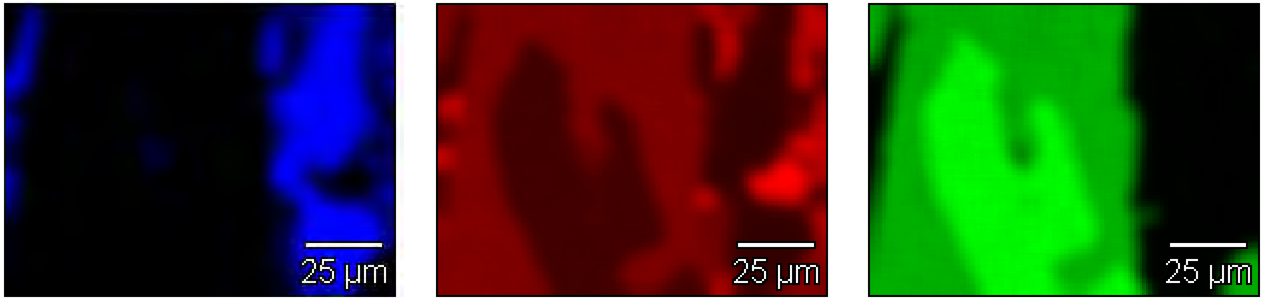
How to maintain the original resolution, but still get enough data in each spectrum to do a decent quantification?

→ Shifted kernels

With this technique you use a N x N kernel, but each pixel gets calculated from the sum of its N by N neighbors. This of courses will generate some smoothing and filtering.



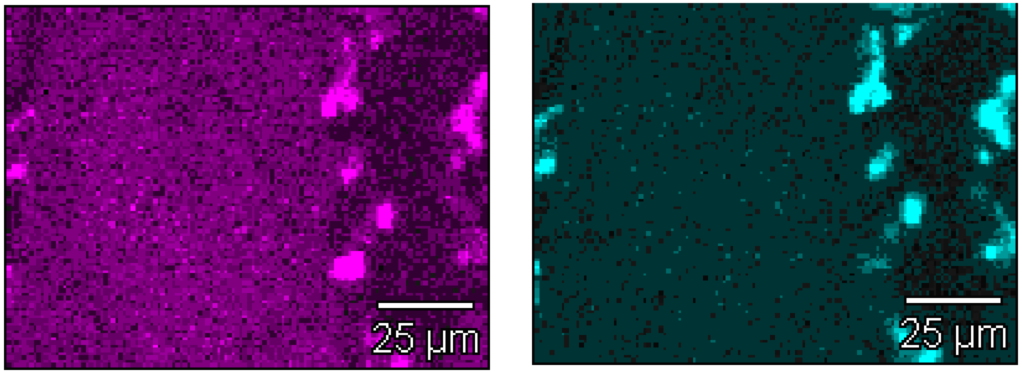
7 x 7 with simple binning



7 x 7 with shifted kernels

Quantitative X-ray mapping: example 1

From the previous dataset, you can find that there is titanium and lanthanum present. So you extract ROI X-ray maps to find out where they are:

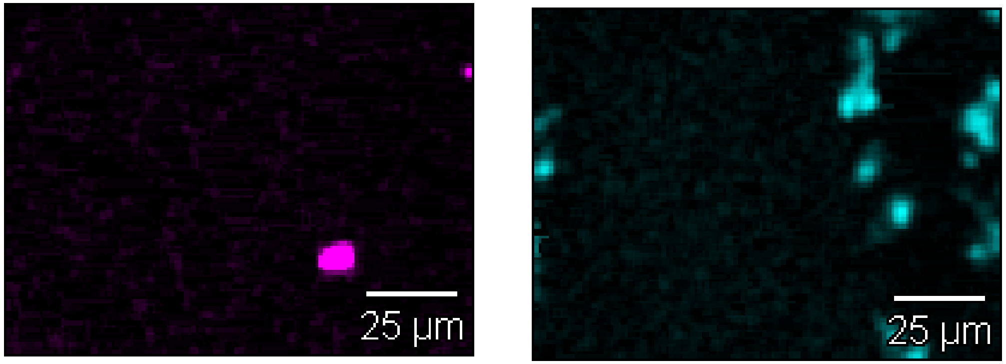


Left (magenta) Ti-Kα

Right (cyan) La-Lα

Very similar right? Too similar: Ti-K and La-L are overlapping.

So we try QuantMapping with 3 x 3 shifted kernels

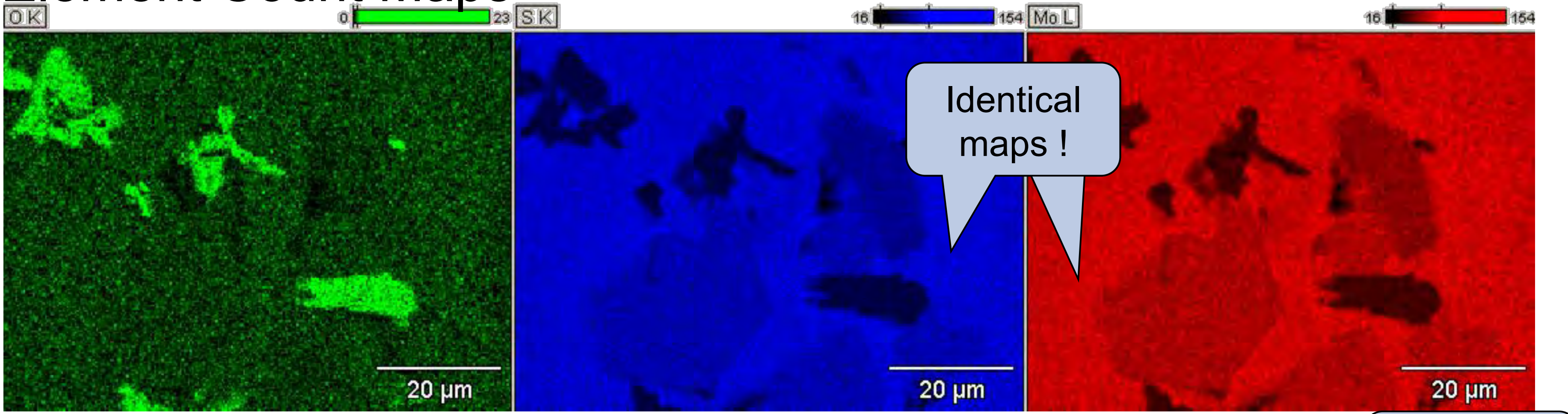


Left (magenta) Ti-Kα

Right (cyan) La-Lα

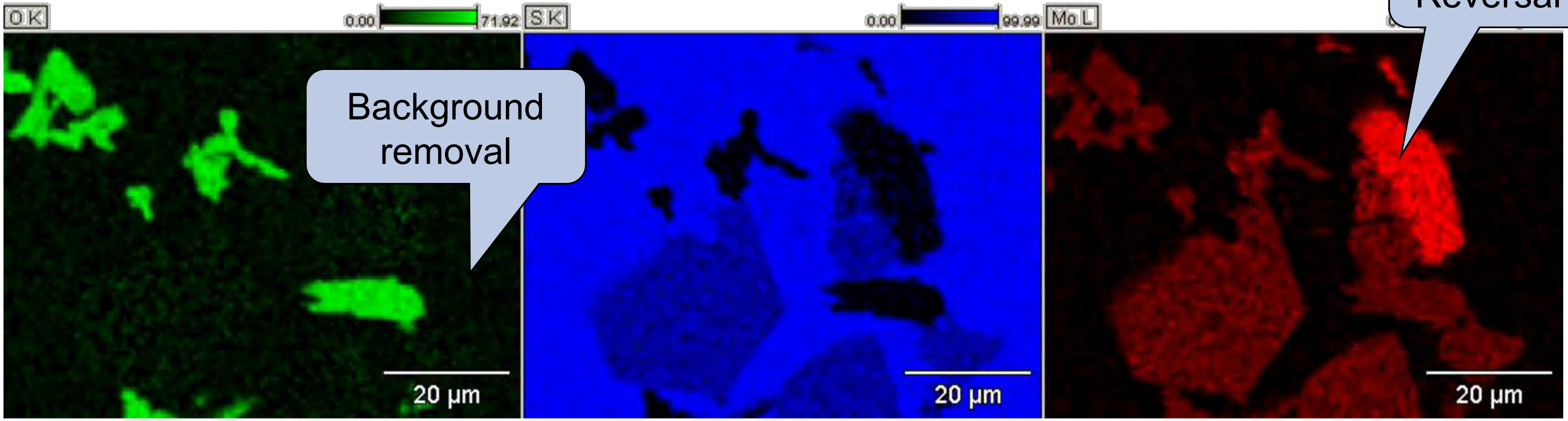
Quantitative X-ray mapping: example 2

Element Count Maps



Identical maps !

Element Weight % Maps

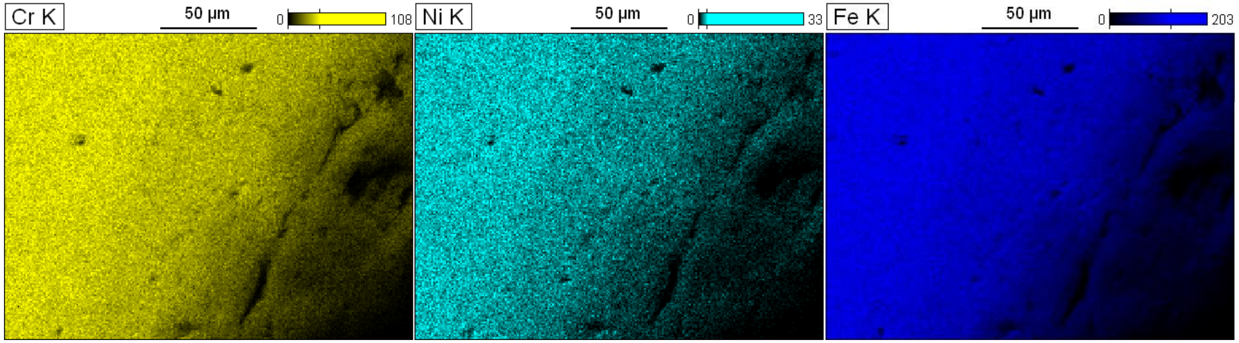


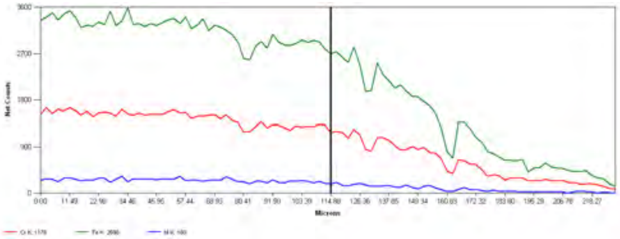
Contrast Reversal !

Background removal

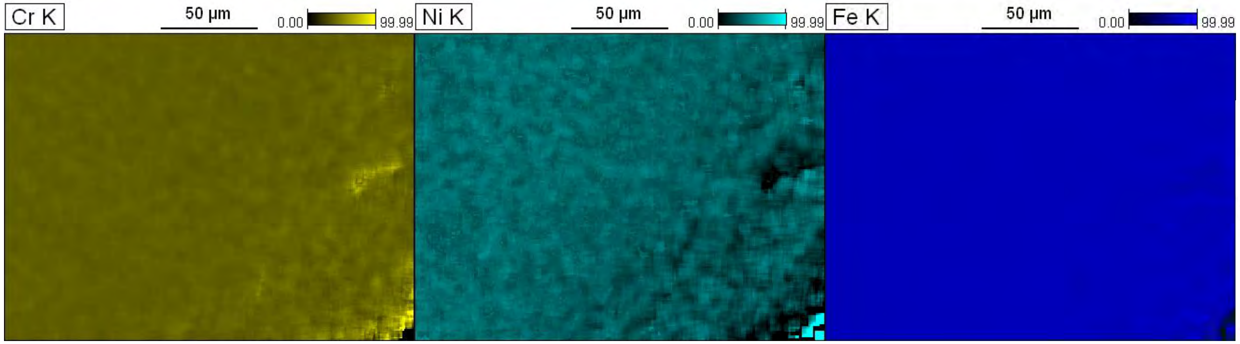
Suppressing Geometry Map Artifacts

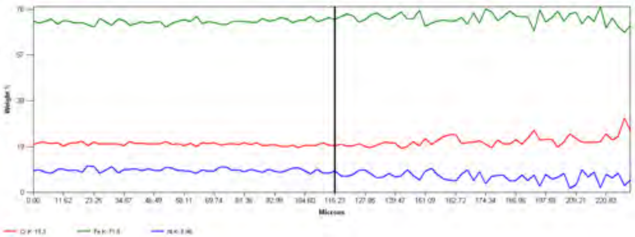
Gross Counts





Weight %





Outline

- X-ray Mapping
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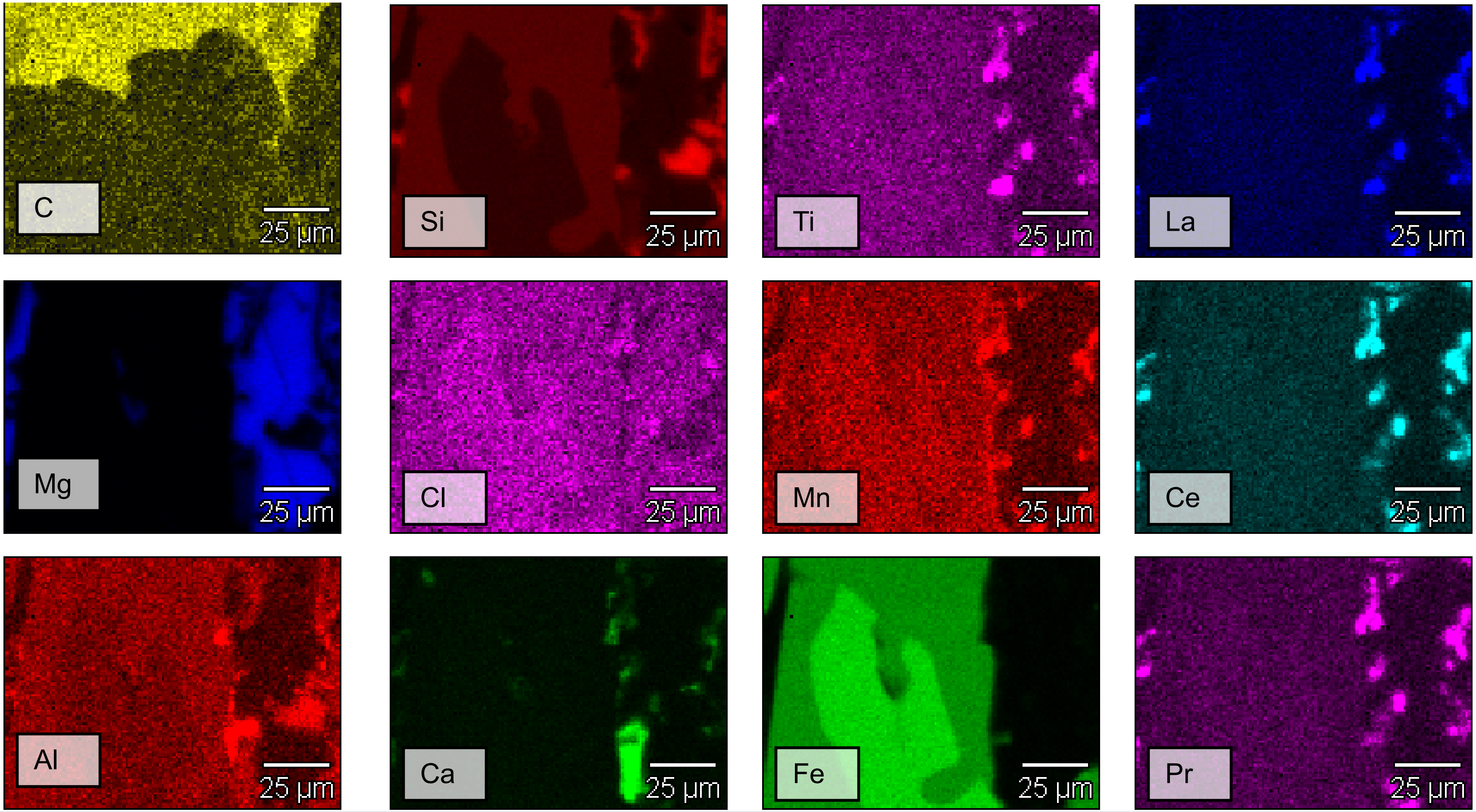
- Quantitative X-ray Mapping
- Phase Mapping

Phase mapping

In this example we have about 12 elements.

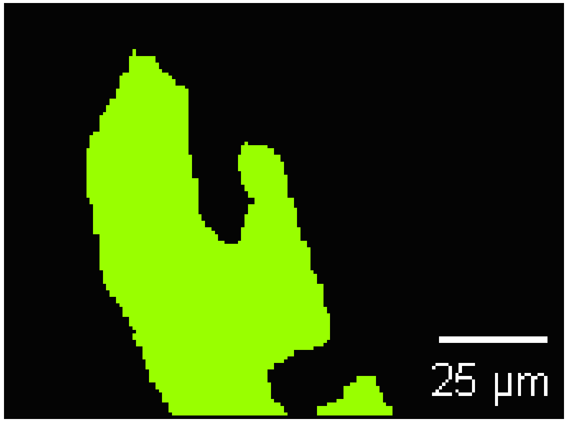
The interpretation is not so easy

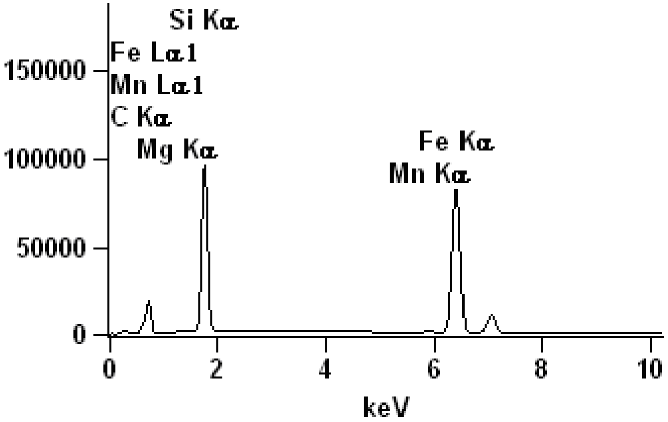


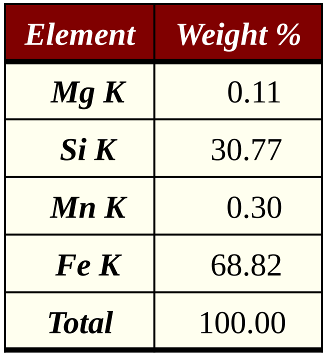
Phase mapping

Phase maps are calculated maps, using X-ray maps (ROI or Quant Maps) as source. A smart software routine will look where intensities are similar, and create phases.

A phase map is binary: a pixel either belongs to a certain phase or not.

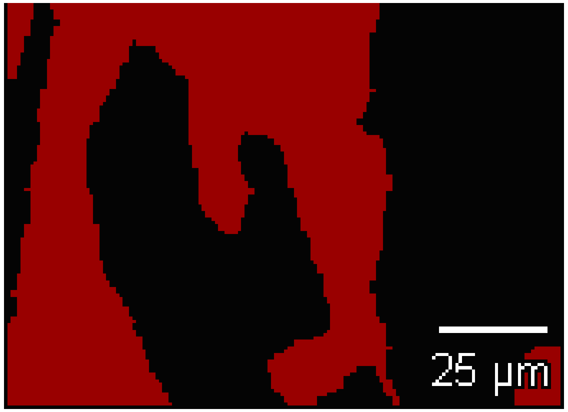


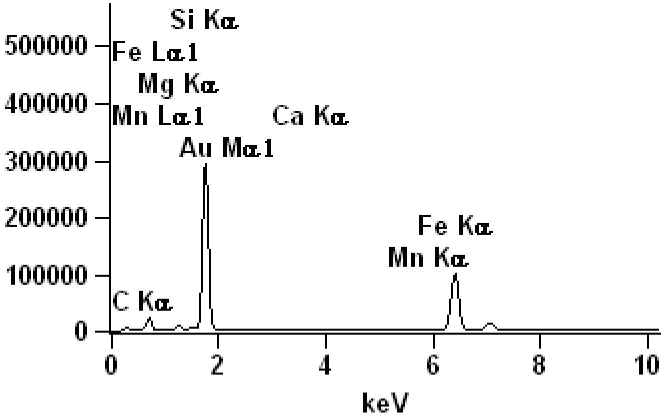




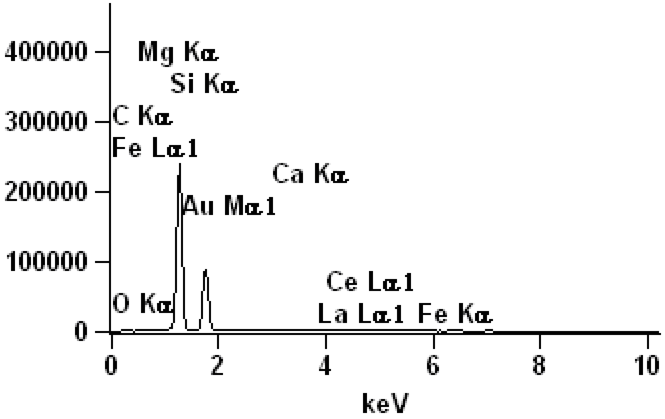
Element	*Weight %*
Mg K	0.11
Si K	30.77
Mn K	0.30
Fe K	68.82
Total	100.00

Phase mapping



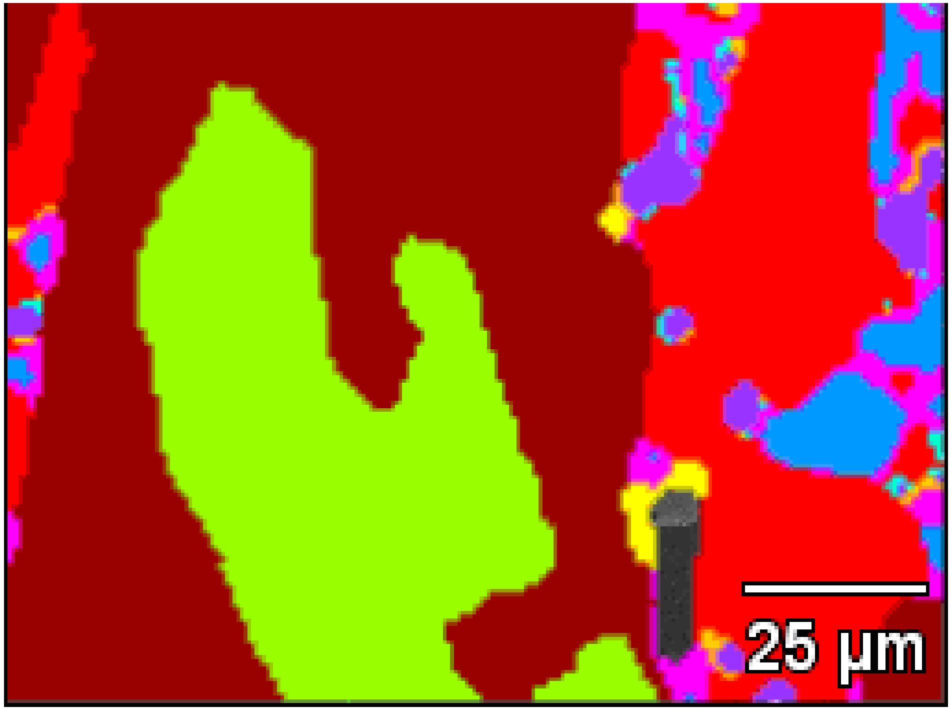


Element Line	Weight %
Mg K	1.27
Si K	51.75
Ca K	0.15
Mn K	0.23
Fe K	45.42
Au L	1.18
Total	100.00



