

# Microanalysis EDS and WDS

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7<sup>TH</sup> CEMM WORKSHOP:

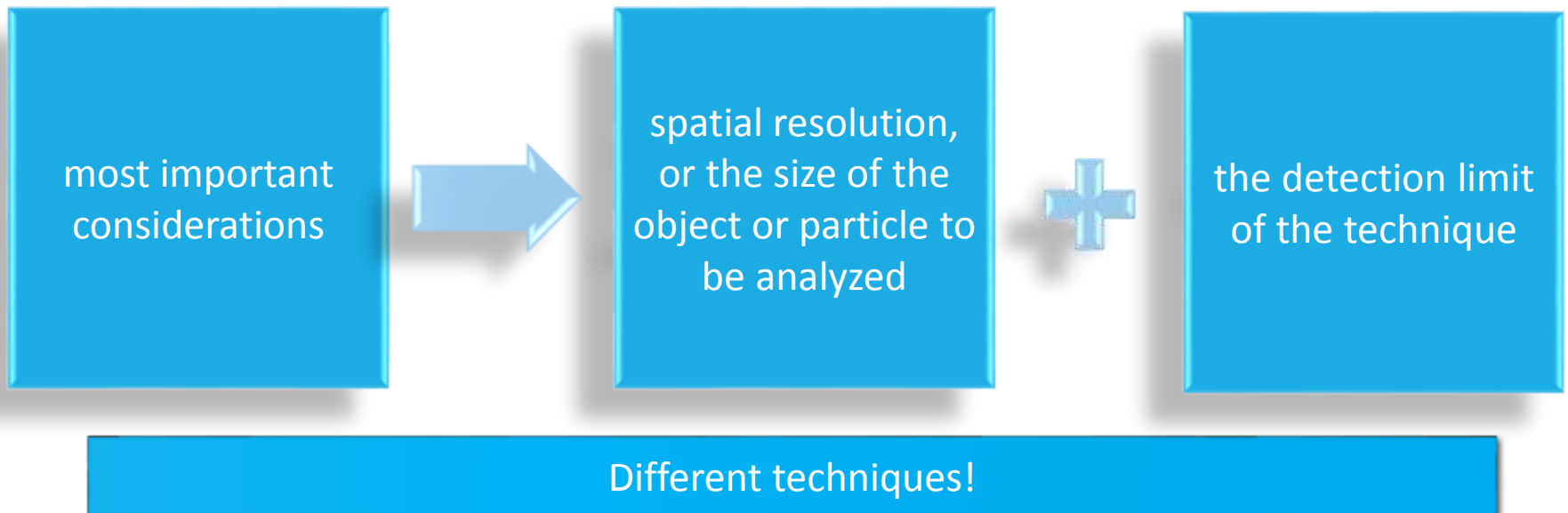
ELECTRON PROBE X-RAY MICROANALYSIS TECHNIQUES

MAJA KOBLAR, SC. ENG. PHYSICS

# What is microanalysis?

identification of the chemical elements present either within or on the surface of an object, and additionally, how the atoms of the elements are arranged with respect to each other. Identification of the elements present may be **qualitative** or **quantitative**.

Figure removed for copyright reasons.



# Commonly used techniques

Which elements?

Light elements: B, C, N, O

Peak overlapping:

Mo ( $L\alpha$ ) = S ( $K\alpha$ )

Ba ( $L\alpha$ ) = Ti ( $K\alpha$ )

Al ( $K\alpha$ ) = Br ( $L\alpha$ )

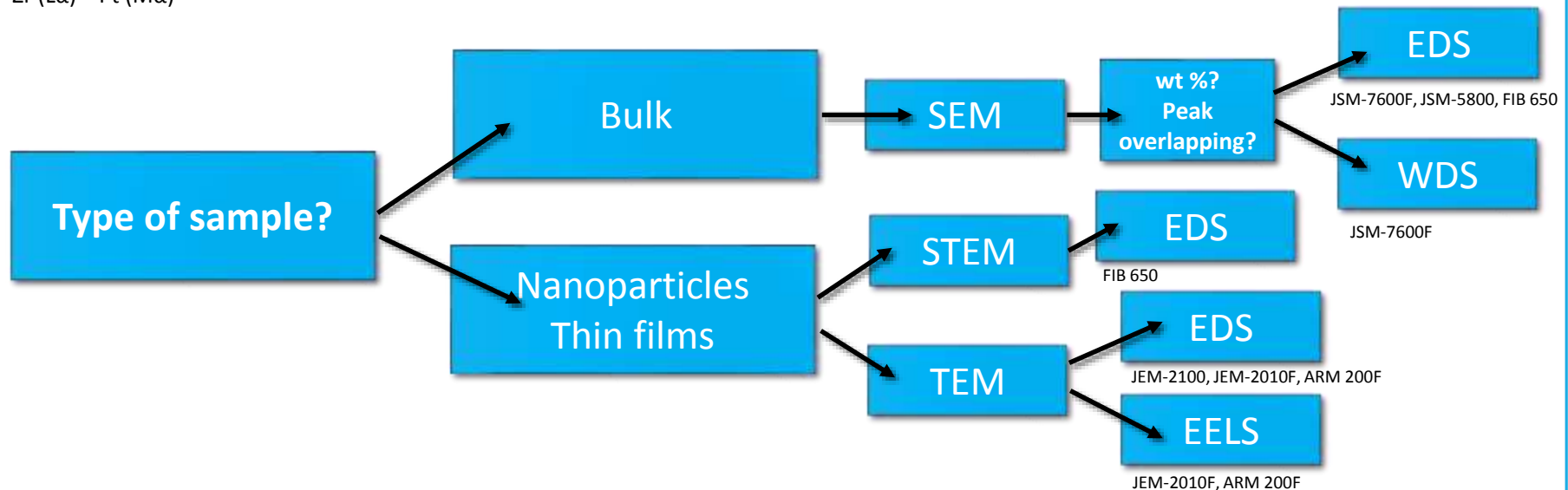
Na ( $K\alpha$ ) = Zn ( $L\alpha$ )

Zr ( $L\alpha$ ) = Pt ( $M\alpha$ )

Qualitative analysis or  
quantitative analysis?

Sample preparation, use of  
standards, evaluating data, ...

**Think! What do I want?**



# What will we talk about?

## The objectives of this workshop are:



To understand that there are different analytical techniques

- To understand the generation of X-rays
- To know what you can get out of EDS, WDS
- How we detect X-rays (EDS, WDS)
- Sample considerations
- How different parameters effect X-ray acquisition
- Spectrum processing and corrections

# Electron specimen interaction

## Elastic:

BSE

## Inelastic:

SE

Characteristic X-rays

Bremsstrahlung X-rays

Auger electrons

Plasmons

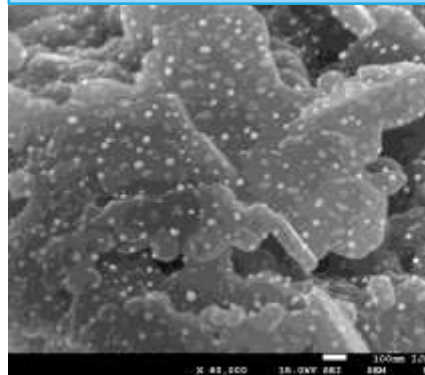
Phonons

Cathodoluminescence

Figure removed for copyright reasons.

Remember the SEM resolution?

What about the EDS and WDS resolution in SEM?



Yellow rings indicates interaction volume for  
low density material

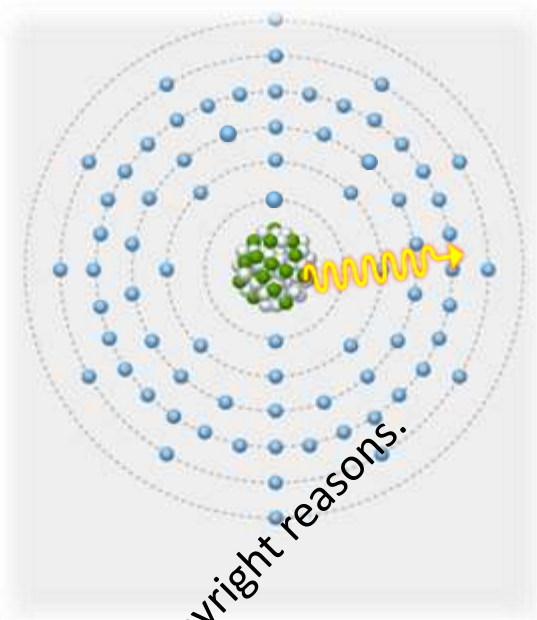
Blue rings show high density material

Dotted lines represent high kV and solid lines  
show lower kV

Density has the largest effect!

# Bremsstrahlung X-ray generation

(Images: ammrfr)



According to Kramer's Law (1923), the **intensity** of the Bremsstrahlung X-rays is **proportional to Z**, the mean atomic number of the specimen. This means that heavier materials like Pb or Au will produce more Bremsstrahlung X-rays than samples made from lighter elements such as C or Al.



## Kramer's law:

$$I \approx i_p \cdot Z \cdot \frac{E_0 - E}{E}$$

Limits:

$$I \approx 0, E = E_0$$

$$I \approx \infty, E = 0$$

$i_p$  ... electron probe current

$Z$  ... mean atomic number

$E$  ... X-ray energy

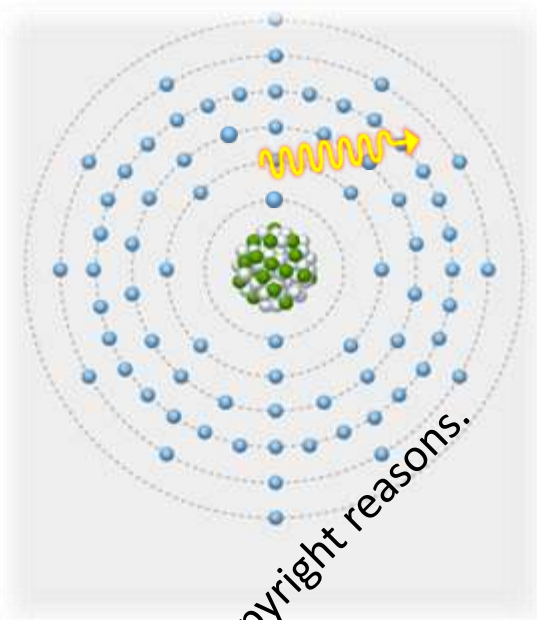
$E_0$  ... incident beam energy

$I$  ... intensity of X-rays

Figure removed for copyright reasons.

(Image: wiki)

# Characteristic X-rays generation



Moseley (1913) associated the atomic number ( $Z$ ) with a certain frequency (**energy**) of the characteristic X-rays!

$$E_K > E_L > E_M > \dots$$

(Image: geology.wisc.edu)

Moseley was researching the characteristic lines of x ray emission from different target materials. He noticed a systematic progression of X ray wavelengths with the increasing atomic number of the material generating the radiation.

(Image: wiki)

# X-ray spectroscopy in SEM

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Records **all** energies simultaneously.

Plots the intensity vs X-ray photon energy.

Uses Bragg reflection on different crystals.

Measures **one** wavelength at a time.

Plots the intensity vs X-ray photon wavelength.

Better spectral resolution.

Figure removed for copyright reasons.

## Spectral resolution:

- EDS from 70 to 130 eV
- WDS from 2 to 20 eV

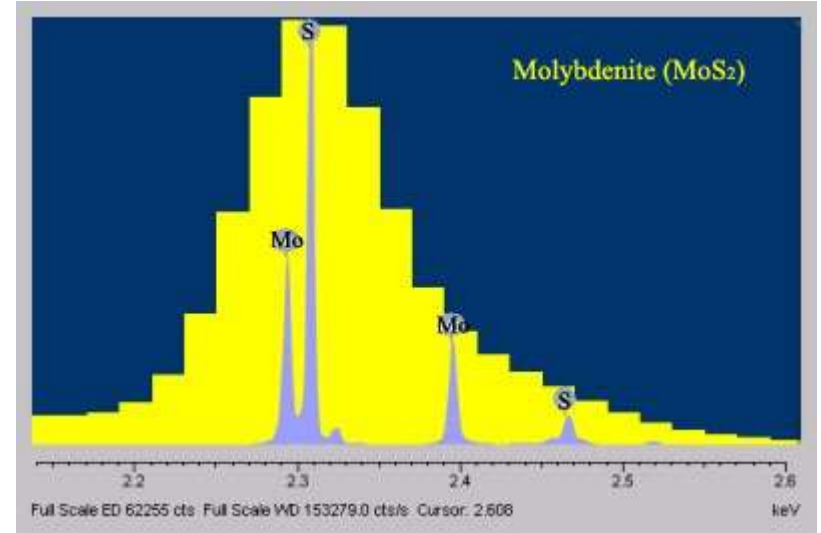
(Image: Goldstein)



# The ED and WD spectrum

Figure removed for copyright reasons.

(Image: ammrif)



(Image: serc.carleton.edu)

# EDS and WDS

$$\text{Max Planck: } E \cdot \lambda = h \cdot c$$

E ... photon energy  
 $\lambda$  ... wavelength  
h ... Planck konst.  
c... speed of light



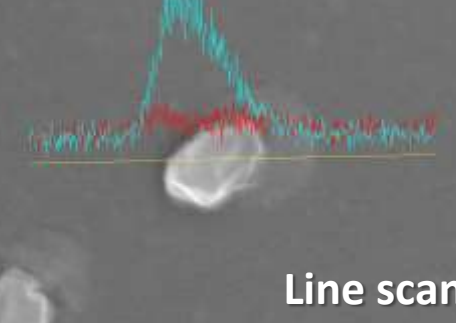
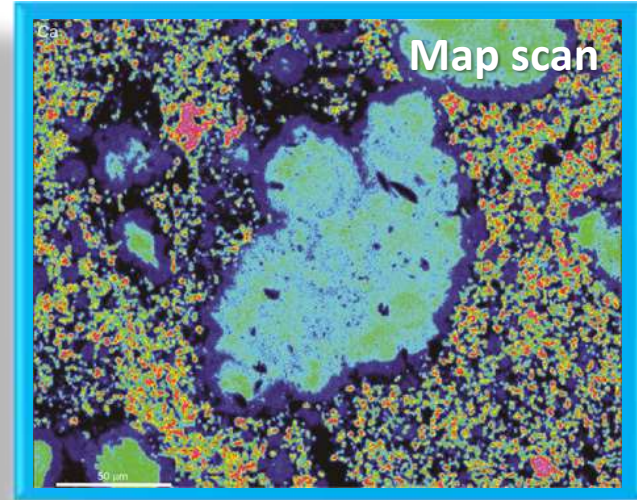
Plank reasoned that if only certain energy levels were possible (quanta), there ought to be a relationship between the energy of an atom undergoing the change and both the energy and the wavelength of the radiation.

