The Abdus Salam International Centre for Theoretical Physics

United Nations Educational, Scientific and Cultural Organization

IAEA
International Atomic Energy Agency

2272-10

Joint ICTP-IAEA School on Synchrotron Applications in Cultural Heritage and Environmental Sciences and Multidisciplinary Aspects of Imaging Techniques

21 - 25 November 2011

SR-(micro/T)XRF for environmental and conservation studies

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Centre for Materials and Microsystems
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Trento
ITALY

SR-(micro/T)XRF for environmental and conservation studies

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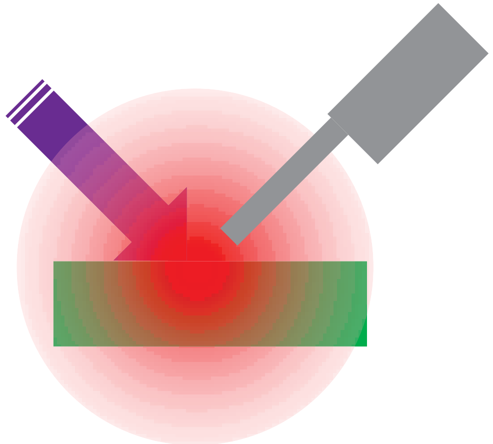
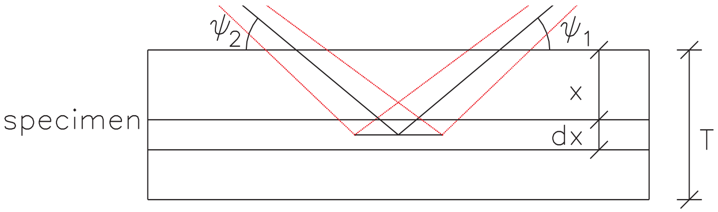
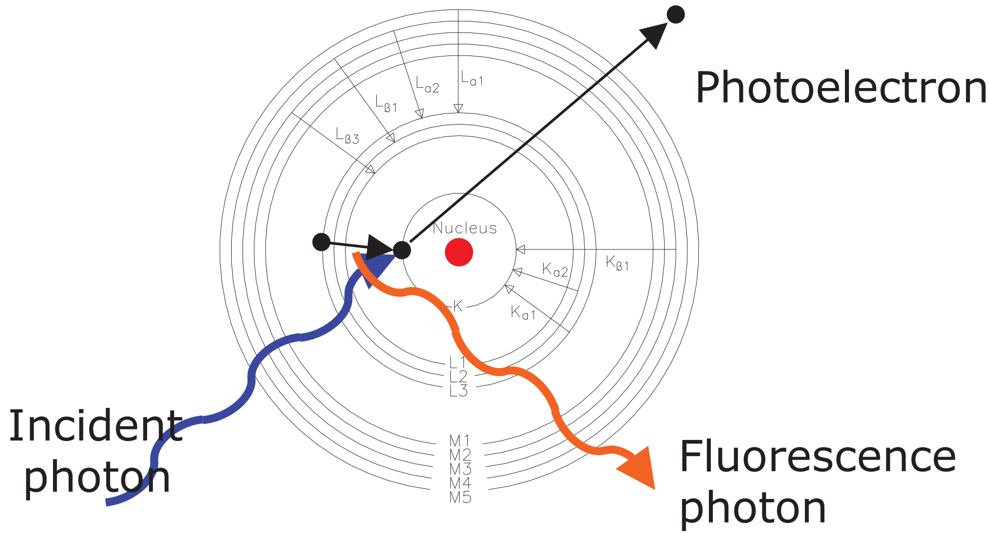
acknowledgement:
Norbert Zoeger – Atominstitut (TU Vienna)
Florian Meirer - FBK

XRF



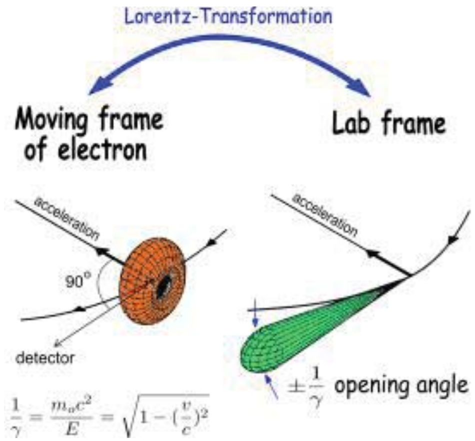




$$I(E_{i,j,k}) = \frac{d\Omega_0 d\Omega_1}{4\pi}\int_0^t \int_{Eedge_{i,j}}^{E\max} \left[I_0(E_0)\exp\left(-\left(\frac{\mu}{\rho}\right)_{s,E_0}\rho_s \frac{x}{\sin\psi_0}\right)\exp\left(-\left(\frac{\mu}{\rho}\right)_{s,E_{i,j,k}}\rho_s\frac{x}{\sin\psi_1}\right)\right.$$

$$\left. W_i \frac{\left(\frac{\tau}{\rho}\right)_{i,E_0}}{\sin\psi_0}\frac{(r_{i,j}-1)}{r_{i,j}}\rho_s\omega_{i,j}p_{i,j,k}\varepsilon_{E_{i,j,k}}\right] dx\,dE_0$$

Synchrotron

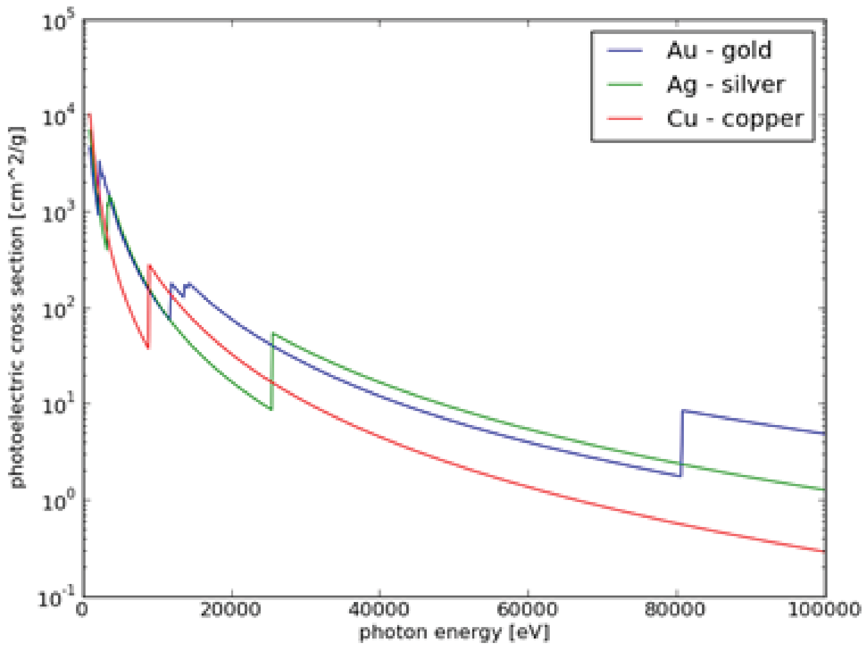


Higher flux:
 - faster measurements (scanning)

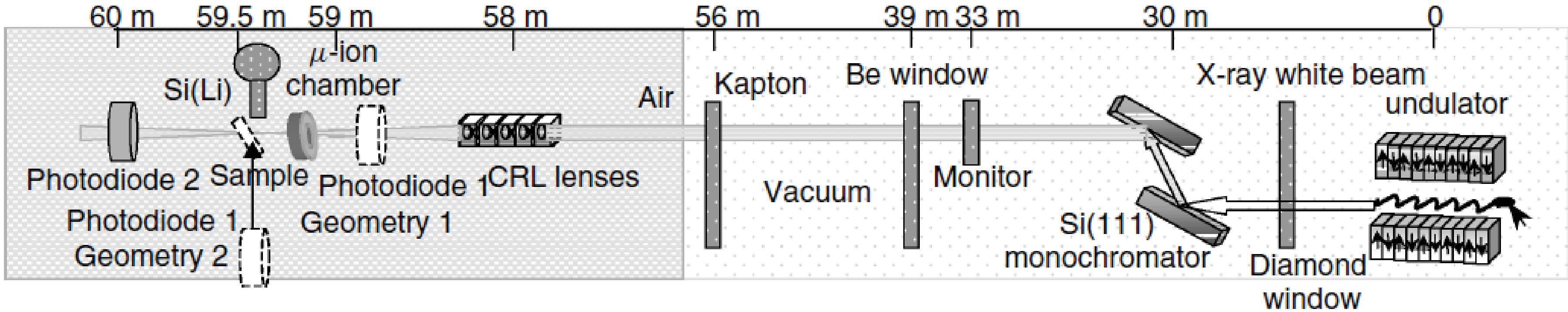
Natural collimation:
 -> high brilliance
 - micro (nano) spots

Polarisation:
 - better peak/background
 - magnetism

Wide spectral range:
 - selective excitation
 - excitation energy vs. sensitivity
 - energy scanning



Synchrotron – microXRF beamline example



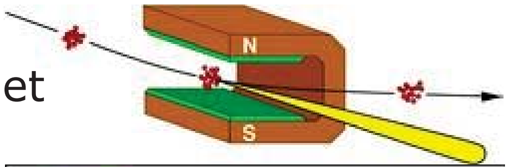
Schematic layout of the ID 18F experimental station. Photodiode 1 is either placed into the sample position if the sample is measured (geometry 1) or in front of the mini-ionisation chamber (geometry 2).

Somogyi, A., Drakopoulos, M., Vekemans, B., Vincze, L., Simionovici, A. and Adams, F. *Nucl. Instrum. Methods B* **199**, 559–564 (2003).

Synchrotron - sources

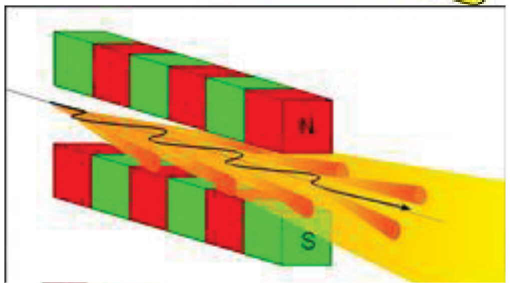
http://hasylab.desy.de/science/studentsteaching/primers/synchrotron_radiation/index_eng.html

Bending magnet



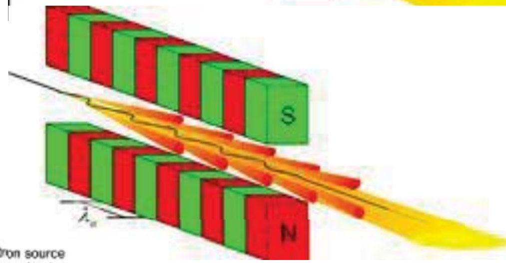
$I \propto n$

Wiggler



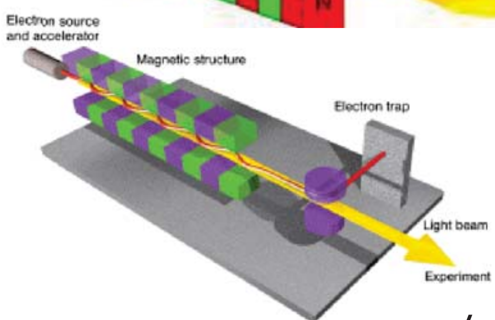
$I \propto N$

Undulator

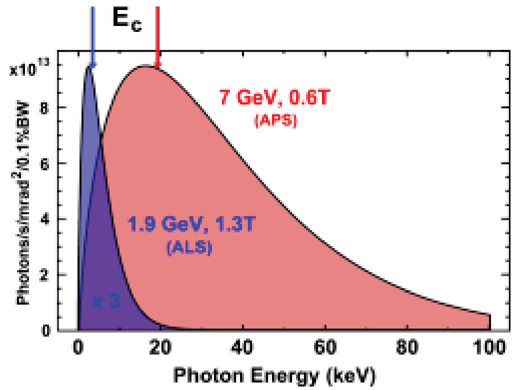


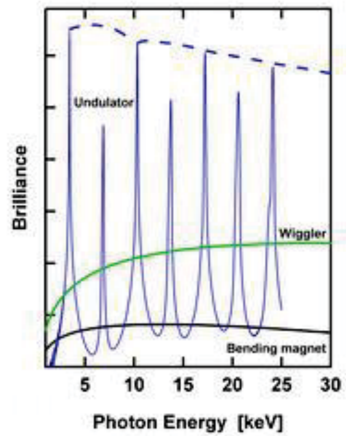
$I \propto N^2$

XFel



$I \propto n^2$





http://xray.bmc.uu.se/spb/

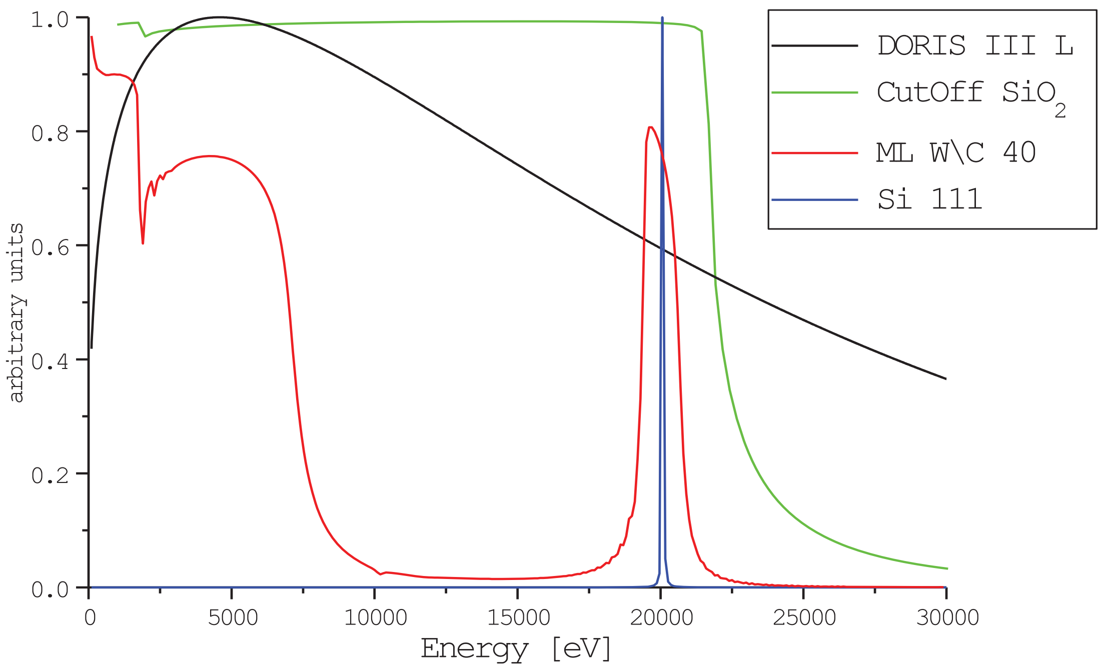
Spectral modifications

Mirrors – total reflection
cut-off, low-pass
(focussing)

Crystals – Bragg reflection
monochromators
$\delta E/E \propto 10^{-3}$ -10^{-4}

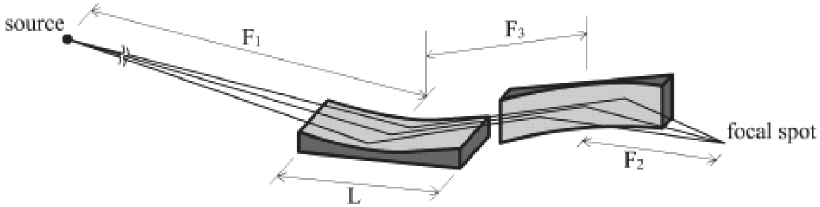
Multilayers – Bragg reflection
monochromators
$\delta E/E \propto 10^{-2}$

Gratings – Bragg reflection
monochromators
$\delta E/E \propto 10^{-3}$ -10^{-4}

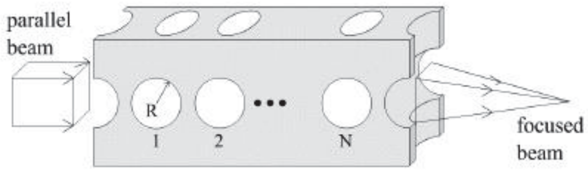


Focussing Optics

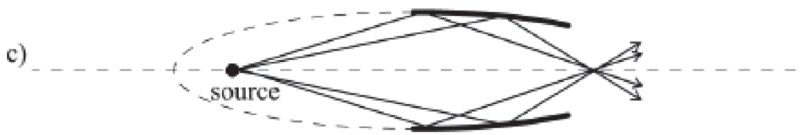
reflective:
Kirkpatrick-Baez



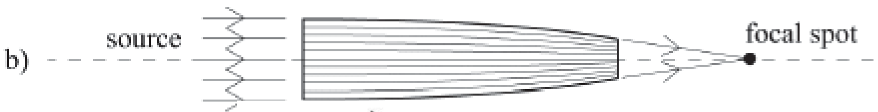
compound refractive lenses



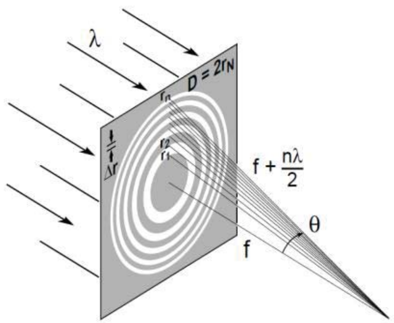
monocapillaries



polycapillaries



zone plates



Flux density gain

Spot size

Energy range

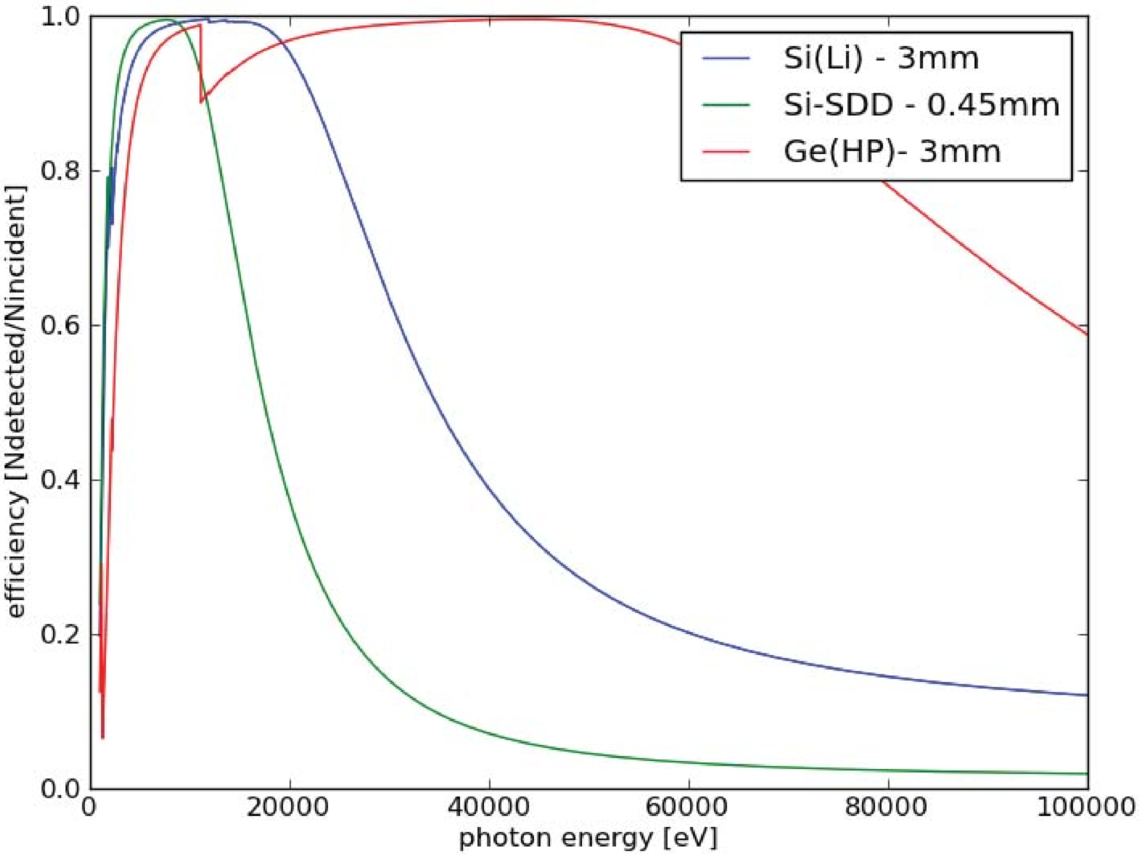
Focal length

Alignment

XRF detectors

Silicon Drift Detectors:
- thin (efficiency)
- fast (up to 1Mcps)
- no LN2

Si(Li) – Ge(HP)
- thick (efficiency)
- not too fast (20-60 kcps)



XAS - detectors

7 element element

30 element

Lytle detector

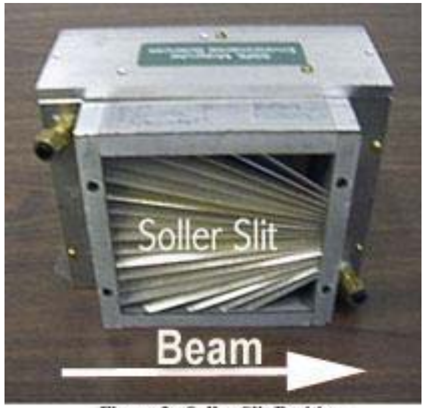


Figure 2. Soller Slit Position

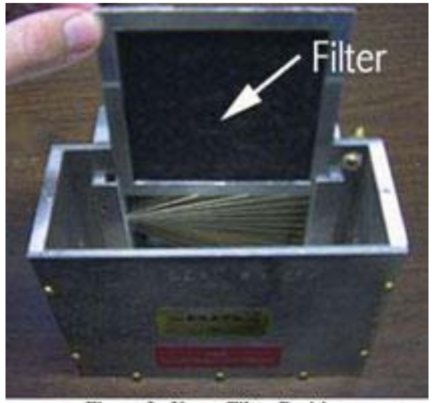
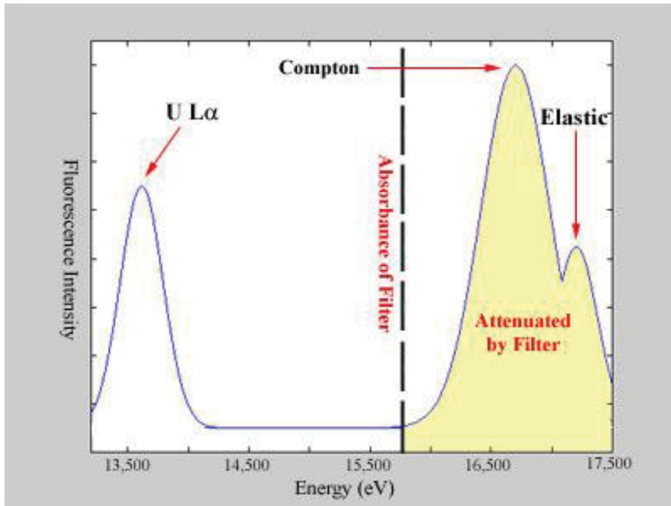
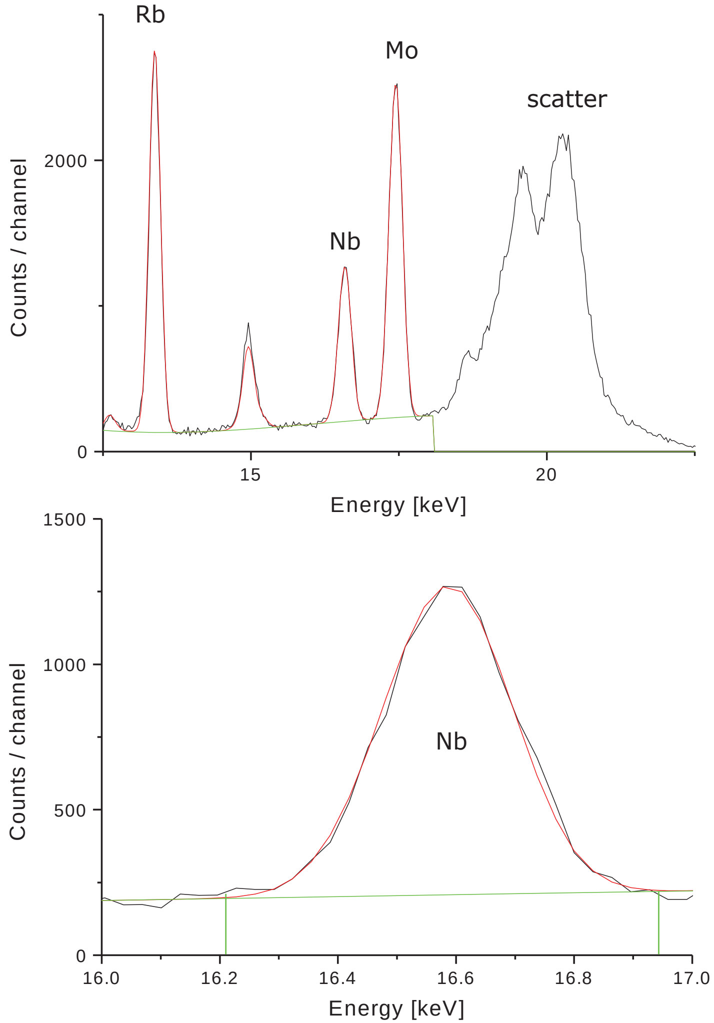


