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X-Ray Fluorescence Analysis
with Ultimate Sources, Optics and Detectors
Applications and Results

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  DESY – Hasylab Hamburg:G. Falkenberg
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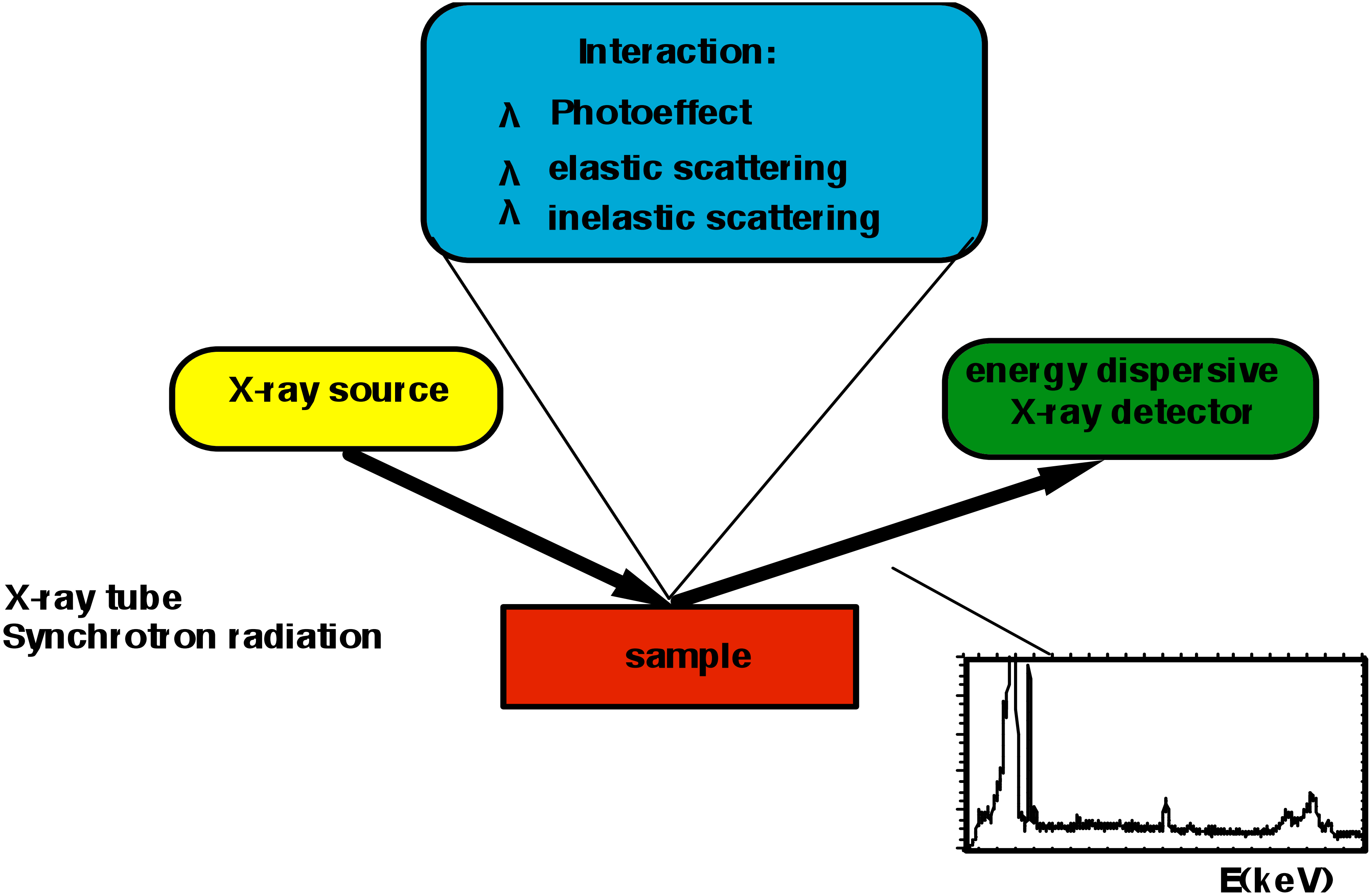
Renaissance of XRF

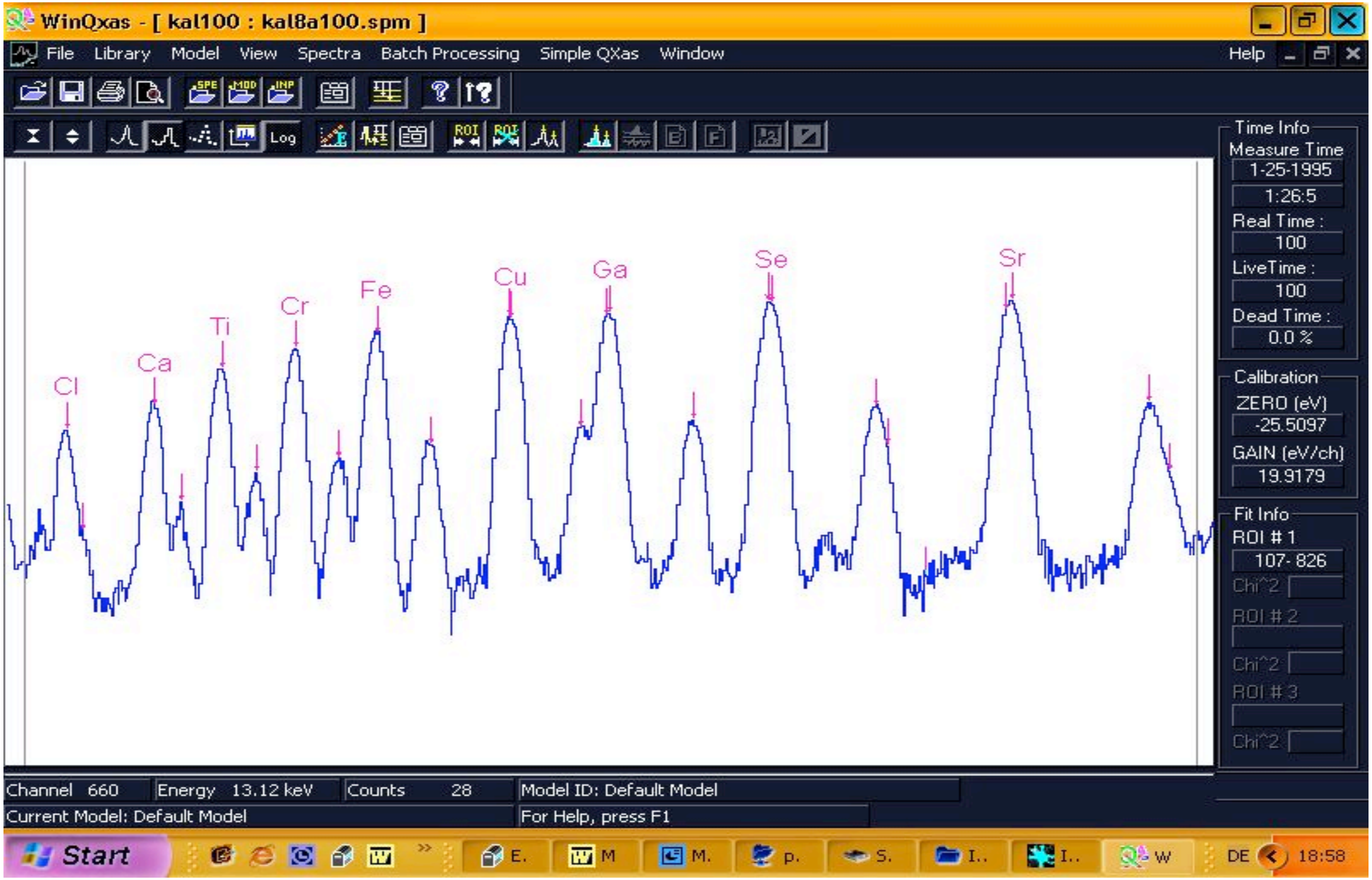
- Elemental range large Be(Z=4) to U Z=(92)
- Simultaneous multielement capacity
- Live time from few s to h 1000s recommended
- Nondestructive in some applications
- Detection limits fg absolute or pg/g

- Why
- New sources X-ray optics
- New detectors
- New structures for monochromatization (Multilayer)
- Fast computers: Spectrum deconvolution
  Quantification
  Absorption correction calculations
  Imaging software

Principle of EDXRS



Multielement spectrum



X-ray Sources

Standing Anodes – Fluorescence and Diffraction tubes

Anode Materials: Cr,Cu,Mo,W, Ag

Special for light element W-M line or Si anode

Focal size 0.04x12mm² line 0.4x0.8 mm² point

Power from few W to 3 kW

Special tubes. Thin window transmission of low E photons – Transmission anode tubes end window

Windowless tubes W- Si anode light element excitation

Rotating anode up to 90 kW

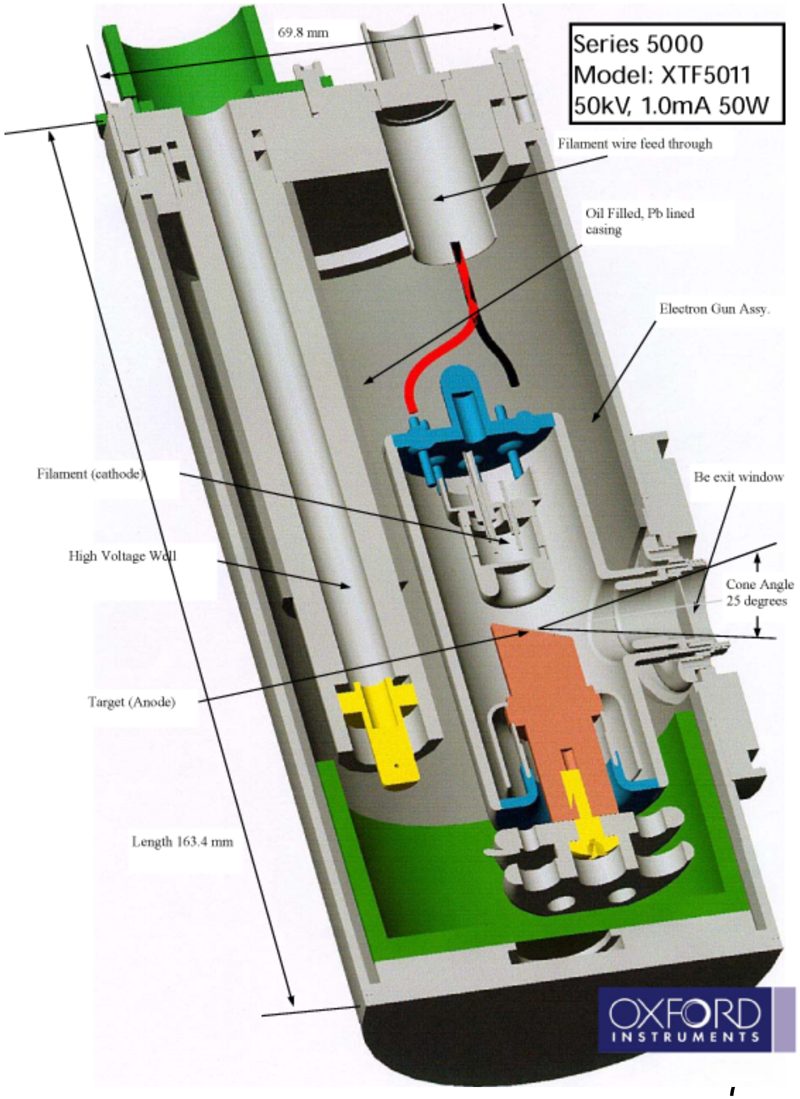
Synchrotron radiation

Femtosecond pulsed laser induced x-rays

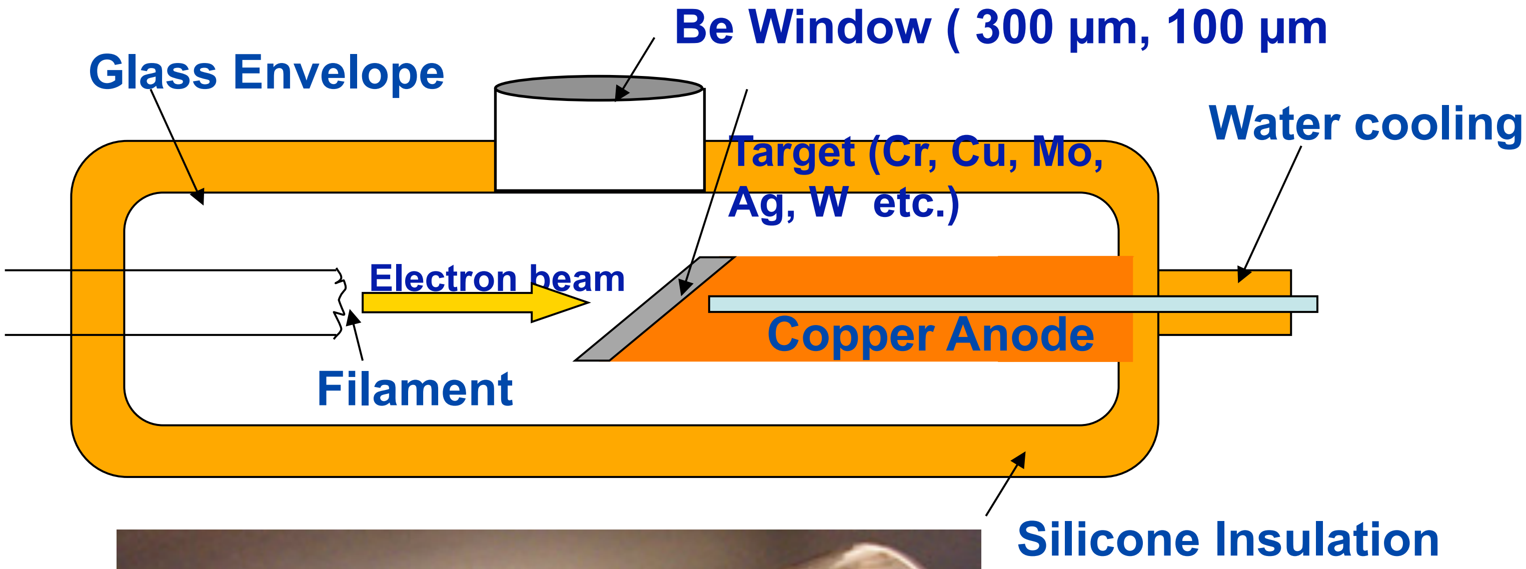
high harmonics or plasma source

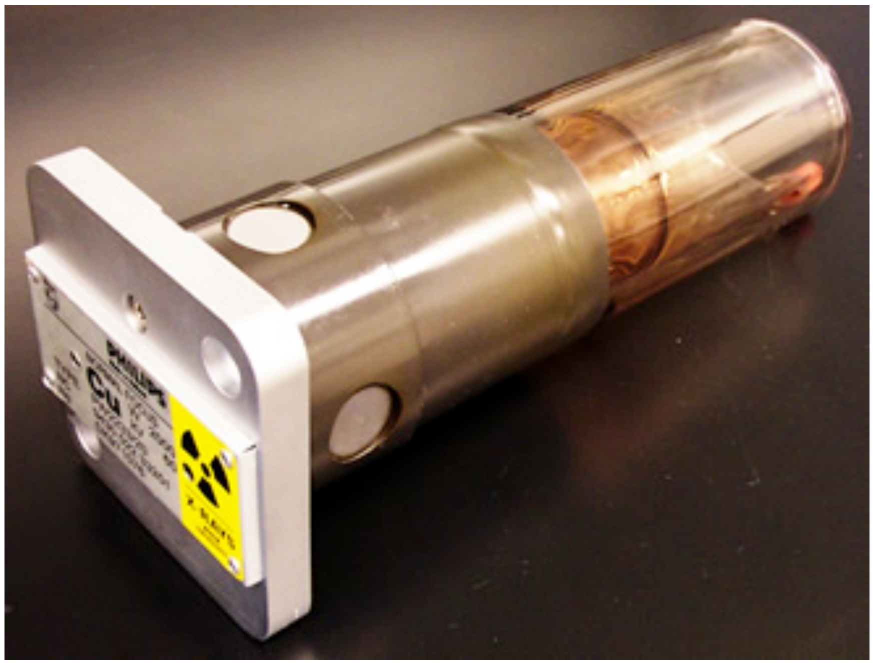
Oxford Low Power tube

• Tube current	0,1mA - 1mA
• Tube voltage	4kV - 50kV
• Max. power	50W kont.
• Cathode	2V - 1,7A
• Focus size	400µm (Pd)
• Exit window	125µm (Be)
• Dimensions	ø70 x165mm
• Air cooling	



Sidewindow tube 2 kW





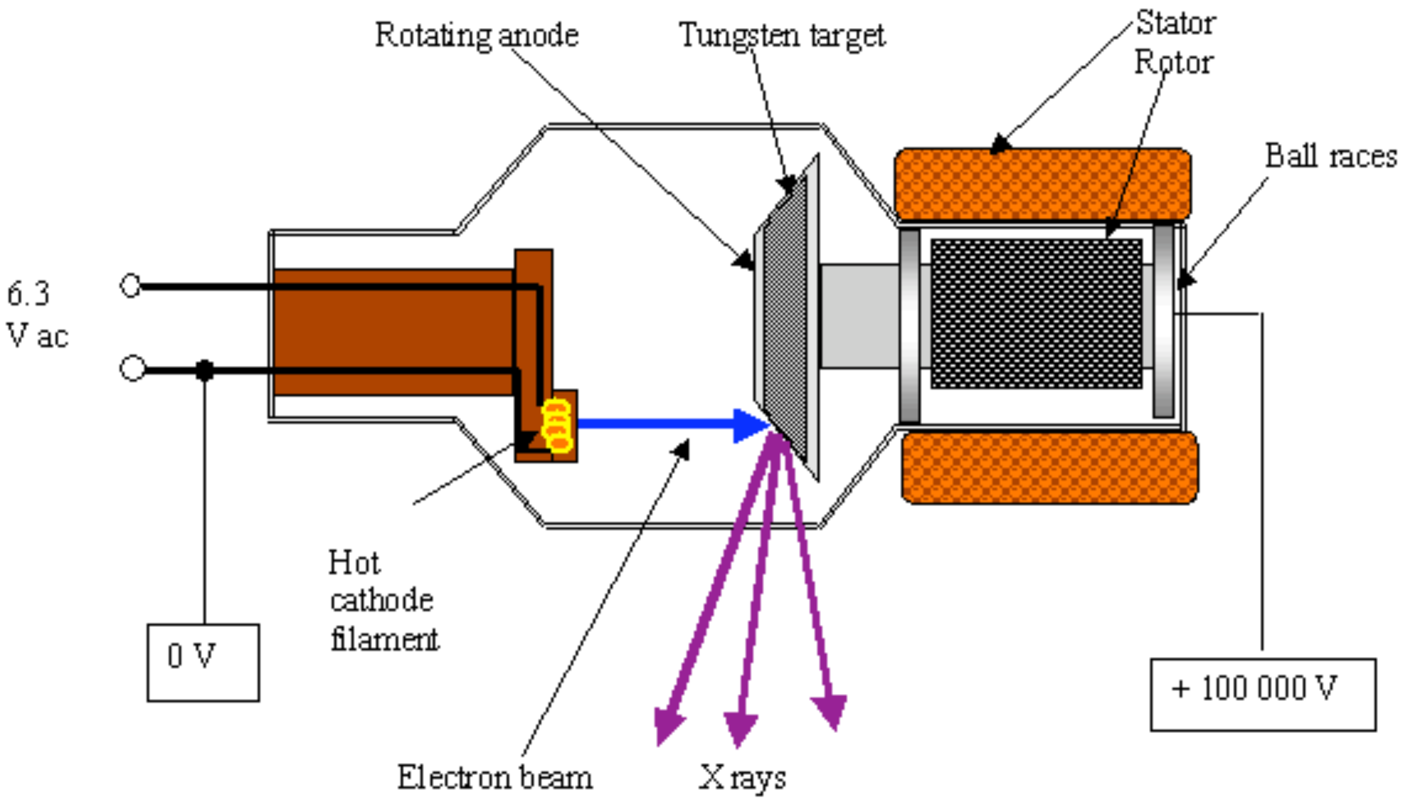
Focal spot:

