X-Ray Energy Dispersive Spectroscopy
In the Electron Microscope

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Micro-Analytical Capabilities
EPMA or SEM

0.1 μm

Volume excited ~ 1 μm³

AEM

10 nm

Volume excited ~ 10⁻⁵ μm³

Thermionic source

100 nm

Volume excited ~ 10⁻⁸ μm³

FEG source

1 nm

10 nm

Spatial resolution ↑ Analytical sensitivity ↓

1 Å?
High Spatial Resolution Quantitative Microanalysis

ANL AAEM #960712c

304 SS GB Composition Profile

Relative Composition Cr, Ni

Relative Composition Fe

10 nm
Brief Review of X-ray Generation

Instrumentation: Detector Systems

Instrumentation: EM Systems

Data Analysis and Quantification:

Additional Topics
The Emission Process:

1-Excitation
2-Relaxation
3-Emission
Schematic Diagram Illustrating Sources of Signals Resulting from Inelastic Scattering
Experimental XEDS, XPS, and EELS data from the Copper L shell. Note the differences in energy resolution, and spectral features.
Nomenclature for Principle X-ray Emission Lines

Characteristic X-ray Line Energy = $E_{\text{final}} - E_{\text{initial}}$

Recall that for each atom every shell has a unique energy level determined by the atomic configuration for that element.

$\therefore$ X-ray line energies are unique.
Relative Intensities of Major X-ray Lines

- $K_{\alpha 1} = 100$
- $K_{\alpha 2} = 50$
- $K_{\beta 1} = 15\text{-}30$
- $K_{\beta 2} = 1\text{-}10$
- $K_{\beta 3} = 6\text{-}15$
- $L_{\alpha 1} = 100$
- $L_{\alpha 2} = 50$
- $L_{\beta 1} = 50$
- $L_{\beta 2} = 20$
- $L_{\beta 3} = 1\text{-}6$
- $L_{\beta 4} = 3\text{-}5$
- $L_{\gamma 1} = 1\text{-}10$
- $L_{\gamma 2} = 0.5\text{-}2$
- $L_{\gamma 3} = 6\text{-}15$
- $L_{\gamma 4} = 3\text{-}5$
- $L_{\eta} = 1$
- $L_{\iota} = 1\text{-}3$
- $M_{\alpha 1,2} = 100$
- $M_{\beta} = 60$
Mosley’s Law

\[ \lambda = \frac{K}{(Z - \sigma)^2}, \]
where \( K \) and \( \sigma \) are constants for a given spectral line.

\[ E \text{ (keV)} = K (Z - 1)^2 \]
where \( Z \) is the atomic number and
- \( K = 1.042 \times 10^{-2} \) for the K-shell
- \( K = 1.494 \times 10^{-3} \) for the L-shell
- \( K = 3.446 \times 10^{-4} \) for the M-shell.
Characteristic X-Ray Spectrum
Illustrating KLM lines

As Z increases the Kth shell line energy increases. If K-shell is excited then all shells are excited (Y, Cu, Ba) but may not be detected. Severe spectral overlap may occur for low energy lines.
Electron Excitation also generates Continuum (background) signal
\[ I = C i_b (E_o - E_c)^p, \]

where \( I \) = intensity of the line of interest,
\( C \) = a constant,
\( i_b \) = beam current,
\( E_c \) = critical excitation potential of the line of interest,
\( E_o \) = accelerating voltage (keV),
and \( p = 1.7 \) for \( E_o < 1.7 E_c \) (and smaller for higher values of \( E_o \)).
Energy Range - Continuous Distribution

Maximum = Incident Electron Energy (Least Frequent)
Minimum = $E_{\text{plasmon}} \sim 15-30\, \text{eV}$ (Most Frequent)

Spectral Distribution will reflect this range, modified by detector response function

\[ \lambda_{\text{swl}} = \frac{hc}{E_0}, \]
where $E_0 =$ accelerating voltage.

\[ I_c = i_b \ Z \ \frac{(E_0 - E)}{E} \]
where $i_b =$ beam current, $E =$ energy of interest, and $E_0 =$ accelerating voltage (keV).
Spectral background will be influenced by:
1.) Specimen composition
2.) Detector efficiency
3.) TEM generated artifacts
Instrumentation: Detector Systems

Wavelength Dispersive Spectrometers (WDS)
Energy Dispersive Spectrometers (EDS)
  Si(Li) Detectors
  HPGe Detectors
  Spectral Artifacts of the EDS System
  Detector Efficiency Functions
  Light Element Detectors
Superconducting Calorimeters/Bolometers
Silicon Drift Detectors

Multichannel Analyzers
Energy Dispersive Spectrometers: (Solid State Detector)

Operates on Energy Deposition Principle

- Simple, Nearly Operator Independent
- Large Solid Angles (0.05-0.5 sr)
- Virtually Specimen Position Independent
- No Moving Parts
- Parallel Detection
- Quantification by Standardless or Standards Methods

- Poor Energy Resolution (~ 130 eV)
  - ** SuperConducting Systems (~ 20 eV)
- Poor Peak/Background Ratios (100:1)
- Detection Efficiency Depends upon X-ray Energy
**Wavelength Dispersive Spectrometers: (Diffractometer)**

**Operates using Diffraction Principles (Bragg’s Law)**

- Excellent Energy Resolution (~ 5 eV)
- High Peak/Background Ratios (10000:1)
- Good Detection Efficiency for All X-rays
- High Counting Rates
- Good Light Element Capabilities

- Complex Mechanical Devices, Operator Intensive
- Specimen Height dependant focus
- Moving Components in the AEM
- Limited Solid Angles (<0.01 sr)
- Serial Detection
- Quantification Requires Standards
WDS system in a TEM
EMMA-4 System

Circa 1972
Modern Applications WDS
Valence Band/Electronic Structure Measurements