# EDS

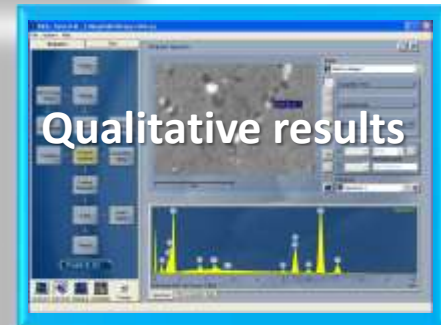
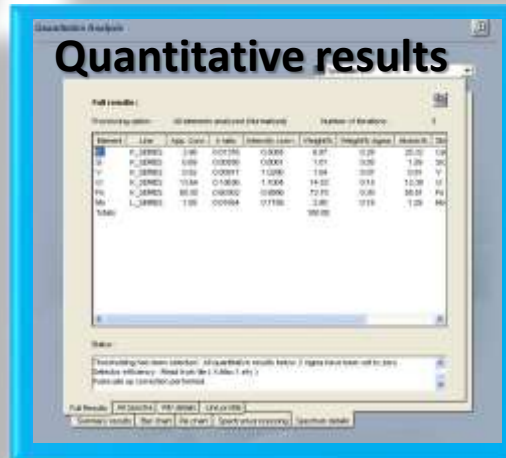
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ENERGY DISPERSIVE X-RAY SPECTROSCOPY  
(EDXS, EDX OR XEDS)

# Spectrum



Line scan



# X-ray detection by EDS

Si(Li)

SDD

JEM-2100



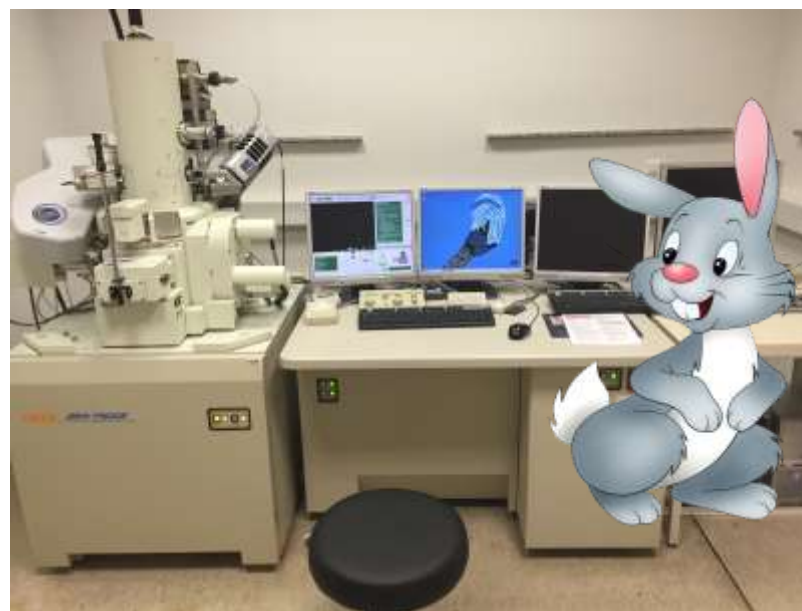
JSM-5800



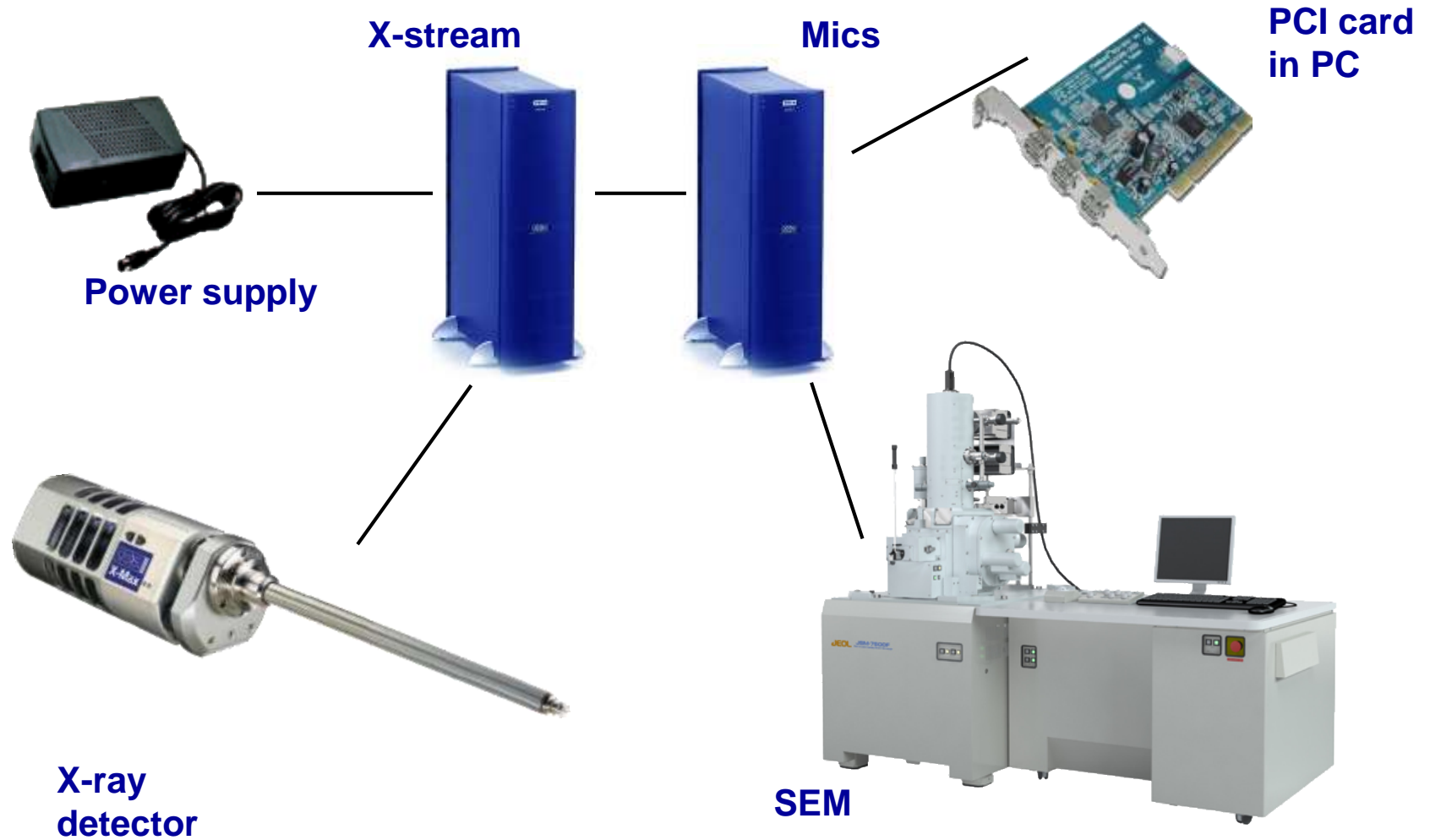
ARM



JSM-7600F



# EDS system components

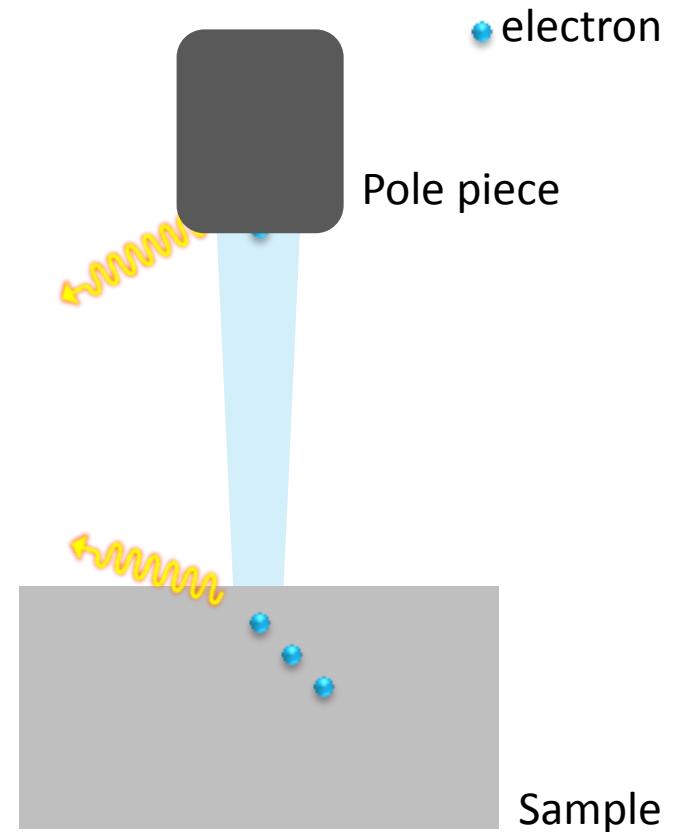
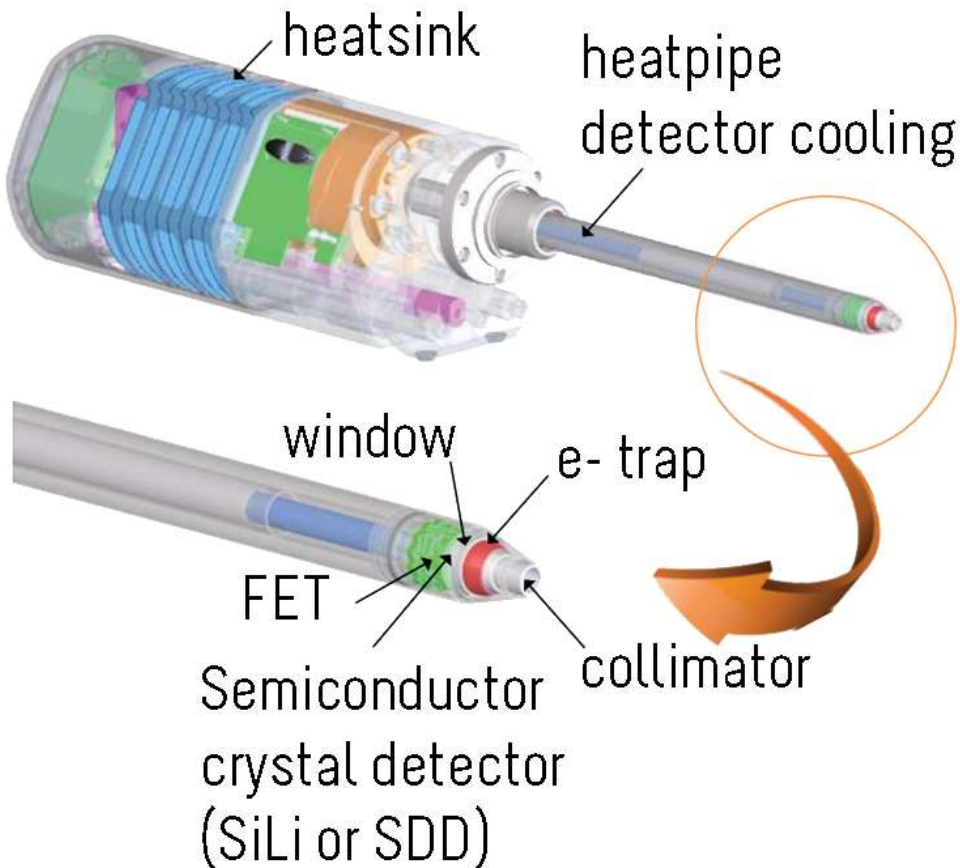


(Images: Steven Hant)



# Components of the detector

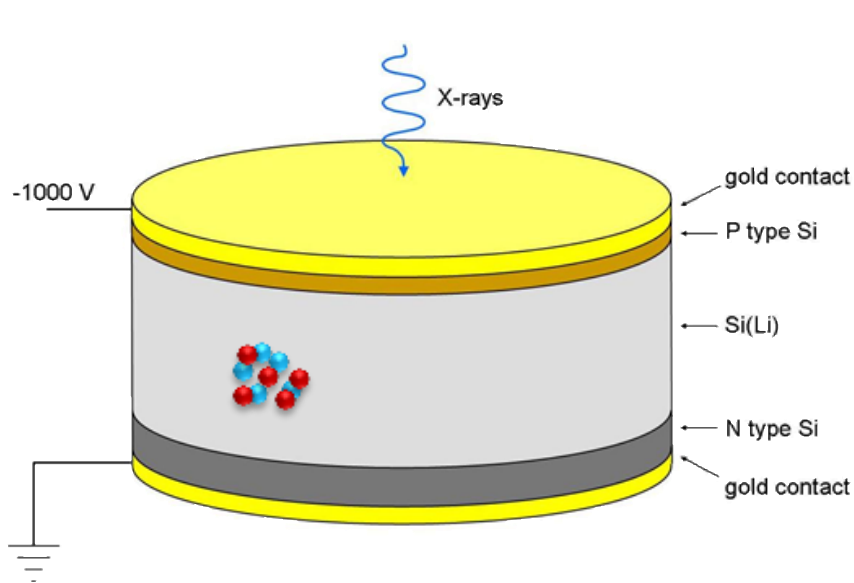
(Image: Oxford)



# Si(Li) detector crystal

## Detector Crystal: **Lithium drifted Silicon semiconductor**

- Cooled to  $\approx -180\text{ }^{\circ}\text{C}$
- An X-ray pulse enters the detector and its energy is converted into electrical energy
- FET collects the charge pulse and amplifies signal



● Electron  
● Hole

For a silicon detector,  $\sim 3.8\text{ eV}$  is used to generate each electron-hole pair ( $\sim 2.9\text{ eV}$  for Ge).

