Joint ICTP-IAEA School on Novel Experimental Methodologies for Synchrotron Radiation Applications in Nano-science and Environmental Monitoring

Evaluation of XRF Spectra

from basics to advanced systems

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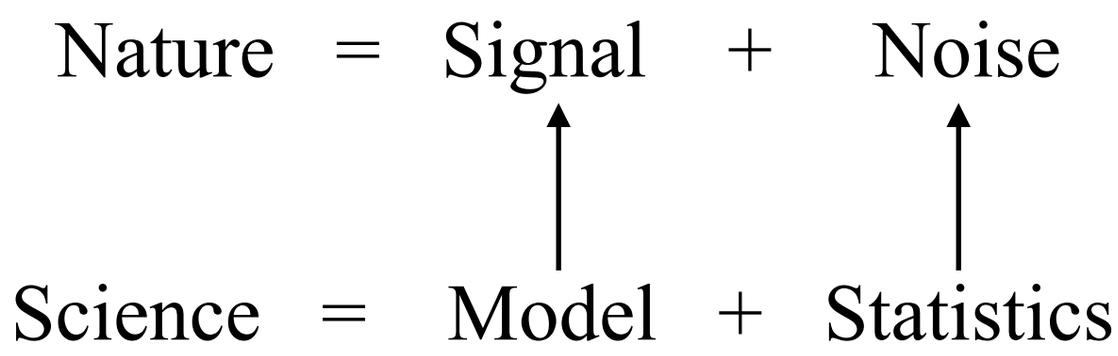
Content

Some basic concepts

Nature and science: a personal view



Why spectrum evaluation?

element concentrations ⇔ **net** intensity of fluorescence lines

interference free
continuum corrected

But:

frequent peak overlap

presence of a continuum

Especially in energy-dispersive spectra

Information content of a spectrum

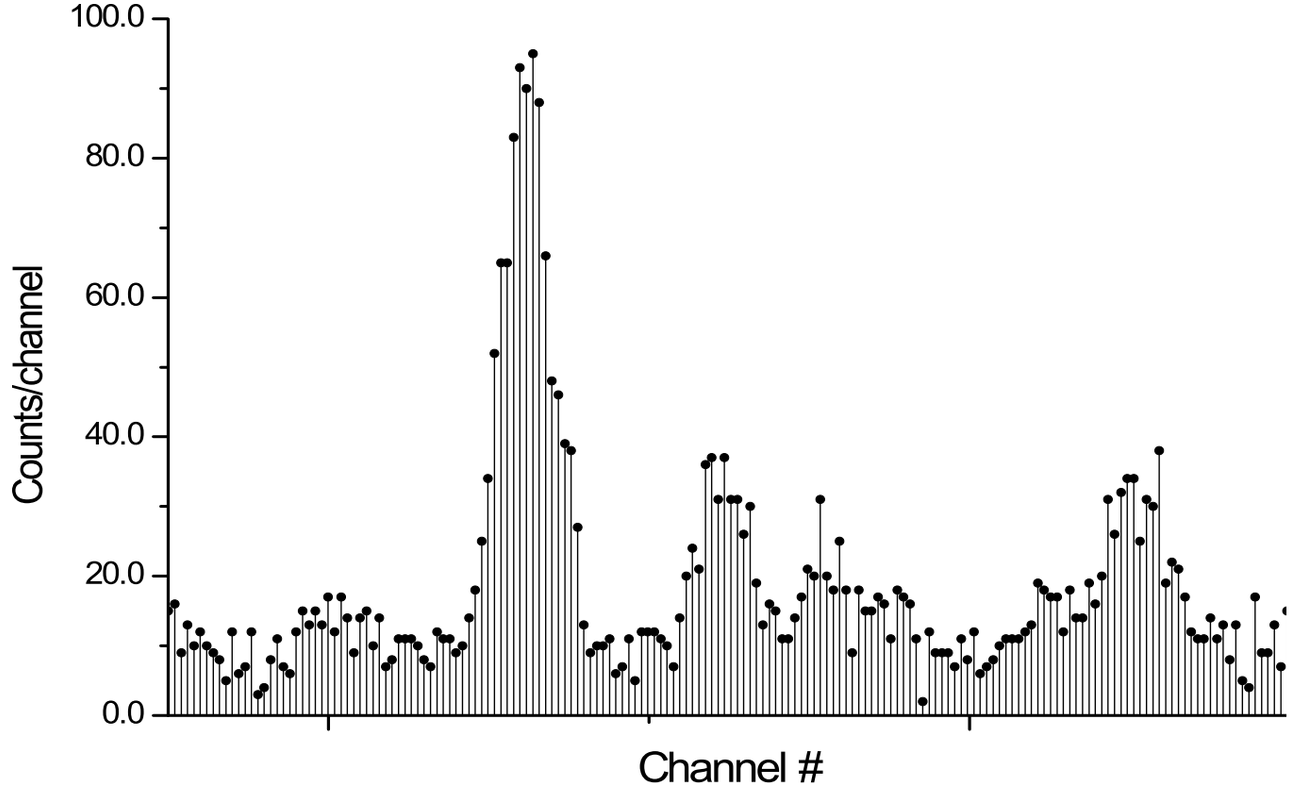
Spectrum contains

- Information: energy and intensity of x-rays — the signal

- Amplitude noise: due to Poisson statistics
  ► fluctuations in the spectrum

- Energy noise: finite resolution of the detector
  ► nearly Gaussian peaks with a width of ~160 eV

— the noise



Amplitude noise

Counting events involves Poisson statistics

Poisson probability density function:

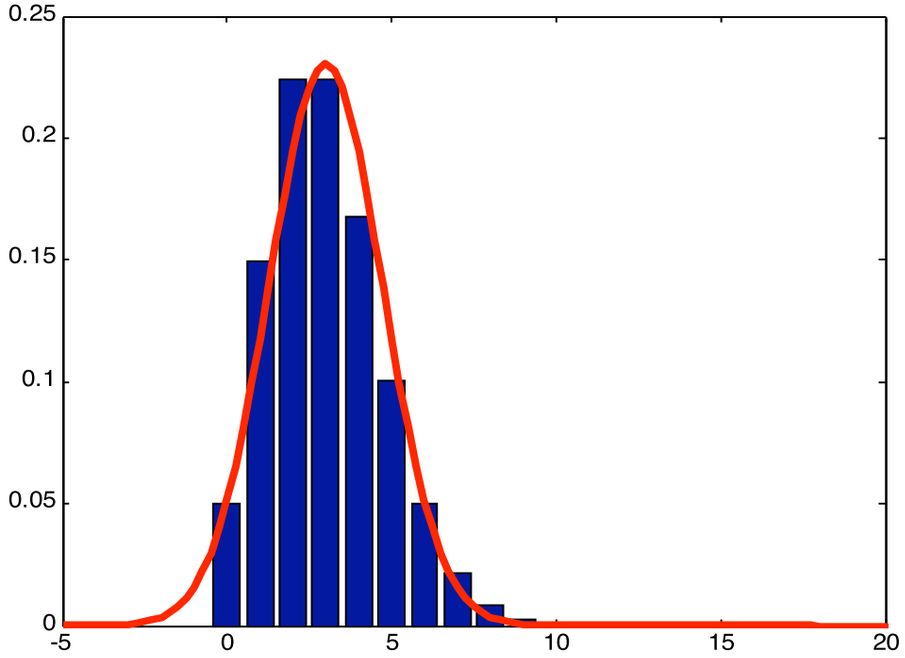
The probability to observe N counts if the true number is μ

$$P(N) = \frac{\mu^N e^{-\mu}}{N!}$$

Property:

$$\sigma_N = \sqrt{\mu} \approx \sqrt{N}$$

$$RSD\% = \frac{\sigma_N}{N} \times 100 = \frac{100}{\sqrt{N}}$$



Poisson : P(N | μ=3)

Normal : P(x | μ=3 σ^2 = 3)

Poisson distribution μ $\cong$ Normal distribution μ and $\sigma^2 = \mu$

approximation is very good for μ (or N) $\geq$ 9

Energy Noise Resolution of ED-XRF spectrometers

Full Width at Half Maximum (FWHM) of a peak

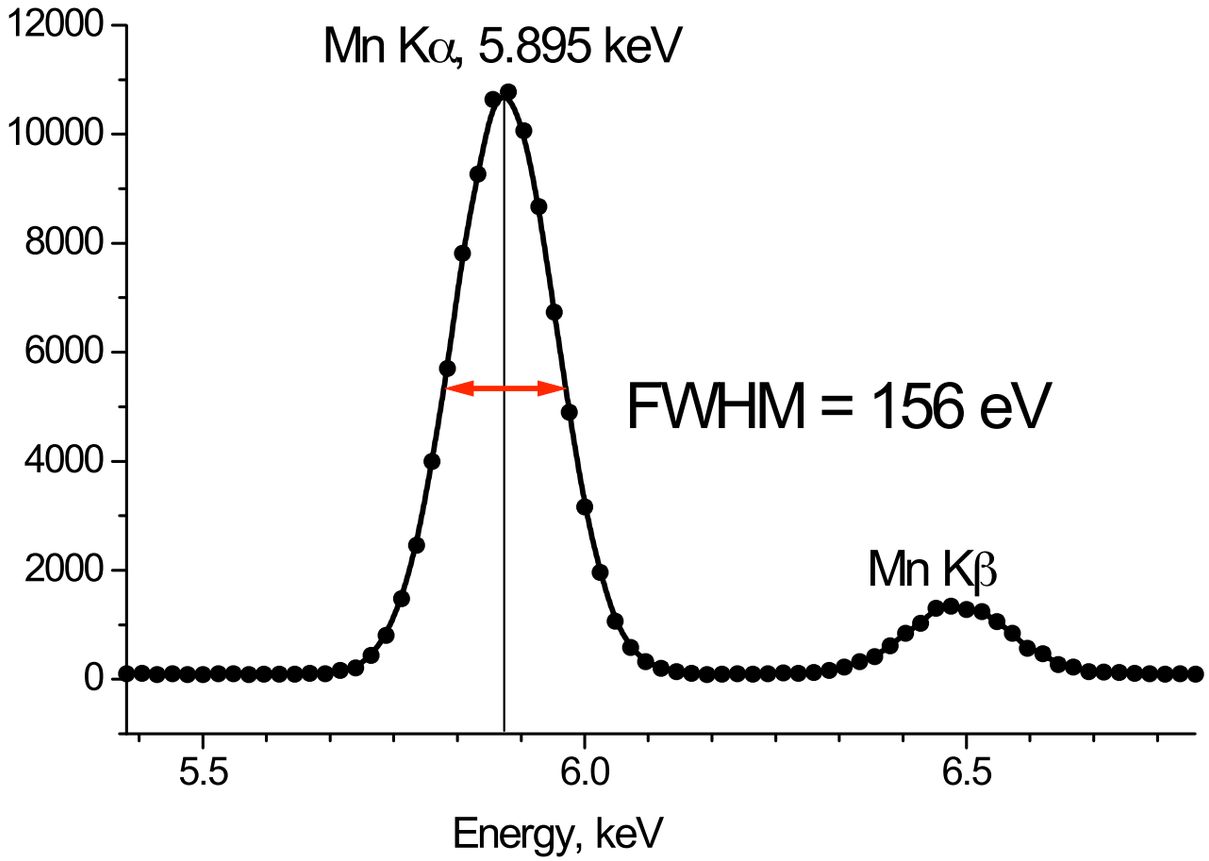
$$\mathrm{FWHM}^2_{\mathrm{Peak}} = \mathrm{FWHM}^2_{\mathrm{Elec}} + \mathrm{FWHM}^2_{\mathrm{Det}}$$

