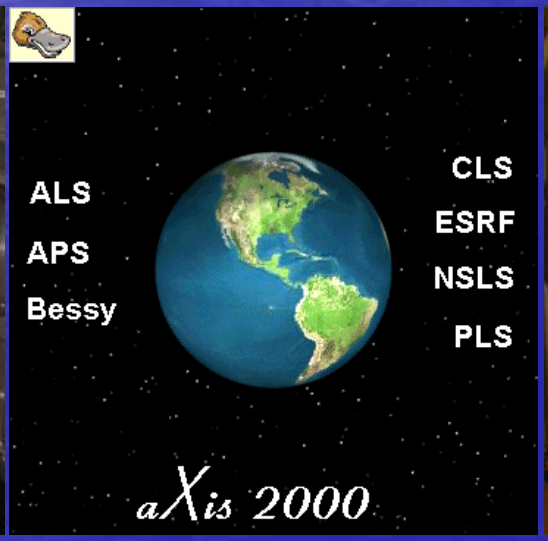
Soft X-ray spectromicroscopy & its analysis with aXis2000 .

Adam Hitchcock - BIMR, McMaster University

GOALS

1. familiarization with Synchrotron spectromicroscopy techniques
2. demonstration of data analysis with aXis2000
3. discussion of potential for your application

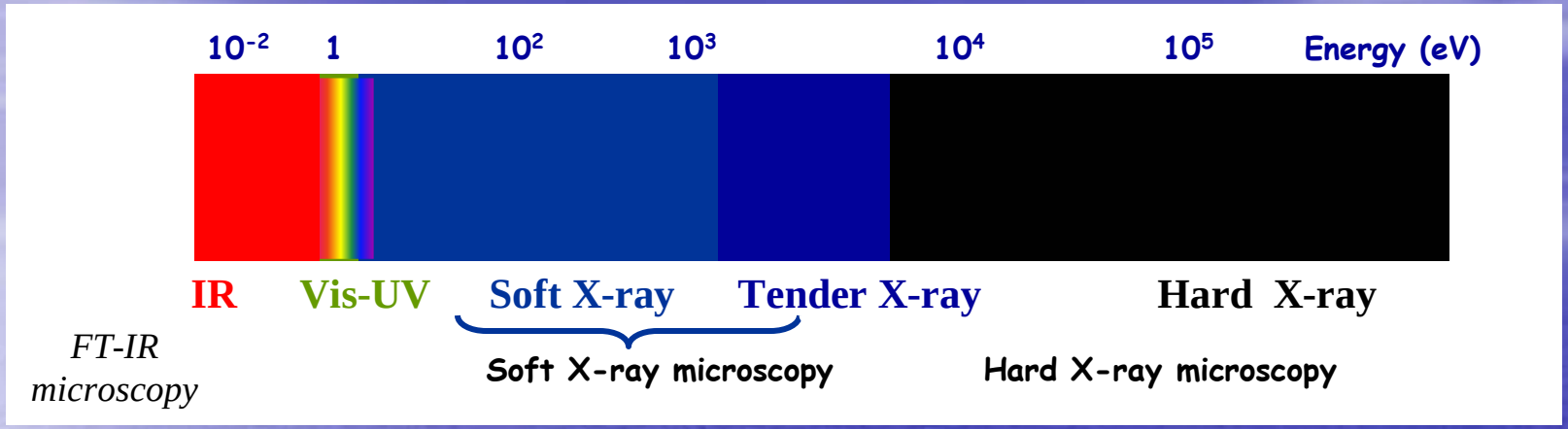


Outline

- Modes & information from X-ray spectromicroscopy
- Data analysis - example from STXM

  chemical mapping of protein on a phase segregated polymer
- structure of aXis2000 widget
- how can you access the power of aXis2000 ?

Basic Principles



* Use **X-ray absorption contrast** for
  * chemically sensitive imaging - "X-ray imaging"
  * spatially resolved chemical analysis - 'Micro-probe"

NEXAFS microscopy

* Use **penetrating power** of X-rays to study
  * wet soft matter (biology, polymers, nano-materials)
  * fluorescence microprobe
  * non-destructive testing; tomography

Soft X-rays ("water window")

Hard X-rays

References:

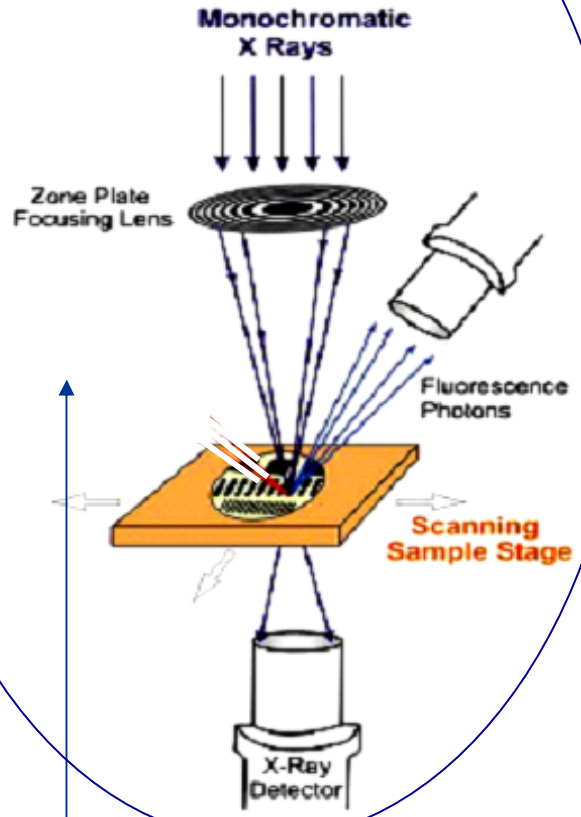
- J. Kirz, C. Jacobsen and M. Howells, Quarterly Review of Biophyisics, 33 (1995) 33
- H. Ade, in *Experimental Methods in the Physical Sciences*, Vol. 32, pp. 225, J.A.R. Samson and D.L. Ederer Ed., Academic Press, 1998
- A.P. Hitchcock, American Laboratory, 33 (2001) 30; J. El. spec. 144 (2005) 259.
- H. Ade and S.G. Urquhart, in "*Chemical Applications of Synchrotron Radiation*" T. K. Sham, ed. (World Scientific Publishing, 2002)

Overview of techniques

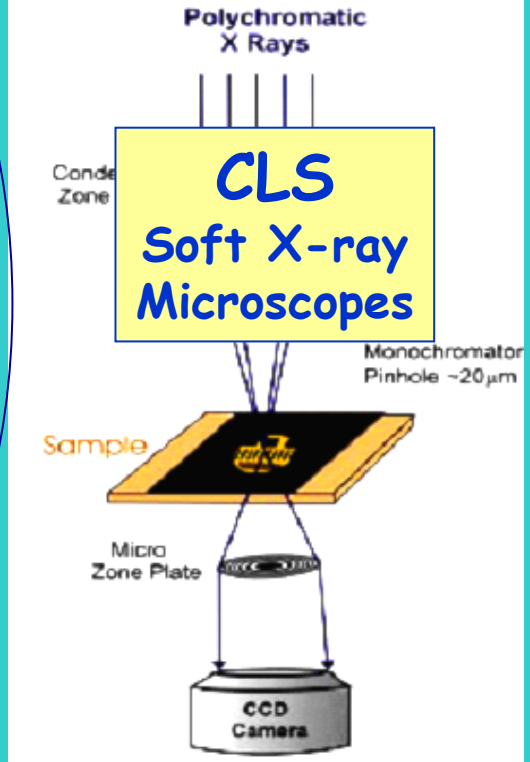
STXM ALS BL 5.3.2; BL11.0, NSLS X1A, BESSY

TXM now at ALS BL 6.1.2 XM-1, BESSY

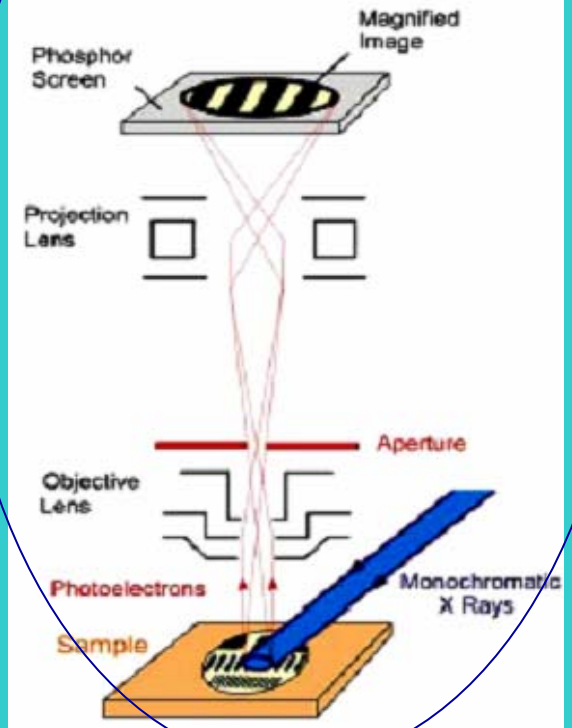
Scanning Transmission X-ray Microscopy - STXM



