AXP

Research group
Analytical X-ray Physics

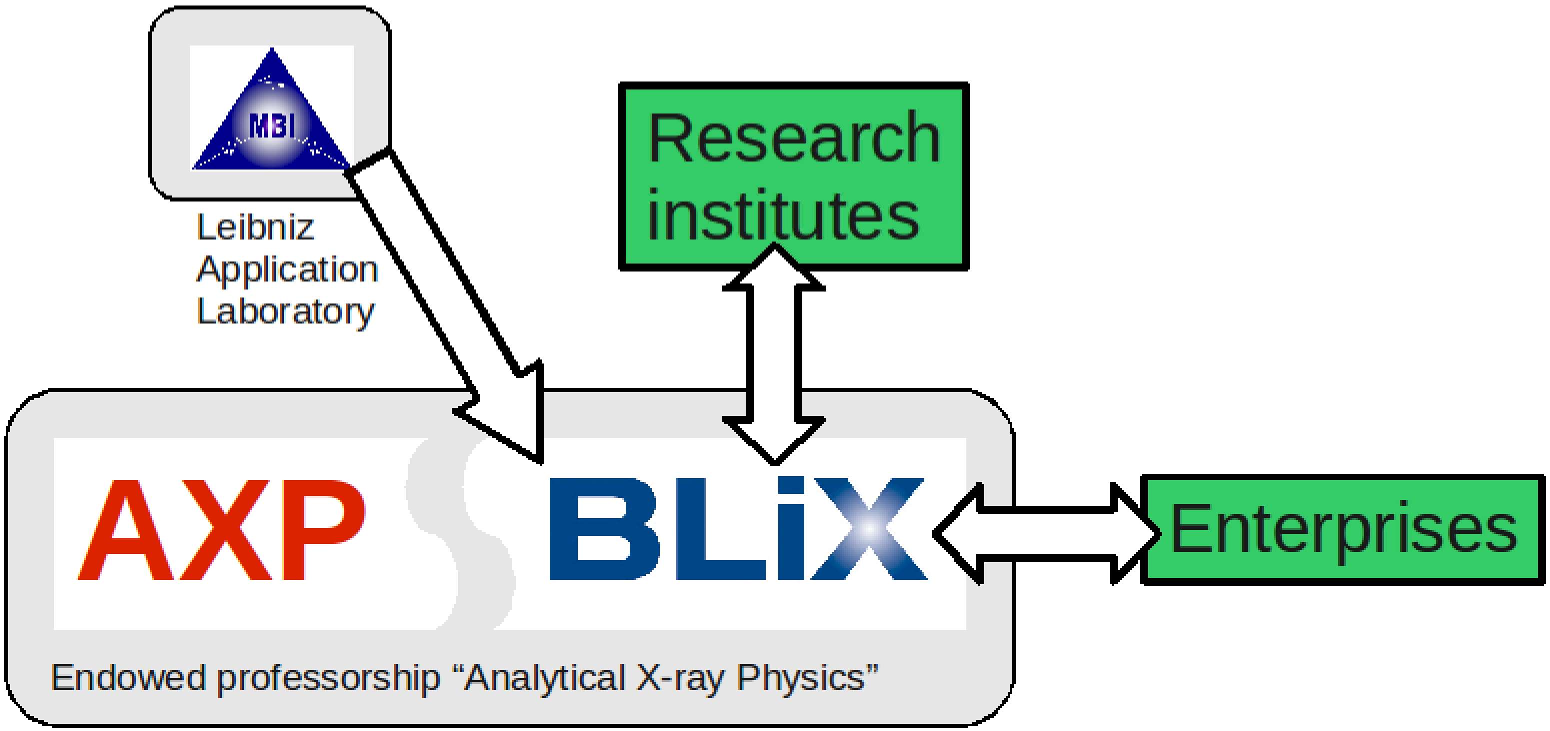
BLiX

Berlin Laboratory for
innovative X-ray Technologies

X-ray Fluorescence Spectrometry

Wolfgang Malzer

AXP and BLiX

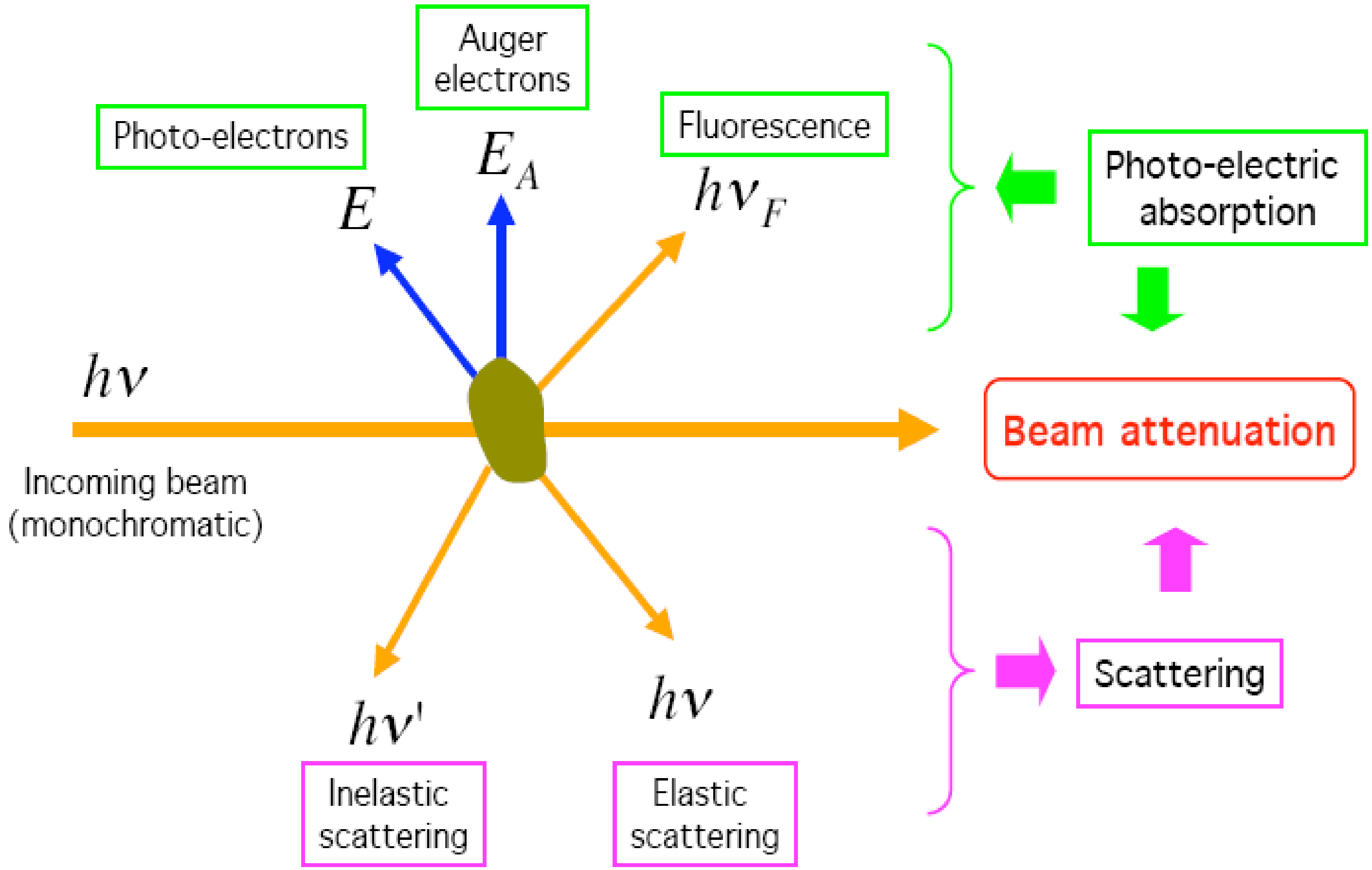

MBI
Leibniz
Application
Laboratory
Research
institutes
AXP
BLiX
Enterprises
Endowed professorship "Analytical X-ray Physics"