M. Terauchi, M. Kawana – Tohoku University

Y. Ito – NIU Physics
## Comparison of EDS and WDS Spectrometers

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Wavelength Dispersive</th>
<th>Energy Dispersive</th>
</tr>
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<tbody>
<tr>
<td>Construction</td>
<td>Mechanical Device</td>
<td>Solid State</td>
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<tr>
<td></td>
<td>moving components</td>
<td>no moving parts</td>
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<tr>
<td>Energy Resolution</td>
<td>5 eV</td>
<td>130 eV</td>
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<tr>
<td>Efficiency</td>
<td>( \leq 30% )</td>
<td>100 % (3-15keV)</td>
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<tr>
<td>Input Count Rate</td>
<td>30-50 K cps</td>
<td>10 K cps</td>
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<tr>
<td>Peak/Background*</td>
<td>10000</td>
<td>100</td>
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<tr>
<td>Atomic Number Range</td>
<td>( Z \geq 4 ) (Be)</td>
<td>( Z \geq 11 ) (Na)</td>
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<tr>
<td></td>
<td></td>
<td>( Z \geq 5 ) (B)</td>
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<tr>
<td>Number of Elements</td>
<td>1 per Detector</td>
<td>All in Energy Range</td>
</tr>
<tr>
<td>Solid Angle</td>
<td>0.001-0.01 sr</td>
<td>0.02-0.3 sr</td>
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<tr>
<td>Collection Time</td>
<td>Tens of Minutes</td>
<td>Minutes</td>
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<tr>
<td>Beam Current</td>
<td>High Stability Required</td>
<td>Low Stability Required</td>
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<tr>
<td>Detector Stability</td>
<td>Good Short Term</td>
<td>Excellent</td>
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<tr>
<td>Spectral Artifacts</td>
<td>Negligible</td>
<td>Important</td>
</tr>
<tr>
<td>Operation</td>
<td>Skilled (?)</td>
<td>Novice</td>
</tr>
</tbody>
</table>

* Values depend on definition, specimen, and operating conditions
Fabrication of Si(Li) Crystals
How is the X-ray Signal Measured?

Properties of Intrinsic Silicon

Attaching HV electrodes to the two surfaces the Si(Li) crystal will act similar to a capacitor with free charges developing on the electrical contacts.

Charge developed in the crystal is $N = E/\varepsilon$. 
($E$= x-ray Energy, $\varepsilon = 3.8$ eV/e-h pair)

$\Rightarrow$ 10 kV X-ray produces ~2630 electrons
= $4.2 \times 10^{-16}$ Coulombs.
Solid State Detector Construction

Using a simple absorption model, define the relative detector efficiency $\varepsilon(E)$ by the following procedure:

$$ I_T = I_o \exp(-\mu x) = I_o \exp(-\left[\frac{\mu}{\rho}\right]\rho x) $$
Calculated Si(Li) Detector Efficiency by Active Layer Thickness & Window Type

\[ \varepsilon(E) = \frac{I_\text{a}}{I_0} = \exp\left( -\sum_{i} \left( \frac{\mu(E)}{\rho} \right)_i \cdot \rho_i \cdot t_i \right) \times \left\{ 1 - \exp\left( -\left( \frac{\mu(E)}{\rho} \right)_j \cdot \rho_j \cdot t_j \right) \right\} \]

- \( \mu(E)/\rho \) = mass absorption coefficient for energy \( E \);
- \( \rho \) = density;
- \( t \) = layer thickness

Detector Parameters
- Be: Window: 8 Microns
- Au Contact: 250 Å
- Si Dead Layer: 1000 Å
- Si Active: 3 mm
- Si Active: 5 mm
Windowless vs. Conventional Detectors
Comparison of XEDS measurement on NiO using a Windowless versus Beryllium Window detector

Note the enhanced detection efficiency below 1 keV for the WL detector. Both spectra are normalized to unity at the Ni Kα Line (7.48 keV)
Windowless vs. Conventional Detectors

K Shell Spectra using Windowless Detector
Boron -> Silicon

L Shell Spectra Using Windowless Detector
Titanium -> Zinc
Note Potential Overlaps with K shell Lines
Comparision
Light Element
Spectroscopy
Resolution
XEDS

316 SS Matrix

TiN in 316 SS

OK
CrL FeL

NiL

NK
TiL
ε = 3.8 eV (in Si) / 2.9 eV (in Ge)

-> But the electrons produced are in a Poisson Distribution this gives rise to a spread in the number of electron

F = Fano Factor ~ 0.1
E= X-ray Energy
Noise = Electronic Noise (mainly in the FET)

Nominal FWHM Values in Modern Si(Li) Detectors:

O Kα (0.52 keV) = 80 to 100 eV
Mn Kα (5.9 keV) = 140 to 160 eV
Mo Kα (17.5 keV) = 210 to 230 eV

Resolution = FWHM = $\sqrt{\text{Noise}^2 + 2.35^2 \epsilon FE}$
Comparison of EDS and WDS Spectra

EDS Spectrum
NBS glass K252

WDS Spectrum
NBS glass K252
Resolution will also vary with Microphonic & Electronic Noise, and Counting Rate!

WL & UTW detectors are particularly sensitive to low energy noise and microphonics. Observe the changes in the spectra (width of the peaks)
The Multi-Channel Analyzer
Silicon Drift Detector

Both sides are reversed biased.
Electrons travel along the central potential well.
Radial drift gradient sweeps electrons to the Anode.

~ 0.3 mm

X-rays
Detector Area = 50 mm²
Peltier Cooled -> No LN₂
Low Capacitance (250 fF)
Silicon Drift Detector Construction

$\Omega_{\text{ANL}} \sim 0.41 \text{ sr}$
Resolution vs Count Rate

Resolution vs Count Rate for Si Ka, Cu Ka, and Mo Ka with Tc = 1 μsec.
Count Rate = ~ 200 Kcps
Time = 100 sec
Integral = 20,000,000 counts!

