Interpretation of EDXRF spectra

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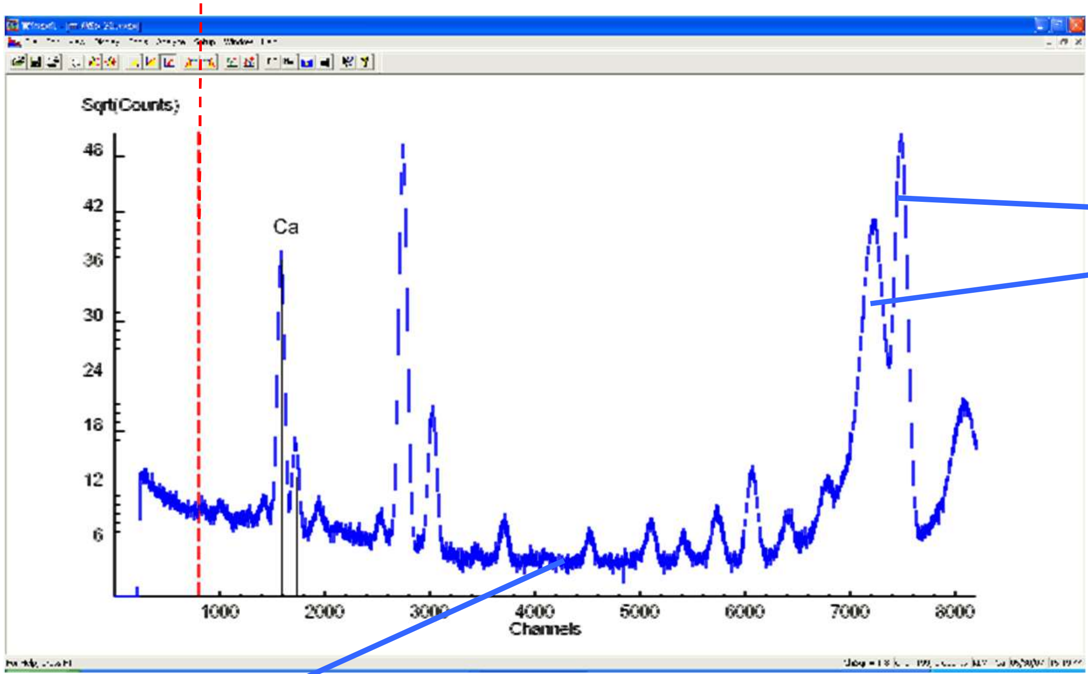
Outline:

- 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

Resolution of ED-XRF spectrometers

Full Width at Half Maximum (FWHM) of a peak

$$FWHM^2_{Peak} = FWHM^2_{Elec} + FWHM^2_{Det}$$

Electronic noise: ~100 eV

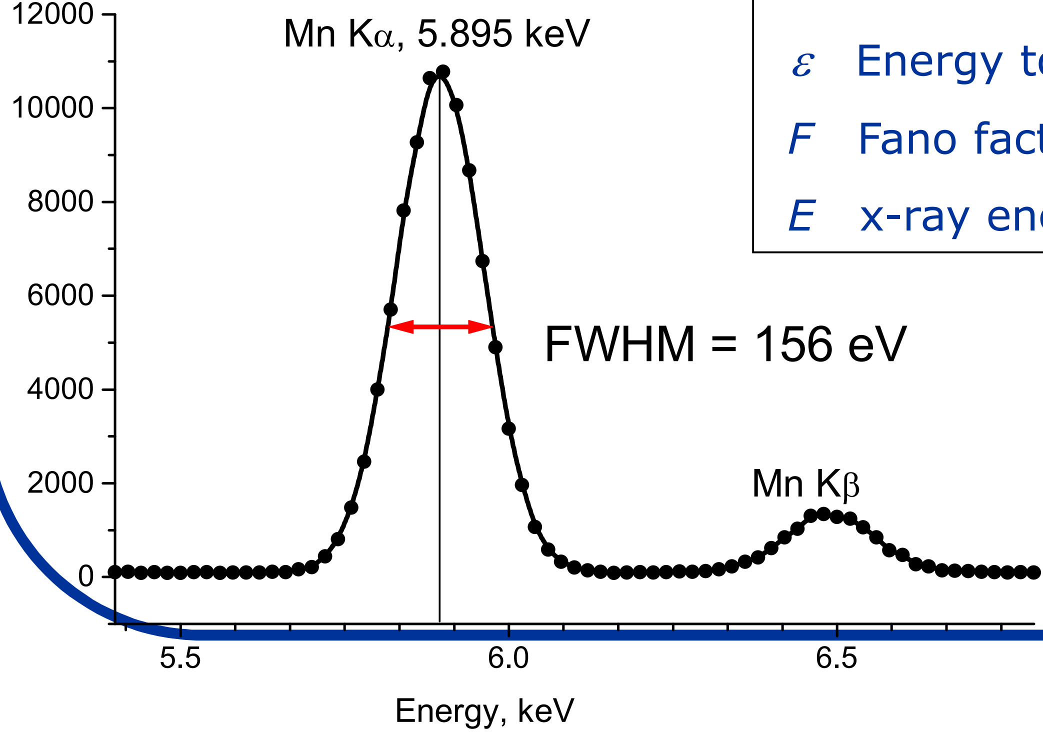
Intrinsic contribution:

$$2.3548\sqrt{\varepsilon \times F \times E}$$

ε Energy to create e-h pair (3.85 eV)

F Fano factor (~0.114)