Team

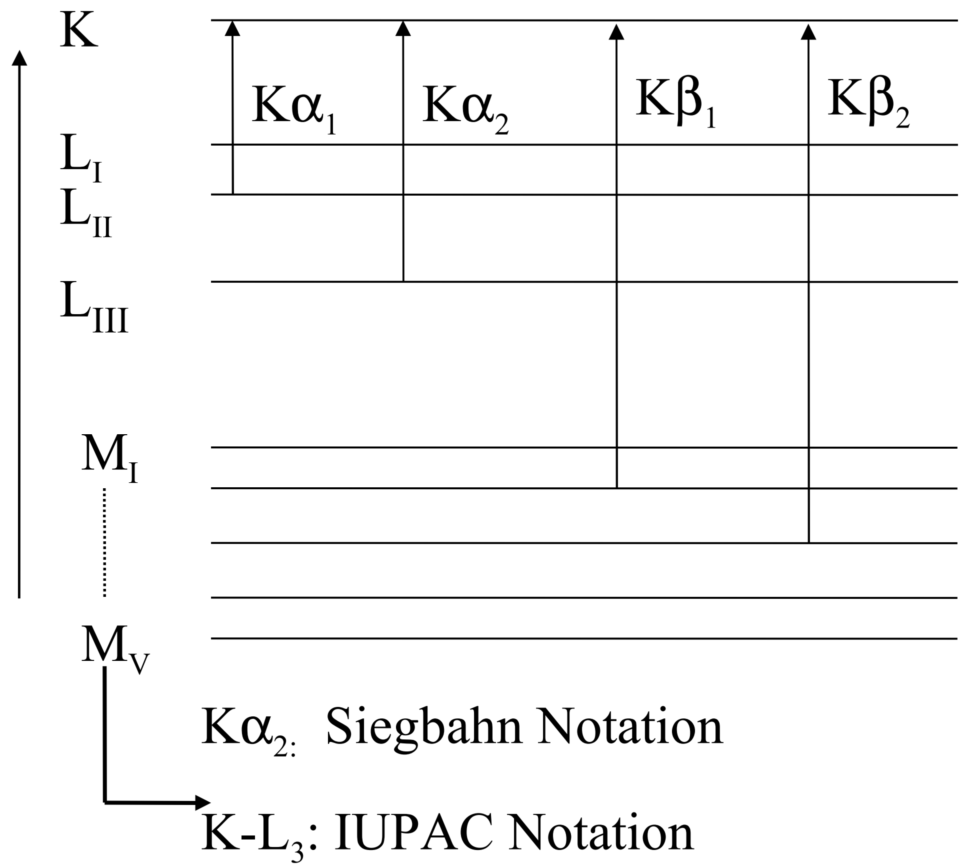
- 3D Micro-XRF
- 3D Micro-XANES
- High resolution X-ray emission spectroscopy
- Characterisation of X-ray optics and sources
- Analytic for photovoltaics
- Laser-Plasma-Sources for the soft X-ray regime
- X-ray microscopy with laser-plasma-source
- Profesional courses

- fields of application: cultural heritage, solar cells, geology, bio-medical

X-rays as a probe



shells



quantum numbers

n	l	j
1	0	1/2
2	0	1/2
2	1	1/2
2	1	3/2
3	0	1/2
3	1	1/2
3	1	3/2

selection rules

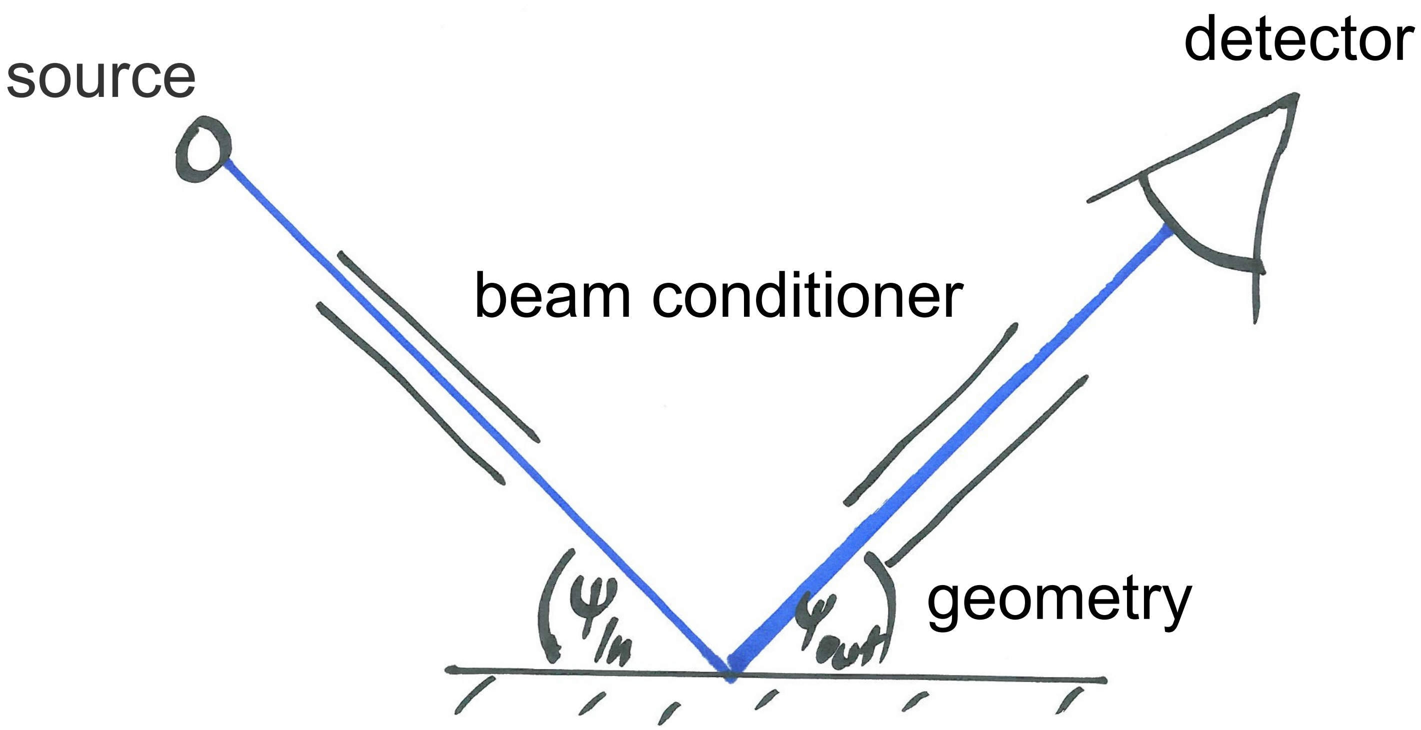
$\Delta l = \pm 1$

$\Delta j = 0, \pm 1$

satellites

- Survey on XRF Instrumentation and Methods
- Quantitative X-ray Fluorescence Analysis
- An Application of Micro-XRF

