Micro X-ray Fluorescence Spectrometer with Low Power Tube and Polycapillary Optics for Light Element Analysis

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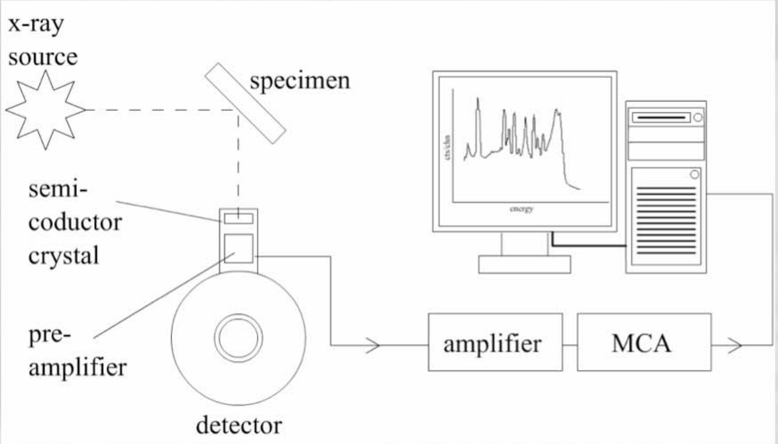
Renaissance of XRF

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

Technique

XRF:

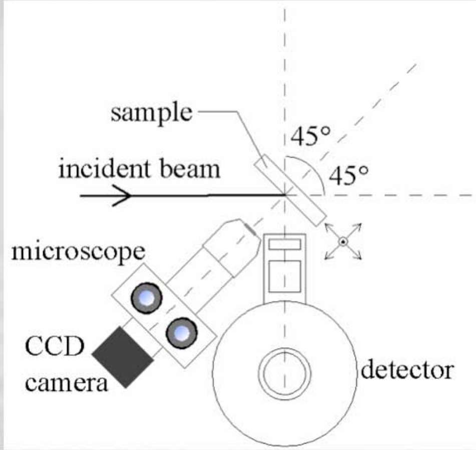


Excitation of characteristic radiation in the Sample by primary X-rays from a suitable source

Recording of characteristic radiation by an energydispersive detector

Signal processing; spectrum storage and evaluation

µ-XRF:



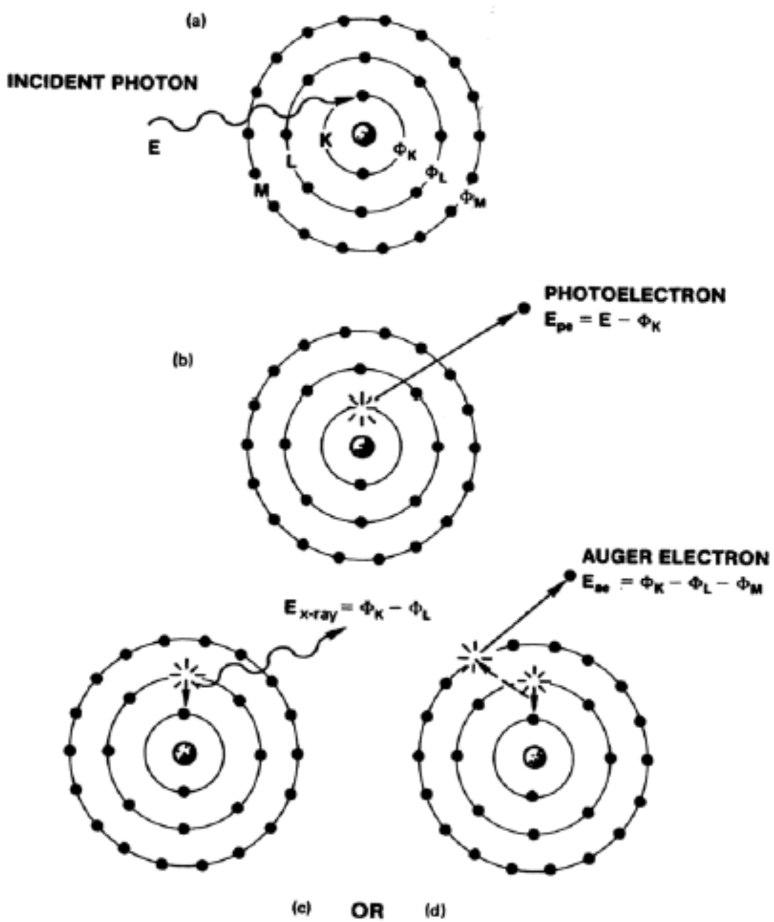
X-ray optics for focussing of incident beam
Spot size in the µm range

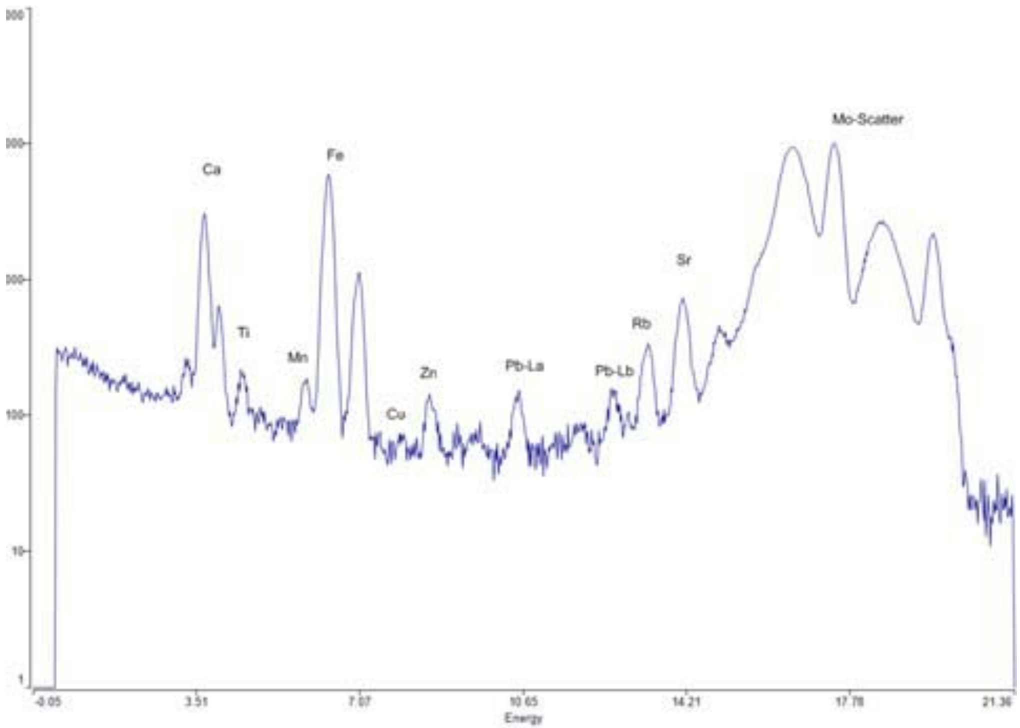
Sample mounted on a sample-stage for spatial resolved measurements

Optical microscope for control of measurement position

Energy Dispersive X-ray Fluorescence Analysis (EDXRF)

Interactions photons/matter < 100keV
Photoeffect
Elastic scattering
Inelastic scattering





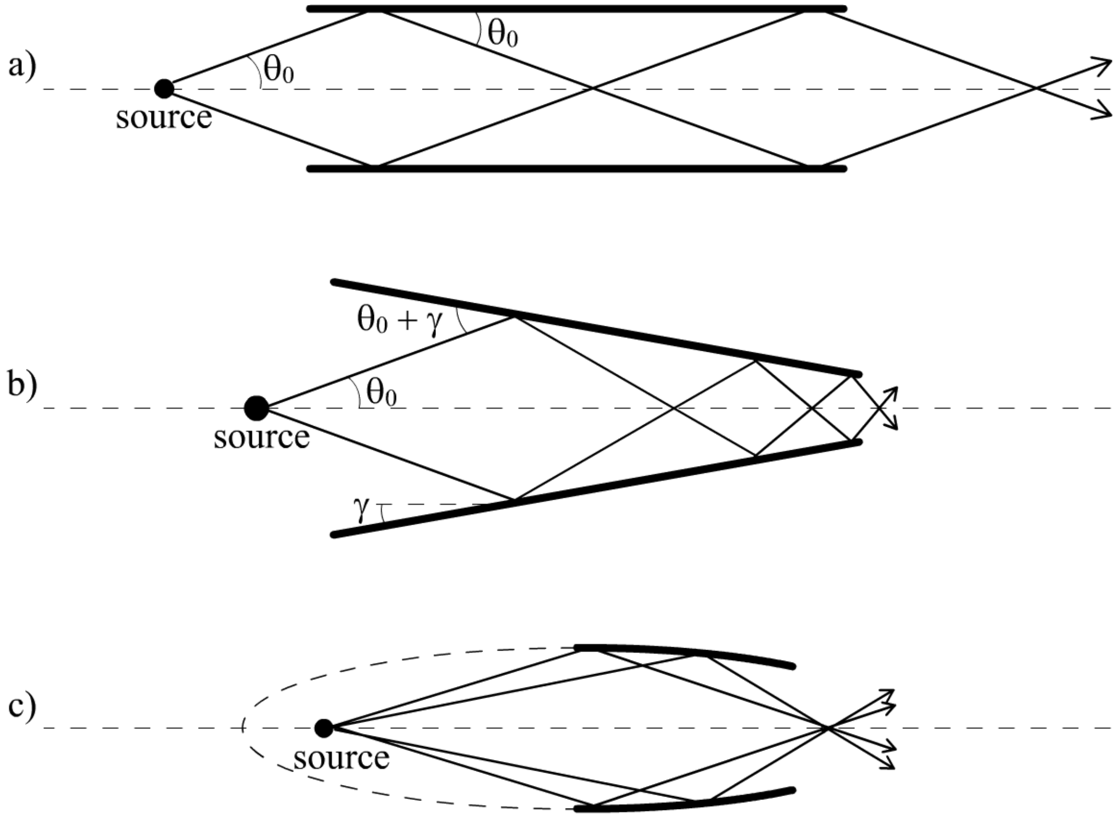
Micro-XRF requirements

- X-ray beam with dimensions in the range of micrometers
- High intensive beam
- Energy high enough to excite the elements
- Linear polarization advantageous
- High throughput detector
- Best energy resolution
- Efficient data management
- Scanning stages for sample
- Optical microscope for position control (depth resolution)

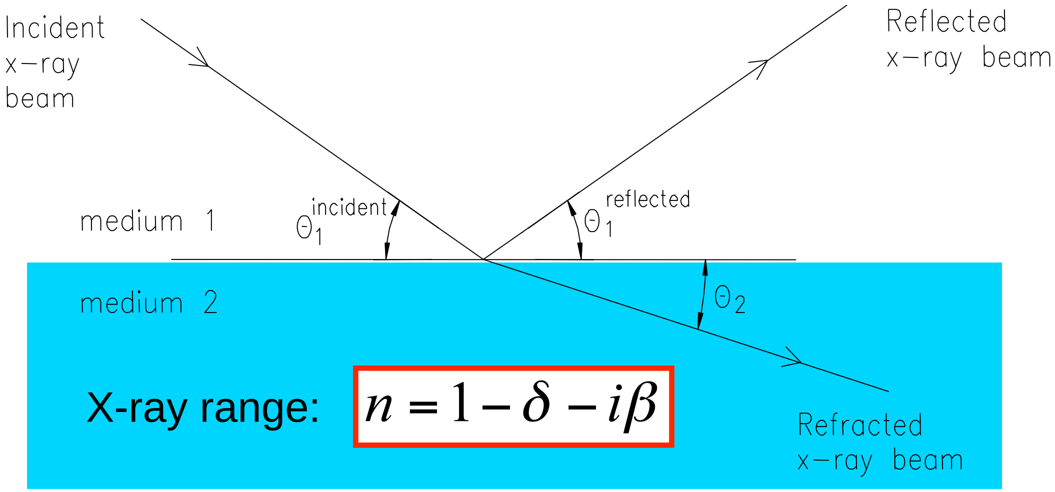
X-ray optical elements

- Single and polycapillaries
- Kirkpatrick – Baez optics
- Compound refractive lenses
- Double curved crystals
- Fresnel lenses
- X-ray waveguides

Monocapillaries



Total (external) reflection of X-Rays



$$\Phi_{crit} \approx \sqrt{2 \cdot \delta} \approx \frac{20.7}{E} \cdot \sqrt{\rho}$$

ϕ_{crit} [mrad], E [keV], ρ [g·cm^{-3}]

φ critical
(Si, 17.5 keV) ≈ 0.1° ≈ 1.75 mrad
(Si, 500 eV) ≈ 3.7° ≈ 64.6 mrad
(Si,12.2 keV) ≈ 0.15° ≈ 2.6 mrad