Element Line	Weight %
O K	0.28
Mg K	68.81
Si K	25.21
Ca K	0.82
Fe K	1.73
La L	0.75
Ce L	1.71
Au L	0.68
Total	100.00

Phase mapping



Combinations	*Area %*
Phase1	22.10
Phase2	0.66
Phase3	3.52
Phase4	23.45
Phase5	0.59
Phase6	0.44
Phase7	2.21
Phase8	4.25
Phase9	41.76

Analysis Considerations

Analysis Considerations

Sample composition

- **The more that you know about the origin and properties of the sample prior to analysis, the easier the analysis will be**
- **What is a possible element?**

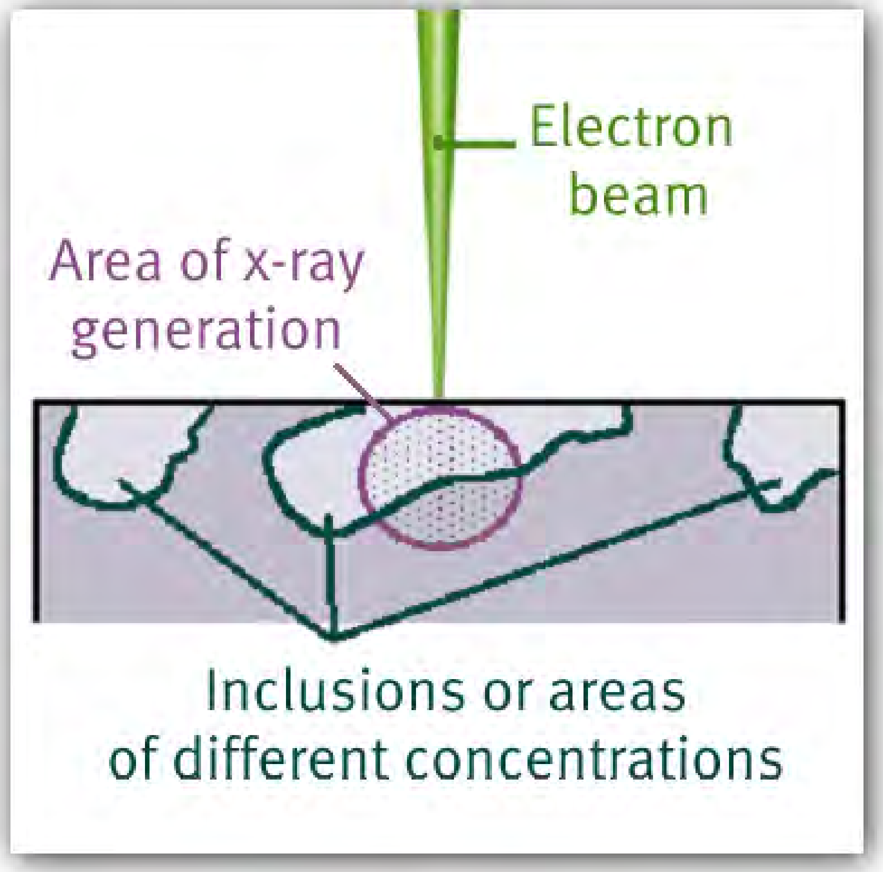
Common sense should be used. If it looks like a piece of steel, then it probably is.

Analysis Considerations

Sample homogeneity

- **The sample must be homogeneous, not with respect to the electron beam, but with the entire interaction volume for an accurate quantitative analysis**

Homogeneous samples are not necessary for qualitative concerns

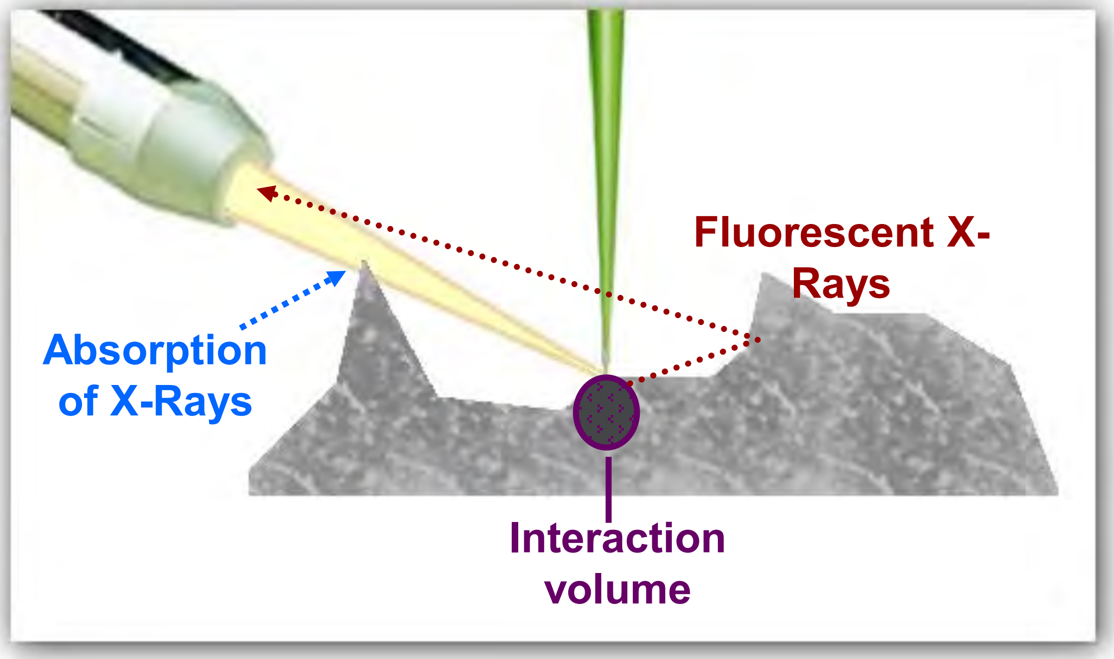


Analysis Considerations

Sample surface condition

- Samples should be flat and polished when possible
- Conditions may affect qualitative and quantitative results

<1 micron polishing media

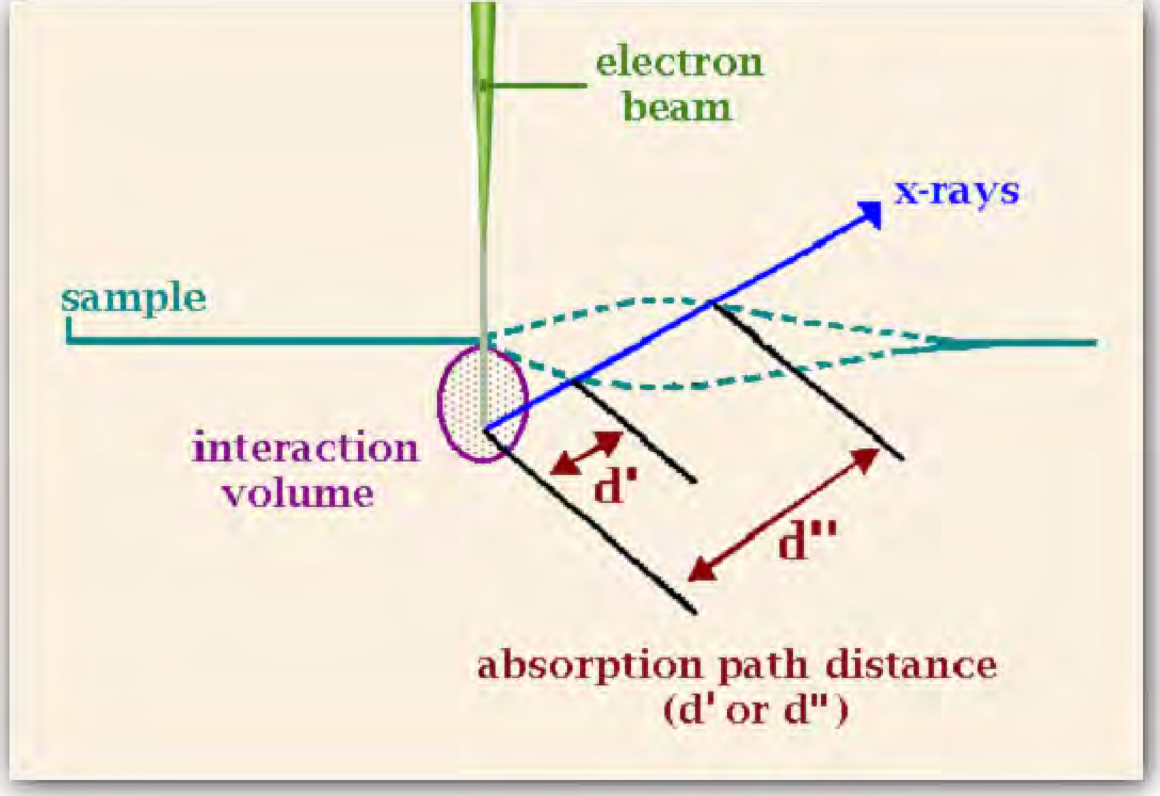


Note: Emergence angle can not be accurately determined for this sample.

Analysis Considerations

Sample surface condition

- **Accurate quantitative results are not possible if the absorption path distance varies or is not accurate**

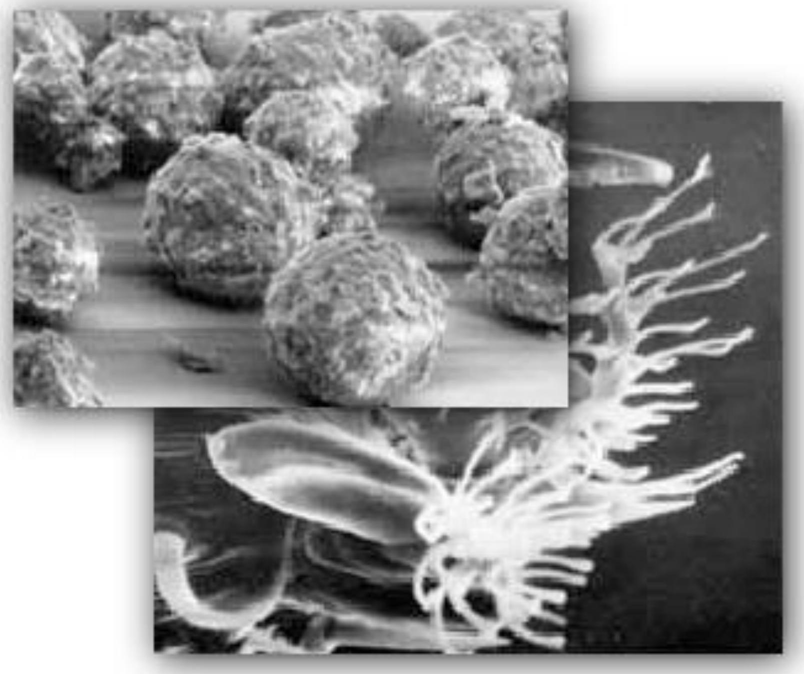


Analysis Considerations

Sample charging

- **Can deflect the electron beam**
- **Effectively will decrease the accelerating voltage**
- **Will make quantitative results inaccurate**

Should be minimized by decreasing the beam current, decreasing the accelerating voltage, coating the sample, or varying the SEM pressure



Analysis Considerations

Sample coating

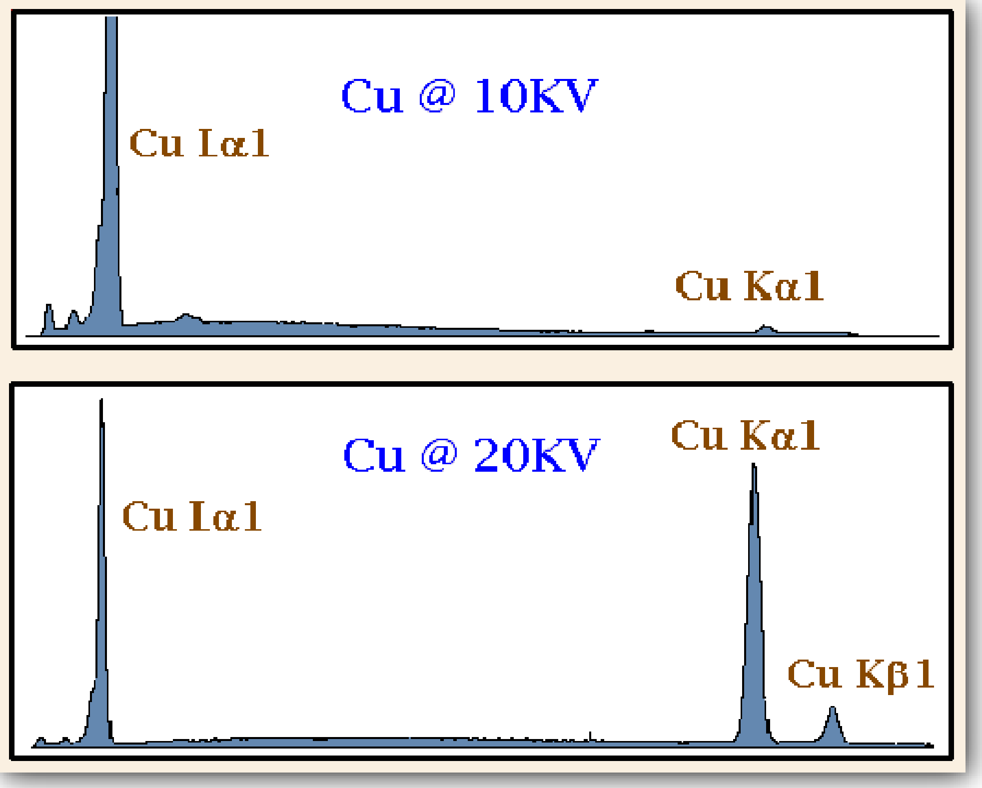
- Always apply a consistent thickness
- Use thinnest useful coating
- Do not coat with a film whose elements are in the sample of interest

Common coating are Carbon or AuPd. Carbon is recommended for EDS since AuPd will absorb low energy X-Rays from the sample

Analysis Considerations

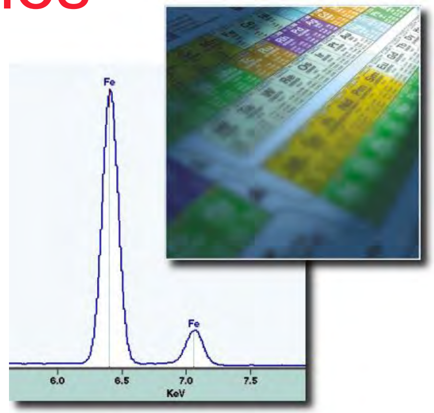
Accelerating voltage

- **Set the accelerating voltage on the SEM to the minimum value to adequately excite the desired elements**
- **Increasing the accelerating voltage will increase the interaction volume**



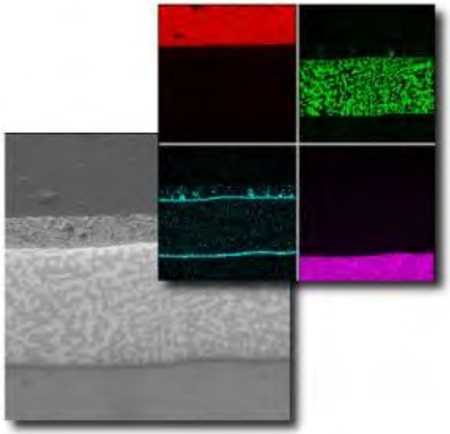
X-Ray Detection Process

Deadtime adjustments: general rules



- **Adjust count rate to achieve a deadtime percentage of approximately 20 with the longest pulse processor rate.**

  Provides best resolution & accuracy.



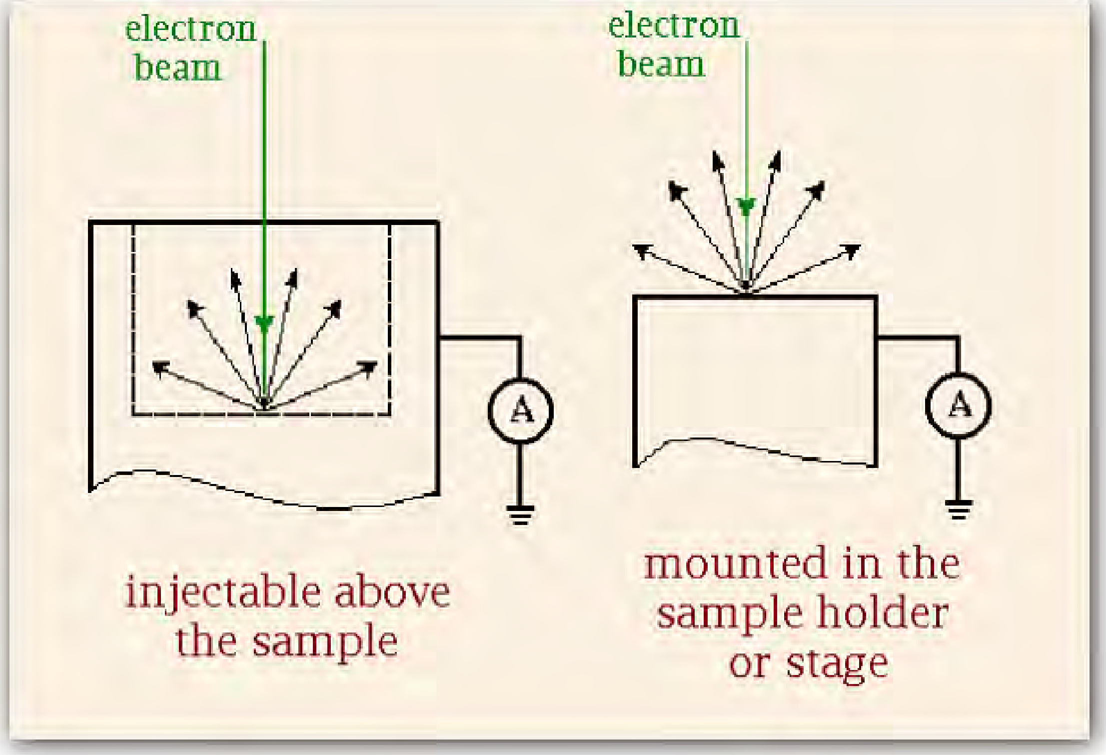
- **Adjust count rate to achieve a deadtime percentage of approximately 50 with the shortest pulse processor rate.**

  Provides maximum throughput, but will degrade resolution.

Analysis Considerations

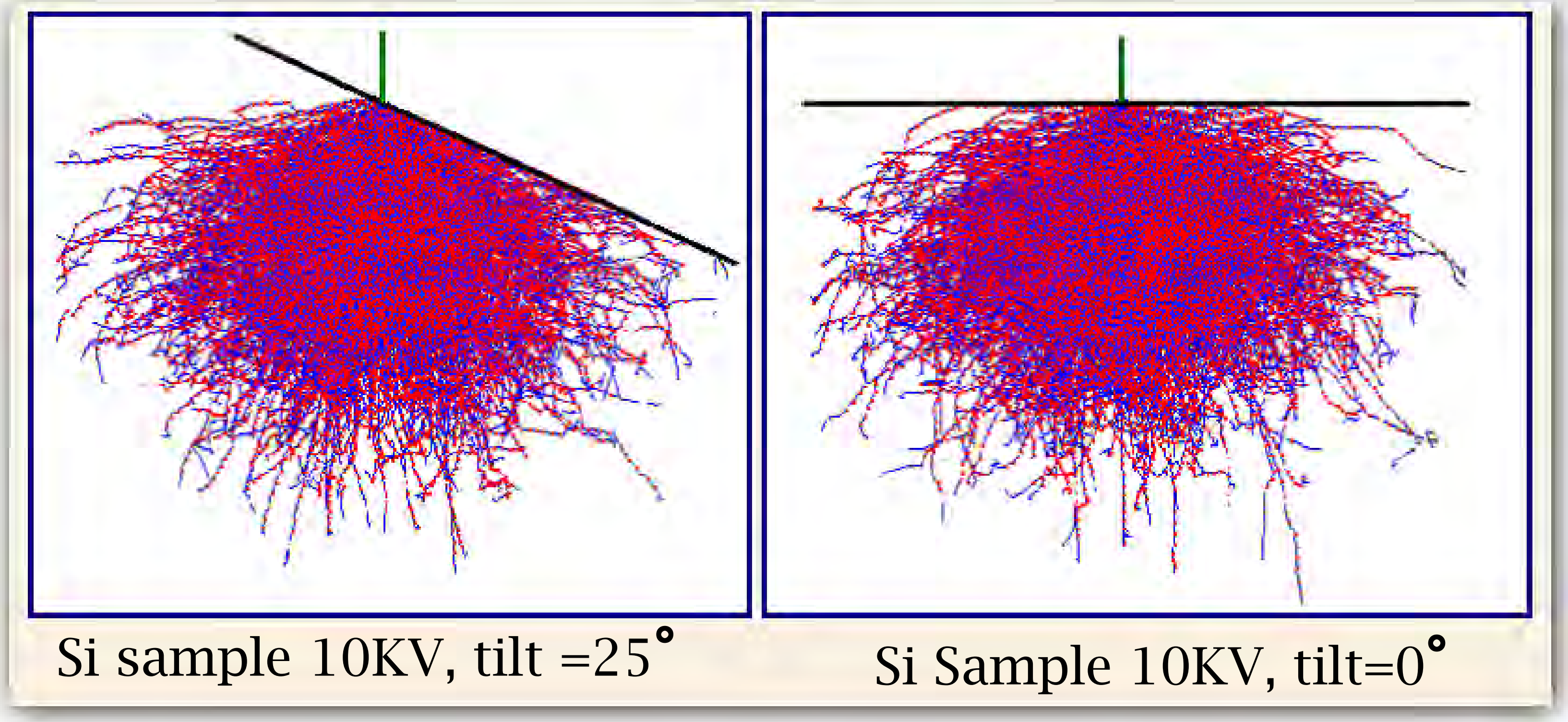
Beam current

- **If the beam current drifts, Quantitative analysis results will be limited by the change in the current**



