X-ray Fluorescence Analysis

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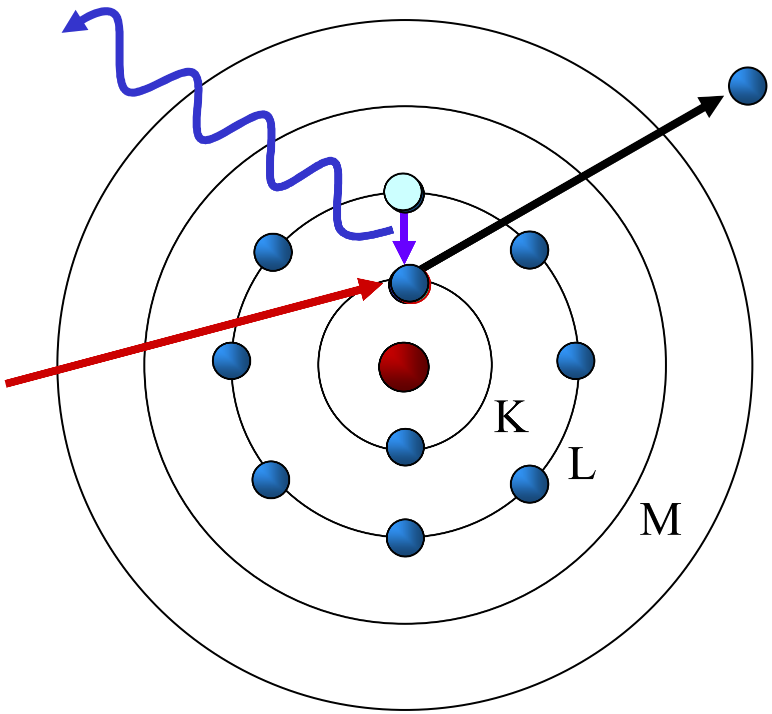
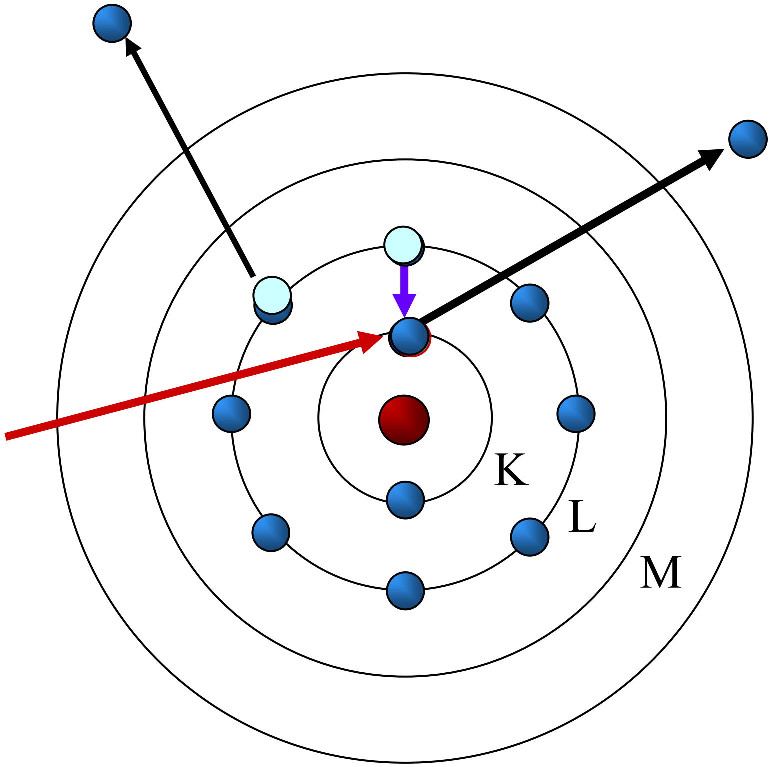
What happens by core hole creation?



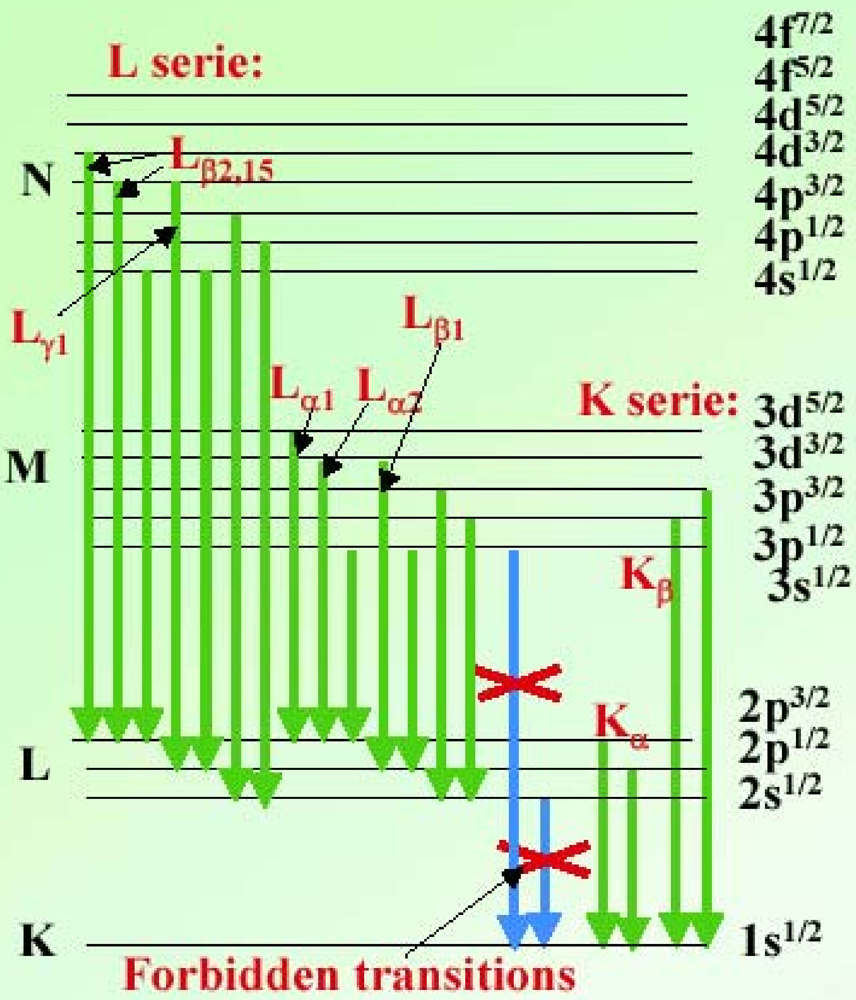
X-ray Fluorescence



Auger electron emission

How does an X-ray spectrum look like?

Diagramm lines



Electric-dipole selection rules

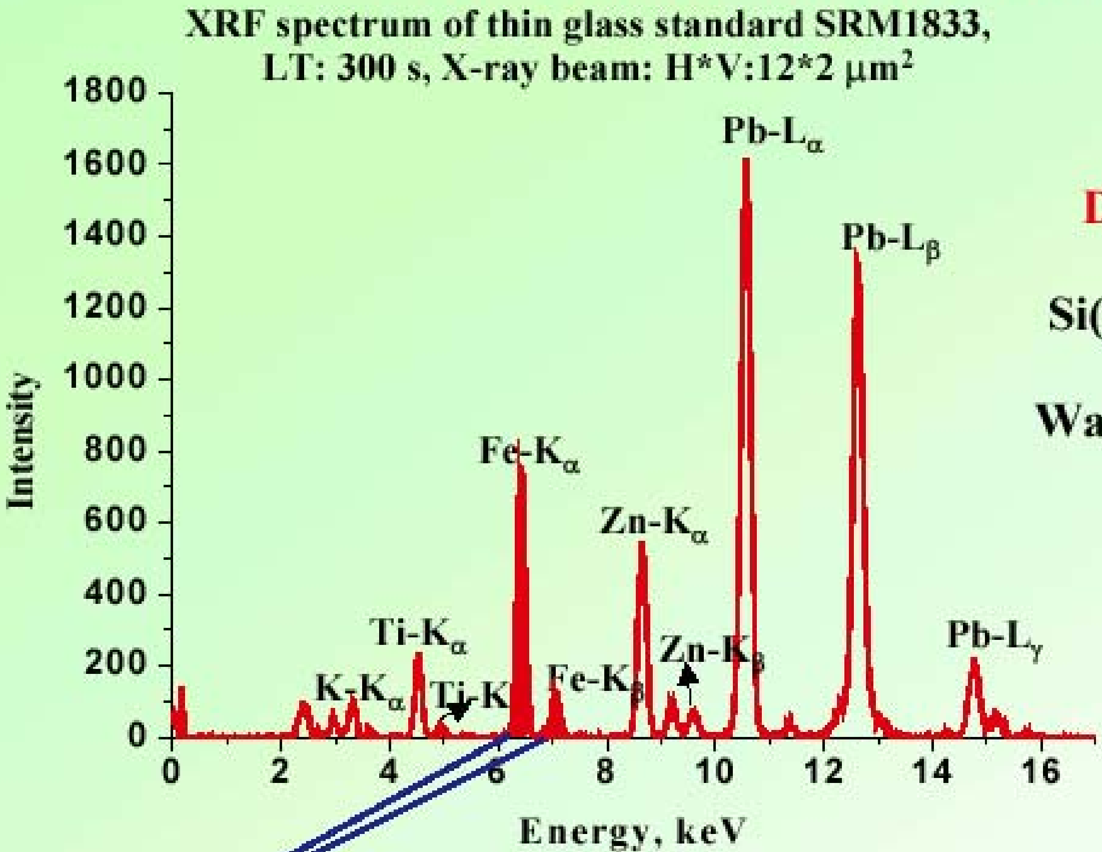
$\Delta l = \pm 1$

$\Delta j = 0, \pm 1$

First 4 elements, H, He, Li, Be have no characteristic X-ray diagramm lines

New transitions become possible with the filling up of the outer electron shells

How does an X-ray spectrum look like?



Detection of XRF spectra:

Si(Li) solid state spectrometer

Wave-length dispersive crystal spectrometer

Energies of the X-ray lines → **qualitative analyzis**

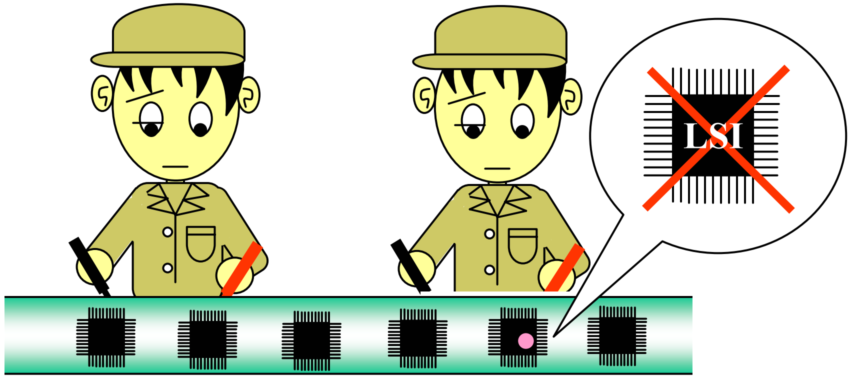
Intensity of a given X-ray line → **~number of a given atom in the excited volume, quantitative analysis**

How can we create core holes?

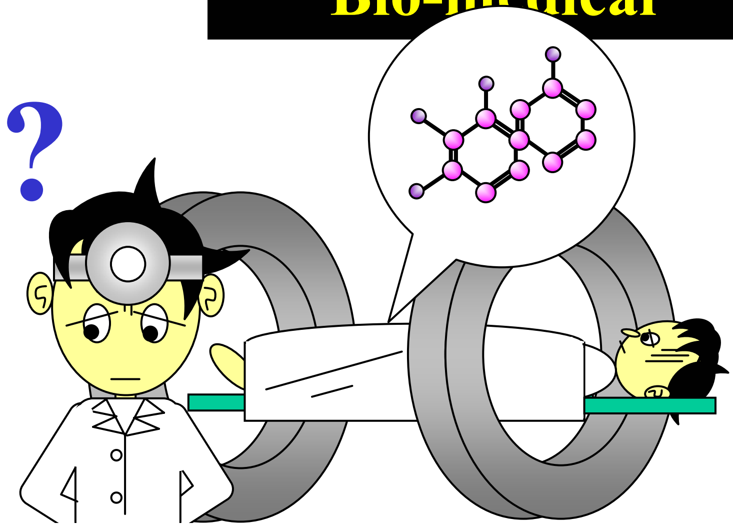
- X-rays, Electrons, Ions which have higher energy than the core electron ionization energies.
- Electrons and ions produces many peaks with multiple excitations. X-ray excitation is preferable.
- Now, X-ray fluorescence analysis by X-ray excitation is a standard technique for trace element alalysis.

How is the Trace Characterization important?

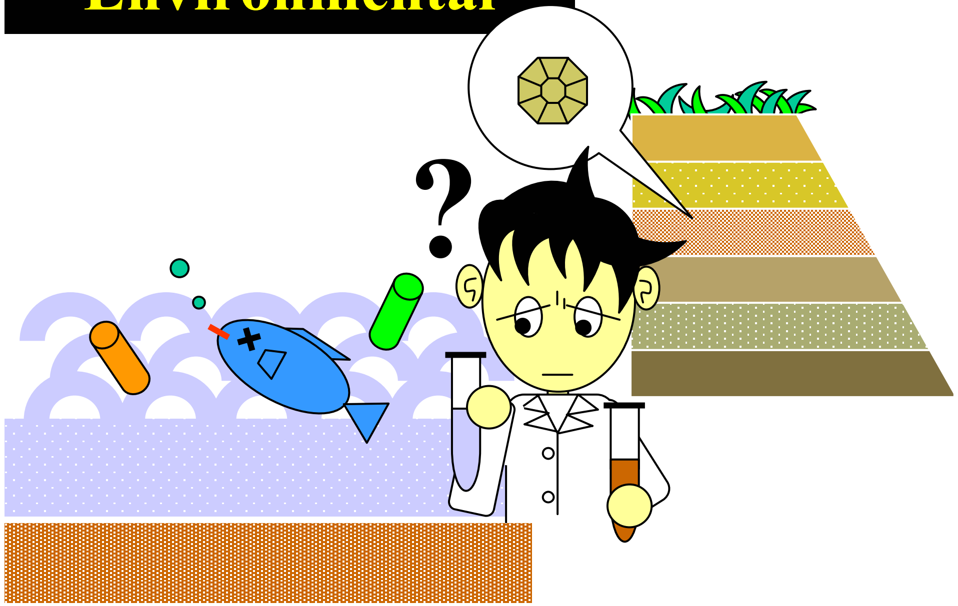
Industrial



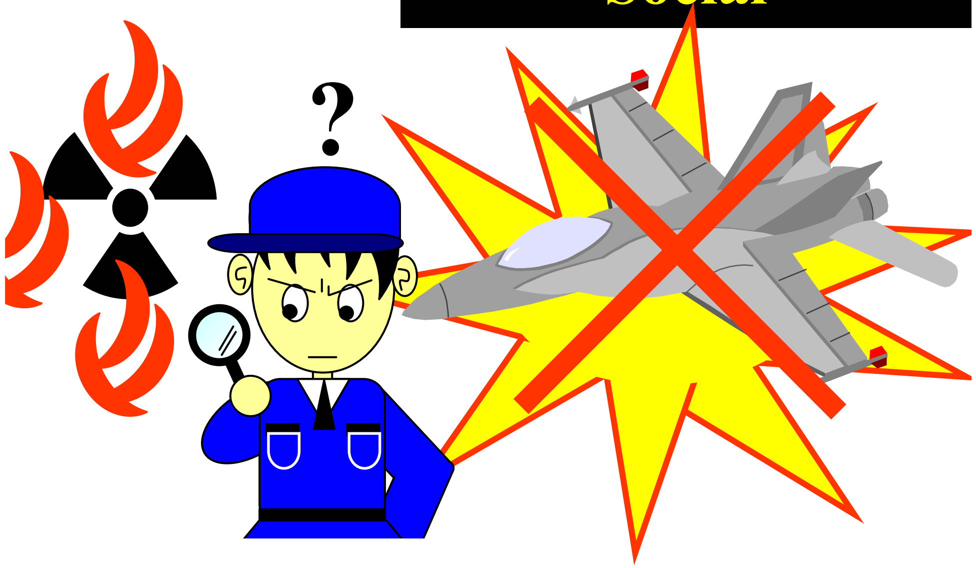
Bio-medical



Environmental



Social



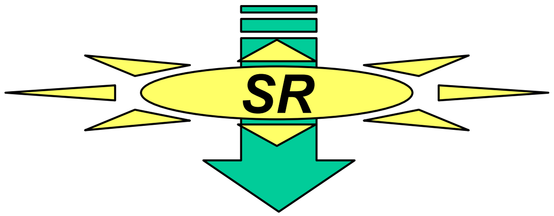
Why synchrotron radiation x-rays ?