Electronic noise
~100 eV

Intrinsic contribution

$$2.35\sqrt{\epsilon \times F \times E}$$

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

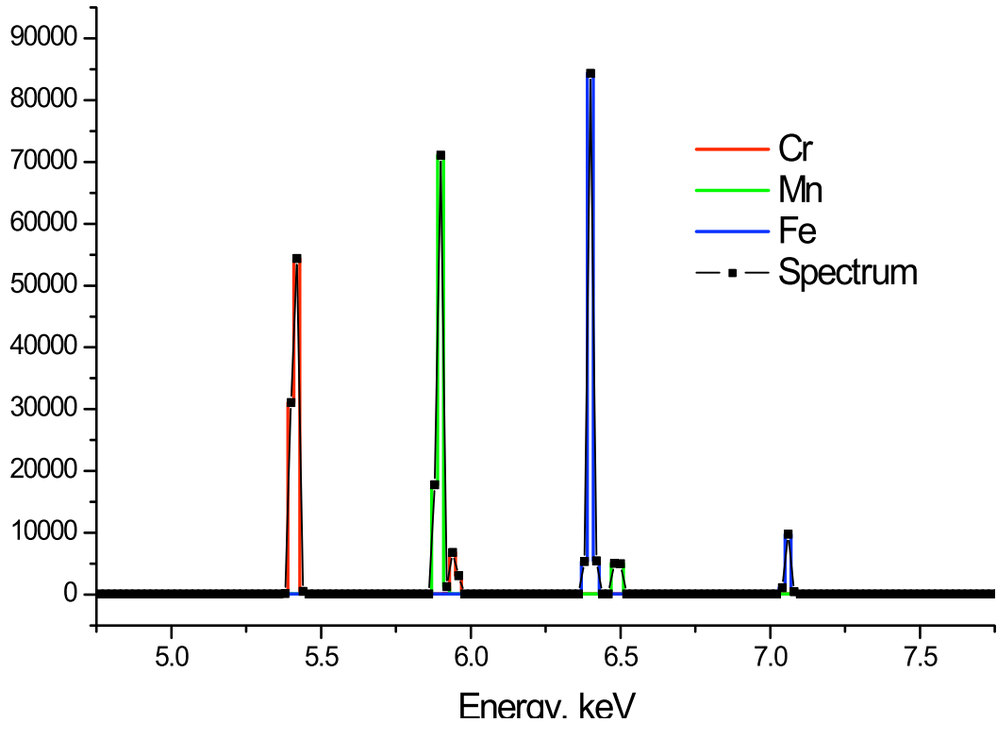
$\mathrm{FWHM}_{\mathrm{Det}}$ = 120 eV

$\mathrm{FWHM}_{\mathrm{Elec}}$ = 100 eV

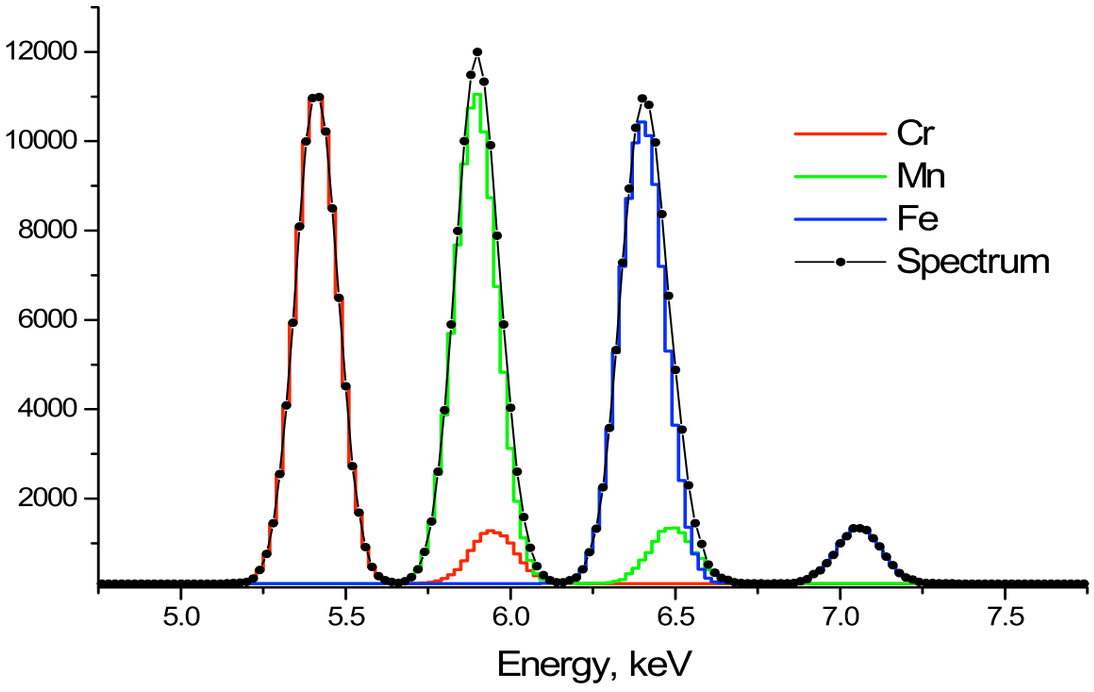
=> $\mathrm{FWHM}_{\mathrm{Peak}}$ = 156 eV

Energy Noise Resolution of ED-XRF spectrometers

Cr – Mn – Fe overlap at ~20 eV



Cr – Mn – Fe overlap at ~160 eV



Without amplitude noise (counting statistics) there would be NO PROBLEM

But it is part of the nature

We can only measure longer or with a more efficient system

Without energy noise there would be LITTLE PROBLEM

The natural line width of x-rays is only a few eV!!!

The observed peak width is the result of the detection process with a fundamental limitation imposed by the Fano factor

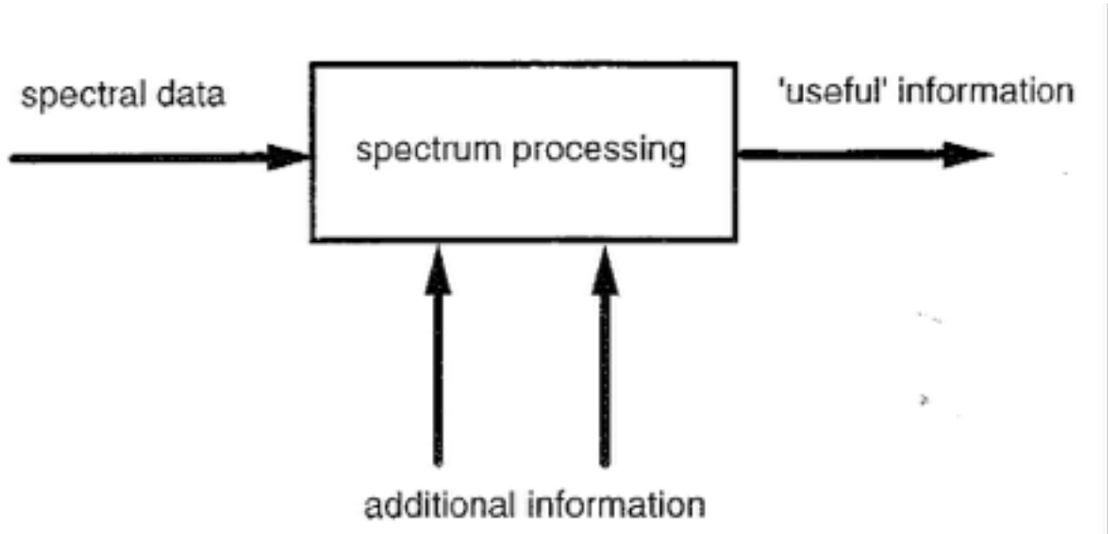
Information content of a spectrum

If no energy noise or no amplitude noise

► could determine the “information” unambiguously

Need methods to extract information in a optimum way

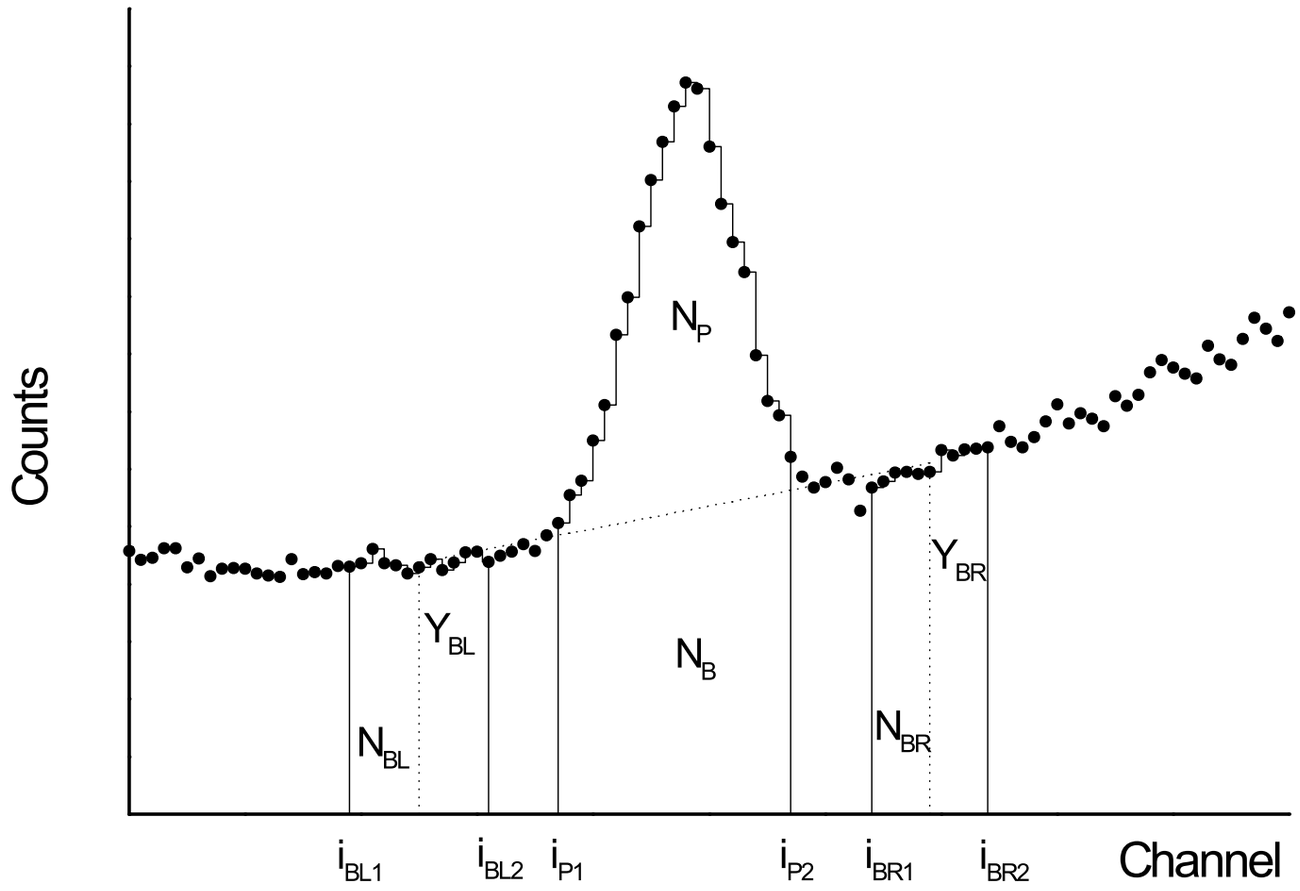
These methods rely on “addition” information (knowledge) to extract the useful information



Not the method itself is important (if implemented correctly) but the correctness of the additional information.

2. Simple peak integration

Simple peak integration



Estimate

$$N_P = \sum_{i_{P1}}^{i_{P2}} \left[y_i - y_B(i) \right] = N_T - N_B$$

Uncertainty

$$s_{N_p} = \sqrt{N_T + N_B}$$

As good as is can get
if the assumptions (model) are correct!

