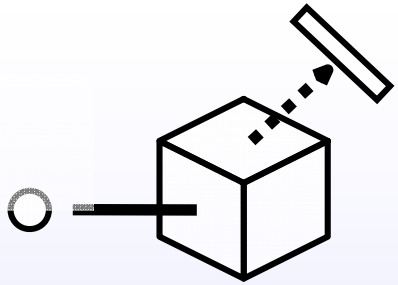
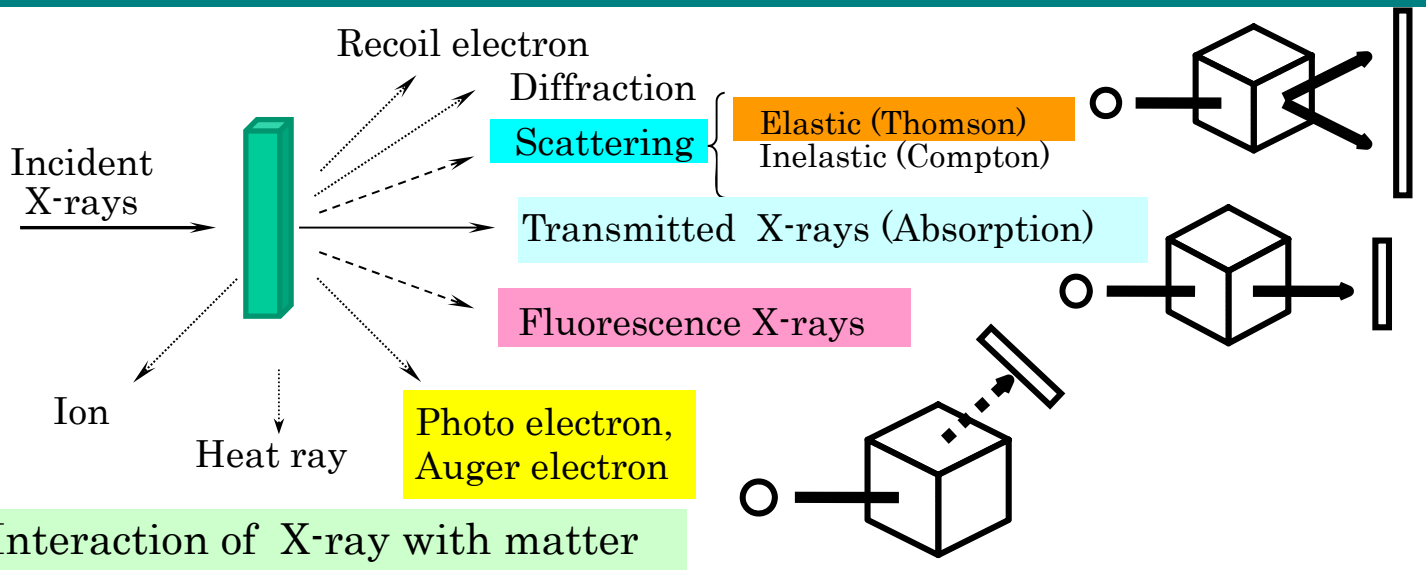
X-ray fluorescence analysis



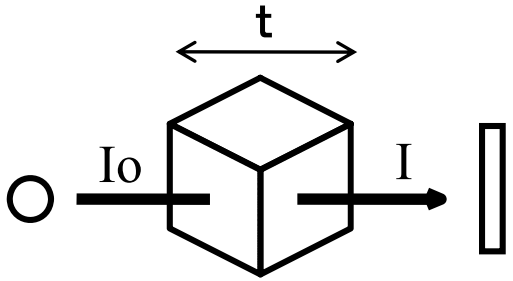
Chiba University, Department of Chemistry
Chiya NUMAKO, Misato KAZAMA
Tokyo University of Science, Department of Applied Chemistry
Izumi NAKAI

- Introduction to XRF
- Characteristics of SR and the advantages in X-ray fluorescence analysis with application examples
  - (1) Highly Brilliant X-ray Source
  - (2) Parallel beam with small divergence : μ-XRF
  - (3) Energy tunability（High Energy）
    - μ –XAFS, HE-XRF
- Conclusion

Principle of X-ray fluorescence spectroscopy (XRF)



Interaction of X-ray with matter



X-ray Absorption

$I = Io \cdot e^{-\mu t}$

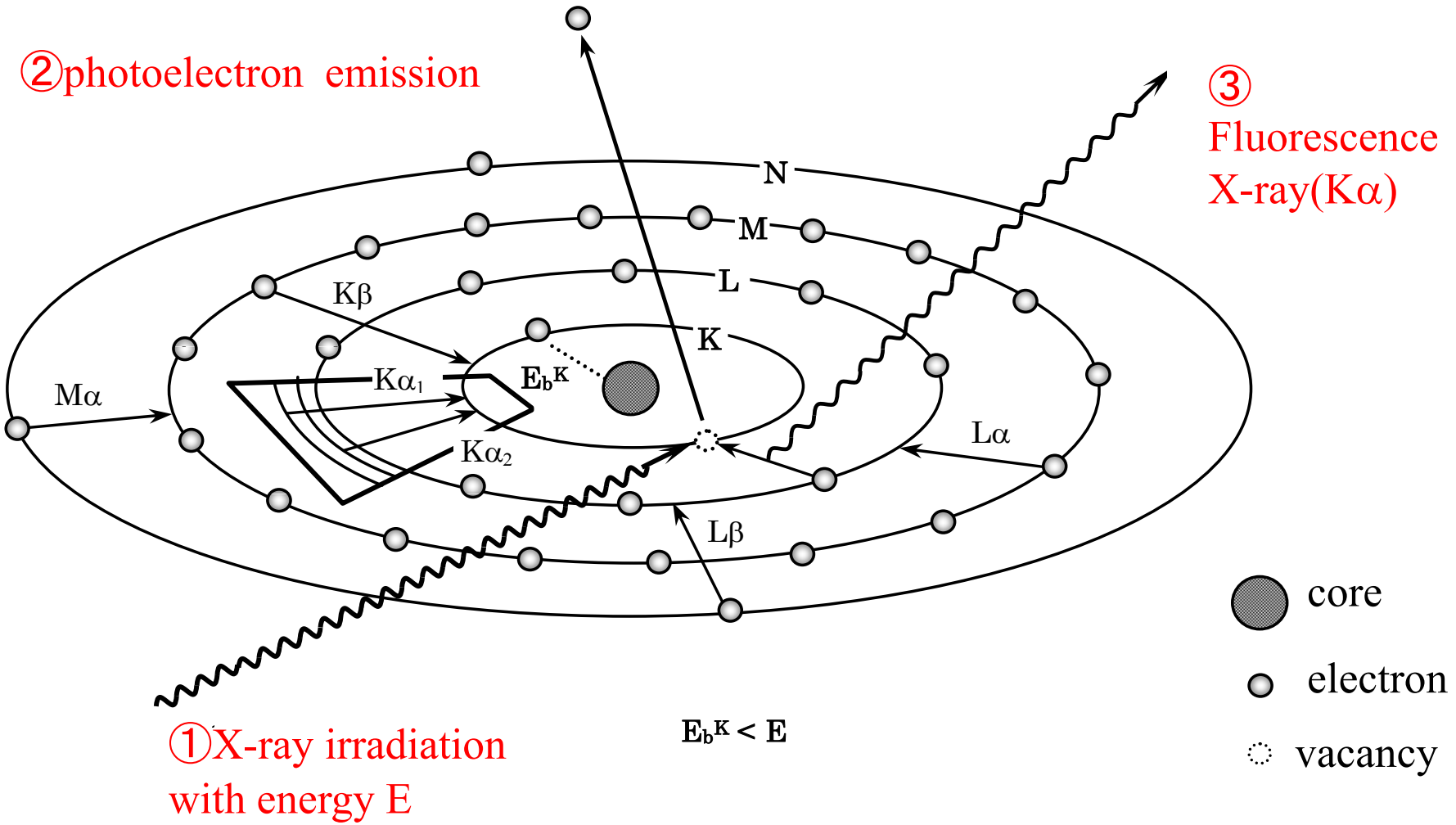
$\mu t = \ln (Io / It)$

Absorption (XAFS)

- Photoelectron effect
  - Photoelectron (XPS)
  - Fluorescence X-rays (XRF)
  - Auger electron (AES)
- Scattering
  - Thomson scattering (XRD)
    *Crystal Structure
    Long-range ordering
  - Compton scattering

X-ray Analyses

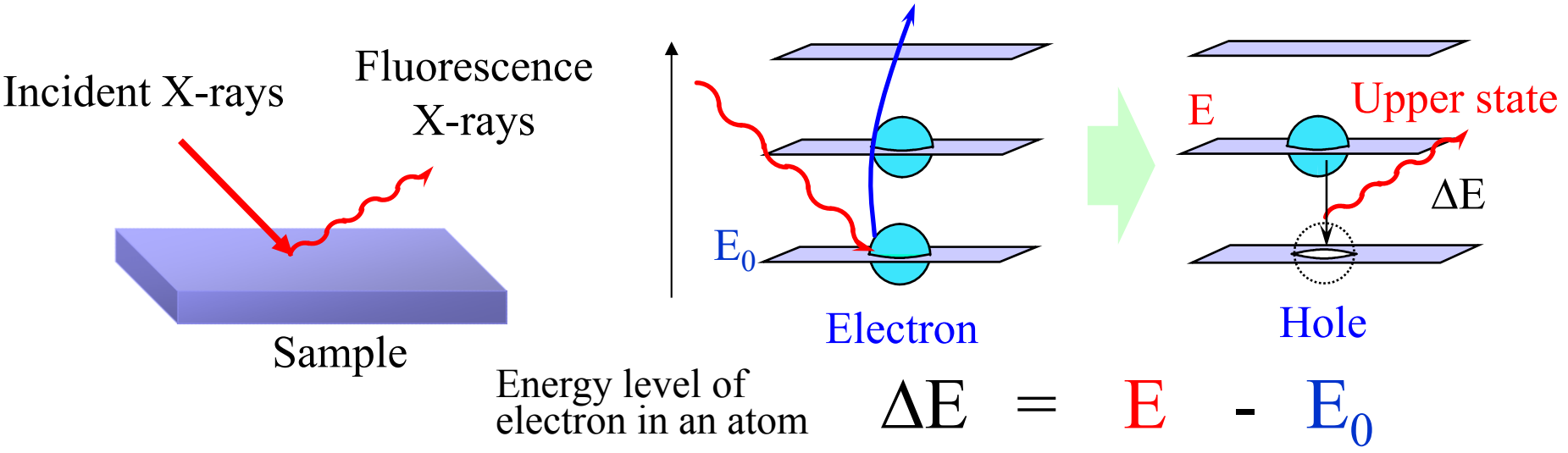
Principle of X-ray fluorescence spectroscopy (XRF)



Bohr model and emission of X-ray fluorescence

X-ray energy E > Binding energy Eb

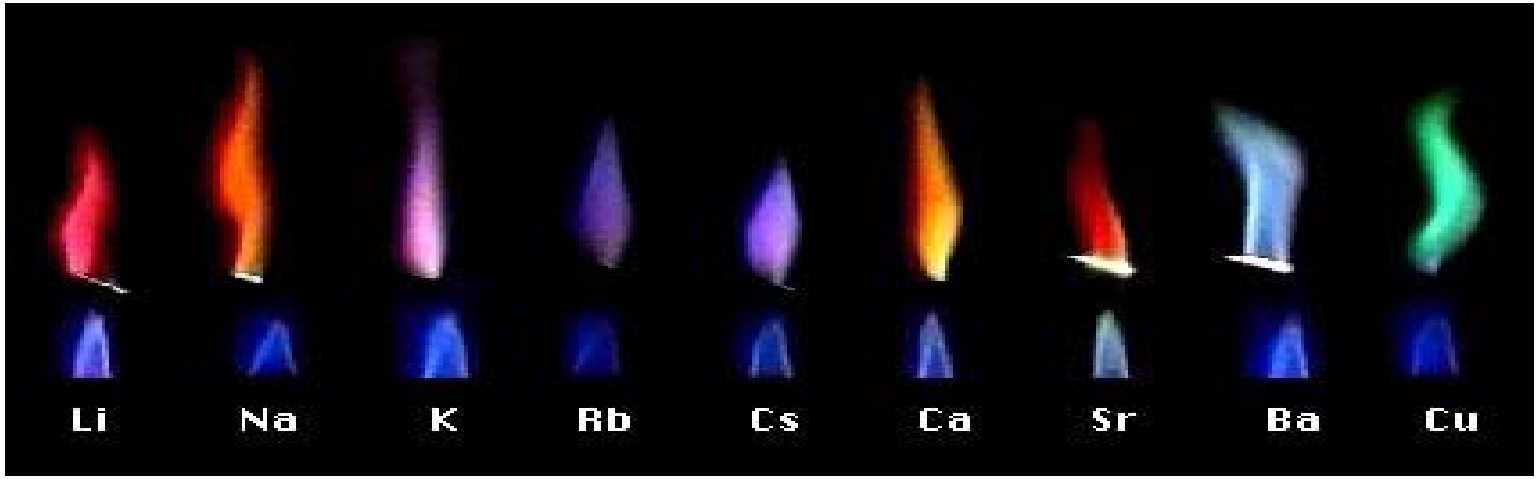
Principle of X-ray fluorescence spectroscopy (XRF)



