SEM Microanalysis

EDS, WDS, EBSD

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Energy Dispersive X-ray Spectroscopy (EDS)

- **E**nergy **D**ispersive X-ray **S**pectroscopy
- **E**nergy **D**ispersive **X**-ray Spectroscopy
- **E**nergy **D**ispersive **A**nalysis of **X**-rays

- Wavelength Dispersive X-ray Spectroscopy

- Electrons in, X-rays out

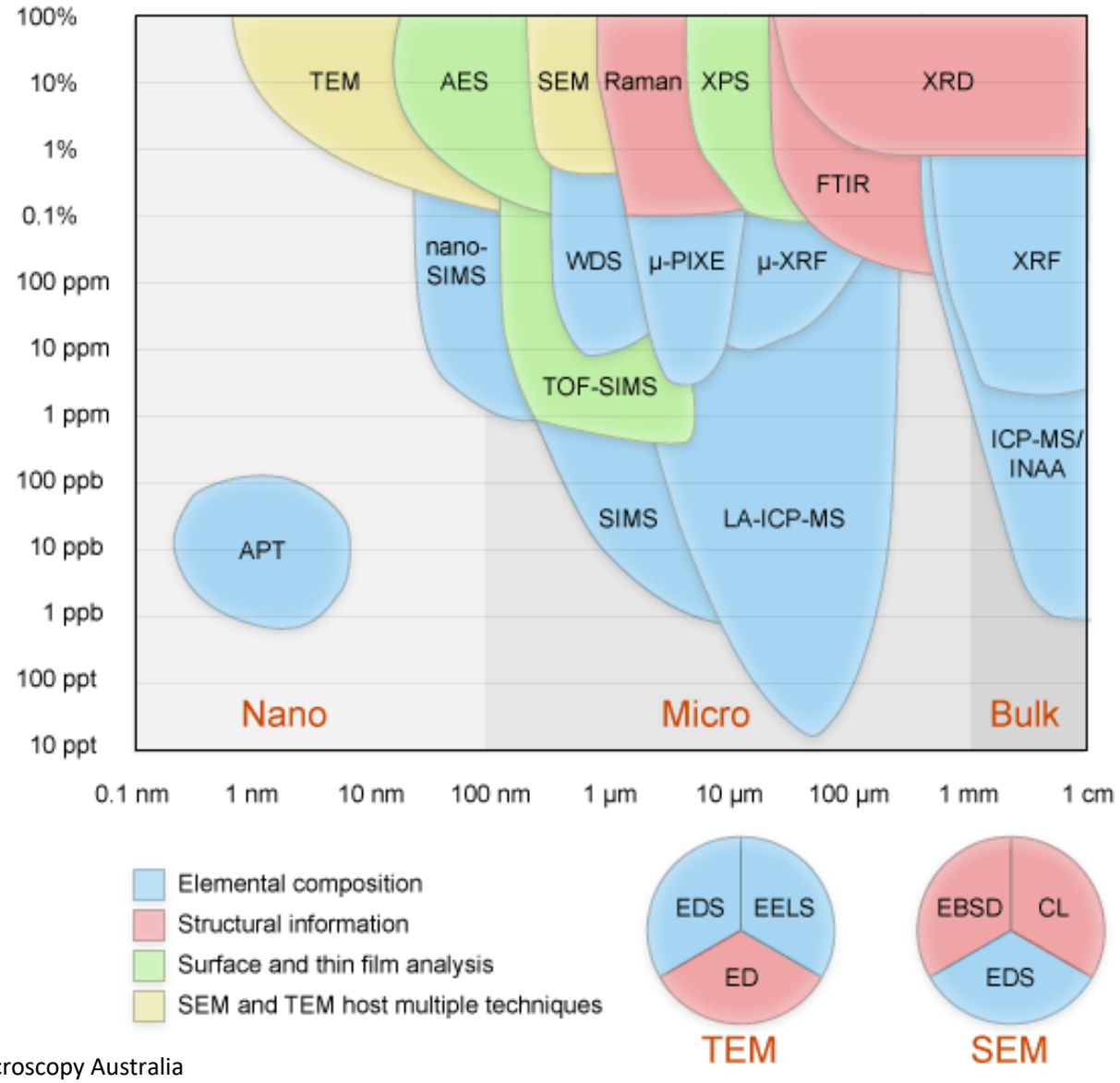
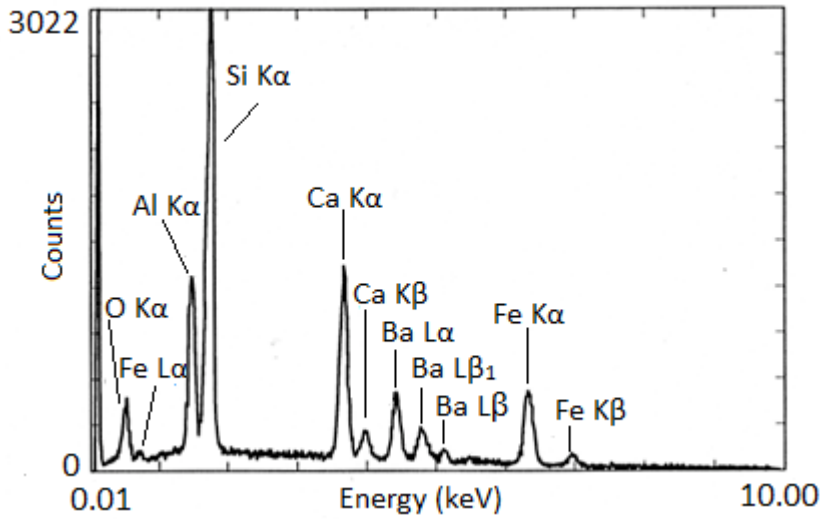
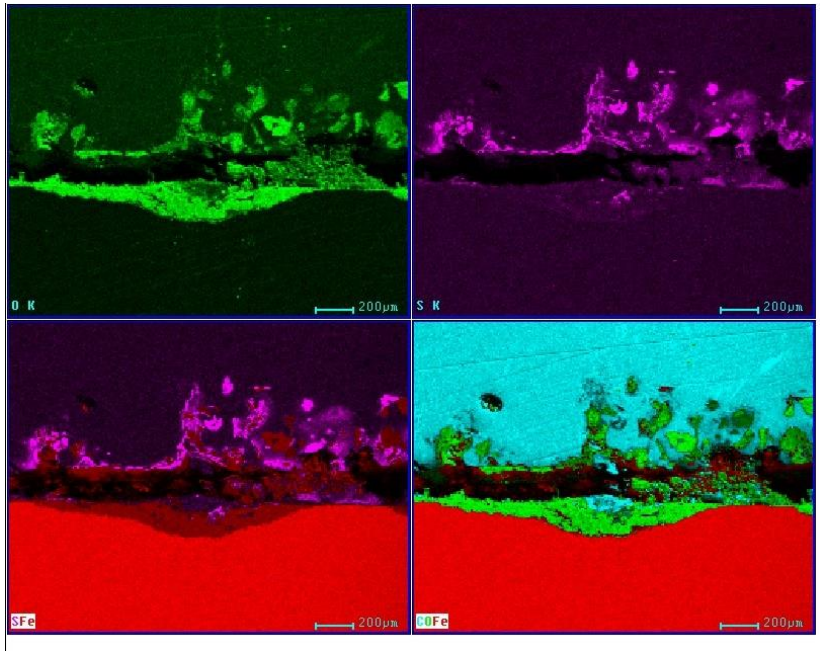


