Outline:

- **EDXRF spectra**
  - Characteristic radiation peaks
  - Scatter peaks
  - Escape peaks
  - Continuum
  - Sum peaks

- **Spectrum fitting algorithms**
  - Least square fit principle
  - Models for peak fit
  - Software for evaluation

- **Interferences**
  - Spectral interferences
  - Environmental interferences
  - Matrix interferences
Typical EDXRF spectrum contains:

- Escape peaks (Ca-Kα – 1.74 keV = 1.95 keV)
- Characteristic radiation
  - K, L or M-lines
- Scatter
  - Coherent
  - Incoherent
- Sum peaks
  - Fe-Kα + Fe-Kα = 12.8 keV
- Continuum radiation
Full Width at Half Maximum (FWHM) of a peak

\[ FWHM_{\text{Peak}}^2 = FWHM_{\text{Elec}}^2 + FWHM_{\text{Det}}^2 \]

Electronic noise: \( \sim 100 \) eV

Intrinsic contribution:

\[ 2.3548 \sqrt{\varepsilon \times F \times E} \]

- \( \varepsilon \): Energy to create e-h pair (3.85 eV)
- \( F \): Fano factor (\( \sim 0.114 \))
- \( E \): x-ray energy in eV

**Mn Kα, 5.895 keV**

\( FWHM = 156 \) eV

\( FWHM_{\text{Det}} = 120 \) eV

\( FWHM_{\text{Elec}} = 100 \) eV

\( \Rightarrow FWHM_{\text{Peak}} = 156 \) eV
Cr – Mn – Fe overlap at \(\sim 160\) eV
Cr – Mn – Fe overlap at ~20 eV
Our need is:

To “estimate” the net peak area with highest possible
• accuracy (no systematic error)
• precision (smallest random error)

How to do it?

Least-squares estimation (fitting):
• unbiased
• minimum variance

Limiting factors:
• counting statistical fluctuations (precision)
• accuracy of the fitting model
Least squares fit of a straight line

Model: \( y(i) = a_1 + a_2 x_i \)

Least squares method: find \( a_1 \) and \( a_2 \)

\[
\chi^2 = \sum_i [y_i - y(i)]^2 = \sum_i (y_i - a_1 - a_2 x_i)^2 = \text{min}
\]

\[
\begin{align*}
\frac{\partial \chi^2}{\partial a_1} &= 0 \Rightarrow \sum_i y_i = Na_1 + a_2 \sum_i x_i \\
\frac{\partial \chi^2}{\partial a_2} &= 0 \Rightarrow \sum_i x_i y_i = a_1 \sum_i x_i + a_2 \sum_i x_i^2
\end{align*}
\]

Set of 2 equations in 2 unknowns \( a_1 \) and \( a_2 \)

\( \Rightarrow \) Normal equations

Data: \( \{x_i, y_i\}, i = 1, 2, \ldots, N \)
Least squares fit of a peak

Peak described by a Gaussian

\[ \chi^2 = \sum_{i=n_1}^{n_2} [y(i) - y_i]^2 \]

\[ y(i) = b + H \exp \left( \frac{(x_i - x_p)^2}{2\sigma^2} \right) \]

Minimum:
No direct analytical solution
Search \( \chi^2 \) for minimum
Spectrum evaluation principle:

Non-linear least squares method:
Search the minimum in $\chi^2$ with an algorithm
  e.g. Marquardt – Leverberg

Real spectrum:
  10 elements
  => 20 x (position, width, height) = 60 parameters

Any search algorithm will fail
  False minima, physical meaningless solution

Need optimal description of the spectrum => fitting model
Fitting function

\[ y(i) = y_{\text{Cont}}(i) + \sum_{j} A_j \left( \sum_{k} R_{jk} P(i, E_{jk}) \right) \]

- Line ratio
  - Theoretical ratio
  - Corrected for sample self-attenuation
- Area
  - Initial guess from counts at maximum and theoretical gaussian area

(Linear parameter)
Fitting function

\[ y(i) = y_{\text{Cont}}(i) + \sum_{j} A_j \left[ \sum_{k} R_{jk} P(i, E_{jk}) \right] \]

- Continuum function

Different approaches:
  - Filtering (iterative averaging of N channels, N \sim FWTM)
  - Fitting (linear, polynomial, exponentials)
Fitting function

\[ y(i) = y_{\text{Cont}}(i) + \sum_{j \text{ Elements}} A_j \sum_{k \text{ lines}} R_{jk} P(i, E_{jk}) \]

