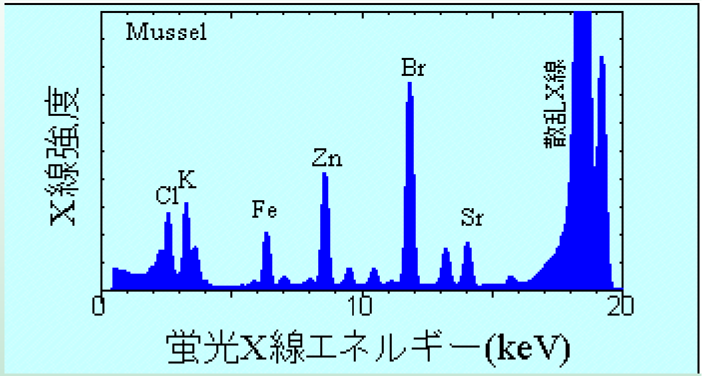
X-ray fluorescence analysis

Chiba University
Department of Chemistry

Chiya NUMAKO



Tokyo University of Science
Department of Applied Chemistry

Izumi NAKAI

Outline of the lecture

- **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

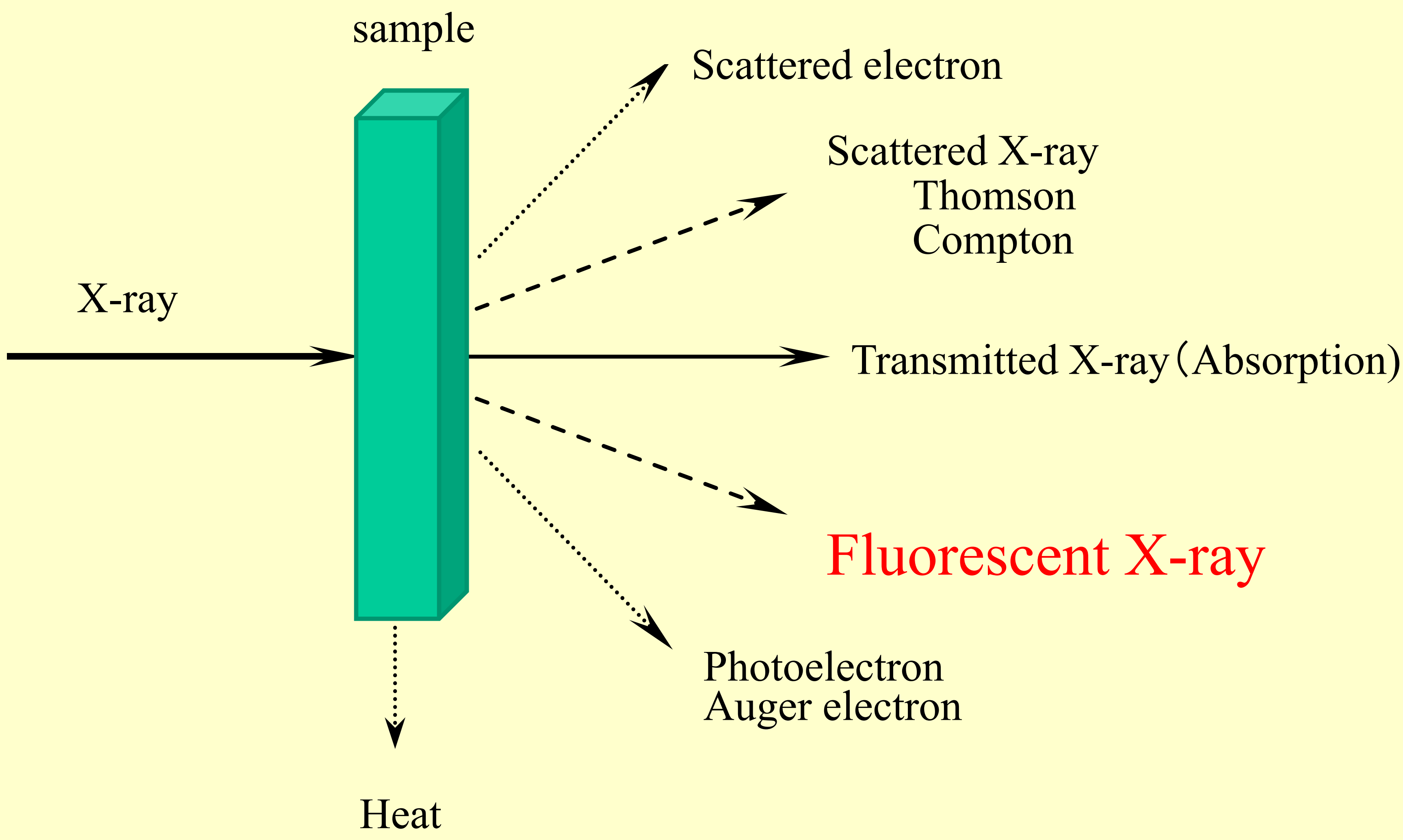
(3) Energy tunability

- Chemical state analysis by Fluorescence –XAFS