Image from My Scope – Microscopy Australia

Qualitative EDS

- Identify peaks based on energy
- Mapping/linescans
- Software standards database





Quantitative EDS

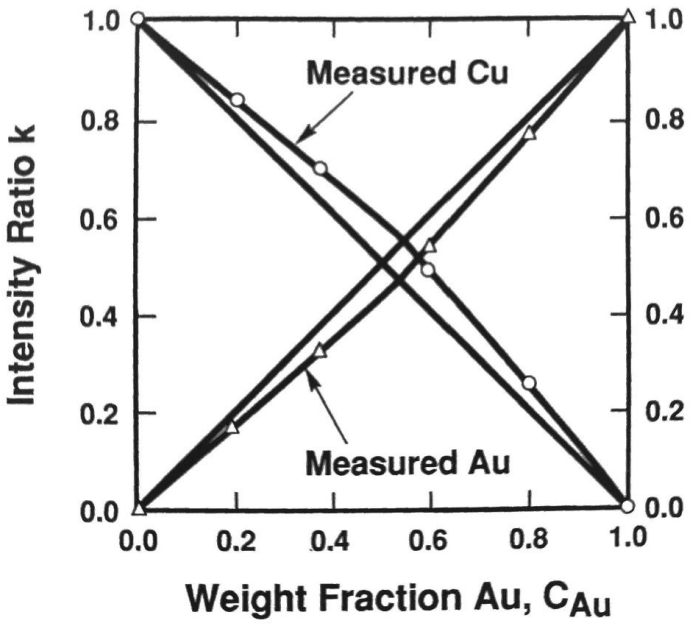
- K ratio
  - $K = I_{sample}/I_{standard}$
  - $C_{sample} = Kc_{standard}$

- ZAF correction (matrix corrections)
  - Z – Differences in atomic number
  - A – differences in absorption of X-rays
  - F – differences in production of secondary x-rays, or x-ray fluorescence

- Sample prep – Flat, homogeneous, conductive, non-porous

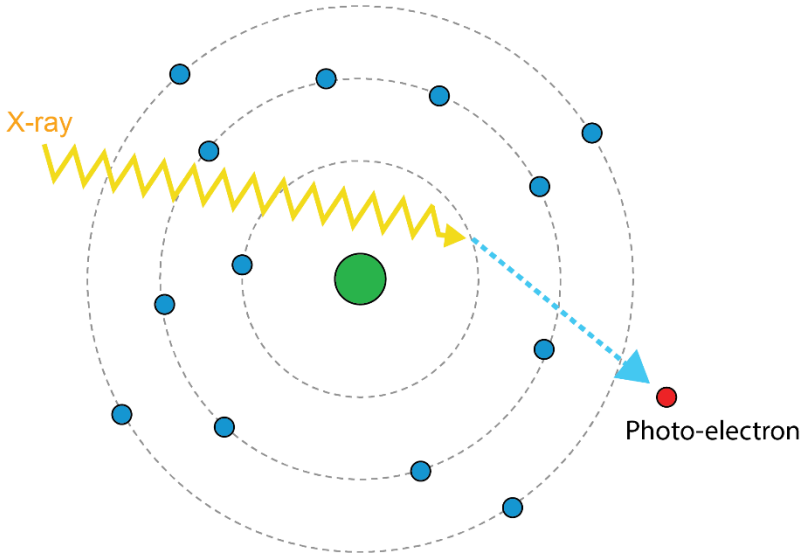
Z Correction

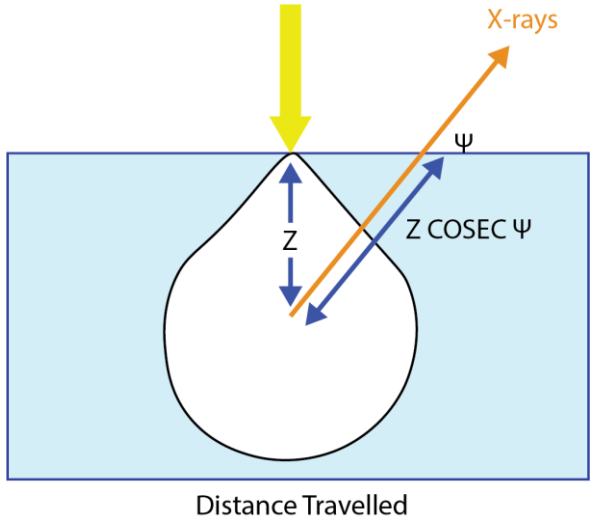
- Backscattering
  - Higher mean atomic number = higher backscatter yield (BSE do not general X-ray)
  - If mean atomic number of the sample is higher than standard, X-ray intensities will be different
- Stopping Power (energy loss)



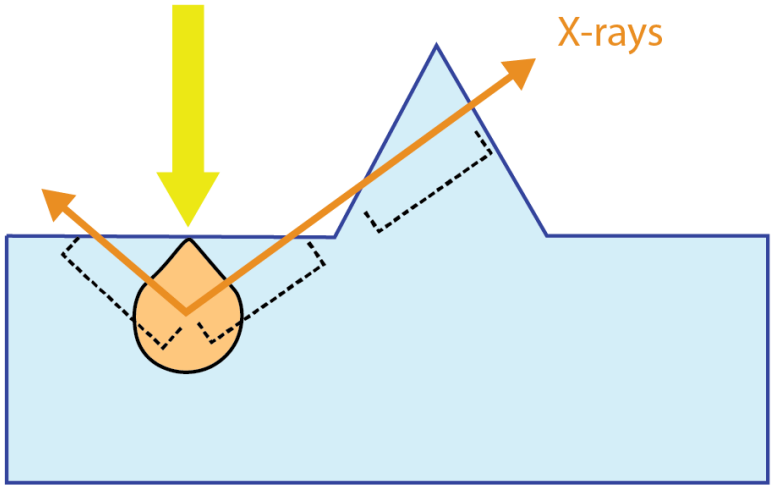
Absorption

- X-ray absorbed by sample
- Energy x-ray equal to ionization energy of an electron shell of another atom
- Depends on
  - Other elements ionization energy in the sample
  - Distance travels through sample before it escapes
- Correction for low Z elements = large
- Corrections for high Z elements = small