Analysis Considerations

Sample tilt



Si sample 10KV, tilt =25°

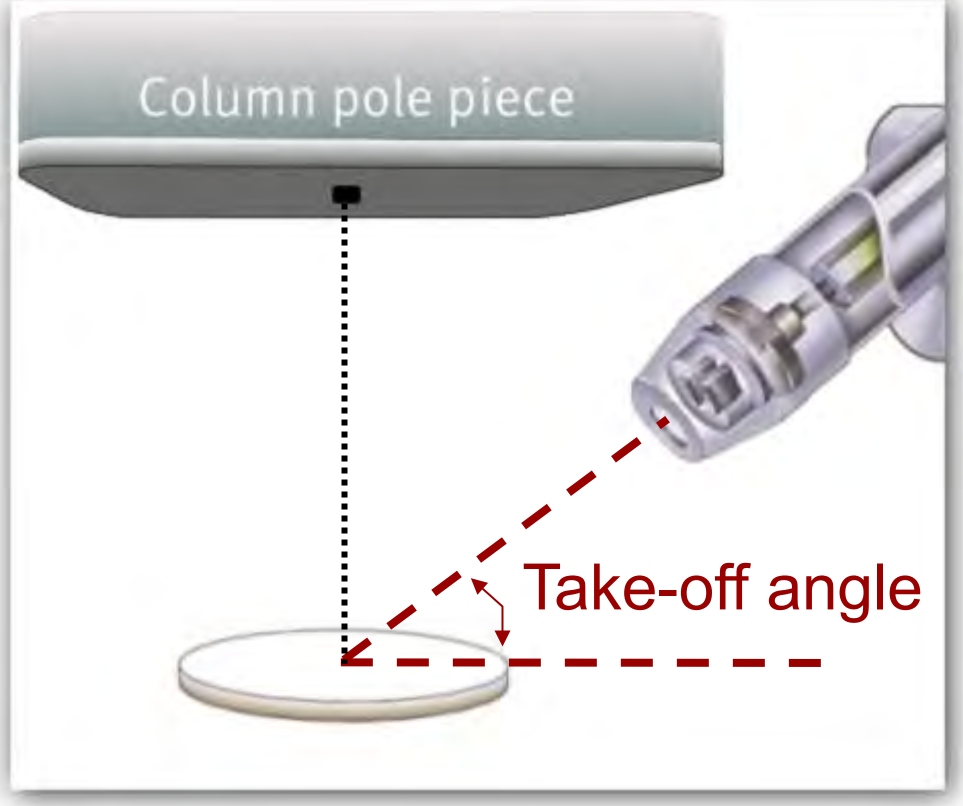
Si Sample 10KV, tilt=0°

The area of the interaction volume in the tilted sample is near the surface. Tilting the sample will change the take-off angle

Analysis Considerations

Geometry: take-off angle

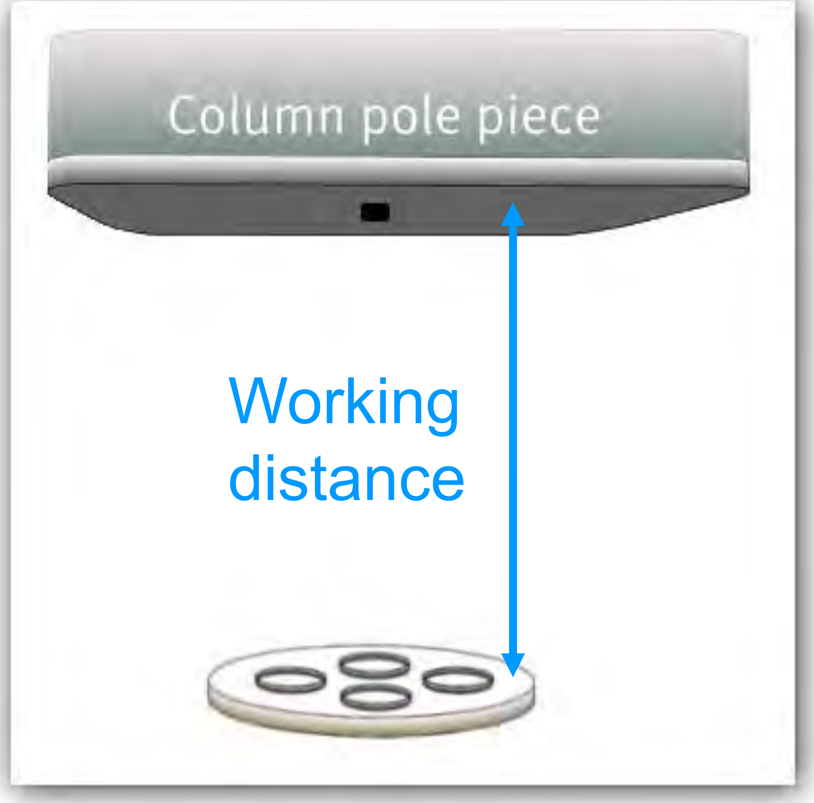
- **The angle between the sample excitation point and the center of the detector crystal**
- **Angle information gained from the detector drawing**



Analysis Considerations

Geometry: working distance

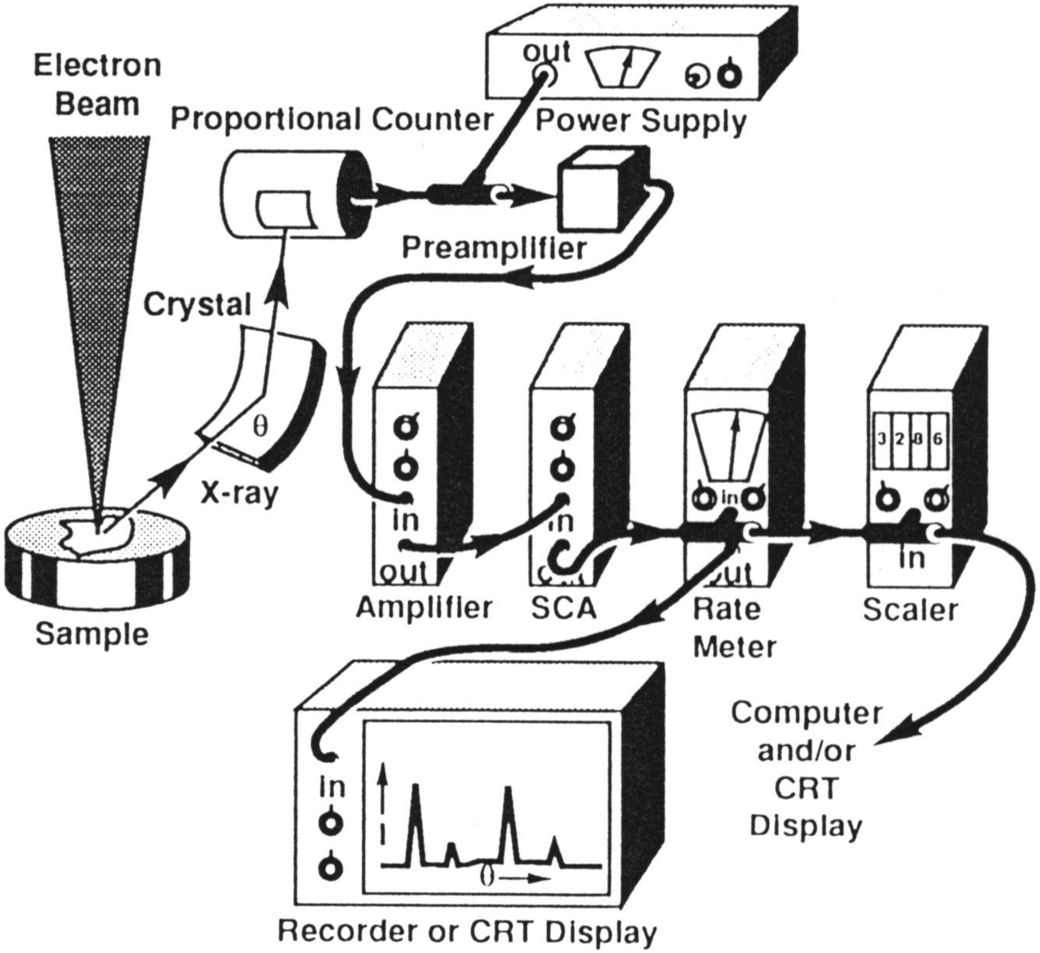
- The distance in mm from the column pole piece to the top of the sample
- The optimum working distance for X-Ray detection is specified on the detector drawing



Outline

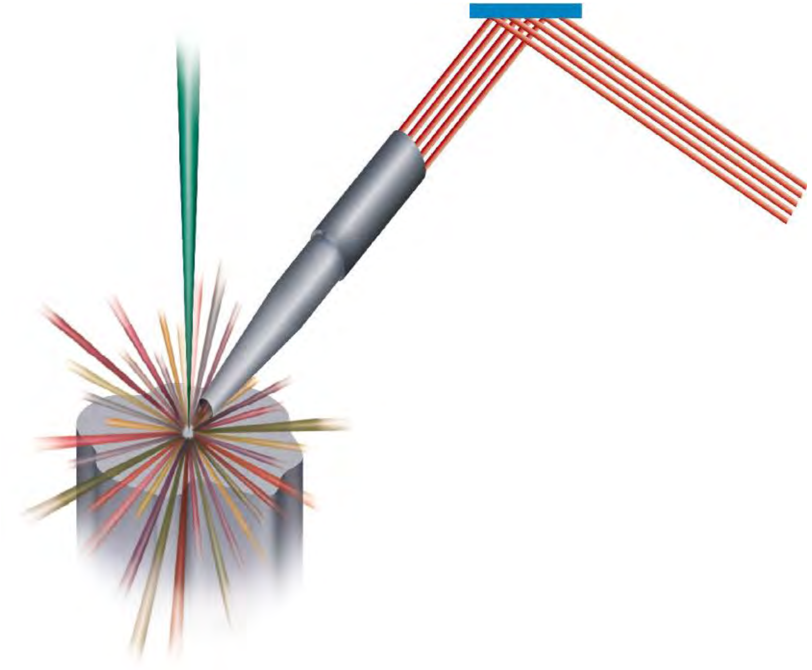
- EDS
- **WDS**
- EBSD
- Conclusions

Basics of WDS



Improving the intensity

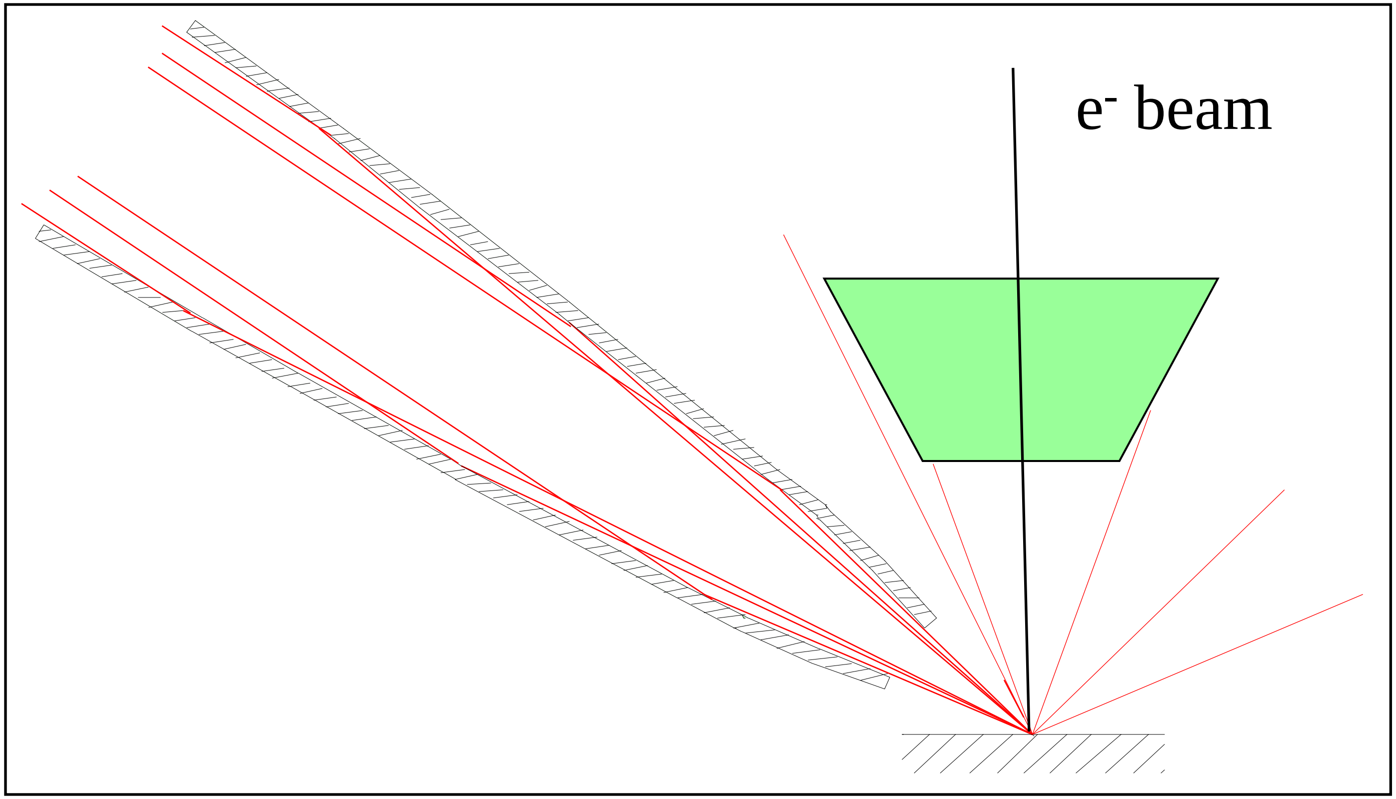
- Use an X-ray lens to capture a large solid angle
- Convert the divergent X-ray beam into parallel beam
- Use large area flat crystals
- Use proportional counter with large entrance window



- 2 types of X-ray lenses:
  - GIXO (Grazing Incidence X-ray Optics)
  - Capillary optics

X-ray lens: GIXO

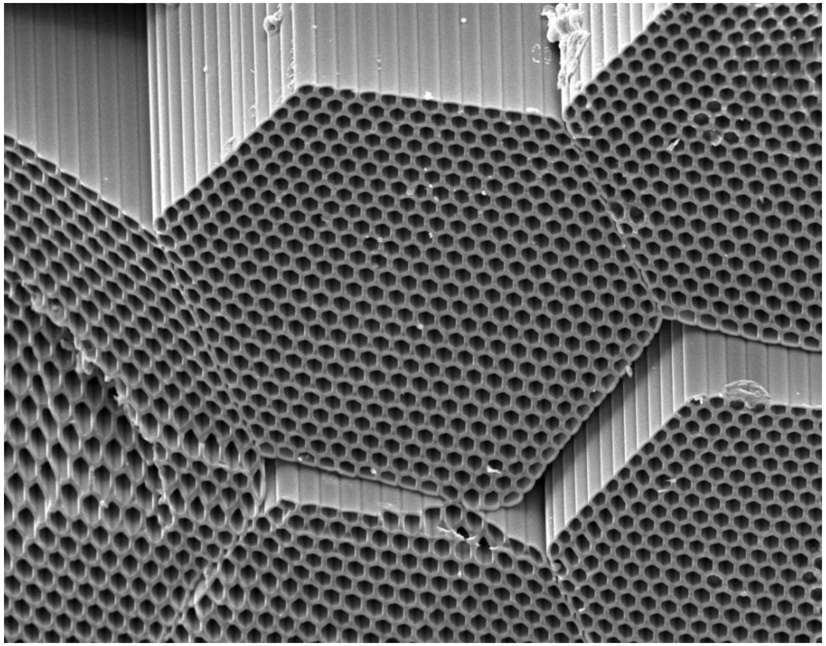
- Metal surface with very fine polish will reflect X-rays

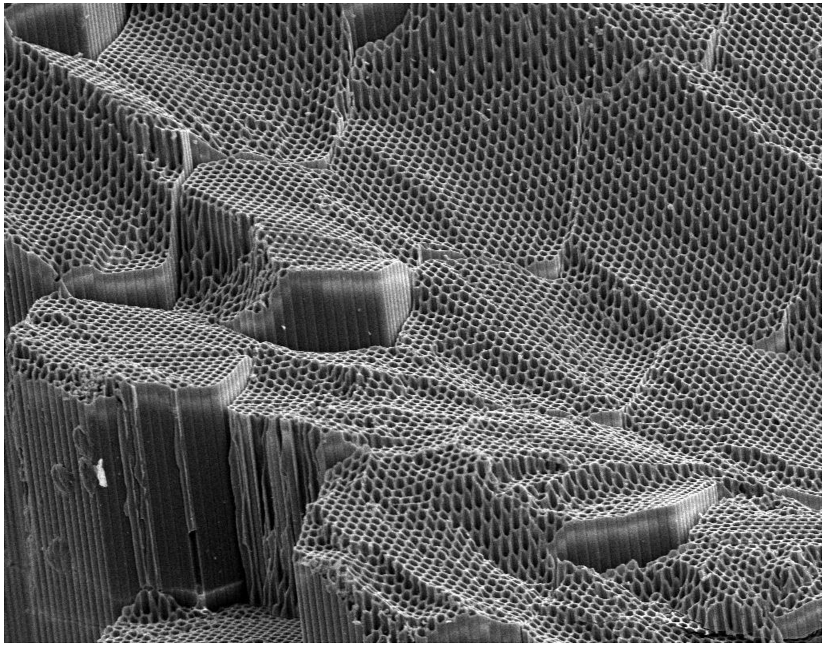


- Limitation of GIXO technology: low energy range only
  - Energy range is 100 – 2200 eV

X-ray Lens: Polycapillary optics

- Bundles of hollow glass tubes
- Diameter of each tube: around 1.5 to 2 micron!





- Each polycapillary lens contains several 100.000's of glass tubes
- Reasonably efficient: certain percentage of X-rays is absorbed

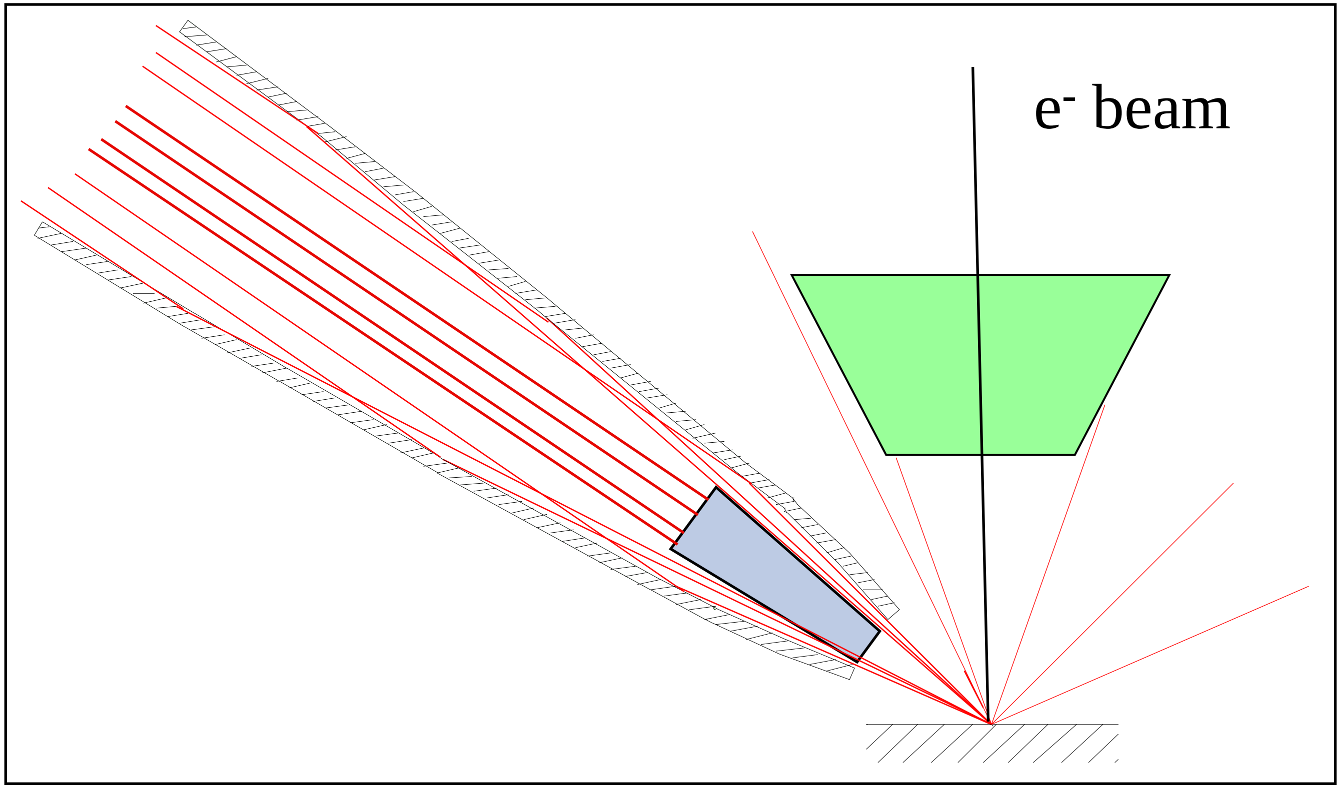
X-ray Lens: Polycapillary optics

- Several manufacturers produce X-ray lenses
- Mainly used in micro-focus XRF

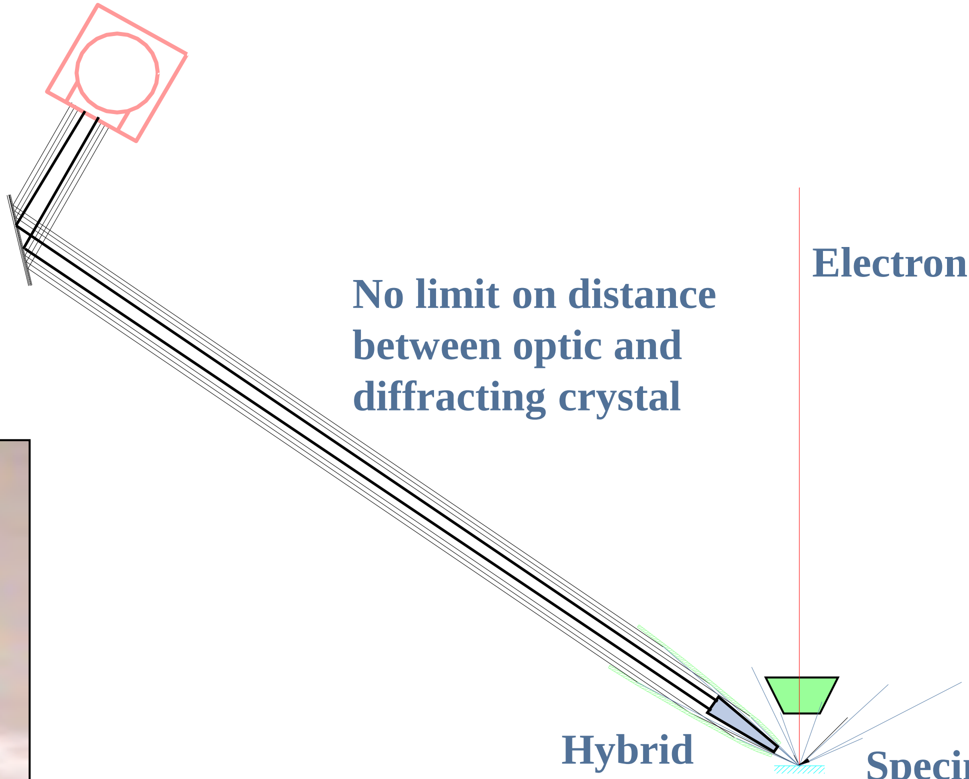
- Typical spotsizes are 20 to 100 micron

Combined GIXO and polycapillary

Energy range: 100 eV ~ 12 keV



The real thing



Large Area
Proportional Counter

Flat
Diffracting
Crystal

Electron Beam

No limit on distance
between optic and
diffracting crystal

Hybrid
Optic

Specimen

Introducing the MagnaRay

Design concepts of MagnaRay

Focus point 1: Ease of use

- Traditional WDS required dedicated WDS operators
- Break with tradition, make WDS available to the non-expert
  - Auto adjustments of all operating parameters
  - Higher confidence in x-ray interpretation:
    - Peak ID of overlapped peaks
    - Quantitative Analysis

Focus point 2: Speed

- Very high-speed mechanical operation
- Minimum need for calibration, bias settings, etc
- Limited need to get standards intensities
- Parallel-beam WDS spectrometer
  - High-efficiency focusing optic
- Fast specimen exchange
  - Small volume to pump

Focus point 3: EDS-WDS integration

- Seamless integration into EDS softtware
  - Not a secondary program
  - Use WDS to enhance EDS performance
  - Use EDS to enhance WDS operation

MagnaRay hardware: crystals

The MagnaRay has 4 standard diffractors, but 2 more can be added for specific applications:

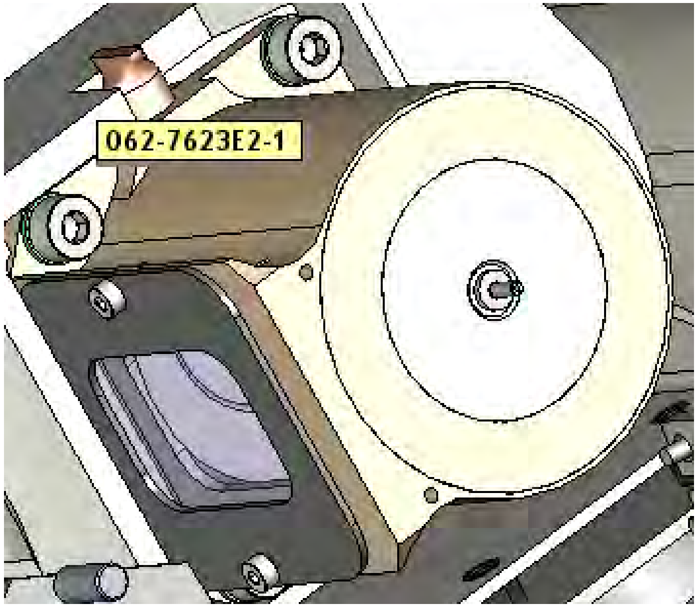
Diffractors	Energy Range	Comment
NiC80	160 eV to 640 eV	Standard
TAP	500 eV to 1.99 keV	Standard
PET	1.47 keV to 5.8 keV	Standard
LIF (200)	3.2 keV to 12 keV	Standard
MoB4C	65 eV to 255 eV	Optional for Be analysis
WSi60	215 eV to 850 eV	Optional for C and O analysis
CrSc80	160 eV to 640 eV	Optional for N analysis
LIF (220)	4.5 keV to 17.9 keV	Optional for improved resolution at high energies

These are flat, plane, large area crystals.