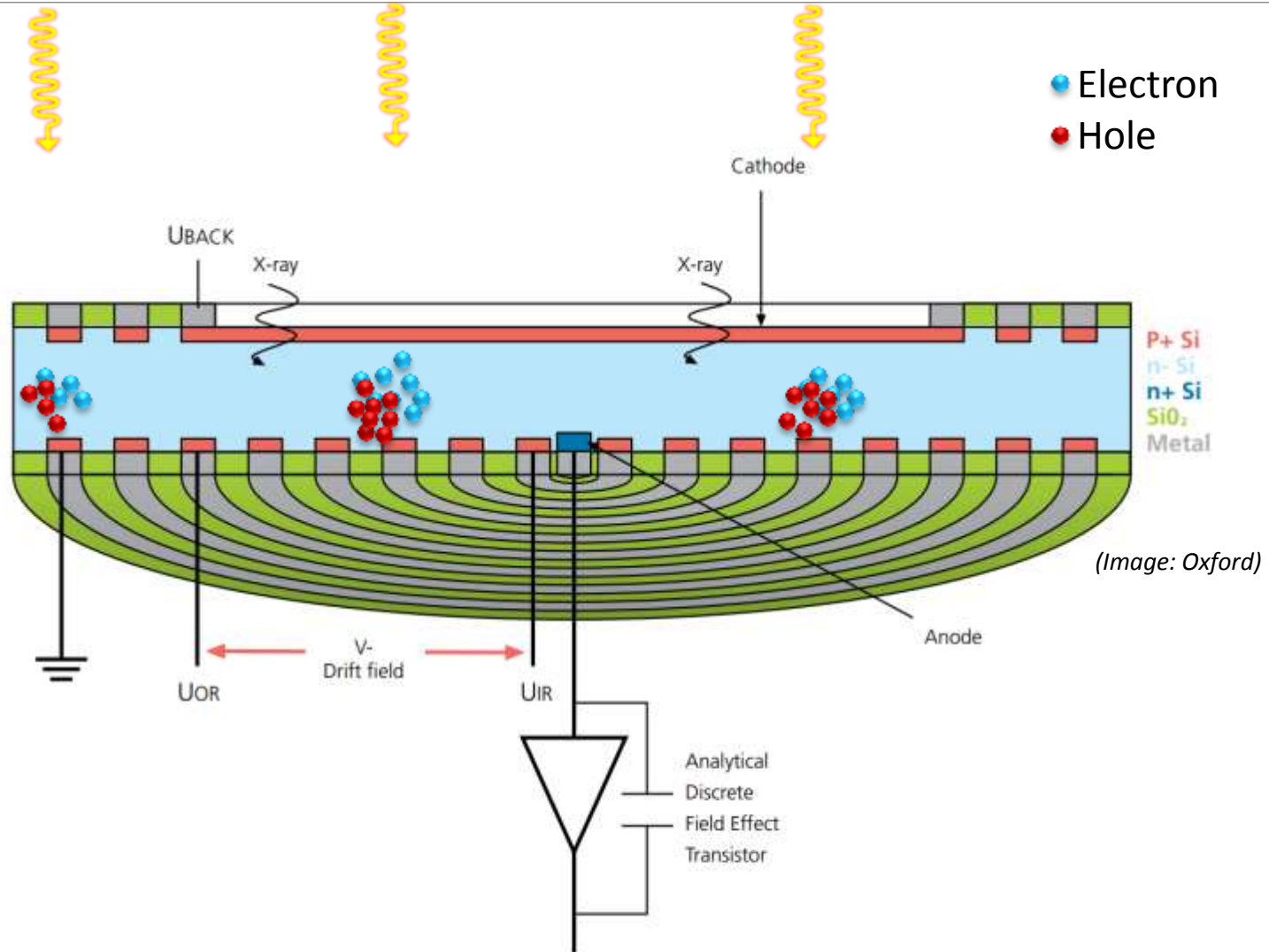
- Ni  $K\alpha$  (7.477 keV)  $\rightarrow$  1968 electron-hole
- Al  $K\alpha$  (1.487 keV)  $\rightarrow$  391 electron-hole pairs

(Image: wiki)



# Silicon Drift Detector

Thermoelectric cooling (Peltier)



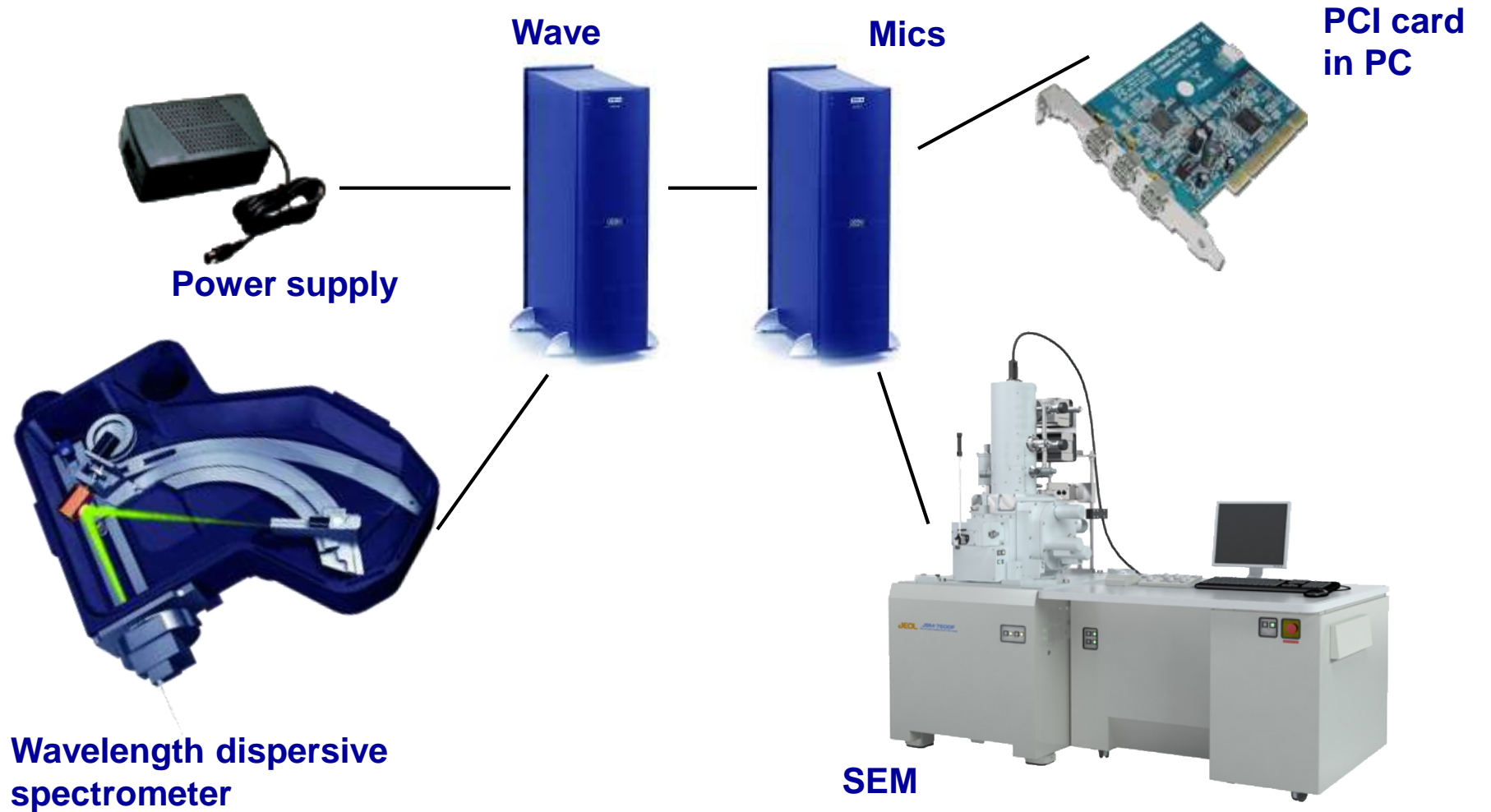
# WDS

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WAVE (WAVELENGTH) DISPERSIVE X-RAY  
SPECTROSCOPY

(WDS OR WDX)

# WDS system components



(Images: Steven Hant)

# X-ray detection by WDS

Wavelength dispersive  
spectrometers



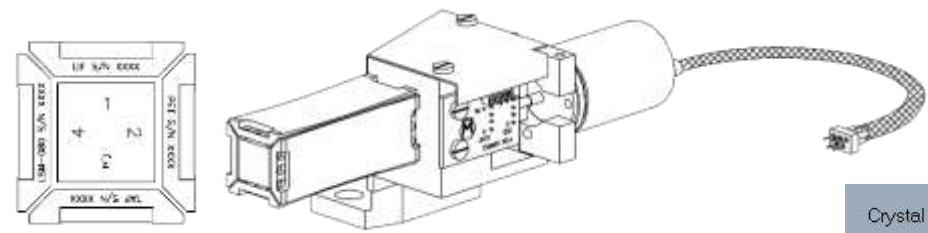
## EPMA -Electron Probe Microanalysis

More spectrometers –  
more elements.  
But in the vertical  
position the X ray counts  
are very sensitive to Z  
focus!

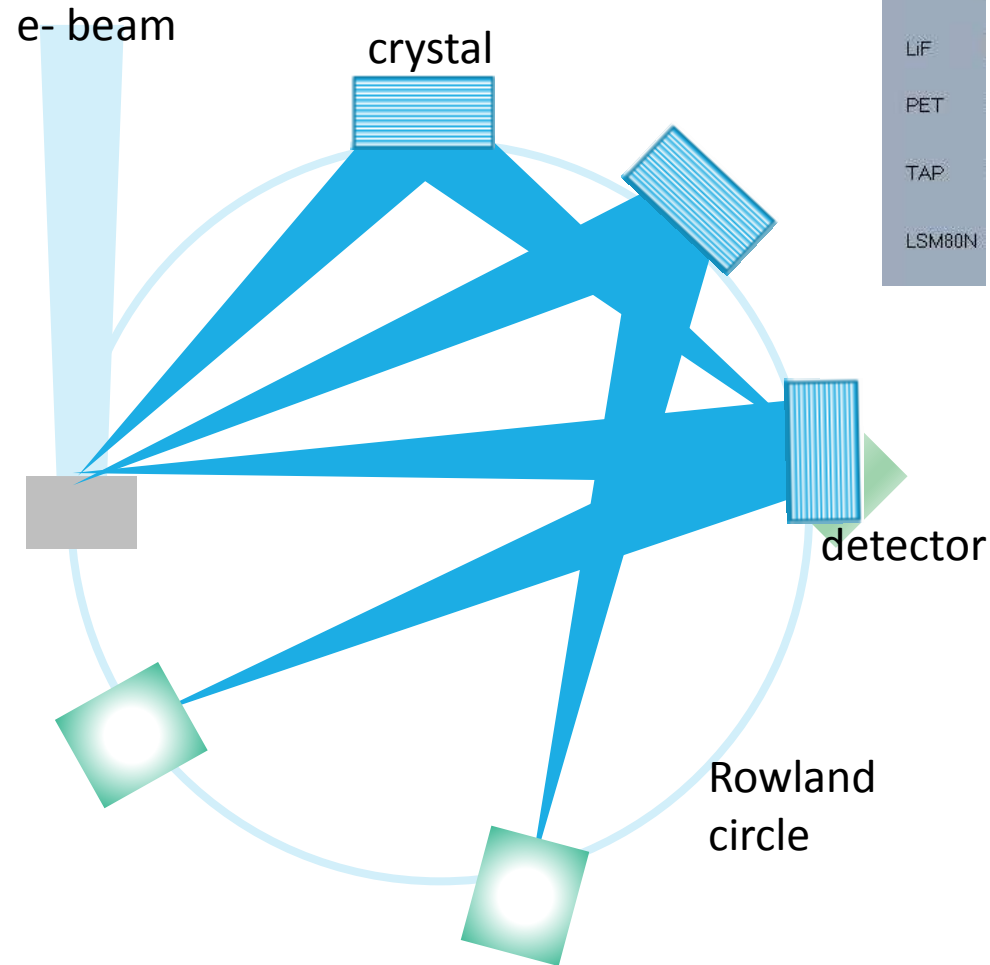
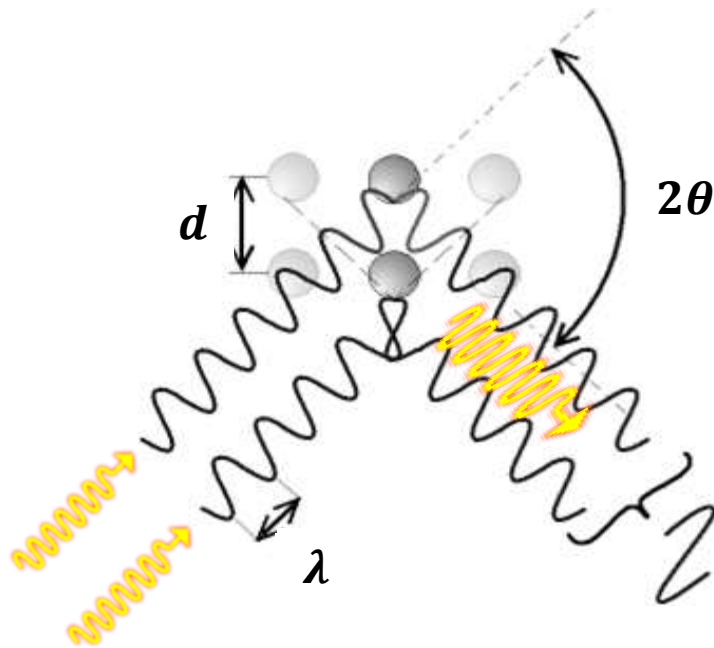
Scanning over one  
wavelength – one  
element at one position