Energy level of electron in an atom

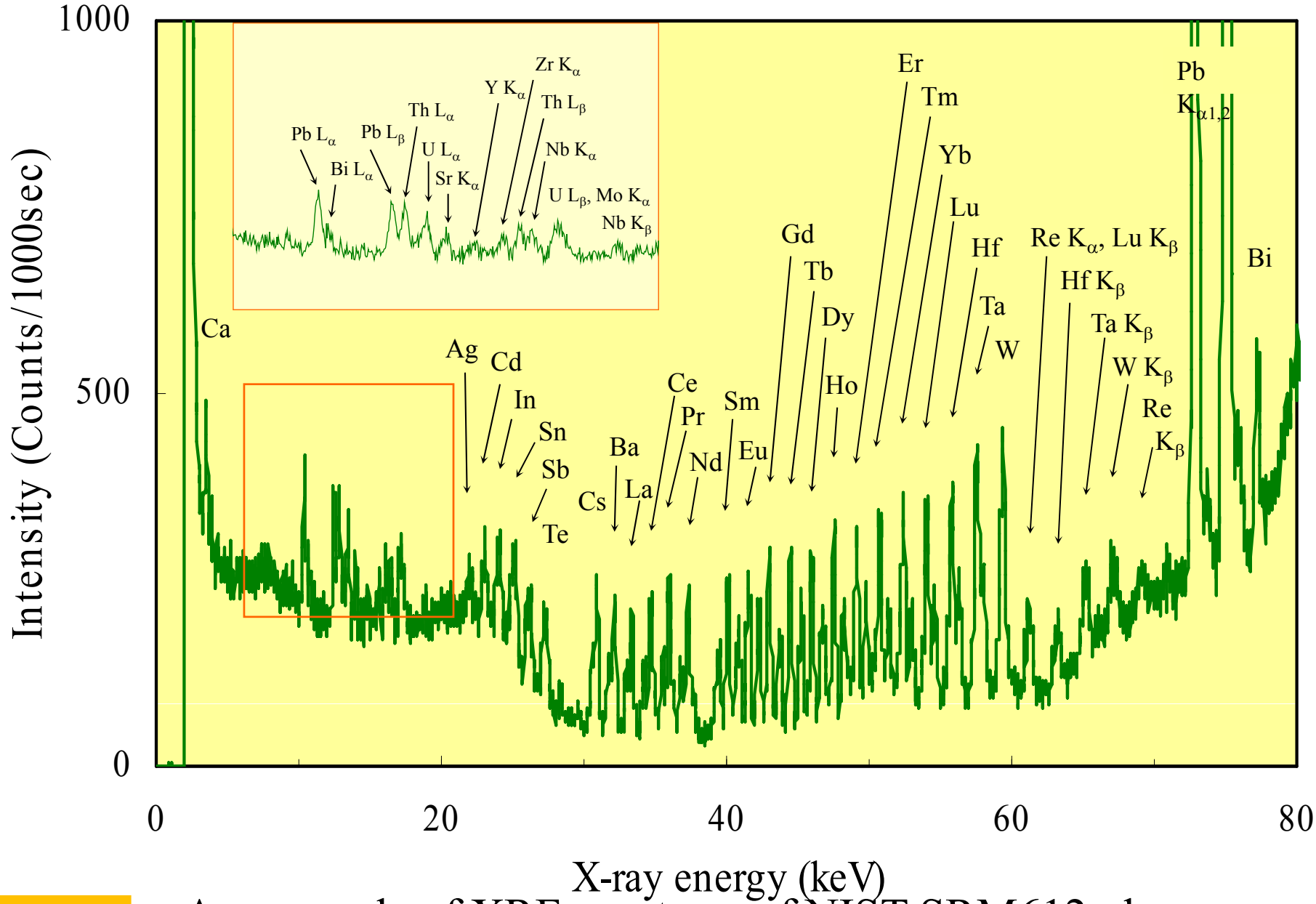
$$\Delta E = E - E_0$$

ΔE is equal to the energy difference between the two electronic state



ex) Flame reaction The color (energy) is unique to element

Principle of X-ray fluorescence spectroscopy (XRF)

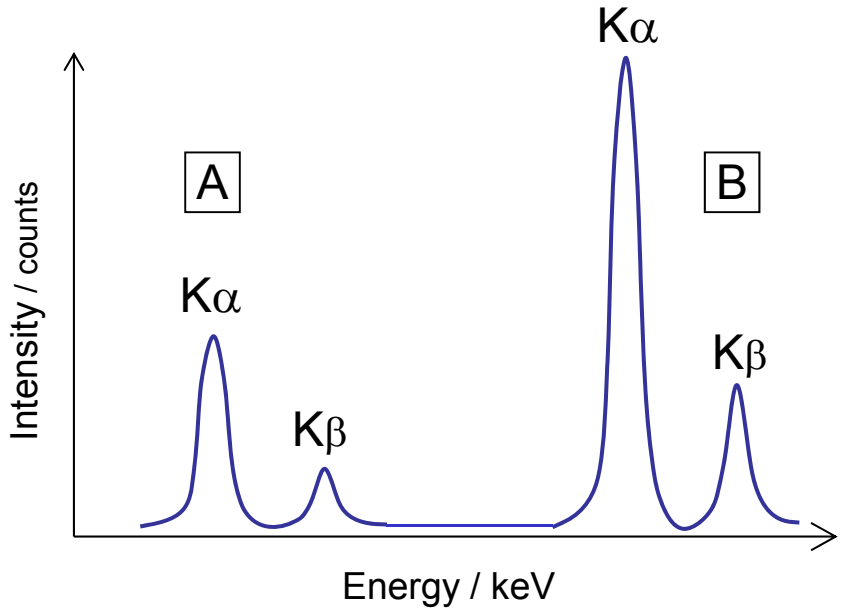


EDS

An example of XRF spectrum of NIST SRM612 glass

Principle of X-ray fluorescence spectroscopy (XRF)

Measuring energy and intensity of XRF signal



Intensity

∝ number of X-ray photons

→ concentration

Quantitative analysis

Energy ΔE

→ characteristic to each element

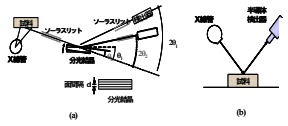
Qualitative analysis

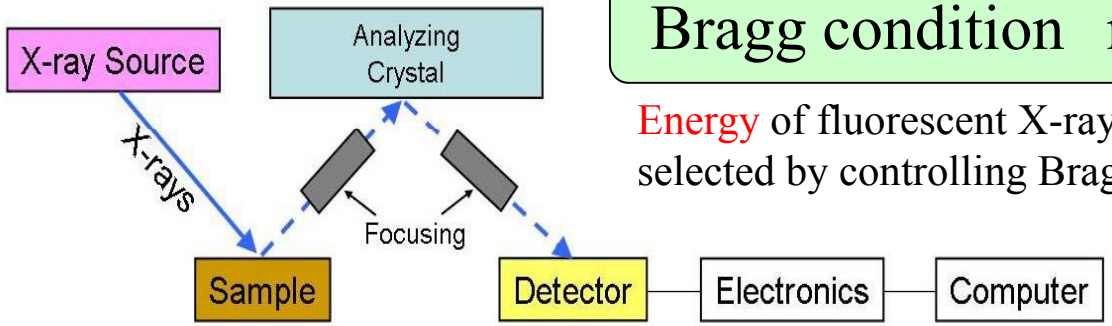
Chemical Composition Analyses

How to measure E and I of the fluorescence X-rays.

(a) Wavelength dispersive spectroscopy

WDS

d-spacing  Analyzing crystal



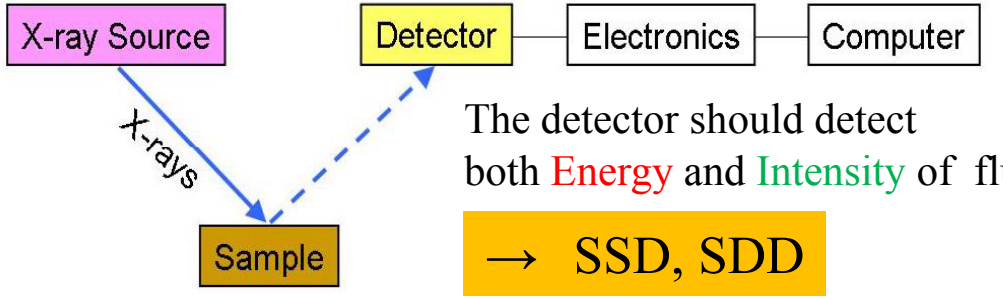
Bragg condition $n\lambda=2d\sin\theta$

Energy of fluorescent X-ray can be selected by controlling Bragg angle.

(b) Energy dispersive spectroscopy

High Efficiency
Multi-elemental detection

EDS



The detector should detect
both Energy and Intensity of fluorescent X-ray

→ SSD, SDD

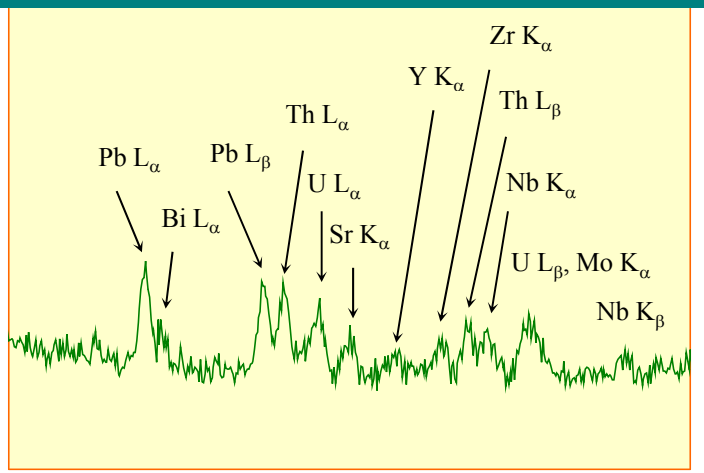
Procedure of X-ray fluorescence Analysis (XRF)

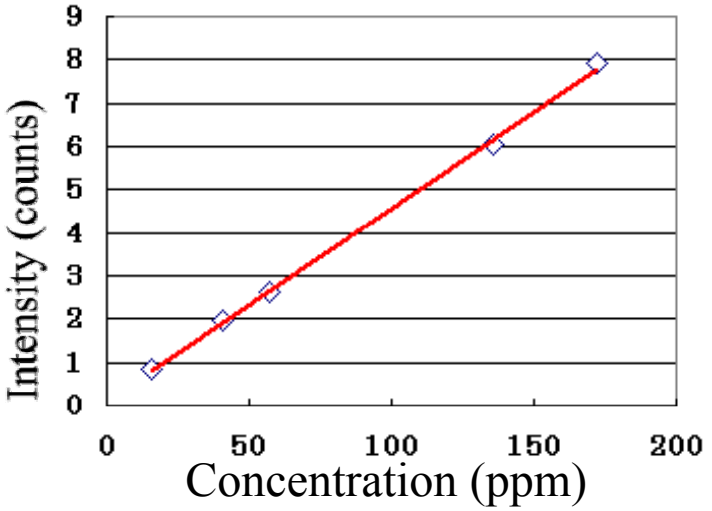
1. Check the chemical composition for samples
   ・・・Qualitative Analysis

2. Select the best condition for XRF analyses
   Combination of X-ray source, Detector, measurement time, etc.

3. Make calibration curve from standards

4. Calculate elemental concentration for the sample from the peak intensity
   ・・・ Quantitative Analysis



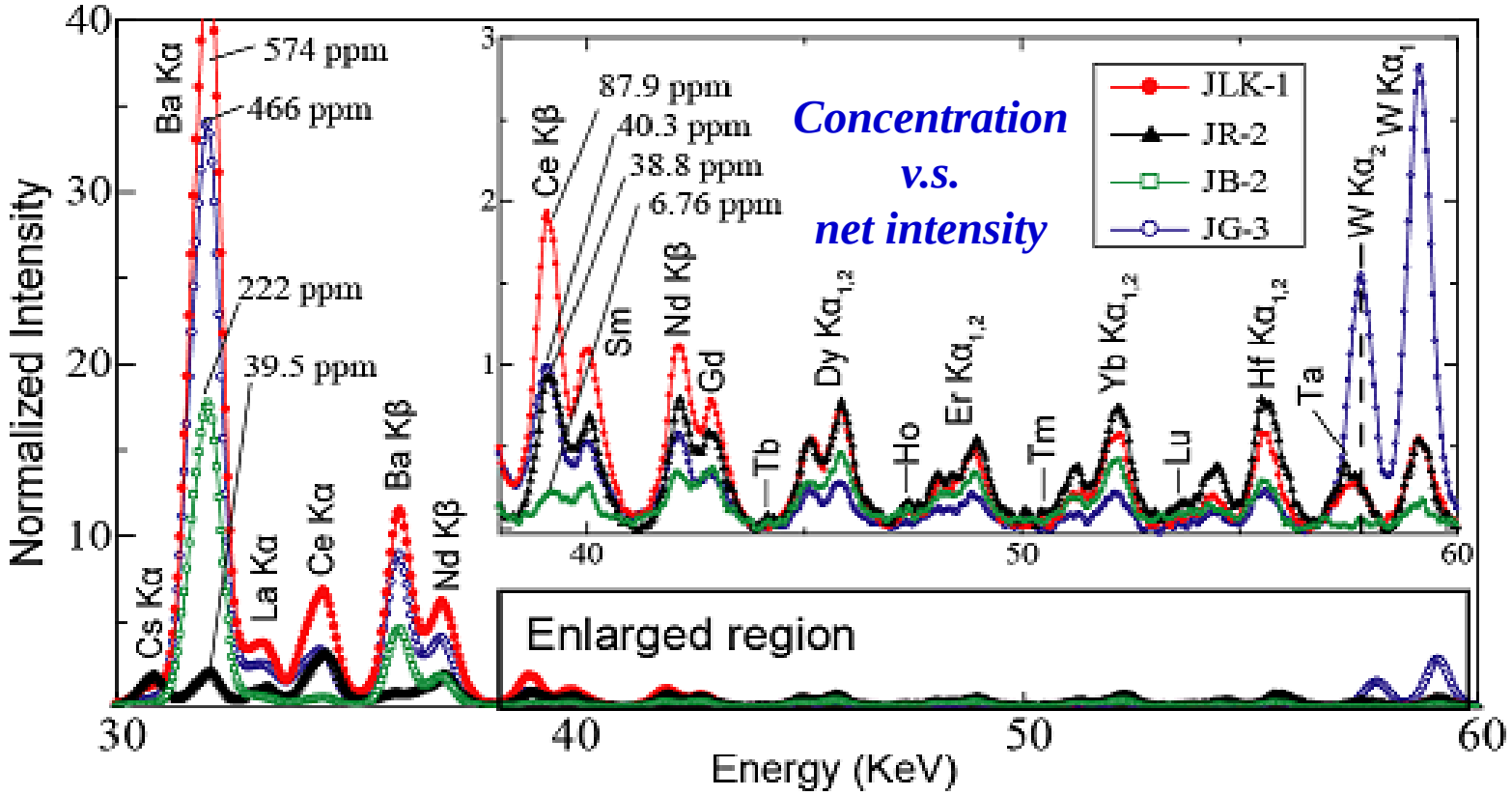


Calibration Curve for Cd

R_2=0.9996, LLD=3.5 (ppm)

Quantitative analysis of HE-SR-XRF: correlation between peak intensities and elements' concentration