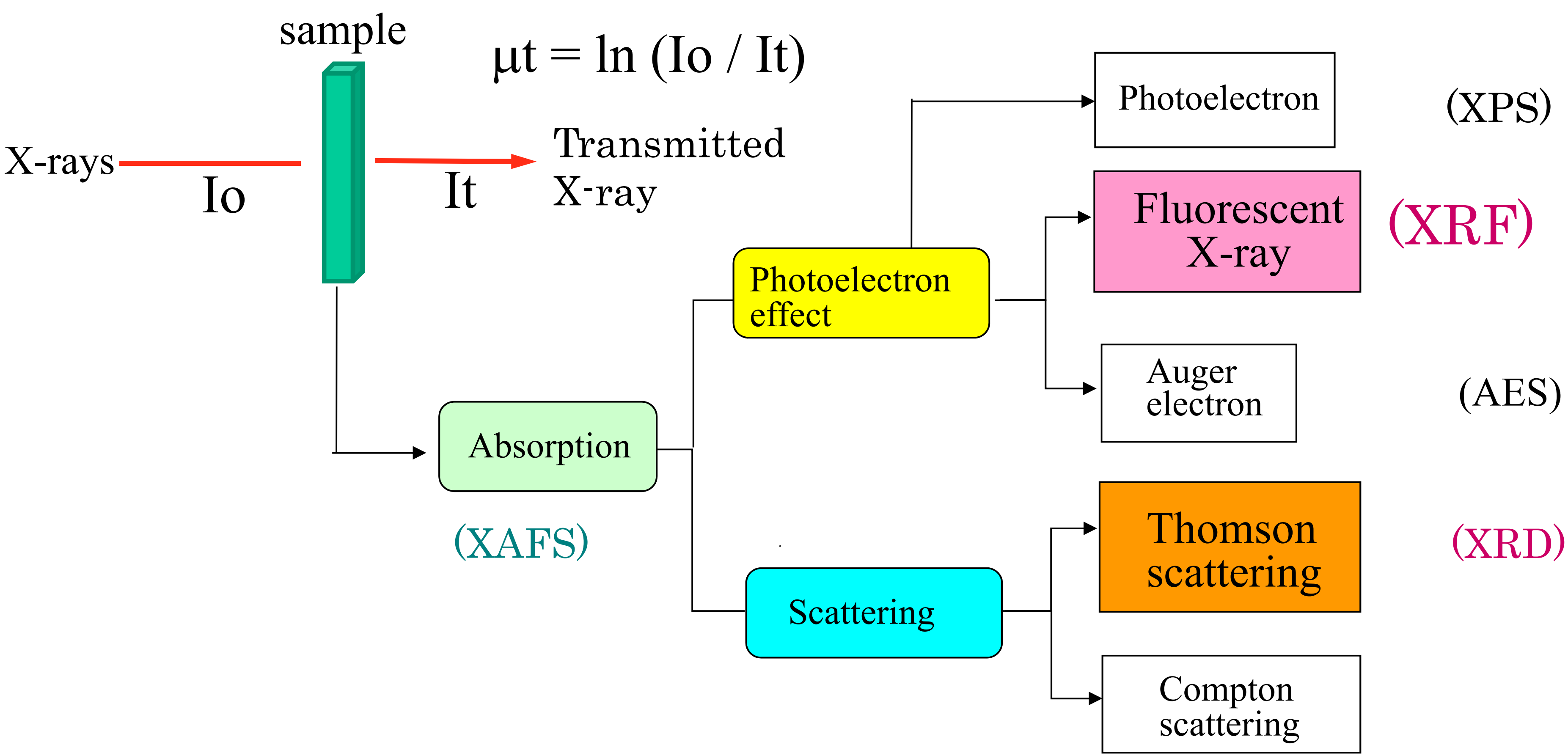
(4) High energy X-ray

(5) Multiple X-ray analytical technique -
A combination of **μ-XRF imaging, μ-XRD, XAFS and SEM**

- Conclusion



Interaction of X-ray with matter



Interaction of X-ray with matter and X-ray analysis

Relationship between λ and E

Particle : energy E [keV]

Wave : wavelength λ[Å]

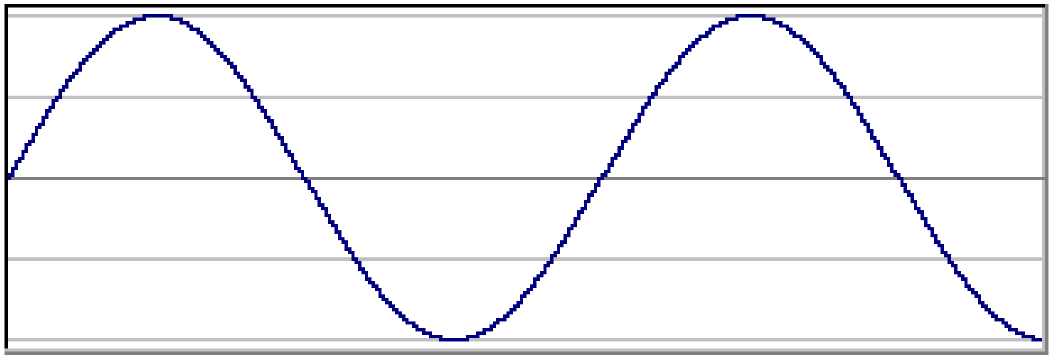
$E = hc/\lambda = 12.398/\lambda$ [keV],