Transmission X-ray Microscopy TXM



X-ray PhotoEmission Electron Microscopy - X-PEEM



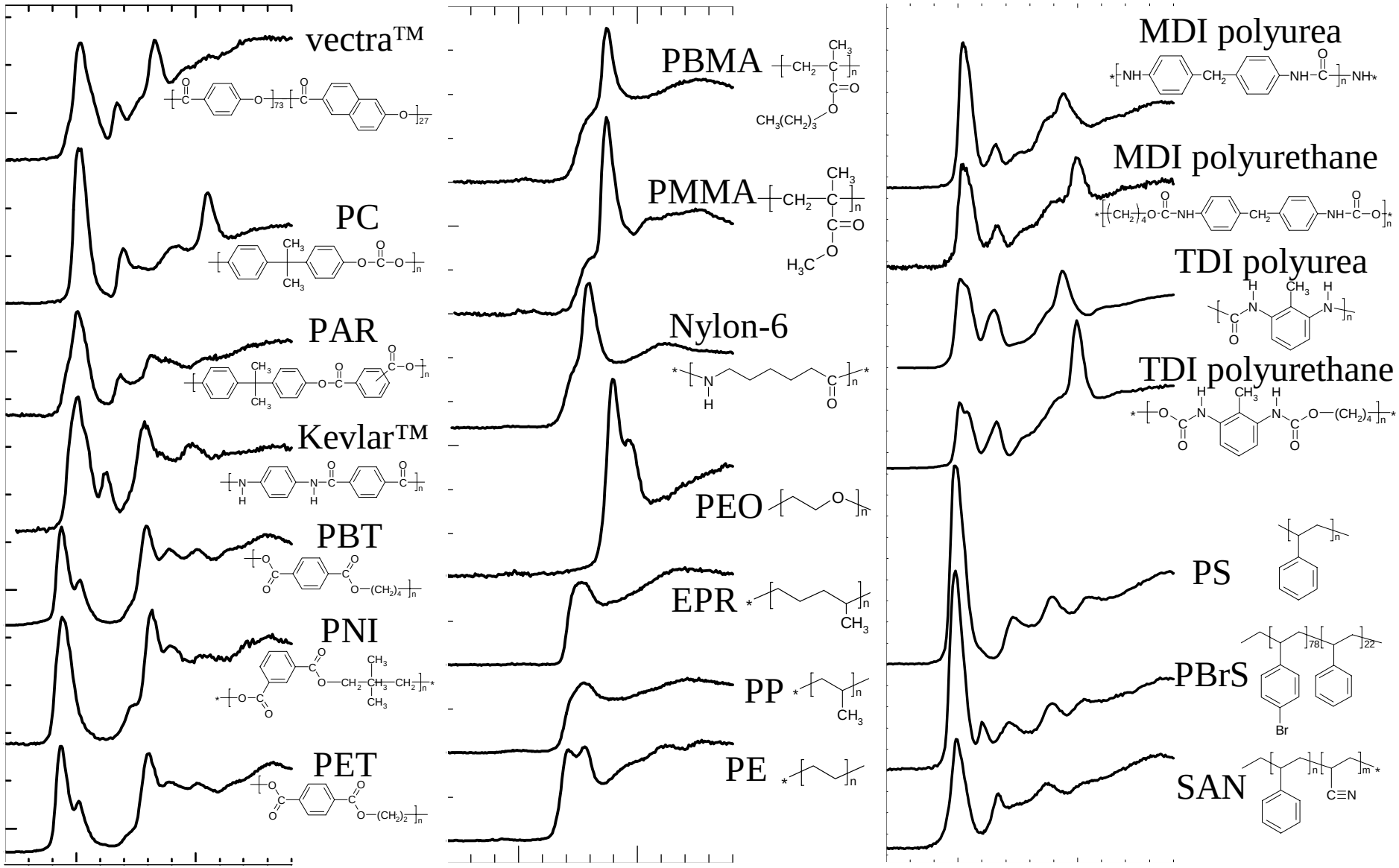
X-PEEM now at ALS BL 7.3.1, SLS, Trieste, SRC

Scanning Photoelectron Microscopy - SPEM

SPEM now at ALS, Trieste, Taiwan, Korea..

Sensitivity of Polymer NEXAFS Spectroscopy

Ade , Urquhart (1997-99)
(nsls X1A stxm)



Electron yield-based soft X-ray microscopies

Primary XAS process produces - **photoelectrons**
Core hole decay produces
- Auger & **secondary electrons**
- photons
- ions
- luminescence photons

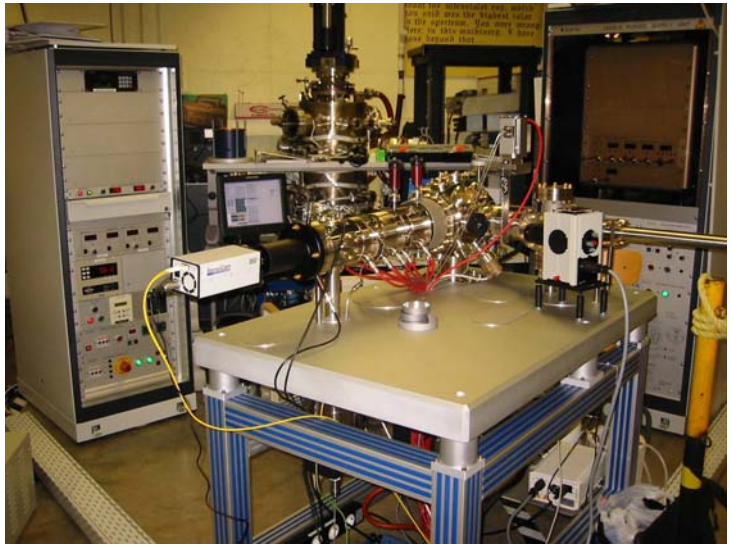
All are being developed as detection channels for analytical X-ray microscopy

SPEM –Scanning PhotoElectron Microscopy

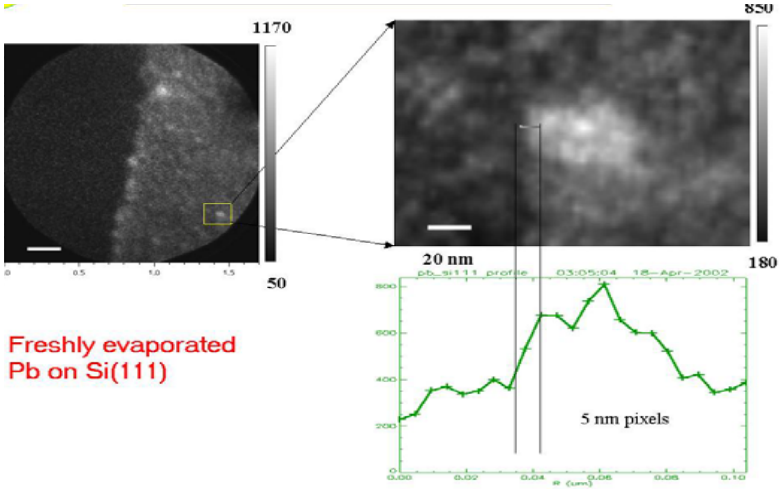
Elettra, Pohang Light Source
ALS BL 7.0.1

PEEM - Photo-Emission Electron Microscopy

Commercially available
* most SR facilities ; BESSY -**SMART**
ALS BL 7.3.1 [PEEM2]



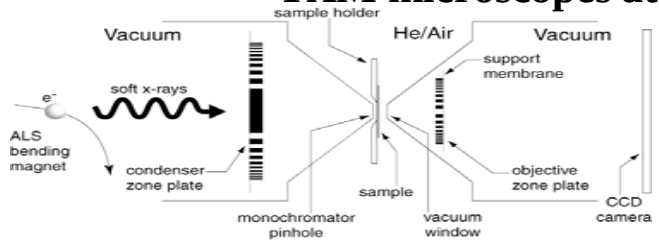
CaPeRS – Canada's Elmitec PEEM
now at CLS