E x-ray energy in eV



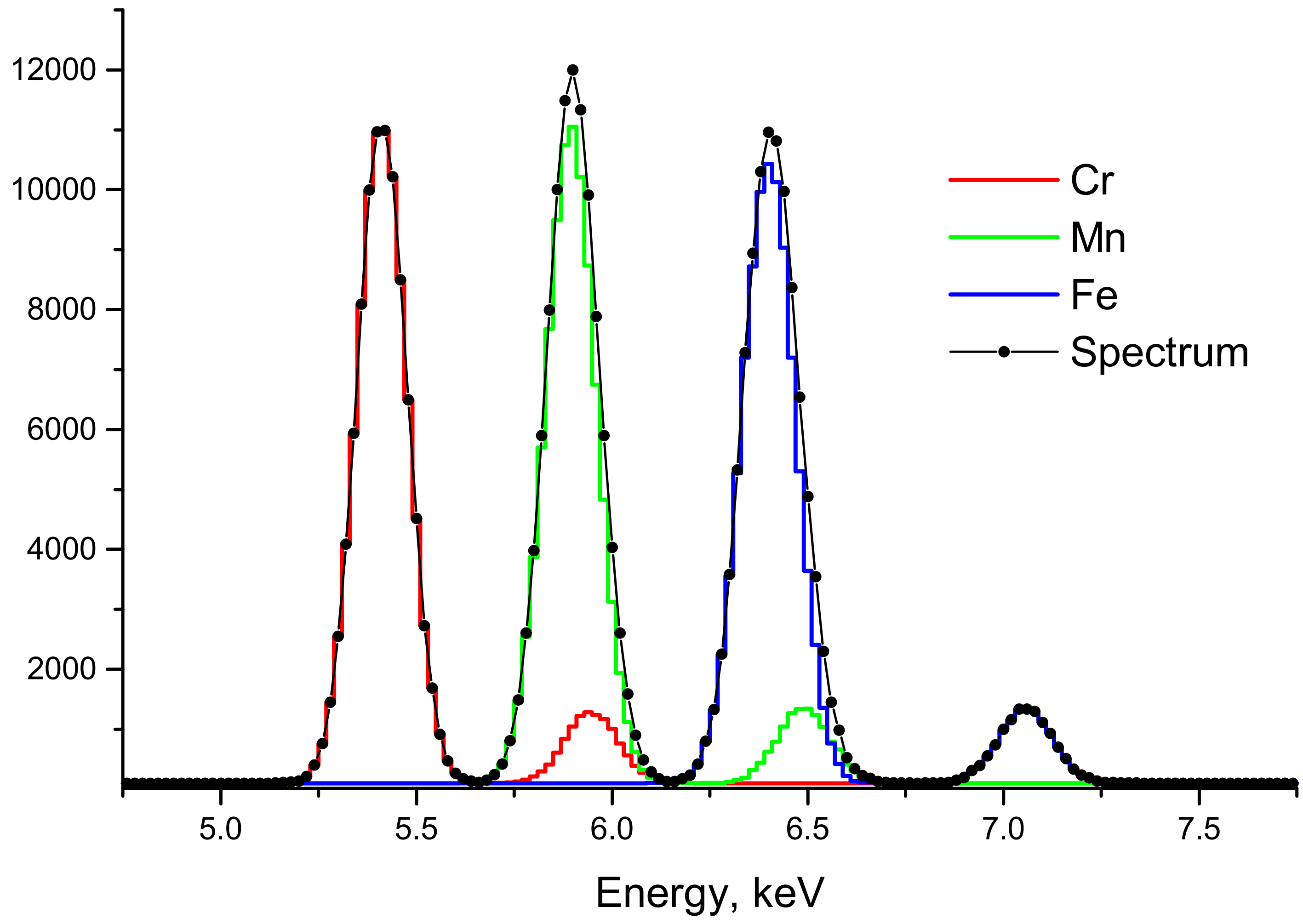
Mn Kα @ 5.895 keV

$FWHM_{Det}$ = 120 eV

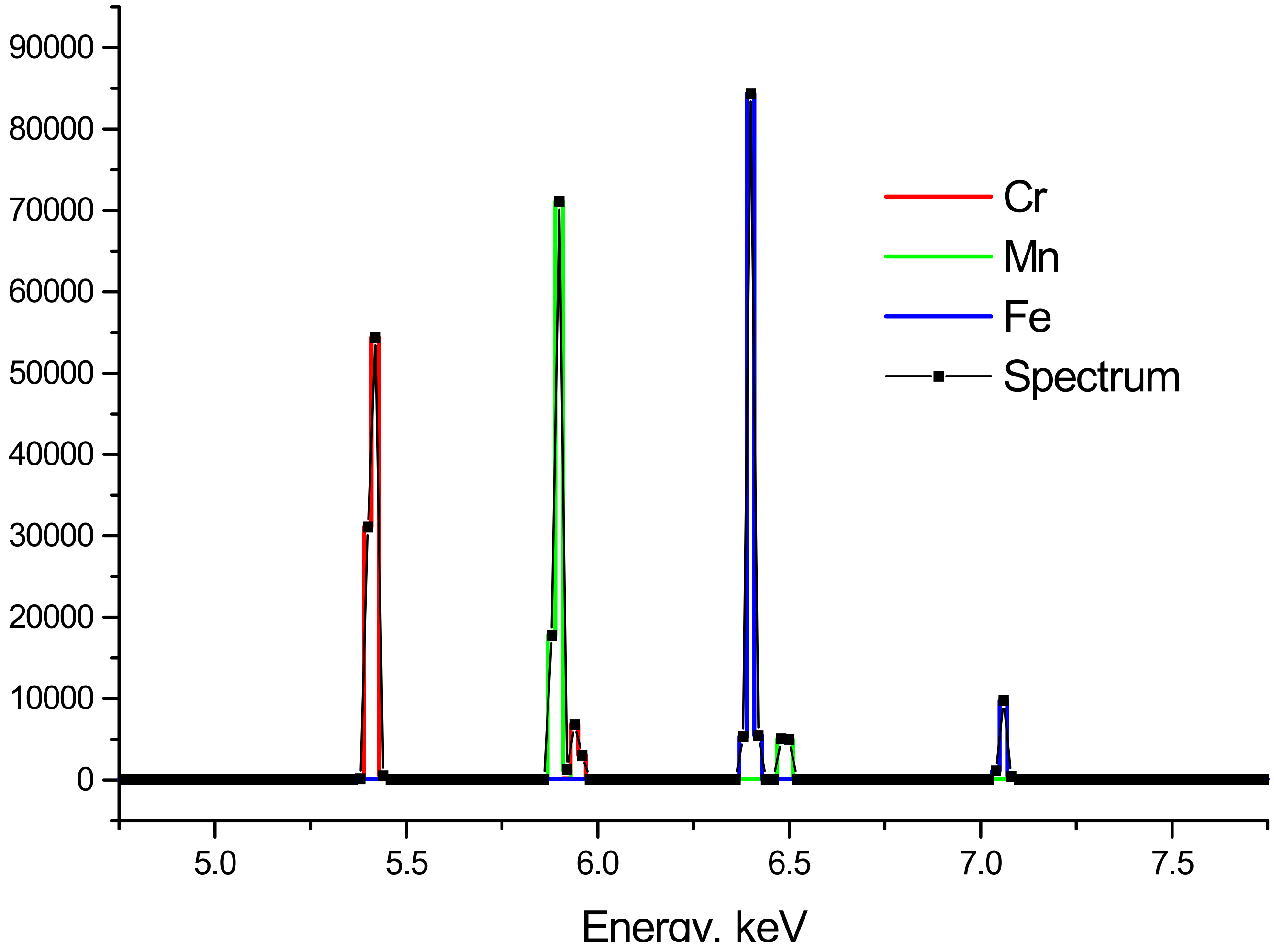
$FWHM_{Elec}$ = 100 eV

=> $FWHM_{Peak}$ = 156 eV

Cr – Mn – Fe overlap at ~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

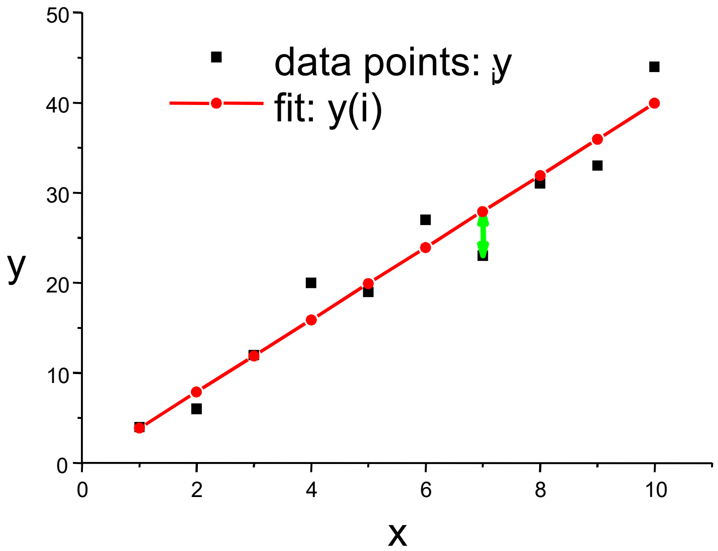
x	y
1	4
2	6
3	12
4	20
5	19
6	27
7	23
8	31
9	33
10	44

Data: $\{x_i, y_i\}$, $i=1, 2, \ldots, N$

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

Least squares method: find a_1 and a_2

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



$$\frac{\partial \chi^2}{\partial a_1} = 0 \Rightarrow \sum_i y_i = N a_1 + a_2 \sum_i x_i$$

$$\frac{\partial \chi^2}{\partial a_2} = 0 \Rightarrow \sum_i x_i y_i = a_1 \sum_i x_i + a_2 \sum_i x_i^2$$

Set of 2 equations in 2 unknowns a_1 and a_2

→ Normal equations

Least squares fit of a peak

Peak described by a Gaussian

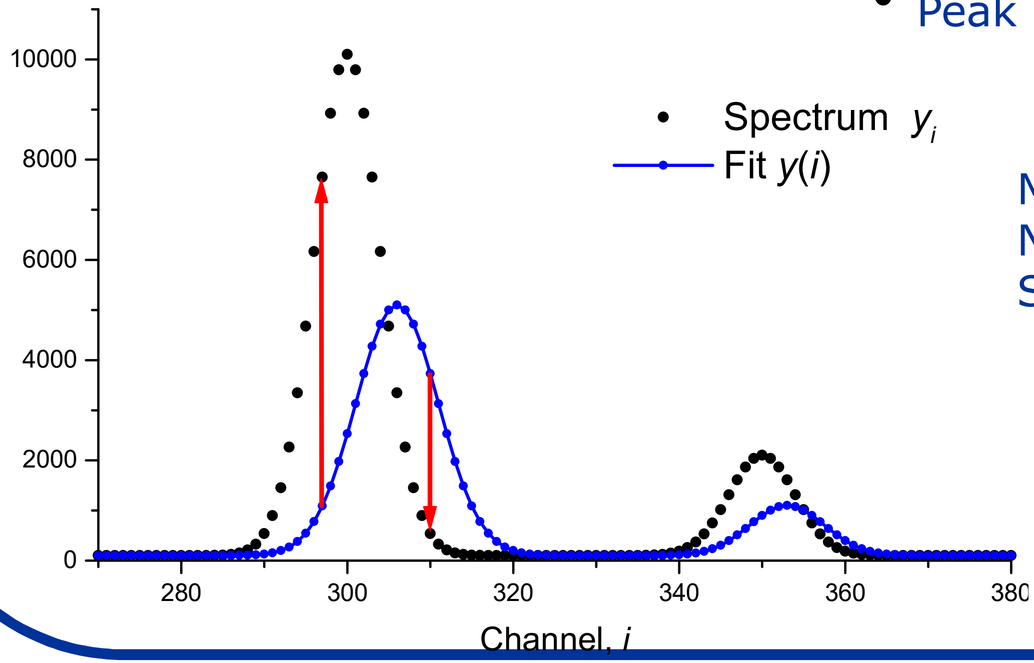
$$\chi^2 = \sum_{i=n_1}^{n_2} \left[y(i) - y_i \right]^2 \qquad y(i) = b + H \exp\left[\frac{(x_i - x_p)^2}{2\sigma^2} \right]$$

Continuum

Peak position

Peak width

Peak height



Minimum:

No direct analytical solution

Search χ^2 for minimum

Spectrum evaluation principle:

Non-linear least squares method:
    Search the minimum in χ^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

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

Line ratio
- Theoretical ratio
- Corrected for sample self-attenuation

Area

(Linear parameter)
- Initial guess from counts at maximum and theoretical gaussian area

Fitting function

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

- Continuum function

Different approaches:

- Filtering (iterative averaging of N channels, N ~ FWTM)
- Fitting (linear, polynomial, exponentials)

Fitting function

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

Peak shape

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

Energy calibration $$E(i) = \underline{Zero} + \underline{Gain} \times i$$

(Nonlinear parameters)

Resolution calibration $$\sigma_{jk} = \left[\left(\frac{\underline{Noise}}{2\sqrt{2\ln 2}} \right)^2 + \varepsilon\, \underline{Fano}\, E_{jk} \right]^{1/2}$$