Wavelength λ

ex. 1 Å = 12.398keV

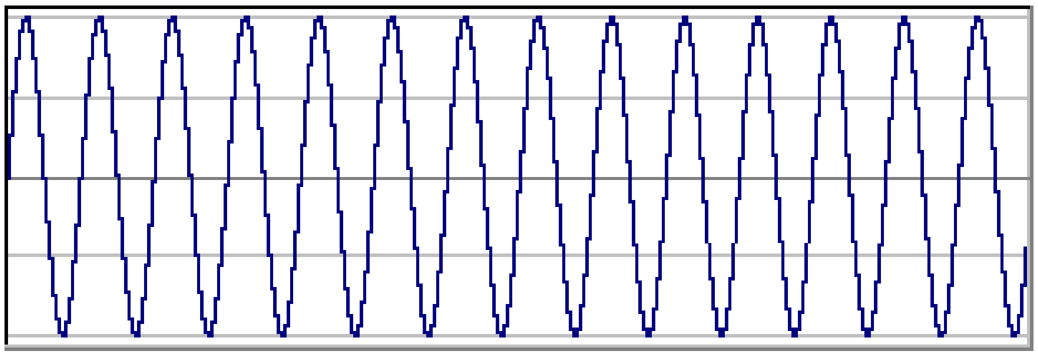
Amplitude

=Intensity



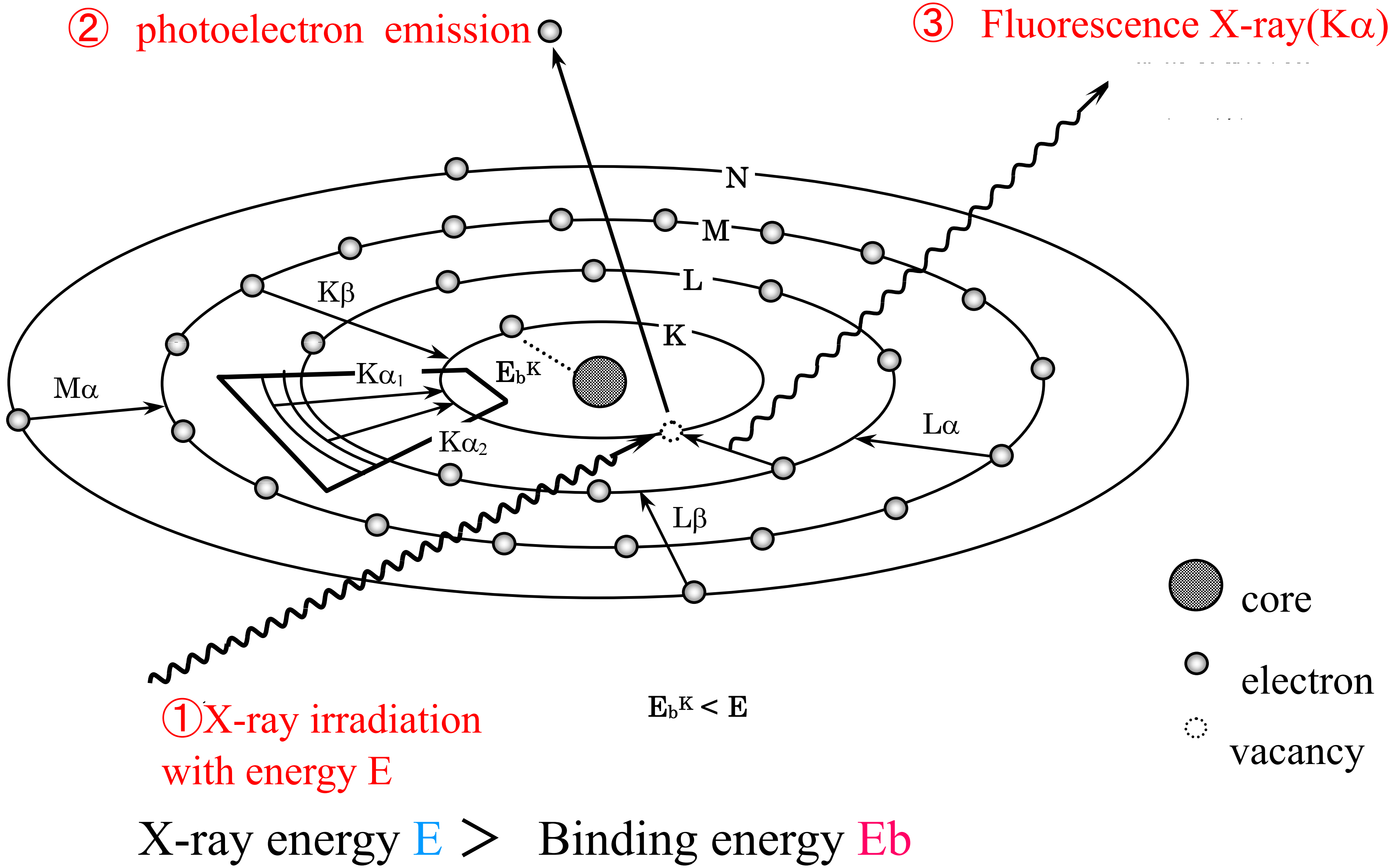
λ = long

Energy = low



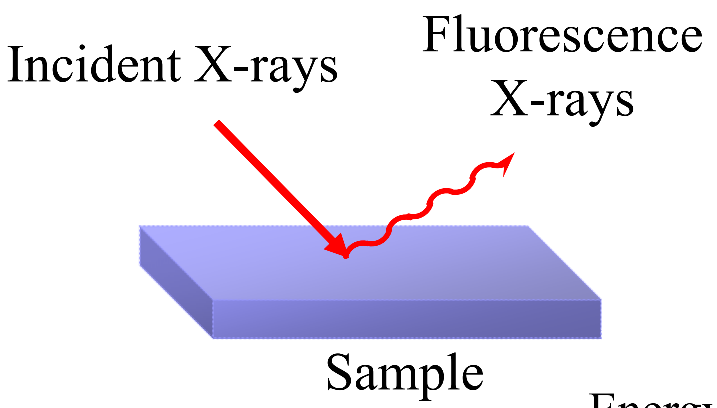
λ = short

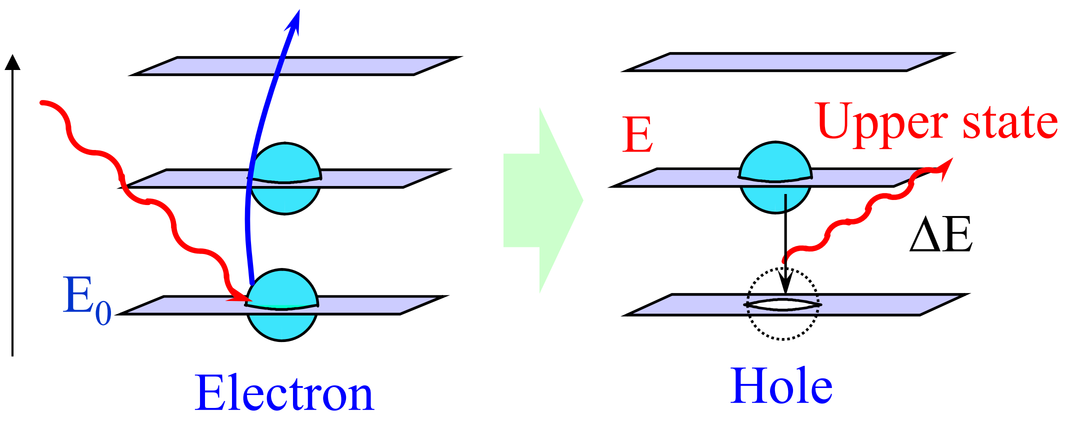
Energy = high



Bohr model and emission of X-ray fluorescence

Principle of X-ray fluorescence spectroscopy (XRF)