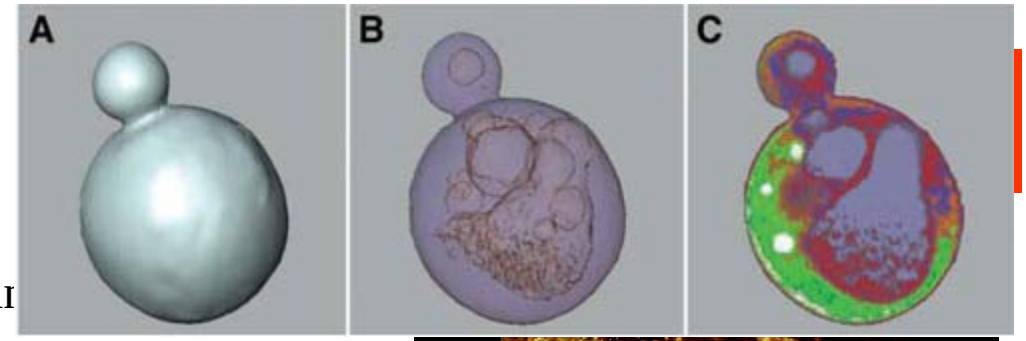


But only ~50 nm with synchrotron light due to e- distribution & chromatic aberration

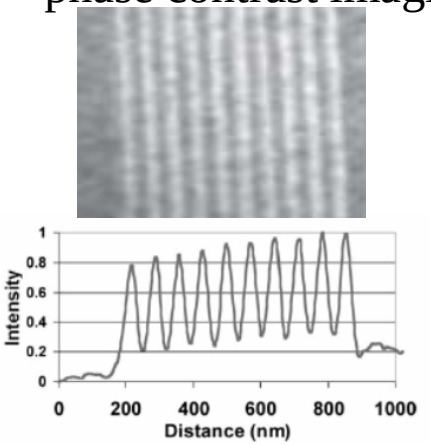
TXM – biological applications

- first demonstrated Gunter Schmäl (Gottenberg) – BESSY (~1986)
- TXM microscopes at ALS (XM-1), Bessy, Aarhaus, Elettra

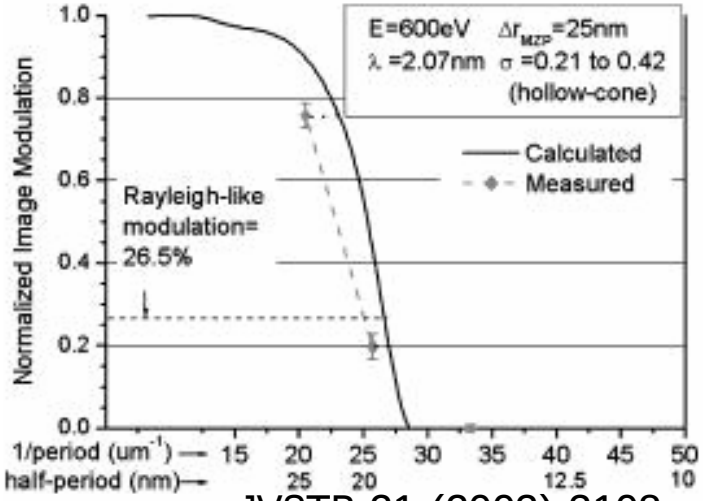




- wet cells: biomaterials & biological imagi
- cryo imaging
- tomography
- XMCD imaging
- phase contrast imaging



Highest spatial resolution
22 nm diffraction limit achieved
test sample: 15 nm lines 4:1 spacing

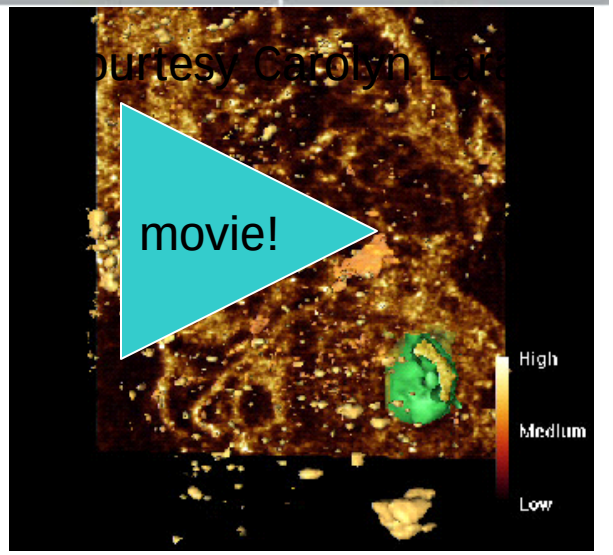


JVSTB 21 (2003) 3108

2 μm

monoclonal antibody / Au-Ag-labeling of cytoskeleton proteins

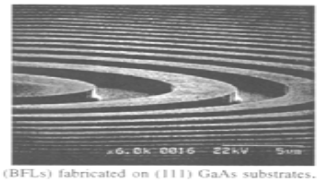
Larabell (UC Davis) ALS 1999

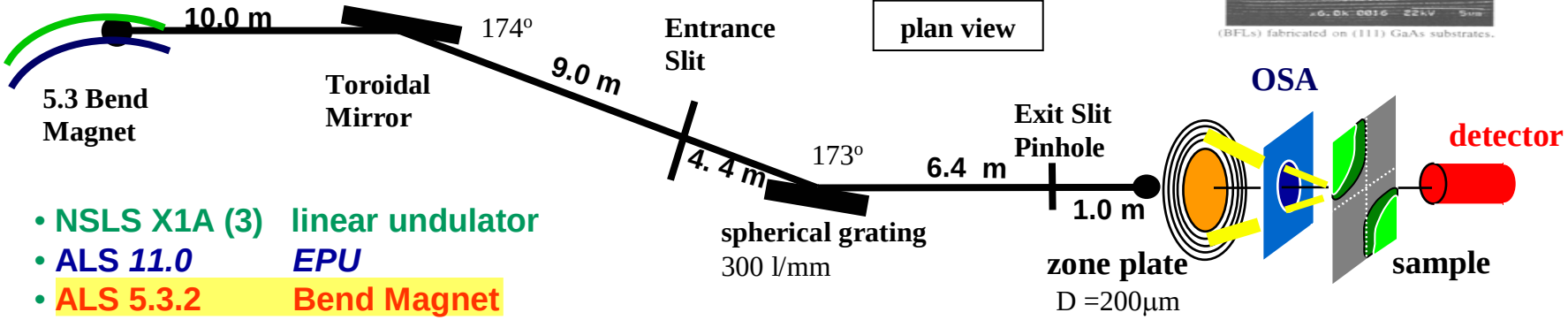


Gerd Schneider, Carolyn Larabel
ALS XM-1 2003

Angle-scan tomography
(cf. Attwood)

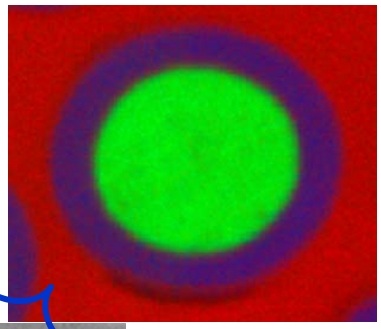
Scanning Transmission X-ray Microscopy (STXM)





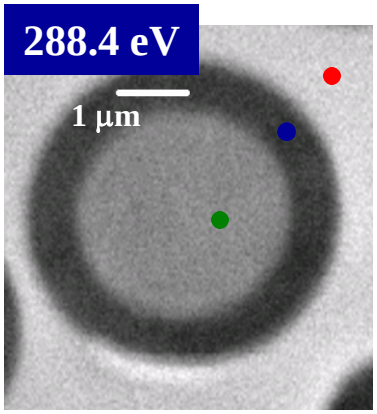
- NSLS X1A (3) linear undulator
- ALS *11.0* *EPU*
- ALS 5.3.2 Bend Magnet

