Materials characterisation using Micro X-ray Fluorescence (BL-16) of Indus-2

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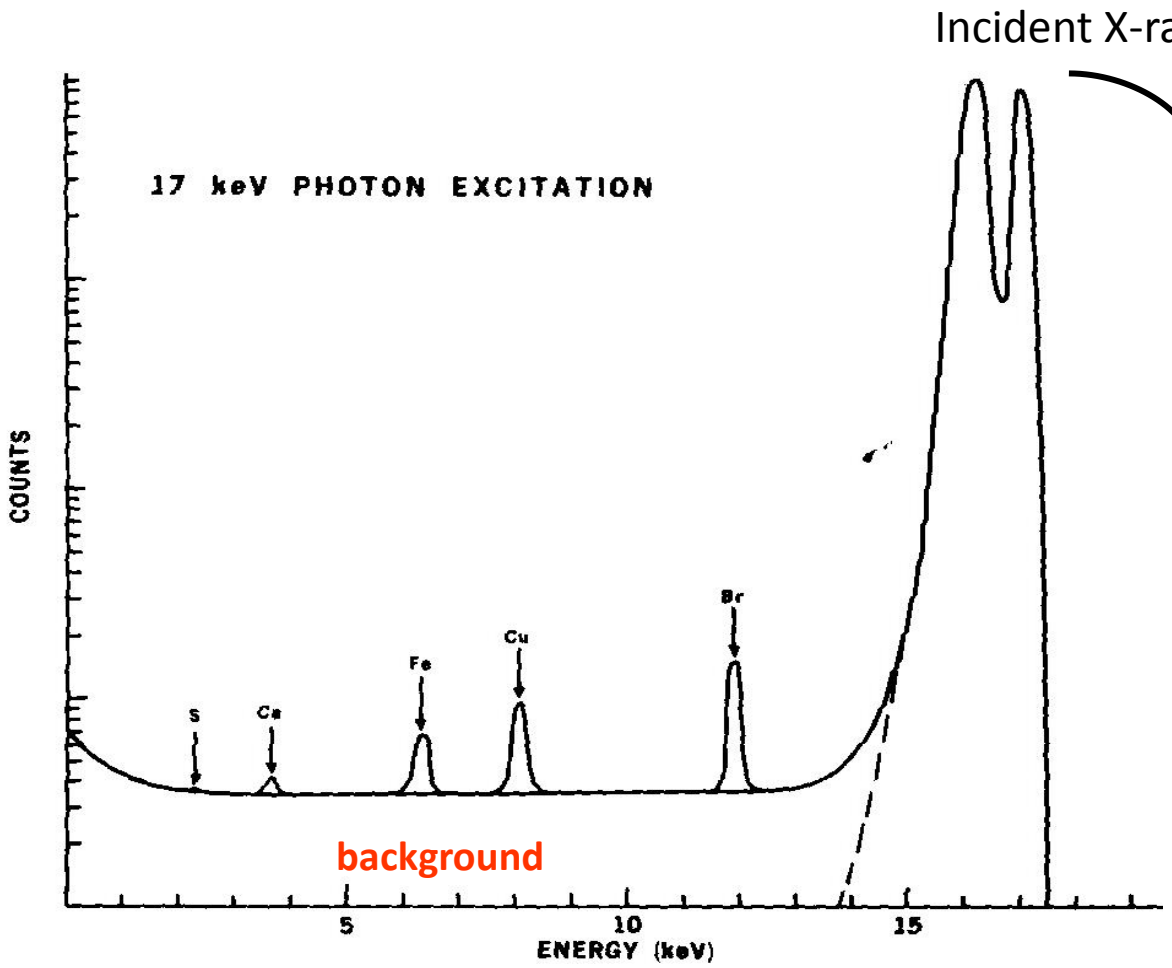
Outline

- **Introduction to EDXRF**
- **Microprobe XRF beamline (BL-16) of Indus-2**
  - **Beamline details, capabilities and salient features**
  - **Possible experiments (XRF, TXRF, μ-XRF)**
  - **Some results**
- **Thin layered materials**
  - ***X-ray reflectivity*, XSW**
  - ***CATGIXRF* program**
- **Future upgrades**

X-ray Fluorescence (XRF) ? : Principle



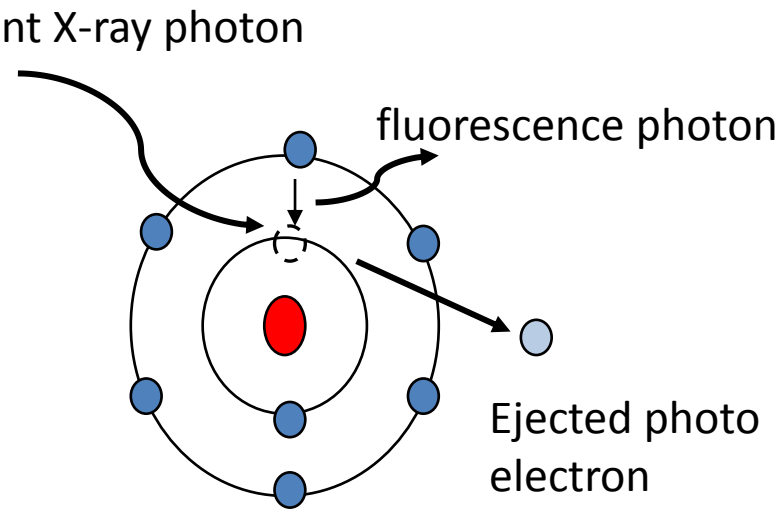
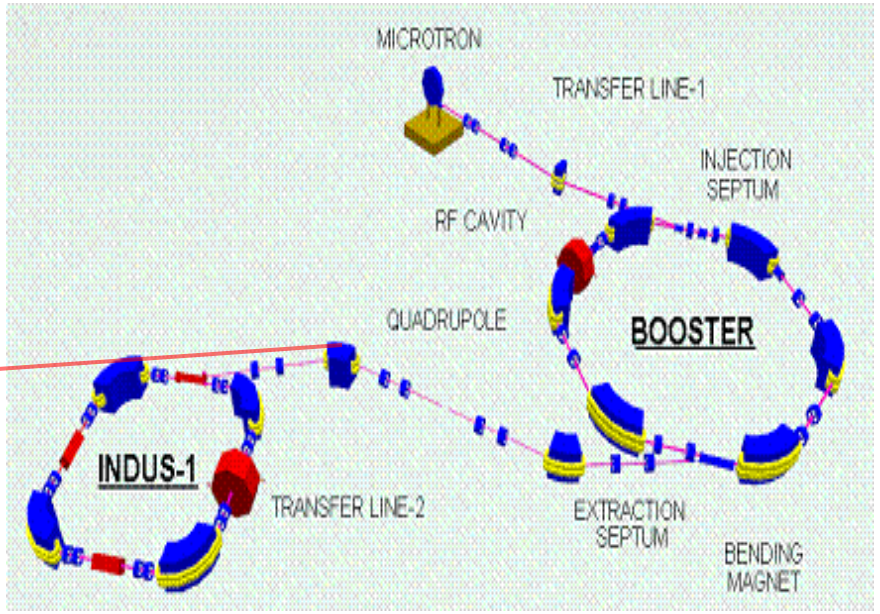


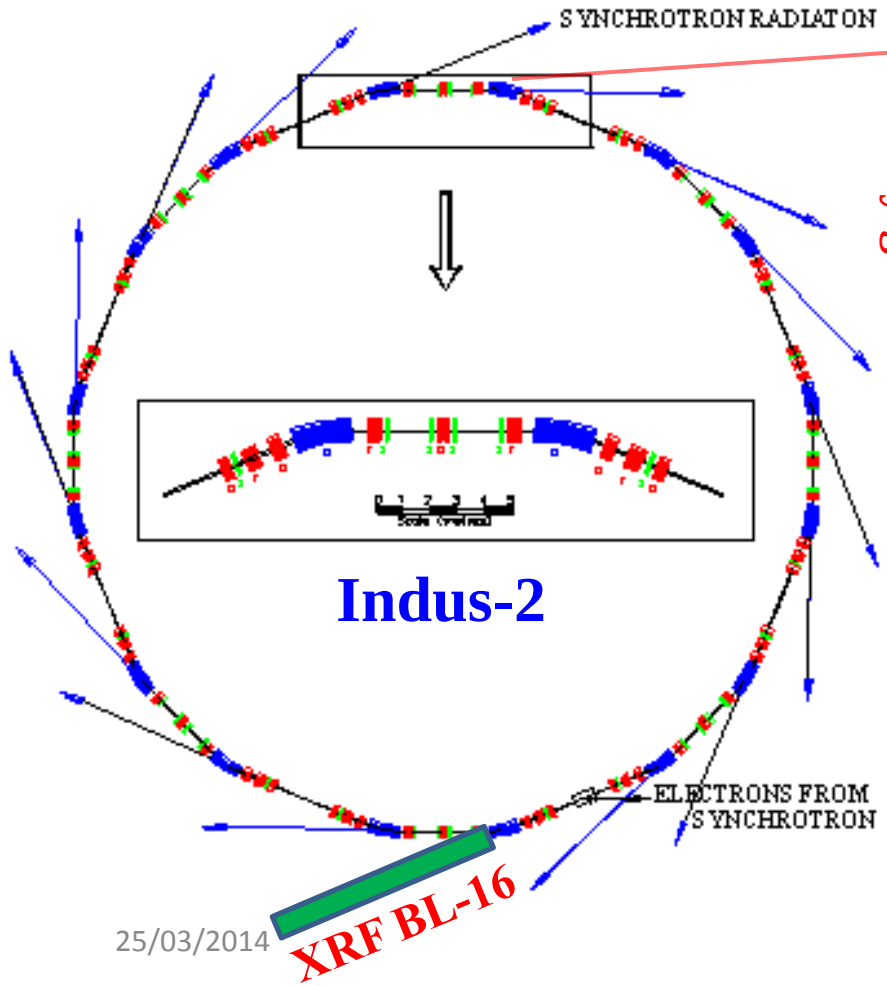
Fig. 1 Spectral background in conventional EDXRF spectrum

Indus SR facility

Indus-1



E = 450 MeV, 100mA
Critical wave length = ~ 61 Å



Entry gate

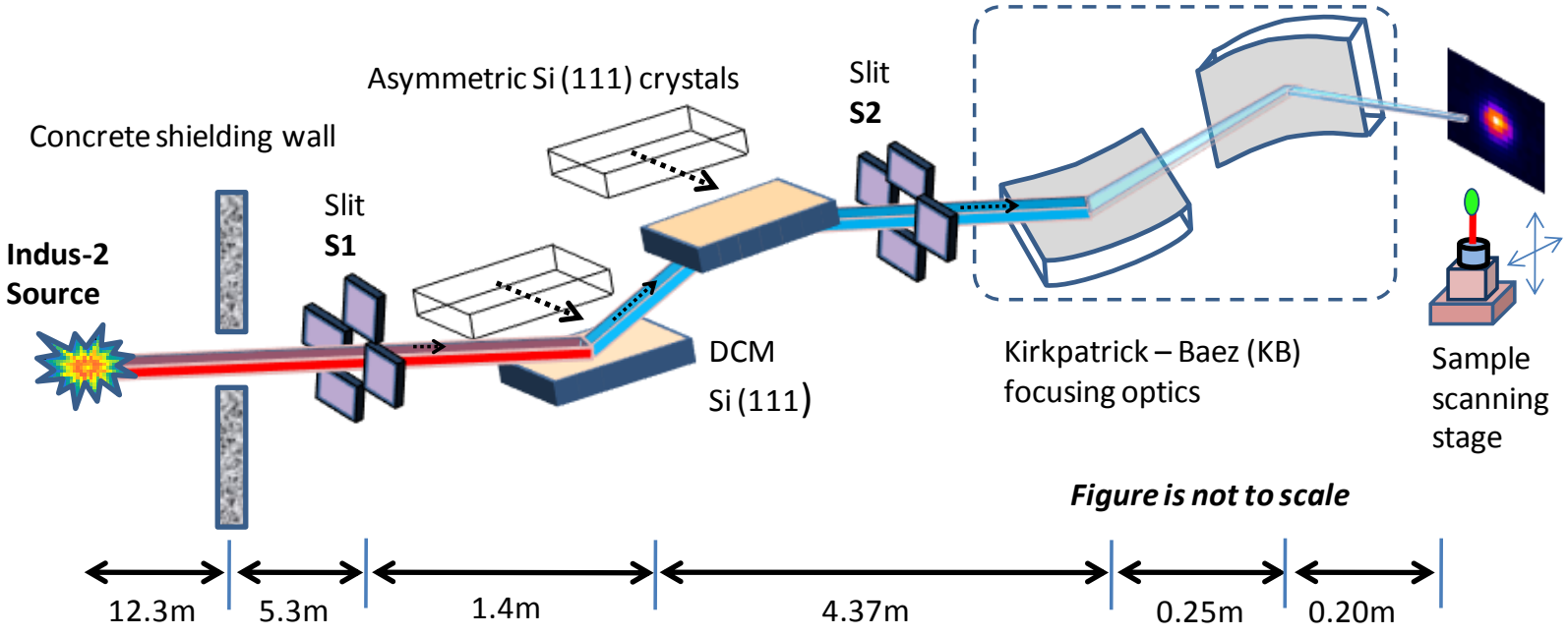
Indus-2

E = 2.5 GeV, 300mA
Critical wave length = ~ 2 Å

E = 2.5 GeV, 100mA

X-ray fluorescence-microprobe beamline (BL-16) on Indus-2

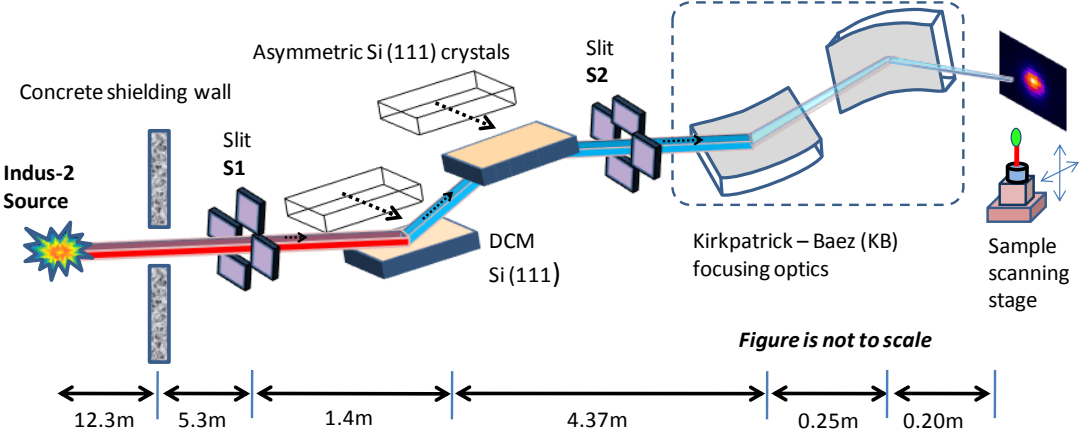
X-ray fluorescence-microprobe beamline (BL-16) on Indus-2



Beamline layout

Beamline parameters

Table 1



Parameters	Values
Working energy range	4 - 20 keV
Beam acceptance	1 mrad (h) x 0.2 mrad (v)
Energy resolution	~ 10^{-3} - 10^{-4}
Beam spot size (*at the sample position*)	: ~ 4.3 μm (v) x 7.5 μm (h) ***(Focused mode)*** : ~ 22 mm (h) x 5 mm (v) ***(Collimated beam mode)***
Photon flux [At 10 keV x-rays/100mA ring current]	: Flux ~ 2 x 10^7 ph/s ***(Focused mode)*** : Flux ~ 1 x 10^8 ph/s/mm^2 ***(Collimated mode)***

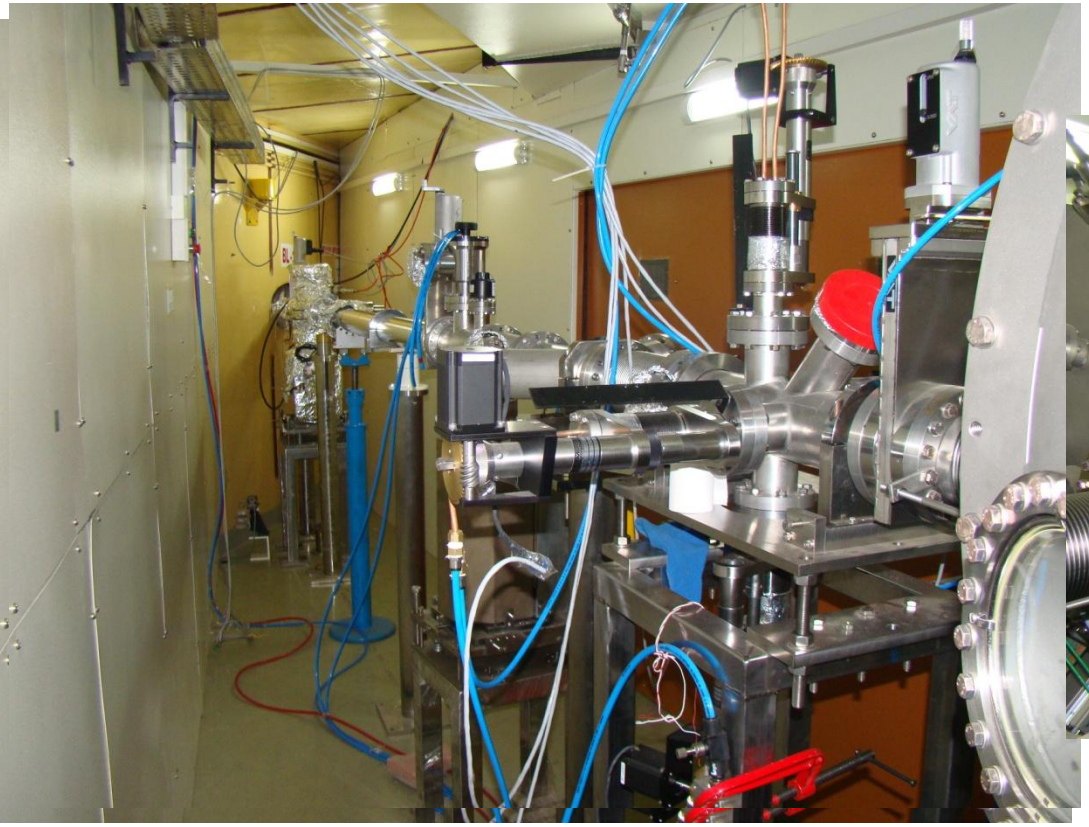
Beamline Optics

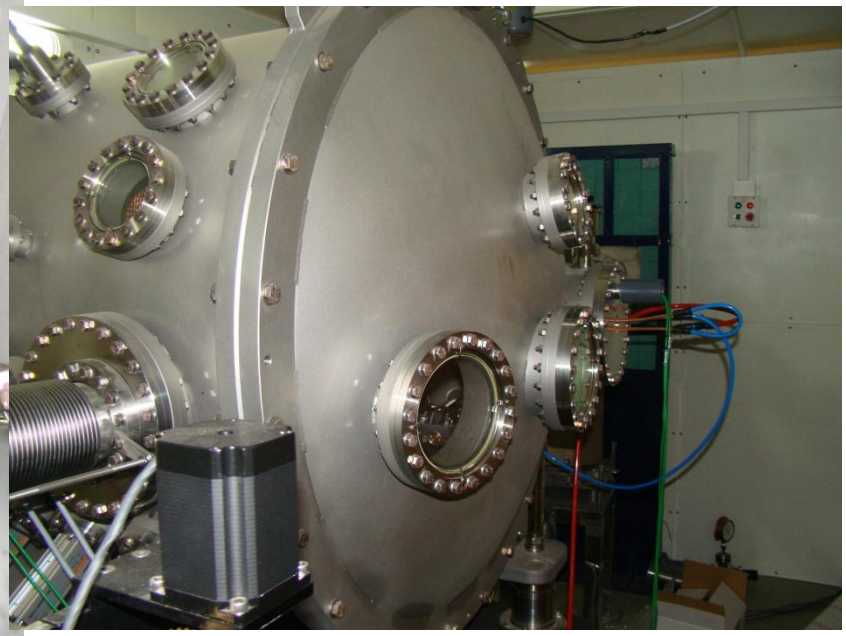
Parameters	Values
Monochromators	: Si 111 double crystal monochromator (***Available***) Energy resolution (ΔE) = ~ 2 – 5 eV : Multilayer monochromator (Mo/Si) ΔE = ~ 100 eV (***Available in due coarse***)
Focusing optics	Kirkpatrick - Baez mirror system (***Available***) system
Experimental stations	: 5-axis sample manipulator (*for micro XRF scanning applications*) (***Available***) : Two circle (theta-2theta) goniometer (*for TXRF, GIXRF and X-ray reflectivity applications)* (***Available***)