We have to make assumptions
- integration limits
- linear background
- no interference

3. Method of Least Squares

Method of least squares

Need to “estimate” the net peak area with highest possible
- correctness (no systematic error)
- precision (smallest random error)

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

Limiting factors:
- counting statistical fluctuations (precision)
- accuracy of the fitting model

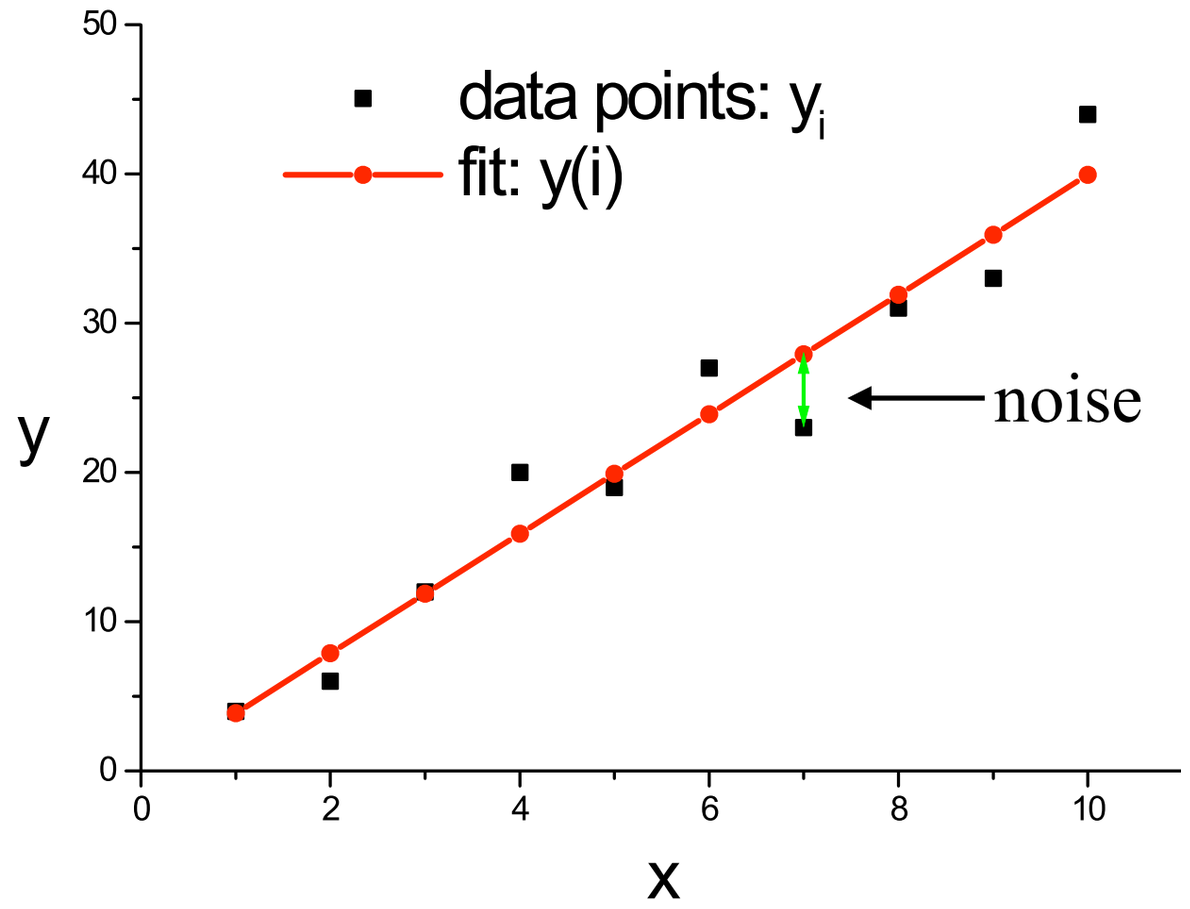
Method of least squares, straight line

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

Model: $y(i) = b_0 + b_1 x_i$

Fitting the model:
estimating b_0 and b_1

Criterion:



$$SS = \sum_i [y_i - y(i)]^2 = \sum_i [y_i - b_0 - b_1 x_i]^2 = \min$$

$$\frac{\partial SS}{\partial b_0} = 0 \quad \rightarrow \quad \sum_i y_i = b_0 n + b_1 \sum_i x_i$$

$$\frac{\partial SS}{\partial b_1} = 0 \quad \rightarrow \quad \sum_i x_i y_i = b_0 \sum x_i + b_1 \sum_i x_i^2$$

Set of 2 equations in 2 unknowns b_0 and b_1

Normal equations

Direct analytical solution

4. Fitting X-ray Spectra

Least-squares estimate of x-ray spectrum parameters

Peak described by a Gaussian

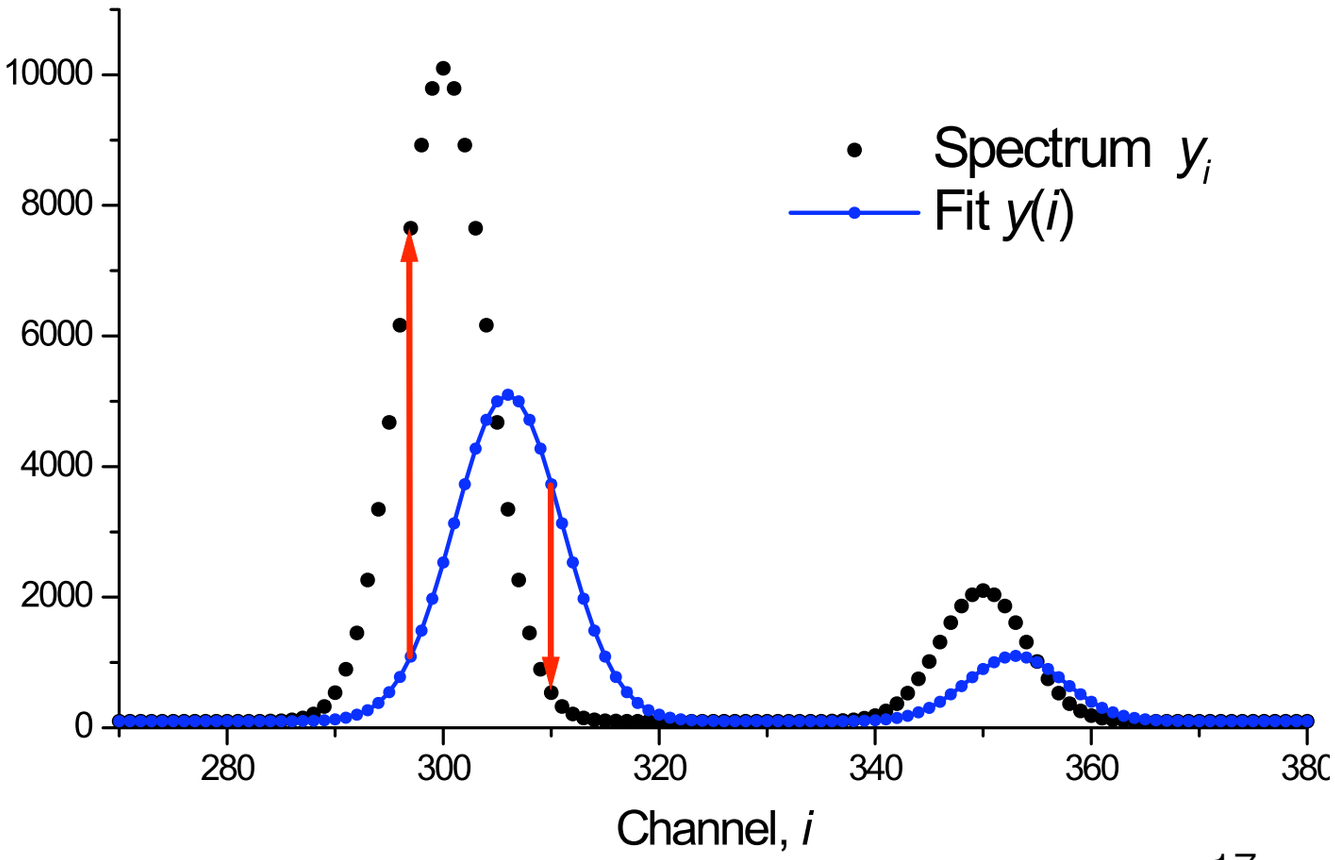
$$y(i) = b + A\frac{1}{\sigma\sqrt{2\pi}}\exp\left[\frac{(x_i - x_p)^2}{2\sigma^2}\right]$$

area: A — position: x_p — continuum: b — width: σ

linear parameter

non-linear

Criterion, agreement between model and data $\chi^2 = \frac{1}{\nu}\sum_{i=n_1}^{n_2}\frac{1}{w_i}\left[y(i) - y_i\right]^2$



Minimum:

No direct analytical solution

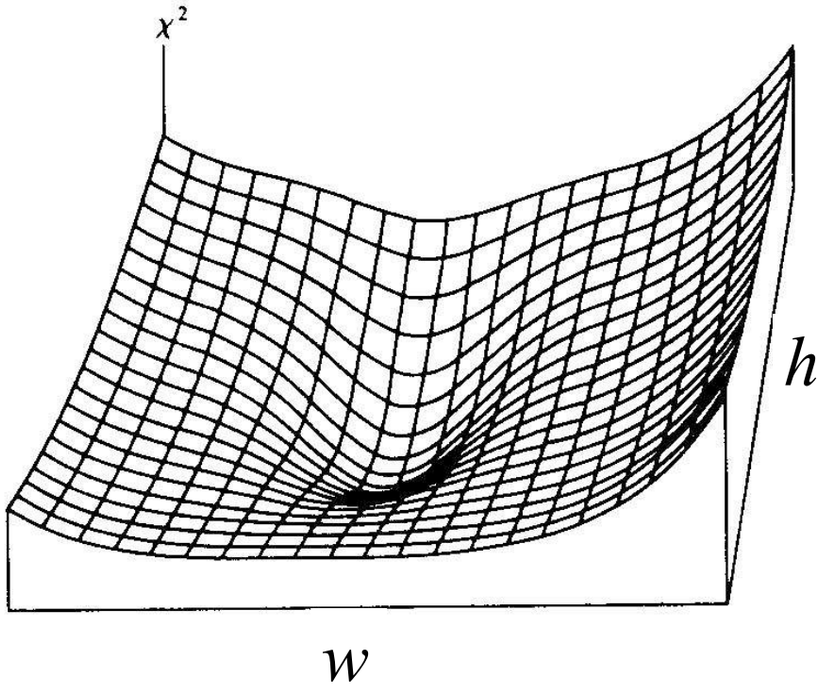
Search χ^2 for minimum

We can still apply the concept of least squares
minimising the square of the differences between the model and the data

$$\chi^2 = \chi^2(b, h, x_0, w) = \frac{1}{\nu} \sum_i \frac{1}{y_i} \left[y_i - y(x_i, b, h, x_0, w) \right]^2$$

The sum of squares is a function of the values of the parameters and for a given set of values should be minimum

In this case SS describes a 4 dimensional hyper-surface in a 5-dimension space



We can only "see" in 3-dimensions but mathematically we can search in a higher dimensional space to locate the minimum

Starting from some initial values we can modify the parameter values until the minimum is reached.

General form of such a search algorithm

1. Select starting values for all parameters b_j and calculate the ch-square $\chi = \chi(\mathbf{b})$

2. Obtain (calculate, guess...) a change (increment or decrement) Δb_j such that one moves towards the minimum: $\chi(\mathbf{b} + \Delta\mathbf{b}) < \chi(\mathbf{b})$

3. Replace the old parameter values with the new ones
   $\mathbf{b} \leftarrow \mathbf{b} + \Delta\mathbf{b}$

4. repeat step 2 until the “true” minimum is found

Iterative process

AXIL = Analysis of X-ray spectra by Iterative Least-squares

$$\chi^2 = \frac{1}{\nu} \sum_{i=n_1}^{n_2} \frac{1}{w_i} \left[y(i) - y_i \right]^2$$

Analytically important parameters: net peak areas

Statistical optimal estimate:

using correct weight (Poisson statistics $w_i = y_i$)

In general $y(i)$ is non-linear → Marquardt – Leverberg algorithm

Gradient search ↔ linearisation

Reliable error estimated

But unstable

10 peaks $\Rightarrow$ > 30 parameters !!!! WANT WORK in practice!!!!

Need parsimony!!!