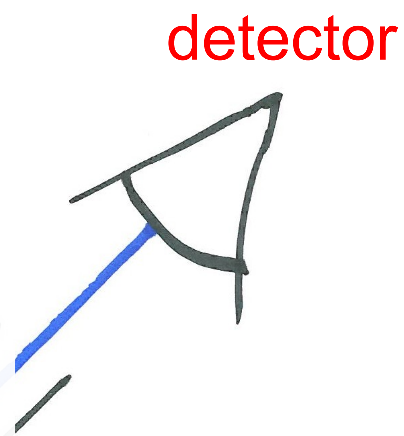
Scheme of a XRF-spectrometer



X-ray detectors

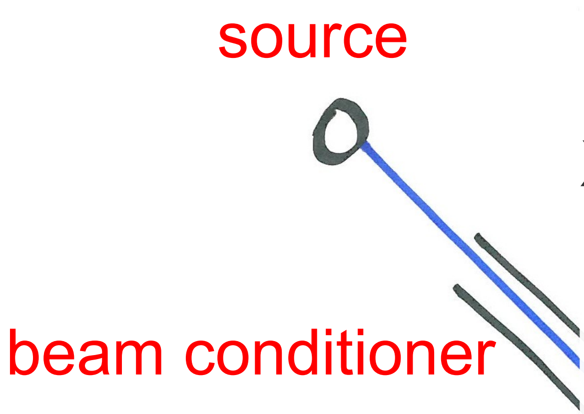
Wavelength **D**ispersive **S**pectrometer

- Crystal or multilayer
- proportional counter, scintillation counter
- Quantitative analysis
- Light element analysis



Energy **D**ispersive **S**pectrometer

- Solid state detector (Si, Ge)
- Small, leightweight detectors (SDD, PIN)
- Qualitative and quantitative analysis
- Range: (B) – Na - U



Syncrotron radiation

- High brillance
- Mikro/Nano-XRF (< 1µm)

X-ray tubes

- Micro focus X-ray tubes
  - Brillance optimised
- Miniature X-ray tubes
  - Portable instrumentation (Handheld)

Other

- Radioactive sources

Standard: Ψ ≥ 45°

Gracing **I**ncidence **XRF**

- Surface sensitive

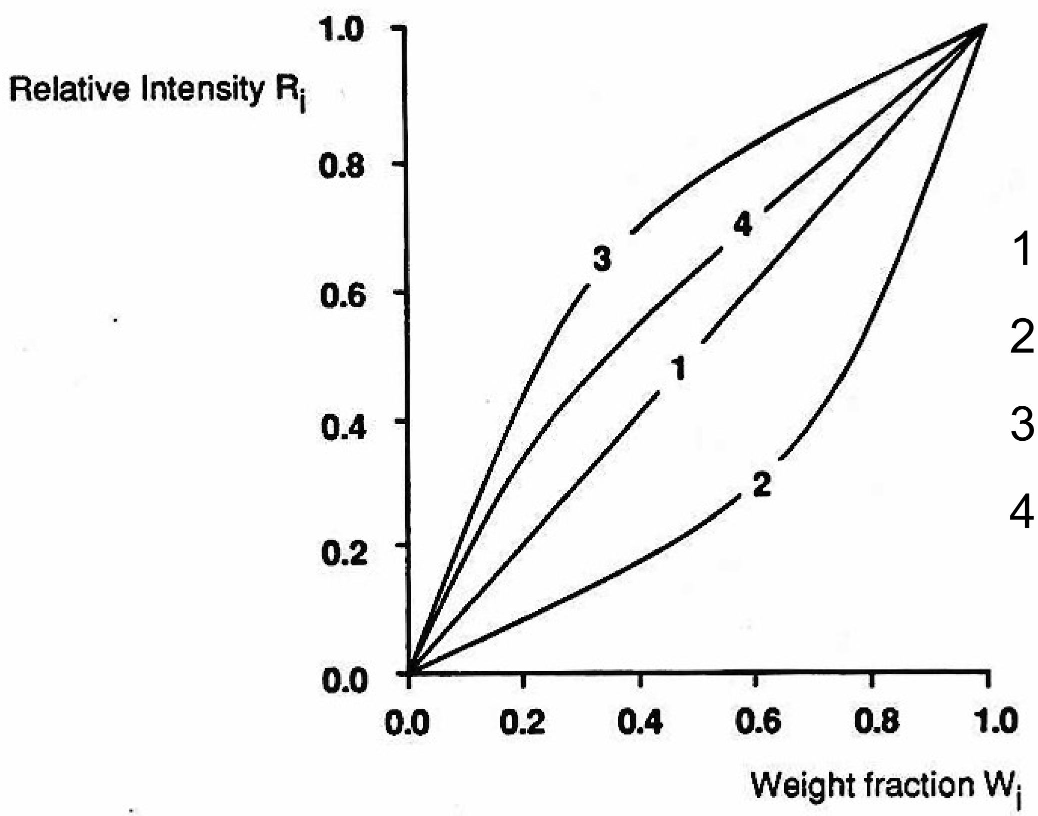
Gracing **E**xit **XRF**

- Surface sensitive

Total reflection **XRF**

geometry

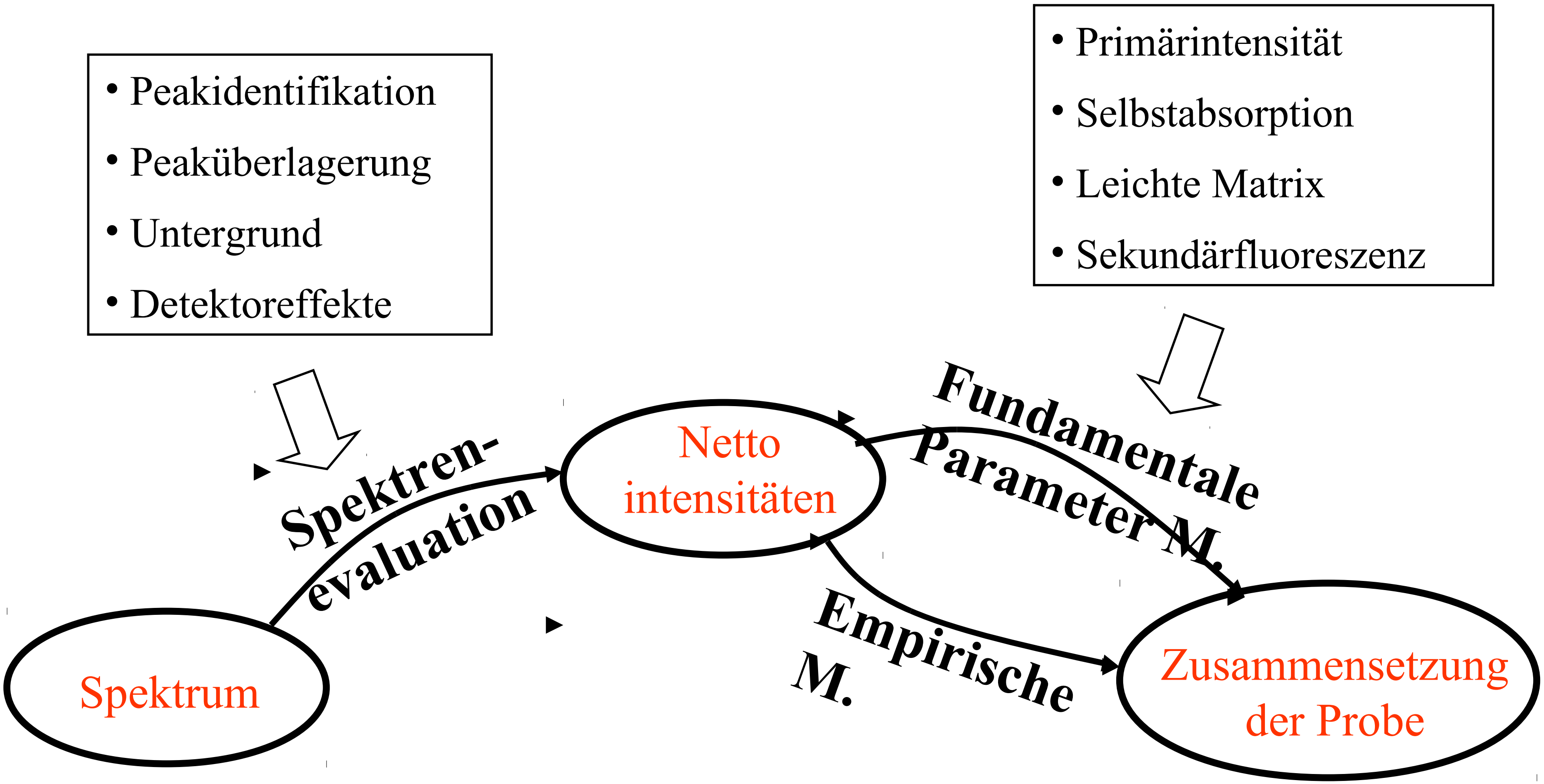
- Survey on XRF Instrumentation and Methods
- Quantitative X-ray Fluorescence Analysis
- An Application of Micro-XRF