- Higher intensity → higher sensitivity
- Energy tunability → Make the analysis easier, chemical state analysis
- Polarizablity → Reduce background
- Directionality → applicable to tiny sample
- → Spectromicroscopy, Imaging

Synchrotron Radiation excited X-ray fluorescence Analysis

Advantages of XRF elemental analysis

- Non-destructive
- multi-elemental analysis
- environmental condition
- high accuracy
- wide dynamic range



•High sensitivity

ng=>fg, ppm=>ppb

•Chemical state analysis

•Micro-beam analysis

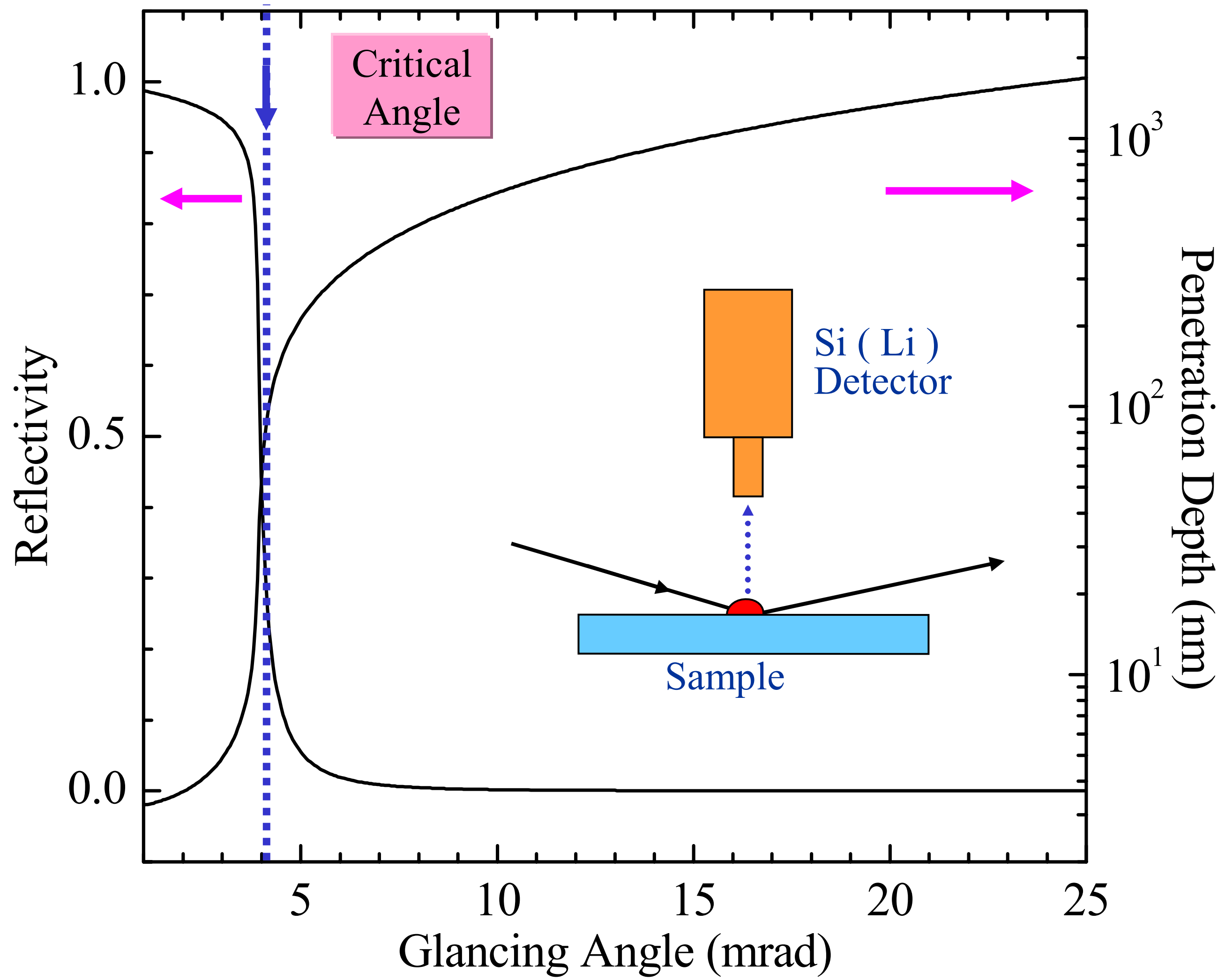
mm=> μm

•Total reflection analysis

10^{15}atoms/cm^2=>10^8atoms/cm^2

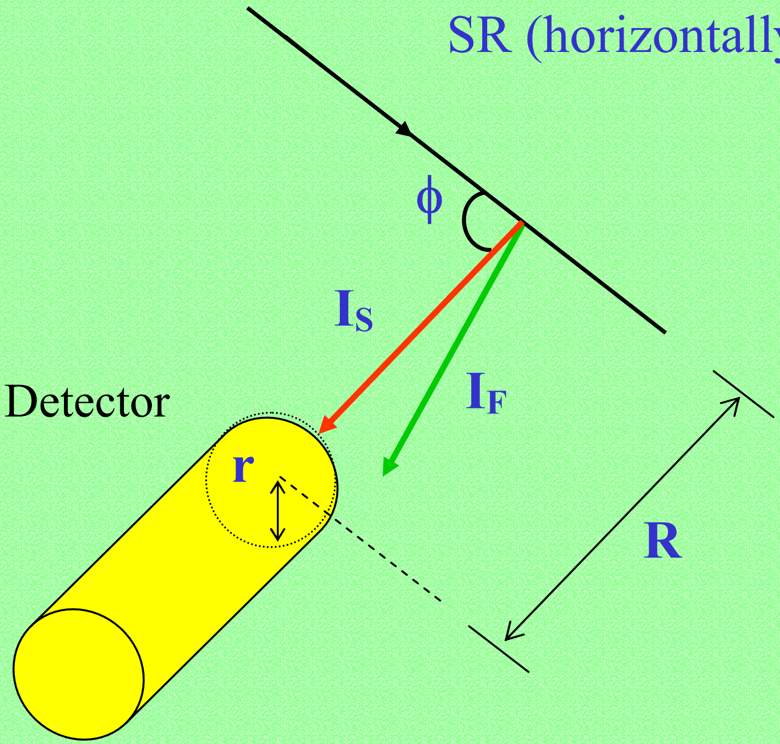
Total-refection X-Ray Fluorescence (TXRF)

Reduction of scattering background from the substrate(1)



Total-refection X-Ray Fluorescence (TXRF)

Reduction of scattering background from the substrate (2)



Fluorescent X-rays

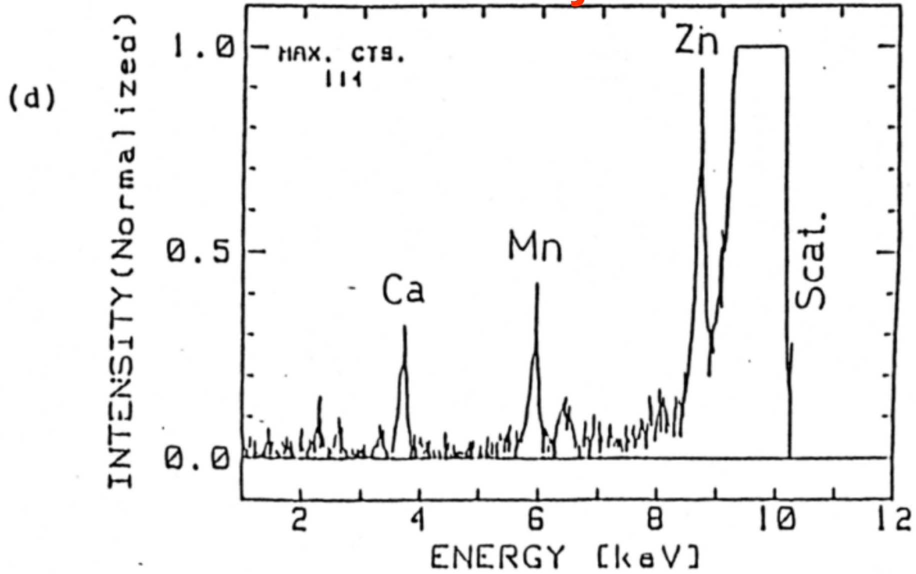
$$I_{fluo} \propto \left(\frac{r}{R}\right)^2$$

Scattered X-rays

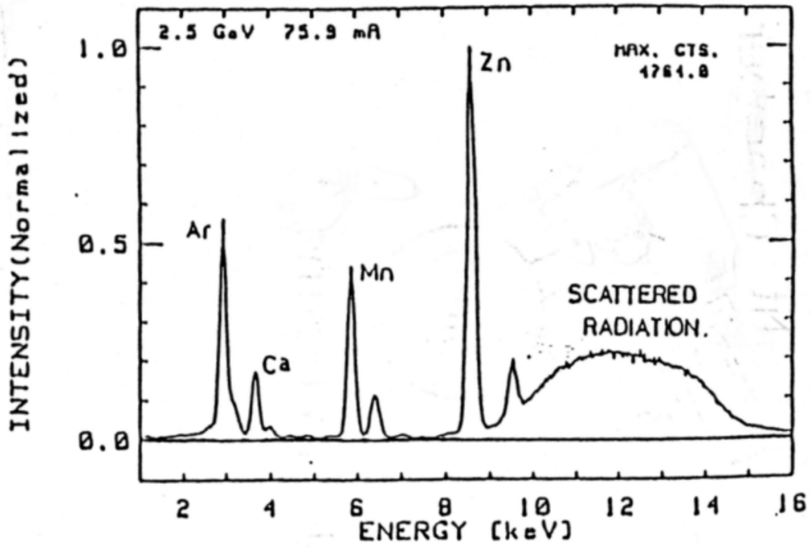
$$I_{scat} \propto 2\cos^2\phi\left(\frac{r}{R}\right)^2 + \sin^2\phi\left(\frac{r}{R}\right)^4$$