But we can do better

We known the energies of the x-ray lines (in most cases)
Where they are depends on the energy calibration
(the same applies to the width of the peaks: resolution calibration)

$\Rightarrow$ Add additional information to the model

Gaussian peak shape $$G(i,E) = \frac{Gain}{\sigma(E)\sqrt{2\pi}} \exp\left[\frac{(E_i - E)^2}{2\sigma^2(E)}\right]$$

Energy relation: $$E(i) = Zero + Gain \times i$$

Resolution relation: $$\sigma(E) = \left[\left(\frac{Noise}{2\sqrt{2\ln 2}}\right)^2 + \epsilon Fano E\right]^{1/2}$$

Only 4 non-linear parameters
For 10 peaks only 14 parameters

Already better, but we know more

We know (to some extend) the ratio between lines of an element

$$\frac{I_{K\alpha 2}}{I_{K\alpha 1}}, \quad \frac{I_{K\beta}}{I_{K\alpha}} \quad \ldots$$

We can group lines together ("peakgroup") with one "area" and fixed intensity ratios

$$y(i) = y_{\mathrm{Cont}}(i) + \sum_j A_j \left\{ \sum_k R_{jk} P(i, E_{jk}) \right\}$$

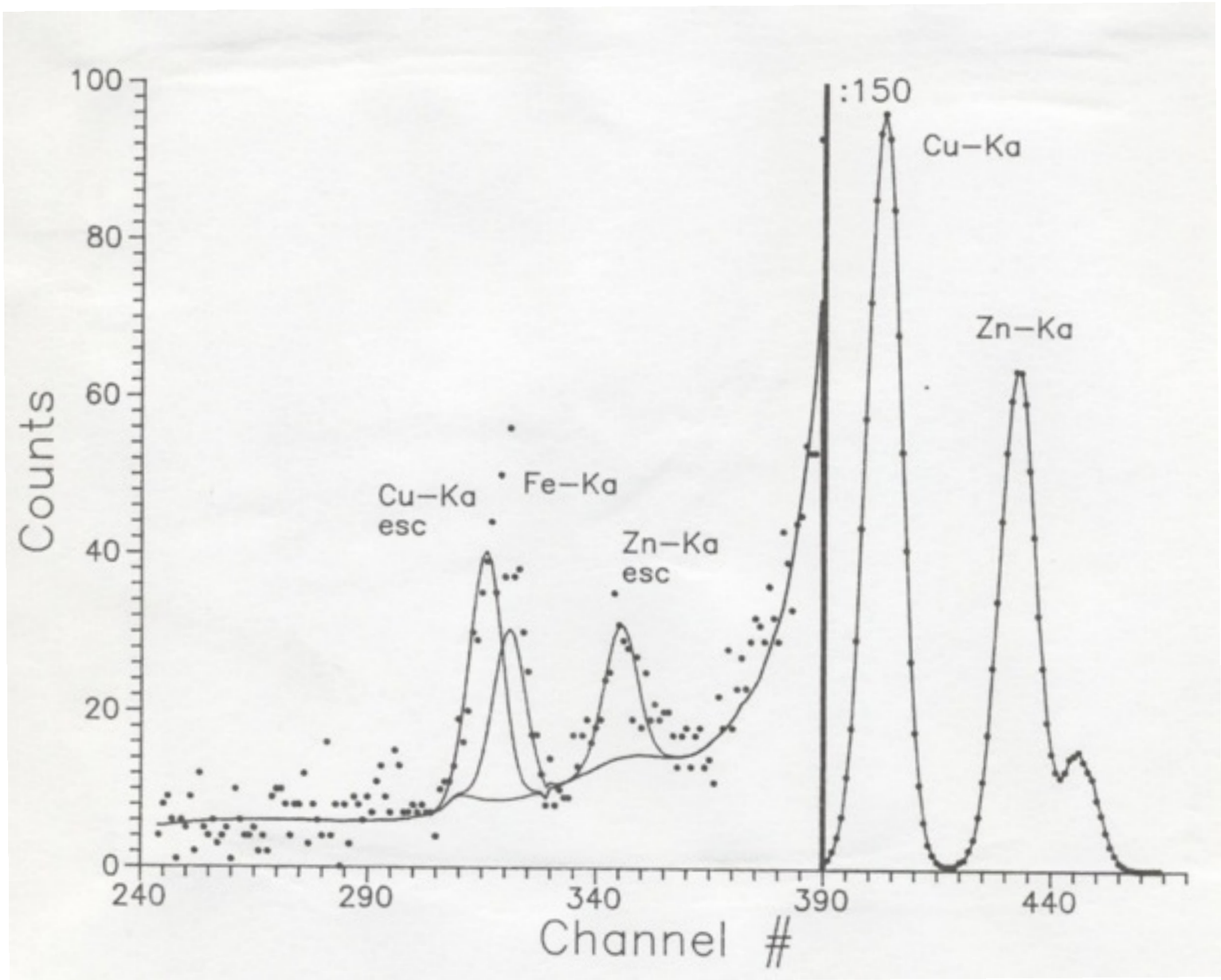
↓ Continuum function ↓ Area ↓ Line ratio ↓ Peak shape

for j elements (or peak groups)

10 elements ⇒ 10 Area's + 4 calibration parameters

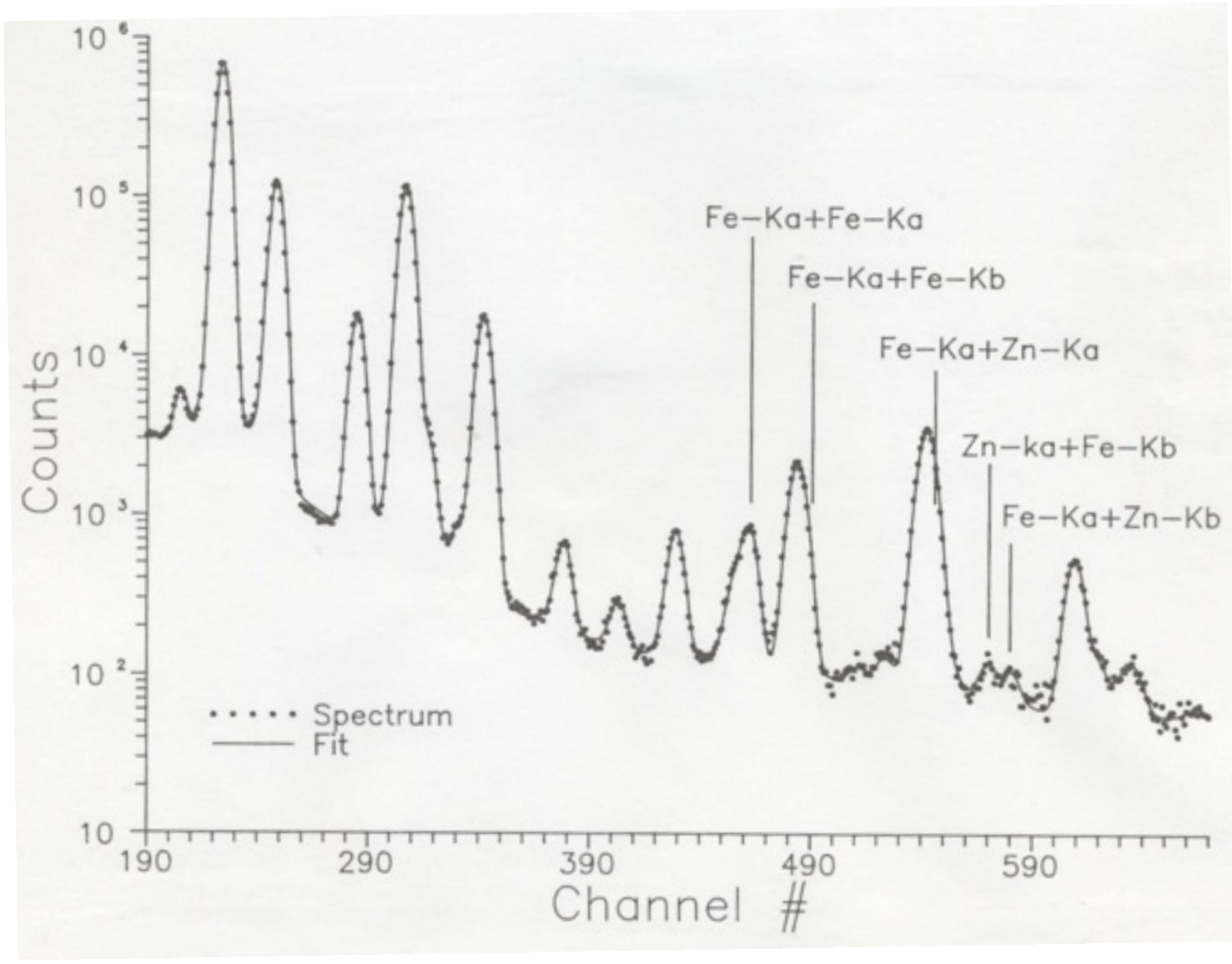
Further refinements: escape peaks

Known
- position (energy)
- intensity (escape probability)