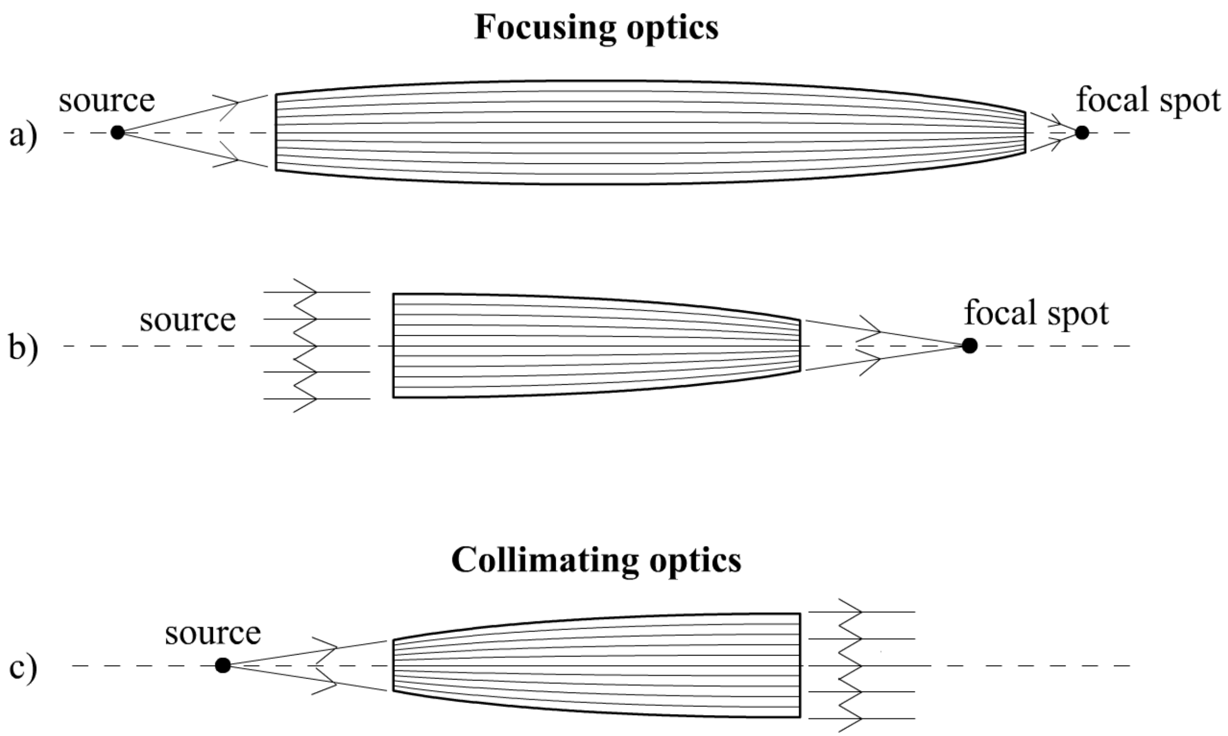
δ ~ 10^{-6} … dispersion: $\delta = K \cdot f_1(E)$

β ~ 10^{-8} … absorption: $\beta = K \cdot f_2(E)$

$$K = \frac{r_0 \cdot \lambda^2}{2\pi} \cdot \frac{N_A}{A} \cdot \rho$$

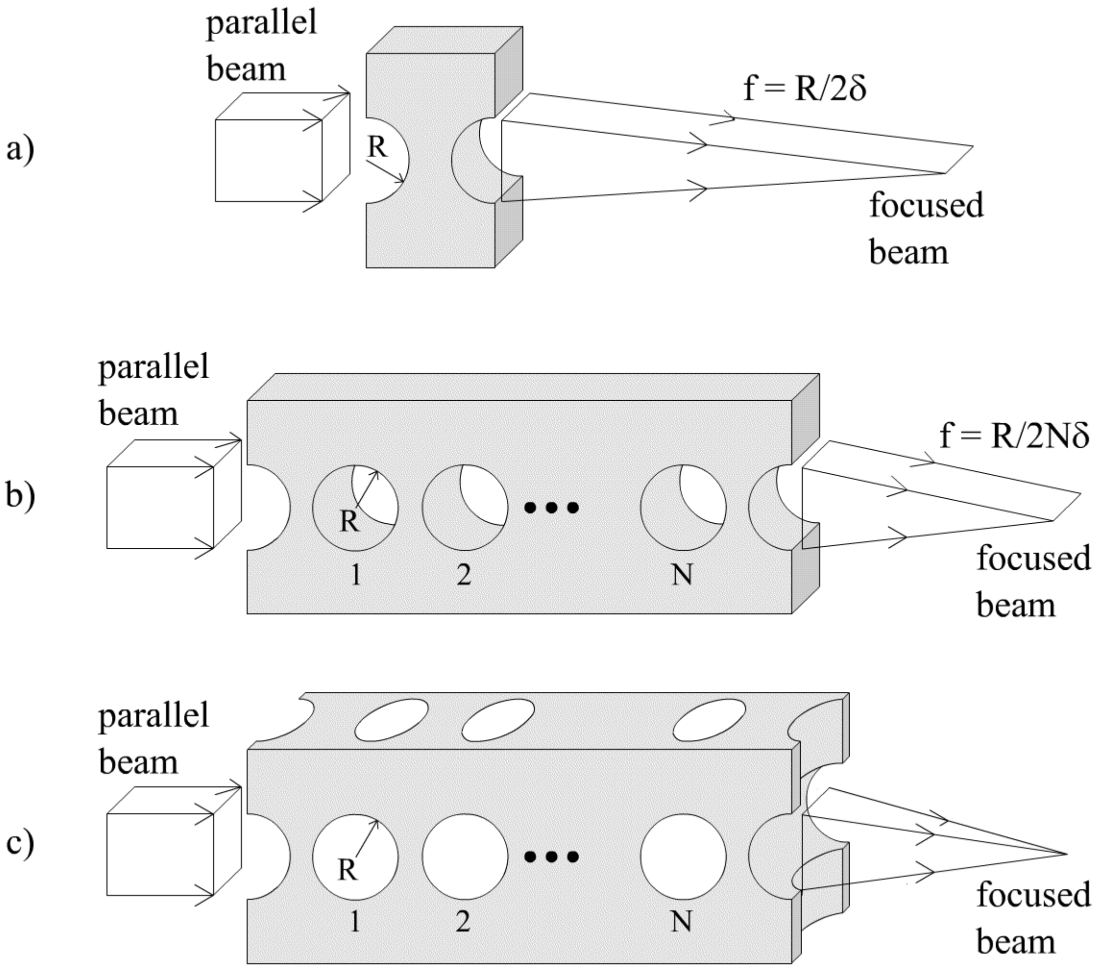
f_i … atomic scattering factor
r_0 … classical electron radius
λ … wavelength of incident beam
N_A … Avogadro‘s constant
A … atomic weigth
ρ … density [g·cm^{-3}]

Polycapillaries

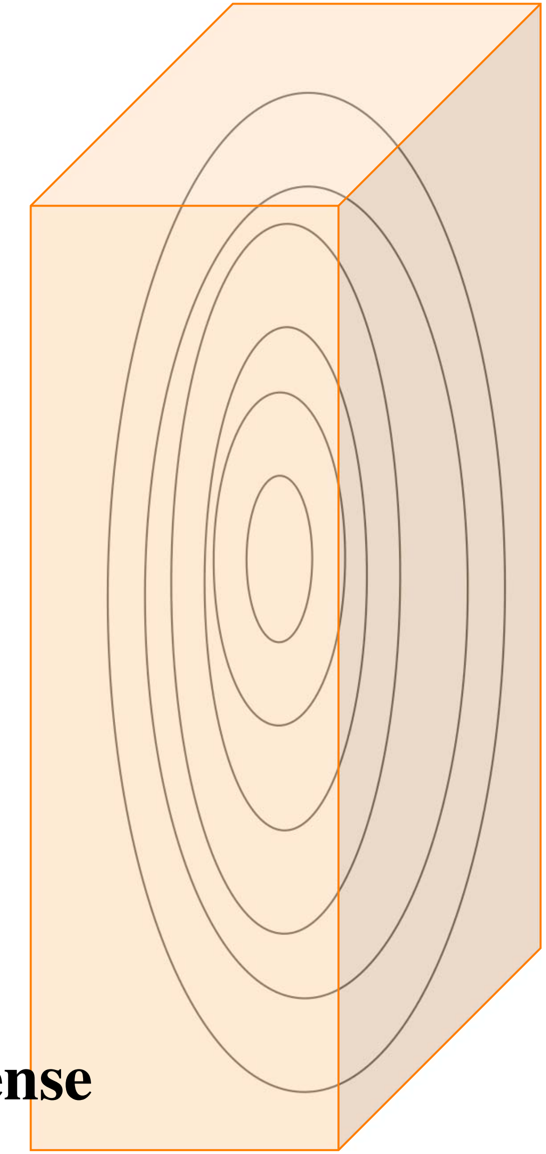


CRL

$n = 1 - \delta - i\beta$

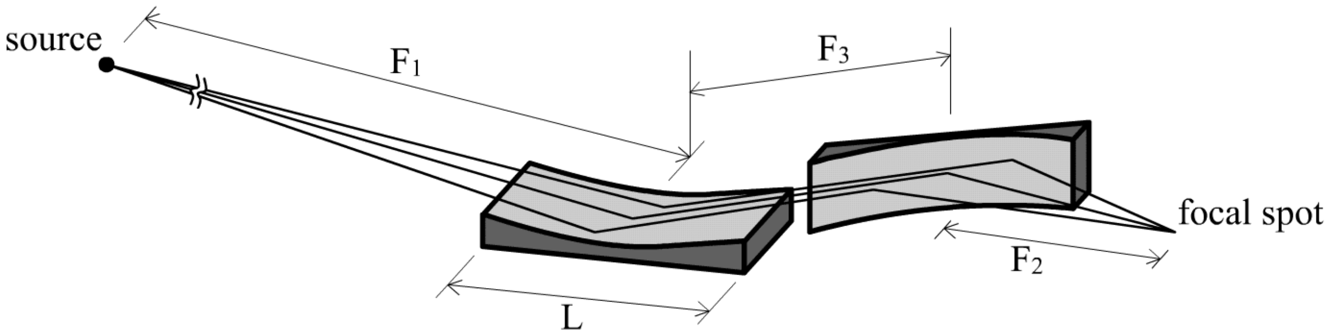


X-ray optics



Fresnel lense

K-B optics



With synchrotron radiation nm spot size achievable

Requirements for light element XRS

- Experiments must be performed in vacuum
- Excitation source with energies close to light element absorption edges
- Detector window Ultra thin polymer to have efficiency in the low energy region

Problems of photoninduced EDXRS of Low Z elements

1. Low intensity of fluorescence radiation:

$$I_K \propto I_0(E) \cdot \tau_K(E) \cdot \omega \cdot \varepsilon \cdot \Omega / 4\pi \cdot m$$

Low for anode materials of conventional X-ray tubes

generally low for low Z elements

special detector required with thin entrance window

2. Possibilities to improve

Synchrotron radiation

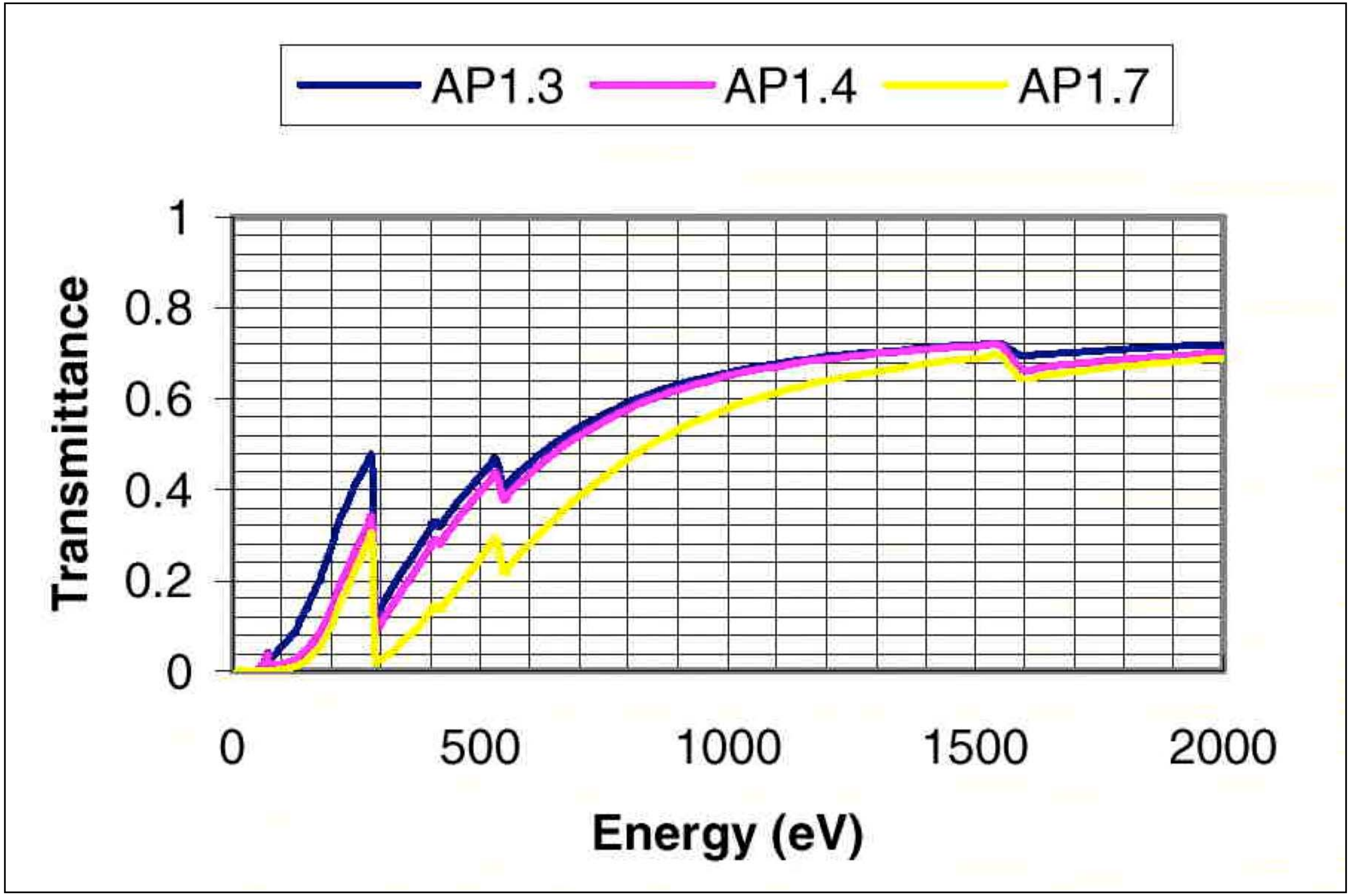
Fs Laser driven source

Special x-ray tubes:

- Low Z anodes
  - Si-K
  - W-M (Rigaku)
  - Al-K
  - Mo-L
- Windowless
- Optimized take-off Angle