HE-SR-XRF spectrum of various reference rock powders, JLK-1, JR-2, JB-2 and JG-3

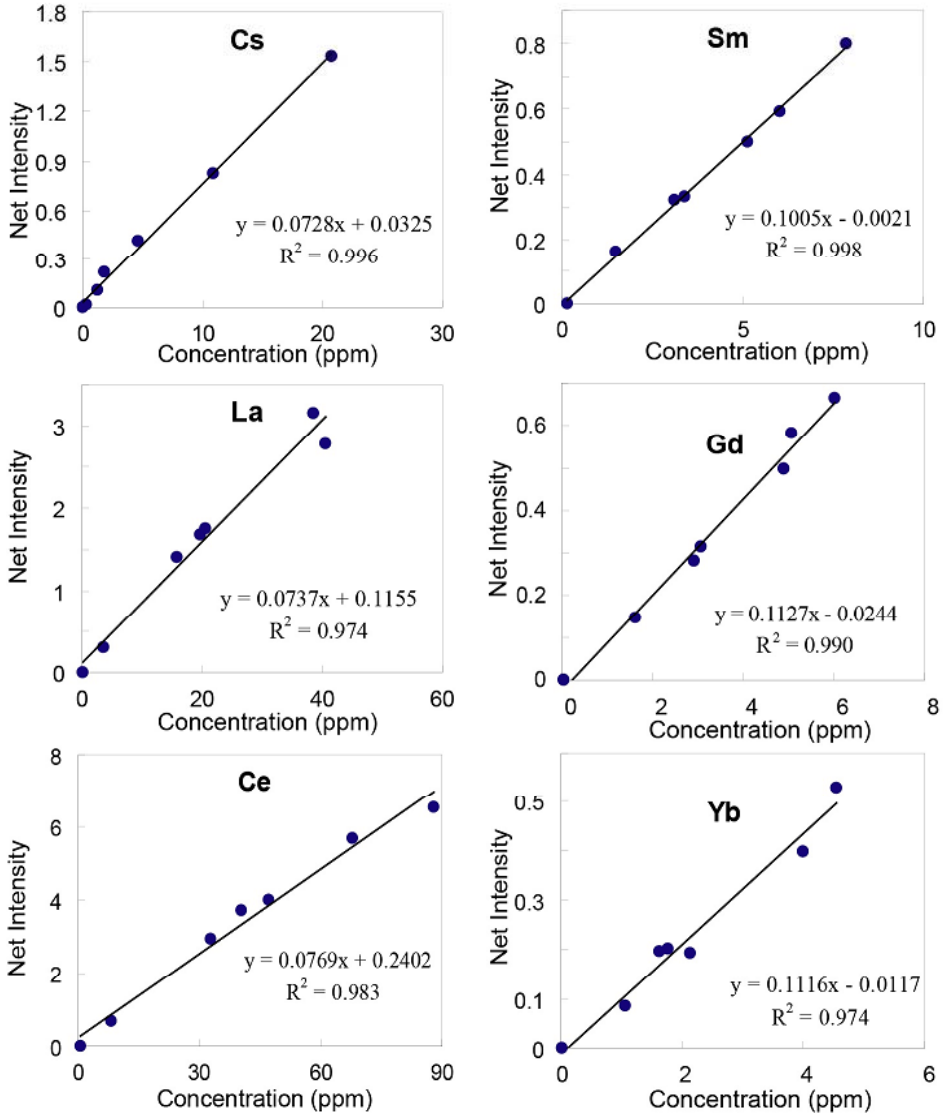


●Energy region between 30 ~ 60 keV: Lowest background, suitable for quantitative analysis for the background can be subtracted accurately.

●Good correlation between the intensity and concentration of the elements

Quantitative analysis by HE-SR-XRF: calibration curve method

Calibration curves: 8 rock reference samples

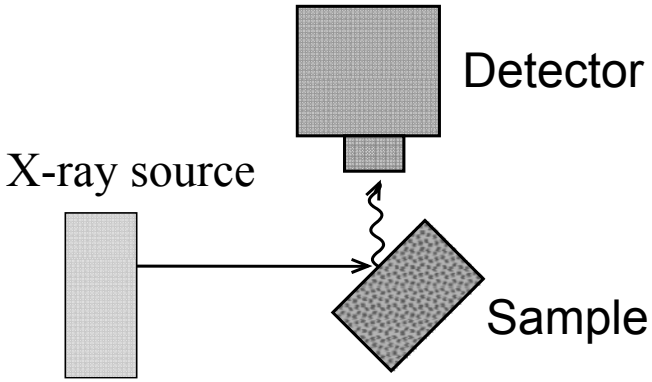


Comparison of HE-SR-XRF results with certified reference value of JR-2

Elements	Concentration/ppm		R^2 values
	HE-SR-XRF	Certified values	
Cs	24.60	25.00	0.996
La	12.71	16.30	0.974
Ce	35.78	38.80	0.983
Nd	18.24	20.40	0.989
Sm	4.84	5.63	0.998
Gd	5.39	5.83	0.990
Dy	7.17	6.63	0.970
Yb	5.65	5.33	0.974

- calibration curves :**Good linearity** with high coefficient of determination (R^2)
- Fair agreement with the certified value of JR-2

Application fields for XRF analyses



Samples:

- Solid, Liquid, and/or Gas
- Crystal and/or Amorphous
- Organic and/or Inorganic
- Non-destructive
- Living sample, Archeological sample

- **Oil**
- **Industrial Waste**
- **Water**
- **Food**
- **Soil, Rock, Mineral**
- **Fly Ash**
- **Glass, Ceramics**
- **Thin film**
- **Courting material**
- **Metal, Jewel**
- **Ink, dye, Cosmetics**
- **Polymer**
- **Medical and Biological**

etc.

- **Elemental Analyses for matrices and impurities**
- **Identification**
- **Forensic analyses**
- **Archeology**

etc.

① How to measure Fluorescence X-ray
② How to select the X-ray source for Incident X-ray
③ How to improve the Signal / Background ratio

Advanced properties of SR for XRF and XAFS analyses

1) Highly brilliant and highly collimated parallel beam

high intensity → signal enhancement, small sample

high collimation → microbeam analysis, total reflection analysis

2) Linear polarization → background reduction

3) White (Bending Magnet) or quasi monochromatic (Undulator) X-rays

monochromatic X-rays → background reduction

continuous energy scanning → XAFS

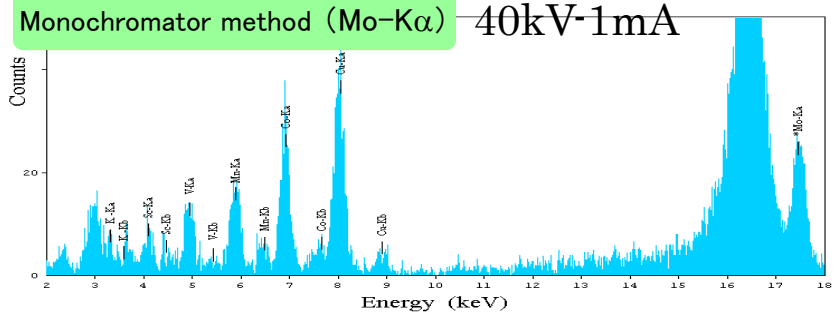
energy tunability → XRF : element selective excitation

The Lower limit of Detection of XRF analysis

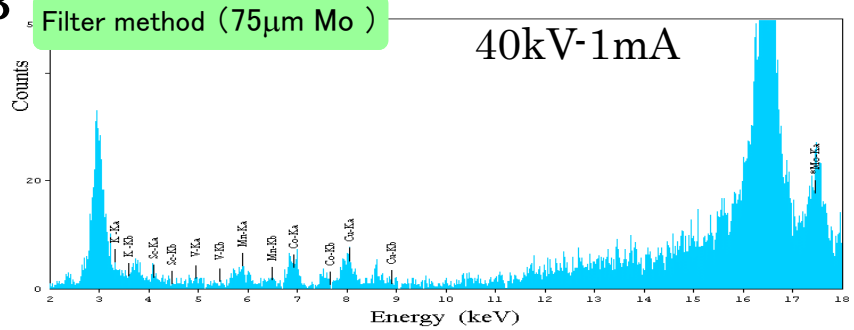
Sample : Cu, Co, Mn, V, Sc, K 0.2ppm
50ml dried up on the holder
Sample holder : Polyethylene 5mm film
X-ray tube : Mo
Measurement time : 200sec

	A	B	C
P.I. (cps)	4.53	0.57	0.57
B.G (cps)	0.08	0.06	2.99
P/B	56.6	9.5	0.2
LLD/ppb	2.65	18.2	129

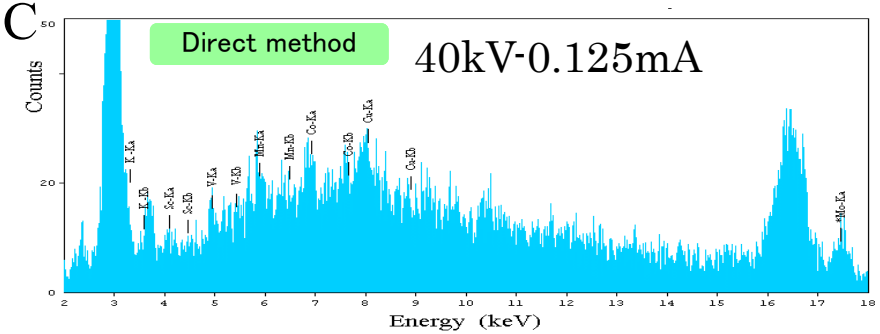
A Monochromator method (Mo-Kα) 40kV-1mA

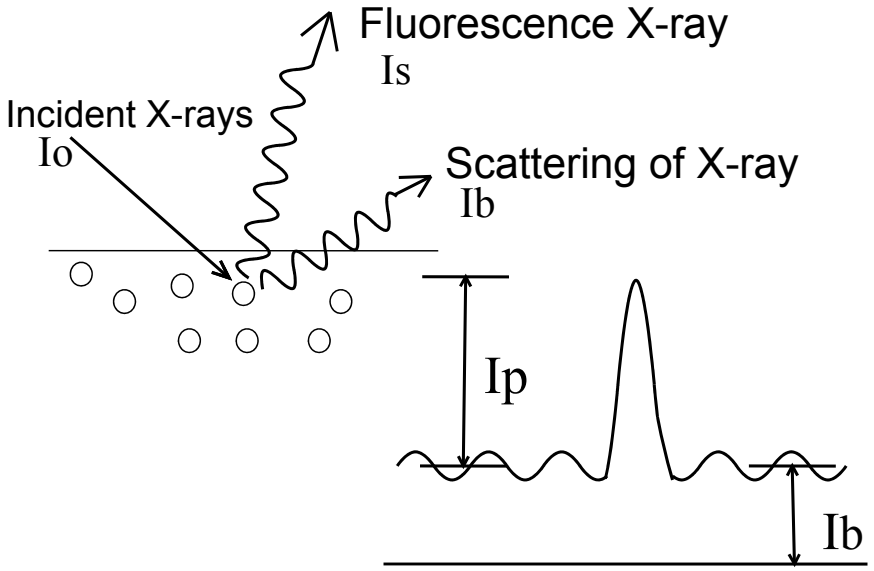


B Filter method (75μm Mo) 40kV-1mA



C Direct method 40kV-0.125mA





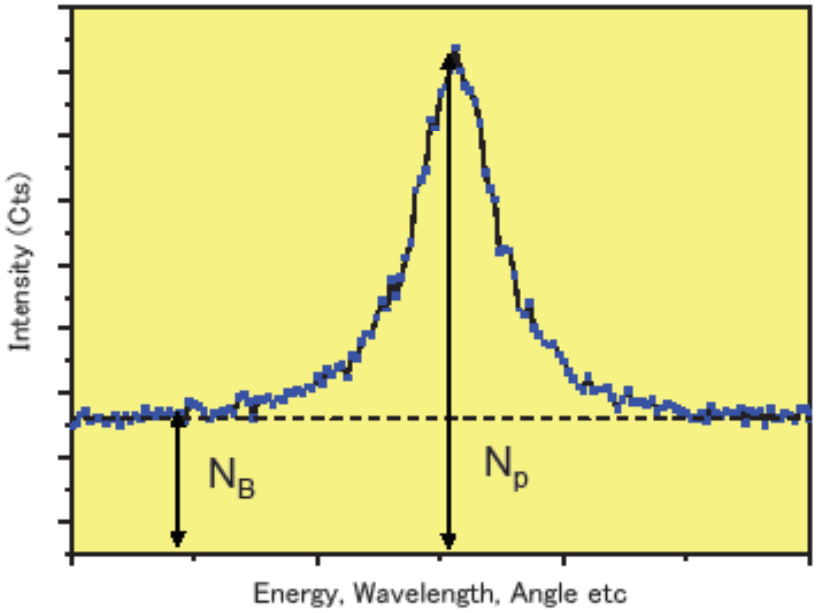
c: concentration of the elements
I_b: background area intensity
I_p: peak area intensity

$$\mathbf{LLD = 3/c \cdot (I_b/I_p)^{1/2}}$$

Improving Signal/Background ratio is most important points for XRF

Sensitivity of XRF analysis is determined by Np and N_B

XRF spectrum



Minimum detection limit (MDL)

$$k = \frac{3C\sqrt{N_B}}{N_p - N_B}$$

Minimum quantification limit (MQL) ($2k$ ~$3.3k$)