Comparison of S/N and S/B ratios

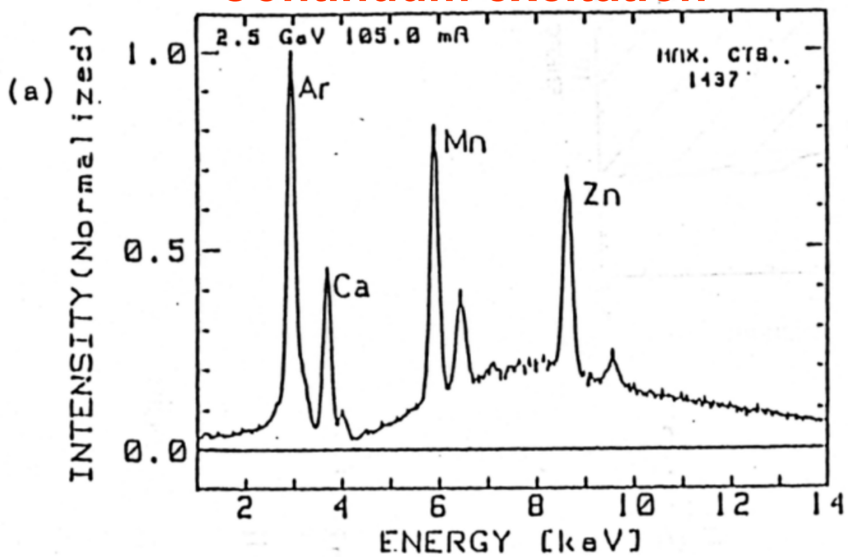
Laboratory source



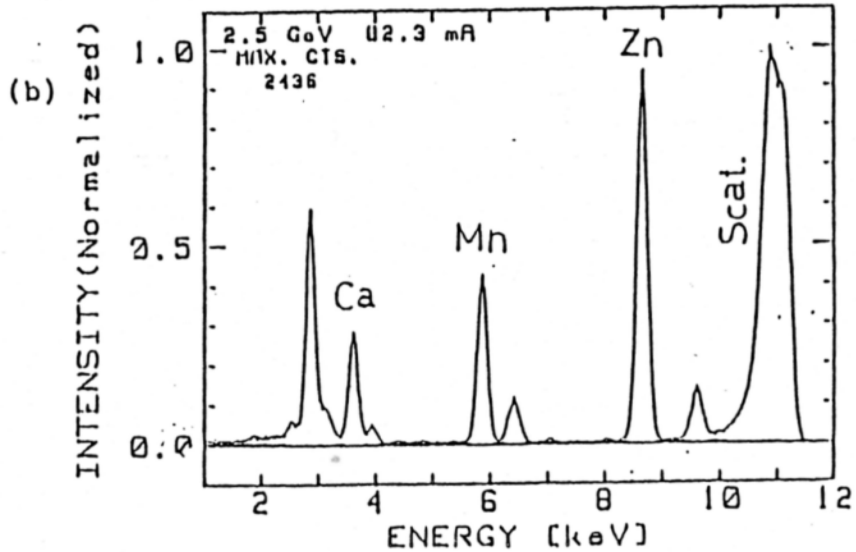
Refl./Trans. Mirrors



Continuum excitation



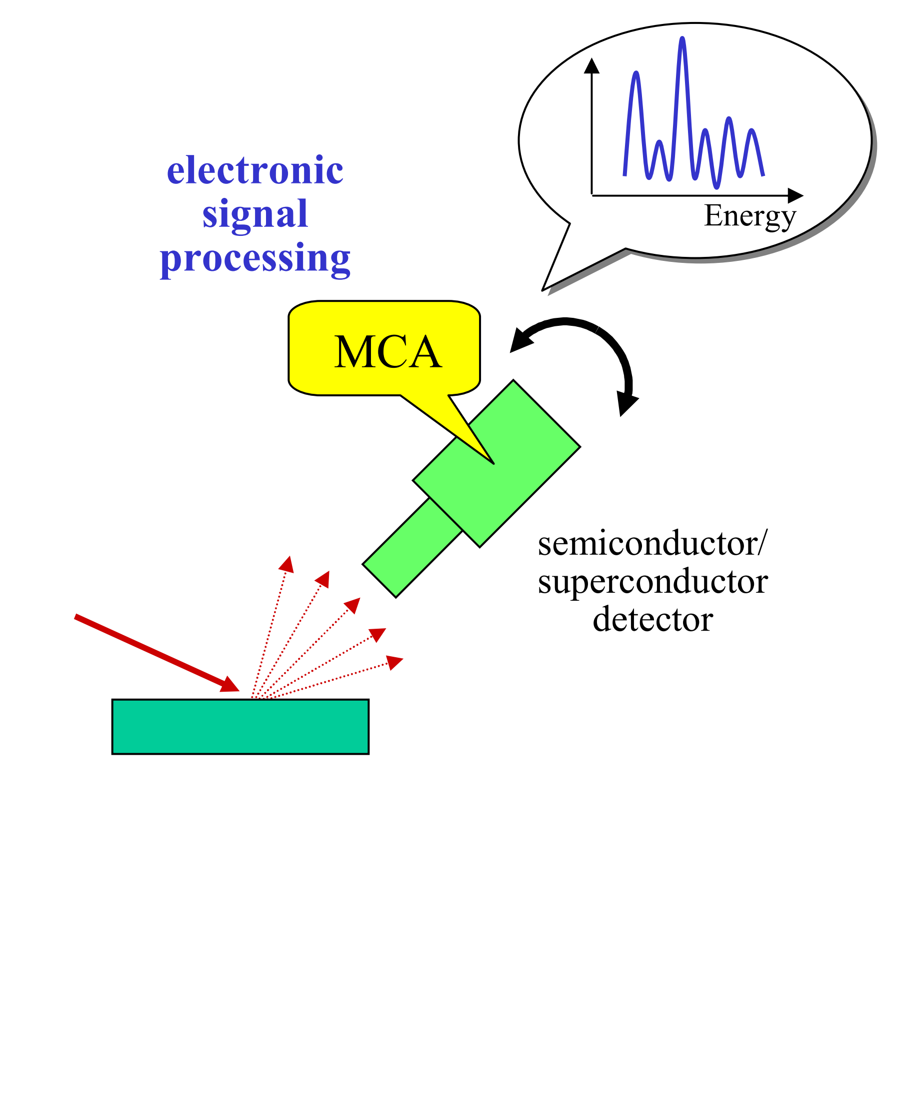
Monochromatic excitation



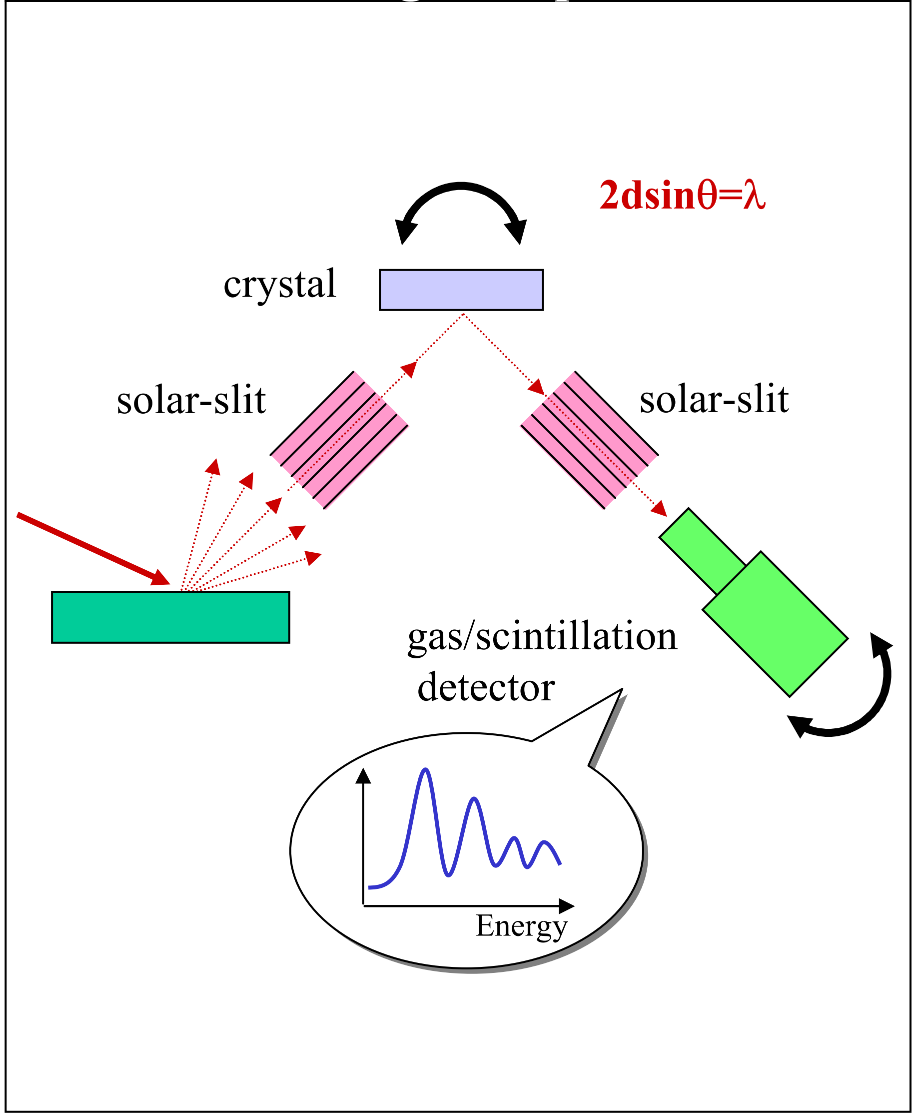
Sample: chelete resin beads

How to analyze X-Ray Fluorescence
Wavelength-dispersive vs. energy-dispersive

Energy-dispersive



Wavelength-dispersive



Chemical Characterization by X-ray Fluorescence Spectra

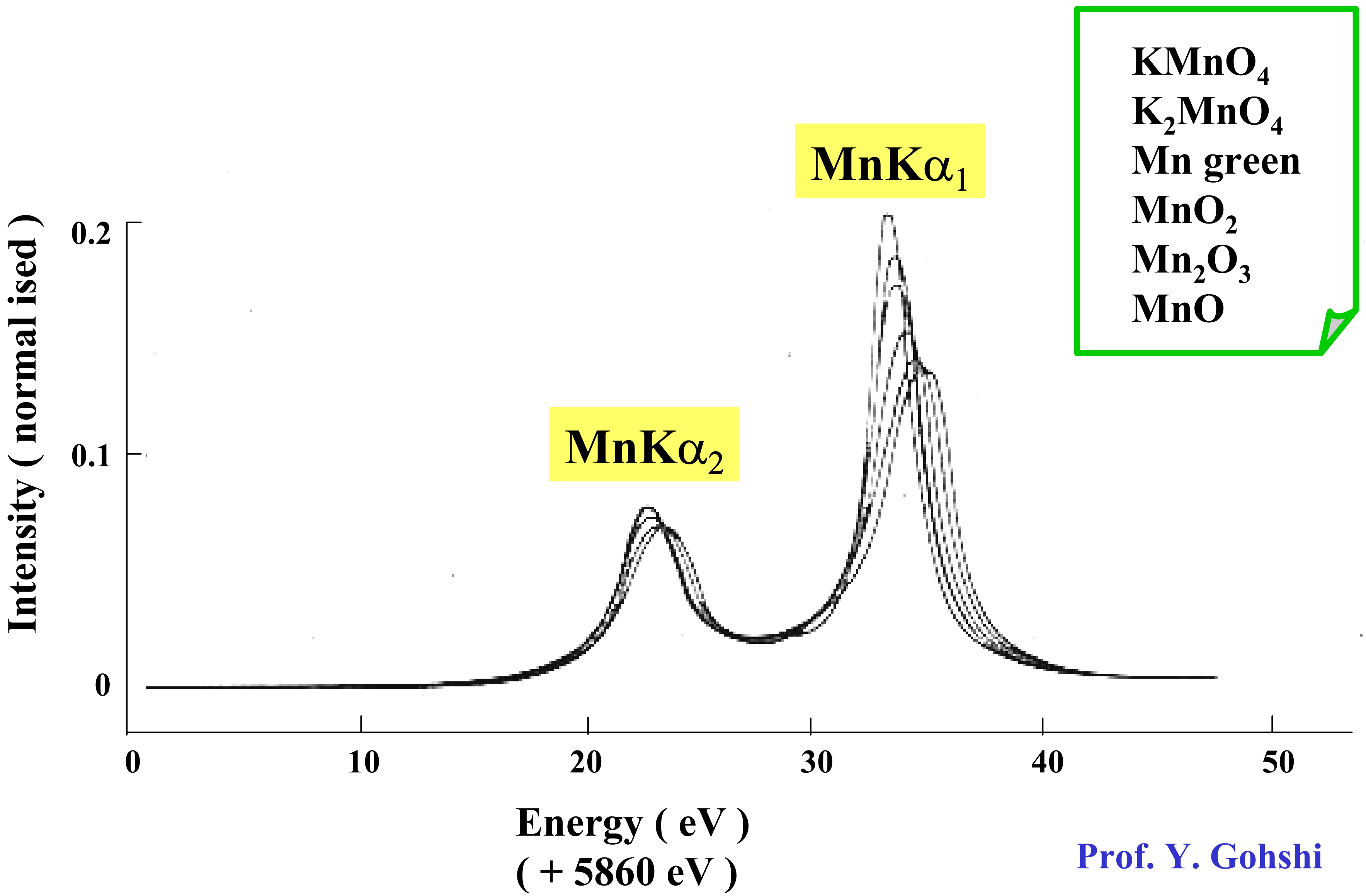
- Qualitative and quantitative analysis —— **Si (Li) detector**
- in terms of XRF

- Intensity changes —— **Single-crystal spectrometer**

- Chemical shifts
- Profile changes and other fine structures
- Satellite lines

} **Double-crystal spectrometer**

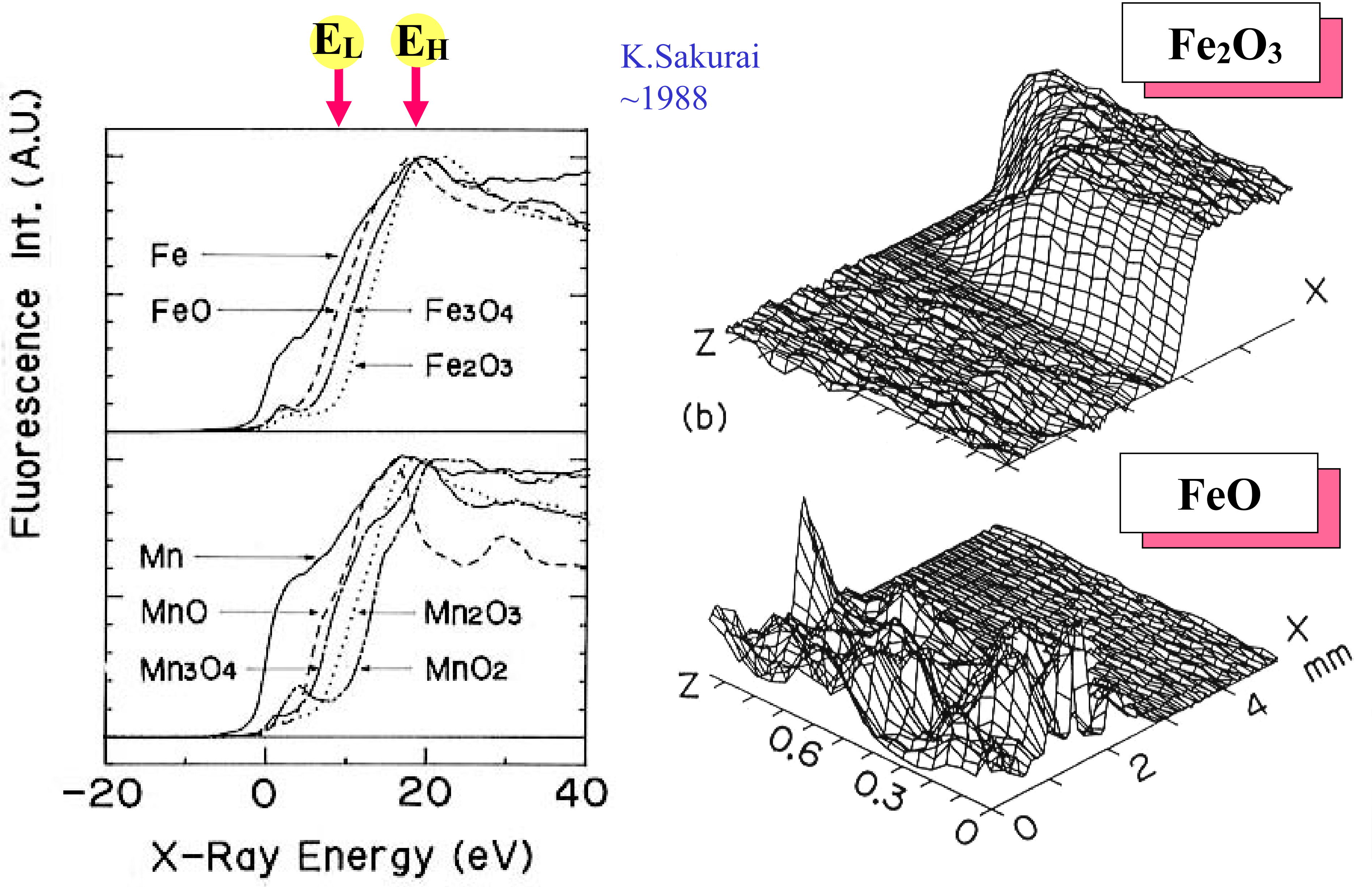
Chemical Shifts and Profile Changes
High resolution X-ray spectrometry