Peak shape

Gaussian peak shape

\[ P = G(i, E_{jk}) = \frac{\text{Gain}}{\sigma_{jk} \sqrt{2\pi}} \exp \left[ -\frac{1}{2} \left( \frac{E(i) - E_{jk}}{\sigma_{jk}} \right)^2 \right] \]

Energy calibration

\[ E(i) = \text{Zero} + \text{Gain} \times i \]

(Nonlinear parameters)

Resolution calibration

\[ \sigma_{jk} = \left[ \frac{\text{Noise}}{2\sqrt{2\ln 2}} \right]^2 + \epsilon Fano E_{jk} \]
Fitting function

Include provision for
• escape peaks
• sum peaks

Implementation
**AXIL** = **A**nalysis of **X**-ray spectra by **I**terative **L**east-squares
• Axil - QXAS, DOS version
• WinAxil, WinQXAS Windows version
Spectrum Evaluation by least-squares fitting

Highly flexible method
- Fit individual lines, multiplets, elements…
- Different parametric and non-parametric continuum models
- Include escape and sum peaks

Quality criteria
- Chi-square of fit
- Uncertainty estimate of parameters

Statistically correct
- Unbiased, minimum variance estimate of the parameters

“Resolving power” is only limited by the noise (counting statistic)

BUT
THE MODEL MUST BE ACCURATE
Deviation from Gaussian peak shape
-> systematic errors for minor and trace elements
Improvement of fitting function

\[ P(i, E_{jk}) = G(i, E_{jk}) + f_S S(i, E_{jk}) + f_T T(i, E_{jk}) \]

**Gaussian:**

\[ G(i, E_{jk}) = \frac{\text{Gain}}{S_{jk} \sqrt{2\pi}} \exp \left[ -\frac{(E_i - E_{jk})^2}{2S_{jk}^2} \right] \]

**Step:**

\[ S(i, E_{jk}) = \frac{\text{Gain}}{2E_{jk}} \text{erfc} \left[ \frac{E(i) - E_{jk}}{\sqrt{2\sigma}} \right] \]

**Tail:**

\[ T(i, E_{jk}) = \frac{\text{Gain}}{2\gamma \sigma \exp \left[ -\frac{1}{2\gamma^2} \right]} \exp \left[ \frac{E(i) - E_{jk}}{\gamma \sigma} \right] \text{erfc} \left[ \frac{E(i) - E_{jk}}{\sqrt{2\sigma}} + \frac{1}{\sqrt{2\gamma}} \right] \]
Determination of step and tail parameters

- Spectrum
- Fit
- Cont.
- Step
- Tail
Lorentzian contribution

Natural line width at high Z elements becomes important e.g. W K ~ 50 eV

![Spectrum](image)

- **Spectrum**
- **Fit**
- **Continuum**
Lorentzian convoluted with Gaussian detector response: Voigt profile

\[
\text{Gain} \frac{K\left(\frac{E(i) - E_{jk}}{\sqrt{2}\sigma}, \frac{\alpha_L}{2\sqrt{2}\sigma}\right)}{\sqrt{2\pi}\sigma} \text{ with } K(x, y) = \text{Re}\left[e^{-\frac{z^2}{2}} \text{erfc}\left(-\frac{iz}{\sqrt{2}}\right)\right], \quad z = x + iy
\]
DOS- AXIL: IAEA, gratis
WinQXAS: IAEA, gratis
WinAXIL: Canberra, ~ 3000 EUR
bAXIL: BrightSpec, ~ 3000 EUR
## Comparison of features

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Spectral interferences:

- Spectral interferences are peaks in the spectrum that overlap the spectral peak (region of interest) of the element to be analyzed.

- Examples:
  - K & L line Overlap
    - S & Mo, Cl & Rh, As & Pb
  - Adjacent Element Overlap
    - Al & Si, S & Cl, K & Ca...

- Resolution of detector determines extent of overlap.
Environmental interferences: Measuring chamber influence

**Spurious peaks**

- Some elements that are present in the chamber or detector materials even at trace concentrations, are efficiently excited by direct or scattered radiation from the source.
- As these materials are close to the detector, ‘spurious peaks’ will be present in blank measurements.
- Solution:
  - Coat inner surfaces with a pure material, which characteristic energies do not interfere, or
  - Measure blanks of the same matrix, to subtract background
Thanks for your time and attention...