Figure 3. X-ray Filter Position

http://ssrl.slac.stanford.edu
/mes/xafs/index.html



XRF – detection limits

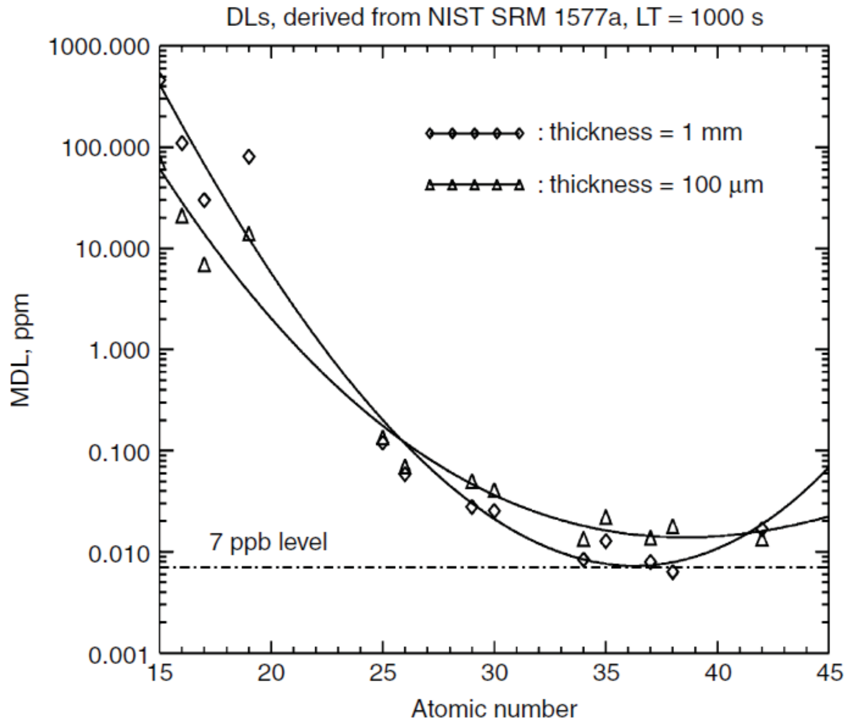


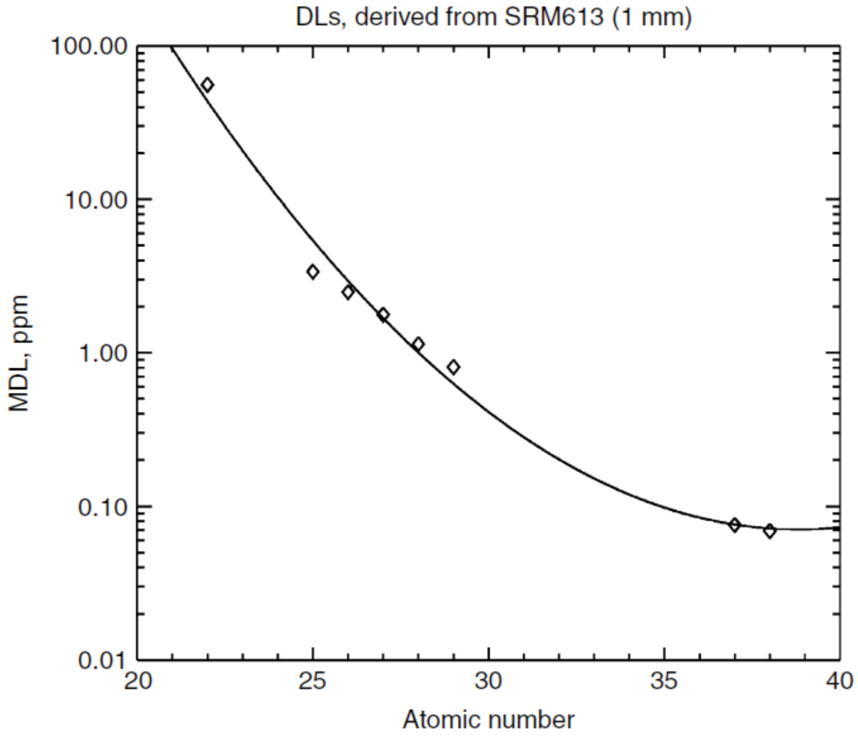
$$DL = 3\frac{\sqrt{Background}}{Net}\,mass$$

$$DL \propto \sqrt{\frac{mass \cdot current}{time}}$$

Results usually normalised to 1000 sec measuring time

Synchrotron – detection limits

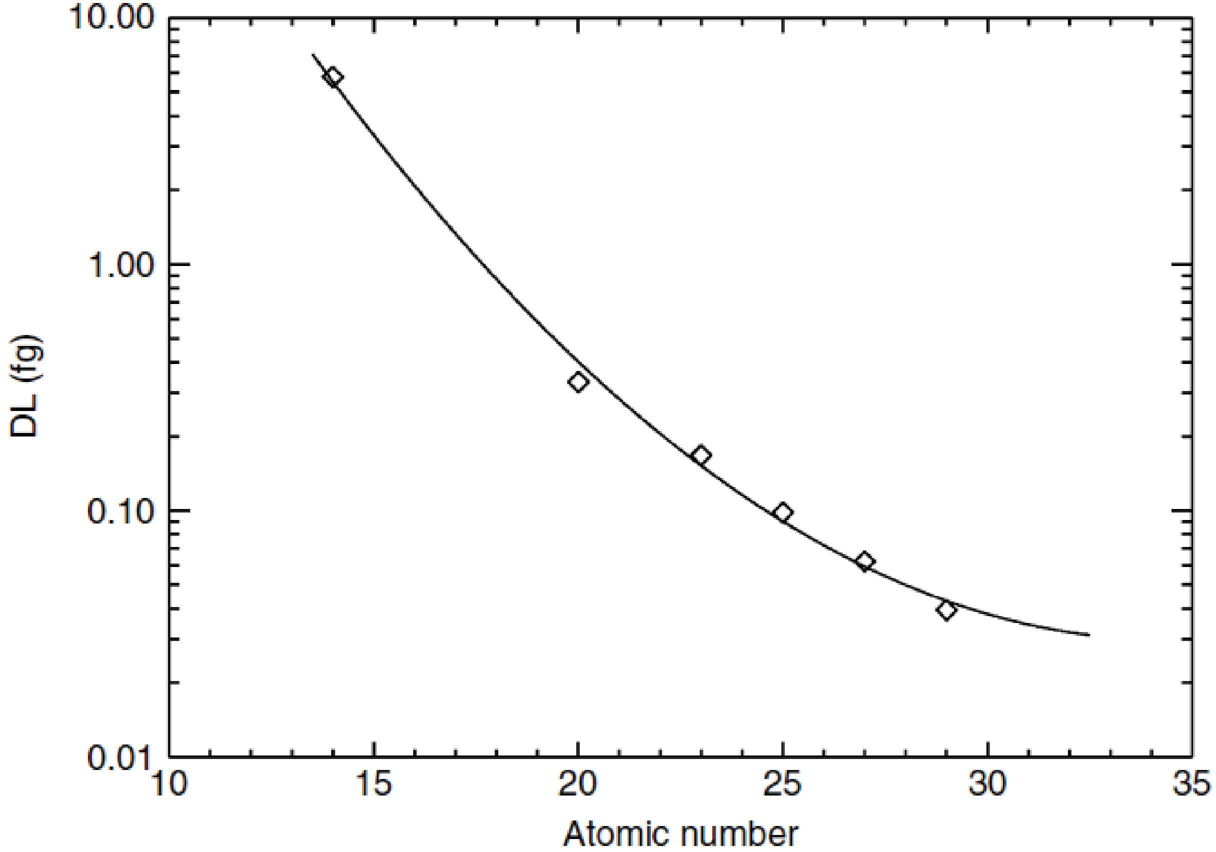




Relative detection limits with ID 18F using a 100 component compound reflective lens set at 21 keV at 2µm × 2µm in biological material (NIST SRM 1577a, bovine liver) and NIST 613 glass SRM 613 (live time measurement of 1000 s).

Somogyi, A., Drakopoulos, M., Vincze, L., Vekemans, B., Camerani, C., Janssens, K., Snigirev, A. and Adams, F. *Xray Spectrom.* **30**, 242–252

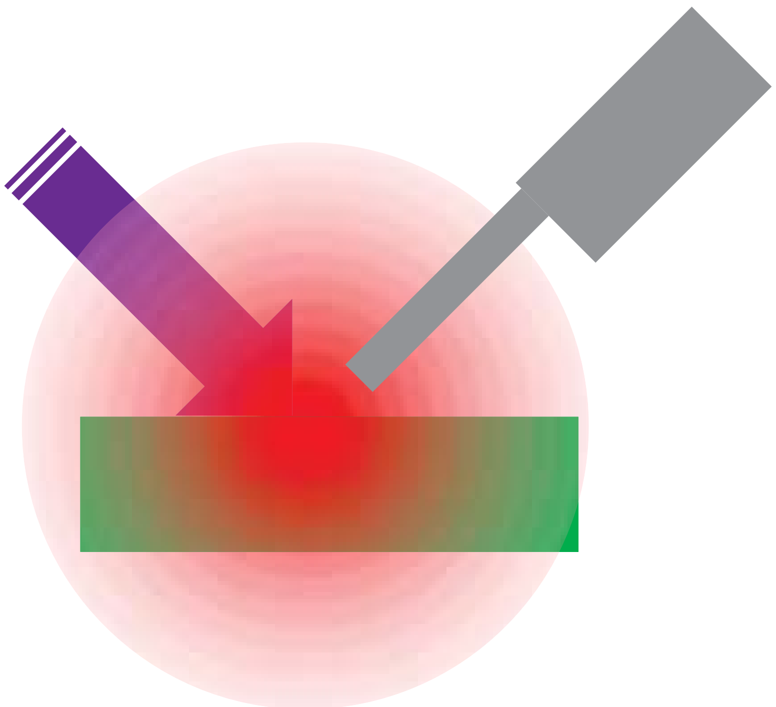
Synchrotron – detection limits



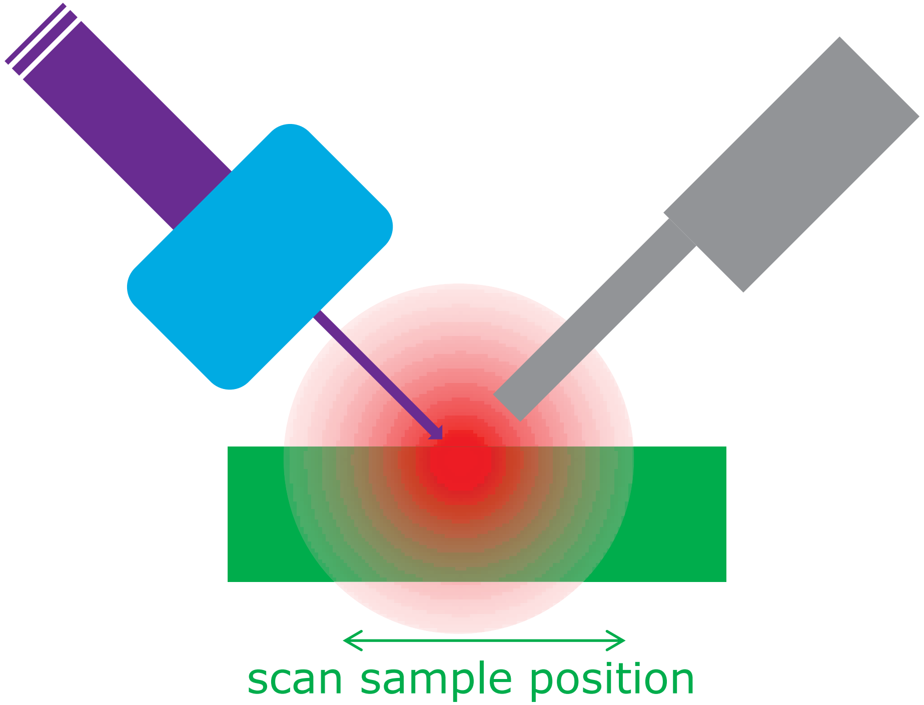
Absolute detection limits with ESRF (ID 13), 21 keV monochromatic radiation at 2μm × 2μm (live time measurement of 100 s). Adapted from Somogyi *et al*. (2001)

Micro - XRF

XRF - microXRF



- homogeneous sample
  (assumed – spinning)
- averaged information
- LD: ppm -> ppb

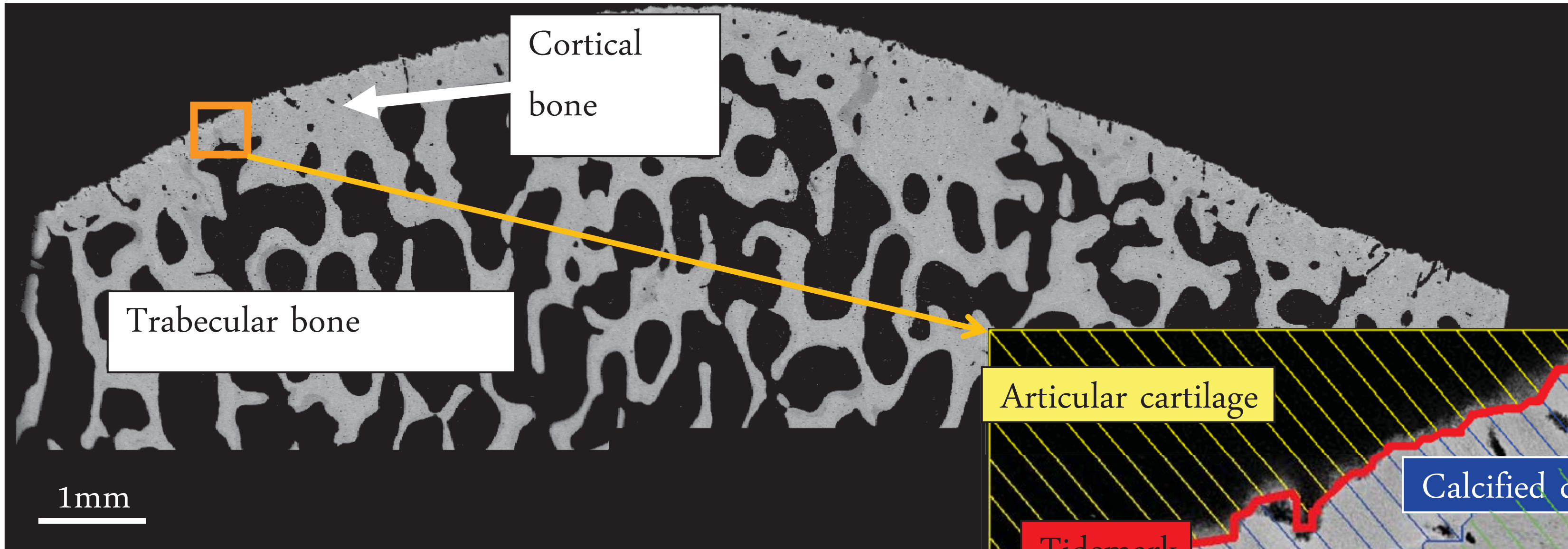


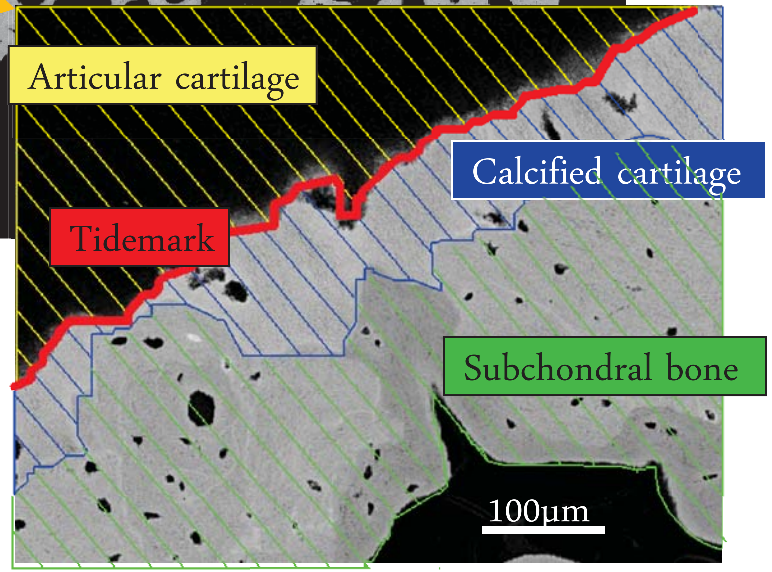
- detect inhomogeneities in sample
- local information -> imaging
- LD: ppm -> ppb ???
- improved signal to background ratio ?
- much more information
  ? data analysis ?

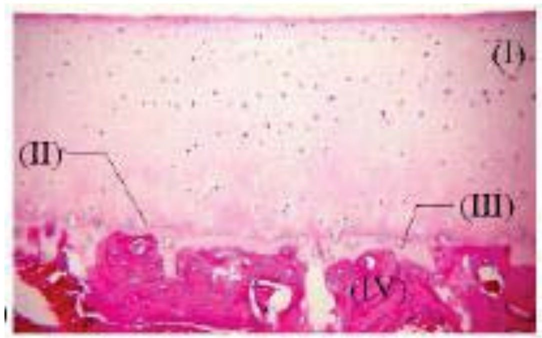
microXRF – example – lead in bone

Most of the work done by Norbert Zoeger for his PhD

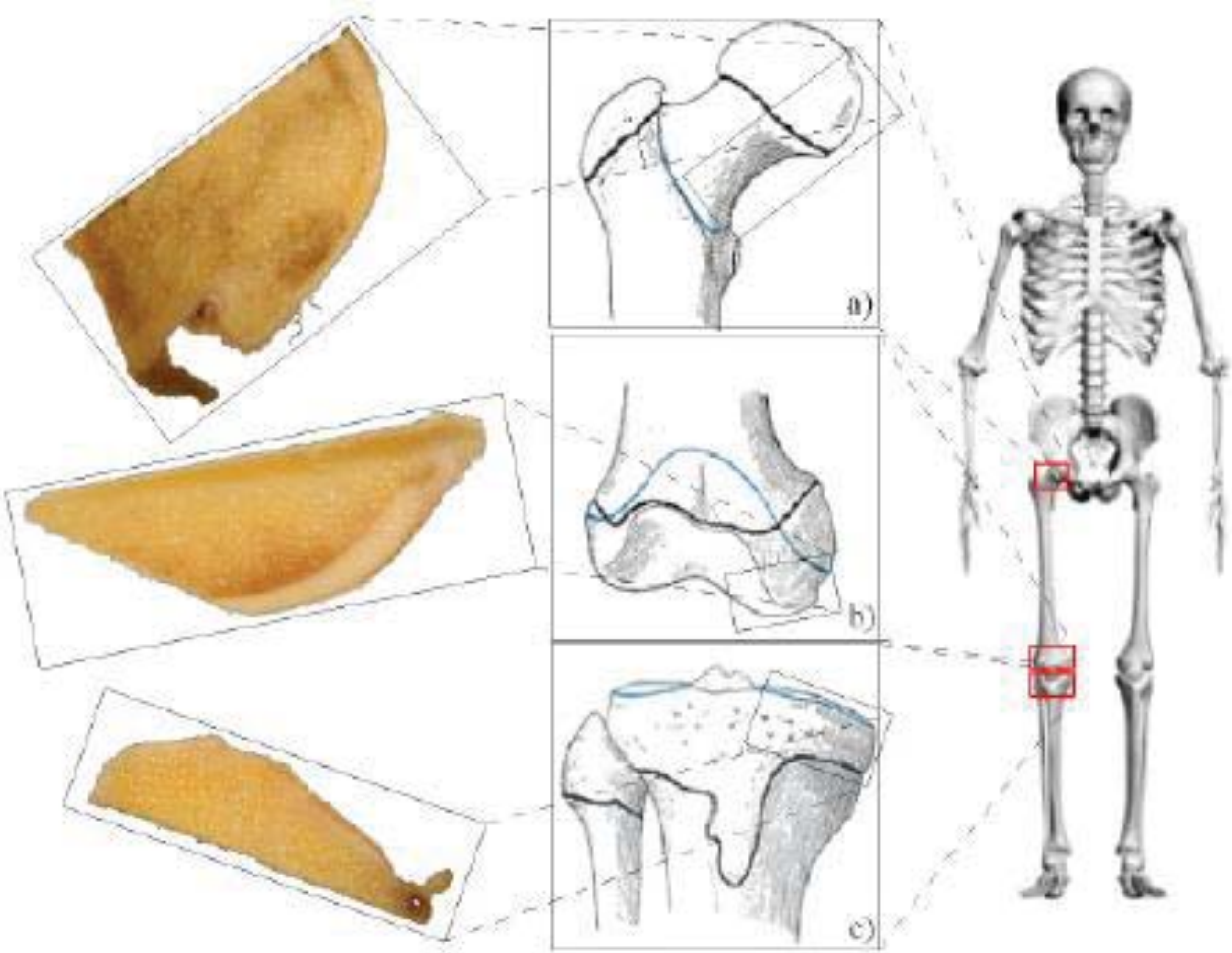
Backscattered Electron Image (BE), Patella