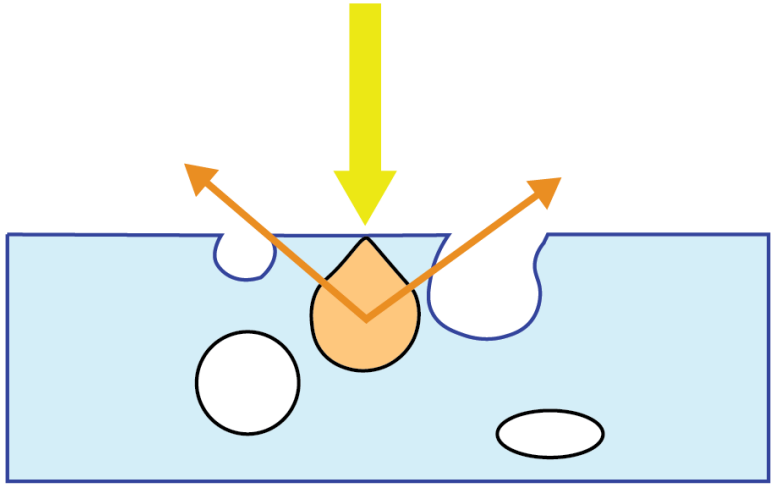




Absorption



X-ray on right under corrected for absorption

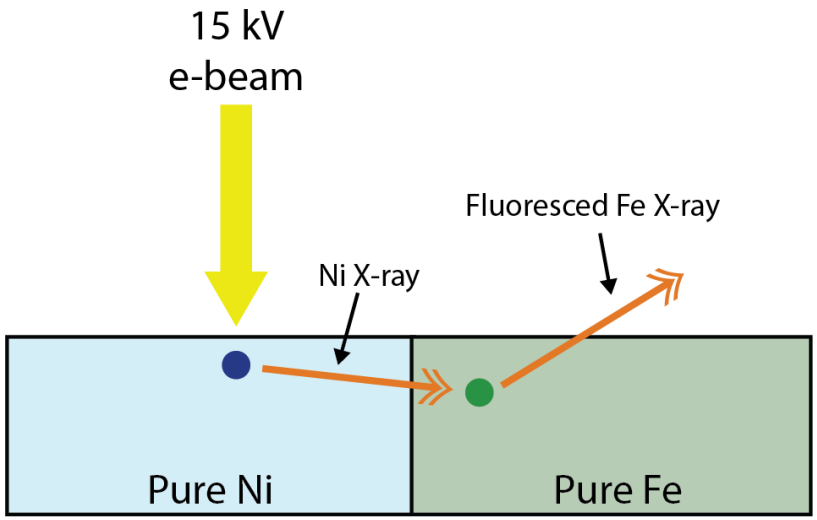


X-rays over corrected for absorption

*Light elements strongly absorbed by the specimen.

Fluorescence

- X-ray traveling through sample has energy $E_x > E_c$ of element B
  - X-ray absorbed by atom B
  - Atom B de-excites
  - Characteristic X-ray emitted from atom B



$E_{NiK\alpha} = 7.47$ kV

$FeK\alpha \rightarrow E_c = 7.11$ kV

$$C^{smpl} = Kc^{std}\, ZAF^{smpl}/ZAF^{std}$$

Standards and Calibration

- Measure beam current or x-ray count rate on pure element
- Measure spectra from standards for element standards under same operating conditions

- AZtec has standard database
- Best that standards measured under same conditions

*EPIC has standards for most pure elements/materials. The best standards, if not pure standards, have similar compositions as the sample.

Mapping Artifacts

- No correction for background or overlapping peaks
  - Higher Z phases give higher background counts
- Aztec TrueMap
  - Differentiates peak overlaps and removes backgrounds

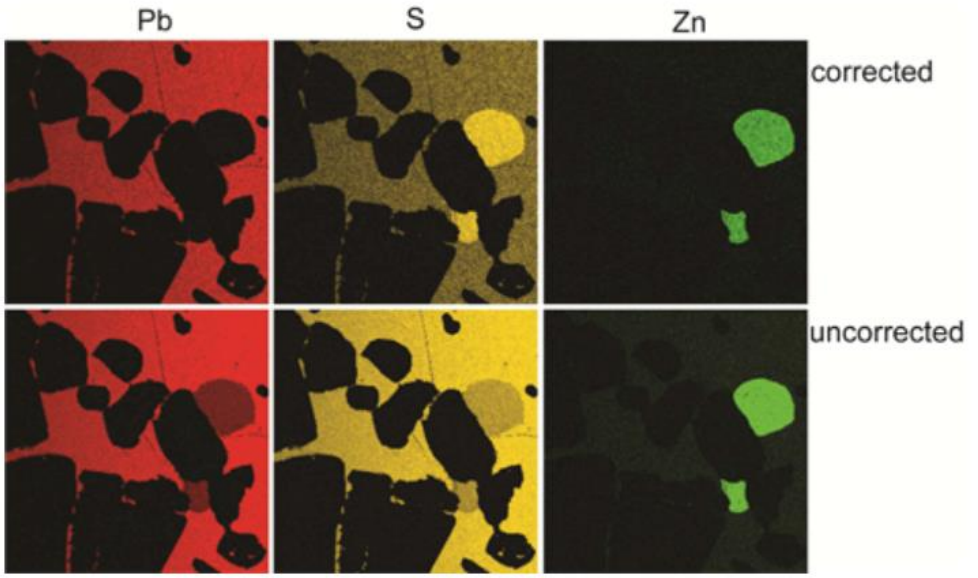
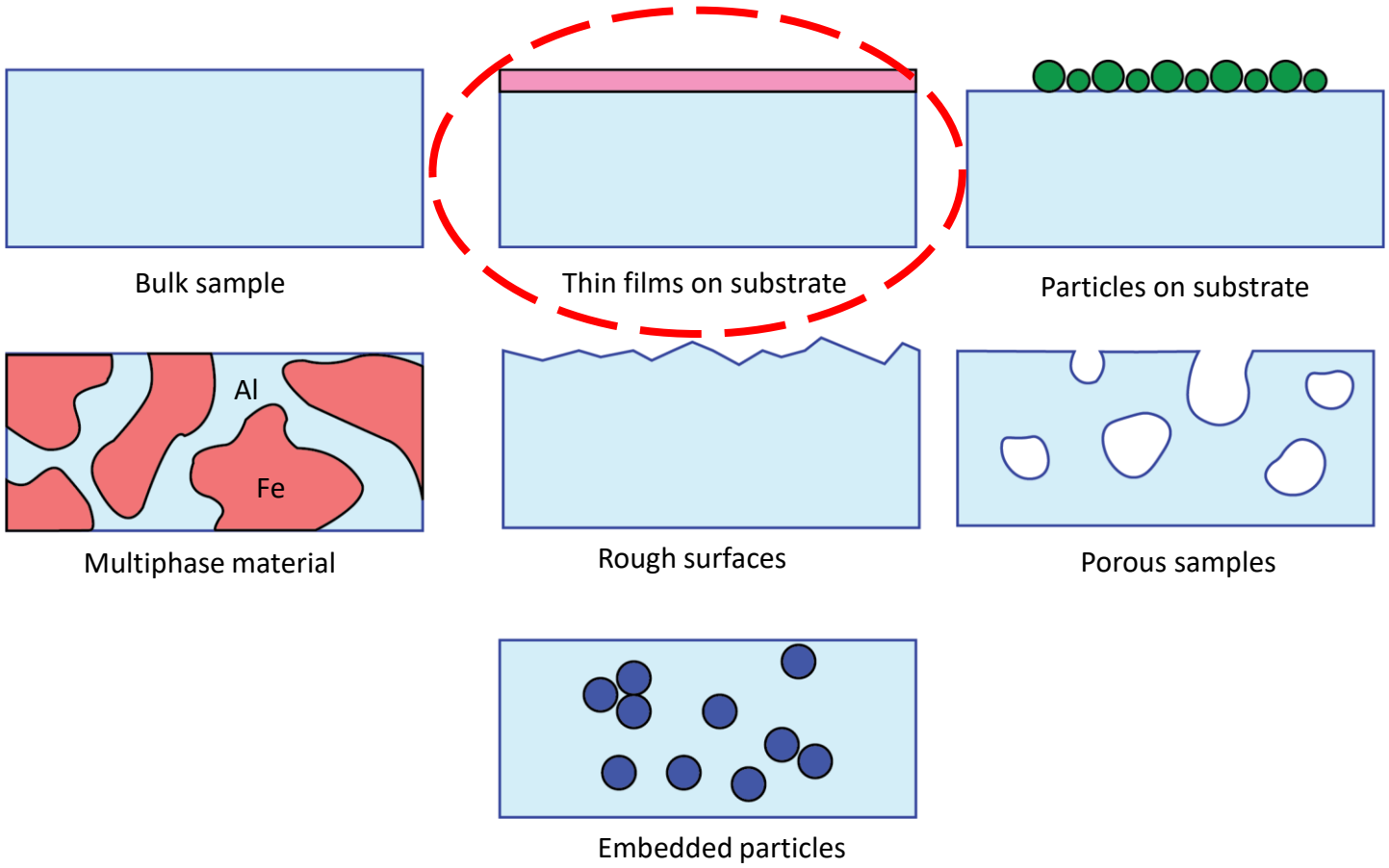