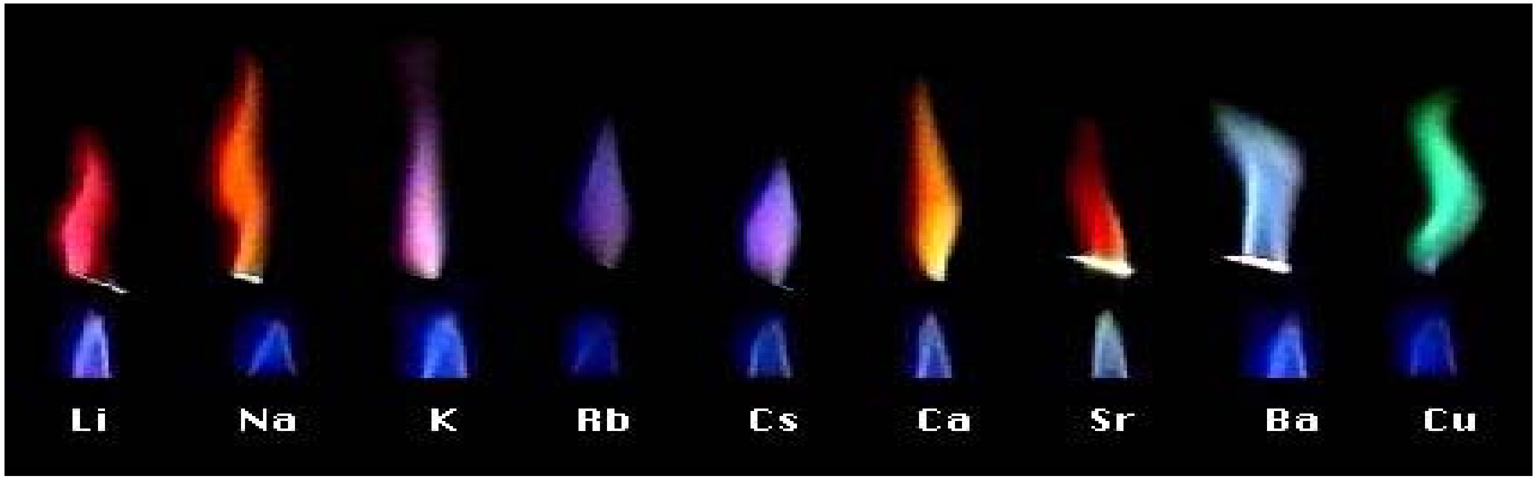




Energy level of electron in an atom

$$\Delta E = E - E_0$$

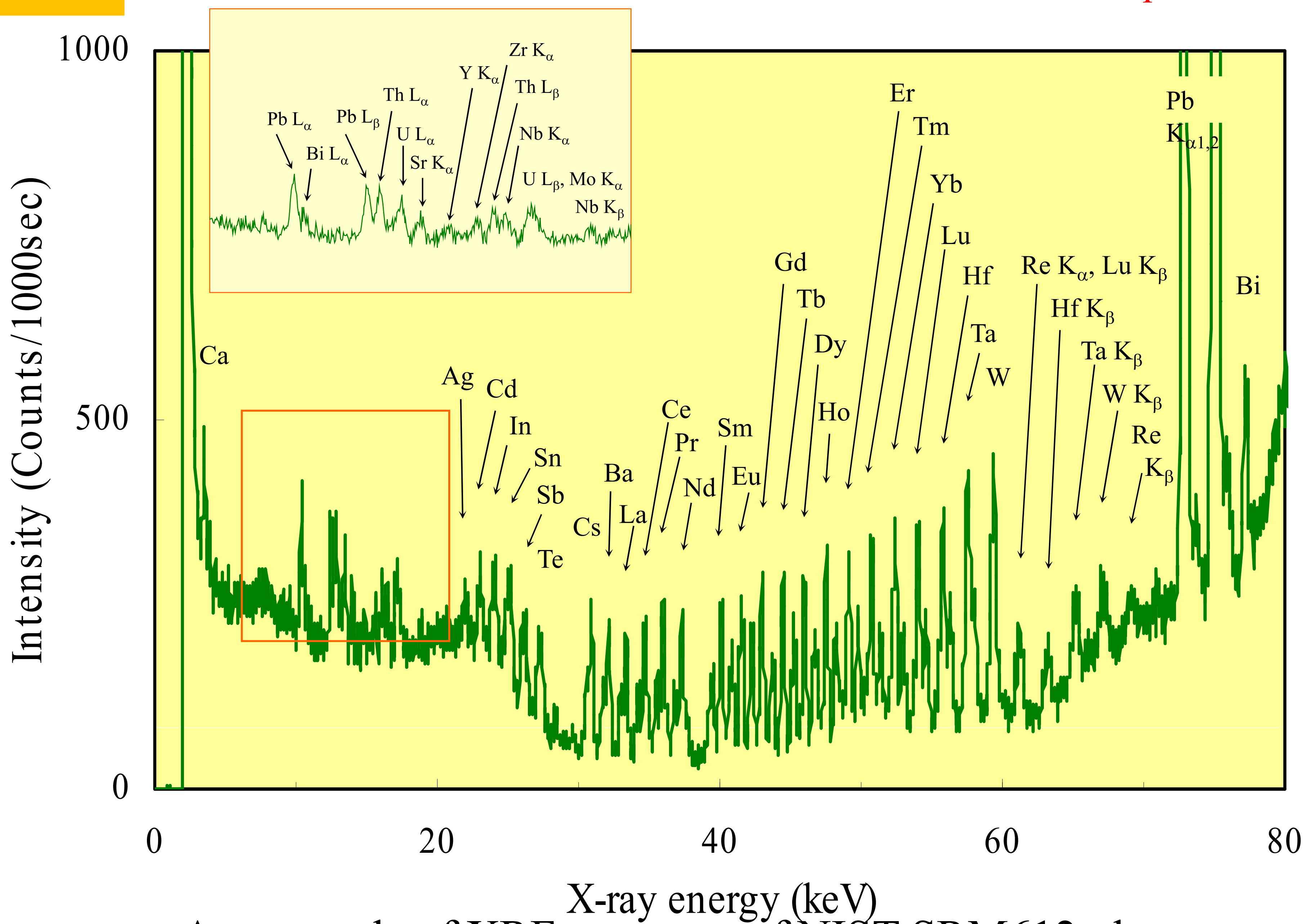
ΔE is identical to the element and chemical condition