8 x 0.4 mm

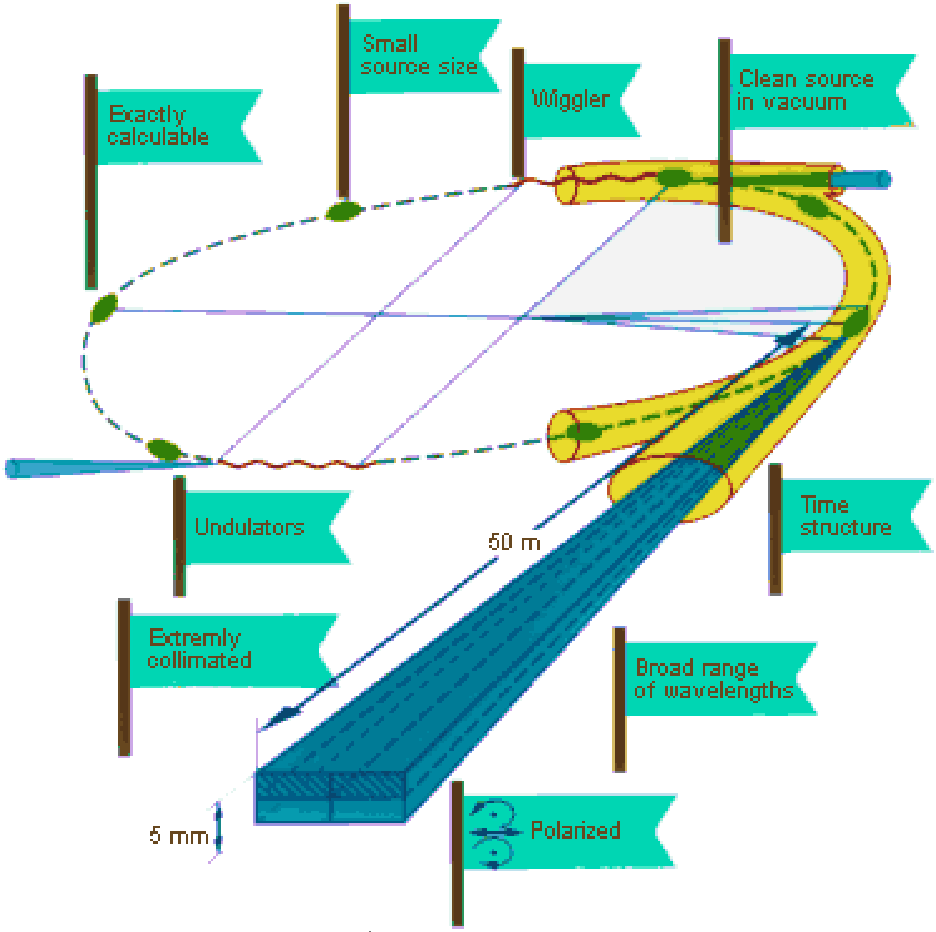
12 x 0.4 mm

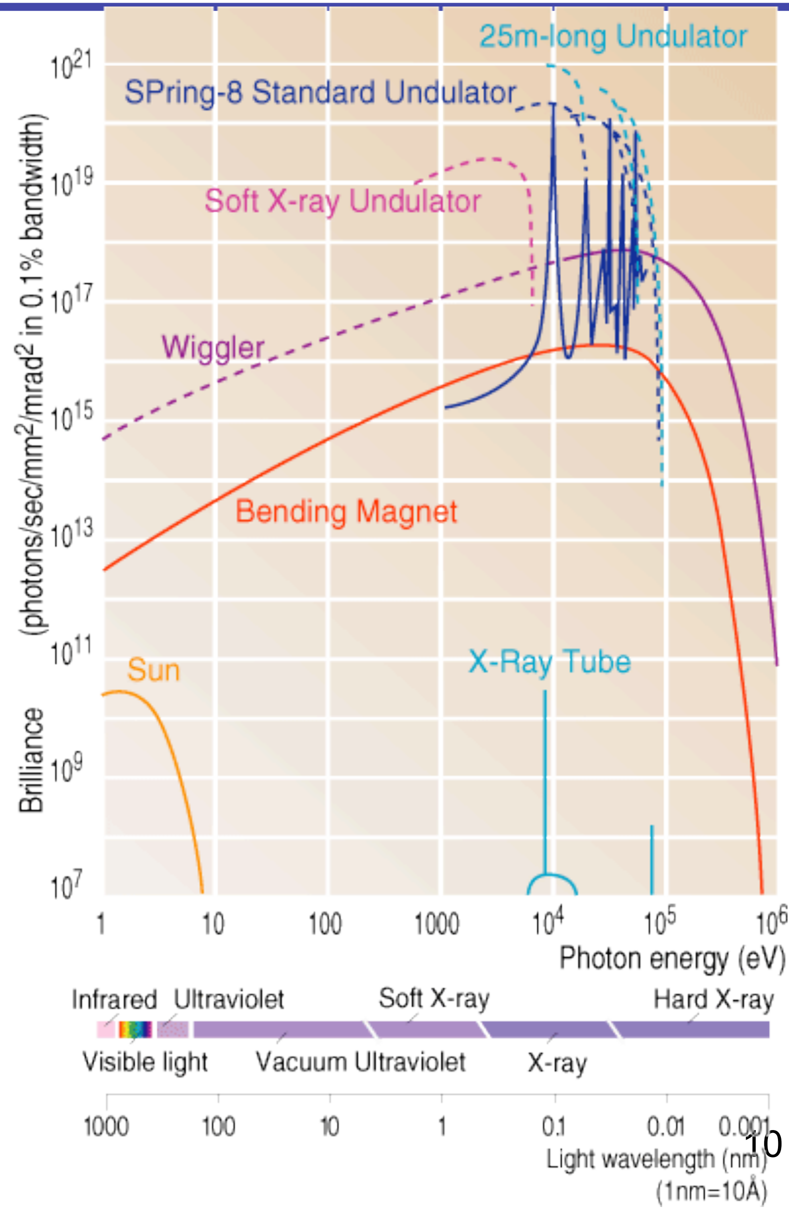
Efficiency: ‰

Rotating anode

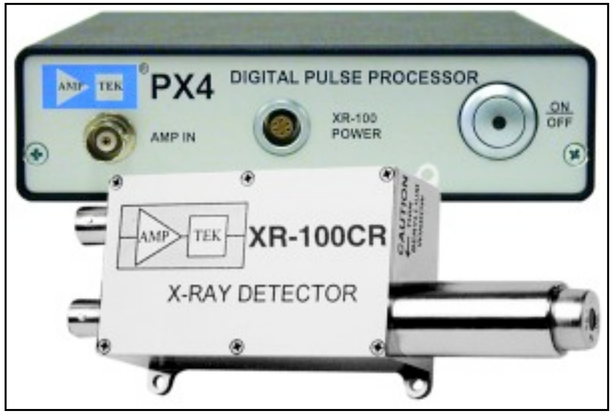


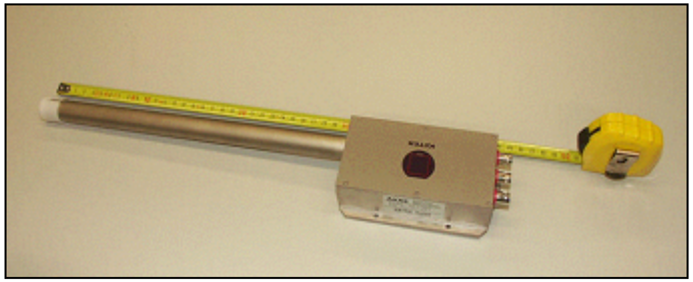
Synchrotron radiation





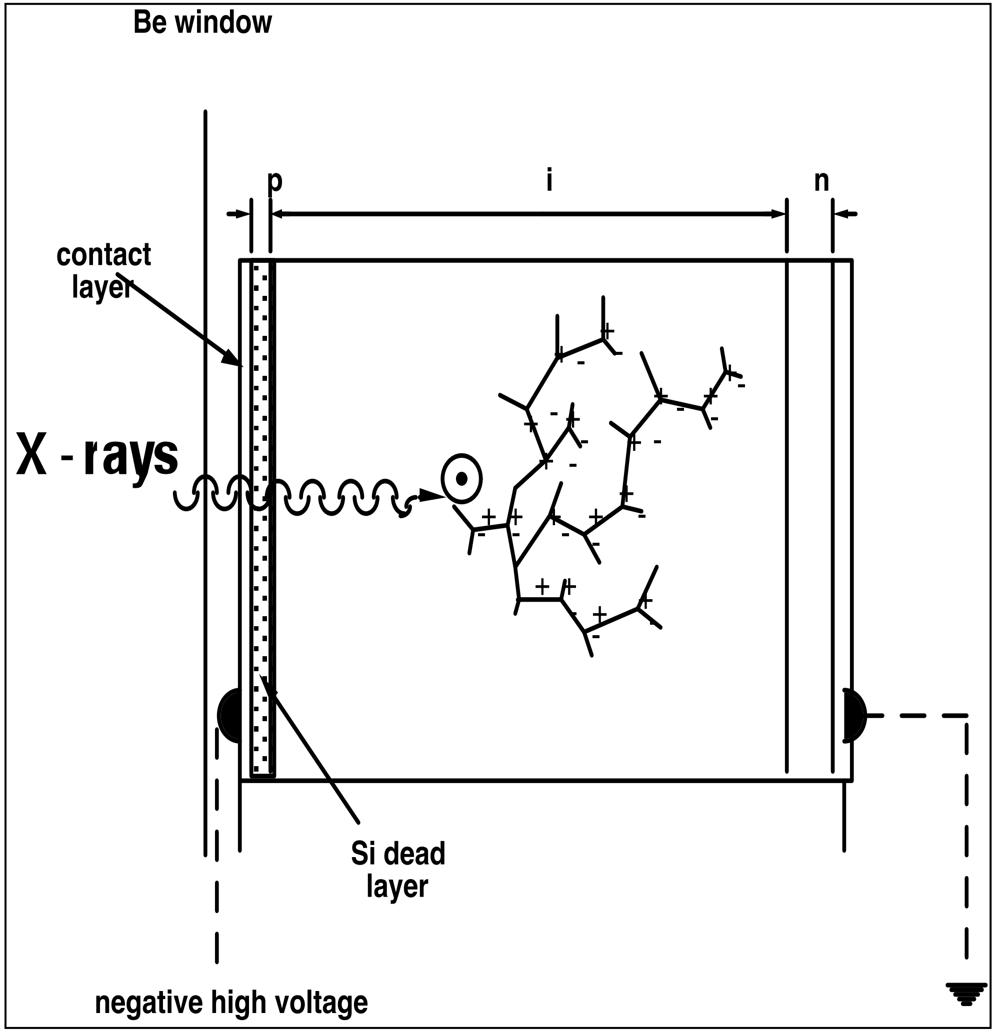
What Detector is this ???



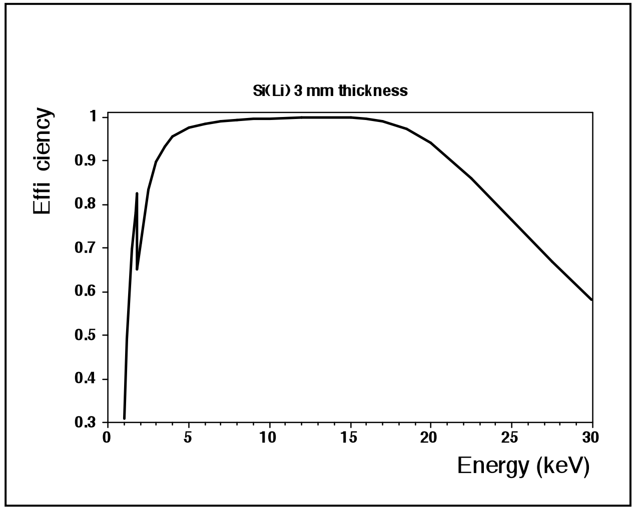


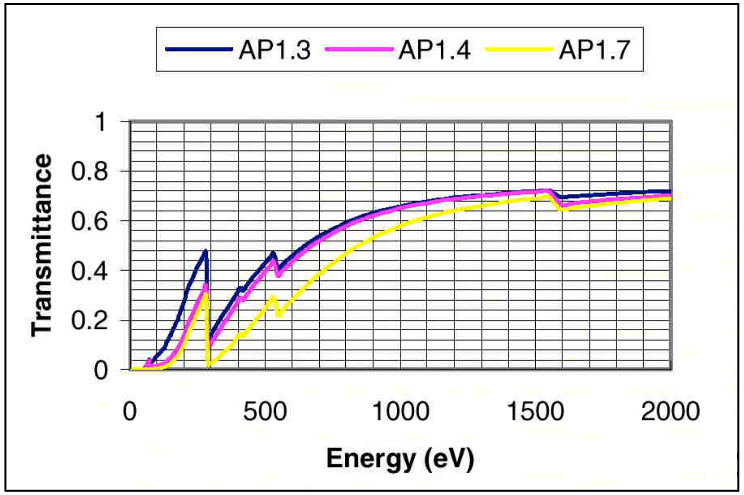
Energy dispersive semiconductor detector

Principle P-I-N type

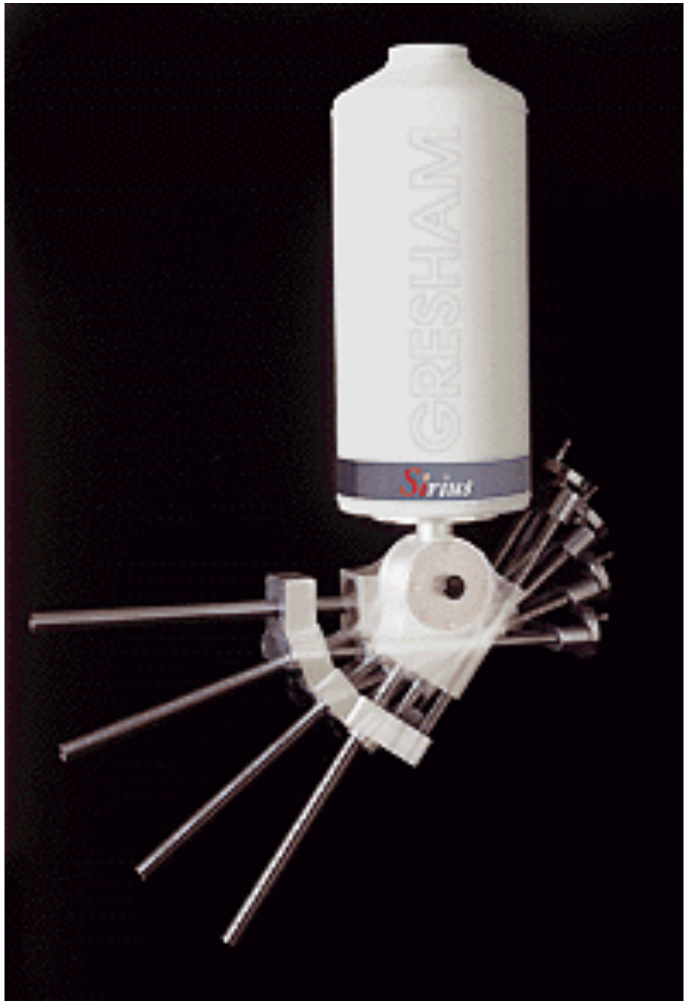


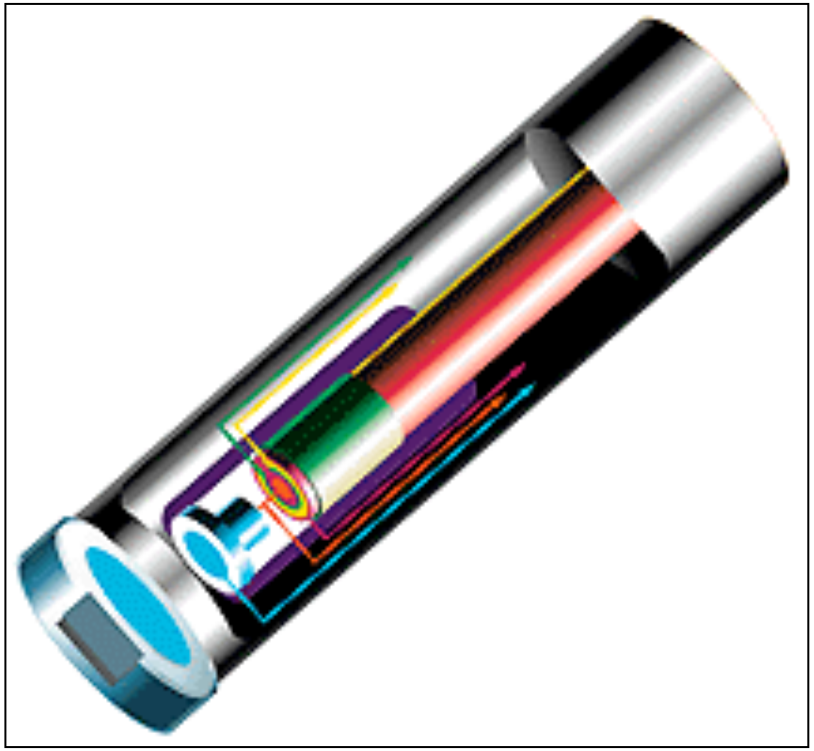
Efficiency





ED detector LN_2 cooled Si(Li)





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Peltier cooled P-I-N type

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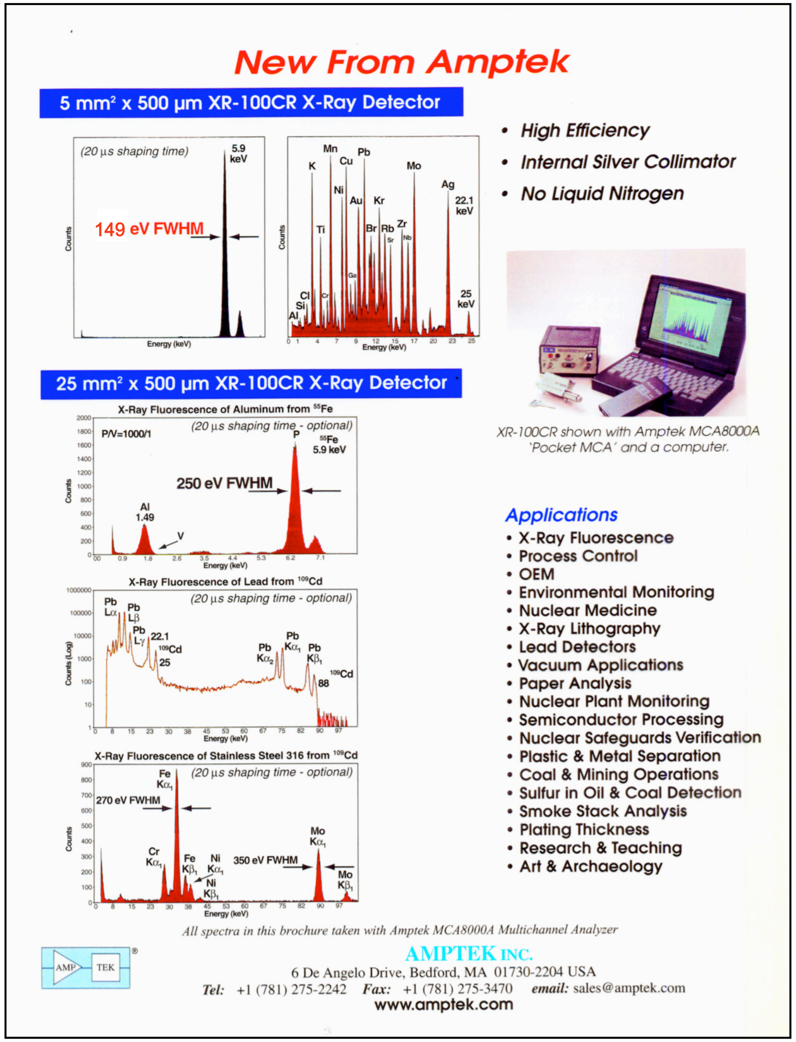
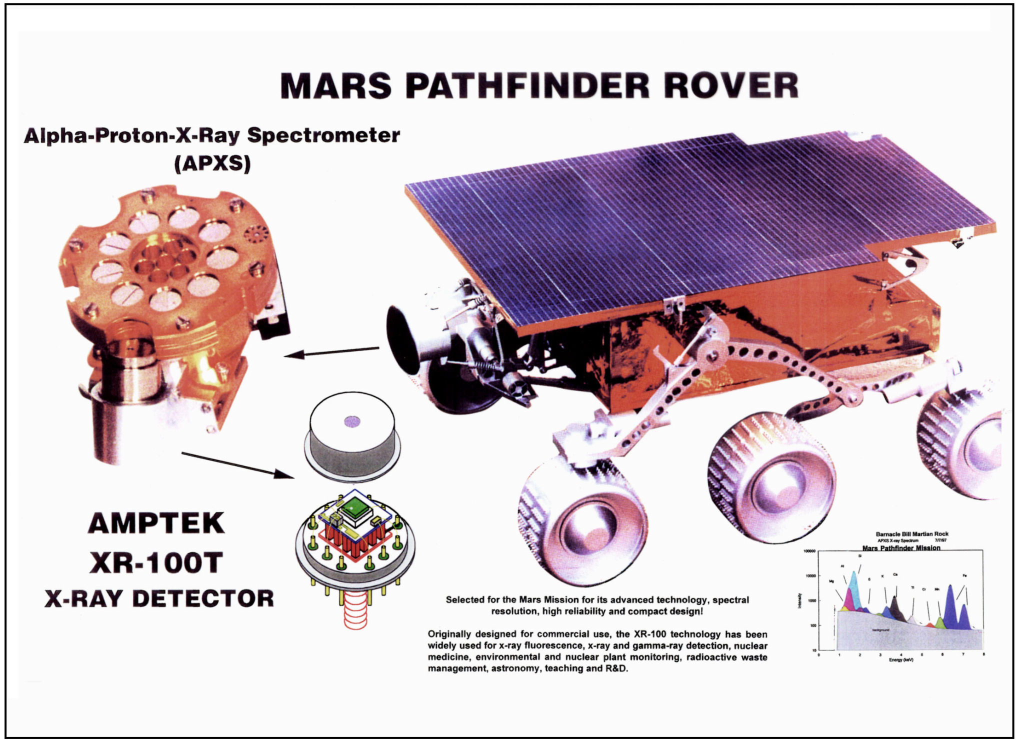
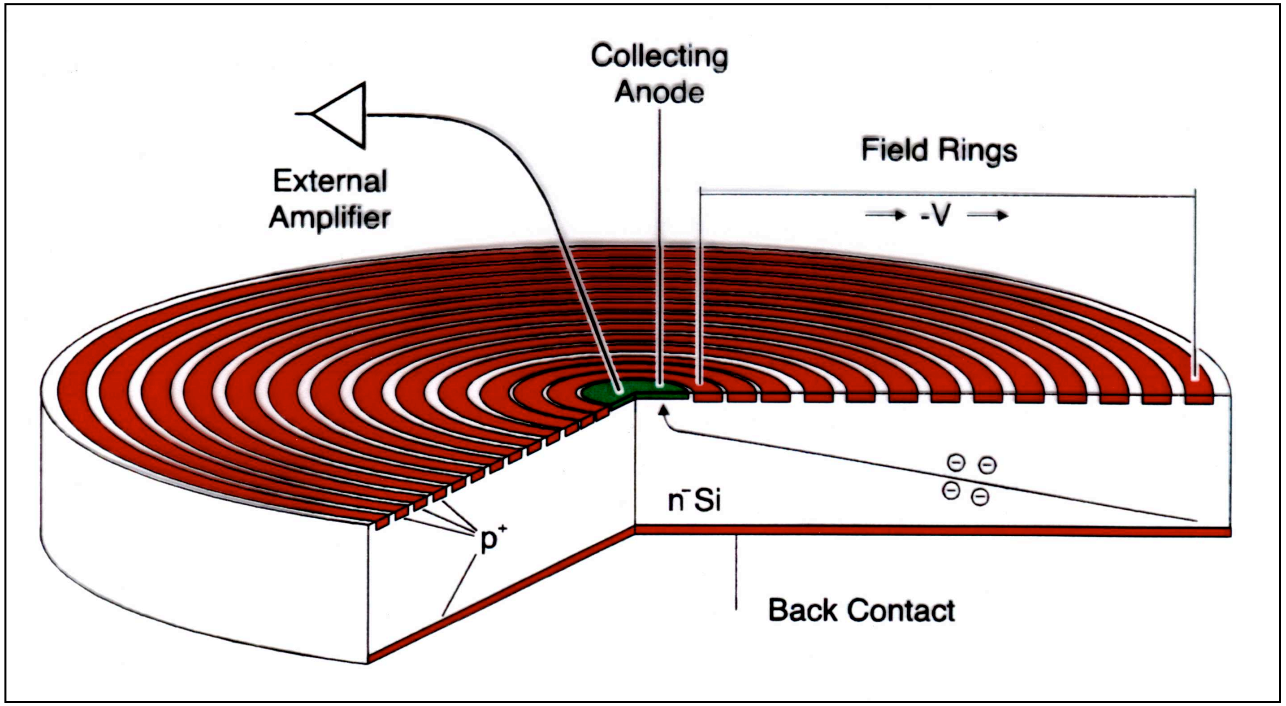
AMPTEK





Silicon Drift Detector with Circular Geometry



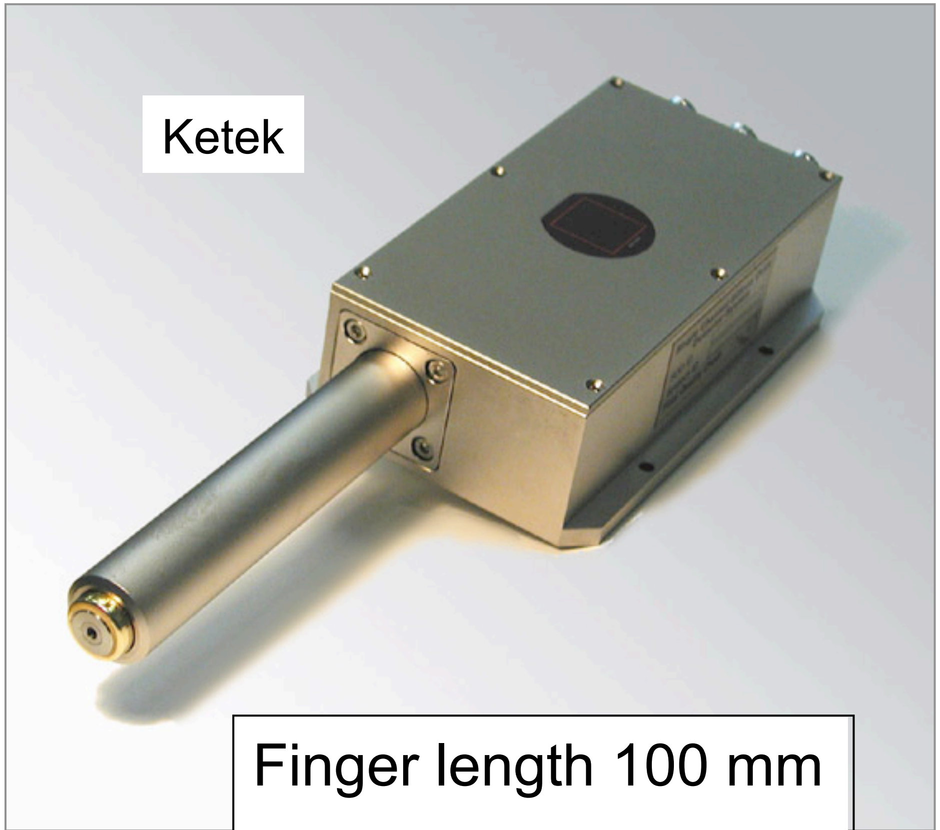
Small size of output capacitance:

- high energy resolution
- high count rate capability

Low leakage current level:

- operation at high temperature

Si drift detector Peltier cooling



Finger length 100 mm

10-80mm^2 active area

(100 mm^2 prototype)

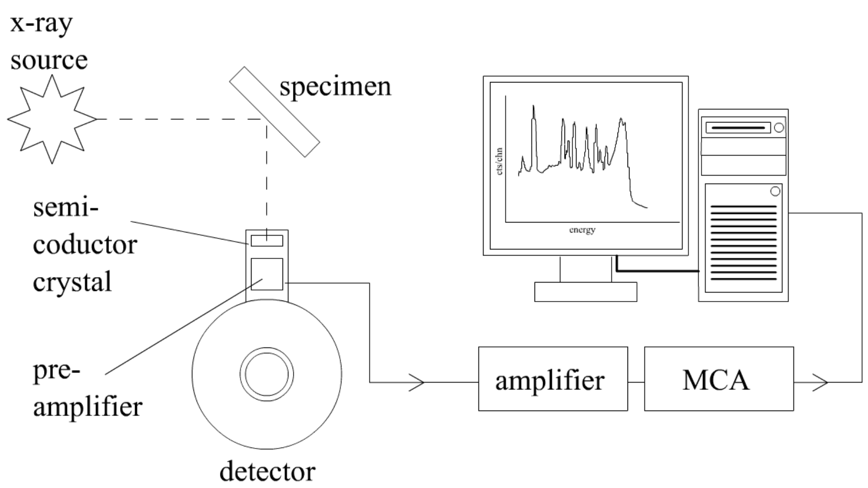
Multi-array design

SII Nano Technology USA Inc.