Sum peaks

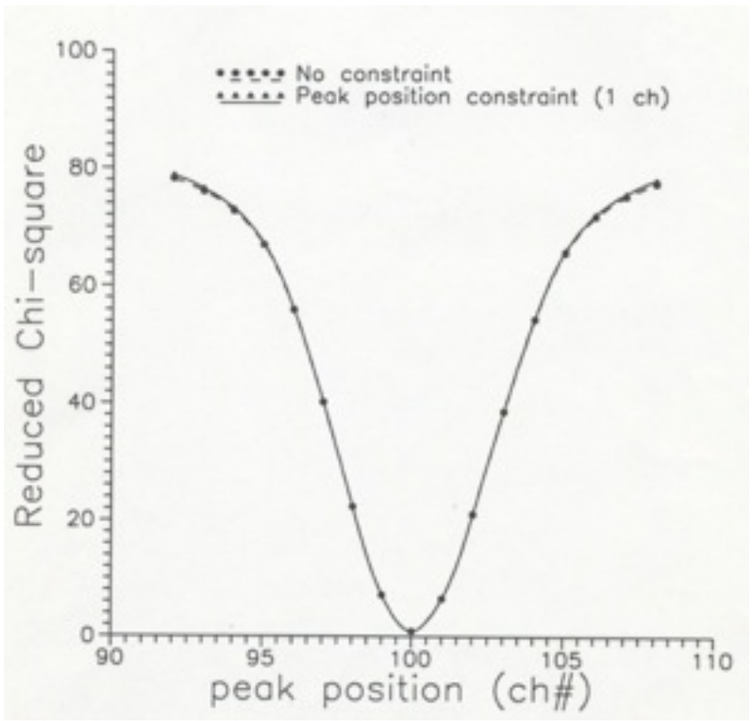
Known
- position
- relative intensity

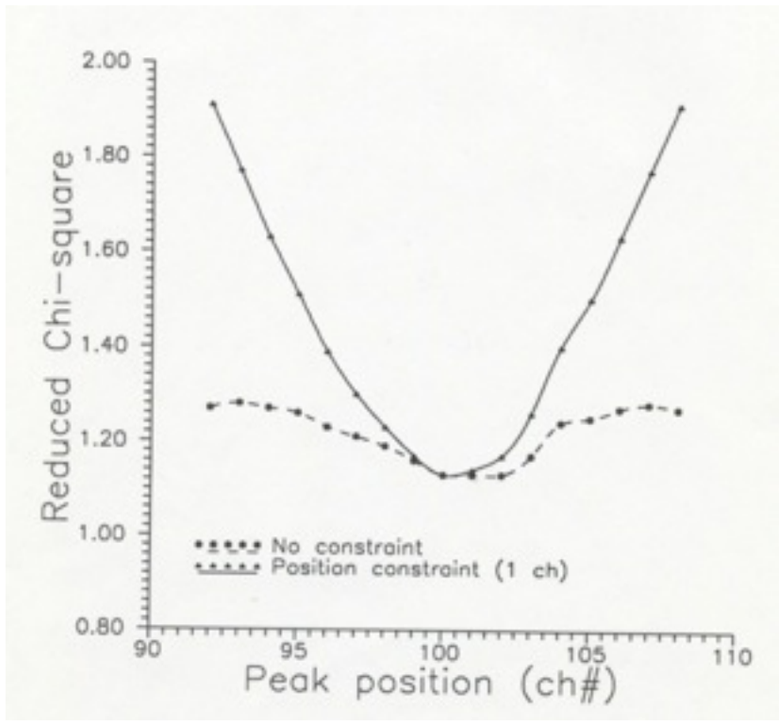


And more

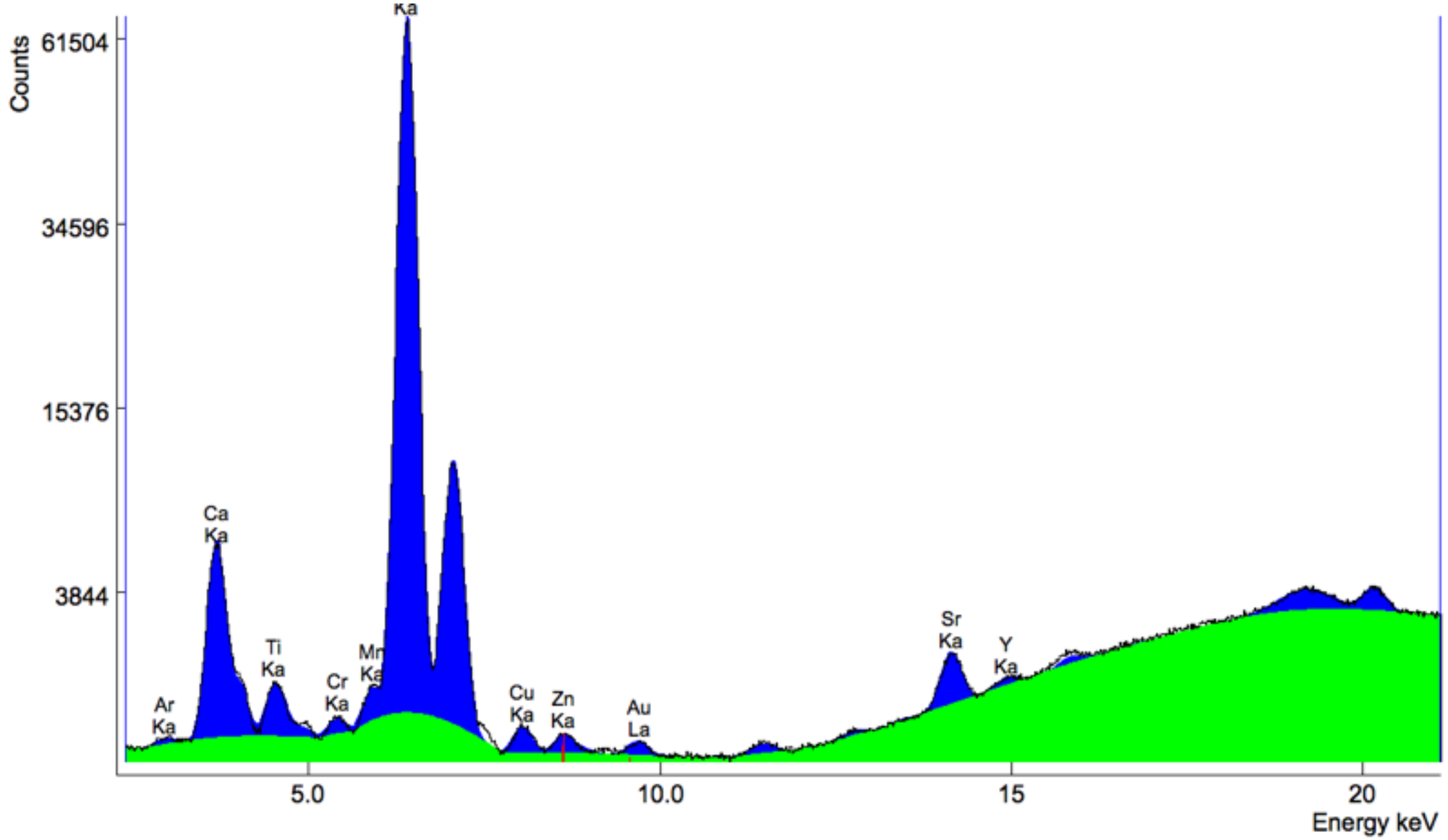
Different background models
- polynomial
- exponential polynomial
- Bremsstrahlung background
- filter background

Parameter constraining





and more...


Counts
61504
34596
15376
3844
Ka
Ca Ka
Ti Ka
Cr Ka
Mn Ka
Ar Ka
Cu Ka
Zn Ka
Au La
Sr Ka
Y Ka
5.0
10.0
15
20
Energy keV

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

5. Improvements to the model

Incorrectness of the model

Not all peaks follow the energy calibration relation

- incoherent (Compton) scatter peaks
- spurious peaks (diffraction, γ-rays)
- even the relation might not be linear

Not all peaks follow the resolution calibration relation

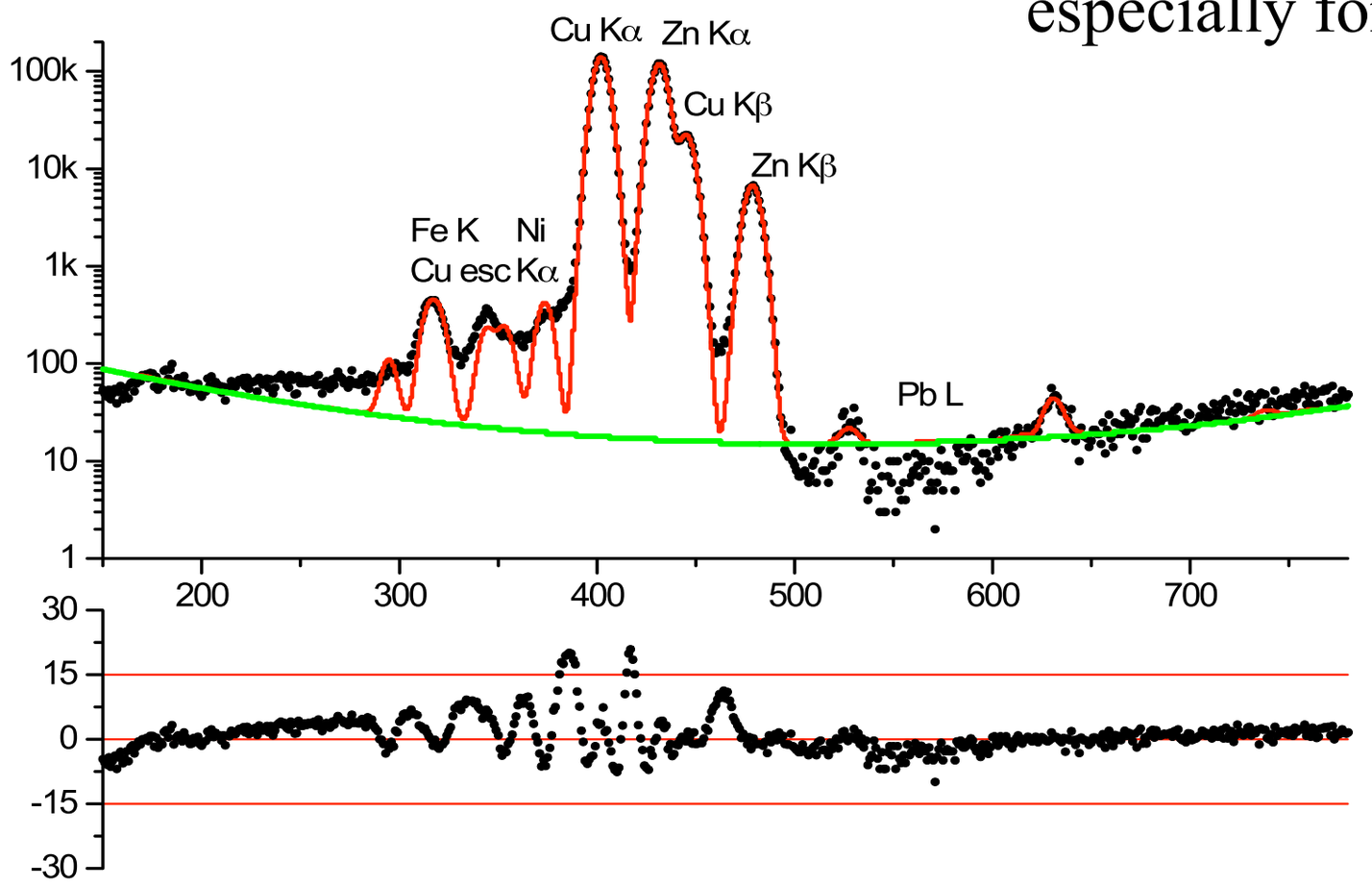
- incoherent scatter peaks (are wider)
- spurious peaks

Peaks are certainly not perfect Gaussians

- shelf (step) due to detector effects (incomplete charge collection)
- tailing due to radiative effects and detector effects
- deviation due to natural line width (Lorentzian)

Incorrect fitting model ⇒ biased results

especially for trace elements



Solution

Adapt the model
(fitting region, which lines to include...)
for each particular case

Very inconvenient
when analyzing
many spectra

Improvements

Improve the peak profile

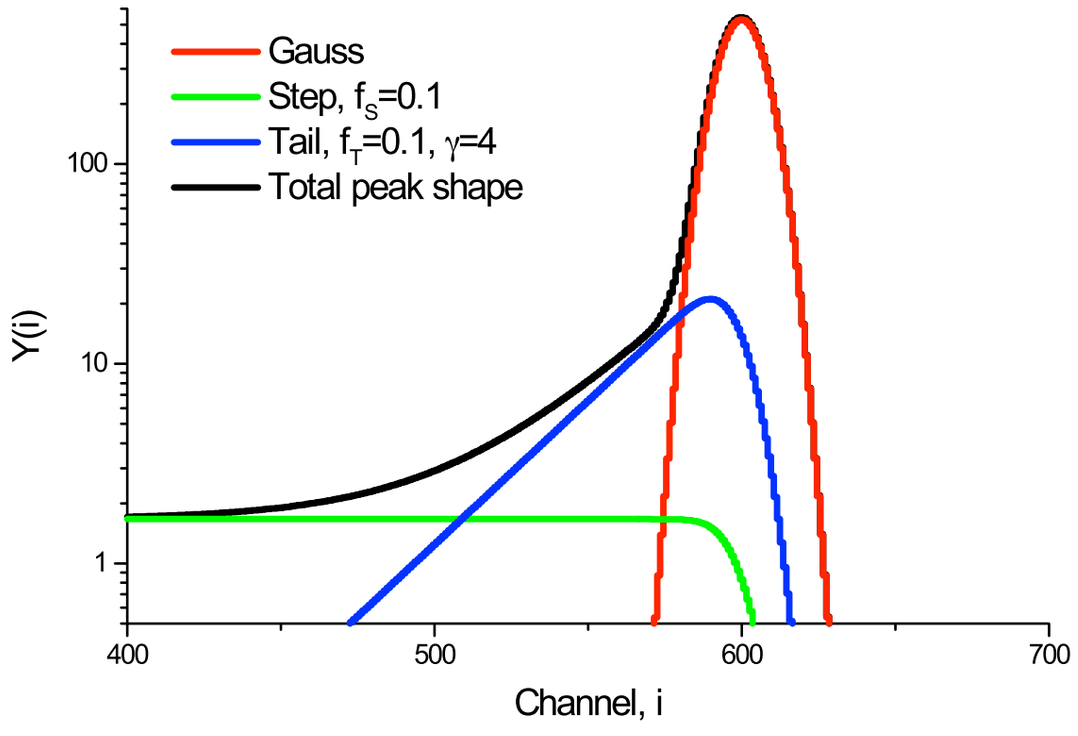
Peak $$P(i, E_{jk}) = G(i, E_{jk}) + f_S S(i, E_{jk}) + f_T T(i, E_{jk})$$

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

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

Adding 1 non-linear
and 2 linear parameters
for each peak!!!

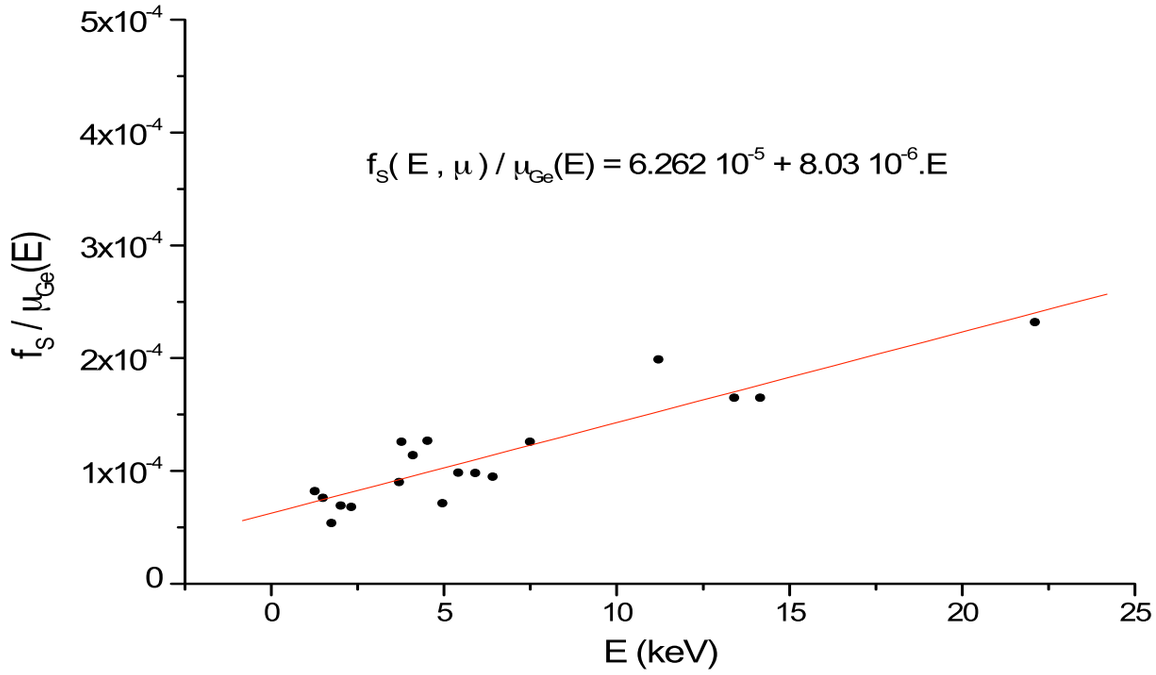
Where is my parsimony gone!!!