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

EDS

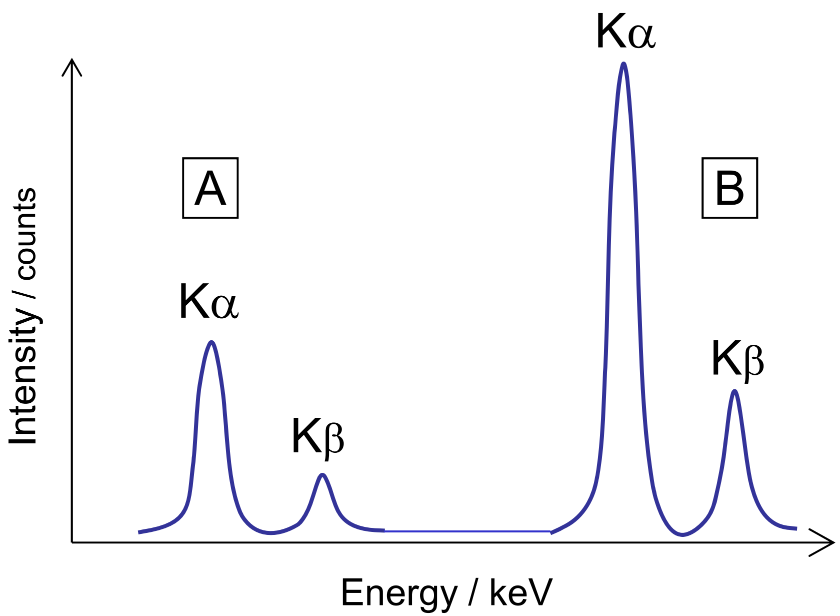
Measurement : Data = XRF spectrum



An example of XRF spectrum of NIST SRM612 glass

Principle of X-ray fluorescence (XRF) analysis

We measure 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

Effective Analytical Method

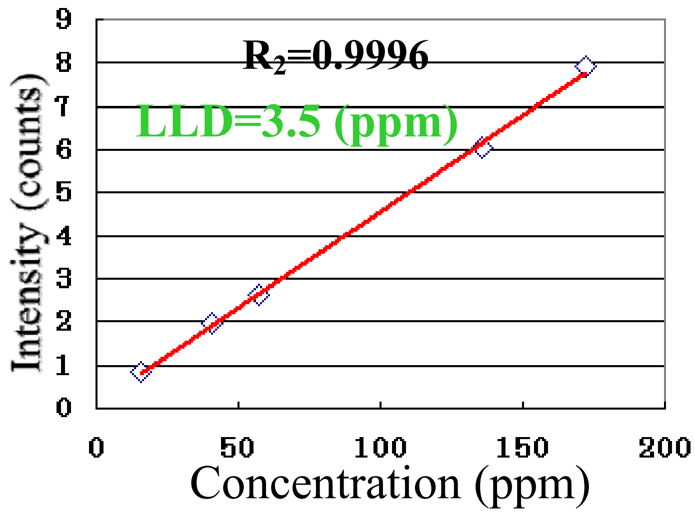
A Procedure of X-ray fluorescence (XRF) analyses

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

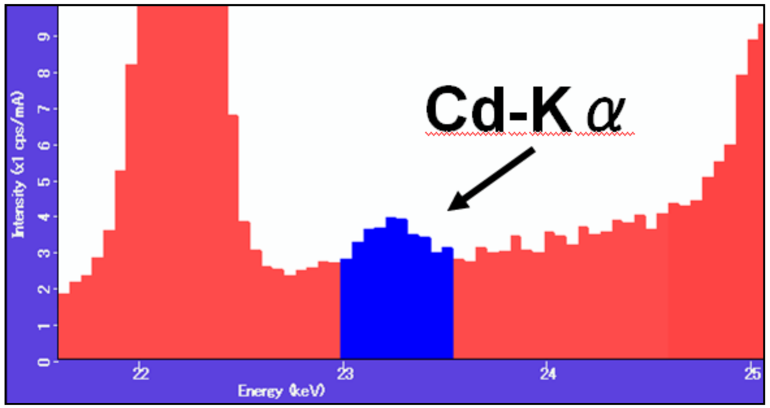
2. Select the best condition for XRF analyses
   Combination of X-ray source, Detector, measurement time, etc.

3. Make calibration curve from standards

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

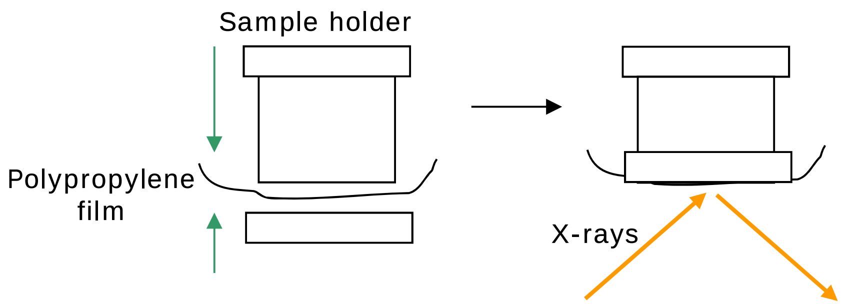


Calibration Curve for Cd



Cd in a Cu-alloy (Analytical data:16ppm)