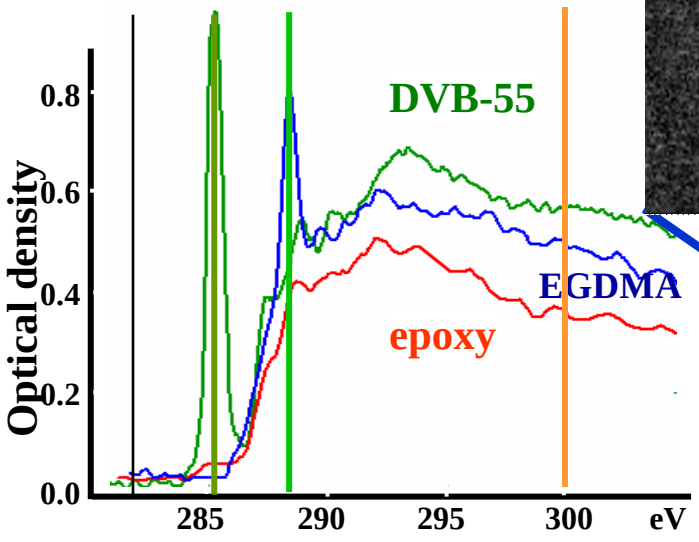
Image sequences *(OD format)*



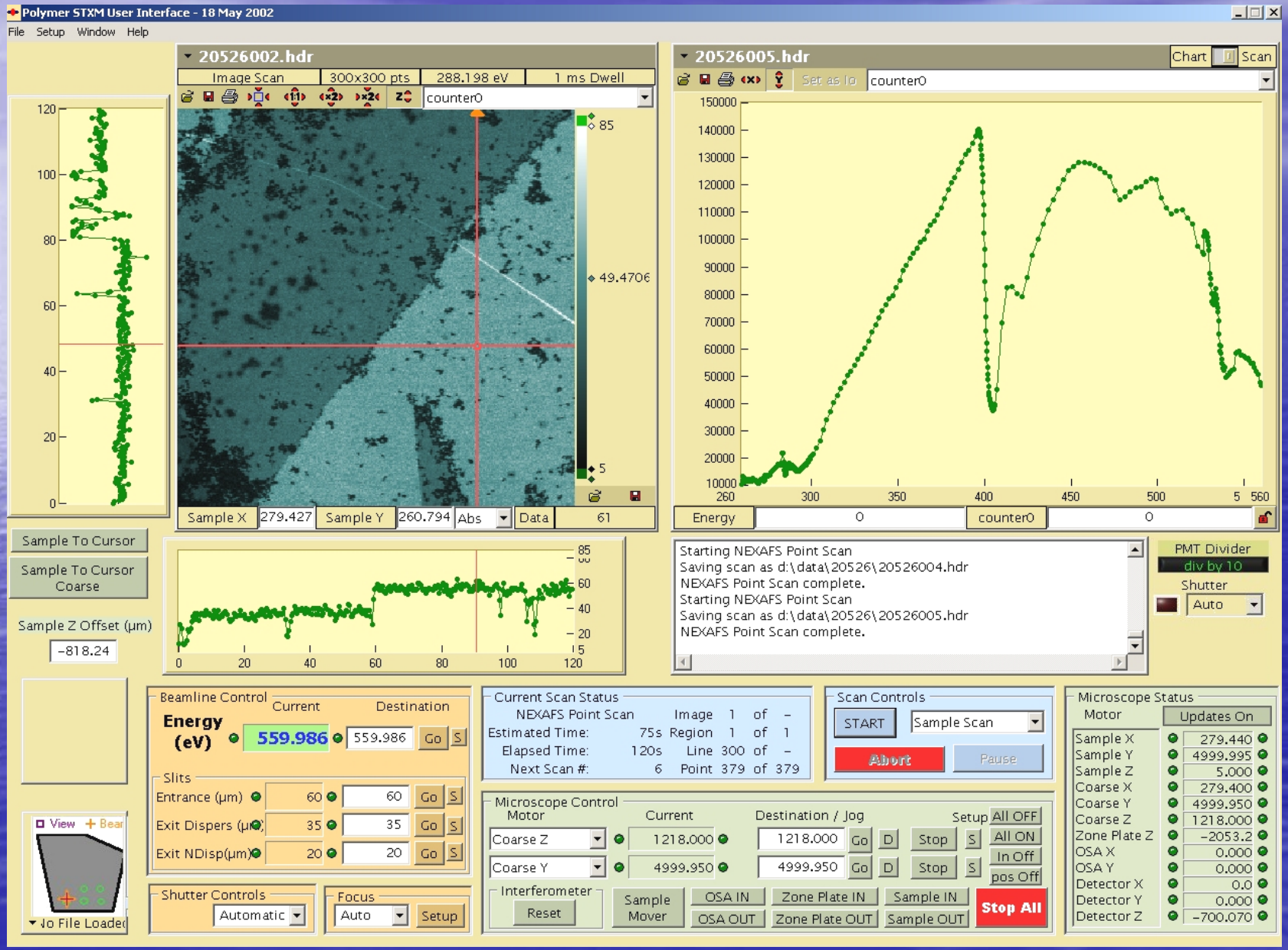
Images
transmitted I(x,y)

Spectra ***ln*(I/Io)**
{point, line, image}



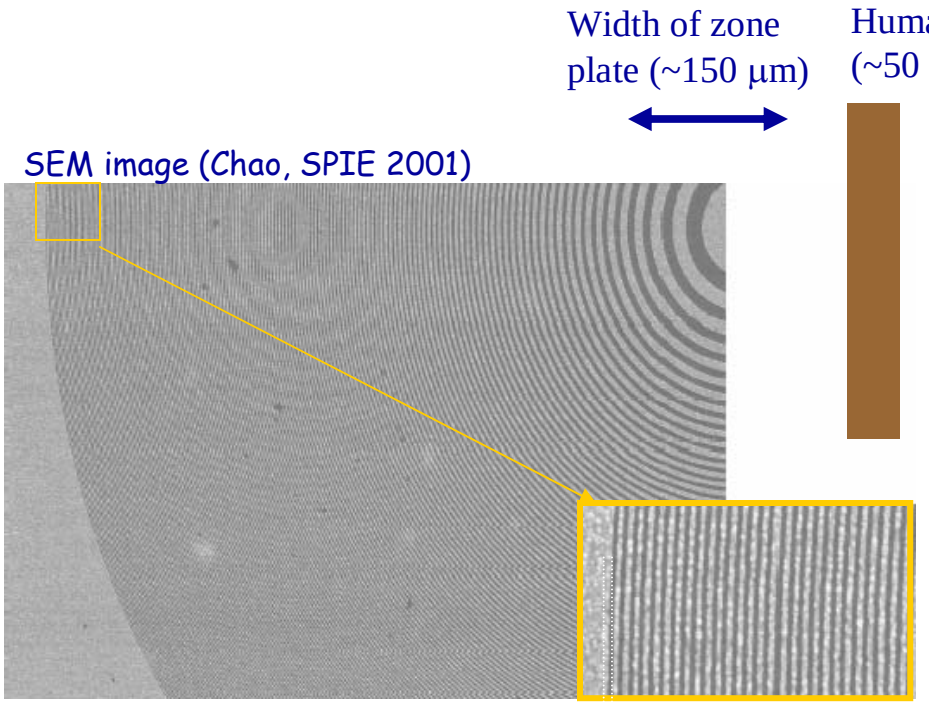


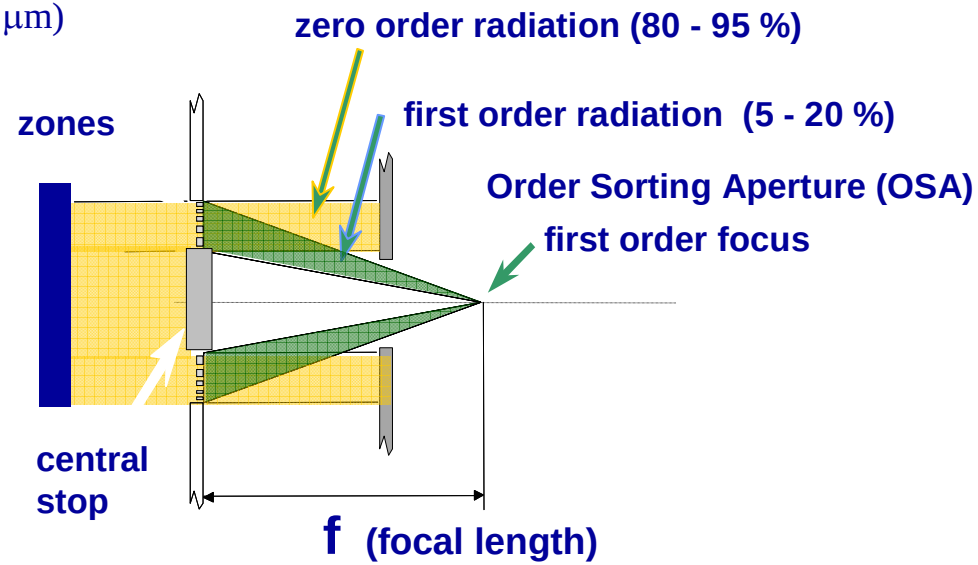
STXM_control - ALS (2), CLS, SLS



Fresnel zone plates: diffractive focusing

A.G. Michette, Optical Systems for soft X-rays, Plenum Press, 1986





$$f = D \cdot \delta r_N / \lambda$$

0.9 -1.2 mm in C 1s region

Typical Values (for current ZP in stxm532)