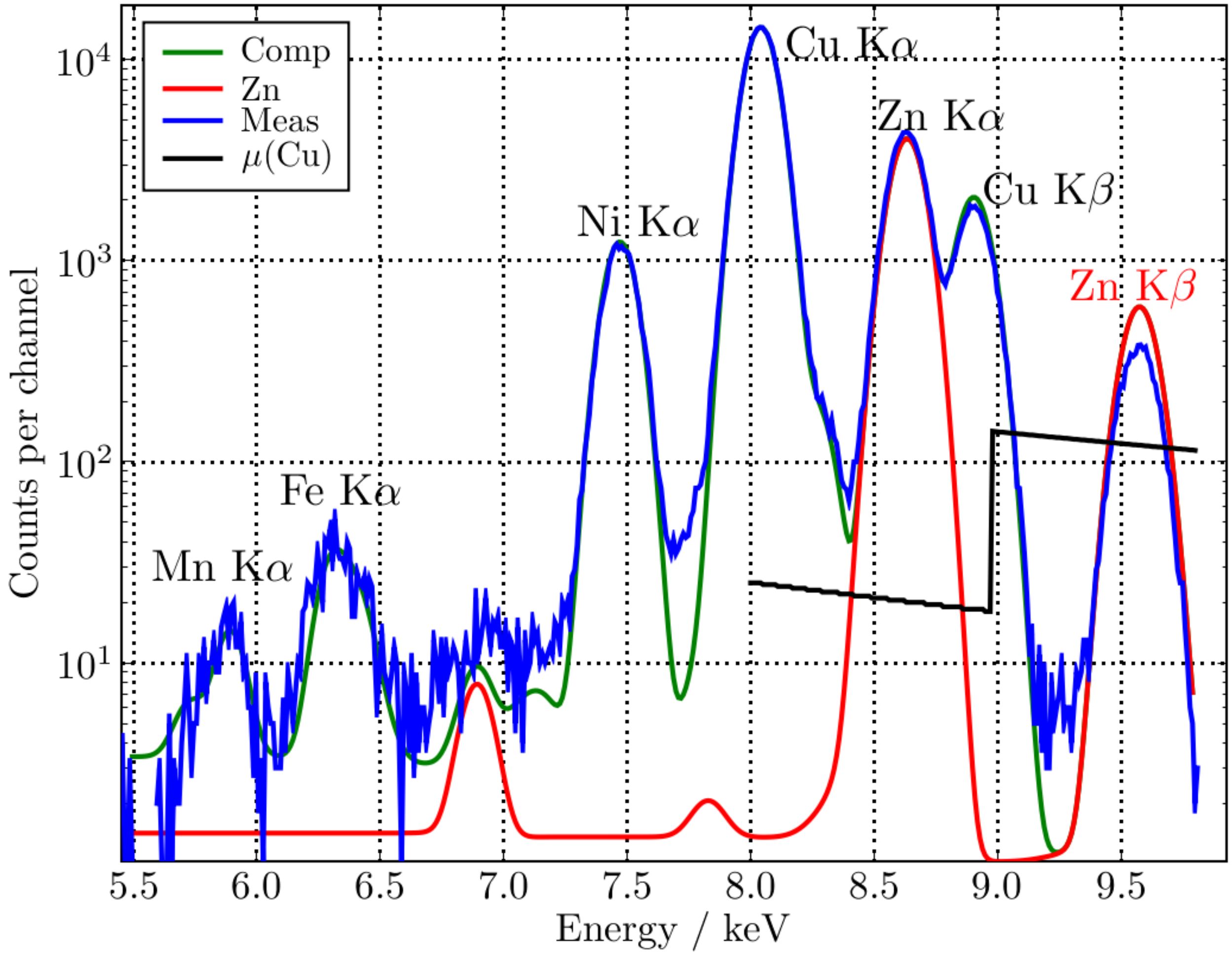
Intensity plots for a 2-element sample

1. No matrix effects
2. Apsorption by matrix dominates
3. Absorption by analyte dominates
4. Analyte line is enhanced by matrix