Figure: Artifacts can result if the element maps are not corrected for overlapping Characteristic X-ray peaks.

The good, bad and ugly of SEM-EDS

- Fast qualitative analysis, mapping
- Quant accuracy
  - With standards and 'good' sample – 1-2% for major constituents
  - Standardless analysis – 10-15% for major constituents
- Spatial resolution
  - Beam energy-dependent – up to several microns
  - Low Z: 1-5 μm^3
  - High Z: 0.2 – 1 μm^3
- Energy resolution
  - >125 eV


Bulk sample
Thin films on substrate
Particles on substrate
Al
Fe
Multiphase material
Rough surfaces
Porous samples
Embedded particles

AZtec LayerProbe

- Thin film and layered sample
- Thickness and composition (2 nm – 2000 nm)
- Model defining layers composition and thickness
- System suggests operating conditions
- Experimental data compared to theoretical spectrum based on model
- Standards – improve accuracy of data

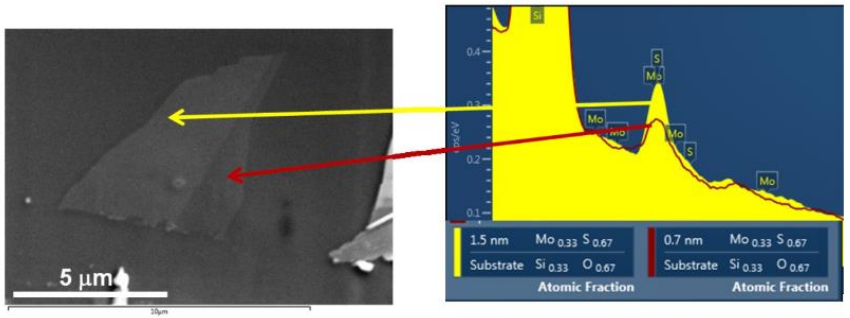
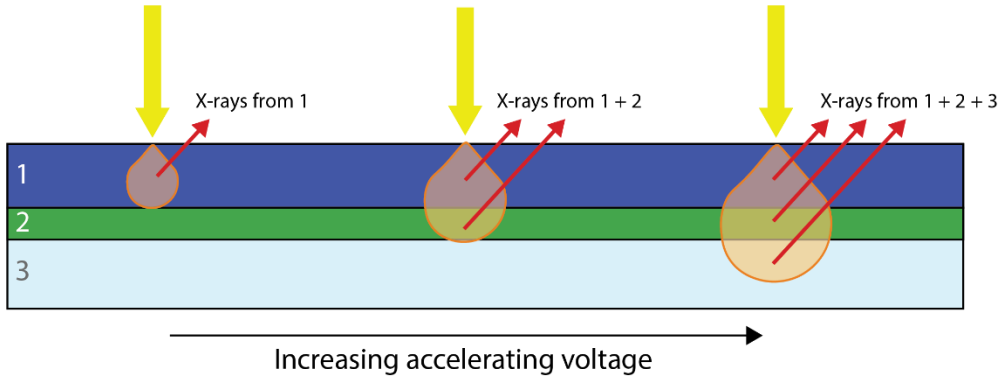


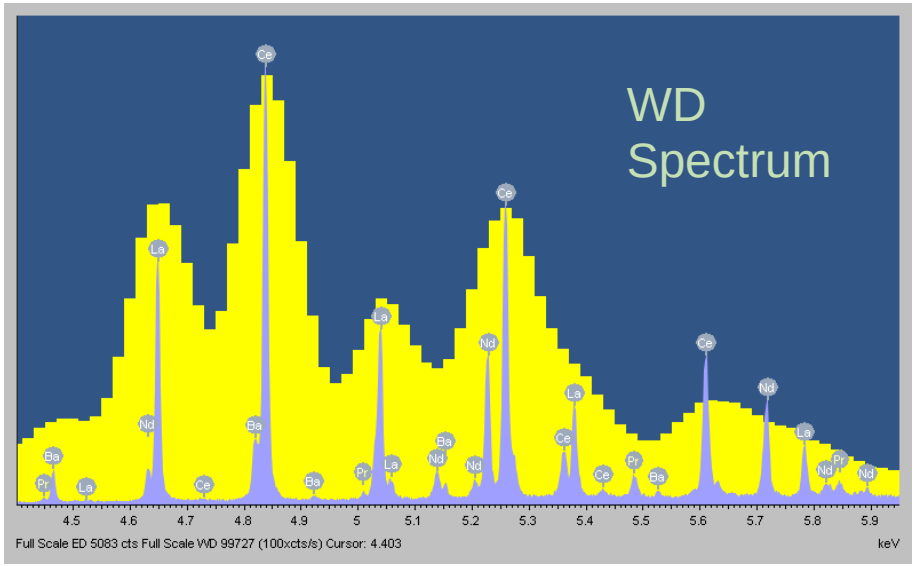
Figure 1. A flake of MoS_2 on an SiO_2 substrate with EDS spectra and resulting layer thicknesses.