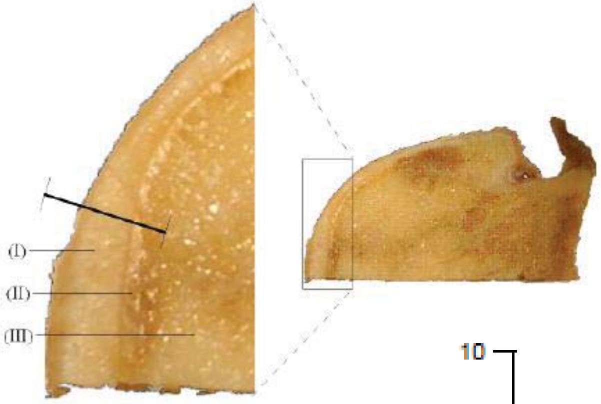




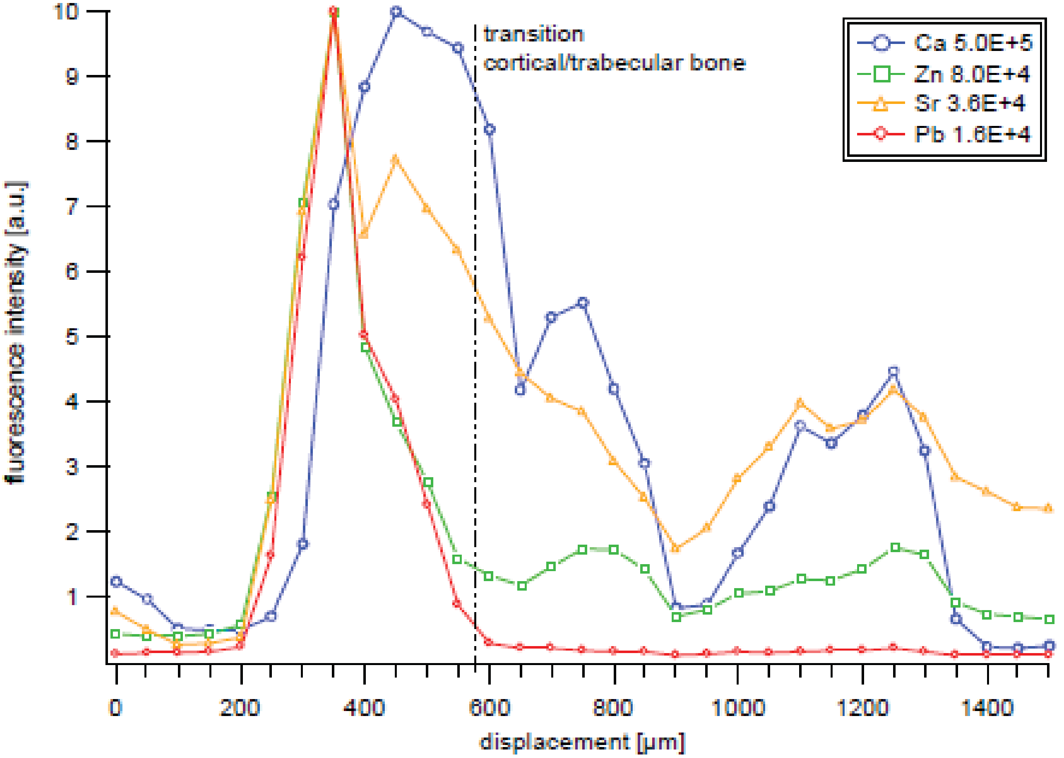
microXRF – example – lead in bone



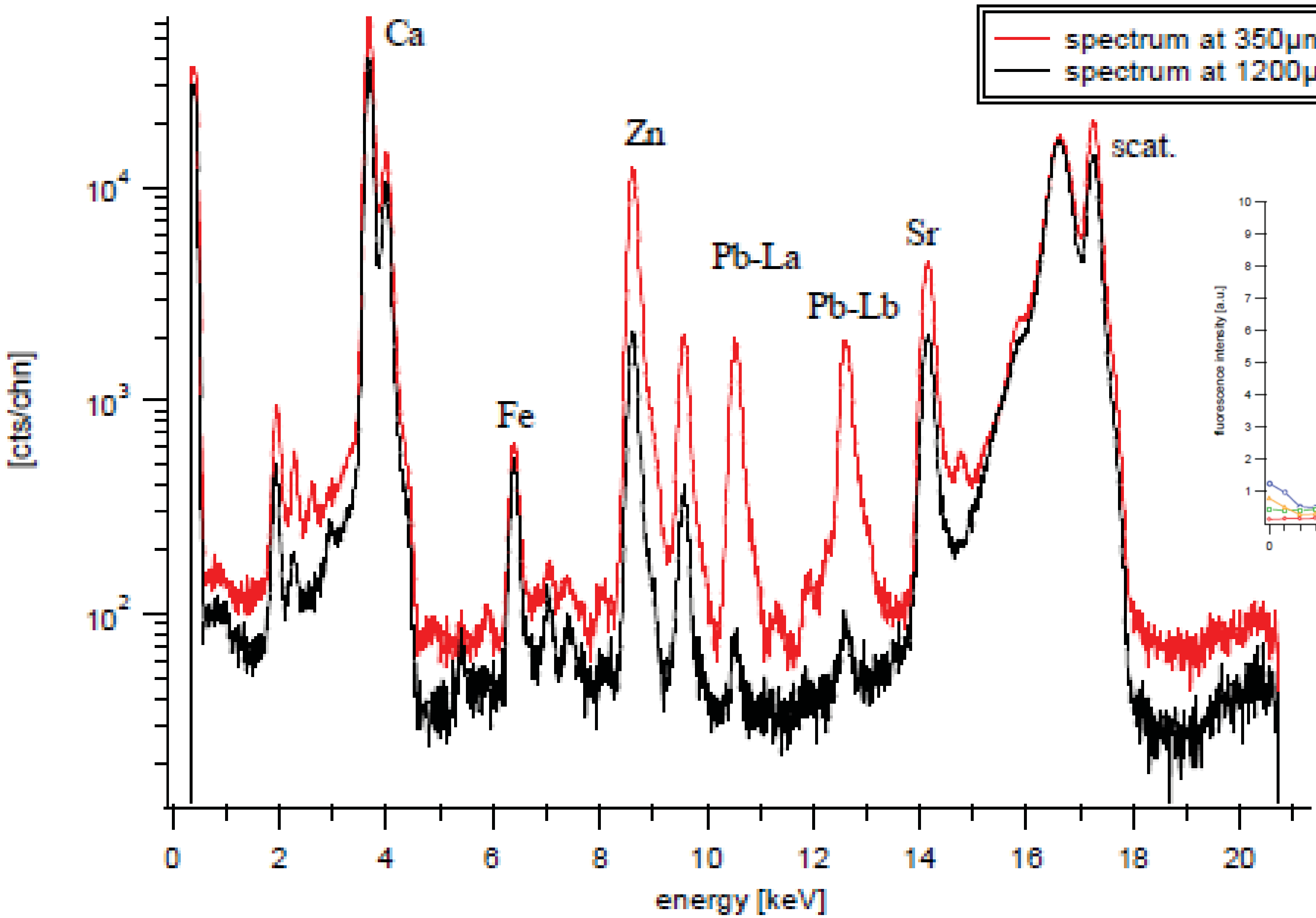
microXRF – example – lead in bone

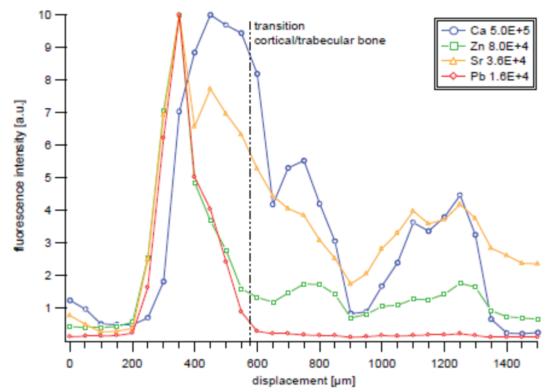


1D scan
mm thick piece



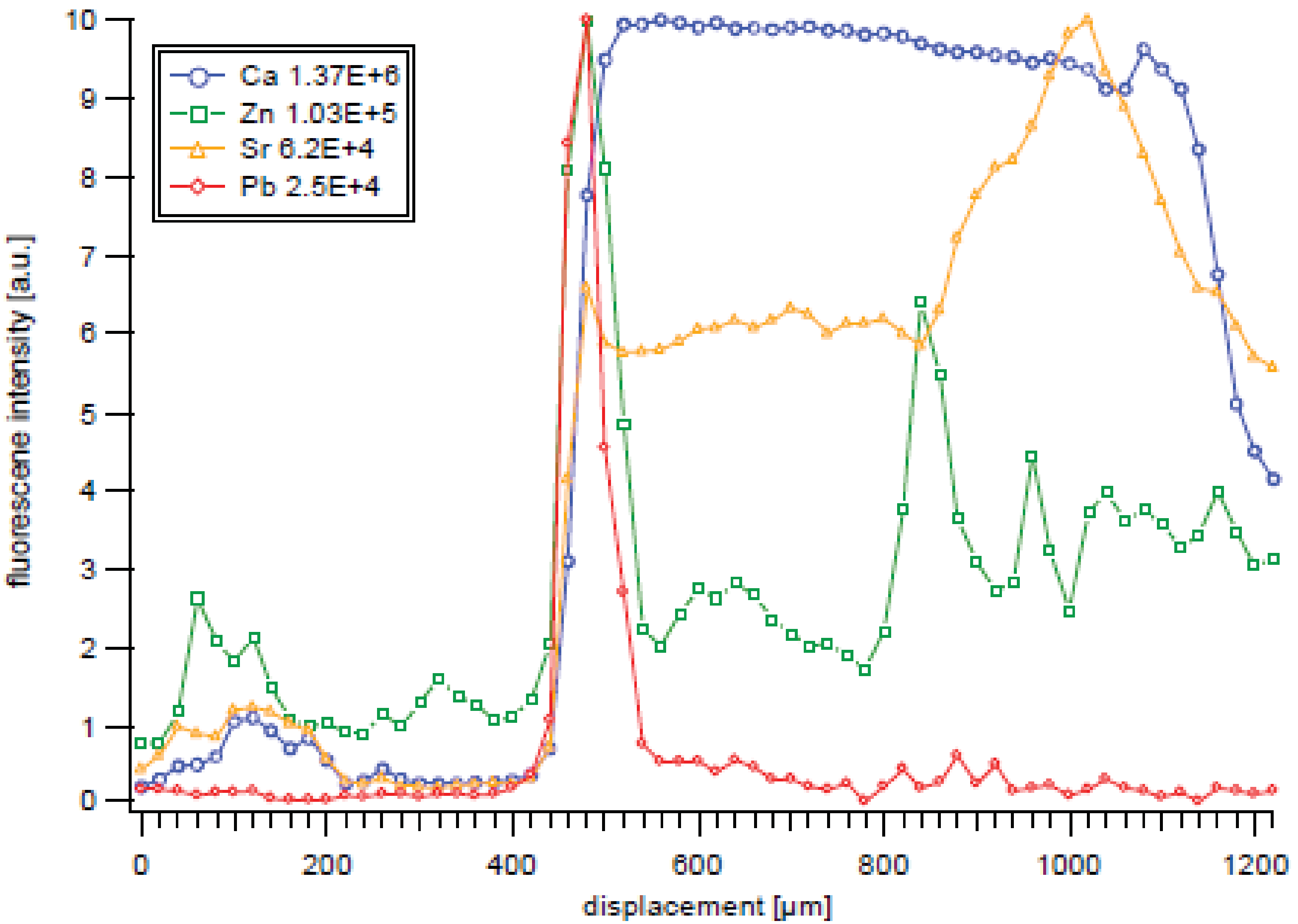
microXRF – example – lead in bone





microXRF – example – lead in bone

1D scan
200 µm thick piece



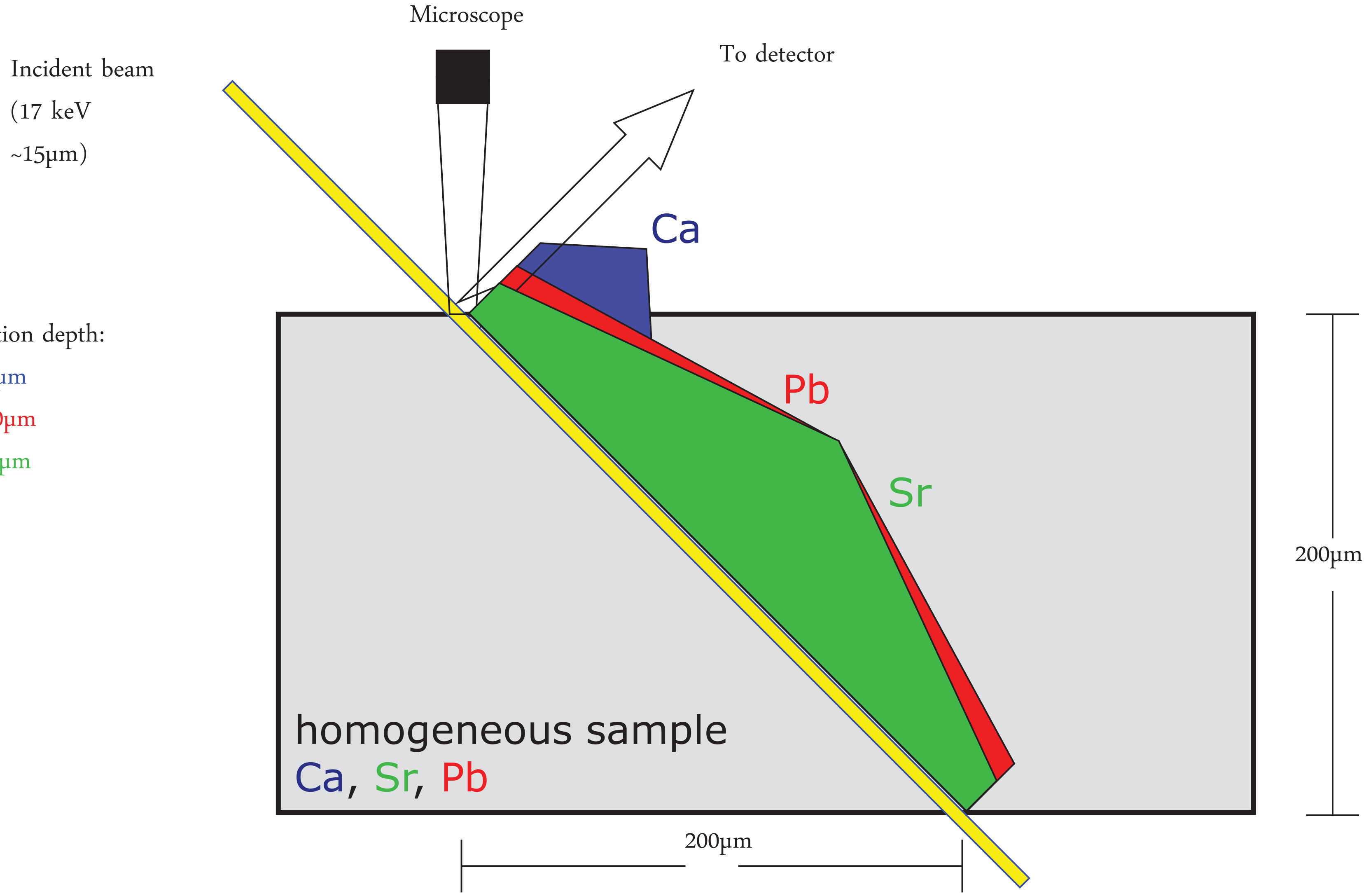
microXRF – artifacts

Information depth:

Ca ~ 40µm

Pb ~ 300µm

Sr ~ 600µm



microXRF – artifacts

Information depth:

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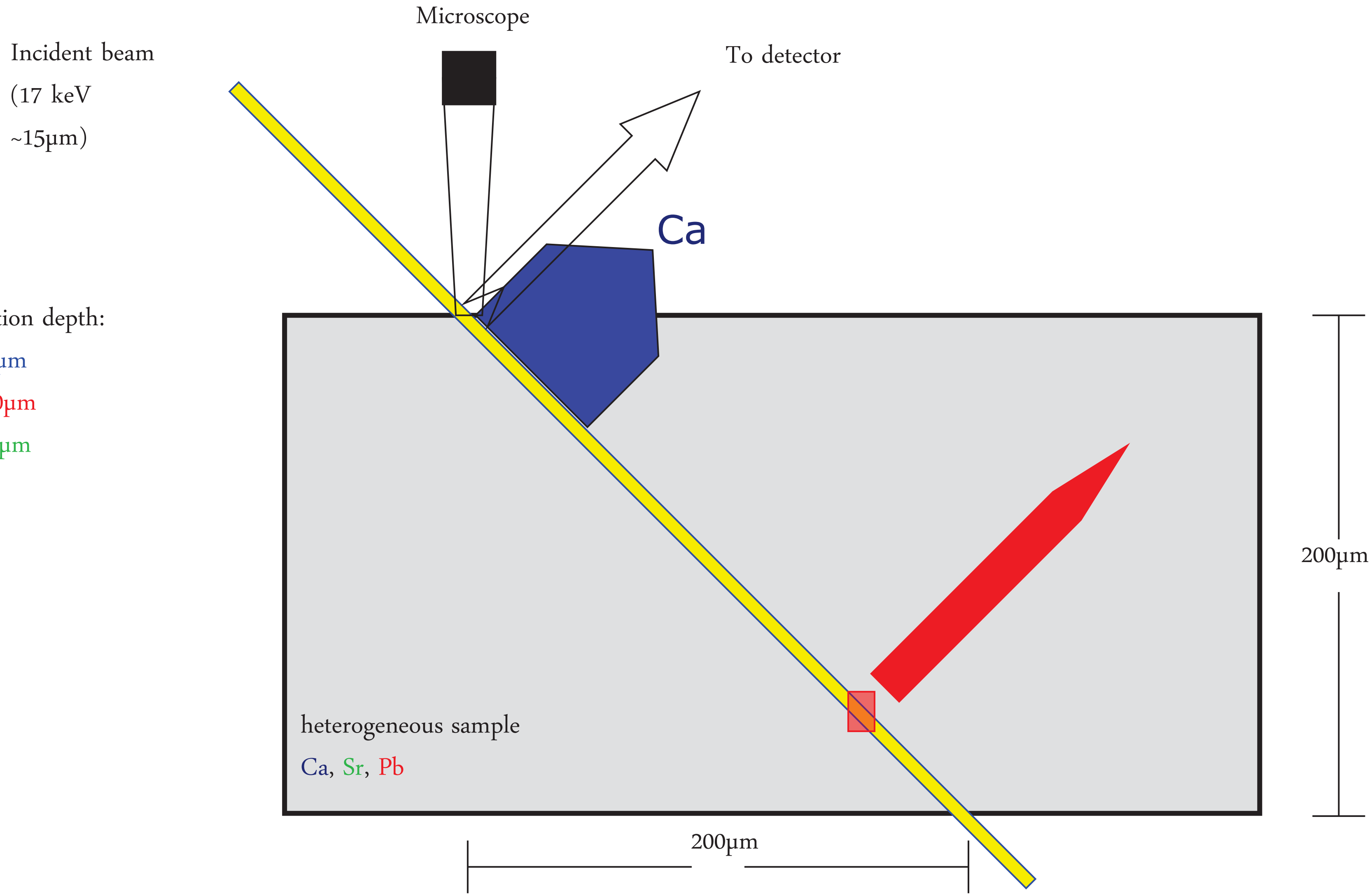
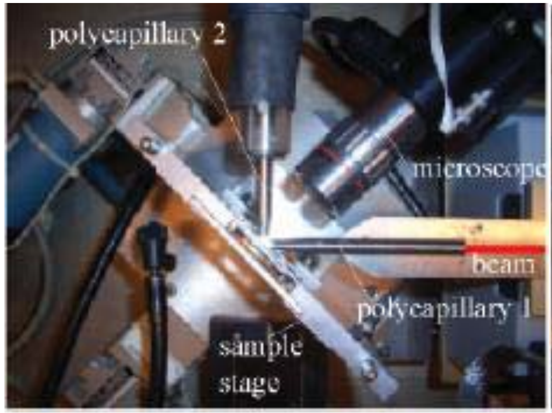


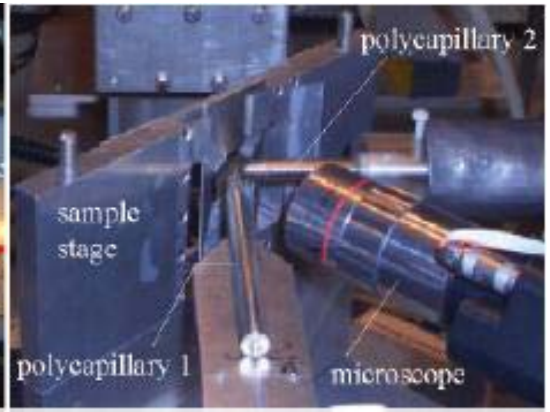
2D -3D

Why 3D?

Because 2D projection can be misleading.

Confocal set-up – hasylab L





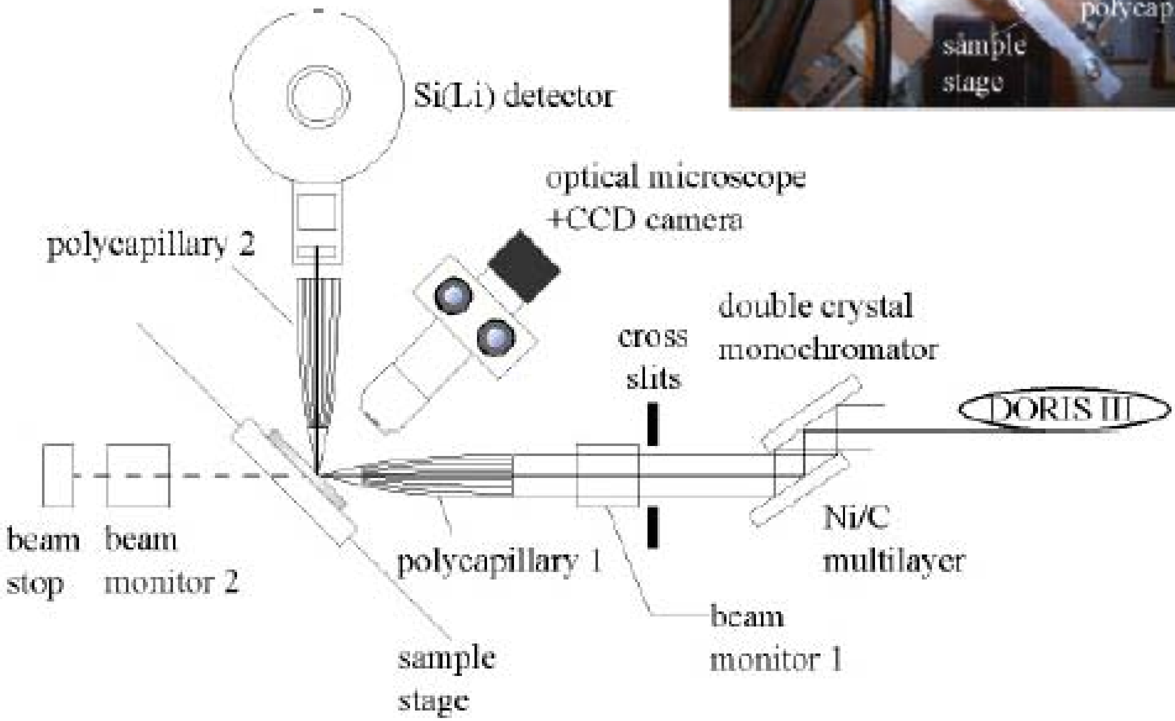
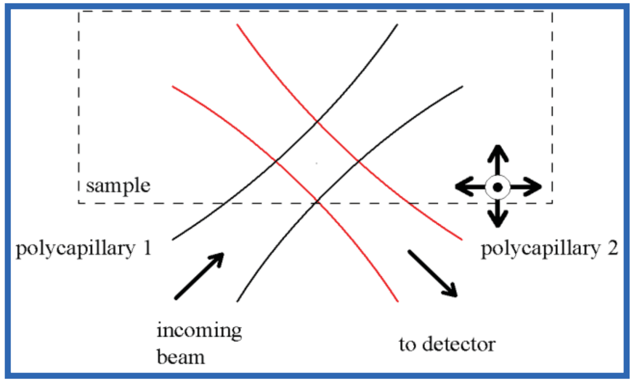


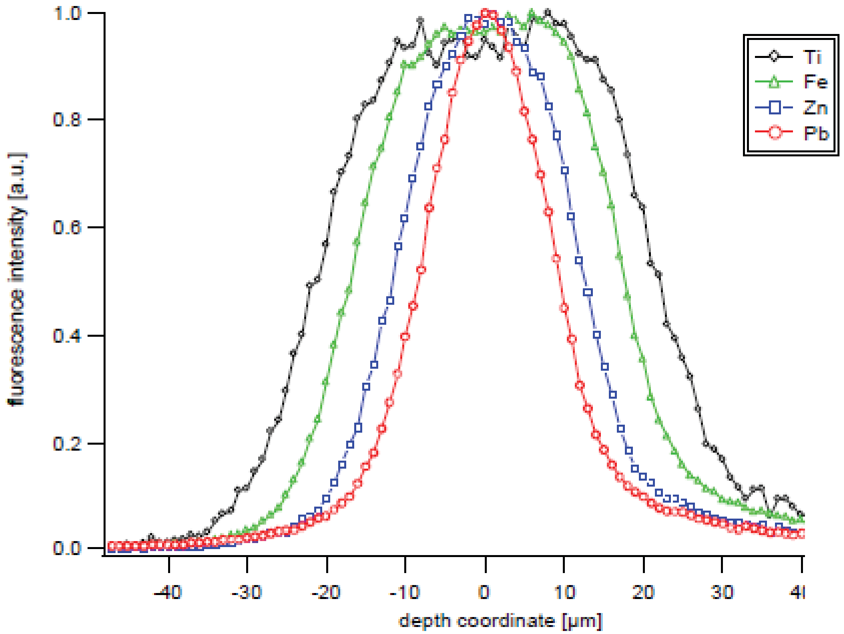
Figure 7.16: Scheme of the confocal setup at HASYLAB, beamline L