Photograph of the μ-XRF experimental setup and beamline shielding hutch

BL-16 Beamline

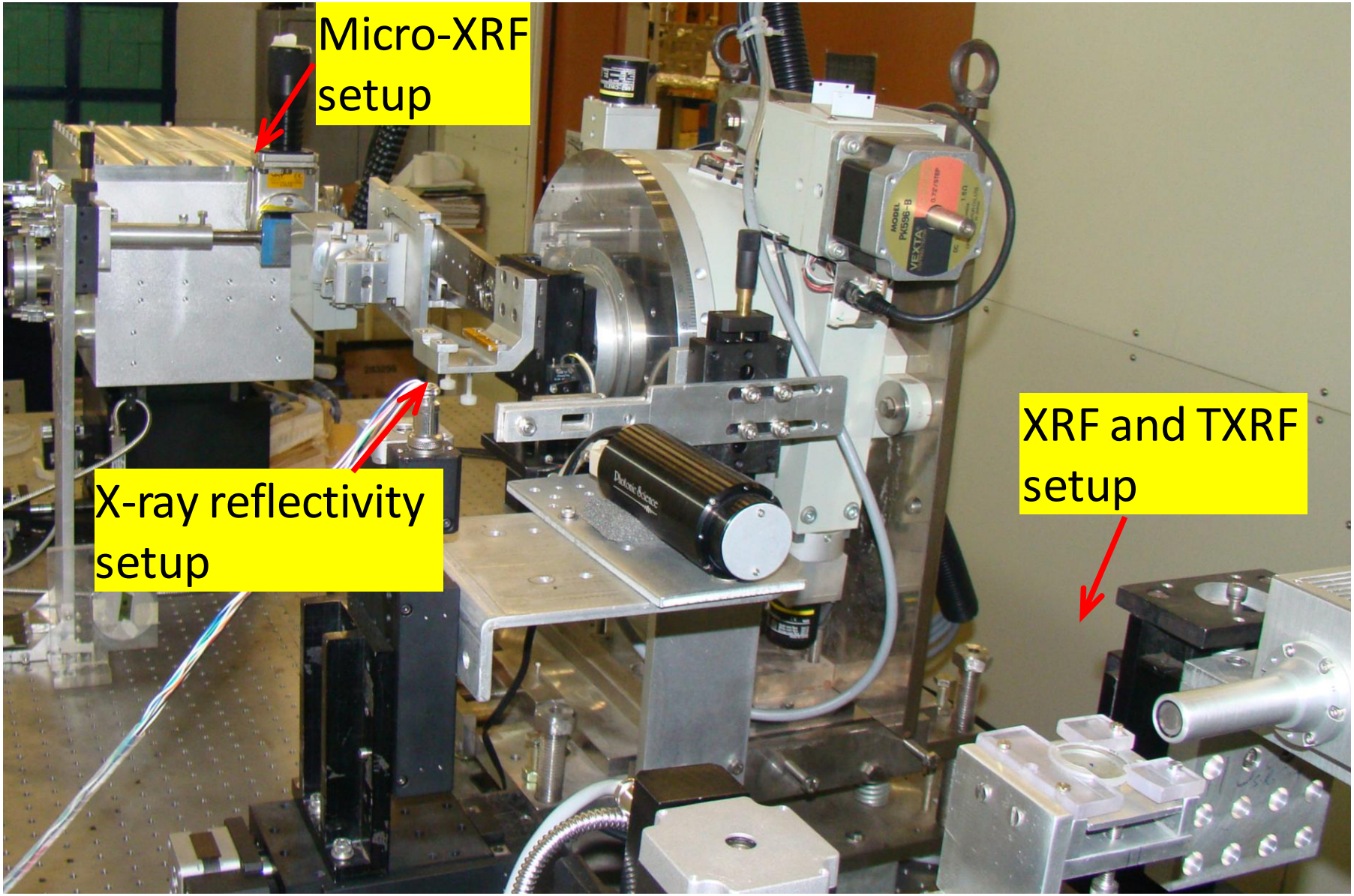
BL-16 Beamline (optics hutch)





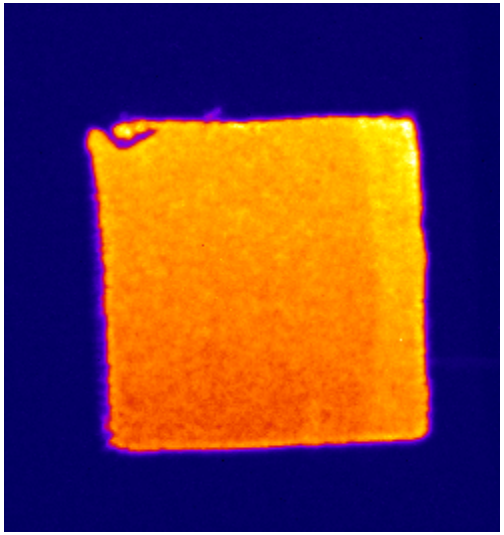
BL-16 Beamline (Expt. hutch)

BL-16 Beamline (Expt. hutch)



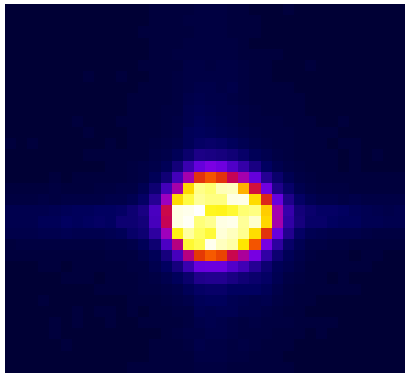
Micro-focus beam at the BL-16 beamline

BL-16 beamline provides microfocus X-ray beam spot at the scanning experimental station of the BL-16 beamline using elliptical bent Kirkpatrick-Baez focusing mirrors.

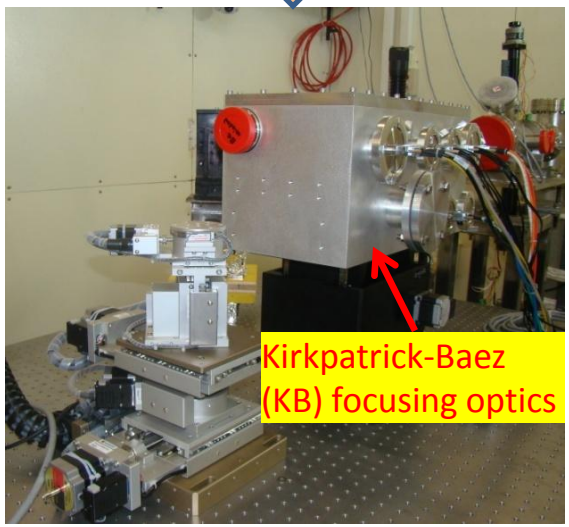


Incident X-ray beam spot: 1x1mm^2

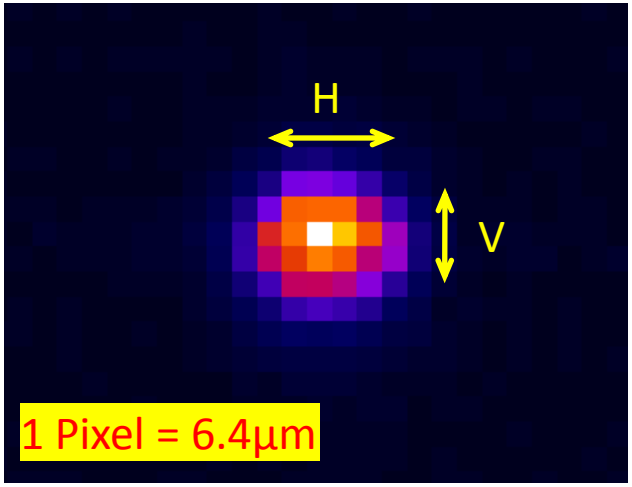
KB Focusing optics



2D Focused beam spot

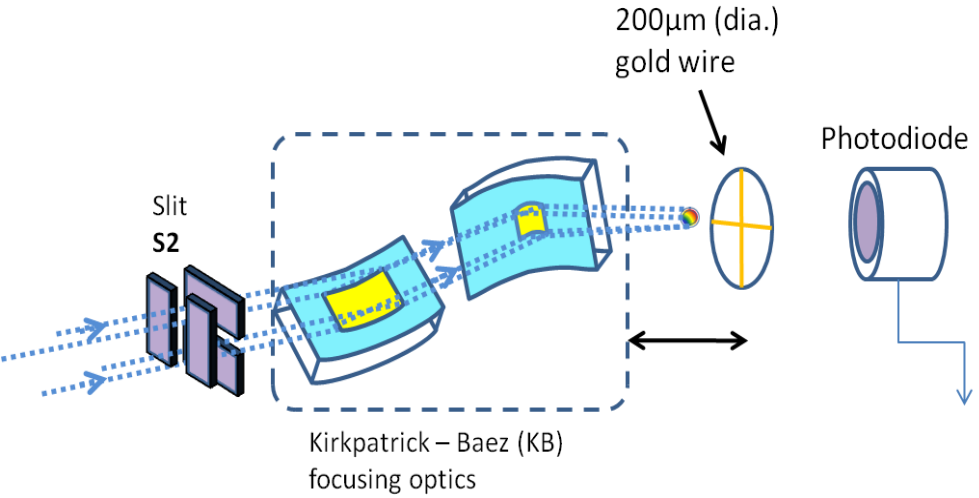


Wire/edge scan measurements

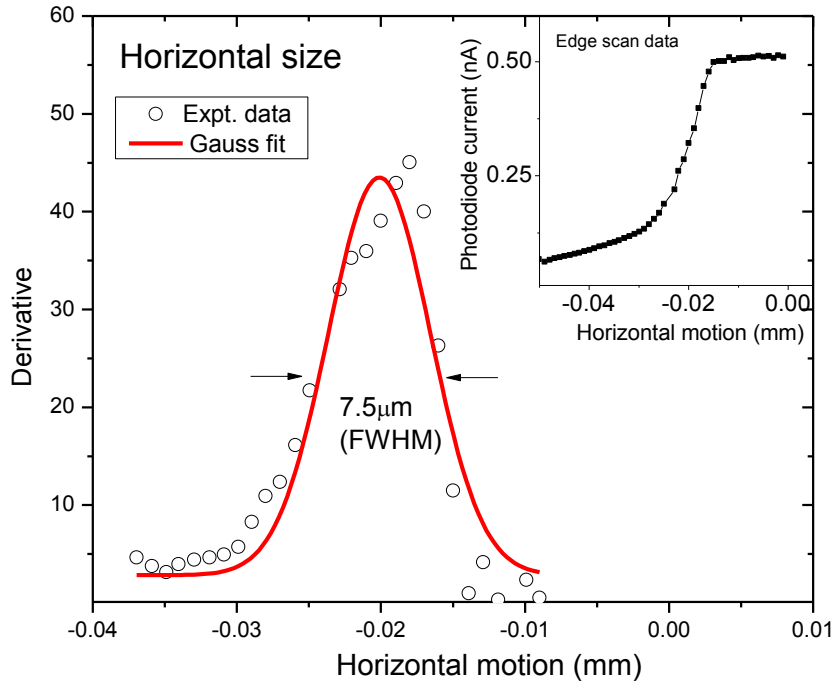


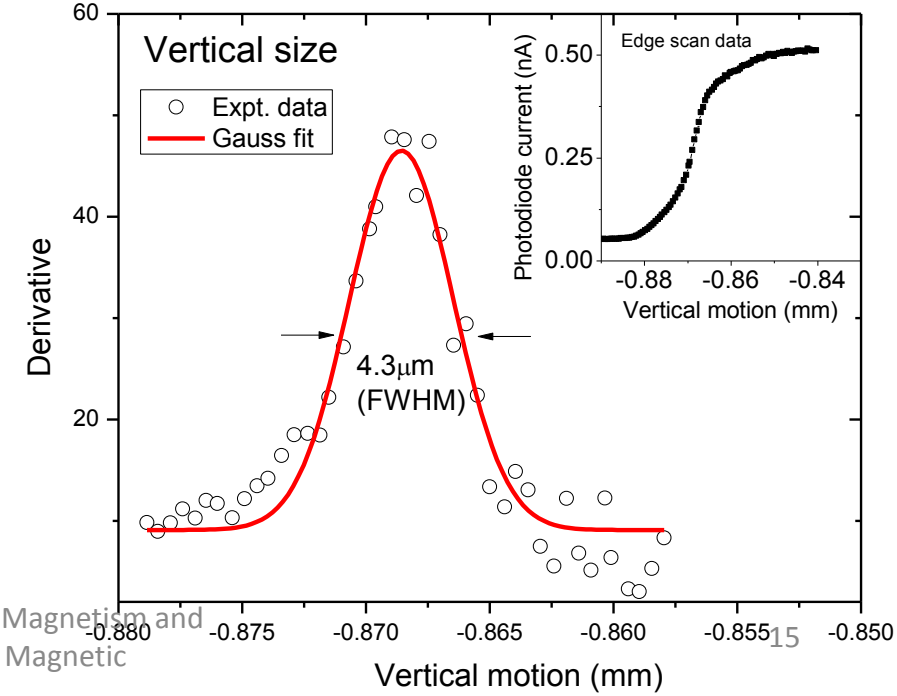
Measured Focused beam size =>

~ 7.5 µm (H) x 4.3 µm (V)

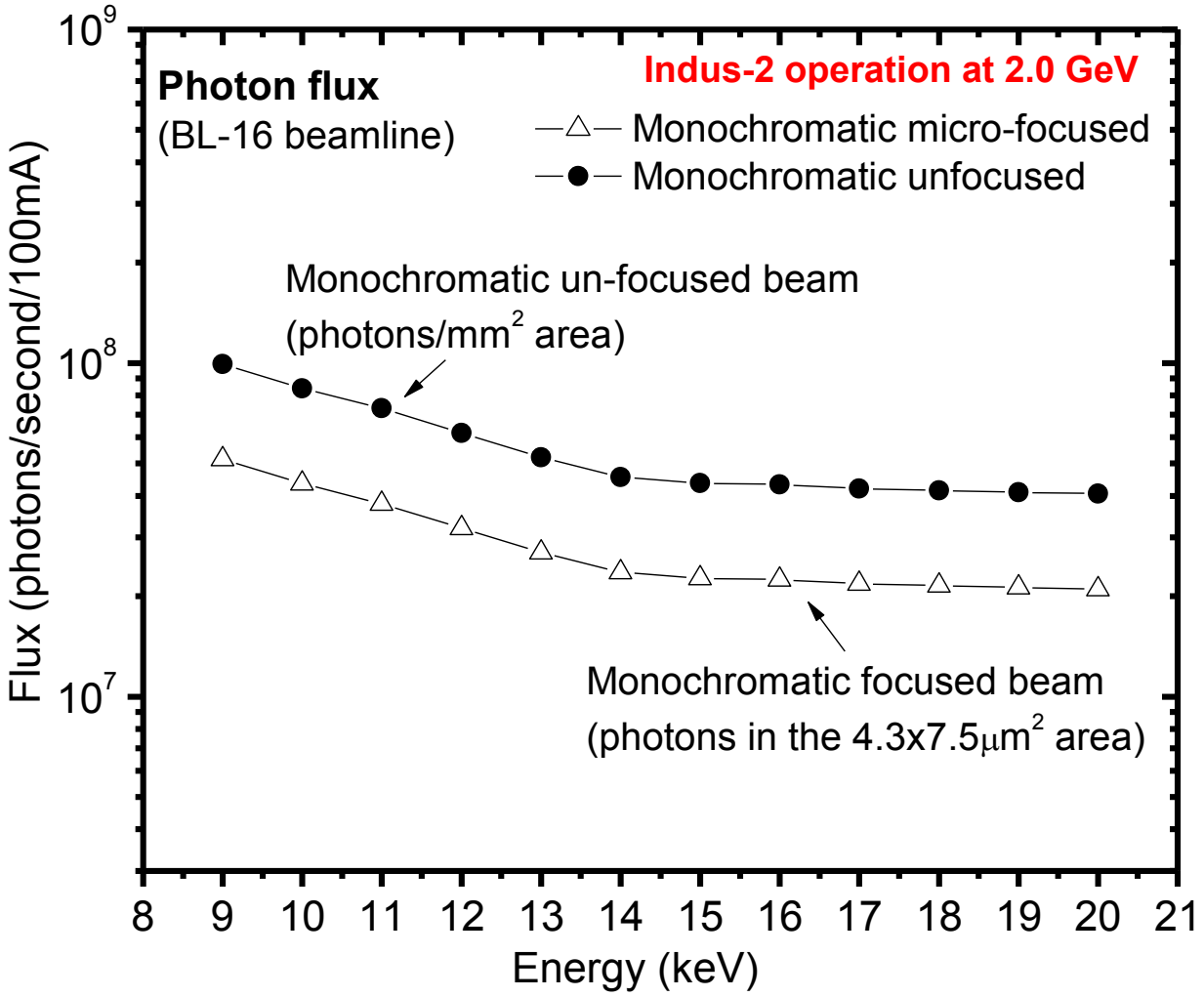


Expt. setup for wire scan measurements





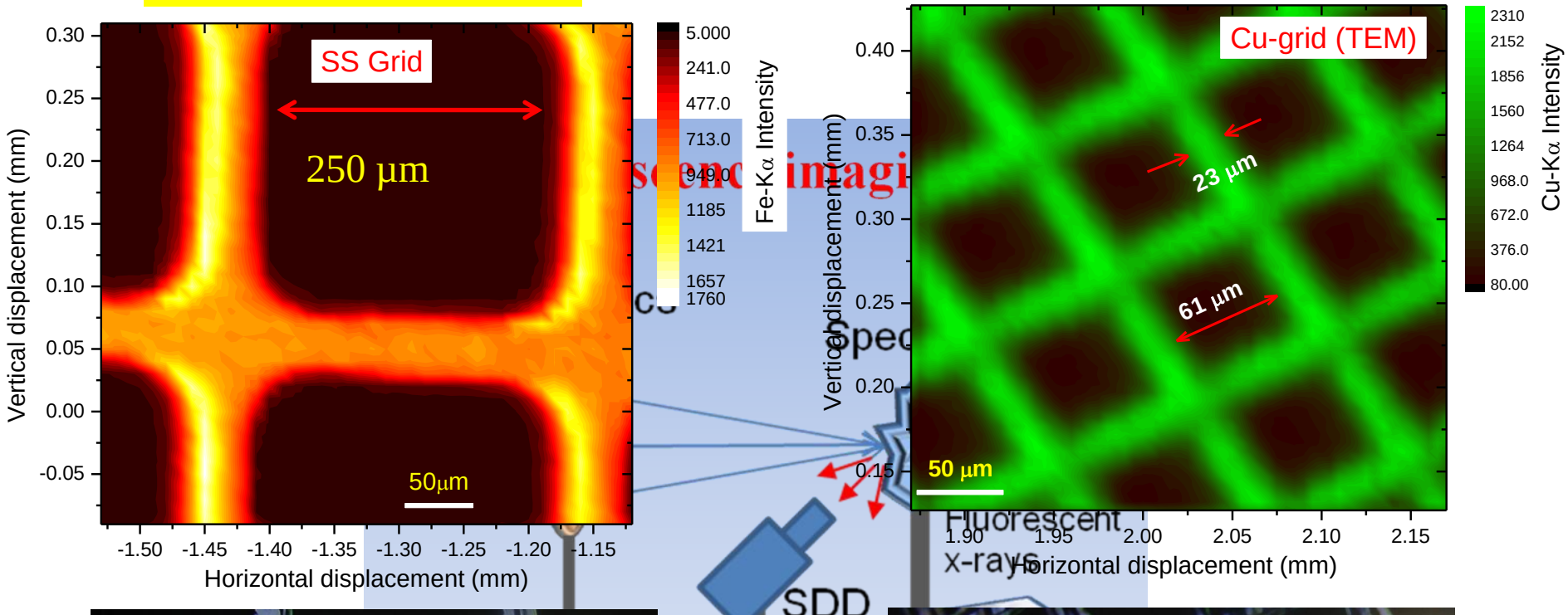
Beamline Photon flux

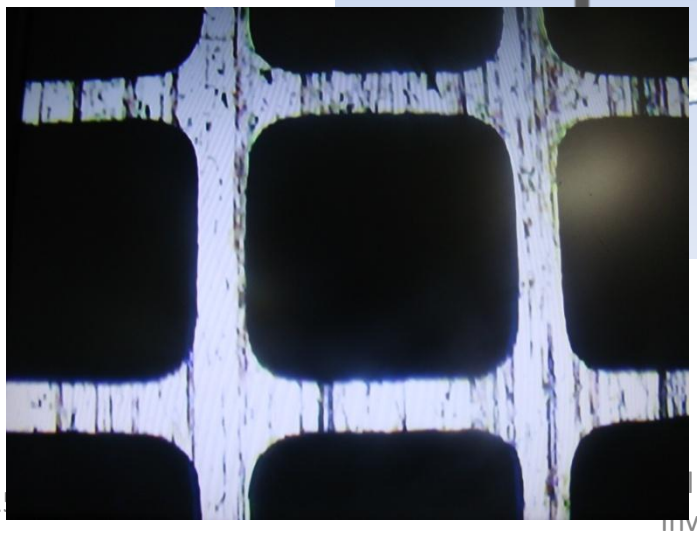


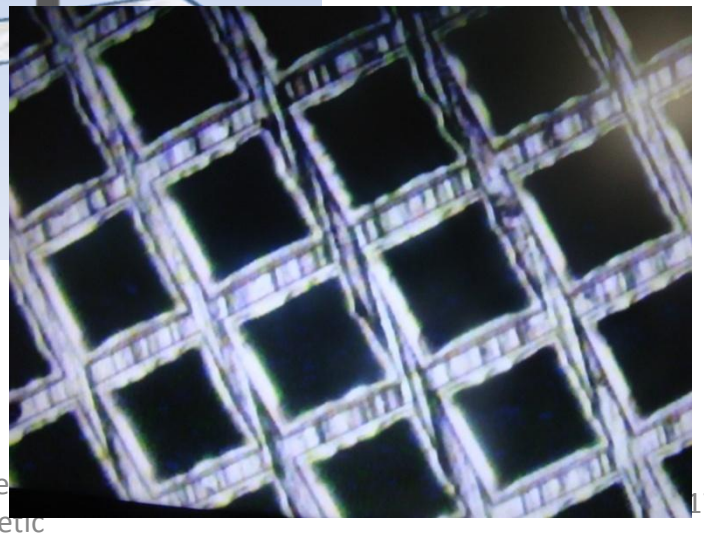
Micro-XRF imaging (SS and Cu test grid structures)

Fe-Kα fluorescence Image of SS grid

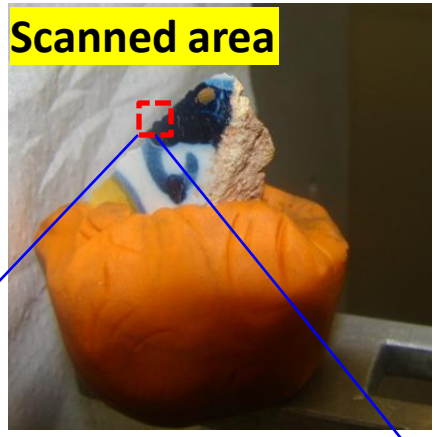
Cu-Kα fluorescence Image of Cu grid



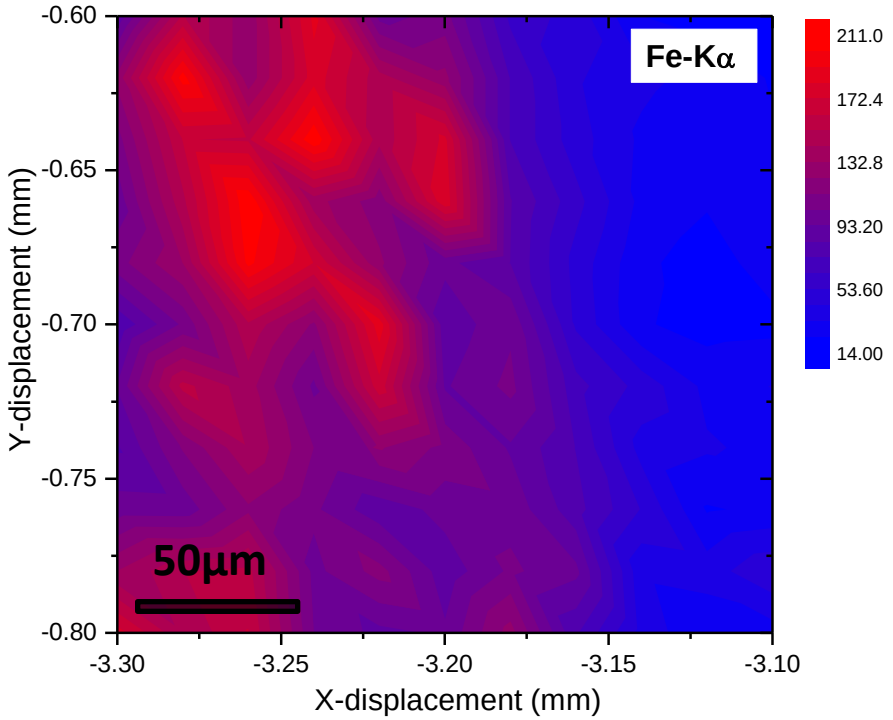




Micro XRF scanning



Measured scanning elemental maps for an archeological tile sample (Goa church ~ 500 yr old). Theses samples were received from the department of Archeological Survey of India. The maps show the distribution of the Pb and Fe elements, measured across the cross sectional area of painted side of the tile sample.