Mo-Si/Cu Slot Grid
Dead Time vs Count Rate

Comparing SDD vs Si(Li) @ Eo = 300 keV

Dead Time (%) vs Input Count Rate (Kcps)
UTW Comparison Si(Li) vs SDD
Instrumentation: AEM Systems

The AEM as a system
Spectral Artifacts in the AEM
  Uncollimated Radiation
  Systems Peaks
  Artifacts at High Electron Energy
Specimen Contamination & Preparation
Optimizing Experimental Conditions
Spectral Artifacts in the AEM
Uncollimated Radiation: The Hole Count

Specimen and Goniometer Stage

Upper Objective Pole Piece

Objective Aperture

Lower Objective Pole Piece

Ni4Mo
Hole Count
• Stnd C1/C2 Apertures

Ni K
Mo L
Fe K
Ni L
Mo K

Energy (keV)

Intensity

15000
10000
5000
0
0
5
10
15
20
3000
2000
1000
0
0
5
10
15
20

Intensity

X-rays
Electrons

Fixed
First Condensor Aperture
Variable
Second Condensor Aperture

Specimen
Spectral Artifacts in the AEM
Uncollimated Radiation Solutions
Spectral Artifacts in the AEM

Hole Count Effects: Modified C₁ and C₂
Apertures

Hole Count Effects: Modified C₁ and C₂ & Non-Beam Defining Apertures

Specimen

Ni₄Mo Specimen
•Thick C₁/C₂ Apertures

Ni₄Mo Specimen
•Thick C₁/C₂ Apertures
•Non-Beam Defining Aperture

Ni L Mo L Ni K Mo K Fe K
e⁻

0 5 10 15 20
Energy (keV)

0 1000 2000 3000
Intensity

0 500 1000 1500
Intensity

0 5000 10000 15000
Intensity

0 5000 10000 15000
Intensity

0 500 1000 1500
Intensity

0 5 10 15 20
Energy (keV)
Optimizing Experimental Conditions

Choice of X-ray Line
  K- series
  L- series
  M- series

Detector/Specimen Geometry
  Elevation Angle
  Solid Angle

Detector Collimation

Choice of Accelerating Voltage
  Relative Intensity
  Peak/ Background
  Systems Peaks/Uncollimated Radiation

Choice of Electron Source
  Spatial Resolution
  Tungsten Hairpin
  LaB$_6$
  Field Emission
Radiative Partition Function \((\Gamma)\) governs the relative intensities
Nominal values (varies slowly with atomic number)

<table>
<thead>
<tr>
<th>K Shell</th>
<th>L Shell</th>
<th>M Shell</th>
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<tbody>
<tr>
<td>(K_{\alpha 1}) = 100</td>
<td>(L_{\alpha 1}) = 100</td>
<td>(M_{\alpha 1,2}) = 100</td>
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<tr>
<td>(K_{\alpha 2}) = 50</td>
<td>(L_{\alpha 2}) = 50</td>
<td>(M_{\beta}) = 60</td>
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<tr>
<td>(K_{\beta 1}) = 15-30</td>
<td>(L_{\beta 1}) = 50</td>
<td></td>
</tr>
<tr>
<td>(K_{\beta 2}) = 1-10</td>
<td>(L_{\beta 2}) = 20</td>
<td></td>
</tr>
<tr>
<td>(K_{\beta 3}) = 6-15</td>
<td>(L_{\beta 3}) = 1-6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_{\beta 4}) = 3-5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_{\gamma 1}) = 1-10</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_{\gamma 2}) = 0.5-2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(L_{\eta}) = 1</td>
<td></td>
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<tr>
<td></td>
<td>(L_{1}) = 1-3</td>
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</table>
XEDS
Collimator
Characteristic X-ray Emission
Angular Dependence (Isotropic Distribution)
Bremsstrahlung Angular Dependence (Anisotropic Distribution)

Detector/Specimen Geometry

Collimator

High Energy

Characteristic ~Isotropic

Continuum
Highly Anisotropic

Low Energy
### Detector/Specimen Geometry

#### TEM

<table>
<thead>
<tr>
<th>Designation</th>
<th>Elevation Angle $\theta_E$</th>
<th>Azimuthal Angle $\theta_A$</th>
<th>Manufacturer</th>
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<tbody>
<tr>
<td>Low</td>
<td>0°</td>
<td>45°</td>
<td>JEOL</td>
</tr>
<tr>
<td></td>
<td>0°</td>
<td>90°</td>
<td>JEOL, FEI, VG</td>
</tr>
<tr>
<td>Intermediate</td>
<td>15-30°</td>
<td>90°</td>
<td>FEI, JEOL, Hitachi, VG</td>
</tr>
<tr>
<td>High</td>
<td>68-72°</td>
<td>0°</td>
<td>Hitachi, JEOL</td>
</tr>
</tbody>
</table>

**Diagram:**
- **e-**: Electron beam
- **Specimen**: Sample for observation
- **Eucentric Height**: Distance from specimen to detector
- **$\theta_E$**: Elevation angle
- **$\theta_A$**: Azimuthal angle
Geometrical / Collection Solid Angle

\[ \Omega = \frac{S}{R^2} = \frac{2\pi \left( a^2 + d^2 - d \sqrt{a^2 + d^2} \right)}{a^2 + d^2} \]

\[ a^* = a \cos(\theta) \]
\[ d^* = d - a \sin(\theta) \]
Geometrical / Collection Solid Angle

\[ \Omega = \frac{S}{R^2} = \frac{2\pi \left( a^2 + d^2 - d\sqrt{a^2 + d^2} \right)}{a^2 + d^2} \]
Comparison of AEM Systems with XEDS Detectors
ANL/UIUC/NU

X-ray Collection Efficiency

X-Ray Photon Energy (eV)

- ANL AAEM
- ANL CM30
- UIUC & ANL
- UIUC
- NU HF2000
Cu? In Steel?
What is the source
Where do Systems Peaks Come from?
Detection of System Peaks
Effects of the Collimator & Stage
Detection & Removal of System Peaks

Removal of Stage System Peaks by use of Beryllium Gimbals

Ge specimen 10,000 in Ge Kα peak in both spectra
Left Standard Single Tilt Cu Stage,  Right Be Gimbal DT Stage
Minimum Detectable Mass

$$MDM \sim \frac{k}{P_x I_o T} = \frac{k^*}{P_x J_o d_o^2 T} -$$

Minimum Mass Fraction

$$MMF \sim \frac{k}{\sqrt{[P_x \left(\frac{P}{B}\right)_x I_o T]}} = \frac{k^*}{\sqrt{[P_x \left(\frac{P}{B}\right)_x J_o d_o^2 T]}}$$