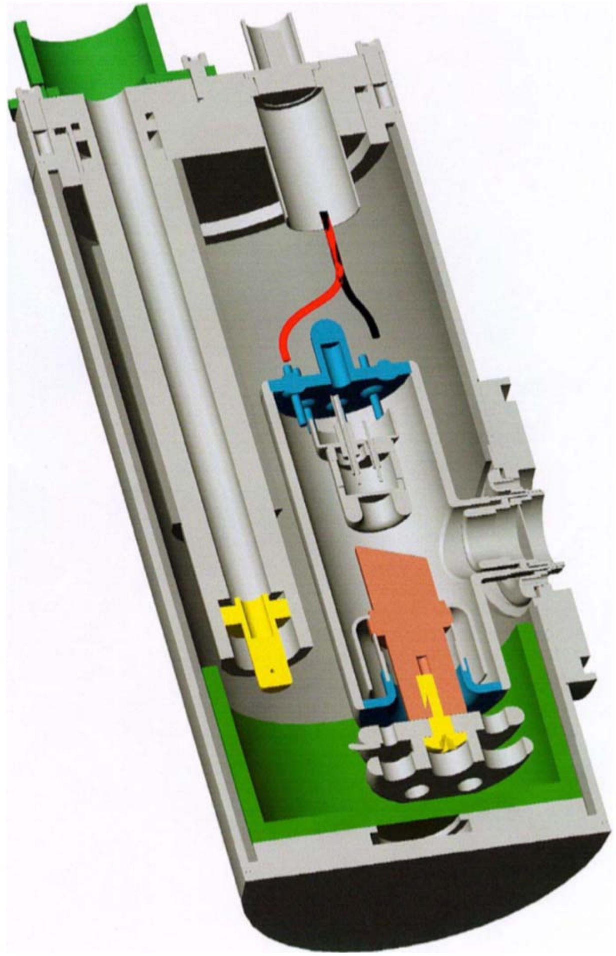
Detector Transmittance with Ultra Thin Window

300nm Polymer window



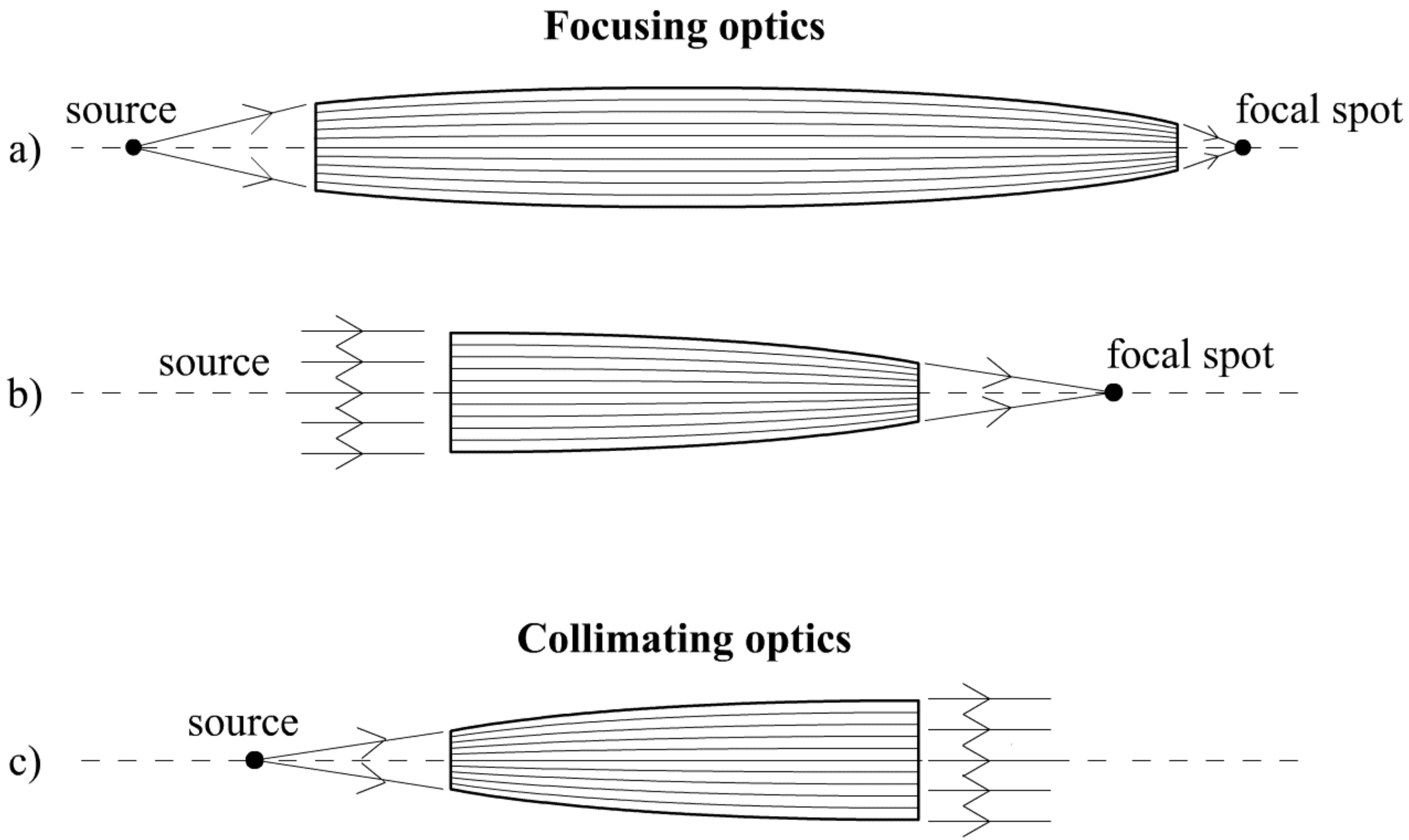
ATI µXRF Spectrometer components

- 50kV/1mA/50W X-ray tube Oxford „Apogee“
  - Mo Anode on HV
  - Cathode grounded
  - Microfocus (35 µm)
  - Thin exit window (125 µm-> Mo-L, 2,3 keV)
  - Air cooled



ATI µXRF Spectrometer

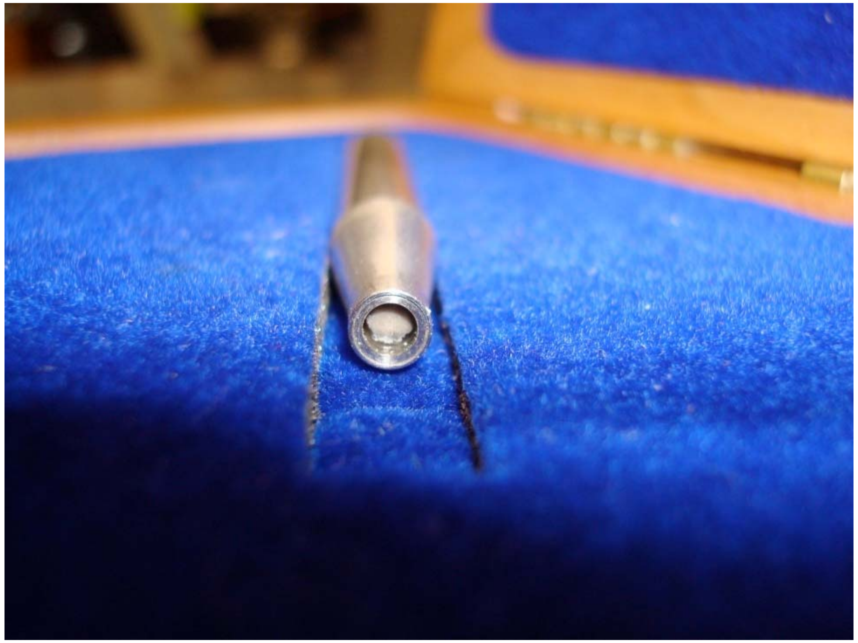
Polycapillary X-ray optic



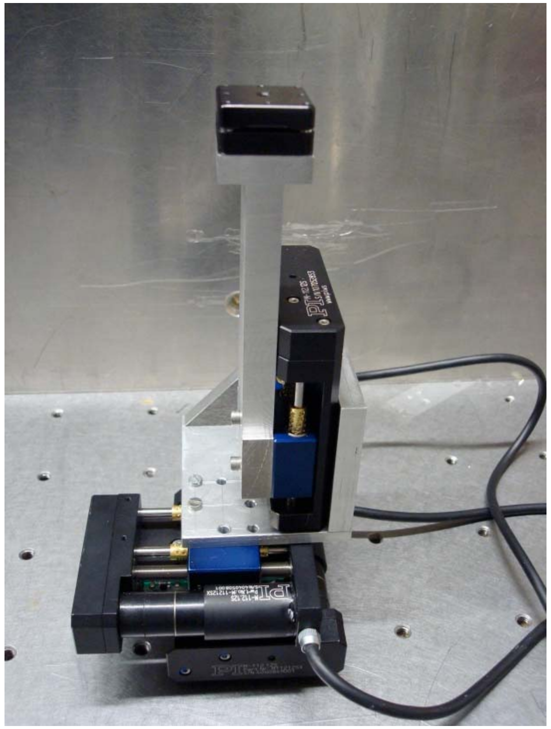
$$n = 1 - \delta - i\beta$$

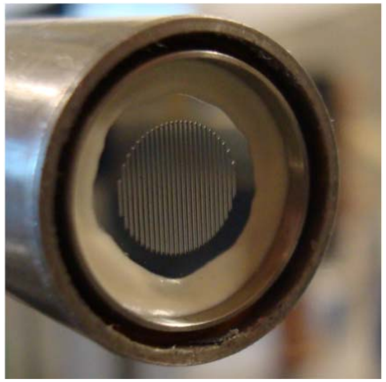
ATI µXRF Spectrometer components

- Polycapillary X-ray optics produced (XOS)
  - Spotsize 32µm @ Mo-Kα (17,44 keV)
  - Intensity gain 39-times (compared to pinhole of 50 µm)
  - 5-Axis adjustable



ATI µXRF Spectrometer components

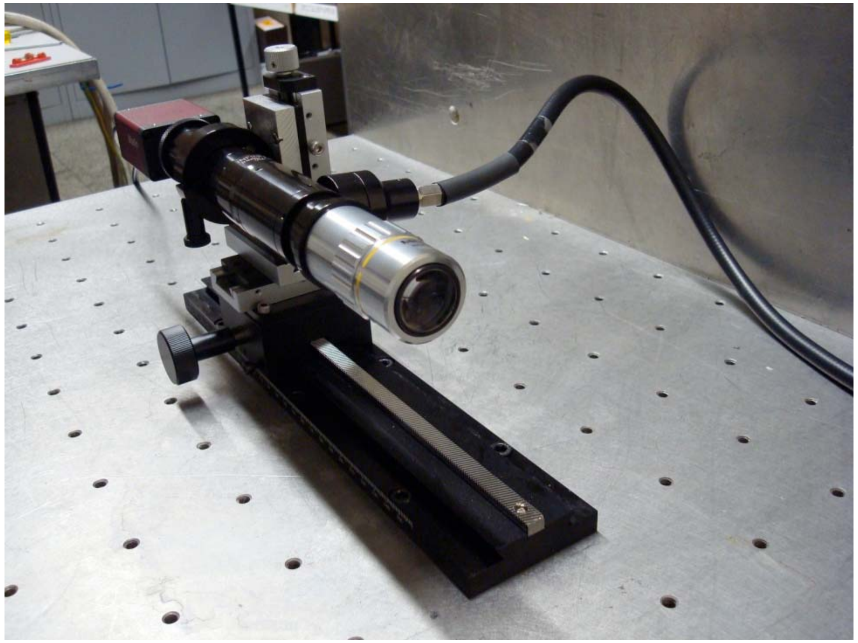




- Motorized sample table (x/y/z)
  - 3 PI M-112.12S 25 mm Translators
  - Magnetic „Kinematic Base“ for easy sample changer
- Si(Li) Detector 30 mm²
  - ultrathin Polymer window (300 nm)
  - Amptek MCA

ATI µXRF Spectrometer components

- 10x Optical Videomicroscope
  - Mitutoyo M Plan Apo
  - shortest depth resolution (3,5 µm)
  - Large working distance (33,5 mm)
  - Manually x/y/z adjustable

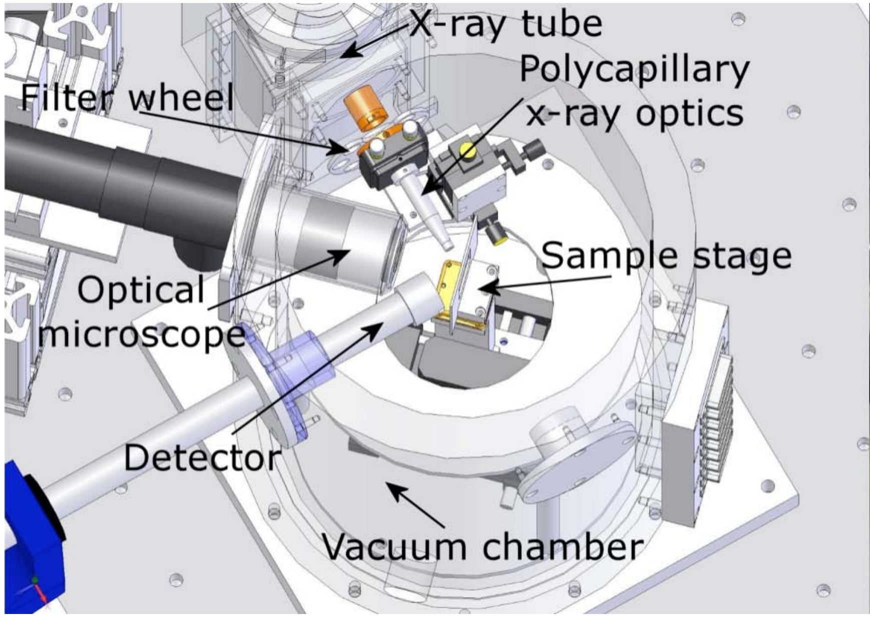


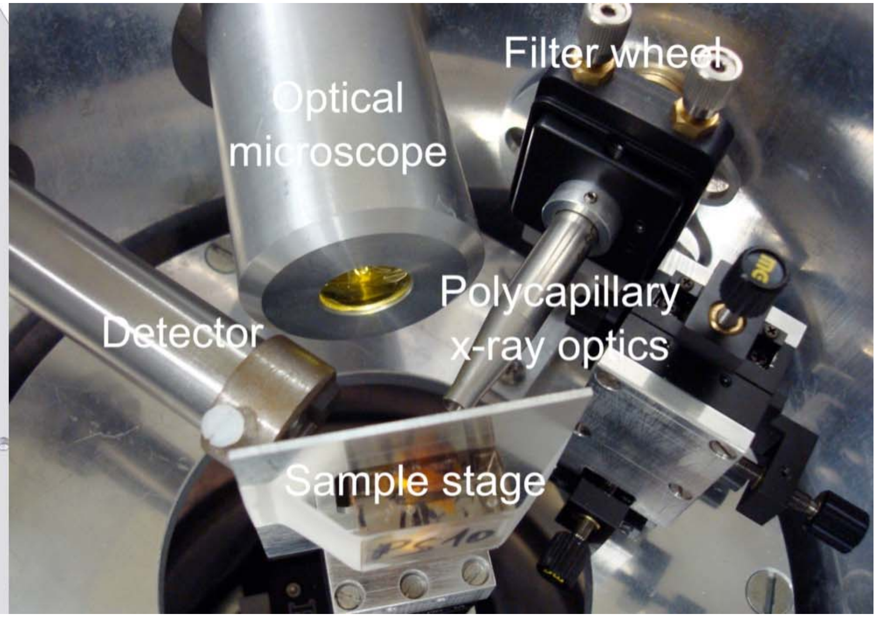
components

- Optional Primary- BeamFilter
  - Reduction of the background
  - Absorption of Mo-L Lines @ 2.3 keV (on S-K)
- Vacuumchamber
  - no absorption of Primary- and Fluorescence radiation in air