Np increase = Signal increase

→ High brilliance source

High flux source

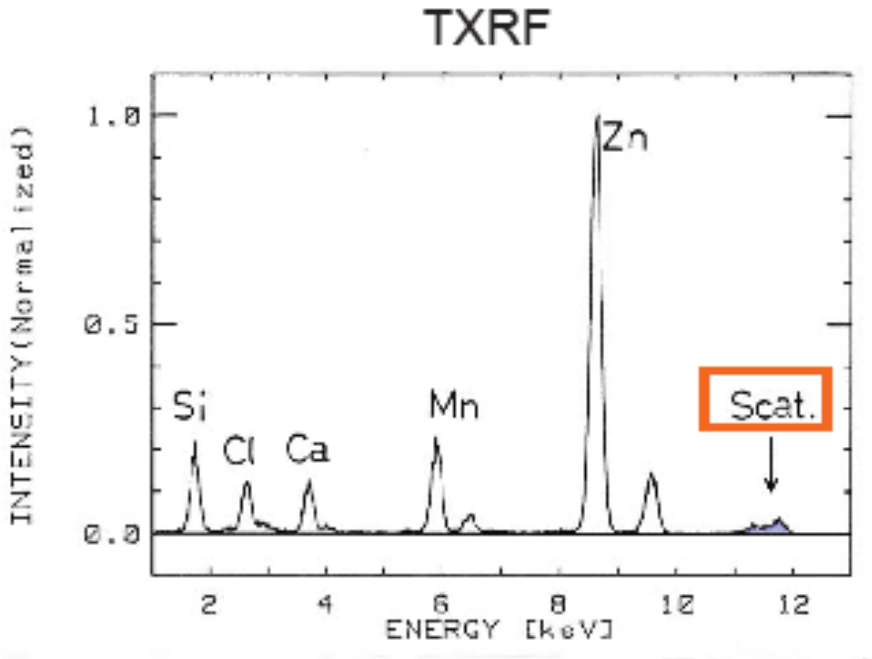
N_B decrease →

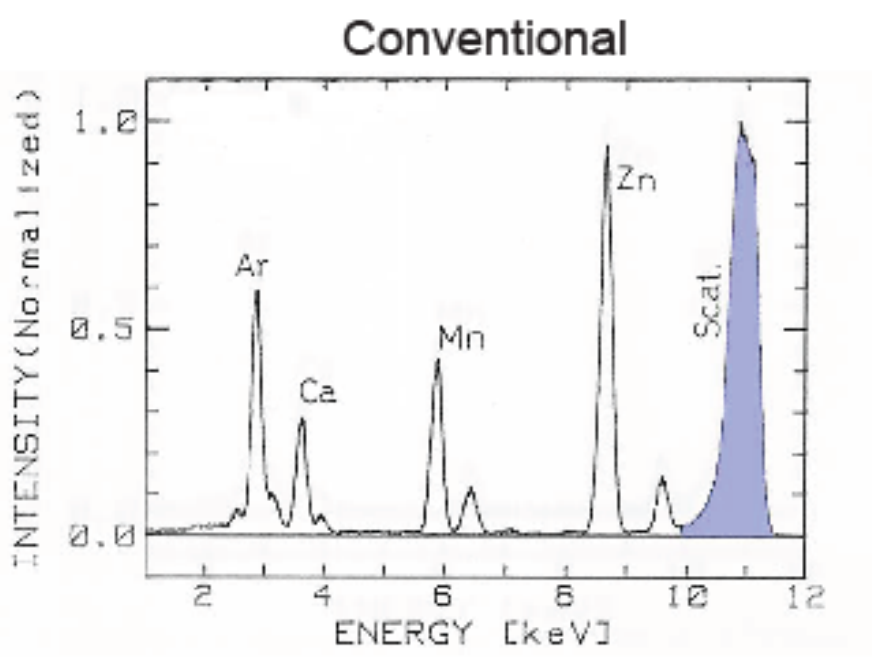
Monochromatic Excitation

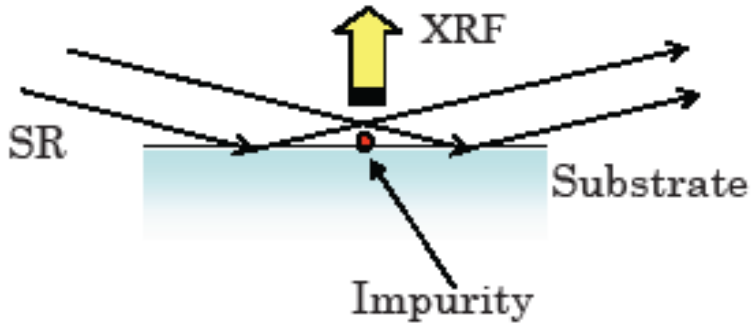
WDX

Total reflection

Total-Reflection X-ray fluorescence analysis
Ultra trace element analysis (TXRF)







Si wafer

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

Advanced properties of SR for XRF and XAFS analyses

1) Highly Brilliant and Highly collimated parallel beam

high intensity → signal enhancement, small sample

high collimation → microbeam analysis, total reflection analysis

2) Linear polarization → background reduction

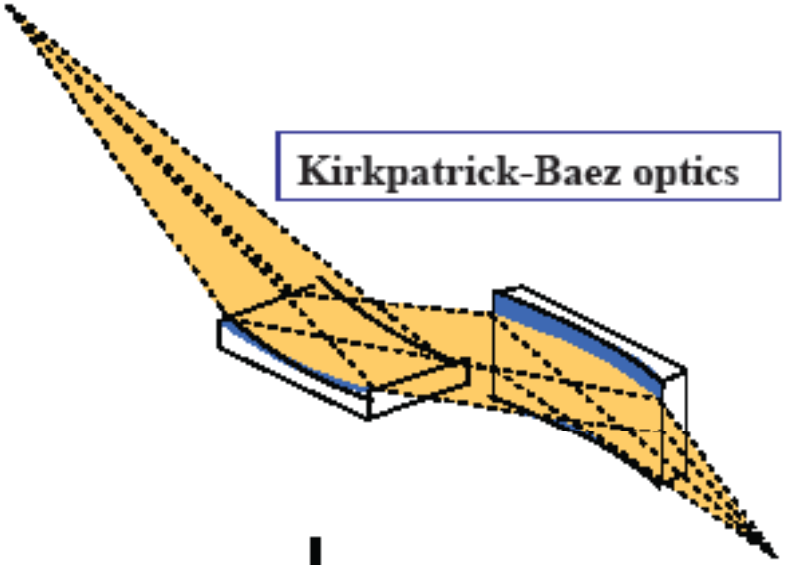
3) White (Bending Magnet) or quasi monochromatic (Undulator) X-rays

monochromatic X-rays → background reduction

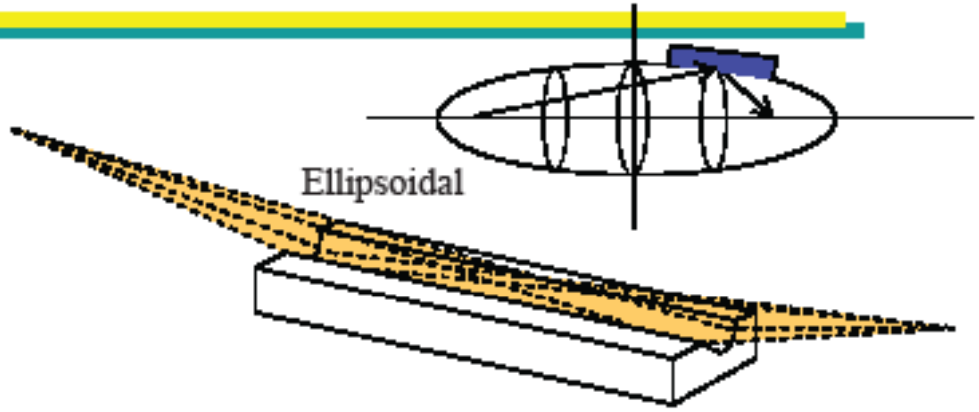
continuous energy scanning → XAFS

energy tunability (high energy) → XRF : element selective excitation

X-ray microbeam Optics

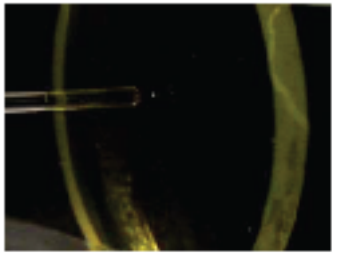


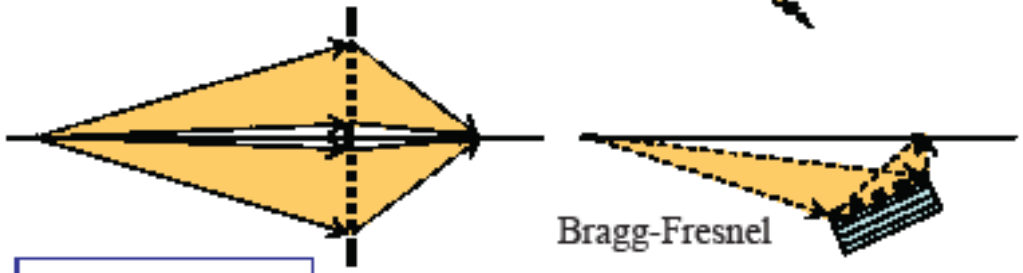
Kirkpatrick-Baez optics



Ellipsoidal

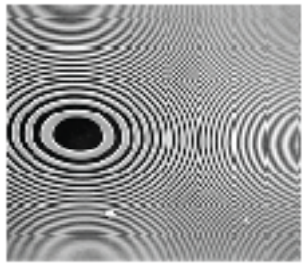
Single tapered capillary



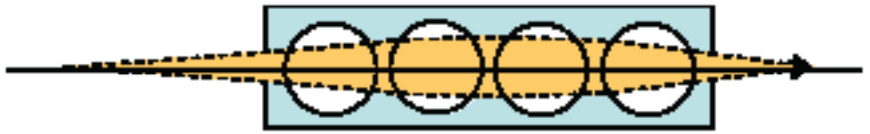


Bragg-Fresnel

Fresnel zone optics



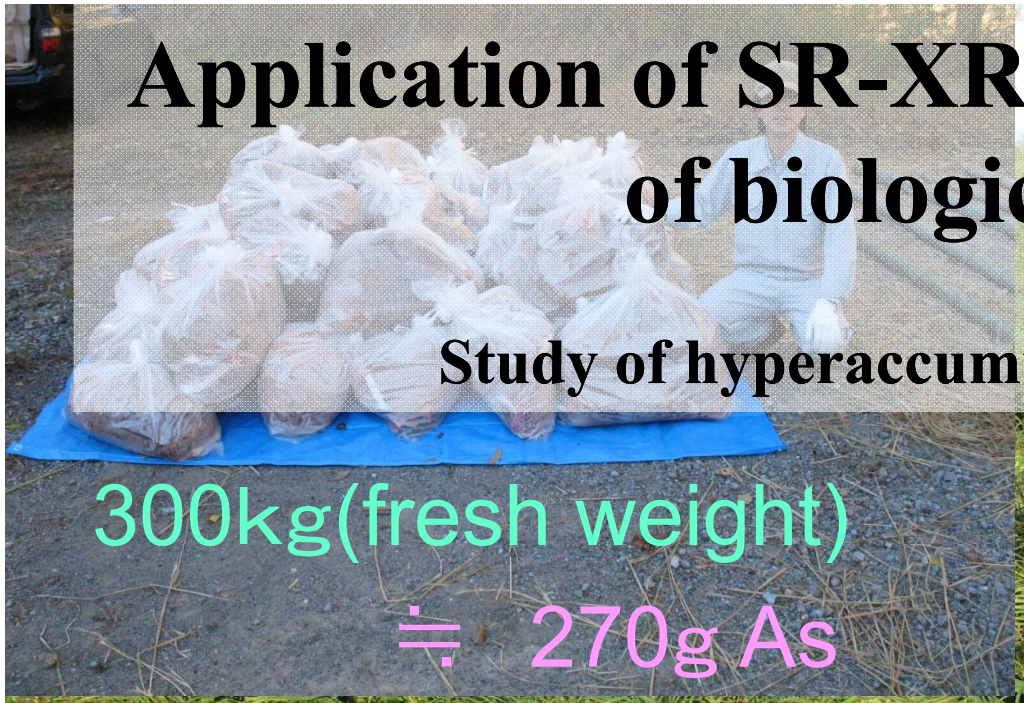
Compound refractive optics



Beam size : mm ~ nm scale

Application of SR-XRF to in vivo analysis of biological sample

Study of hyperaccumulator plants of As



300kg(fresh weight)

≒ 270g As

A. Hokura, R. Onuma, Y. Terada, N. Kitajima,
T. Abe, H. Saito, S. Yoshida and I. Nakai

Journal of Analytical Atomic Spectrometry, 21, 321-328 (2006)

Chinese brake fern (*Pteris vittata* L.)

As: *ca.* 22,000 μg /g dry weight

Phytoremediation

plant　　remediate

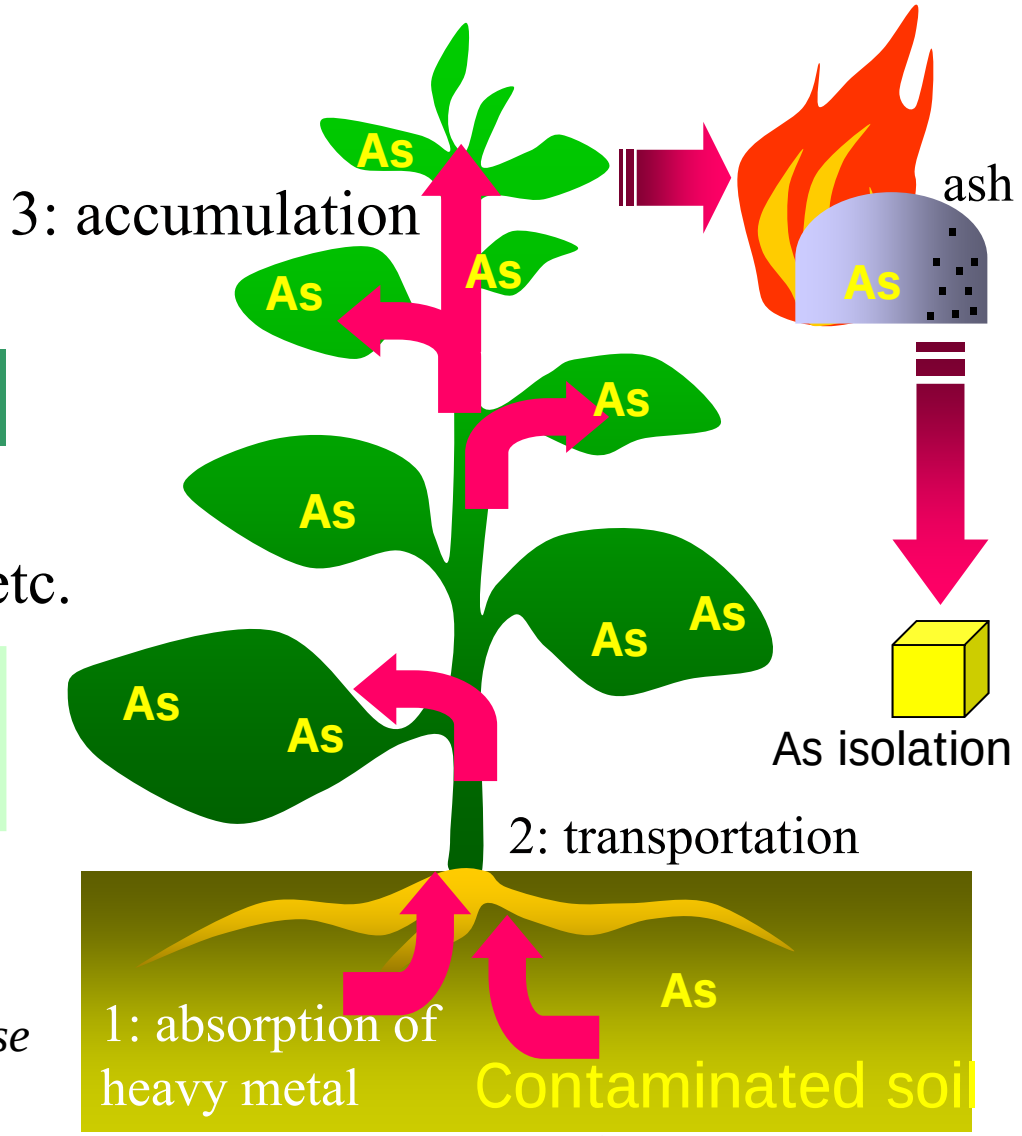
Green technology by plant

Merit: no damage, low cost
preservation of surface, etc.