Example: XRF analyses for Cd in rice



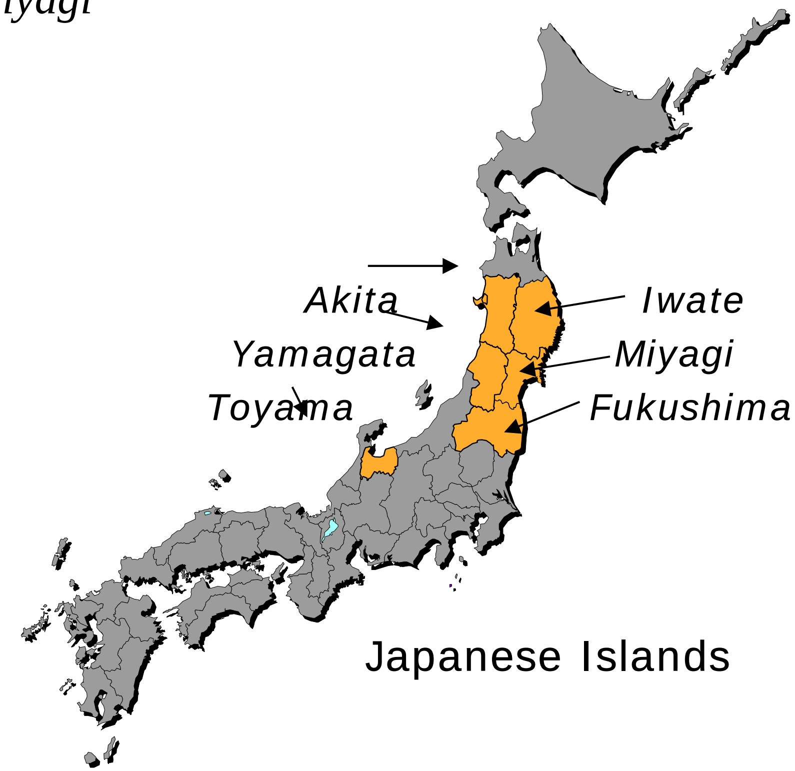
- Standards
  - <u>Rice Flour-Unporished</u>
    <u>(NIES CRM No.10 a,b,c)</u>