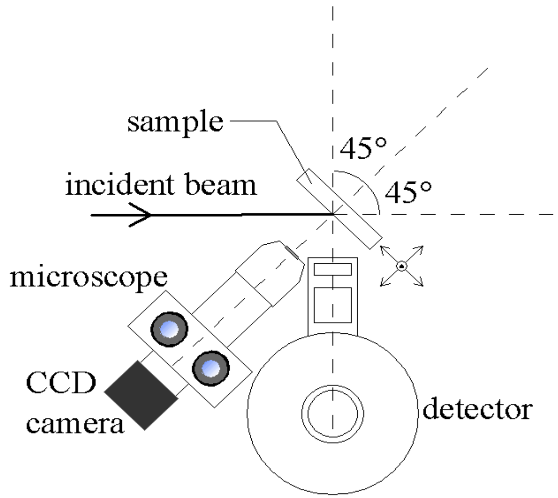
Up to 1 Mcps
Area 50 mm²
FWHM 140 eV @ 5,9 keV

EDXRF-setups

XRF:



μ-XRF:



Excitation of characteristic radiation in the Sample by primary X-rays from a suitable source

Recording of characteristic radiation by an energydispersive detector

Signal processing; spectrum storage and evaluation

X-ray optics for focussing of incident beam
Spot size in the μm range

Sample mounted on a sample-stage for spatial resolved measurements

Optical microscope for control of measurement position

Polycapillary optics

- 200.000 Boron Silicate glass tubes polycapillary

- Focal diameter available
- 30 – 200 µm according to task

- Inside the glass wall total reflection

$$R_{(\varphi)} \approx R_{(\theta)}^{\varphi/2\theta}$$

- Critical bending radius

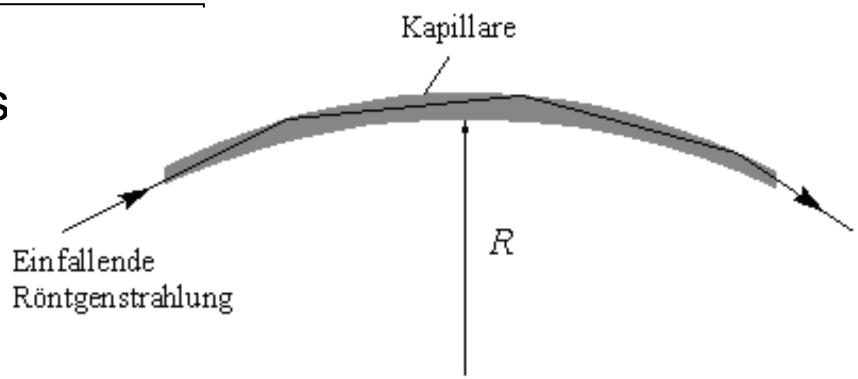
$$R_c = \frac{4 \cdot r}{\theta_c^2}$$

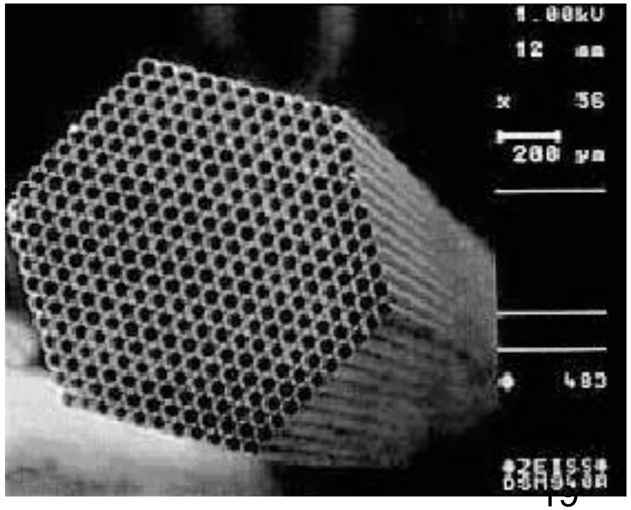
- Focal size energy depending

$$\varphi_c = \frac{L}{R_c}$$

- Compared to pinhole gain factor up to 1000 depending to design

- High energy limit due to critical angle of total reflection ~30keV





Portable EDXRS spectrometer

☞Design aim: nondestructive analysis of art and cultural heritage objects:

- Low power tube (Pd target, 50 W)
- Vacuum chamber
- 10 mm2 SDD
- Polycapillary/ 2mm collimator
- Low Z capability

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Positioning of sample

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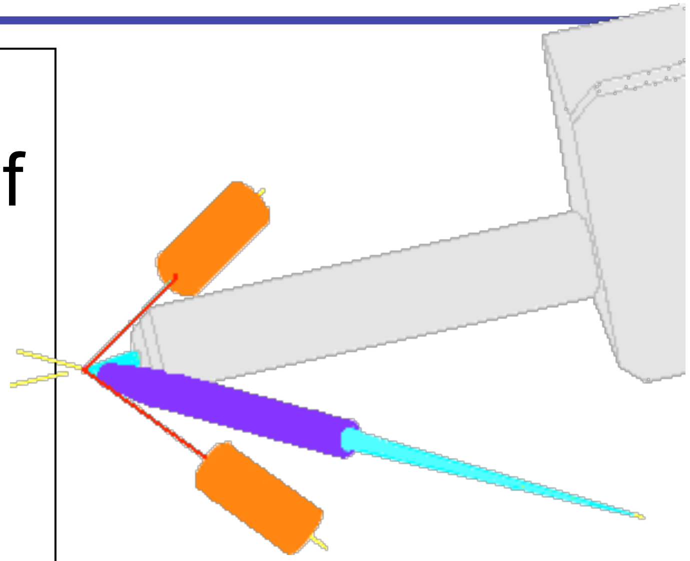
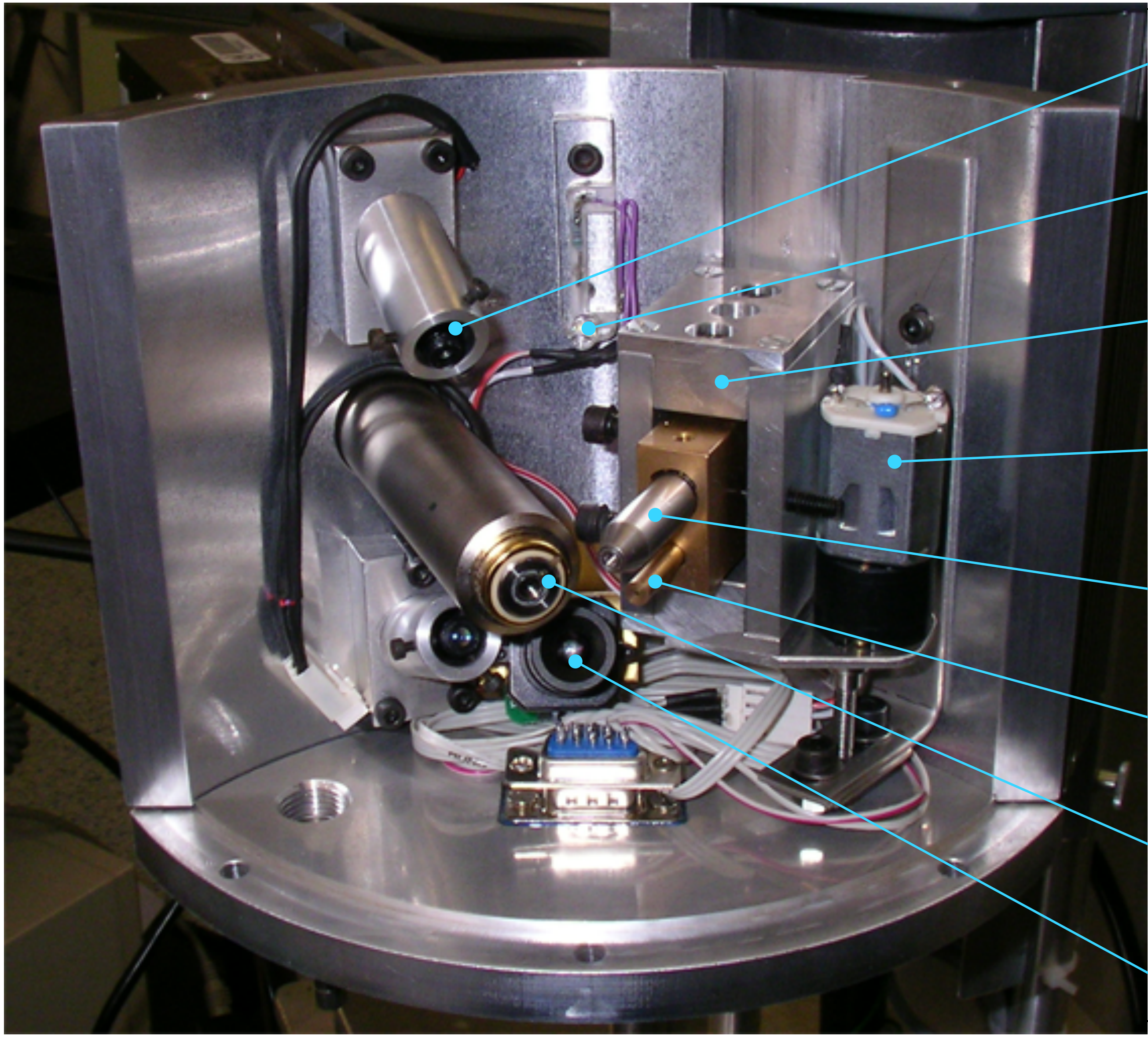
- Coincidence of x-ray beam – detector axis – sample point of interest
- Use of 2 laser beams + x-ray phosphor
- CCD camera
- 2 Lasers form one point on the screen with the spot of the x-ray beam „perfect“



Inside view of evacuable spectrometer design Diploma Thesis G. Buzanich



Laser

LED

changer colli polycap

gearmotor

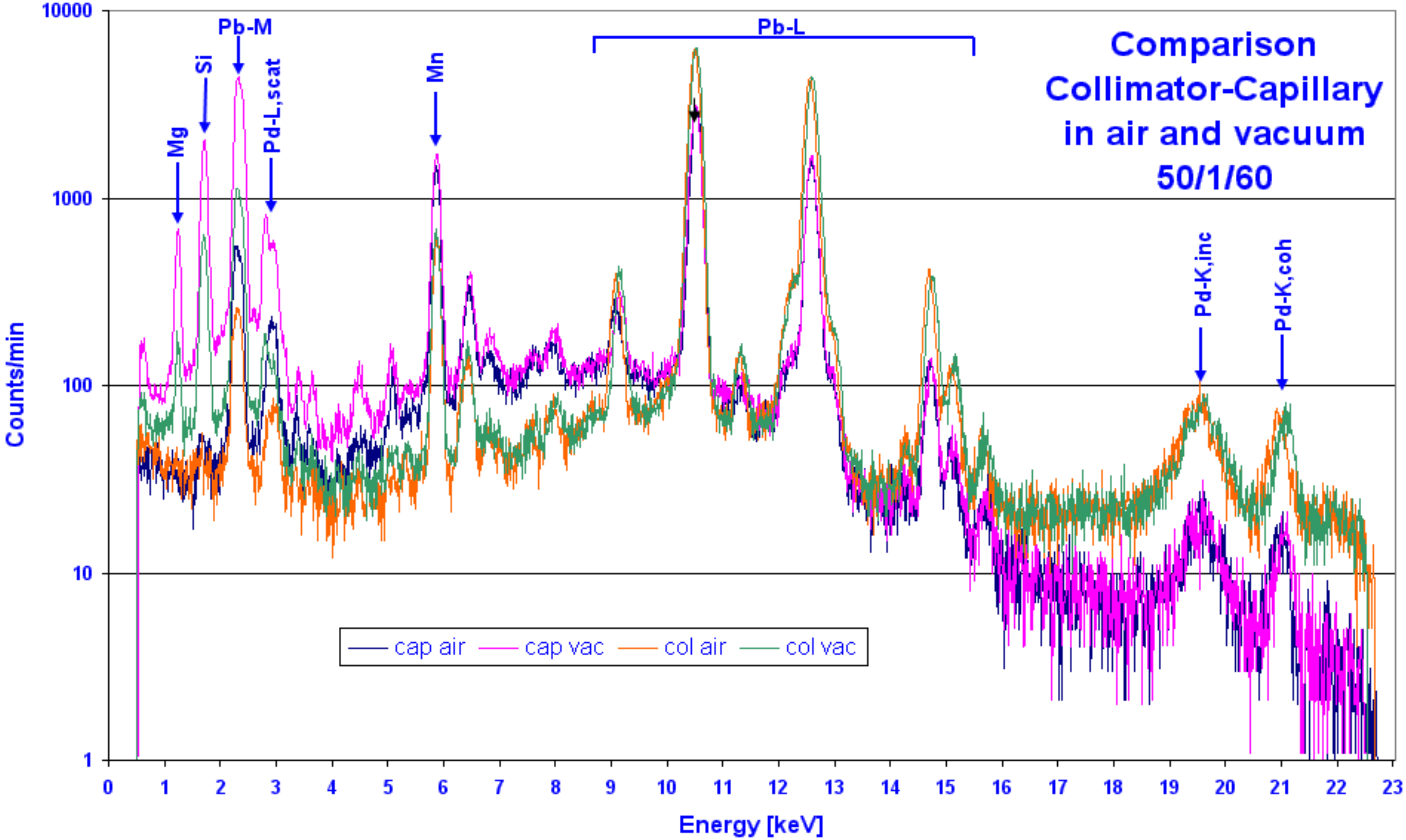
x-ray optics

Collimator

Detector

CCD camera

Comparison air - vacuum capillary Optics-collimator



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Spectrometer analyzing various samples cooperation IAEA Seibersdorf and Museum of fine ArtsVienna, K.Uhlier M. Griesser

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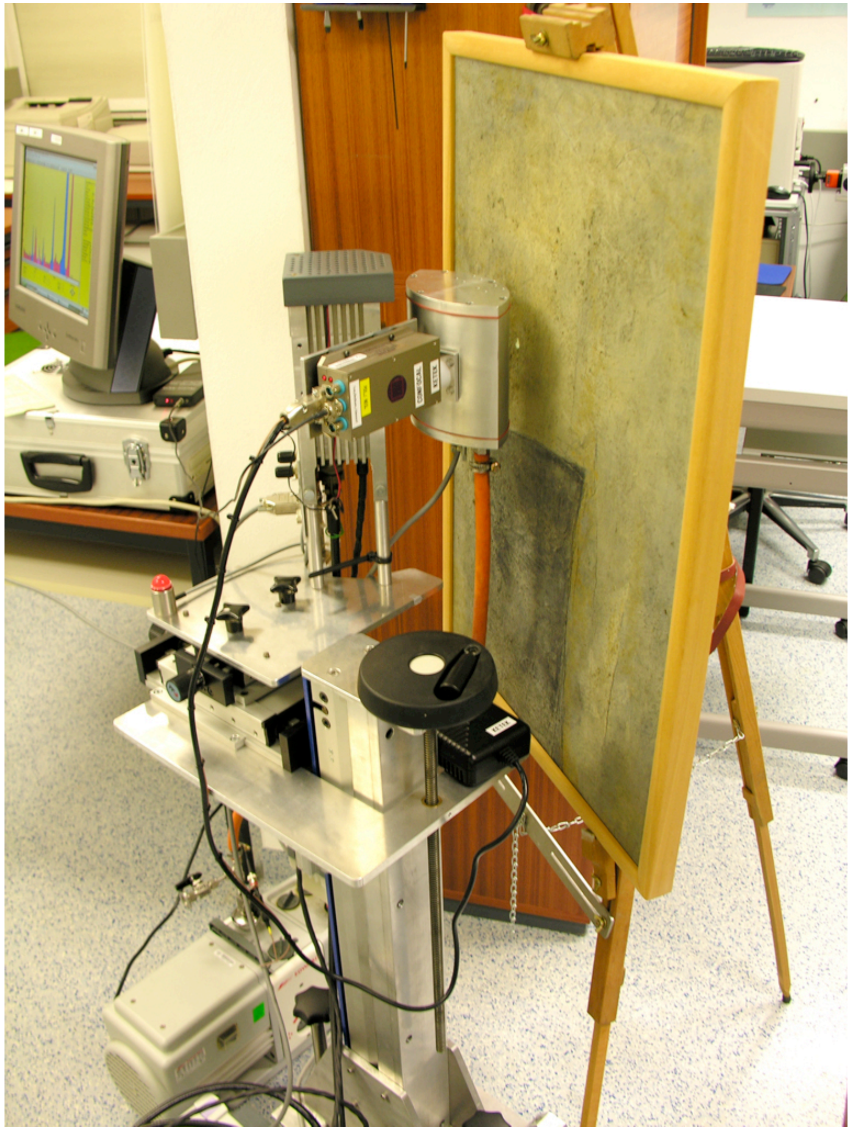


Improvements of detection limits

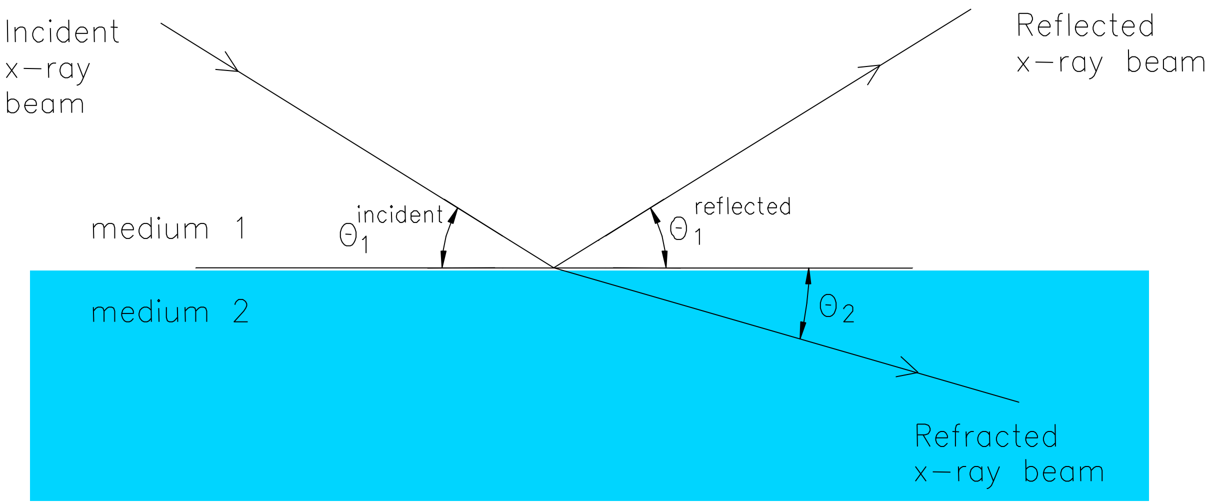
Detection Limits TXRF

1975 → ng

1985 → pg

1995 → fg

Total external reflection



n (x-ray range) $= 1 - \delta - i\beta$

$\delta \sim 10^{-6}$ decrement $\delta \propto f_1(Z)$

$\beta \sim 10^{-8}$ absorption part

$\varphi_{critical} \approx \sqrt{2\,\delta} \propto \sqrt{\rho}/E$

$\varphi_{critical}$

(Si, 17.5 keV) ≈ 0.1° ≈ 1.75 mrad

(Si, 500 eV) ≈ 3.7° ≈ 64.6 mrad

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TXRF vs EDXRF

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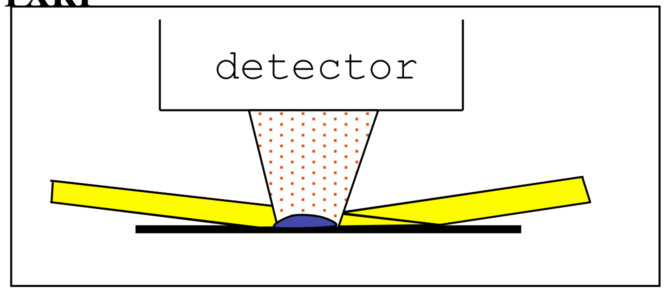
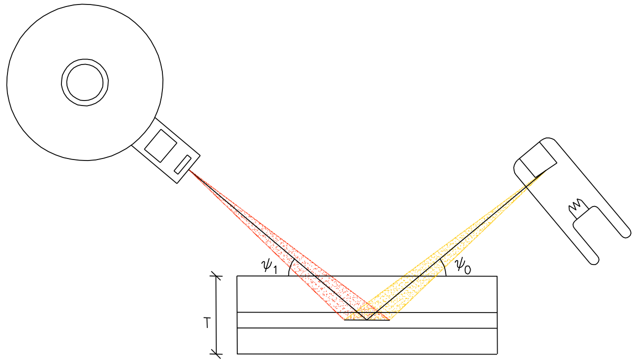
TXRF



EDXRF

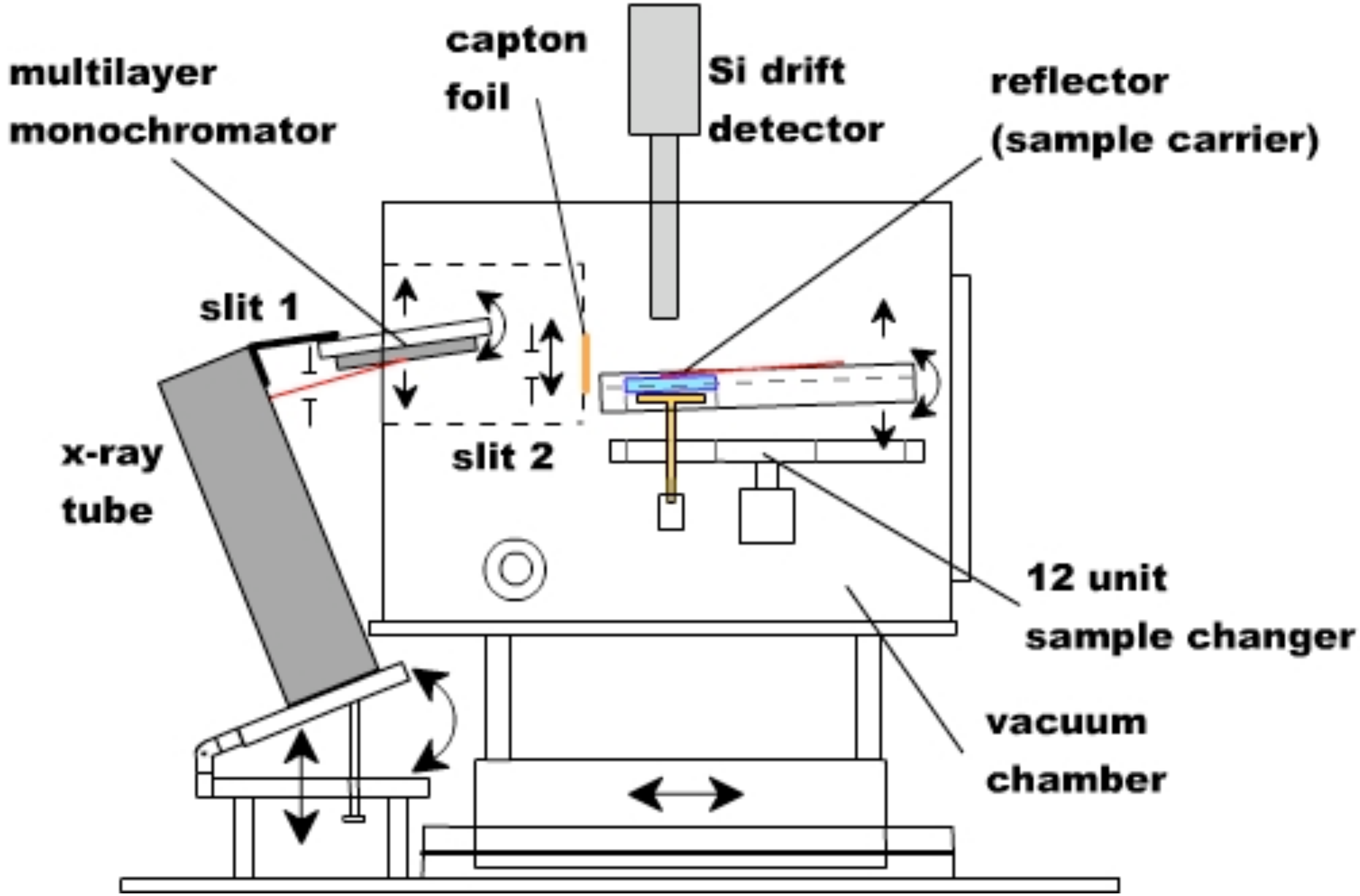


- **background reduction**
- **double excitation of sample by both the primary and the reflected beam**
- **small distance sample - detector (~1mm) : large solid angle**

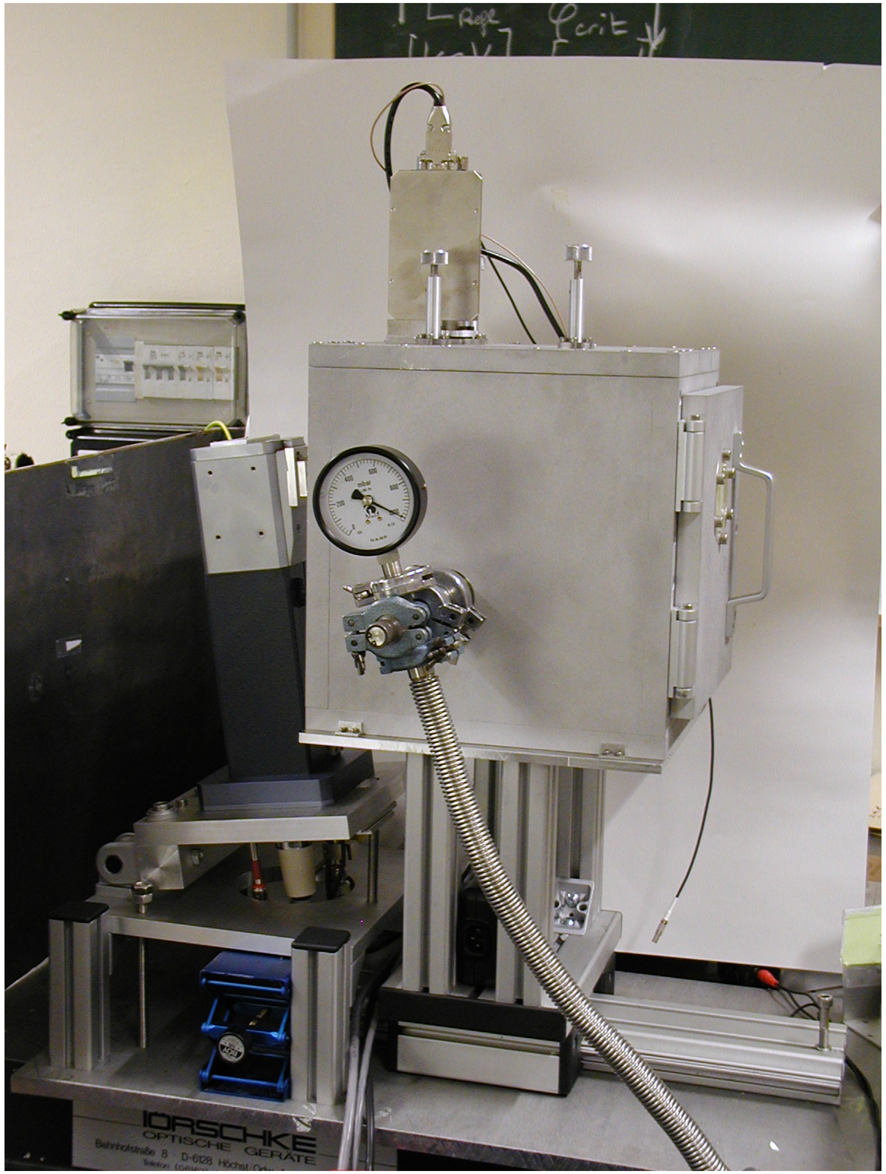
Analytical features:

- **small sample amounts required (ng, some µl)**
- **detection limits in the pg range with X-ray tube excitation**
- **detection limits in the fg range with Synchrotron radiation excitation**
- **Simple quantification (thin film approximation) by adding internal standard**
- **angle dependence of fluorescence signal : particle – film - implantation**

WOBISTRAX:Schematic view

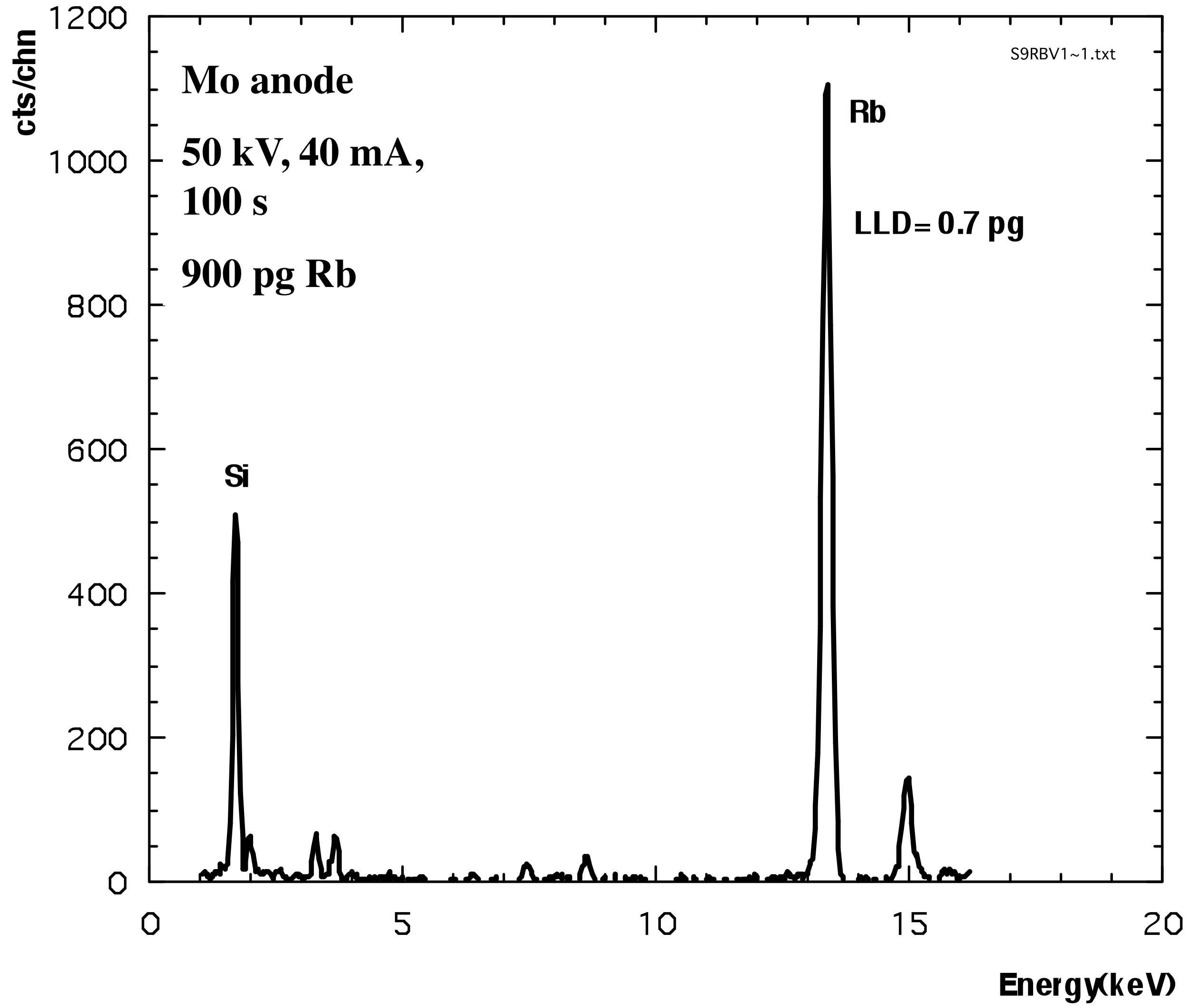


WOBISTRAX



Detection limits: AXIL deconvolution

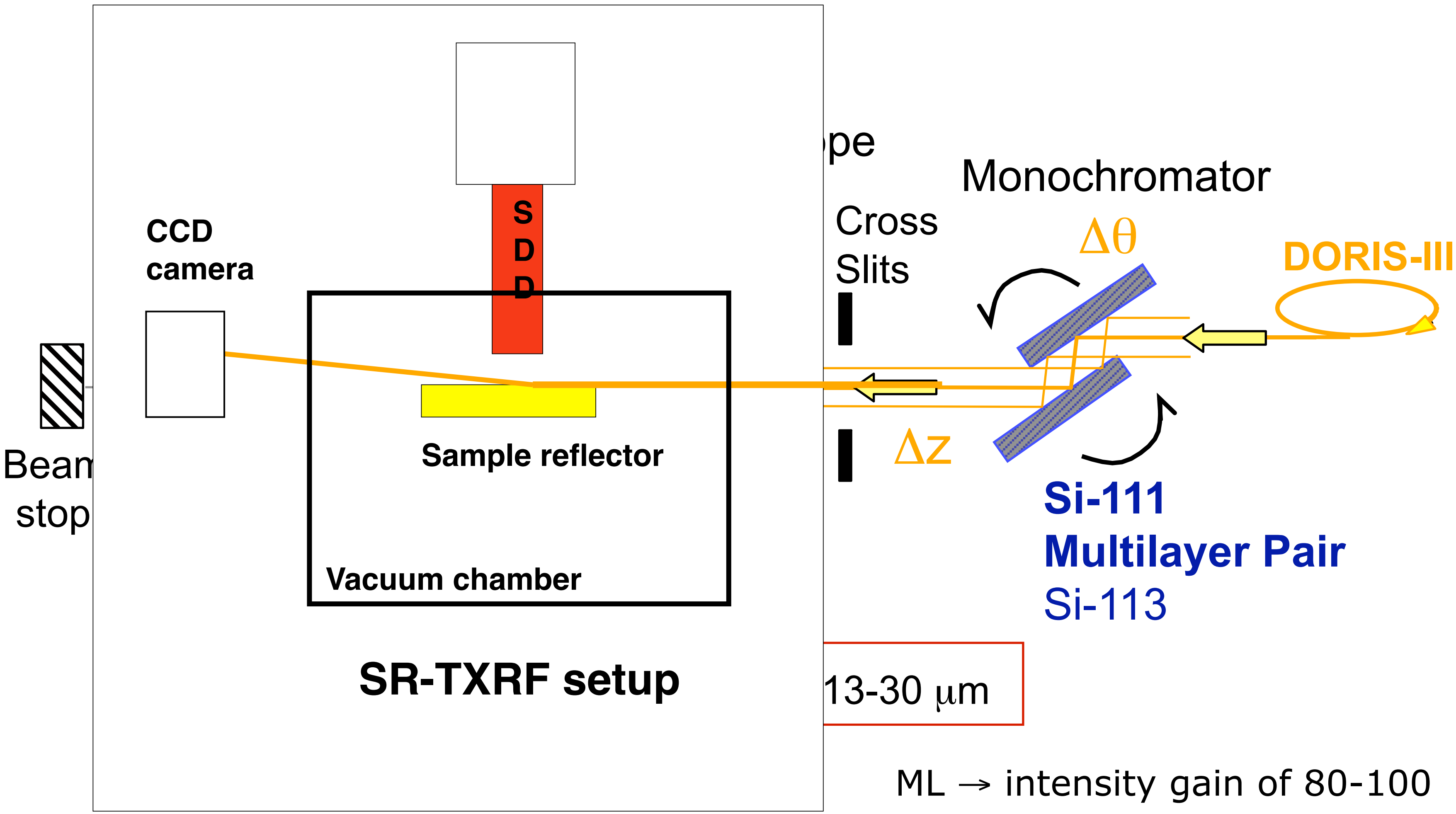
Standard : Mo-tube



Advantages of Synchrotron radiation induced- TXRF

- high flux
- wide spectral range – excitation from low Z to high Z
- wide range of detectable elements – choice of suited detector
- linear polarisation in orbital plane - reduction of background
- low detection limits (fg range)
- minute sample mass required (pg to ng)

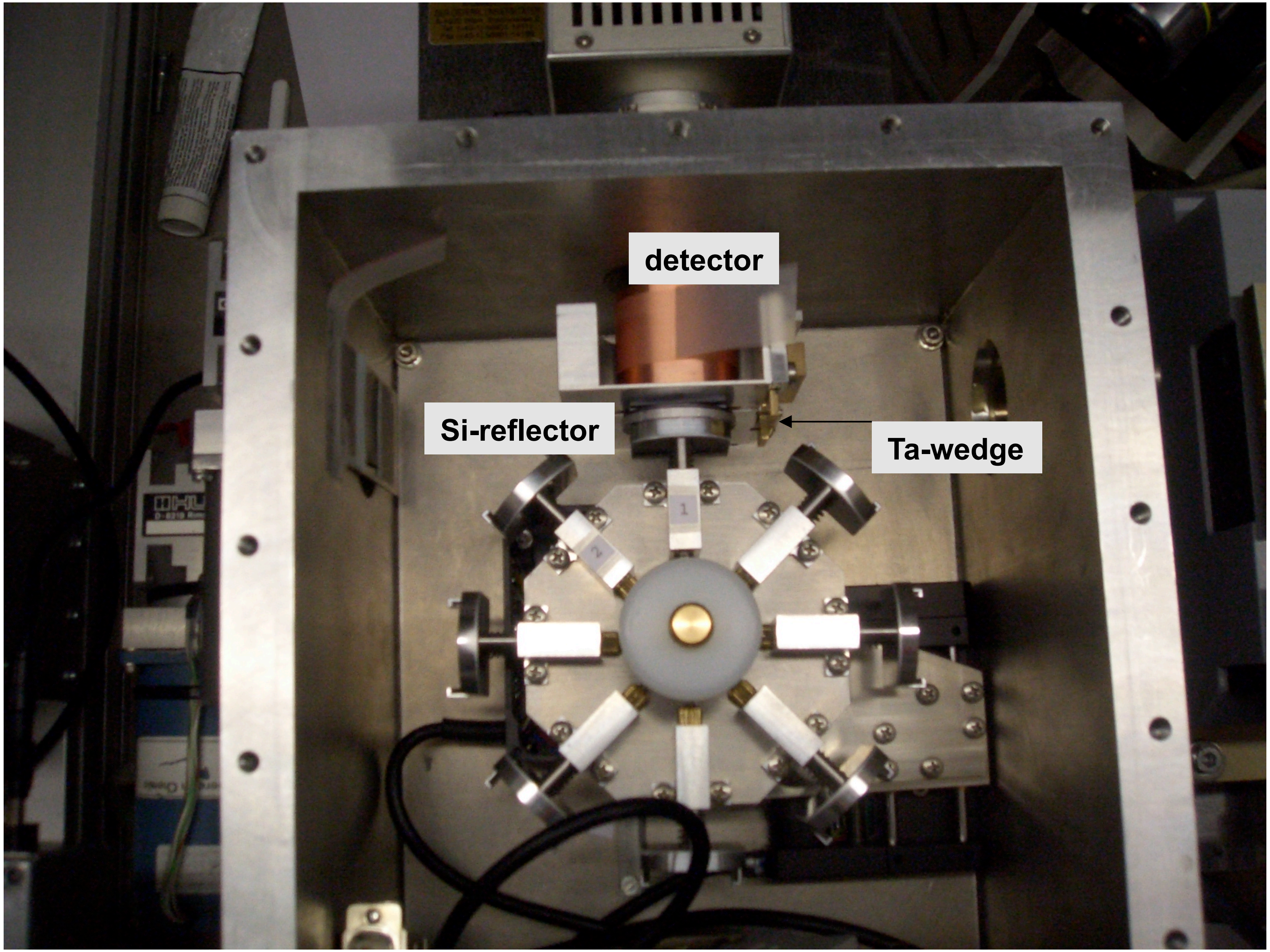
Experimental Setup @ HASYLAB beamline L



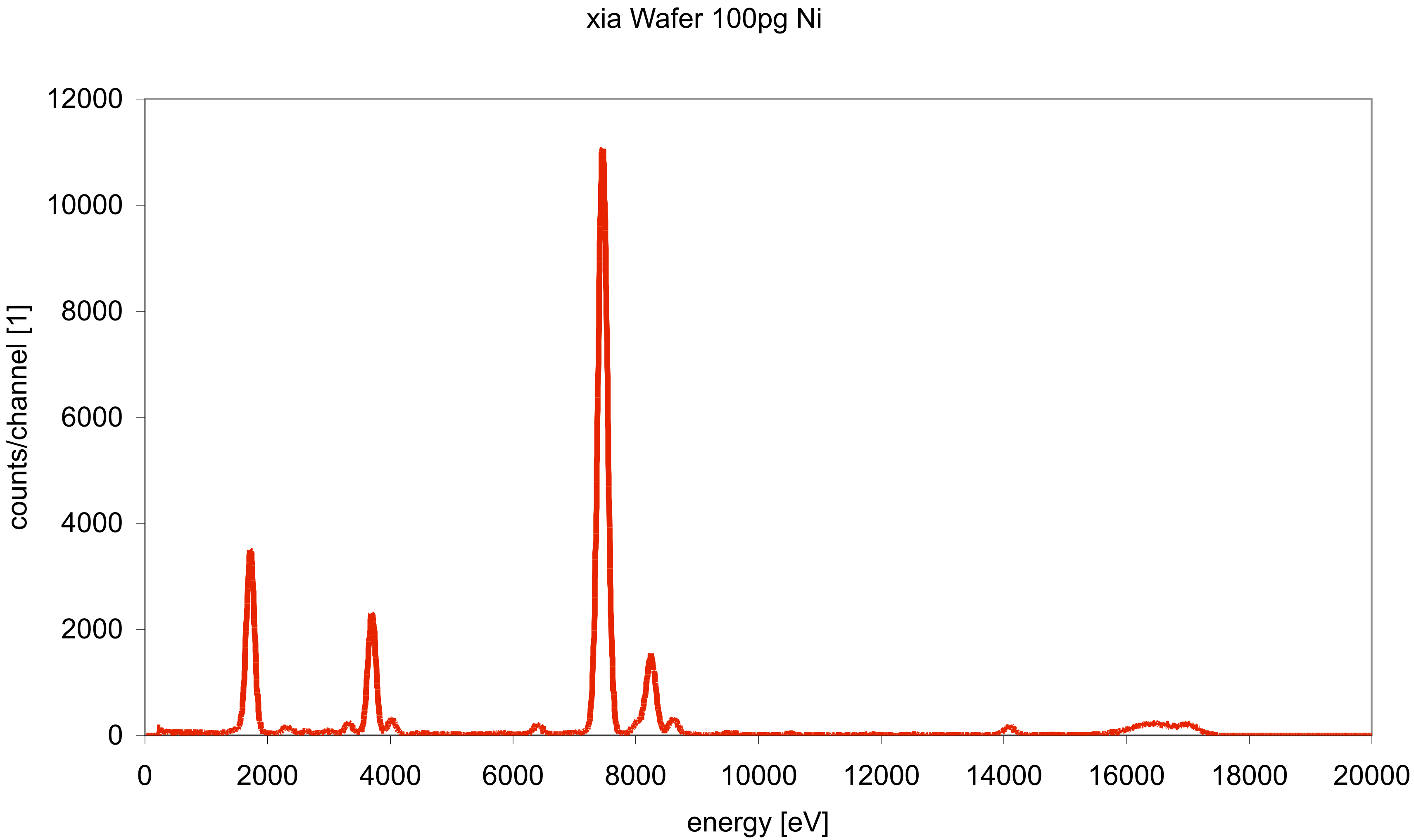
ML → intensity gain of 80-100

only small increase of scatter peak

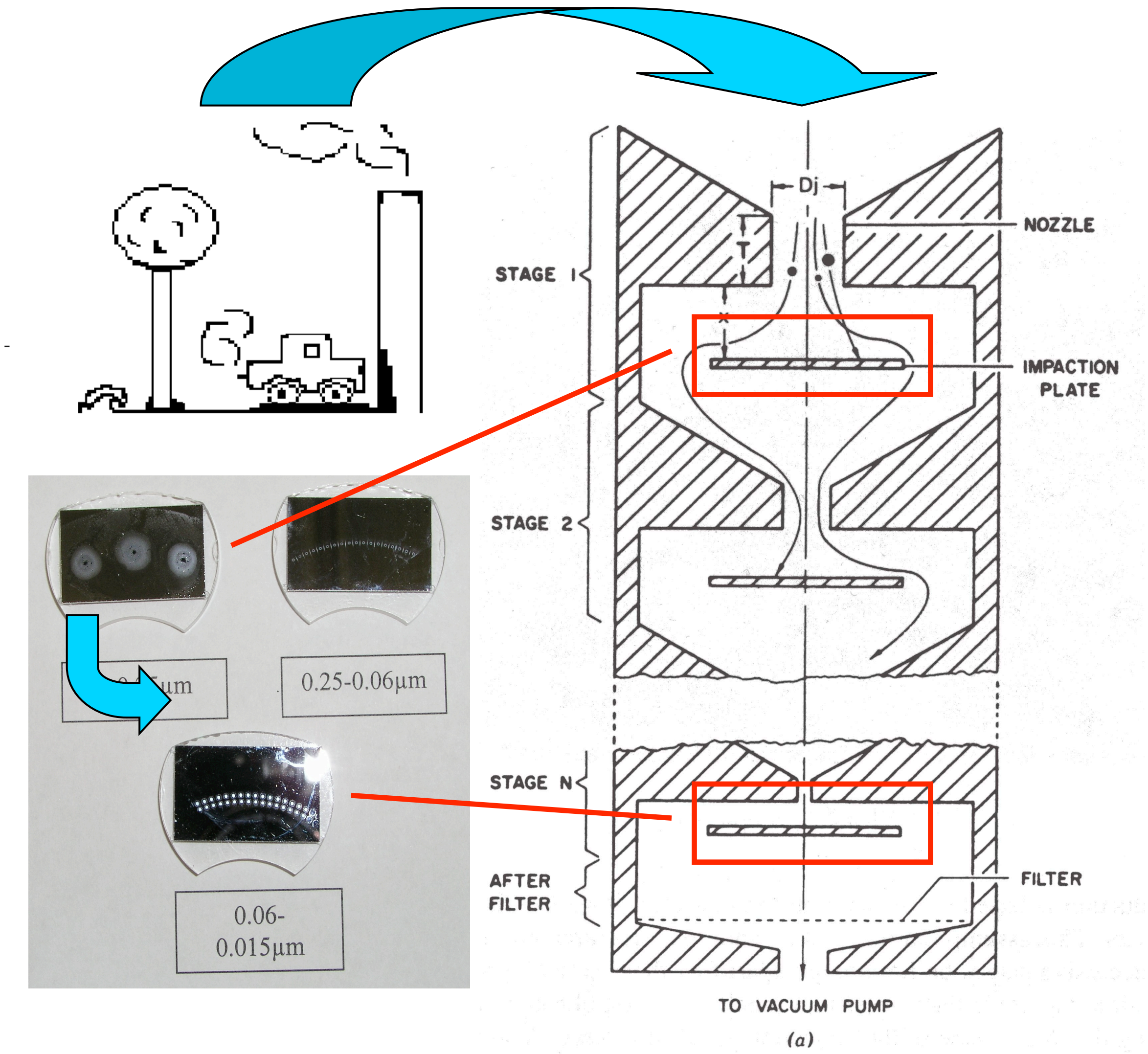
sample changer
8 stages



LLD with Vortex 50 mm^2 detector



analysis of aerosols: coop Dr. Fittschen



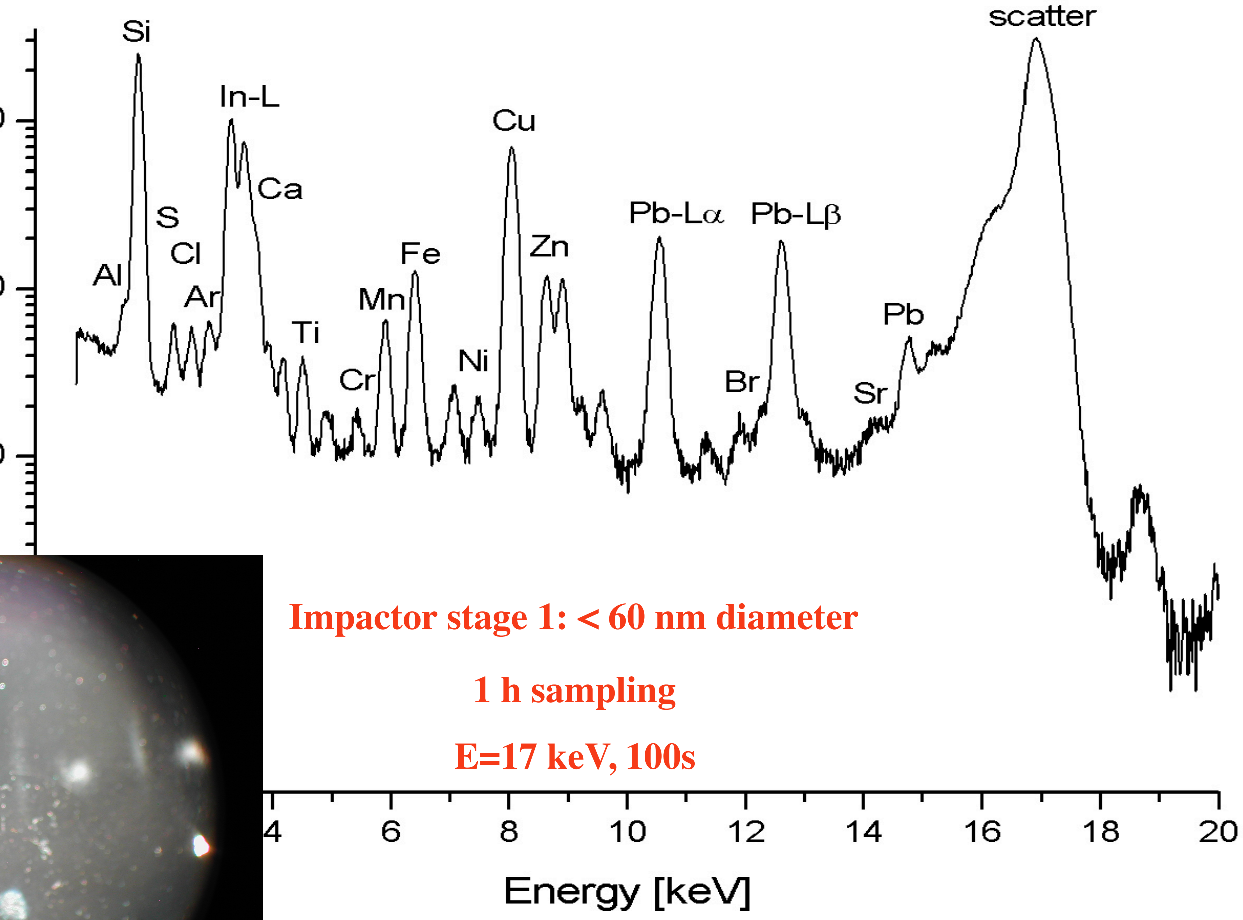
Motivation:

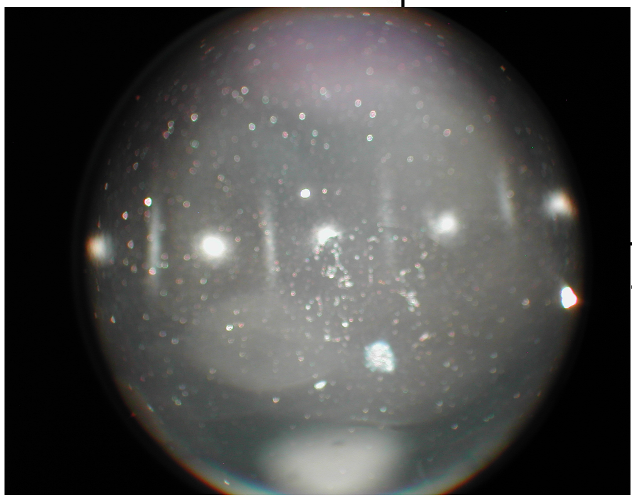
To understand the effect of aerosols on global climate a detailed understanding of sources, transport, fate and the physical and chemical properties of atmospheric particles is necessary.

The chemical speciation of the toxic elements is of relevance for the environmental impact.