ATI µXRF Spectrometer

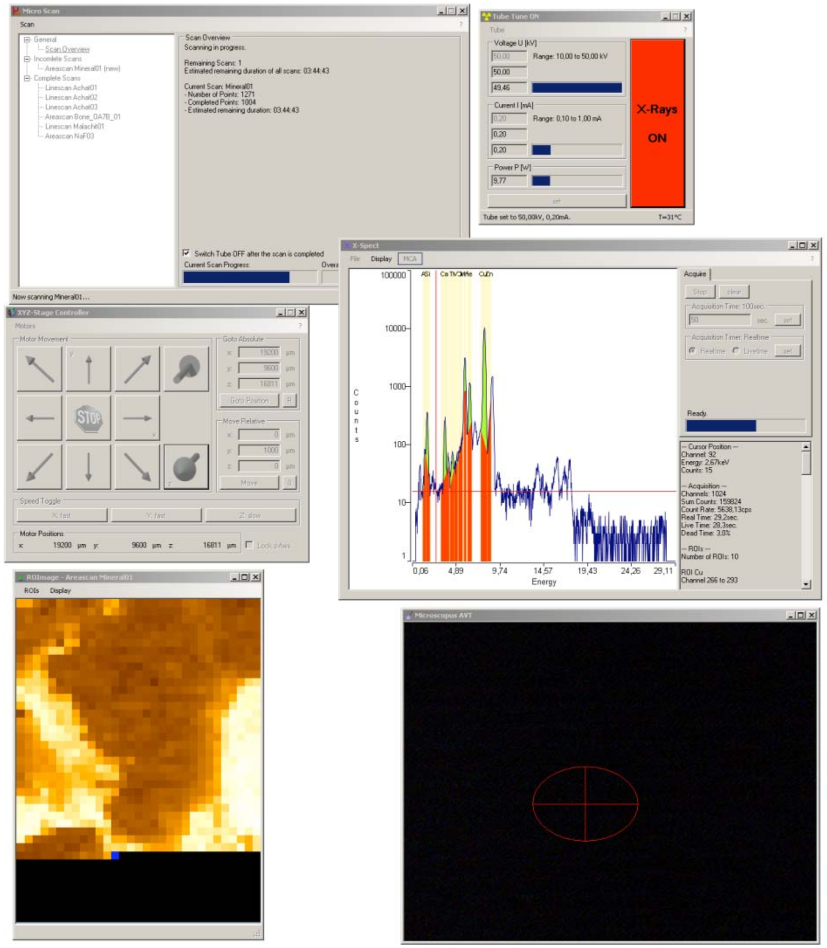
Design





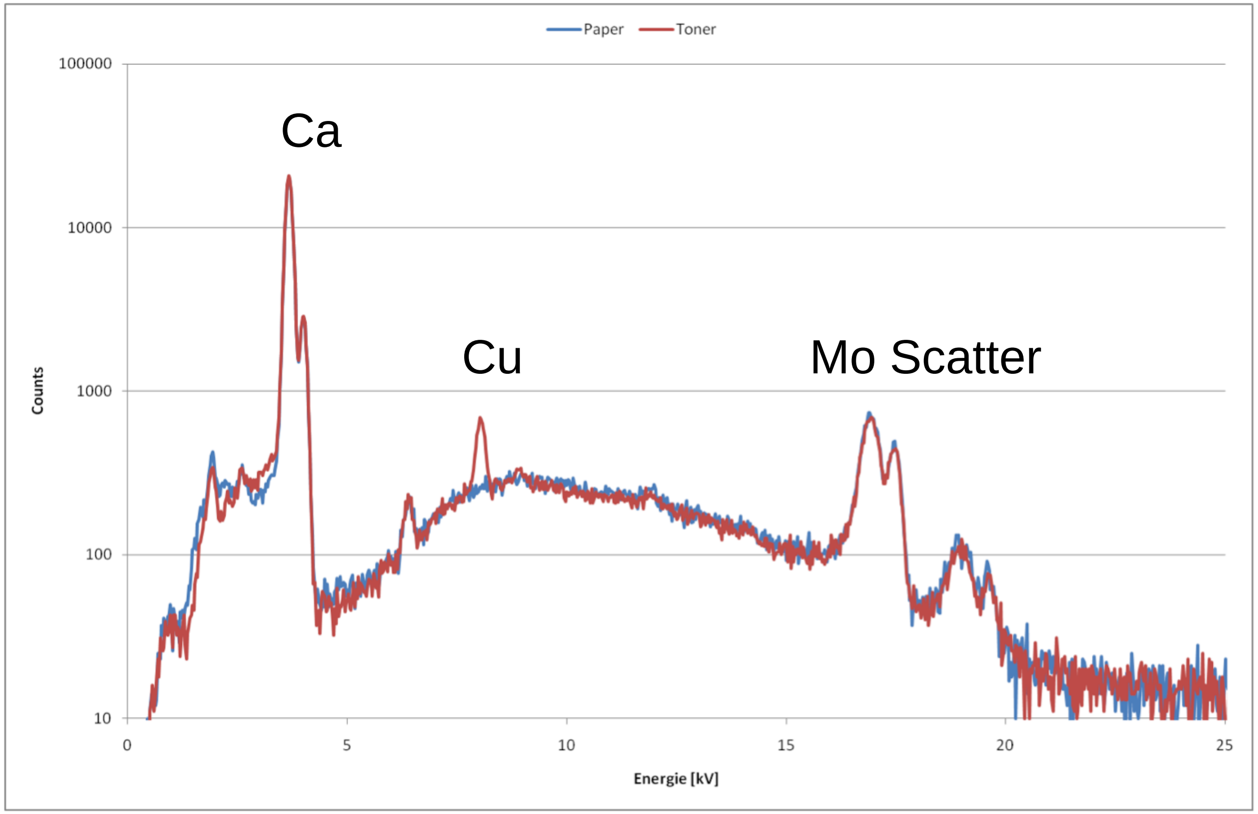
ATI µXRF Spectrometer

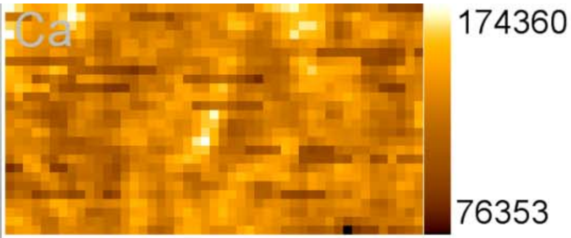
Software

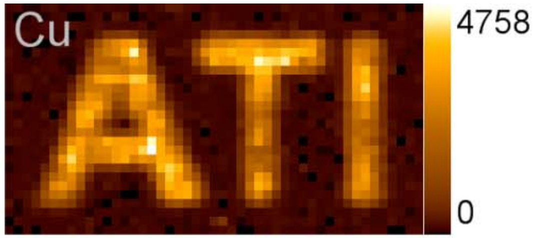


- Software for automatic Mapping of a sample
- Automatic Region of Interest (ROI) Spectrum evaluation with live-preview
- All Spectra stored for later evaluation with software packages as(AXIL,...)

Micro-XRF (µXRF)



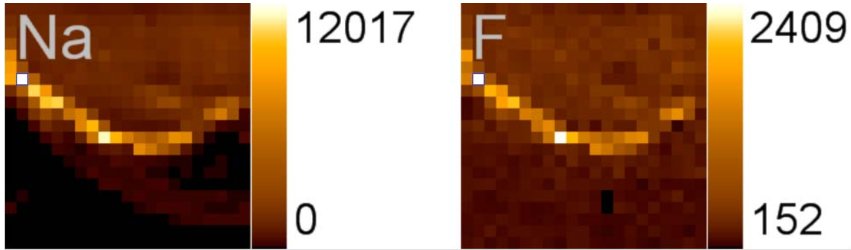


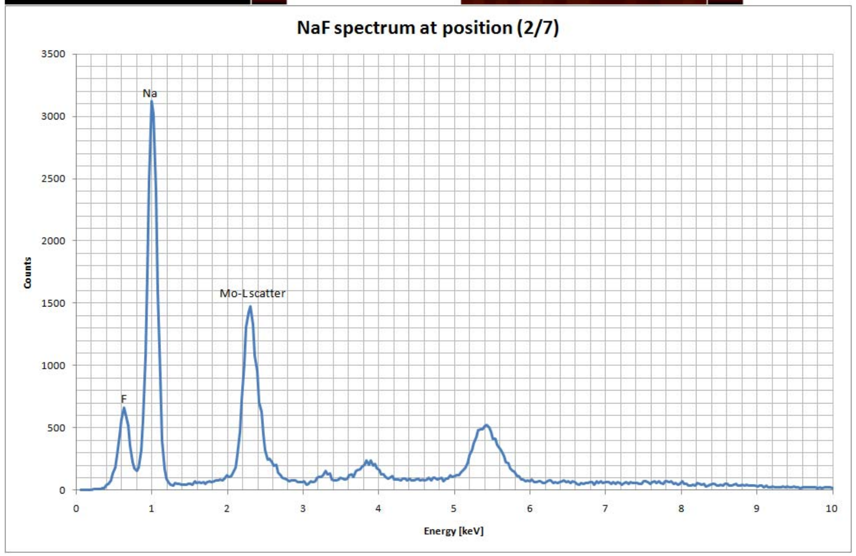


Name: ATI
Scan size: 47x26 pixel
Resolution: 40µm per pixel.
Counting time: 150sec. per pixel
Tube parameters: 50kV, 1mA

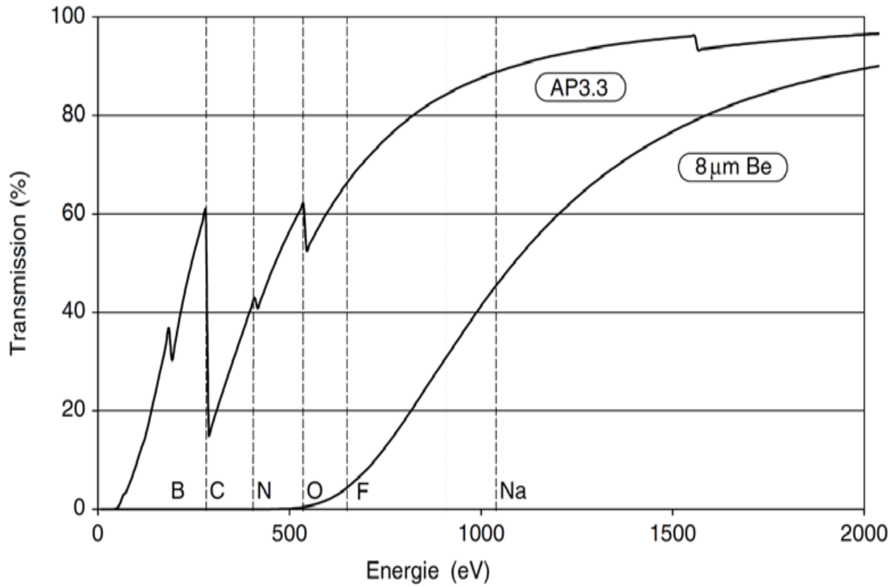
ATI µXRF Spectrometer

low-Z

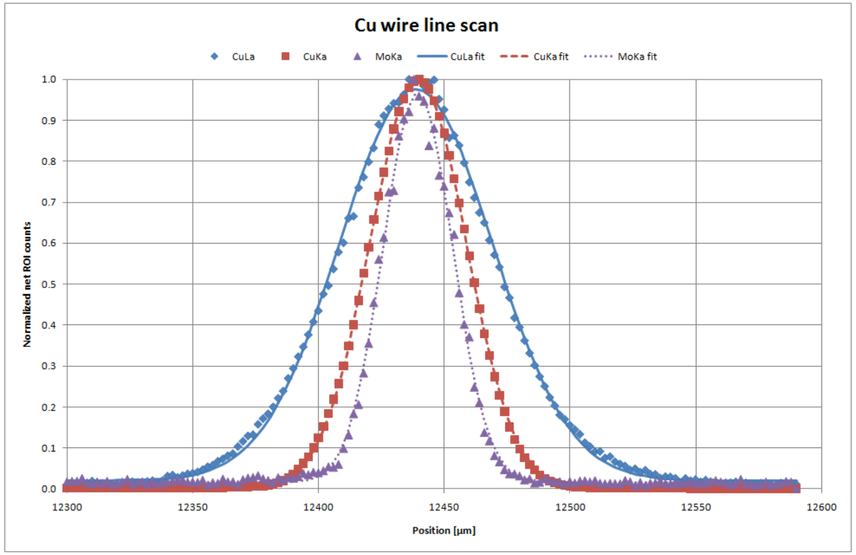




- Analysis of elements with low Z :
  - Mo-L excitation
  - Vacuum
  - UTW Detektor