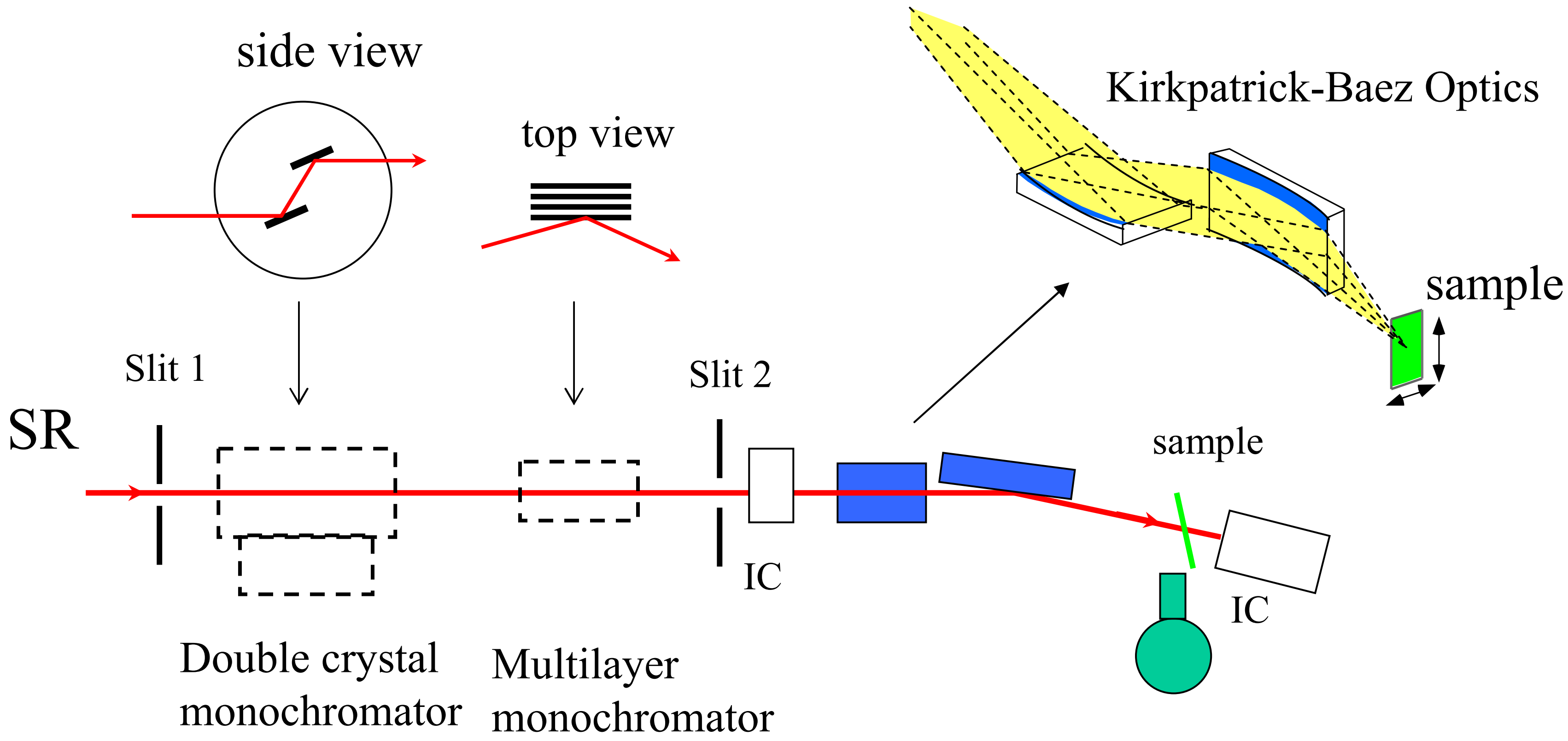
Prof. Y. Gohshi

Selectively Induced X-Ray Emission Using Edge Shifts

Use of tunable monochromatic synchrotron source



Synchrotron X-Ray Microbeam



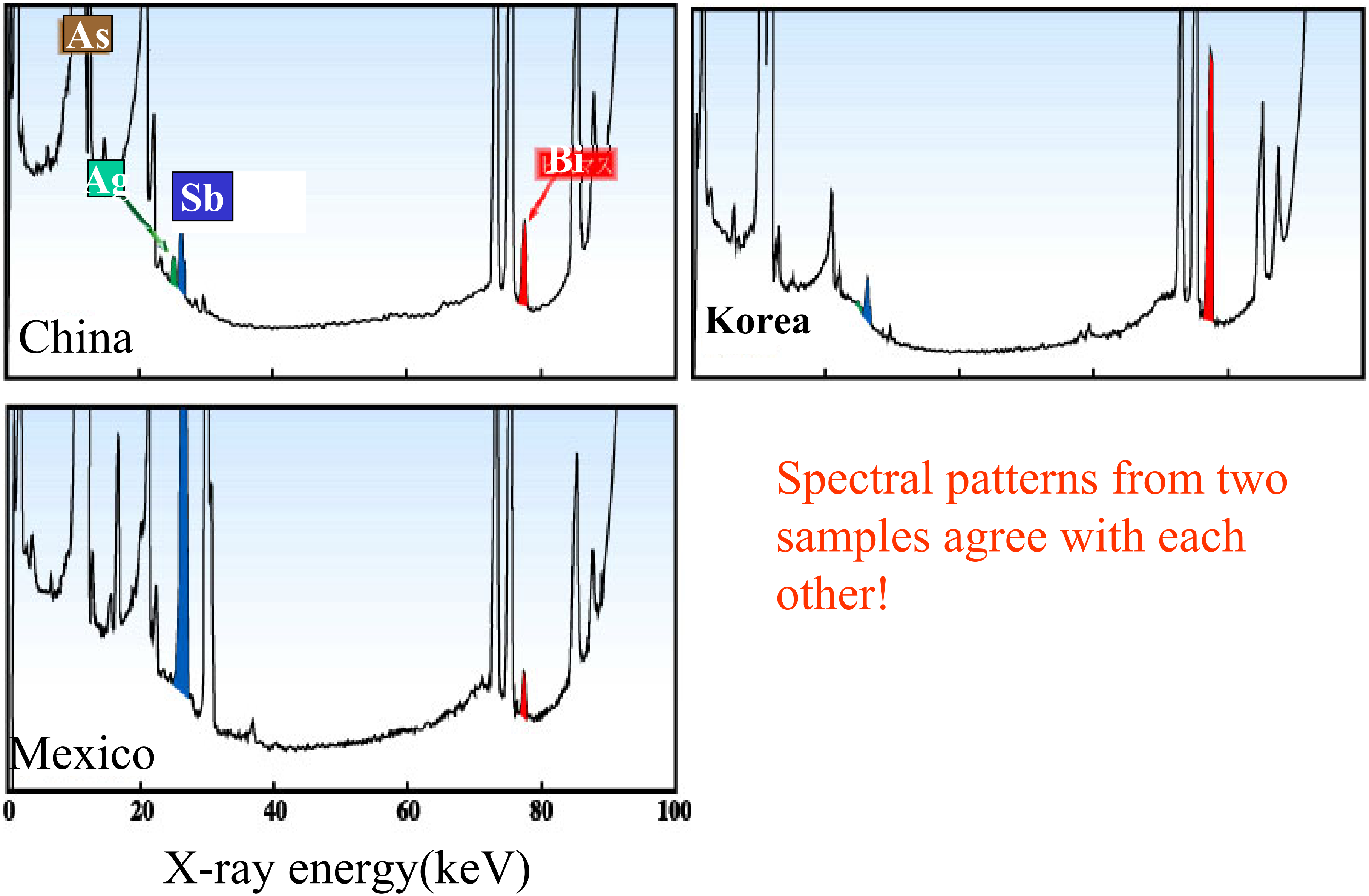
Beam size 5~6 μm^2 (1 μm min)

Photon Flux(Max) 10^{10} (Multilayer) 10^8 (DXM)

Application to criminology

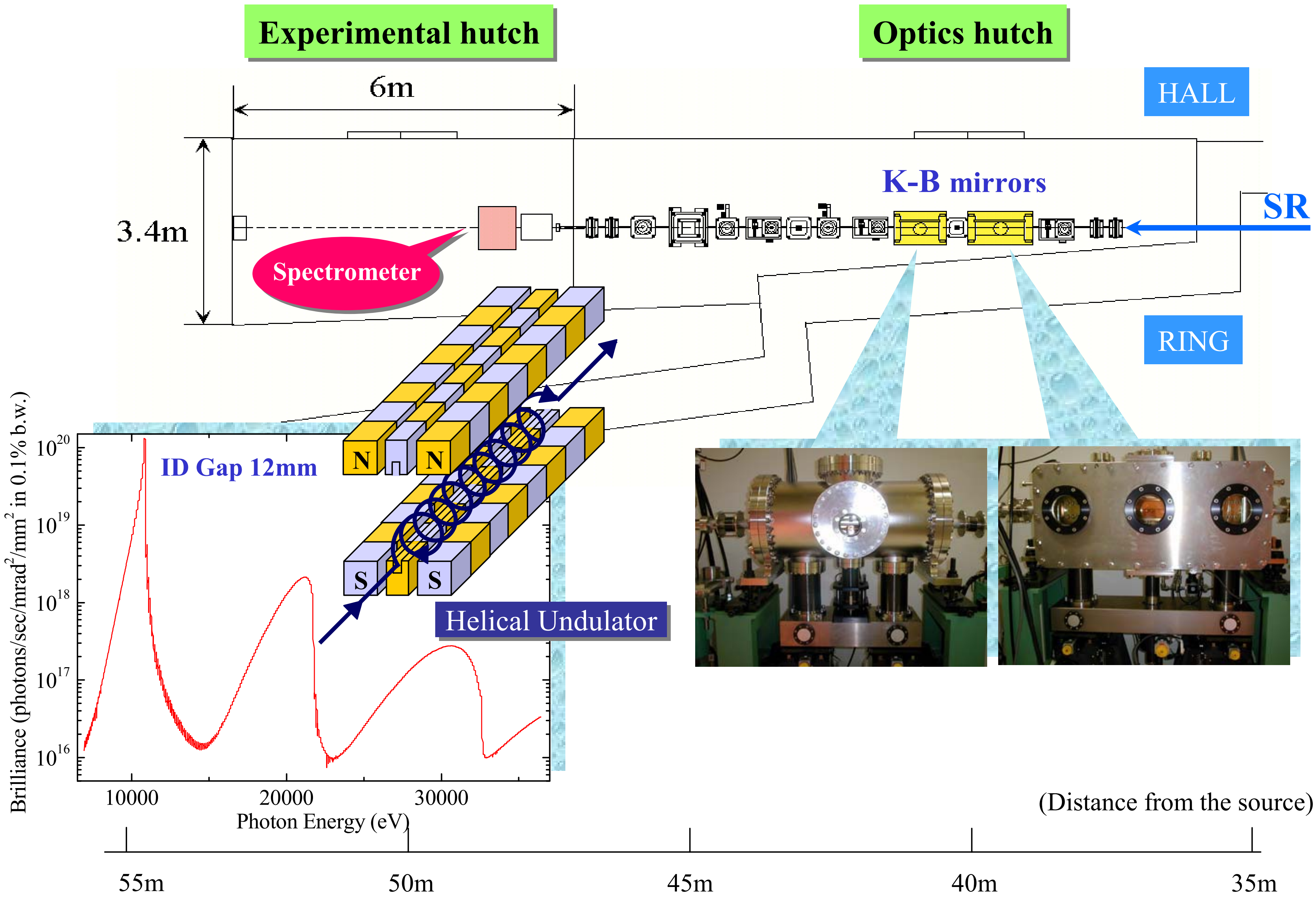
- A serious case of murder happened in a small town in Japan in 1999.
- White arsenic(arsenic oxide) was mixed in curry and 5 kids died of arsenic poisoning.
- No wittness and no confession, only presumptive evidence
- XFS technique works effectively.

XFS of white arsenic produced in various countries



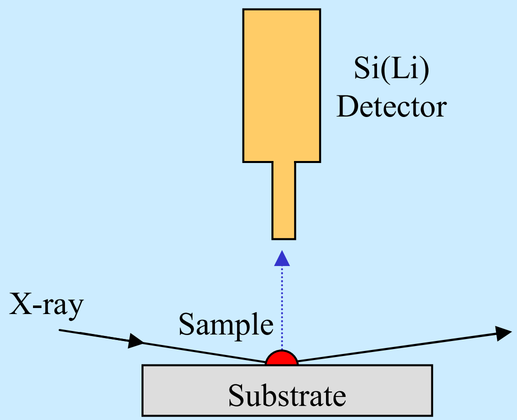
Spectral patterns from two samples agree with each other!

Plan View of Beamline 40XU at SPring-8



From Energy-dispersive to Wavelength-dispersive Spectrometer
To further upgrade signal to background ratio

Energy-dispersive TXRF



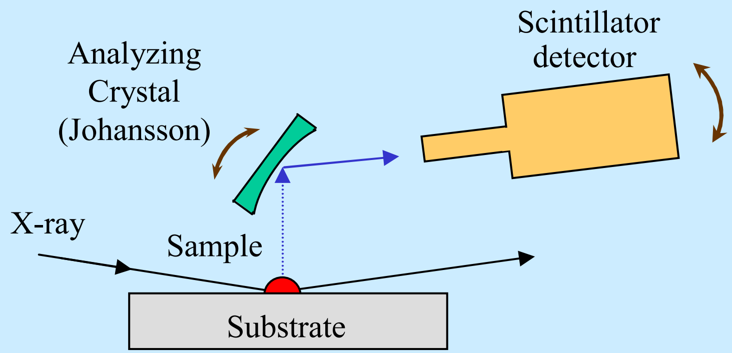
Advantages

- Large solid angle (High detection efficiency)
- Collecting whole XRF spectra simultaneously

Disadvantages

- Low energy-resolution
- Limitation of counting-rate
- Scattering background

Wavelength-dispersive TXRF



Advantages

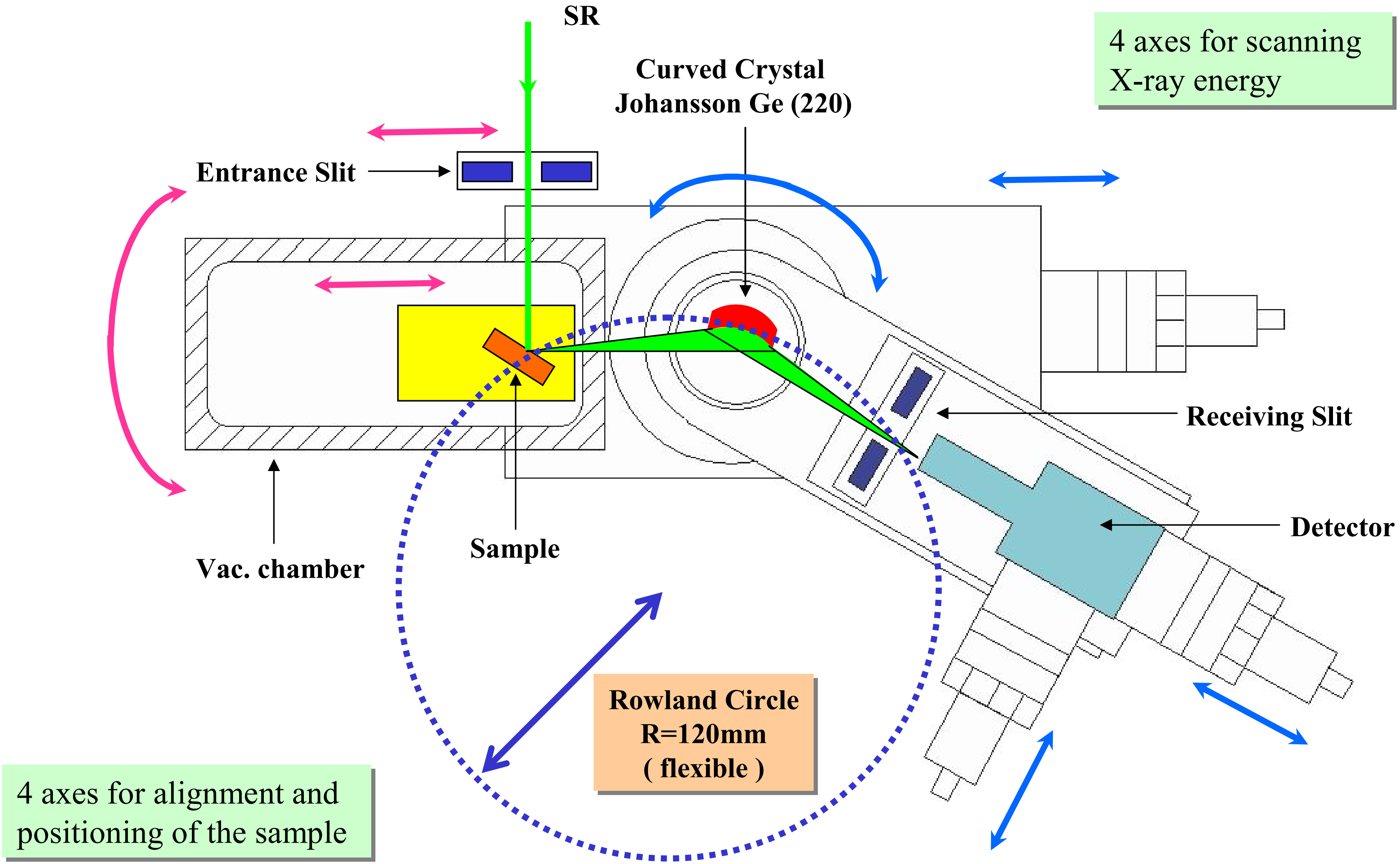
- High energy-resolution
- Good signal to background ratio