Aerosol particle sampling device, 12-stage, round nozzle **Berner low-pressure impactor** for **particle sizes of 0.06-12 µm** (aerodynamic particle size);

analysis of aerosols: coop Dr. Fittschen





Impactor stage 1: < 60 nm diameter

1 h sampling

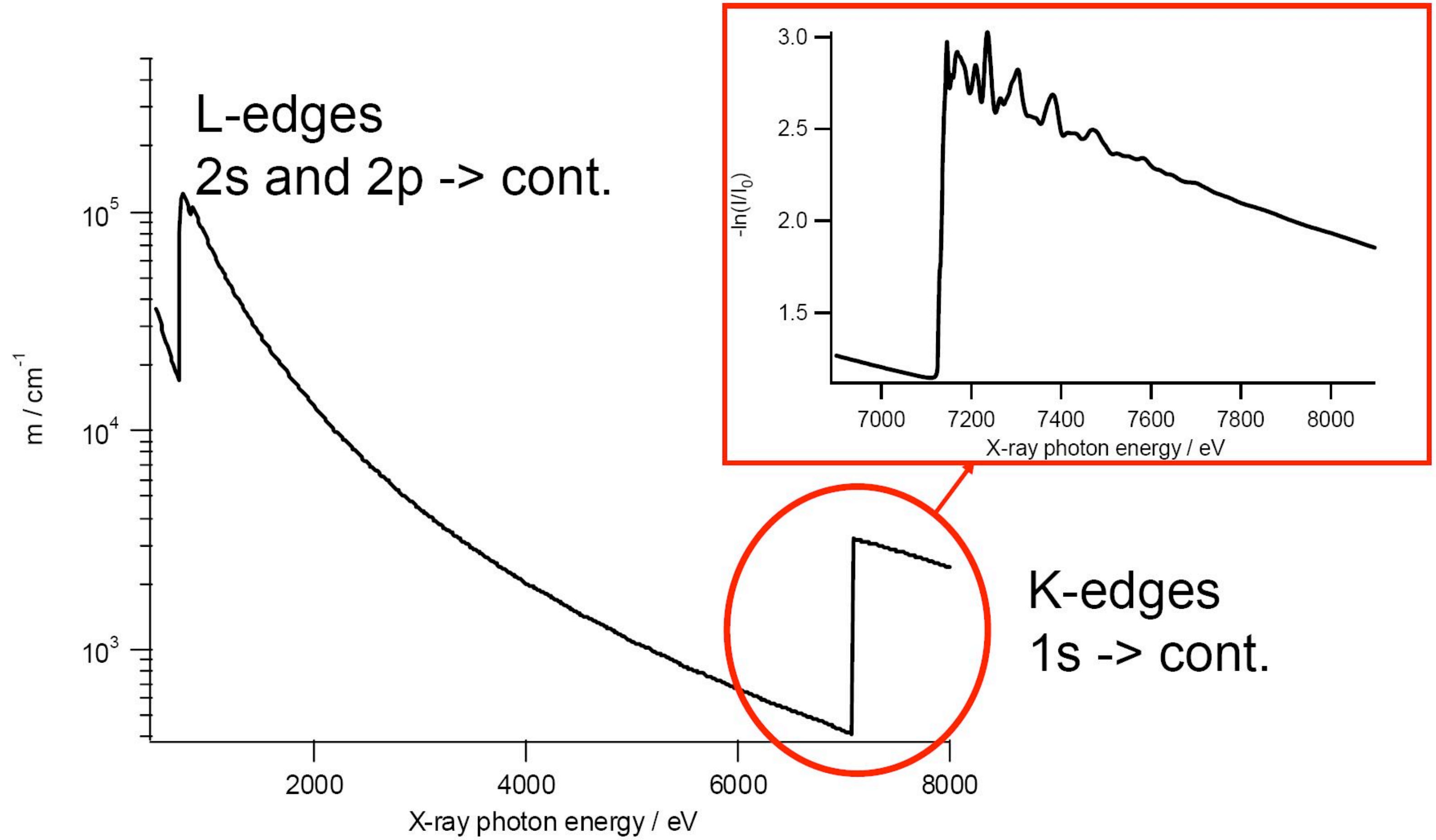
E=17 keV, 100s

Quantification is a problem!

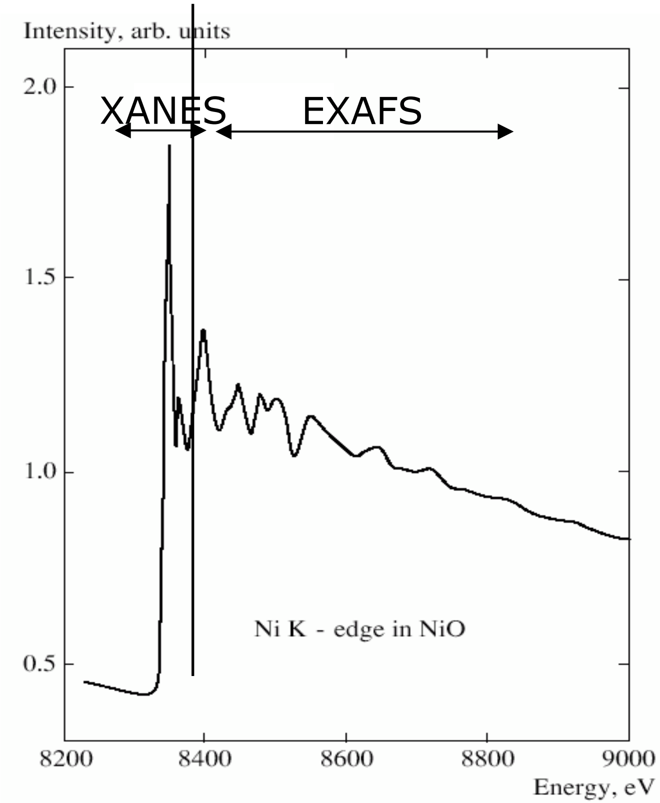
Advantages of SR-TXRF:

- only small sample volumes are required
- sampling time can be diminished ⇨ time resolved investigation of atmospheric events
- simple sample preparation (aerosols directly collected on reflectors)
- **TXRF offers good sensitivity for XANES chemical speciation of traces**

Example: The X-ray Absorption Fine Structure (XAFS) of an Fe-foil



X-ray Absorption Spectroscopy



The x-ray absorption spectrum shows a fine structure if it is sampled with a high resolution.

absorption involves electronic transitions

fine structure affected by energy and density of electronic states and transition probabilities

influence of the environment: neighbouring atoms (EXAFS), bond type (XANES)

$$W_{if} = \frac{2\pi}{\hbar} \underbrace{\left| \langle \Psi_i | \hat{H}_I | \Psi_f \rangle \right|^2}_{\text{EXAFS}} \underbrace{\rho\left(E_f\right)}_{\text{XANES}}$$

XANES: **X**-Ray **A**bsorption **N**ear **E**dge **S**tructure, ends 50-100 eV above the edge

EXAFS: **E**xtended **X**-Ray **A**bsorption **F**ine **S**tructure, starts 50 - 100 eV above the edge

What we have …

Samples:

• with very low elemental concentrations (ppb)

• which are only available in low amounts (µl)

(e.g. xylem sap, aerosols, pollen,…)

TXRF

… what we want …

Elemental speciation:

⇦ information about

• oxidation states

• ligand type

XANES

…and what we get:

TXRF-XANES

XANES spectra recorded in TXRF geometry

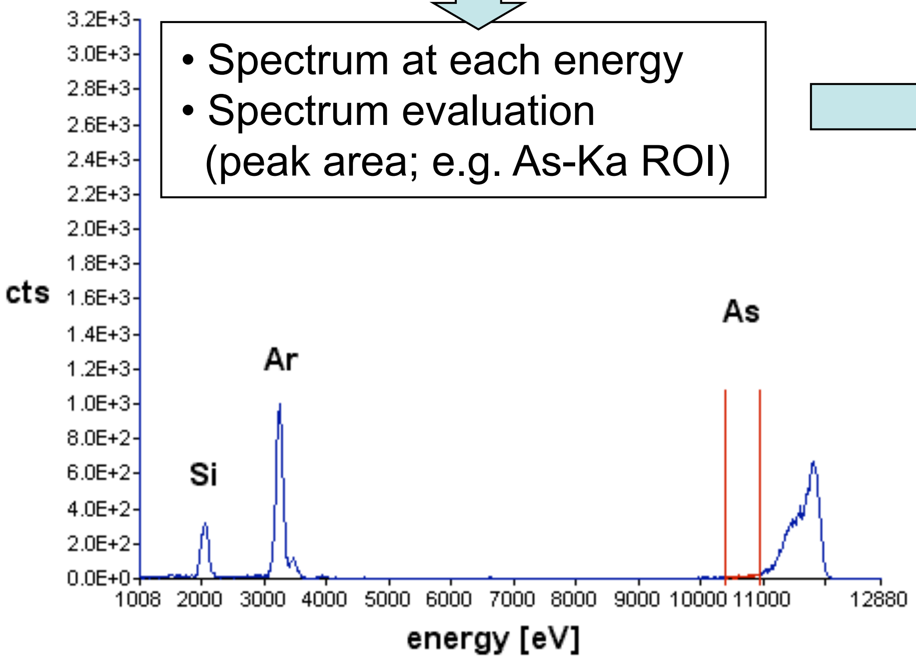
• method used as a fingerprint method

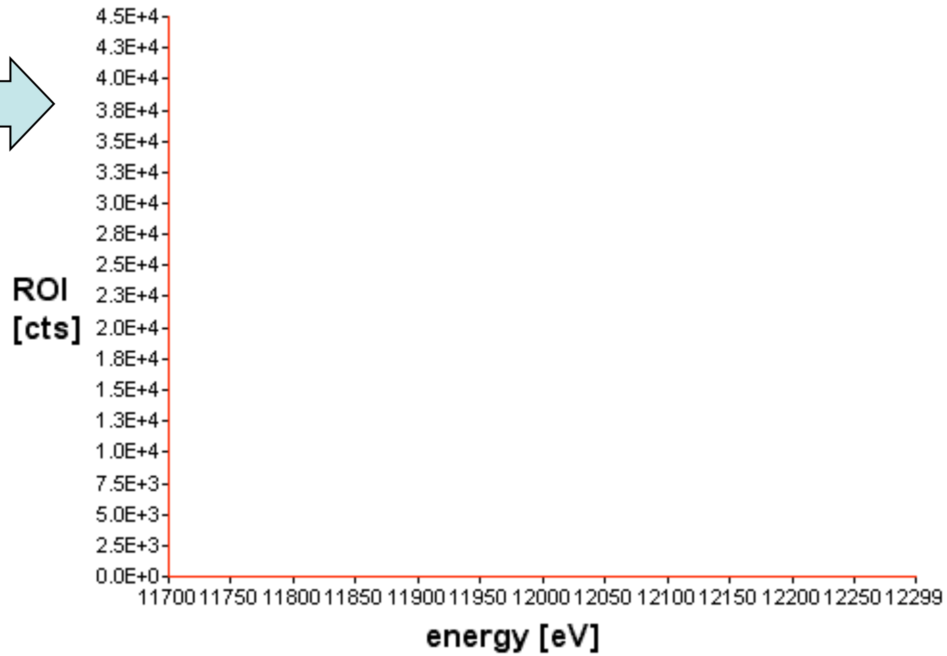
• analysis based on linear combinations of known spectra from “model compounds”
⇨ ratios of oxidation states

Introduction - The EXAFS Experiment

Variation of excitation energy

- Spectrum at each energy
- Spectrum evaluation
  (peak area; e.g. As-Ka ROI)





EXAFS **XANES**

$$W_{if} = \frac{2\pi}{\hbar} \left| \langle \Psi_i | \hat{H}_I | \Psi_f \rangle \right|^2 \rho\left(E_f\right)$$

EXAFS equation, Fingerprint method (XANES)

- XANES: bond type
- EXAFS: neighboring atoms

- **Wafer surface analysis with SR-TXRF XANES (TXRF-XANES)**

M. Zaitz, IBM, Hopewell Junction, USA

- F. Meirer et al., *Feasibility study of SR-TXRF-XANES analysis for iron contaminations on a silicon wafer surface*
Surface and Interface Analysis (2008), accepted

- **Analysis of Aerosols (SR-TXRF & TXRF-XANES)**

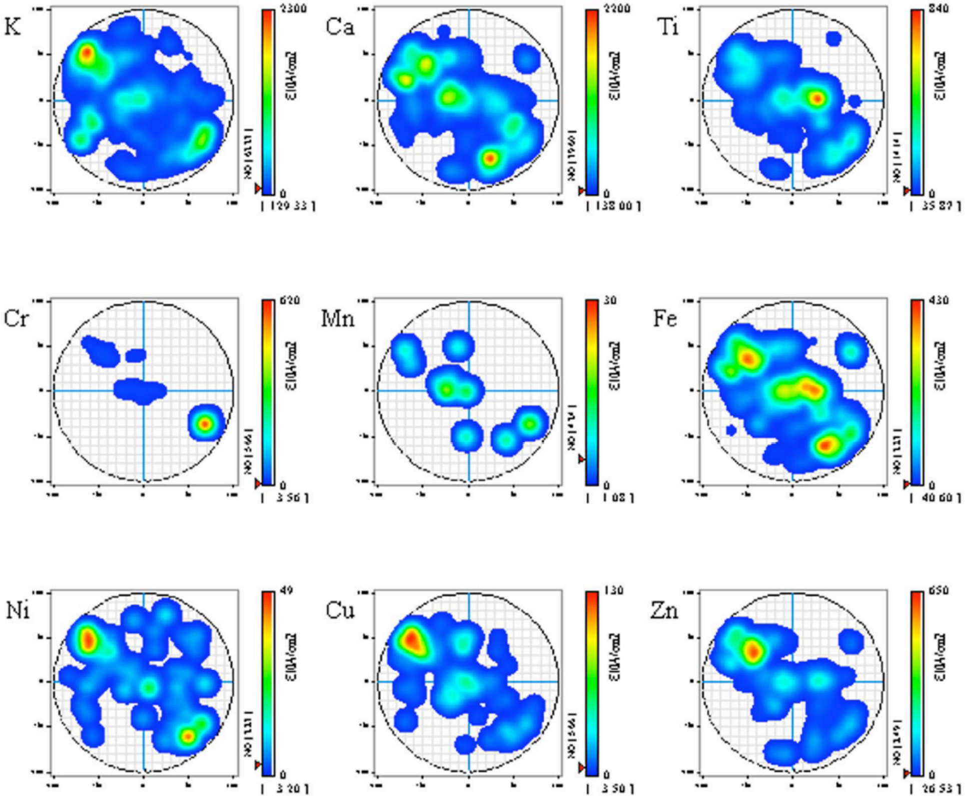
Prof. J. Broekaert, Institut für Anorganische und Angewandte Chemie, University of Hamburg, Germany

- U.E.A. Fittschen et al., *Characterization of Atmospheric Aerosols using SR-TXRF and Fe K-edge TXRF-XANES*,
Spectrochimica Acta Part B (2008), submitted

Wafer surface analysis with SR-TXRF XANES

Coop: MaryAnn Zaitz

TXRF contamination map with Lab system



Maps of elemental distribution on 200mm Si-Wafer
Map: 229 points X-Ray: 30kV 300mA Beam: W-Lβ Sampletime: 5sec
Scale: E10 atoms/cm²

Motivation:

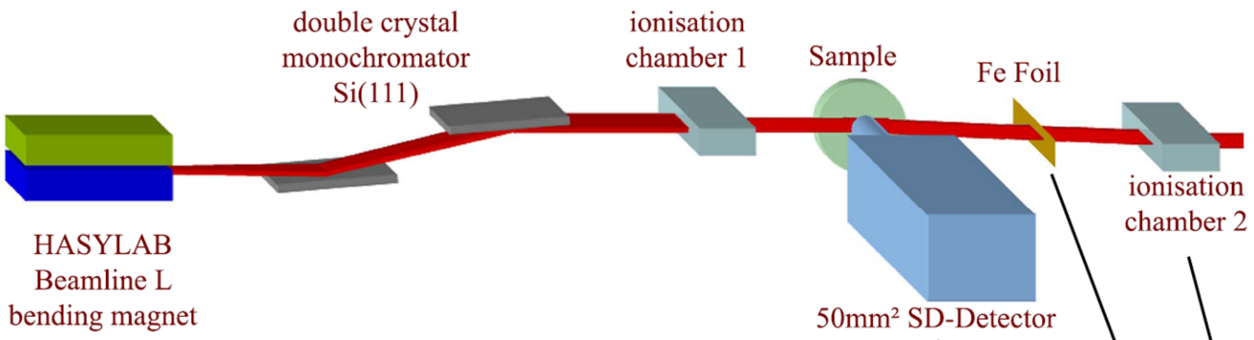
- Surface contamination levels are very low
⇨ SR-TXRF (LLD in the fg-range)

- Not only the contaminating element is of relevance, also chemical information of the contaminant
⇨ SR-TXRF XANES

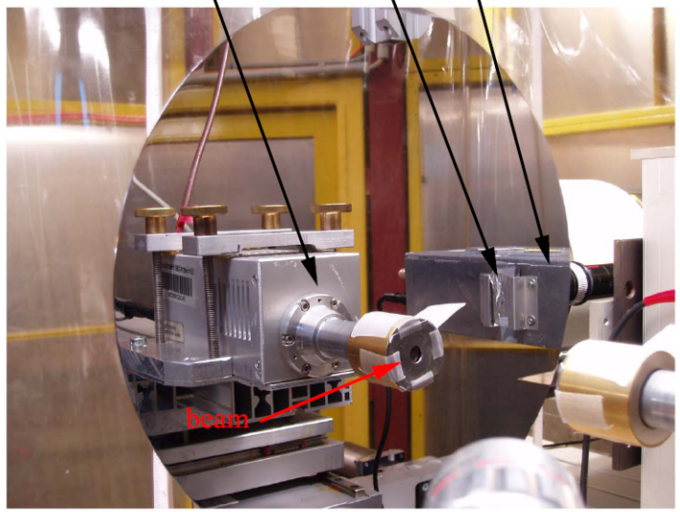
Aim:

- Determination of location and oxidation states of iron-contaminations **to trace possible sources.**

Experimental setup:

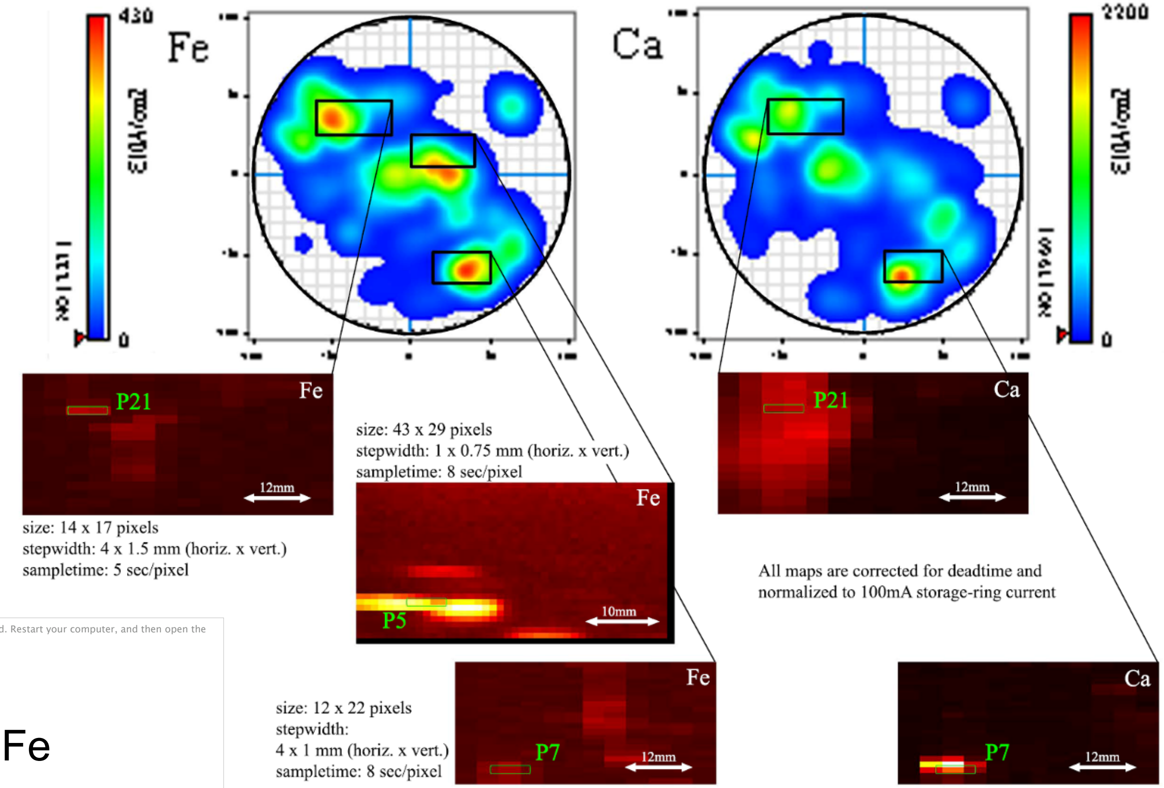


Setup in clean environment
at HASYLAB Beamline L



IBM Wafer maps:

SR-TXRF Wafer mapping to localize Fe-contaminations:



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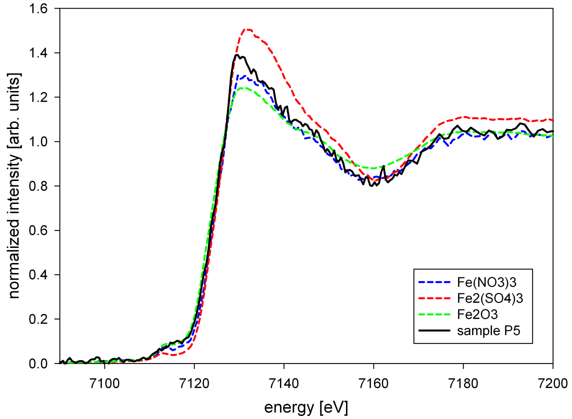
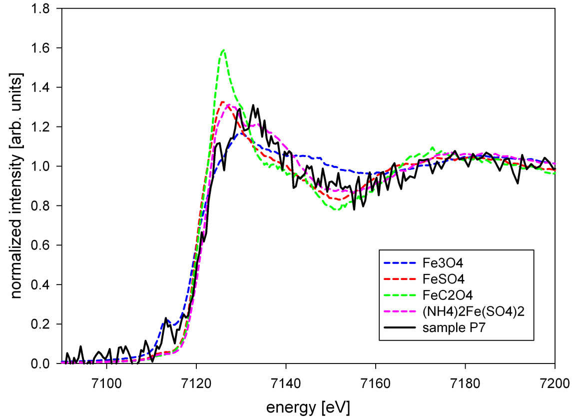
Ca

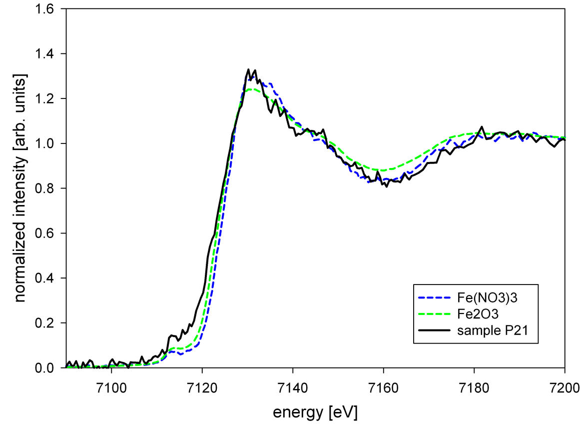
Fe

SR-TXRF spectra of Fe-contamination found at P7

Wafer surface analysis







Result of Linear Combination Fit for P5:

	Fe2O3 [%]	Fe(NO3)3 [%]	Fe2(SO4)3 [%]	R-factor	chi-square
P5	26 ±7	48 ±8	26 ±10	0.001424	0.1478

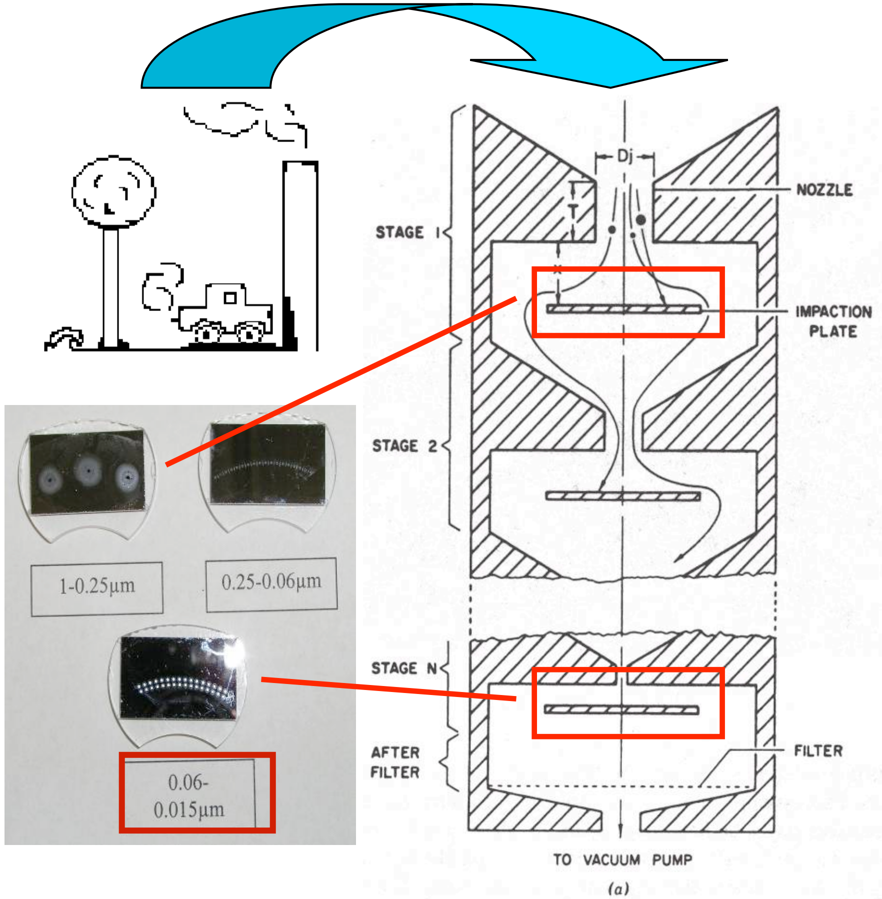
	compound	edge position [eV]
FeS	Iron(II)-sulfide	7117
FeCl2	Iron(II)-chloride	7119
FeSO4	Iron(II)-sulfate	7119.5
Fe3O4	Iron(II,III)-oxide	7119.5
FeC2O4	Iron(II)-oxalate	7120.5
(NH4)2Fe(SO4)2	Ammonium-Iron(II)-sulfate	7122.5
NH4Fe(SO4)2	Ammonium-Iron(III)-sulfate	7123
Fe2O3	Iron(III)-oxide	7123.5
Fe(NO3)3	Iron(III)-nitrate	7125
Fe2(SO4)3	Iron(III)-sulfate	7126
Wafer at P5	Fe(III)	7125
Wafer at P7	Fe(II)	7121.5
Wafer at P21	Fe(III)	7124.5

Advantages of SR-TXRF XANES:

- multielement-analysis of Si-Wafer surface contaminations
- wafer surface mapping (time consuming)
- determination of contamination type (residual, surface layer, bulk)
- analysis of the oxidation state of an element of interest at 4E12 atoms/cm2 level for Fe
- All analyses can be done nondestructiveley within the same setup

TXRF- (& XANES) analysis of aerosols

Coop: Univ. Hamburg, Prof. Broekaert, Dr. Ulla Fittschen



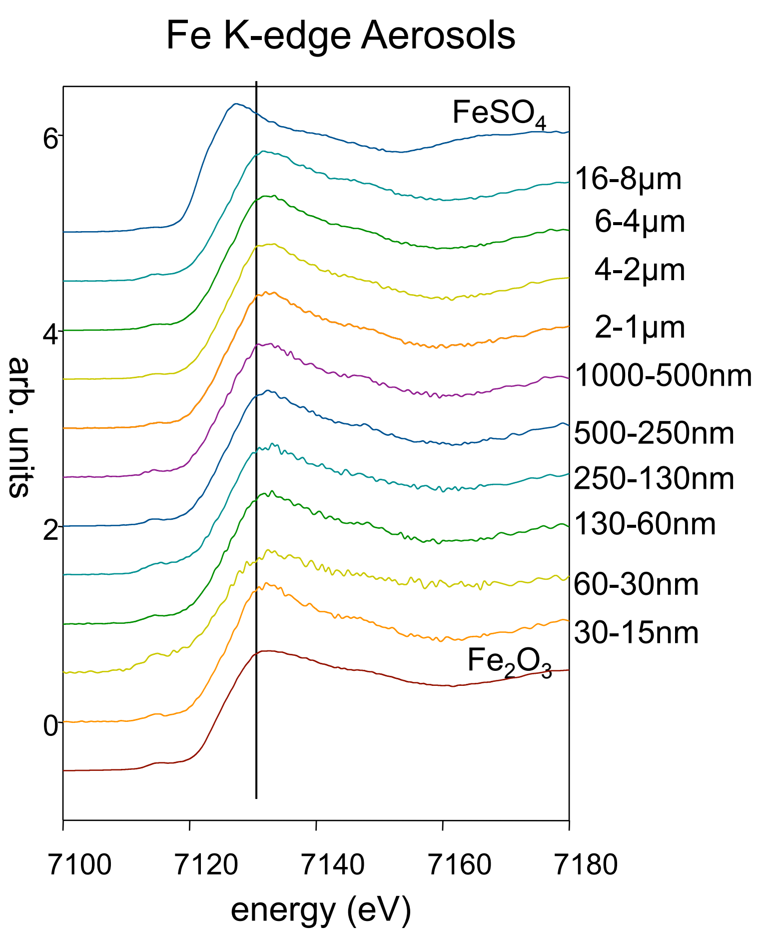
Berner impactor 10 stages

16 µm – 0.015 µm

Motivation:

To understand the effect of aerosols on global climate a detailed understanding of sources, transport, fate and the physical and chemical properties of atmospheric particles is necessary.

