Quantification in X-ray fluorescence analysis and the contribution of Monte Carlo simulations

Mateusz Czyzycki, Pawel Wrobel, Dariusz Wegrzynek and Marek Lankosz

Joint ICTP-IAEA Workshop on Advances in X-ray Instrumentation for Cultural Heritage Applications
13-17 July 2015, Trieste, Italy

Outline

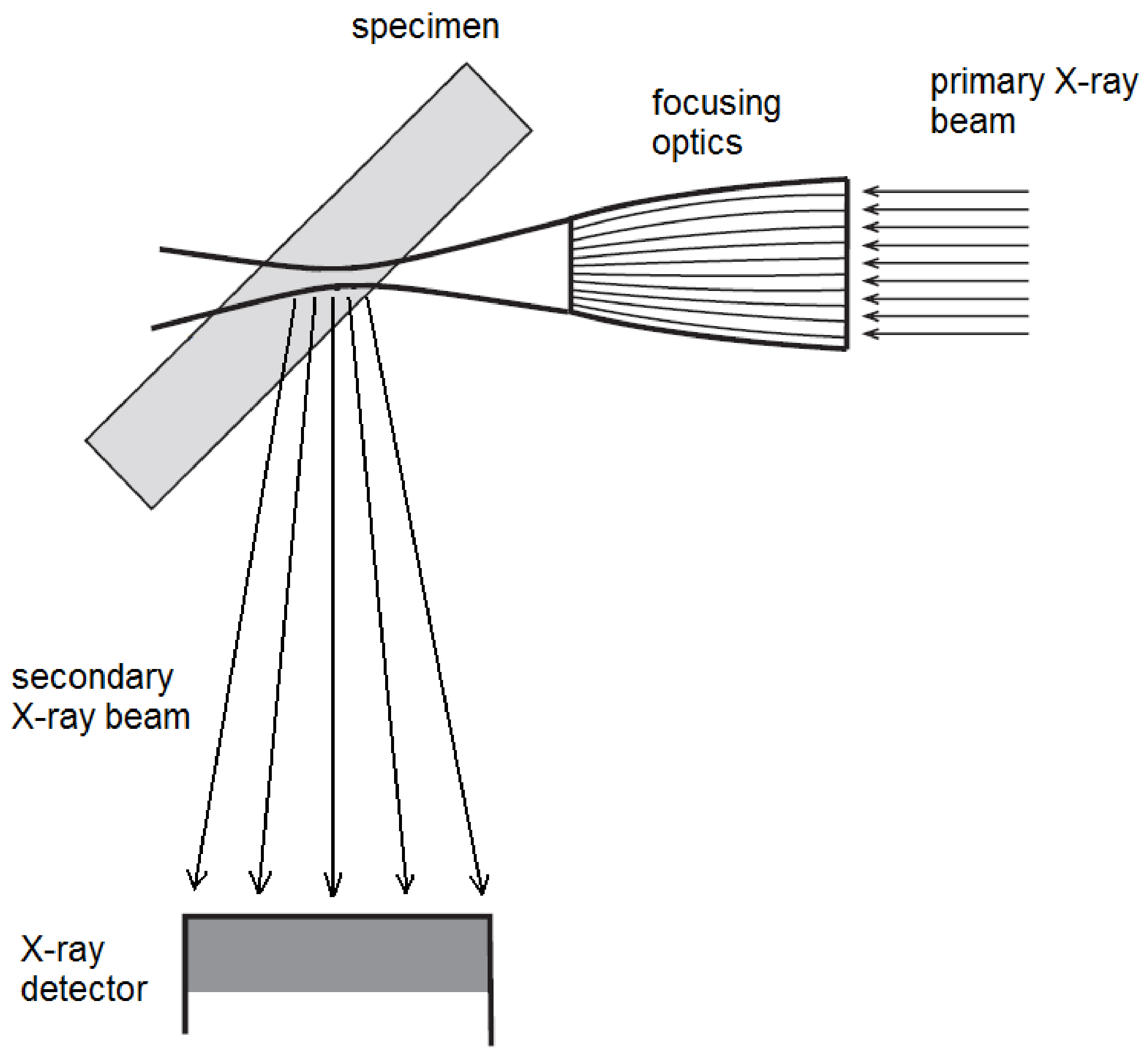
- Confocal XRF spectroscopy in tilted geometry
- Fundamental Parameters model
- Monte Carlo simulations
- Examples
  - Multi-layers with low-Z matrices,
  - Multi-layers of alloys.

Multi-layer materials

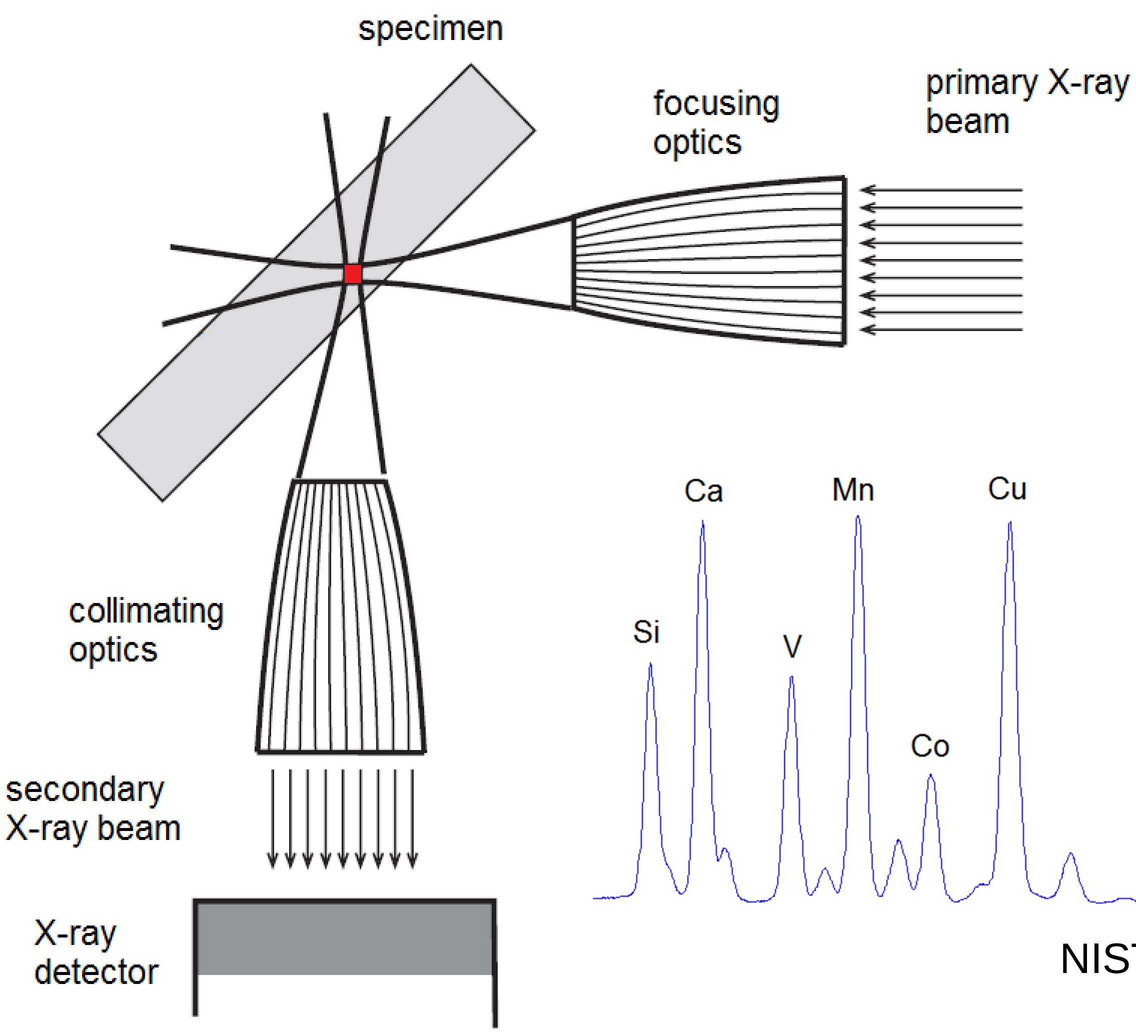
- electronics
- energy production & storage
- optics
- environmental solutions
- petroleum industry
- automotive industry
- building industry
- biomedical applications