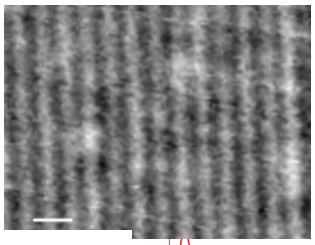
- λ **(photon wavelength)** 1 to 6 nanometers (~1240/**E**)
- **D (ZP diameter)** = 155 microns
- δr_N **(outer zone width)** = 35 nanometers
- **Number of zones** ~ 1000
- **Central stop diameter** = 80 microns
- **OSA diameter** = 55 microns

Spatial resolution (diffraction limited)

$$\Delta r = 1.22 \cdot \delta r_N$$

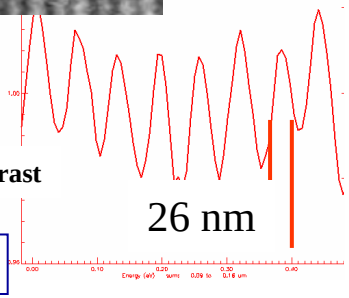
5.3.2 STXM Performance

- Diffraction limited spatial resolution (40 nm)
- 50 meV spectral resolution
- 50 nm CHEMICAL resolution via interferometry



Slits:
E/XD/XND
150/25/**25** μm

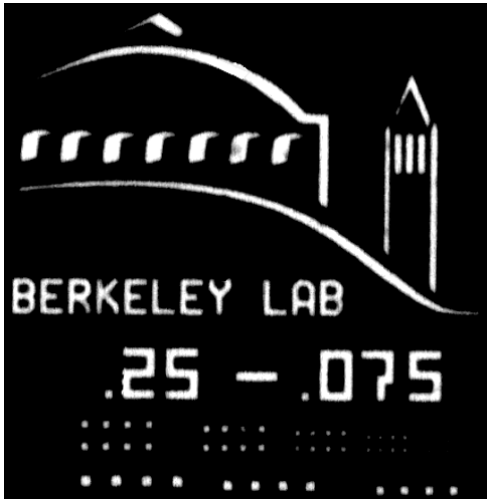
100 nm

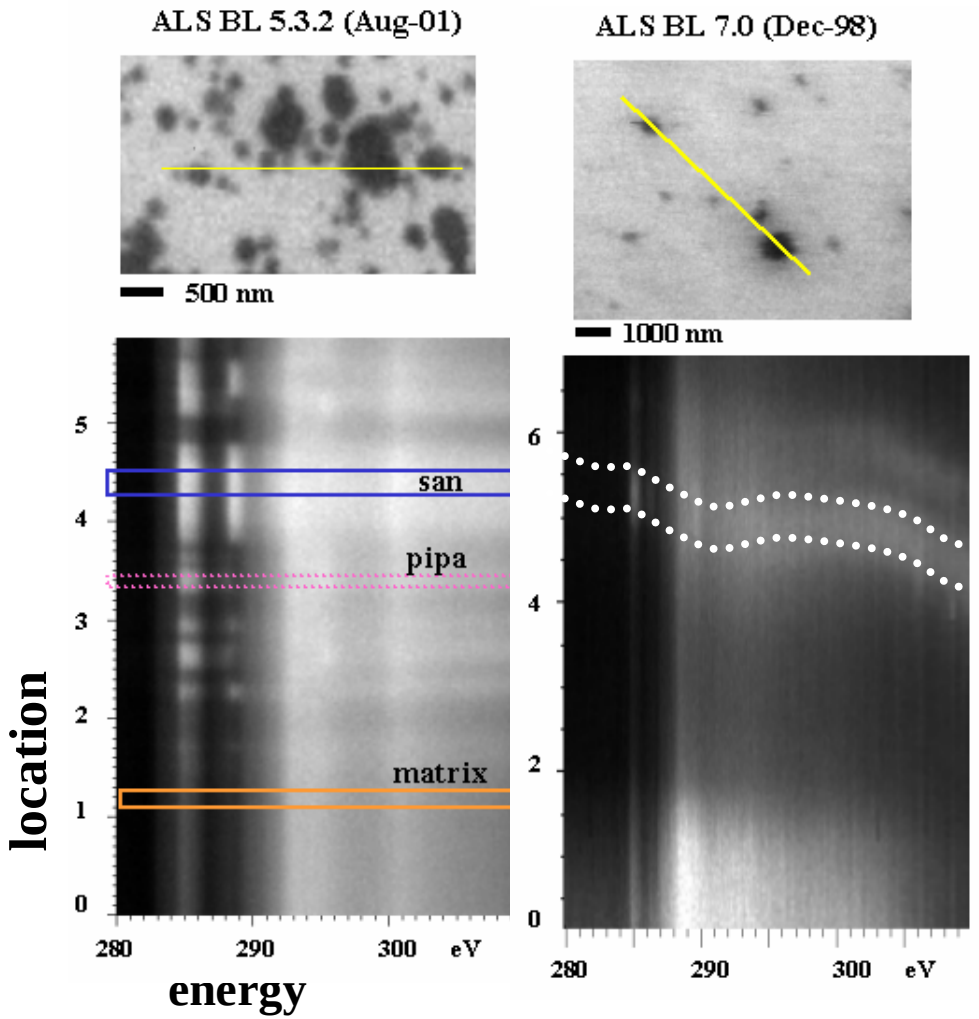


~10% contrast

26 nm

Nov 2002





Advanced Light Source

Tony Warwick
Mike Kirschner
Keith Franck

NC STATE UNIVERSITY

David Kilcoyne
Harald Ade (NCSU)

McMaster University

Tolek Tyliszczak
Adam Hitchcock
Peter Hitchcock

STXM-11: state-of-art performance

December 2003 - BREAKTHROUGH in ZP technology !

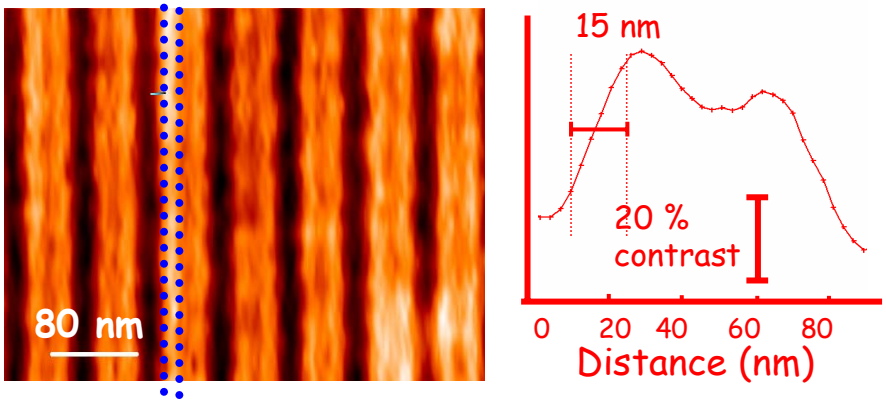
25 nm diffraction limited zone plates

Recent advances in CXRO zone plate fabrication has resulted in new STXM zone pates with significant improvements in

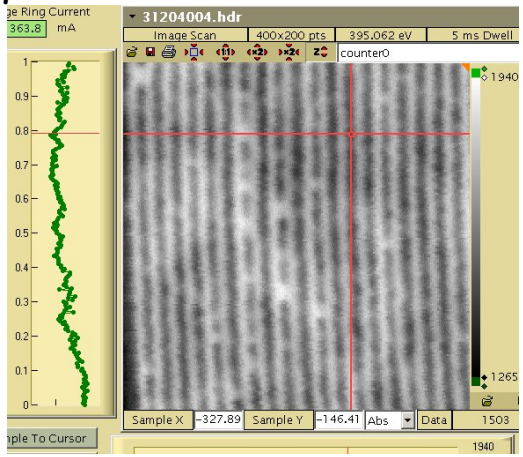
- spatial resolution
  - due to narrower outer most zones (**25 nm** instead of 35 nm)
- performance at high photon energy
  - due to higher aspect ratio (**7:1** instead of 3:1)

The performance of the interferometrically controlled STXM - in particular its thermal and temporal stability, as well as precision of tracking over variable photon energy - has been found sufficient to take advantage of the improved zone plate performance.