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

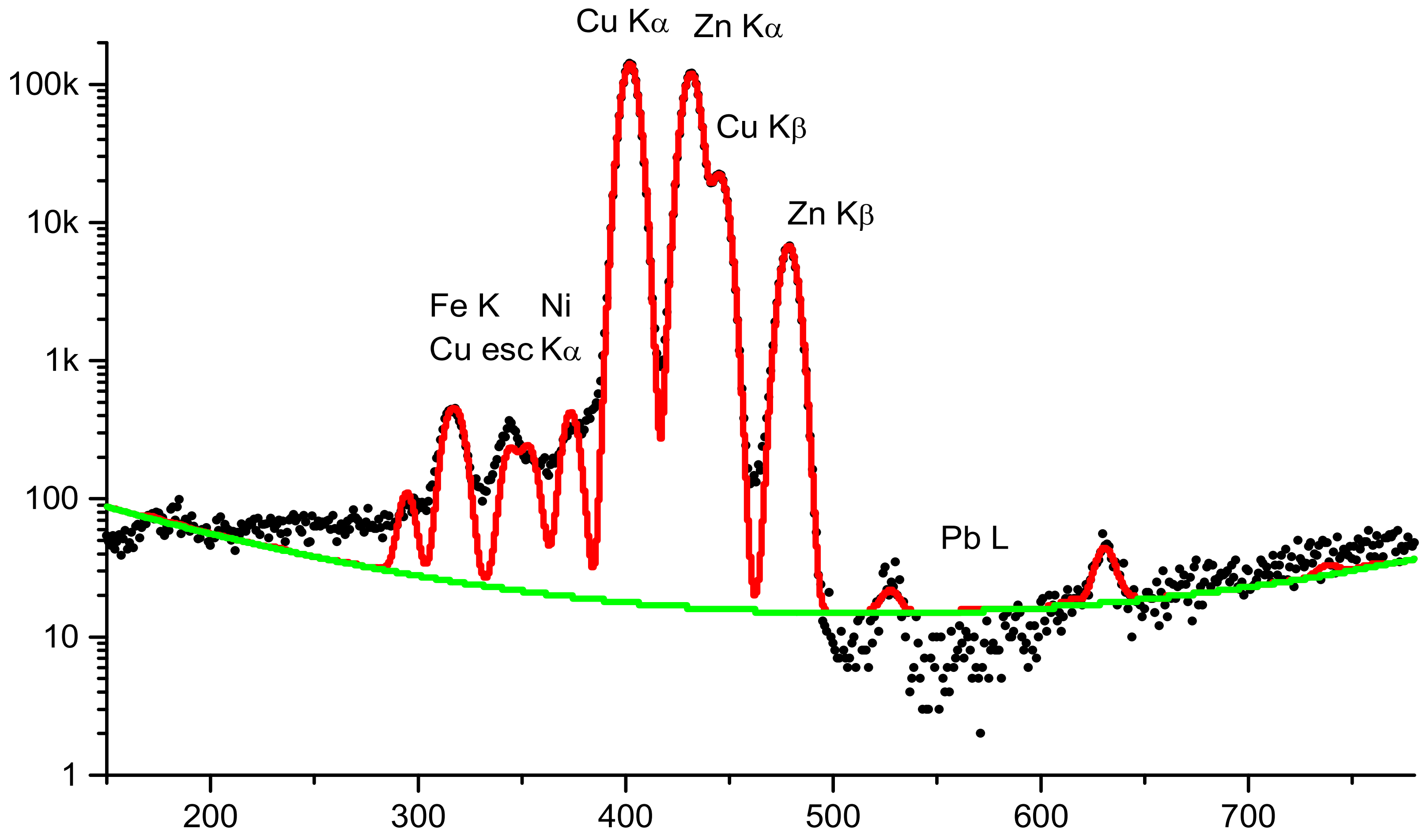
- unbiased, minimum variance estimate of the parameters

“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

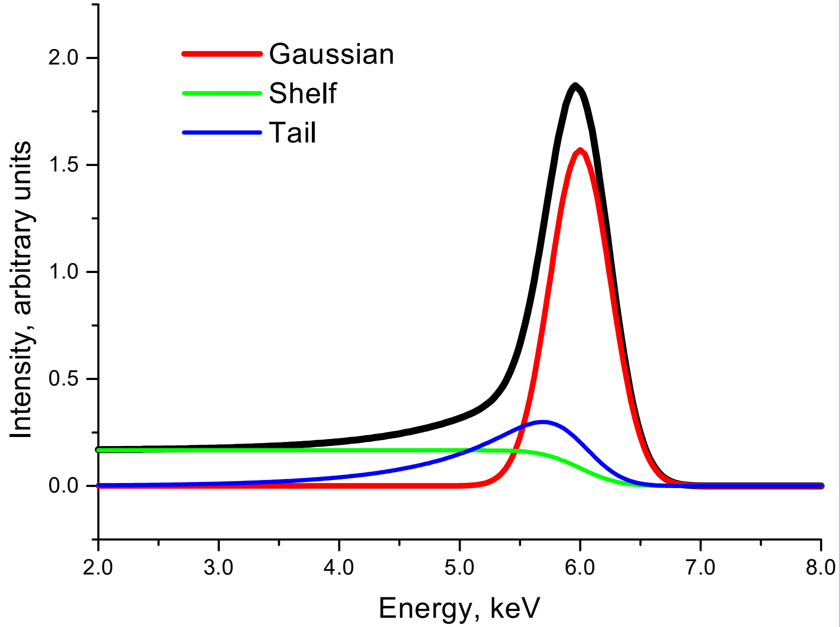


Improvement of fitting function

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

Gaussian:

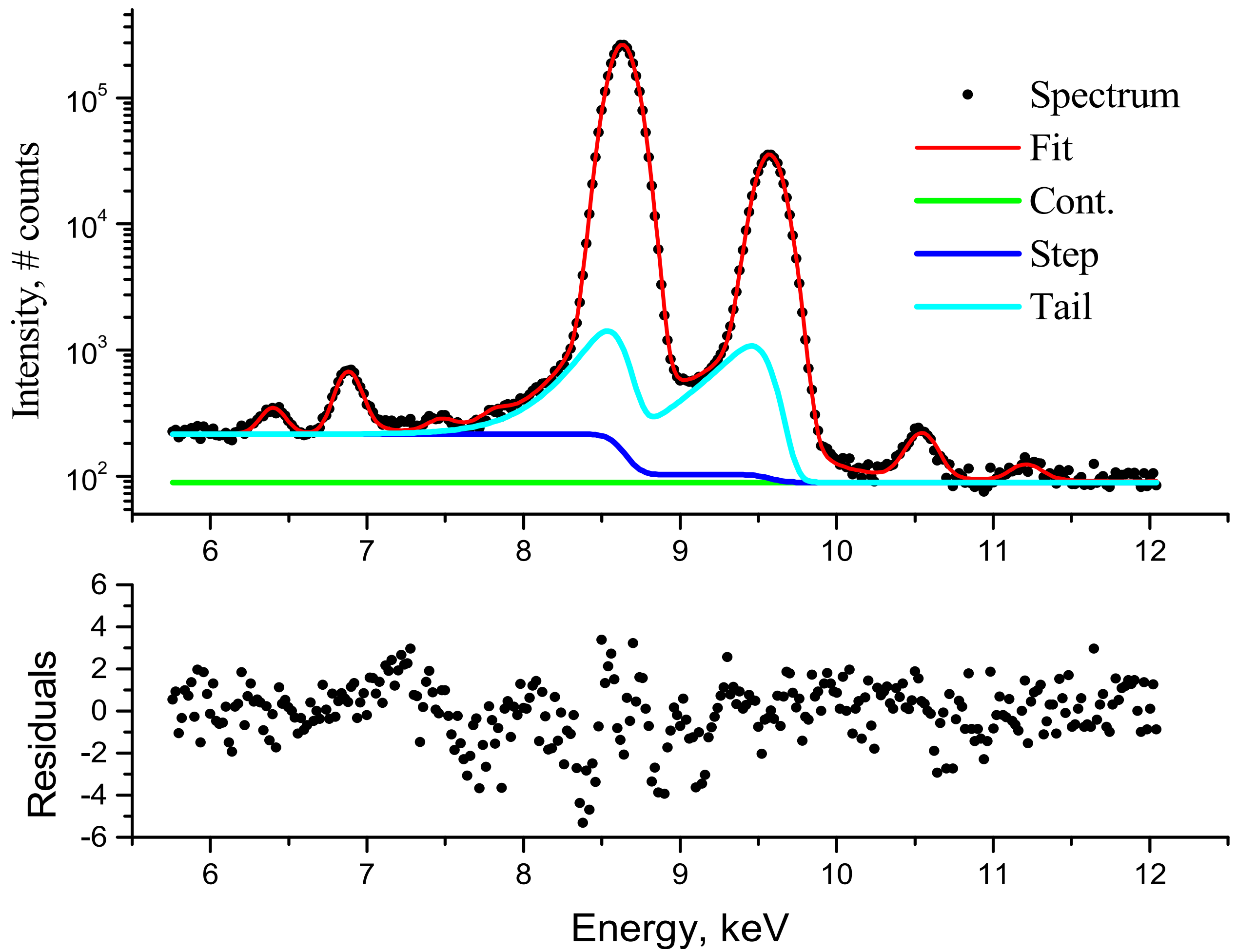
$$G(i,E_{jk}) = \frac{Gain}{S_{jk}\sqrt{2\pi}} Exp\left[-\frac{(E_i - E_{jk})^2}{2S_{jk}^2}\right]$$



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

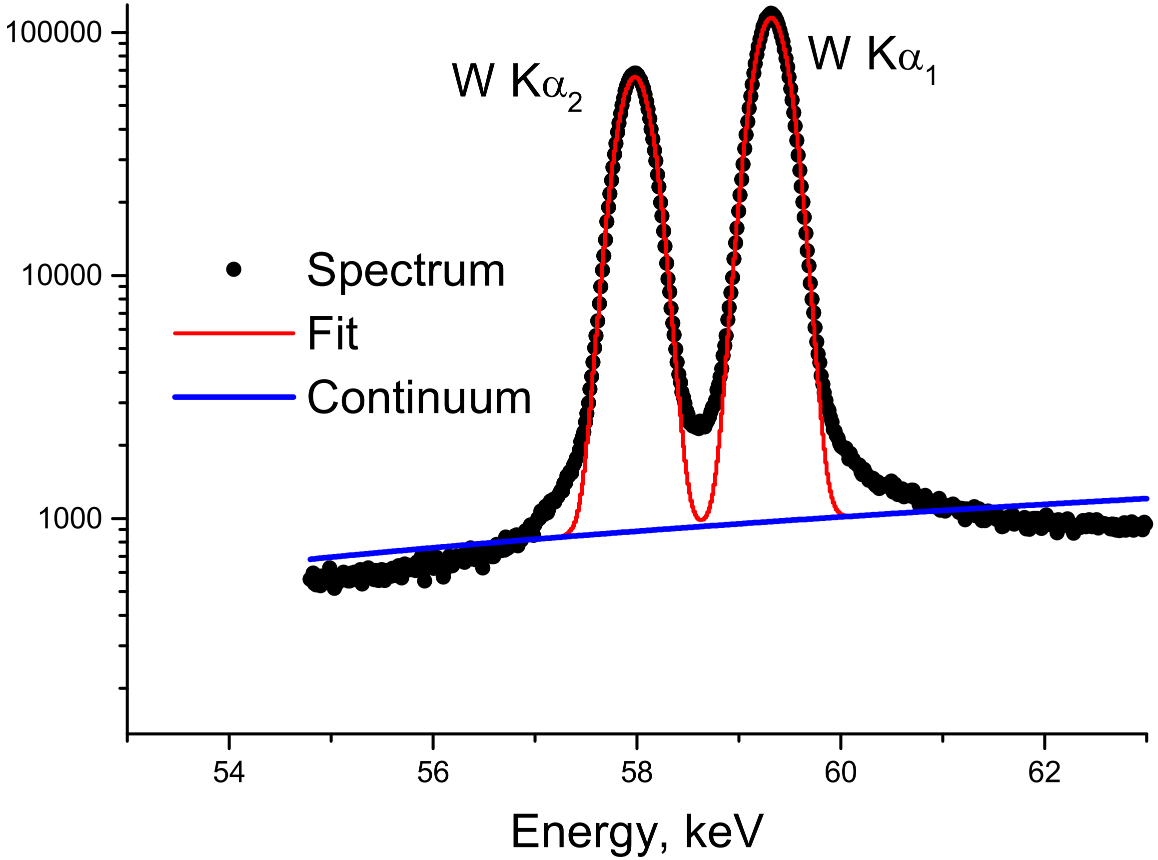
Tail: $T(i,E_{jk}) = \frac{Gain}{2\gamma\sigma \exp\left[-\frac{1}{2\gamma^2}\right]} \exp\left[\frac{E(i) - E_{jk}}{\gamma\sigma}\right] \mathrm{erfc}\left[\frac{E(i) - E_{jk}}{\sqrt{2}\sigma} + \frac{1}{\sqrt{2}\gamma}\right]$