50µm

BL-16 beamline publication

electronic reprint

Journal of Synchrotron Radiation

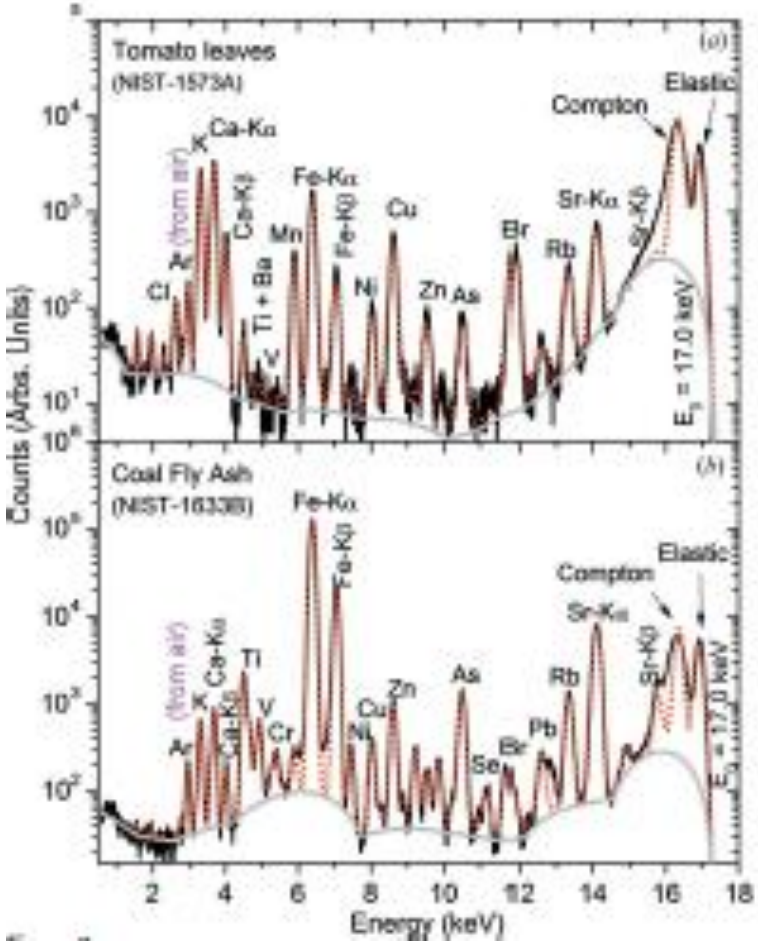
ISSN 0909-0495

Editors: G. E. Ice, I. Schlichting and J. F. van der Veen

A microfocus X-ray fluorescence beamline at Indus-2 synchrotron radiation facility

M. K. Tiwari, P. Gupta, A. K. Sinha, S. R. Kane, A. K. Singh, S. R. Garg, C. K. Garg, G. S. Lodha and S. K. Deb

J. Synchrotron Rad. (2013). **20**, 386–389



User's experiments

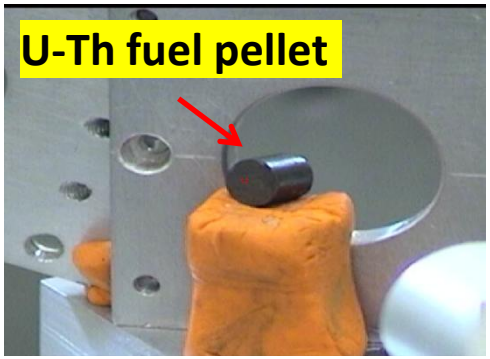
Characterization of U-Th AHWR fuel pellets using micro-XRF beamline (*Fuel Chemistry Division, BARC*)

U-Th fuel pellets are prepared by two processes;

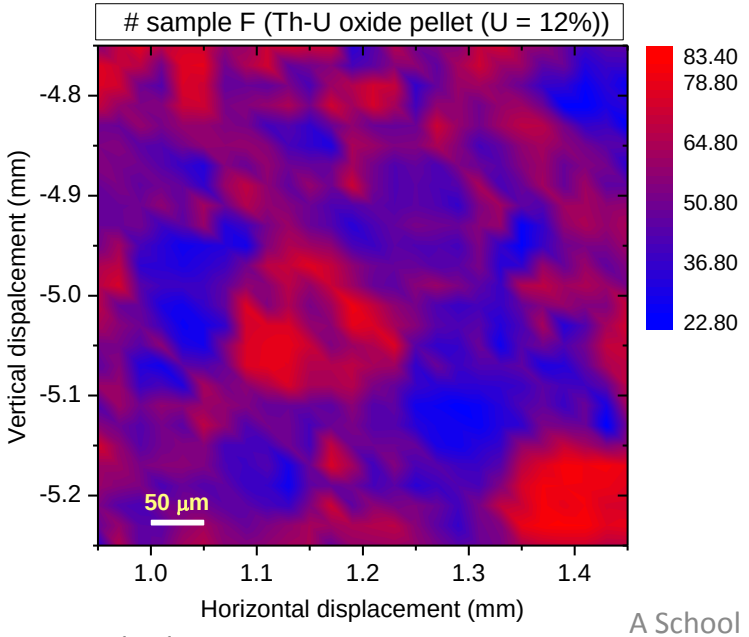
(1) Power Metallurgy Process (PMC)

(2) Coated pellet agglomeration (CAP)

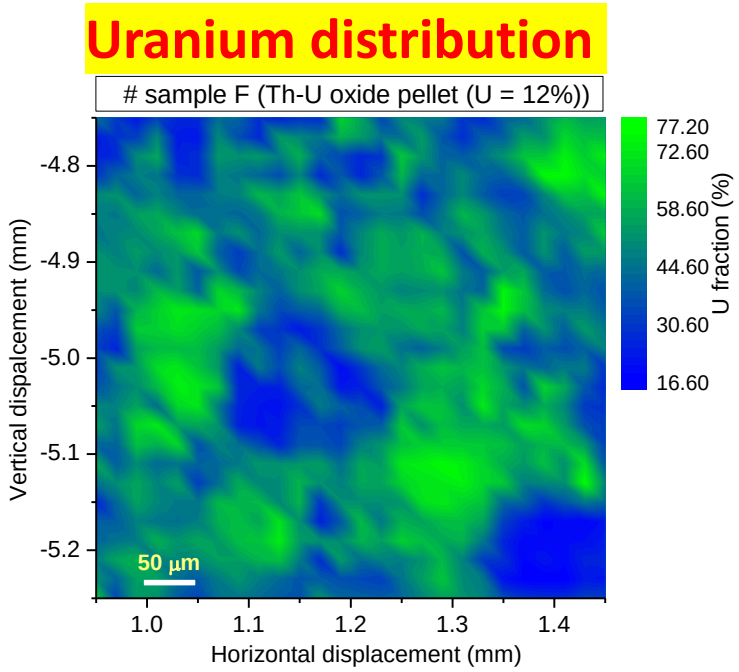
XRF and microprobe X-ray fluorescence analysis were performed for the determination of concentration in-homogeneity



Thorium distribution

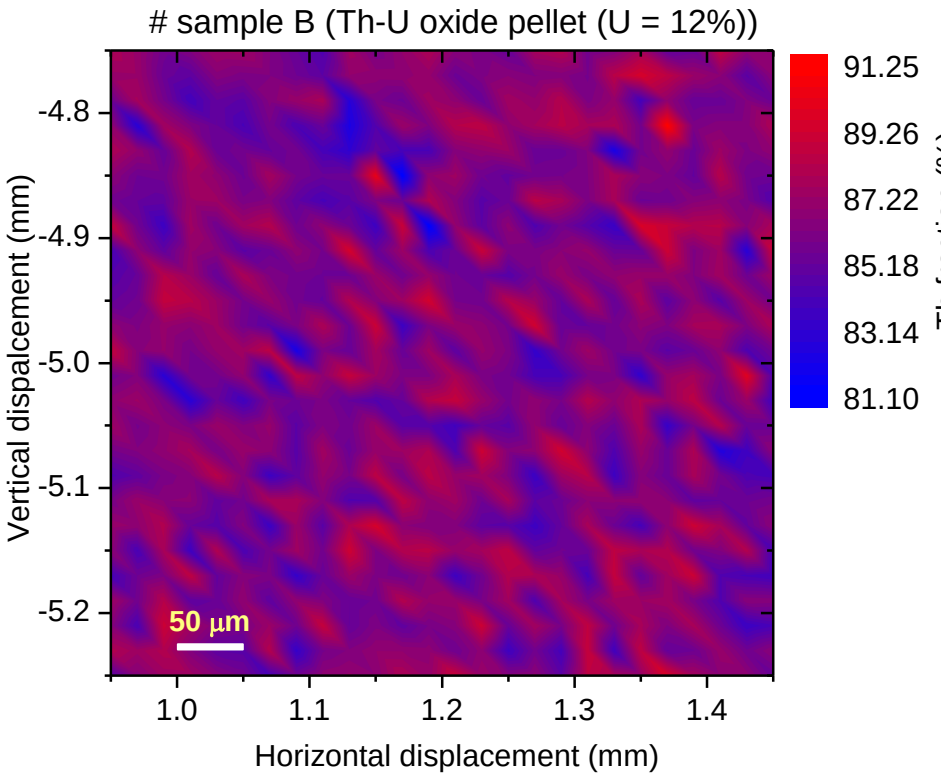


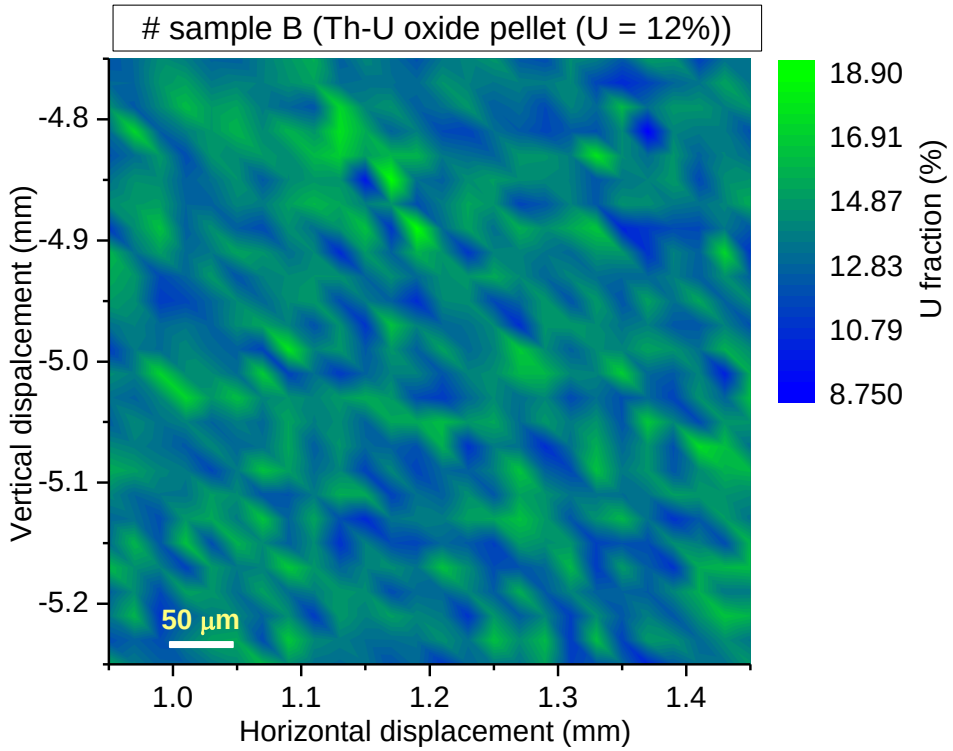
Uranium distribution



U-Th fuel pellets prepared by CAP method

Micro-XRF images of the U-Th fuel pellets prepared by PMC method





Thorium distribution

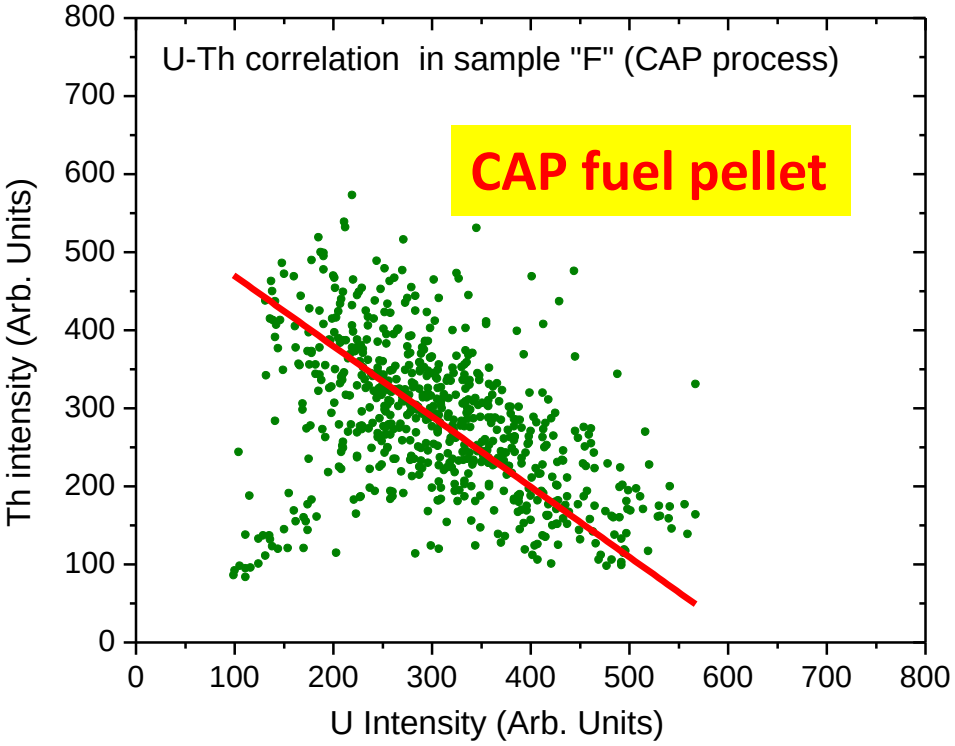
Uranium distribution

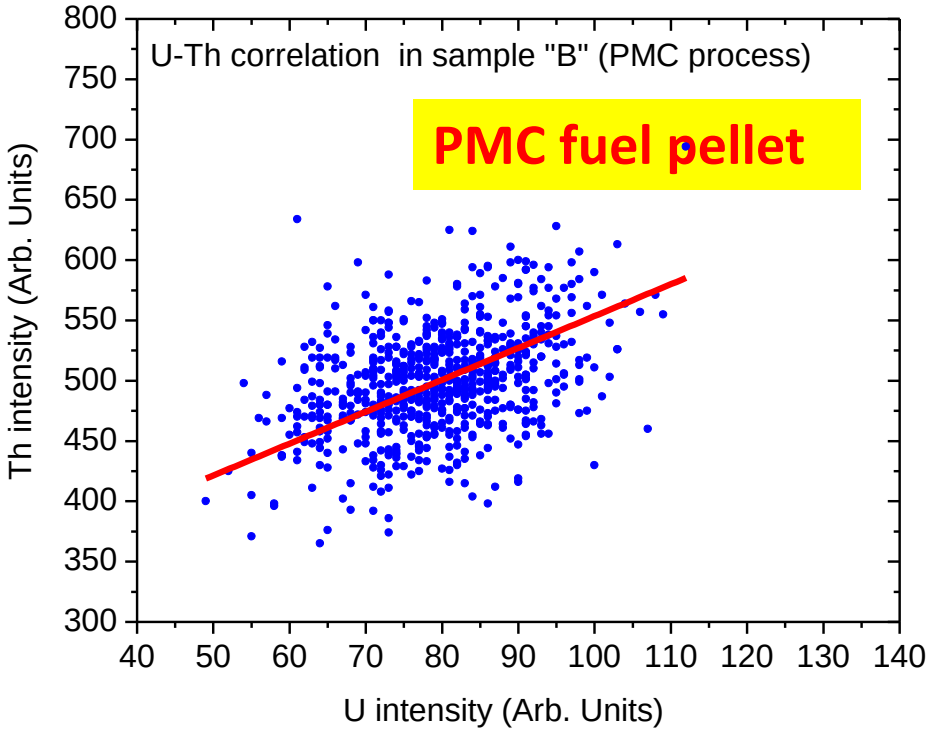
"Synchrotron μ-XRF study on compositional uniformity of uranium-thorium oxide pellets prepared by different processes"

N.L. Misra, M. K. Tiwari, Bal Govind Vats, S. Sanjay Kumar, Ajit Kumar Singh, G. S. Lodha, S.K. Deb, P.D. Gupta and S.K. Aggarwal

X-ray Spectrometry, (2014) DOI: 10.1002/xrs.2532

Correlation between U-Th distribution in CAP and PMC fuel pellet

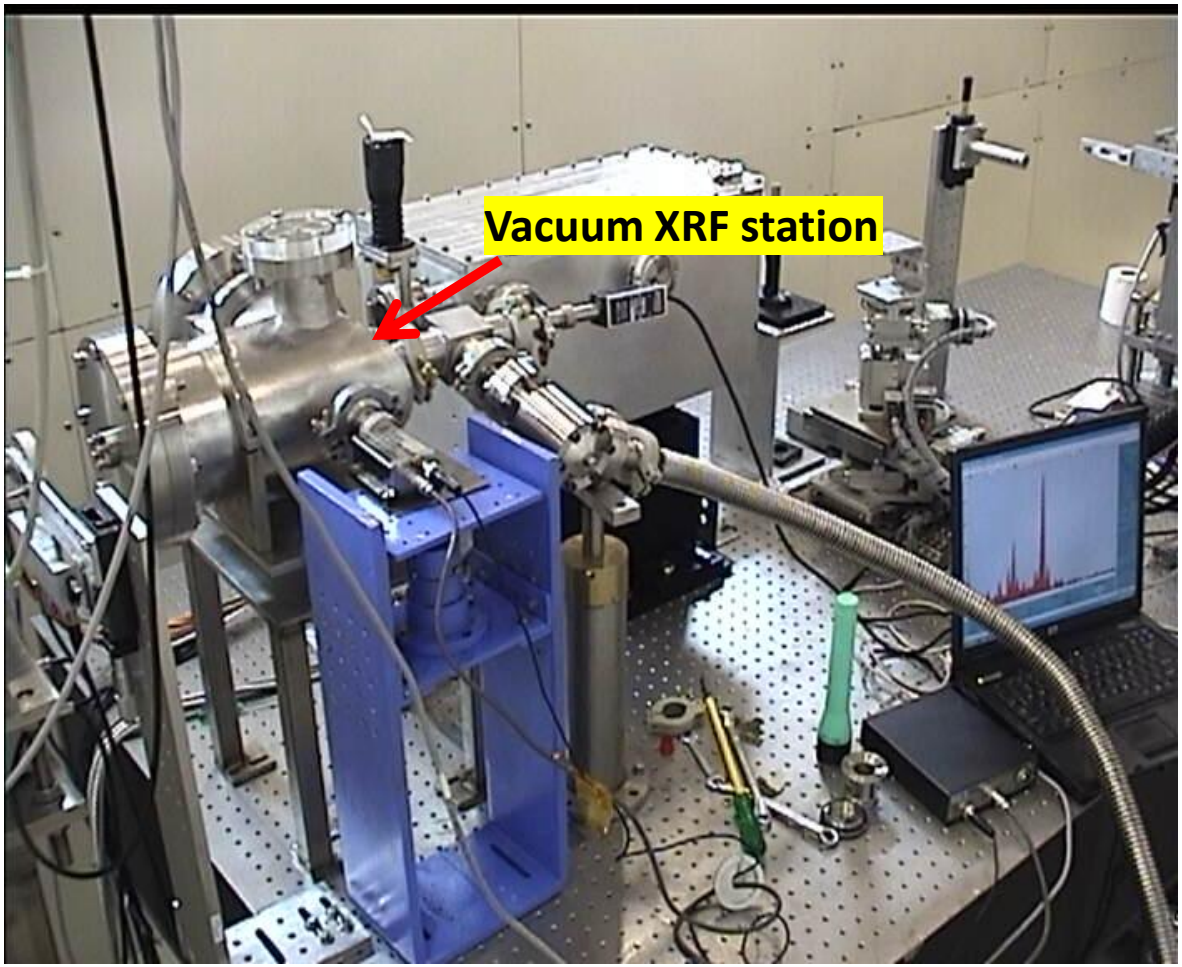




- Non-uniformity in the CAP process ~ 60%
- Non-uniformity in the PMC process ~ 10%
- U-Th distribution is correlated in PMC process
- U-Th distribution is anti-correlated in CAP process