$k, k^*$ = Constants

$P_x$ = Characteristic Signal from element X

$(P/B)_x$ = Peak to Background ratio for element X

$I_o$ = Incident electron flux

$J_o$ = Incident electron current density

$d_o$ = Probe diameter

$T$ = Analysis time
Experimental Peak/Background Variation with Voltage

- Normalized Peak/Background Ratio vs. Accelerating Voltage (kV)
- Graphs show variation of peak/background ratio with accelerating voltage for different materials:
  - Germanium
  - Chromium
  - Aluminium

- Aluminium Peak/Background Ratio vs. Accelerating Voltage (kV)
  - Curves for Aluminium with different thickness:
    - Al P/B 400Å
    - Al P/B 1200Å
    - Al P/B 3000Å
\[ d_{o*} \sim \frac{k^*}{\text{MMF}^* \sqrt{[P_X (\frac{P}{B})_x J_0 \tau]}} \]
What is your spatial resolution?
Spatial Resolution /Beam Spreading Monte Carlo Calculations

DC Joy's MC Program

100 kV

Aluminium

Gold
Monte Carlo Calculations of $\beta$ (Newbury & Myklebust -1979)

<table>
<thead>
<tr>
<th>Element</th>
<th>$Z$</th>
<th>10nm</th>
<th>50nm</th>
<th>100nm</th>
<th>500nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>6</td>
<td>0.22</td>
<td>1.9</td>
<td>4.1</td>
<td>33.0</td>
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<tr>
<td>Aluminium</td>
<td>13</td>
<td>0.41</td>
<td>3.0</td>
<td>7.6</td>
<td>66.4</td>
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<tr>
<td>Copper</td>
<td>29</td>
<td>0.78</td>
<td>5.8</td>
<td>17.5</td>
<td>244.0</td>
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<tr>
<td>Gold</td>
<td>79</td>
<td>1.71</td>
<td>15.0</td>
<td>52.2</td>
<td>1725.0</td>
</tr>
</tbody>
</table>
**Analytic Formulation** (Elastic Scattering - Goldstein et al 1977)

\[ B = 625 \frac{Z}{E_0} \frac{\sqrt{\rho}}{A} t^{3/2} \]

- \( b \): Beam Broadening [cm]
- \( Z \): Atomic Number
- \( E_0 \): Accelerating Voltage [kV]
- \( \rho \): Density [gms/cm\(^3\)]
- \( A \): Atomic Weight
- \( t \): Thickness [cm]

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>10nm</th>
<th>50nm</th>
<th>100nm</th>
<th>500nm</th>
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<tbody>
<tr>
<td>Carbon</td>
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<td>0.16</td>
<td>1.8</td>
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<td>0.26</td>
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<tr>
<td>Gold</td>
<td>79</td>
<td>15.5</td>
<td>17.3</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

*model invalid at higher kV and/or high scattering angles*
What are the Limits - Today?
Example:

- The figure at the right shows the results of contamination formed when a 300 kV probe is focused on the surface of a freshly electropolished 304 SS TEM specimen.

- The dark deposits mainly consist of hydrocarbons which diffuse across the surface of the specimen to the immediate vicinity of the electron probe. The amount of the contamination is a function of the time spent at each location. Here the time was varied from 15 - 300 seconds.
Plasma Cleaning of Electropolished 304 SS

• Untreated Specimen

• After 5 minutes Argon Processing

• After 5 minutes of additional Oxygen Processing
Specimen Preparation Artifacts

Electropolishing: HCl residue

Ion Milling: Redeposition of Fe, Ni, Cu from SS holder
Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects:
  Absorption
  Fluorescence
Spectral Processing : XEDS

Spectrum = Characteristic Peaks + Background

Data Reduction
- Simple: Linear Background Fit & Integration
- Curve Fitting: Non-Linear Background & Profile Matching
- Frequency (Digital) Filtering: Background Suppression & Reference Spectra Fitting

Deconvolution: Fourier Method for Resolution Enhancement

Background Modeling
- Simple - Linear and/or Polynomial Interpolation
- Modeling - Parametric Fits of Analytic Expressions
  - Phenomenological Expressions
  - Modified Bethe Heitler Model
  - Digital Filtering - Mathematical Supression
Spectral Processing : XEDS
Simple Data Reduction

Note: Must use peak integrals (I) and not peak amplitudes (A)

Recall that for a Gaussian Peak

\[
I = \int_{-\infty}^{+\infty} \exp\left(-\frac{x^2}{2\sigma^2}\right) \, dx = \sqrt{2\pi \sigma} \cdot A
\]

Hence for the ratio of Intensities

\[
\frac{I_1}{I_2} = \frac{\sigma_1 \cdot A_1}{\sigma_2 \cdot A_2} \neq \frac{A_1}{A_2}
\]
Spectral Processing: XEDS

Background Modeling:
Power Law/Parametric Fits

Polynomial expansion of Kramers Law

\[ B_{\text{gnd}} = \varepsilon^* \left( A \left( \frac{E-E_0}{E} \right)^2 + B \left( \frac{E-E_0}{E} \right) + C \right) \]
- Remove Background
- Describe Peaks as Gaussians

\[ I(E) = A \exp \left( \frac{-(E - E_c)^2}{2\sigma_{Ec}^2} \right) \]

\[ \sigma(E_c) = \frac{FWHM}{2.355} \]

- Implement a Least-Squares Minimization to Theoretical or Reference Spectra
- Linear Modeling:
  Solve for best \( A \) with \( E_c, \sigma_{Ec} \), as known values
- Non-Linear Modeling:
  Solve for best values of \( A, E_c, \sigma_{Ec} \)
Spectral Processing: XEDS
Curve Fitting: Linear Modeling

Let

\[ G_{ij} = \exp \left( \frac{-(E_j - E_i)^2}{2\sigma_{Ei}^2} \right) \]

then

\[ Y_1 = A_1 G_{11} + A_2 G_{21} + A_3 G_{31} \]
\[ Y_2 = A_1 G_{12} + A_2 G_{22} + A_3 G_{32} \]
\[ Y_3 = A_1 G_{13} + A_2 G_{23} + A_3 G_{33} \]