Disadvantages

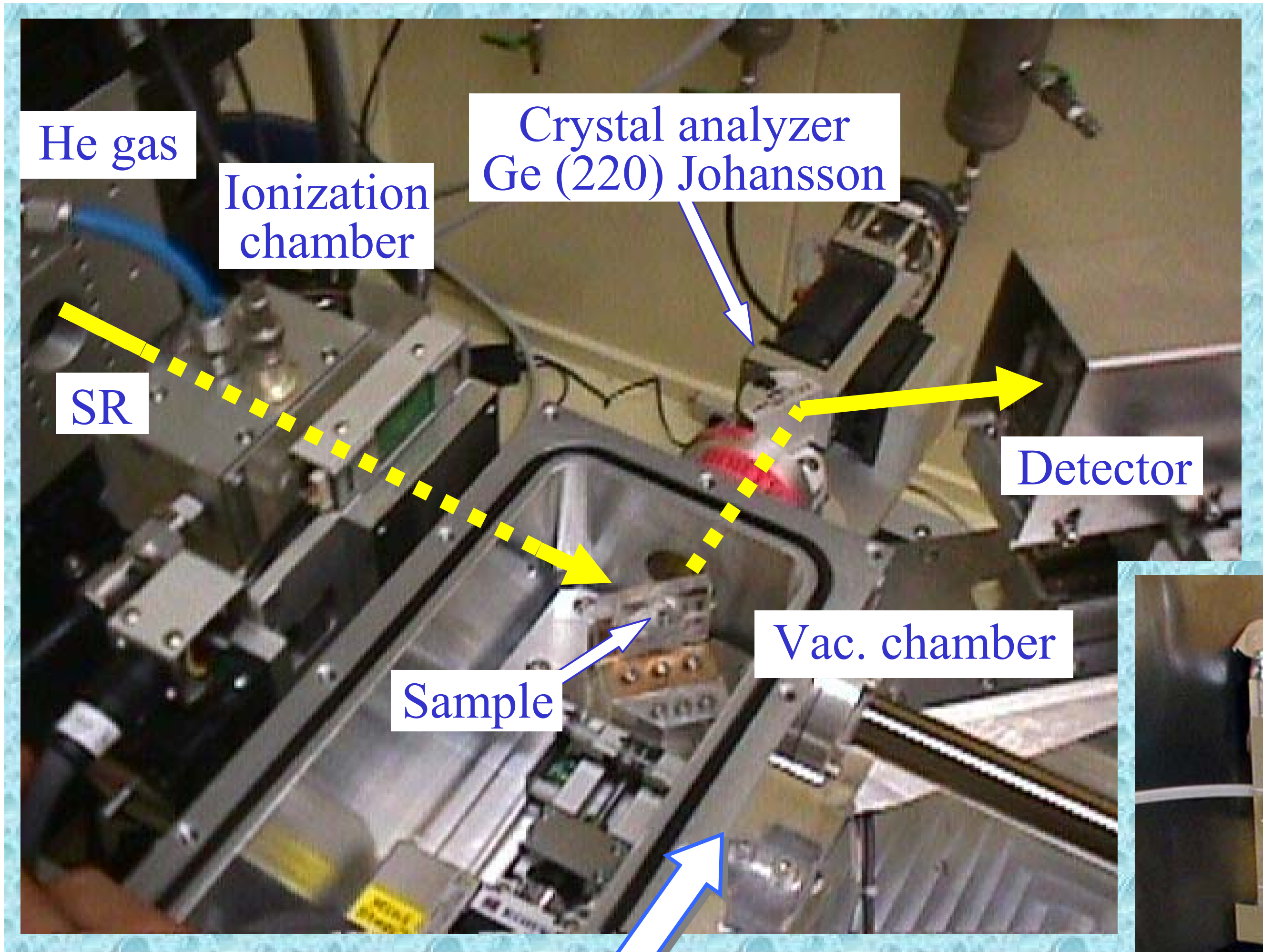
- Low detection-efficiency

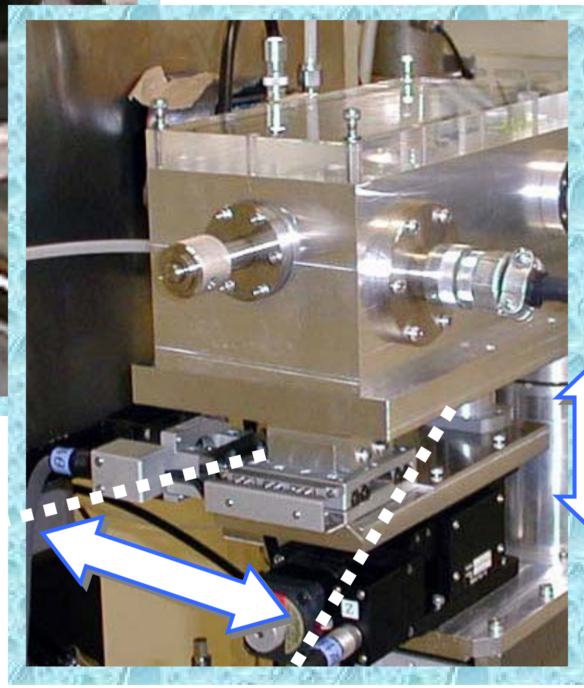
Design Considerations

Flexibility and feasibility for practical analytical applications



Compact Johansson X-ray Fluorescence Spectrometer

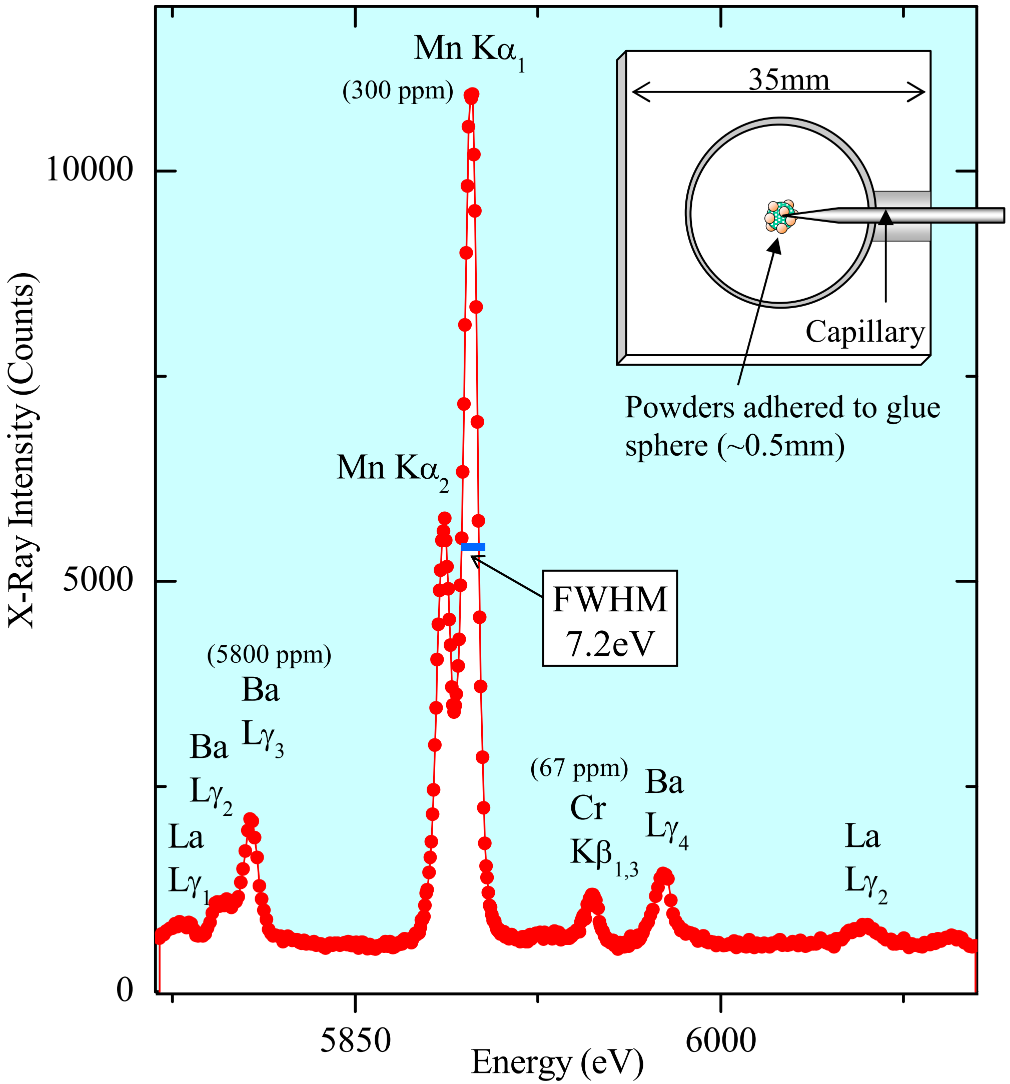




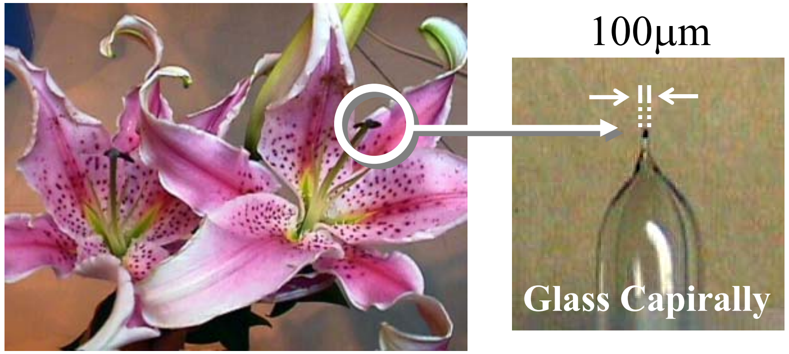
Performance of the Spectrometer

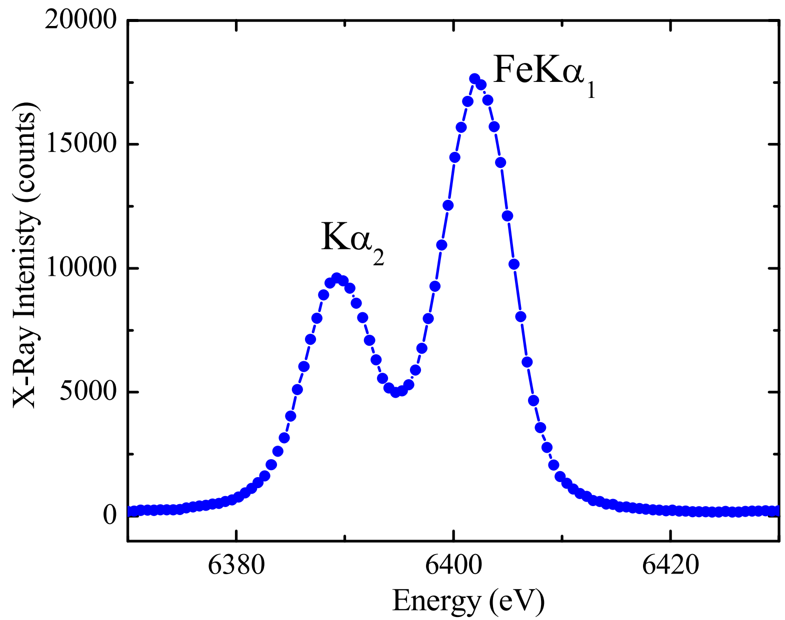
Feasibility for the analysis of trace elements in small samples

Coal Fly Ash (NIST SRM-2690)



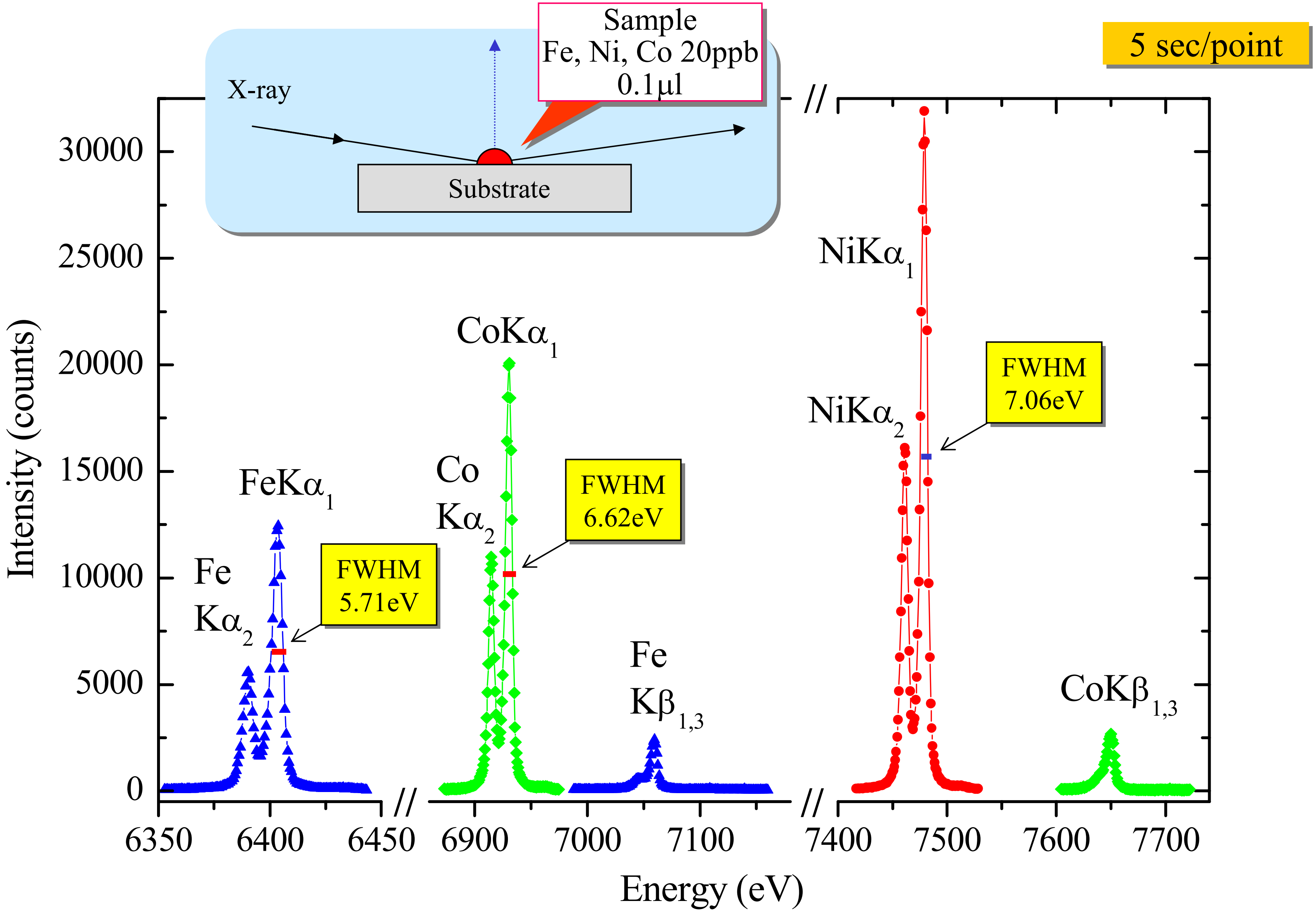
Lily Pollen (20 particles.)





WD-TXRF Spectra for Trace Elements in Micro Drop

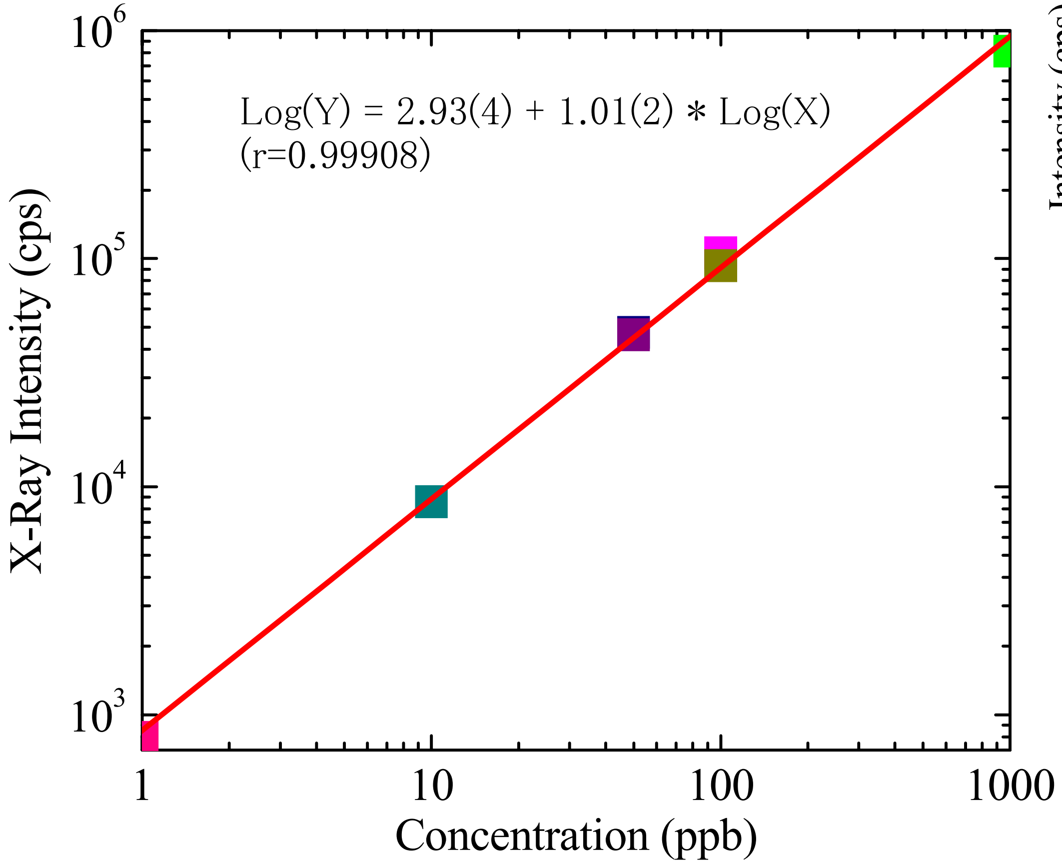
Significant enhancement of signal to background ratio