* Macroscopic concentration distribution in uniform in both the processes

Vacuum assisted XRF experimental station at BL-16 beamline

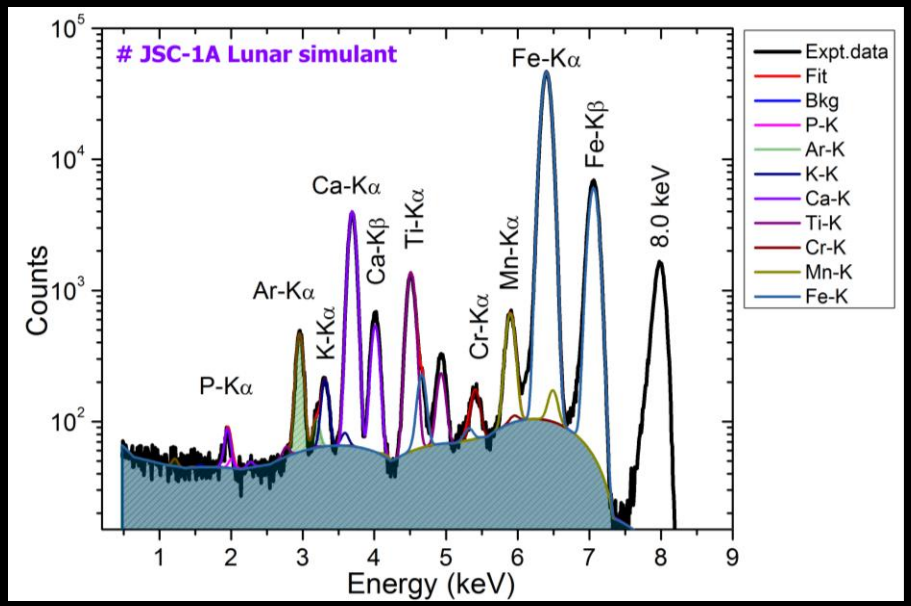


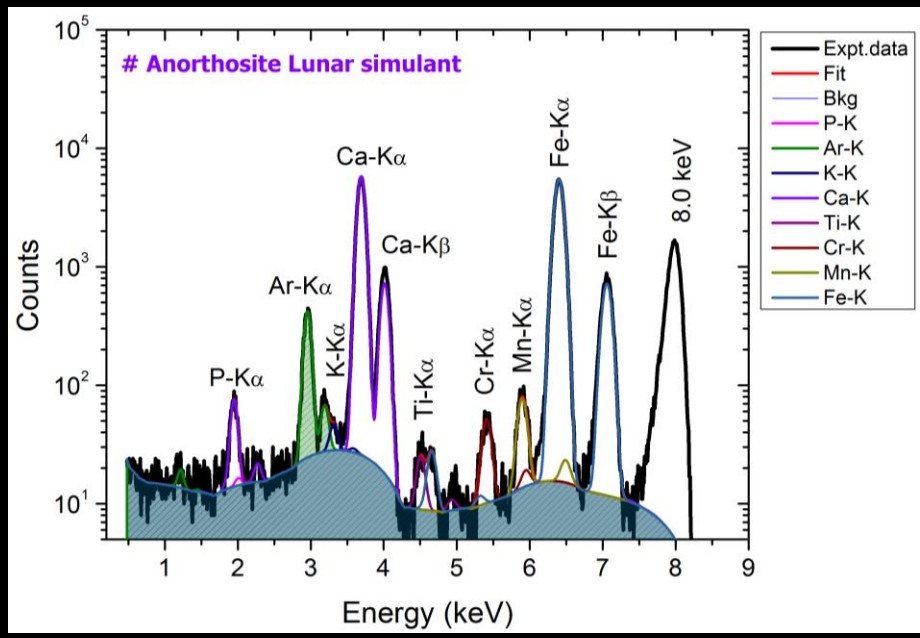
Indian Space Research Organisation

Aim of the experiment

- Calibrate detectors to be used for the Chandra yan -2 project

Experiments done at RRCAT using Microprobe-XRF (BL-16)

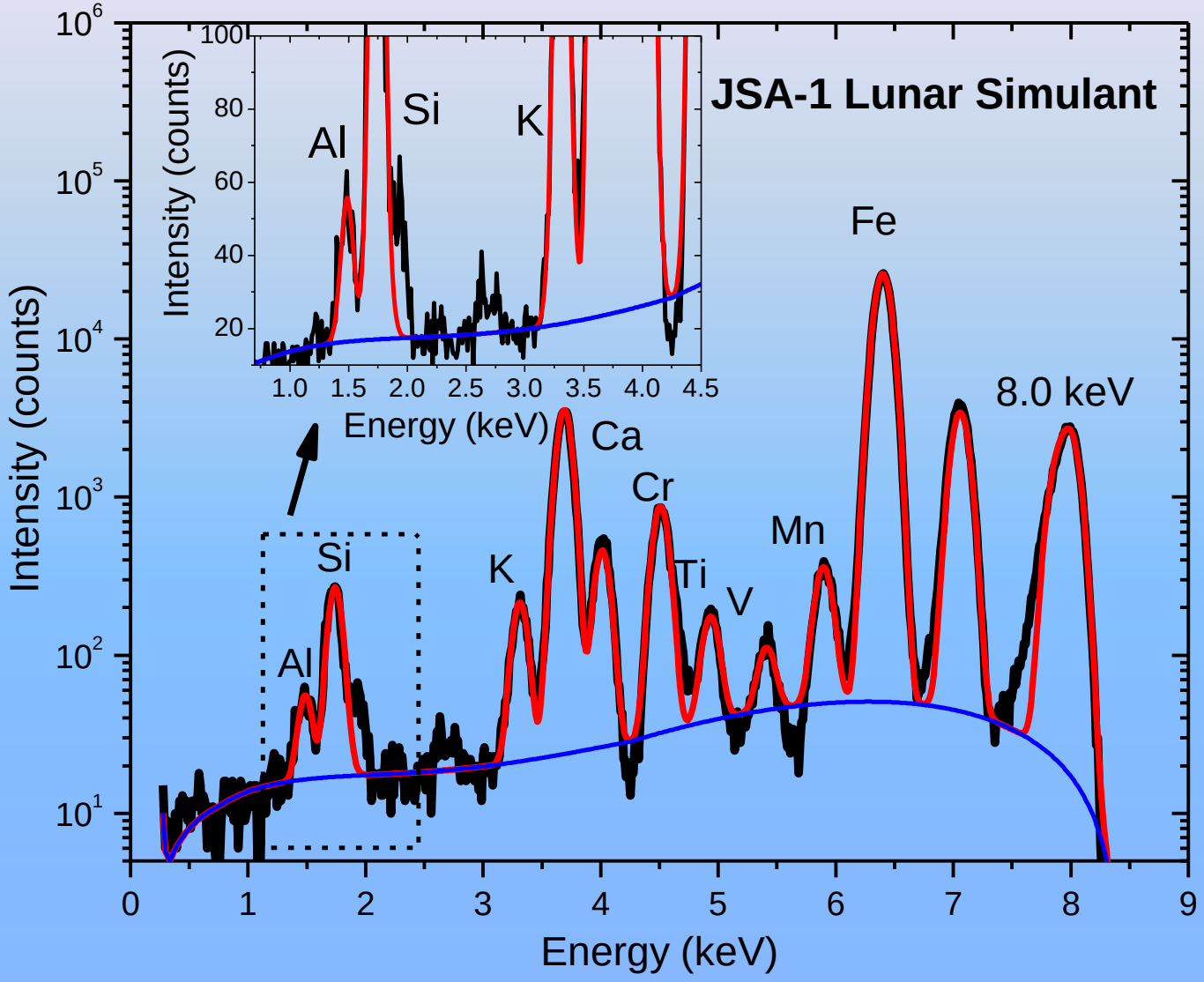




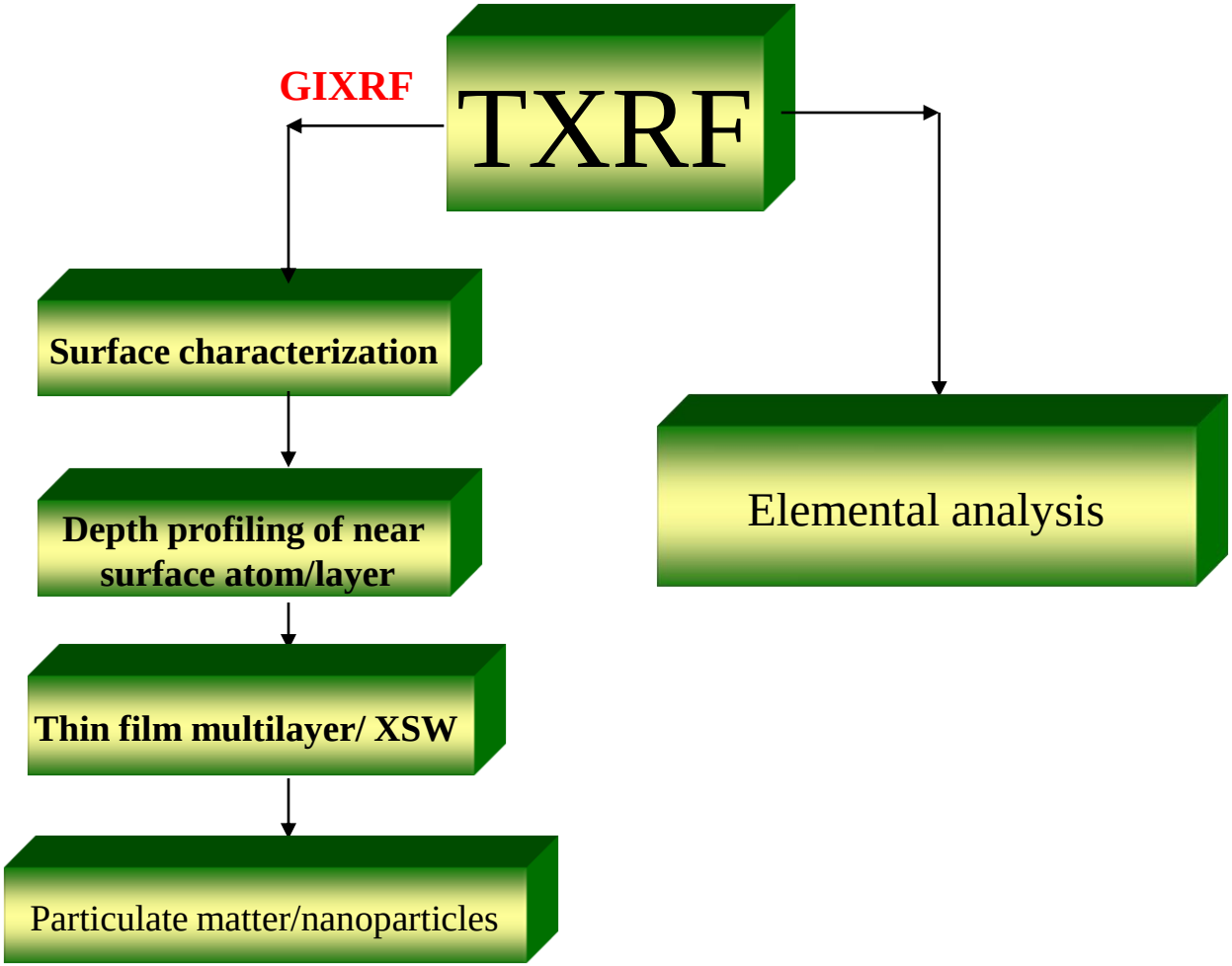
Measured SRXRF spectrum from a Lunar JSC-1A and anorthosite simulants

"Experimental validation of XRF inversion code for Chandrayaan-1"
P.S. Athiray, M. Sudhakar, M.K. Tiwari, S. Narendranath, G. S. Lodha, S. K. Deb, P. Sreekumar, S.K. Dash
Planetary and Space Science **89** 183–187 (2013).

Vacuum XRF measurements for ISRO



TXRF applications

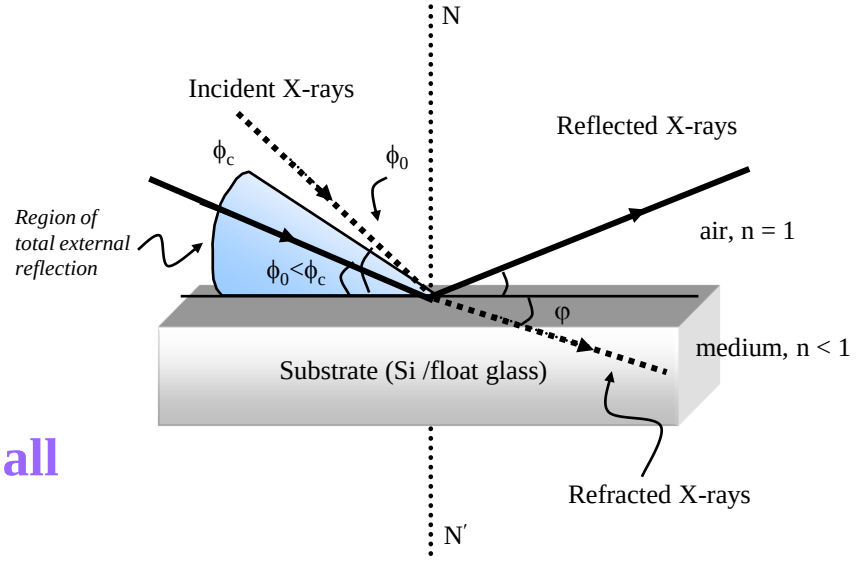


Total Reflection XRF (theory)

Snells law : $n = \frac{Cos\phi}{Cos\varphi}$

At $\phi = \phi_c$ ⇒ $\varphi = 0$

$$n = Cos\phi_c$$



For X-rays, the refractive index n of all materials is slightly <1.

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

$$\delta = \frac{N_A}{2\pi} r_e \rho \frac{Z}{A} \lambda^2 = decrement \quad \beta = \frac{\lambda}{4\pi}\left(\frac{\mu}{\rho}\right)\rho = absorption$$

Values of δ and β range in 10^{-3} to 10^{-6} and β< δ

$$\phi_c = \sqrt{2\delta} \approx \frac{1.65}{E}\sqrt{\frac{Z}{A}\rho}$$

For total external refection condition

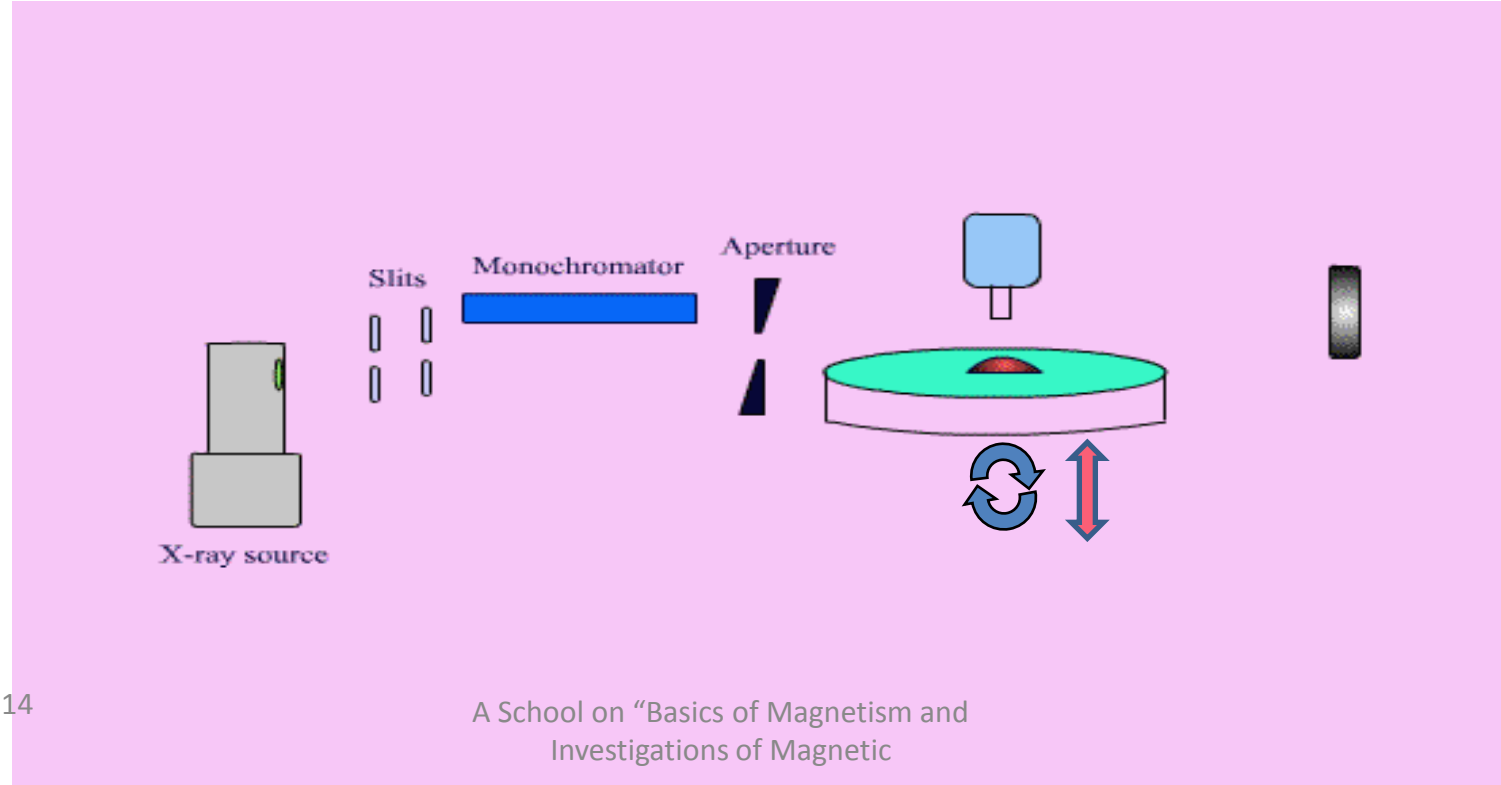
$$\phi < \phi_c$$

For quartz glass ϕ_c=0.21˚@ 8.047 keV X-rays

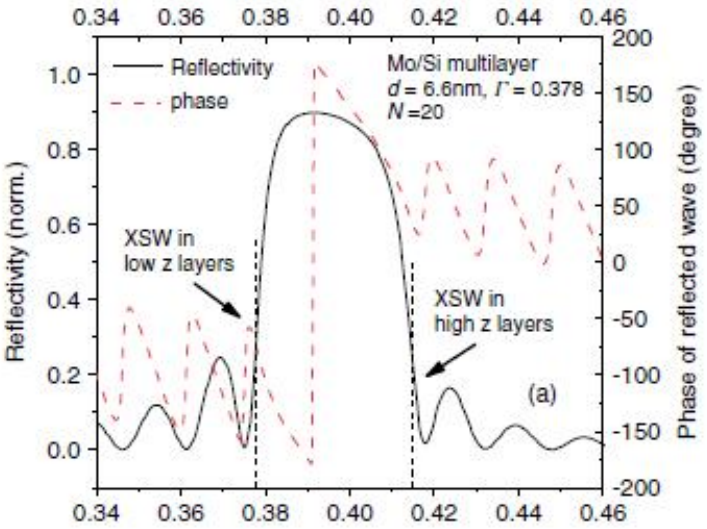
Requirements for GIXRF measurements

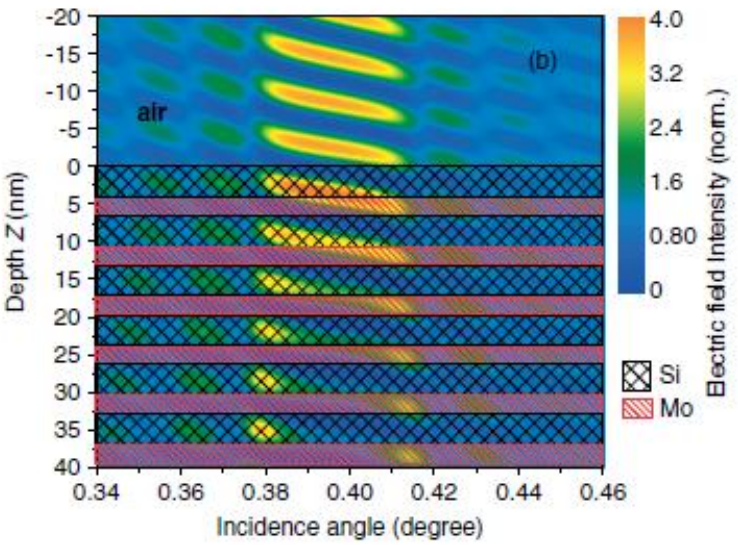
- Incidence angle: Grazing angle (~0 - 2^0) step < 0.005^0
- X-ray beam divergence: ~0.005^0
- Primary X-ray beam : monochromatic ($\Delta E/E \sim 10^{-2}$ -10^{-4})

  (multilayer monochromator or Natural crystal etc.)
- Very good mechanical stability for each optical elements of TXRF spectrometer