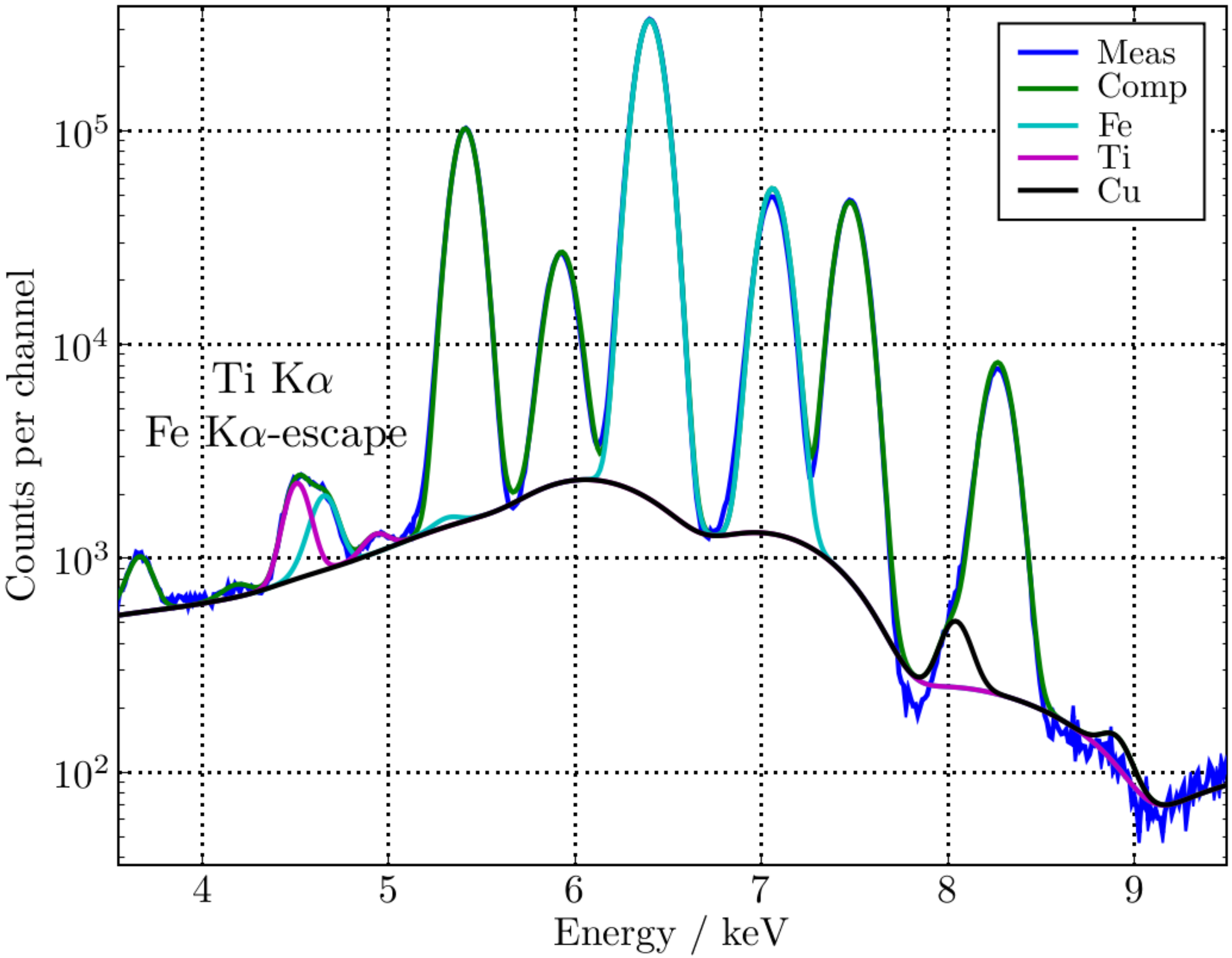
Routes and Steps of Quantification



Spectra of solid state det. And of wavelength systems detail


Comp
Zn
Meas
μ(Cu)
Cu Kα
Zn Kα
Cu Kβ
Ni Kα
Zn Kβ
Fe Kα
Mn Kα
10⁴
10³
10²
10¹
Counts per channel
5.5
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
Energy / keV

Enhanced uncertainty due to overlap with escape peak



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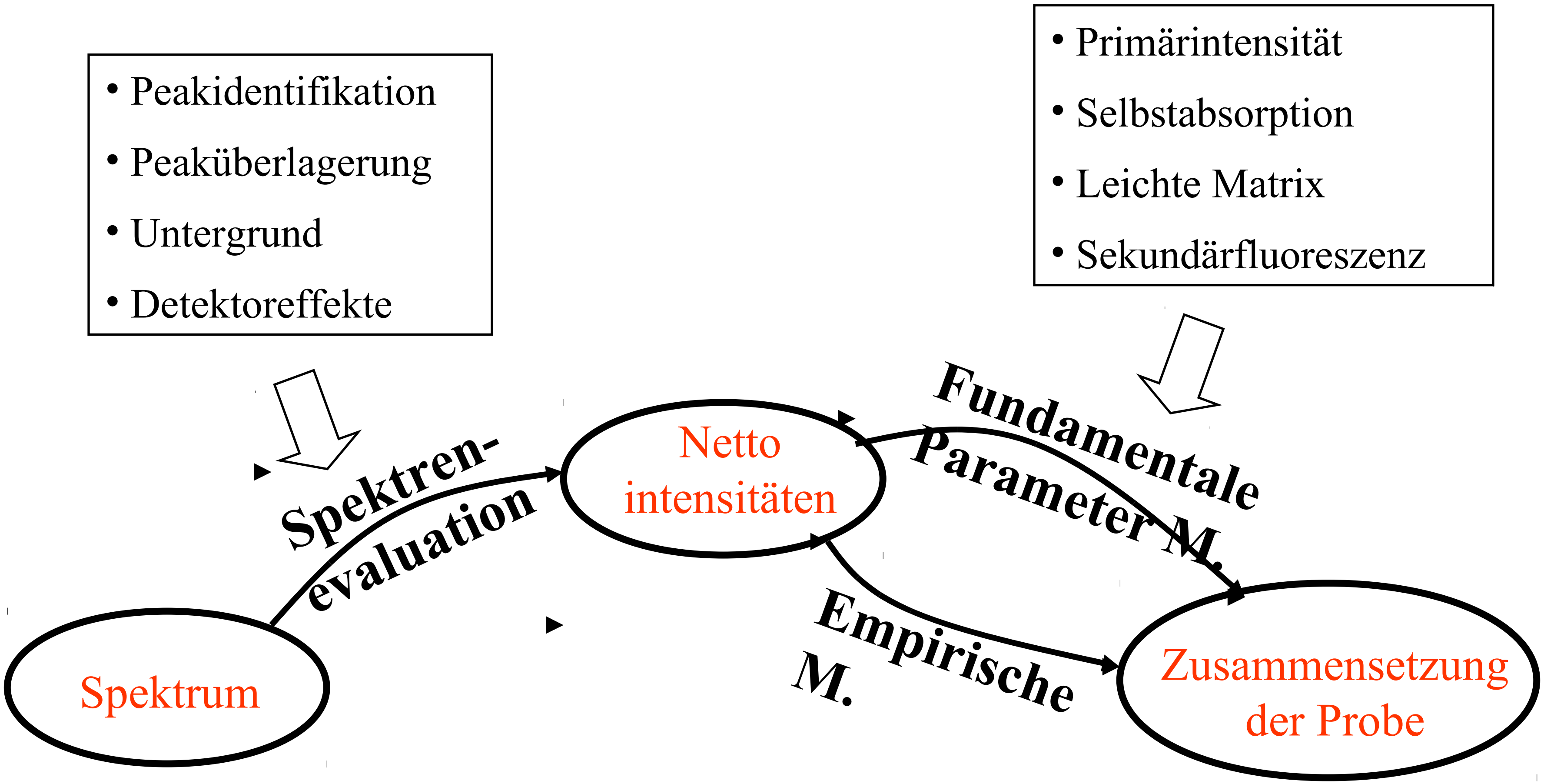
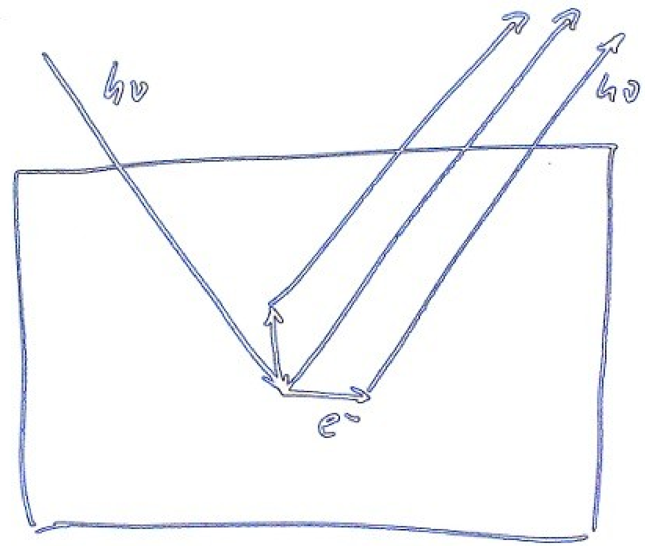
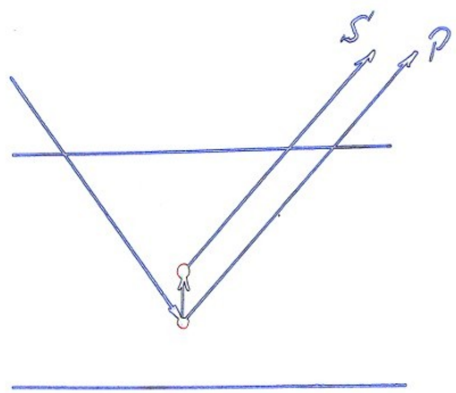


• Peakidentifikation
• Peaküberlagerung
• Untergrund
• Detektoreffekte
• Primärintensität
• Selbstabsorption
• Leichte Matrix
• Sekundärfluoreszenz
Spektrum
Spektren-evaluation
Netto intensitäten
Fundamentale Parameter M.
Empirische M.
Zusammensetzung der Probe