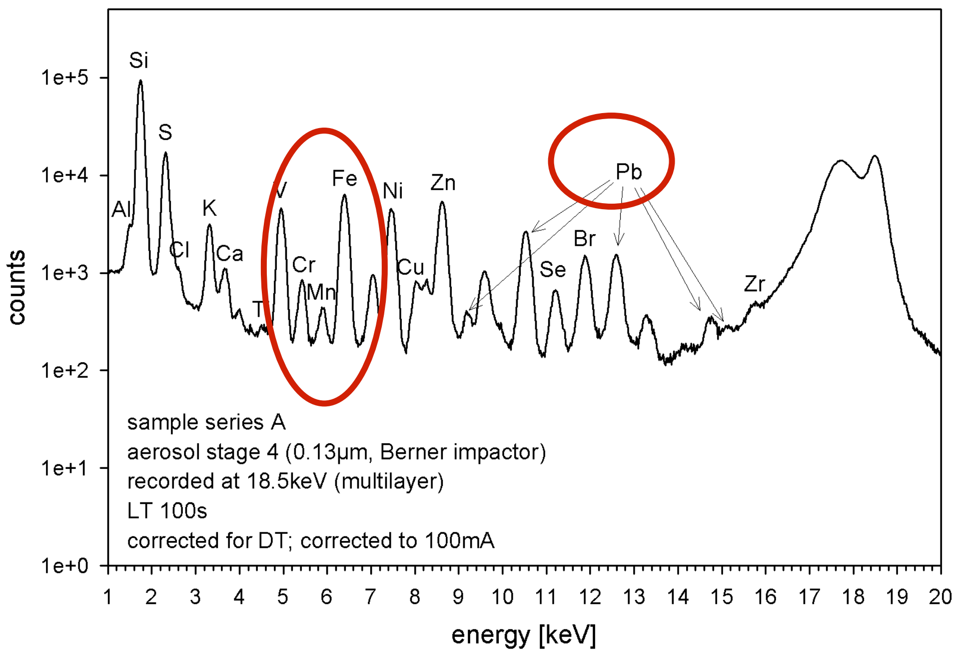
The chemical speciation of the elements is of relevance for the environmental impact.



All stage showed Fe(II)!

Advantages of SR-TXRF:

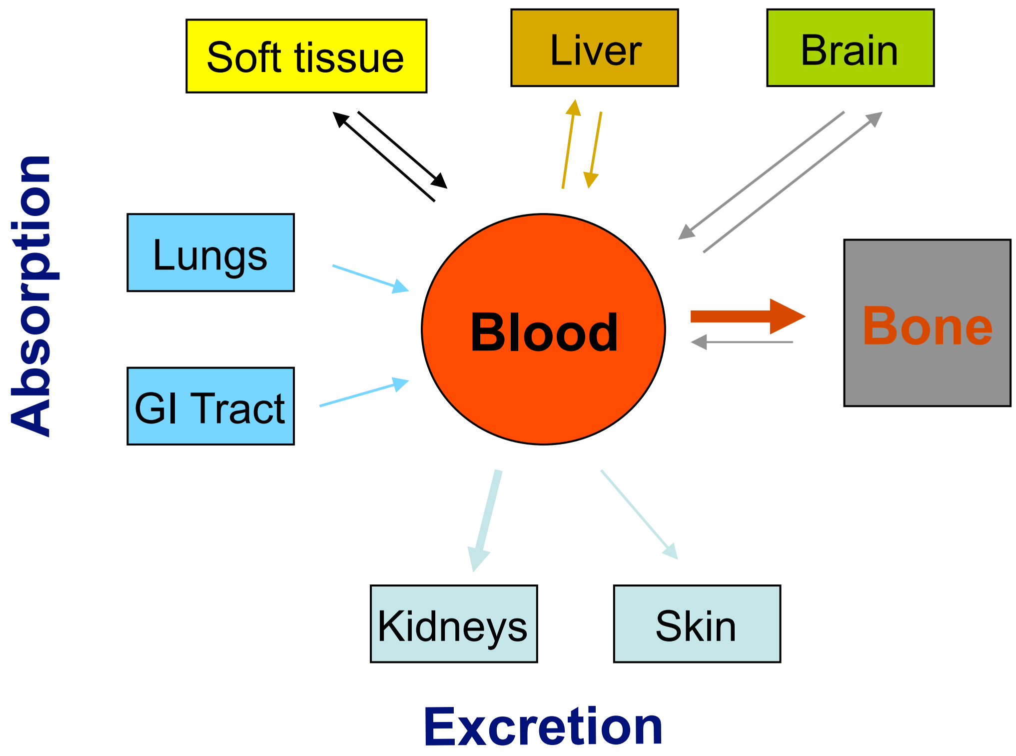
- only small sample mass required
- sampling time can be diminished
  ⇨ time resolved investigation of atmospheric events
- simple sample preparation
  (aerosols directly collected on reflectors)
- TXRF offers good sensitivity for XANES speciation of traces



Elemental distribution µm resolved
N.Zoeger

- Line scans – 2-D and 3-D representations of elemental distributions in a sample
- Tomography vs confocal measurements
- 3kW lab source vs synchrotron radiation
- Human bone and brain elemental distribution - Pb and others

Pb Metabolism in Man,coop Med. Univ. Vienna W.Osterode



Cognitive deficiencies

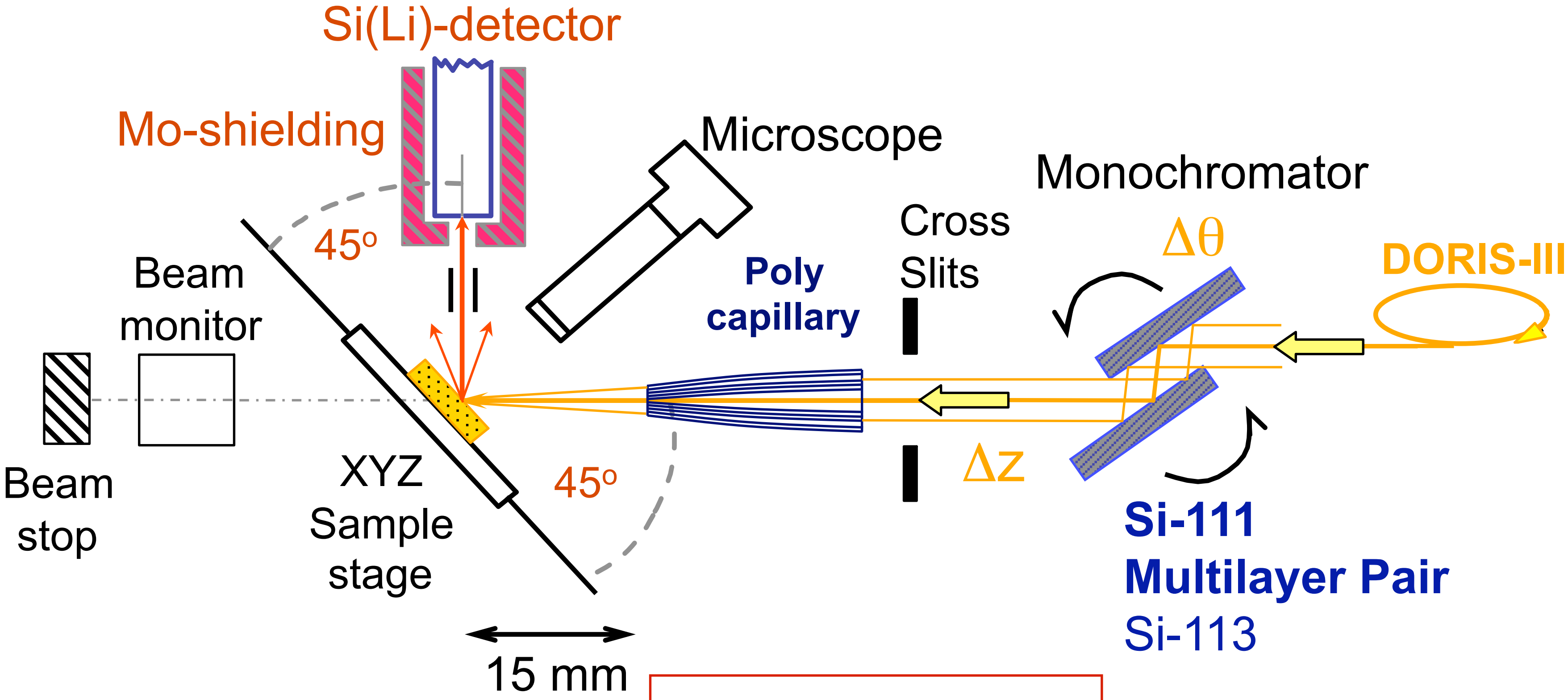
? Pb detection in bone ?

? Spatially resolved measurements to study elemental distribution in bone ?

Estimated concentration of Pb in bone:
low ppm range (about 10ppm)

2D imaging at Hasylab

Experimental Setup @ HASYLAB beamline L

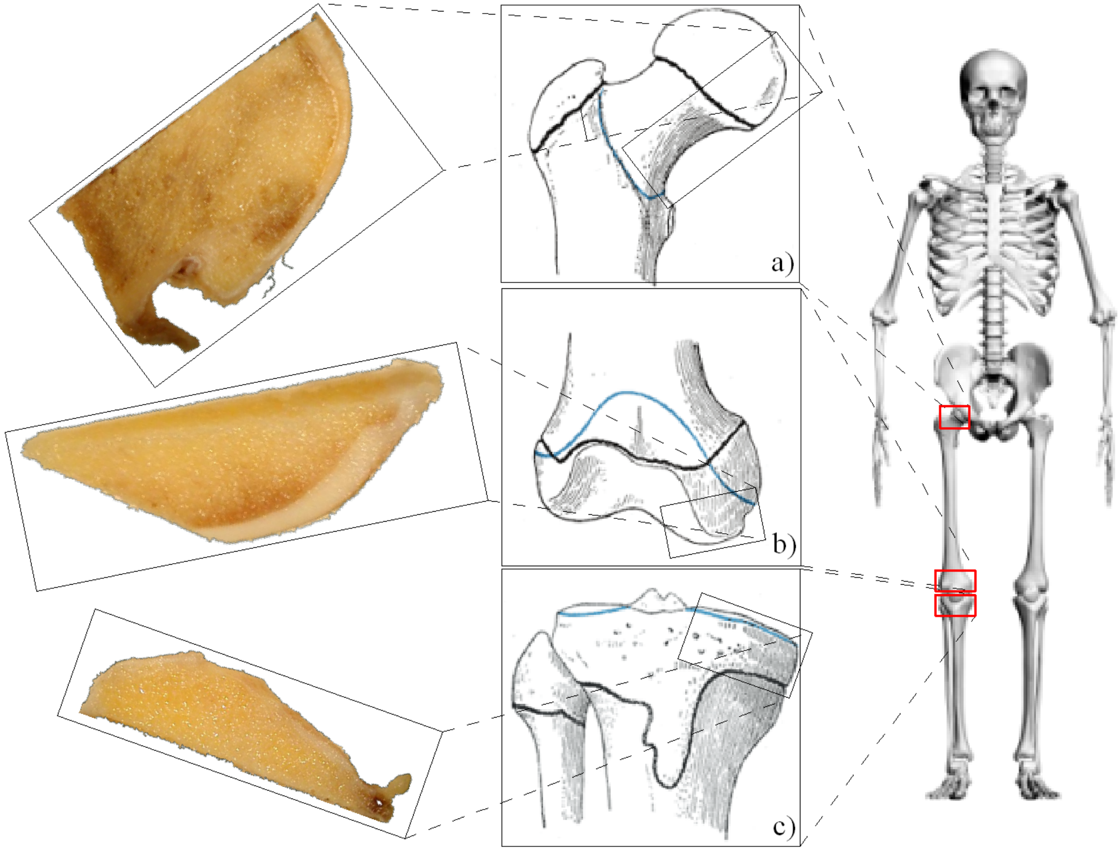


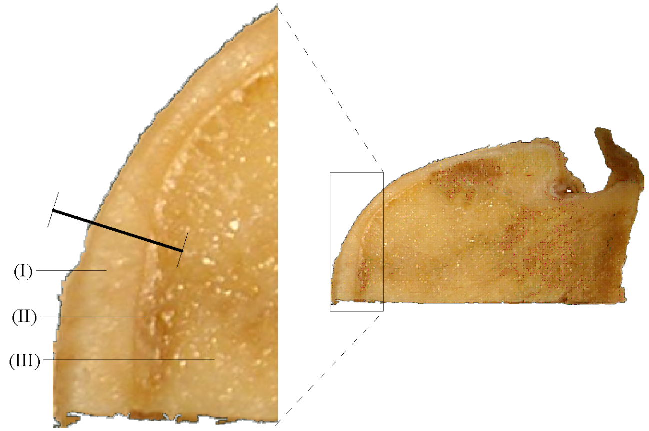
Focal size: 13-30 μm

ML → intensity gain of 80-100

only small increase of scatter peak

Samples





(I) Non-calcified cartilage
(II) Cortical bone
(III) Trabecular bone

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Sample Preparation/Samples

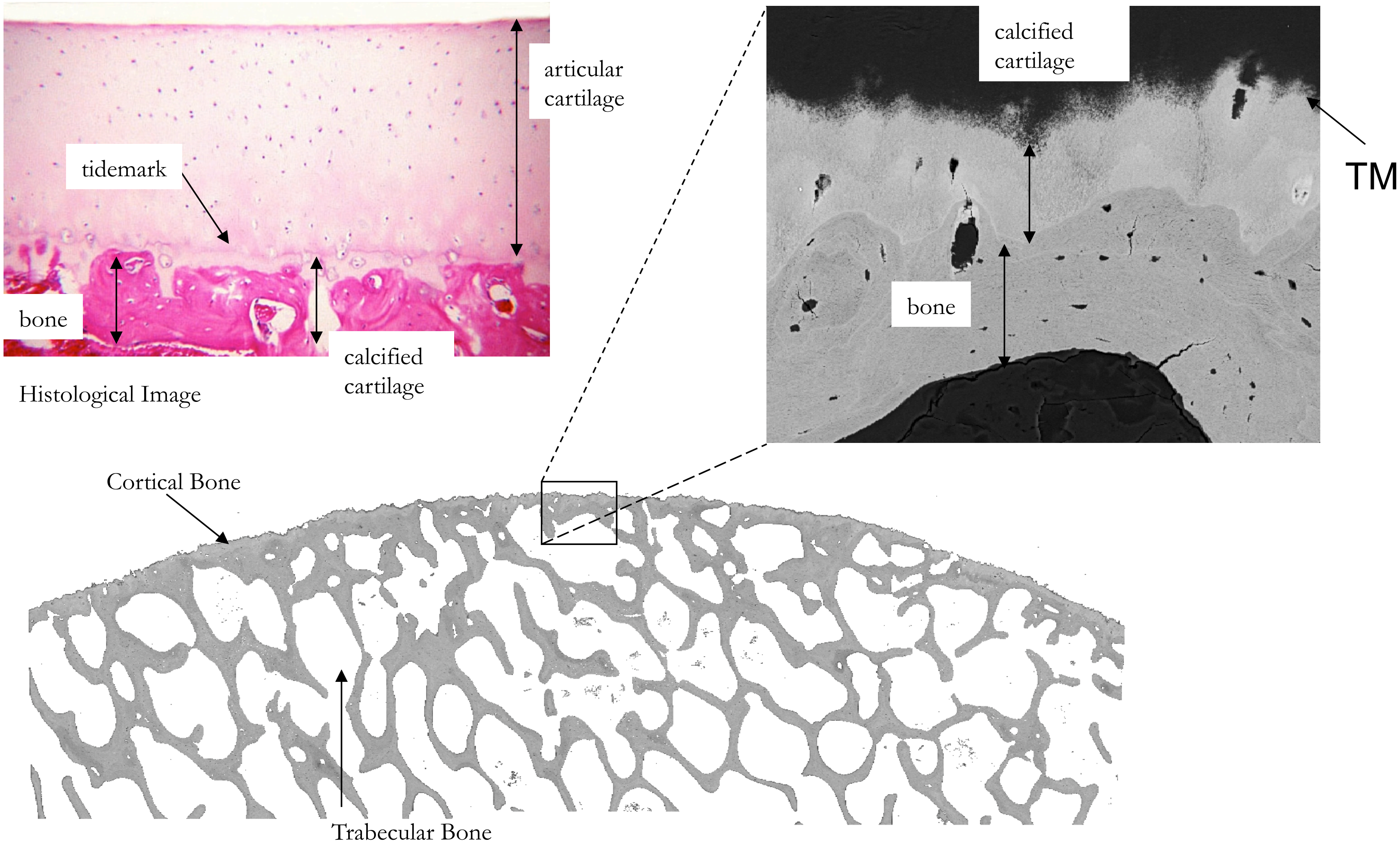
UKH Meidling

TECHNISCHE UNIVERSITÄT WIEN
VIENNA UNIVERSITY OF TECHNOLOGY

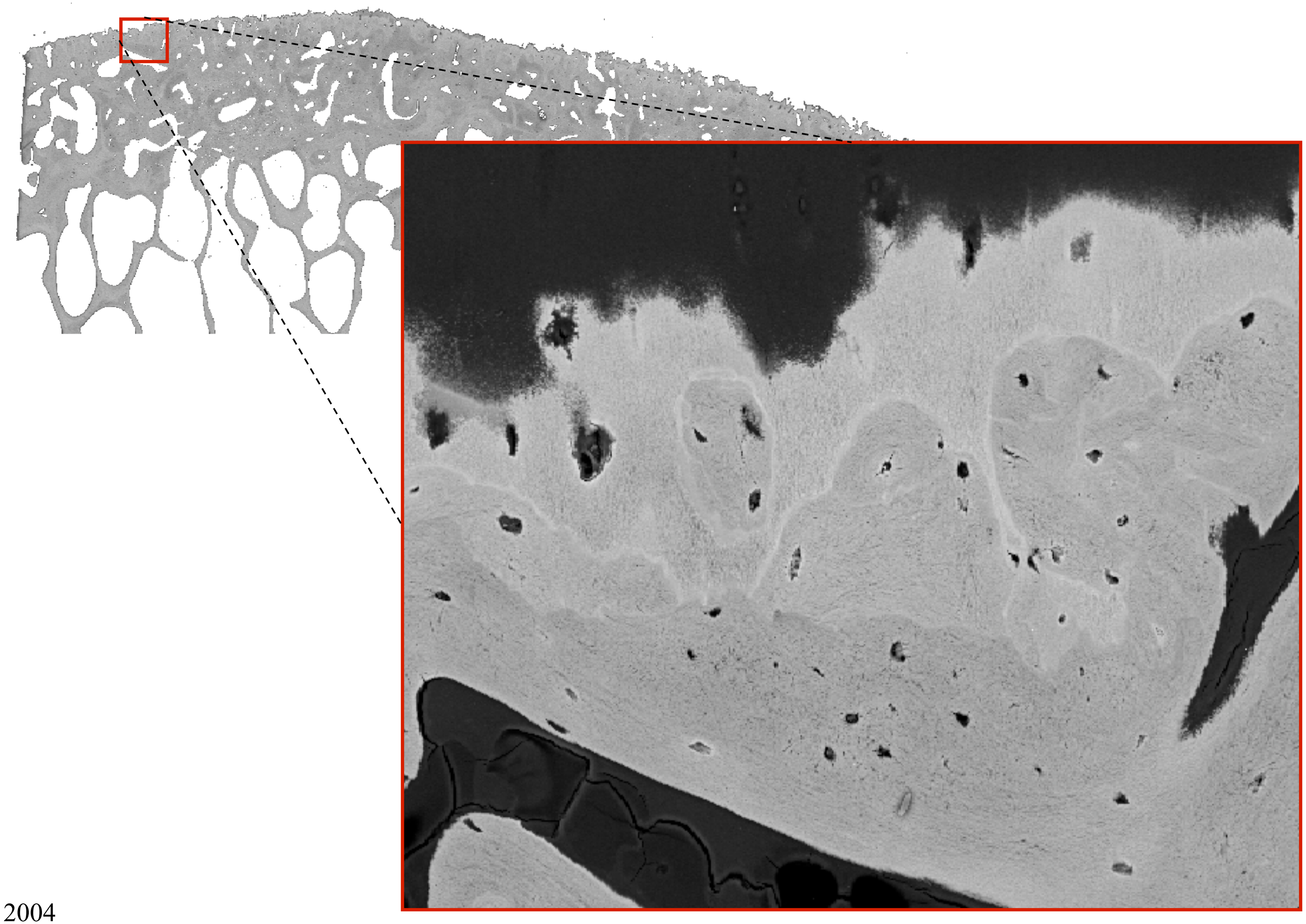
- Dehydration in a graded series of alcohol
- Embedding in polymethylmethacrylate (PMMA)
- Diamond saw cutting, grinding and polishing
- Carbon coating for BEI

- 5 bones from HIP HEAD
- 3 bones from PATELLA
- All samples contained trabecular bone, cortical bone as well as calcified and non-calcified cartilage
- **Sample thickness: 200µm**