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

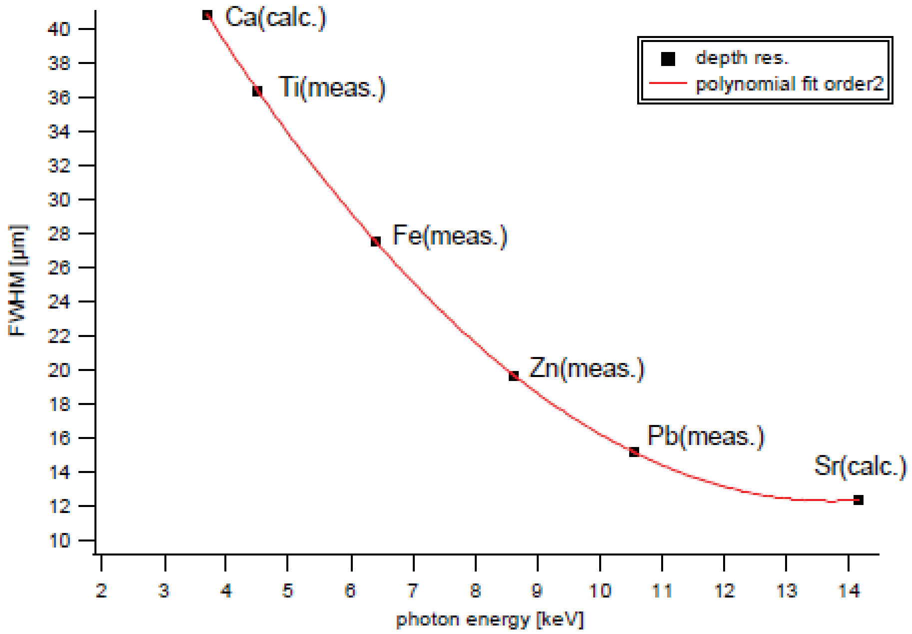
for Au La

Confocal set-up – hasylab L

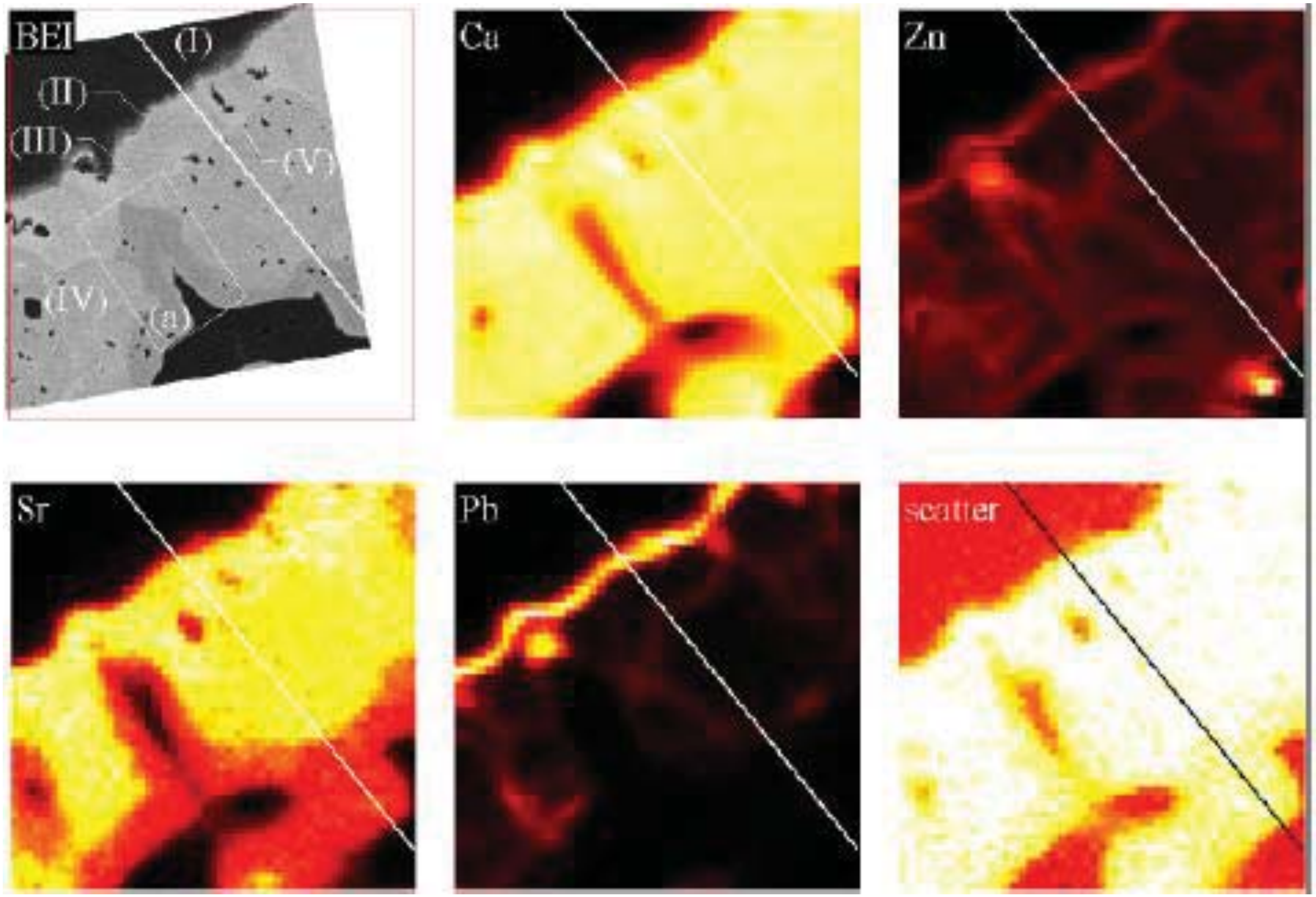


Detection volume

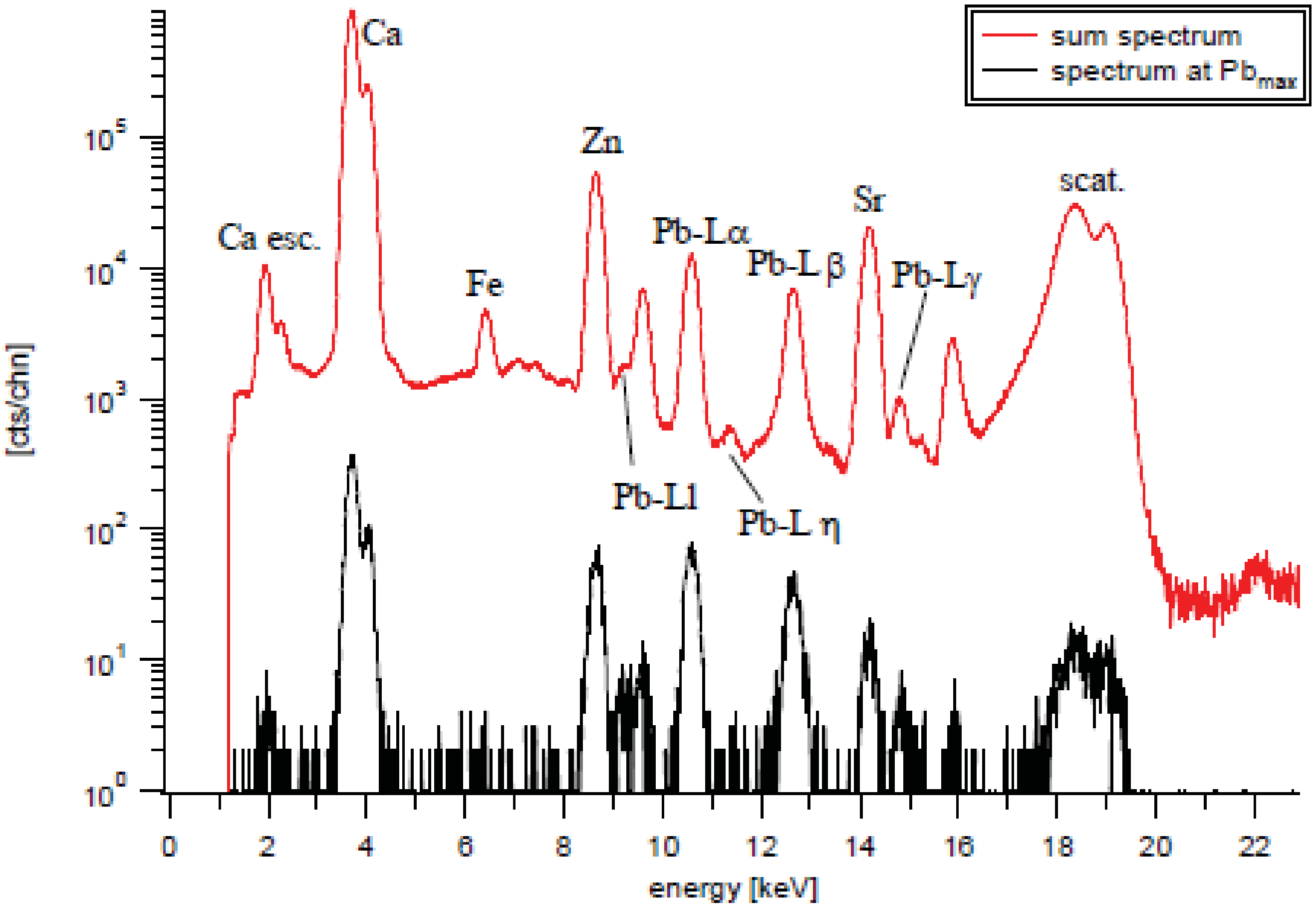
spatial resolution



Confocal set-up – hasylab L

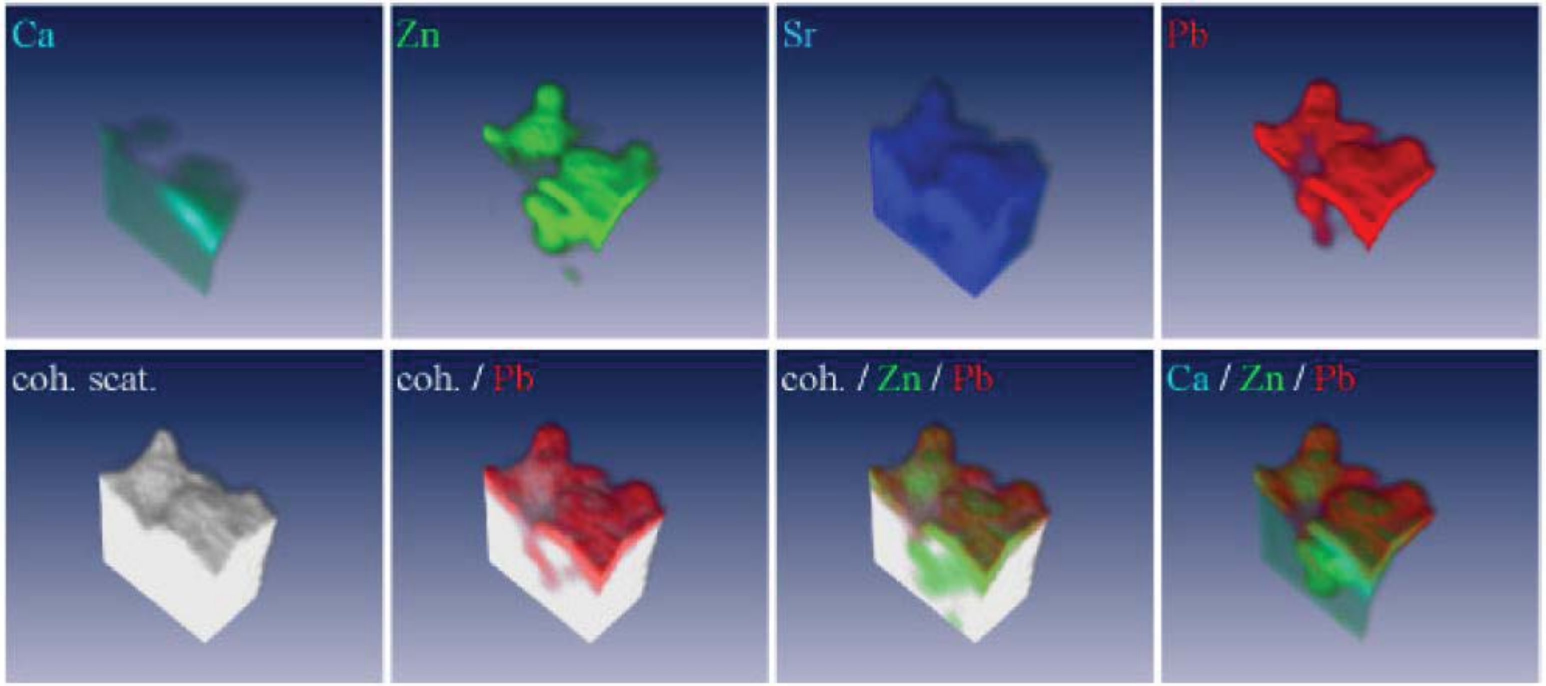


Confocal set-up – hasylab L



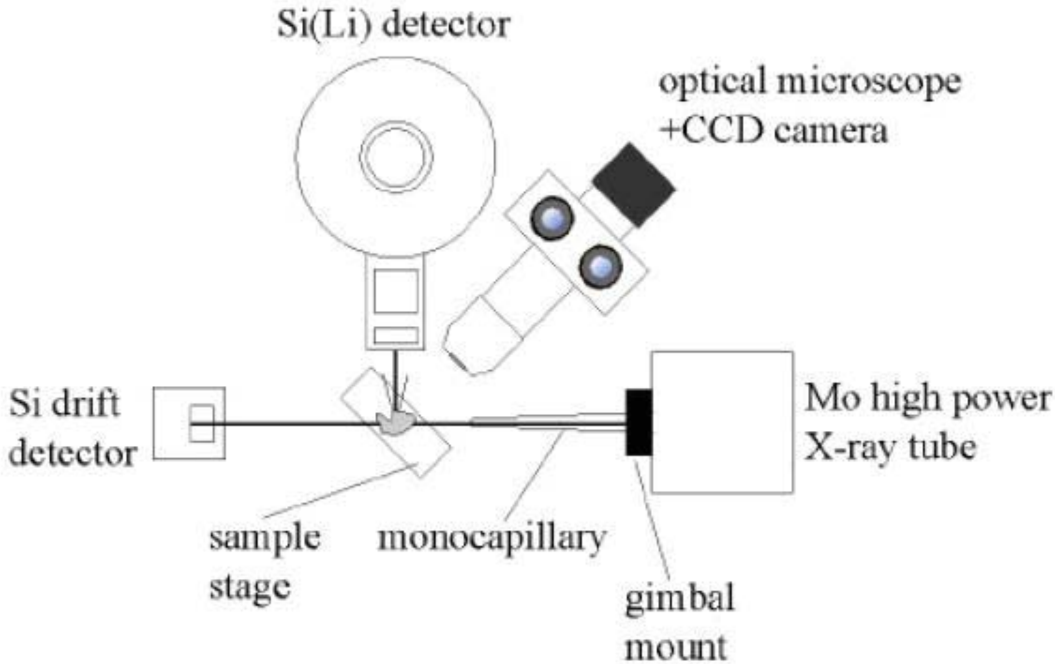
all (2601) fluorescence spectra from the area scan (red) compared with the single spectrum at the maximum of Pb (black), obtained in 5s measuring time