25 nm 1:1 lines as test object



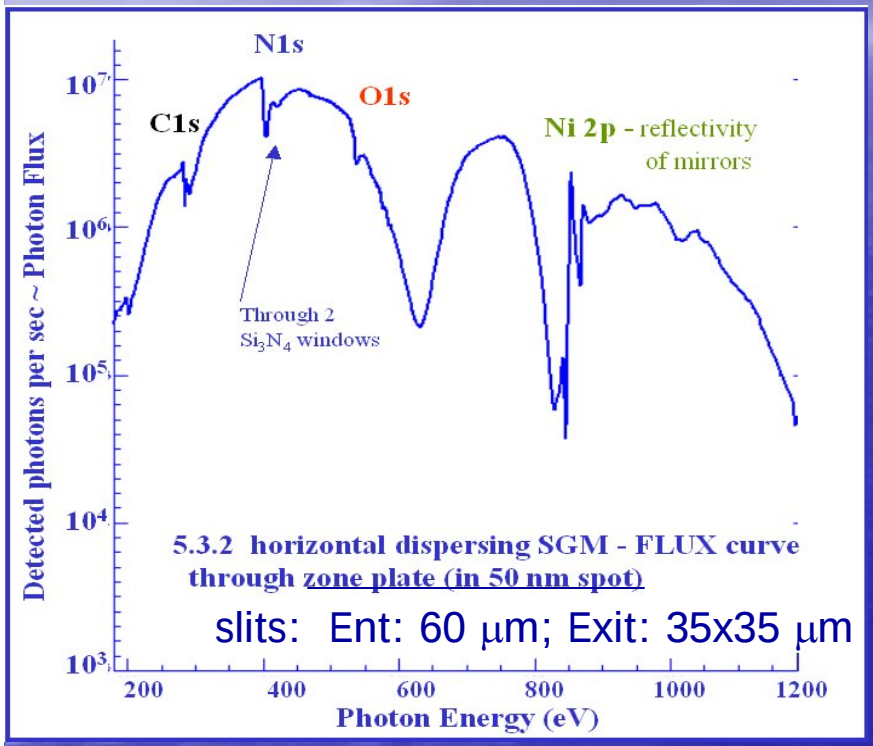
25 nm zone plate as test



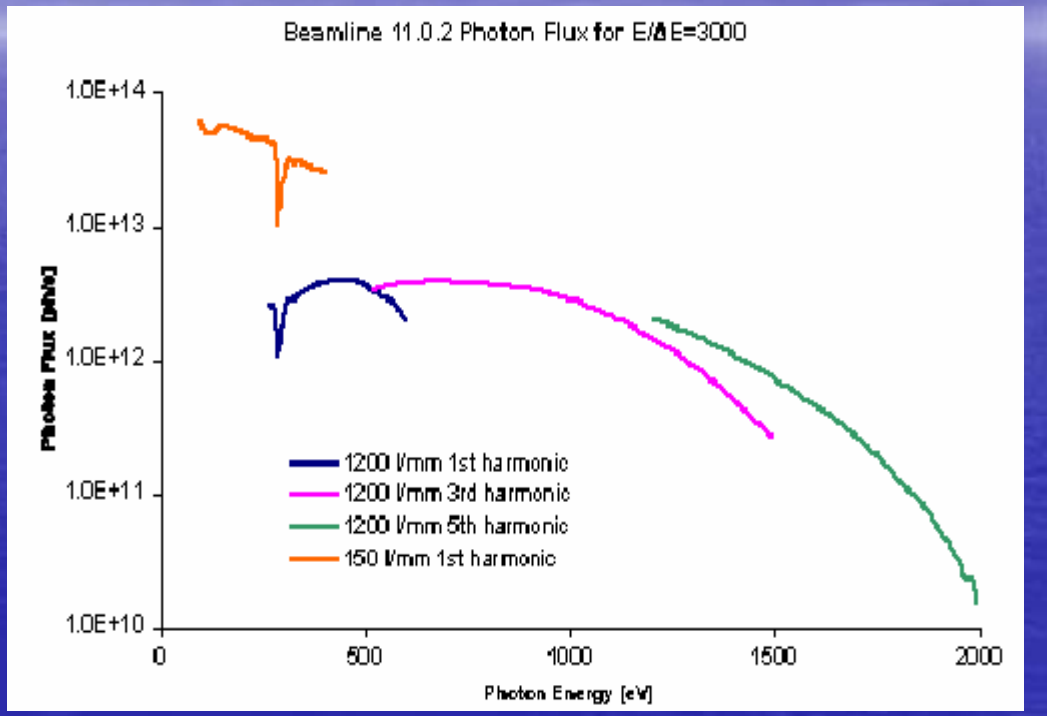
STXM532 - can mount 25 nm ZPs
- usually 35 nm ZPs (intensity)

ALS STXMs: Energy range, flux

BM STXM 5.3.2



Undulator STXM 11.0.2



with 90/60/60 slits it is easy to get **> 10^8 ph/s in ~60 nm spot on sample at 390 eV**

exit slits are typically 5-30 μm **> 10^9 ph/s ~40 nm spot on sample at 390 eV**

Spectromicroscopy at the CLS

Insertion device: Elliptically Polarized Undulator (EPU)

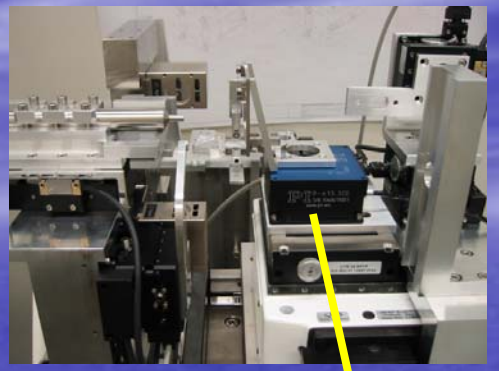
Monochromator: Plane Grating, no entrance slit (modified SX-700)

Energy range: 250 - 1900 eV

Resolving power: 5000

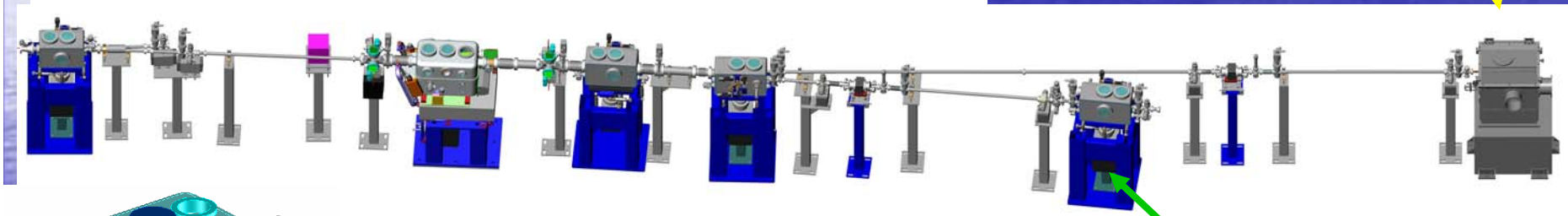
Flux: **PEEM**: 10^{11} - 10^{12} photon/s in 20 micron spot

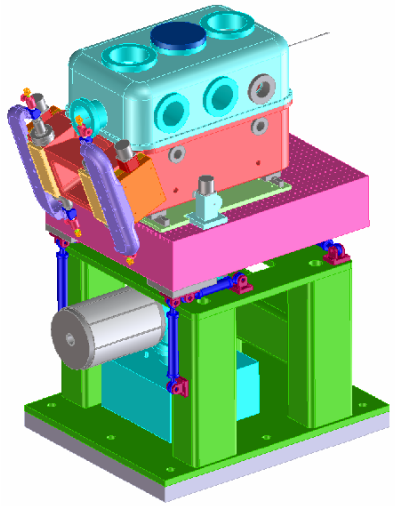
STXM: 10^{8} photon/s in 50 nm spot



STXM: modified 5.3.2 design

ALS assistance: monochromator & mirror holders similar to BL 11.0.1





X-PEEM (*Stephen Urquhart*)
- operated Apr02-Mar05 at SRC (Madison, WI)
- now at CLS
- to run on SGM summer 2005