Determination of step and tail parameters



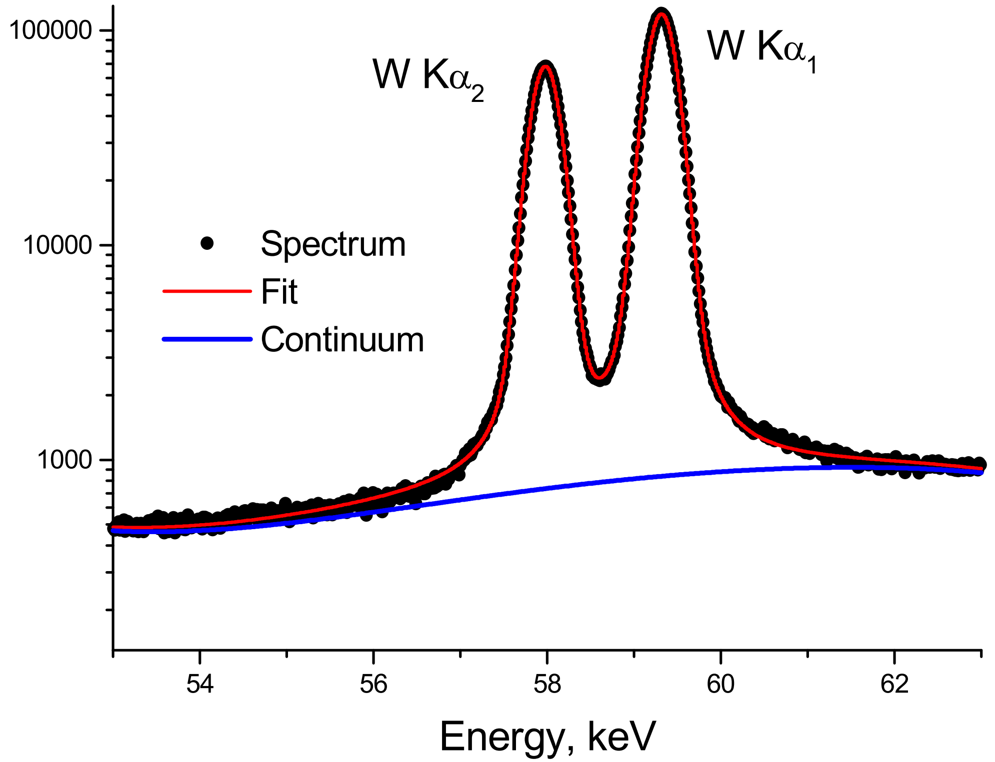
Lorentzian contribution

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

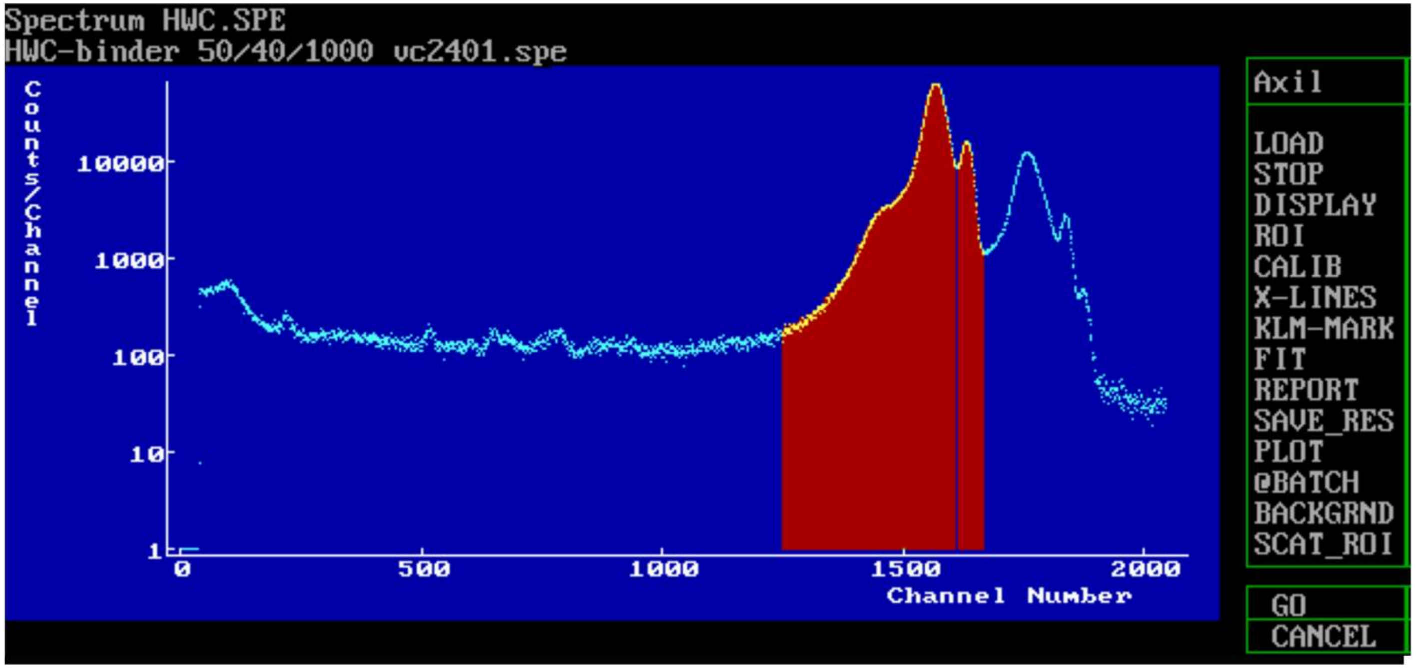


Lorentzian convoluted with Gaussian detector response: Voigt profile

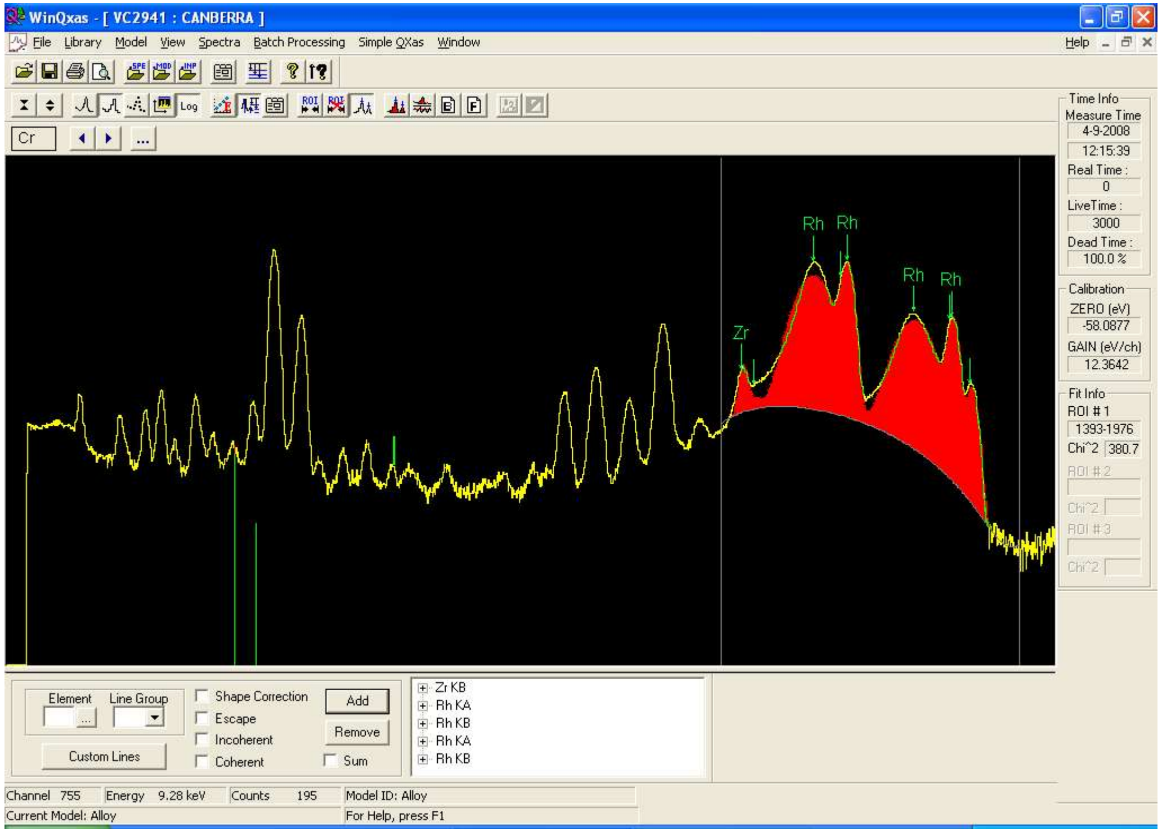
$$\frac{Gain}{\sqrt{2\pi}\sigma}\mathrm{K}\left(\frac{E(i)-E_{jk}}{\sqrt{2}\sigma},\frac{\alpha_L}{2\sqrt{2}\sigma}\right) \quad \text{with} \quad K(x,y)=\mathrm{Re}\left[e^{-z^2}\,\mathrm{erfc}(-iz)\right],\ z=x+iy$$