Structure of Cortical Bone



Patella - line scan



n.zoeger 2004

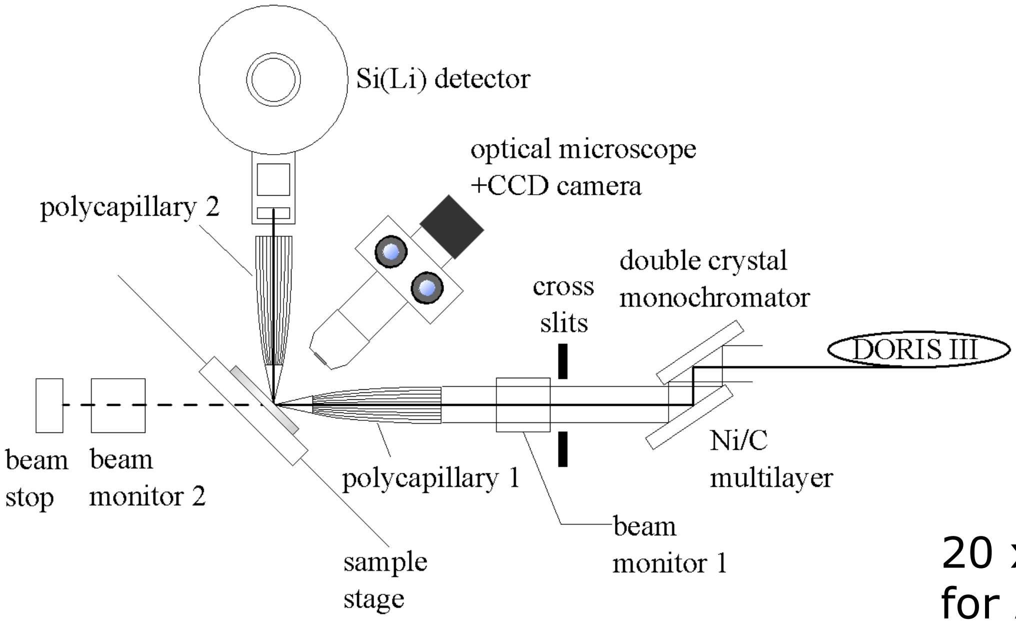
3 D imaging

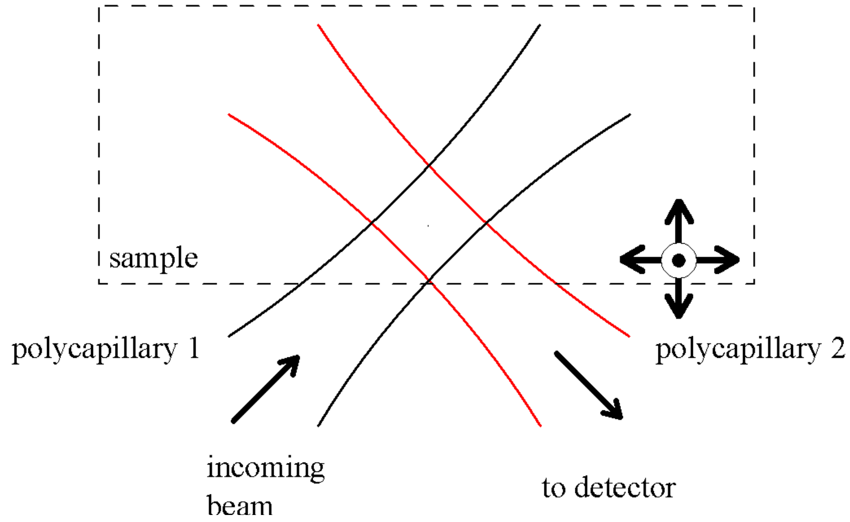
•Tomography: absorption – fluorescence

•Complicated mathematical
•reconstruction algorithm

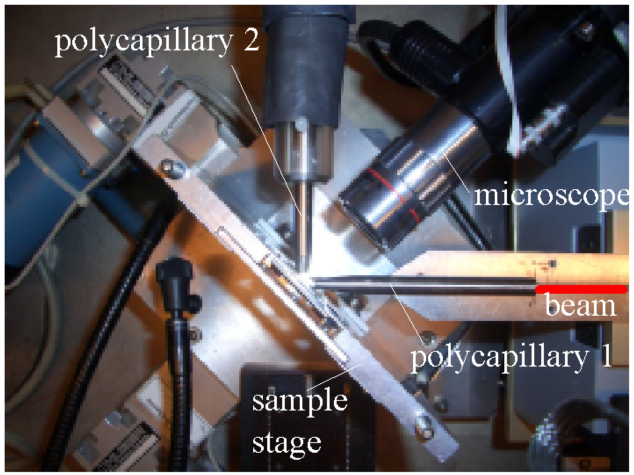
•Confocal imaging

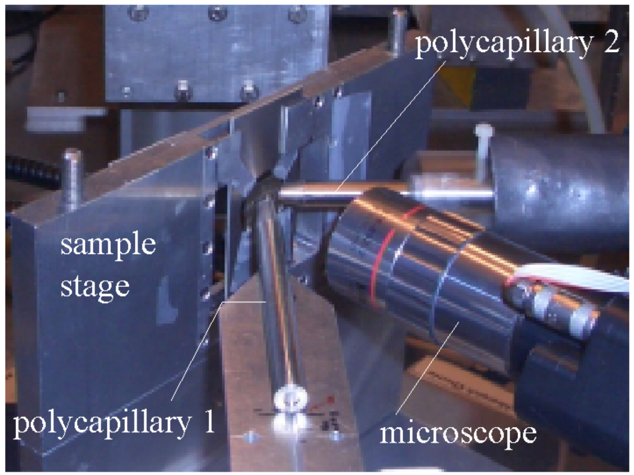
Confocal setup Hasylab



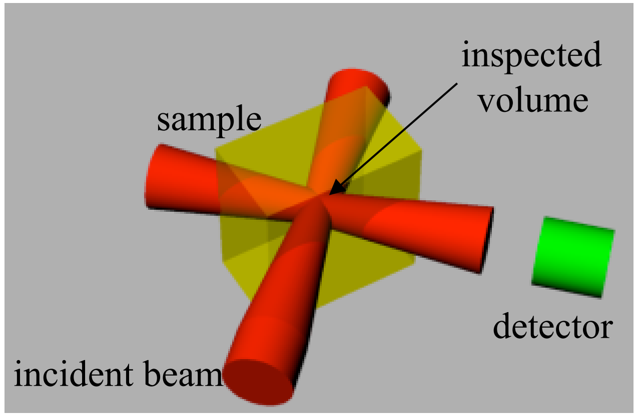


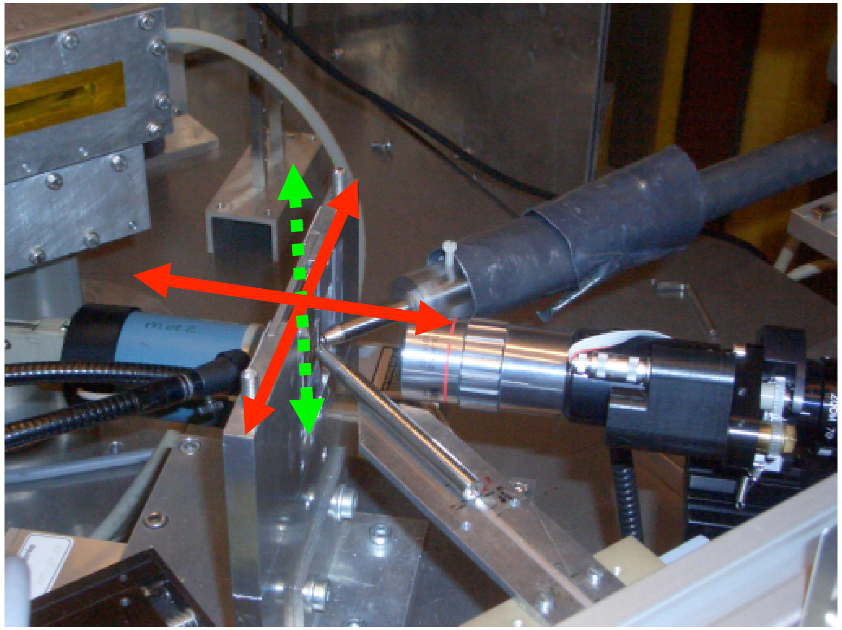
20 x 22 x 14 µm^3 (lateral x depth x height) for Au Lα



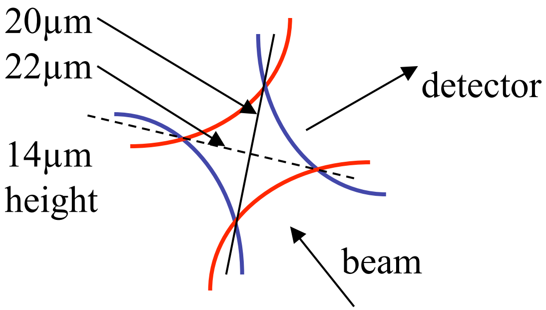


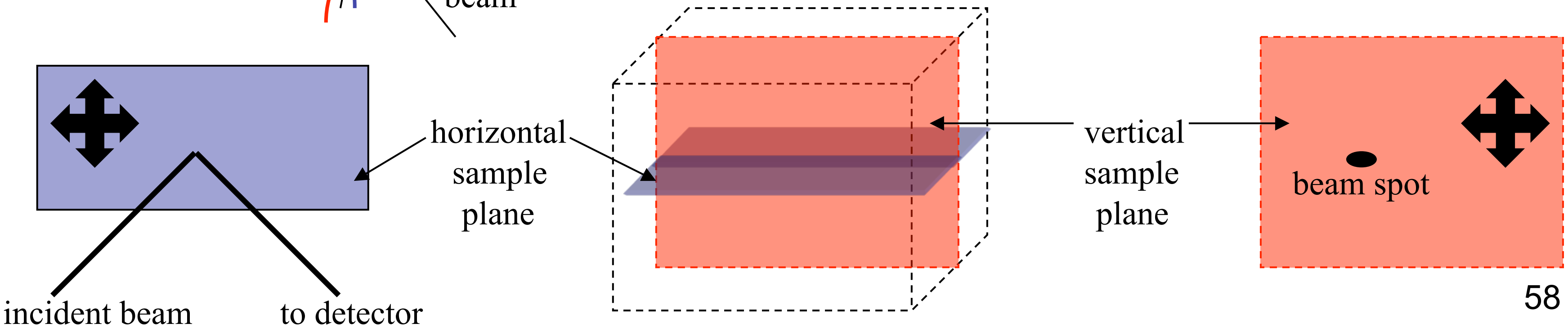
Inspected Volume





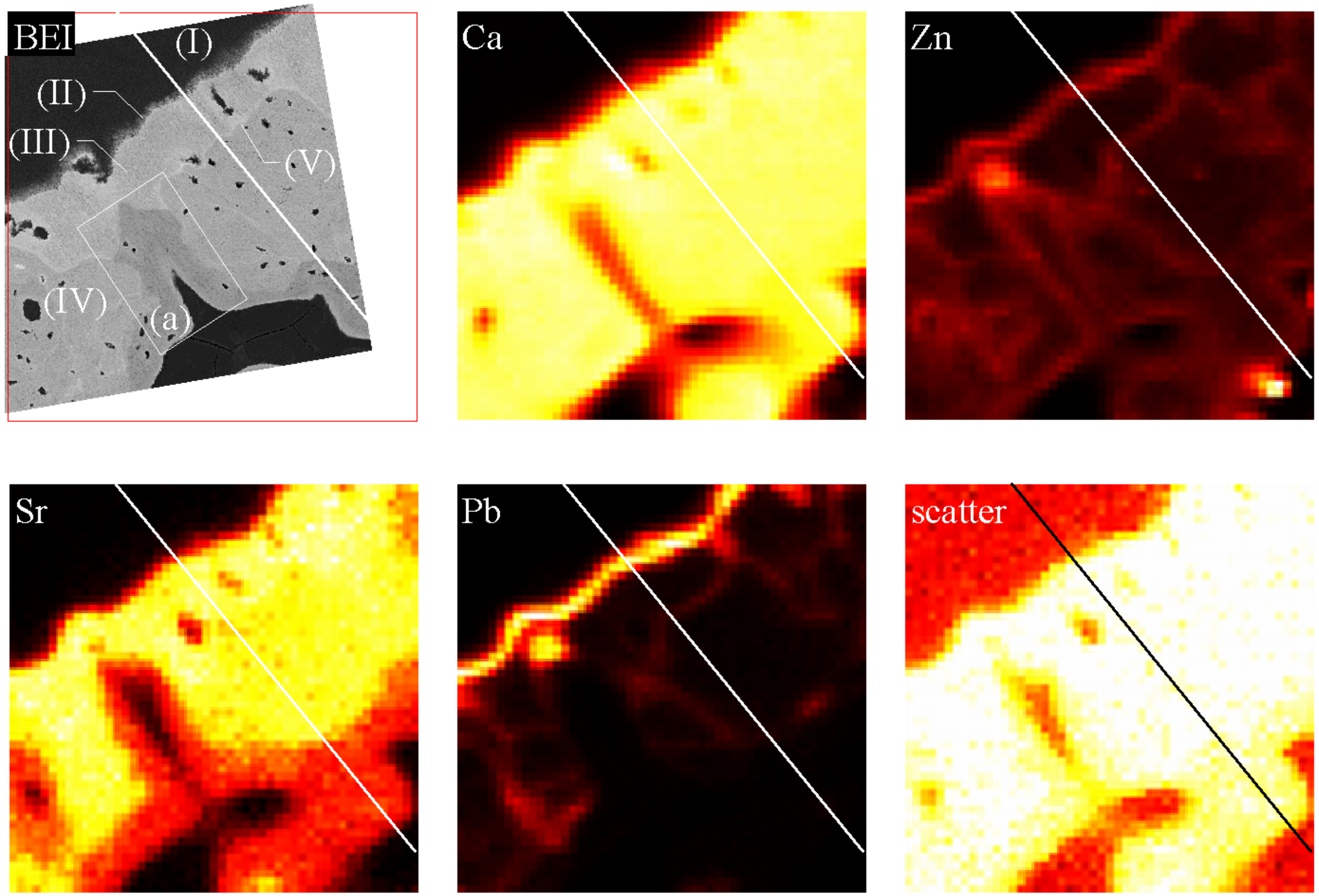
For Au La



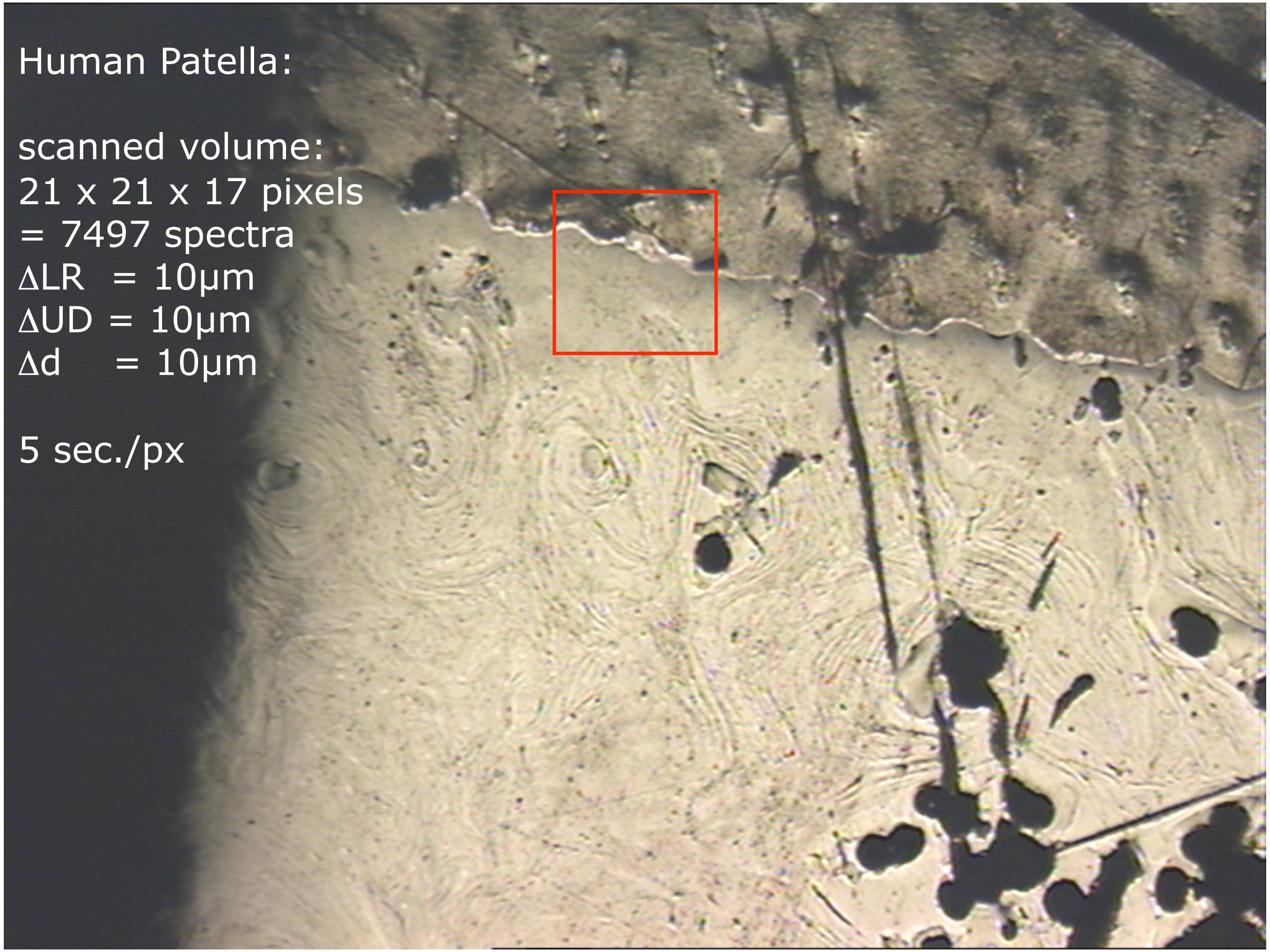


Results Patella Element Maps from surface layer

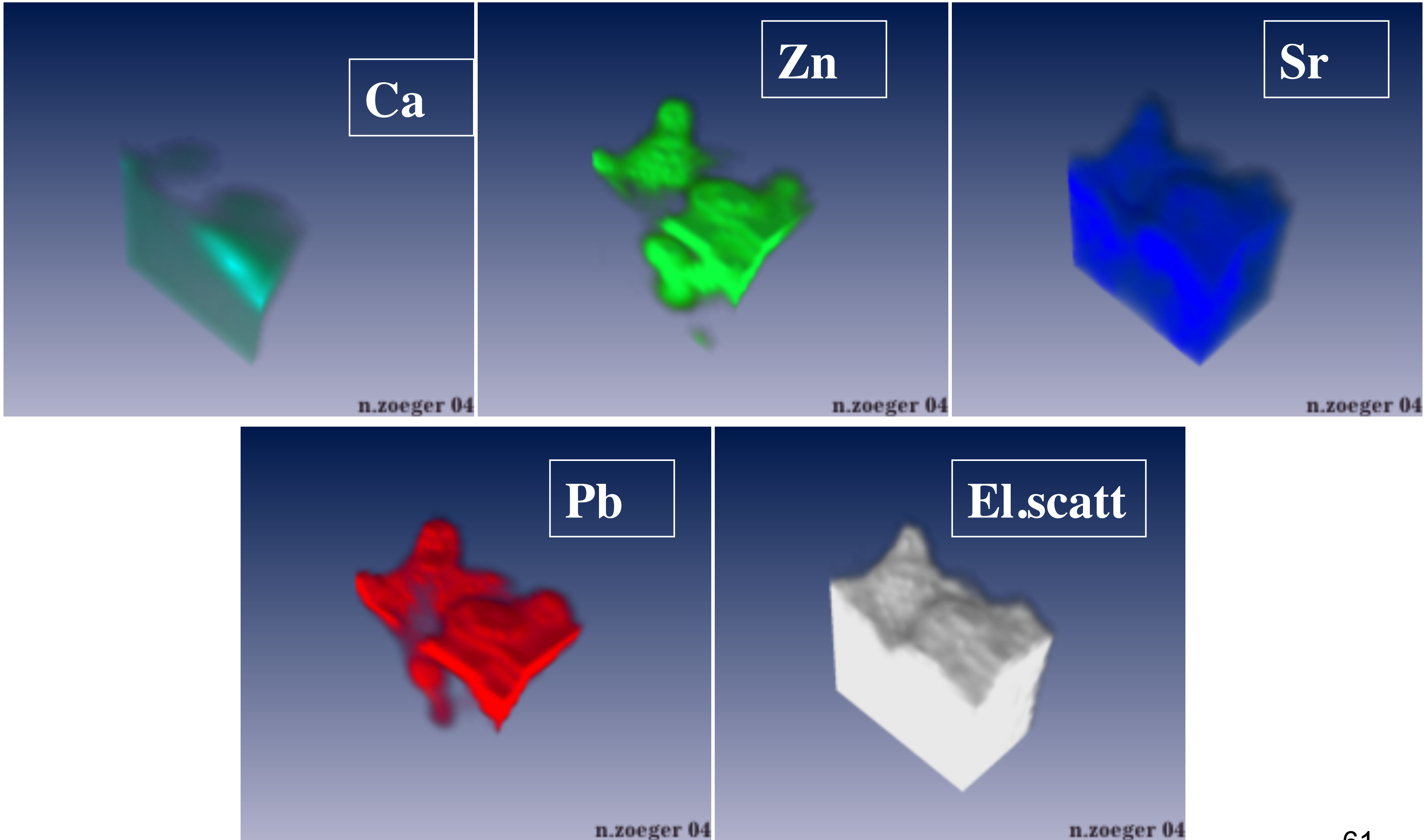
51 x 51 px
5s /px



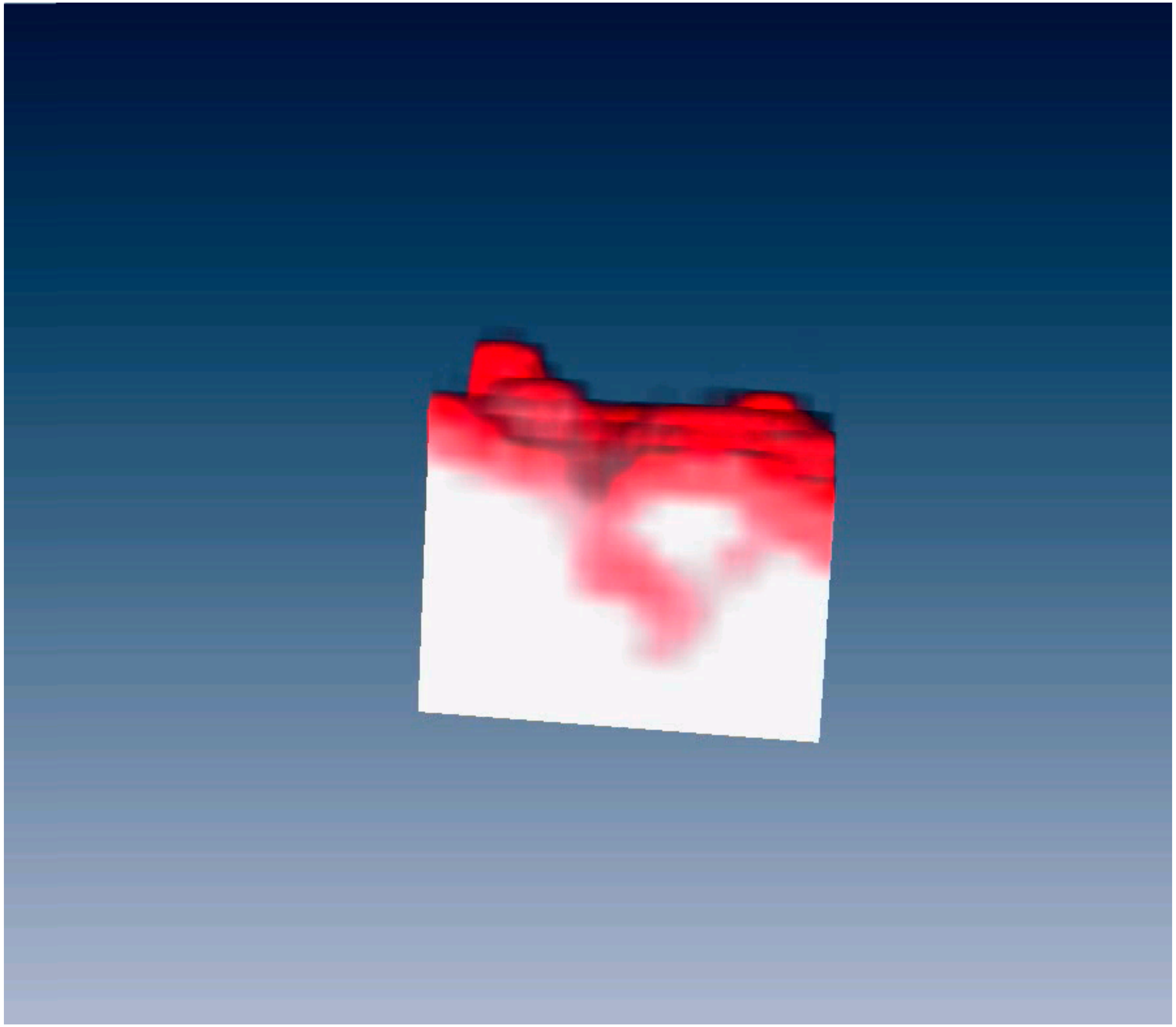
3D Element „maps“



results


Ca
n.zoeger 04
Zn
n.zoeger 04
Sr
n.zoeger 04
Pb
n.zoeger 04
El.scatt
n.zoeger 04

Result of a volumetric scan Pb and scattered Intensities



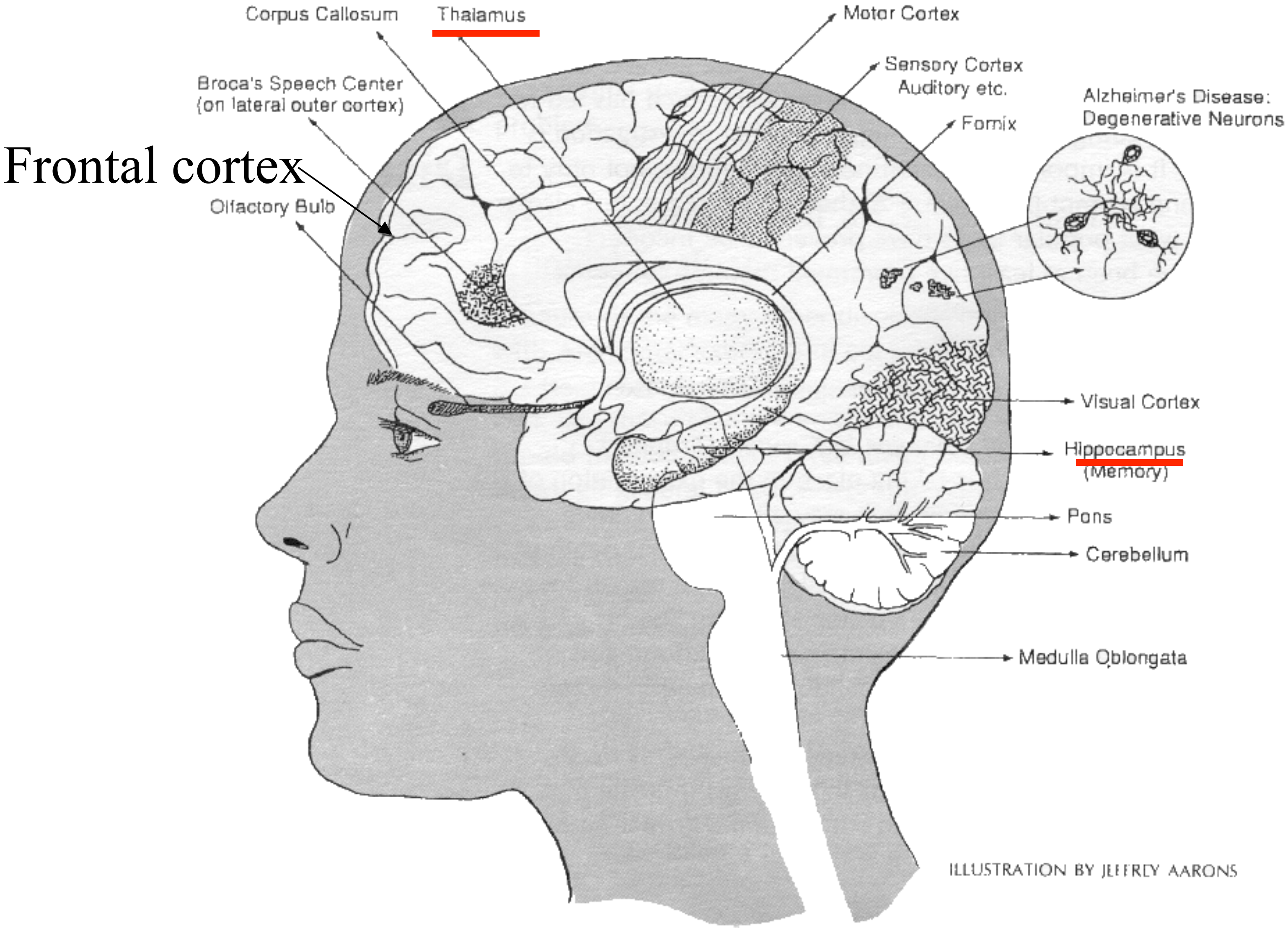
Advantages of confocal experiments

- Confocal micro XRF allows deconvolution of structural and elemental inhomogeneities
- 3-D imaging possible without reconstruction algorithm
- Sample preparation much easier
- Lateral sample dimension can be larger as in fluorescence / absorption tomography