Determination of embedded impurity in a Mo/Si multilayer

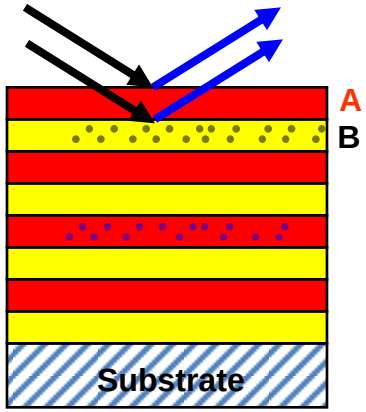




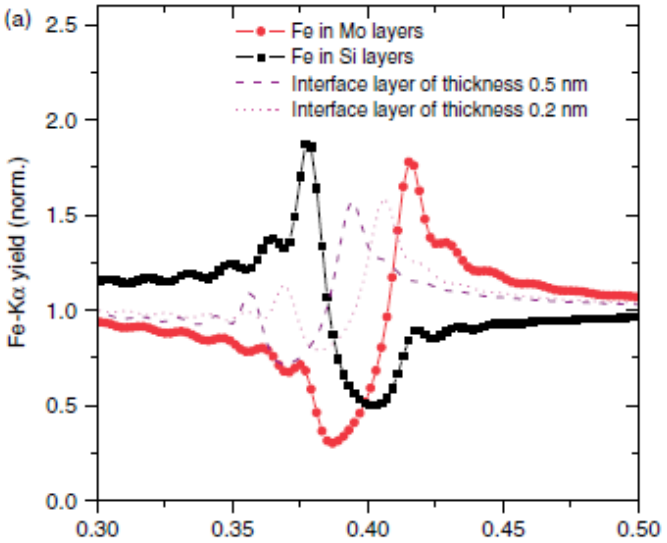
XSW under Bragg condition

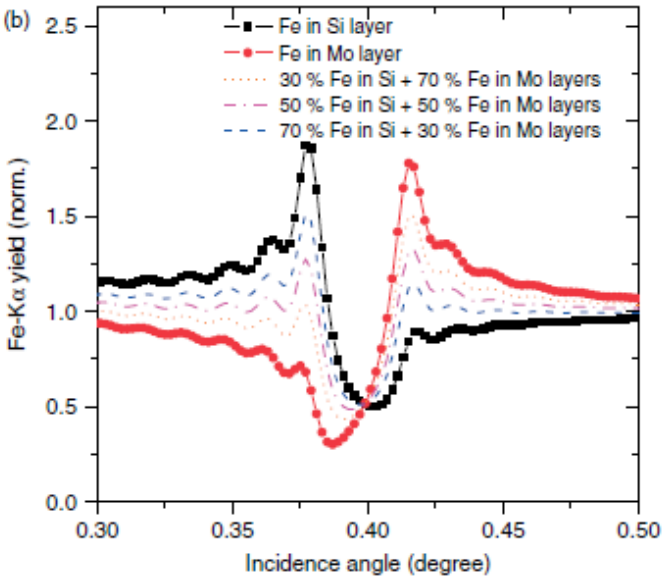
Different forms/profiles of impurity diffusion

Multilayer structure

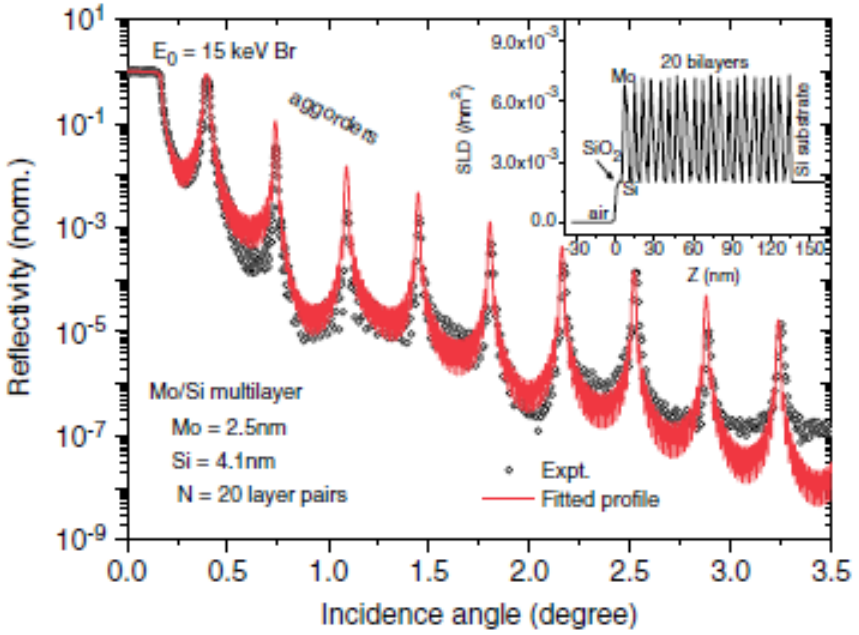


Impurity atoms

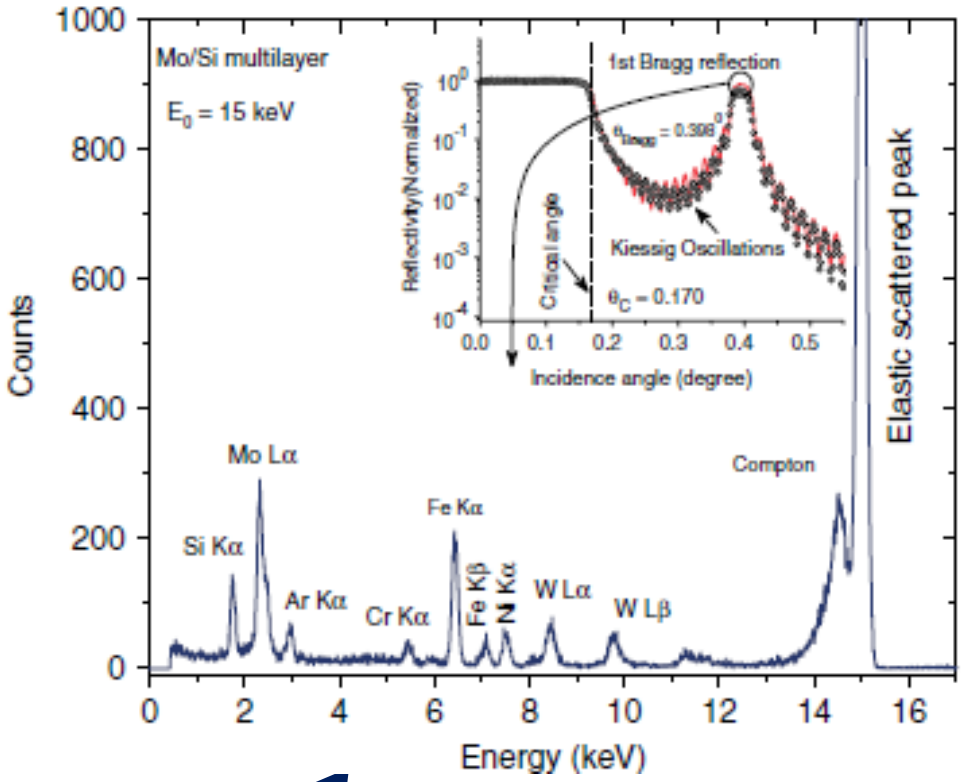




Determination of embedded impurity in a Mo/Si multilayer



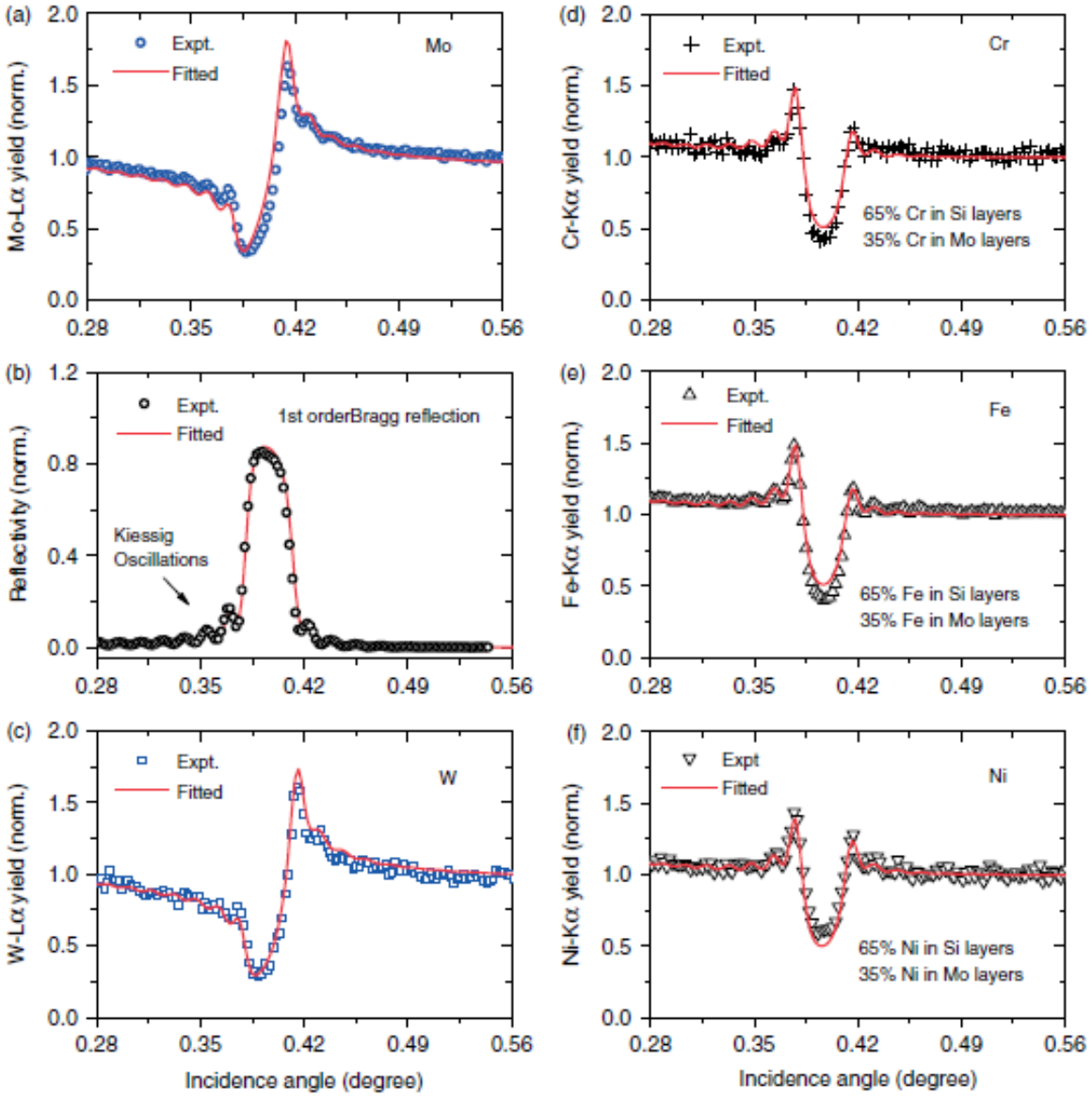
Measured and fitted XRR profiles for Mo/Si multilayer



These measurements were done at Diamond Light Source UK on B16 beamline

Measured XRF spectrum at Bragg position showing presence of different elemental impurities

Measured and fitted XSW profiles of different elements



More details can be found….

Research Article

SURFACE and INTERFACE ANALYSIS

Received: 13 October 2009 Revised: 1 December 2009 Accepted: 2 December 2009 Published online in Wiley Interscience: 13 January 2010

(www.interscience.wiley.com) DOI 10.1002/sia.3178

Characterization of trace embedded impurities in thin multilayer structures using synchrotron X-ray standing waves

M. K. Tiwari,[a,b]* K. J. S. Sawhney[a] and G. S. Lodha[b]

A CATGIXRF Program is developed XSW and GIXRF characterization of thin layered materials

Research Article

X-RAY Spectrometry

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Applications of the 'CATGIXRF' computer program to the grazing incidence X-ray fluorescence and X-ray reflectivity characterization of thin films and surfaces

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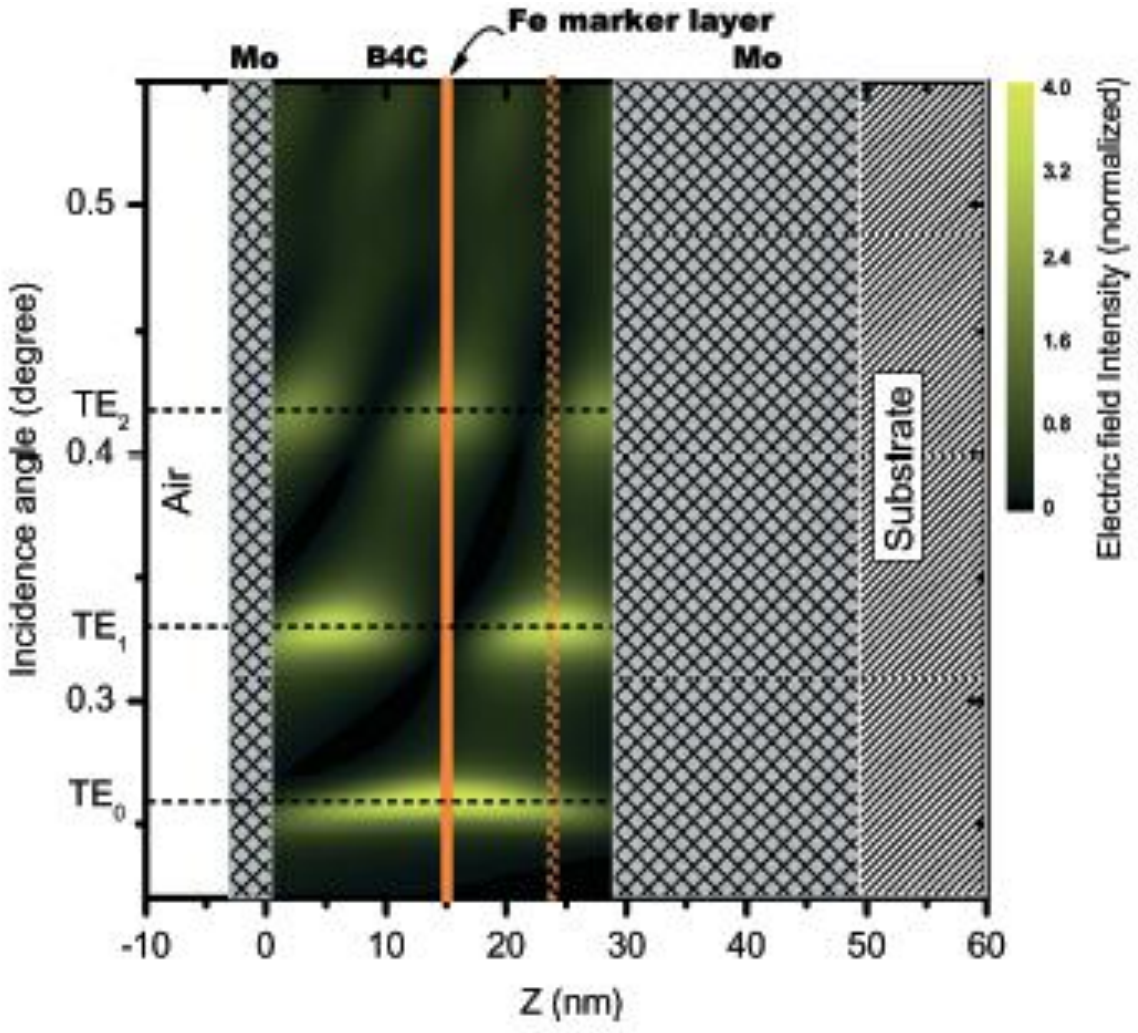
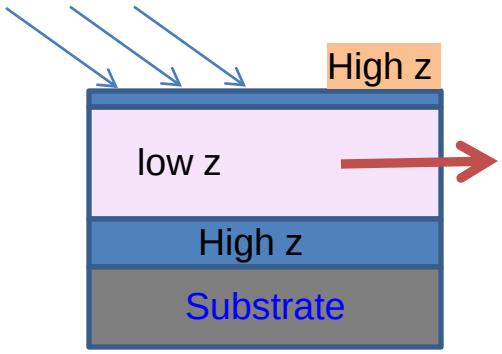
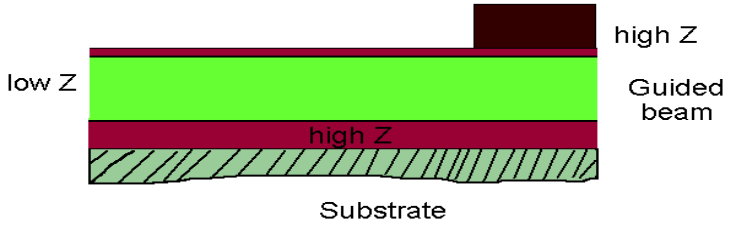
Thin film X-ray waveguide structure



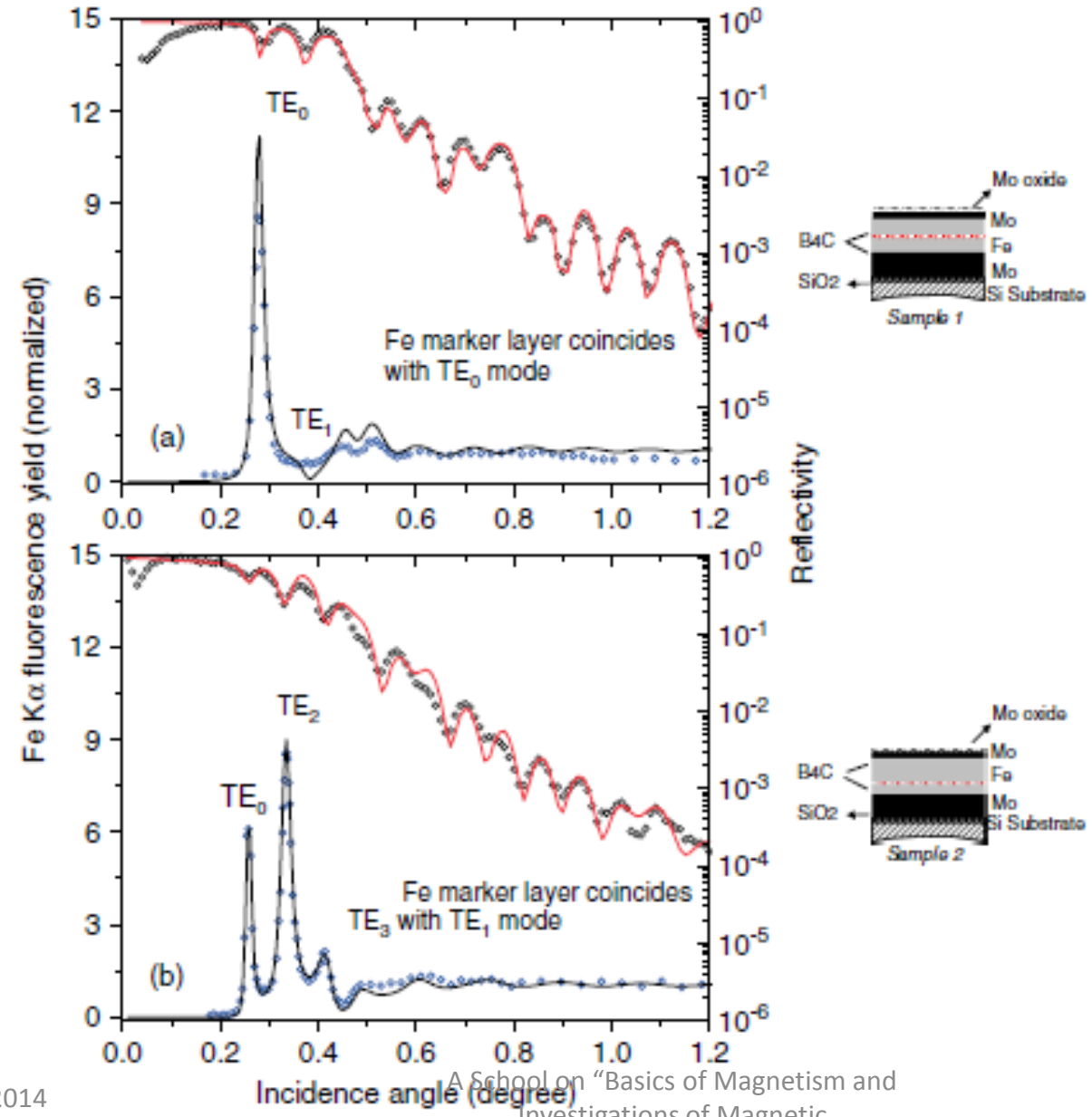
Wave guide structure



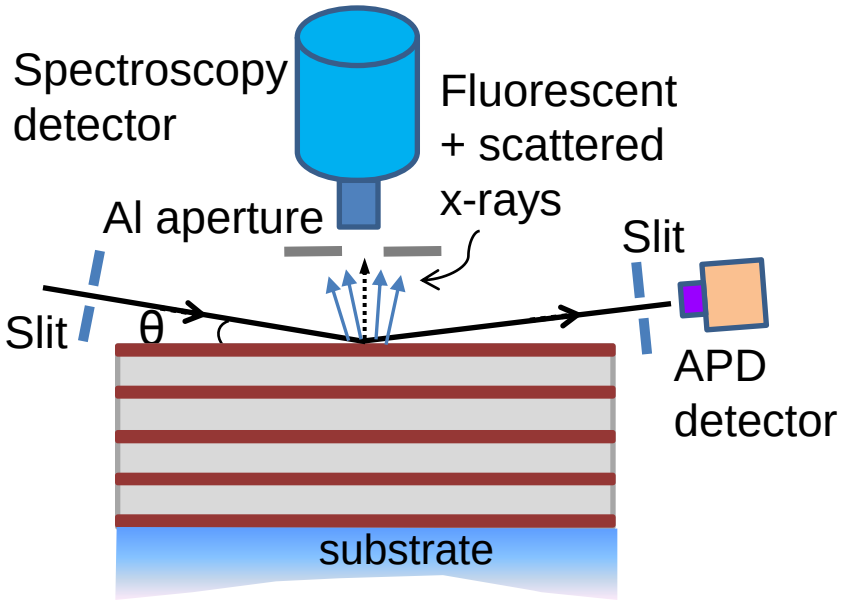
AGif - UNREGISTERED

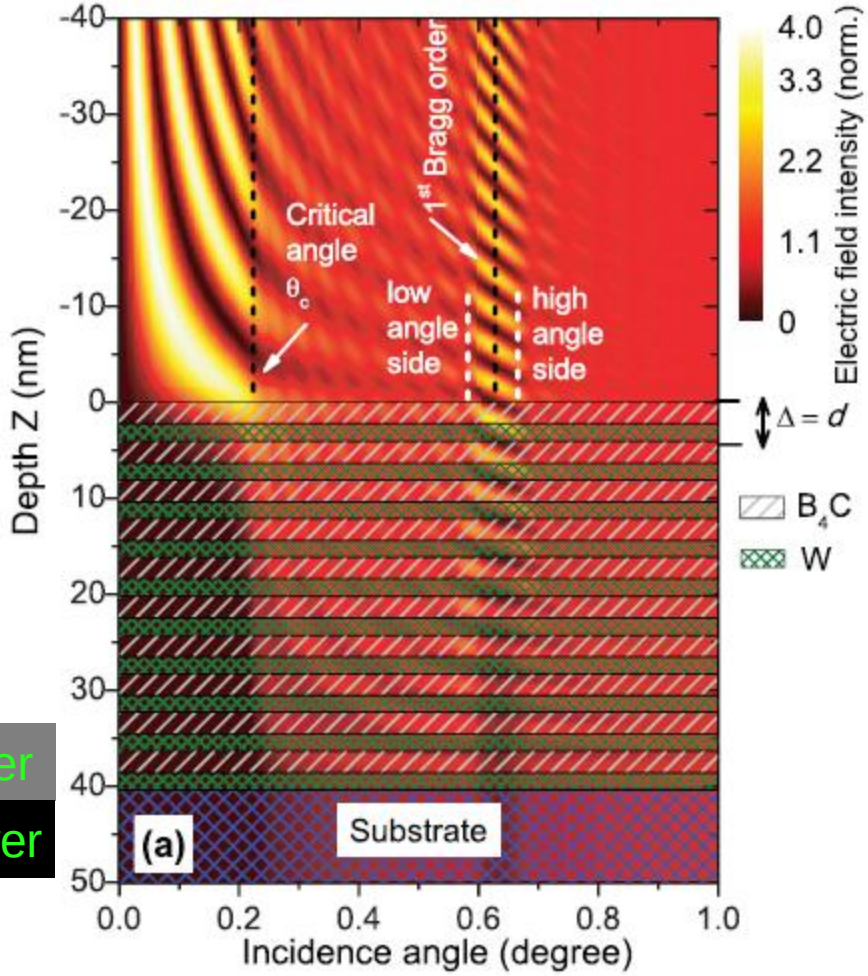


Thin film X-ray waveguide structure



X-ray standing wave induced Compton and elastic scattering from thin periodic multilayer structures