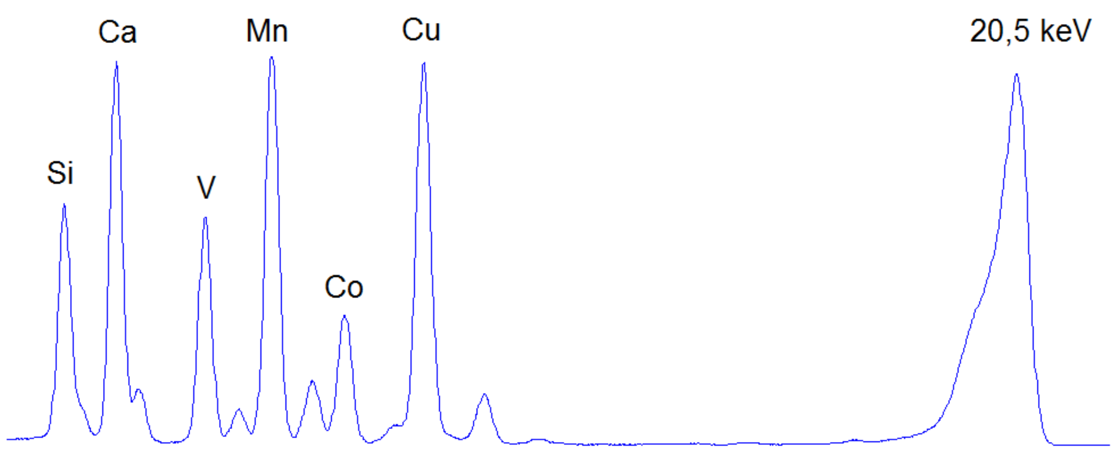
- **cultural heritage**

Conventional geometry



Confocal geometry





NIST SRM 1832

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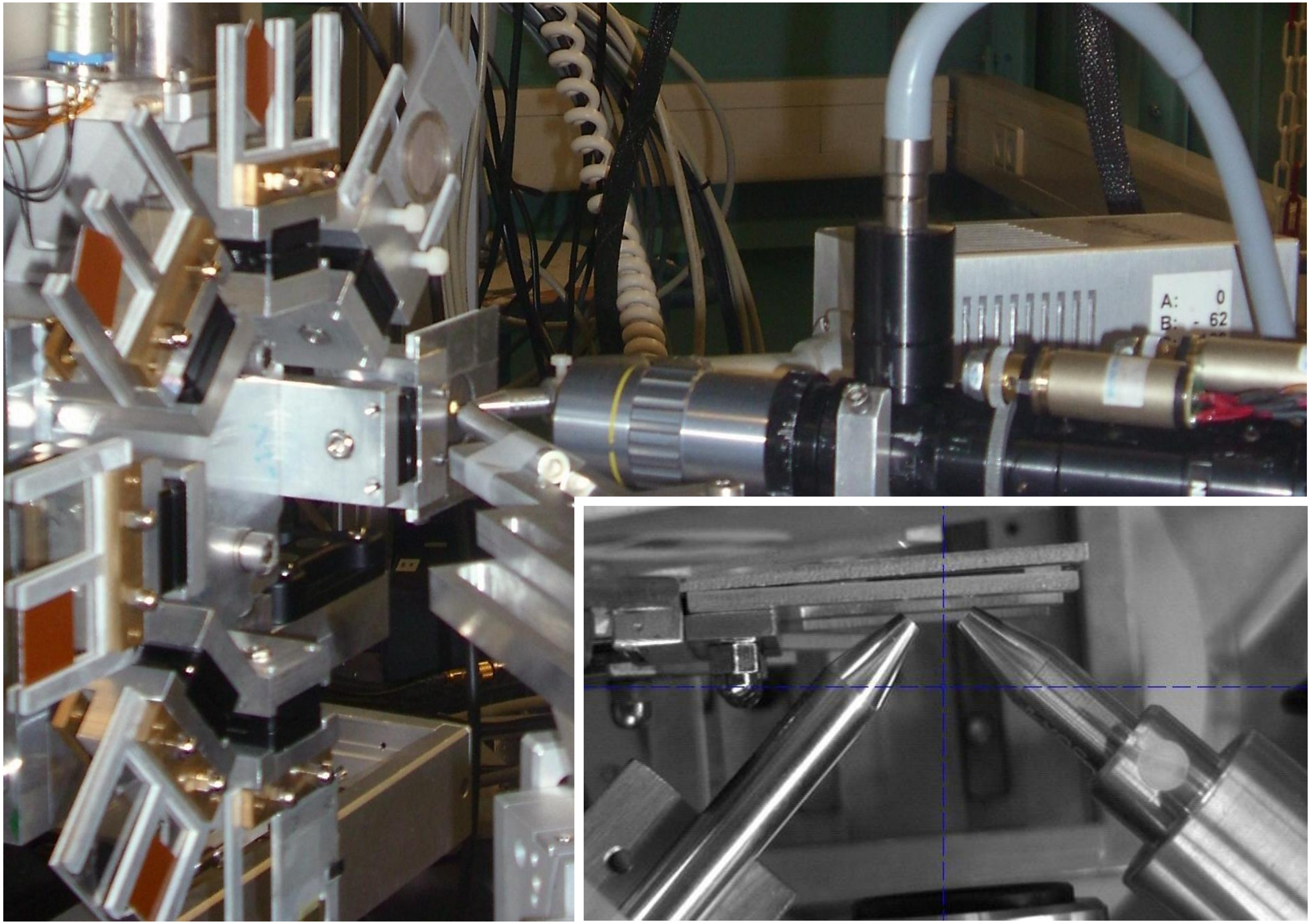
Experimental endstation



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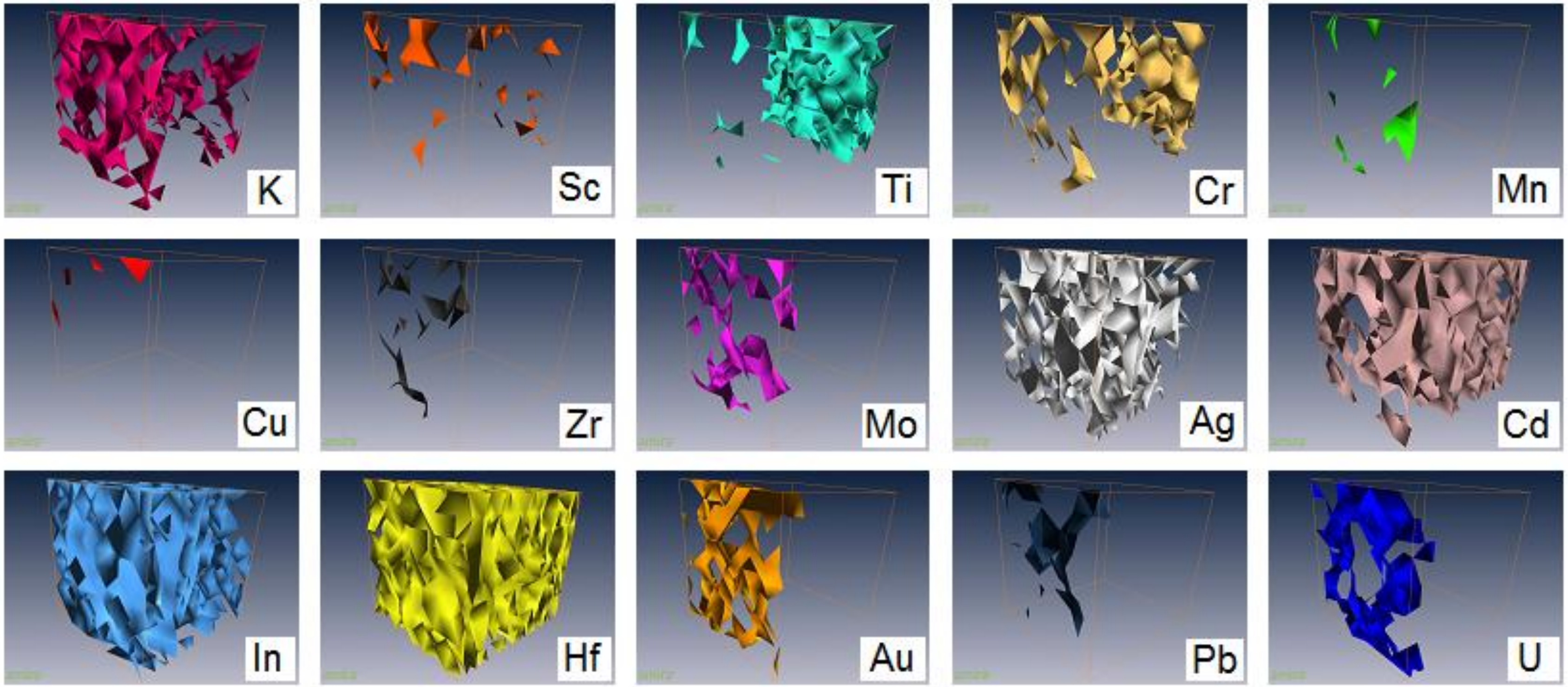
NIST SRM 611



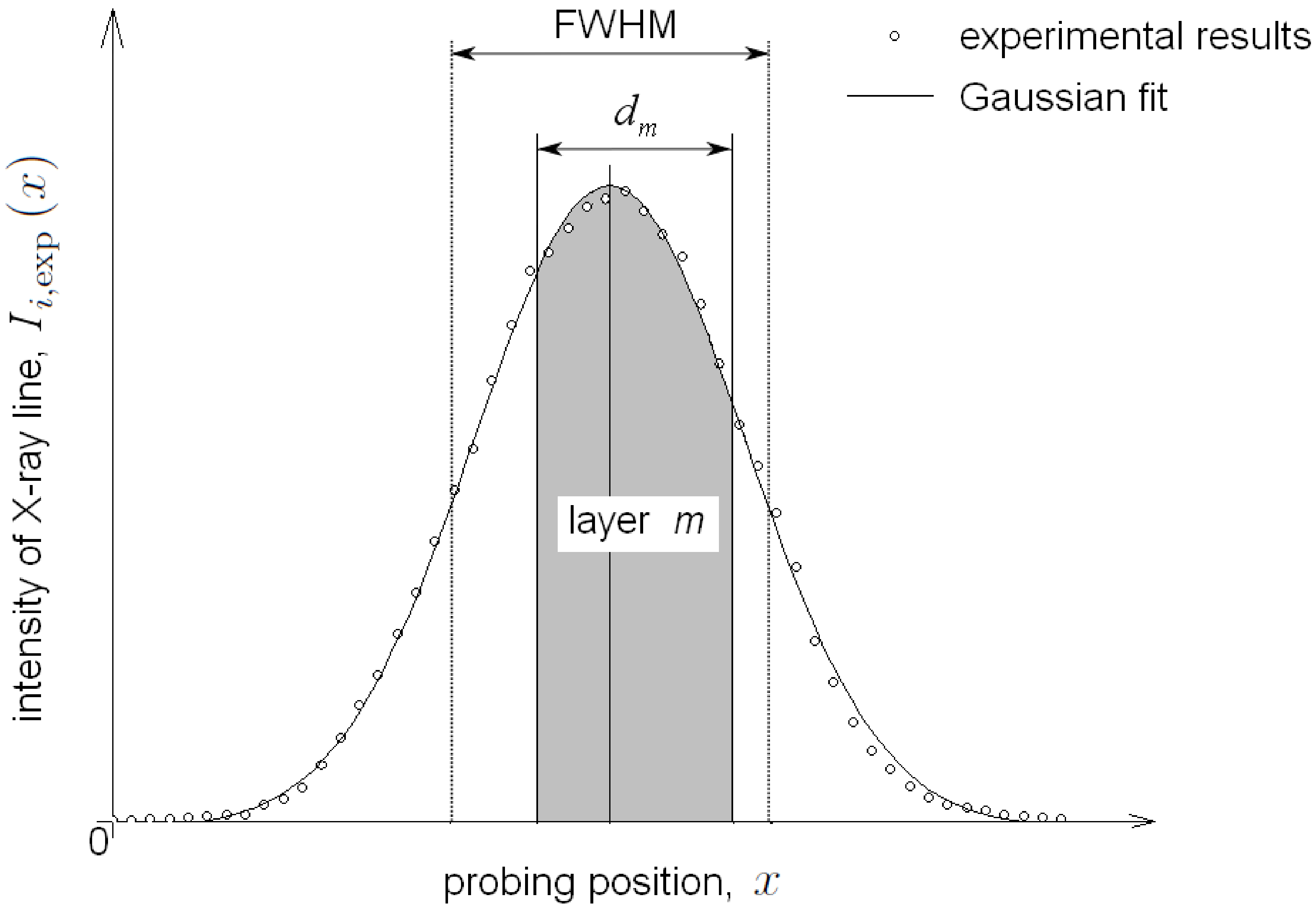
HASYLAB, DESY, DORIS III, beamline L

NIST SRM 611 glass standard. Scanned volume: 135 µm / 135 µm / 150 µm

Incident X-ray beam: 6.7 µm, 21 keV.