MagnaRay hardware: X-ray Counter

The MagnaRay uses a sealed Xenon counter.

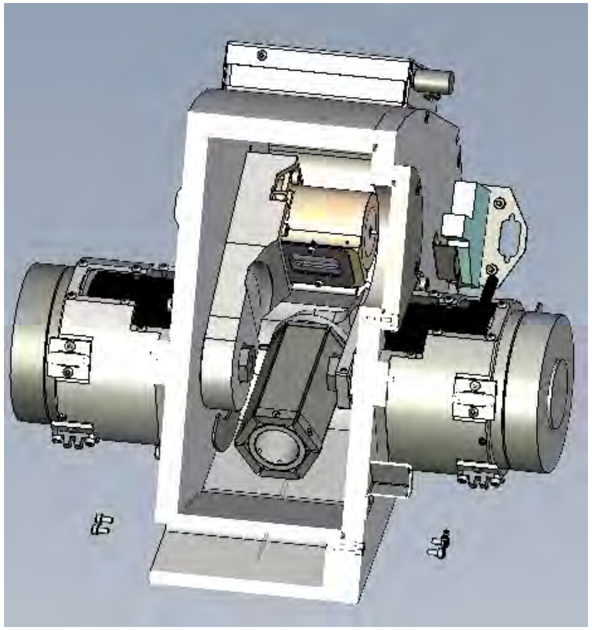
- Life-time over 10-15 years
- Light-element window for detection from Be-Ka
- Absolute zero leakage into SEM chamber
- Factory designed fixed specifications



Benefits:

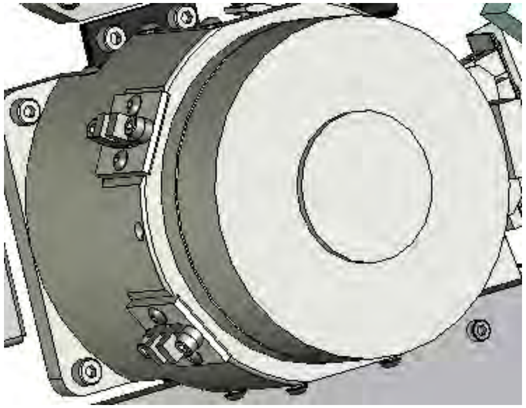
- No P10 gas as needed with flow-counters
- Very constant pressure, thus constant efficiency
- Standard intensities remain valid for a long time
- Significantly faster quantitative analysis
- Fixed settings for gain and bias: no calibration needed
- No special SEM pump requirements

MagnaRay hardware: Motors



The MagnaRay has its motors outside the vacuum

- Direct drive motors
- No moving o-rings
- Ferro-fluidic feed-through
- Very fast motors
- High precision encoders on each motor
  - 0.001 degree accuracy
- Powerful motors
  - 14° -77° movement in 0.25 seconds
  - Diffractor change in less than 3 seconds



Benefits:

- Very quick start of data acquisition
- Very silent motors
- No vibrations or anything

MagnaRay hardware: Alignment

Any WDS has a limited focus range. When you get out of this range the diffraction conditions are not optimal, generating a loss of intensity. On most WDS systems this means you have to follow a tedious routine to place the specimen at the exact X, Y, Z coordinates. Quantification is difficult as small deviations from the hotspot generate intensity losses.

The MagnaRay has 3 powerful high-precision motors to move the spectrometer:

- Insert
- Tilt
- Pan

This alignment is done with EDS assistance

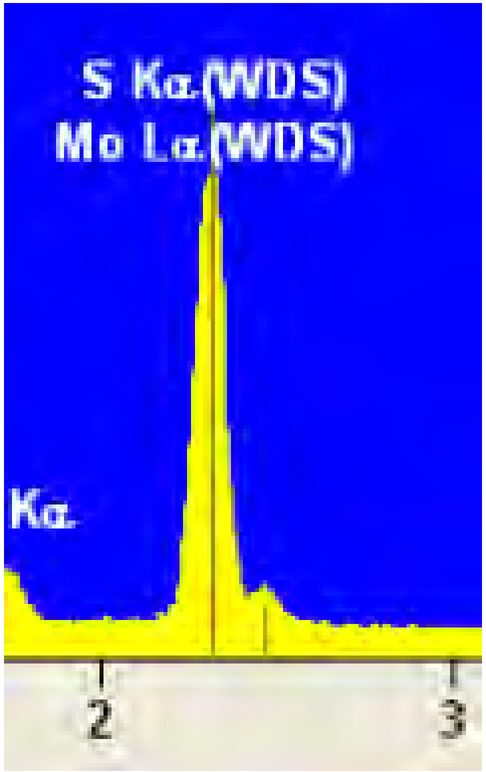
Benefits:

- Very fast finding of the optimum acquisition conditions
- Not dependant on stage movement accuracy, hysteresis problems, etc.
- Reliable quantification results

MagnaRay software: WDS assisted ElementID

Routine to use WDS to assist ElementID with EDS

- EDS acquisition begins
- MagnaRay determines potential overlaps
- MagnaRay measures overlaps using optimum WDS parameters
- EDS peak identification perfected using WDS
- Optional WDS scan taken and overlapped on EDS spectrum

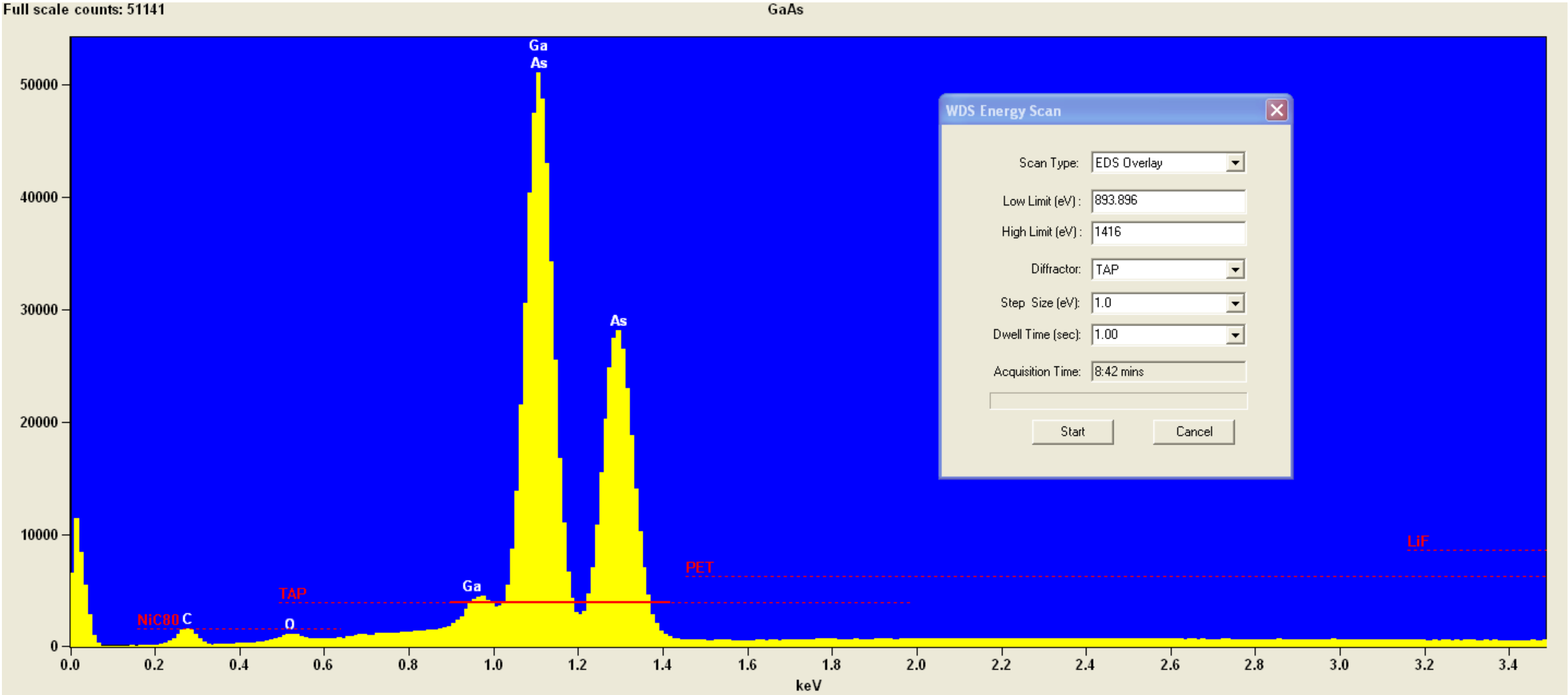


Benefits:

- Reliable ElementID for all samples
- 100% Confidence in your results

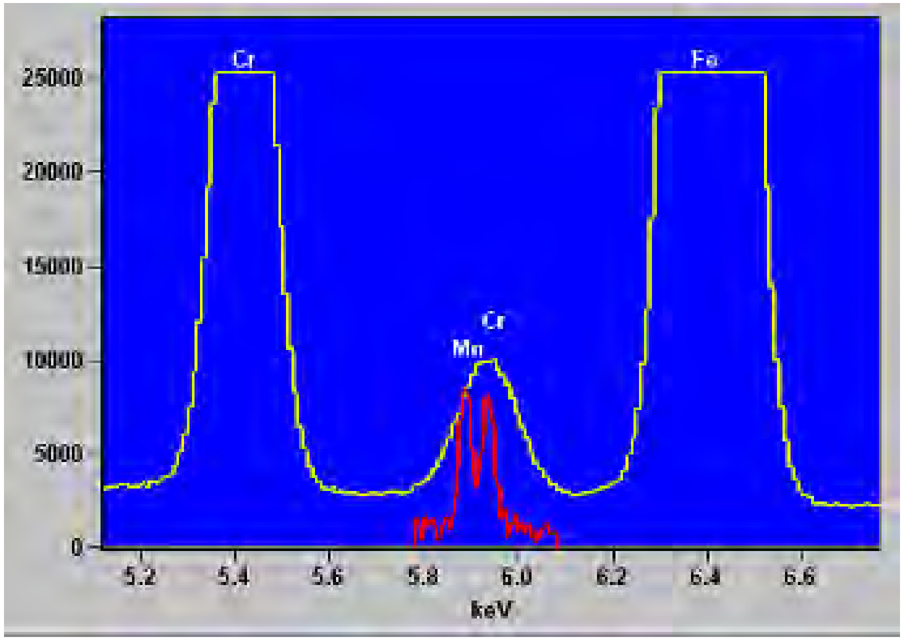
MagnaRay software: Trace element search

To find a trace element, just select an energy range and press start:



Scan Type: EDS Overlay
Low Limit (eV) : 893.896
High Limit (eV) : 1416
Diffractor: TAP
Step Size (eV): 1.0
Dwell Time (sec): 1.00
Acquisition Time: 8:42 mins

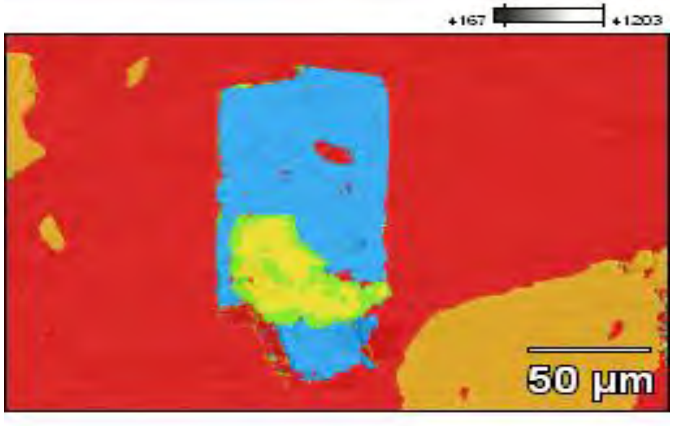
MagnaRay software: Trace element search



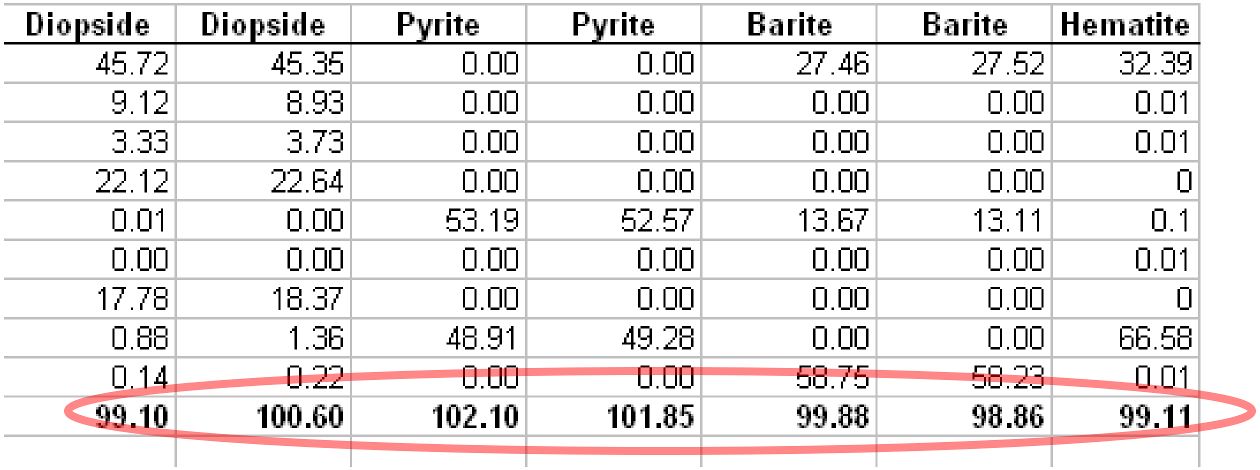
The WDS spectrum is overlaid with the EDS spectrum

MagnaRay – Full standards quantification

Complex multi-element geological sample



🟥 Phlogopite
🟧 Diopside
🟦 Barite
🟨 Pyrite
🟩 Hematite



Diopside	Diopside	Pyrite	Pyrite	Barite	Barite	Hematite
45.72	45.35	0.00	0.00	27.46	27.52	32.39
9.12	8.93	0.00	0.00	0.00	0.00	0.01
3.33	3.73	0.00	0.00	0.00	0.00	0.01
22.12	22.64	0.00	0.00	0.00	0.00	0
0.01	0.00	53.19	52.57	13.67	13.11	0.1
0.00	0.00	0.00	0.00	0.00	0.00	0.01
17.78	18.37	0.00	0.00	0.00	0.00	0
0.88	1.36	48.91	49.28	0.00	0.00	66.58
0.14	0.22	0.00	0.00	58.75	58.23	0.01
99.10	**100.60**	**102.10**	**101.85**	**99.88**	**98.86**	**99.11**

Microprobe Accuracy!

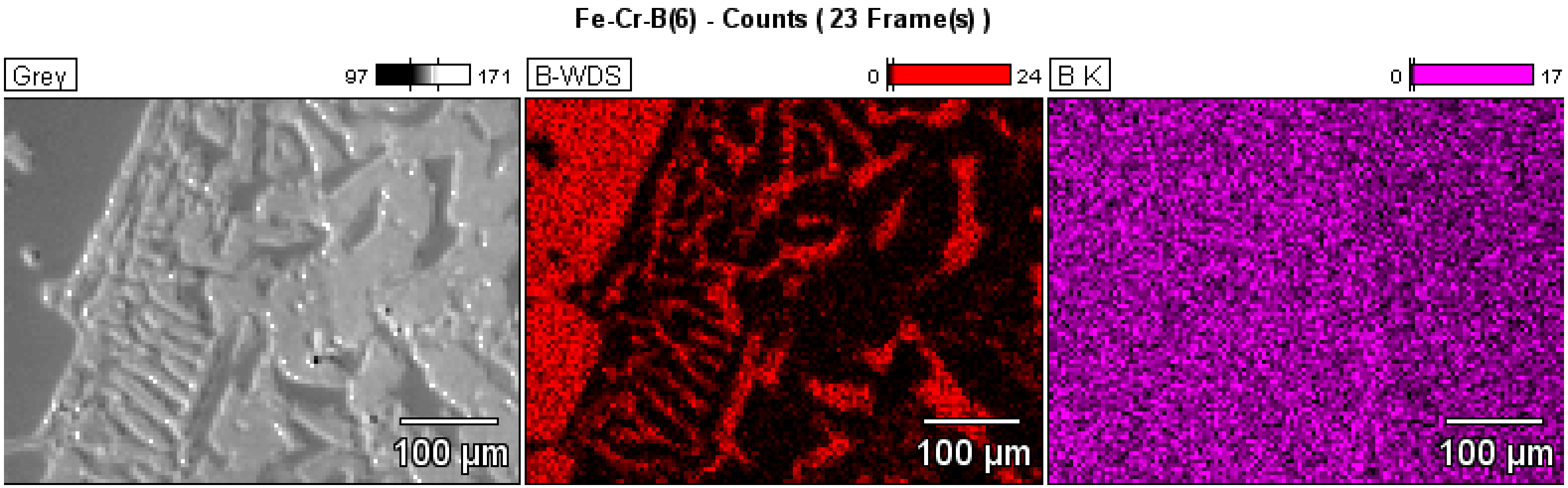
MagnaRay software: X-ray mapping

X-ray mapping:

- Select which element to do the MagnaRay mapping
- Software will take care of the rest

Benefits:

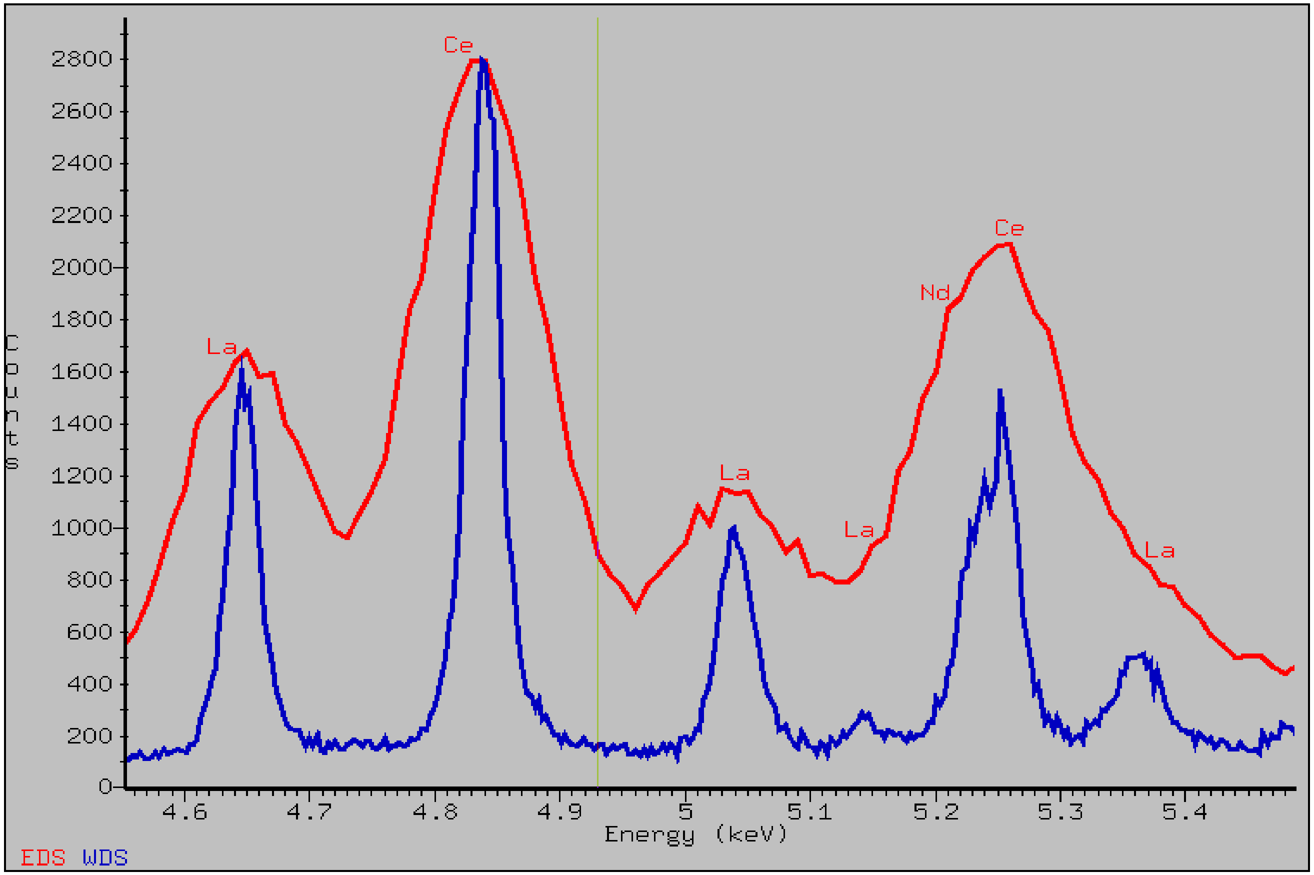
- WDS map acquired simultaneously with EDS data
- Integrated with Spectral Imaging
- Very high efficiency: See Boron maps below