Resolution



$$FWHM_{beam} \approx \sqrt{FWHM_{profile}^2 - d_{wire}^2}$$

- Determination of minimum beam diameter with a 10µm Cu wire:
  - @ Mo-Kα (17,44 keV): 31 µm
  - @ Cu-K (8,98 keV): 44 µm effektiv
  - @ Cu-L (1,1 keV): 71 µm effektiv

LLD

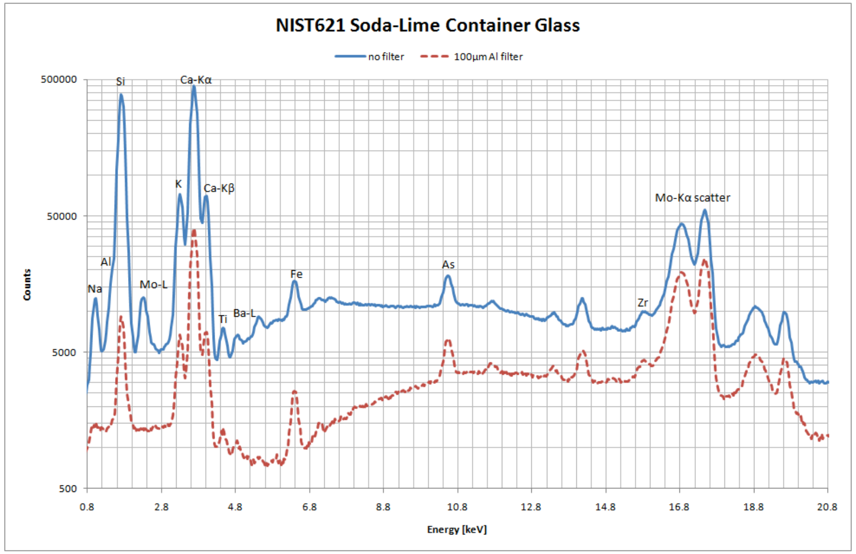
Determination of lower limits of detection by means of thin foils:

$$m = \frac{\pi}{2} d^2 x \rho \qquad LLD = m \frac{3\sqrt{N_B}}{N_N}$$

Sample - beam - info			Operating conditions			LLD		
Element	Beam diameter [µm]	Thickness of foil [µm]	V [kV]	I [mA]	Filter	single Spot [pg]	Areal mass density [µg/cm²]	Atomic area density [Atoms/cm²]
Ni	44	4	50	0,1	100µm Al	11	0,5	5E15
Ni	44	4	50	0,4	100µm Al	13	0,6	6E15
Ni	44	4	50	1	100µm Al	14	0,7	7E15
Zn	44	4	50	0,4	100µm Al	10	0,5	4E15
Al	70	0,8	50	1	100µm Al	102	1,9	4E16
Al	70	0,8	50	1	no	8	0,1	3E15
Al	70	0,8	20	1	no	7	0,1	3E15
Au	40	1	50	0,4	100µm Al	25	1,4	4E15

ATI µXRF Spectrometer

Determination of (LLD) using Standard Reference Material NIST621 Soda-Lime Container Glass:



S. Smolek, C. Streli, N. Zoeger, P. Wobrauschek, Improved Micro-XRF Spectrometer for Light Element Analysis, REVIEW OF SCIENTIFIC INSTRUMENTS **81**, 053707 2010

Project supported by “Innovative Projekte” of TU Wien

LLD

Element	LLD [ppm]	LLD (100µm Al filter) [ppm]
Na	878	36409
Al	115	4898
Si	95	2513
K	22	148
Ca	15	81
Ti	8	17
Fe	5	6
As	4	5
Zr	2	4
Ba	54	145

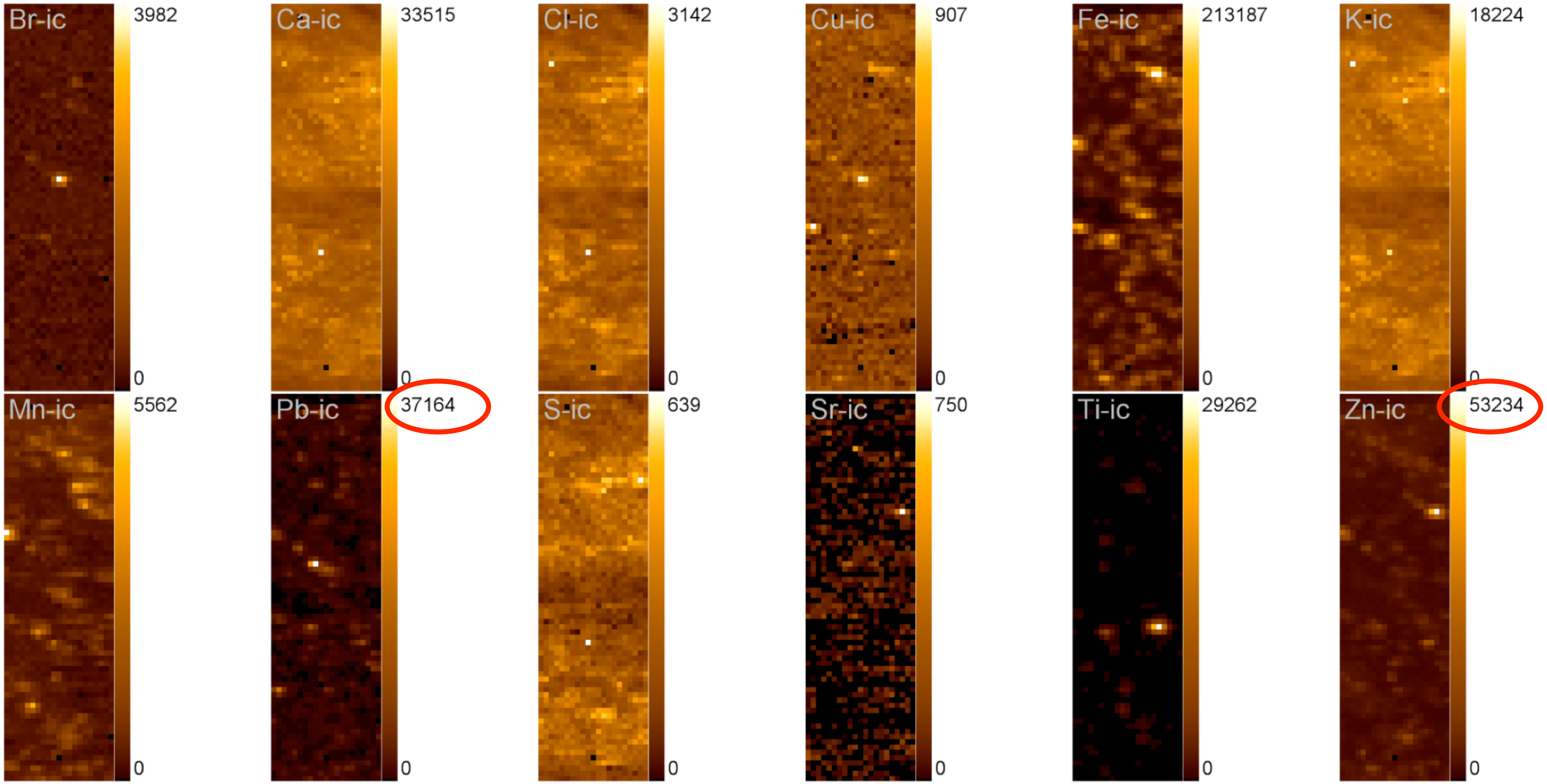
$$LLD = m\frac{3\sqrt{N_B}}{N_N}$$

Phytoremediation

- Phytoremediation: Extraction of metallic contaminations from soil by plants
- Determination of the Elemental distribution in the leaves of *Dittrichia viscosa* growing in the tail region of the mines
- Comparison with a control group

In collaboration with E. Marguí, Laboratory of X-ray Analytical Applications (LARX).
Institute of Earth Sciences "Jaume Almera", CSIC. Solé Sabarís s/n. 08028 Barcelona, Spain

Phytoremediation

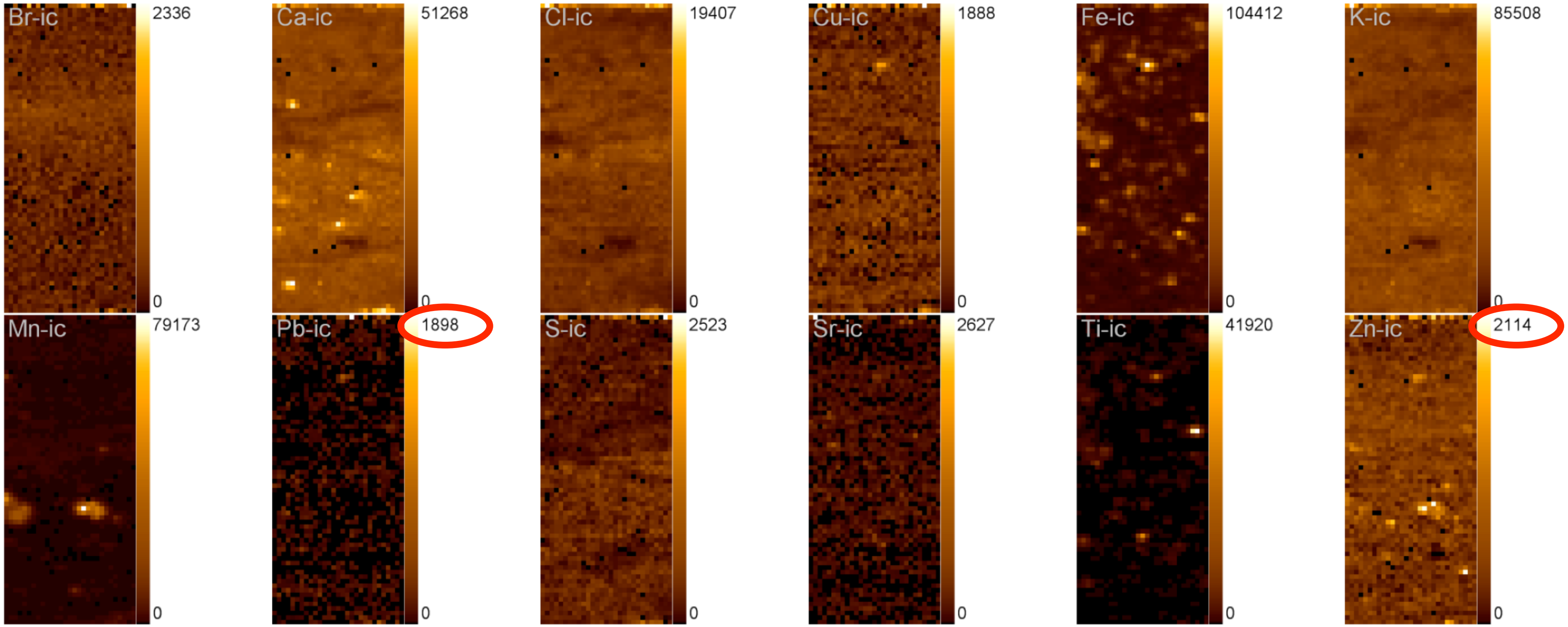


Name: Leaf04_
Scan size: 21x74 pixel
Resolution: 50µm per pixel.
Counting time: 50sec. per pixel.
AXIL fit, dead time corrected, divided by inc scatter.

From mining activites (Pb, Zn)

ATI µXRF Spektrometer

Phytoremediation

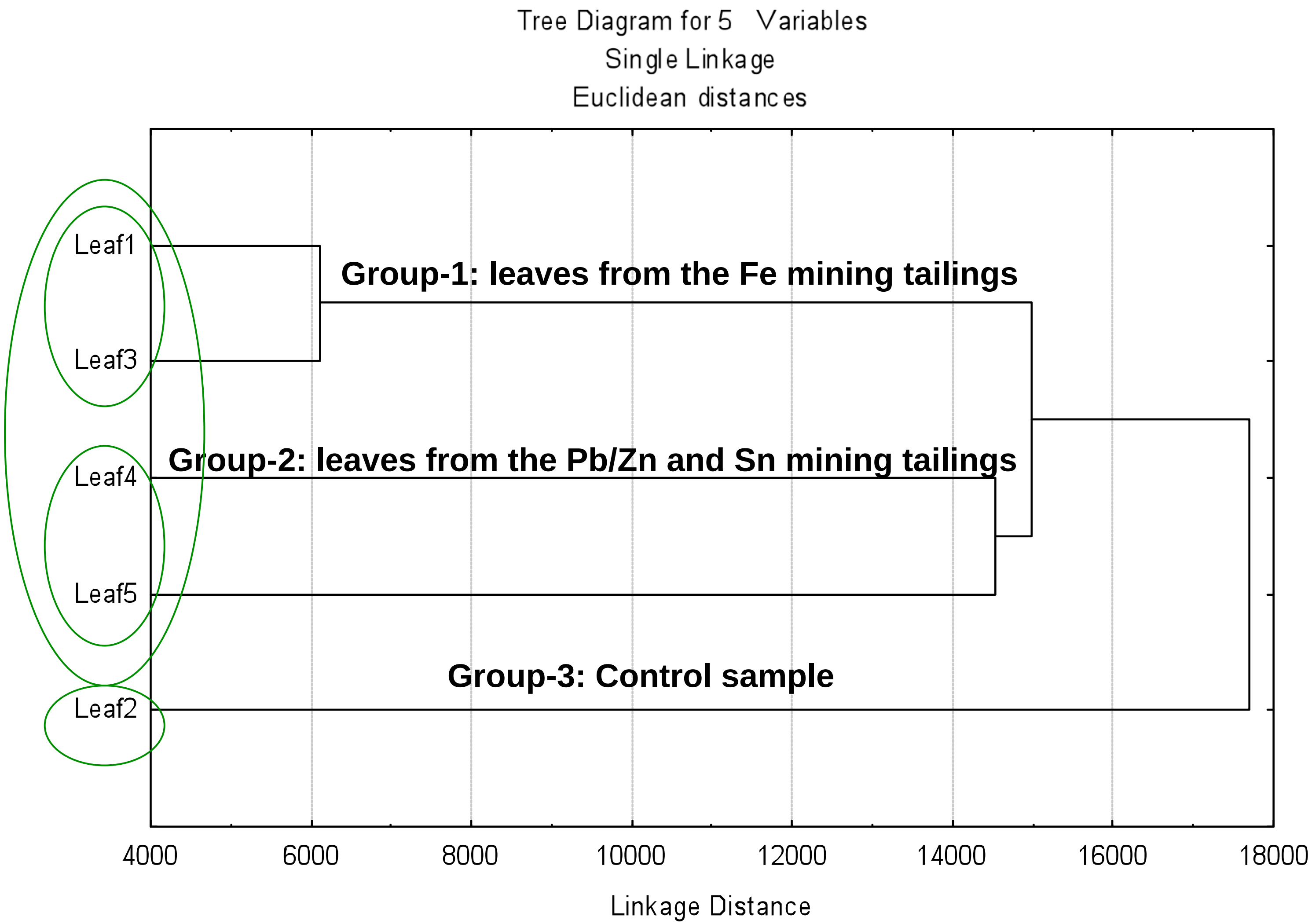


Name: Leaf02_
Scan size: 29x68 pixel
Resolution: 50µm per pixel.
Counting time: 50sec. per pixel.
AXIL fit, dead time corrected, divided by inc scatter.