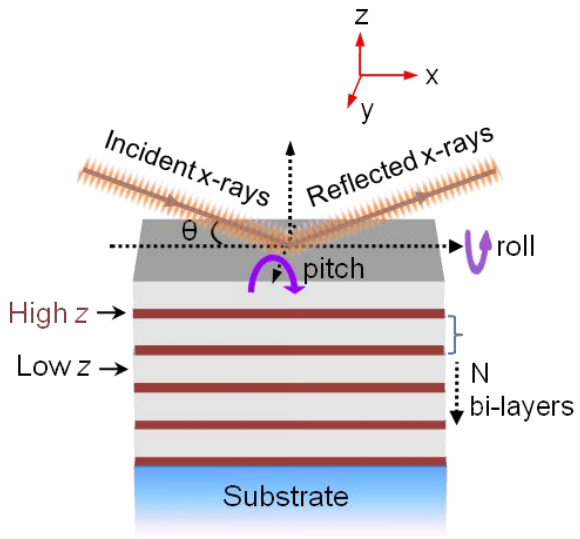


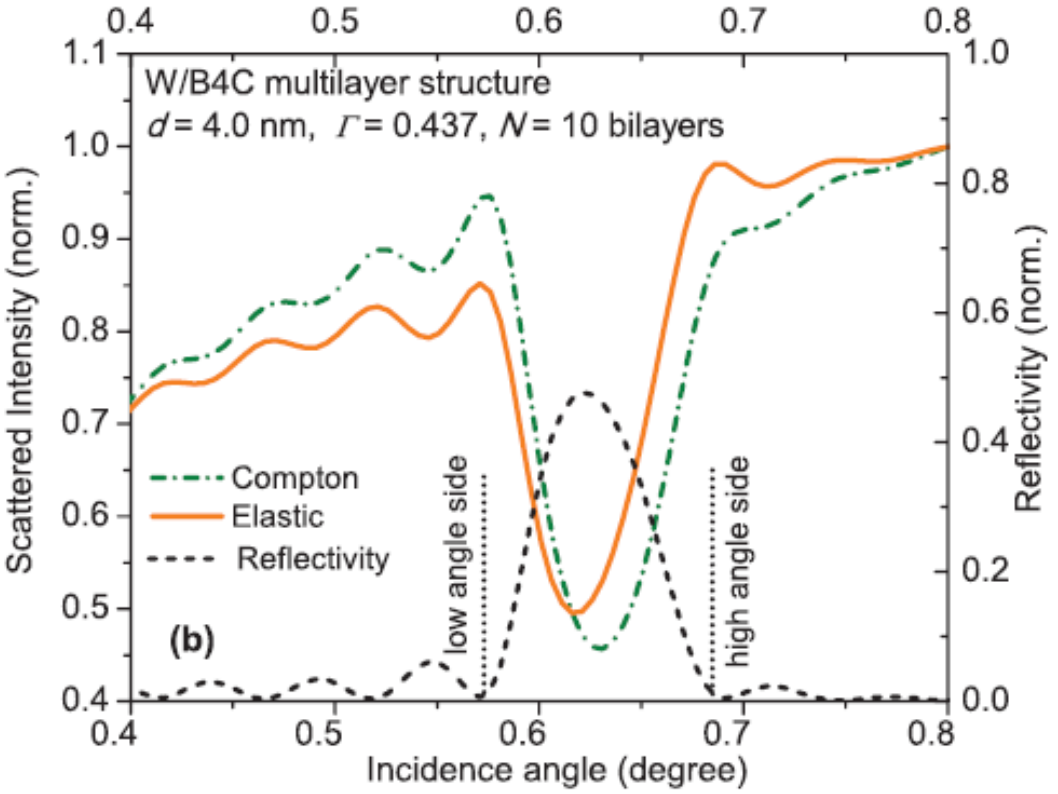


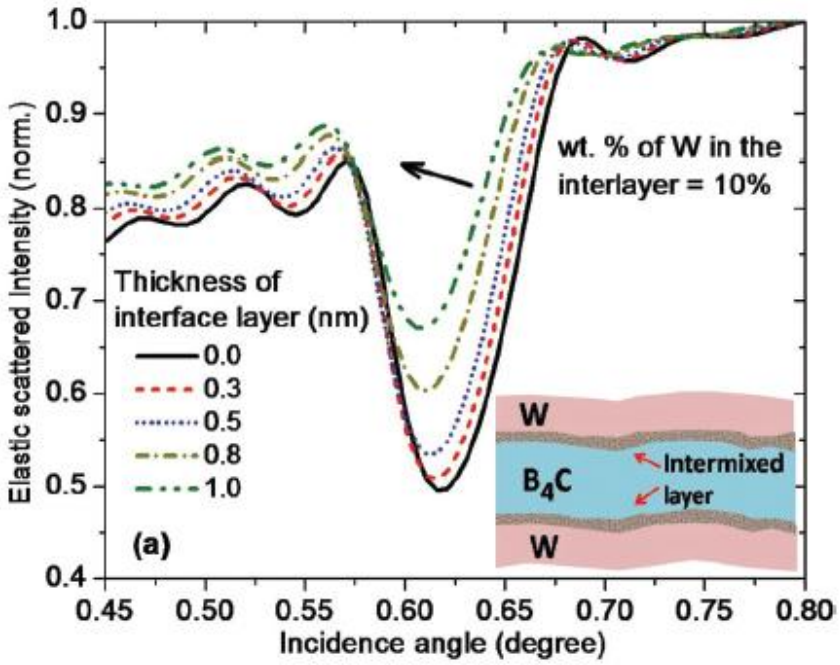
Compton scattered x-rays → Low Z layer

Elastic scattered x-rays → High Z layer

W/C periodic multilayer structure

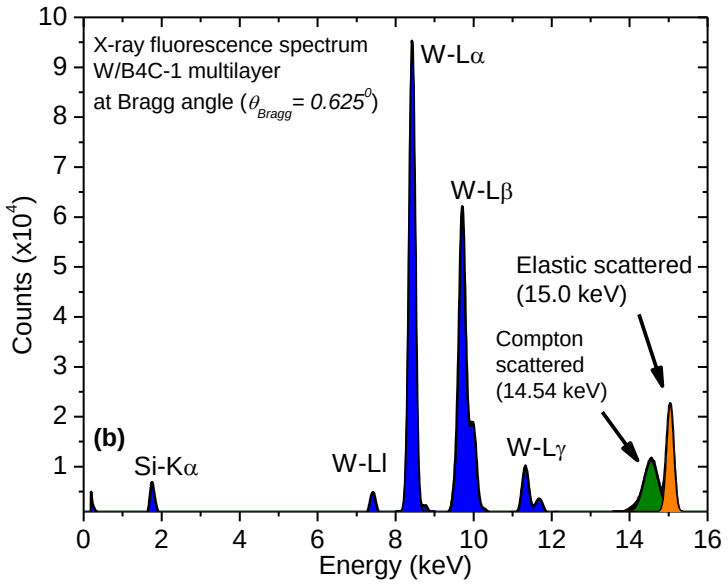


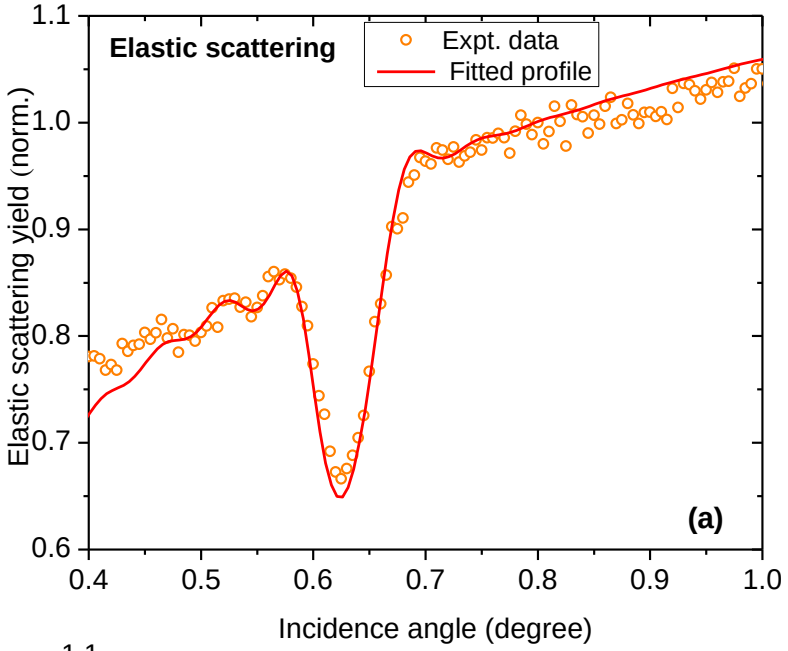


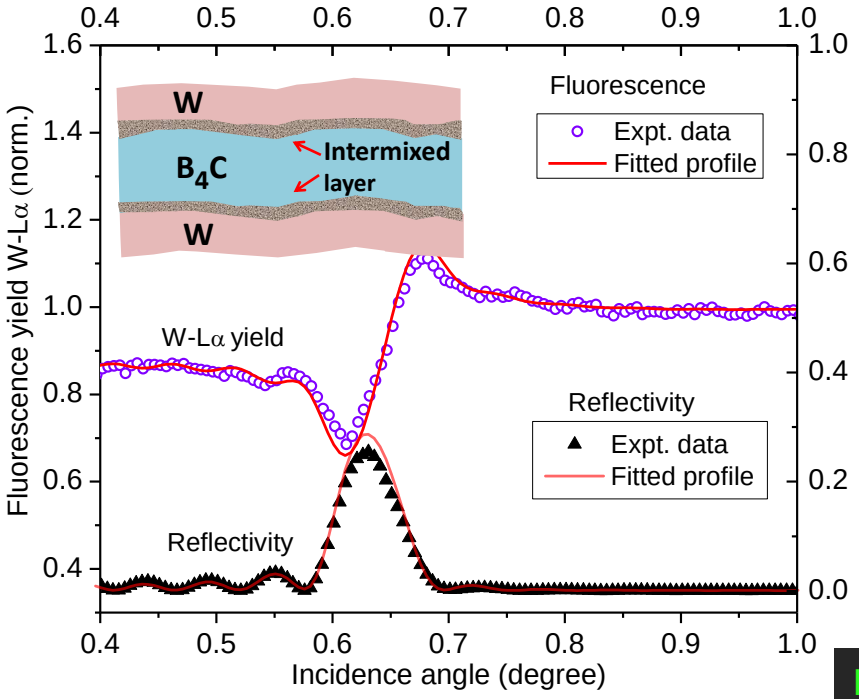


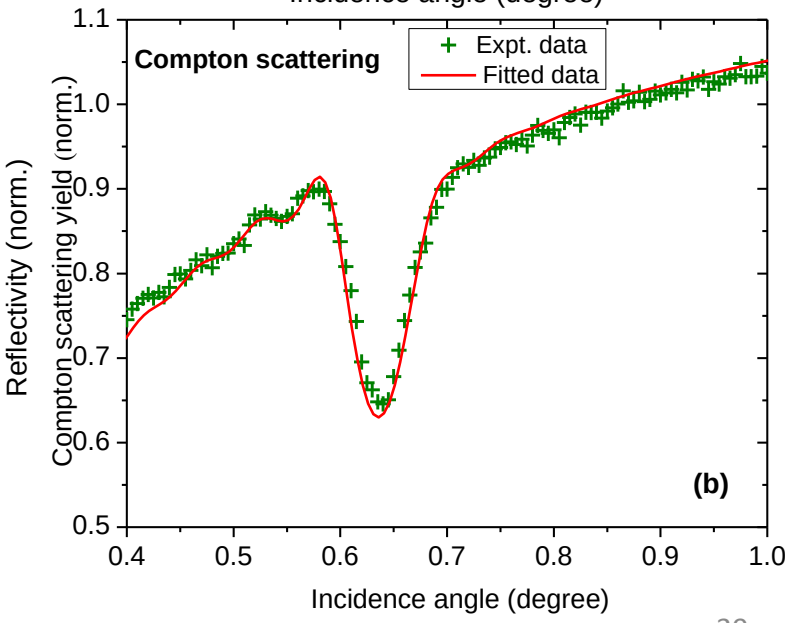
W/B4C periodic multilayer structure (d = 4.0 nm, structure factor = 0.437, number of bilayers N = 10)

W/C periodic multilayer structure…..





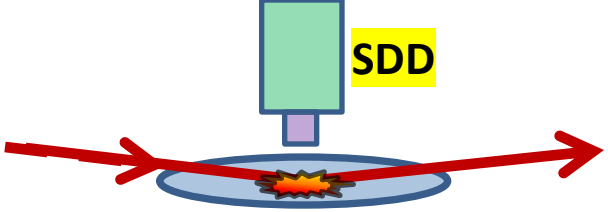


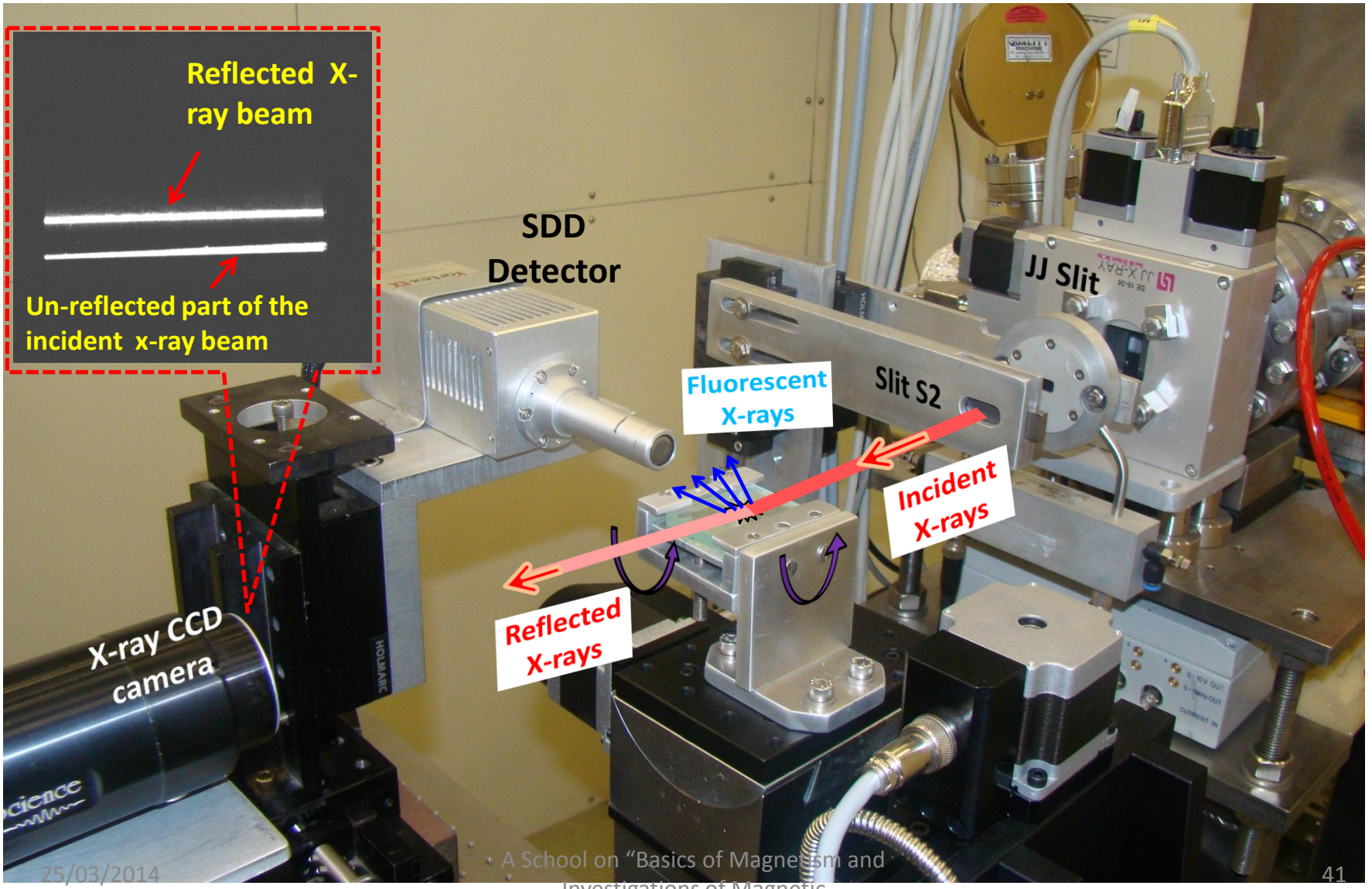


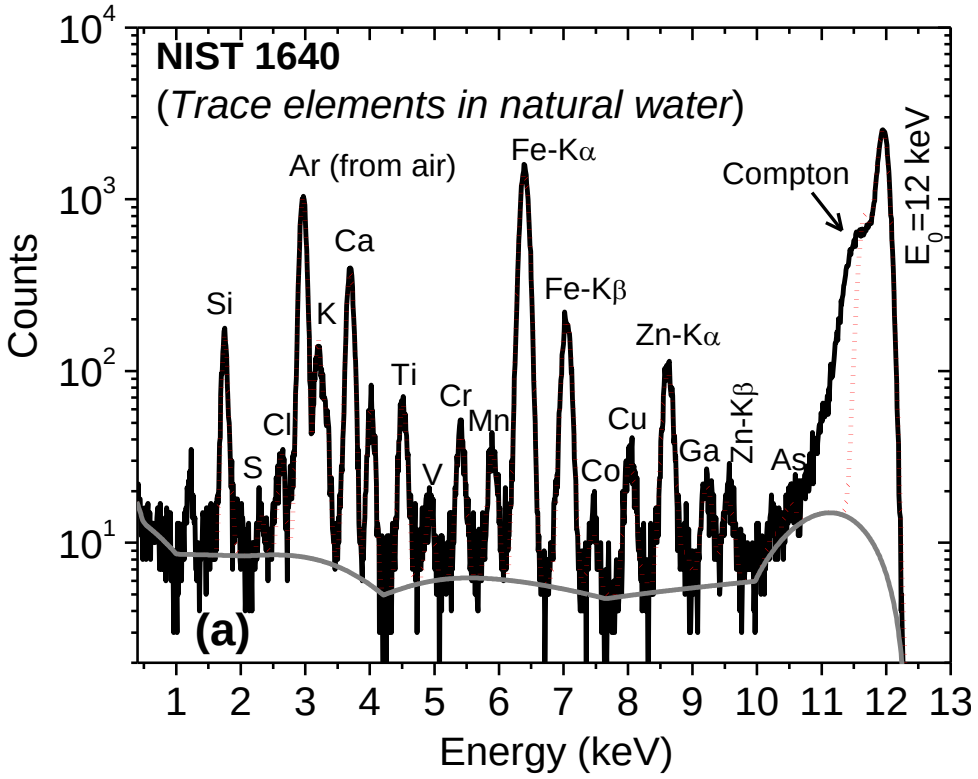
M K Tiwari et. al. Phys. Rev. B 87, 235401 (2013)