Lang et al., 2015

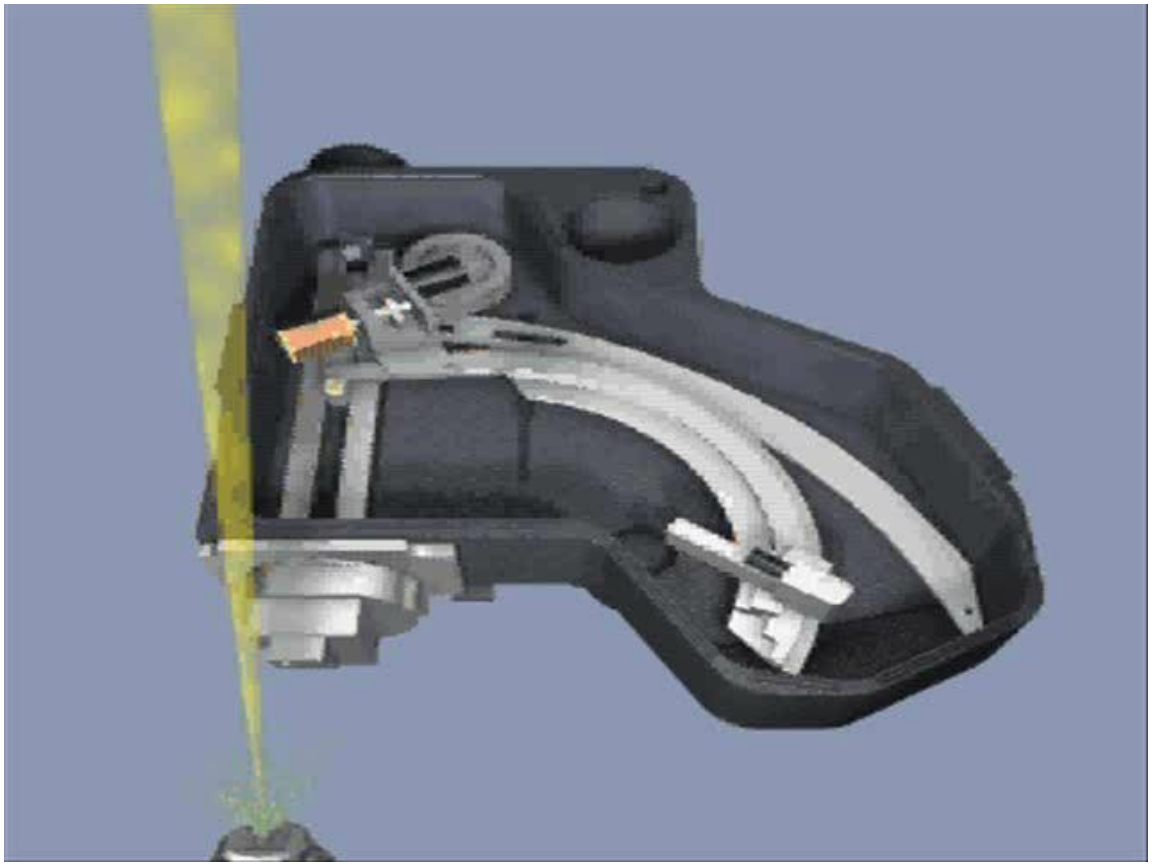


Wavelength Dispersive X-ray Spectroscopy

- Micro-analysis ~10x more sensitive than EDS
  - Detection limit 0.01%
- Energy resolution ~13 eV
  - Separate peak overlaps
- Higher count rates on element
- High sensitivity for light element detection
- Standard based analysis



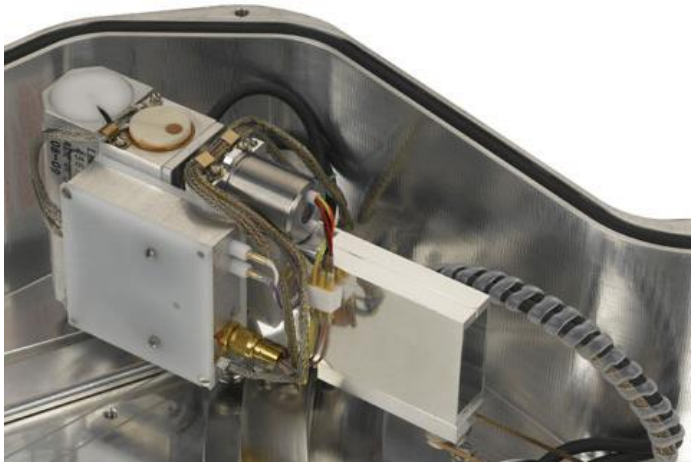
- Powder Sample containing CeLaNdBaPr
- Lots of heavily overlapped peaks in a small spectral range

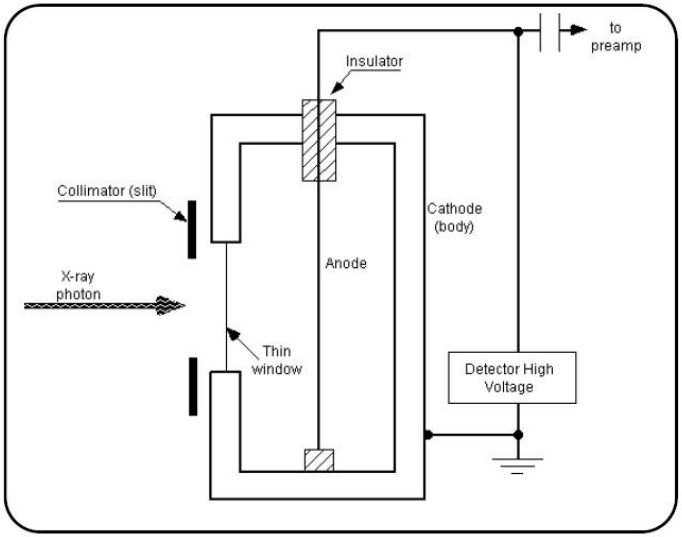


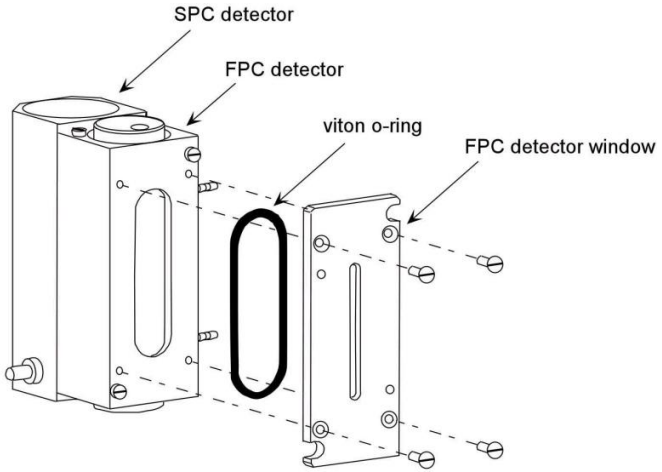
- Separating characteristic x-rays by X-ray diffraction using a crystal of known lattice spacing d
- The angle of diffraction needed to collect X-rays of a particular wavelength is predicted using Bragg's Law

WDS Detectors

- Flow Proportional Counter (FPC)
  - Flowing P-10 (10% CH_4 balance Ar)
    Low Energy x-rays (<Fe Kα)
- Sealed Proportional Counter (SPC)
  - Sealed Xe gas
    Good for high Energy X-rays (>Fe Kα)
- Positioned in Series so high energy X-rays not measured by FPC pass to SPC.