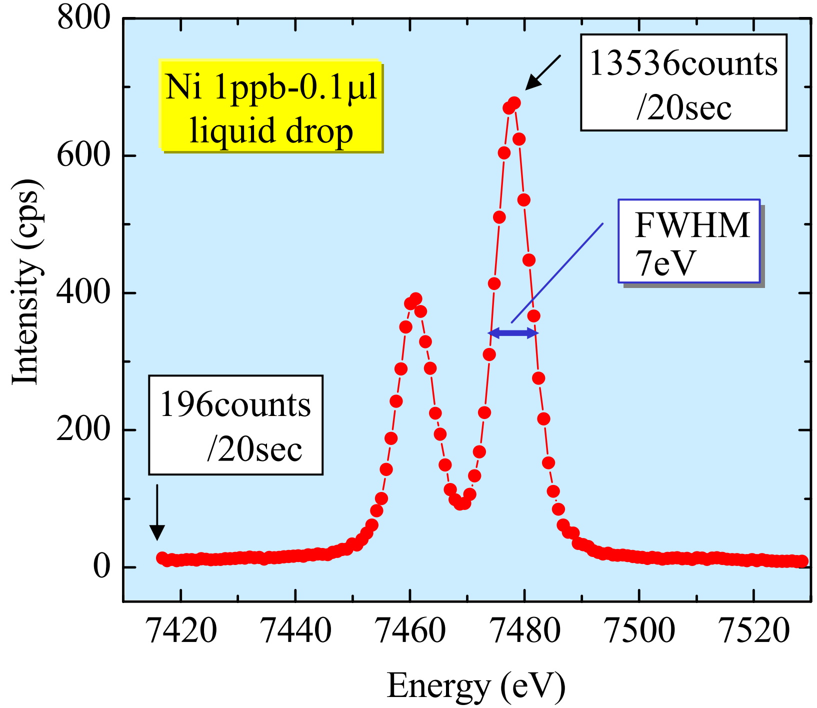
Performance of Wavelength-Dispersive TXRF

ppt level detection limit with less than 10eV energy

Calibration curve



Ni in 0.1 µl solution



Detection Limit

	Absolute amount	Concentration of solution of 0.1µl
Ni	0.31fg	3.1ppt

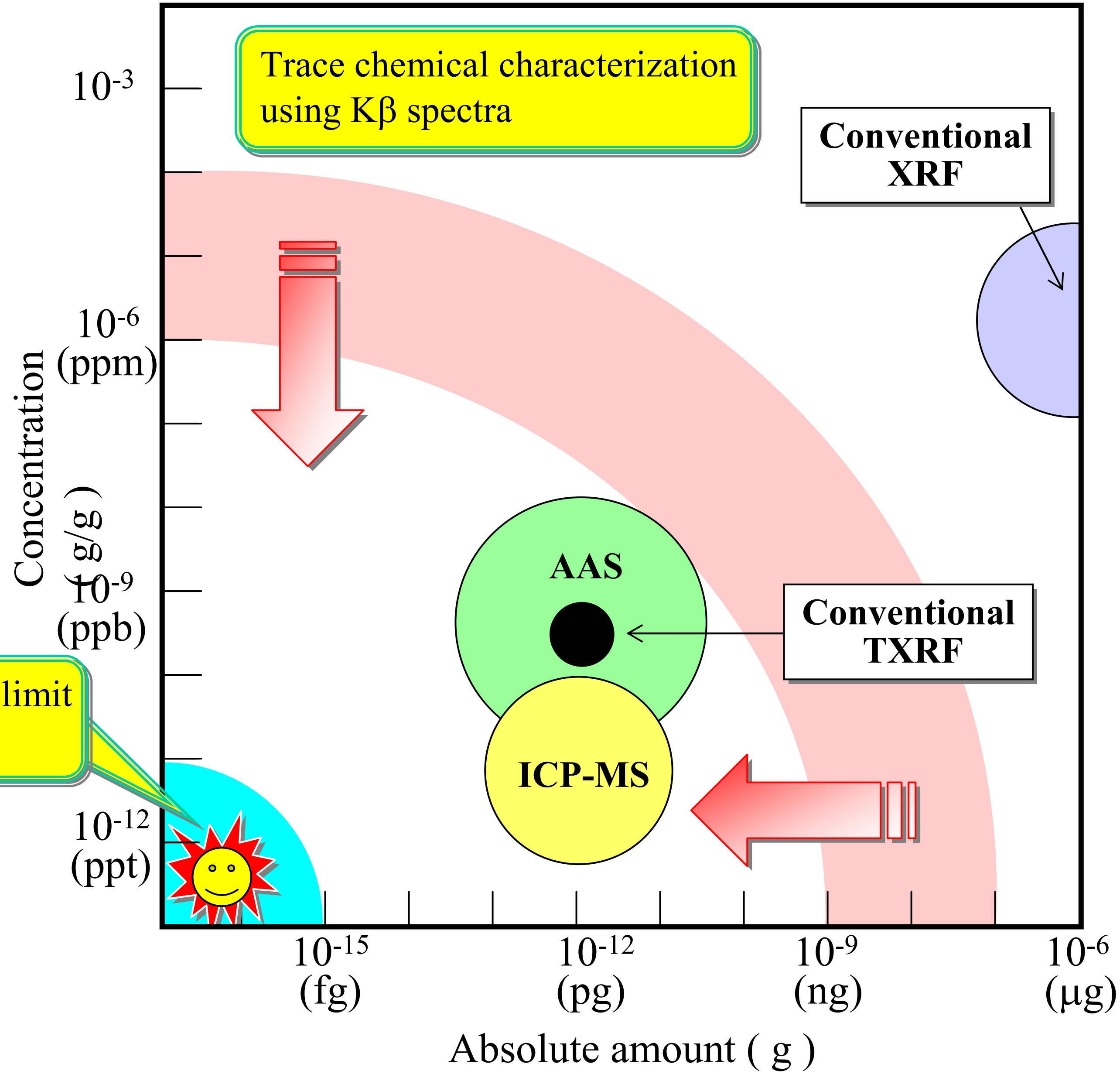
Summary
Towards ppt chemistry

Reducing scattering background as well as parasitic X-rays due to contamination is extremely important.

Downsized wavelength depressive XRF spectrometer is effective to enhance both detection efficiency and energy resolution.

~10^{-16}g
~10^{-12}(ppt)
For 0.1μl

Present detection limit (SR-WD TXRF)



X-ray fluorescence analysis

A. Somogyi
ID22, European Synchrotron Radiation Facility, ESRF, Grenoble France

Outline

- What is X-ray fluorescence analysis (XRF)?
- Micro-X-ray fluorescence analysis
- Application of scanning μ-XRF
- X-ray fluorescence tomography and applications
- Combination of μ-XRF with other μ-X-ray techniques (μ-XRD, μ-XANES, μ-tomography)
- Conclusion

Collaborators:

- J. Susini, M. Salome, R. Baker, ID21
- B. Golosio, S. Bohic, M. Drakopoulos, S. Labouré, ID22/ID18F
- R. Toucoulou, ID21/ID22
- B. Fayard, A. Simionovici(CNRS)

Synchrotron radiation induced scanning μ-XRF

ID21, ID22 beam-lines of the European Synchrotron Radiation Facility (ESRF)

	ID21 X-Ray Microscopy	ID22/ID18F Micro-XRF,Imaging, Diffraction
•Energy range:	2-8 keV	6-70 keV
•Spatial resolution:	0.1 - 1.0 μm	1.5 - 3.0 μ m
•Monochromator:	Si 111 or Si 220	Si 111 or Si 311
•Detection:	parallel multiple detection	
•Fluorescence:	HPGe	Si(Li)
•Transmission:	photodiode	photodiode, ion. chamber
	operation in air/vacuum	operation in air
•Detectable elements:	Z<26 (Fe) K-lines	14<Z<72 (Hf) K-lines
(by XRF)	Z<64 (Gd) L-lines	72<Z L-lines

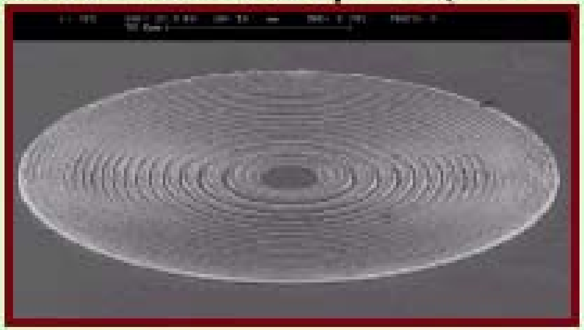
Applications:

Geochemistry, Biology, Environmental Sciences, Materials Science…

Micro-X-ray fluorescence spectrometry
Focusing devices

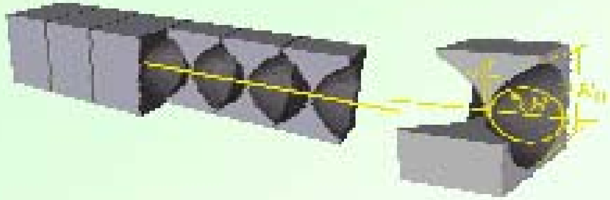
Fresnel Zone Plates (FZP)
Diffractive Optics

- diffraction gratings of increasing linear density
- 50-60 % efficiency
- spot size:< 0.1 x 0.1μm^2 (for low E)

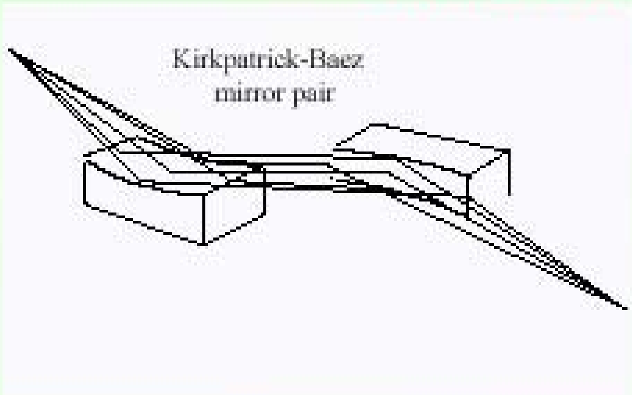


Compound Refractive Lenses (CRL)
Refractive Optics

- parabolic lenses - reduced aberrations
- variable n assemblies: tune f and L_2
- high yield for high E
- spot size: ~2 x 12 μm^2

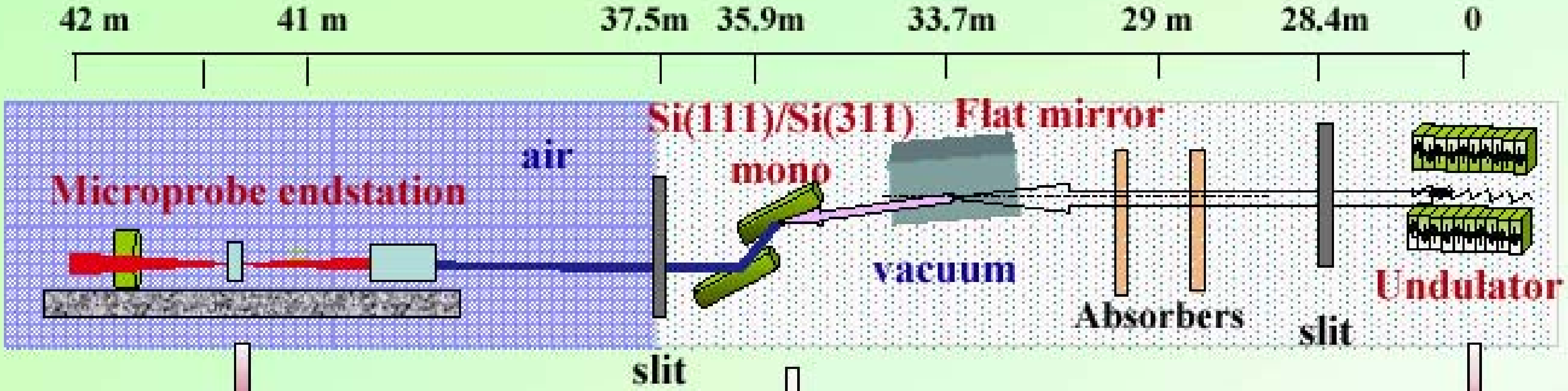


Bent mirrors Kirkpatrick-Baez, (KB mirror pair)
Reflective optics



- 60-70 % efficiency
- acchromaticity
- Multilayer mirror for high energy
- spot size: ~1 x 3 μm^2

Schematic layout of the ID22 beam line and the microprobe end-station

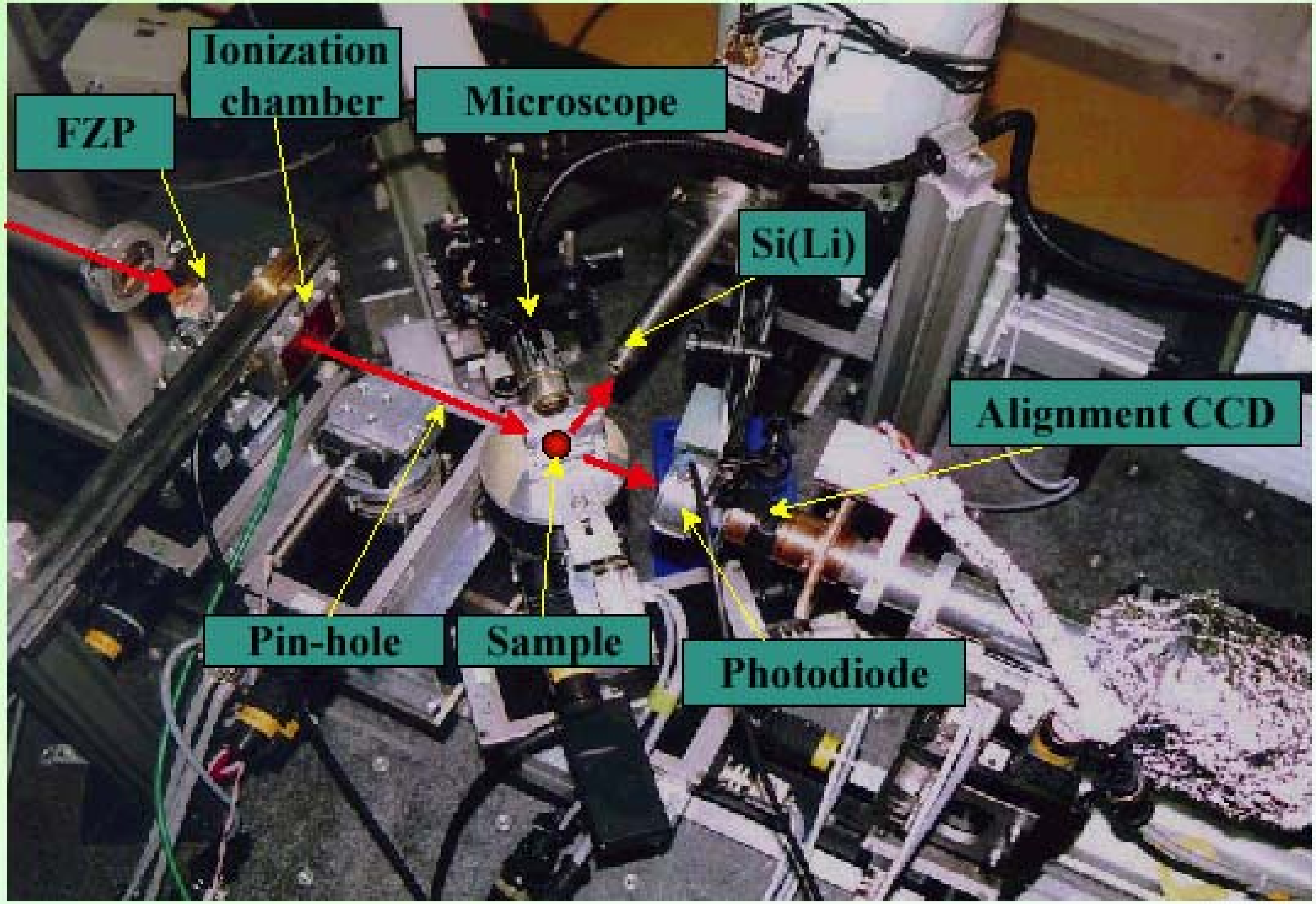


Focused micro-beam,
Spot-size (H×V): 3 × 1.5 μm²
Flux: 10^{10} - 10^{11} ph/s

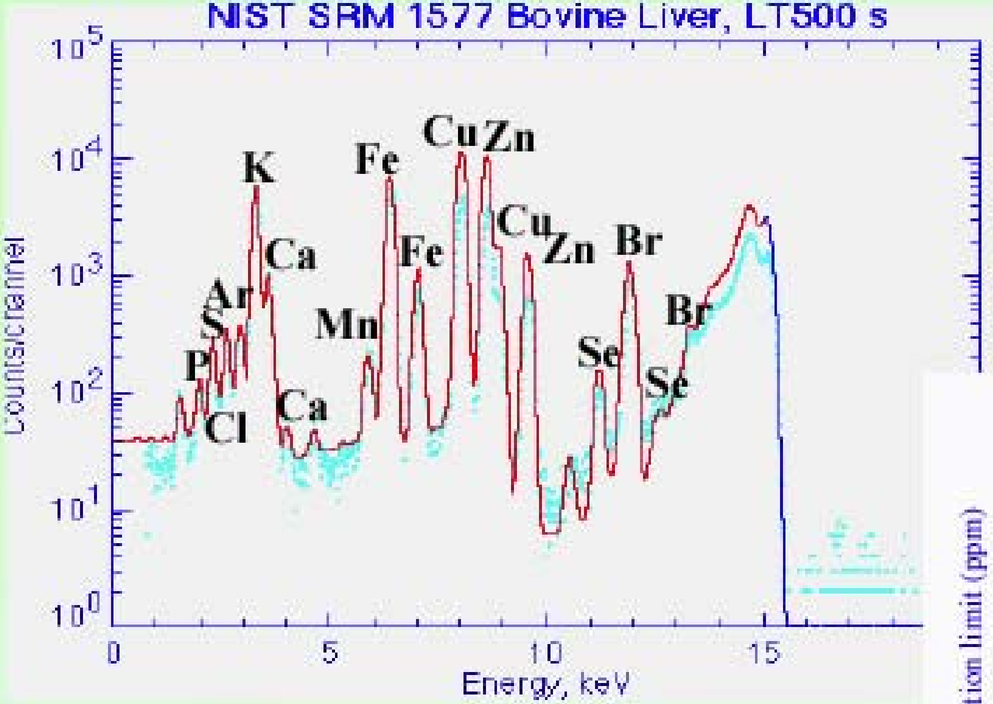
High beta section
Source size (H×V): 700 × 30 μm²
Div. (H×V): 30 × 20 μrad²