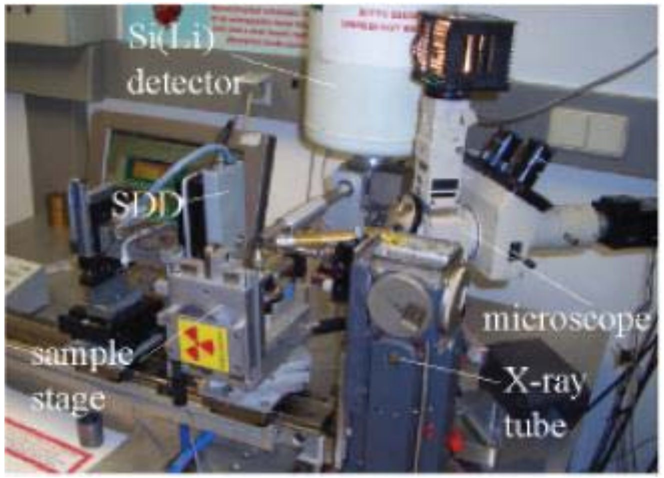
Confocal set-up – hasylab L

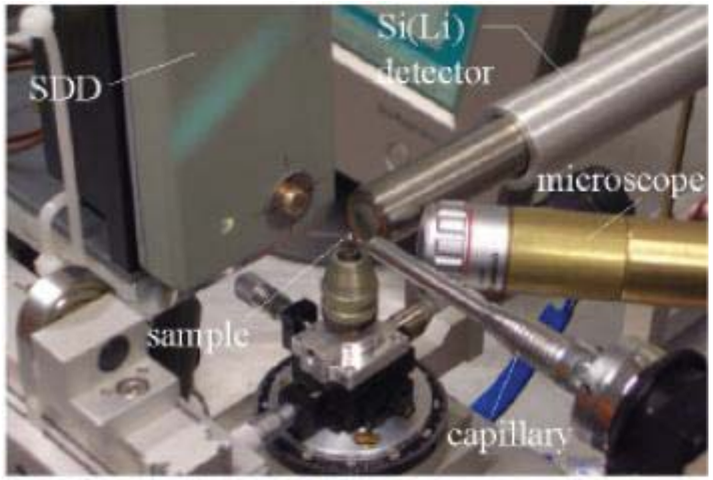


Three-dimensional element distribution in human patella

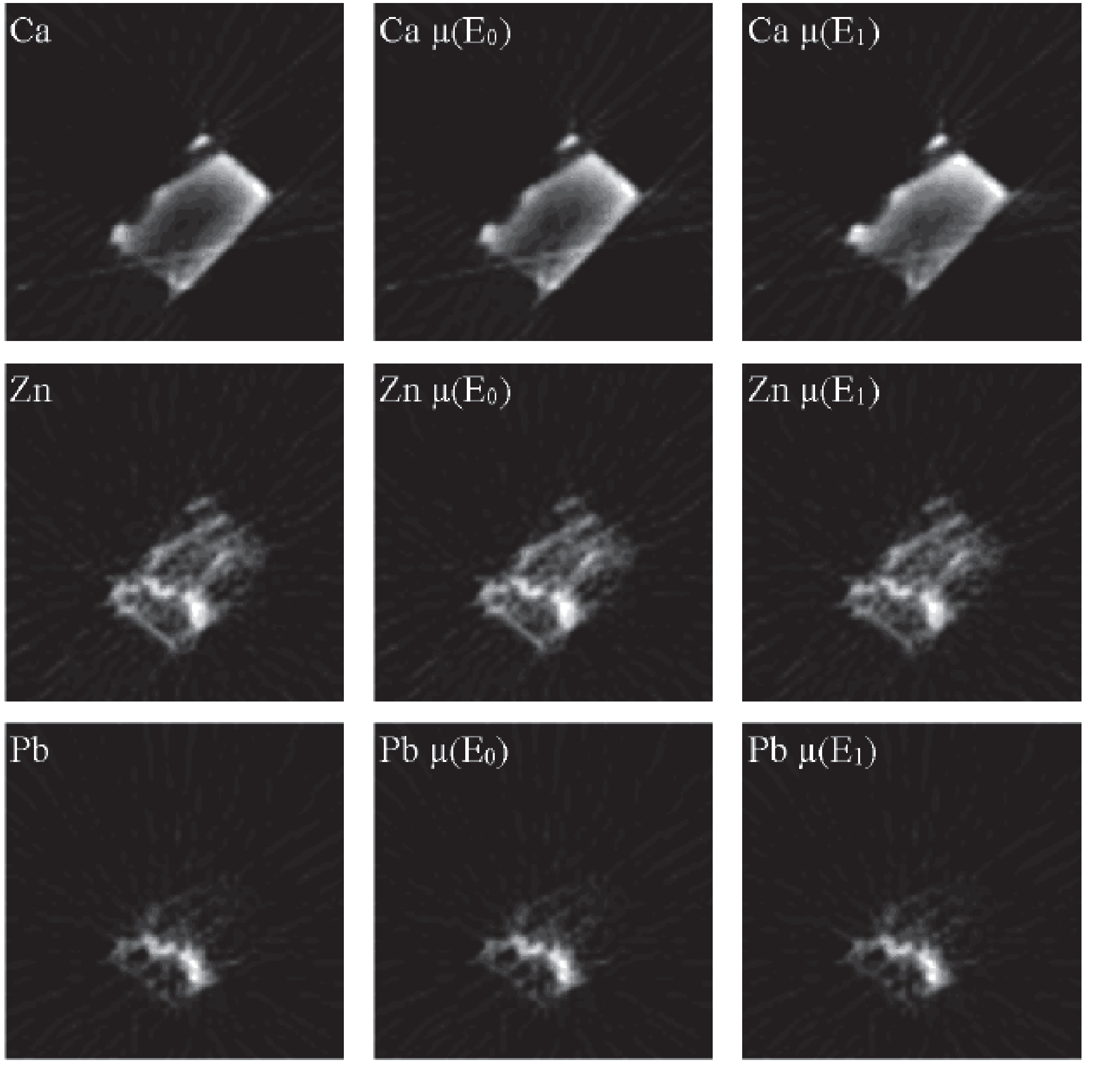
Tomo set-up – ANKA



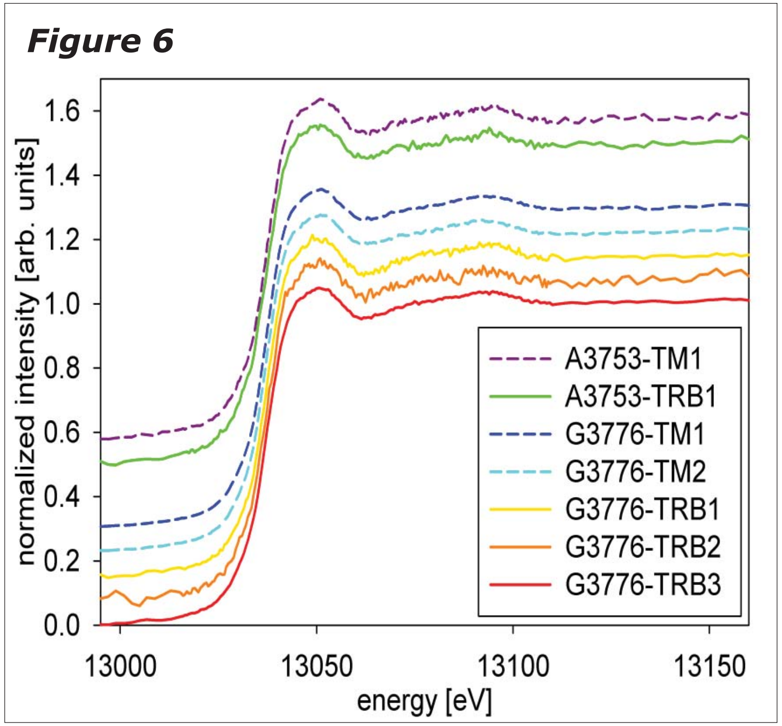




Tomo set-up – ANKA



Pb XANES – ANKA



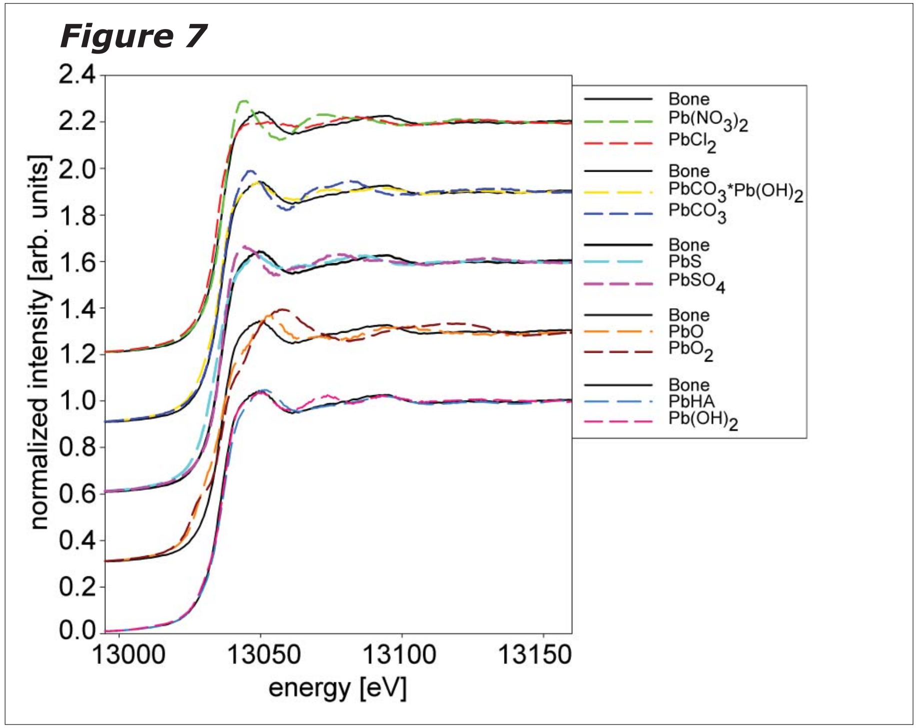
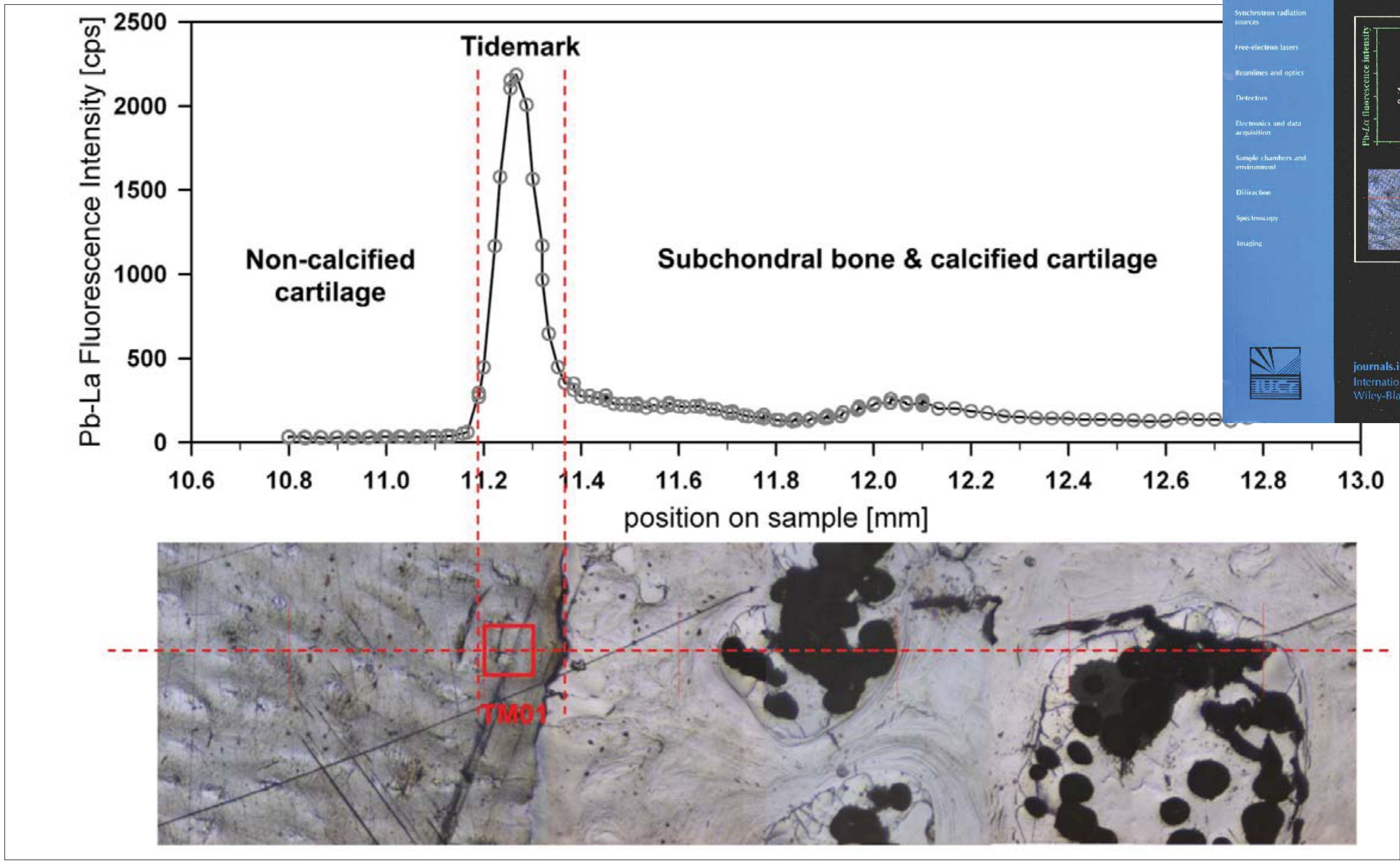


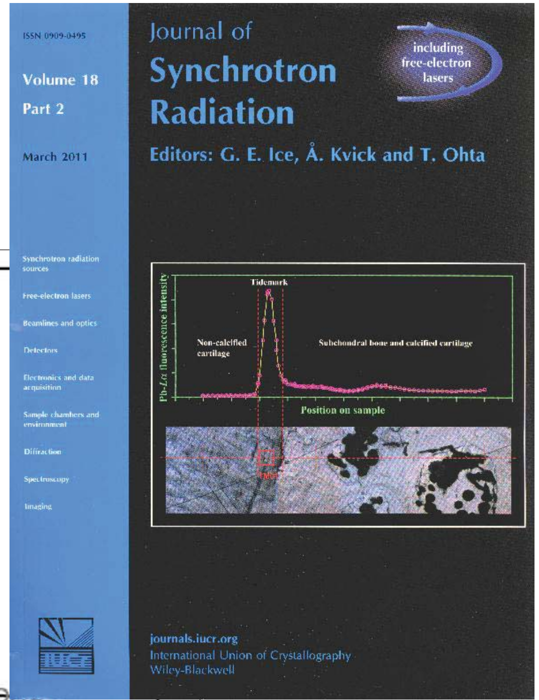
Figure 6: *Comparison of XANES spectra recorded at different tidemark (TM) positions and different regions in the trabecular bone (TRB) of the human patella (G3776) and femural head (A3753) sample [2].*

Figure 7: *Comparison of bone XANES spectra (black) - because TM and TRB spectra of Fig. 6 show no differences they have been merged for further evaluation - with spectra of reference compounds [2].*

FONDAZIONE BRUNO KESSLER

Pb XANES – ANKA

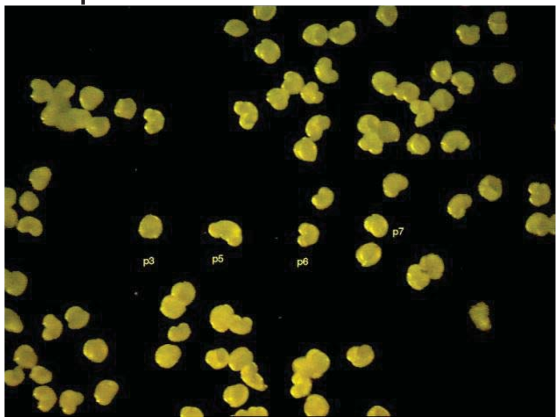


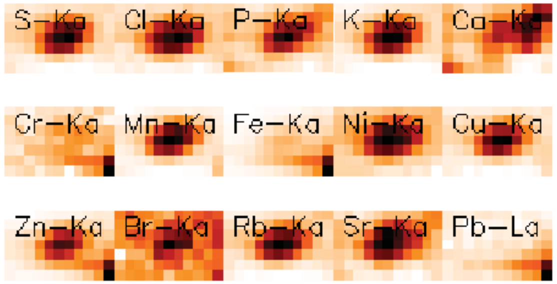


March 2011 cover

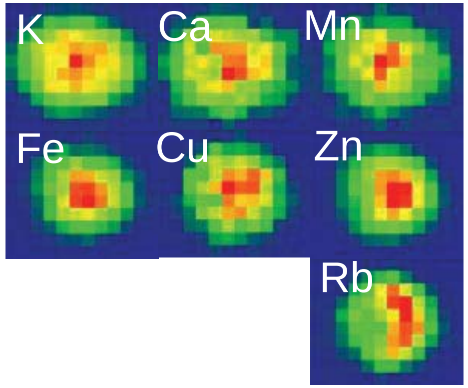
microXRF - pollen

Sample PR11

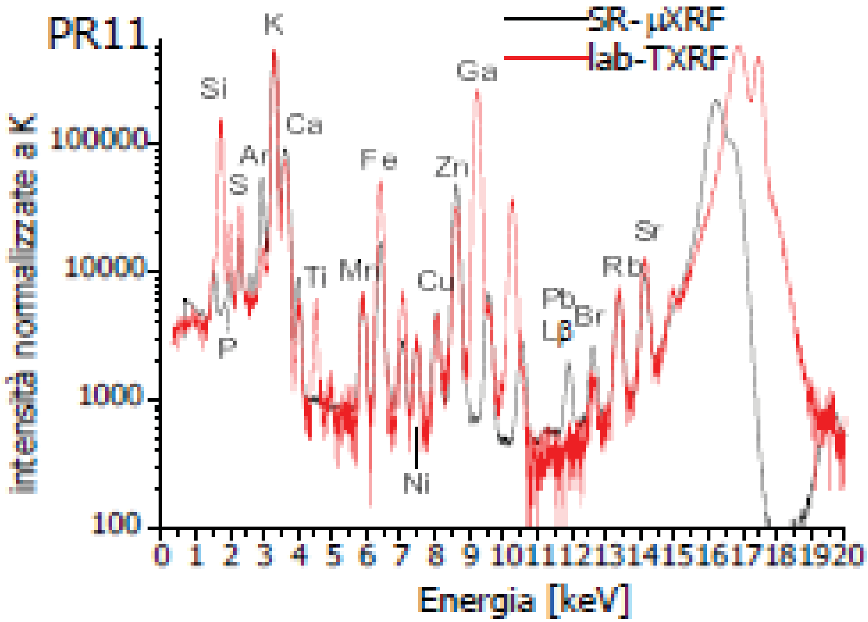




Polycapillary micro-XRF

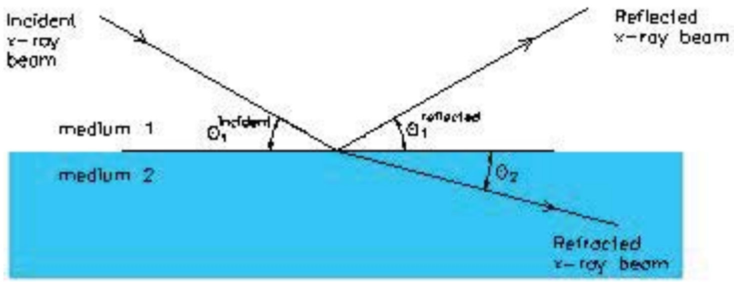


confocal micro-XRF



TXRF
Total Reflection X-Ray Fluorescence

Total external reflection

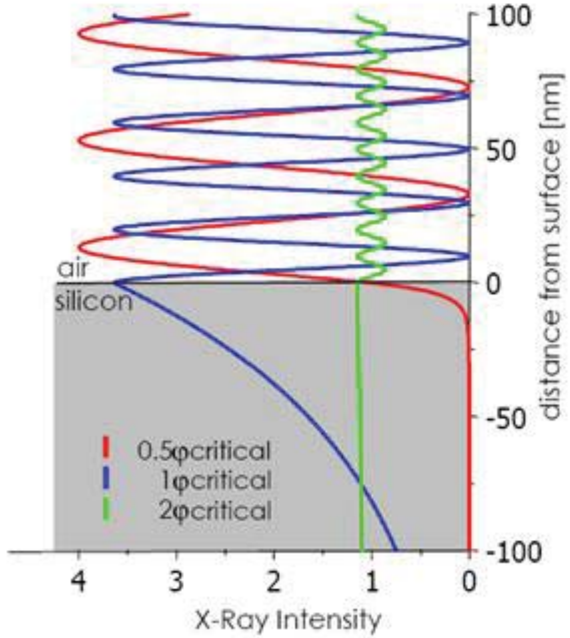


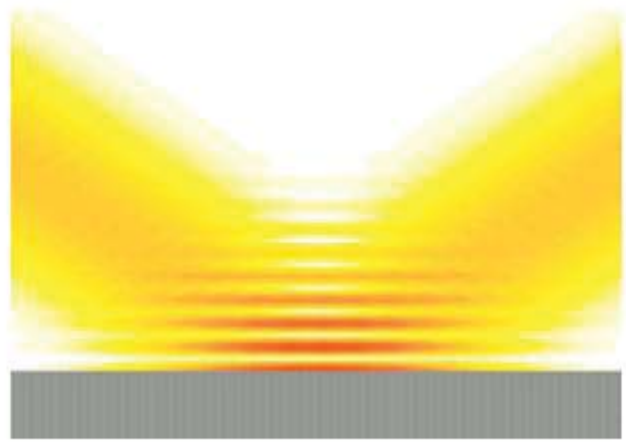
n (x-ray range) $= 1 - \delta - i\beta$

$\delta \sim 10^{-6} \quad \beta \sim 10^{-8}$

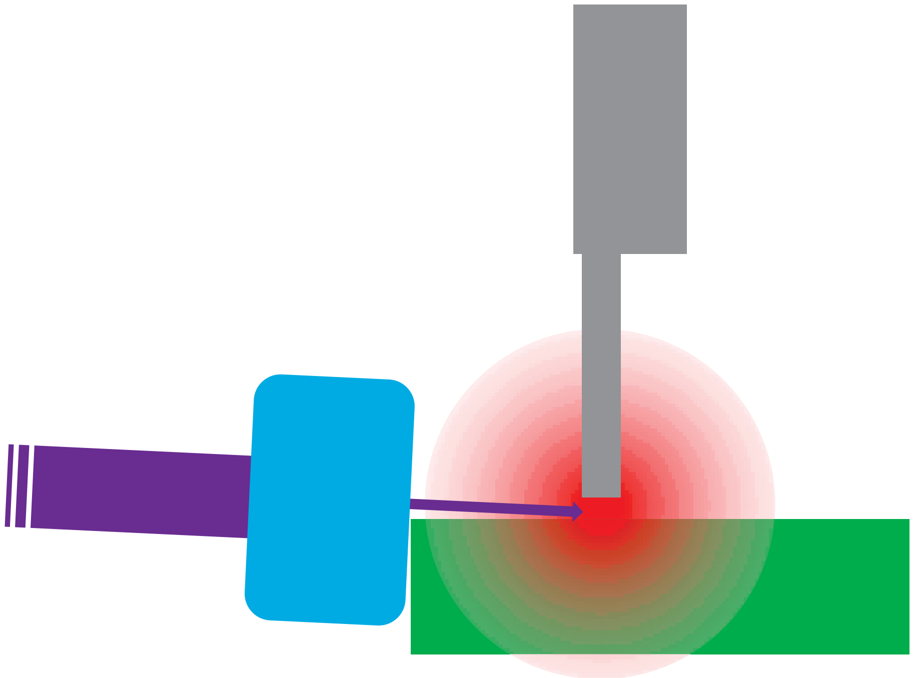
φ critical $\approx \sqrt{2\delta}$

φ critical
(Si, 17.5 keV) $\approx$ 0.1° $\approx$ 1.75 mrad
(Si, 500 eV) $\approx$ 3.7° $\approx$ 64.6 mrad

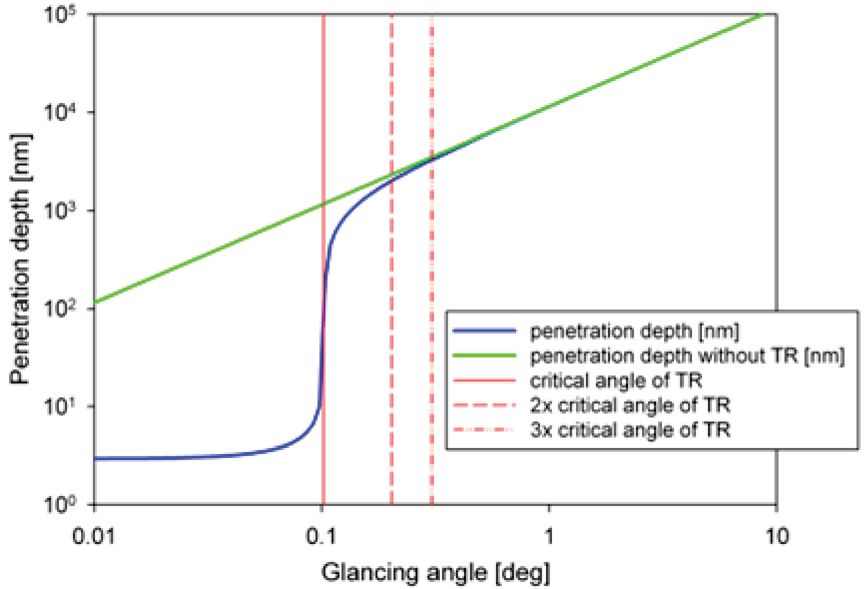




TXRF



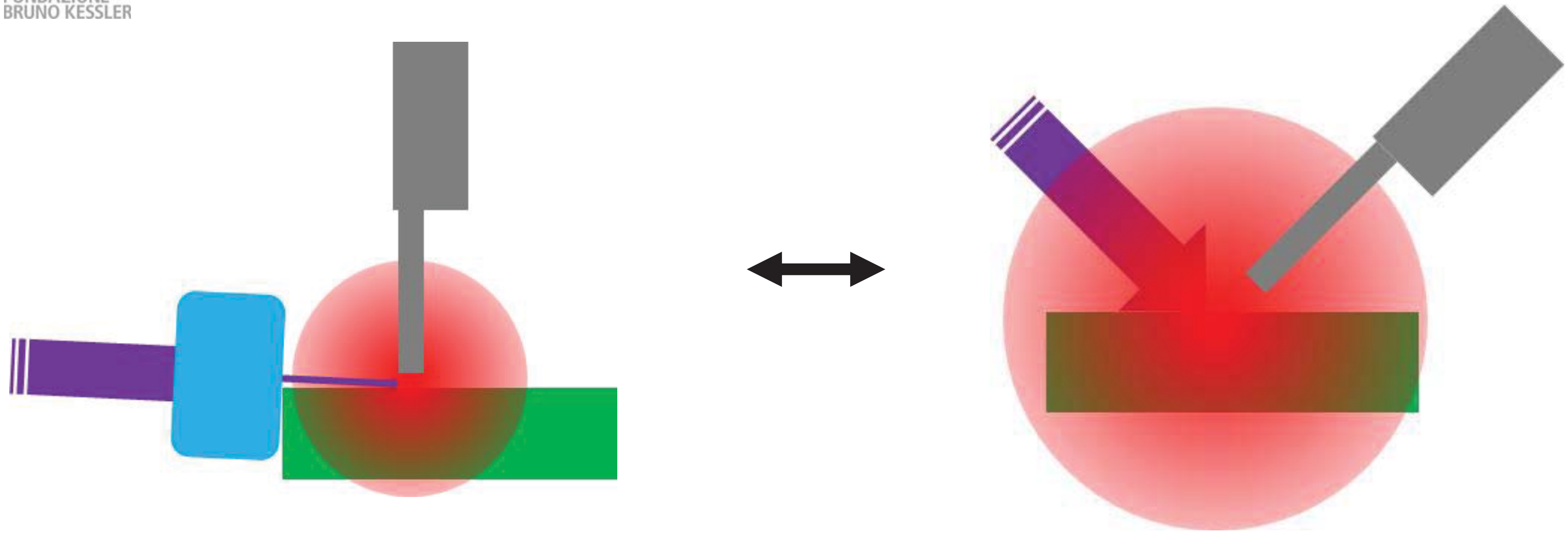
flat smooth surface (reflector)



Idea: - analyse impurities-contamination of polished surfaces

- deposit sample on a reflector and carry out analysis of the sample

TXRF



- background reduction
- double excitation of sample by both the primary and the reflected beam
- small distance sample - detector (~1mm) : large solid angle
- small sample amounts required
- detection limits in the pg range with X-ray tube excitation
- detection limits in the fg range with Synchrotron radiation excitation
- “no” matrix effects ?

TXRF – cultural heritage studies

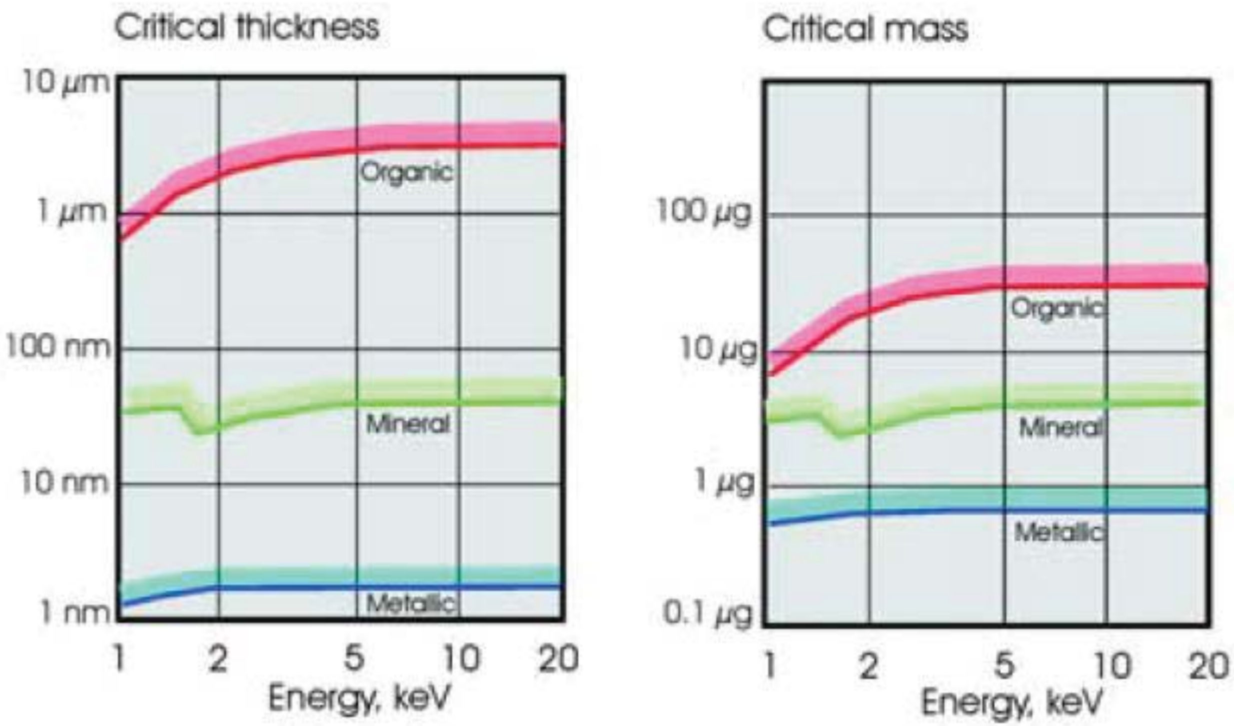
e-PS, 2004, 1, 23-34
ISSN: 1581-9280

TOTAL REFLECTION X-RAY FLUORESCENCE SPECTROMETRY - A VERSATILE TOOL FOR ULTRA - MICRO ANALYSIS OF OBJECTS OF CULTURAL HERITAGE

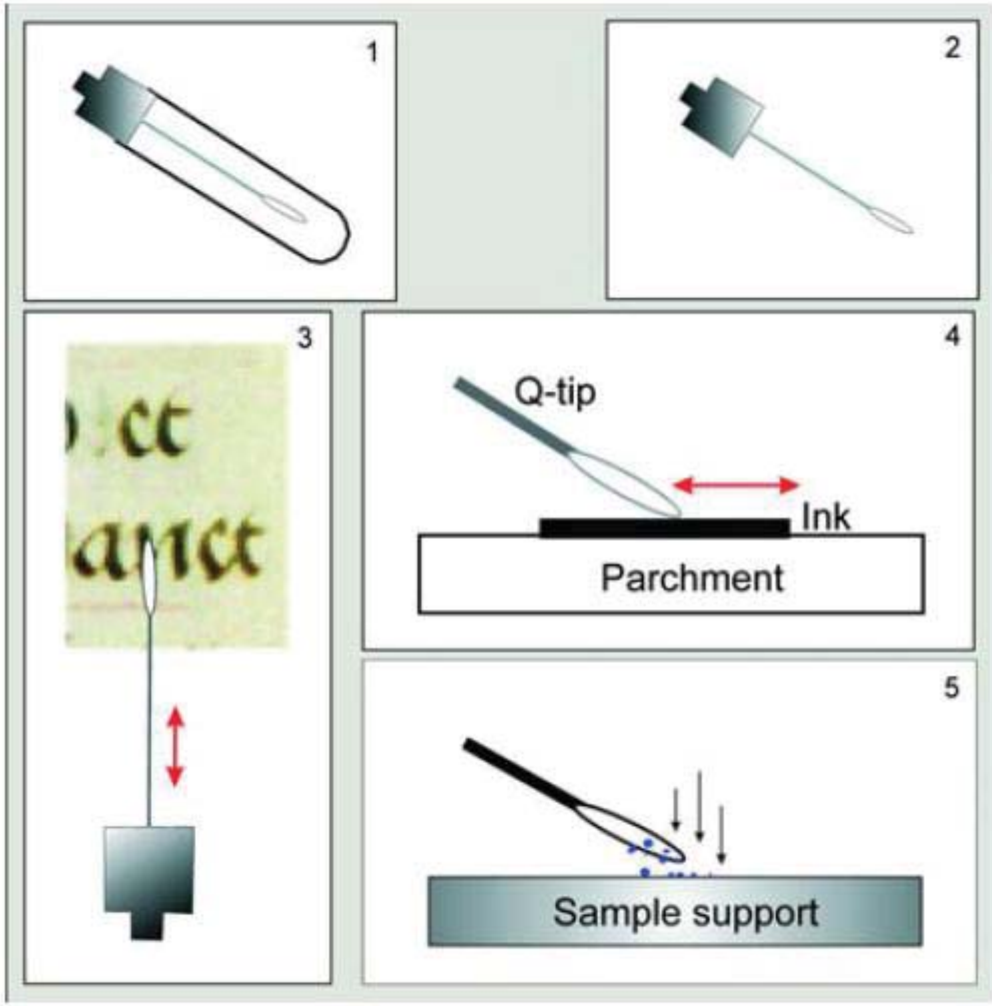
A. VON BOHLEN[1]