Control group

ATI µXRF Spectrometer

Phytoremediation



Phytoremediation

- Metals accumulate in „Hot-Spots“
- Significant higher Intensities in leaves from contaminated regions compared to the control group
- Correlations of metals found from contaminations in leaves

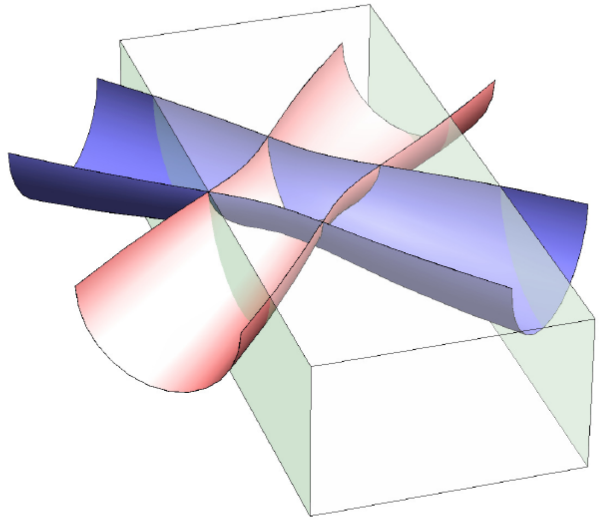
ATI µXRF Spectrometer

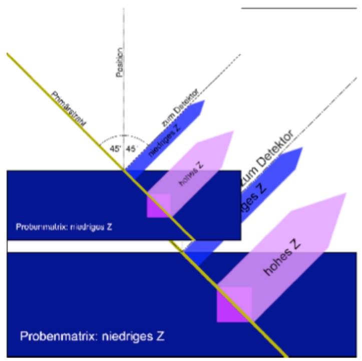
future aspects

- confocale Extension of the Spectrometer
- Determination of the effective Spotsize (Volume) for different Elements
- Determination of the Transmissionfunction of Polycapillaries
- Quantificationmodels
- Measurement of various samples open projects (ANNA, …)

Confocal µXRF

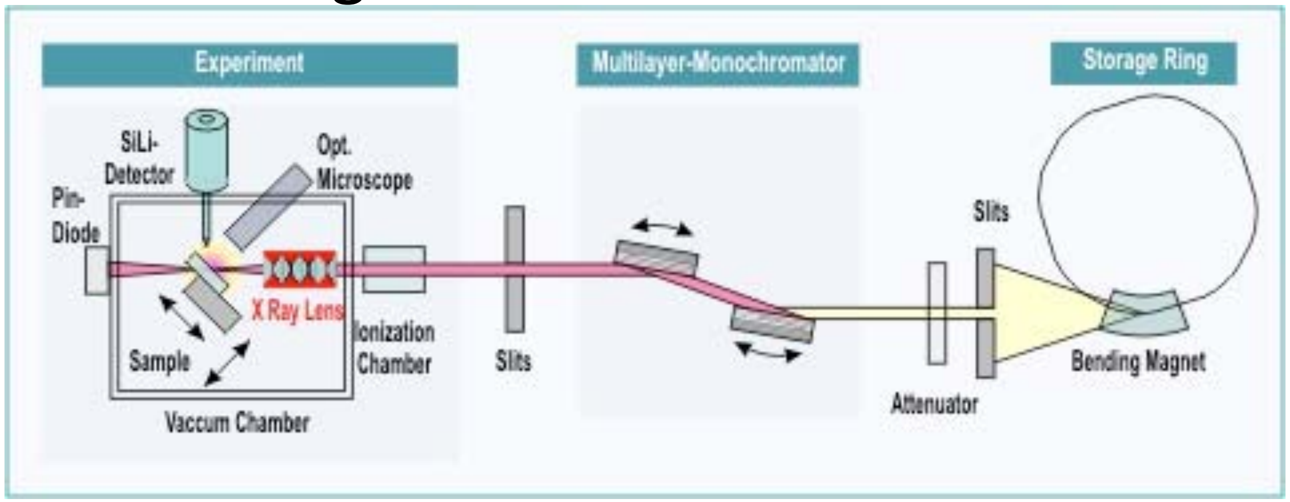
- Measuring in a defined Micro volume
- 3D Analysis
- Information depth for thick samples solved as the actual depth is known





Synchrotron radioation induced µXRF (SR-µXRF)

- Synchrotron radiation: high Brillance, natural collimation, linear polarised;
- Monochromatization -> low background, better detection limits
- Small beam dimensions (few µm even 30-100 nm), short measuring time



ANKA
Karlsruhe
Germany

SR-µXRF

Sr in bone

Levels and spatial distribution of trace elements in trabecular bone following strontium treatment in calcium deficient rats

B. Pemmer[1], F. Meirer[1,2], J. G. Hofstaetter[3,4], S. Smolek[1], P.Wobrauschek[1], R. Simon[5], R. K. Fuchs[6,9],

M. R. Allen[6], K. W. Condon[6], S. Reinwald[6], D. McClenathan[7], B. Keck[7], R. J. Phipps[7], D. B. Burr[6,9], P. Roschger[3], E. Paschalis[3], K. Klaushofer[3], C. Streli[1]

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[4] Department of Orthopaedic Surgery, Vienna General Hospital, Medical Univ. of Vienna, 1090 Vienna, Austria

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[7] Procter and Gamble Pharmaceuticals, Mason, OH, USA

[8] Department of Physical Therapy, School of Health and Rehabilitation Sciences, Indiana University, Indianapolis, IN, USA

[9] Department of Orthopaedic Surgery, Indiana University School of Medicine, Indianapolis, IN, USA

SR-µXRF

Sr in bone

- Sr treatment in cases of Osteoporosis to improve production of bone material
- Where is Sr STORED IN BONE? (Comparison with qBEI electron backscatter images)
- Influence of diet Ca levels on Sr uptake?
- 5 Groups:
  - Group 1: untreated Control group
  - Group 2: low Sr Dose, normal Ca diet
  - Group 3: low Sr Dose, low Ca diet
  - Group 4: high Sr Dose, normal Ca diet
  - Group 5: high Sr Dose, low Ca diet

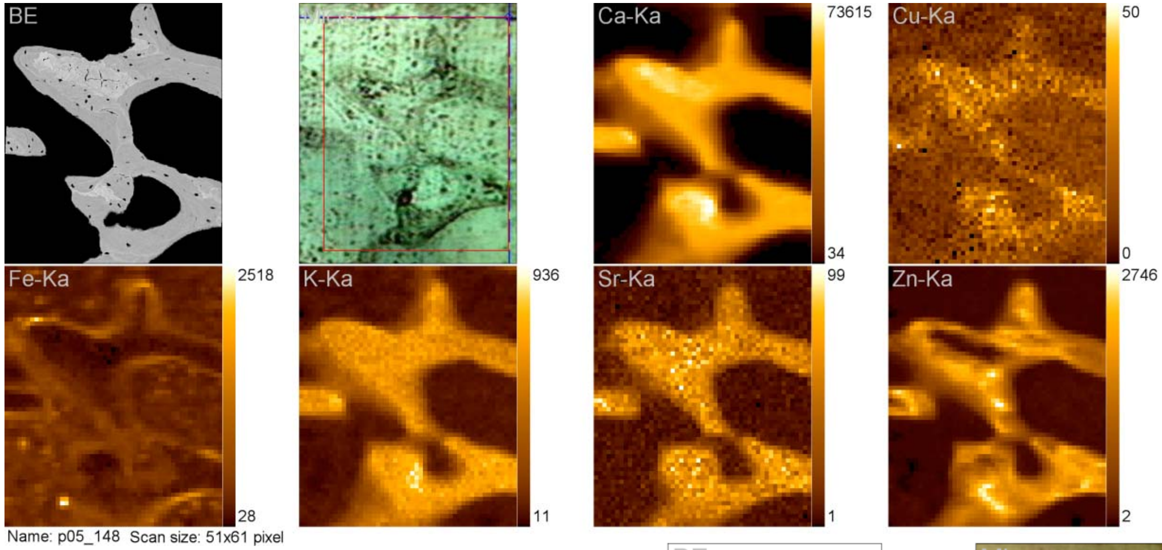
SR-µXRF

Sr in bone

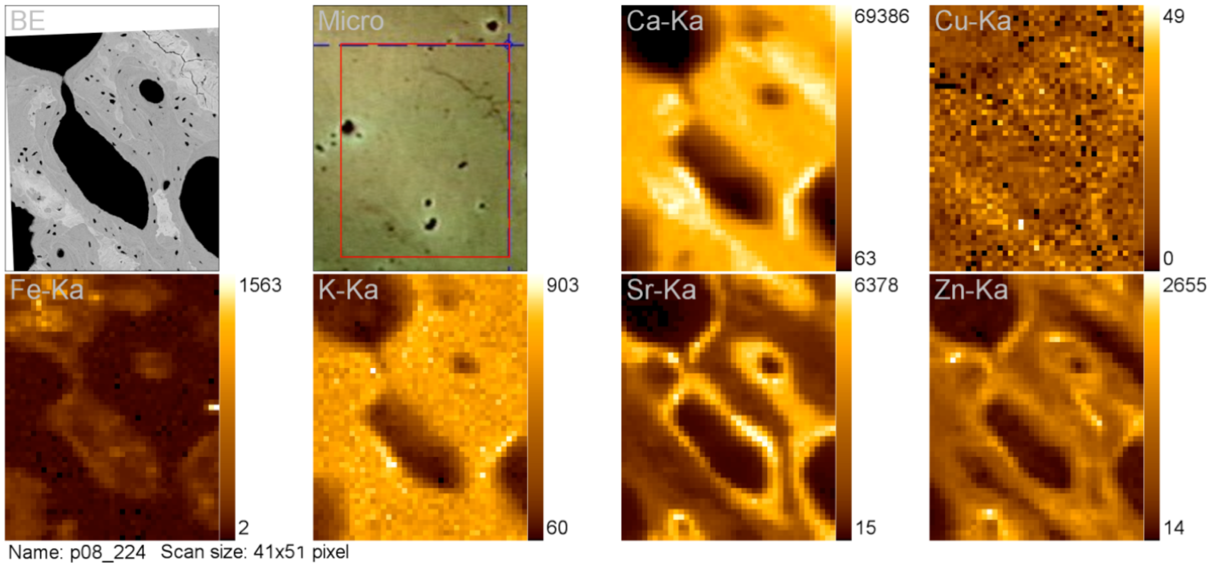
- Confocal setup FLUO, ANKA
- 2 polycapillary half lenses
- Resolution 10 x 10 x 12 μm^3 @ Sr-Kα (14,2 keV)
- Excitation energy 17,7 keV with Multilayer
- 50 mm^2 SDD Detector (Vortex)
- 1 s Measuring time per Pixel