Some PB-WDS Applications

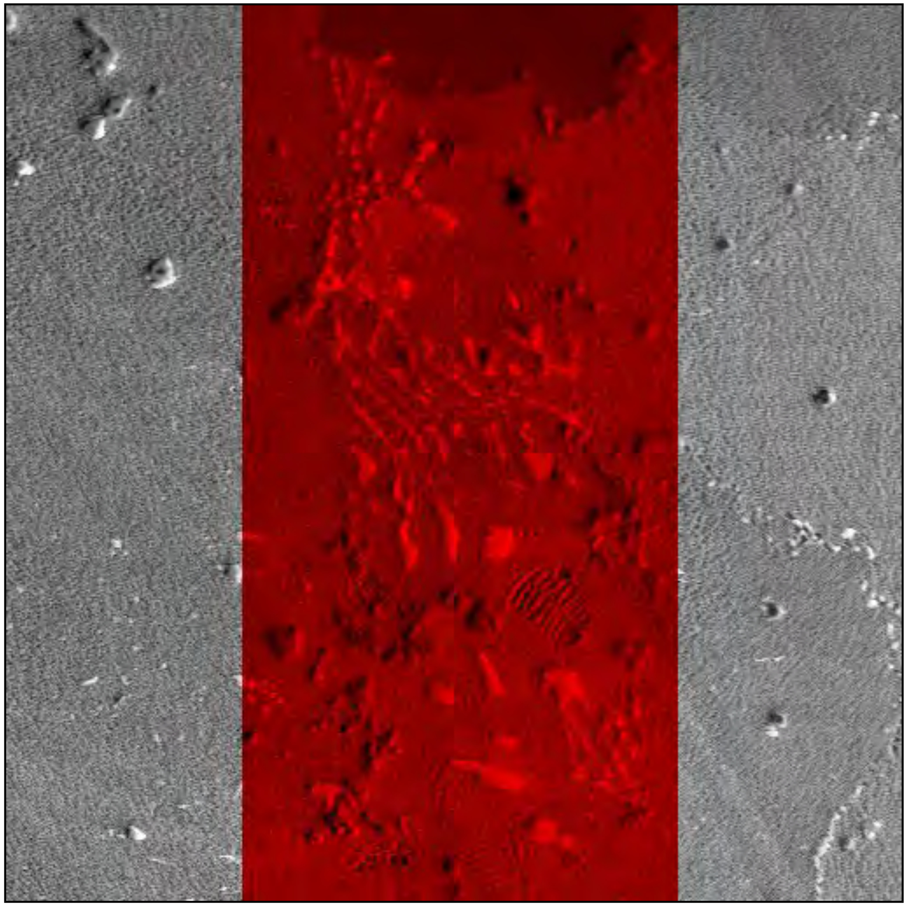
- Multiple peak overlaps that EDS cannot easily separate
- B-Mapping on joint (15kV, 4nA)
- Fe-F overlap – 15 kV, 2nA
- Na-Zn overlap – 15 kV, 2nA
- N in Glass fibers – 15kV

Multiple peak overlaps that EDS can not easily separate

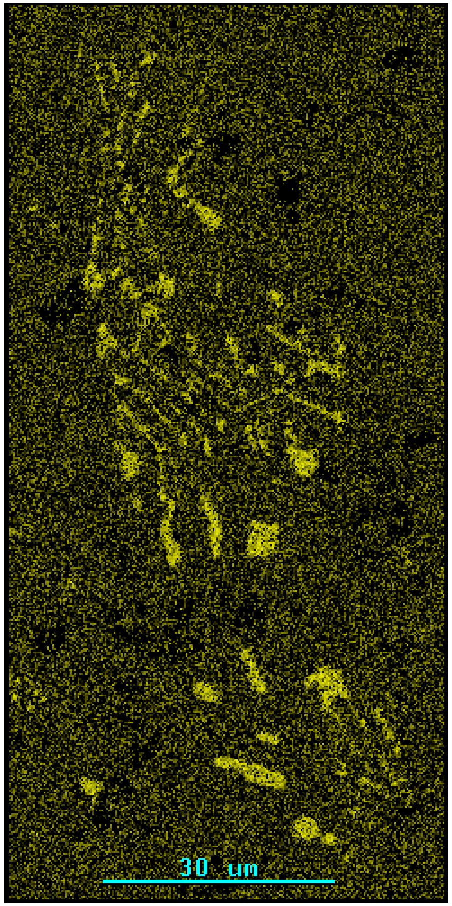


Monazite, PBS-blue 3 seconds 2eV per channel, EDS-red 129eV resolution

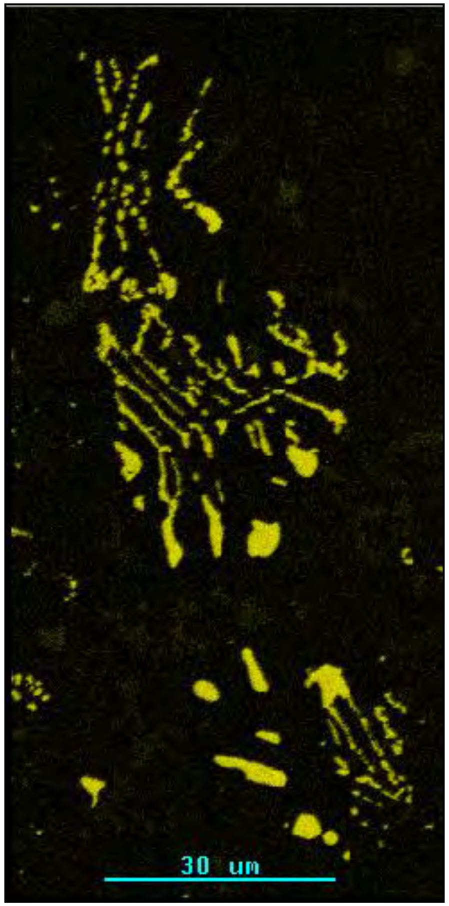
B-Mapping on joint (15 kV, 4 nA)



Red = area of interest

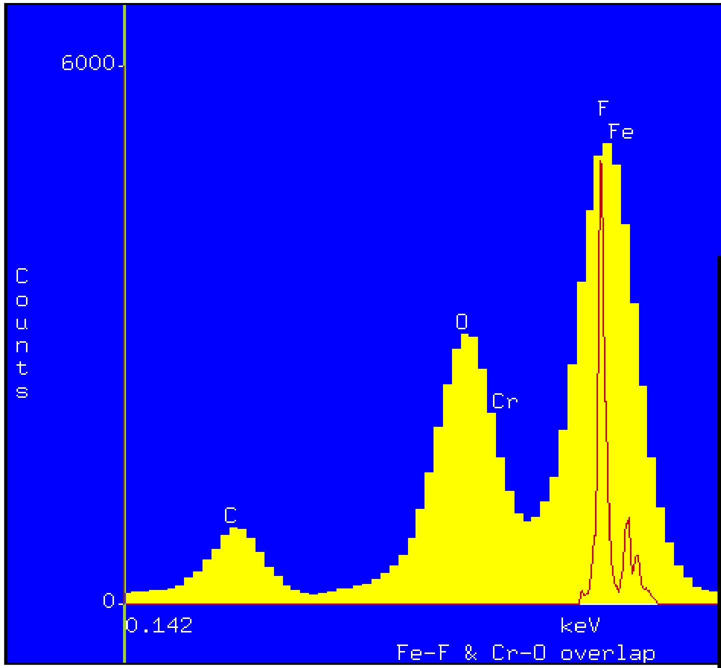


B - EDS

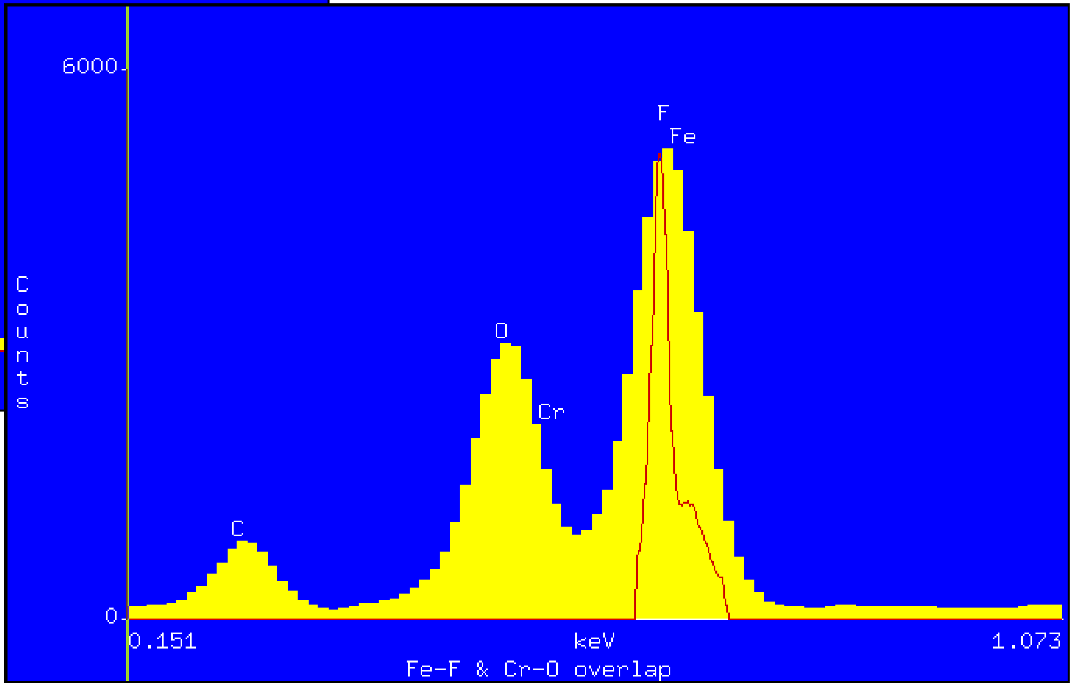


Boron – PB-WDS

Fe-F overlap – 15 kV, 2nA

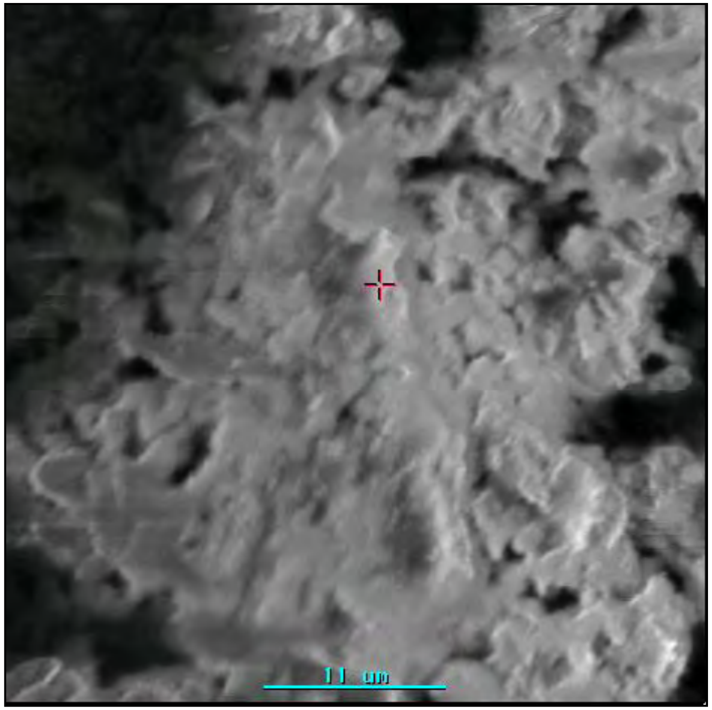


Overlap between EDS + WDS (TAP crystal)

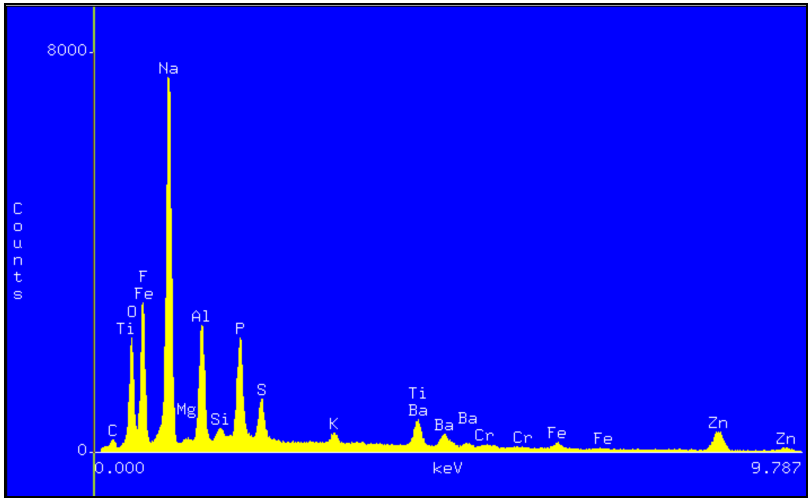


Overlap between EDS + WDS (WSi60 crystal)

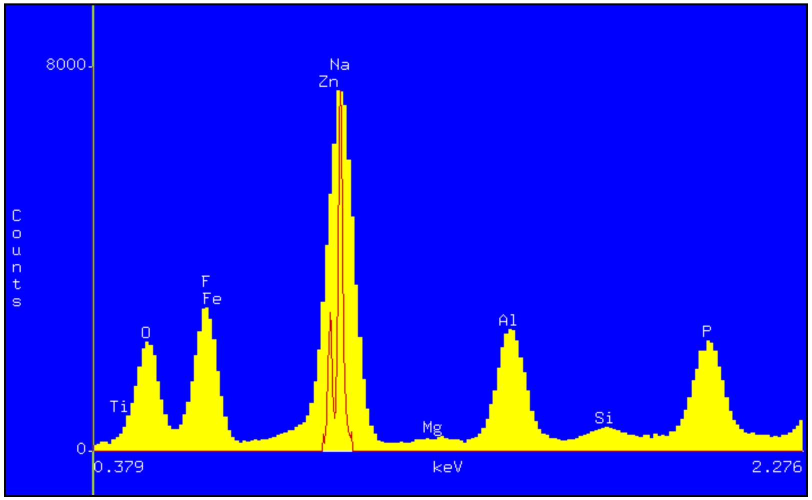
Na-Zn overlap – 15 kV, 2nA



Electron image

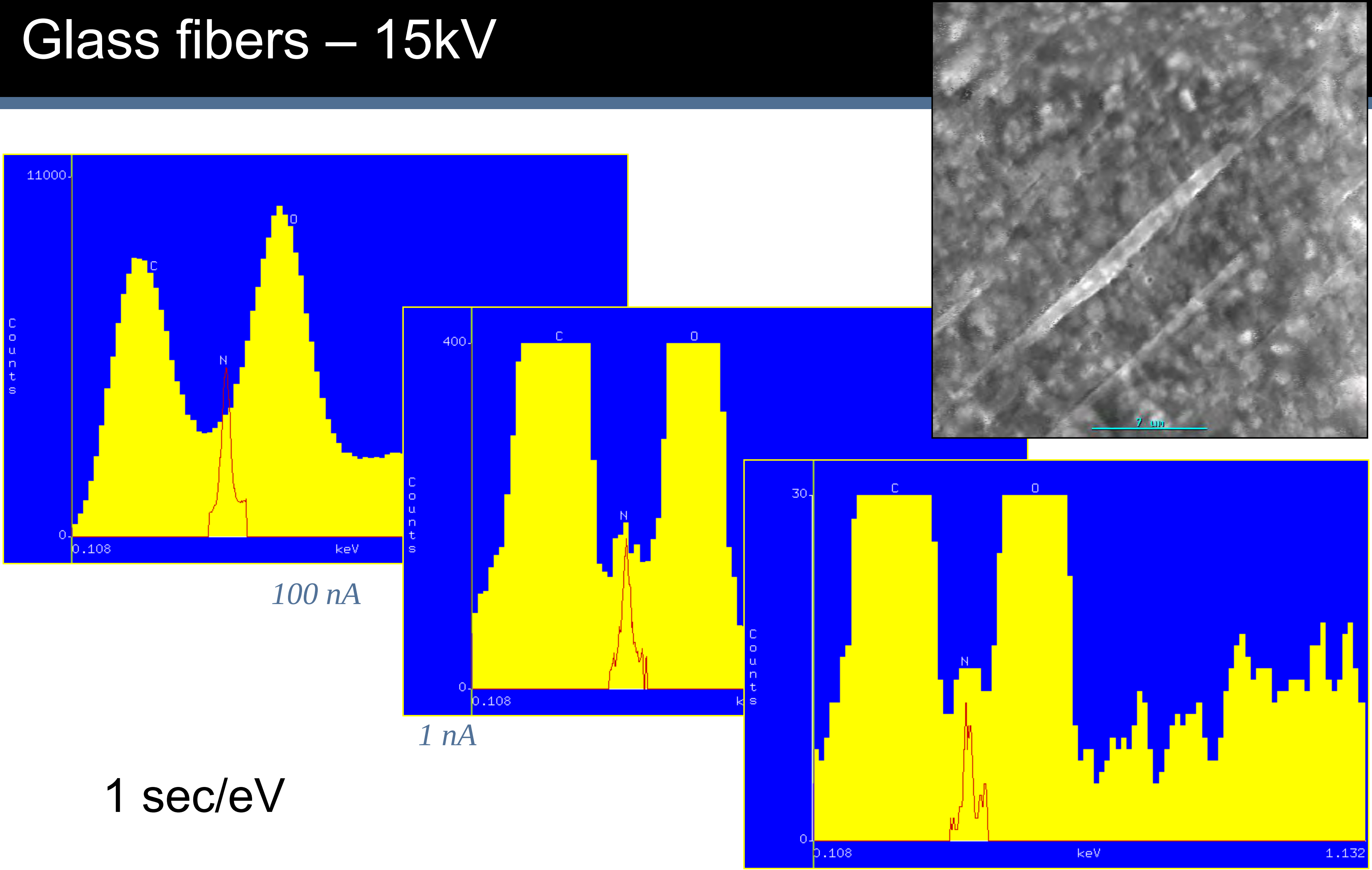


EDS Spot analysis



Overlay between EDS + WDS (TAP Crystal)