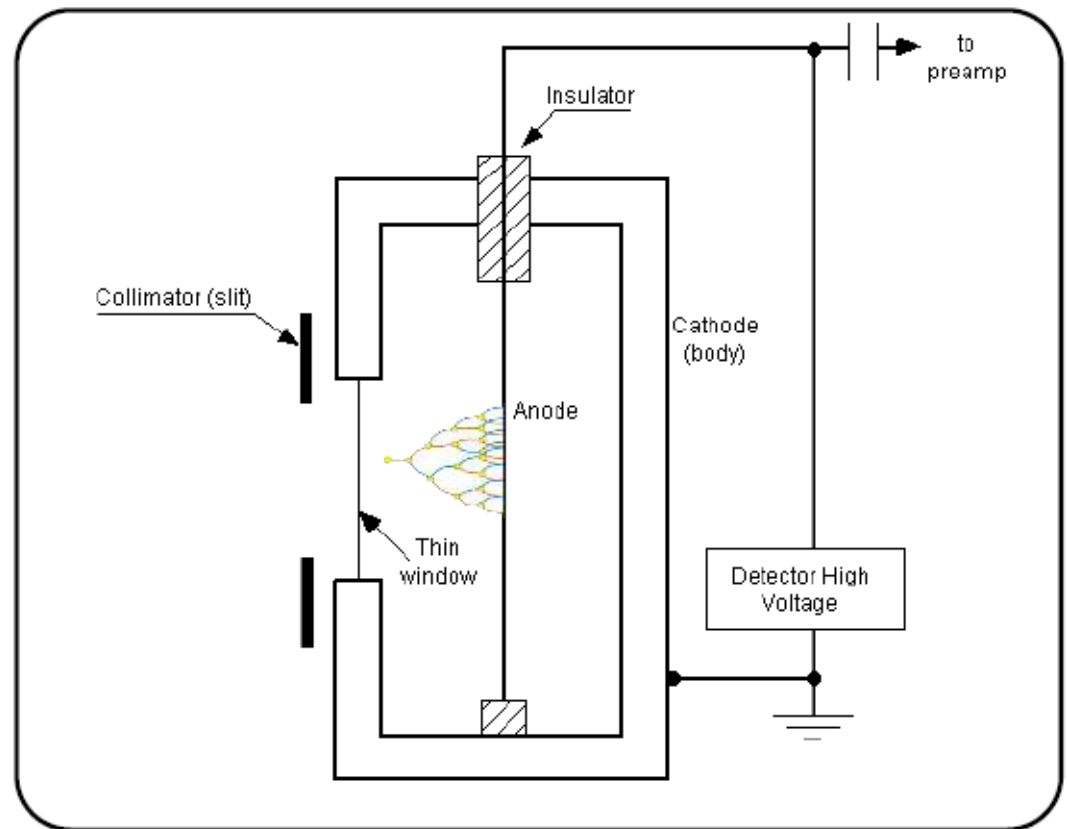
# Diffraction



$$\text{Bragg's law: } 2 \cdot d \cdot \sin \theta = n \cdot \lambda$$



# Detectors



Low energy X-ray lines - Gas Flow Proportional Counter (FPC)

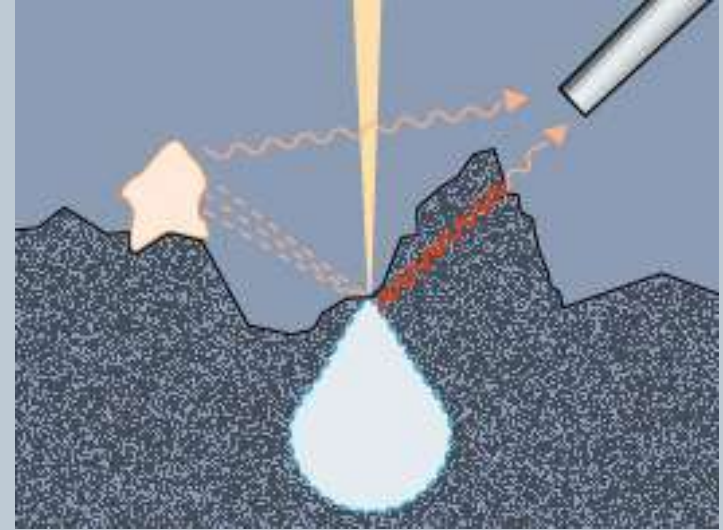
High energy X-ray lines - Sealed proportional counter (SPC)

Standard: Fe for calibration





*(Images: Oxford)*



# Sample preparation

How to prepare a good sample for EDS

# Samples must be:

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- 1) Vacuum compatible
- 2) **Conductive** and stable under the beam (heating)
- 3) Flat - polished, no shadowing (geometry and height for multiple samples must be taken into account)
- 4) **Homogeneous** in the area of the analysis! Multi phase?

Figure removed for copyright reasons.

(Image: ammrj)



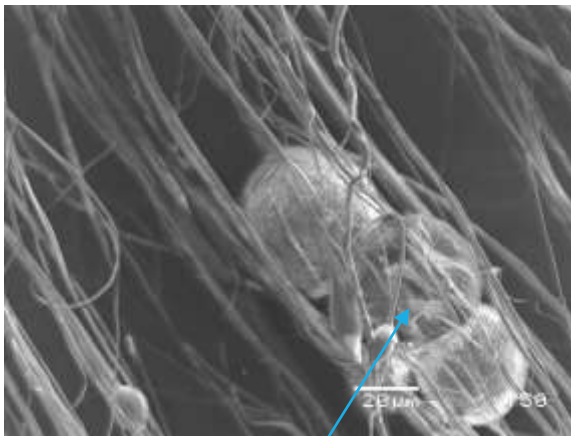
## 2) Sample charging

A layer of negative charge develops on the sample surface

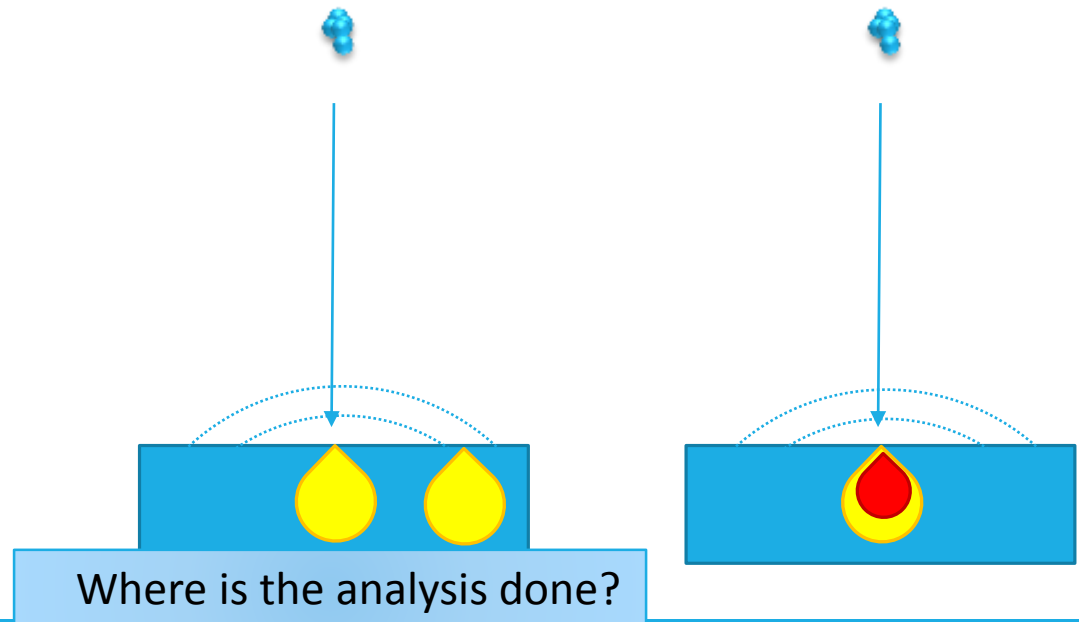
• electron

- A. decreases image quality
- B. deflects the beam when doing spot analysis
- C. reduces the effective accelerating voltage

important: XPP calculates using the kV value from Column Control but the reduction alters the interaction volume!

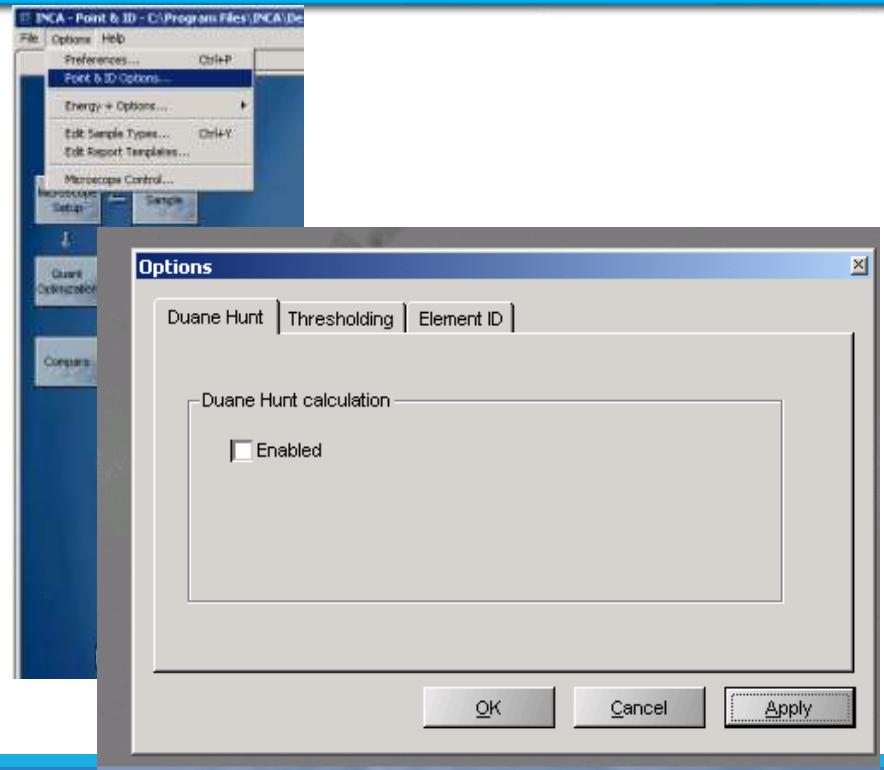
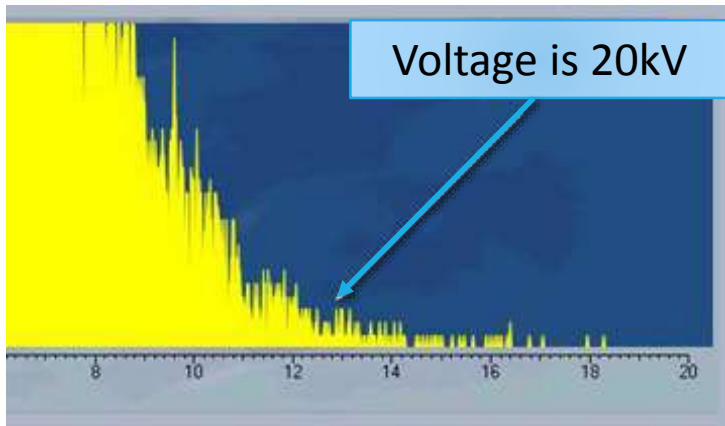


Charging lines



# How to be sure you have a problem with the conductivity?

1. Check the upper energy cut off - Duane Hunt limit.
2. Have the Duane Hunt tab Enabled – it will warn you when the spectrum high energy cut off is less than the accelerating voltage.



# How to reduce sample charging?

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1. Coat with carbon (low X-ray absorption factor)
2. Reduce probe current or spot size
3. Reduce accelerating voltage. But think about the overvoltage ratio!
4. Scan the beam rather than spot mode. But only if you are analyzing bulk areas, not good for particles
5. Tilt the sample
6. \*Low Vacuum SEM: ok, but will cause beam spreading so you will get X-rays from a larger area and you will get absorption of x-rays in the gas.