Using simple matrix algebra solve for \( A \)

• Fast and simple procedure

• Presumes operator knows all elements present

* System must be calibrated
  (i.e. \( E_c \) and \( \sigma_E \) must be accurately known)
Spectral Processing : XEDS
Curve Fitting : Linear Modeling
Background Suppression by Mathematical modeling
- Replace Data by new spectra formed by the following linear operation.

\[ G(x_1) = [F(x_1) - 2 \cdot \frac{W^-}{W^+} \cdot F(x_0) + F(x_{-1})] \quad \text{where } F(x_j) = \sum f(x_j) \]

First Order (Top Hat) Digital Filter

Operator independent
Introduces severe spectral distortion
Spectral Processing: XEDS
Digital Filtering

Original Spectrum

Ti
Ni
Cu
CuAl

Digitally Filtered

0 Energy (keV) 10
Data Analysis and Quantification:

Spectral Processing
Thin Film Quantification Methods
Specimen Thickness Effects:
Okay we can detect elements
How do we Quantify things?

Figure 9. Energy dispersive spectrum of the final reaction product of cellulase activity (Bal, 1972; Weaves & Bal, 1972).
\[
\text{X-rays Detected} = \text{X-rays Emitted} \times \text{Efficiency of Collection} \times \text{Efficiency of Detection}
\]

\[
\begin{align*}
\text{X-rays Generated} & \times \text{Fraction of X-rays which leave Specimen} \\
\text{X-rays Generated per Atom per Electron} & \times \text{Number of Incident Electrons} & \text{Number of Atoms} \times (1 + \text{Fraction Generated by Secondary Sources})
\end{align*}
\]

\[
\begin{align*}
\text{Number of "K" Shell Ionizations per Atom per Electron} & \times \text{Number of "K" X-rays per Ionization} & \text{Fraction of Total "K" X-rays Measured}
\end{align*}
\]
### Quantitative Analysis Equations

**For a thin specimen**

\[
I_A^{K\alpha} = \{\sigma_A(E,Z)\Gamma_A\omega_A\} C_A \left\{ \frac{N_o \rho}{W_A} \right\} \eta_o t \| \varepsilon A \| \Omega
\]

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I_A)</td>
<td>Measured x-ray intensity per unit area</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>(K^{\text{th}})-shell ionization cross-section</td>
</tr>
<tr>
<td>(\omega)</td>
<td>(K^{\text{th}})-shell fluorescence yield</td>
</tr>
<tr>
<td>(\Gamma)</td>
<td>(K^{\text{th}})-shell radiative partition function</td>
</tr>
<tr>
<td>(W)</td>
<td>Atomic Weight</td>
</tr>
<tr>
<td>(N_o)</td>
<td>Avagadro's number</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Density</td>
</tr>
<tr>
<td>(C)</td>
<td>Composition (At %)</td>
</tr>
<tr>
<td>(\eta_o)</td>
<td>Incident electron flux</td>
</tr>
<tr>
<td>(t)</td>
<td>Specimen thickness</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Detector efficiency</td>
</tr>
<tr>
<td>(\Omega)</td>
<td>Detector solid angle</td>
</tr>
</tbody>
</table>
For K Shells

\[ Q_K = \frac{a_K \times b_K \times \left\{ \ln \left( c_K \frac{T_O}{E_C} \right) - \ln(1-\beta^2) - \beta^2 \right\}}{T_O \times E_C} \]

\[ T_O = 1/2 \, m_o c^2 \beta^2, \quad E_C = \text{Shell Excitation Energy}, \quad \beta = \frac{v}{c} \]

For L Shells

\[ Q_L = \frac{a_L \times b_L \times \left\{ \ln \left( c_L \frac{T_O}{E_C} \right) - \ln(1-\beta^2) - \beta^2 \right\}}{T_O \times E_C} \]

Note: The parameters \( a_x, b_x, c_x \) are generally different for each element and Shell, although their variation is slow with \( Z \). Experimental & theoretical parameterizations exist for many elements, others are obtained by extrapolation.
X-ray Fluorescence Yield has Systematic Variation With Atomic Number

$\omega_K$ shell

$\omega_K$ vs $\omega_L$ shell
Radiative Partition Function ($\Gamma$) Governs the Relative Intensities
Nominal Values (Varies slowly with Atomic Number)

<table>
<thead>
<tr>
<th>K Shell</th>
<th>L Shell</th>
<th>M Shell</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_{\alpha1} = 100$</td>
<td>$L_{\alpha1} = 100$</td>
<td>$M_{\alpha1,2} = 100$</td>
</tr>
<tr>
<td>$K_{\alpha2} = 50$</td>
<td>$L_{\alpha2} = 50$</td>
<td>$M_{\beta} = 60$</td>
</tr>
<tr>
<td>$K_{\beta1} = 15-30$</td>
<td>$L_{\beta1} = 50$</td>
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</tr>
<tr>
<td>$K_{\beta2} = 1-10$</td>
<td>$L_{\beta2} = 20$</td>
<td></td>
</tr>
<tr>
<td>$K_{\beta3} = 6-15$</td>
<td>$L_{\beta3} = 1-6$</td>
<td></td>
</tr>
<tr>
<td>$L_{\beta4} = 3-5$</td>
<td>$L_{\gamma1} = 1-10$</td>
<td></td>
</tr>
<tr>
<td>$L_{\gamma3} = 0.5-2$</td>
<td>$L_{\eta} = 1$</td>
<td></td>
</tr>
<tr>
<td>$L_{\iota} = 1-3$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Invoke the Intensity Ratio Method, that is consider the ratio of x-ray lines from two elements

\[
\frac{I_A}{I_B} = \frac{\kappa_A \varepsilon_A C_A}{\kappa_B \varepsilon_B C_B} = k_{AB}^{-1} \frac{C_A}{C_B}
\]

\[
\kappa_A = \frac{\sigma_A \omega_A \Gamma_A}{W_A}
\]

\[
\frac{\kappa_A \varepsilon_A}{\kappa_B \varepsilon_B} = k_{AB}^{-1} \text{ (k-factor)}
\]

This simple equation states that the relative intensity ratio of any two characteristic x-ray lines is directly proportional to the relative composition ratio of their elemental components multiplied by some "constants" and is independent of thickness.