Step parameterisation

Step fraction f_S is related to the MAC of the detector crystal

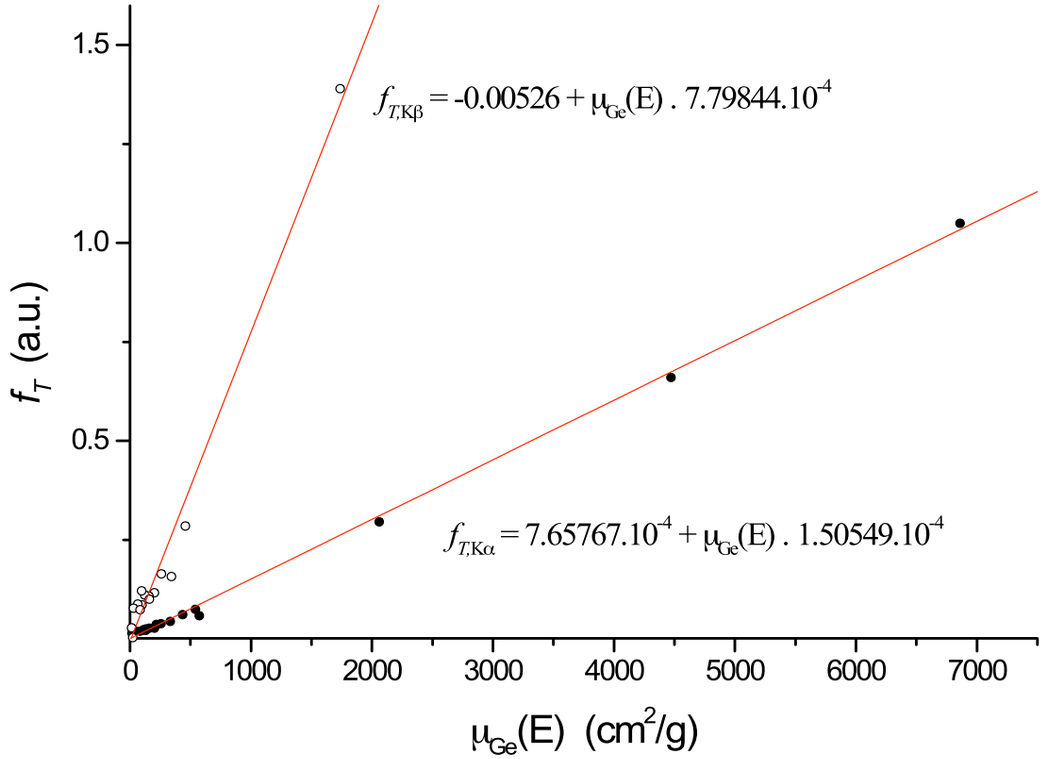
Step is a fundamental aspect of the detector (charge loss by photo-electrons near the surface of the detector)



Tail fraction parameterisation

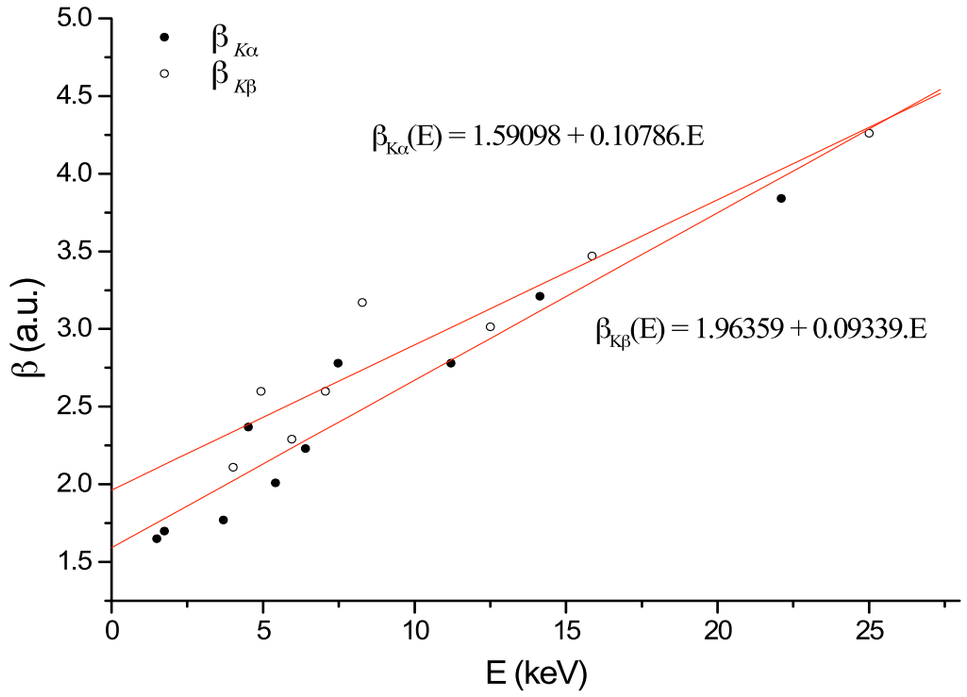
Tail fraction f_T is related to the MAC of the detector and the type of radiation (Kα and Kβ)

The tail has a component due to the detector and a radiative component



Tail width parameterisation

similar magnitude over the entire energy range



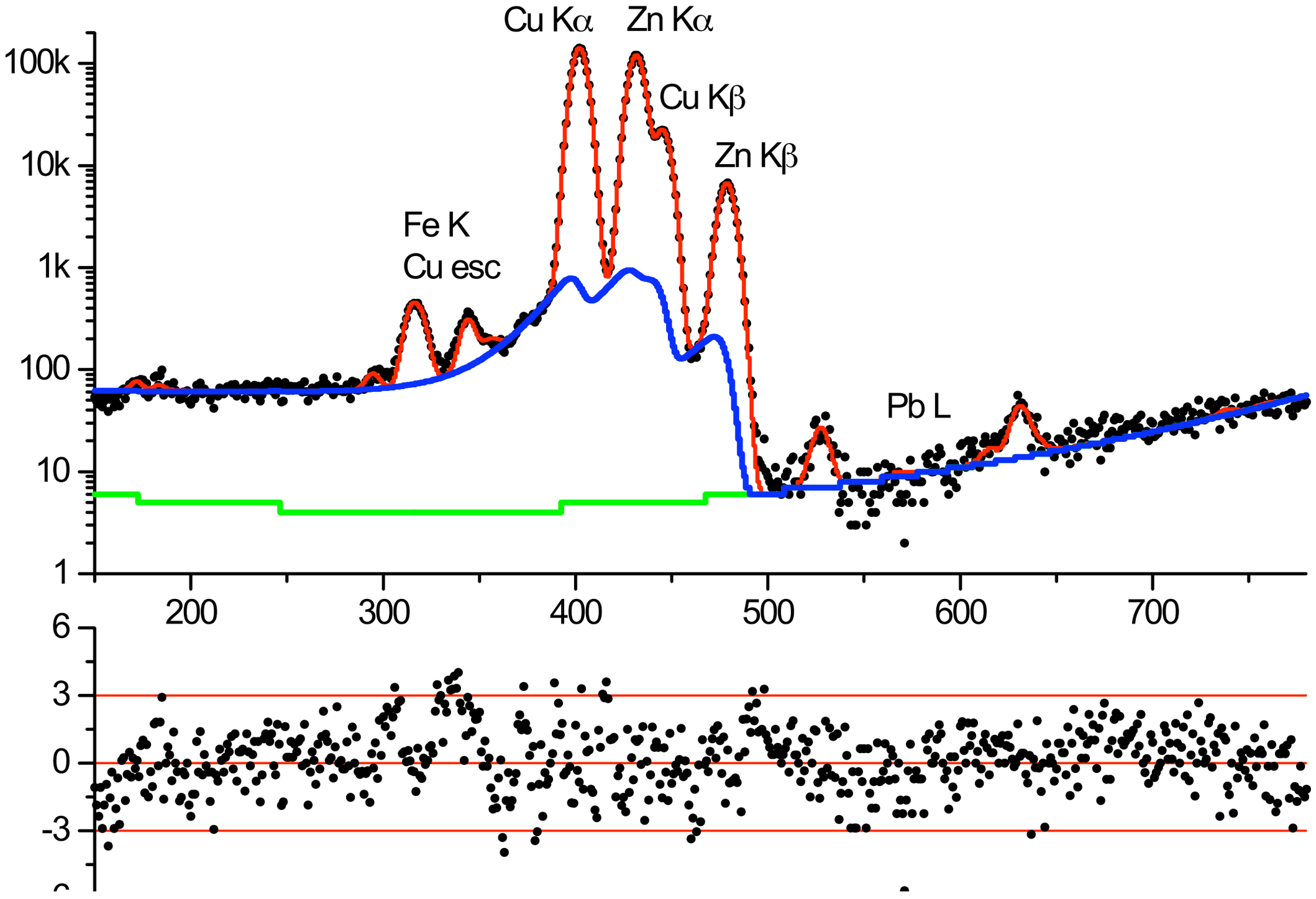
$\Rightarrow$ Fitting parameters a_0, a_1, b_0, b_1, c_0, c_1, d_0, d_1

$$
\begin{aligned}
f_S(E_{jk}) &= \mu_{\mathrm{Det}}(E_{jk})\,(a_0 + a_1 E_{jk}) \\
f_{TK\alpha}(E_{jk}) &= b_0 + b_1 \mu_{\mathrm{Det}}(E_{jk}) \\
f_{TK\beta}(E_{jk}) &= c_0 + c_1 \mu_{\mathrm{Det}}(E_{jk}) \\
\beta(E_{jk}) &= d_0 + d_1 E_{jk}
\end{aligned}
$$

(compare to Zero, Gain, Noise and Fano)

improvement

Fit of a NIST SRM 1106 Brass spectrum (SpecTrace 5000, Rh tube)



To account for peak shift and peak broadening

Need to make the peak profile still a bit more complicated

$$G(i,E) = \frac{Gain}{\gamma\sigma(E)\sqrt{2\pi}} \exp\left[\frac{(E_i - E(i) + \delta E)^2}{2\gamma\sigma^2(E)}\right]$$

δE peak shift parameter (normally 0.00)

γ peak broadening parameter (normally 1.00)