## 4) Multi-phases and **homogeneity** of the sample

- Size of the grain?
- What is the shape underneath the surface?
- Are the X-rays coming from the grain or the matrix or a different grain?
- **Quantitative analysis is based on a homogeneous sample!!!**

Spectrum Label	N	Mg	Al	Ti	Cr	Fe	Total
Grain 1	22.87	0.30	0.39	74.29	0.44	1.71	100.00
Grain 2	22.31		0.19	75.02	0.62	1.85	100.00
Grain 3	23.08			70.21		6.71	100.00
Grain 4	25.37			44.32	4.17	26.14	100.00
Max.	25.37	0.30	0.39	75.02	4.17	26.14	
Min.	22.31	0.30	0.19	44.32	0.44	1.71	

1. use the “X-ray Generation Region” tool in Point and ID to give you a rough idea
2. Make several spot analysis of ‘similar’ grains and compare the results, if the results vary by more than **a few percent**, you could be getting matrix elements
3. reduce the accelerating voltage to reduce penetration depth and repeat several spot analysis

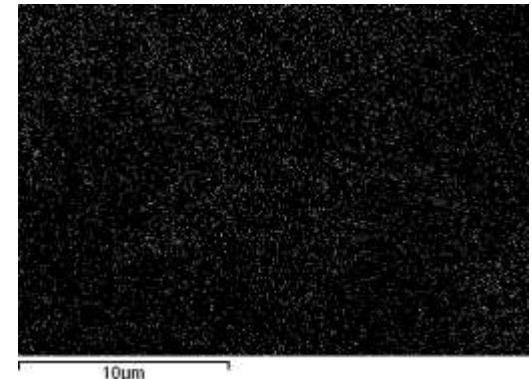
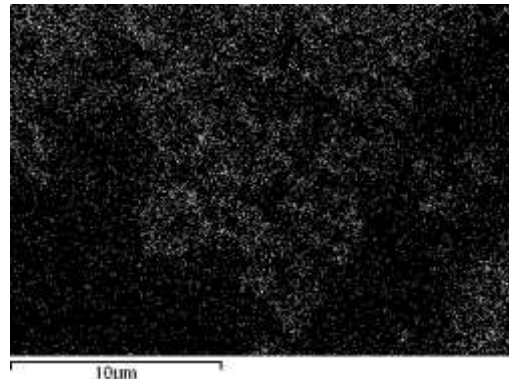
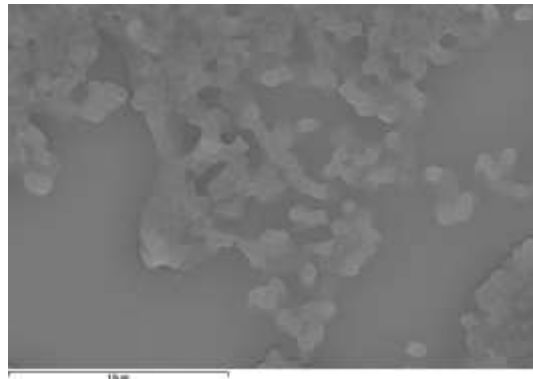
# Sample concentrations

## Concentration

- major amounts ( $> 10$  wt%) will have major peaks
- minor (1-10 wt%) or
- trace amounts ( $< 1$  wt%) will have small or undetectable peaks in the spectrum.

Typical detection limit of EDS in bulk material is 0,1\* wt % or 1000\*ppm!

Never do mapping for trace elements!





(Image: JEOL)

# Practical part: SEM parameters

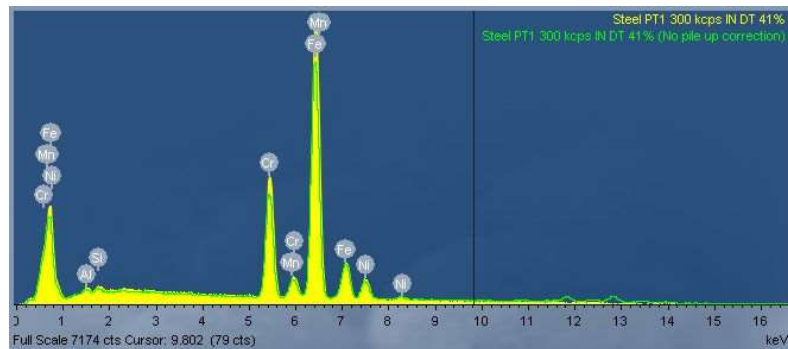
You want a

*great,  
superior,  
excellent,  
superb,  
outstanding,  
magnificent,  
exceptional,  
marvelous,  
wonderful*

ED  
spectrum!

## What defines the perfect EDS? X ray intensity

The height of the Characteristic X-ray peaks in an ED spectrum, given in cts!



Question:

Is the height of the X-ray peak in the spectrum proportional to the concentration of the element in the sample??

- SEM – not necessarily
- TEM – of course

# Overvoltage ratio - U

the ratio of the energy of the electrons in the beam ( $E_o$ ) to the critical excitation energy ( $E_c$ )

Example:

$$E_o = 15 \text{ keV}$$

$$E_c = 7.11 \text{ keV (Fe K}\alpha \text{ 6,398 keV)}$$

$$U = \frac{E_o}{E_c} = 2.11$$

Figure removed for copyright reasons.

Figure removed for copyright reasons.

Effect on the spatial resolution!

$\lambda$  = 25 kV - Well stimulated X-rays for Si & Cu  
 $\lambda$  = 15 kV - Well stimulated X-rays for Si but  
Under stimulated X-rays for Cu

(Images: ammrif)



# Accelerating voltage

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A good starting point is 20 kV.

If you know your sample – consider the overvoltage ratio.

For thin layers and small particles - lower the kV, but more problems if you have peak overlapping.

Figure removed for copyright reasons.

*(Images: ammrif)*

# Probe current, aperture

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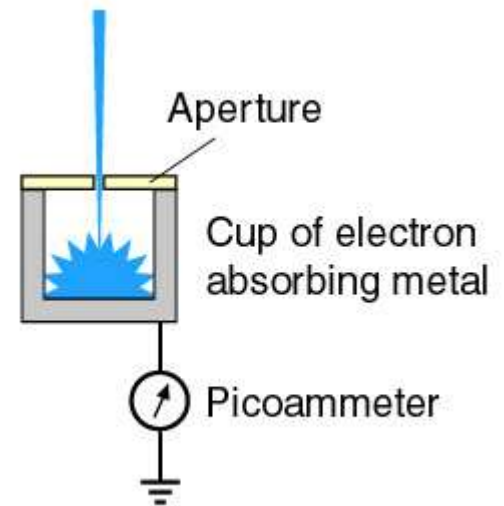
↑PC will ↑ **X-rays cts**, but relative heights stay the same

If doing WDS have higher currents (nA) – bigger aperture.

Figure removed for copyright reasons.

INCA (SDD) we can use **much higher currents** than with Link ISIS (SiLi)!

# Measuring the current



## HOLDER



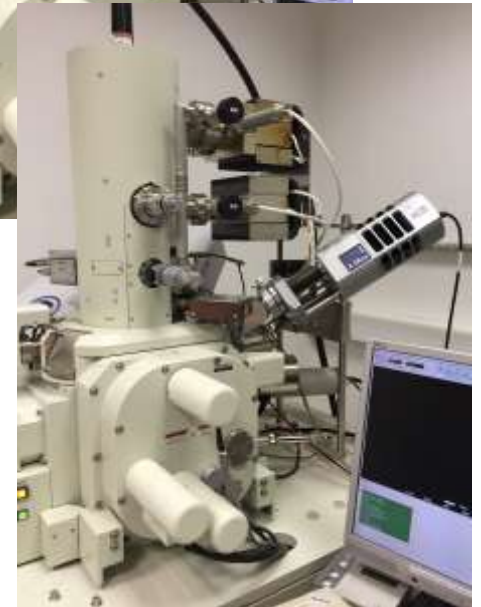
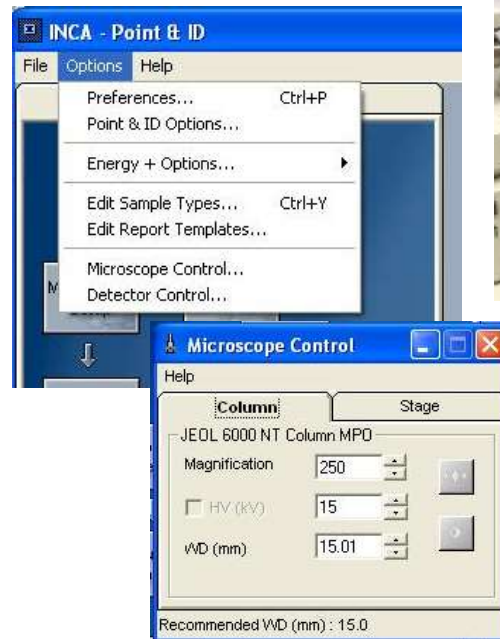
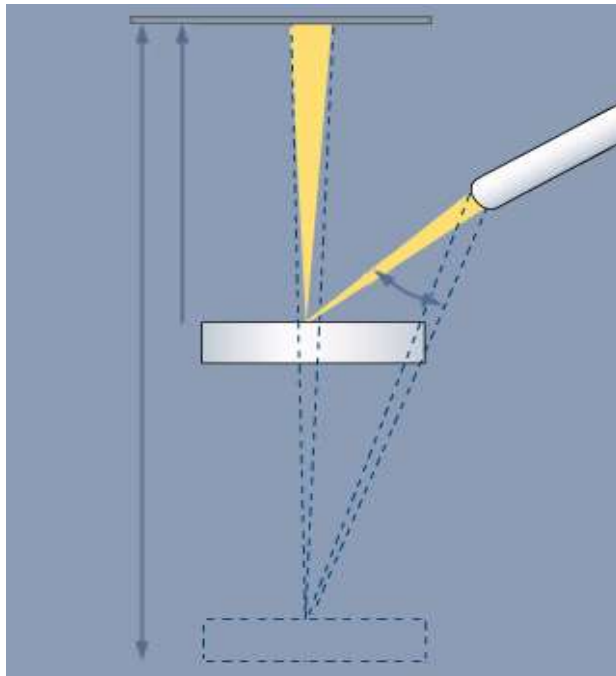
## XENOS FARADAY CUP



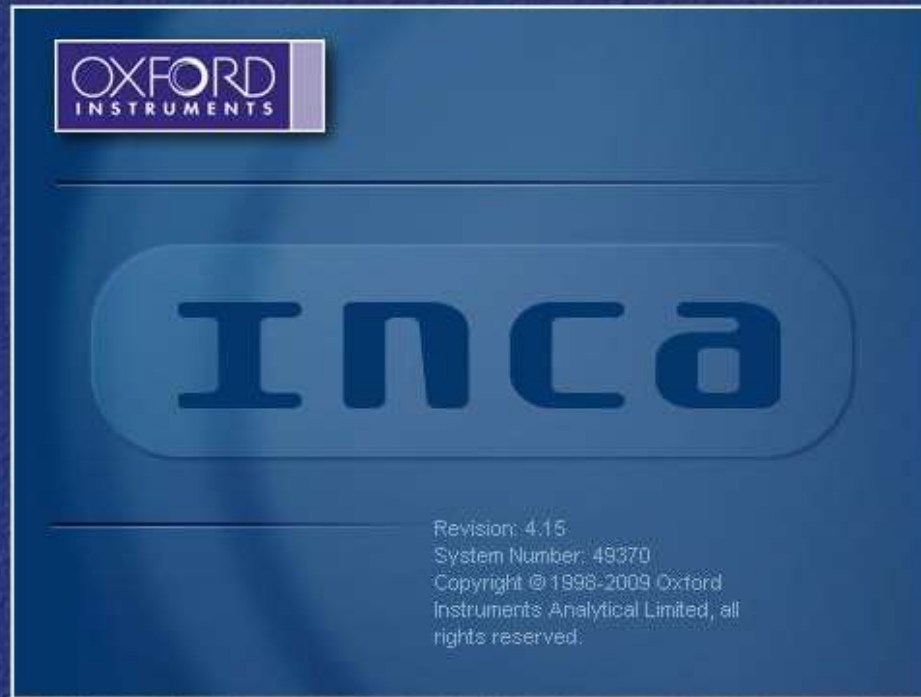
# Proper parameters on SEM

The geometry of the EDS/WDS:

- **WD** (7600F 15 mm, FIB 5 mm)
- EDS detector inserted and cooled



(Image: Oxford)



# EDS/WDS: Oxford INCA

# How to start - Steps

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SEM parameters:

- **Voltage** (depending on the interaction volume – small grains, sample lower voltage, but if the low x ray lines are overlapping go to higher voltages and think about the overvoltage)
- **Aperture**, spot size or **probe current** (more electrons more x-rays – more counts – better statistics) check on Cu, Co to get the dead time to 35%.

- EDS parameters:

- **Process time** (depending on the type of the detector: from 3-5)
- Set **life time** (not real time) – time depends on counts
- **Dead time 30%** (Remember different samples will give different count rates and dead times for the same beam current – therefore optimum dead time 30%!)
- Use the program to see if the AUTO ID did its job.

# Optimal pulse processor settings

Process time (PT)		
	X-max SDD	Si(Li) or X-act SDD
Quantitative analysis	3 or 4	5
X-ray mapping	2 or 3	4

Number of channels: 2K if low cps 1K

Spectrum range:

- 0 - 20 keV, if working at above 10 keV (15, 20, 25, 30 keV)
- 0 - 10 keV, if working below 10 keV

If interested in light elements or low keV peaks  
( lower than 2keV) use PT 5 or 6!





# Where can we use the program INCA?

Oxford Instruments **X-Max** Silicon Drift Detector

JEOL 7600F

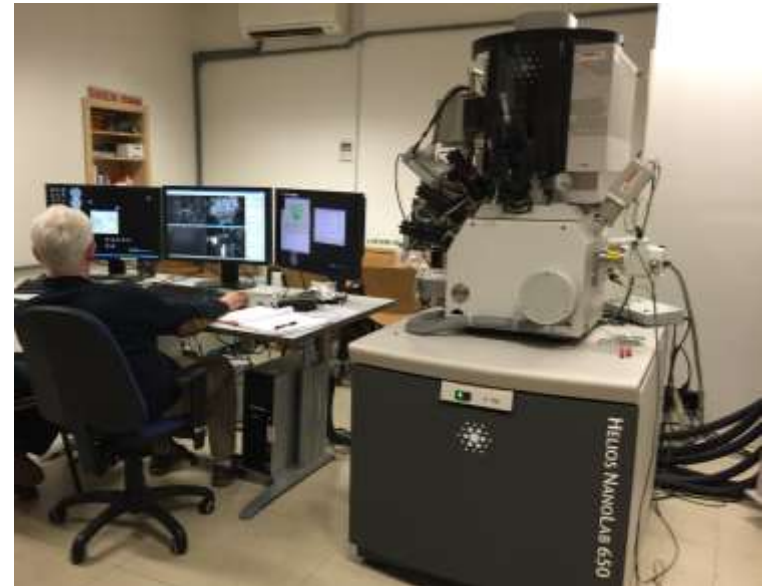
SDD 20 mm<sup>2</sup>



SEM

FEI HELIOS NANOLAB 650

SDD 50 mm<sup>2</sup>



SEM

STEM



# Workflow for **semi-quantitative** analysis

Describe the project in **“Project”** and the sample in **“Sample”**



Select appropriate pulse processor settings in **“Acquisition Setup”**



Adjust the SEM conditions in **“Microscope Setup”**



**“Quant Optimization”** (Co, Ti, Si or Cu tape)



Collect a reference image in **“Site of interest”**



Start spectral acquisition in **“Acquire Spectra”** by selecting appropriate tool (spot, rectangular region, etc.) and clicking on the region of interest.