M. Czyzycki et al., unpublished work

Confocal experiment on a single layer



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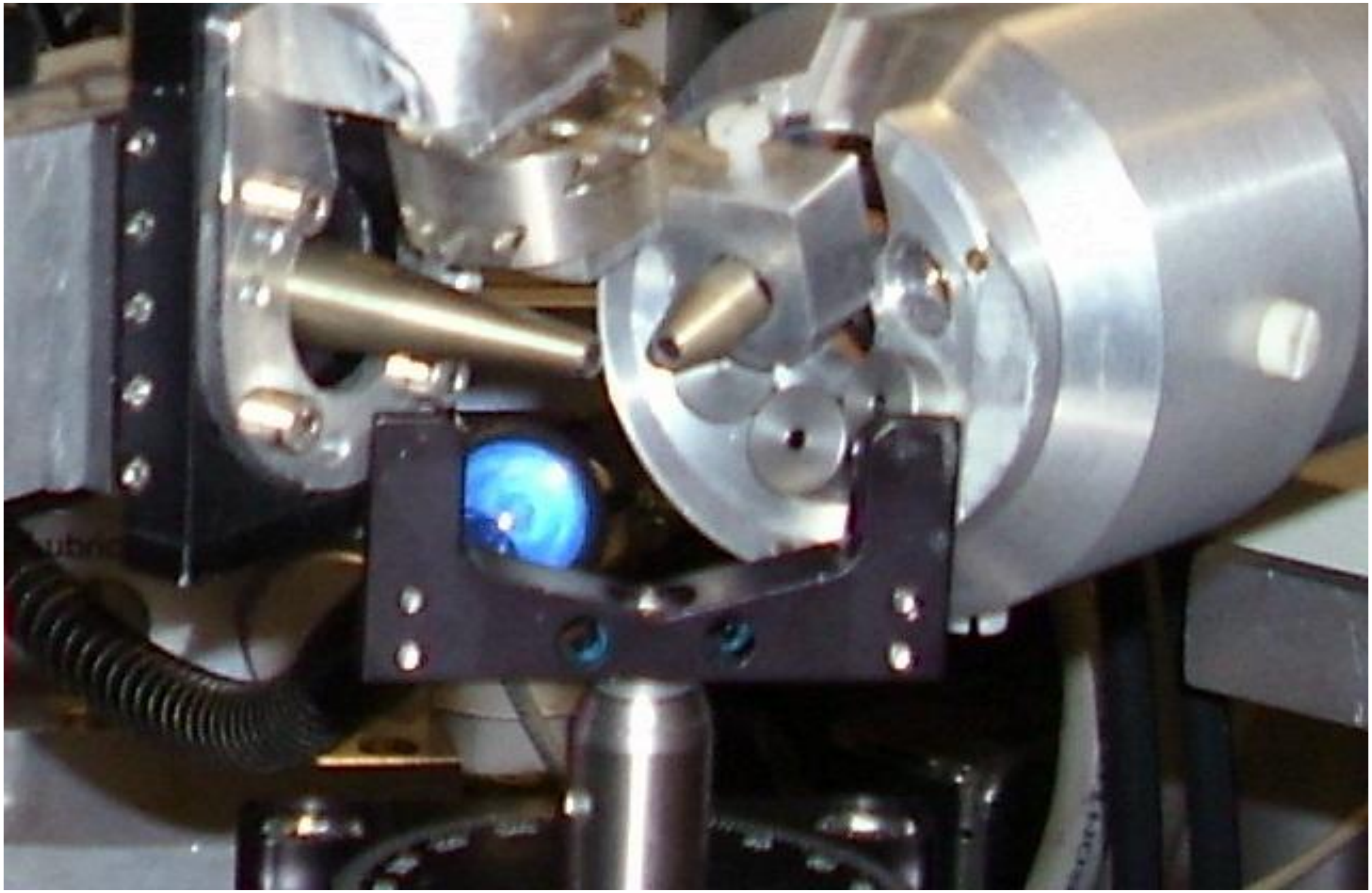
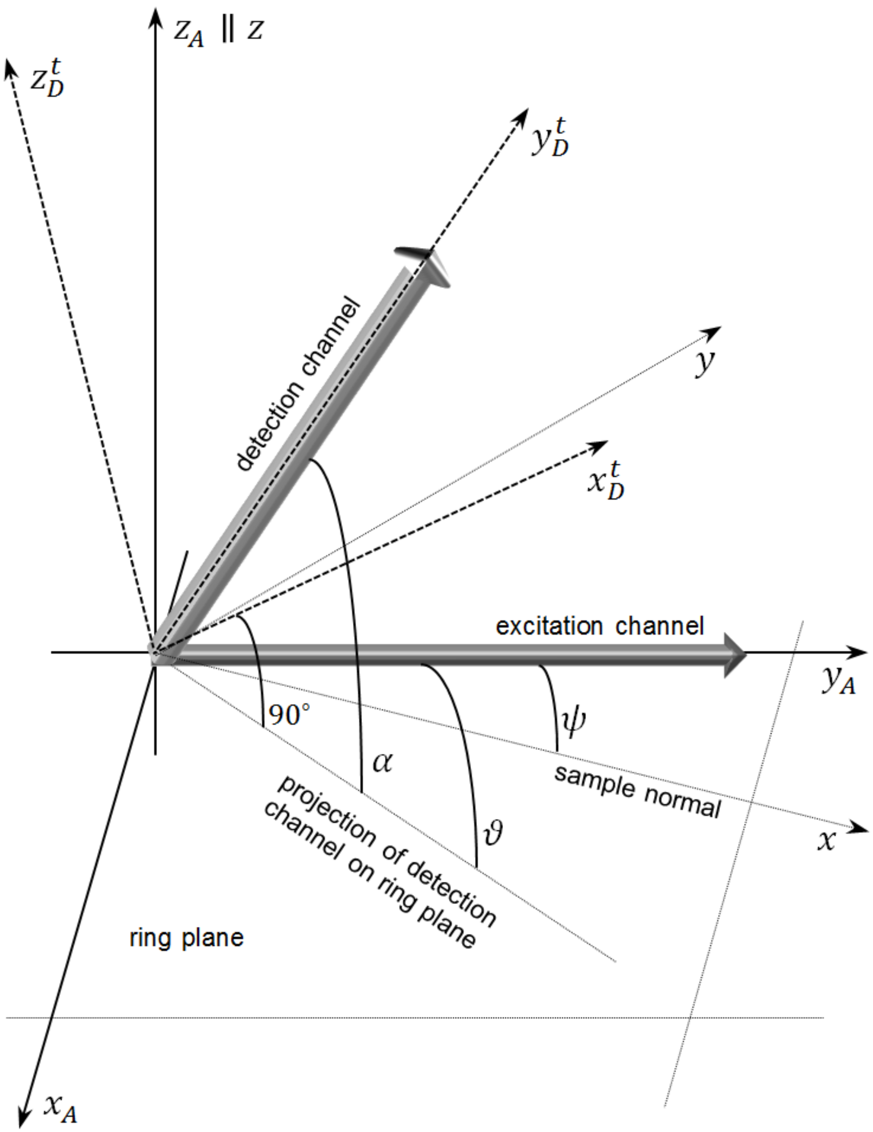
Equipment in tilted geometry



Tilted geometry – schematic drawing



Fundamental parameter model – general

$$\eta_A(\vec{r}_A) = \frac{T_A}{2\pi\sigma_A^2}\exp\left(-\frac{x_A^2 + z_A^2}{2\sigma_A^2}\right)$$

$$\eta_D(\vec{r}_D^{\,t}) = \frac{\Omega}{4\pi}T_D\varepsilon\exp\left(-\frac{\left(x_D^t\right)^2 + \left(z_A^t\right)^2}{2\sigma_D^2}\right)$$

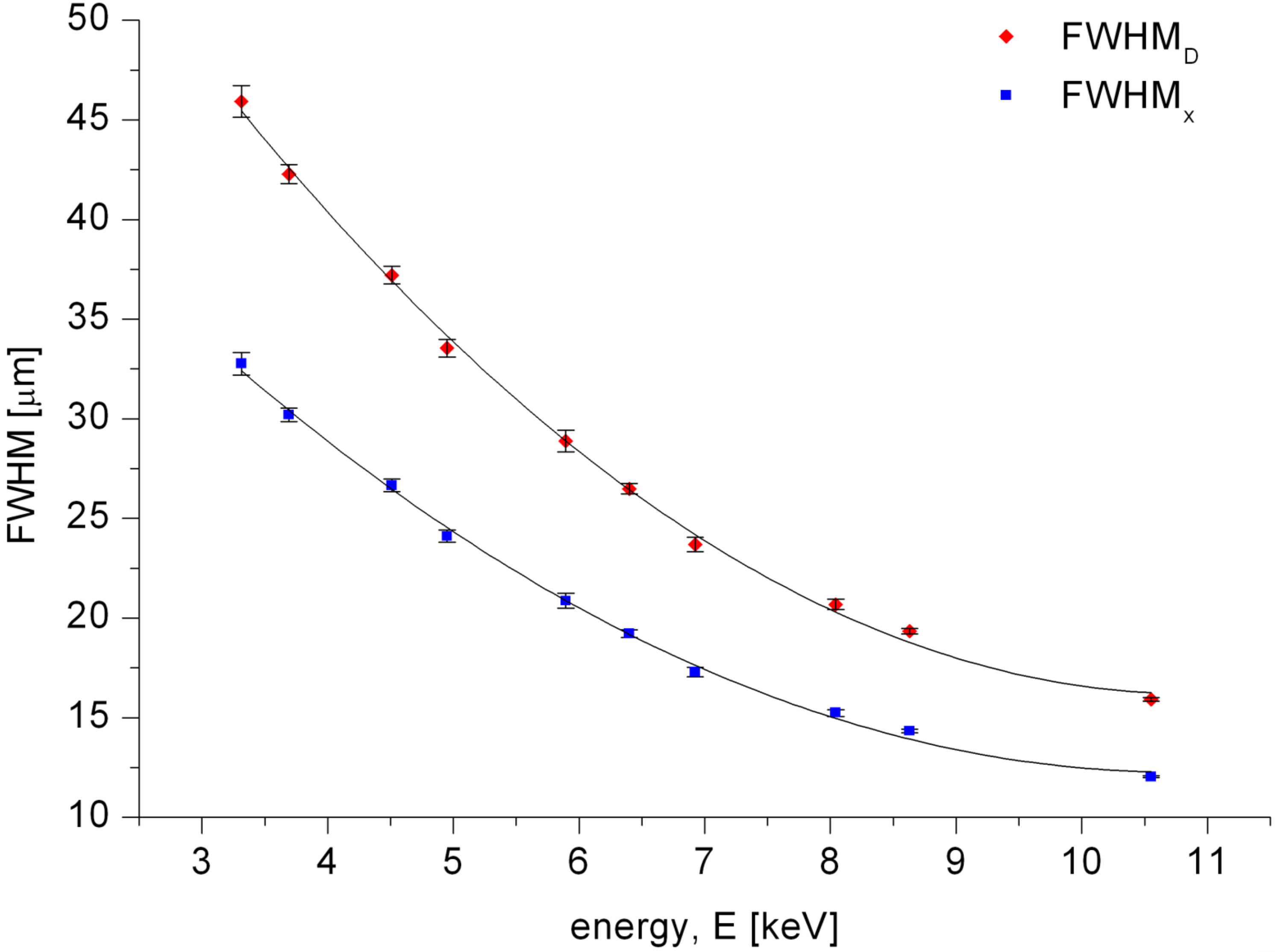
$$\eta(\vec{r}_A) = \eta_A(\vec{r}_A)\cdot\eta_D(\vec{r}_A)$$

$$\tilde{\eta} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\eta(\vec{r}_A)\mathrm{d}x_A\mathrm{d}y_A\mathrm{d}z_A = \frac{T_A T_D \Omega\varepsilon}{\sqrt{8\pi}}\frac{\sigma_D^2}{\sqrt{\sigma_A^2 + \sigma_D^2}}$$

$$\eta_x(x) = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\eta(\vec{r})\mathrm{d}y\mathrm{d}z = \frac{\tilde{\eta}}{\sqrt{2\pi}\sigma_x}\exp\left(-\frac{x^2}{2\sigma_x^2}\right)$$