Institute of Spectrochemistry
and Applied Spectroscopy
ISAS, Bunsen-Kirchhoff-Str. 11,
D – 44139 Dortmund, Germany

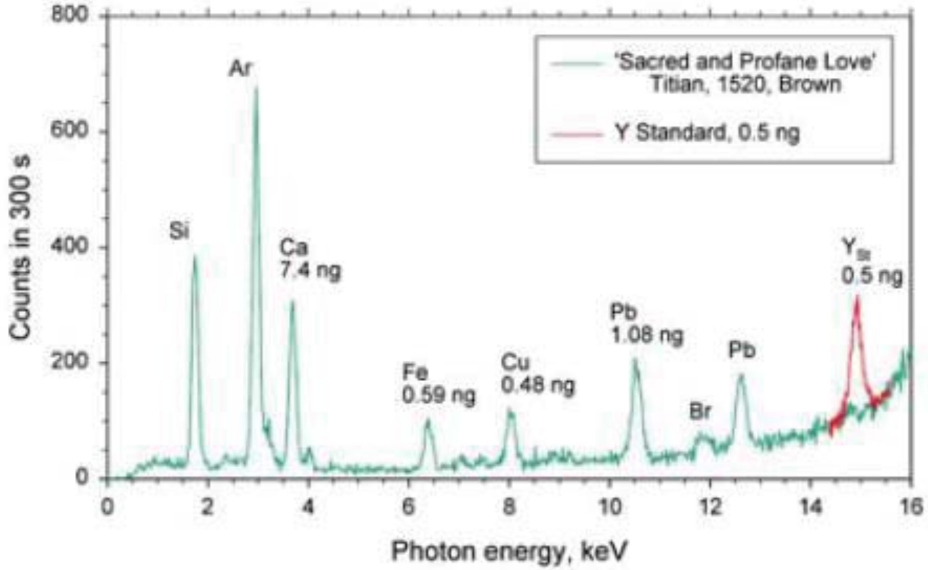
TXRF – critical thickness/mass



TXRF – cultural heritage studies - sampling



TXRF – cultural heritage studies



FONDAZIONE BRUNO KESSLER

TXRF – cultural heritage studies

White Pigments

Antimony white	Sb_2O_3
Lithopone	$ZnO + BaSO_4$
Permanent white	$BaSO_4$
Titanium white	TiO_2
White lead	$2PbCO_3 \times Pb(OH)_2$
Zinc white	ZnO
Zirconium oxide	ZrO_2
Chalk	$CaCO_3$
Gypsum	$CaSO_4 \times 2H_2O$

Yellow Pigments

Auripigmentum	As_2S_3
Cadmium yellow	CdS
Chrome yellow	$2PbSO_4 \times PbCrO_4$
Cobalt yellow	$K_3[Co(NO_2)_6] \times 1.5H_2O$
Lead-tin yellow	Pb_2SnO_4 / $PbSn_2SiO_7$
Massicot	PbO
Naples yellow	$Pb(SbO_3)_2$ / $Pb_3(SbO_4)_2$
Strontium yellow	$SrCrO_4$
Titanium yellow	$NiO \times Sb_2O_3 \times 20TiO_2$
Yellow ochre	$Fe_2O_3 \times nH_2O$ (20% - 70%)
Zinc yellow	$K_2O \times 4ZnO \times 4CrO_3 \times 3H_2O$

Red Pigments

Cadmium red	$CdS + CdSe$
Cadmium vermilion	$CdS + HgS$
Chrome red	$PbO \times PbCrO_4$
Molybdate red	$7PbCrO_4 \times 2PbSO_4 \times PbMoO_4$
Realgar	As_2S_3
Red lead	Pb_3O_4
Red ochre	Fe_2O_3 (up to 90%)
Vermilion	HgS

Green Pigments

Basic copper sulfate	$Cu_x(SO_4)_y(OH)_z$
Chromium oxide	Cr_2O_3
Chrysocolla	$CuSiO_3 \times nH_2O$
Cobalt green	$CoO \times 5ZnO$
Emerald green	$Cu(CH_3COO)_2 \times 3Cu(AsO_2)_2$
Guignet green	$Cr_2O_3 \times nH_2O + H_3BO_3$
Malachite	$CuCO_3 \times Cu(OH)_2$
Verdigris	$Cu(CH_3COO)_2 \times nCu(OH)_2$

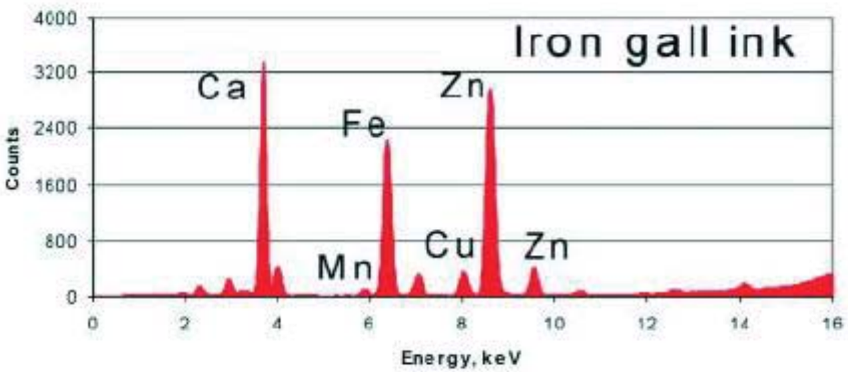
Blue Pigments

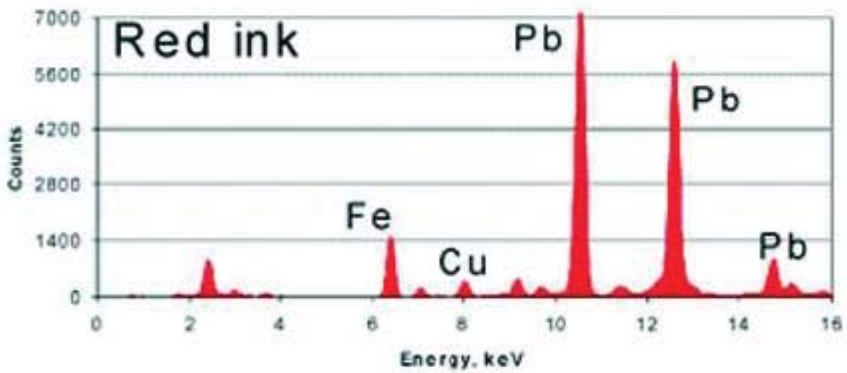
Azurite	$2CuCO_3 \times Cu(OH)_2$
Cerulean blue	$CoO \times nSnO_2$
Cobalt blue	$CoO \times Al_2O_3$
Cobalt violet	$Co_3(PO_4)_2$
Egyptian blue	$CaO \times CuO \times 4SiO_2$
Manganese blue	$BaSO_4 \times Ba_3(MnO_4)_2$
Prussian blue	$Fe_4[Fe(CN)_6]_3$
Smalt	Co-glass ($K_2O + SiO_2 + CoO$)
Ultramarine	$Na_{8..10}Al_6Si_6O_{24}S_{2..4}$

Black Pigments

Antimony black	Sb_2O_3
Black iron oxide	$FeO \times Fe_2O_3$
Carbon black	C (95%)
Cobalt black	CoO
Ivory black	$C + Ca_3(PO_4)_2$
Manganese oxide	$MnO + Mn_2O_3$

TXRF – cultural heritage studies





TXRF – cultural heritage studies

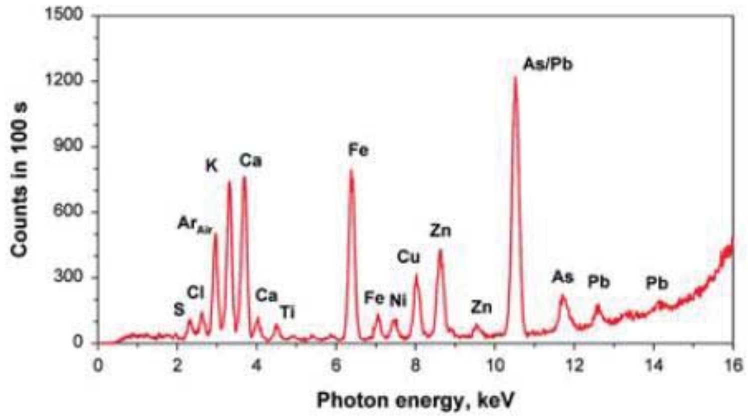


Figure 11. Scroll of a Cello made by L. Maugin, 19th century and TXRF spectrum of the original varnish.

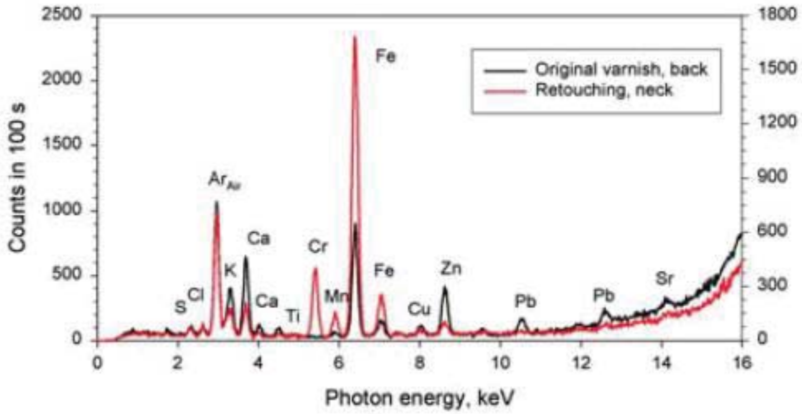


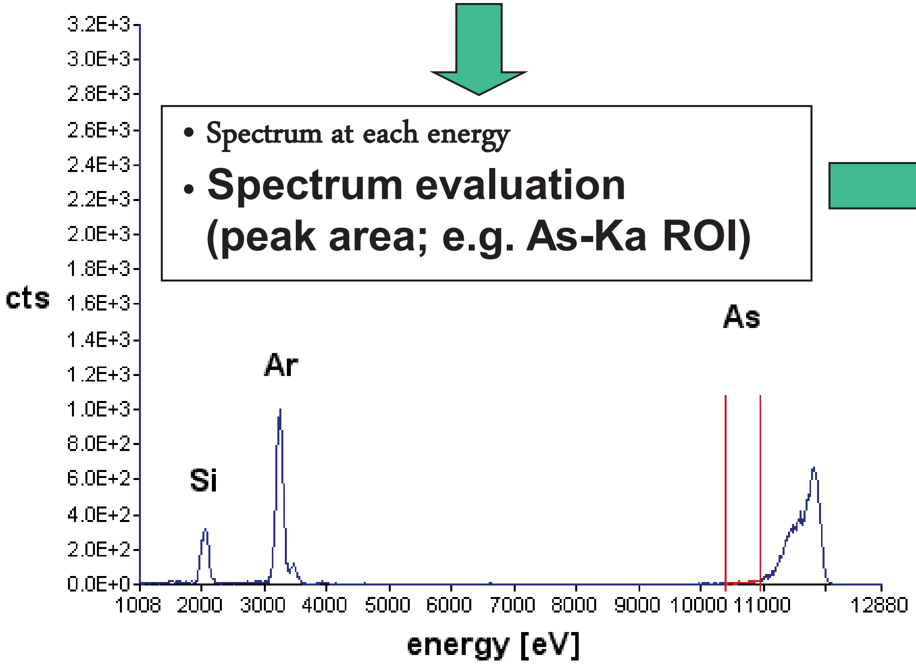
Figure 12. TXRF spectra of an original and retouched violin varnish from a violin made by Th. & S. Thompson, London, about 1780.

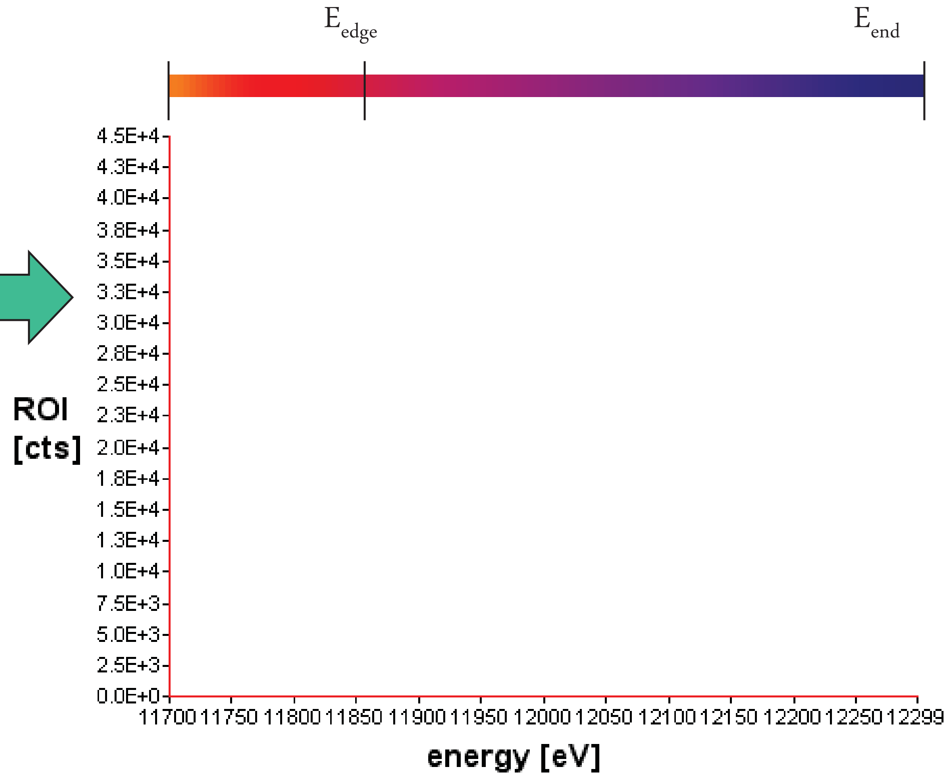
TXRF-XANES

The measurement: Example – TXRF-XANES of As droplet sample on Si reflector

Variation of excitation energy

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





EXAFS XANES

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

EXAFS equation, Fingerprint method (XANES)

- XANES: chemical state
- EXAFS: local structure

Example I

Arsenic speciation in cucumber (*Cucumis sativus* L.) xylem sap by K-edge TXRF-XANES

Giancarlo Pepponi

C. Streli, P. Wobrauschek, F. Meirer,

V.G. Mihucz, G. Zaray, V. Czech,

J. Broekaert, U. Fittschen

and G. Falkenberg

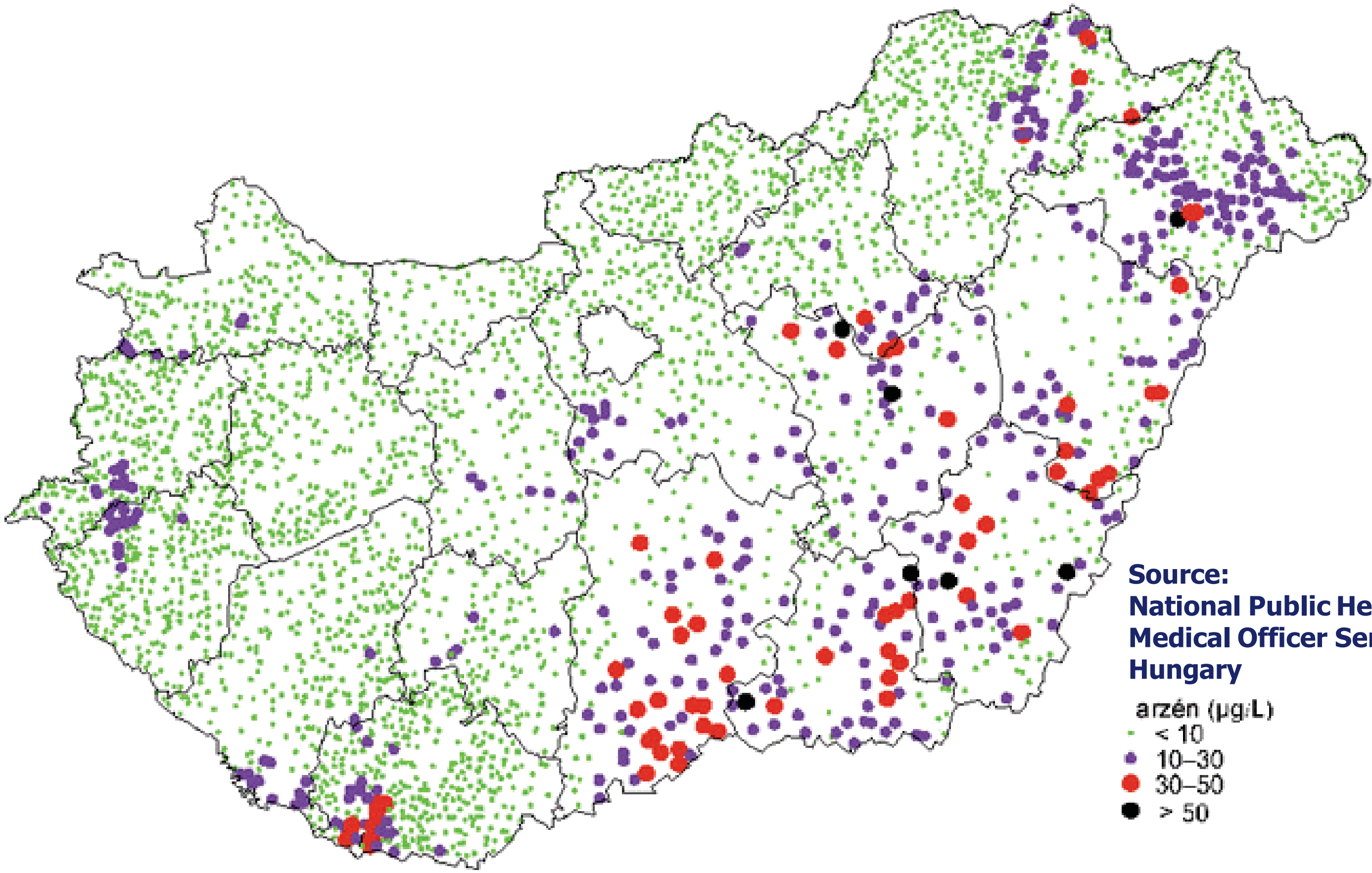
Application of synchrotron-radiation-induced TXRF-XANES for arsenic speciation in cucumber (Cucumis sativus L.) xylem sap

F. Meirer, G. Pepponi, C. Streli, P. Wobrauschek, V. G. Mihucz, G. Záray, V. Czech, J. A. C. Broekaert, U. E. A. Fittschen, G. Falkenberg

X-Ray Spectrometry, Volume 36, Issue 6, pages 408–412, 2007

Cucumber xylem sap - motivation

- Arsenic is contained in groundwater in Eastern Hungary in concentrations that can exceed 50 µg/L



Source:
National Public Health and Medical Officer Service, Hungary

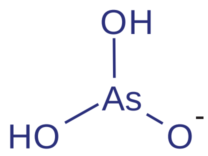
Cucumber xylem sap - motivation

- different species of As have different toxicity

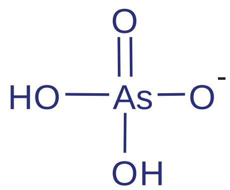
Compound	LD_{50} mg/kg
As_2O_3	20
Na_3AsO_3	60
Na_3AsO_4	120
$CH_3AsO(OH)_2$ (MMA)	700
$CH_3AsO(ONa)_2$	1800
$(CH_3)_2AsO(OH)$ (DMA)	1600
$(CH_3)_2AsO(ONa)$	2600
$(CH_3)_3As^+CH_2COO^-$ (As-betaine; AsB)	4500

Cucumber xylem sap - motivation

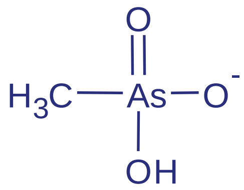
Occurrence of As species in plants, lichens, fungi, algal species and microorganisms **Source: V.M. Dembitsky, T. Rezanka, Plant Science 165, 2003, 1177-1192**



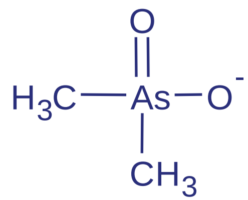
Arsenic (III) arsenite



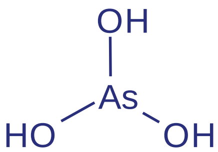
Arsenic (V) arsenate



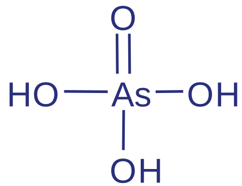
Methylarsonate



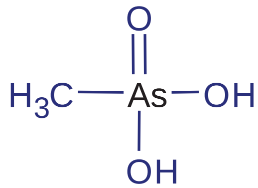
Dimethylarsinate



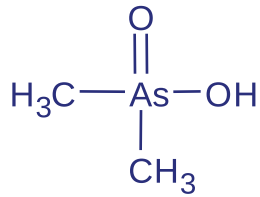
Arsenous acid



Arsenic acid



Methylarsonic acid



Dimethylarsonic acid

Speciation of the As is important to . . .