Use the Reconstruction Overlay tool to verify peak identification in **“Confirm elements”**



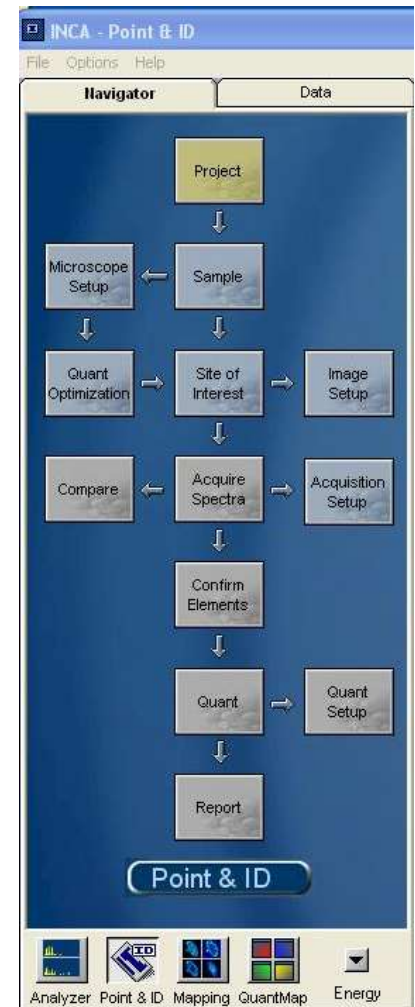
Set the conditions for quantization in **“Quant Setup”**



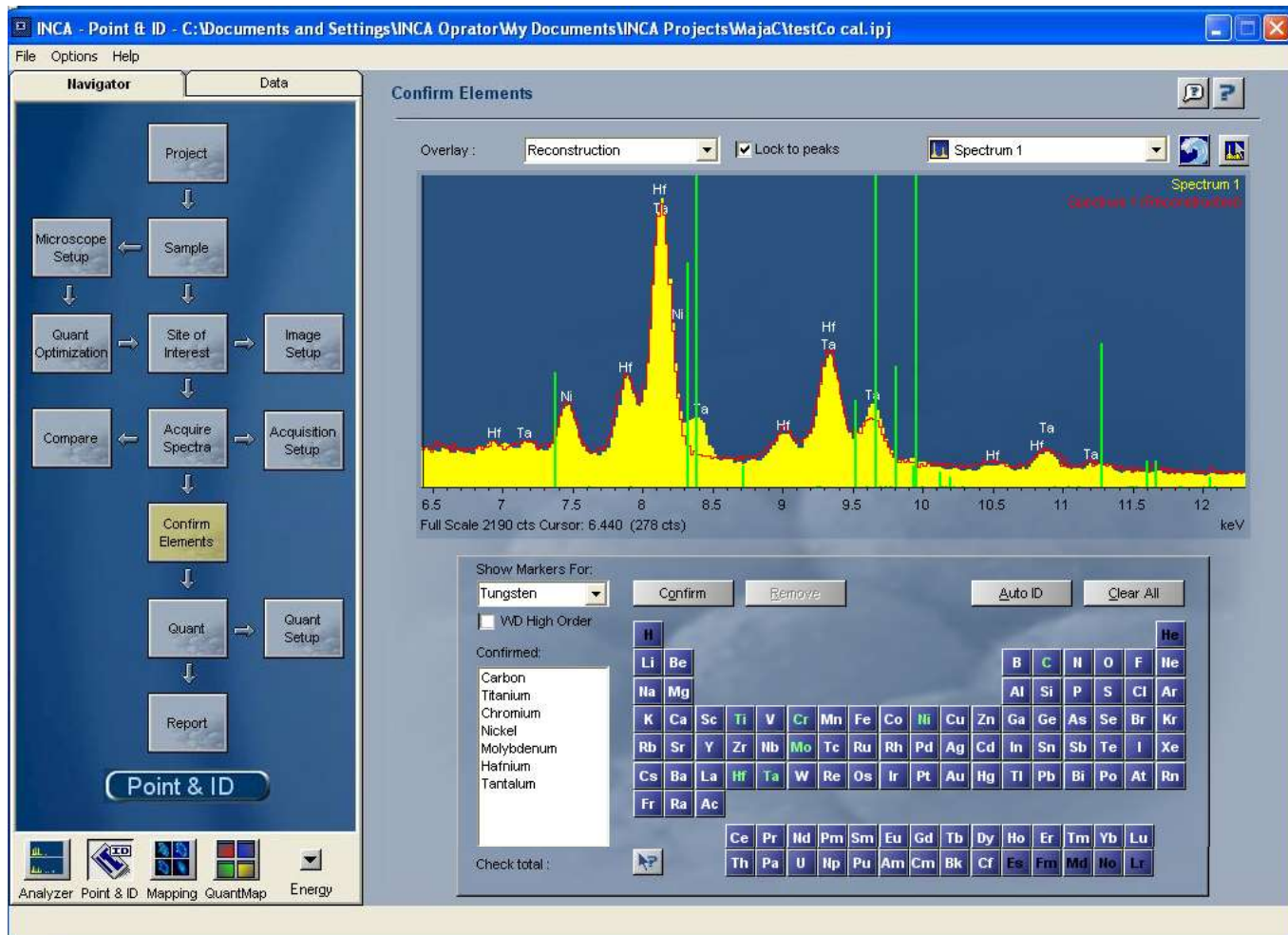
**“Quant”**



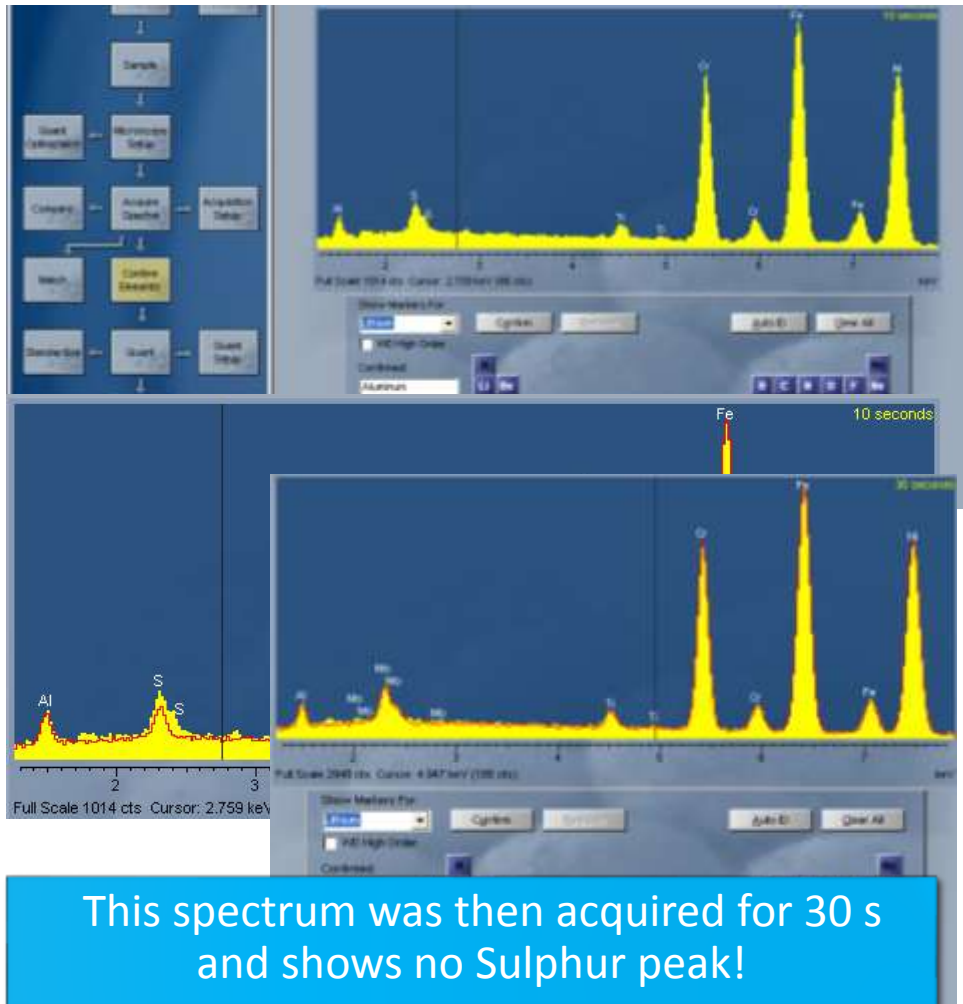
Make a report in **“Report”**



# Confirm the elements



# Reliable peak ID (accuracy)



This spectrum was acquired for 10 s and shows a Sulphur peak giving the quantitative result below!

## Summary results :

Element	Weight%	Atomic%
Al	1.45 +/- 0.22	2.95
S	1.09 +/- 0.19	1.86
Ti	1.14 +/- 0.18	1.31
Cr	17.75 +/- 0.41	18.74
Fe	34.88 +/- 0.58	34.28
Ni	43.70 +/- 0.65	40.87
Totals	100.00	100.00

BUT when you overlay with the shape of the spurious

## Summary results :

Element	Weight%	Atomic%
Al	1.36 +/- 0.12	2.84
Ti	1.15 +/- 0.10	1.36
Cr	17.75 +/- 0.24	19.20
Fe	33.76 +/- 0.34	34.00
Ni	42.11 +/- 0.39	40.34
Mo	3.86 +/- 0.32	2.26
Totals	100.00	100.00

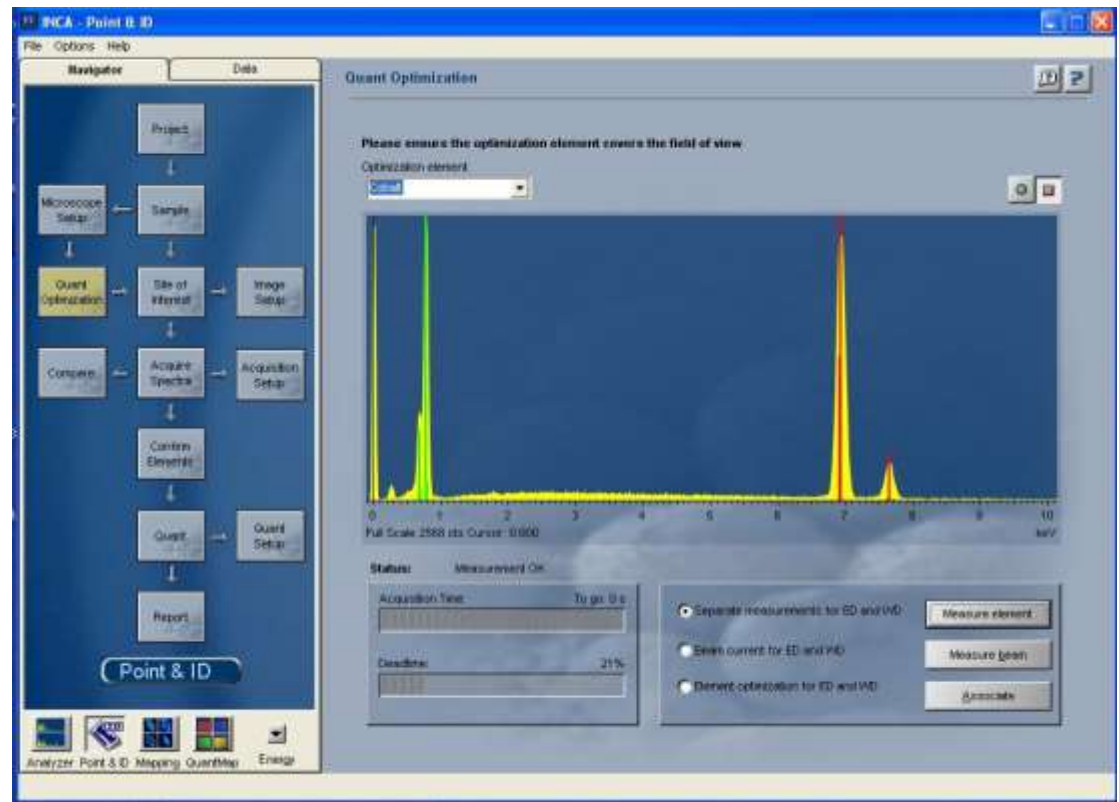
# When do you need to do it?

The screenshot displays the INCA - Point & ID software interface. On the left, a 'Navigator' pane shows a workflow diagram with steps: Project, Sample, Microscope Setup, Quant Optimization, Site of Interest, Image Setup, Compare, Acquire Spectra, Acquisition Setup, Confirm Elements, Quant, Quant Setup, and Report. The 'Acquire Spectra' pane on the right shows a dark image area and a dropdown menu for 'Image' set to 'Electron Image 1'. A 'Quant Optimization' dialog box is open, displaying an information icon and the text: 'The range has changed optimization. Press R optimization'. It includes a checkbox labeled 'Don't warn me about' and a 'Retry' button. At the bottom of the dialog, it says 'Not optimized for this range' with a question mark icon. The bottom status bar of the software shows 'Spectrum' and 'VWD Acquisition Data'.

Ambient temperature changes  
Beam current may vary with time  
To determine exact peak positions, and the resolution of the system  
If peaks overlap, the relative sizes of individual peaks can only be calculated accurately if the width and position of each peak is accurately known.  
By measuring the position of one known peak, the system can be optimized to determine the position of all other peaks.