These parameters are constrained to vary within a certain range

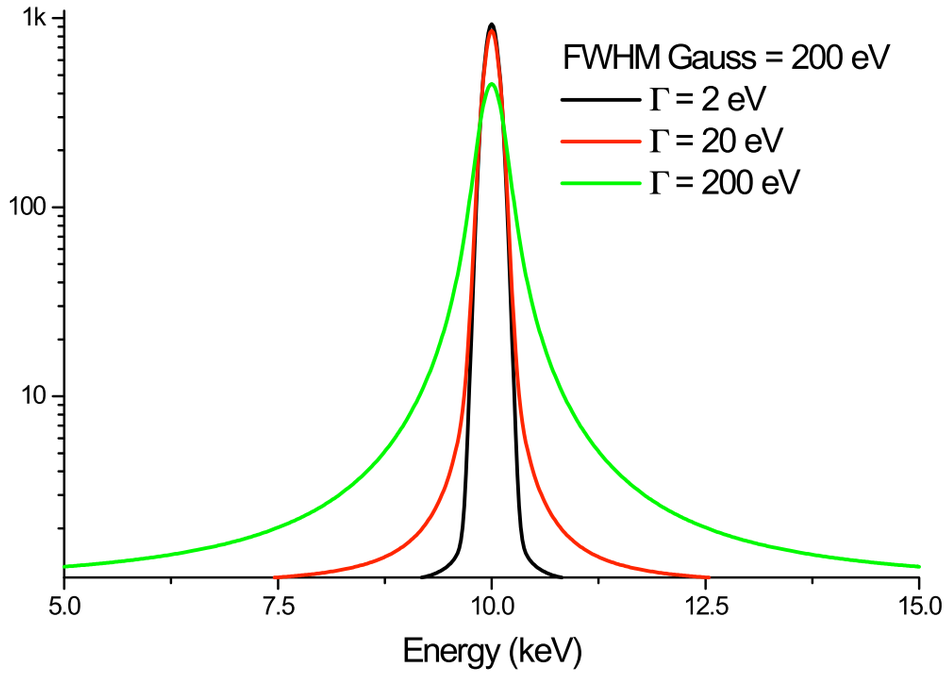
$$\delta E_{ini} - \Delta\delta E \leq \delta E \leq \delta E_{ini} + \Delta\delta E$$

$$\gamma_{ini} - \Delta\gamma \leq \gamma \leq \gamma_{ini} + \Delta\gamma$$

The last step

For high Z elements the natural line width becomes substantial relative to the detector resolution

Z	Element	Lorentz Width eV	FWHM	Ratio in%
13	Al	0.85	115	0.74
30	Zn	2.70	171	1.58
40	Zr	5.64	212	2.66
47	Ag	8.70	243	3.58
50	Sn	11.5	257	4.49
74	W	41.3	376	10.98
79	Au	56.0	403	13.88



Replace Gaussian with the convolution of a Gaussian with a Lorentzian

= Voigt profile

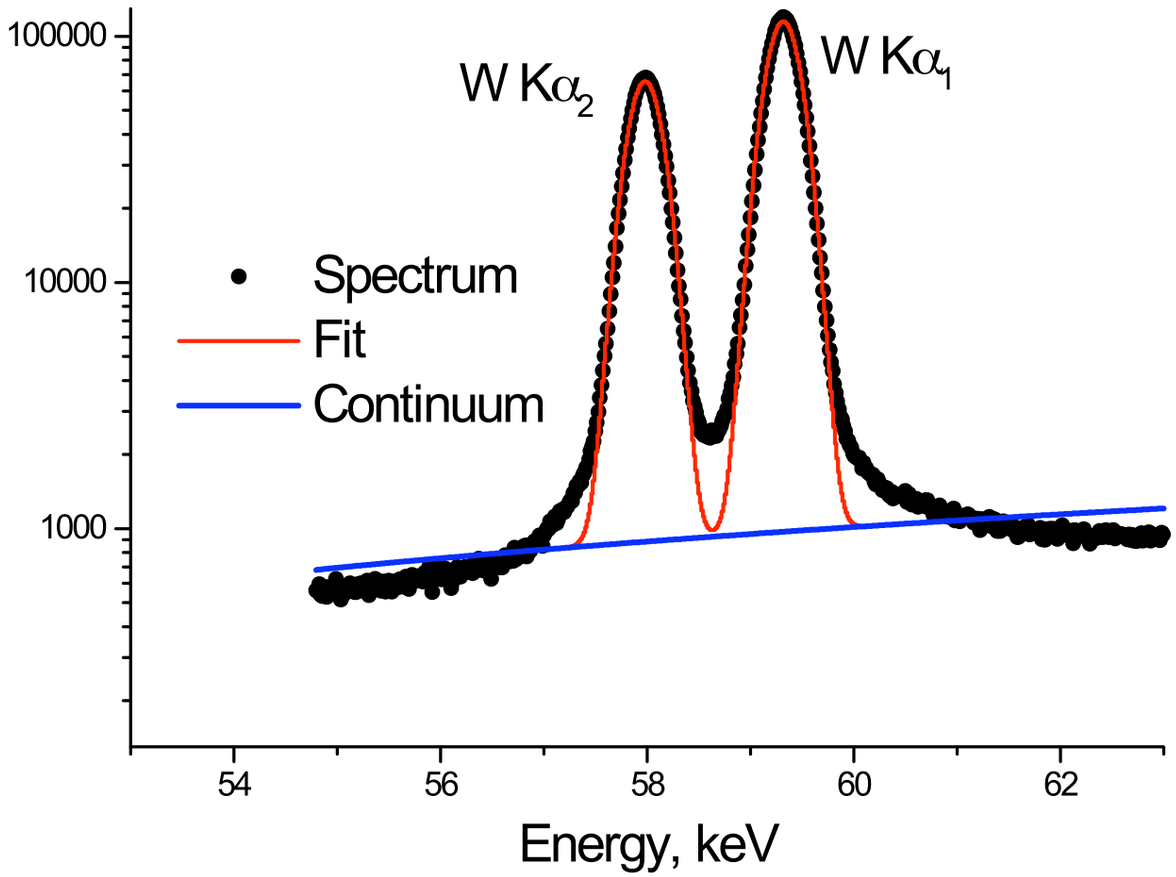
$$\frac{Gain}{\sigma_{jk}\sqrt{2\pi}} K\left(\frac{E(i)-E_{jk}}{\sigma_{jk}\sqrt{2}}, \frac{\alpha_L}{2\sigma_{jk}\sqrt{2}}\right)$$

with *K*(...) the complex error function

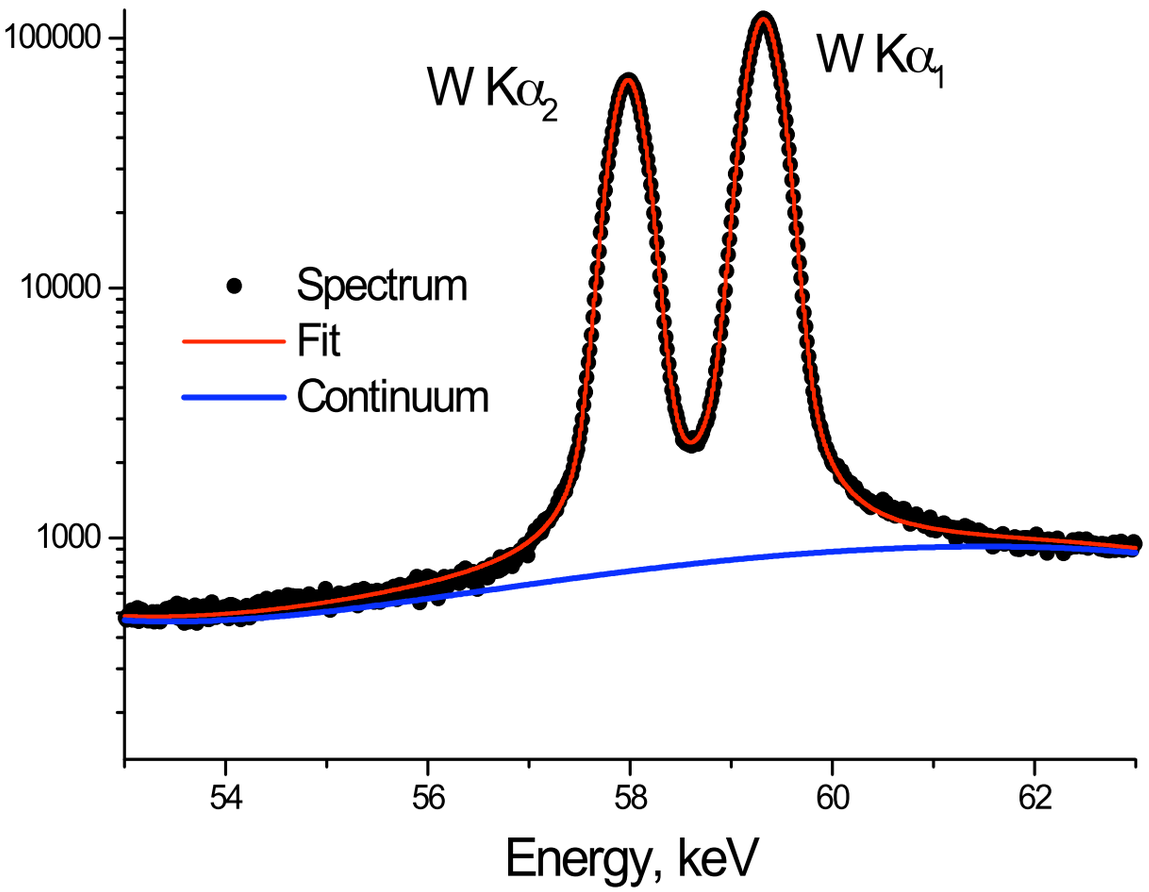
$$K(x,y) = \mathrm{Re}\left[\exp(-z^2)\mathrm{erfc}(-iz)\right] \qquad z = x + iy$$