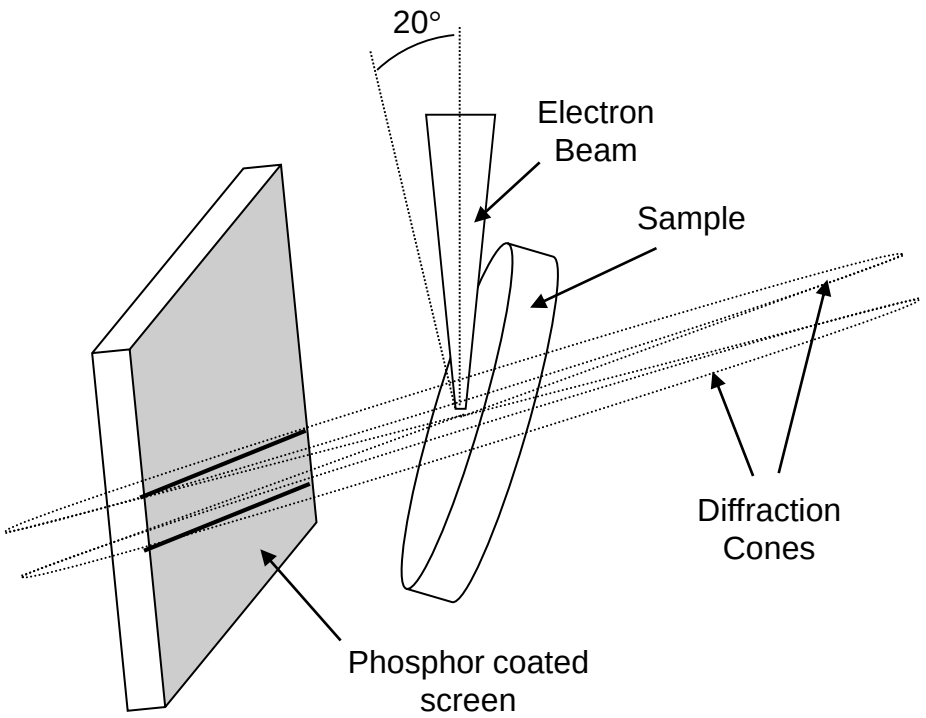
WDS/EDS

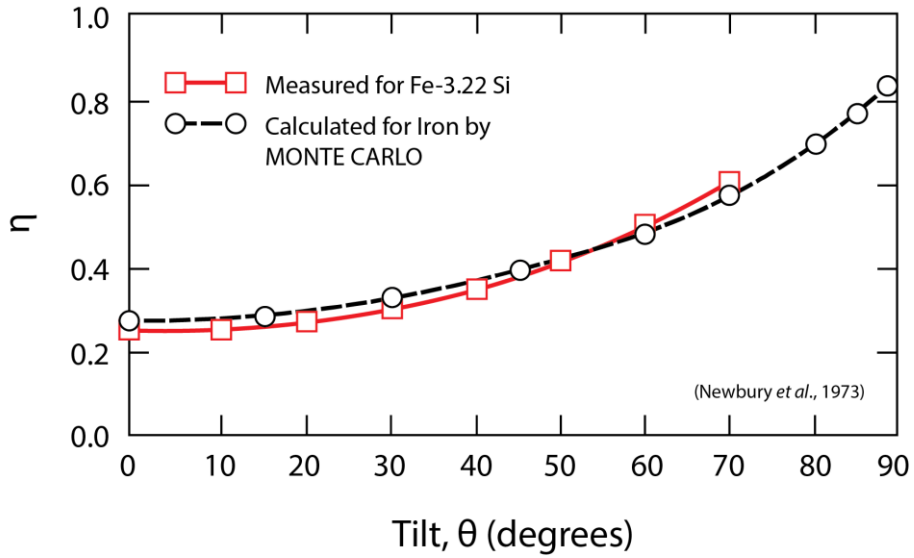
- Extends Analytical capability of SEM close to that of an Electron Microprobe

- SEM with both ED and WD combines their strengths
  - ED for major elements
    - Fast analysis
    - Sample Overview
  - WD for overlaps and minor/trace elements
    - High Resolution Analysis
    - High Sensitivity Quantitative Analysis

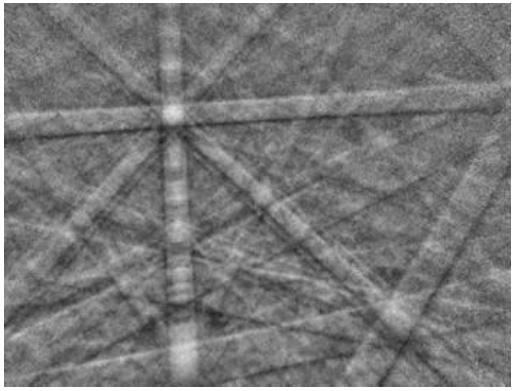
Element	Data type	Weight%	Atomic%
Na	ED	2.28 +/- 0.17	2.09
Al	ED	9.26 +/- 0.16	7.23
Si	ED	31.27 +/- 0.24	23.46
K	ED	10.10 +/- 0.16	5.44
Ca	ED	0.20 +/- 0.08	0.11
Fe	WD	0.07 +/- 0.01	0.03
O		46.82 +/- 0.27	61.65
Totals		100.00	100.00

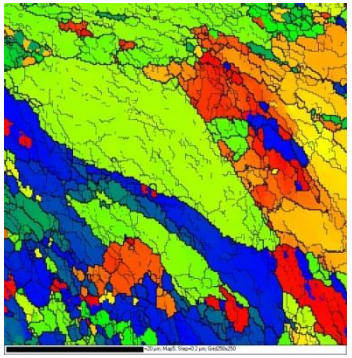
Electron Backscatter Diffraction (EBSD)

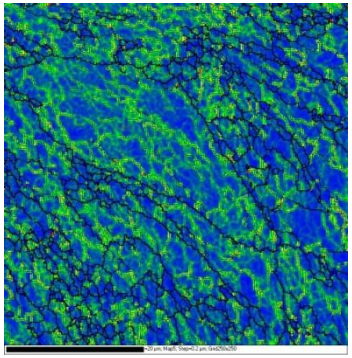


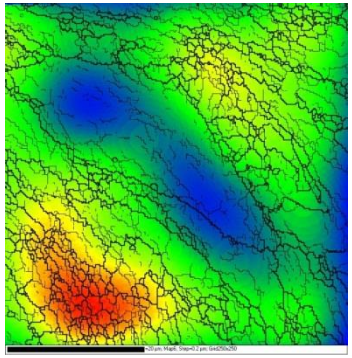


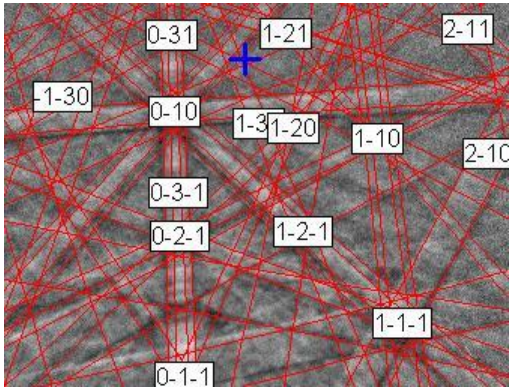
Electron Backscatter Diffraction (EBSD)