W. Malzer, B. Kanngiesser, *Spectrochim. Acta Part B* 2005; 60, 1334-1341

Spatial resolution in confocal geometry



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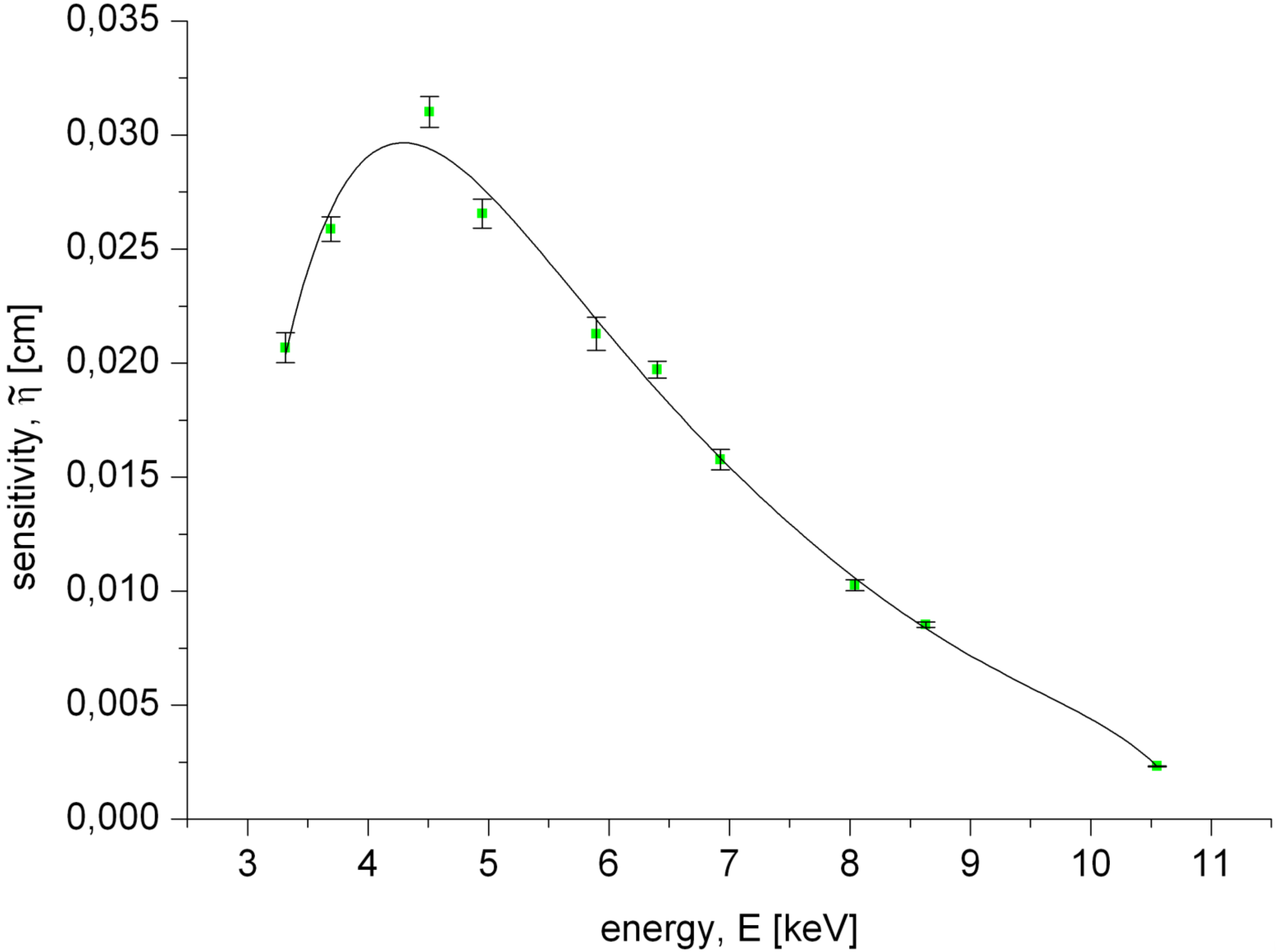
Integral sensitivity



Fundamental parameter model – in tilted geometry

$$\sigma_x = \sqrt{\chi \sigma_A^2 \sin^2 \psi + \sigma_D^2 \cos^2 \psi}$$

$$\chi = \frac{\sigma_A^2 \cos^2 \alpha + \sigma_D^2}{\sigma_A^2 + \sigma_D^2}$$

$$\Phi_l(x) = \Phi_0 \sigma_F \int_0^D \eta_x(\zeta - x)\rho(\zeta)\exp\left[-\int_0^\zeta \mu_{\mathrm{lin}}(\xi)\mathrm{d}\xi\right]\mathrm{d}\zeta$$

$$\mu_{\mathrm{lin}} = \sum_i \rho_i \left(\frac{\mu_{0,i}}{\cos \vartheta_A} + \frac{\mu_{j,i}}{\cos \alpha \cos \vartheta_D}\right)$$

M. Czyzycki, P. Wrobel, M. Lankosz, *Spectrochim. Acta Part B* 2014; 97, 99-104

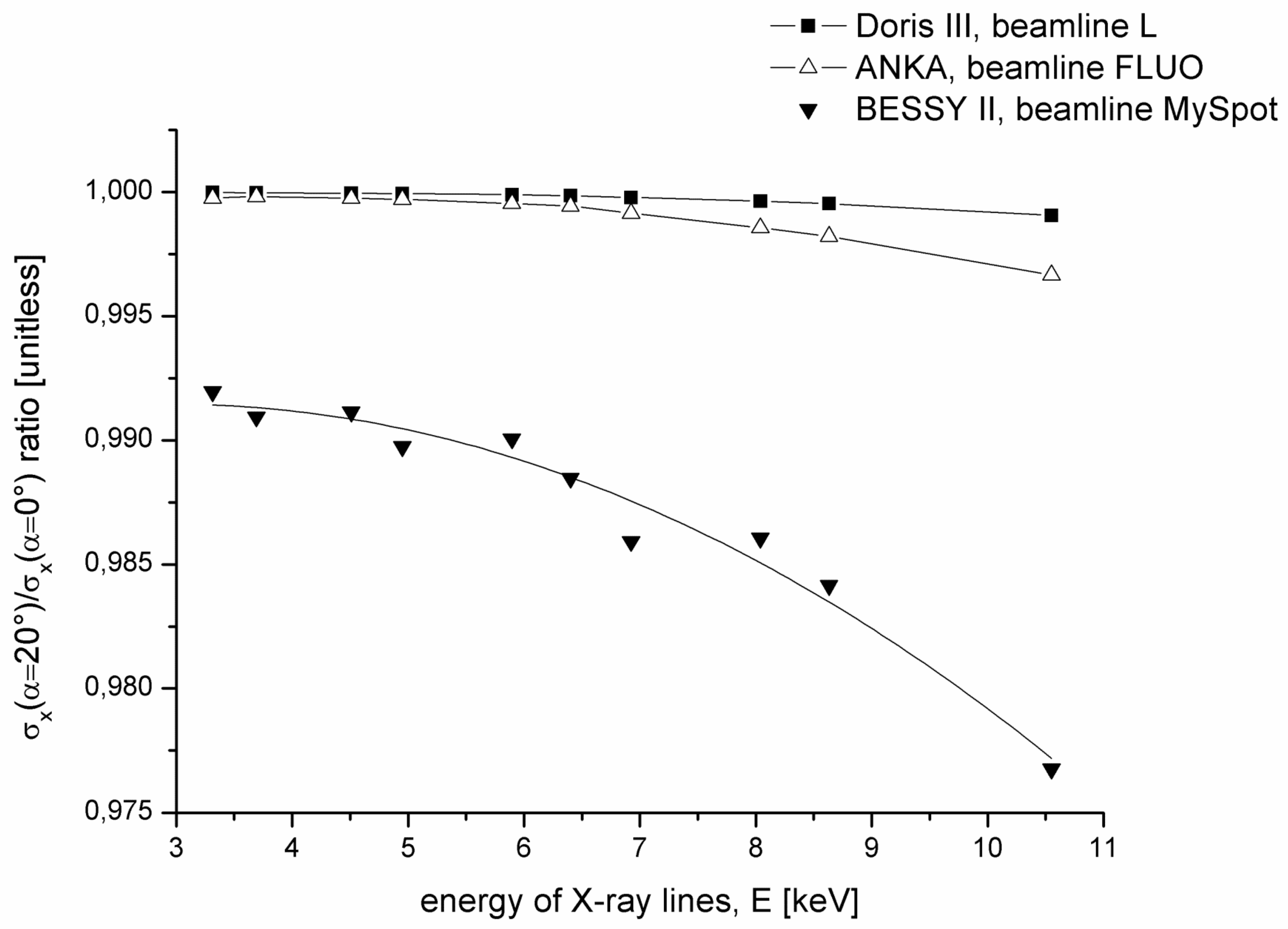
Fundamental parameter model

$$\Phi_l(x) = \frac{\Phi_0 \tilde{\eta} \sigma_F \rho}{2} \exp(-\mu_{\text{lin}} x) \exp\left(\frac{(\mu_{\text{lin}} \sigma_x)^2}{2}\right) \times \left\{ \text{erf}\left(\frac{D + \mu_{\text{lin}} \sigma_x^2 - x}{\sqrt{2}\sigma_x}\right) - \text{erf}\left(\frac{\mu_{\text{lin}} \sigma_x^2 - x}{\sqrt{2}\sigma_x}\right) \right\}$$

$$\Phi(x) = \sum_{l=1}^{n} \Phi_l(x) \prod_{k=1}^{l-1} \exp\left(-\mu_{\text{lin},k} D_k\right)$$

I. Mantouvalou, W. Malzer, I. Schaumann, L. Lűhl, R. Dargel, C. Vogt, B. Kanngiesser, *Anal. Chem.* 2008; 80, 819-826

Spatial resolution in tilted geometry



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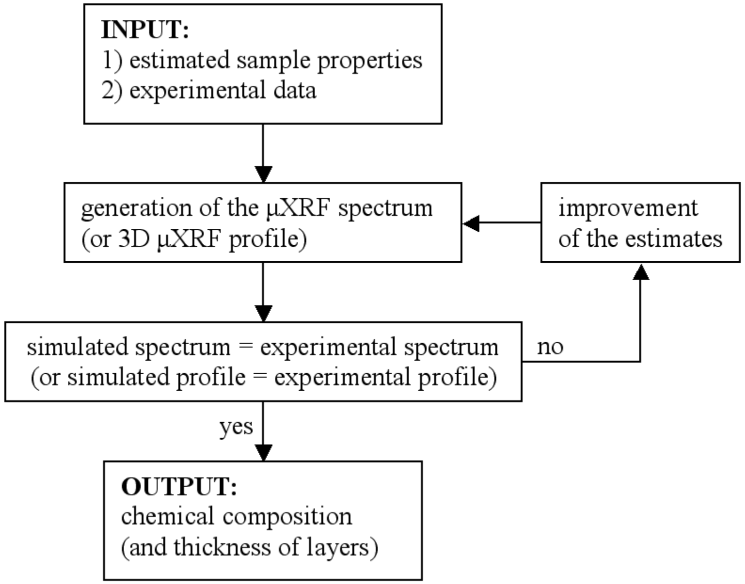
Monte Carlo simulation – Why to use?