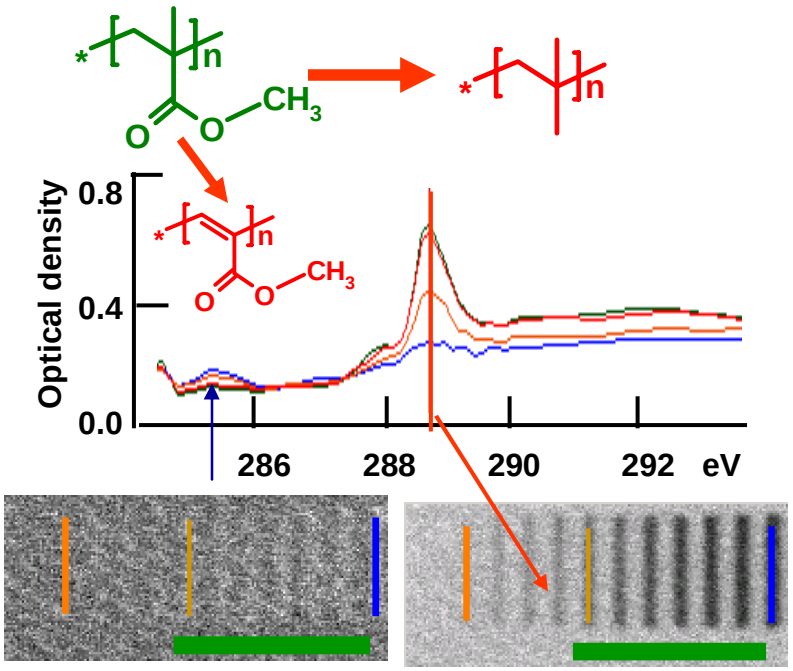
see talk and poster by Kaznatcheev (MSC)

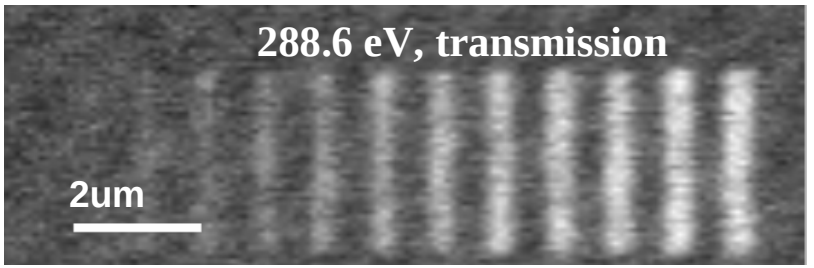
Radiation damage in STXM: PMMA

*** 4 um** line pairs; spaced at 1 um

** Exposed in linescan mode at 300 eV;
~2 MHz in detector

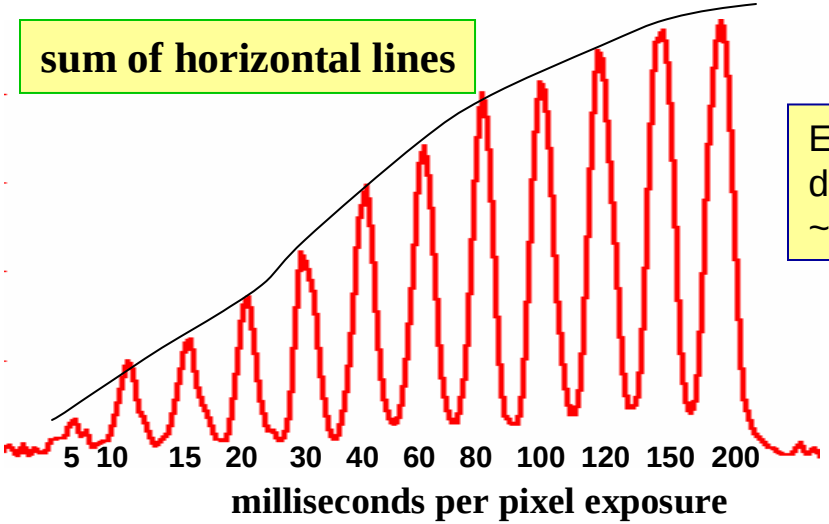
PMMA = polymethylmethacrylate





stxm 5.3.2

sum of horizontal lines



Exposure to damage 1/e ~50 ms !!!

Damage control measures in STXM 5.3.2

a) Hardware

- 1 msec in-vacuum piezo shutter
- Closed between successive scan lines
- fast scanning: 0.2 - 1.0 msec/pixel dwell

b) Acquisition strategy

- Defocused beam (if suitable) – point, line, image modes
- Multi-region acquisition
- Short stacks / SVD

STXM is optimal for quantitative chemical analysis of soft matter

✓ **High Spatial Resolution**

Zone plate properties determine resolution. Typically ~30-40 nm

✓ **High Spectral Resolution = high chemical resolution**

All instruments achieve ~ natural line width (0.1 eV in C 1s)

✓ **Quantitative compositional analysis**

Beer's Law response – Absorbance (OD) proportional to concentration in column / pixel

✓ **Adaptable to many environments**

Fully solvated systems – water window
Magnetic fields
Vacuum – surface analysis

✓ **Significantly lower radiation damage** than TEM-EELS . . .

Quantitative comparison indicates 10^2 – 10^3 advantage on basis of information / unit damage

PET – Rightor et al J. Phys. Chem. B 101 (**1997**) 1950

see poster by Wang (MSC)

. . . and TXM *(In STXM, the inefficient Zone Plate optic is BEFORE the sample)*

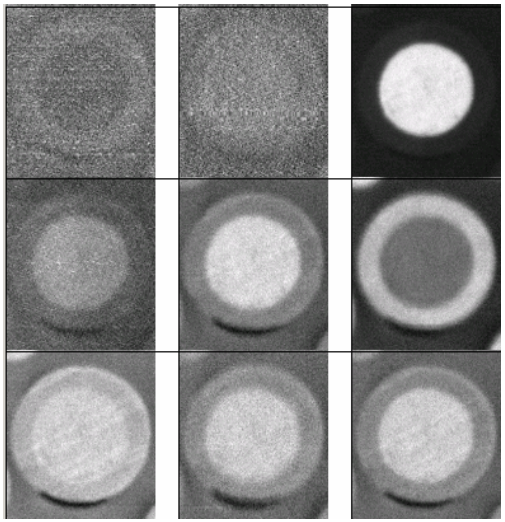
Quantitative Chemical Mapping

From pixel-by-pixel fits to reference spectra

Implemented in aXis2000

Core shell particles: (with Stöver)
see *Macromolecules* 34 (**2001**) 4424

1. Record image sequence (stack)

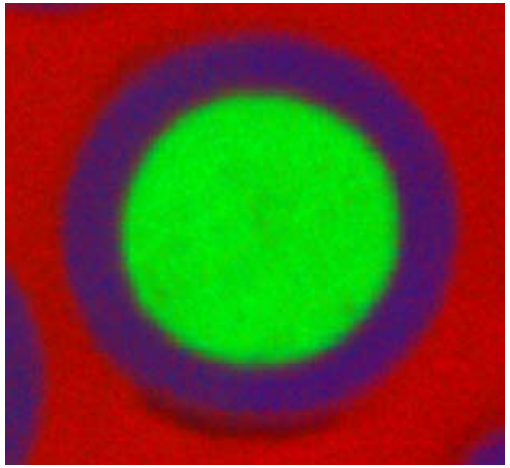


3. Generate component maps

$$OD(j,k) = \sum_i a_i(j,k) * (reference)_i$$

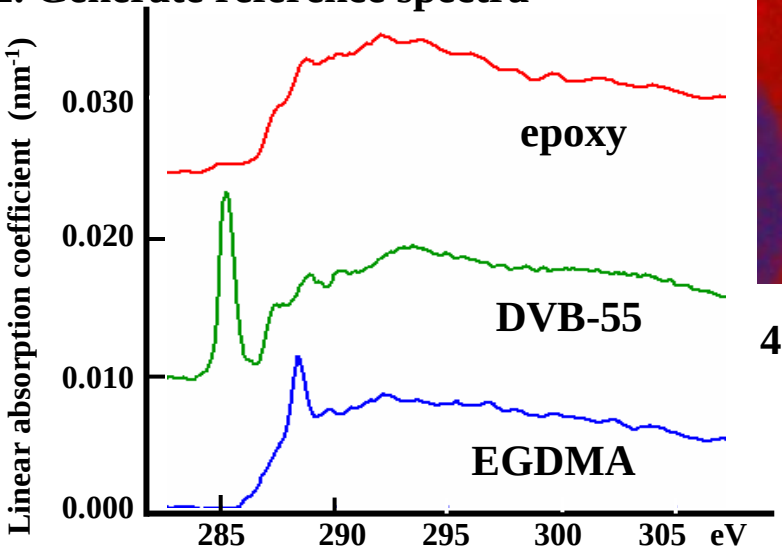
with a_i (j,k) = *THICKNESS* **(nm) at (jk)**