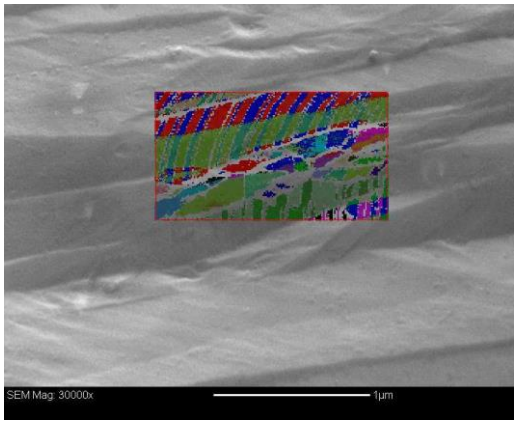


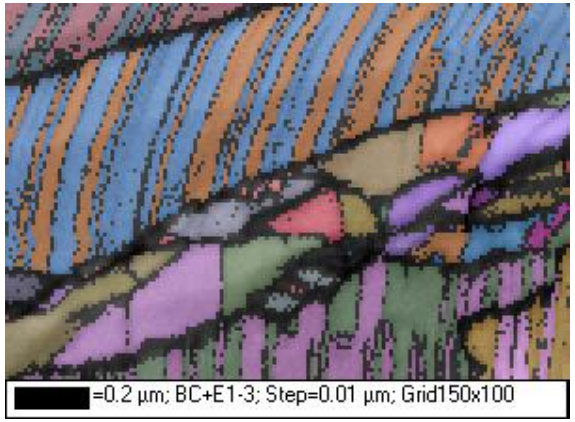












Specimen requirements for EBSD

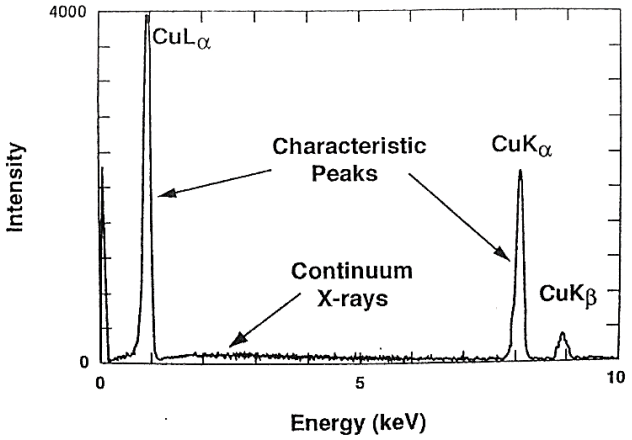
- Flat (<1 µm)
- Pristine surface – free of mechanical damage and oxidation
- Known structure(s)
- Stable preparation (no carbon tape)
- Conductive (or use VP-SEM)

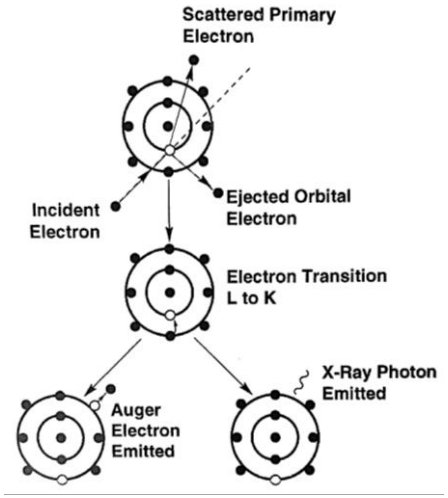
Questions?

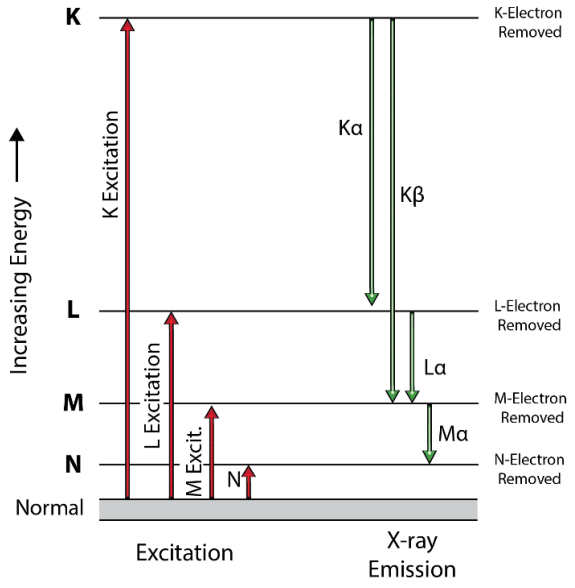
Extra Slides

X-ray Emission

- Large λ – low spatial resolution in SEM
  - Thin film
  - Low E_o
- Characteristic X-rays
  - Inner shell ionization – element specific energy
- Bremsstrahlung
  - "Braking radiation" – x-ray background