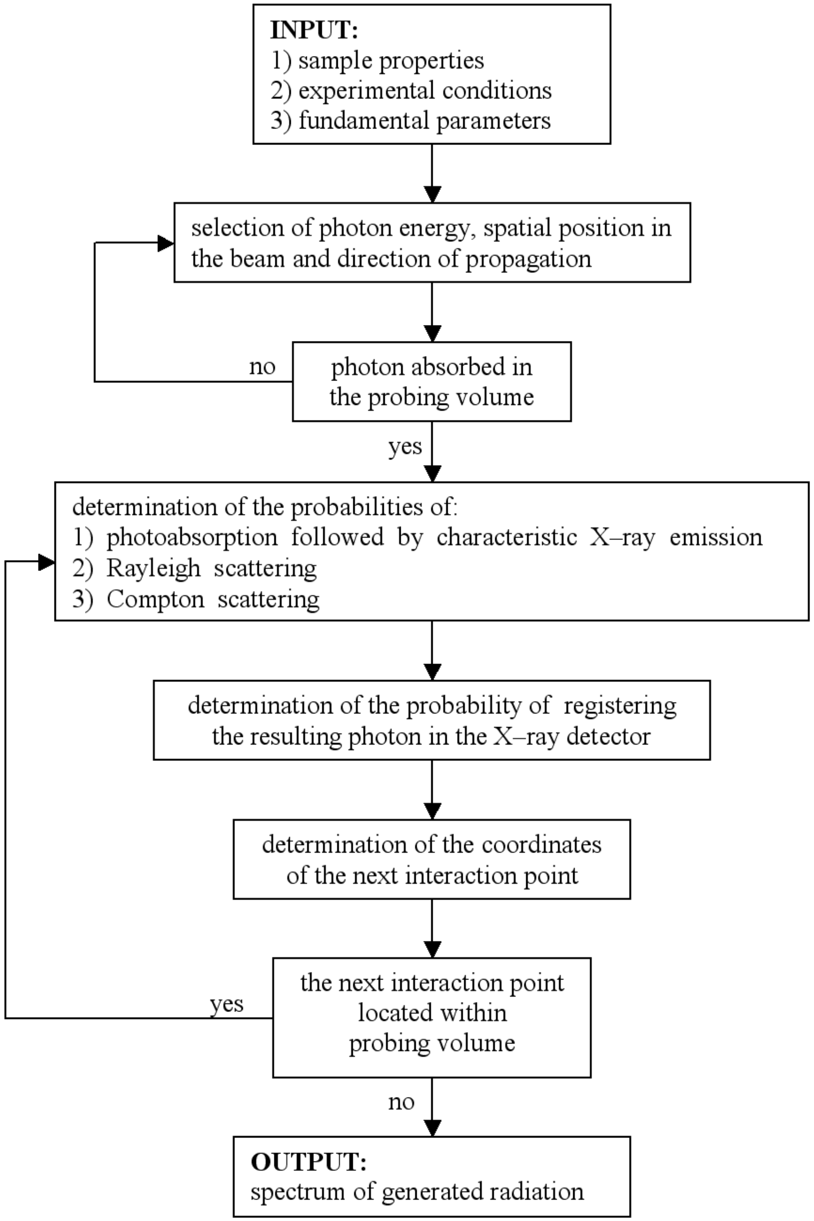
1. Morphology of the sample:
   shape, sizes, inner structure, inhomogeneities, layers

2. Experimental conditions:
   spectral and spatial distribution of X-ray beam, polarisation effects, unlimited geometries

3. Interaction of X-rays with matter:
   photoabsorption, scattering effects

Monte Carlo algorithm





Quantitative reconstruction of layers

Element concentrations:

$$w_i^{(k+1)}(x) = w_i^{(k)}(x) \frac{Y_{i,\exp}(x)}{Y_{i,\mathrm{MC}}^{(k)}(x) \sum_{j=1}^{N_m} w_j^{(k)}(x) \frac{Y_{j,\exp}(x)}{Y_{j,\mathrm{MC}}^{(k)}(x)}}$$

Thicknesses:

$$d_m^{(k+1)} = \frac{d_m^{(k)}}{N_x N_X} \sum_x \sum_{i=1}^{N_X} \frac{Y_{i,\exp}(x)}{Y_{i,\mathrm{MC}}^{(k)}(x)}$$

M. Czyzycki, D. Wegrzynek, P. Wrobel, M. Lankosz, *X-Ray Spectrom*. 2011; 40, 88-95

Computing cluster

> ***Software***

C, Perl, Unix, *xraylib* library

> ***Hardware***

IBM BladeCenter HS21 cluster
112 Intel Dual-core processors
2GB RAM/core
2.4 Tflops

Academic Computer Centre

CYFRONET AGH, Cracow, Poland

Multi-layer Zn standard on polymer matrix

9 individual layers

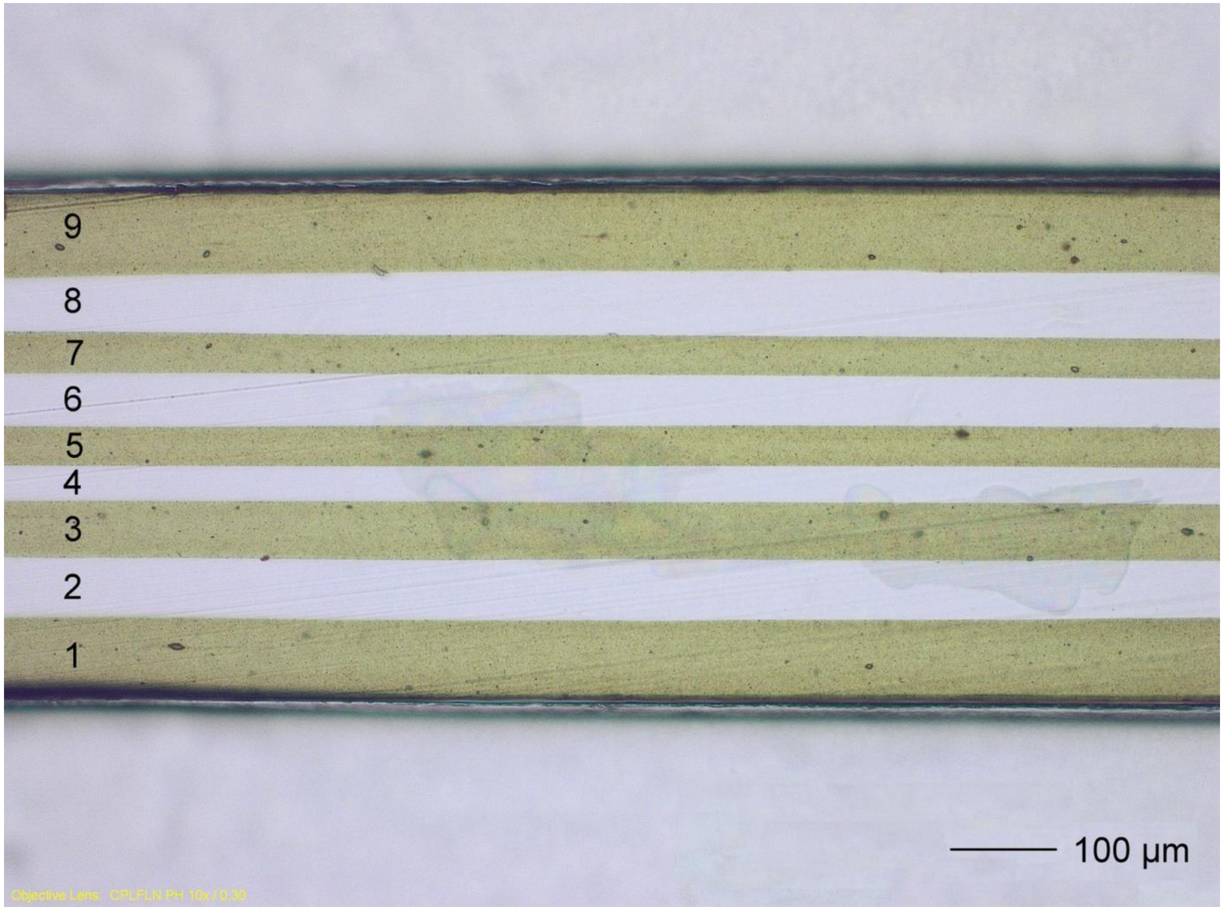
odd layers:

$(CH_2)_n$ – 95.02%

ZnO – 4.98%

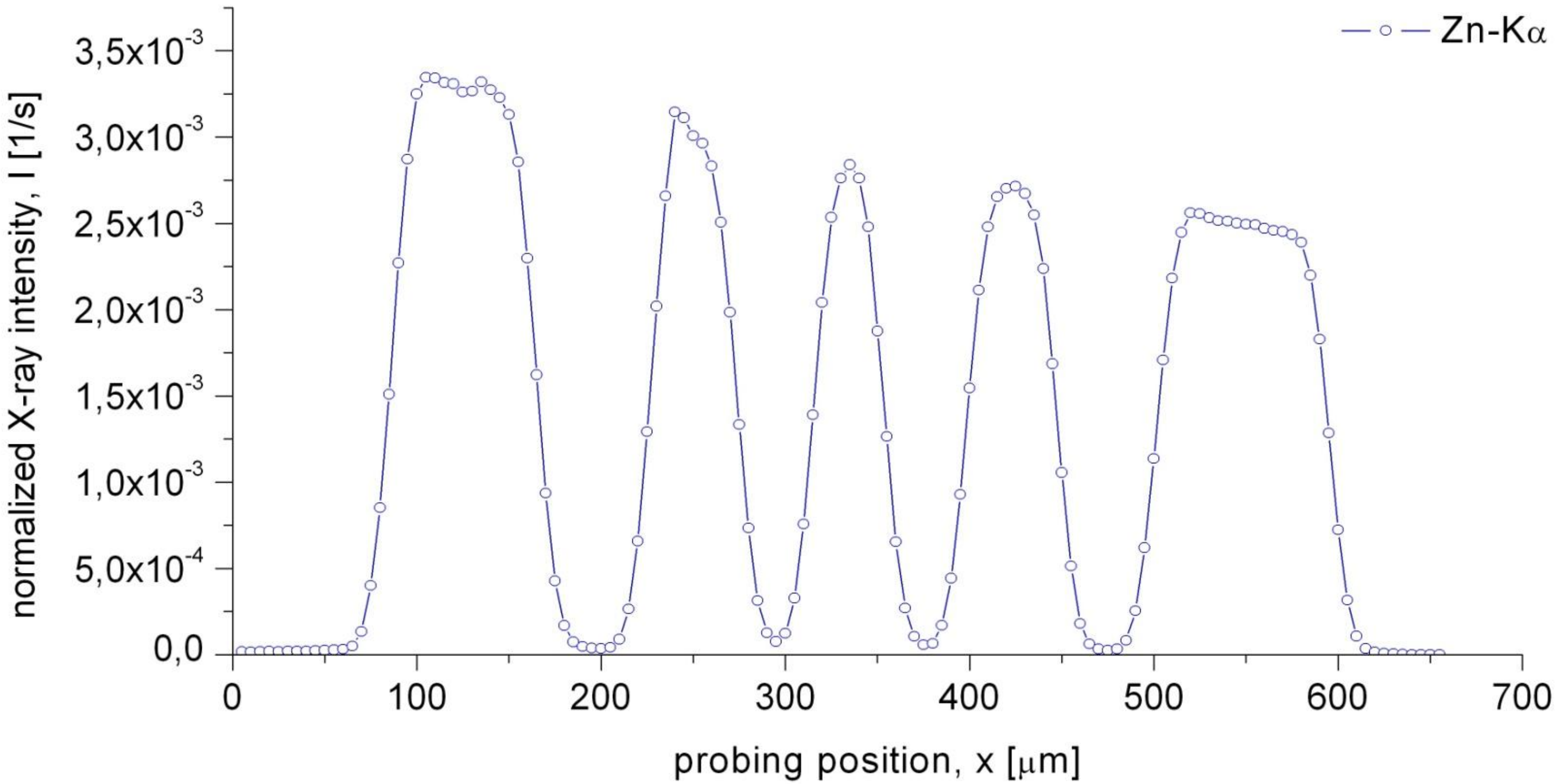
even layers:

$(CH_2)_n$ – 100%



M. Czyzycki, P. Wrobel, M. Szczerbowska-Boruchowska, B. Ostachowicz, D. Wegrzynek, M. Lankosz, *X-Ray Spectrom*. 2012; 41, 273-278

Depth-sensitive scan on Zn standard



HASYLAB at DESY, DORIS III, beamline L

Spatial resolution in depth-scan: 14.3 μm (Zn-Kα)

Reconstruction of multi-layer Zn standard

Layer no.	ZnO weight fraction determined by MC [%]	Layer thickness MC [µm]	Layer thickness Optical microscope [µm]
1	4.98 (0.07)	80.5 (0.6)	80.2 (0.3)
2		63.2 (0.5)	62.4 (0.4)
3	5.06 (0.06)	45.9 (0.4)	45.3 (0.4)
4		43.8 (0.4)	43.6 (0.5)
5	4.84 (0.15)	38.7 (0.3)	38.8 (0.9)
6		45.9 (0.4)	46.5 (0.6)
7	4.76 (0.07)	49.9 (0.4)	51.3 (1.1)
8		55.0 (0.4)	54.8 (0.5)
9	4.95 (0.05)	96.8 (0.8)	97.3 (0.6)
nominal	4.98		

Multi-layer Zn/Cu standard on polymer matrix

9 individual layers

odd layers:

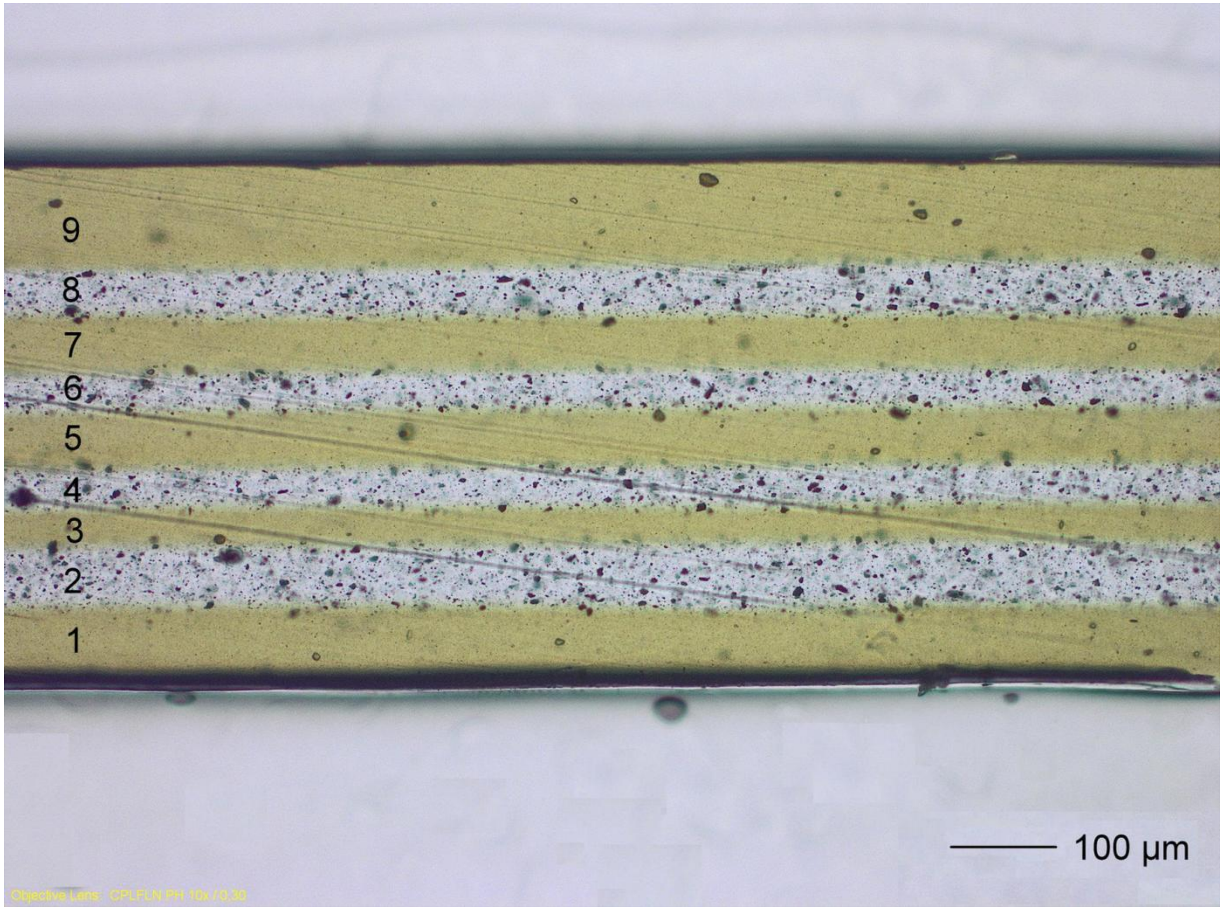
$(CH_2)_n$ – 95.02%

ZnO – 4.98%

even layers:

Cu_2O – 4.50%

$(CH_2)_n$ – 95.50%



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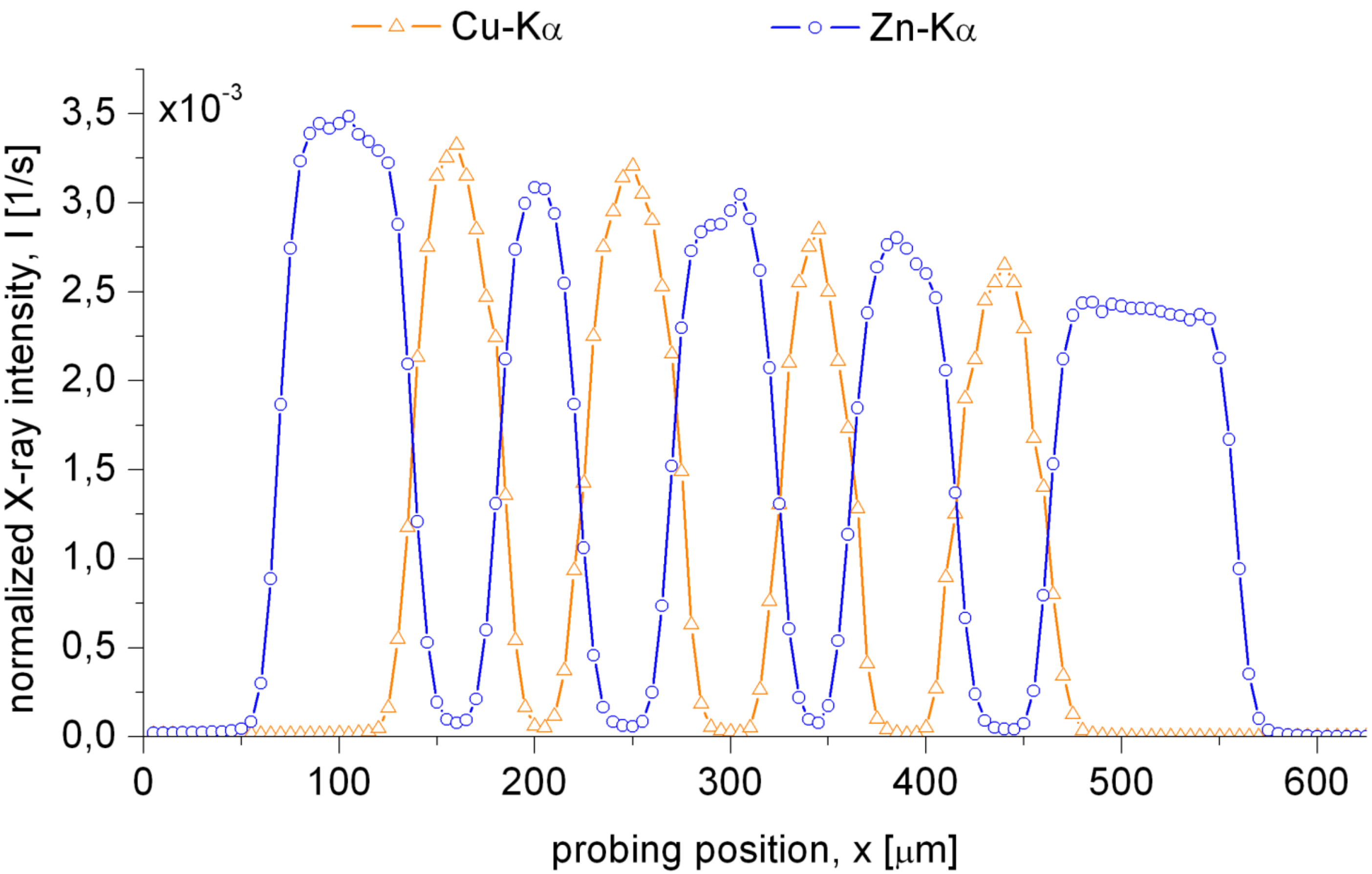
Depth-sensitive scan on Zn/Cu standard



HASYLAB at DESY, DORIS III, beamline L

Spatial resolution in depth-scan: 15.2 μm (Cu-Kα) and 14.3 μm (Zn-Kα)