SR-µXRF

Sr in Bone



Untreated
Control group

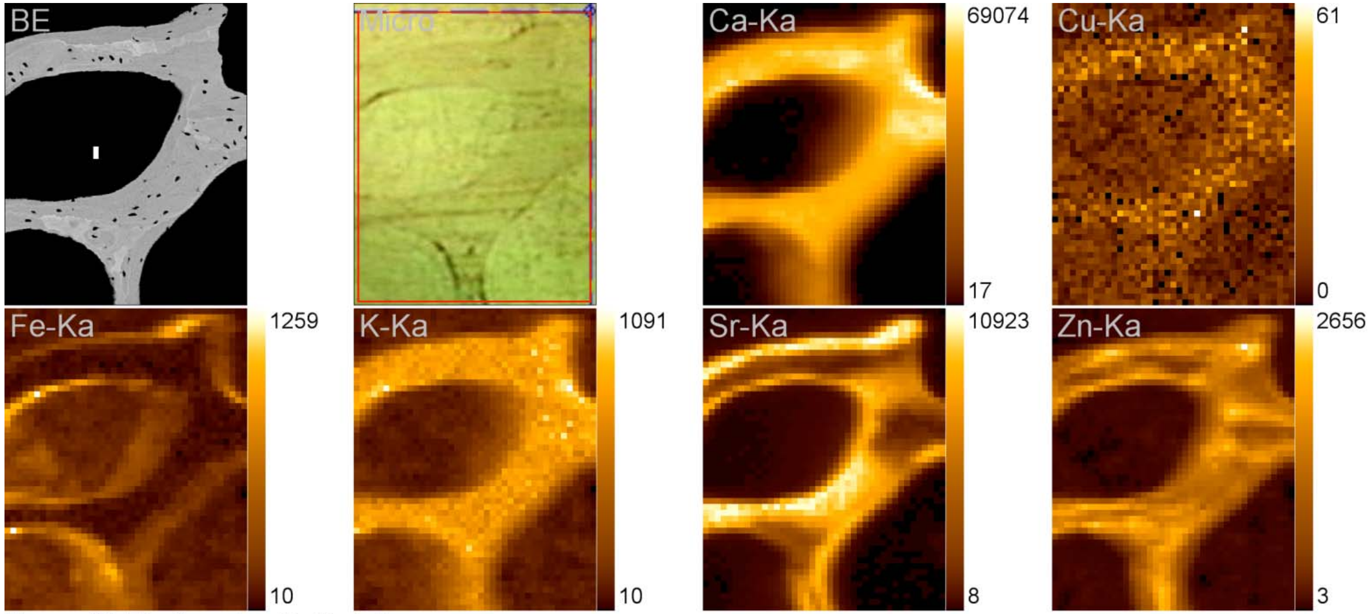


Low Sr Dose,
low Ca
diet

SR-µXRF

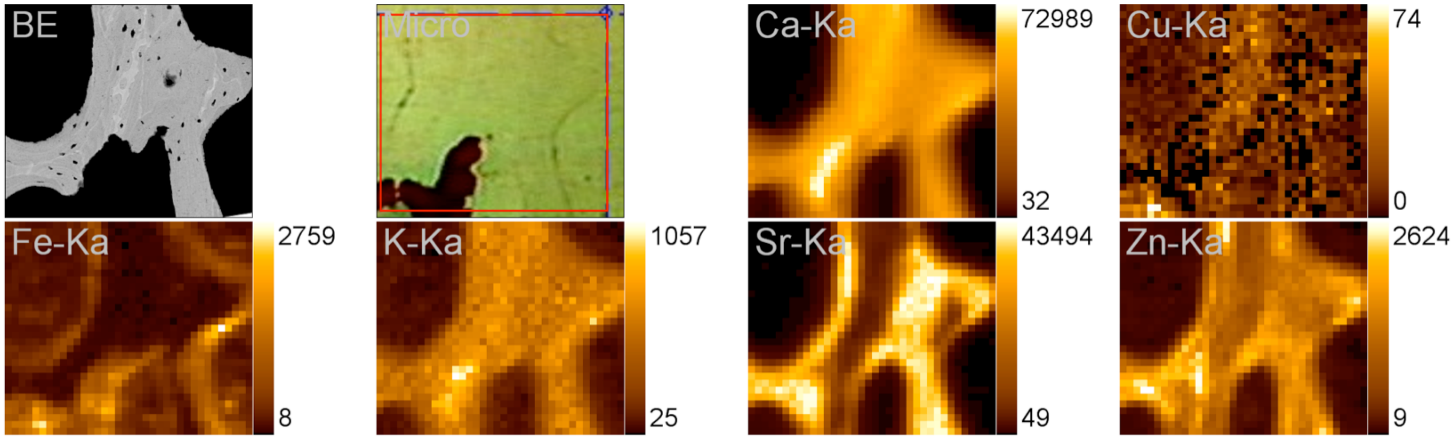
Sr in bone

High Sr Dose, normal Ca diet



Name: p01_98 Scan size: 41x51 pixel

High Sr Dose, deficient Ca diet

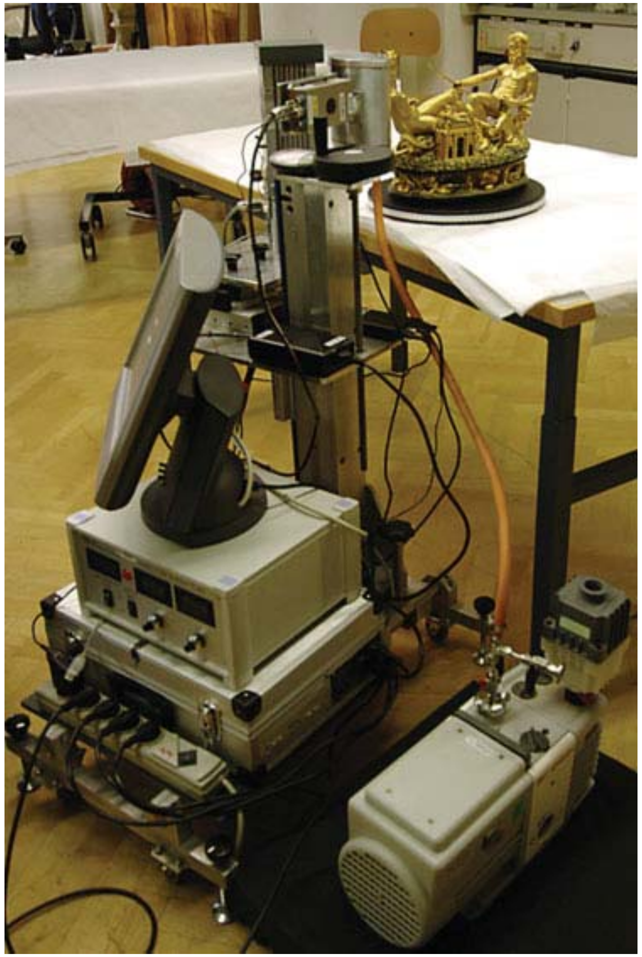


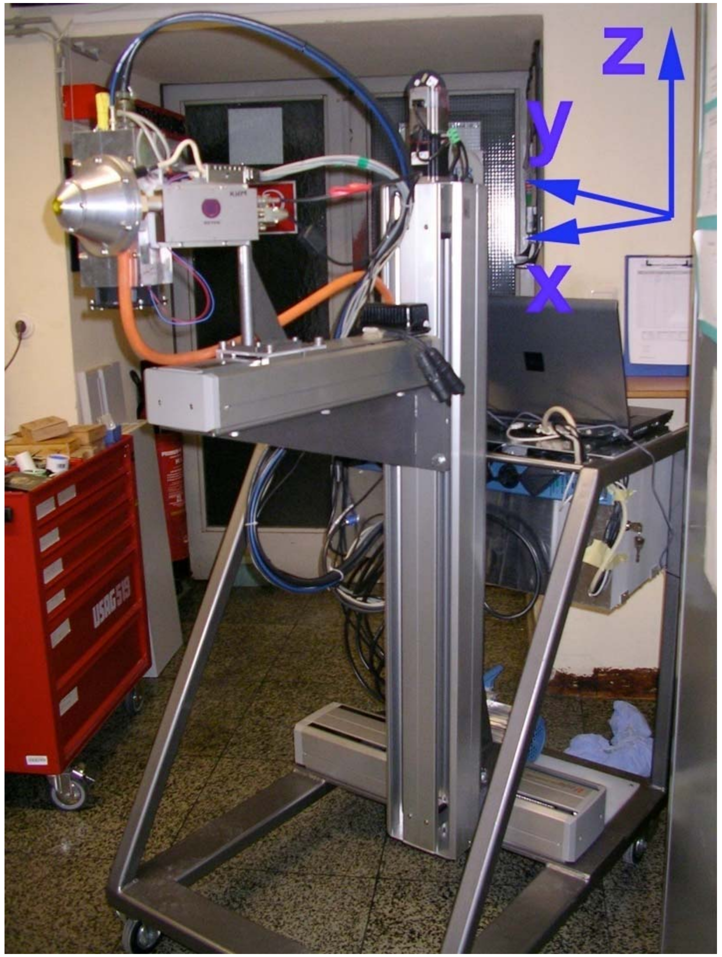
Name: p02_112 Scan size: 36x31 pixel

Sr in bone Conclusions

- Sr is located and built in the new bone matrix
- Almost no Sr in old bone
- The groups could be successfully correlated by their ratios Sr/(Sr+Ca) .
- Highest Sr countrates at high Sr Dose and deficient Ca diet -> Ca deficient diet leads to high incorporated Sr.

Portable ART analyzer
(PART I & II)



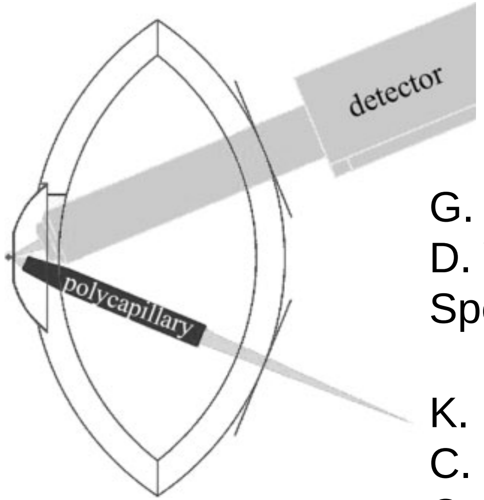


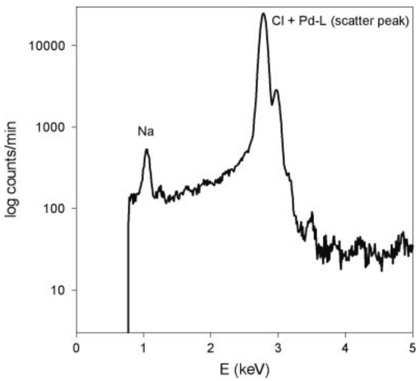
In cooperation with Art History Museum Wien and IAEA

PART I

Saliera B. Cellini 1540-43 produced

- 50kV/1mA Pd x-ray tube
- Polycapillary x-ray optic (160µm) or collimator (1mm)
- Ketek SDD, $10mm^2$, 8µm Be
- Vacuum chamber



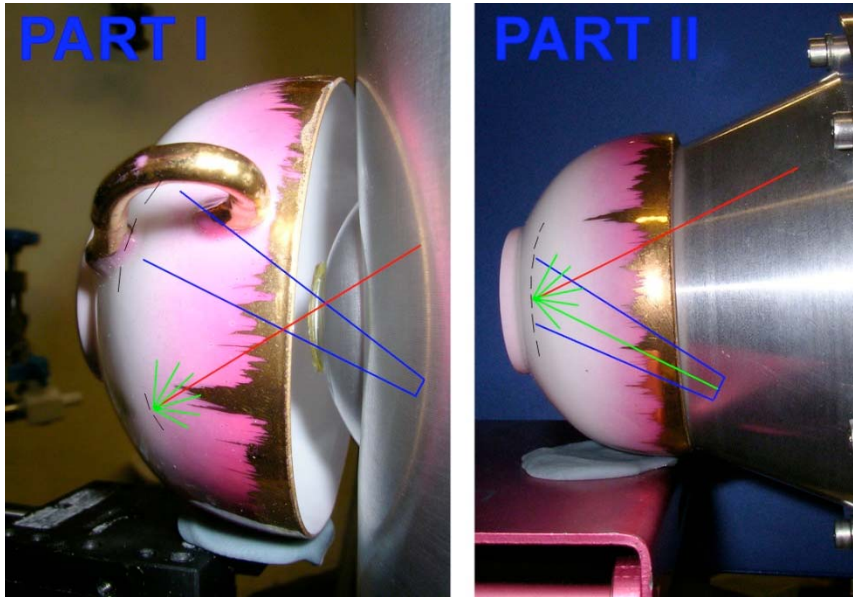


G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, S. Bamford, Spectrochimica Acta Part B 62 (2007) 1252 –1256

K. Uhlir, M. Griesser, G. Buzanich, P. Wobrauschek, C. Streli, D. Wegrzynek, A. Markowicz, E. Chinea-Cano, X-Ray Spectrom. 2008; 37: 450–457

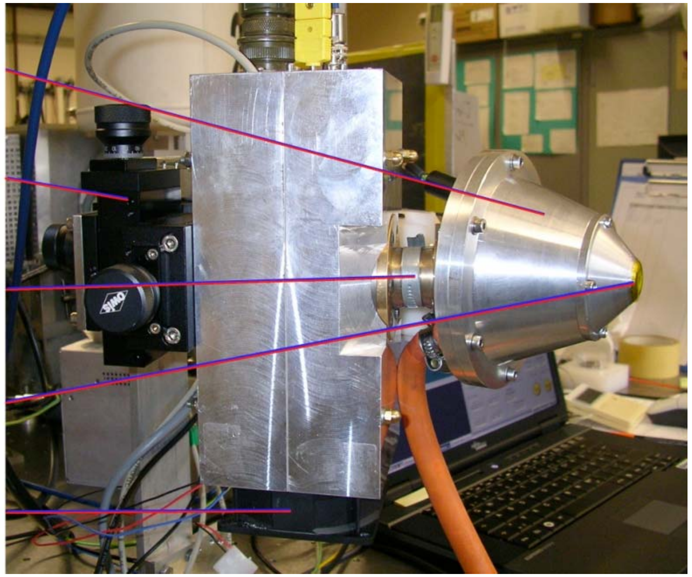
PART I: Problems

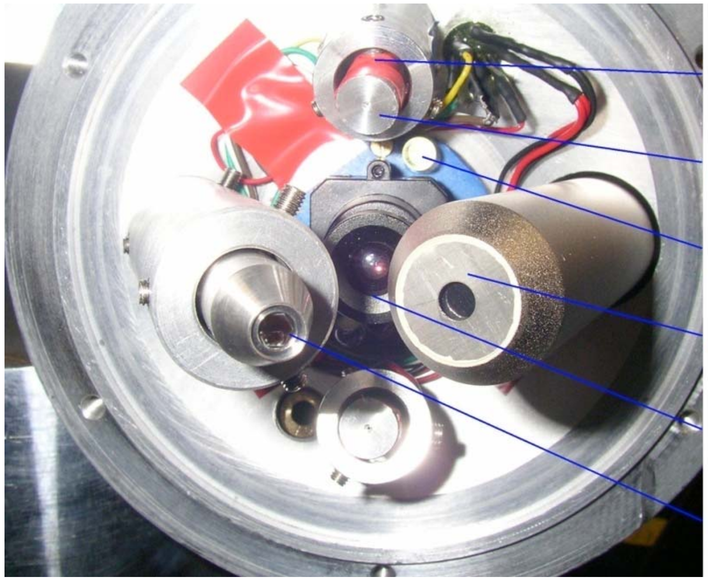
- Too large shaped Vacuum chamber – not all interesting point on the object could be reached.
- Problems measuring paintings due to base holder of the chamber.
- Kapton™ window is bending towards inside and increases air gap, light elements as Na absorption in air.
- Laserspots were too large for 150 µm optic undefined position.