- understand how plants metabolise and transform As
- assess the health risk caused by As entering the food chain

In aerobic soils arsenate [As(V)] is the most stable form

Cucumber xylem sap - experimental

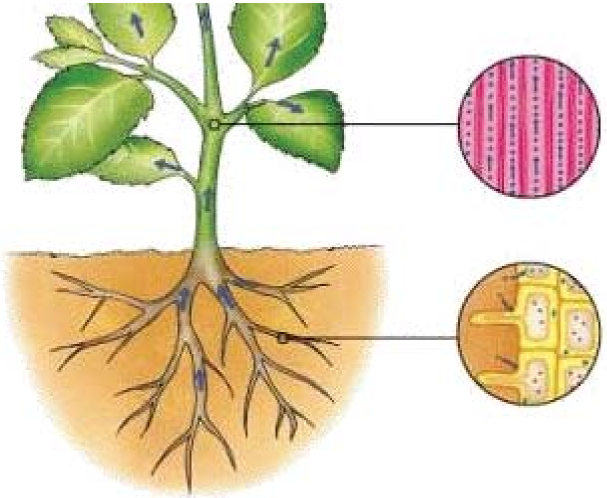
- At two leaf stage:
transferred in solution with arsenic compounds and diminished phosphate concentration

- After 30 days from germination (17 d arsenic):
  - stem cut 2 mm above root neck
  - sap collected with micropipettes for 1 hour into PE vials immersed in ice salt bath

→ Flow Injection Analysis (FIA)
HPLC-HR-ICP-MS

→ TXRF-XANES

Cucumber xylem sap - experimental



water is “pulled up” through the xylem

water is taken in through the roots

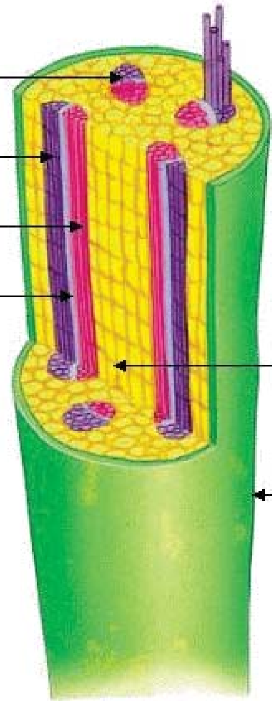
Source:
http://www.fairchildgarden.org/EduProfDev/Leaf_anatomy.html

vascular bundle

phloem

xylem

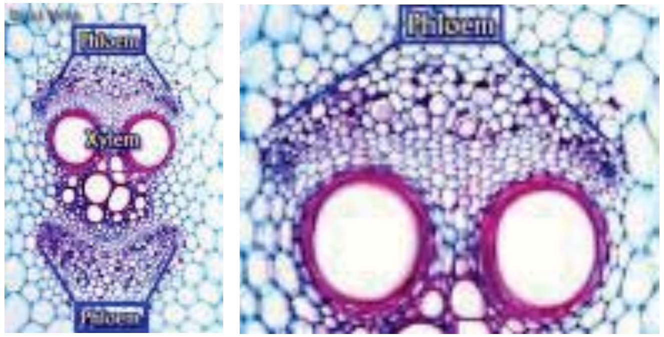
cambium



cortex

epidermis

cucumber vascular bundle



Source:
http://www.botany.hawaii.edu/faculty/webb/BOT410/410Labs/LabsHTML-99/Xylem/Labxyphlo99.html

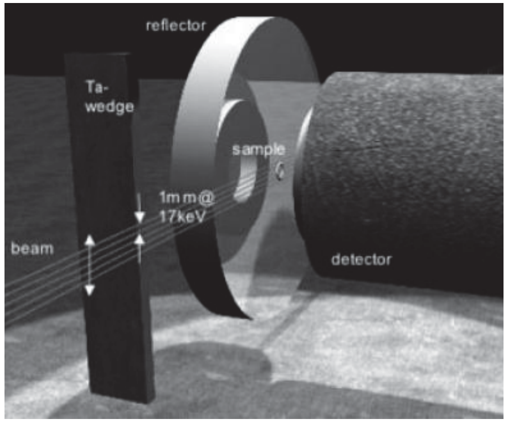
Cucumber xylem sap - experimental

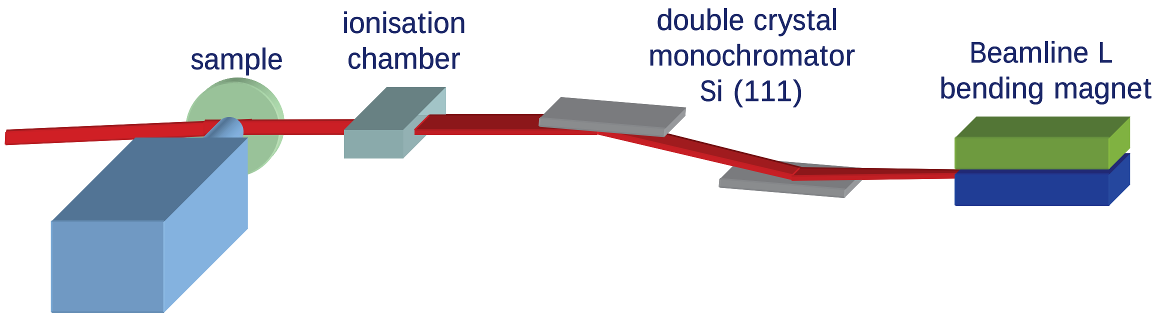
Solutions were

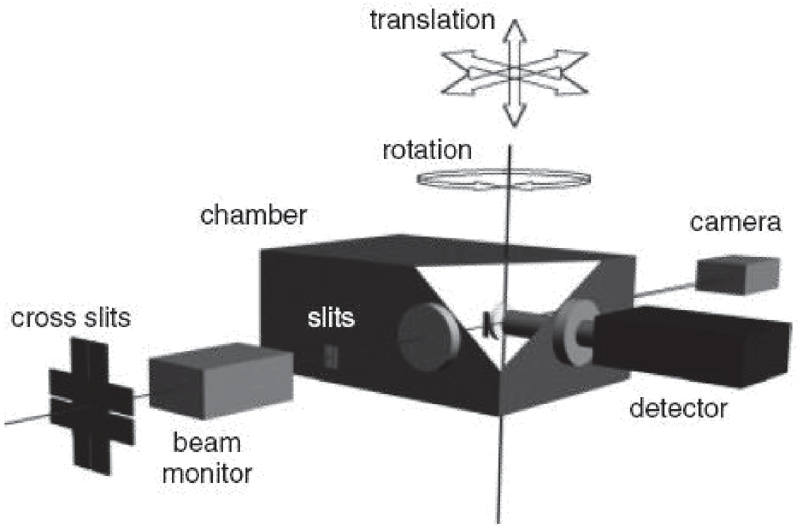
pipetted onto quartz reflectors
vacuum dried
sent in inert atmosphere (Ar)

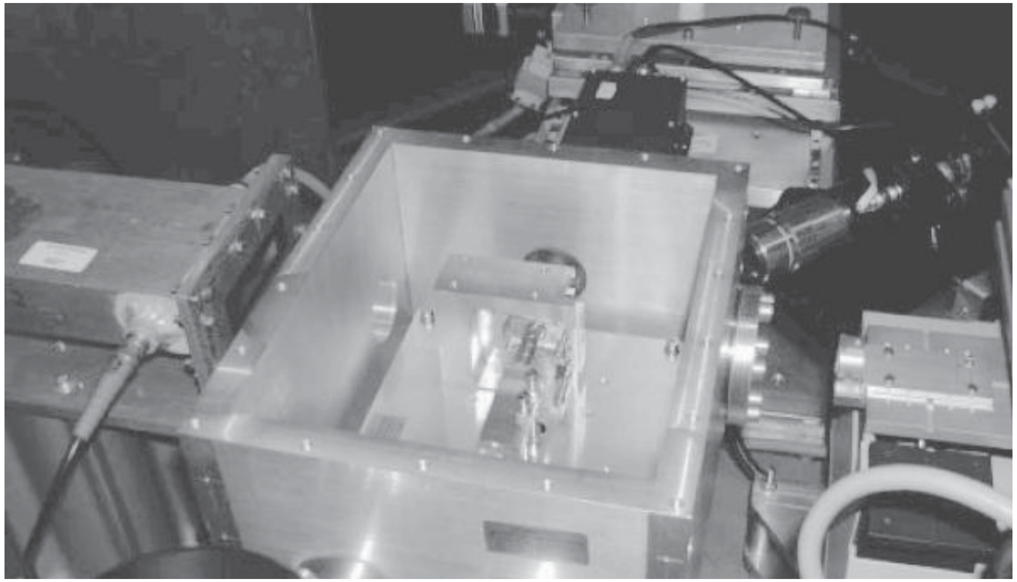
reflector	sample	oxidation number	concentration [ppb]	volume [µl]	mass As [ng]
117	standard solution	3	10000	20	200
122	nutrient solution	3	150	20	3
101	nutrient solution	3	150	10	1.5
124	xylem sap	3	50	20	1
121	standard solution	5	10000	20	200
123	nutrient solution	3	150	20	3
115	xylem sap	5	30	10	0.3

HASYLAB L - setup

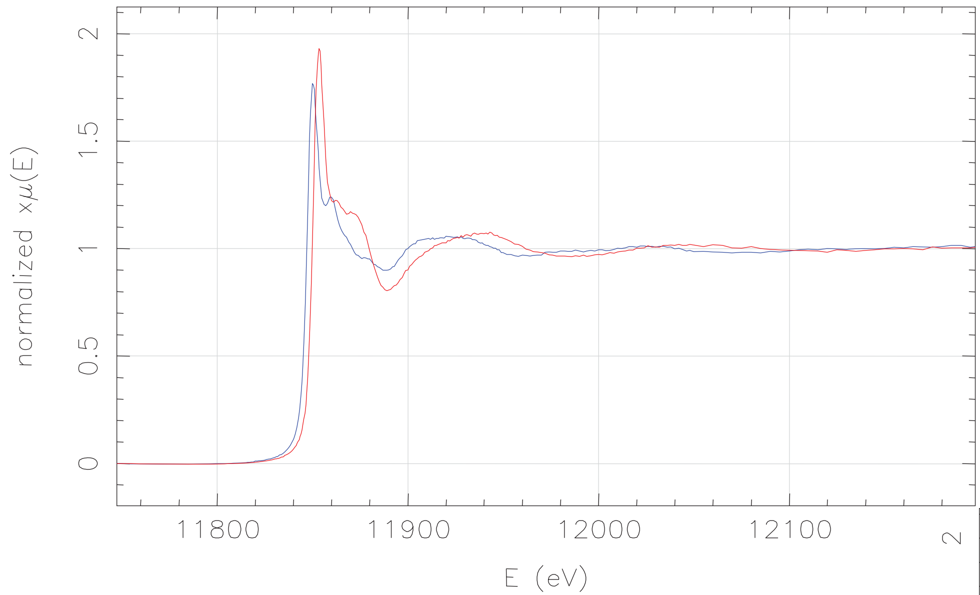




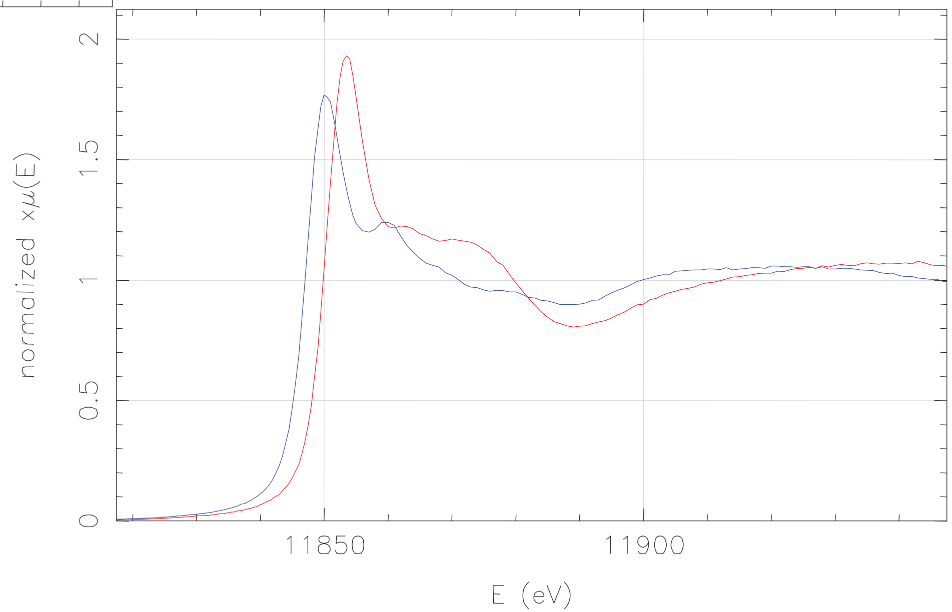




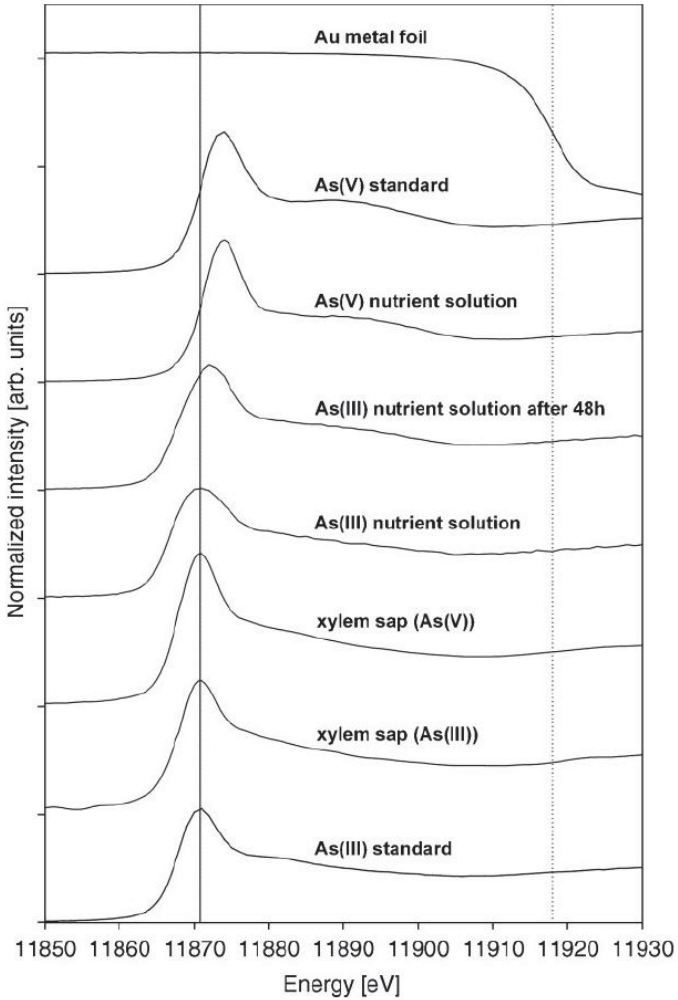
As standard solutions - XANES

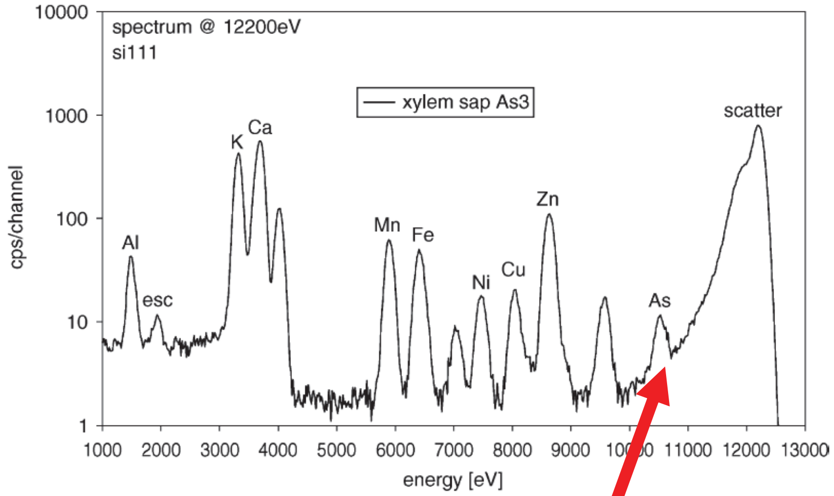


- standard solution As(III)
- standard solution As(V)



Fluorescence signal extraction





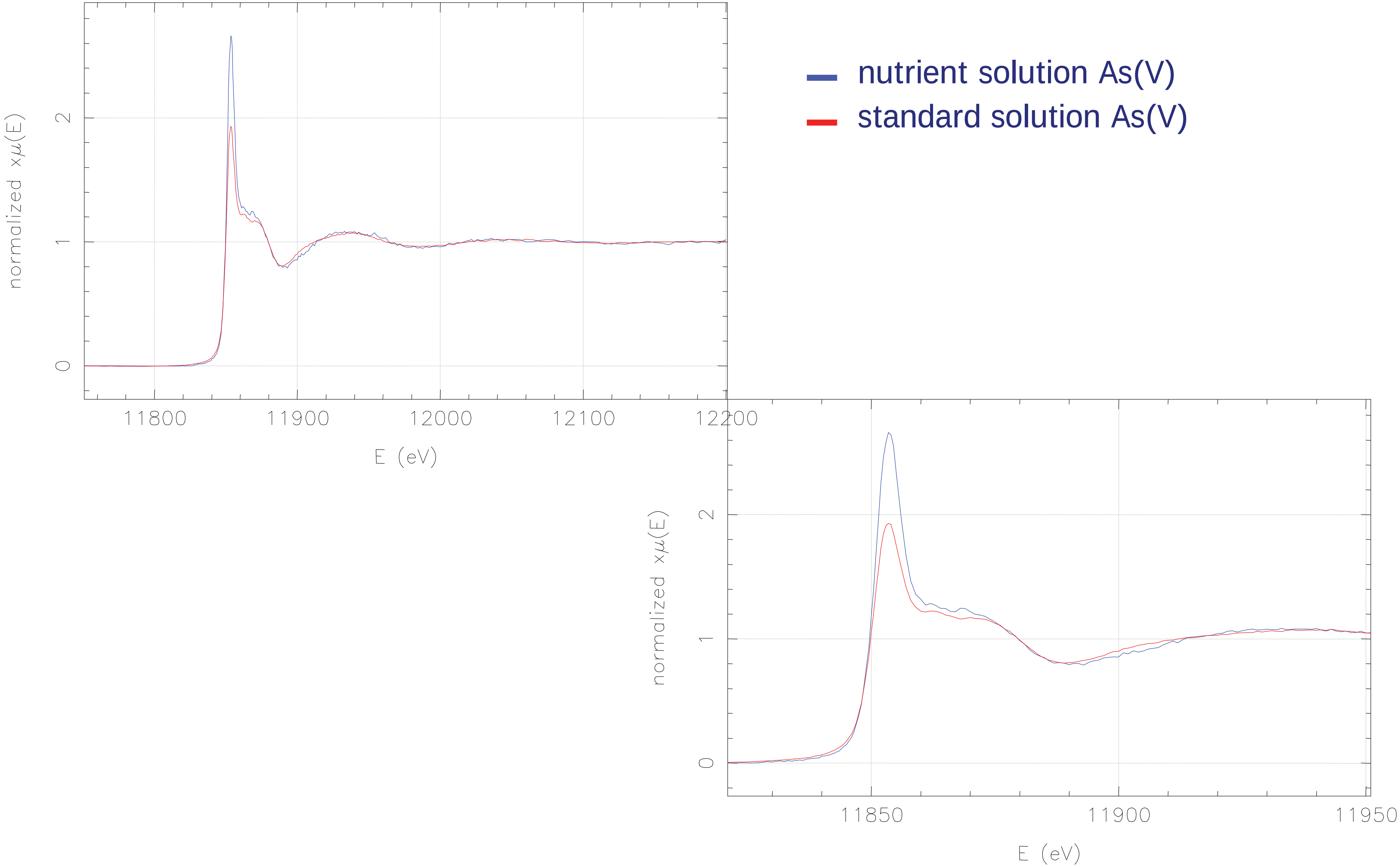
Results:

- Speciation of As was possible down to the 30ppb level
- As(III) in nutrient solutions oxidises easily to As(V)
- Cucumber roots convert As(V) to As(III)

Sample	As(III) [%]	As(V) [%]	R-factor	χ^2	reduced χ^2
xylem sap (As(III))	88 ± 3	12 ± 3	0.0155	1.09	0.0115
xylem sap (As(V))	83 ± 3	17 ± 3	0.0143	1.06	0.0112
As(III) nutrient solution	100 ± 3	0 ± 3	0.0103	0.68	0.0072
As(III) nutrient solution after 48h	71 ± 3	29 ± 3	0.0080	0.60	0.0063
As(V) nutrient solution	2 ± 2	98 ± 2	0.0065	0.63	0.0066

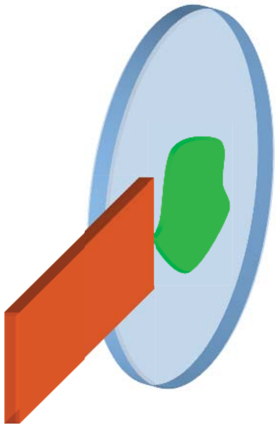
F. Meirer et al., X-Ray Spectrometry 36 (2007) 408-412.

A strange? result



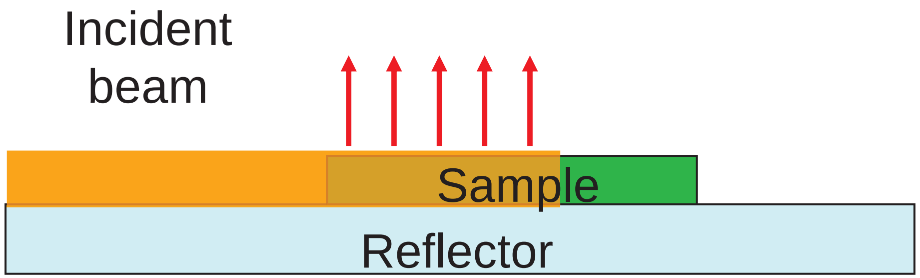
Self Absorption

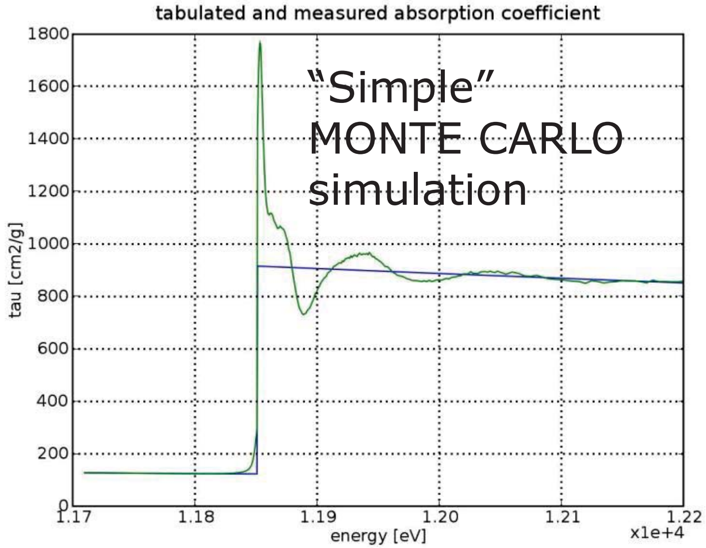
$$I(x) = I_0 \exp(-\mu x)$$

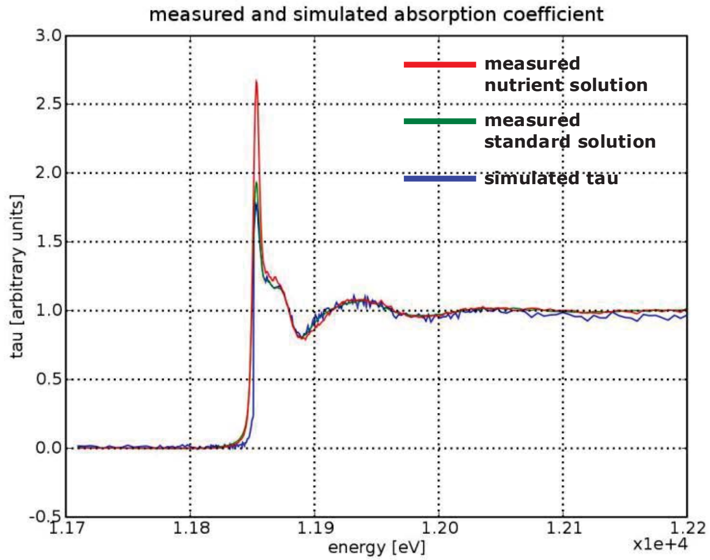


Sample (droplet) size becomes thickness, i.e. path that the primary beam crosses

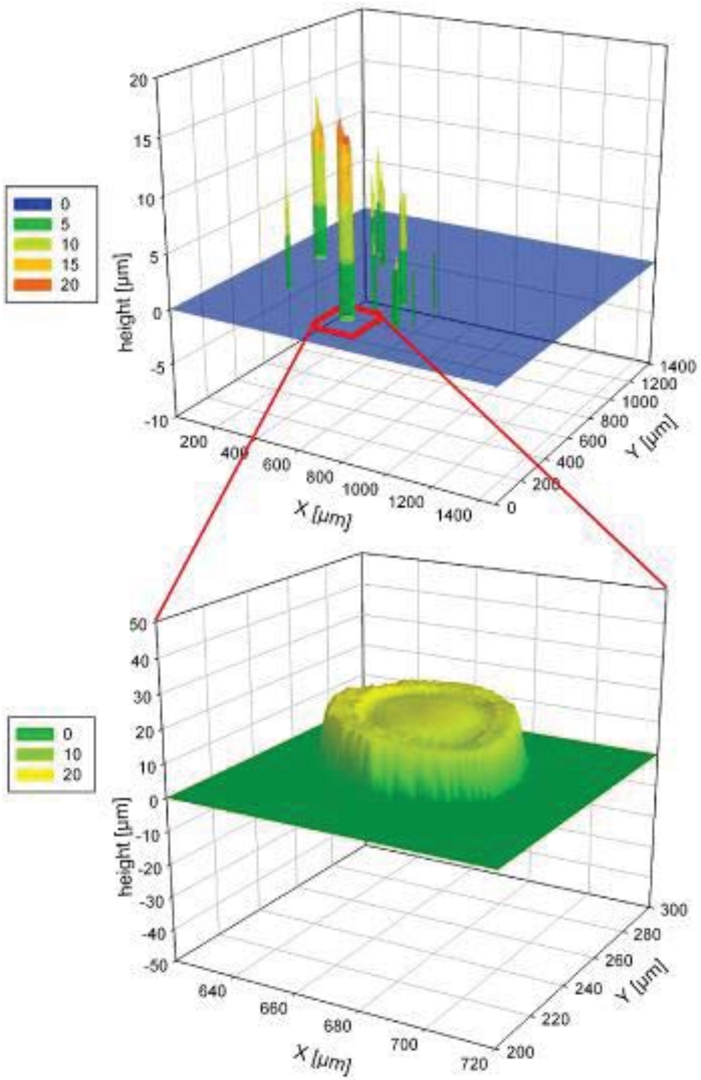
⇨ Large or highly concentrated samples: penetration depth of incident beam < sample size