Synchrotron GIXRF and TXRF activities on Indus-2

TXRF SETUP

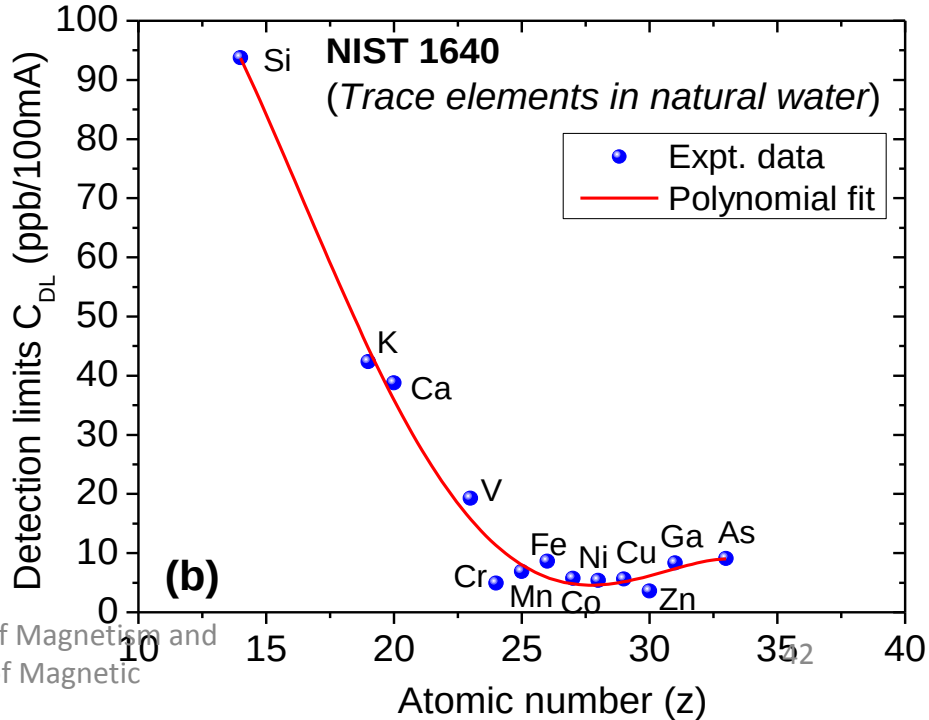

SDD


Reflected X-ray beam
Un-reflected part of the incident x-ray beam
SDD Detector
JJ Slit
Slit S2
Fluorescent X-rays
Incident X-rays
Reflected X-rays
X-ray CCD camera

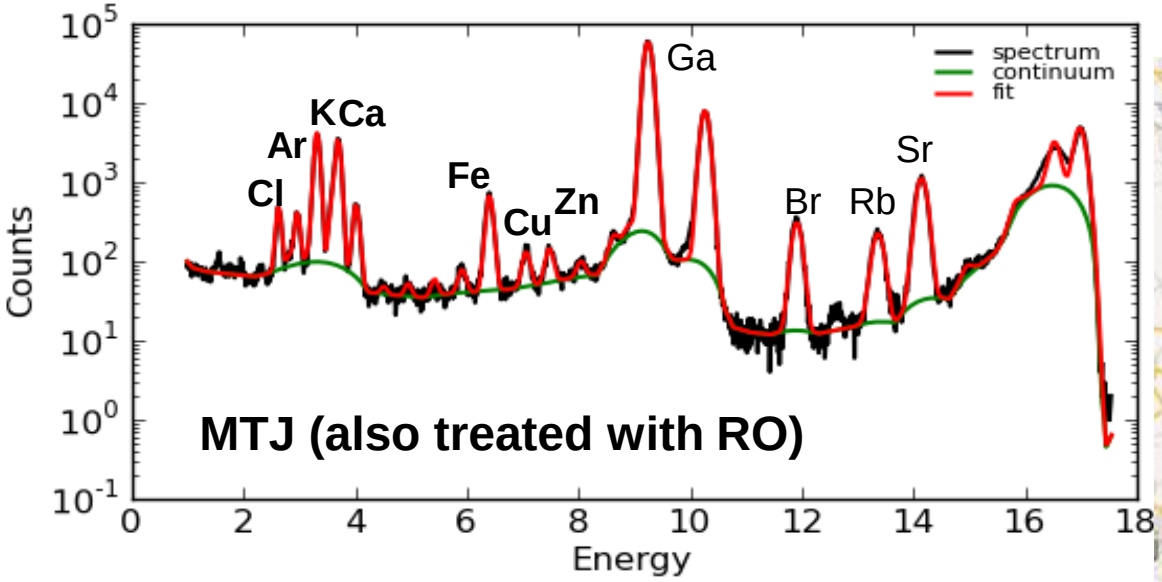


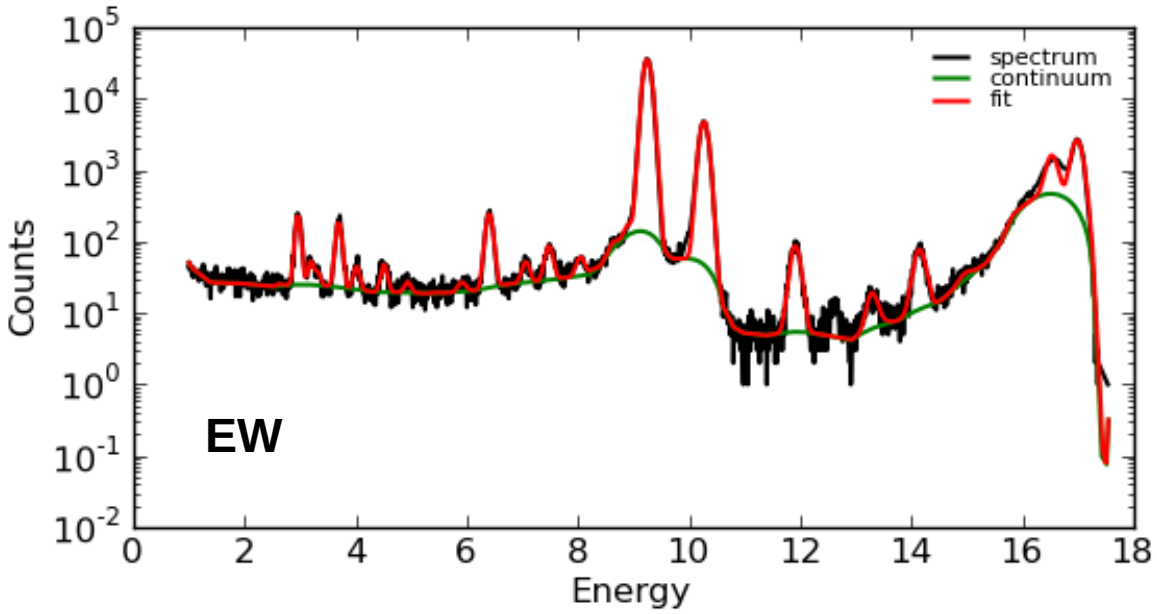
(a) Measured TXRF spectrum of a NIST-1640 sample at monochromatic x-ray energy of E_0 = 12 keV. Black solid line is experimental data, dotted lines are fitted data and the thick grey lines represent an estimation of the spectral background.

(b) Variation of element detection sensitivities as function atomic number z. These detection sensitivities were derived for a sample-to-detector distance of ~ 30mm.

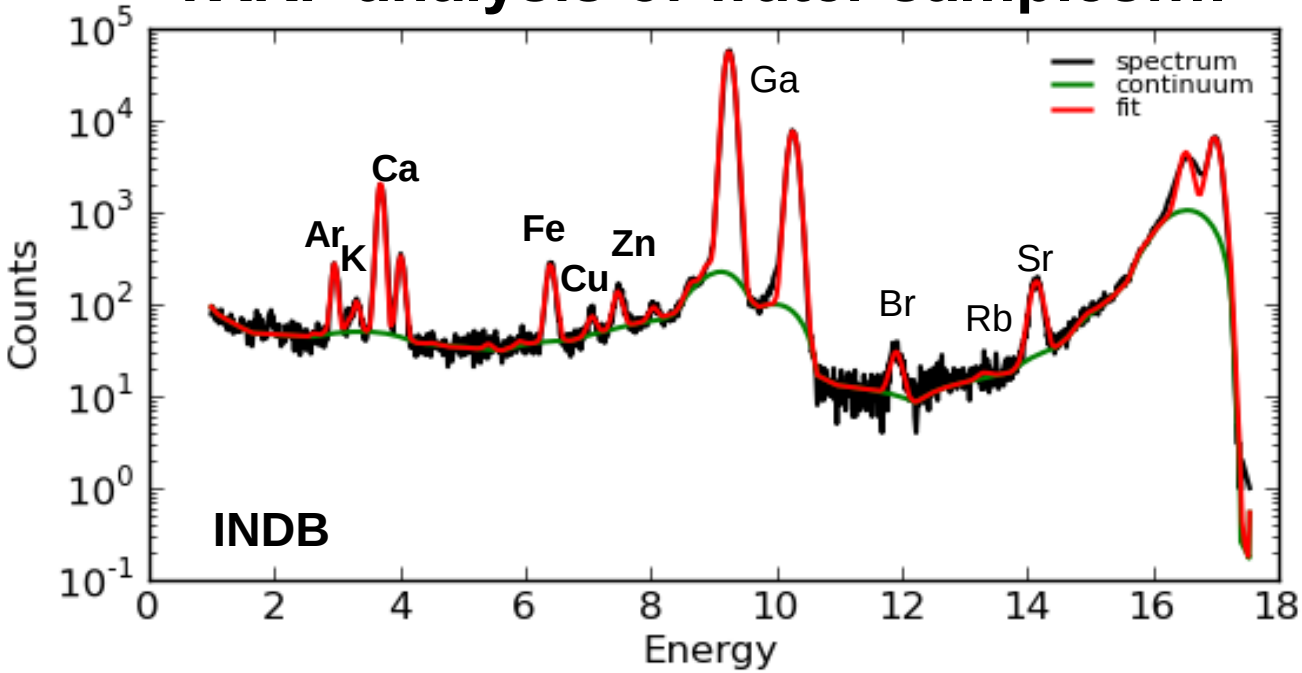


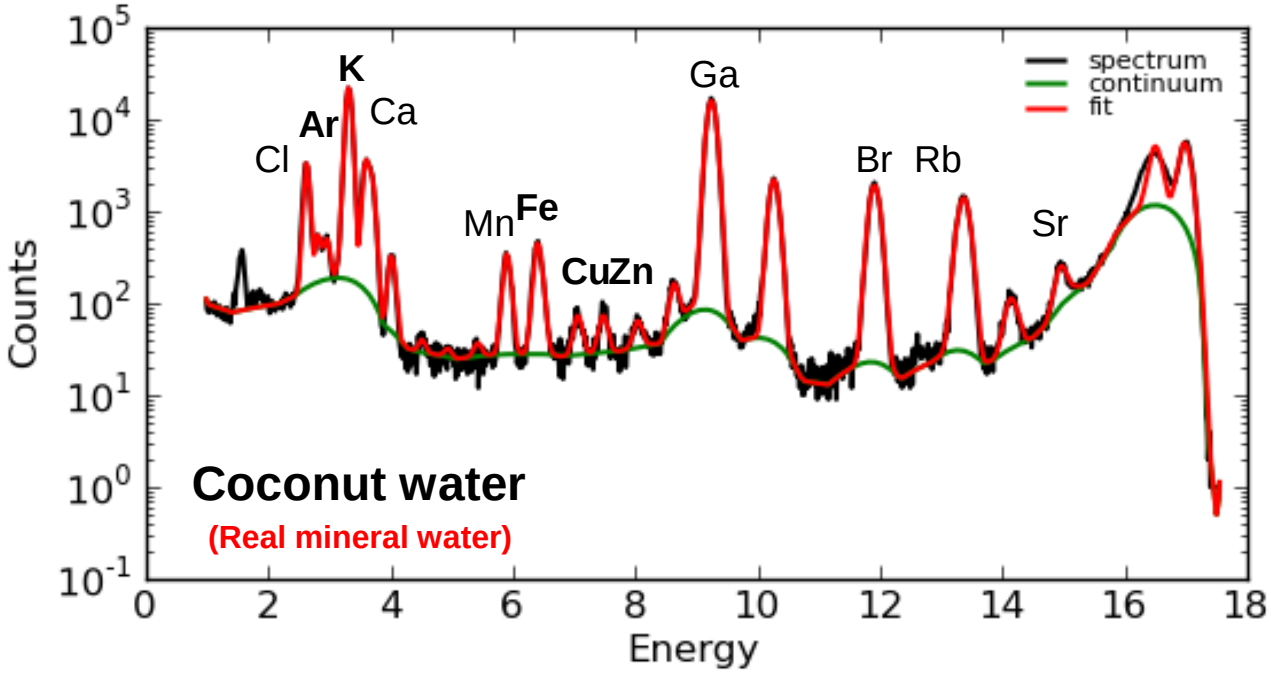
TXRF analysis of water samples





TXRF analysis of water samples….



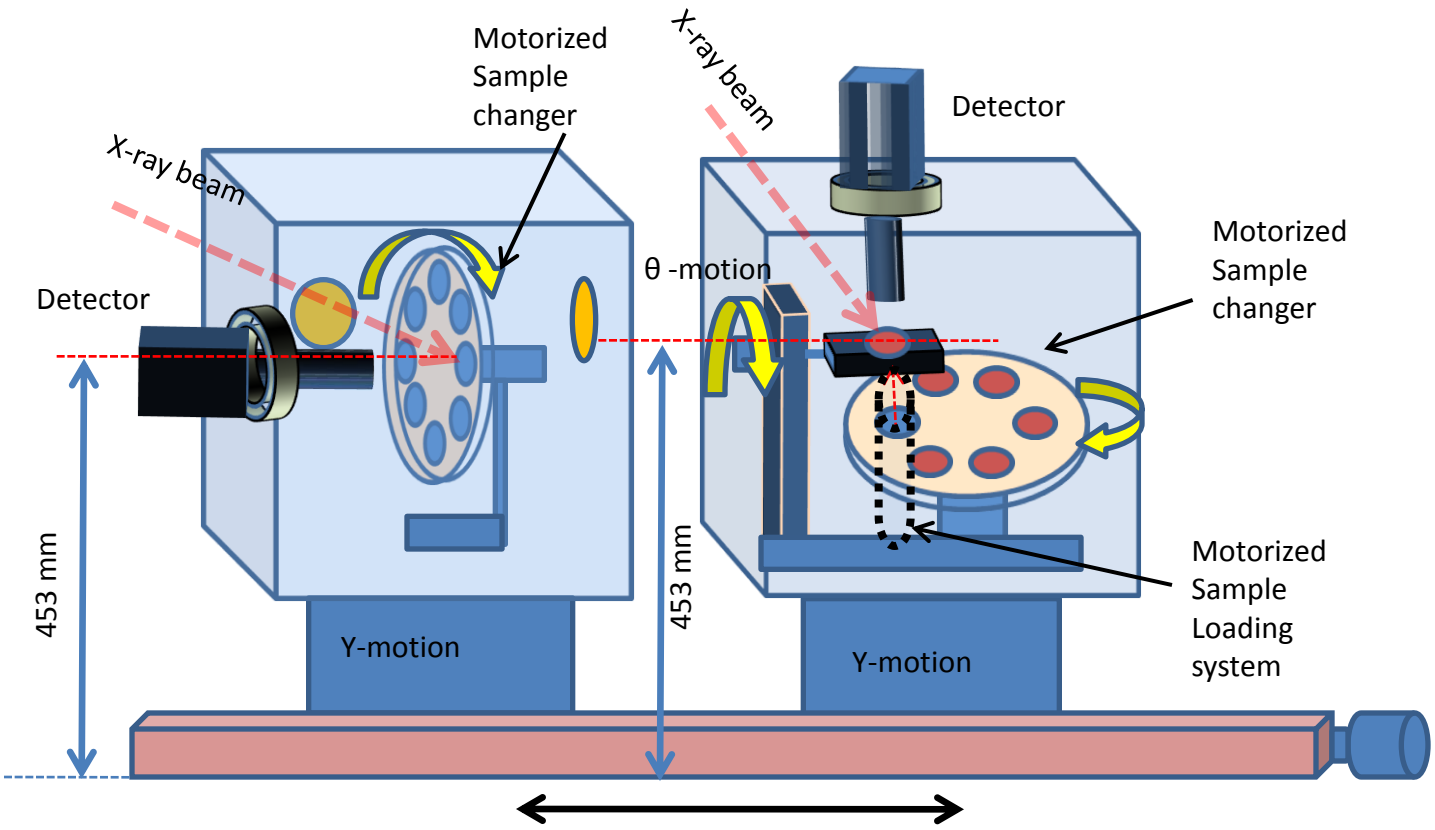


TXRF analysis of water samples….

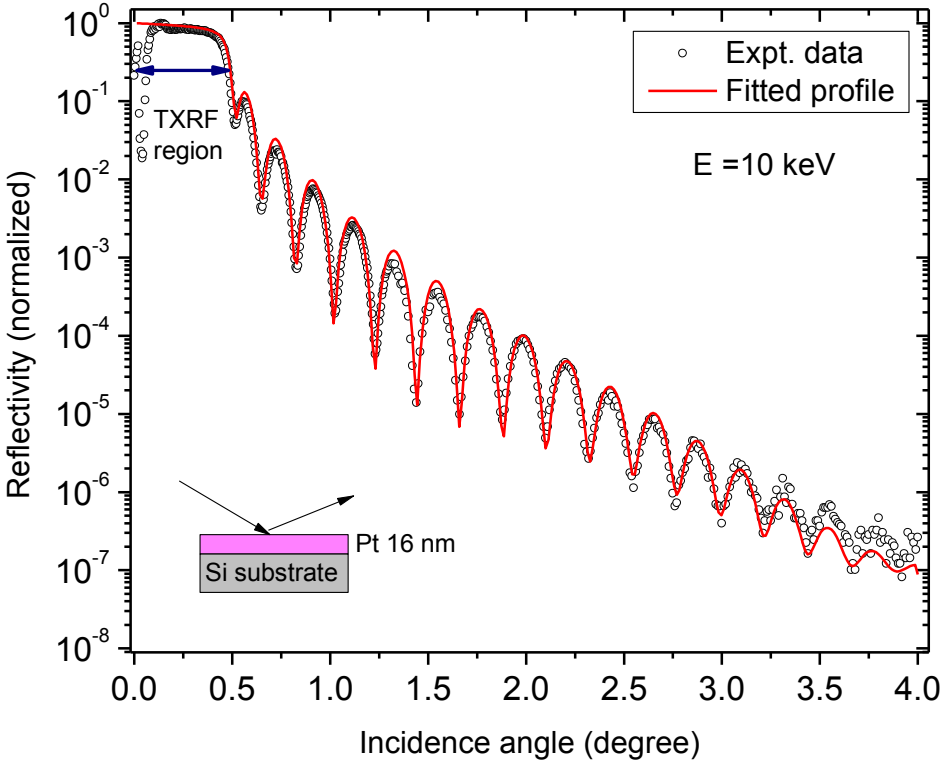
Element	#Water INDB-Narmada	#Water MTJ	#Water EW	#Water Coconut	WHO guidelines (for drinking water)
Cl	0.083	8.61	0.042	264.7	≤ 5
Ar	5.6	7.8	7.6	29.7	-
K	0.92	67.55	0.37	1367.4	Not defined * (recommended daily requirement is greater than 3000 mg)
Ca	19.6	31.0	3.0	67.8	≤ 100, (100-300 may change taste of water)
Ti	0.02	0.04	0.17	0.13	
V	--	0.014	--	0.031	
Cr	0.006	0.017	0.003	0.02319	≤ 0.05
Mn	0.005	0.053	0.012	1.7	≤ 0.4
Fe	0.3	0.8	0.55	1.81	0.5 - 50
Ni	0.075	0.0786	0.083	0.158	≤ 0.07
Cu	0.023	0.0265	0.0256	0.091	≤ 2
Zn	0.020	0.050	0.029	0.258	0.01 – 0.05
Ga	36.433	36.433	36.433	36.433	-
Br	0.008	0.153	0.072	3.61	≤ 0.05
Rb	0.6ppb	94.7ppb	1 ppb	2455 ppb	
Sr	0.094	0.639	0.062	0.183	

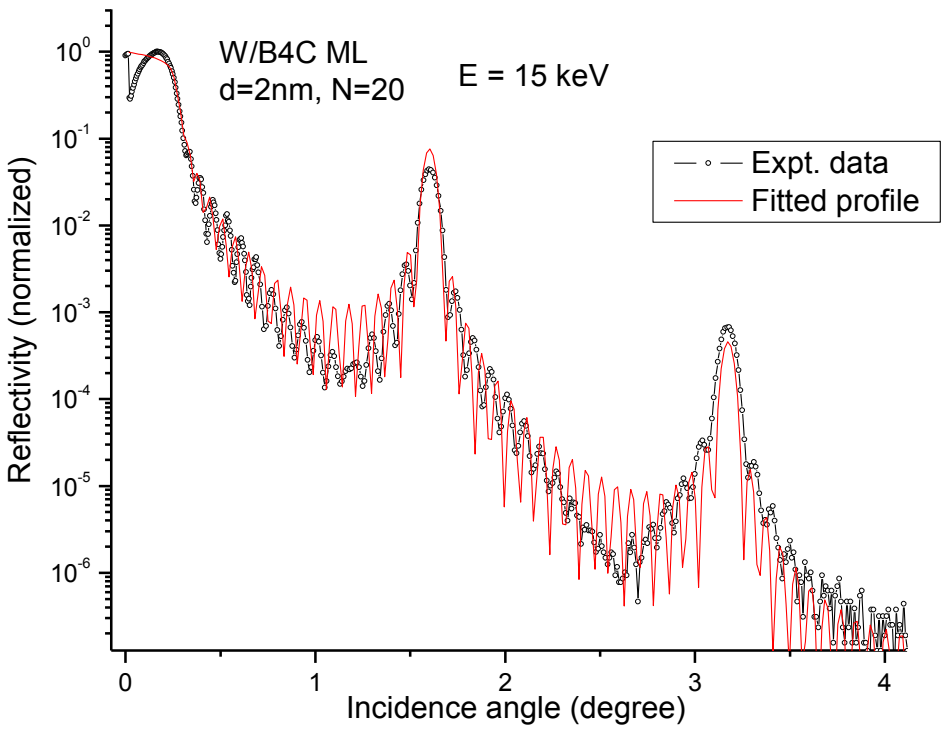
All quantities are in (mg/liter)

Assembly of the chambers



XRR

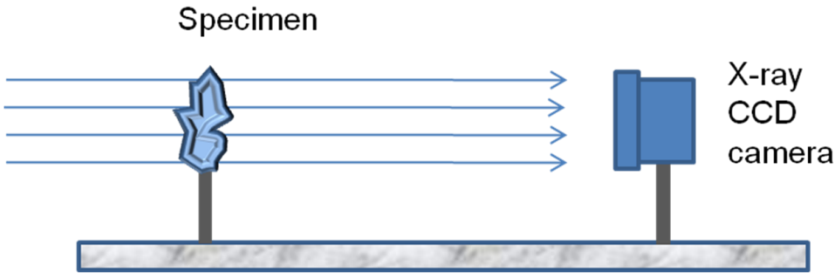

Expt. data
Fitted profile
E =10 keV
TXRF
region
Pt 16 nm
Si substrate
Reflectivity (normalized)
Incidence angle (degree)