Tunable, monochromatic X-ray beam
E range: 6-70 keV
E resolution: $\Delta E/E \approx 10^{-4}$
or
Mirror reflected pink beam: one full undulator harmonics

X-ray microprobe set-up at ID22

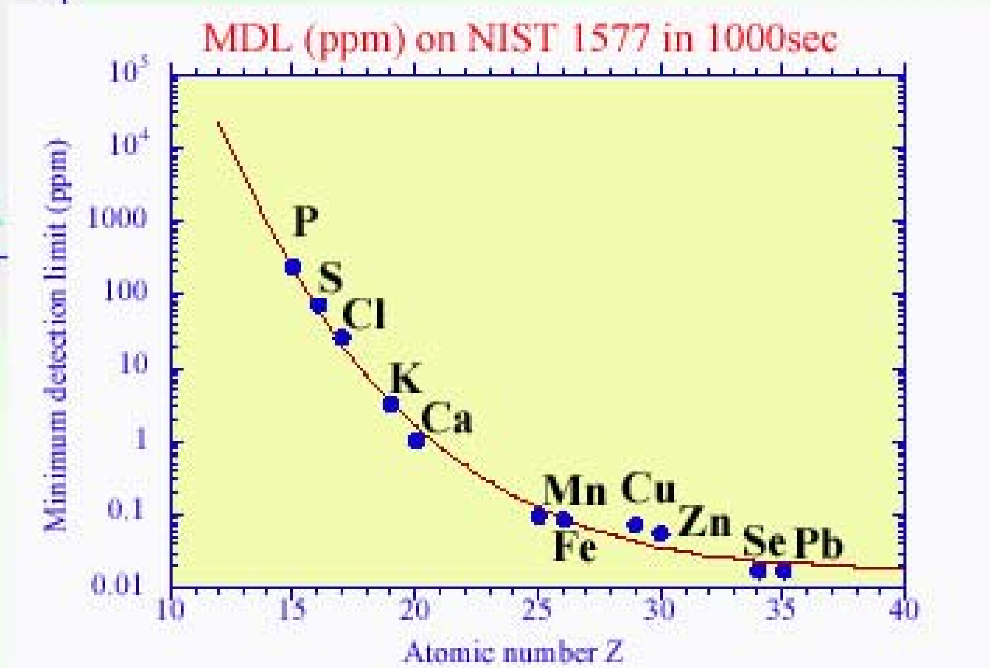


X-ray microprobe set-up at ID22, ESRF
Minimum limit of detection



Detection limit/1000 s:
≈20 ppb
≈0.4 fg

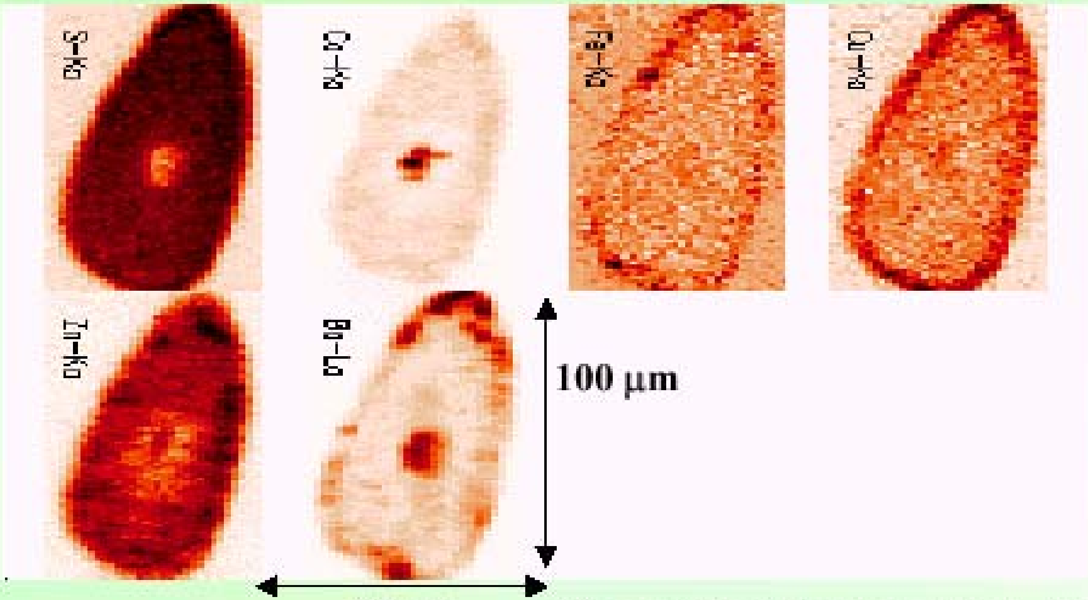
E=15 keV, 1 x 5 μm²



10^{10}-10^{11} photons/s in the focused beam

Scanning micro-XRF, biological applications
XRF mapping of hair sections, ID18F

In collaboration with S. Bohic, ID22, ESRF, France, Y. Duvault: L'Oréal, P. Dumas: LURE, France



Aim of the study:

Anomalies of elemental distribution: stress? Chemicals?

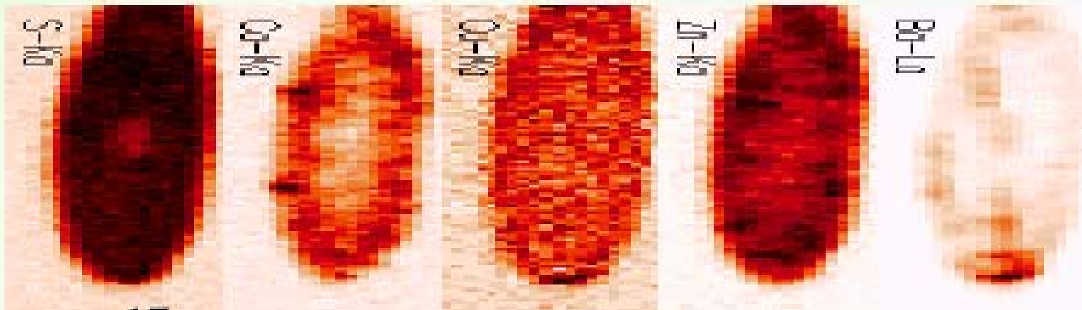
Effect of cosmetics, new developments

Medical diagnostics?

10 µm thick hair sections, E: 17 keV, spot size 2x4 µm², LT:7 s/pixel

Needed:

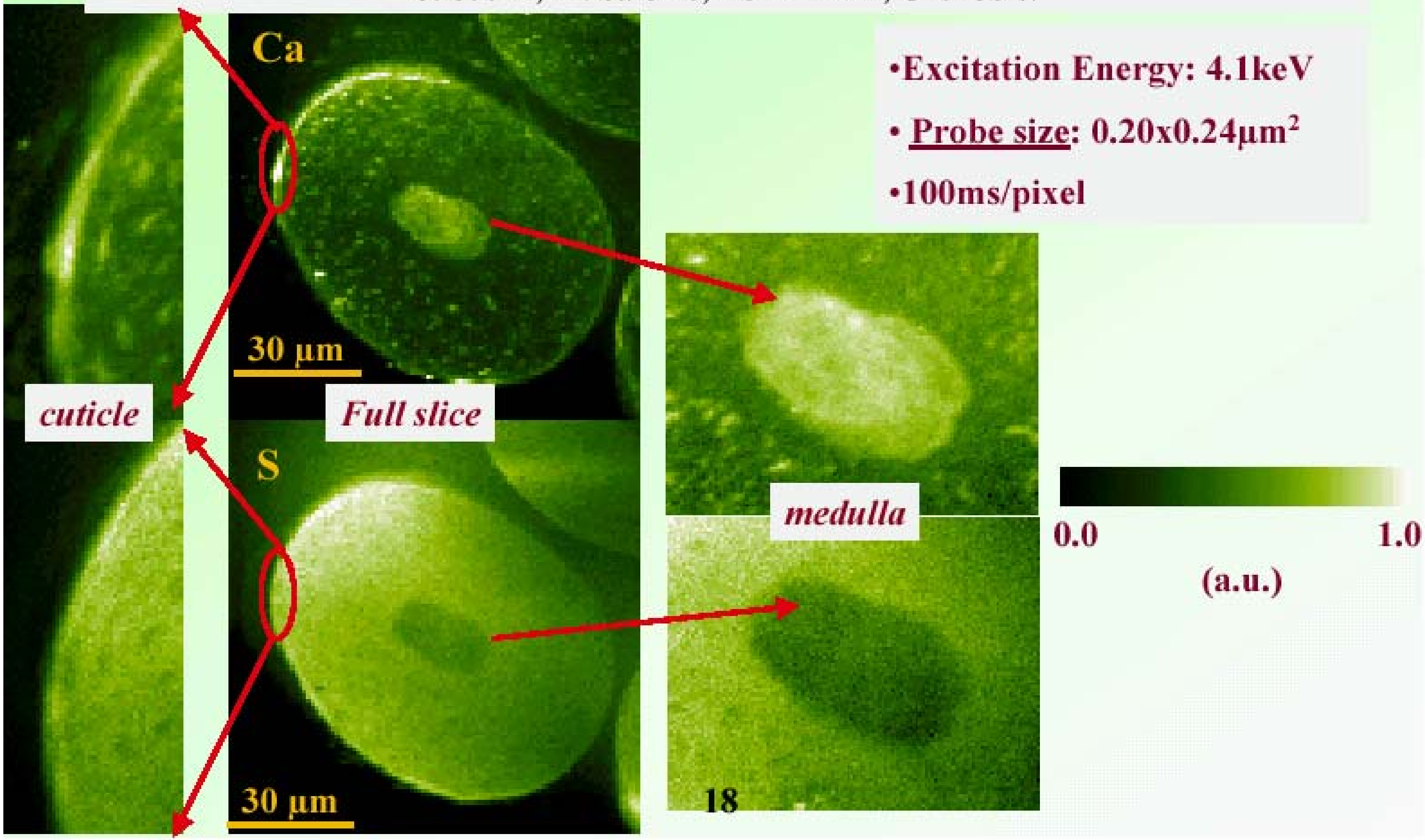
Large number of samples !!!
Complementary techniques, SAX, IR
Careful sample preparation



XRF mapping of hair sections, ID21

C. Mérigoux, F. Briki, L. Kreplak, J. Doucet, LURE, Orsay.
J. Susini, M. Salomé, ESRF-ID21, Grenoble.

- Excitation Energy: 4.1keV
- Probe size: $0.20 \times 0.24 \mu m^2$
- 100ms/pixel



Scanning micro-XRF, biological applications
Single cell spectroscopy

S. Bohic, A. Simionovici, ESRF, Ortega R - Devès G. , CNRS, Bordeaux CNRS Bordeaux,
Medical beamline, IBS, CHU-G

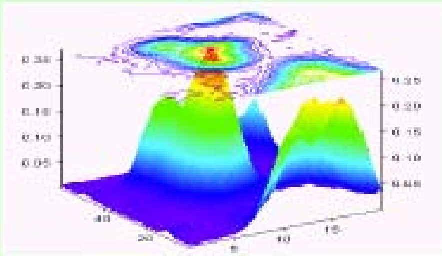
Aim: study of the

- biological effects
- intracellular distribution
- anticancer action

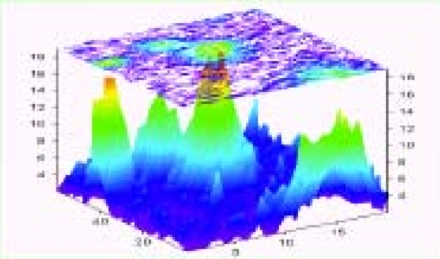
of various high Z labelled anticancer drugs used at pharmacological doses

anticancer drugs: low 1 mg/ml conc.

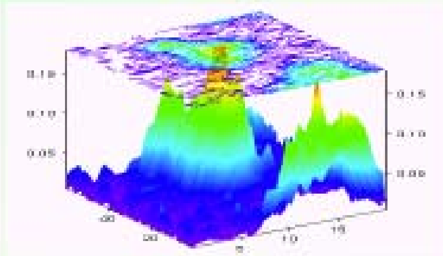
Ovarian cancer cell



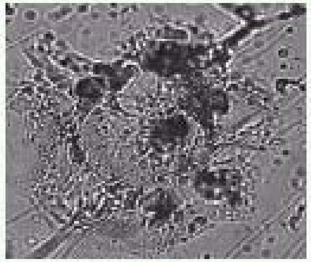
K K_α



Fe K_α



I L_β

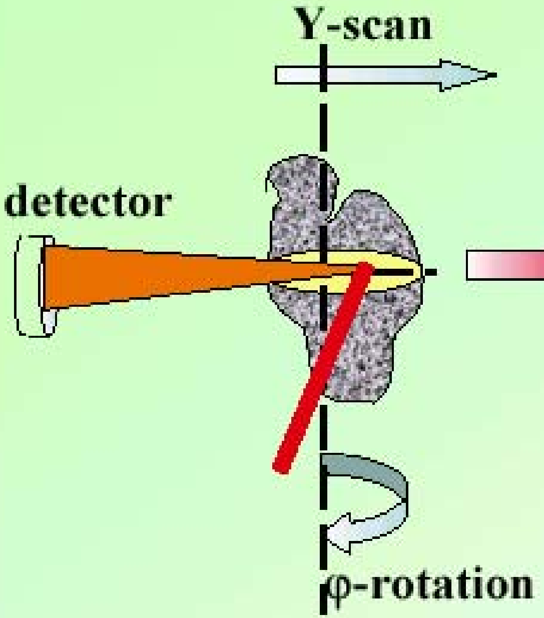


optical img

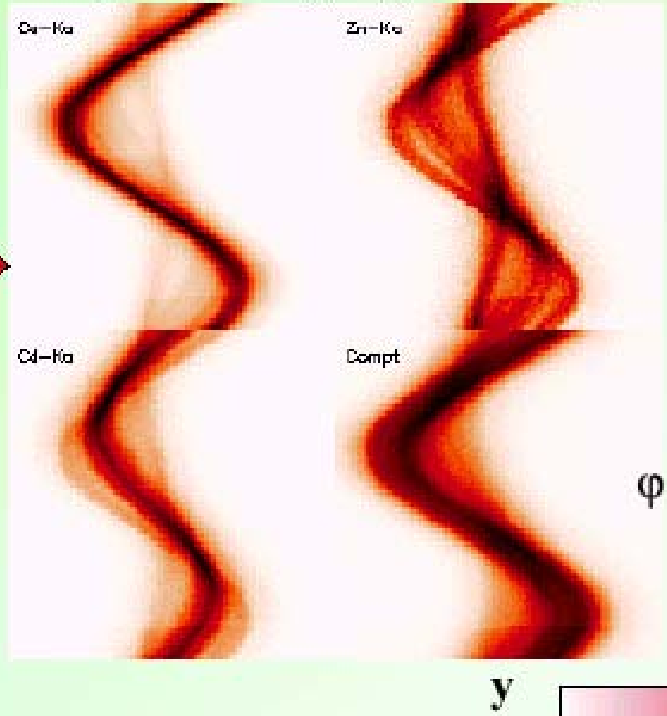
PINK beam:	1 x 5 µm (min), flux $\geq 5 \cdot 10^{11}$ ph/s , CRL lenses
Non-destructive:	dry or freeze-dry samples, $t \leq 5$ µm
Mapping:	2-4 hours, 1-2 sec./point (PINK),
	$t > 20$h (monochromatic)