**NOTE:** The \( k_{AB} \) factor is not a universal constant!! Only the ratio of \( \kappa_A/\kappa_B \) is a true physical constant and is independant of the AEM system. The ratio of \( \varepsilon_A/\varepsilon_B \) is not a constant since no two detectors are identical over their entire operational range. This can cause problems in some cases as we shall see.
The analysis to this point has only yielded the relative compositions of the specimen. We need one additional assumption to convert the relative intensity ratio's \( \frac{I_i}{I_j} \) into compositions namely:

\[
\sum_{i=1}^{N} C_i = 1.0
\]

One now has a set of \( N \) equations and \( N \) unknowns which be solved algebraically solved for the individual composition values.

Thus for a simple two element system we have:

\[
\frac{I_A}{I_B} = k_{AB}^{-1} \frac{C_A}{C_B}
\]

and

\[
C_A + C_B = 1.
\]

or

\[
C_B \left( \frac{C_A}{C_B} + 1 \right) = 1
\]

Solving for \( C_B \) and \( C_A \)

\[
C_B = \left( \frac{1}{1 + \frac{C_A}{C_B}} \right) = \left( \frac{1}{1 + \frac{I_A}{I_B} \cdot k_{AB}} \right) \quad \text{and} \quad C_A = C_B - 1
\]
Variation in Measured Composition on 308 SS for Different Labs

Example in which K-factor is stable
Cr, Fe, Ni

Note: Detector efficiency ~ 100% in this energy range
Variation in K-factor with AEM/Detector System
Specimen: Uniform NiO film on Be Grid

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Experimental K -Factor</th>
<th>Apparent Variation in Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.17</td>
<td>80.9/19.1</td>
</tr>
<tr>
<td>2</td>
<td>1.56</td>
<td>56.1/43.9</td>
</tr>
<tr>
<td>3</td>
<td>1.25</td>
<td>50.6/49.4</td>
</tr>
<tr>
<td>4</td>
<td>1.25</td>
<td>50.6/49.4</td>
</tr>
<tr>
<td>5</td>
<td>1.24</td>
<td>50.4/49.5</td>
</tr>
<tr>
<td>6</td>
<td>1.13</td>
<td>48.1/51.9</td>
</tr>
<tr>
<td>7</td>
<td>1.10</td>
<td>47.4/52.6</td>
</tr>
<tr>
<td>8</td>
<td>1.03</td>
<td>45.8/54.2</td>
</tr>
<tr>
<td>9</td>
<td>0.74</td>
<td>37.8/62.2</td>
</tr>
</tbody>
</table>

From: Comparison of UTW/WL X-ray Detectors on TEM/STEMs and STEMs

Thomas, Charlot, Franti, Garratt-Reed, Goodhew, Joy, Lee, Ng, Plichta, Zaluzec.
Analytical Electron Microscopy-1984
Determining the $k_{AB}^{-1}$ Factor

**Experimental Measurements**

Prepare thin-film standards of known composition then measure relative intensities and solve explicitly for the $k_{AB}$ factor needed. Prepare a working data base.

This is the "best" method, but
- specimen composition must be verified independently
- must have a standard for every element to be studied

**Theoretical Calculations**

Attempt first principles calculation knowing some fundamental parameters of the AEM system

Start with a limited number of $k_{AB}$ factor measurements, then fit the AEM parameters to best match the data. Extrapolate to systems where measurements and/or standards do not exist.

- **Method 1.** (Goldstein et al) Assume values for $\Gamma, \omega, \varepsilon$ and determine the best $s$ to fit $k_{AB}$. This procedure essentially iterates the fit of $s$ to the data.

- **Method 2.** (Zaluzec) Assume values for $\Gamma, \omega, \sigma$ determine the best $e$ to fit $k_{AB}$. This procedure essentially iterates the fit of $e$ (detector window parameters) to the data.
Sources of values for $k_{AB}$ Calculations

$W$ - International Tables of Atomic Weights

$\Gamma (K)$ - Schreiber and Wims, X-ray Spectroscopy (1982)
Vol 11, p. 42

$\Gamma (L)$ - Scofield, Atomic and Nuclear Data Tables (1974)
Vol 14, #2, p. 121

$\omega (K)$ - Bambynek etal, Rev. Mod. Physics, Vol 44, p. 716
Freund, X-ray Spectrometry, (1975) Vol 4, p.90


$\sigma (E_0)$ - Inokuti, Rev. Mod. Physics, 43, No. 3, 297 (1971)
- Goldstein etal, SEM 1, 315, (1977)
- Chapman etal, X-ray Spectrometry, 12,153,(1983)

$\varepsilon (E)$ - Use mass absorption coefficients from:
- Thinh and Leroux; X-ray Spect. (1979), 8, p. 963
Quantitative Analysis using XEDS
Thin Film Standards Method

Invoke the Intensity Ratio Method, but now consider the ratio of the same x-ray line from two different specimens, where one is from a standard of known composition while the other is unknown:

\[ \frac{I_u}{I_s} = \frac{\eta_u \rho_u t_u}{\eta_s \rho_s t_s} \times \frac{C_u}{C_s} \]

\[ C_u = \frac{\eta_s \rho_s t_s}{\eta_u \rho_u t_u} \times \frac{I_u}{I_s} \times C_s \]

This simple equation states that the relative intensity ratio of same characteristic x-ray line is directly proportional to the relative composition ratio of the two specimens multiplied by a some new parameters.