	Cd concentration
#1	0.023 ±0.003 ppm
#2	0.32 ±0.02 ppm
#3	1.82 ±0.06 ppm

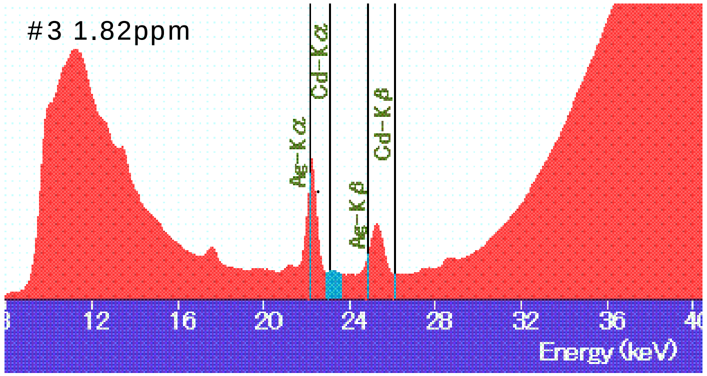
- Samples

Koshihikari#1 Yamagata
Akitakomachi#1 Akita
Hitomebore Miyagi

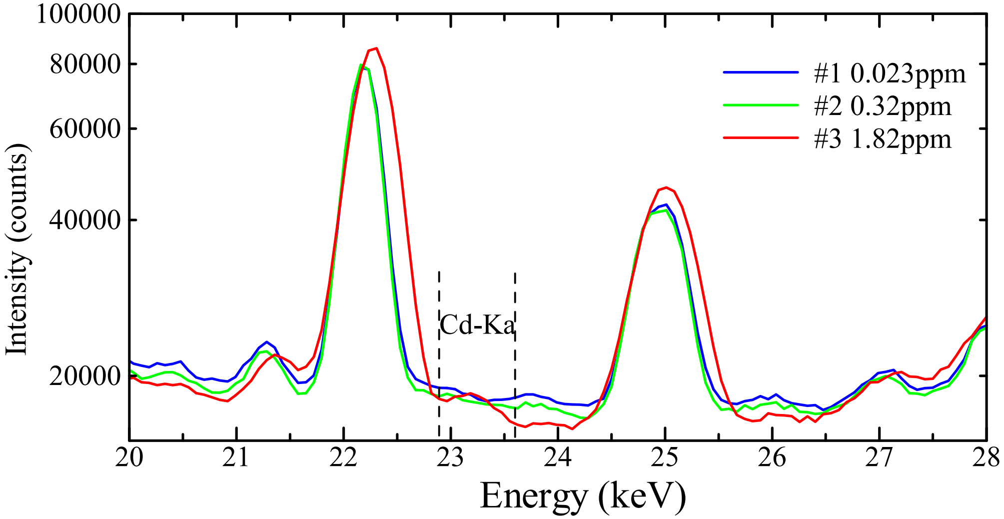
MT:1000s

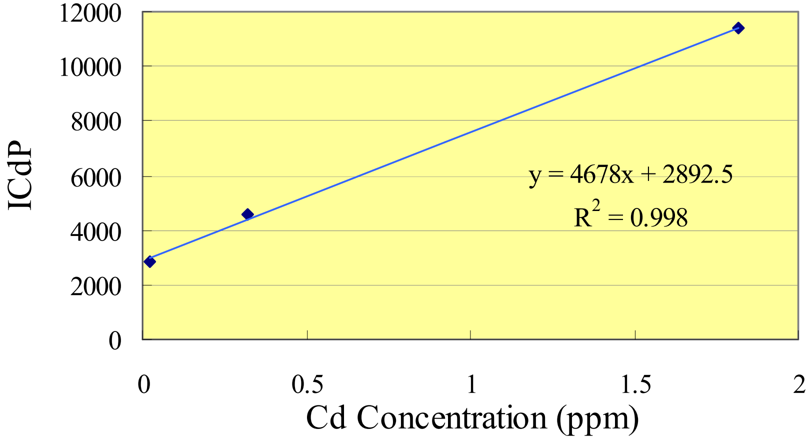


Results (1) Calibration Curve for Cd with the Rice flour Standards



	Cd Conc.(ppm)	Dead Rate(%)	ICR/OCR (Mcts)	Cd Ka Intensity (cts/100sec)		LLD (ppm)	ICdP/IB	ICdP+IB
				Peak	BG			
#1	1.82	12.5	134.2 /88.7	11371	171787	0.1990	0.0662	183158
#2	0.32	12.9	138.8 /90.5	4604	175110	0.0873	0.0263	179714
#3	0.023	13.2	142.8 /92.0	2821	181999	0.0104	0.0155	184820