Some specific kinds of plants are known to be heavy metal hyperaccumulator

Element	conc./ ppm	plant
As[*1]	**22,630**	*Pteris vittata L.*
Cd	**11,000**	*Athyrium yokoscense*
Pb	**34,500**	*Brassica juncea*

*1　L. Q. Ma, et al., *Nature*, (2001) , **409**, 579.



Application of SR X-ray analyses

- **μ･Two dimensional multi-element nondestructive analysis in cell level**
  →XRF imaging

- **Chemical state analysis in cell level**
  → μ-XAFS

Cultivation of fern

arsenic-contaminated soil

As level in soil：481 μg g^{-1}dry

Term： ～ 3 weeks

Average As level ：～720 μg /gdry

culture medium containing As
(1 ppm 4days)

As level*

pinna：2800 - 4500 μg g^{-1}dry

midrib of a frond：84 - 250 μg /g dry

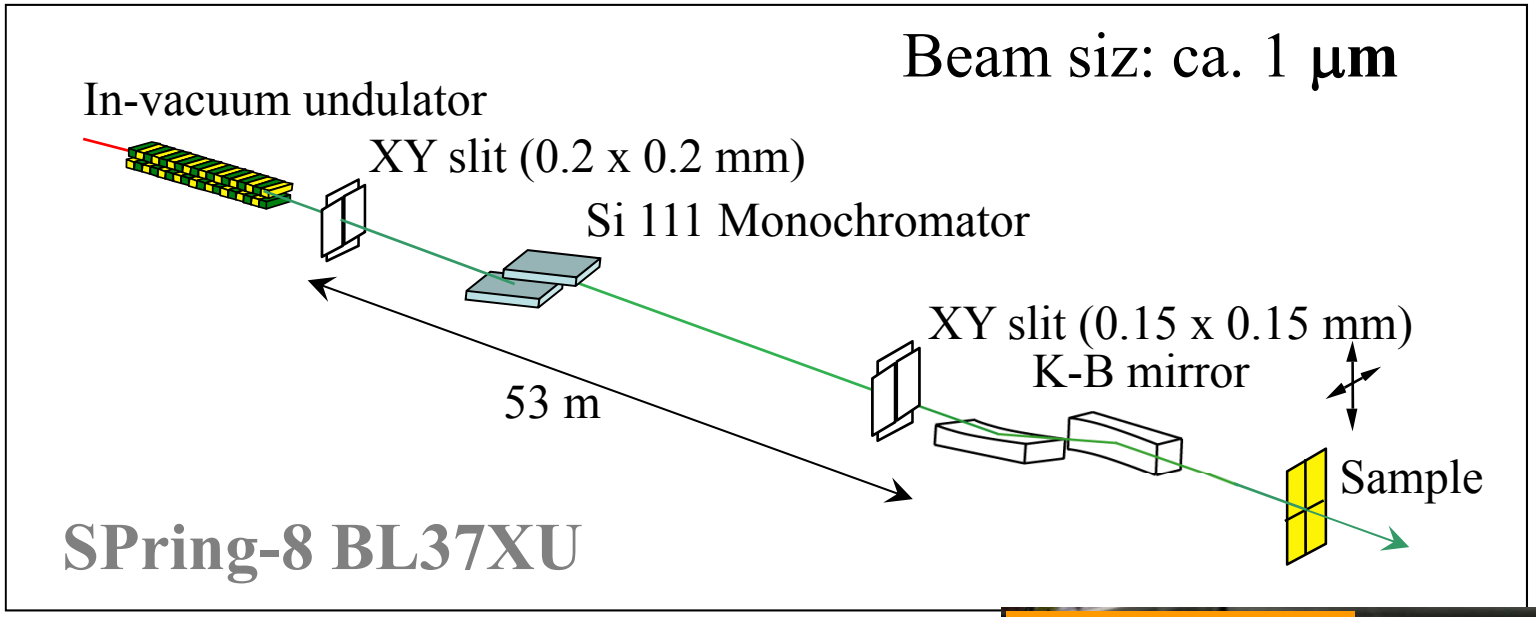
* Anal. By AAS

μ-XRF, μ-XANES

X-ray energy

As: 12.8keV

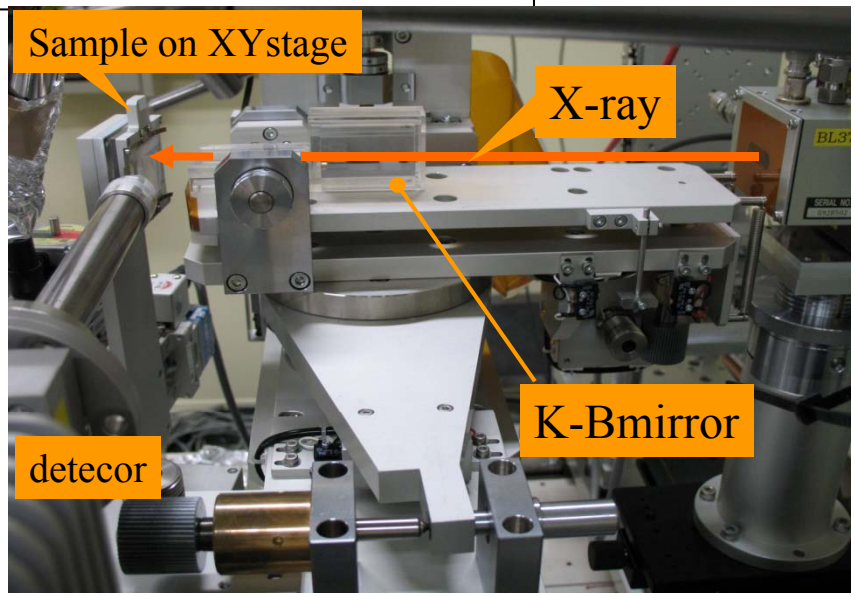
Cd: 37.0keV



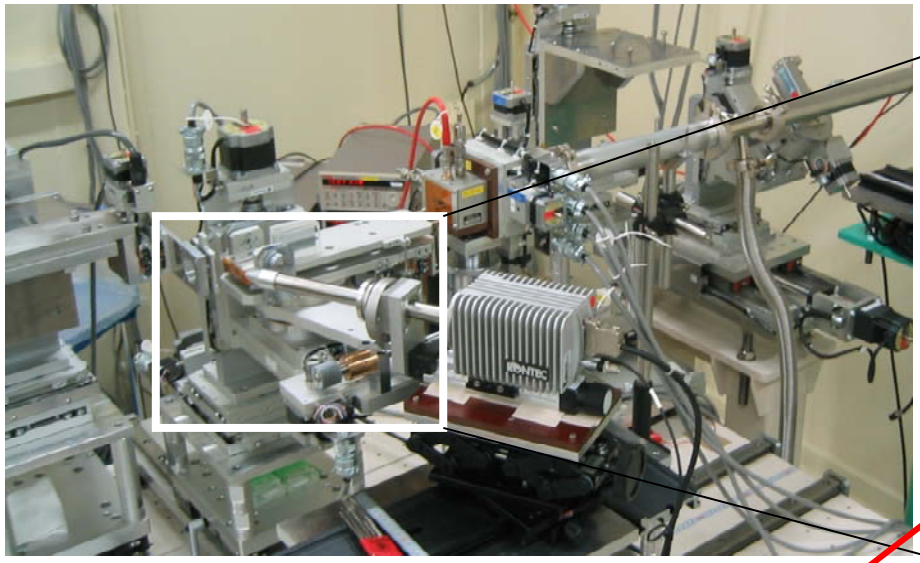
- BEAMLINE DESCRIPTION -
The light source : In-vacuum type undulator
(Period length : 32 mm, the number of period : 140)
Monochromator : Double-crystal monochromator
located 43 m from the source

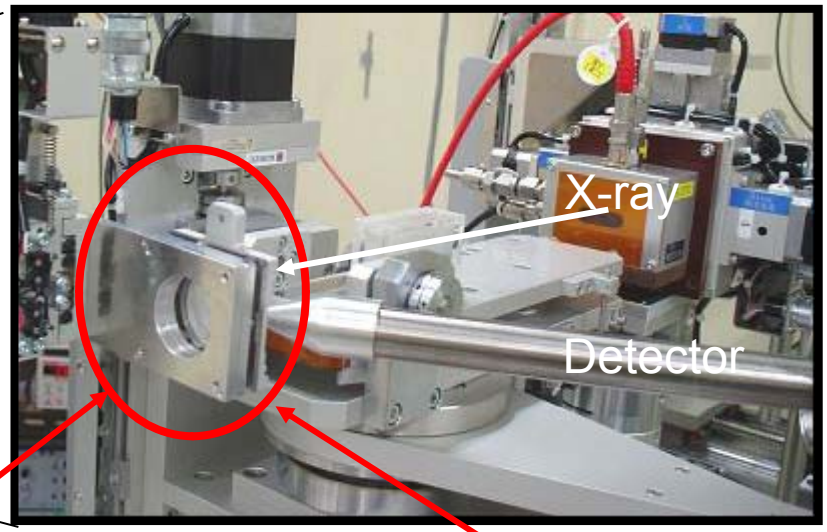
Table Details of focusing optics by K-B mirror

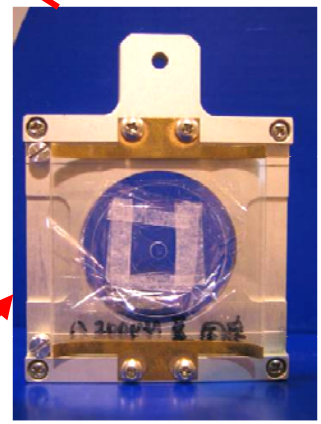
	37 keV[1]	12.8 keV
Material	fused quartz	fused quartz
Surface	platinum coated	platinum coated
Focal length (1st mirror)	250 mm	100 mm
(2nd mirror)	100 mm	50 mm
Average glancing angle	0.8 mrad	2.8 mrad