Line scan to 2-D Area scan

- Area scan in 2-D is achieved by a set of line scans

Brain Areas



Corpus Callosum
Thalamus
Motor Cortex
Broca's Speech Center
(on lateral outer cortex)
Sensory Cortex
Auditory etc.
Fornix
Alzheimer's Disease:
Degenerative Neurons
Frontal cortex
Olfactory Bulb
Visual Cortex
Hippocampus
(Memory)
Pons
Cerebellum
Medulla Oblongata
ILLUSTRATION BY JEFFREY AARONS

Samples prepared and selected in Cooperation with W.Osterode AKH Vienna

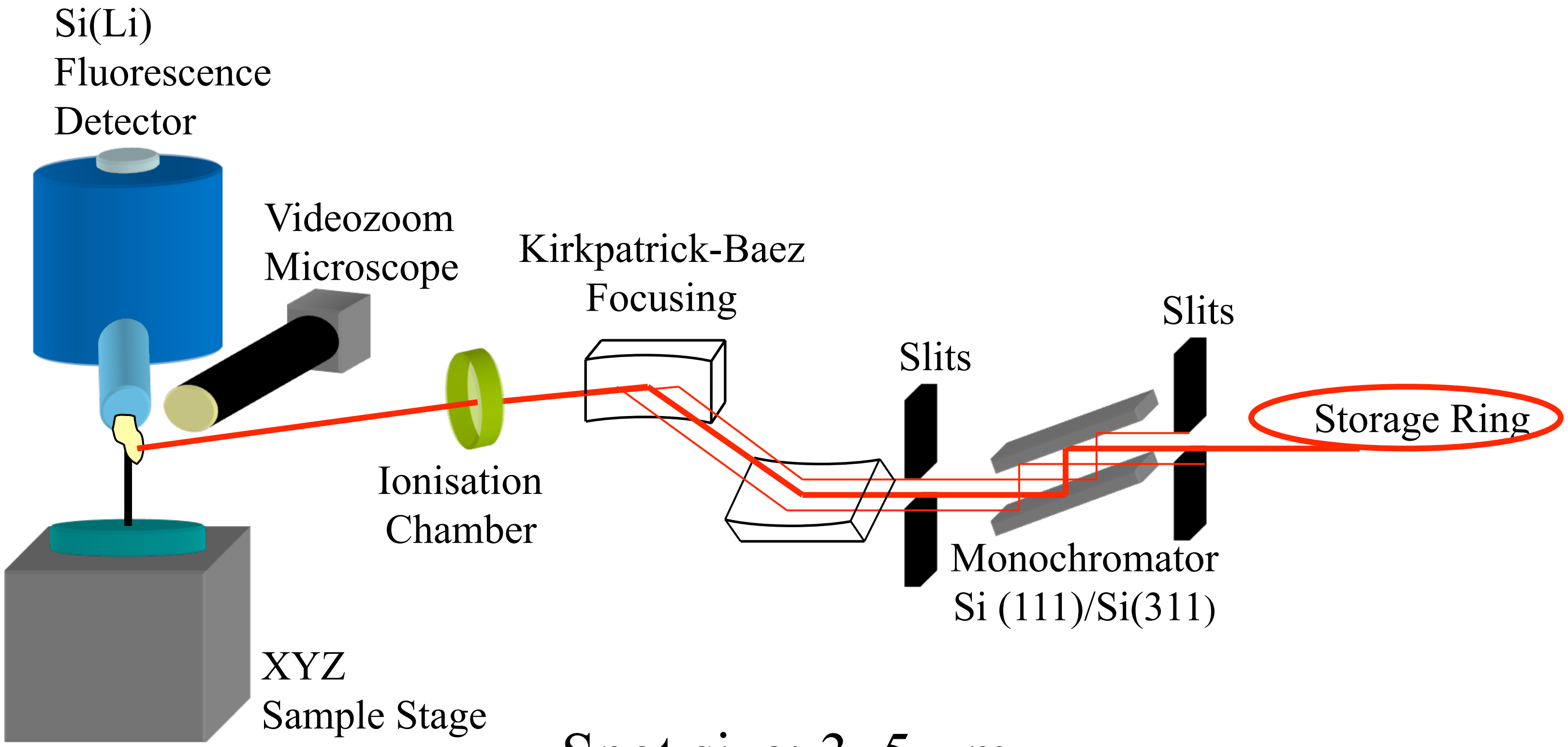
- samples from prefrontal cortex, hippocampus & thalamus

- embedded in paraffin

- cut by microtome (20µm thickness)

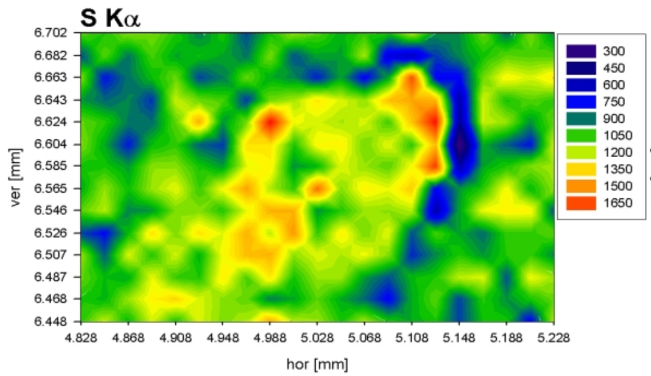
- mounted on frames between capton foil

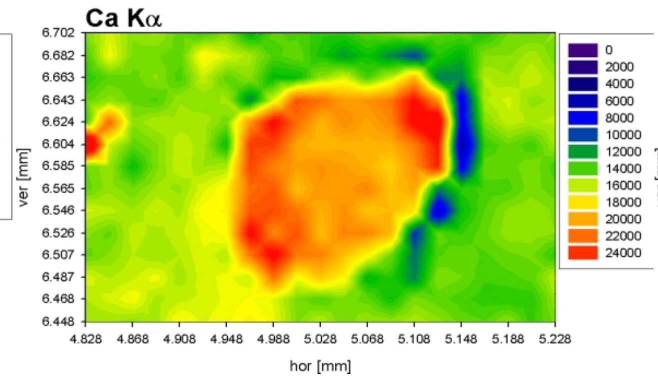
Experimental Setup ID-22, ESRF

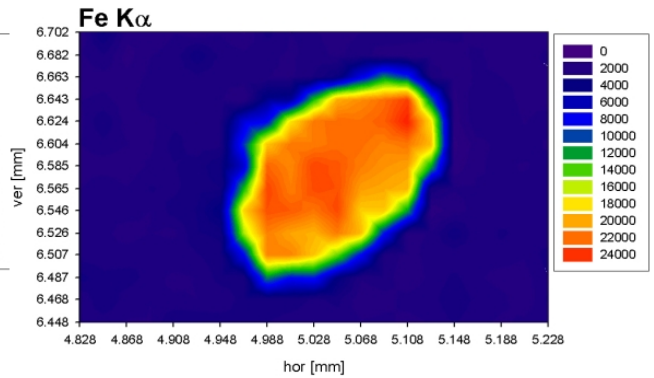


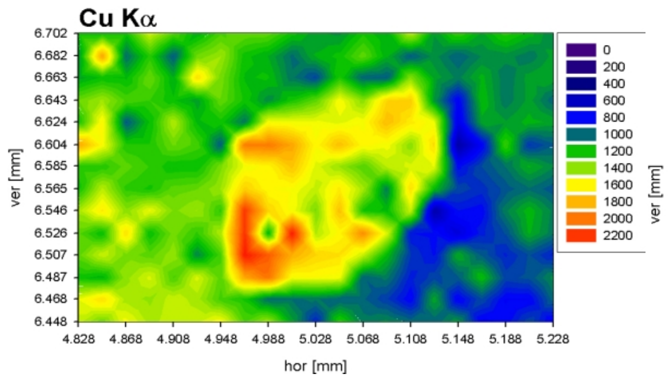
Spot size: 3x5 µm
Flux: E11 ph/s

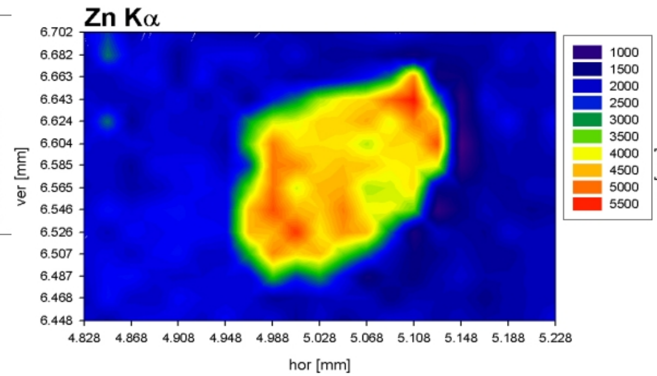
Blood Vessel in the Hippocampus area

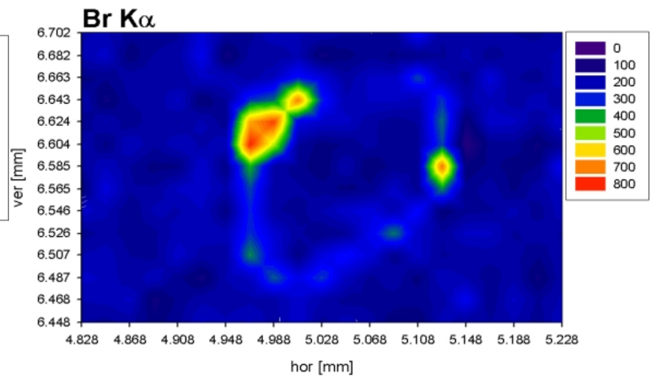


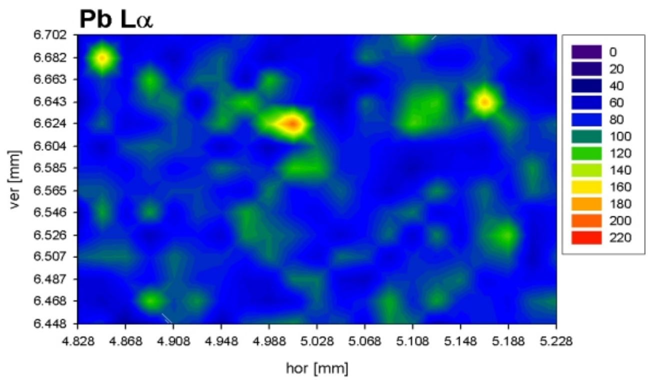


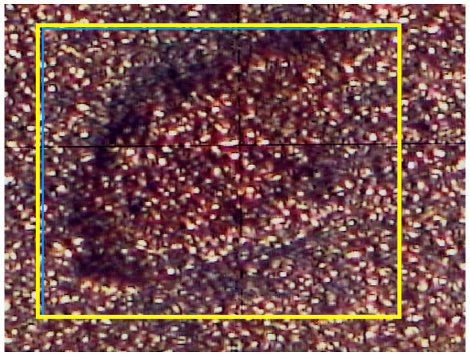






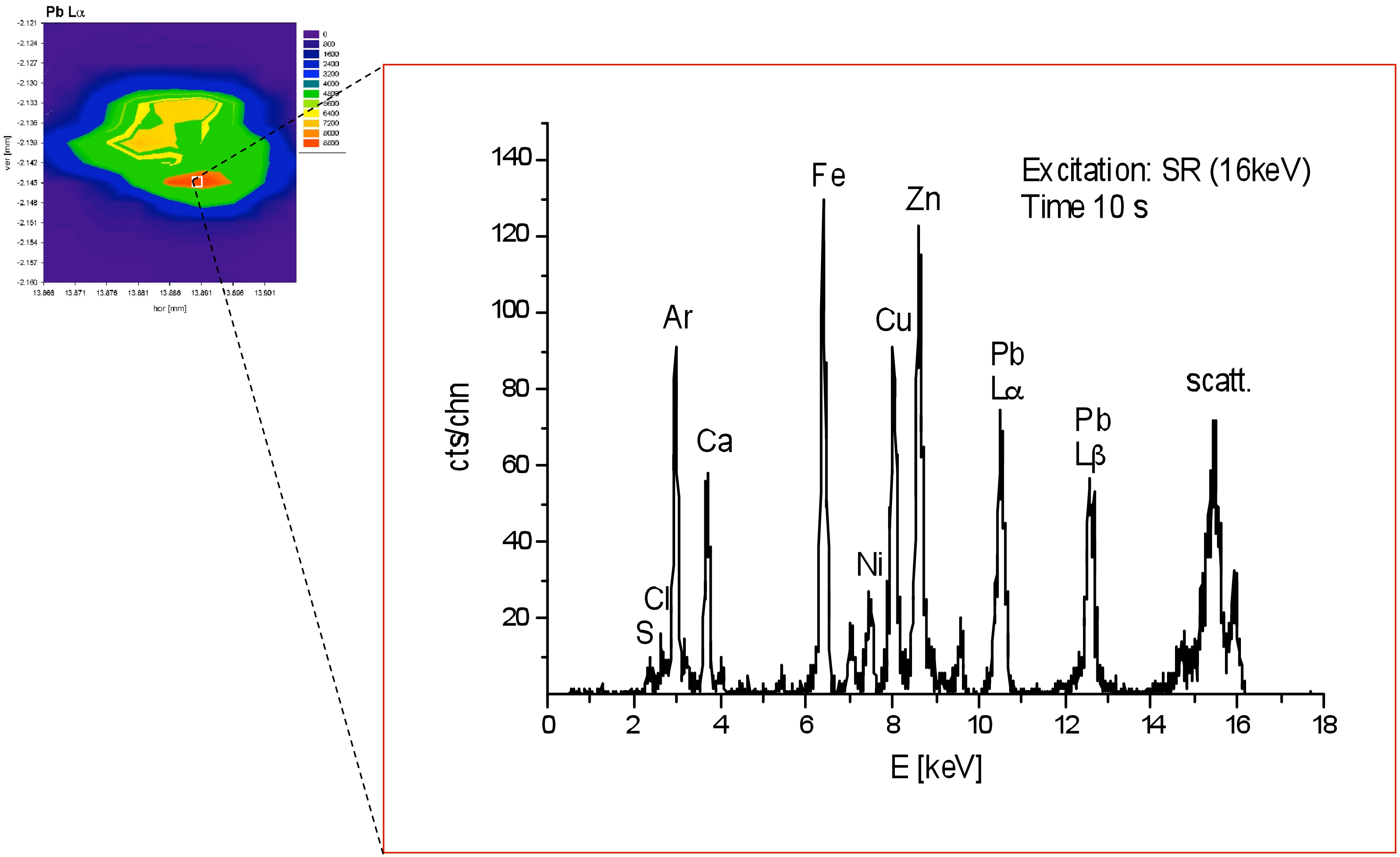






Microscope image

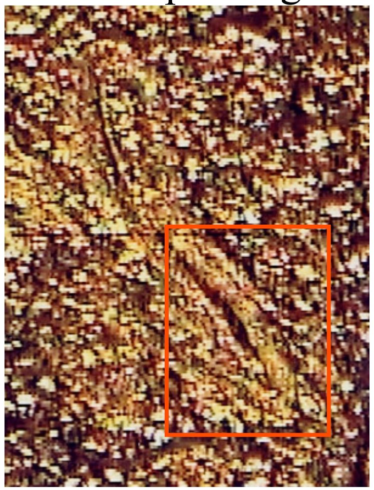
Spectrum at Maximum of Pb

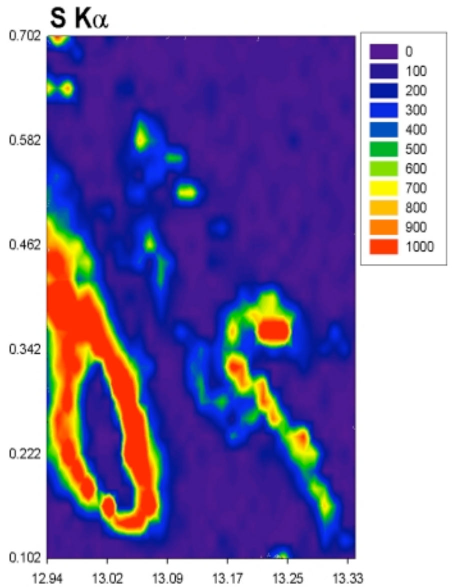


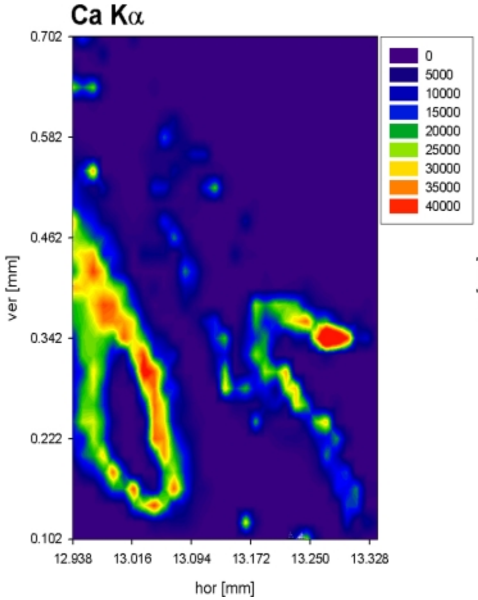
Plexus Choroidei in the Thalamus area

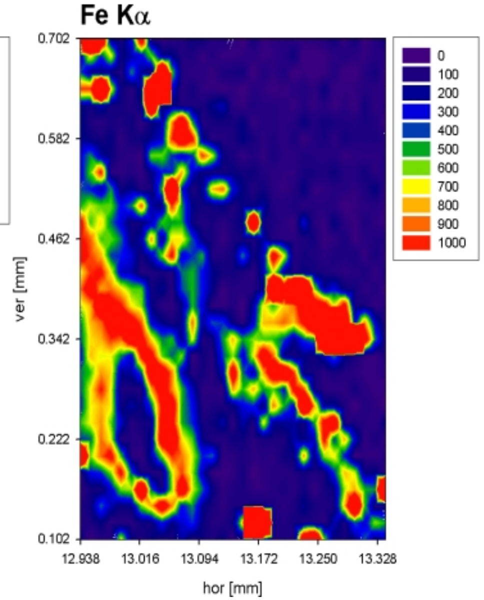
a meshwork of vessels where the liquor cerebrospinalis is generated

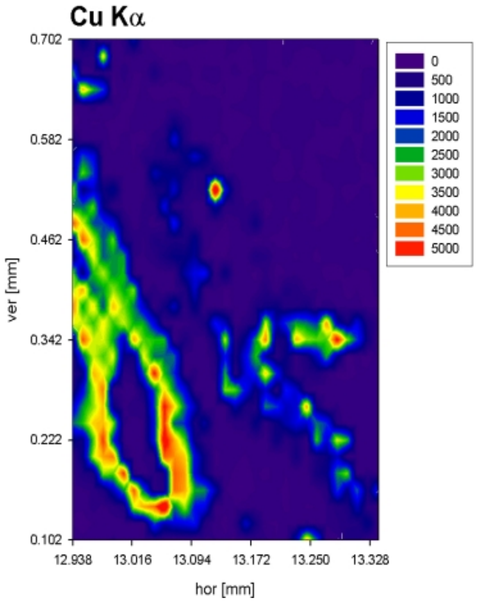
Microscope image

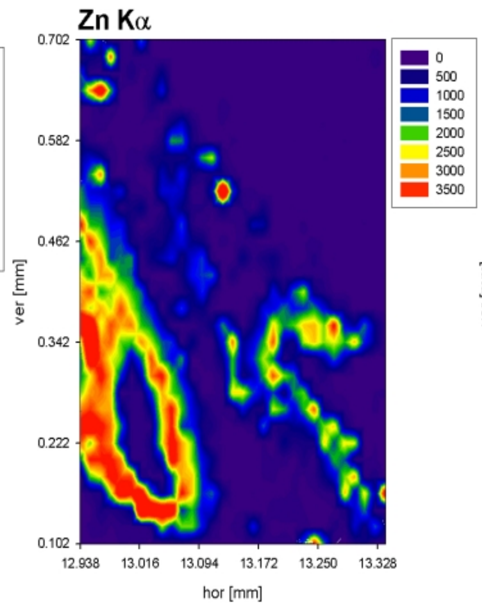


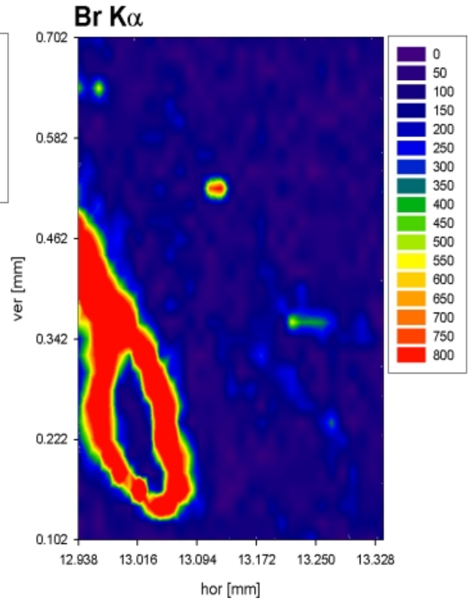


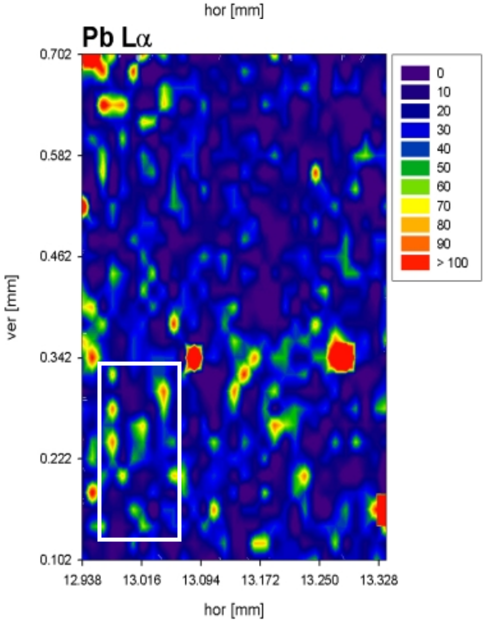












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Conclusions

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Low power sources + SDD   portable XRF instruments

TXRF with lab sources pg detection limits

TXRF with SR sources fg detection limits

TXRF with SR and Si crystal chemical speciation with XANES

SR - micro XRF 1D, 2D and 3D elemental distribution

In confocal XRF without reconstruction algorithm

Speciation by XANES with Synchrotron radiation

3rd generation Synchrotron sources flux up to E 11 ph/sμm2

☺ New world for interdisciplinary activities!

ID22
P
Thank You
for your
Attention