Glass fibers – 15kV



100 nA

1 nA

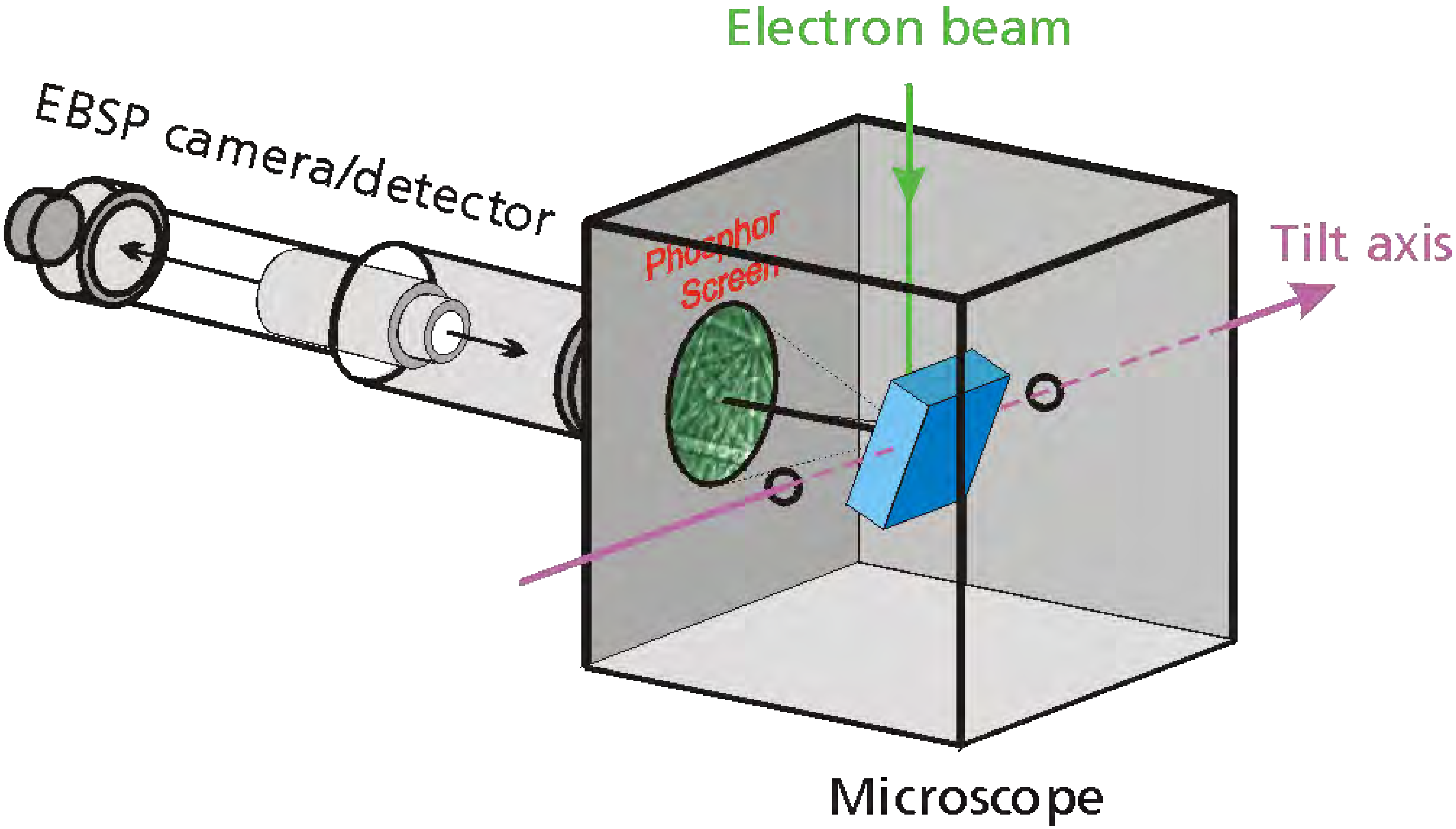
0.2 nA

1 sec/eV

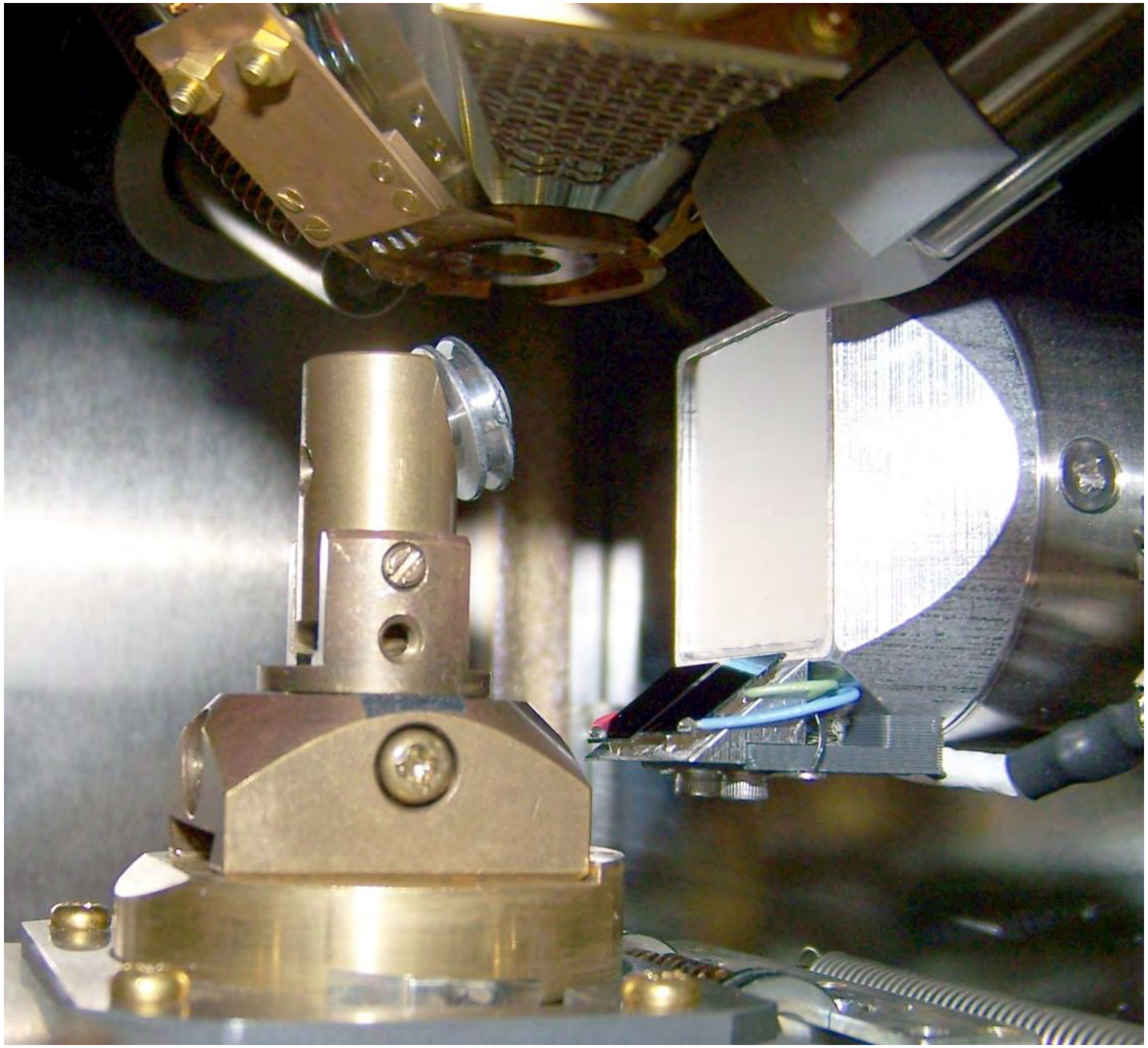
Outline

- EDS
- WDS
- **EBSD**
- Conclusions

If a specimen is tilted ~70 degrees to the incoming electron beam, the backscatter electrons display a pattern, caused by the crystal planes in a sample.



EBSD



EBSD pattern formation

- Electron beam strikes specimen

  Scattering produces electrons travelling in all directions

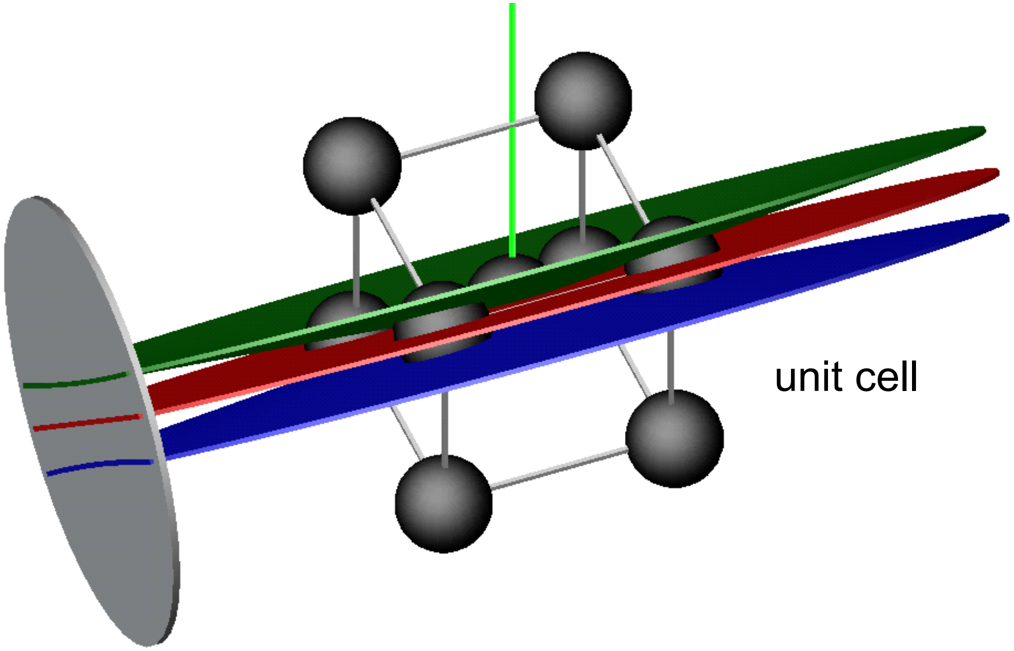
- Electrons that satisfy the Bragg condition ($n\lambda=2d.\sin\theta$) for a plane are channeled ⇒

  Kikuchi bands

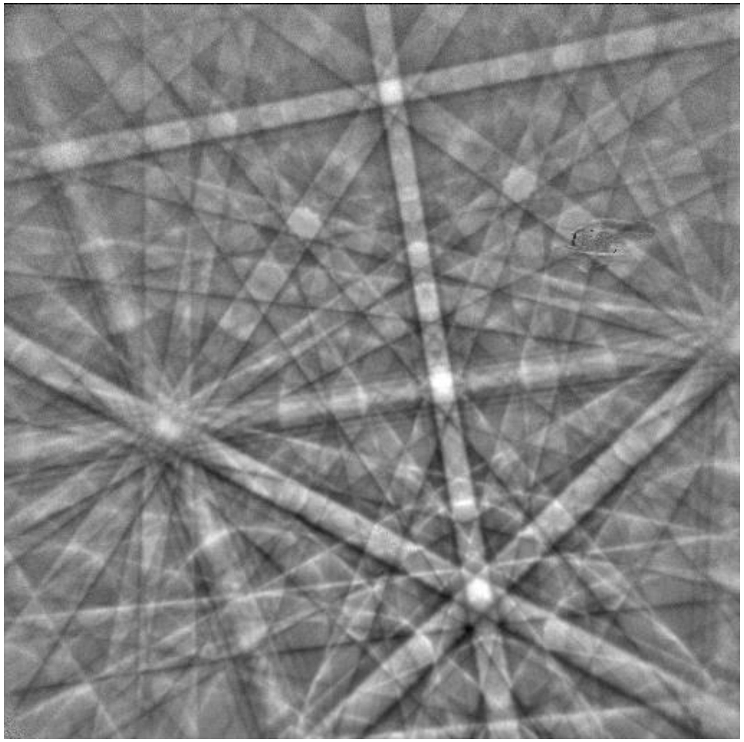
- Electrons strike the phosphor screen and produce photons

- These photons are detected by the CCD camera

- The resulting EBSD pattern is analysed by the computer



EBSD



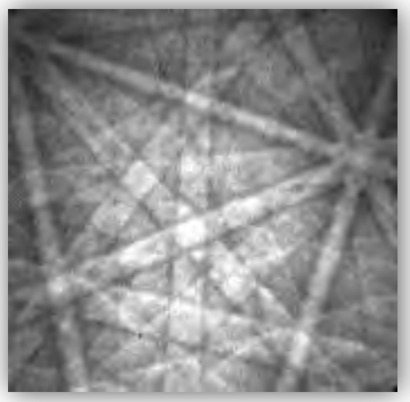
The electron patterns are recorded using a fluorescence screen and a CCD camera. Sophisticated software then processes the pattern to identify the crystal structure and orientation.

Background Removal

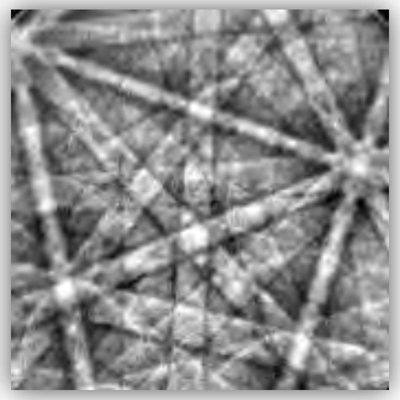
- Scans over multiple grains eliminate diffraction information.
- Watch out for variations in Z contrast when doing background averages
- Background division or background subtraction

Pattern

Background



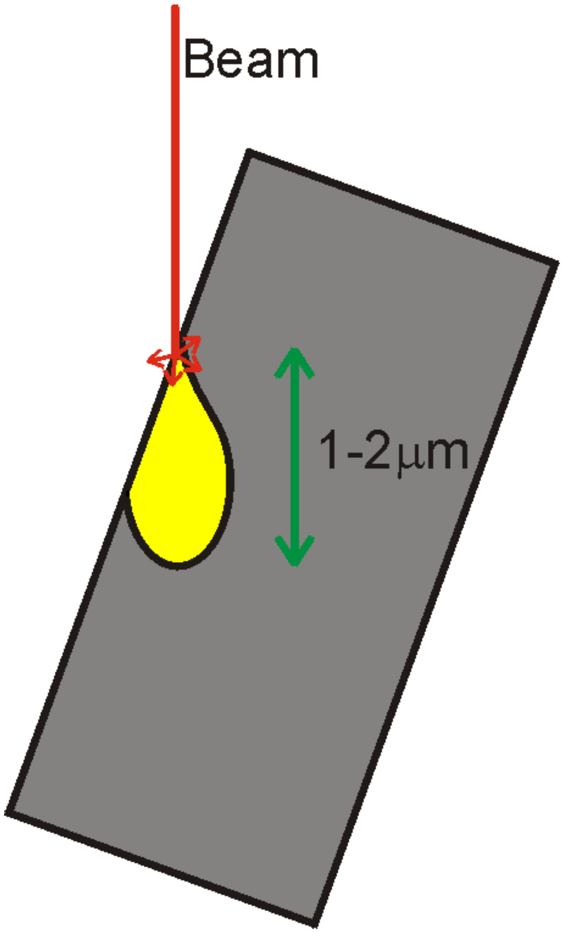
Background subtraction



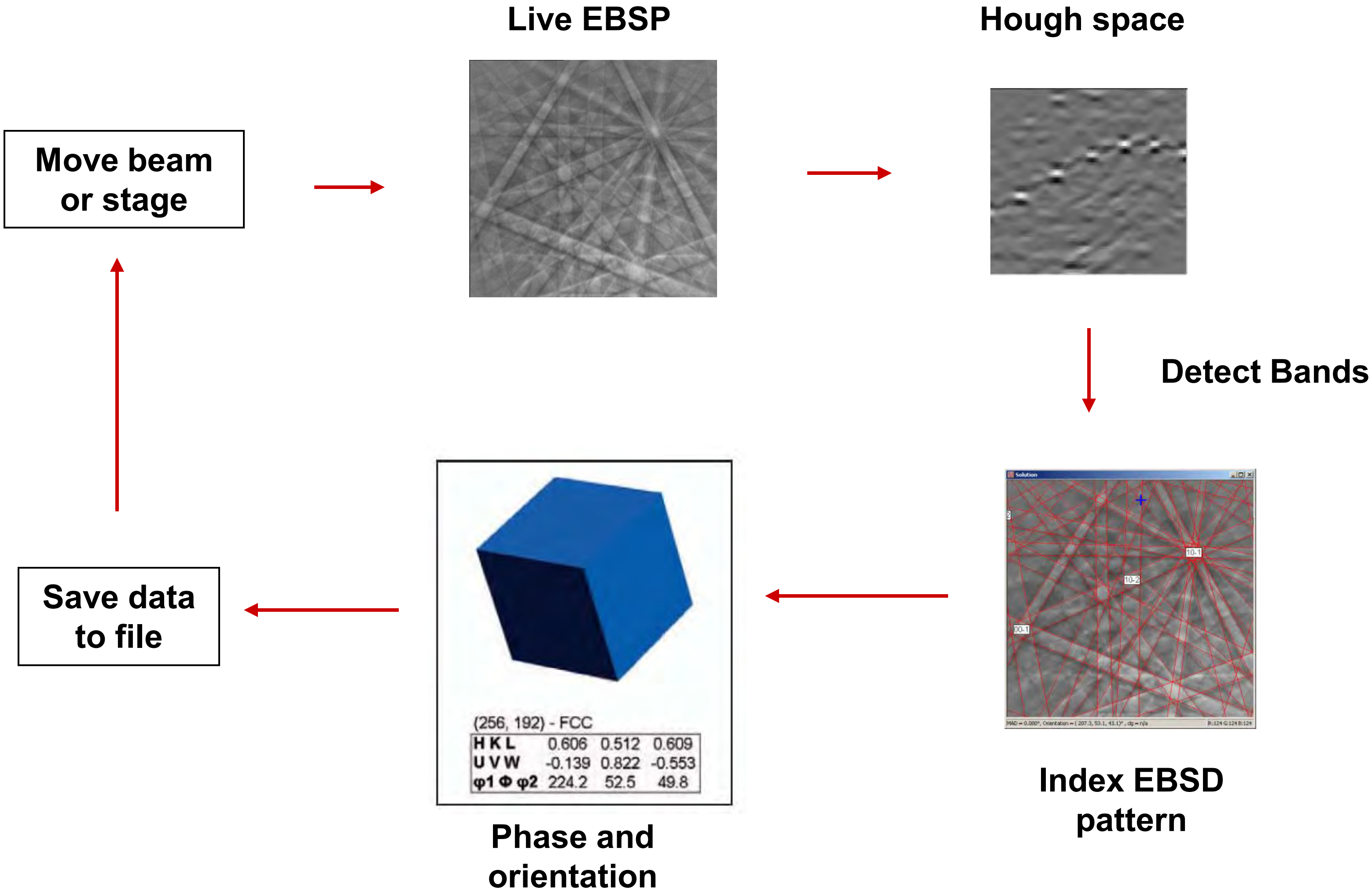
Background division

EBSD spatial resolution

- Although EBSD patterns are created by backscattered electrons, the signal does not come from the whole BSE interaction volume
- Most BSE do not have any crystallographic information
- Only BSEs that were generated close to the surface have crystallograpic information: the top few nm
- This means that the EBSD technique can obtain very high resolutions (<20nm), much smaller than with EDS



EBSD Mapping



Live EBSP

Hough space

Detect Bands

Index EBSD pattern

Solution

MAD = 0.080°, Orientation = (207.3, 53.1, 43.1)° , dg = n/a R:124 G:124 B:124

(256, 192) - FCC

H K L	0.606	0.512	0.609
U V W	-0.139	0.822	-0.553
φ1 Φ φ2	224.2	52.5	49.8

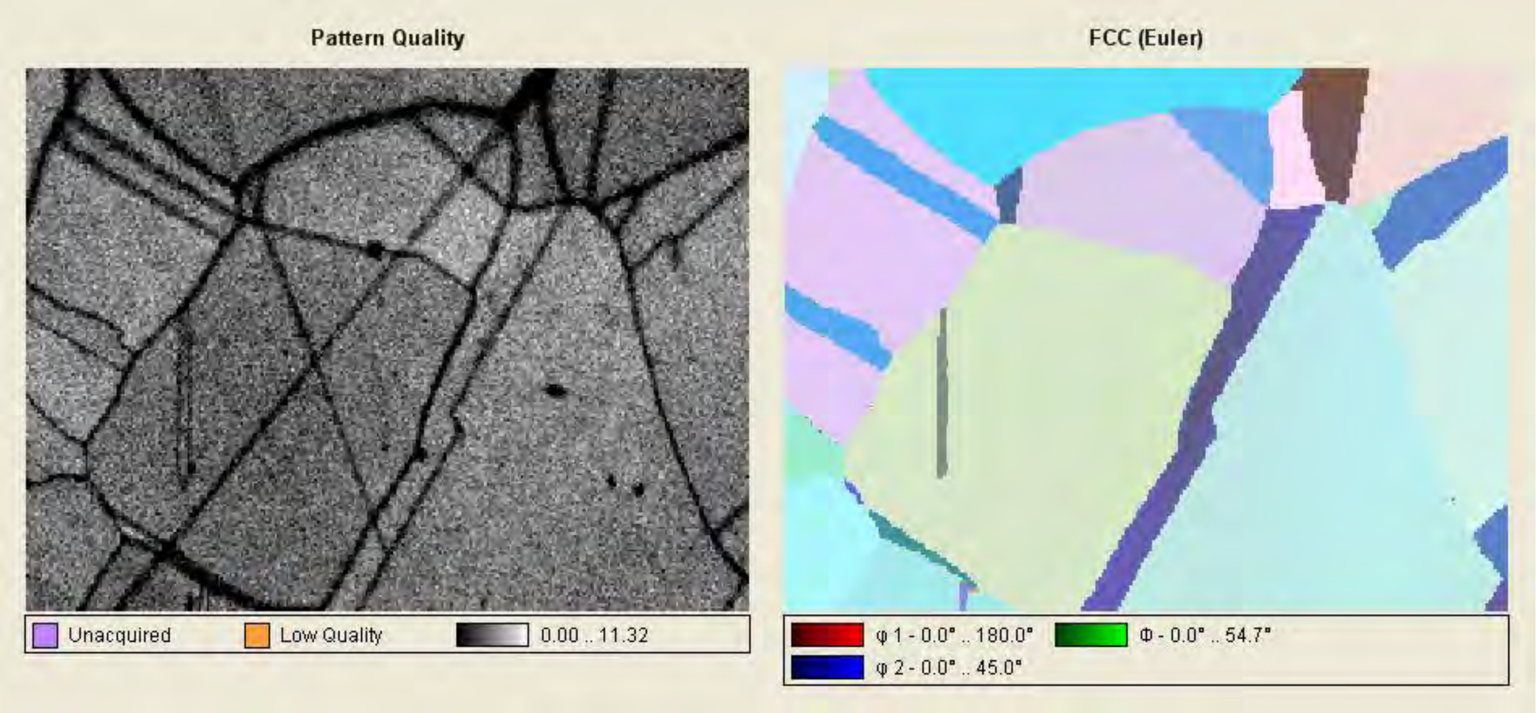
Phase and orientation

Save data to file

Move beam or stage

EBSD

By scanning the electron beam over the sample and identifying the crystal orientation at each pixel EBSD maps van be created.



This allows the operator to distinguish grains and measure a range of material properties, like orientation distribution functions.

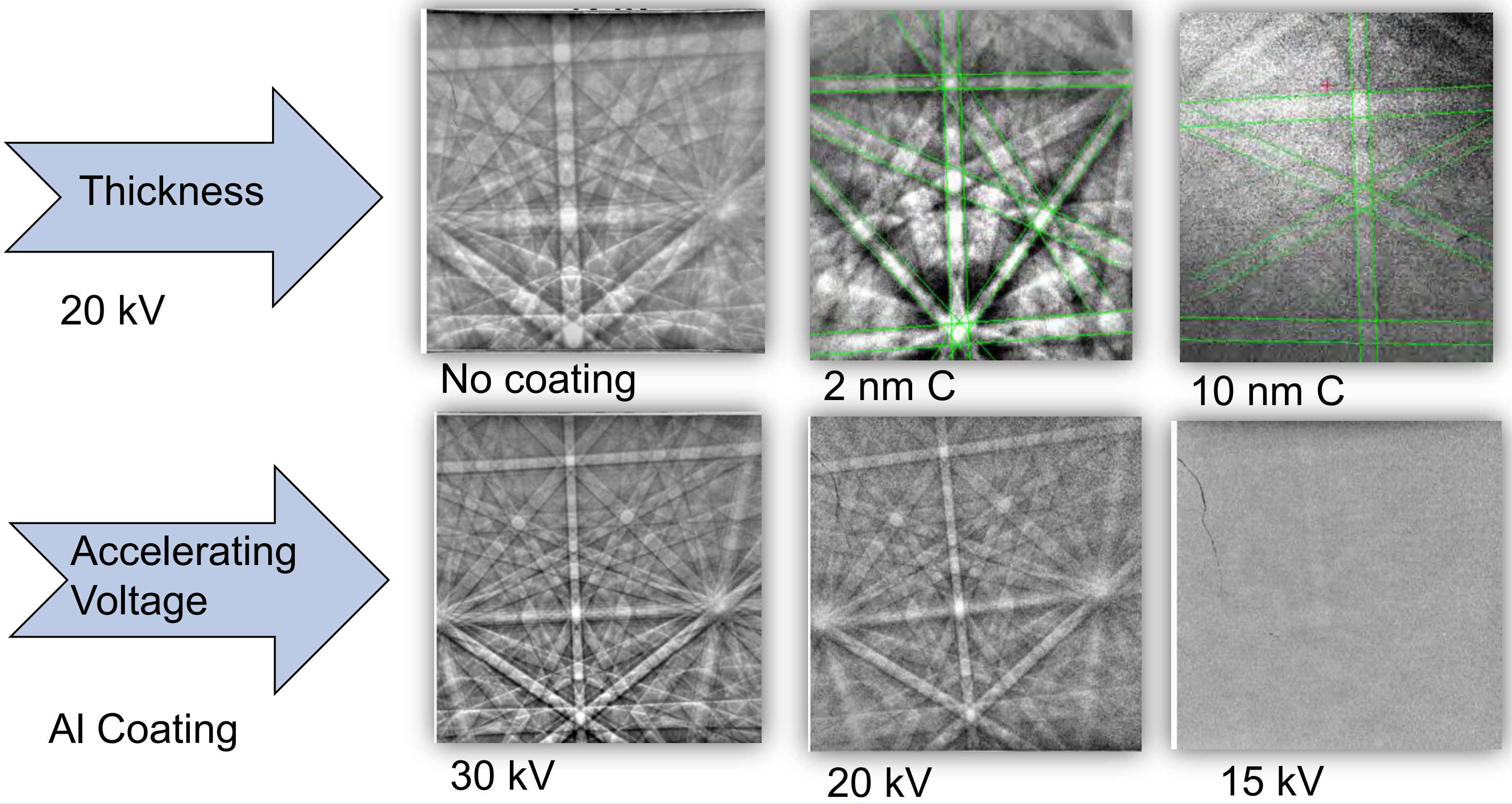
Sample Limitations

- Crystalline material
  - Amorphous material does not provide meaningful patterns.
- Minimum grain size
  - The interaction volume must be contained within a single crystal.
  - Multiple crystals produce an overly complex pattern.
- Uncoated surface
  - Any coating acts like a blurring filter on the emerging pattern.
  - Low vacuum operation is a potential workaround.
- Deformation-free surface
  - Defects in the crystal within the interaction volume bend the atomic planes and blur the pattern.
  - Defects can originate from material processing or sample preparation.