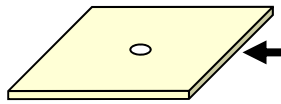


Instrument ~SPing-8 BL37XU~

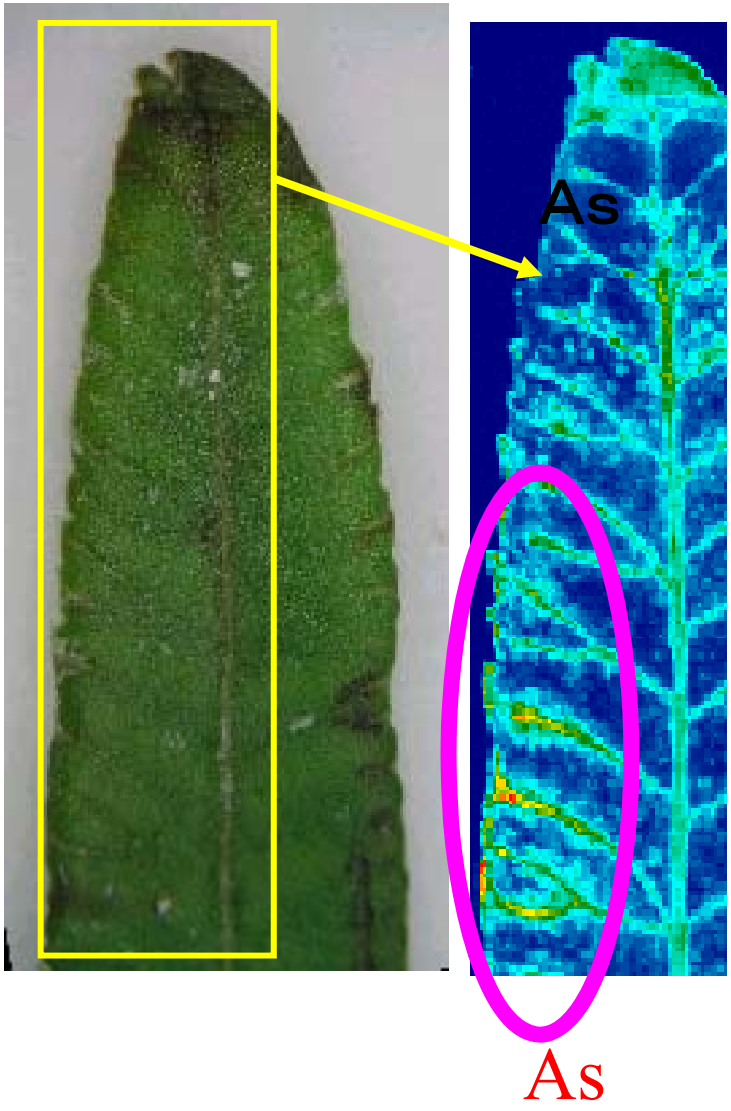


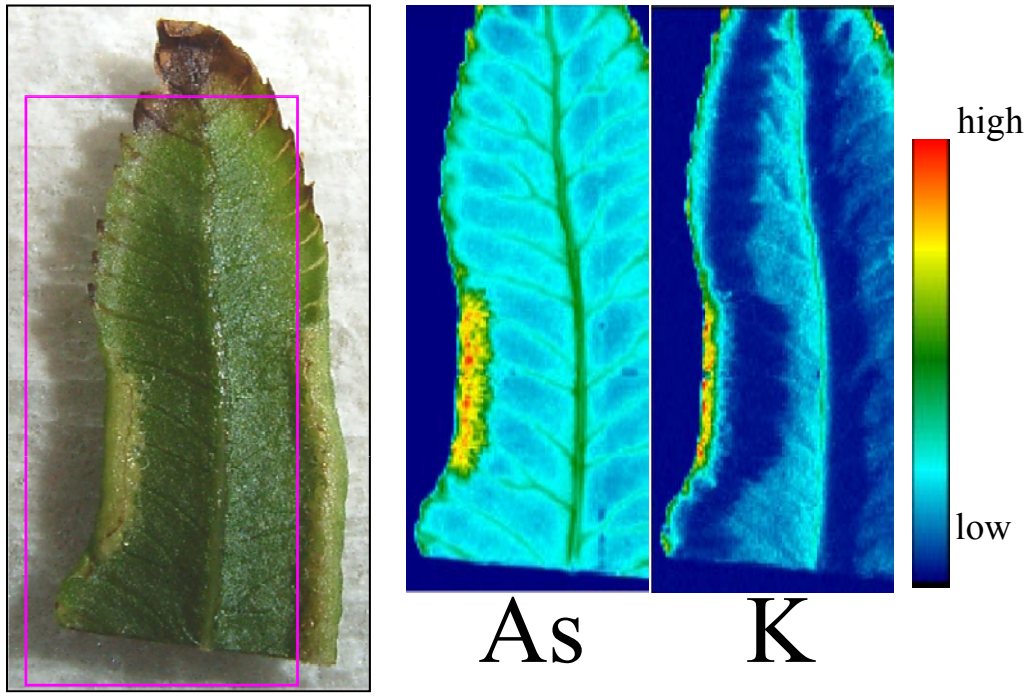


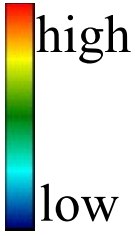




XRF imaging for As, K, and Ca of pinnae

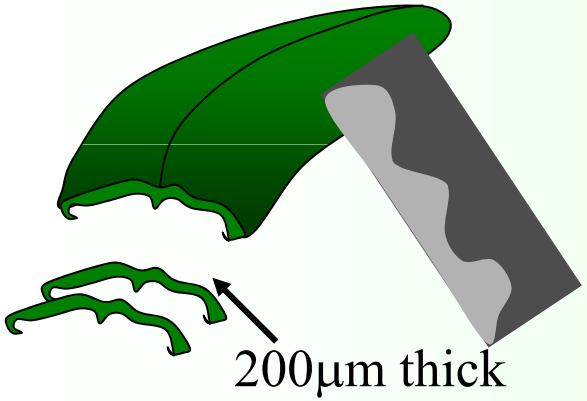




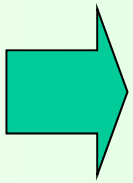


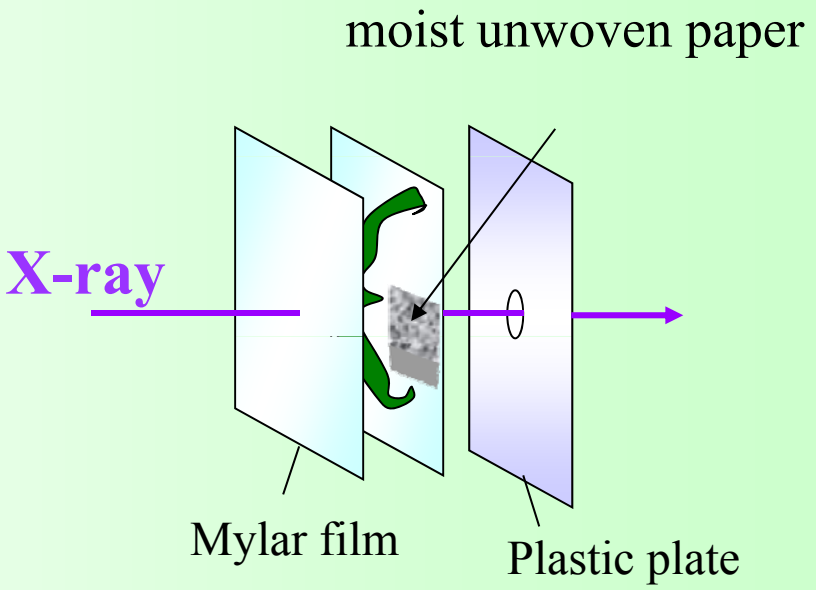
Accumulation of As at Fertile with spores along marginal parts

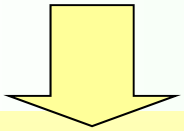
Sample preparation for microbeam analysis



vertical slicer
(Model HS-1, JASCO Co.)

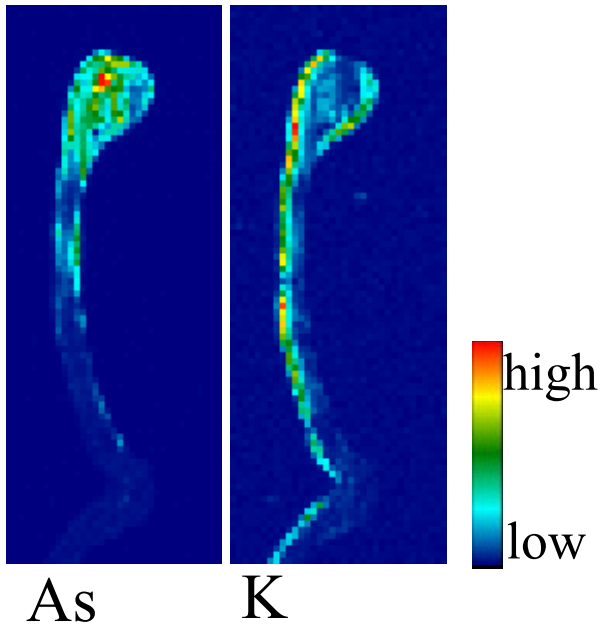


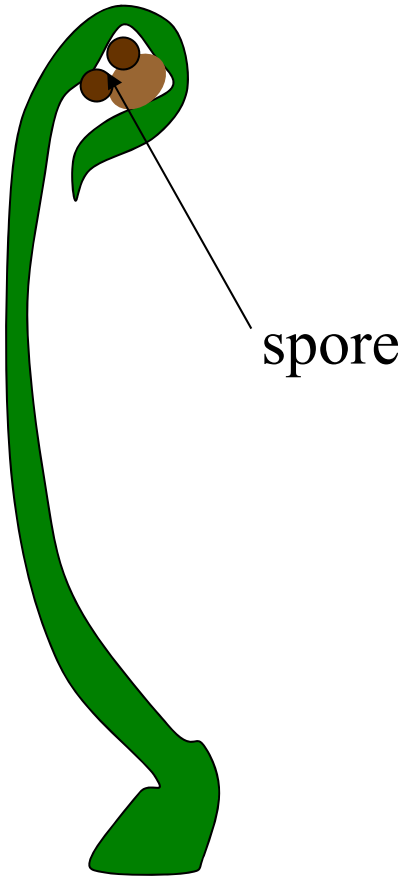




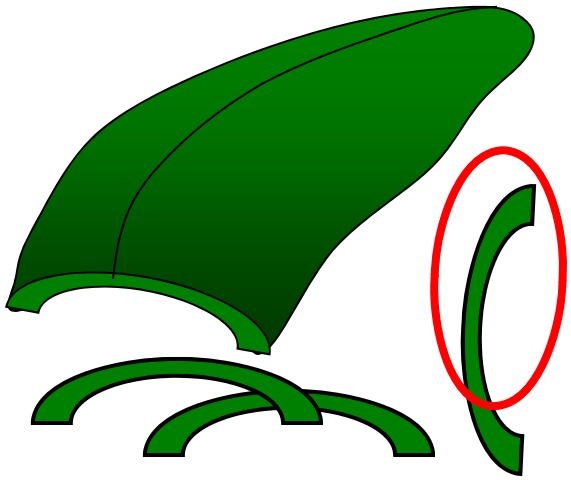
freeze dry of frozen

A section of pinna





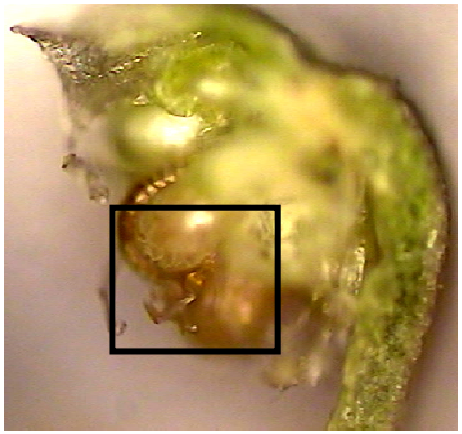
frond

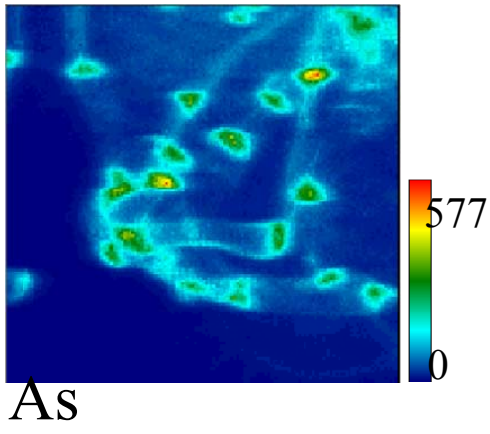


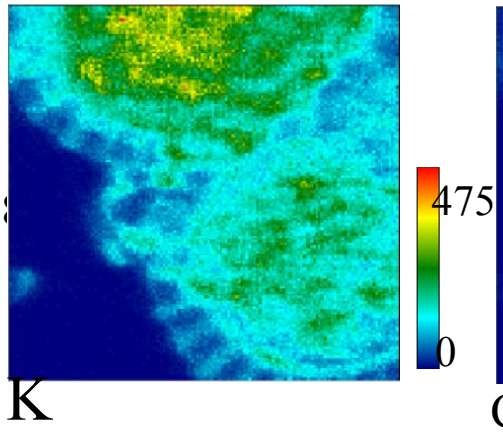
X-ray Energy : **14.999 keV**
Beam size : **50 μm × 50 μm**
Step number : **35 point × 90 point**
measurement time : **1 sec/point**

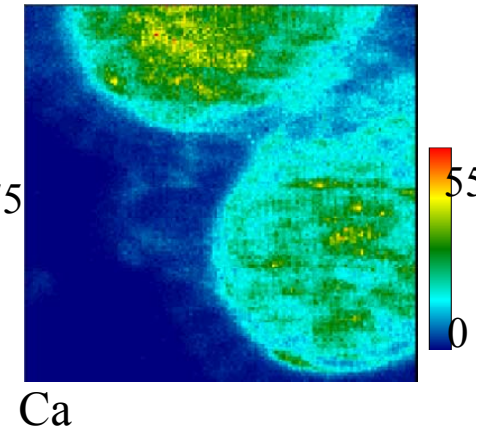
X-ray Energy : 12.8 keV
Beam size : 1.5 μm ×1.5 μm
Exposure time : 0.2 sec. / point
Point : 150 point ×150 point

μ－XRF imaging at SPring-8



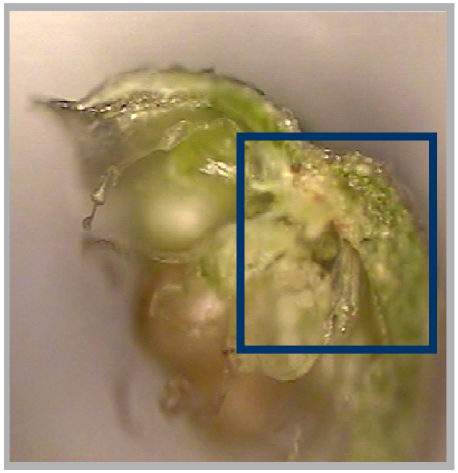


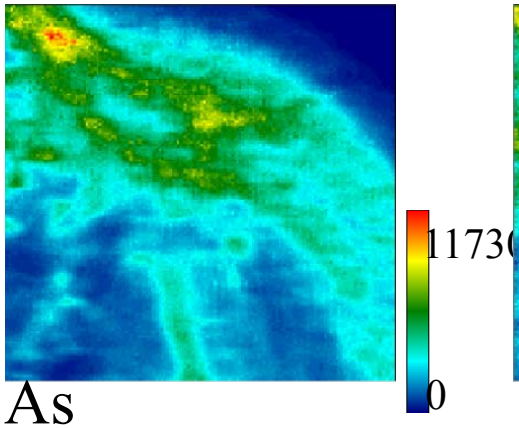


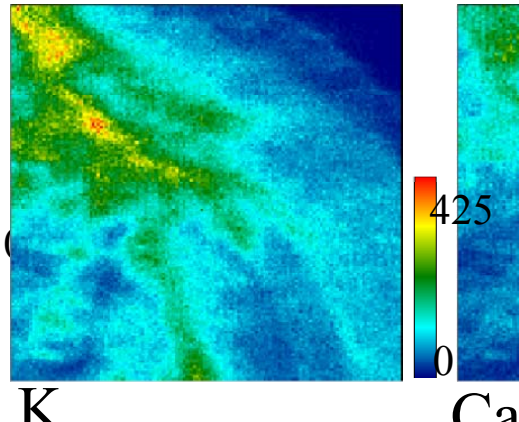


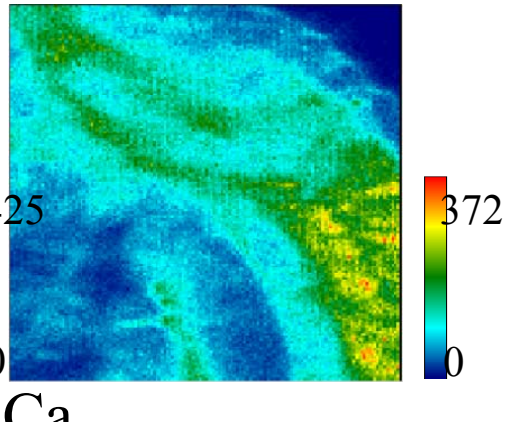
X-ray Energy : 12.8 keV
Beam size : 1.5 μm ×1.5 μm
Exposure time : 0.2 sec. / point
Point : 150 point ×150 point