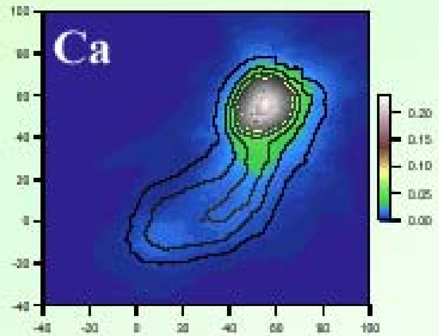
Scanning micro-XRF, 2D/3D internal elemental distribution

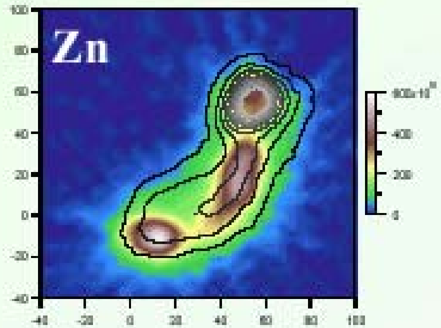
Fluorescence tomography

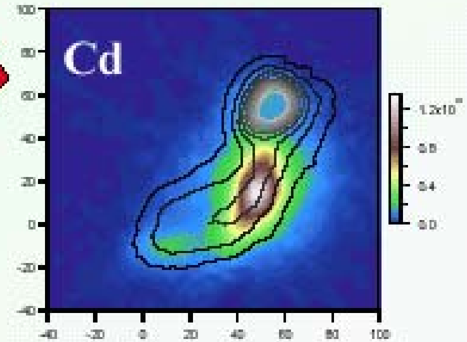


Sinogram: 2D (y- φ) intensity map









Several slices: complete 3D distribution, time-consuming

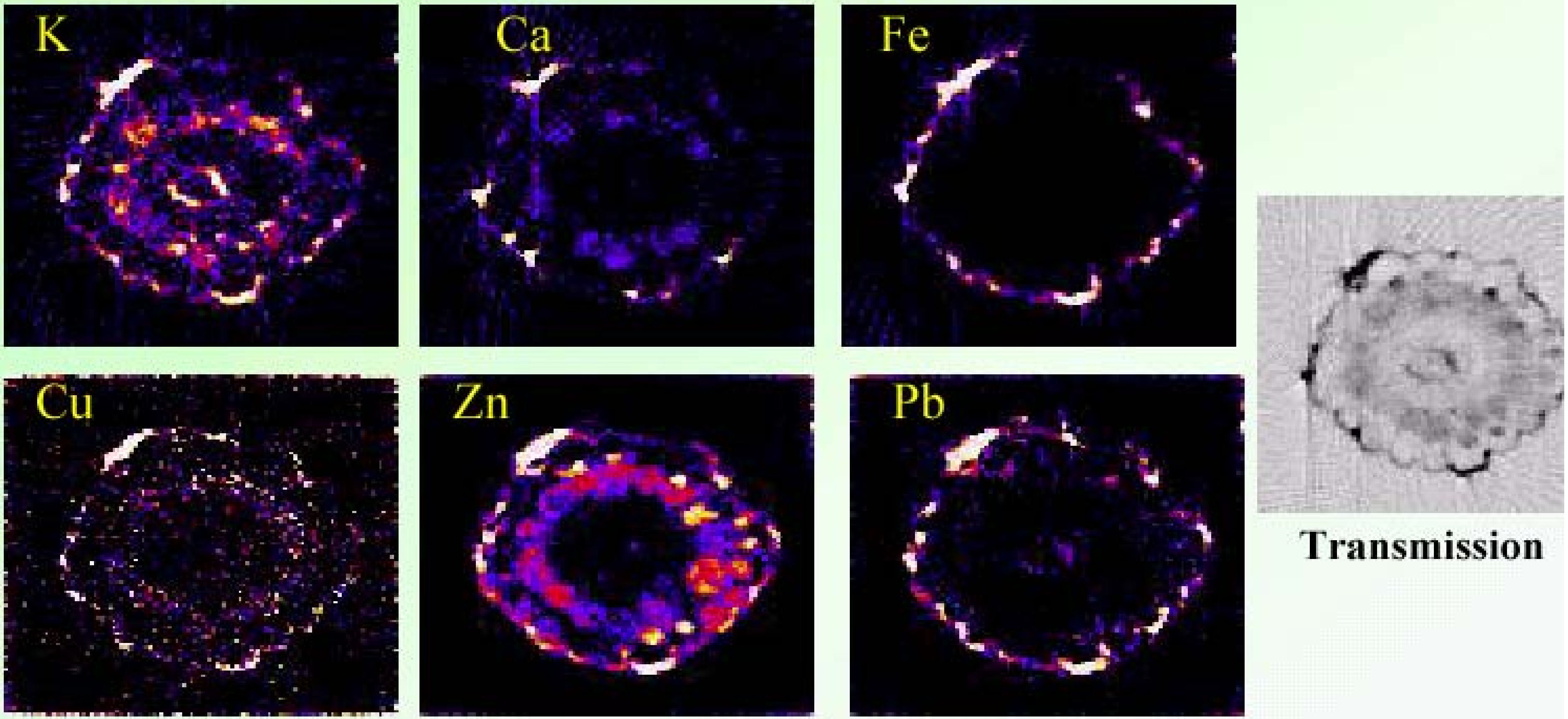
Reconstruction algorithm 2D, (x-y) internal intensity (concentration) distribution

Fluorescence tomography, biological application

W. Schröder, FZ Julich, Ch. Schroer, T.F. Günzler, B. Lengeler, RWTH Aachen, A. Simionovici, CNRS

Study of ion transport in plants

Mycorrhizal root of tomato plant root - Ø < 0.5 mm; resolution ≈ 1 µm



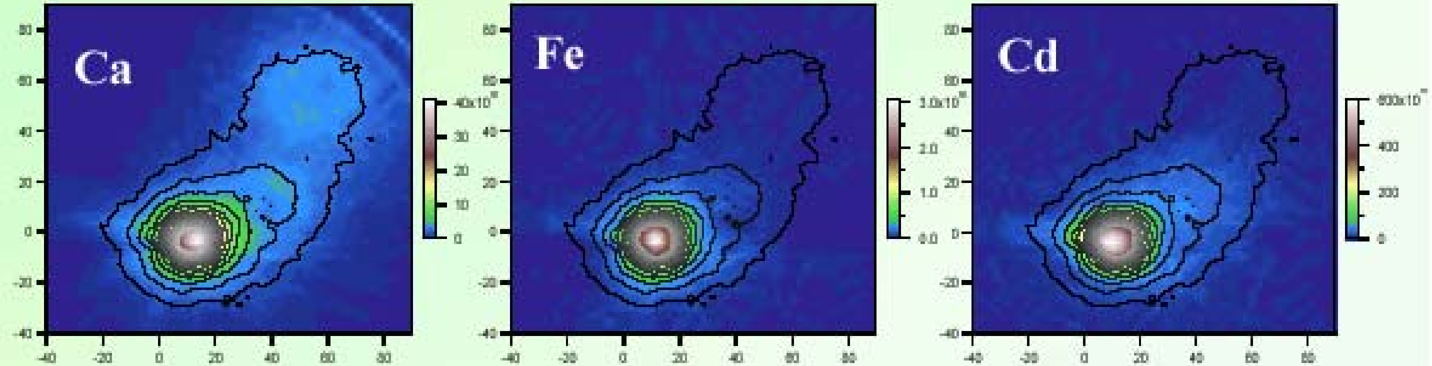
Transmission

Scanning µ-XRF + Combined techniques

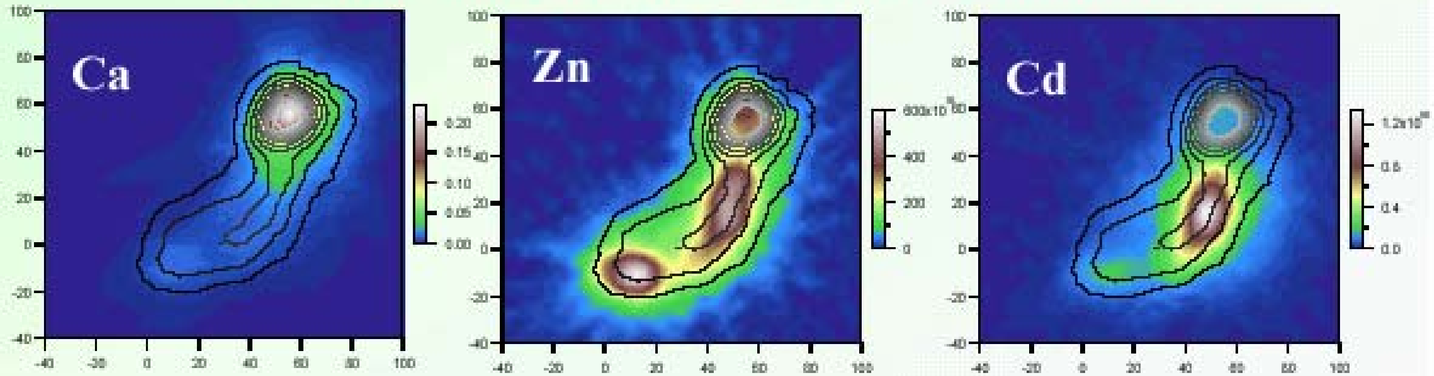
Environmental application, investigation of individual fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. of Techn., Göteborg, Sweden, B. Golosio, A. Simionovici, ID22

Internal elemental distribution within Slice2



Internal elemental distribution within Slice1



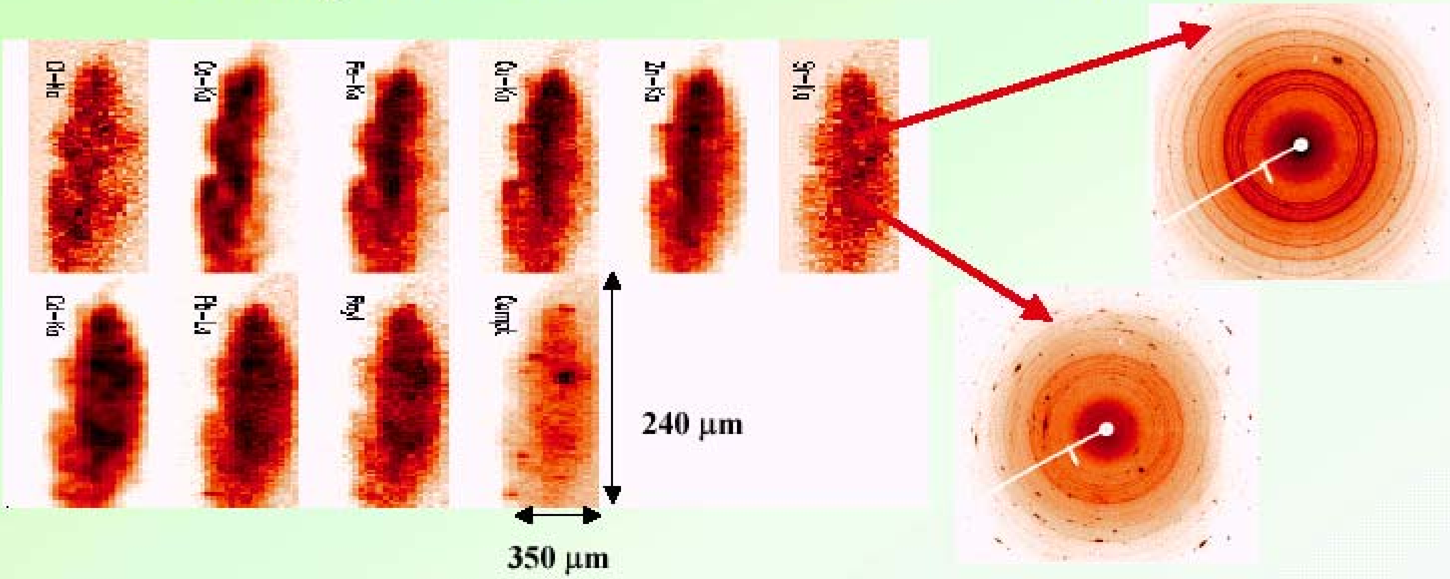
Scanning μ-XRF + Combined techniques

Environmental application, investigation of individual fly ash particles

In collaboration: C.M. Camerani, B.M. Steenari, O. Lindquist Chalmers Univ. , Göteborg, Sweden, B. Golosio, S. Ansell, A. Simionovici, ID22

Crystalline structure: micro-XRD

Scanning-Micro-XRF | **Micro-XRD**

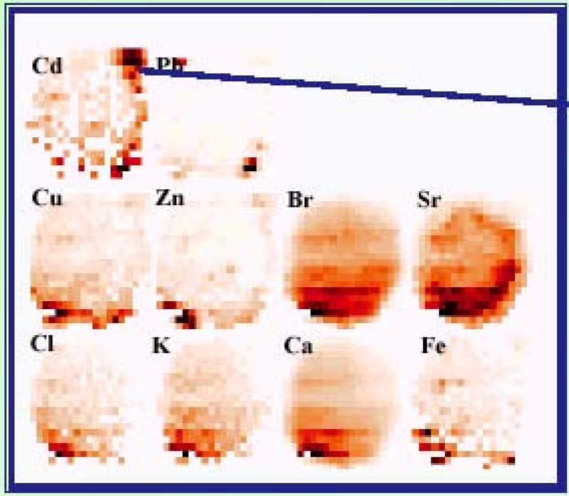


Single waste fly ash particles, LT:6 s, step-size H*V:14*3 μm^2, ID18F/ID22

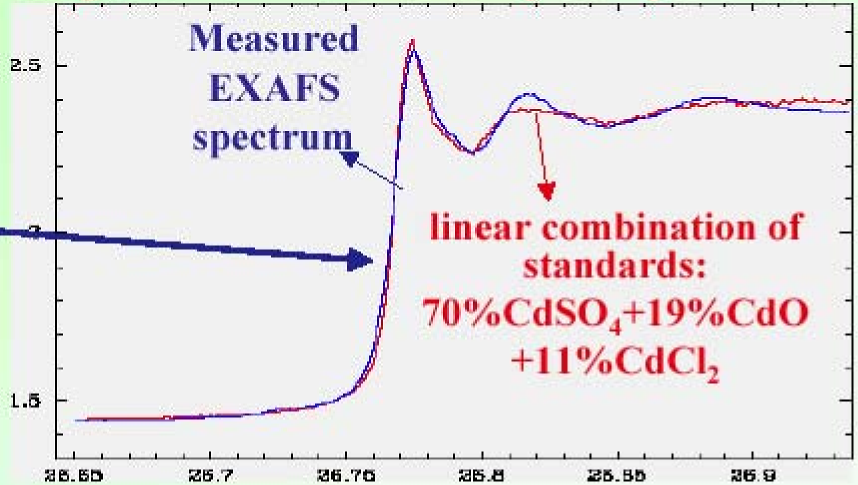
Scanning μ-XRF + Combined techniques

Environmental application, investigation of individual fly ash particles

Scanning-μ-XRF

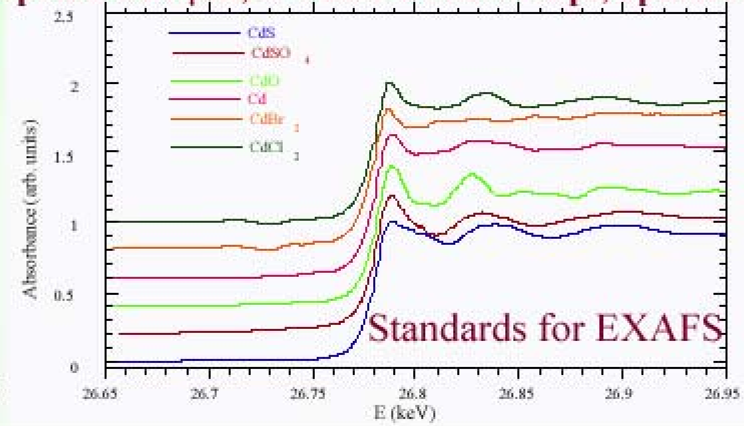


Spot: 8 x 8 μm², E = 27 keV,LT:6 s/pt



Spot: 3 x 20 μm, E = 26.6-27 keV 1 s/pt, 3passes

Chemical speciation and coordination number of Cd in the chosen pixel: μ -EXAFS



Conclusions

SR-X-ray XRF technique is very powerful.

- Low detection limit down to fg, ppt level
- applicable to samples of limited size
- well analyzed due to energy tunability and high energy resolution
- Development of XRF imaging
- Combination with different micro techniques (XRD, XANES and EXAFS)