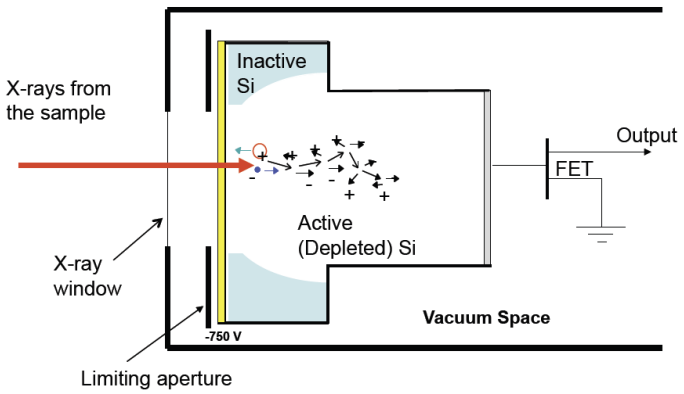


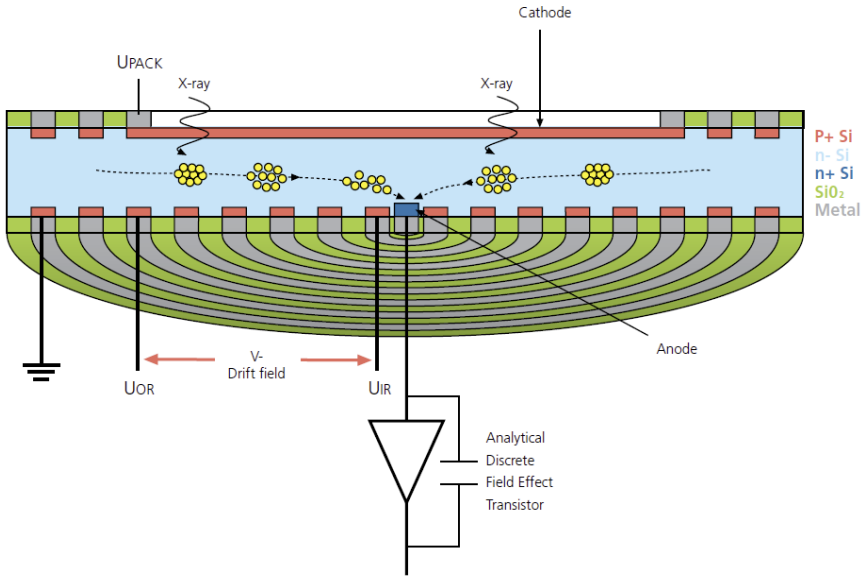




EDS Detectors

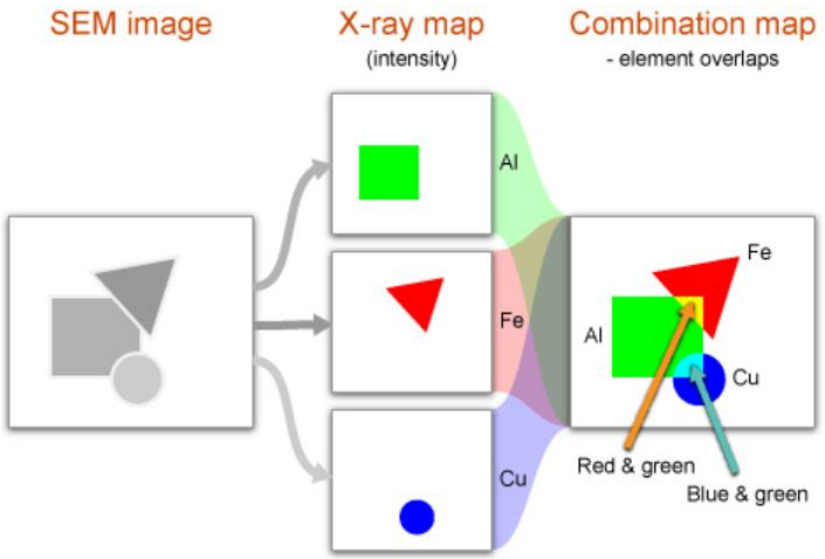
- Si(Li)
  - LN2 cooled
  - Limited count rates
  - Limited active area
- SDD
  - Peltier cooled
  - High count rates
  - Large area





EDS Mapping

- ED spectrum for each pixel
- Pixel dwell time faster than point analysis
  - Better for major elements
- Acquisition time depends on map pixel resolution
  - Long maps require no beam current shift
  - Beam stability harder to maintain on cFEG (Hitachi 4800/8030)



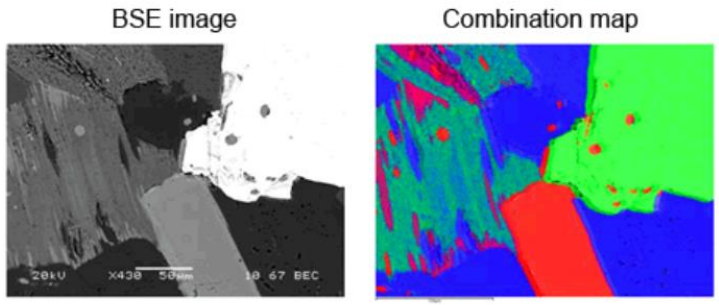
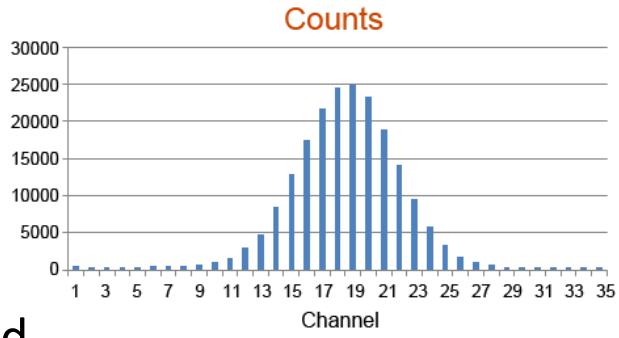
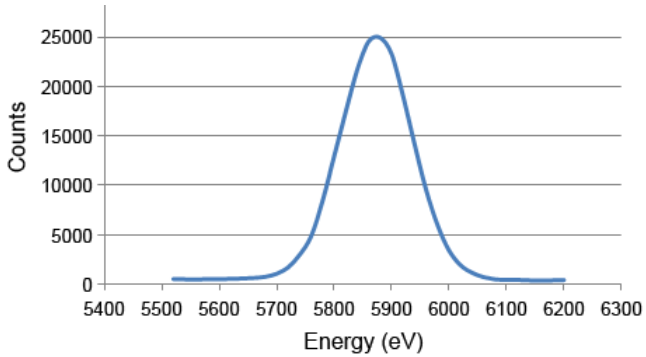


Figure: A combination map for phases in a sample of granite.

EDS Spectra

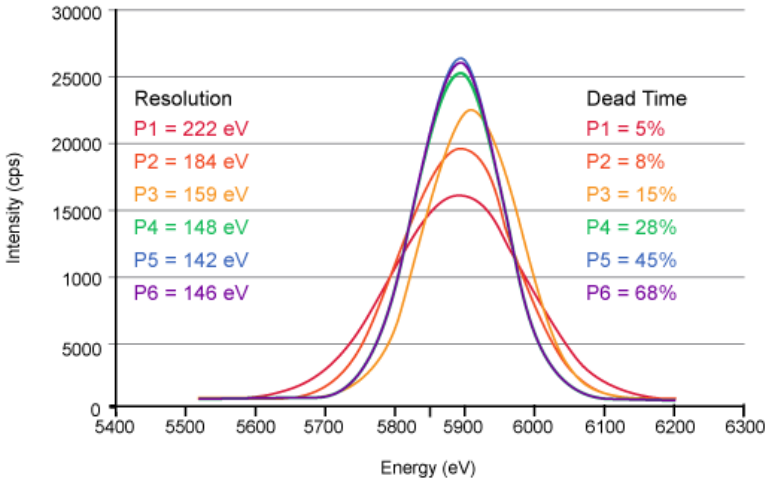




- Energy range of spectrum divided into channels (1024, 2048, 4096 on AZtec)
  - Energy width changes depending on energy range and number of channels
- Intensity vs. Energy
- Peaks for each characteristic x-ray of elements in sample

Spectral Artifacts

- Spectral resolution
  - FWHM – Width at half peak height
  - Process time – improve spectral resolution
- Peak Overlaps
- Escape peaks
- Sum peaks

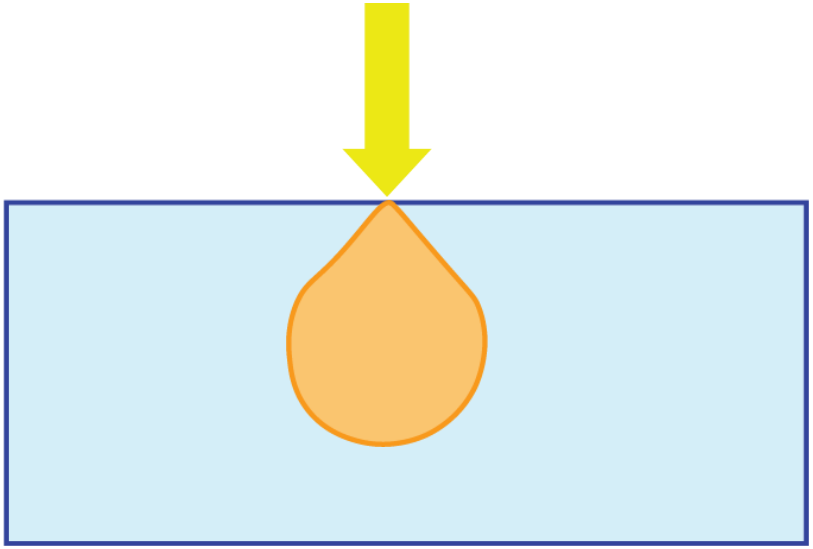


Ideal specimen satisfies 3 assumptions:

1. Intensity differences between standard and element due to compositional differences and not surface roughness, size, shape, and thickness (“geometric factors”)

2. Specimen is homogeneous over full extent of interaction volume.

3. Specimen is stable under beam and not altered by beam interaction (e.g. polymers and biological samples)



- Information from WDS and EDS combined in a single result
  - Uses same matrix correction algorithm for both EDS and WDS data

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