As level is low at spore

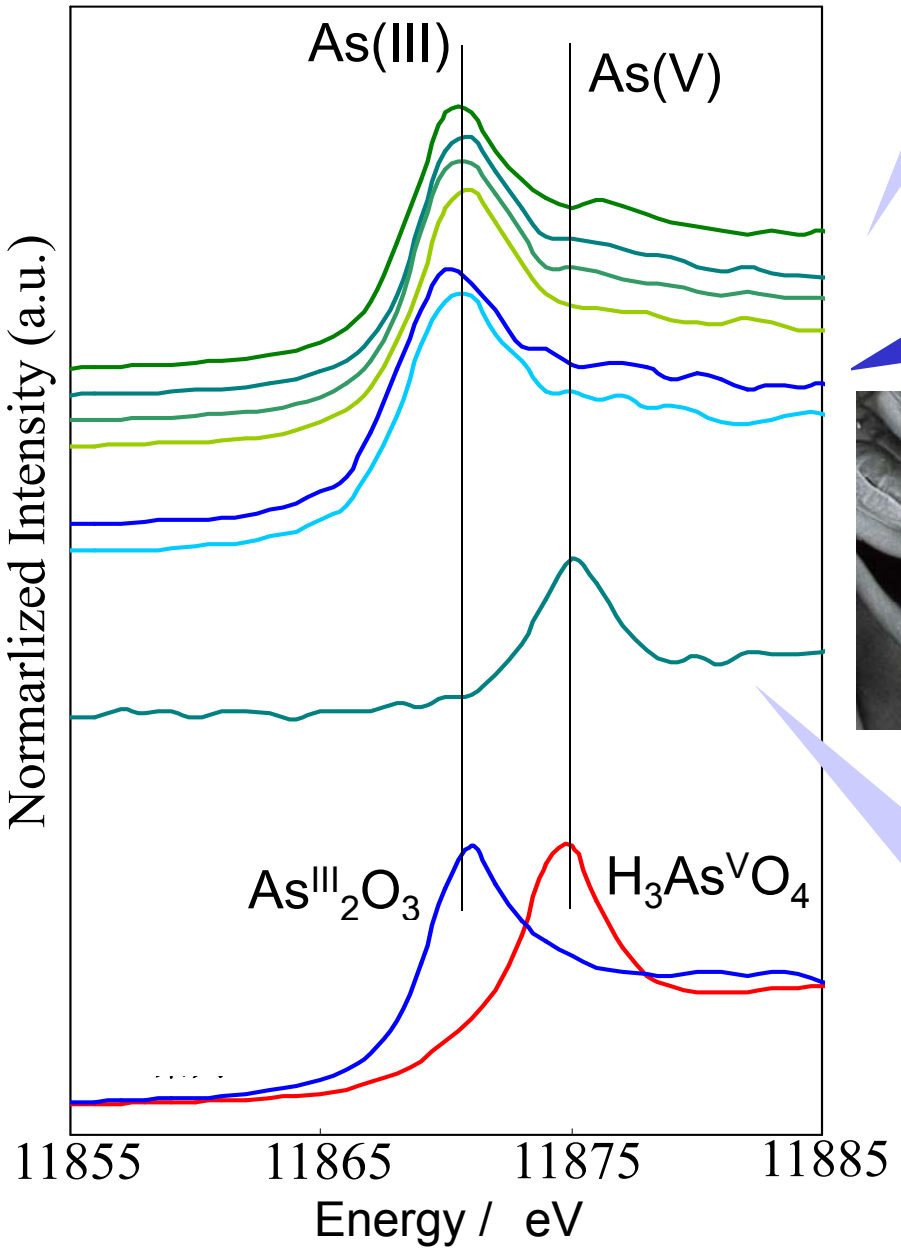


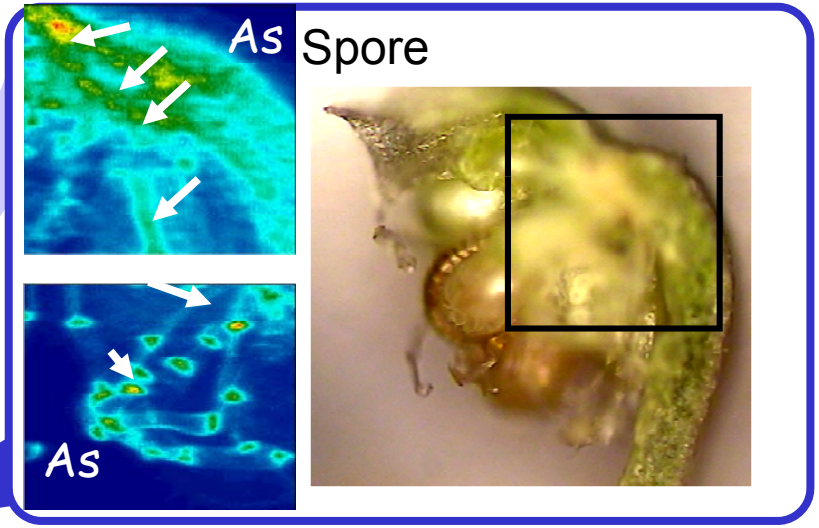


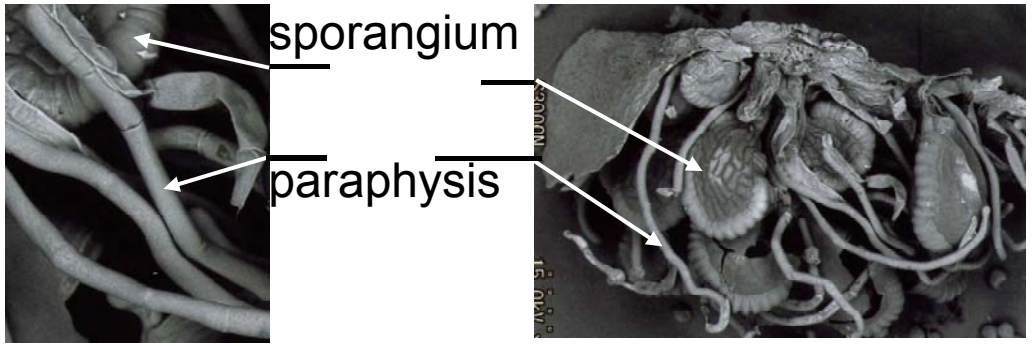




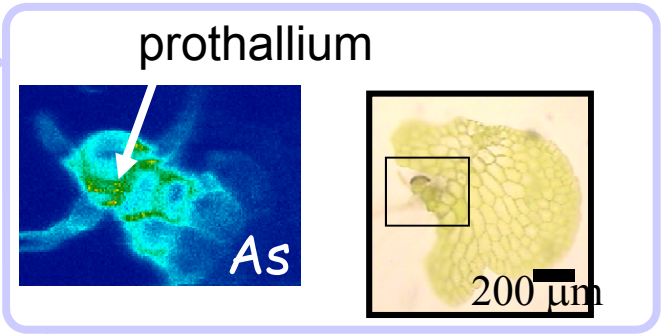
As K-dge XANES







As exits as As^{3+}



As(V)

Advanced properties of SR for XRF and XAFS analyses

1) Highly Brilliant and Highly collimated parallel beam

high intensity → signal enhancement, small sample

high collimation → microbeam analysis, total reflection analysis

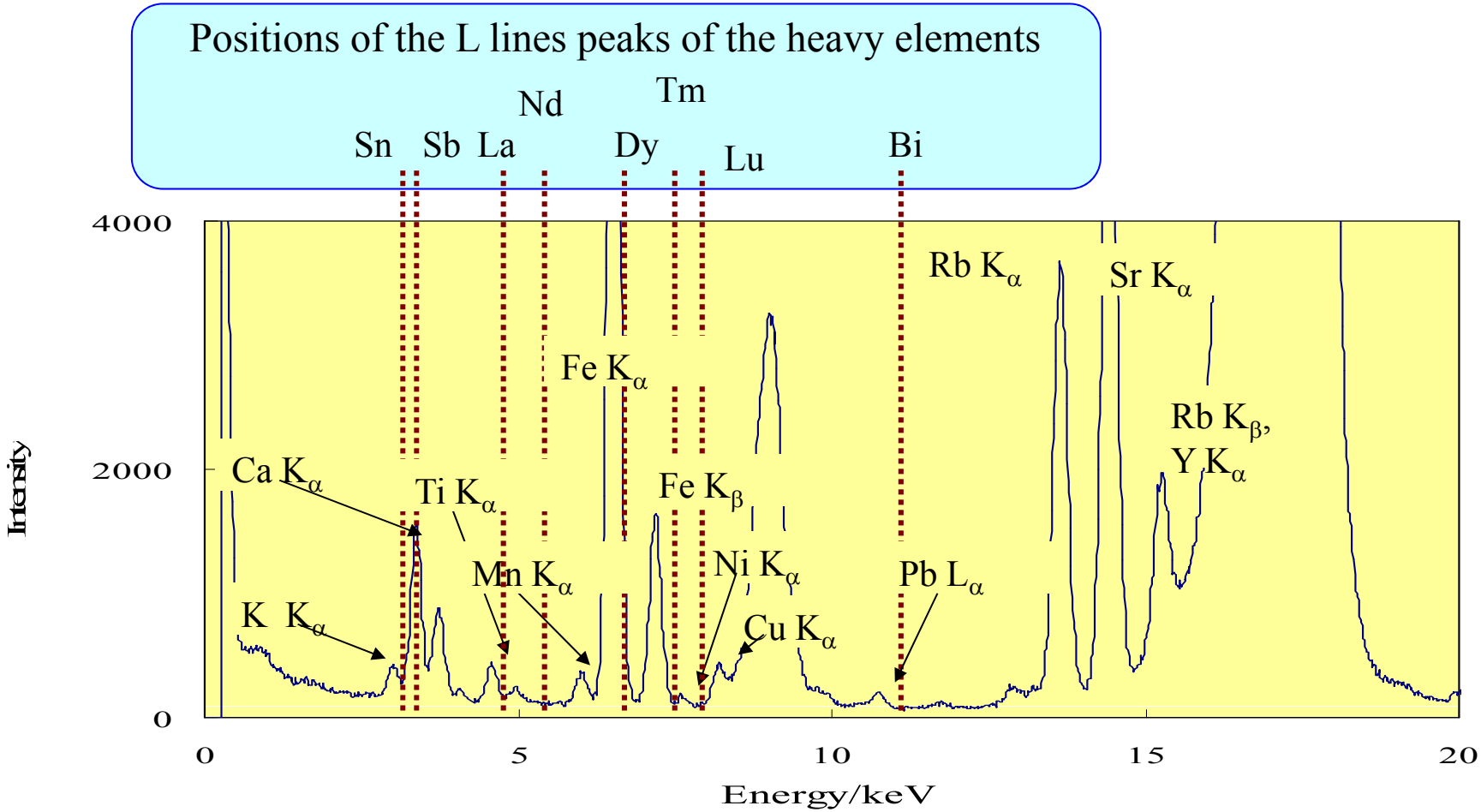
2) Linear polarization → background reduction

3) White (Bending Magnet) or quasi monochromatic (Undulator) X-rays

monochromatic X-rays → background reduction

continuous energy scanning → XAFS

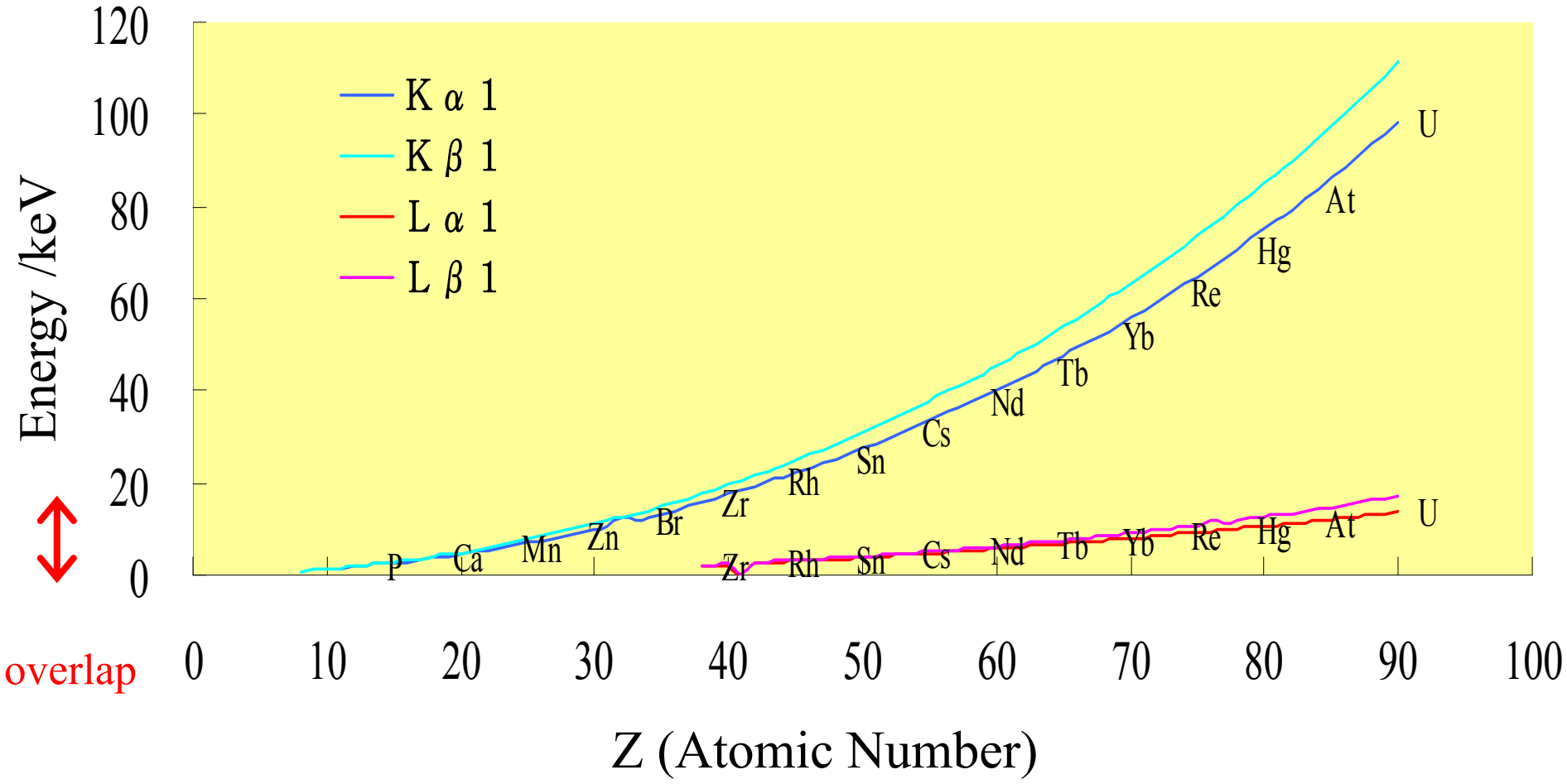
energy tunability (high energy) → XRF : element selective excitation