# How to do quant optimization?

1. Co, Cu, Ti or Si
2. spot mode on SEM
3. set the parameters
4. acquire a spectrum
5. click on “Measure element”
6. undo spot mode



# Workflow for **quantitative** analysis

Describe the project in **“Project”** and the sample in **“Sample”**



Select appropriate pulse processor settings in **“Acquisition Setup”**



Adjust the SEM conditions in **“Microscope Setup”**



**“Quant Optimization”** (Co, Ti, Si or Cu tape)



Acquire a spectrum from a standard in **“Standardize”**



Start spectral acquisition in **“Acquire Spectra”** by selecting appropriate tool (spot, rectangular region, etc.) and clicking on the region of interest.



Use the Reconstruction Overlay tool to verify peak identification in **“Confirm elements”**



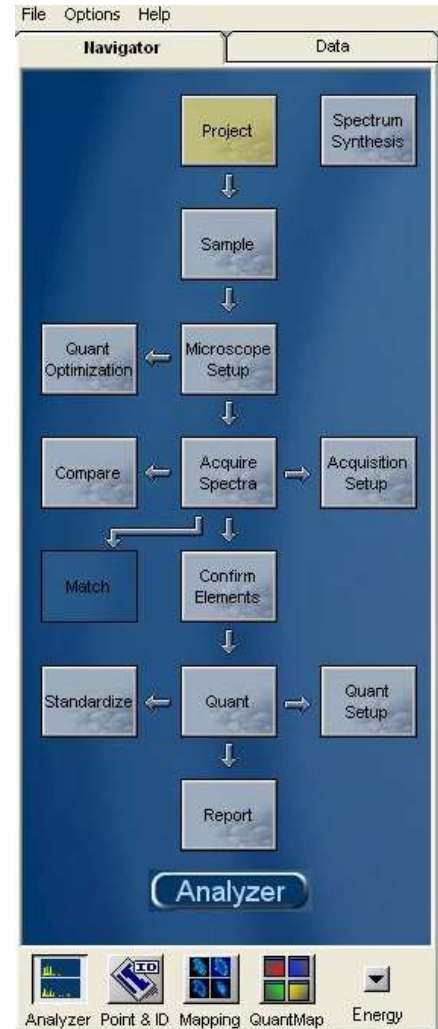
Set the conditions for quantization in **“Quant Setup”**



**“Quant”**



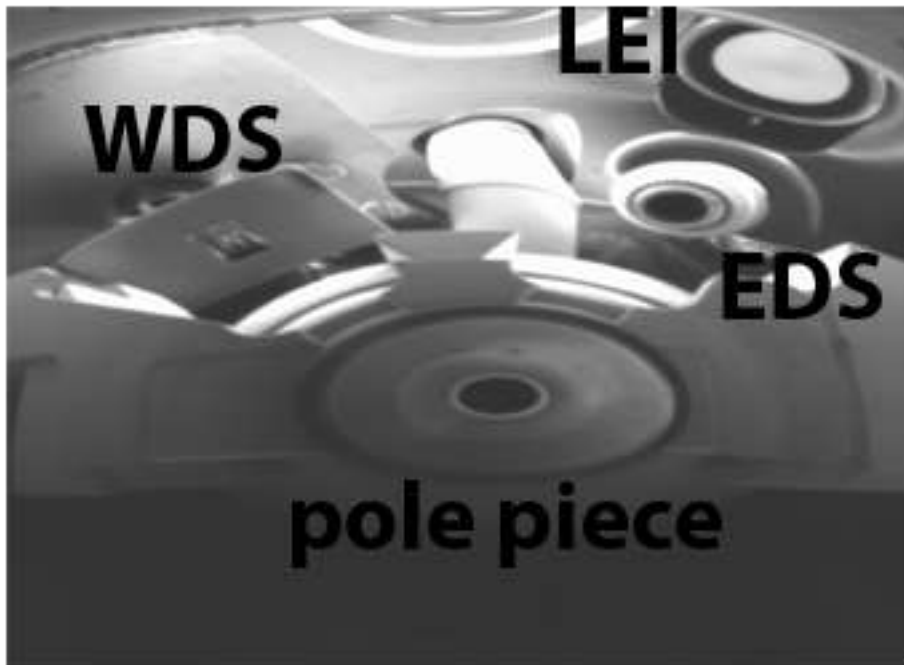
Make a report in **“Report”**





# Inside JSM-7600F

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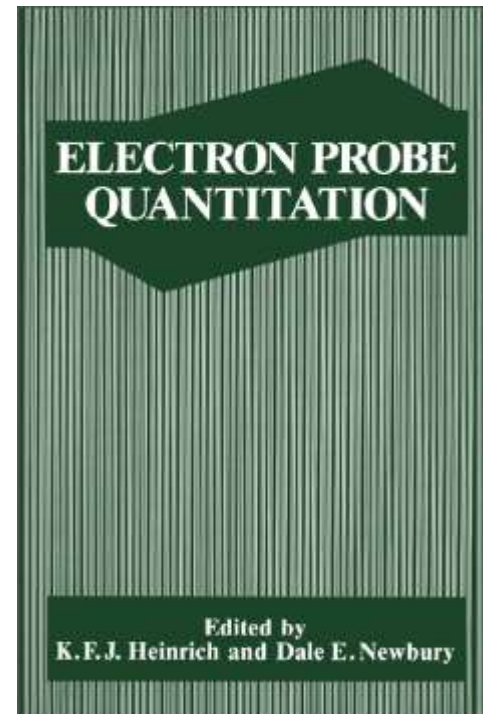


With Matejka Podlogar K7

# Spectrum processing

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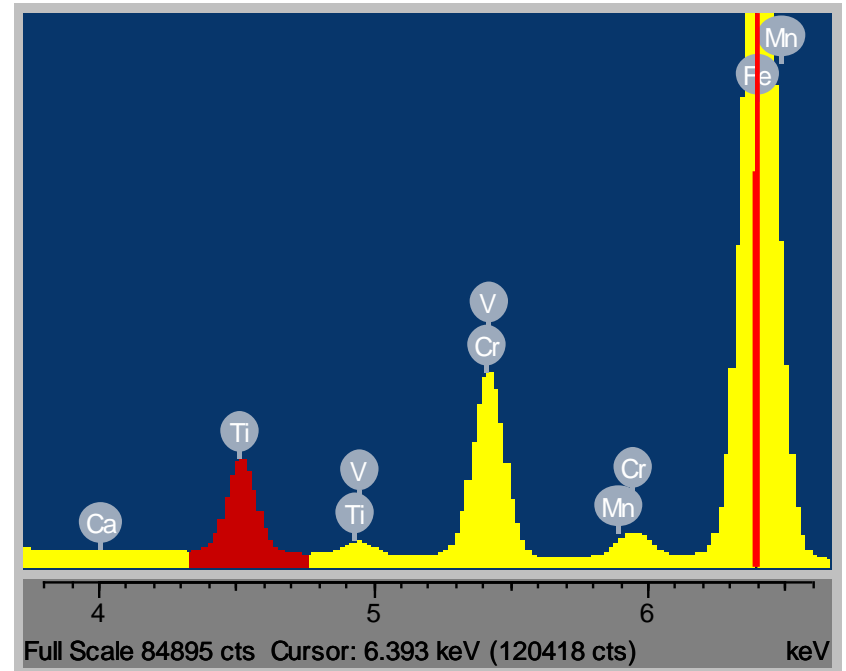
*(Image: cartoonstock)*





# Spectrum processing

- The peak area is directly related to the amount of each element
- We need to measure the integrated peak intensity (P-B) from each elemental peak in the sample
- The background (B) is removed by digital filtering
- The sample spectrum peaks can then be compared with pre-recorded **(virtual)** standard peaks supplied with the INCA Energy system (Standardless)



(Image: Steven Hant)

$$\frac{P-B_{\text{sample}}}{P-B_{\text{standard}}} = \frac{wt\%_{\text{sample}}}{wt\%_{\text{standard}}}$$

Complicated! But not a “black box”

# EMPA - Castaing

Raimond Castaing under the mentorship of Andre Guiner (X-ray crystallographer) started studying defects in Al metals - inclusions Cu in Al.

PhD: finding the inclusion composition by electron beam using TEM

His thesis laid out the basics of EMPA!

Castaing's first approximation

$$k = \frac{I_i^{unknown}}{I_i^{standard}} \sim \frac{C_i^{unknown}}{C_i^{standard}}$$

(Images: microscopy.org)

# Only k factors?

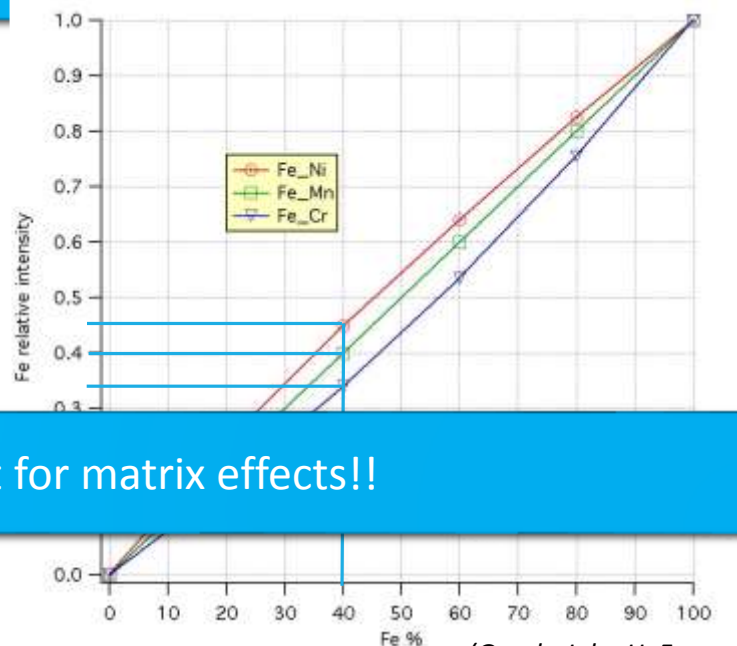
using k factors we simplify the analysis, because

- Counts or the measured intensity of the unknown sample and standard sample on the **same instrument** and under the **same conditions, cancel other physical parameters of the machine**

But is that all?

Example: Three Fe alloys plotted in Fe  $K\alpha$  X-ray intensity data

Ni ( $K\alpha$  7,5 keV) produces additional Fe  $K\alpha$  lines (6,4 keV) by secondary fluorescence!



We must correct for matrix effects!!

(Graph: John H. Fournelle)

# Z A F

## Atomic number

- **Z** correction deals with differences in the behavior of incident electrons between an unknown sample and a standard sample. In most cases describes how the electron beam penetrates in the sample and loses energy.

## Absorption

- **A** correction deals with differences in the degree of X-ray absorption between an unknown sample and a standard sample. This correction gives consideration to the mass absorption coefficient, incident electron energy, an X-ray take-off angle.

## Fluorescence

- **F** correction needs to be considered if the characteristic X-rays from an element, B, are at the short-wavelength (high-energy) side of the absorption edge of another element, A. In this case, the X-rays from element B may excite element A. The same is true with fluorescence excitation by continuous X-rays, but the effect usually is negligible..

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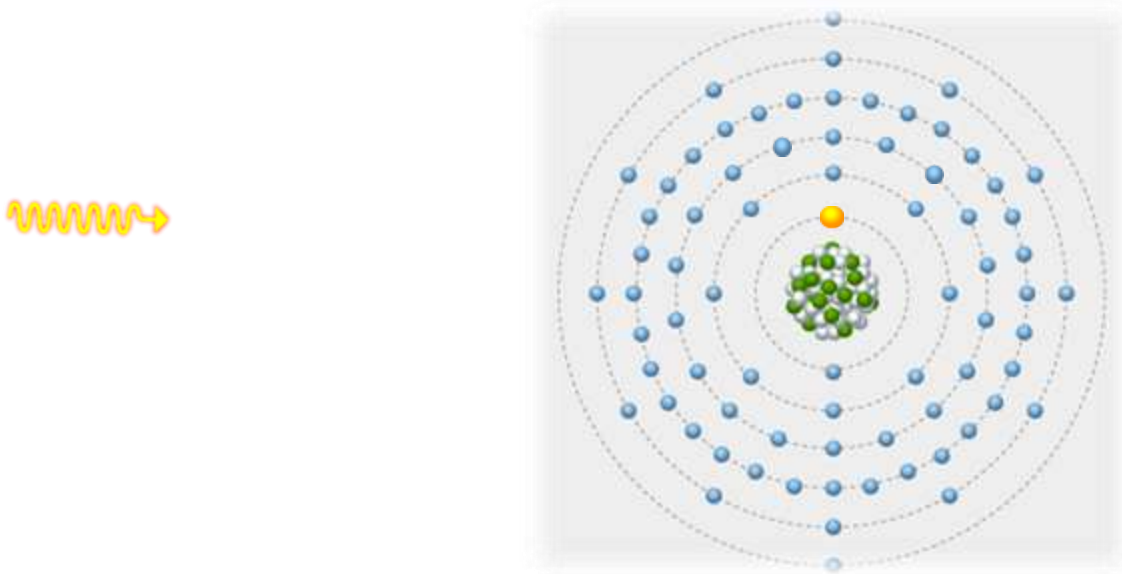
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(Images: ammrif)

# Absorption

X-rays may be absorbed by other elements in the sample due to the photo-electric effect!

If the energy of an X-ray photon is equal to the critical ionization energy of an electron in another element in the sample then there is a high probability that the X-ray will be absorbed and a photo-electron produced.