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

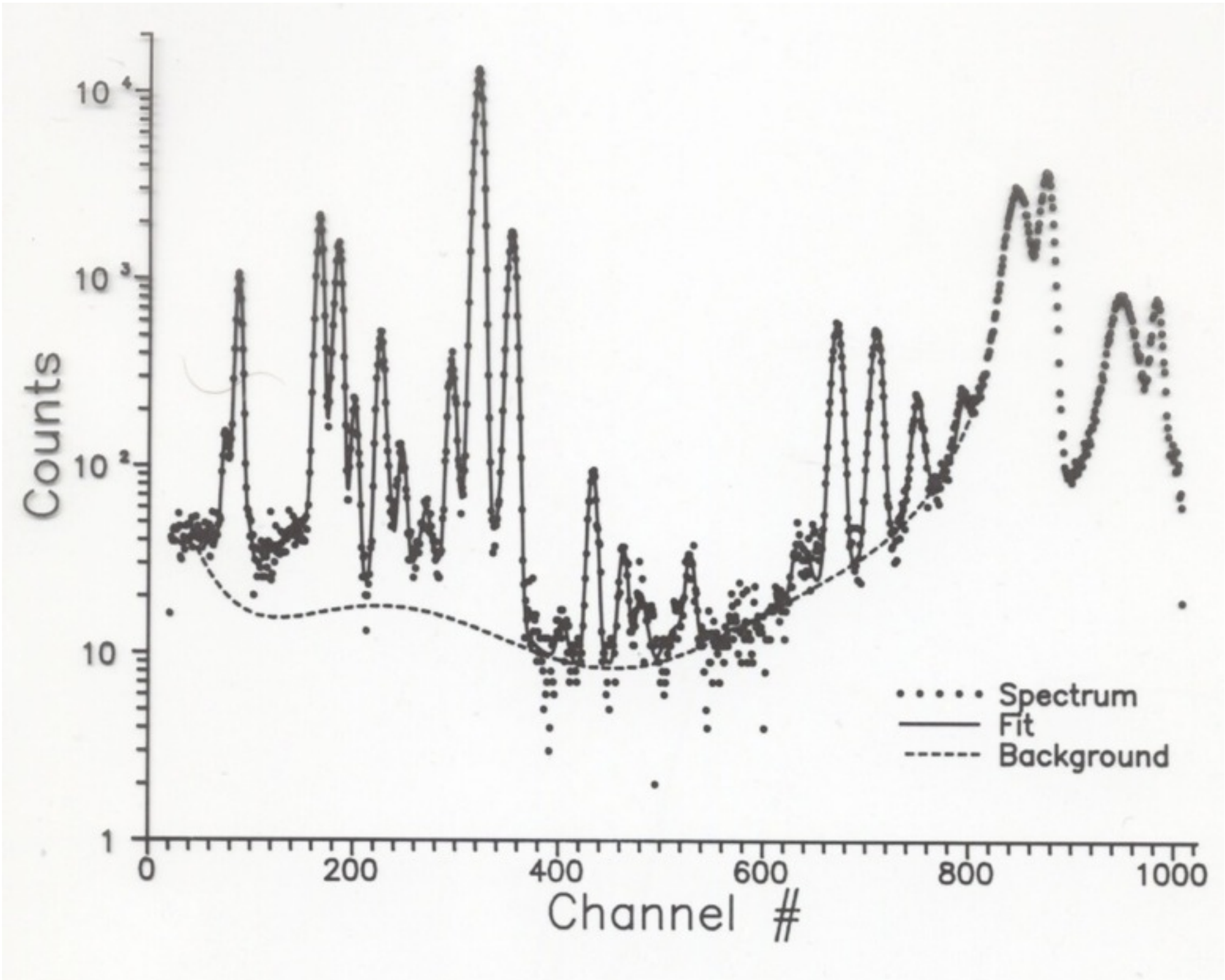
Gaussians



Voigts

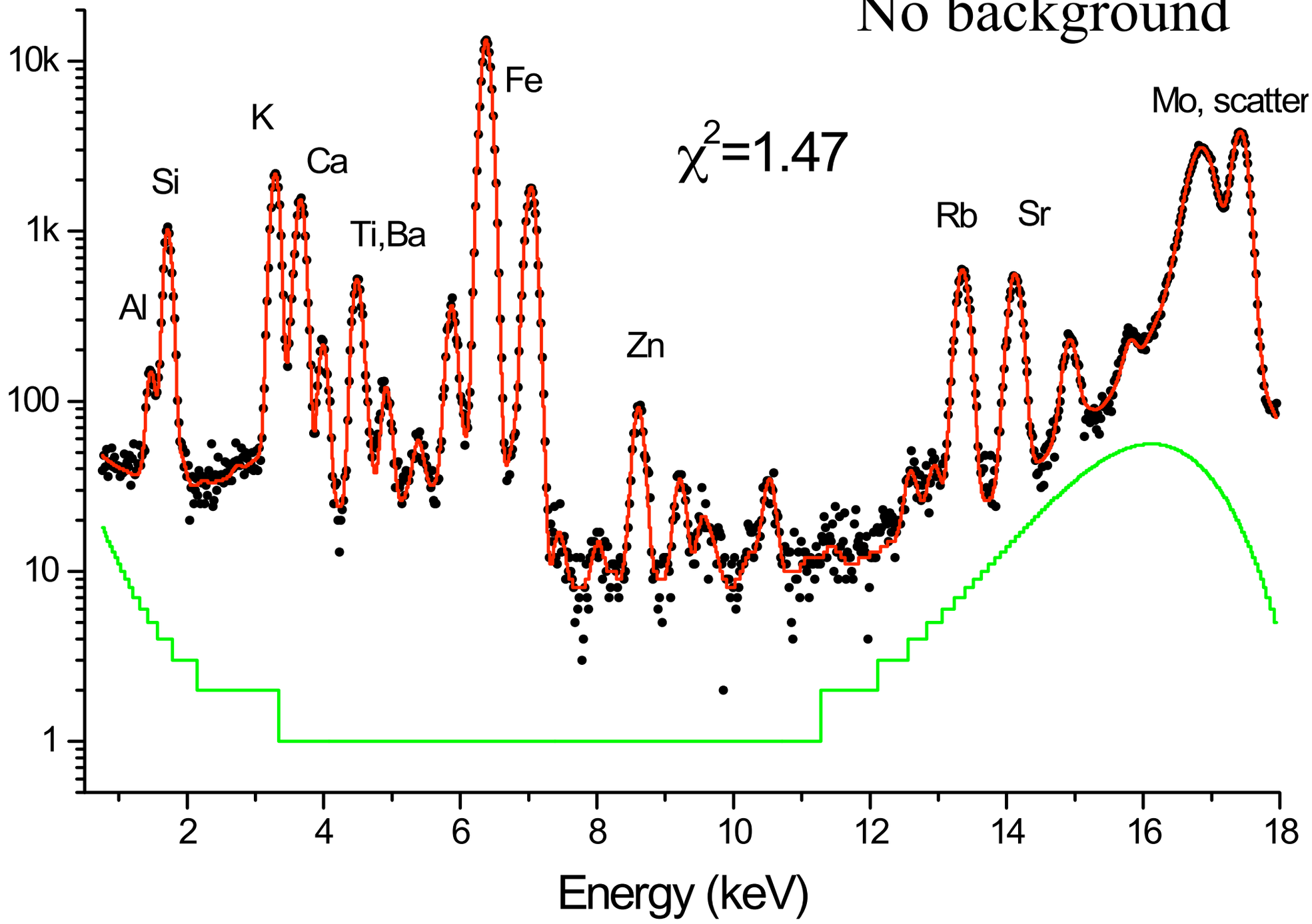


Original fit of a geological standard (JG1)

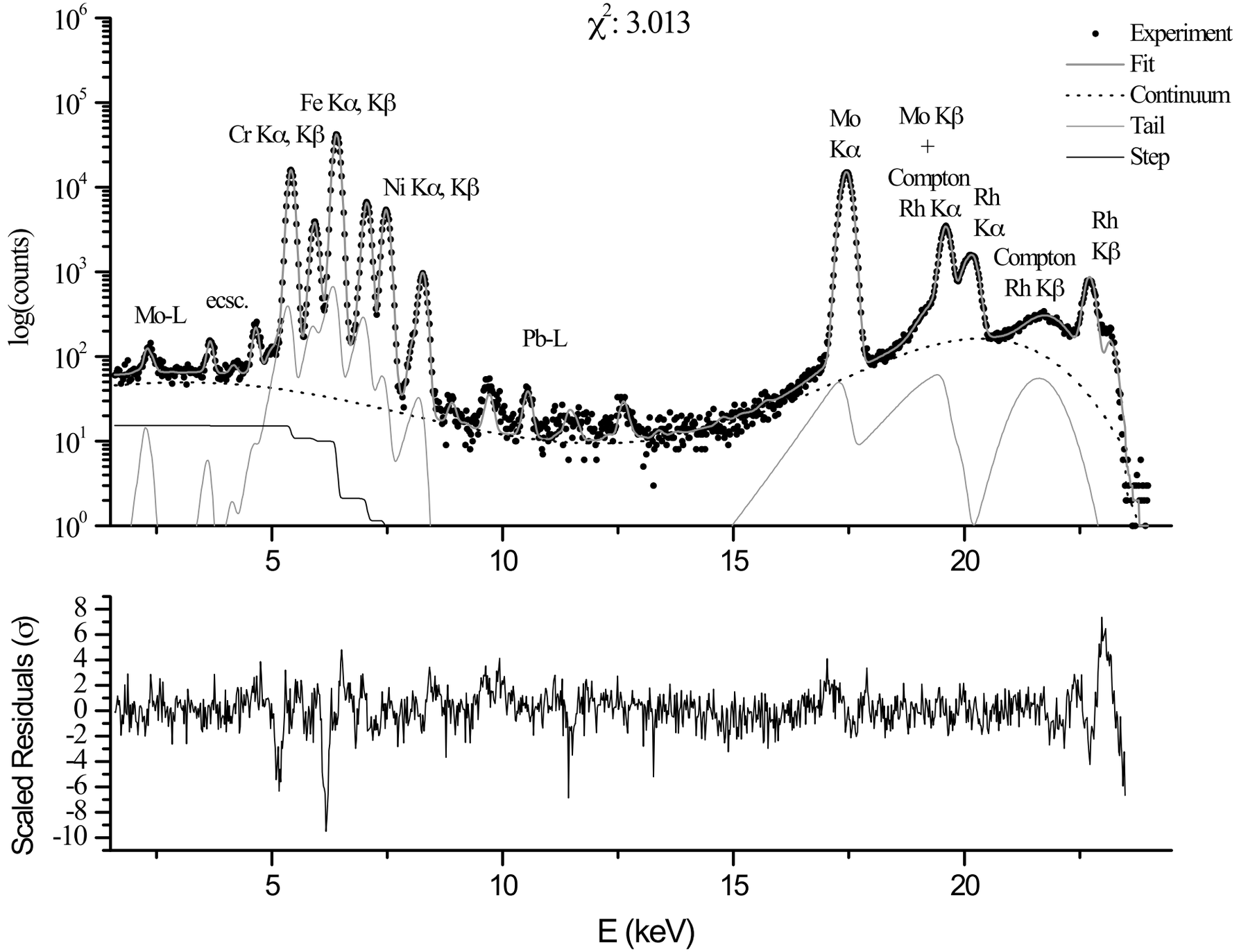


Improved fit of the geological standard (JG1)

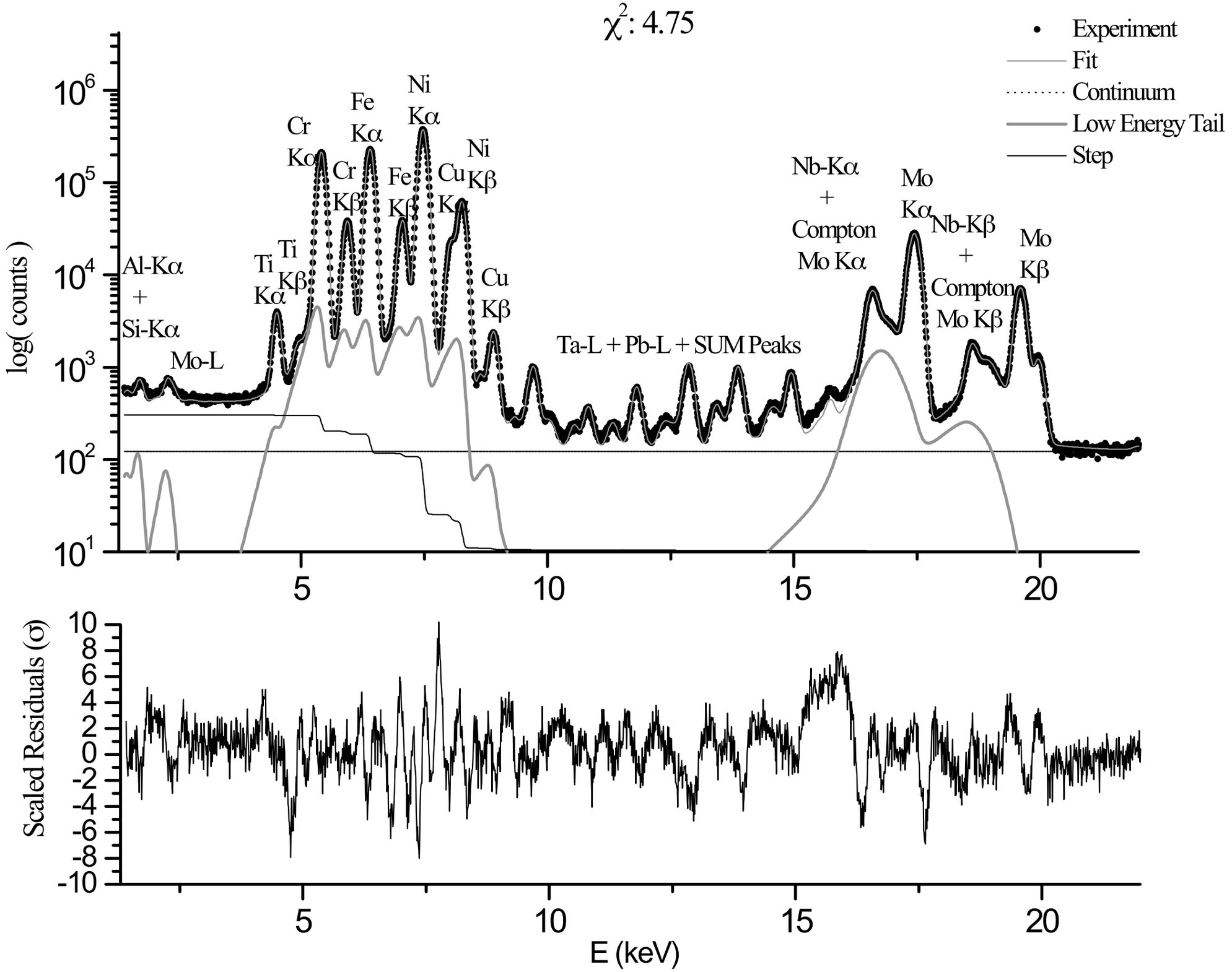
Mo secondary target
No background



NIST SRM 1155



NIST SRM 1247



More Details

Handbook of X-ray Spectrometry
R. Van Grieken, A. Markowicz
Marcel Decker, N.Y. 2002
ISBN: 0-8247-0600-5

Chapter 4: Spectrum Evaluation

Some final remarks: The future

Non-linear least-squares works

if you have a good parsimonious model

if you have TIME

X-ray fluorescence imaging:

256 x 256 image = 65536 x-ray spectra

@ 1 s / spectrum

= 65536 seconds

= 1092 minutes

= 18 hours !!!!

Need to explore new methods

Linear models?

Multivariate models?

6. Final remarks

Thanks for your attention