\( \eta = \text{incident beam current} \)
\( \rho = \text{local specimen density} \)
\( t = \text{local specimen thickness} \)
X-ray Absorption

\[ \mu = \tau + \sigma \]

where \( \mu = \) bulk mass absorption coefficient, 
\( \tau = \) photoelectric absorption coefficient, 
\( \sigma = \) Compton scattering coefficient.

\[ I = I_0 e^{-\mu pt} \]

where \( I_0 = \) initial intensity (cps), 
\( I = \) final intensity (cps), 
\( \mu = \) bulk mass absorption coefficient of the material (cm\(^2\)/g), 
\( \rho = \) density of the material (g/cm\(^3\)), 
and \( t = \) thickness of the material (cm).
Consider simple absorption model for x-rays leaving the specimen

\[ I(t) = \int I_0(t) \exp(-\mu t) \, dt \]

\[ = \int I_0(t) \exp(-w t) \, dt \]

**Parallel Slab Geometry**

- \( d \) = Absorption Pathlength from the specimen to detector
  - \( t = \frac{\sin(\beta)}{\cos(\beta - \theta_E)} \)
- \( \chi \) = Geometrical factor multiplied by average mass absorption coefficient for the measured x-ray line in the compound
  - \( \frac{\chi x_{\text{Spec.}}}{\rho} = \frac{|\mu|}{\rho} x_{\text{Spec.}} + \frac{\sin(\beta)}{\cos(\beta - \theta_E)} \)
- \( \left( \frac{|\mu|}{\rho} \right) x_{\text{Spec.}} \) = Weighted average mass absorption coefficient
  - \( = \sum_{i=1}^{N} \left( \frac{|\mu|}{\rho_i} \right) * C_i \) (Note: composition dependent)
Now rederive the standless equations to include absorption.

\[
\frac{I_A}{I_B} = \frac{\varepsilon_A}{\varepsilon_B} \times \frac{\kappa_A}{\kappa_B} \times \frac{\delta_A}{\delta_B} \times \frac{C_A}{C_B}
\]

with

\[
\frac{\delta_A}{\delta_B} = \frac{\left(\frac{\mu}{\rho}\right)_A}{\left(\frac{\mu}{\rho}\right)_B} \frac{\left(1 - \exp(-\chi \rho t^*)^\infty\right)}{\left(1 - \exp(-\chi \rho t^*)^\infty\right)}
\]

\[
t^* = t_0 \frac{\sin(\beta)}{\cos(\beta - \theta_E)}
\]

\[
\chi = \left(\frac{\mu}{\rho}\right) \text{ x-ray in Compound} = \sum_{i=1}^{N} \left(\frac{\mu}{\rho}\right)_i \times C_i
\]

\[
\beta = \text{ Electron Incidence Angle}
\]

\[
= \text{ Function of Stage Tilts: } \phi_x, \phi_y, \text{ & Detector Azimuth } \theta_A
\]

\[
\theta_E = \text{ Detector Elevation Angle}
\]

Define the Thin Film approximation: \( \chi \rho t^* < 0.1 \)
Thin Film approximation: $\chi \rho t^* < 0.1$

$$t^* \leq \frac{0.1}{\chi \rho}$$
Effect of Tilting Specimen on Absorption

For a plane parallel slab specimen, tilting has the effect of increasing the Specimen Thickness. Different Detector/Specimen Geometries will enhance/reduce the Absorption Effects.
In the "real" world few specimens have the shape used to derive this correction. Next consider two representative geometries:

**Symmetric Wedge Geometry:**

Replace all $\beta$'s by $\beta \pm \alpha/2$, where $\alpha$ is the wedge angle of the specimen.

* $+\alpha/2$ variant applies when the detector is positioned such that the pathlength *increases* relative to the parallel slab model.

* $-\alpha/2$ variant applies when the detector is positioned such that the pathlength *decreases* relative to the parallel slab model.
Attempt a Wedge Model Correction using previous formulae.

<table>
<thead>
<tr>
<th>Path #1</th>
<th>Path #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{I_{Ni}}{I_{Al}} = 2.64$</td>
<td>$\frac{I_{Ni}}{I_{Al}} = 5.18$</td>
</tr>
<tr>
<td>Thin Film Model</td>
<td>Thin Film Model Error!</td>
</tr>
<tr>
<td>Ni = 60.9</td>
<td>Ni = 60.5</td>
</tr>
<tr>
<td>Al = 39.1</td>
<td>Al = 39.5</td>
</tr>
<tr>
<td>Parallel Slab</td>
<td>Parallel Slab</td>
</tr>
<tr>
<td>Ni = 45.3</td>
<td>Ni = 60.5</td>
</tr>
<tr>
<td>Al = 54.7</td>
<td>Al = 39.5</td>
</tr>
<tr>
<td>Wedge Model</td>
<td>Wedge Model</td>
</tr>
<tr>
<td>Ni = 50.6</td>
<td>Ni = 42.6</td>
</tr>
<tr>
<td>Al = 49.4</td>
<td>Al = 57.4</td>
</tr>
<tr>
<td>$\chi \rho t_{Ni} = 0.016$</td>
<td>$\chi \rho t_{Ni} = 0.081$</td>
</tr>
<tr>
<td>$\chi \rho t_{Ni} = 0.925$</td>
<td>$\chi \rho t_{Ni} = 4.24$</td>
</tr>
</tbody>
</table>

Absorption Correction has limited applications keep $\chi \rho t < 1$
Quantitative Analysis using XEDS
Specimen Thickness Effects

For finite thickness specimens, what is a thin film?

Previous Assumptions:
- Energy loss,
- X-ray absorption,
- No X-ray fluorescence

\[ I = I_0 e^{-\mu t} \]
where 
- \( I_0 \) = initial intensity (cps),
- \( I \) = final intensity (cps),
- \( \mu \) = bulk mass absorption coefficient of the material (cm²/g),
- \( \rho \) = density of the material (g/cm³),
and \( t \) = thickness of the material (cm).
X-Ray Fluorescence Correction

\[ I_A^{\text{Measured}} = I_A^{\text{Electron}} + I_A^{\text{XRF by B}} \]

\[ I_A^{\text{Measured}} = I_A^{\text{Electron}} \left( 1 + \frac{I_A^{\text{XRF by B}}}{I_A^{\text{Electron}}} \right) \]
Next, rederive the standardless equations to include x-ray fluorescence and you can show:

\[
\frac{I_A}{I_B} = \frac{\varepsilon_A}{\varepsilon_B} \times \frac{\kappa_A}{\kappa_B} \times \frac{\delta_A}{\delta_B} \times \frac{\gamma_A}{\gamma_B} \times \frac{C_A}{C_B}
\]

as in the case of x-ray absorption this requires iterative solution because the ratio of \(\gamma\)'s are composition dependent.