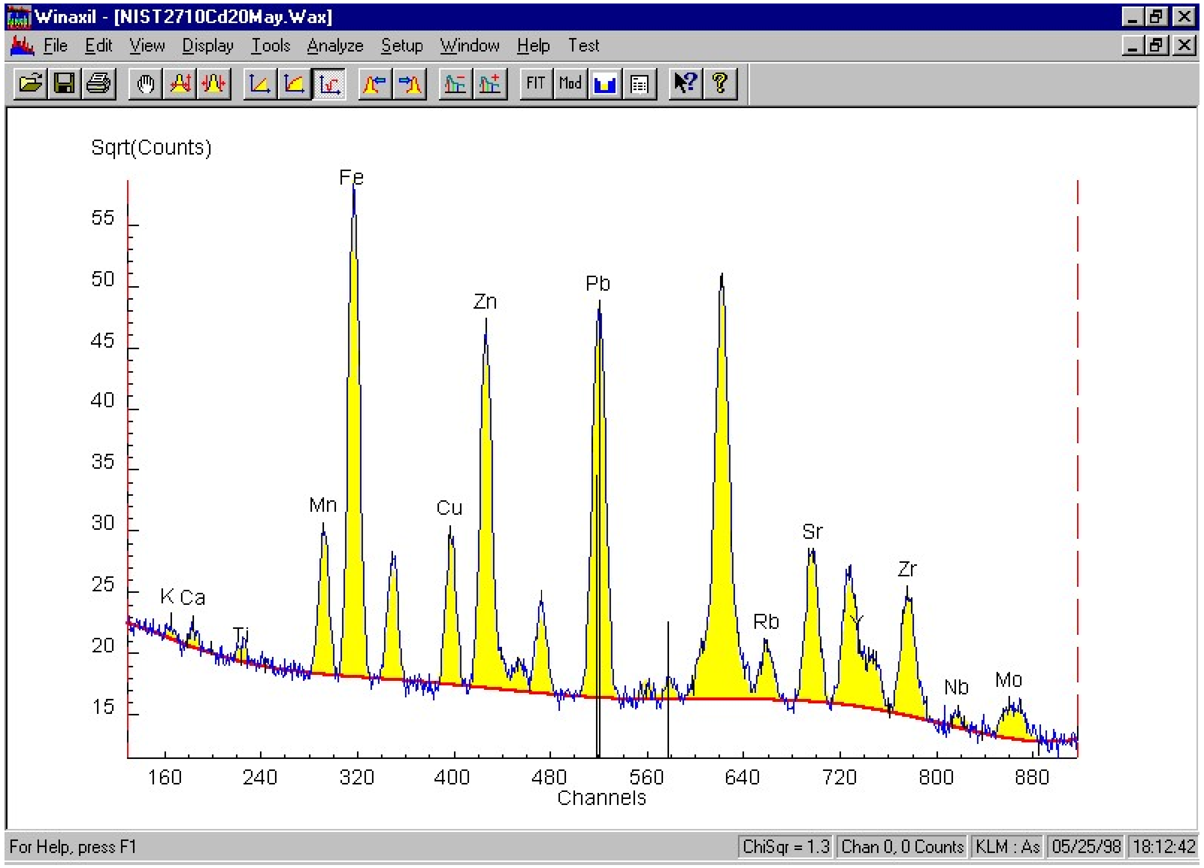
DOS- AXIL: IAEA, gratis



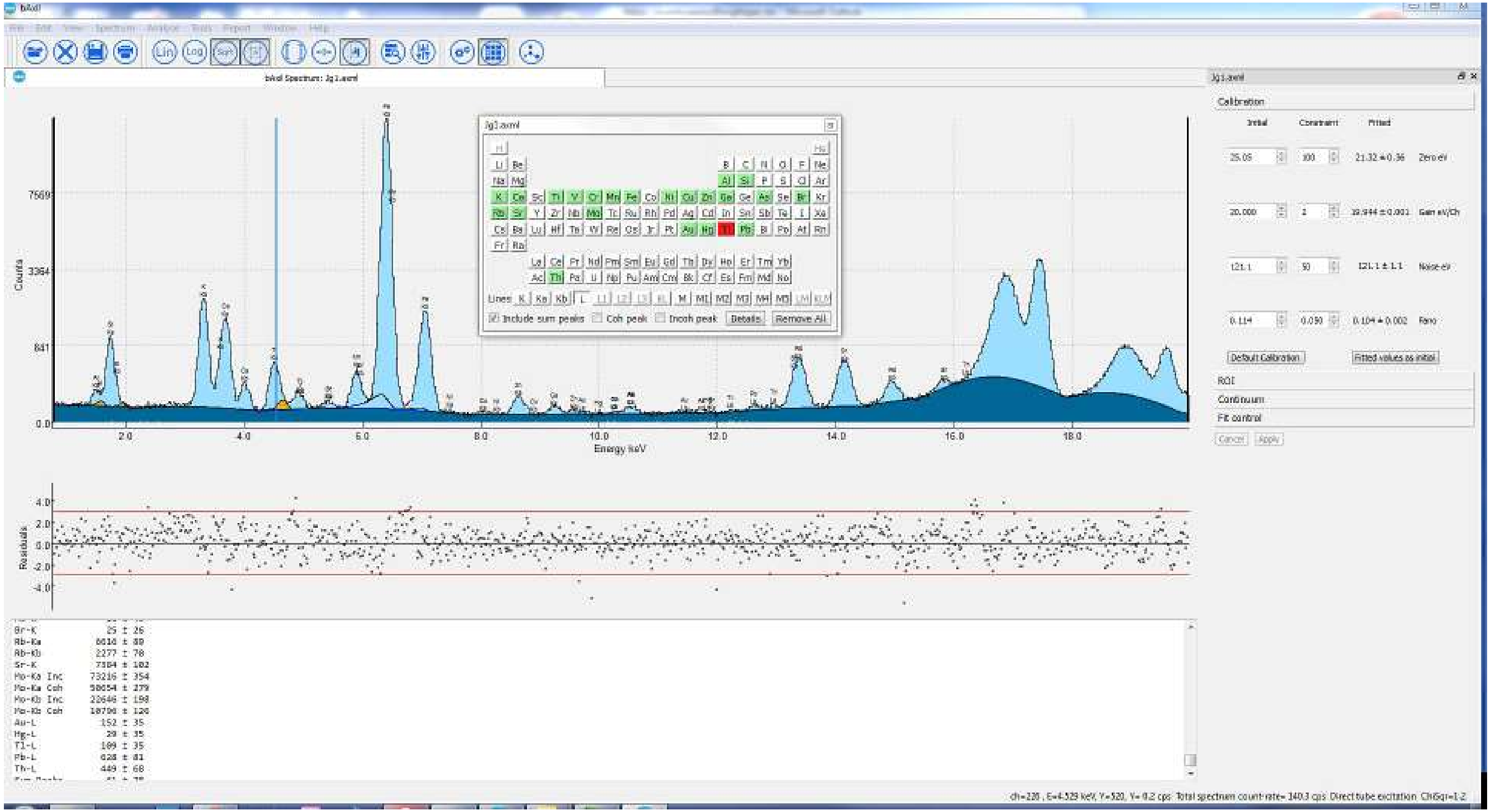
WinQXAS: IAEA, gratis



WinAXIL: Canberra, ~ 3000 EUR



bAXIL: BrightSpec, ~ 3000 EUR

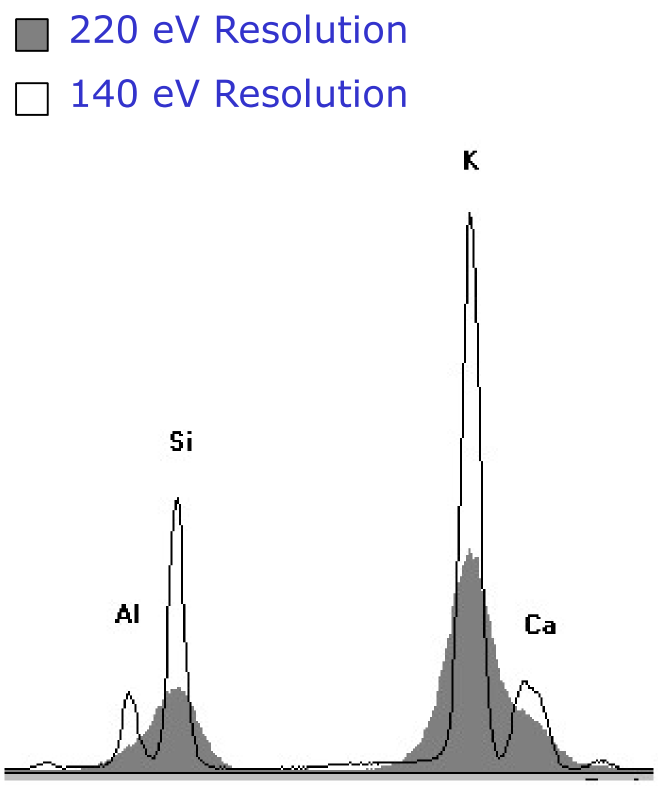


Comparison of features

	AXIL-QXAS	WinQXAS	WinAXIL	bAXIL
Environment	DOS	WINDOWS	WINDOWS	Windows
User interface	Old fashion, but friendly	Friendly	Friendly	Friendly
Multiple ROIs	Only successive	Allowed	Not allowed	Not allowed
Scatter peaks	- Integral - As COH INCOH	- Integral - As Line,COH, Line,INCOH	None	Yes, advanced model
Format conversion	Wide	Limited	Limited	Wide selection
Quantitative programs	Multiple choice	Only Elemental Sensitivity	Fundamental Parameter (MET)	Fundamental Parameter (MET) Elem. Sens.

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.



Adjacent Element 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 bakground

Thanks for your time and attention…