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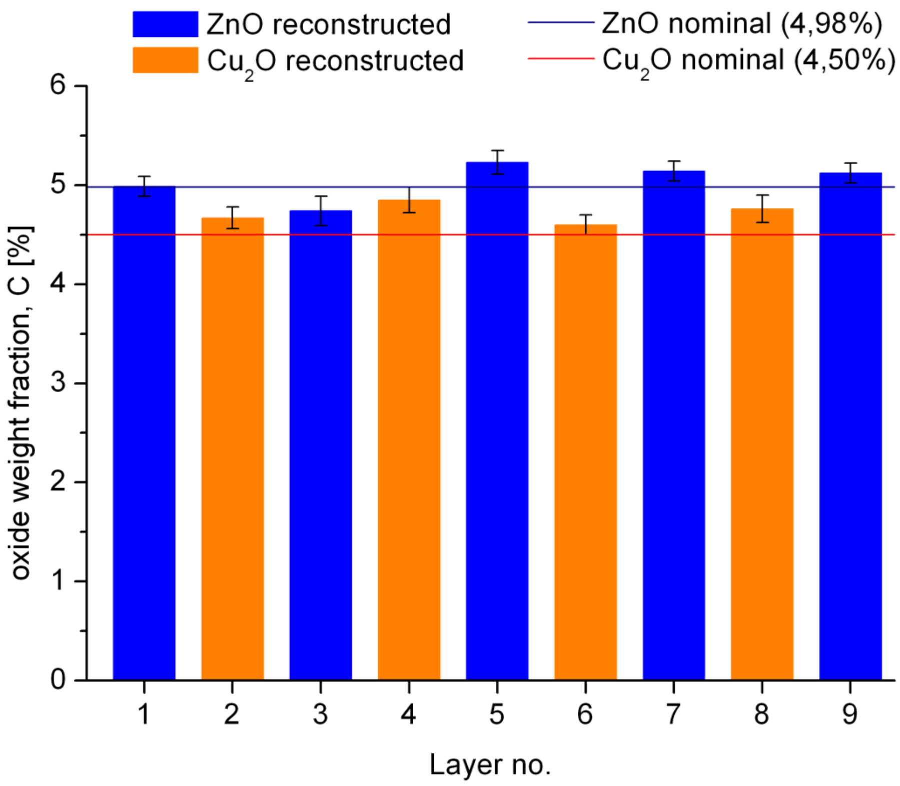
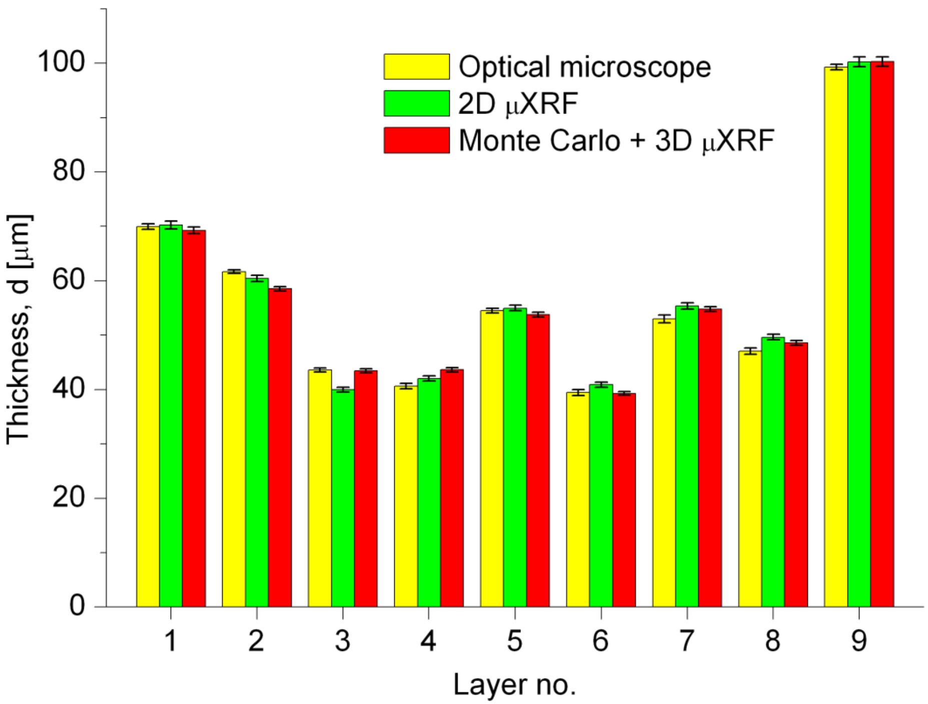
Reconstruction of multi-layer Zn/Cu standard





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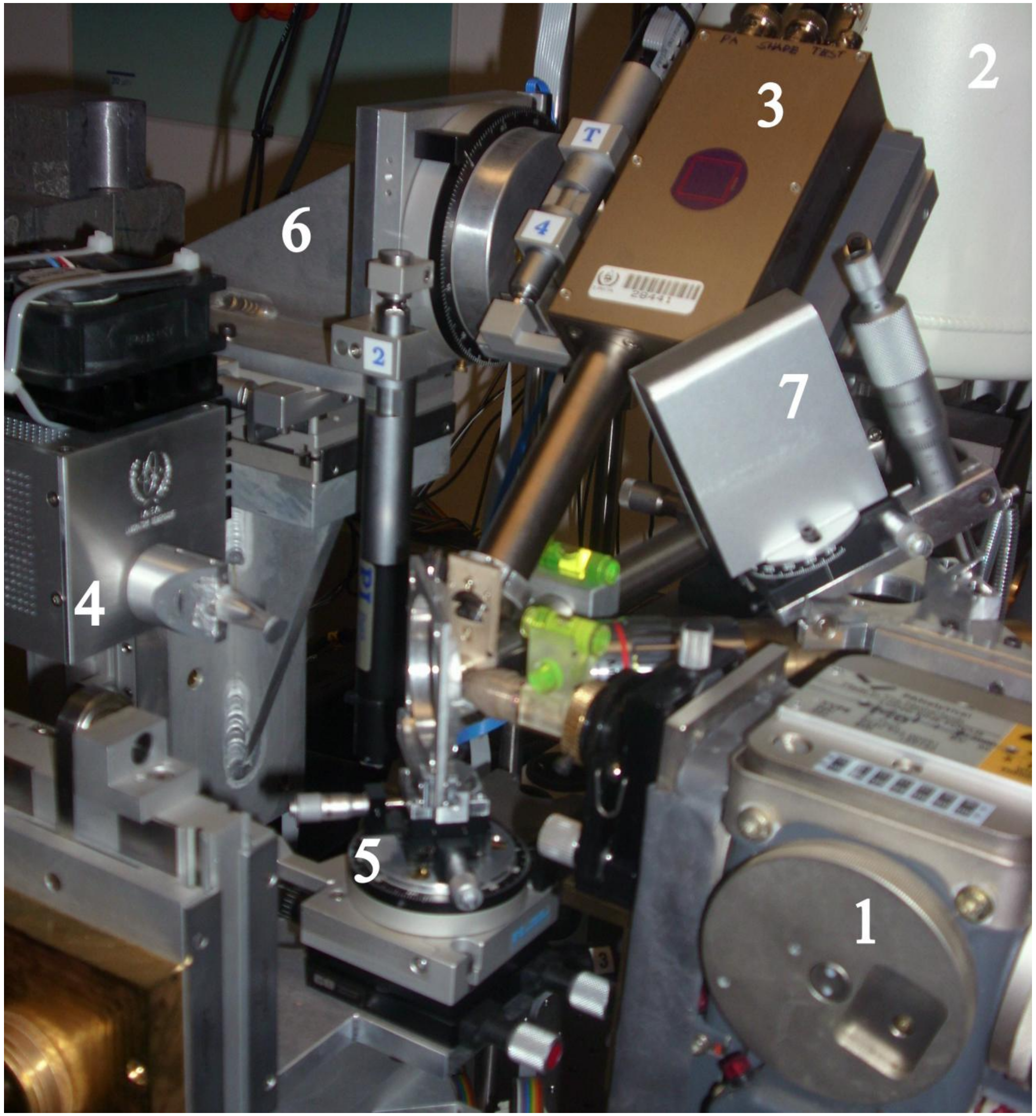
Confocal XRF spectrometer in the IAEA lab



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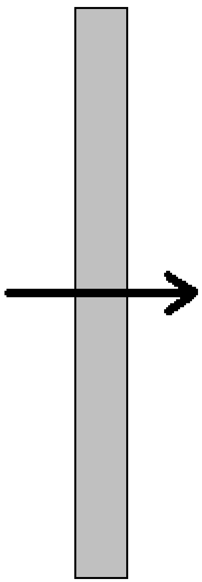
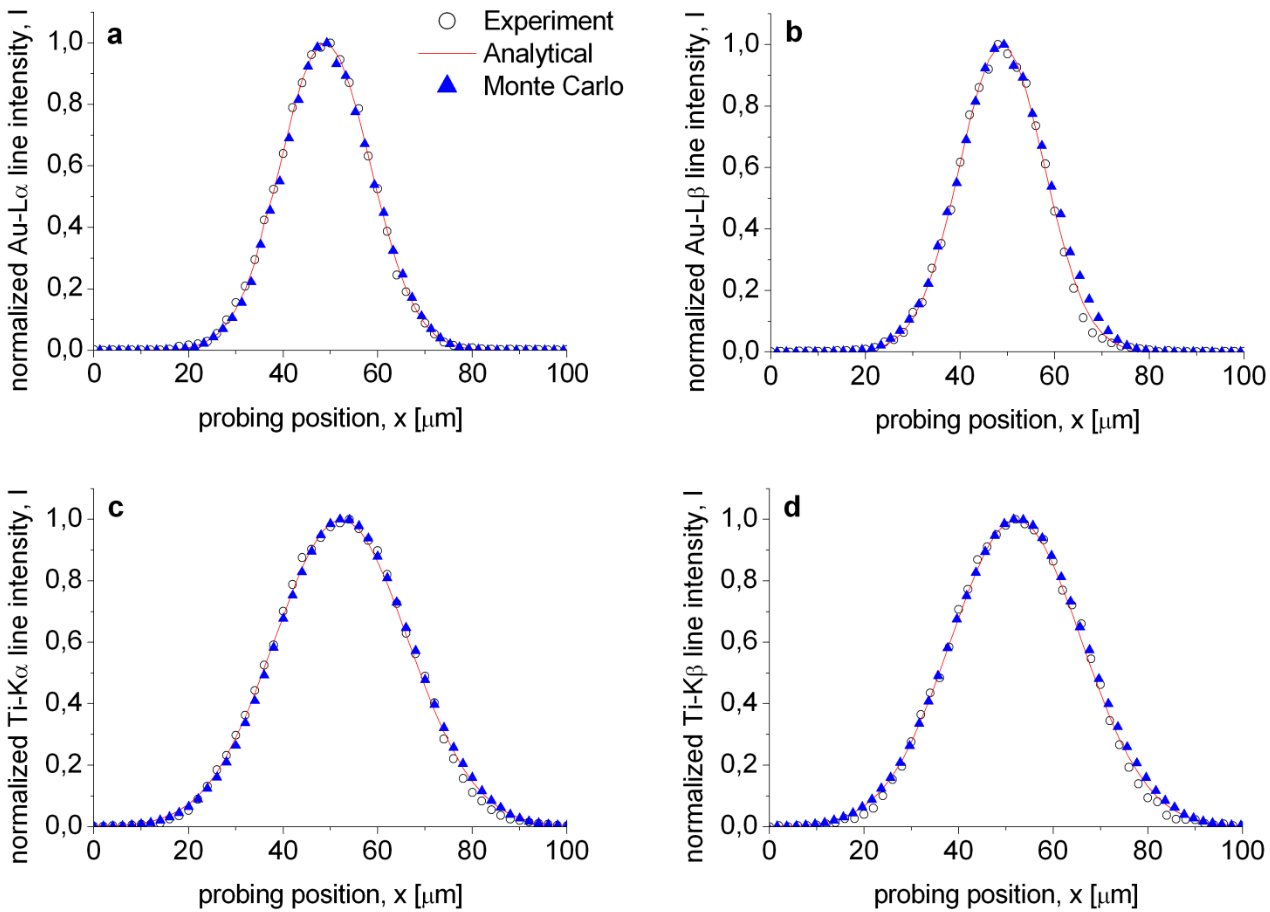
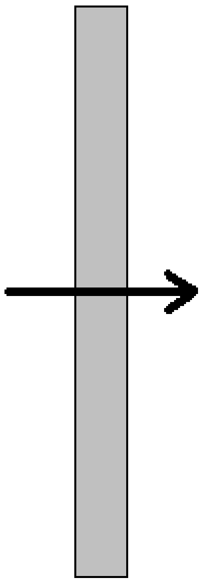
Mono-layers of high-Z matrix (1)