(Image: ammrif)

# But ...

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Sample considerations:

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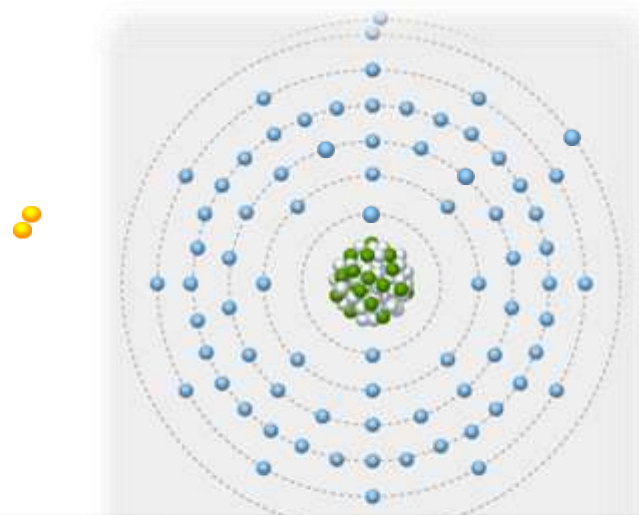
ZAF corrections – flat surface

# Fluorescence Yield ( $\omega$ )

Two-stage process:

- Ionization
- Relaxation
  - **Auger e<sup>-</sup>** emission ( $\alpha$ )
  - or **X-ray** emission ( $\omega$ )

Figure removed for copyright reasons.



Competition to stabilize the ionized atom!

(Image: cime)

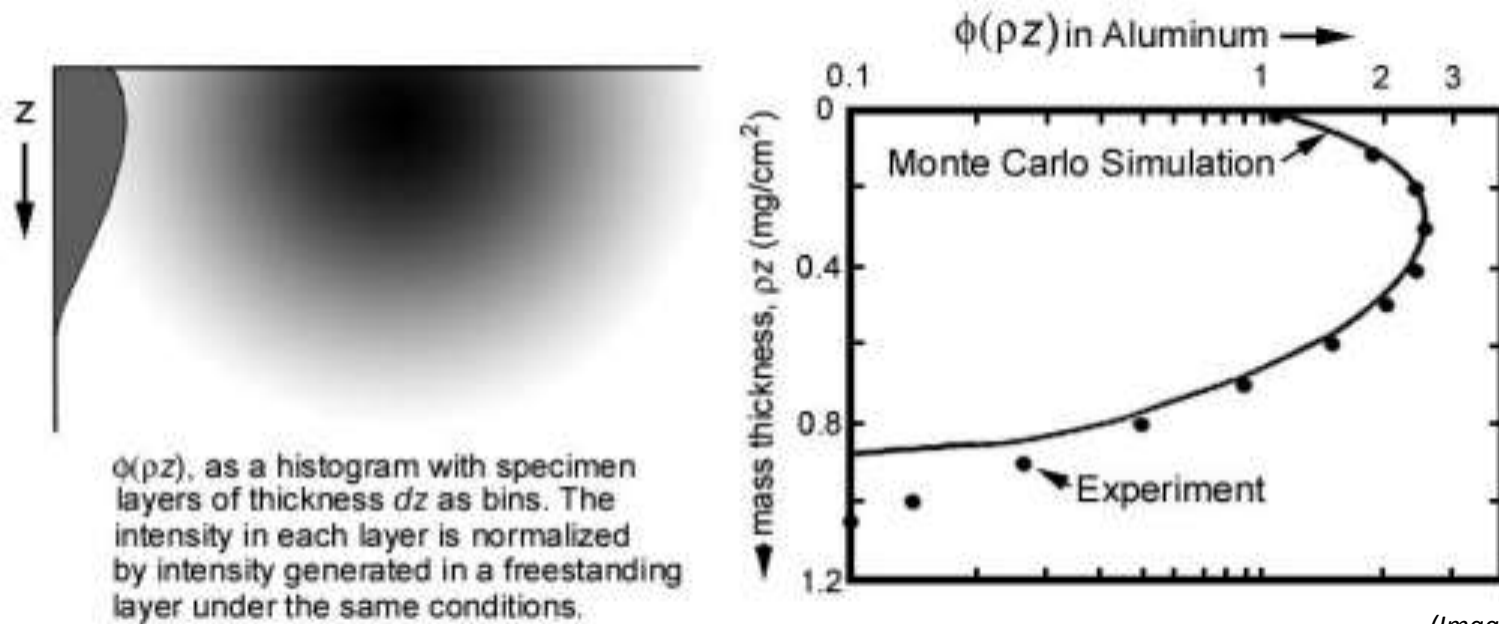
The fluorescence yield ( $\omega$ ) is the relative yield or ratio of X-rays to Auger electrons. Elements with low ionization energies ( $Z < 11$ ), have low fluorescence yields.

# Commercial correction models

In 1950s Castaing developed models for absorption ( $\phi(\rho z)$  curves)...

With the PC processing improvements ...

**ZAF corrections** are replaced by  **$\Phi(\rho z)$  models**:



(Images: mit)



# Correction methods for matrix

## $\alpha$ factors

- Were popular early on when online-data reduction using complicated algorithms was fairly slow due to limited computer processing speeds and memory
- Bence and Albee 1968, Armstrong 1988



## ZAF

- more rigorous physical model (ZAF, CITZAF)
- assumes a linear relation between concentration and x-ray intensity
- Goldstein 1992, Armstrong 1995

## $\Phi(\rho-z)$

- based upon depth profile (tracer) experiments and simulations
- PROZA, PAP, XPP, XPHI, PRZ
- Pouchou and Pichoir 1991, Brown 1991, Packwood 1991, Armstrong 1995



# Correction models in TEM

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K factor

Cliff Lorimer

- JEM 2100, JEM 2010F, ARM 200F

$\zeta$  factor

Monte Carlo simulation

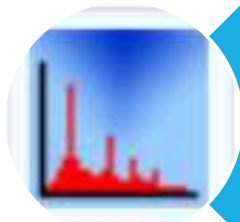
# Microscopy software



## CASINO

- Free Monte Carlo simulation

<http://www.gel.usherbrooke.ca/casino/What.html>



## Win X-ray

- Free Monte Carlo simulation

<http://montecarlomodeling.mcgill.ca/software/winxray/winxray.html>



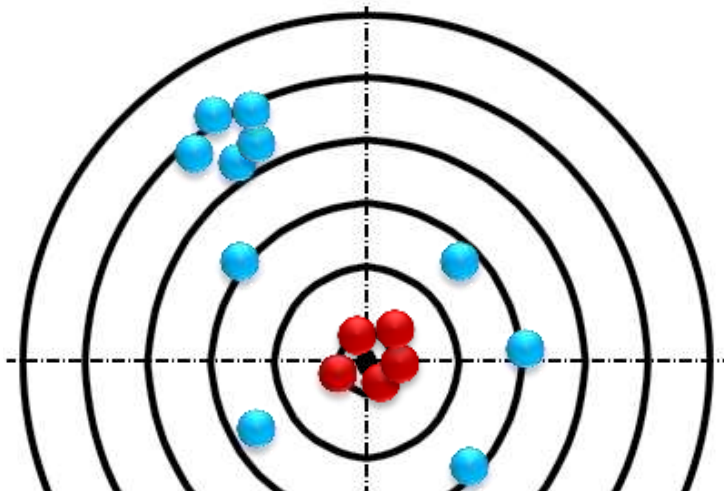
## NIST

- Free EDS software

<http://www.cstl.nist.gov/div837/837.02/epq/dtsa2/index.html>

# Accuracy and Precision

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Precise, not accurate

Accurate, not precise

**Improving Accuracy? Standardize with suitable standard material!**

Then the microanalysis system after standardization should give accuracy of approximately  $\pm 2\%$  relative, or better, for most elements.

**Problems with light elements!**

Light element analysis Boron, Carbon, Nitrogen and Oxygen will be significantly improved to accuracies of a few % although light element analysis is always less reliable due to variations in sample conditions.

# What is the error?

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## Random errors include:

- random nature of X-ray generation and emission
- instrumental (random) instability
- operator inconsistency
- sample surface roughness
- interaction volume intersecting two phases
- secondary fluorescence from hidden (below surface) phases

## Systematic errors include:

- instrumental instability
- inappropriate matrix correction
- poor electrical ground of either standard or unknown
- beam change
- difference in peak shape/position (standard vs unknown)
- peak or background interference

# EDS precision

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Assuming the sample is **conductive, homogeneous, stable and flat** and the appropriate measuring **conditions** have been selected

Then the microanalysis system, as received, should give

- Accuracy of approximately  $\pm 5\%$  relative, or better, for most elements
- For example if an element is measured in the sample to be 50 wt % then the accuracy should be within  $50 \pm 2.5$  ( that is in the range 47.5 to 52.5 wt%)
- But Light element analysis with Boron, Carbon, Nitrogen and (O) is likely to be far less accurate

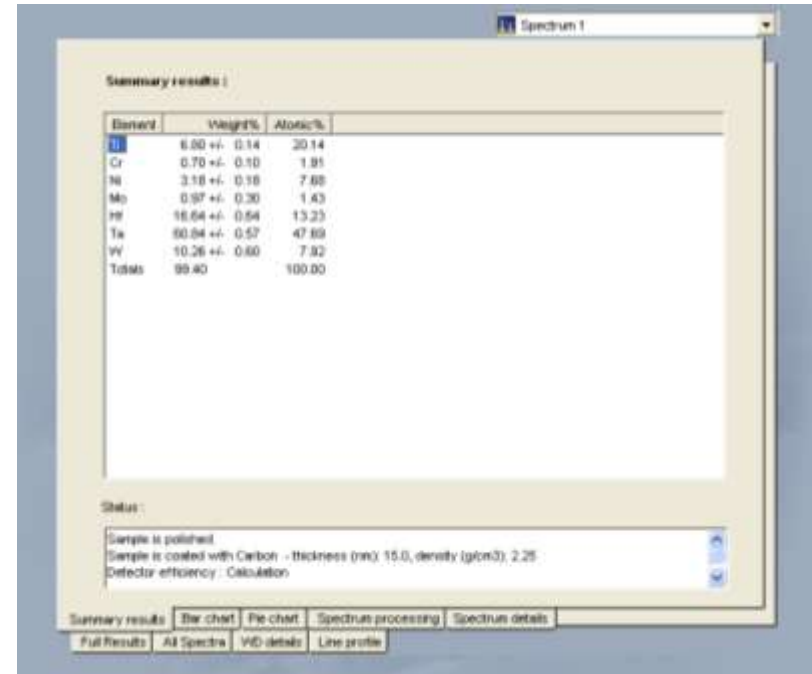
*However, we must be much more careful about the term accuracy.  
In Inca quant, the  $\pm$  column is the precision of the analysis!*

# Summary results

The  $\pm$  error originates from the counting statistics of the peak!

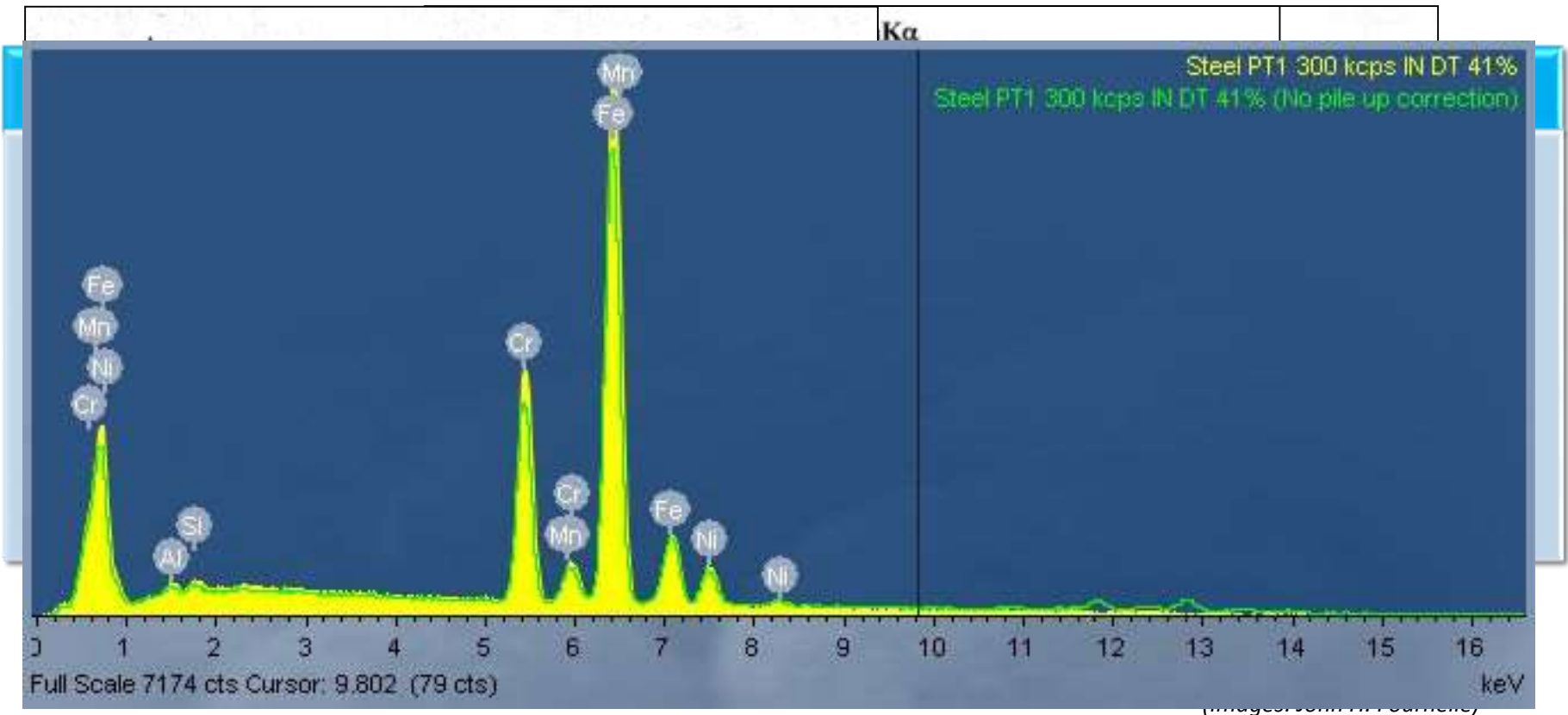
A measure of precision shown as  $1\sigma$  confidence limit

By increasing the number of counts statistics may improve, but we may also increase systematic errors



# Spectral artifacts

Several artifacts can be produced in EDS X-ray spectra because of the way the X-rays are detected and processed. Three common artifacts are:





# Set the acquisition setup