W/B4C ML
d=2nm, N=20
E = 15 keV
Expt. data
Fitted profile
Reflectivity (normalized)
Incidence angle (degree)

X-ray Imaging at BL-16

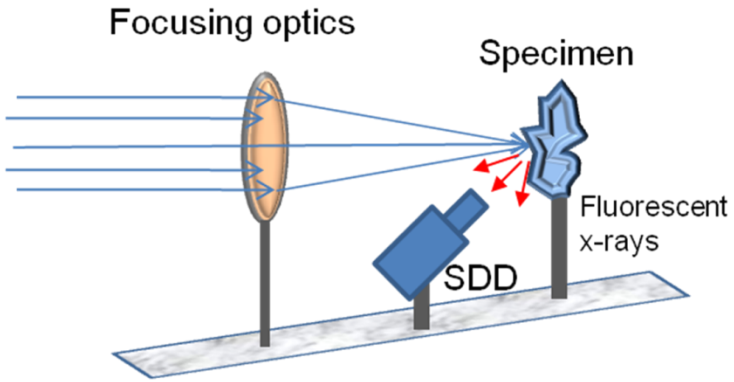
Experimental schemes

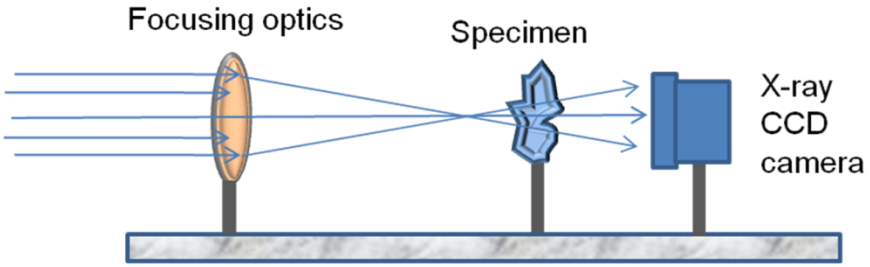
Absorption contrast x-ray imaging



Collimated beam illumination

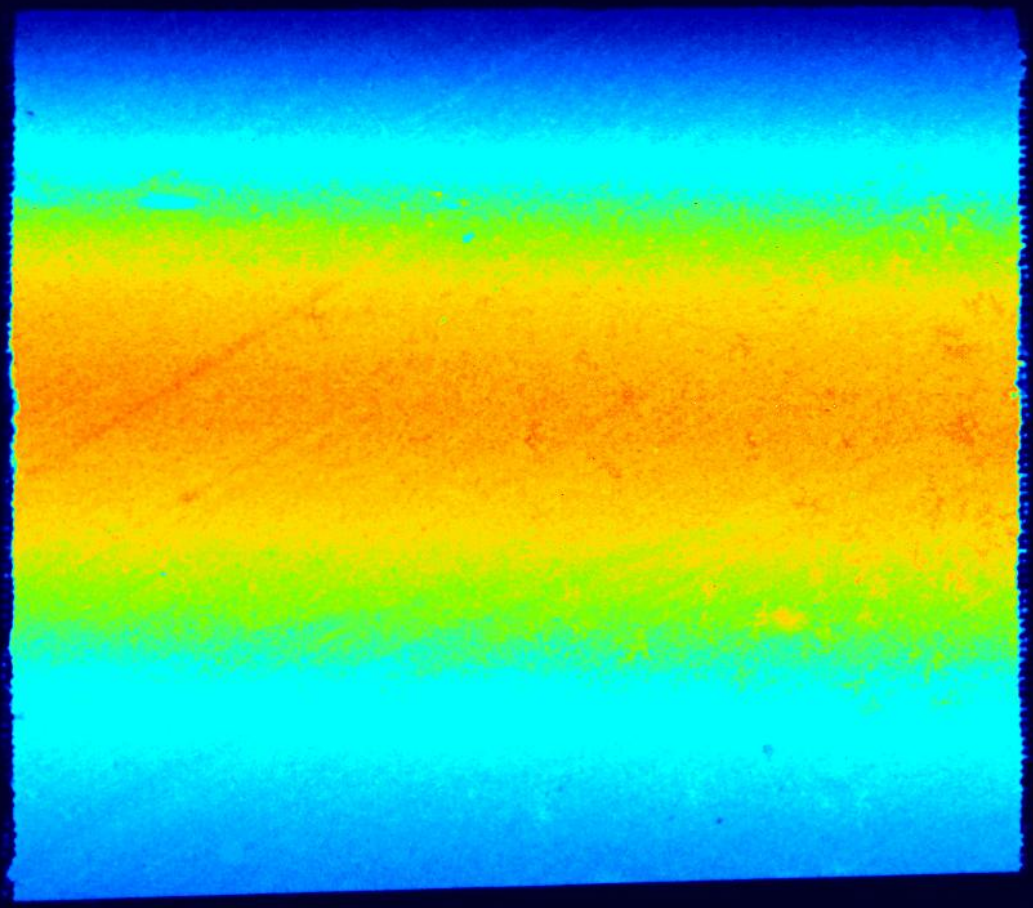
Fluorescence imaging

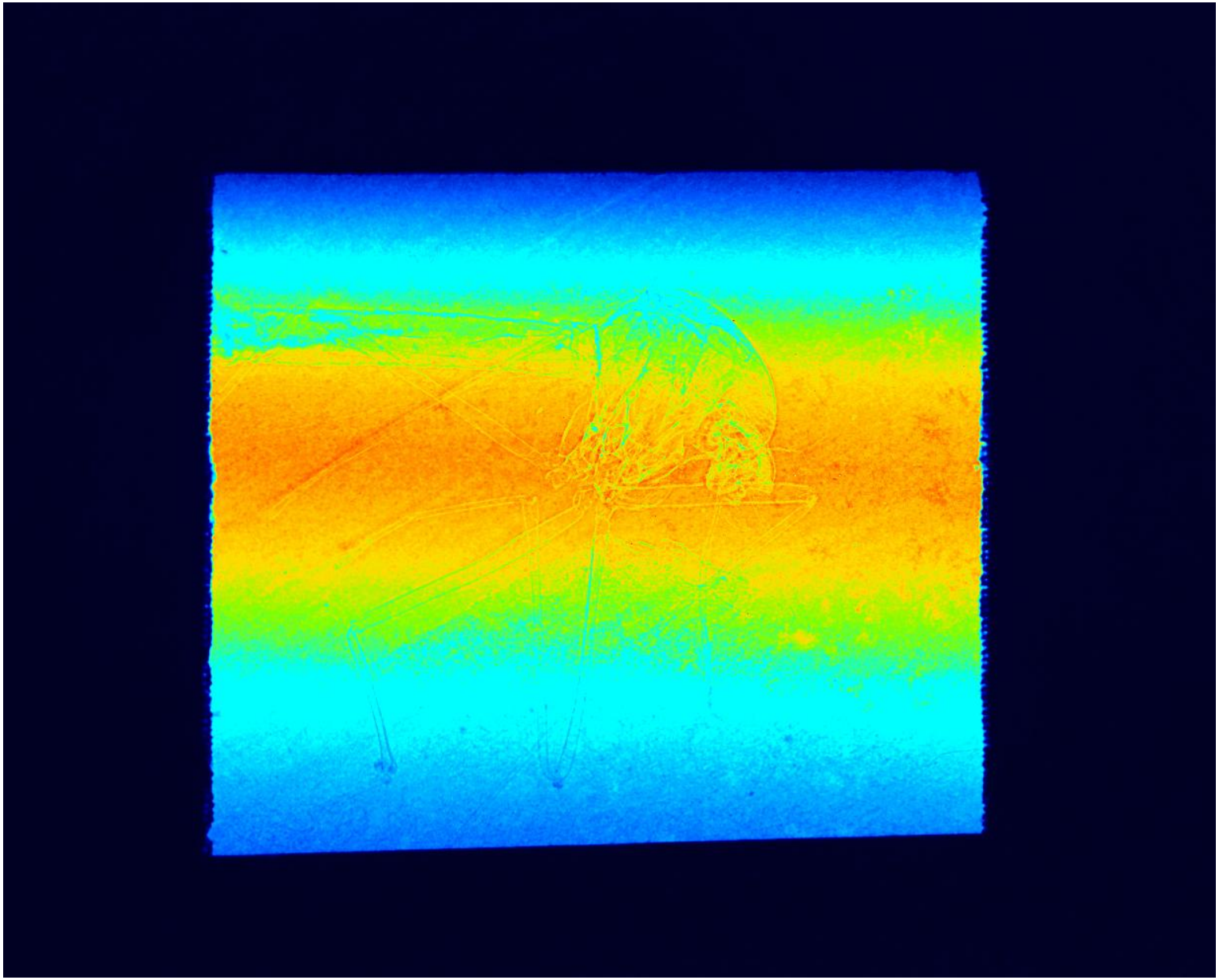




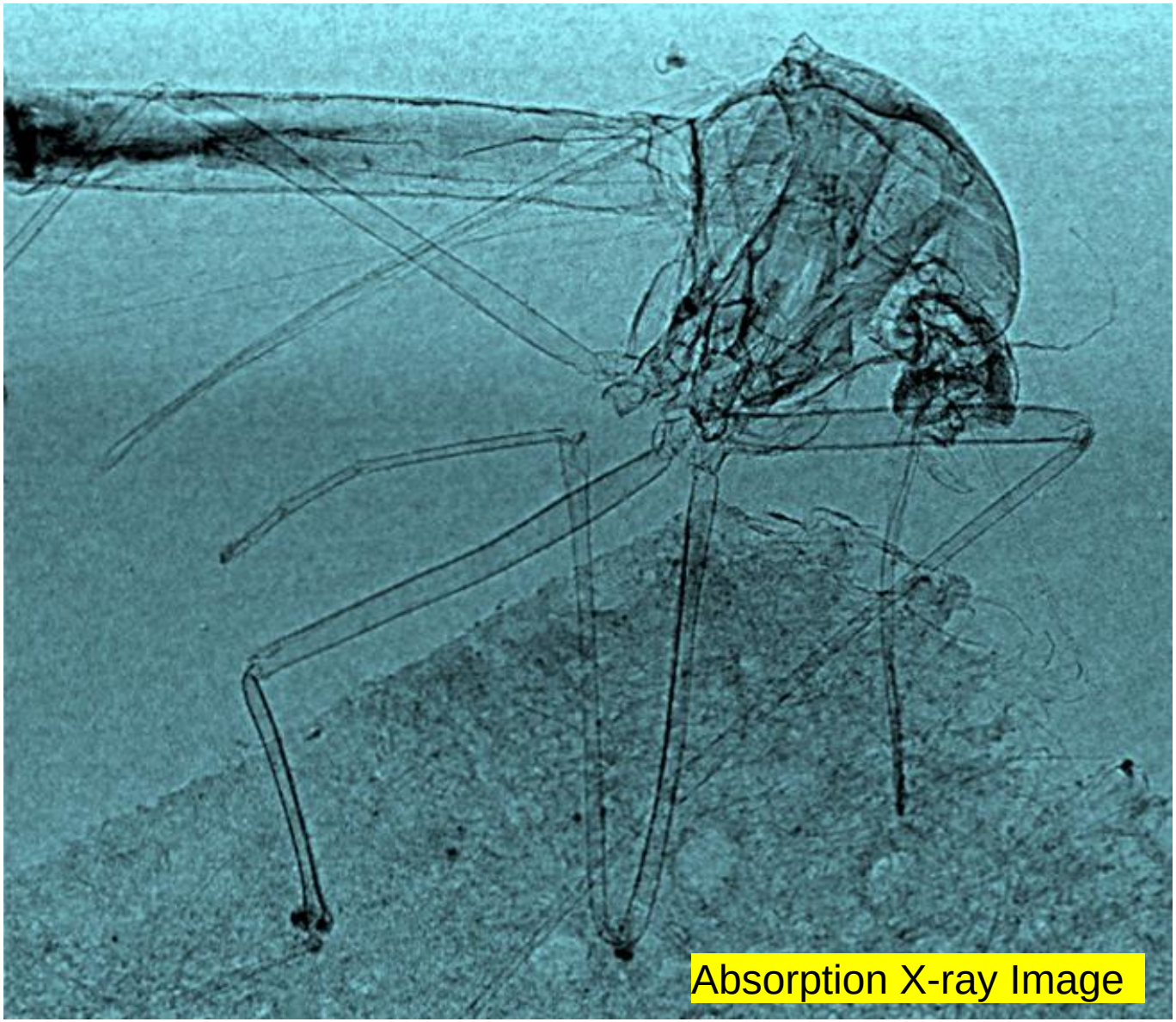
Projection Imaging (using BL-16 KB optics)

Beam size = 5 mm (v)× 5 mm (h)





X-ray Image of a Mosquito (At E= 12 keV)

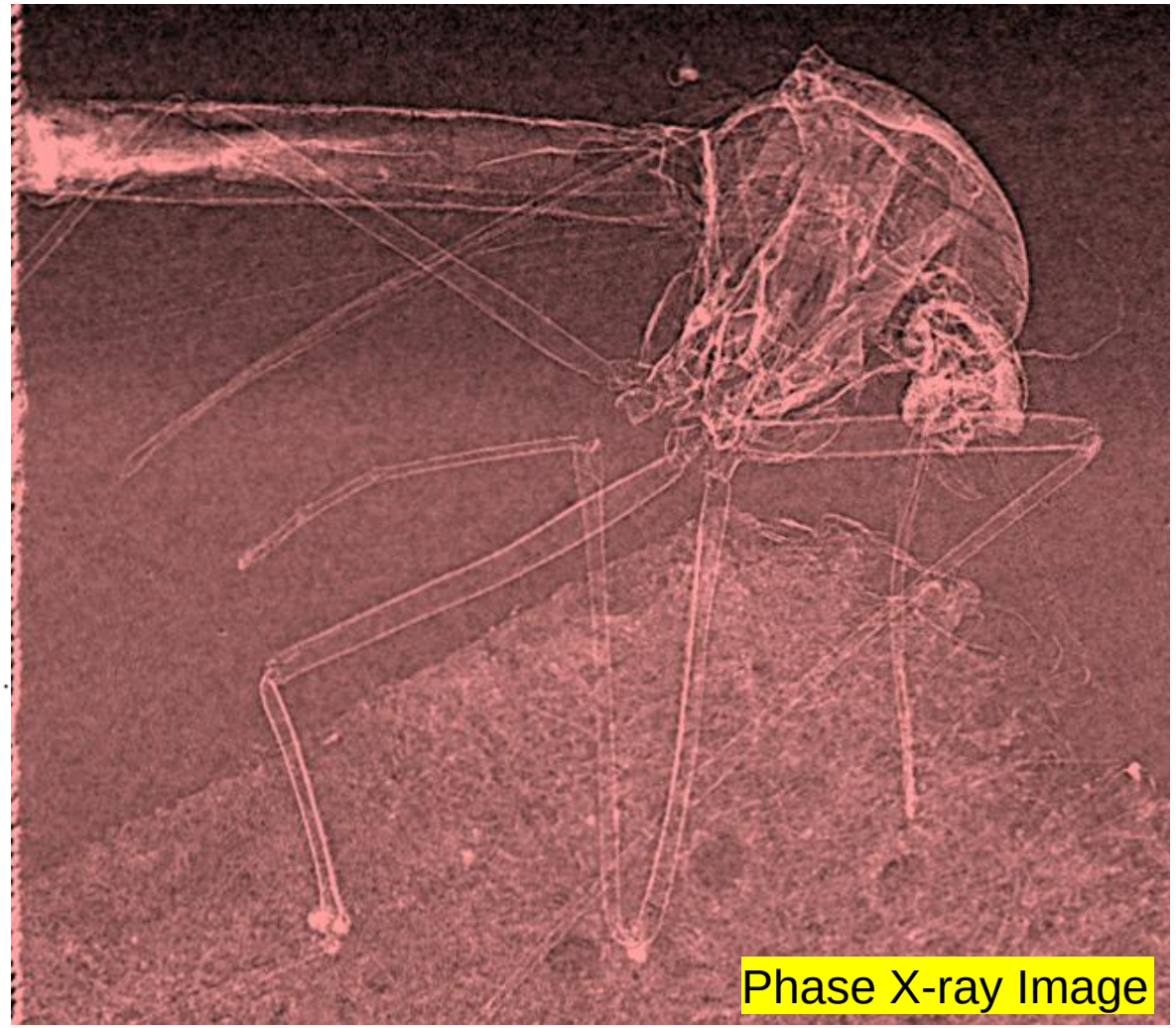


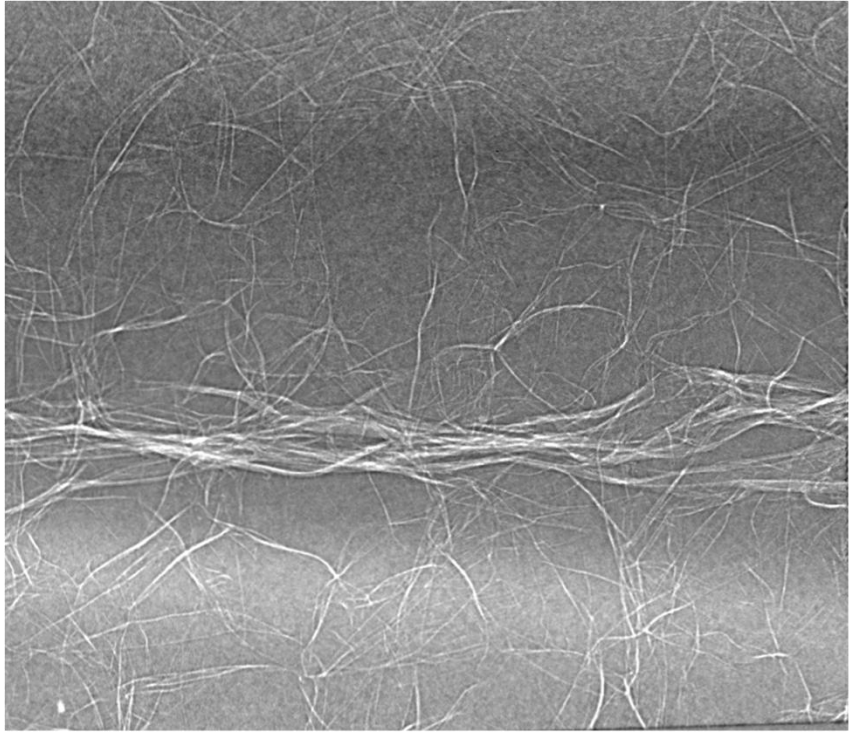
X-ray Image of a Mosquito (At E= 12 keV)

$$t(x,y) = -\frac{1}{\mu}\ln\left(\mathcal{F}^{-1}\left[\frac{\mu\,\mathcal{F}[I(x,y)/I_0(x,y)]}{\mu + z\delta(u^2+v^2)}\right]\right)$$

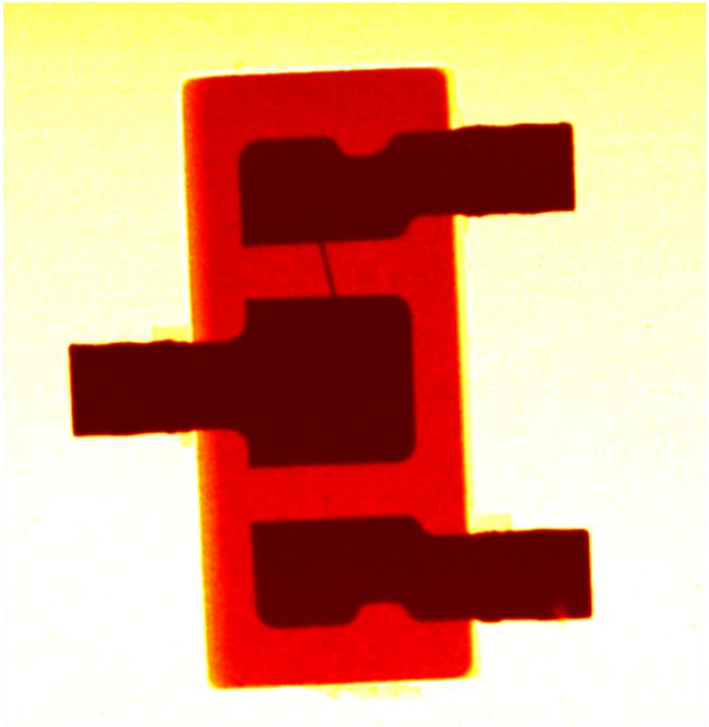
$$\varphi(x,y) = -\frac{2\pi\delta}{\lambda}\,t(x,y)$$

$$\varphi(x,y) = \frac{1}{2}\ln\left(\mathcal{F}^{-1}\left\{\frac{\mathcal{F}\left[I(x,y)/I_0(x,y)\right]}{\beta/\delta + [\lambda z/(4\pi)](u^2+v^2)}\right\}\right).$$

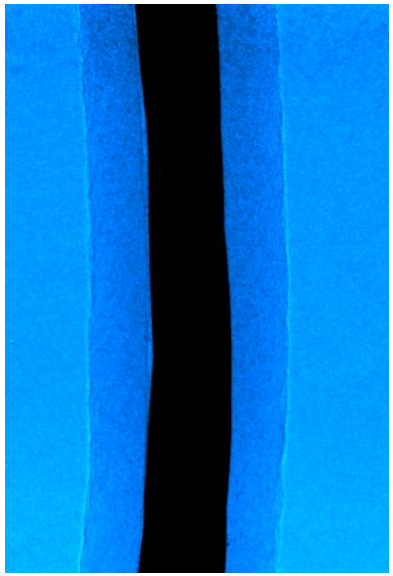




Polymer fibers in foam structure



Zener diode



A thin electrical wire

Summary

- Microprobe XRF beamline (BL-16) commissioned on the Indus-2 synchrotron source can be for materials characterization (trace element analysis, bulk and thin layered materials, etc.)

- Beamline offers several modes of XRF analysis (*viz*. normal EDXRF, TXRF and microprobe elemental mapping)

- BL-16 beamline is running in the user operation mode. A user an access this beamline by requesting a user beam time

- Vacuum compatible TXRF and GIXRF experimental stations are being setup on BL-16 beamline (will be ready for use ~1 year time)


Thank you