Deformation-free sample preparation is crucial !!

Conductive Coatings

- Conductive coatings can be used to eliminate charge
- Z dependent – C is ideal
- Higher KeV is key
- Coating prior to polishing in some cases



Thickness

20 kV

No coating

2 nm C

10 nm C

Accelerating Voltage

Al Coating

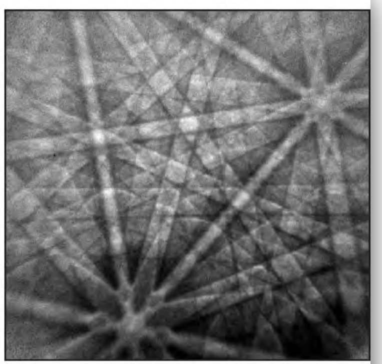
30 kV

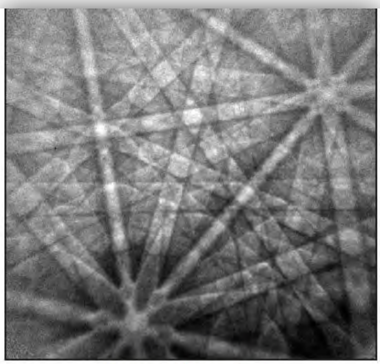
20 kV

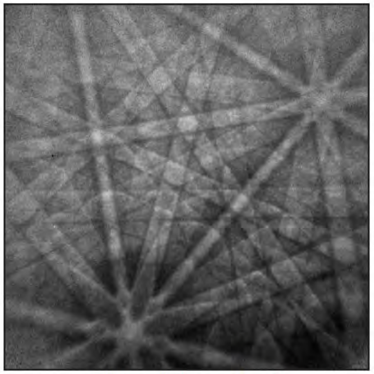
15 kV

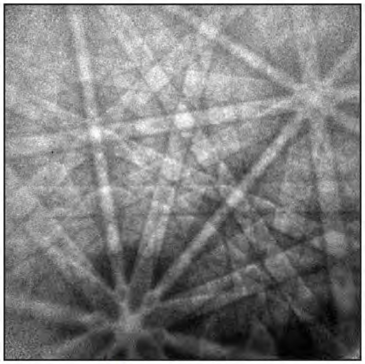
Variable Pressure

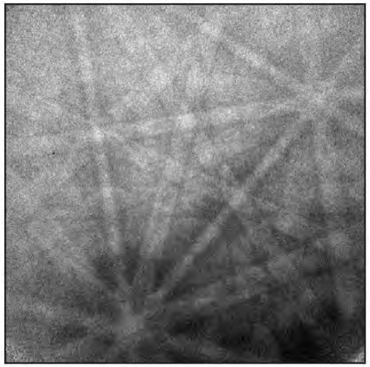
- Static charge can lead to drift and degradation of pattern quality
- High pressure leads to intensity impairment
- 20 Pa is sufficient to eliminate static charge

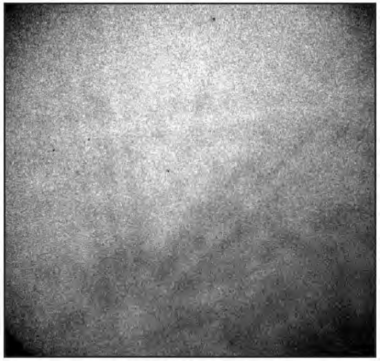

High vacuum


10 Pascal (75 millitorr)


20 Pascal (150 millitorr)

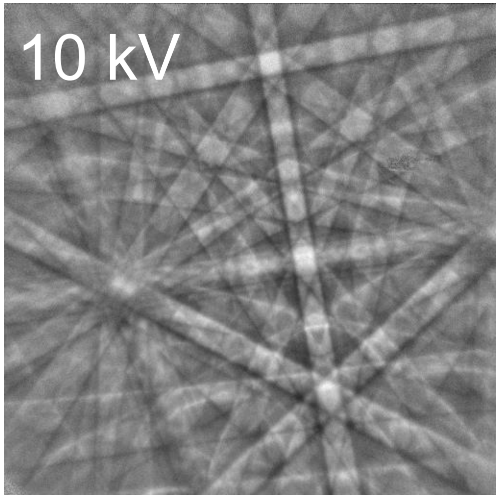

50 Pascal (375 millitorr)

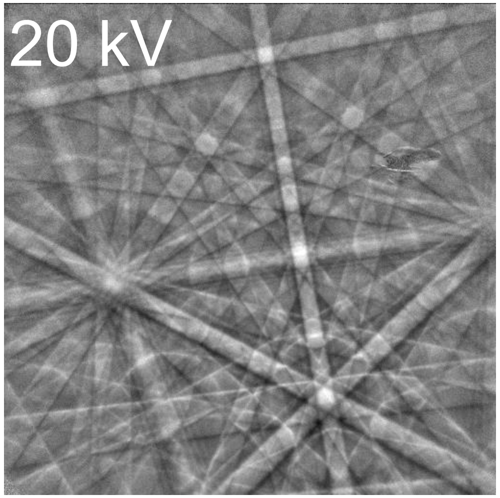

100 Pascal (750 millitorr)

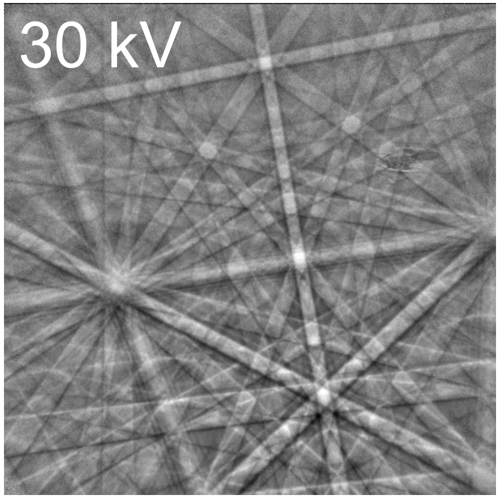

200 Pascal (1500 millitorr)

Accerlating Voltage

- Higher kV =>shorter wavelength => increase 1/d







- Screen intensity increases with accelerating voltage
- Interaction volume increases
  - Conductive layers
  - Capture multiple phases

Examples: Acquisition conditions

Samples were polished to a very high degree, finalized with 15 to 60 minutes vibration polishing.

FEG-SEM with pre-tilted sample holder.

20 kV Accelerating voltage.

Beam current varied to obtain high EDS countrate.

EBSD detector, CCD, 640 x 480 pixels
EDS detector, SDD, 30 mm2 active area
WDS detector, 6 diffractors

EBSD camera exposure 2 to 5 milliseconds (200 – 500 fps)

EBSD camera set to 4 x 4 or 8 x 8 binning

Example 1: NbC precipitates in Ni-based alloy

Aim:

- Detect precipitates
- Determine their compositions
- Determine if their crystal orientation is random
- Determine if their crystal orientation is related to the Ni-alloy matrix

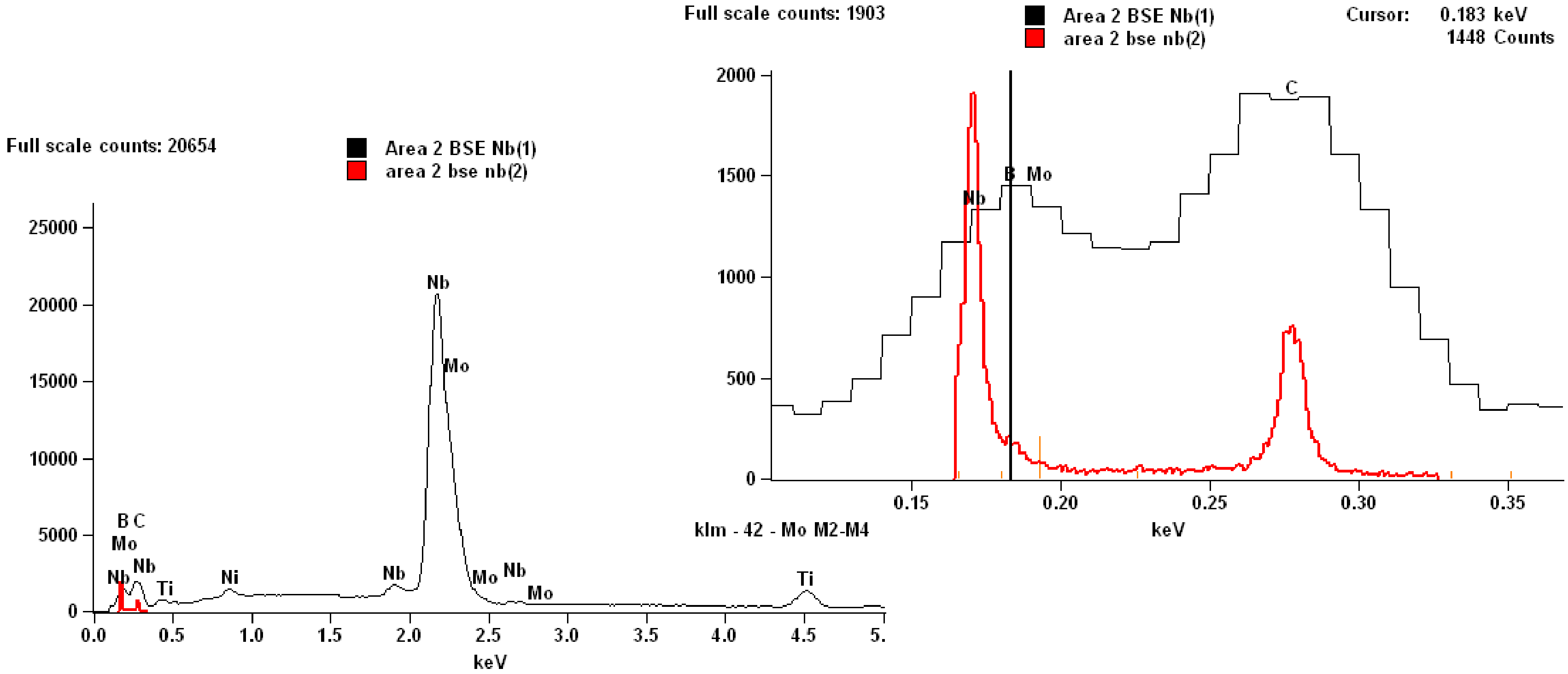
SE image clearly showed carbides, as their extreme hardness made them stick out above the alloy matrix.

BSE image also revealed bright inclusions because of the heavy elements inside carbides.

Example 1: NbC precipitates in Ni-based alloy

Composition: Nb and C were easily confirmed

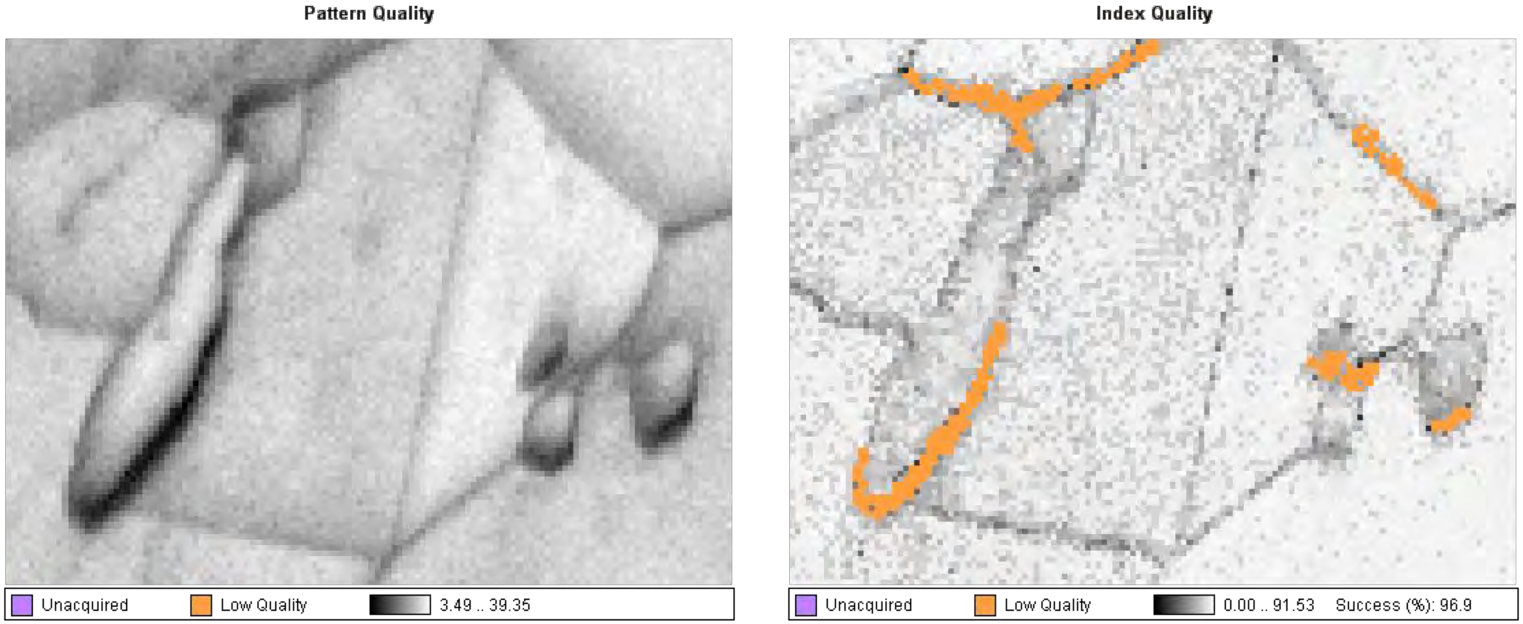
WDS was used to verify the peak at the B-Ka position was actually the Nb-M X-ray line:



Example 1: NbC precipitates in Ni-based alloy

EBSD analysis:

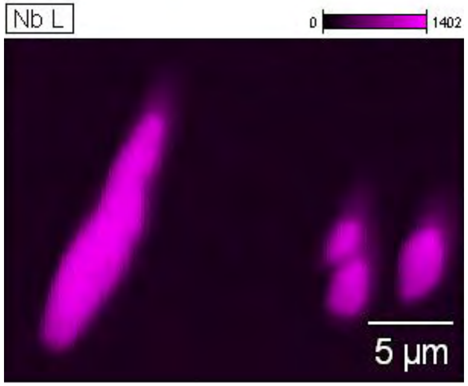
- Overall pattern quality was very good.
- At the edge of the precipitates pattern quality was poor, due to shadowing effects (precipitates sticking out above matrix)



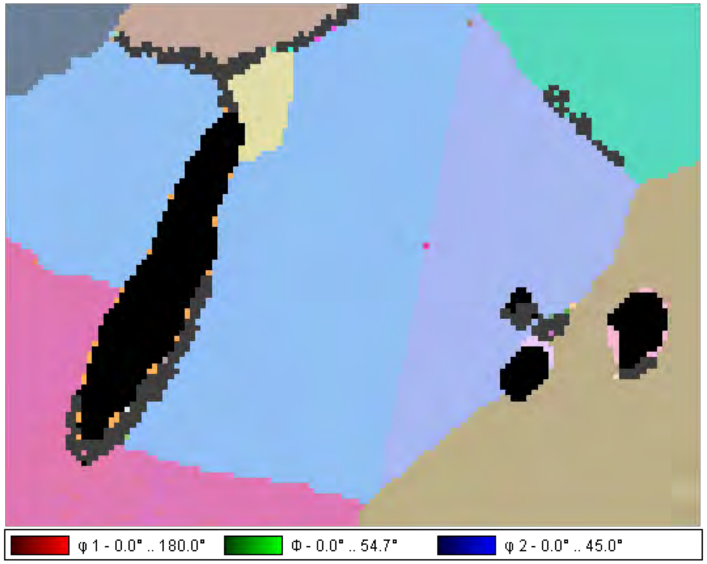
Example 1: NbC precipitates in Ni-based alloy

EBSD analysis:
- Good indexing of Ni matrix
- Good indexing of NbC
- Good match with EDS map

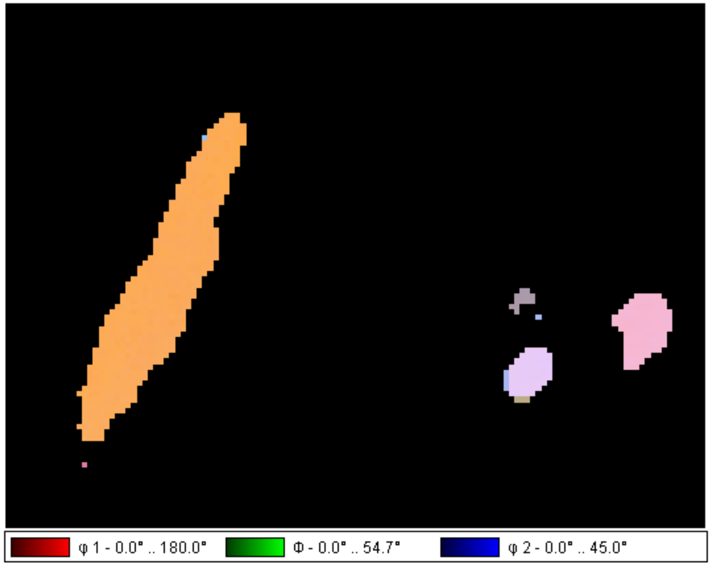
Conclusion: Random orientation of NbC particles without relation to matrix orientation



Ni (Euler)



Niobocarbide (Euler)



Example 2: Dual-phase steel

Alloy A2205 is a dual-phase stainless steel

Aim:

- Detect microstructure and chemistry of the two phases
- Determine volume ratio between the 2 phases

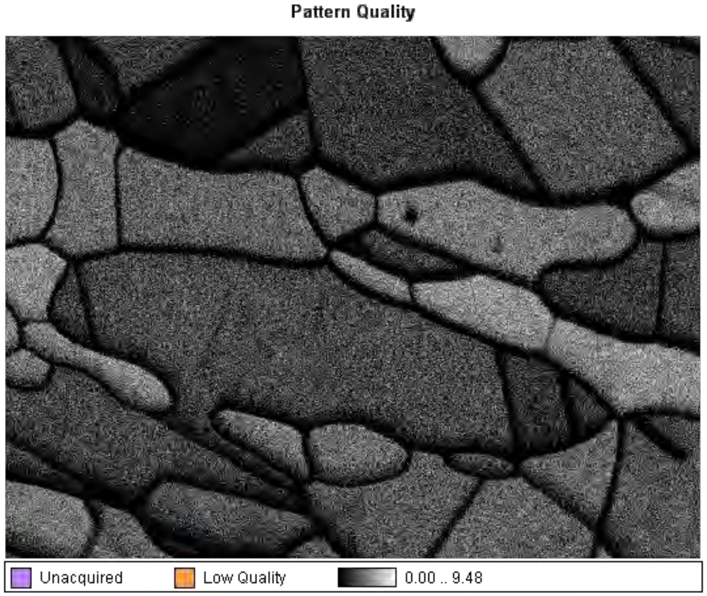
SE image clearly showed no detail at all.

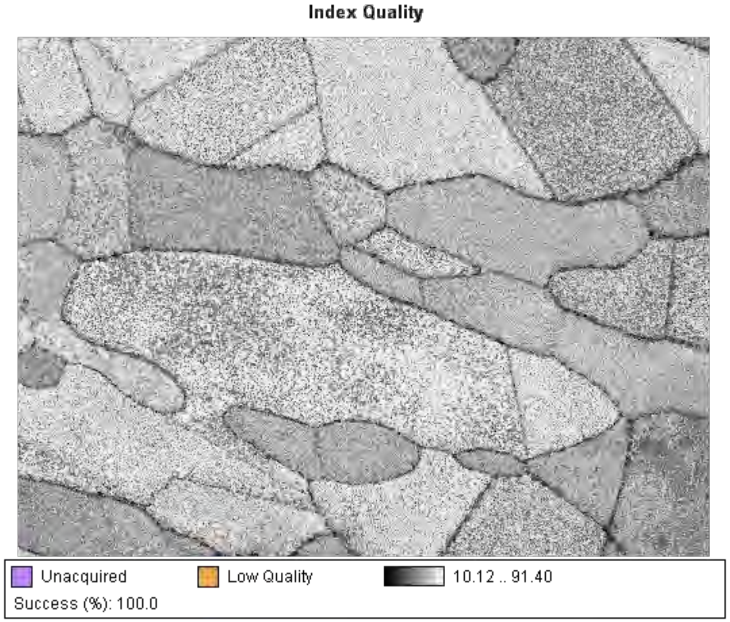
BSE image also did not reveal anything, as the 2 phases are very similar in atomic weight.

Example 2: Dual-phase steel

EBSD analysis:

- Overall pattern quality was very good, except at phase boundaries.

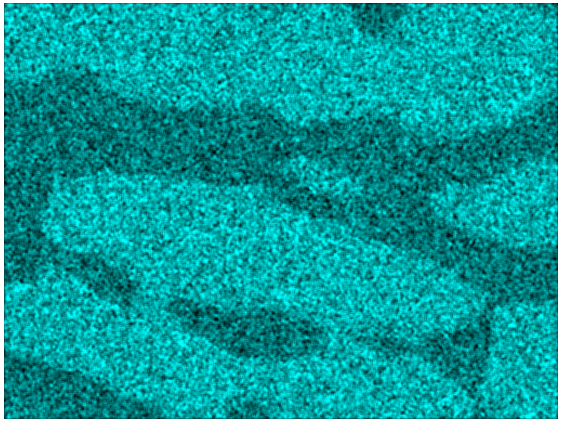

Pattern Quality


Index Quality

Example 2: Dual-phase steel

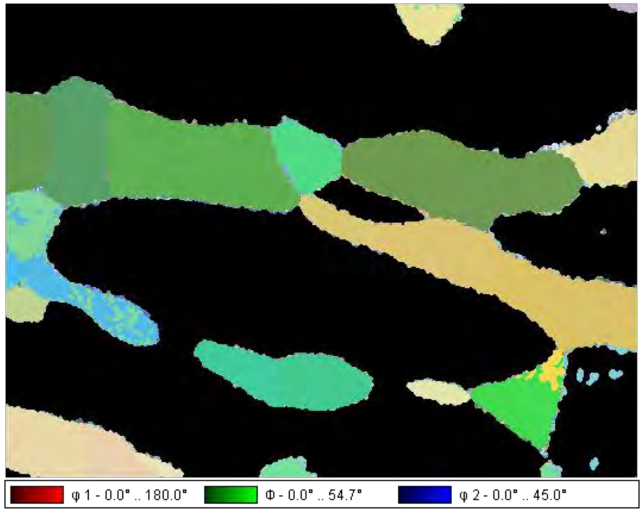
EBSD analysis:
- FCC and BCC phase were found
- More twinning in FCC phase

EDS analysis:
- Ni enrichment and Cr depletion in FCC phase
- Ratio FCC : BCC about 65 : 35

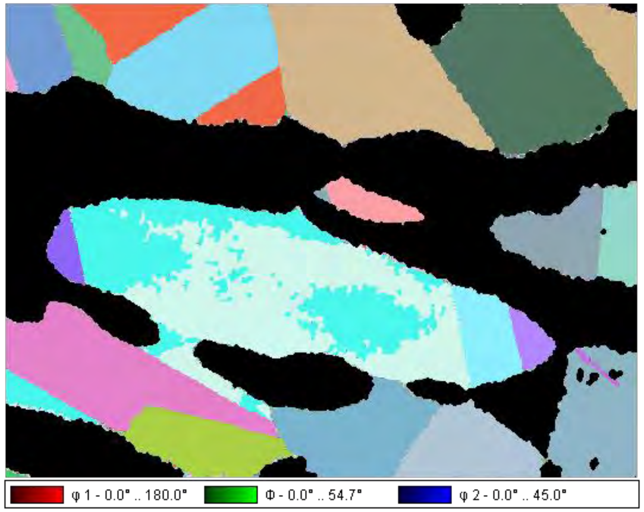


Ni map EDS

Conclusion: Sample fully characterized



BCC (Euler)



FCC (Euler)

QuasOr EBSD

- Full suite of EBSD acquisition and processing software
- Up to 600fps indexed
- Completely integrated into NS7
- Simultaneous spectral imaging and EBSD
- No compromises

X-ray microanalysis in the TEM

An EDS detector has to be specifically designed for TEM use.