Complex radiation transport

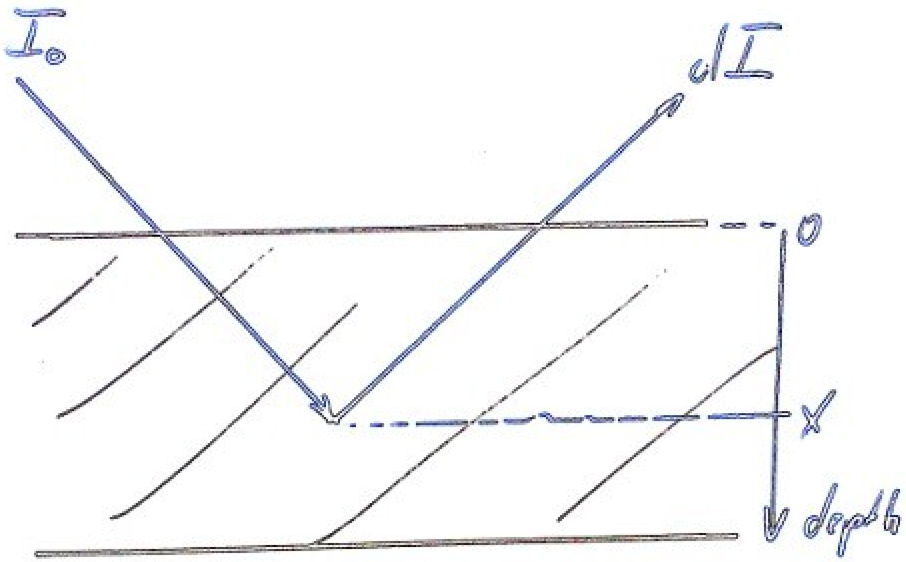
is simplified to



primary fluorescence intensity

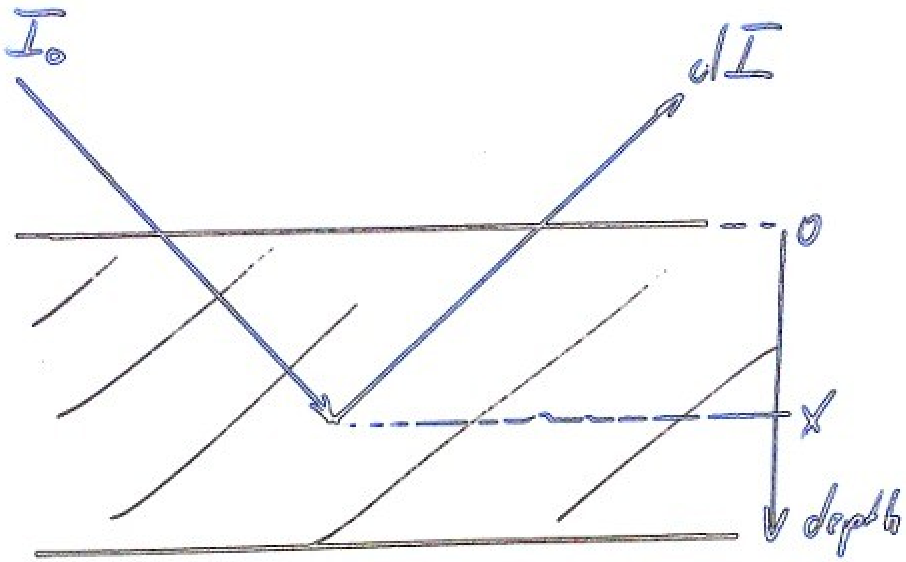
+

secondary fluorescence intensity



- Model for X-ray fluorescence production
- Integration over sample thickness

$$dN_i = w_i \varepsilon_i \frac{\Omega}{4 \cdot \pi} \frac{\tau_i}{\sin \Psi_0} j_i \omega_i p_i N_{I_0} \exp\left(-\frac{\mu_S(E_0)\rho x}{\sin \psi_0} - \frac{\mu_S(E_i)\rho x}{\sin \psi_{\det}} \right) \rho dx$$



- Integration over excitation spectrum N_{I_0}
- Sample is flat and homogeneous

$$N_i = w_i K_i \frac{\tau_i}{\mu_i^*} N_{I_0} \quad \text{with} \quad \mu_i^* = \sum_j w_j \left(\frac{\mu_{0j}}{\sin\psi_0} + \frac{\mu_{ij}}{\sin\psi_{\det}} \right)$$

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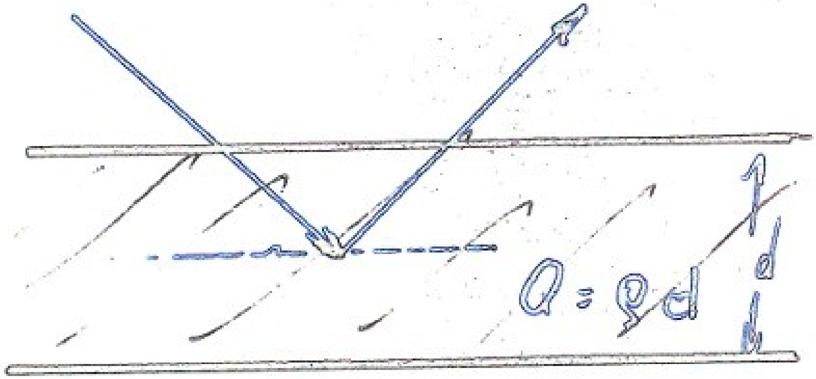
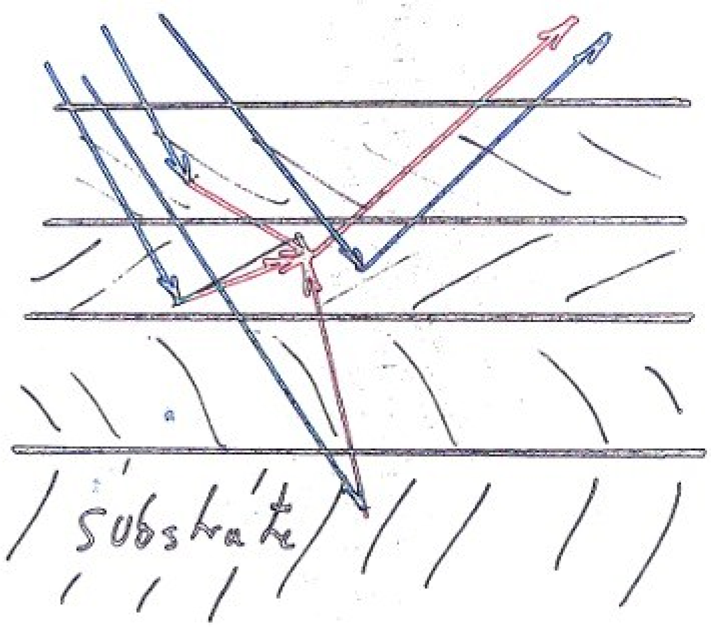
$$w_i = \frac{N_i}{\frac{K_i \tau_i N_{I_0}}{\mu_i^*}\left(1+S_i\right)} \quad \text{but} \quad \mu_i^* = f(\mathbf{w})$$

- Initial guess for **w**
- Iterative solution

- Sketch primary intensity



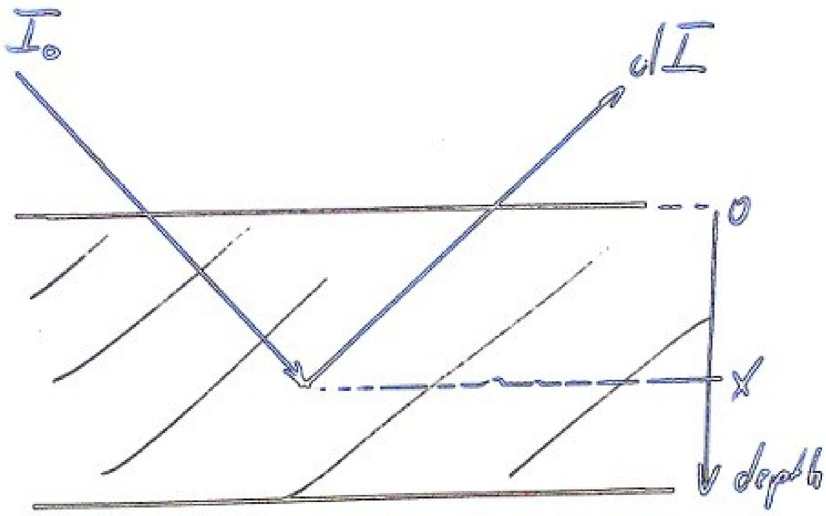
$$N_i = w_i K_i \tau_i \frac{1-\exp\left(-\mu_i^* Q\right)}{\mu_i^*} N_{I_0}$$



Primary fluorescence intensity
+ intra-layer enhancement
+ inter-layer enhancement

What is the information depth of my sample?