-> solution: New design PART II

PART II: Components

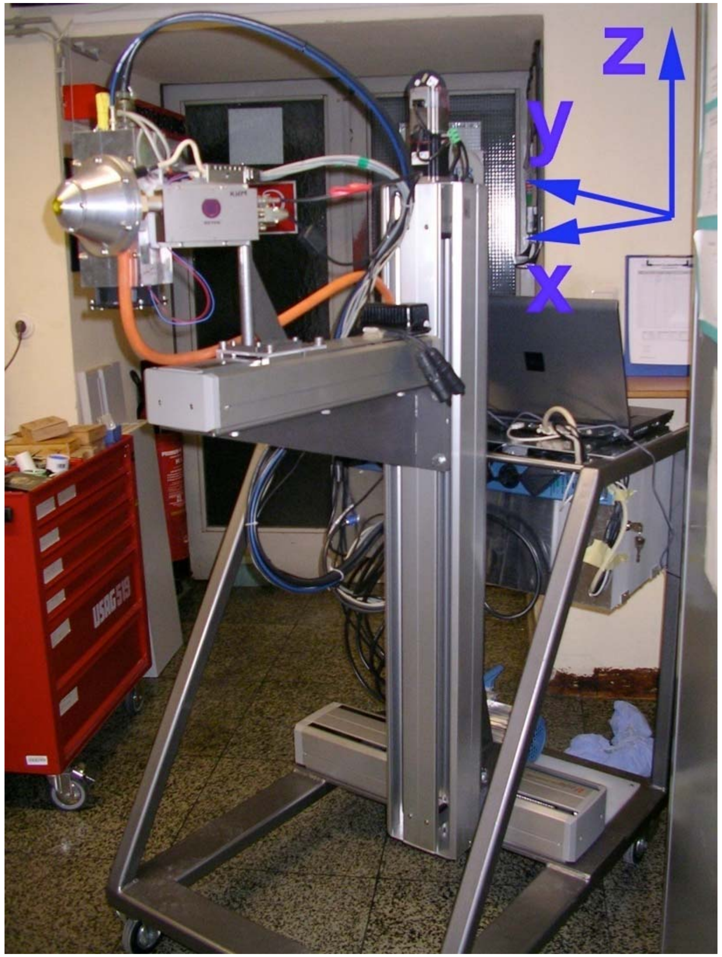




- Exchangeable x-ray tube (Mo /Cr) 50W
- Polycapillary x-ray optic (XOS), 145µm for Cr-Kα (5.41 keV)
- Ketek SDD, 20mm², 8µm Be
- Vacuumchamber

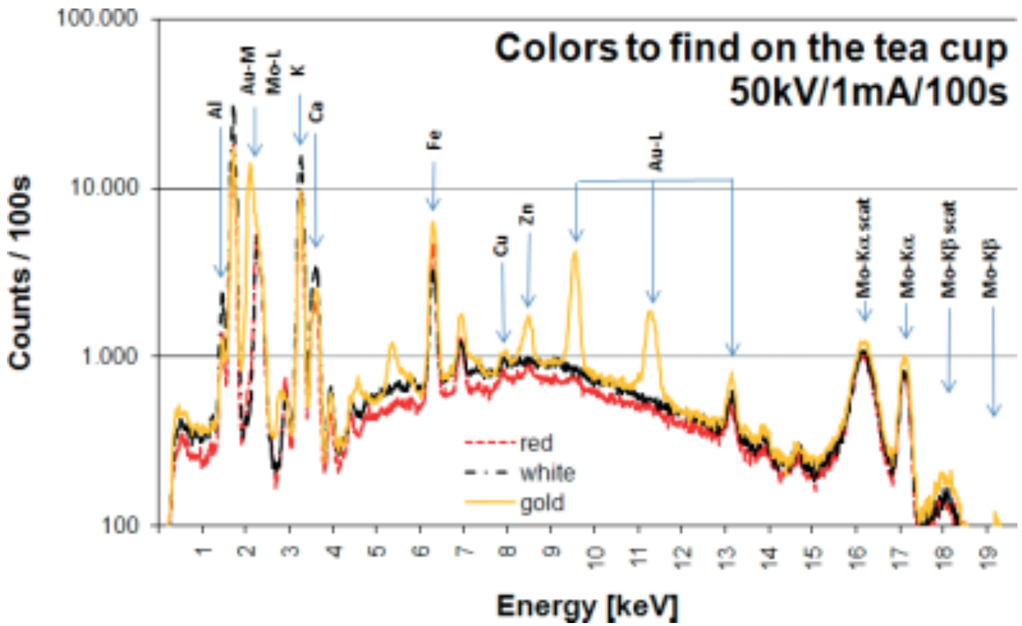
G. Buzanich, P. Wobrauschek, C. Streli, A. Markowicz, D. Wegrzynek, E. Chinea-Cano, M. Griesser and K. Uhlir, X-Ray Spectrom. 2009; 39: 98-102

PART II: Setup



- Spectrometer motorized positioning (200 mm / 300 mm / 1000 mm depth x width x Height)
- Stable design of stand
- User friendly control

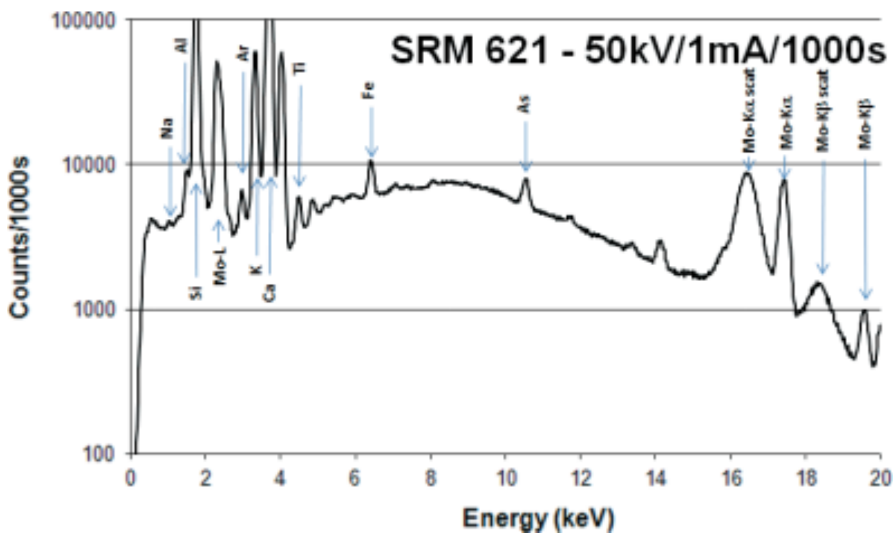
PART II: Tea cup



- Elemental composition of various colors of the tea cup:
  - Whíte: base material
  - Red: Higher Fe Gehalt, probably red Ockre. Small amounts of Zn point to a cup of the last century.
  - yellow: Gold

PART II: Detection limits LLD

Determination of detection limits (LLD) with NIST621 Soda-Lime Container Glass:



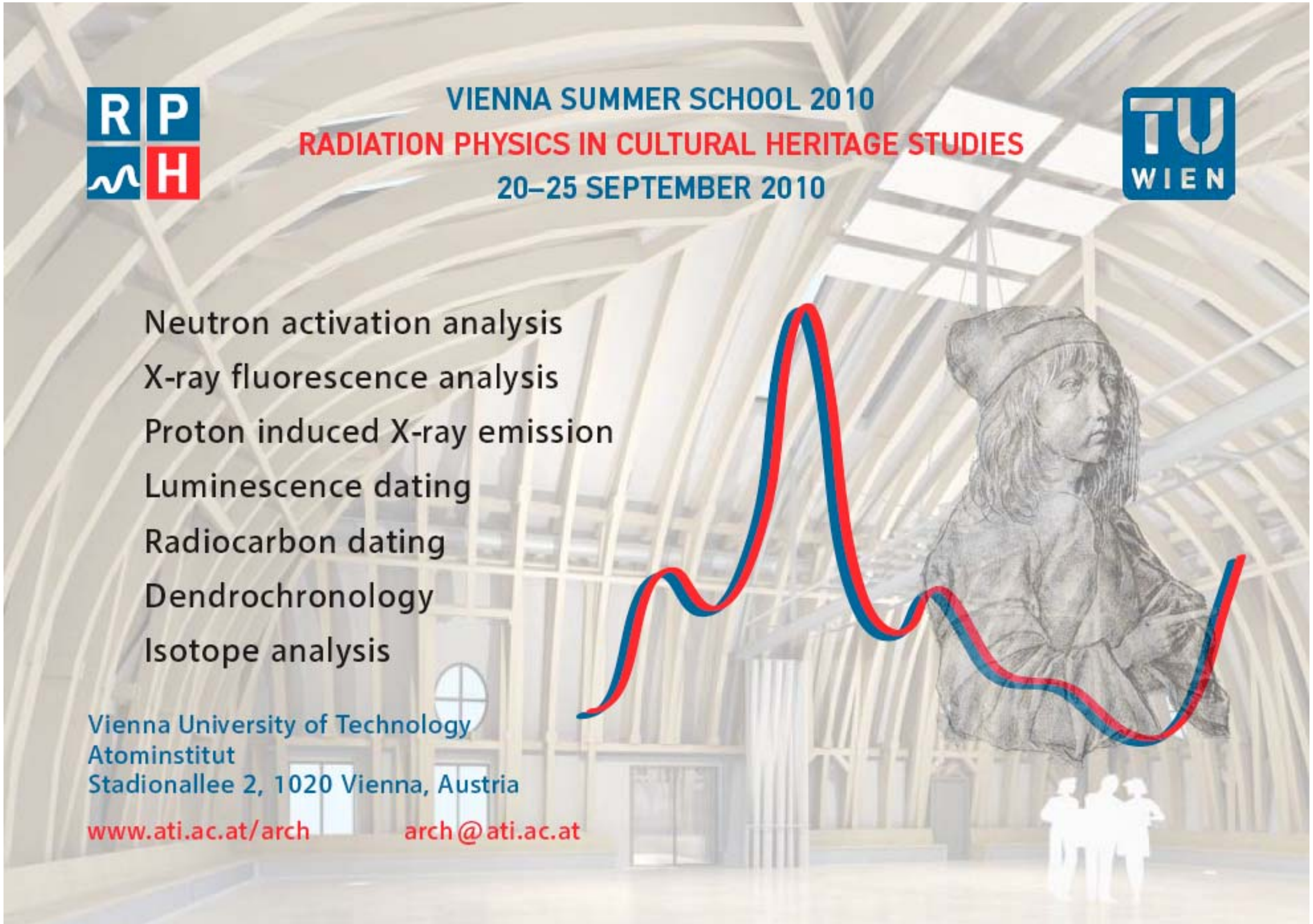
Element	LLD [ppm]
Na	7,69%
Al	452
Si	205
K	39
Ca	28
Ti	4
Fe	6
As	6

$$LLD = m\frac{3\sqrt{N_B}}{N_N}$$

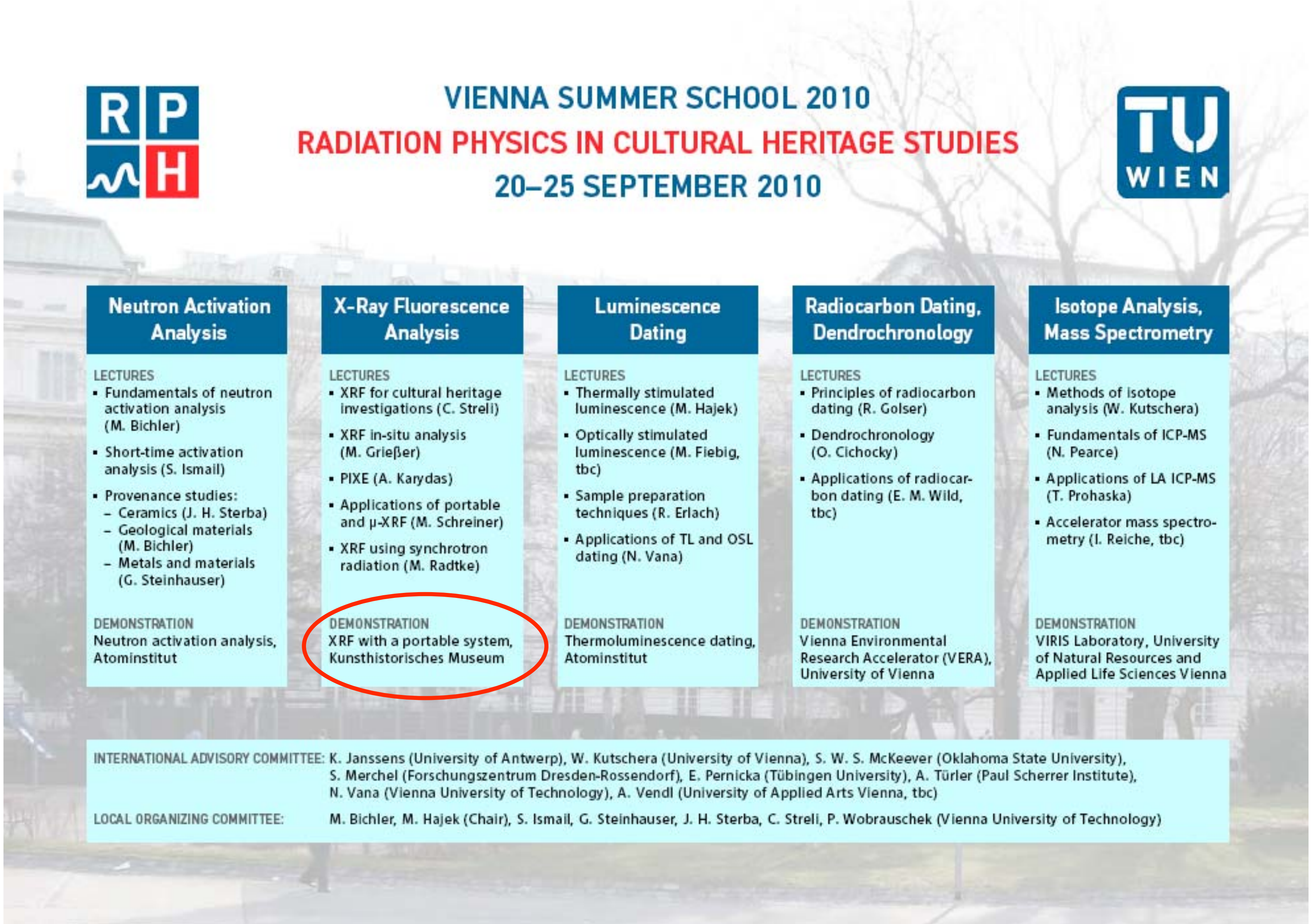
PART II has got officially the radiation protection certificate !!

Thanks for your attention!

Summer School



Summer School



SR-µXRF

Sr in bone