In general X-ray countrate will be very low, so the detector will be designed to get very close to the specimen.
The Si(Li) or HP-Ge crystal will be large, usually 30 mm^2.

Special care needs to be taken to prevent high-energy BSE to enter the detector. Some TEMs offer automatic protection mechanisms, or one can use retractable EDX detectors.

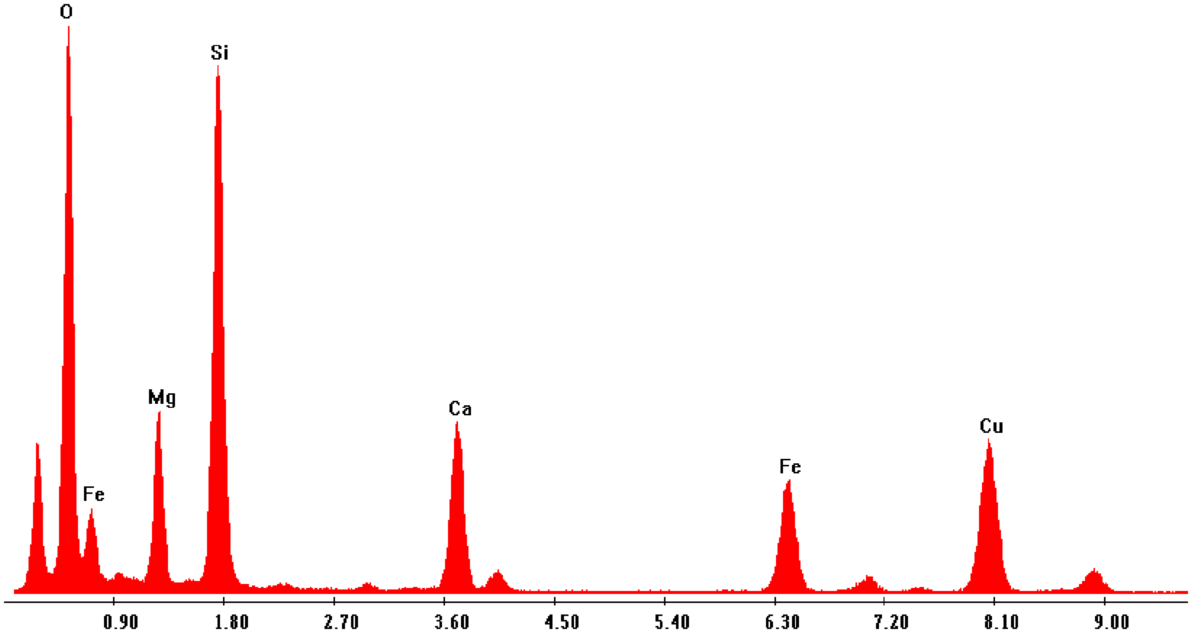
X-ray safety shielding is vital !

TEM X-ray detector

X-ray spectra

EDX spectra from the TEM look similar to SEM spectra. But there are some small differences:

- lower background due to thin specimens
- different relative peak heights due to the high kV.



TEM quantification: Materials Science

The most common method to quantify a spectrum in the TEM is the ratio method, or Cliff-Lorimer method, or K_{AB}-method.

This method is based on the intensity ratio of one element compared to the other elements in the sample.

The main equation is surprisingly simple. In a binary sample with elements A and B:

$$\frac{\mathrm{C_A}}{\mathrm{C_B}} = K_{AB} \bullet \frac{I_A}{I_B}$$

TEM Quantification: Cliff-Lorimer method

So all we need to do is determine the K_{AB} factor for all elements present in the sample.

There are 3 routes to take now:

1. Use some set of measured data published in literature. Make sure this set matches the kV that you are using, and that the detector window type is the same. Some EDS systems have a built-in set of values, recorded e.g. at 200 kV.

2. Calculate the K_{AB} factors from first principles.

3. Determine the K_{AB} factors yourself by using a set of standards.

K_{AB} factors : 2. Theoretical values

The basic idea behind the Cliff-Lorimer correction is that the intensity generated in a specimen can be calculated as:

$$I_A = const \bullet \frac{\omega_A \bullet P_{IJ} \bullet Q_A}{A_A} \bullet C_A \bullet t$$

Where ω is the fluorescence yield, P_{IJ} is the fraction of the total K, L, or M-line that is measured, Q is the ionization cross-section, A is the atomic weight, t is the specimen thickness.

I_A is of course the number of counts in a peak, per livesecond acquisition time, per unit beam current.

K_{AB} factors : 2. Theoretical values

Since we do not know the specimen thickness or the constant, we take the ratio:

$$\frac{I_A}{I_B} = \frac{const \bullet \dfrac{\omega_A \bullet P_{IJ} \bullet Q_A}{A_A} \bullet C_A \bullet t}{const \bullet \dfrac{\omega_B \bullet P_{IJ} \bullet Q_B}{A_B} \bullet C_B \bullet t}$$

Which we can rewrite as:

$$\frac{C_A}{C_B} = \frac{\omega_B \bullet P_{IJ\,B} \bullet Q_B \bullet A_A}{\omega_A \bullet P_{IJ\,A} \bullet Q_A \bullet A_B} \bullet \frac{I_A}{I_B}$$

K_{AB} factors : 2. Theoretical values

So far the we only talked about the generated intensity. But of course we measure the intensity in the detector, which has a certain efficiency. On their way from the sample to the Si(Li) detector the X-rays have to pass several layers (polymer, Al-coating, metal contact layer, Si dead layer), so the efficiency is less than 100%, and dependant on the X-ray energy.

$$I_{\text{detector}} = \varepsilon \bullet I_{\text{generated}}$$

So we end up with:

$$\frac{C_A}{C_B} = \boxed{\frac{\omega_B \bullet P_{IJ\,B} \bullet Q_B \bullet A_A}{\omega_A \bullet P_{IJ\,A} \bullet Q_A \bullet A_B} \bullet \frac{\varepsilon_B}{\varepsilon_A}} \bullet \frac{I_A}{I_B}$$

K_{AB} factors : 2. Theoretical values

In this equation we can easily determine the values of A, ω, P_{IJ} and ε. They can be found in standard table books, or calculated once the detector parameters are known.

The only disputed parameter is Q, the ionization cross-section. Most authors agree on the overall equation to calculate this factor:

$$Q = \frac{6.51 \cdot 10^{-20}}{E_c^2 \bullet U} n_s \bullet b_s \bullet \ln(c_s \bullet U)$$

Where E_C is the critical (ionization) energy, U is the overvoltage, n_K=2, n_L=8, n_M=18, etc., and b and c are constants.

The determination of the parameters b and c is still open for discussion:

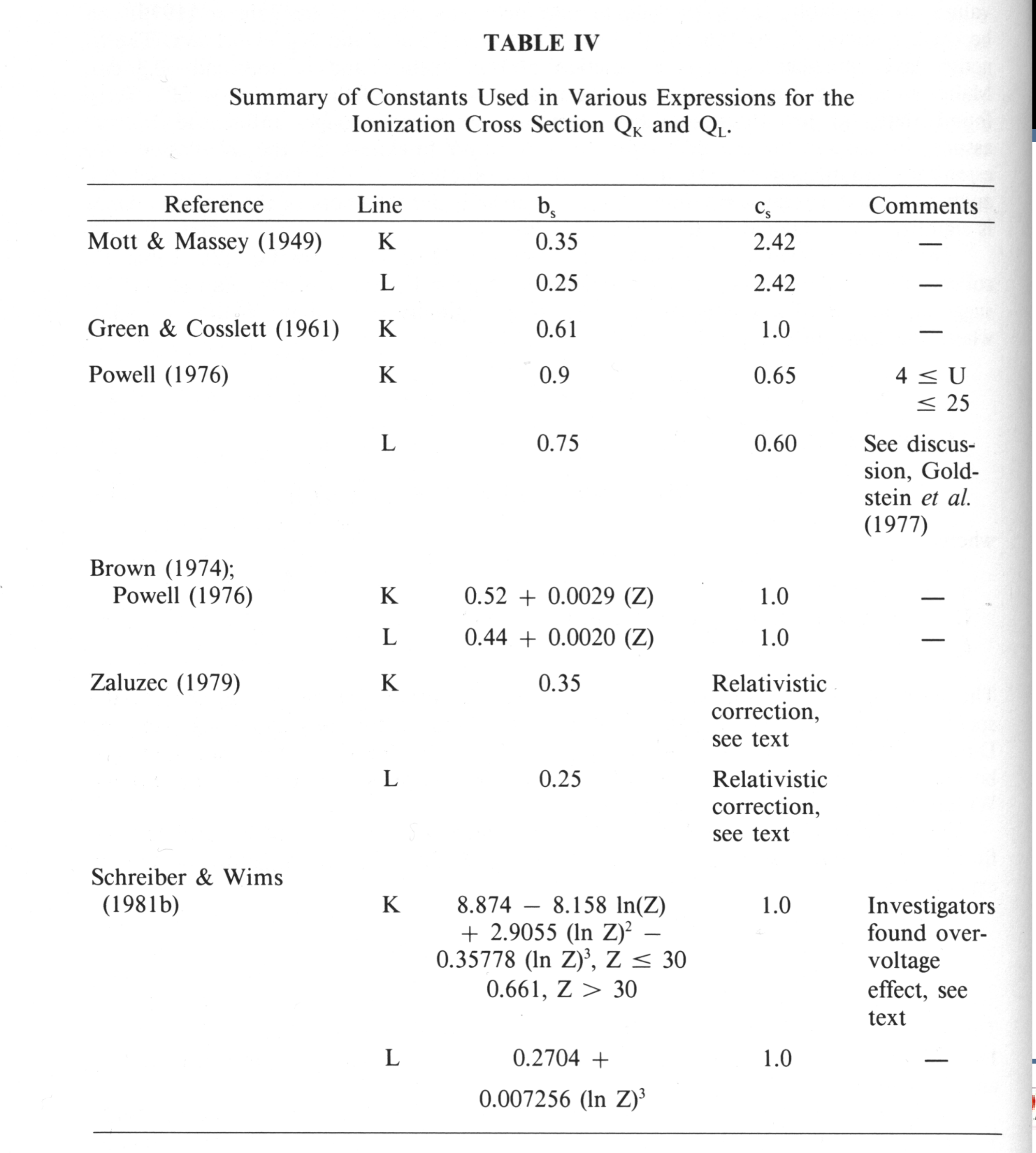


TABLE IV

Summary of Constants Used in Various Expressions for the Ionization Cross Section Q_K and Q_L.

Reference	Line	b_s	c_s	Comments
Mott & Massey (1949)	K	0.35	2.42	—
	L	0.25	2.42	—
Green & Cosslett (1961)	K	0.61	1.0	—
Powell (1976)	K	0.9	0.65	$4 \leq U \leq 25$
	L	0.75	0.60	See discussion, Goldstein *et al.* (1977)
Brown (1974); Powell (1976)	K	0.52 + 0.0029 (Z)	1.0	—
	L	0.44 + 0.0020 (Z)	1.0	—
Zaluzec (1979)	K	0.35	Relativistic correction, see text	
	L	0.25	Relativistic correction, see text	
Schreiber & Wims (1981b)	K	$8.874 - 8.158 \ln(Z) + 2.9055 (\ln Z)^2 - 0.35778 (\ln Z)^3$, $Z \leq 30$ 0.661, $Z > 30$	1.0	Investigators found overvoltage effect, see text
	L	$0.2704 + 0.007256 (\ln Z)^3$	1.0	—

K_{AB} factors : 2. Theoretical values

So if you want to use theoretically calculated K_{AB} factors you can do the hard work yourself, and calculate them using the parameters according to some literature equations.

Alternatively, most commercial EDX systems have one or more of these equations built in.

In my personal experience, the Zaluzec and the Schreiber/Wims model gives good results.

K_{AB} factors : 3. Standards

Determine the K_{AB} factor yourself by using a set of standards.

This is easier said than done, since it requires that for compound you would need to have a unique standard. That is very hard to achieve unless you have a single-purpose analysis topic.

Fortunately: $K_{AB} = \frac{K_{AC}}{K_{BC}}$ for C we often choose Si or Fe

This means we need to have a set of Si-compounds or Fe-compounds. If we then analyse Al-Cu we use the Al-Si and the Cu-Si standards.

Standards need to be very thin.

K_{AB} factors : 3. Standards

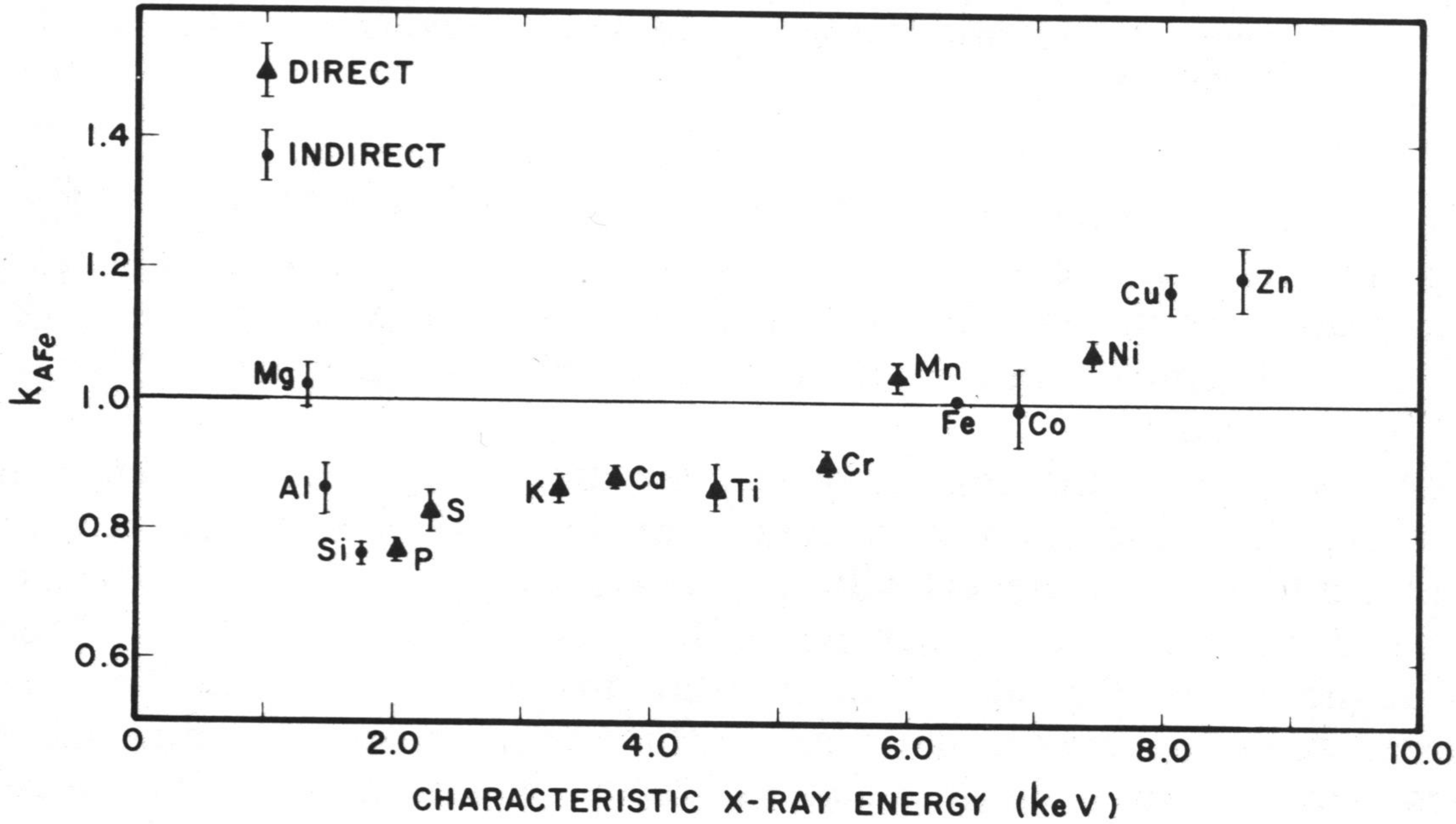


Figure 2 Experimental k_{AFe} factors for K_α lines of Wood *et al.* (1984) for a 120-keV operating potential.

Absorption correction

So far we have assumed that the generated X-rays can leave the sample without hindrance. But that is only valid for very thin samples, and if the mass-absorption coefficients are low. For thicker specimens or if ultra-light elements are involved, then you need to take absorption of X-rays into account.

Absorption takes place according to the basic Lambert-Beer law:

$$I = I_0 \bullet e^{-\frac{\mu}{\rho} \bullet \rho \bullet z}$$

Where μ/ρ is the mass-absorption coefficient.

But of course X-rays are generated over the whole specimen depth, so we need to do some integration mathematics.

Absorption correction

If you fill in all the data, and re-shuffle a bit, then we end up with the following absorption equation:

$$K_{AB} = K_{AB\perp Thin-film} \bullet \frac{\left[\mu \middle/ \rho\right]_A}{\left[\mu \middle/ \mu\right]_B} \bullet \frac{1 - e^{-\left[\frac{\mu}{\rho}\right]_B \bullet \operatorname{cosec}(\alpha)\rho \bullet t}}{1 - e^{-\left[\frac{\mu}{\rho}\right]_A \bullet \operatorname{cosec}(\alpha)\rho \bullet t}}$$

Where α is the take-off angle of the EDX detector, and t is the specimen thickness. The EDX software can do all the absorption calculations, but the main problem is the specimen thickness t. In some cases also the specimen density ρ is not known accurately enough. Often it can be estimated with sufficient accuracy by simply taking the weighted average of the constituents.

But how do we find out the specimen thickness?

Specimen thickness

In literature you can find several methods for determining the specimen thickness, both none of these methods are universally applicable and accurate:

1. EELS (electron-energy-loss spectroscopy). From an EELS spectrum one can retrieve the specimen thickness, but not every TEM has an EELS attached to it…

2. Contamination spot method. With this method you leave the electron beam on the un-tilted sample for a certain amount of time, during which 2 carbon contamination spots will be created on the top and bottom surface of the specimen. By tilting the specimen and then measuring the distance between the spots an estimate of the specimen thickness can be calculated. This method is extremely inaccurate, as this method tends to overestimate the sample thickness by 25 to 200%.

Specimen thickness

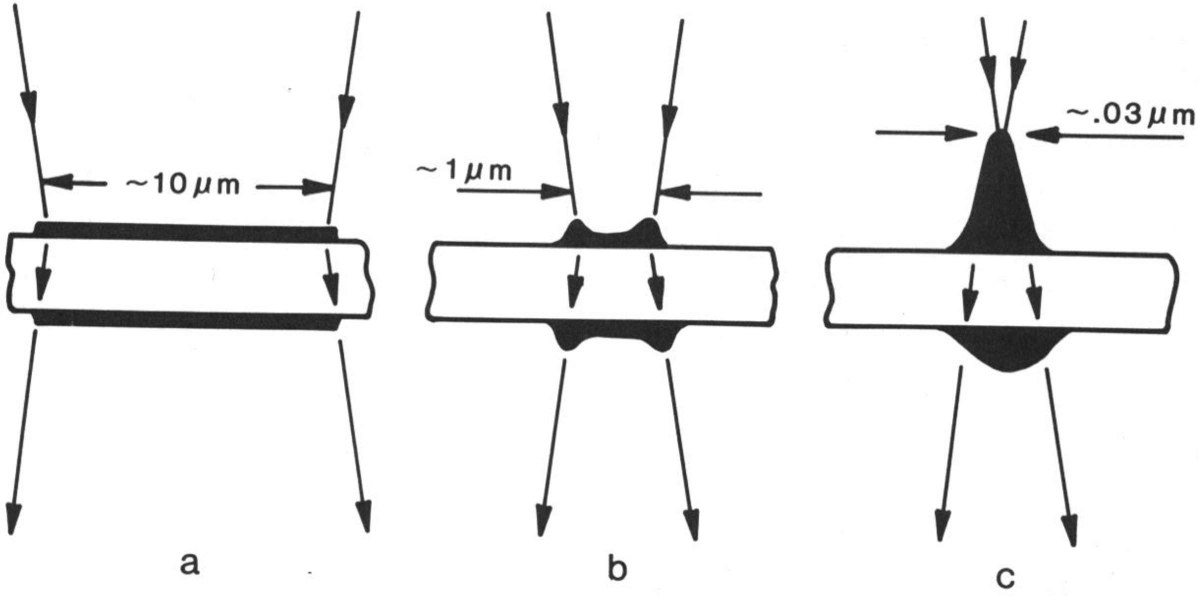


Figure 3 Schematic illustration of the change in appearance of the contamination deposit with different beam sizes. Note the change in scale from (a) to (c).

Contamination spot method

Specimen thickness

3. Measure the spacing of the Kossel-Mollenstedt fringes in CBED (convergent beam electron diffraction) patterns. This requires the sample to be crystalline, and you need a double-tilt holder to obtain the right CBED conditions. It is also limited to a certain thickness range: too thin or too thick and you don’t get the right CBED patterns,

4. Compare the X-ray intensity to a bulk standard of known composition. This does require the possibility to measure the beam current (e.g. analytical holder) with a very wide range (less than a pico-amp up to several nano-amp.

5. For compounds like minerals the ionic compound method can be useful (see later in this presentation).

6. Several even more exotic techniques can be found in literature, but they are even less widely applicable.

Summary: Quantification in Materials Science

For very thin specimens the Cliff-Lorimer correction offers an easy to use quantification procedure.

The C-L factors can be calculated from theory, or can be determined by the user.

For thicker specimens it is necessary to apply absorption correction, but this requires that the specimen thickness and density are known.

End of the Course

End of the Course???

Sorry to disappoint you, but this is not the end of the Course.

Learning Microanalysis will continue in your own lab, every day you use a Microanalysis system, for as long as you keep working with the system!.

I hope you enjoyed the Course, and that you found what you were looking for!

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