Is the homogeneity of my sample sufficient?



Definition of information depth:

Half of the total intensity comes from above

Simplifications:

* Only consider attenuation of fluorescence line
* $1/2 \approx 1/e$

Mean free path length $1/\mu\rho$ is an estimate for the information depth

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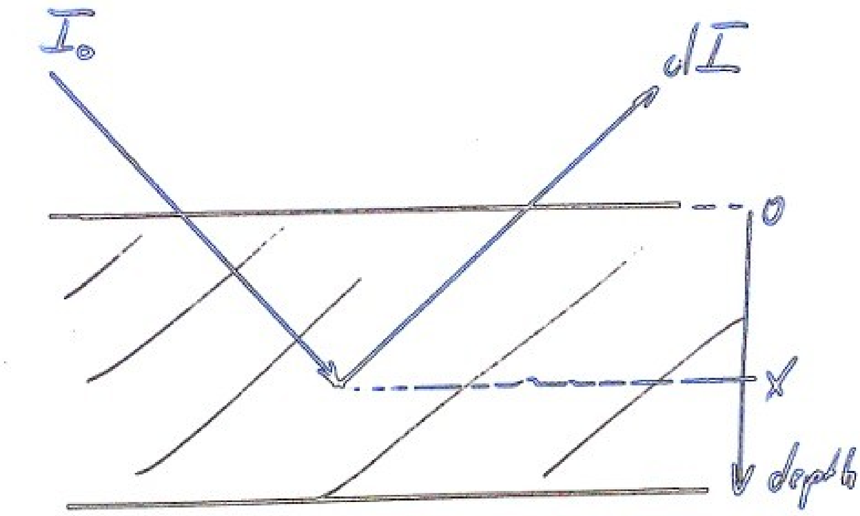
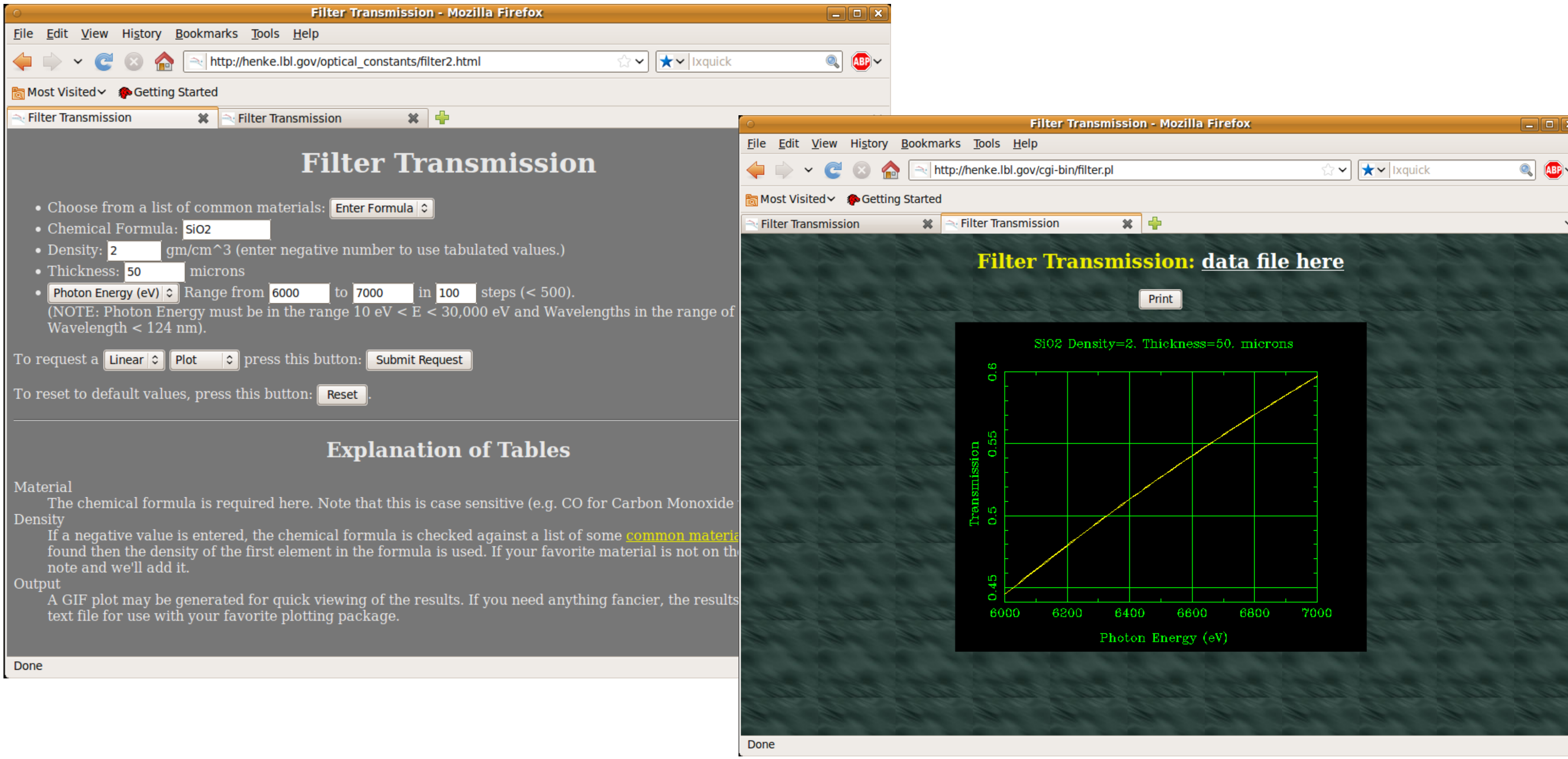


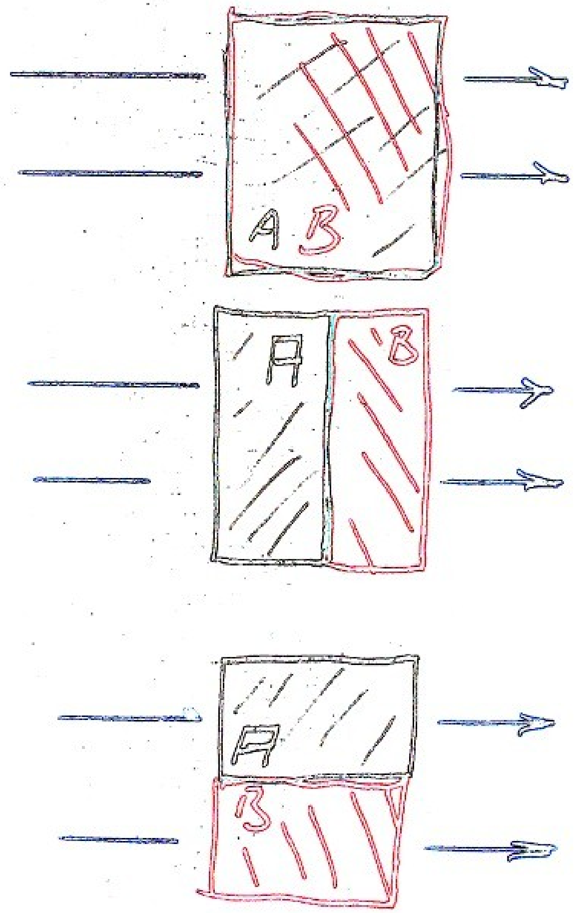
Mean free path in µm	Fe	Sn
SiO_2 (2 g/cm³)	70	3,500
O (1 g/cm³)	440	19,000