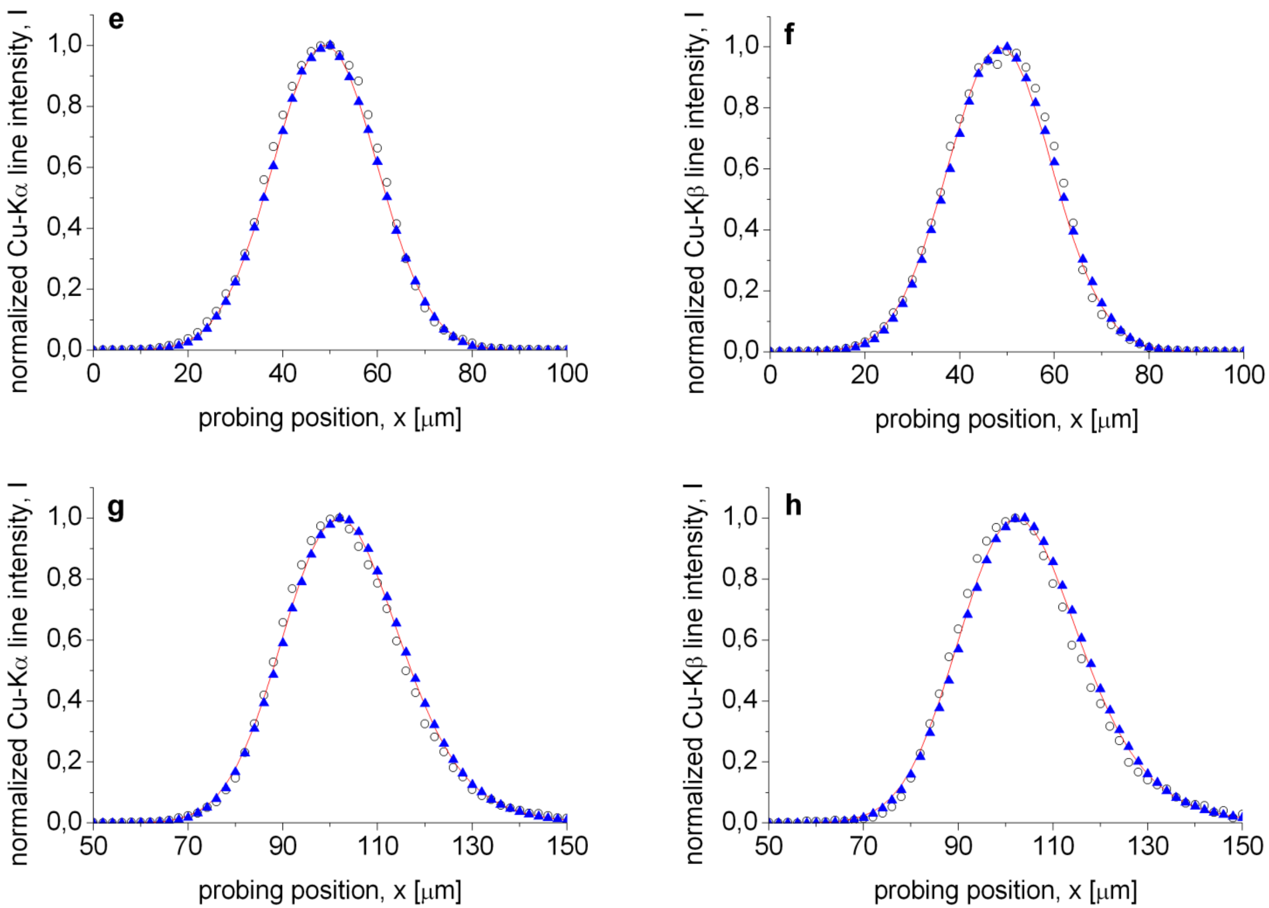




IAEA Seibersdorf a,b – Au foil, 0,02 μm c,d – Ti foil, 6 μm

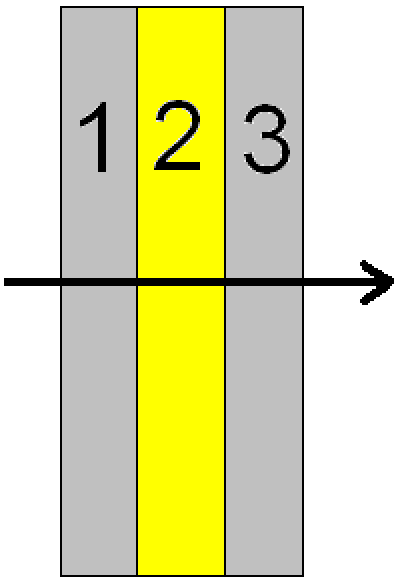
Mono-layers of high-Z matrix (2)

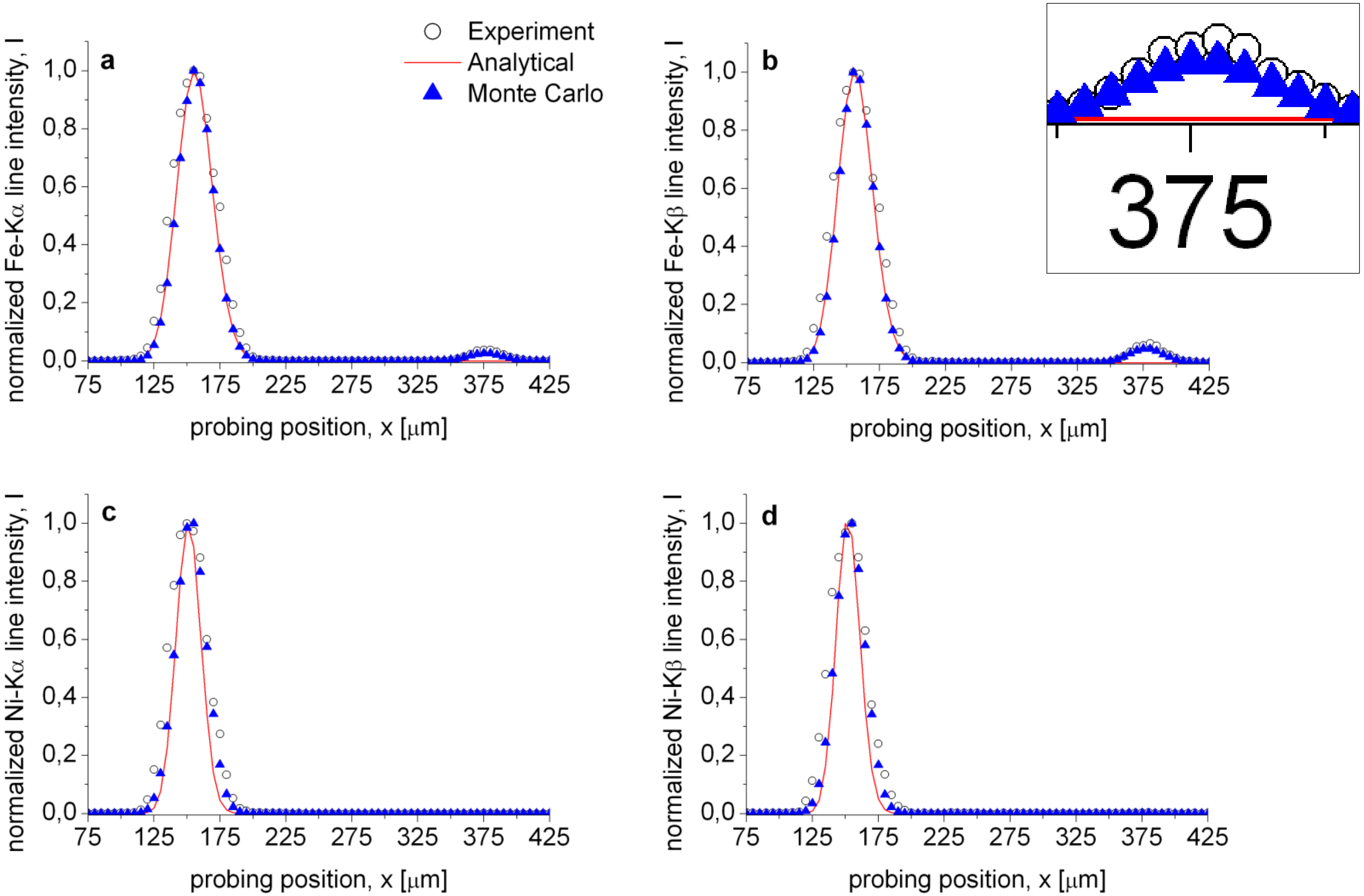




IAEA Seibersdorf e,f – Cu foil, 7 µm g,h – Cu sheet, 2 mm

Three-layer alloy standard





#1 i #3 – $Fe_{0.64}Ni_{0.36}$ alloy foil, 25 μm

#2 – $(C_3H_6)_n$ foil, 220 μm

Conclusion

Confocal µXRF spectroscopy can be sucessfully used to discover the elemental composition of materials studied (in particular multi-layers).

Monte Carlo simulation is a reliable tool for the simulation of scanning confocal µXRF experiments and for the qualitative and quantitative interpretation of experimental results.

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Thank you for your attention!