When is the XRF Correction important?

- When fluorescing line is near the absorption edge of the lower energy line. Typically within a few atomic numbers (i.e. \(Z+2\) to \(Z+6\))
- When specimen is thick or path length is long

Define a thin film approximation for XRF as:

\[
\frac{I_{A_{\text{XRF by i}}}}{I_{A_{\text{Electron}}}} < 0.05
\]

\[
C_i \omega_i \Gamma_i \frac{A_A}{A_i} \frac{Q_i}{Q_A} \left(\frac{\Delta \mu}{\mu}\right)_A \left(\frac{\mu_i}{\rho}\right)_A \frac{\rho T}{2} \left[1.12 + \left(\frac{\mu_i}{\rho}\right)_A \cdot \frac{\rho T}{4} - \ln\left(\left(\frac{\mu_i}{\rho}\right)_A \cdot \rho T\right)\right] < 0.05
\]
In this and all other derivations we have assumed that over the excited volume, as well as along the exiting pathlength, the specimen is homogeneous in composition. If this assumption is invalid, one must reformulate the absorption correction and take into account changes in: $\frac{\mu}{\rho}$, $\rho$, and $t$ along the exiting pathlength.

**Effects of Beam Broadening**

- **Parallel Slab Model:** No Change in absorption pathlength
- **Wedge Model:** There is a correction the magnitude of which varies with the wedge angle.

**Effects of Irregular Surface**

This cannot be analytically modeled but must be understood!
Additional Topics

Heterogeneous Specimens
Composition Profiles
Electron Channeling
Radiation Damage
Spectral Imaging
All quantitative analysis equations were derived assuming that the specimen is homogeneous over the exited volume.

Application of the these equations to heterogenous specimens effectively averages the composition over the excited volume.
Grain Boundary Segregation

Distance (nm)

-200

+200

Cr

Ni

Fe

-200

Distance (nm)

+200

Cr

Ni

Fe
Fig. 9. Typical Concentration Profiles for Chromium, Nickel, and Iron Across a Grain Boundary of Type 304 Stainless Steel Softened at 875°C for 230 hours. Comparison of (a) and (b): 20°C/Ms on Duration by Energy Dispersive X-ray Analysis with a JEOL 100X Electron Microscope Specimen for STEM Operation. The error bars represent the uncertainties associated with the counting statistics only.
\[ C^*(x,y) = C(x,y,z) \ast d(x,y,z) \]

- \( C^*(x,y) \) = Apparent profile measured
- \( C(x,y,z) \) = Actual composition profile
- \( d(x,y,z) \) = Incident beam profile
- \( \ast \) = Convolution operator
- \( F,F^{-1} \) = Fourier and Inverse Fourier Transforms

In the 2 dimensional limit one can deconvolute the measured profile using:

\[ C(x,y) = F^{-1} \left[ \frac{F\{C^*(x,y)\}}{F\{d(x,y)\}} \right] \]

Realistically, it is better to decrease the probe diameter and specimen thickness
• Characteristic X-ray Emission is not truly isotropic in crystalline materials!

• Original Observations of Effect
  – Duncumb ‘62, Hall ‘66, Cherns et al ‘73

• Predicted Applications
  – Cowley ‘64, ‘70

• ACHEMII Technique
  – Tafto ‘79, Spence & Tafto ‘83

• Multi-Variate Statistical Analysis
  – Rossouw et al., Anderson and others
    late80’-90’s
High Angular Resolution Electron Channeling X-ray Spectroscopy
Orientation Dependance in Homogeneous Alloys
Applications in Ordered Systems

Compare Ni/AL <110>/<100>

NIK/AIK Intensity Ratio

g
ALCHEMI
Atom Location by CHanneling EMIssion
Tafto & Spence - Science 1982

(Mg$_{0.90}$Fe$_{0.10}$Ni$_{0.004}$Mn$_{0.002}$)$_2$SiO$_4$

Note: Mn prefers Si Sites and Ni prefers Mg Sites
Spectral Imaging

FEI Tecnai F20

20nm

Nb FeSmCoCr

MgO
How much data is generated in PRD Expt's
Compare with Spectrum Imaging

<table>
<thead>
<tr>
<th>XY</th>
<th>128²</th>
<th>256²</th>
<th>512²</th>
<th>1024²</th>
</tr>
</thead>
<tbody>
<tr>
<td>256</td>
<td>4M</td>
<td>16M</td>
<td>67M</td>
<td>262M</td>
</tr>
<tr>
<td>512</td>
<td>8M</td>
<td>32M</td>
<td>134M</td>
<td>524M</td>
</tr>
<tr>
<td>1024</td>
<td>16M</td>
<td>64M</td>
<td>268M</td>
<td>1G</td>
</tr>
</tbody>
</table>
Spectrum Imaging

Energy

Position/Angle

E1
E2
E3
E4
E5
En

AI K
Si K
U M
Three Dimensional Spectrum Imaging Profiles
Using the ANL AAEM System

XY Slices Along E Axis Yield Composition Distributions

Line Scans along the Energy Axis Yield Complete Spectral Profiles
Spectrum Imaging allows for Off-line Projections/Summations Operations

But it requires massive data storage

<table>
<thead>
<tr>
<th>E</th>
<th>XY</th>
<th>128²</th>
<th>256²</th>
<th>512²</th>
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<tr>
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<td>4 M</td>
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<tr>
<td>1024</td>
<td>16 M</td>
<td>64 M</td>
<td>268 M</td>
<td>1 G</td>
<td></td>
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<tr>
<td>t</td>
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<td>256</td>
<td>512</td>
<td>1024</td>
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<td>65 ms</td>
<td>0.26 s</td>
<td>1.05 s</td>
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<tr>
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<td>65 s</td>
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<td>~3 days</td>
<td>~12 days</td>
<td></td>
</tr>
<tr>
<td>1 min</td>
<td>~11 days</td>
<td>~1.5 mnths</td>
<td>~6 mnths</td>
<td>~2 yrs</td>
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