Calculation of transmission

http://henke.lbl.gov/optical_constants/filter2.html



Sample inhomogeneity



-

$$\exp\left(-(w_A\mu_A + w_B\mu_B)Q\right)$$

$$=$$

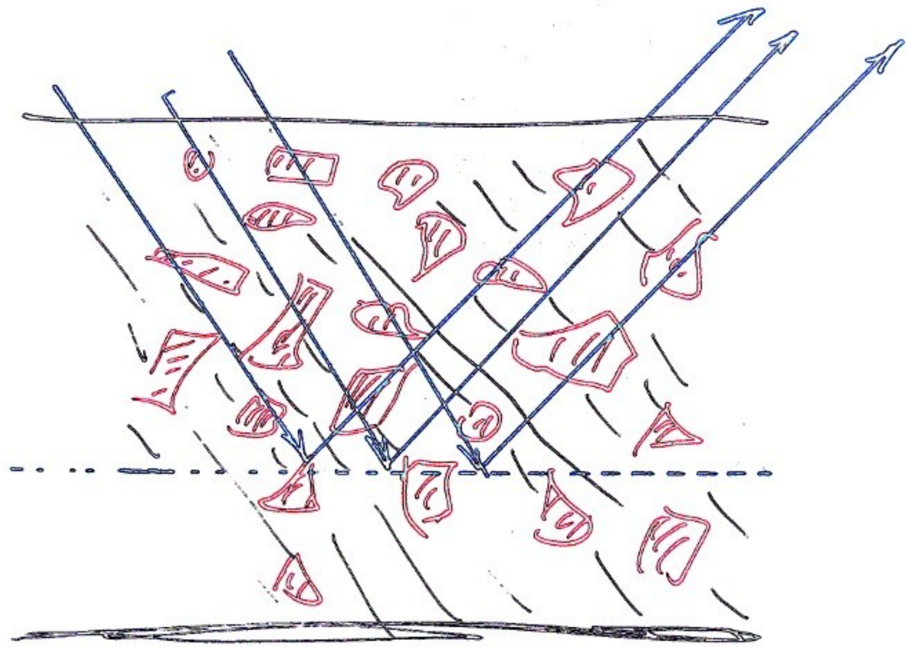
$$\exp\left(-w_A\mu_A Q\right)\exp\left(-w_B\mu_B Q\right)$$

$$\neq$$

$$\exp\left(-w_A\mu_A Q\right) + \exp\left(-w_B\mu_B Q\right)$$

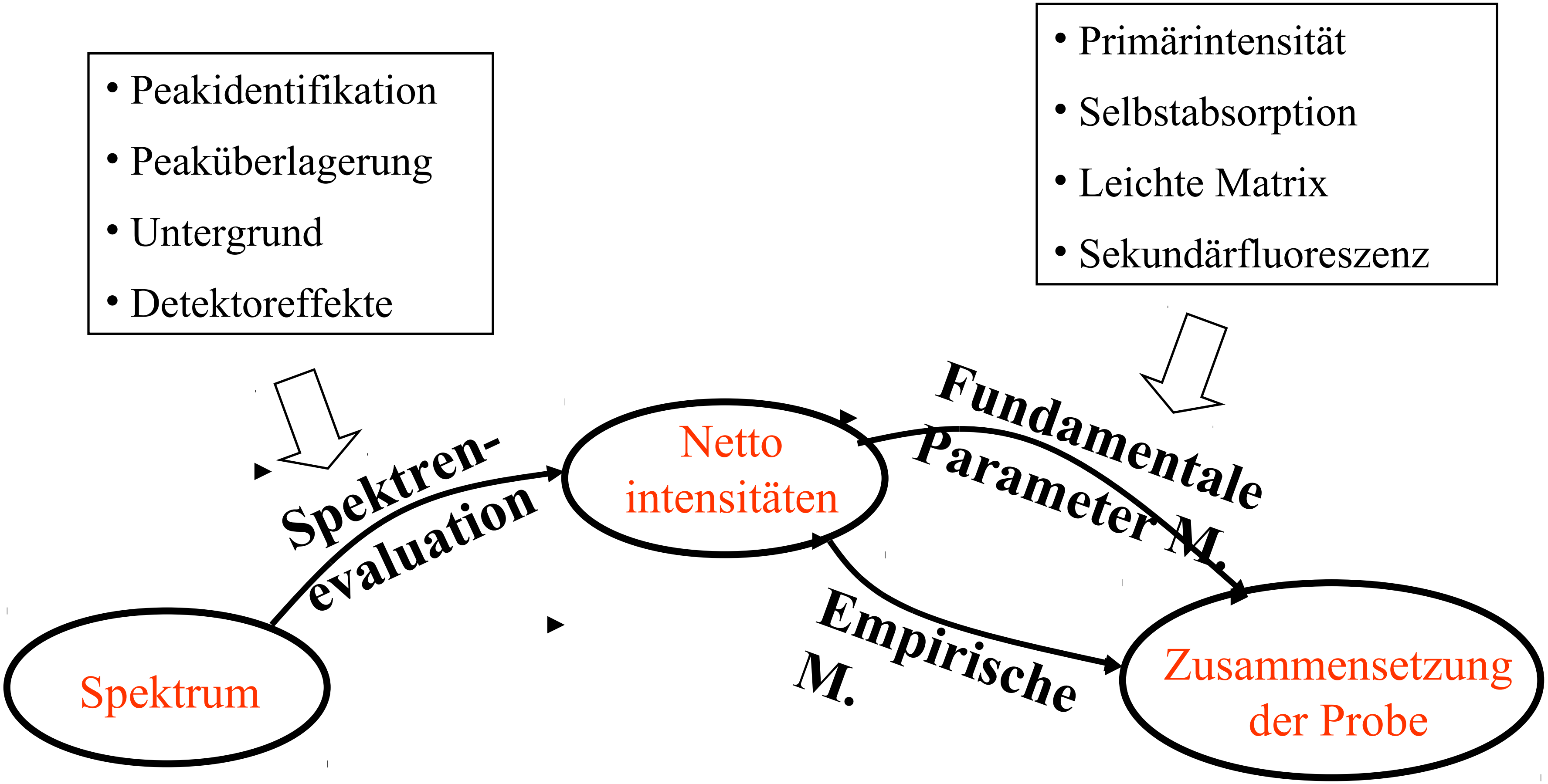
$$Q = \rho d$$

Sample inhomogeneity



particle size « particle mean free path length
information depth » sample mean free path length

Routes and Steps of Quantification



- Standard addition, internal standard, etc.
- Fingerprint
- Influence coefficients method

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$$w_i = w_{0i} + m_i N_i \left(1 + \sum_j \alpha_{ij} w_j\right)$$

$$w_i = w_{0i} + m_i N_i \left(1 + \sum_j m_{ij} I_j\right)$$

- Best precision achievable (< 1%)
- Two reference materials per coefficient
- Applied in analysis of steel, gold, concrete production

Fin

Part 1