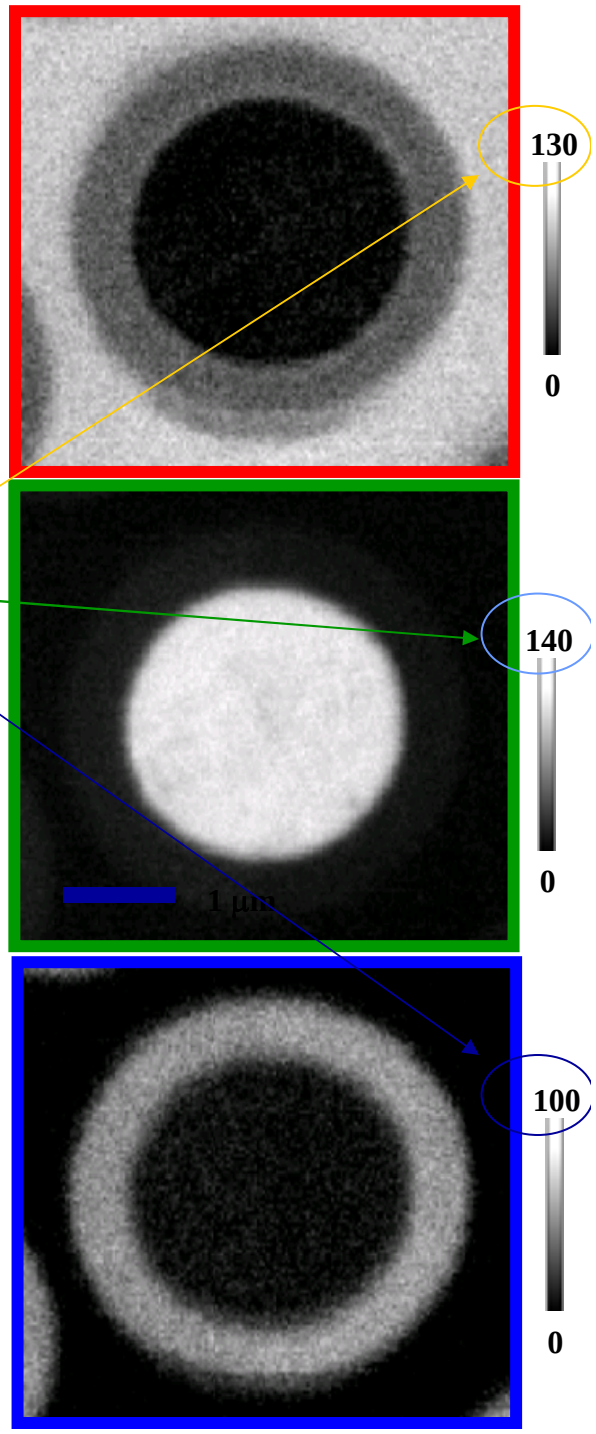
when reference spectra are absolute (nm^{-1})



4. Generate RGB-composite component "image"

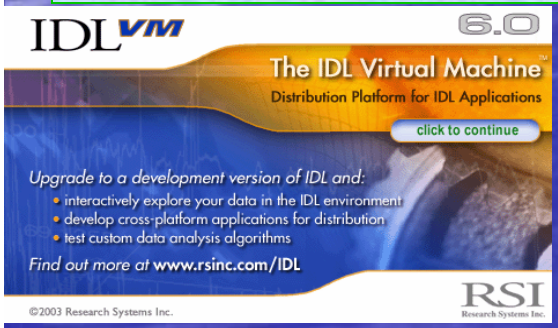
2. Generate reference spectra



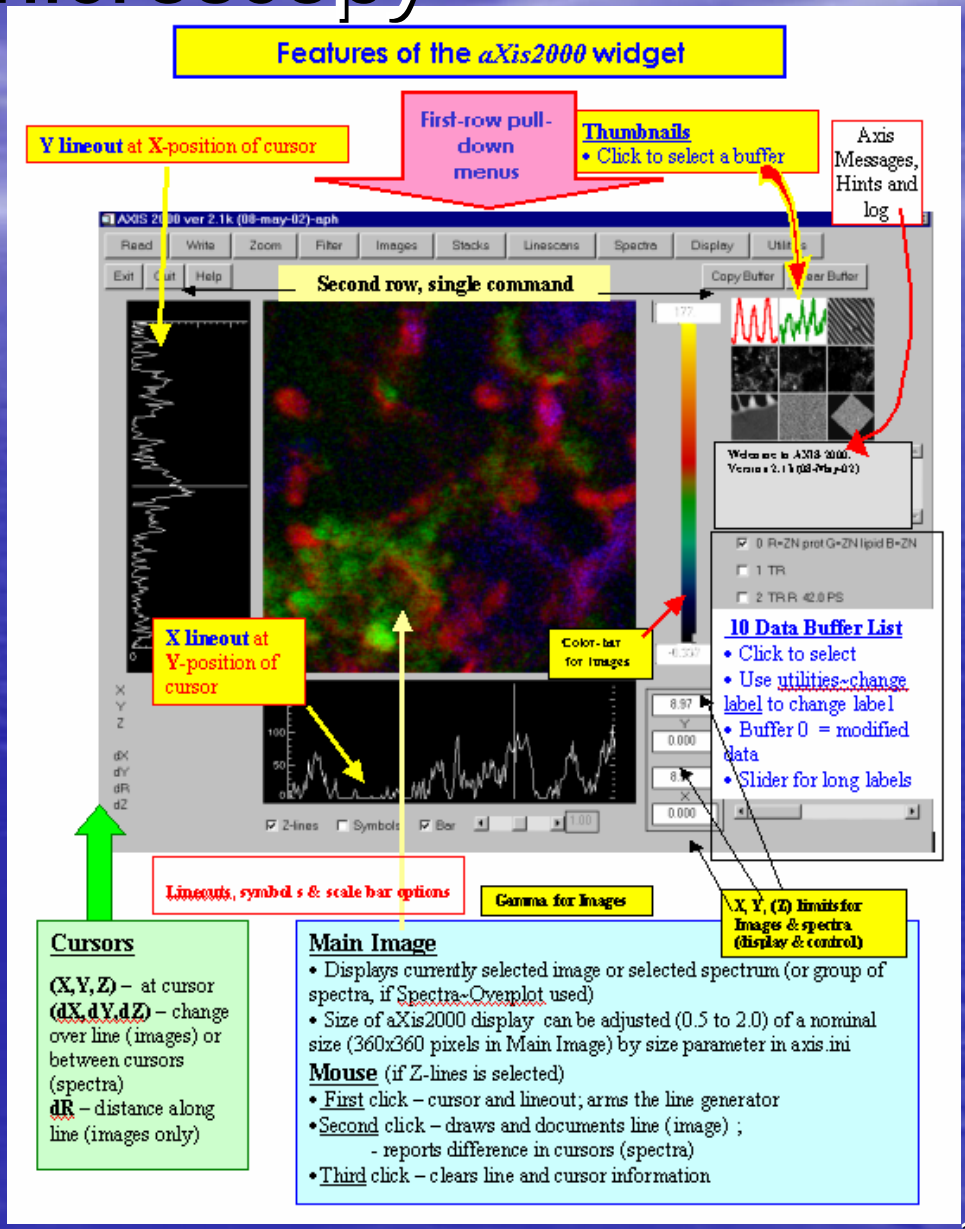


Analysis software for soft X-ray spectromicroscopy

(http:unicron.mcmaster.ca/aXis2000.html)



aXis2000 is free for non-commercial use



5.3.2 STXM can be viewed and even run remotely (with training & permission) over the net (***'Fedex' synchrotron microscopy)***

BREAK TIME !