Problem of conventional XRF analysis (E<20 keV) →

Overlapping of heavy elements L lines with light elements K lines

Sample porcelain , Source : Mo Kα X-ray 40 kV-40 mA , time:1000sec



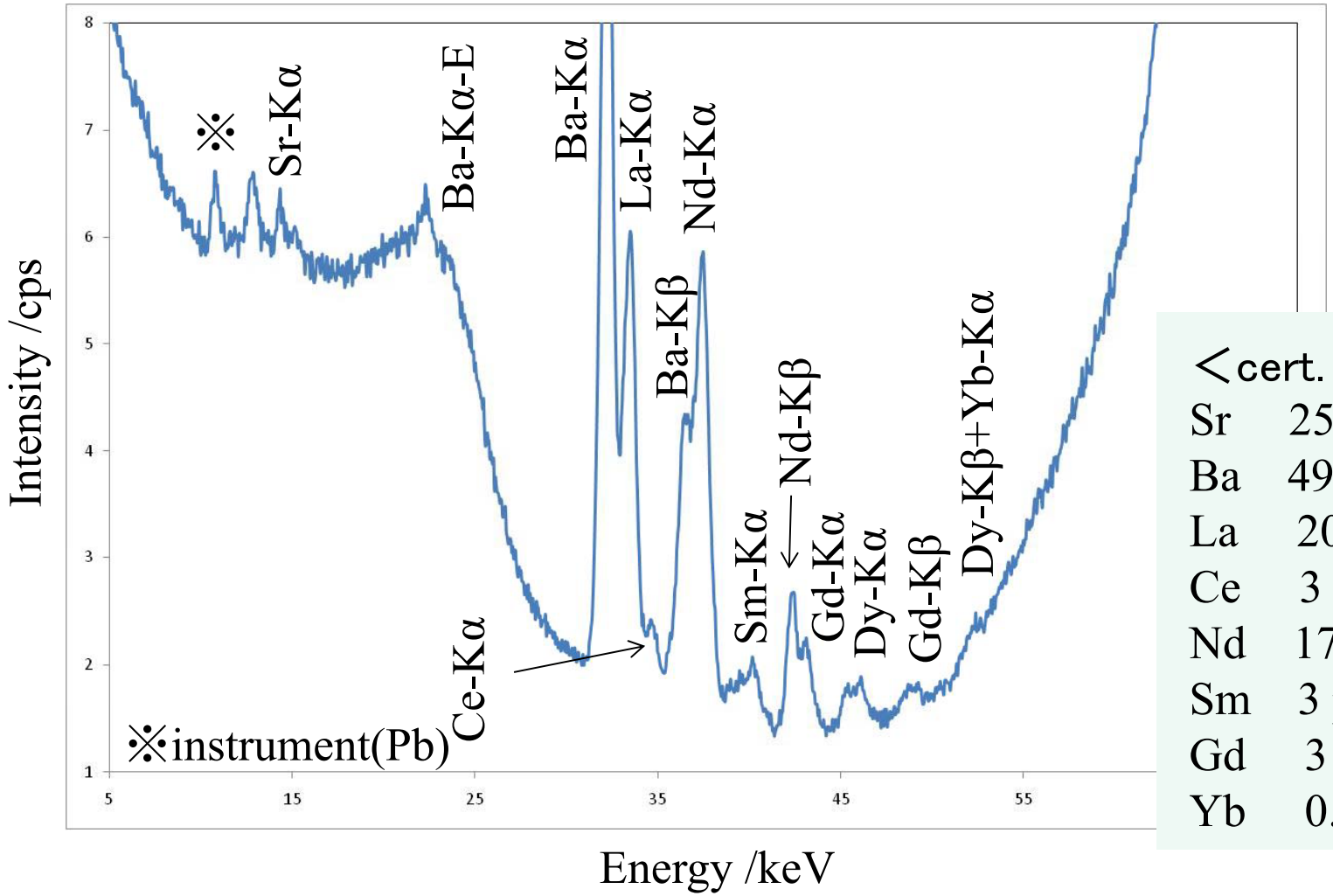
X-ray fluorescence energies of K & L lines v.s. atomic number

L lines for all elements < 20 keV

Above 20 keV → K line only

→suitable for analysis of elements heavier than Rh Kα (= 20.17 keV)

Apple leaves (NIST SRM 1515)

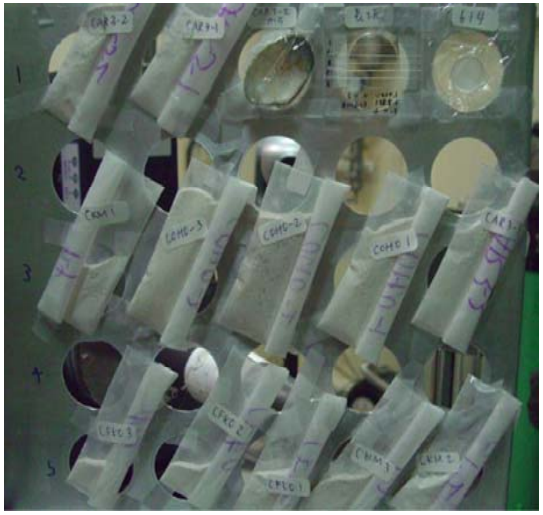


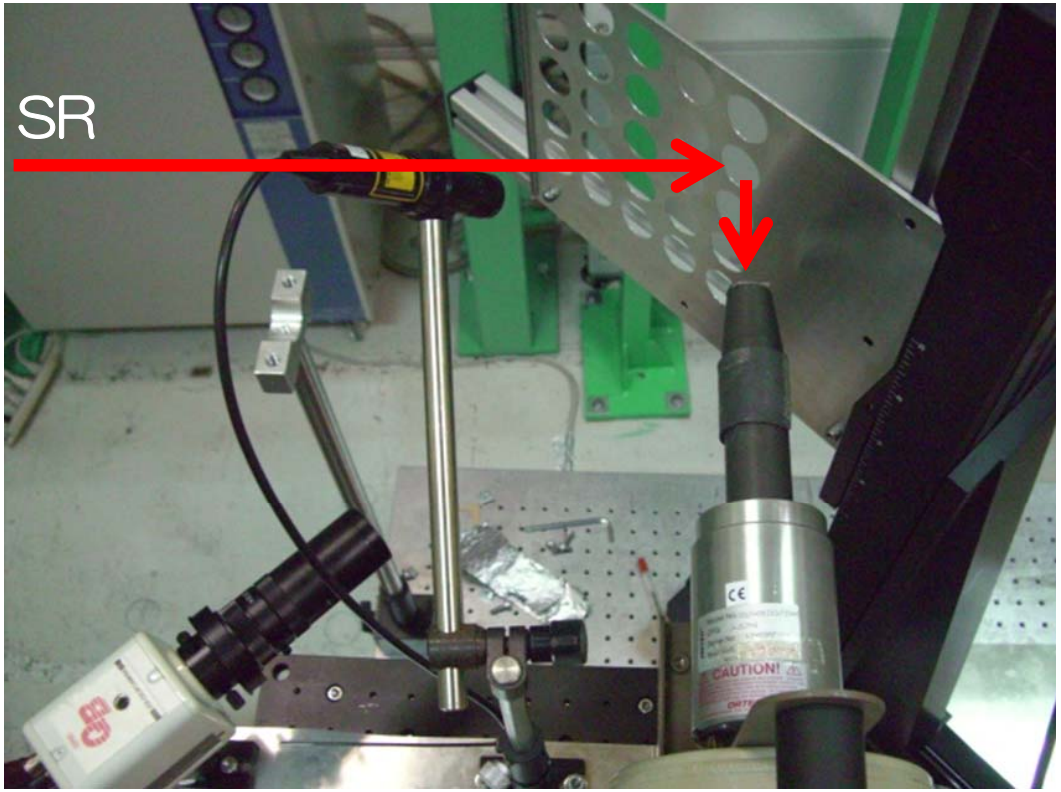
＜cert. v.＞

Sr	25 ppm
Ba	49 ppm
La	20 ppm
Ce	3 ppm
Nd	17 ppm
Sm	3 ppm
Gd	3 ppm
Yb	0.3 ppm

HE-SR-XRF at @SPring-8 BL08W

25 samples





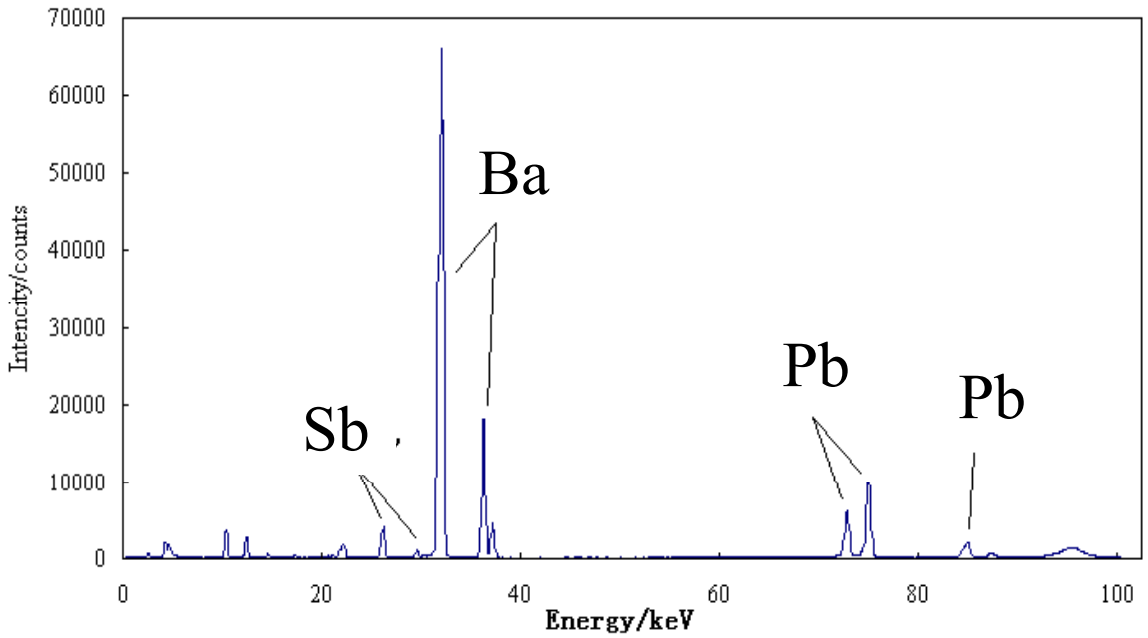
Detector

Slit 200 μm×200 μm、 meas. Time 600～2000 sec

Forensic application

S&W Gunshot Residue

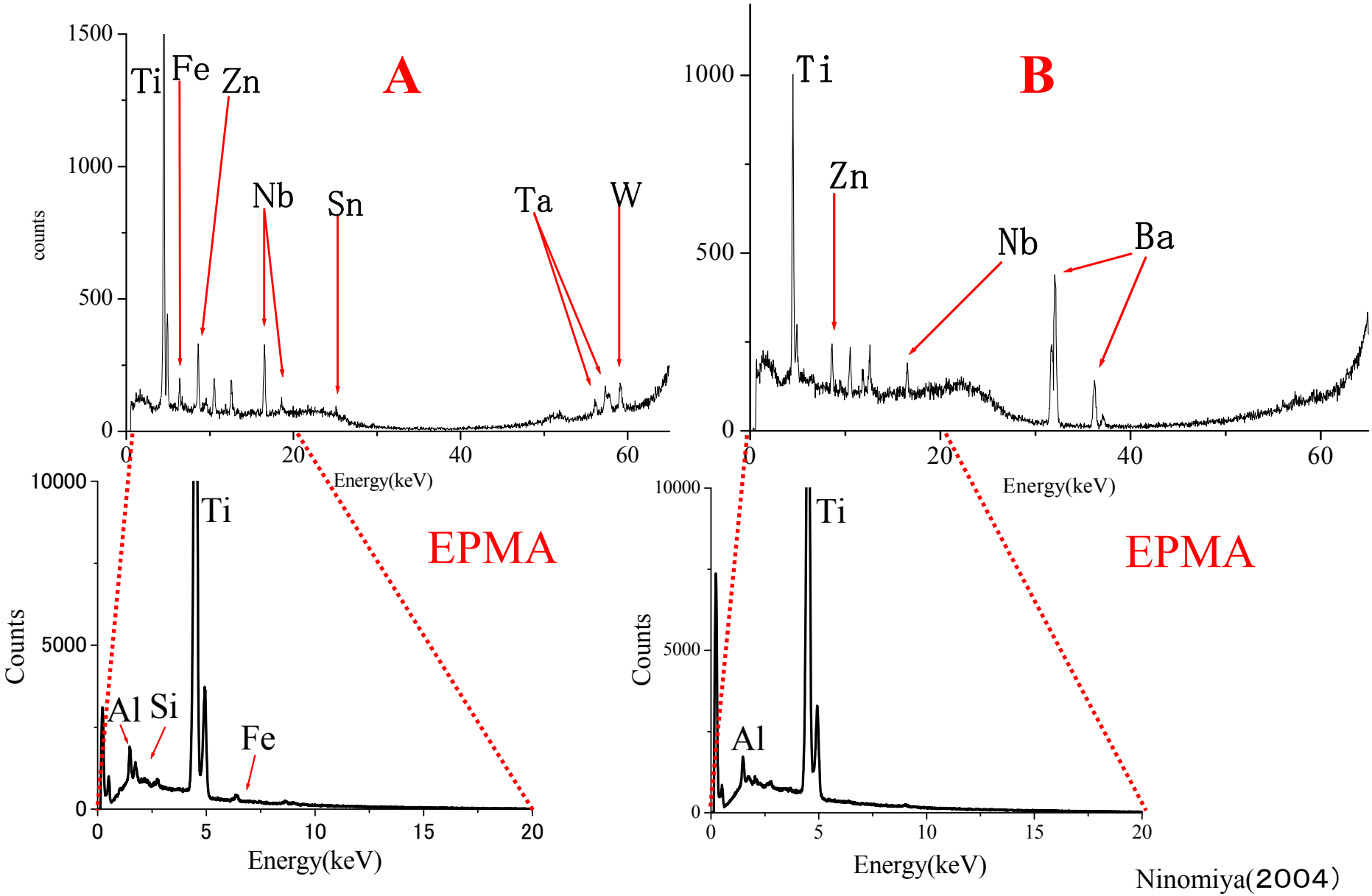
Characteristic element: Ba,Sb, Pb



SPring-8 BL08W

High energy SR-XRF characterization of trace gunshot residue

High energy XRF characterization of trace heavy elements in white car paints (paints A & B) compared with X-ray microprobe (bottom)



Ninomiya(2004)

Conclusion

Limitation of the SR-XRF

1. **Microbeam analysis**

   i) the thickness of the sample should be in the order of beam size

   → preparation of thin sample is not easy

   ii) it takes long hours to carry out two dimensional mapping

   because of large numbers of measurement points

2. **Low excitation efficiency for light elements**
3. **Special efforts is necessary to carry out quantitative analysis**
4. **Sample damage should be considered if you use brilliant Undulator SR Source or white X-ray radiation. Especially, care must be taken about photo-reduction/oxidation of the component elements.**

However!

Attractiveness of (SR)-XRF

1. Nondestructive analysis, multielemental analysis
2. Two dimensional resolution
3. Easy to carry out the analysis and easy to understand the results
4. Basic optical system for EDS analysis is simple

   SR → Monochromator → sample → detector
5. We can analyze almost any samples

   size → from cell level to sculpture, paintings

   in situ、in vivo、in air at any temperature
6. Information

   concentration: major(%), minor, trace(ppm) elements C ～Na ～ U

   distribution: from nm level to cm level

   chemical state (oxidation state, local structure) C ～ Si ～ U
7. Multiple SR-X-ray analysis: combination with X-ray diffraction and XAFS

Conclusion

Attractiveness of SR-X-ray analyses

1. **Nondestructive multielemental analysis with cell level resolution**

2. **In vivo analysis in air is possible**

3. **Information**

   concentration: major(%), minor, trace(ppm) elements Na ～ U

   distribution: from nm level to cm level

   chemical state (oxidation state, local structure) Al ～ U

   crystal structure & identification of crystalline phase

New direction of SR-X-ray analyses for practical application

1. **Combination of multiple techniques**

   XRF-XAFS-XRD from the same sample

2. **Use of an automated sample system**

   130 diffraction data /day 100 SR-XRF data /day

Conclusion

Attractiveness of SR-X-ray analyses

X-ray is only electromagnetic wave which gives the information of chemical composition, chemical state, crystal structure, and internal structure(X-ray CT) from the same sample nondestructively with high spatial resolution.