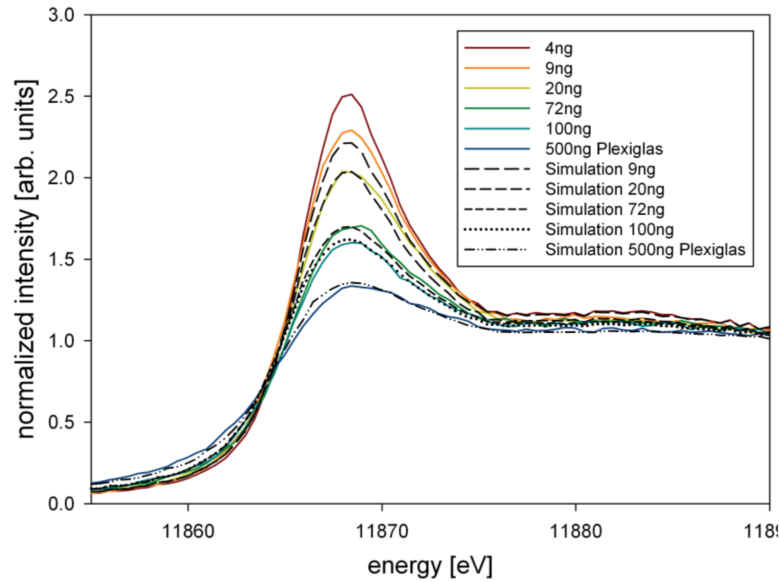


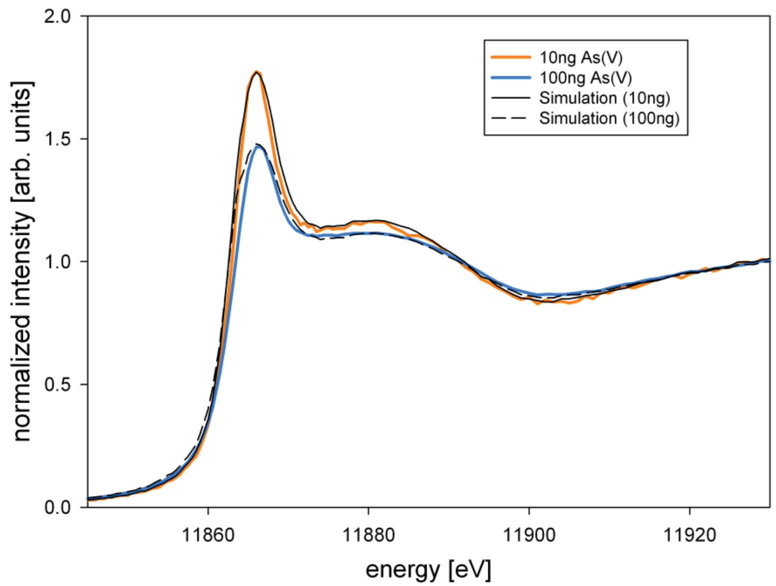




Self Absorption

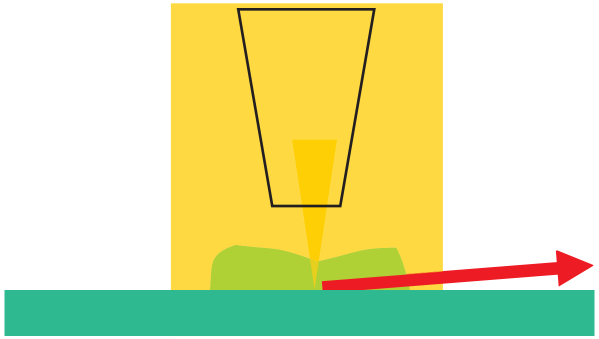




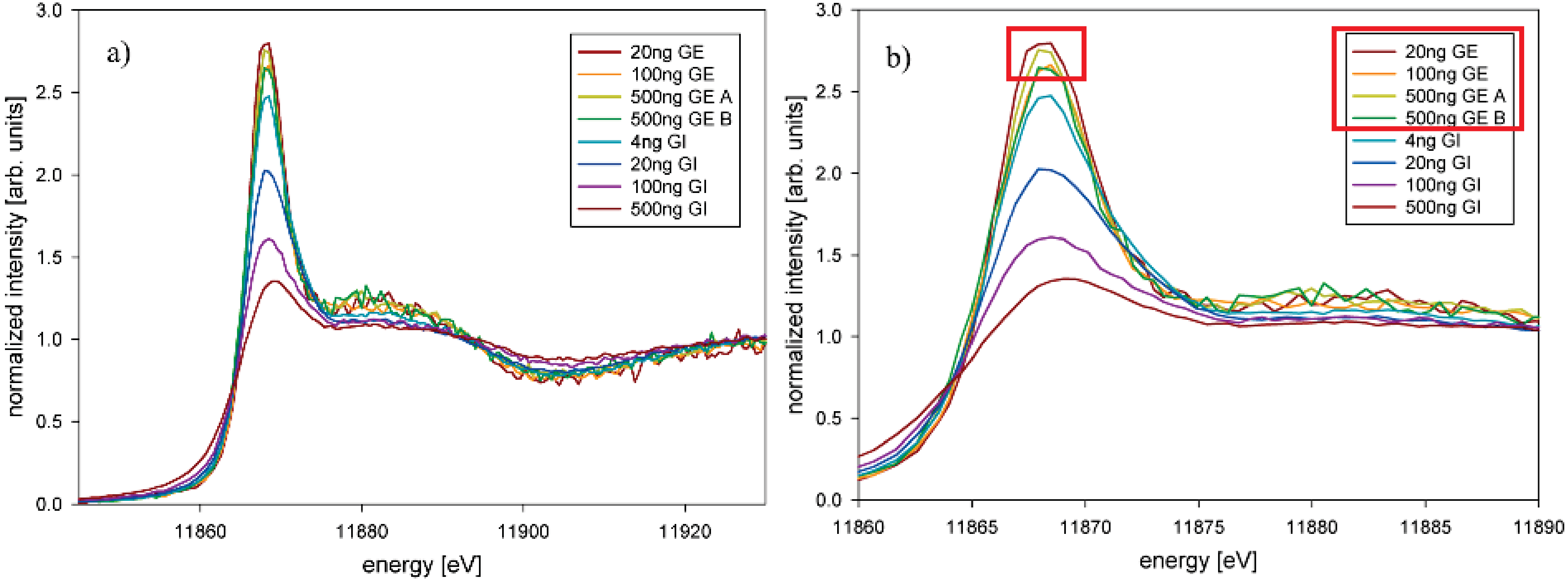


F. Meirer et al., Spectrochimica Acta Part B 63 (2008) 1496–1502

Self Absorption – grazing exit



- GE setup suffers minimally from self-absorption effects
- Shows lower sensitivity than GI-setup
  ⇒ difficult to apply to XAFS analysis of trace amounts (few nanograms) of samples



F. Meirer et al., J. Appl. Phys. 105, 074906 (2009)

Example II

Speciation of copper and zinc in size-fractionated aerosol samples using TXRF-XANES

J. Osán[1], F. Meirer[2,3], S. Török[1], D. Ingerle[2], C. Streli[2] and G. Pepponi[4]

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[2]Atominstitut, Vienna Univ. of Technology, Stadionallee 2, A-1020 Vienna, Austria
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Speciation of copper and zinc in size-fractionated atmospheric particulate matter using total reflection mode X-ray absorption near-edge structure spectrometry

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Particulate matter - motivation

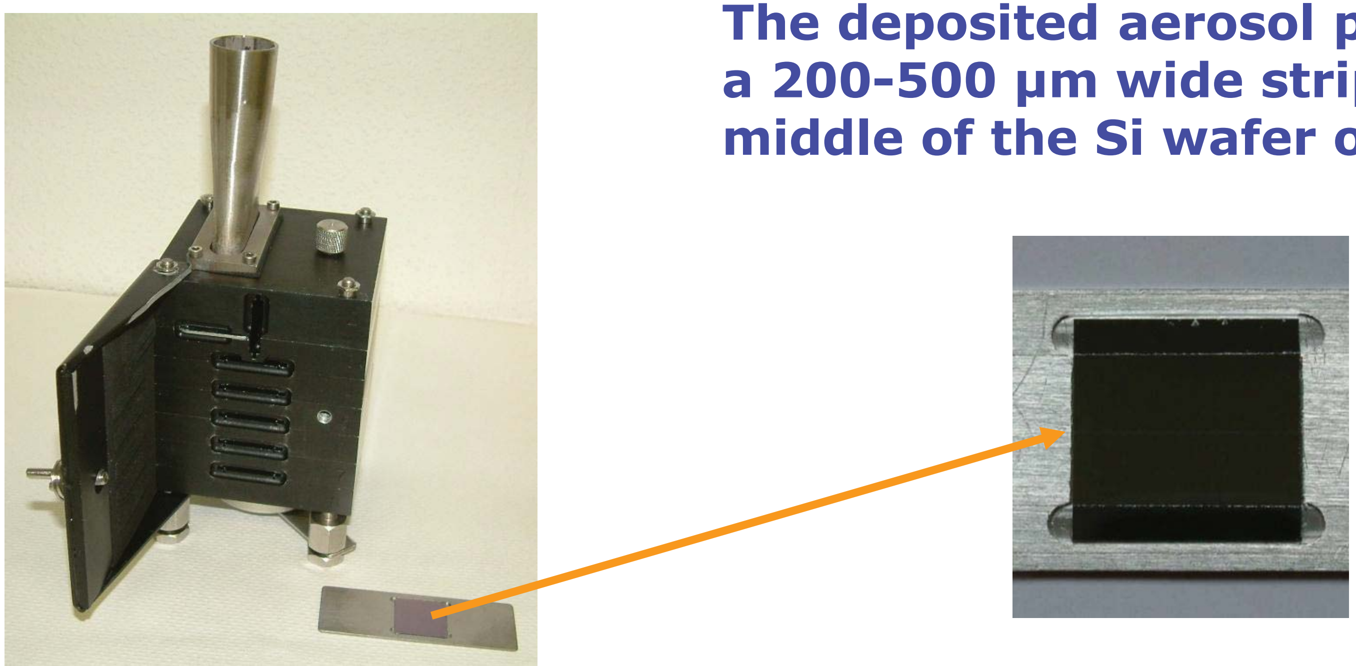
- Health effects of aerosol depend on the size distribution and the chemical composition of the particles
- Heavy metals of anthropogenic origin are connected to the fine ($PM_{2.5}$) aerosol fraction
- Determination of copper and zinc speciation in size-fractionated aerosols from a short sampling period
- Relation of the size distribution of Cu and Zn speciation to the aerosol sources

Particulate matter - experimental

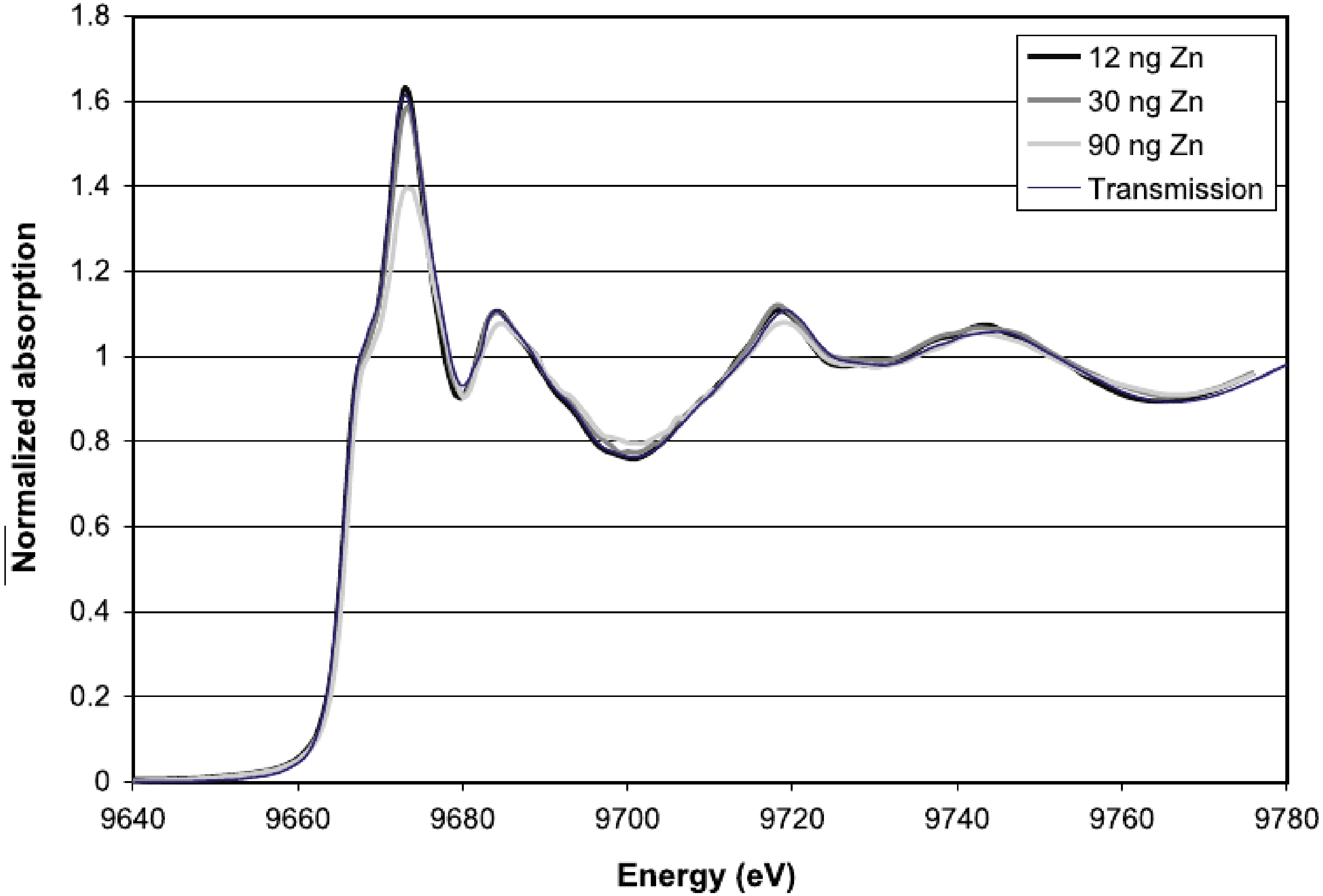
Size fractioned aerosol sampling

- 7-stage May-type cascade impactor
- cut-off diameters: 16, 8, 4, 2, 1, 0.5, 0.25 µm for stages 1–7 at 20 lpm flow rate
- sampling 20–3200 l air depending on stages and aerosol concentration

The deposited aerosol particles form a 200-500 µm wide strip in the middle of the Si wafer of 20x20 mm²



Particulate matter – self absorption



Particulate matter – Zn XANES

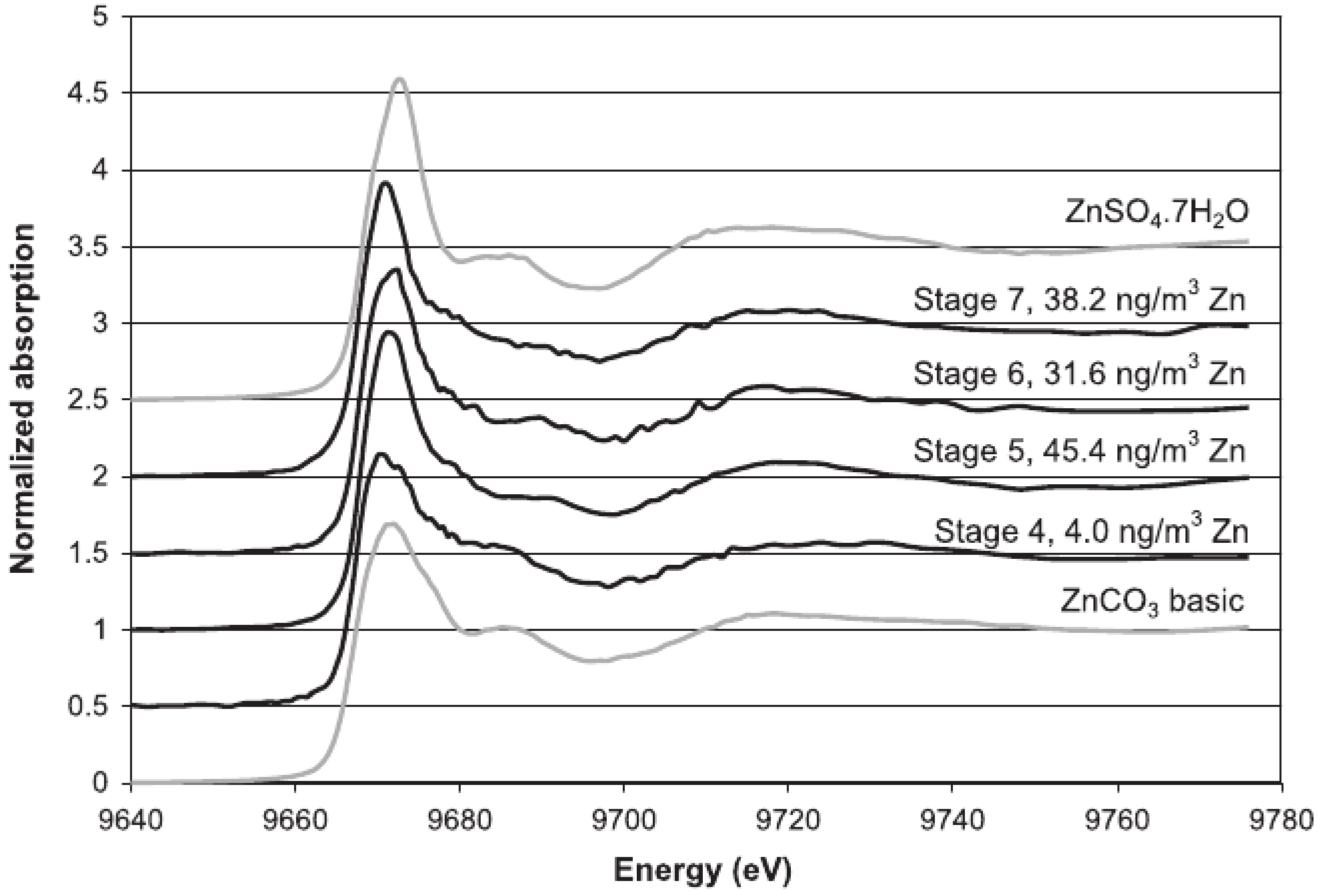


Fig. 5. Zn–K edge TXRF-XANES spectra of the aerosol sample set collected at the airport of Budapest on 12 01 2006; zinc sulfate and carbonate standard spectra are plotted for comparison.

Particulate matter – Cu XANES

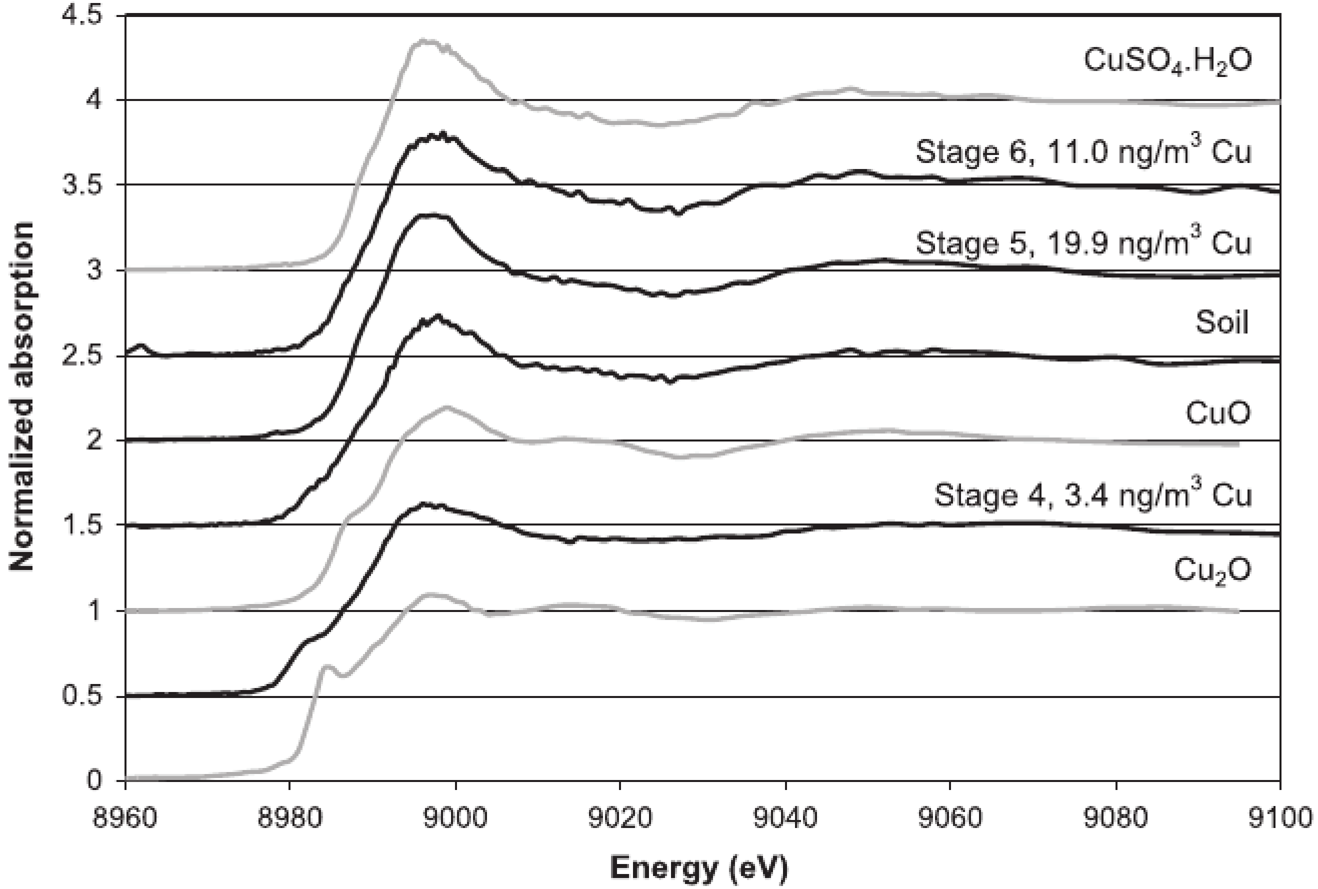


Fig. 6. Cu–K edge TXRF-XANES spectra of the aerosol sample set collected at the airport of Budapest on 12 01 2006; standard spectra of Cu(II) sulfate, Cu(II) oxide and Cu(I) oxide are plotted for comparison.

Particulate matter – conclusions

The combination of TXRF-XANES and direct sampling of aerosol particles onto Si wafers using a May-type cascade impactor was found to be well applicable for non-destructive speciation of transition metals in atmospheric particulate matter.

Cu and Zn chemical forms could be identified from air concentrations as low as 140 pg/m^3 for a collected air volume of 1 m^3 (50 min sampling time).

Speciation of metals with air concentrations in the ng/m^3 range is possible in the time scale of a few minutes, allowing the tracing of mobile sources variable in time.

Cu and Zn were found to be bound to secondary aerosol particles in the form of sulfates and nitrates in the fine fraction.

Sources of soil resuspension and brake pad wear erosion could be distinguished based on the chemical form of copper in the coarse fraction (2μm).

TXRF XANES conclusions

TXRF XANES good for:
- small sample amount (mass)
- diluted samples
- solutions/suspensions
- particulate matter

Speciation performed down to:
- 30 ng/ml   (xylem sap)
- 140 pg/m^3 (fine particulate matter)

Weaknesses:
- self absorption in “highly” concentrated samples (standards)
- alignment can be time consuming