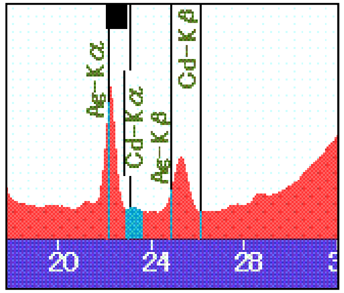




The Calibration Curve for Cd

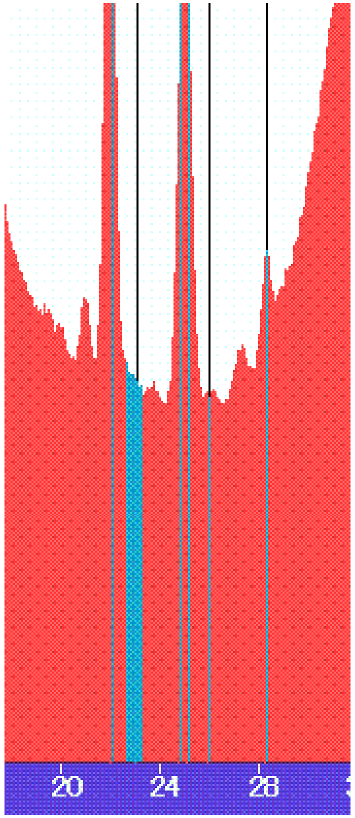
$$C_{(ppm)} = 0.0002 \times I - 0.6157$$

Results (2) Rice Specimens

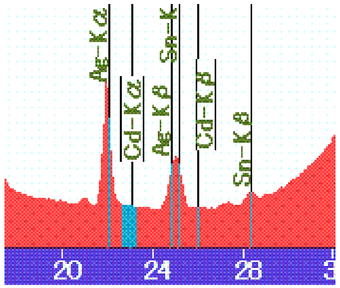


Rice Flour Standard #3

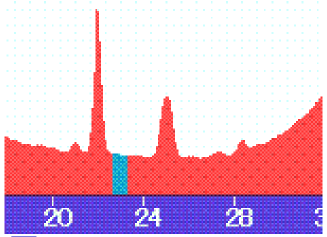
■Unpolished Rice



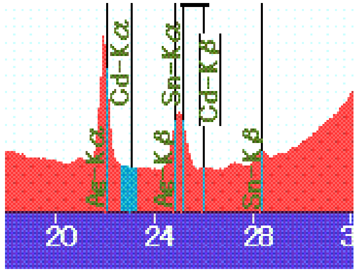
□*Koshihikari#1*



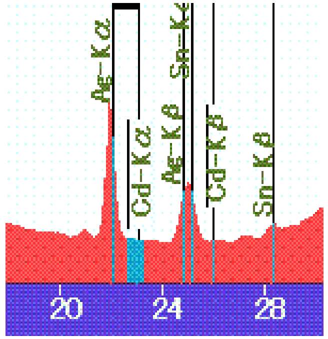
□ *Koshihikari#2*



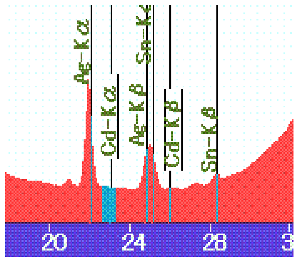
□ *embryo*



□*Akitakomachi#1*

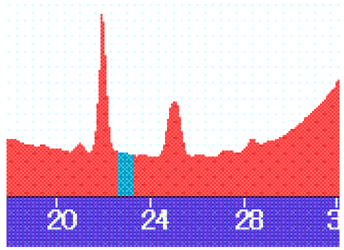


□*Akitakomachi#2*



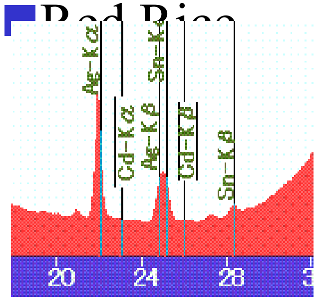
□*Hitomebore*

■Black Rice



□*#1 Toyama*

■Red Rice

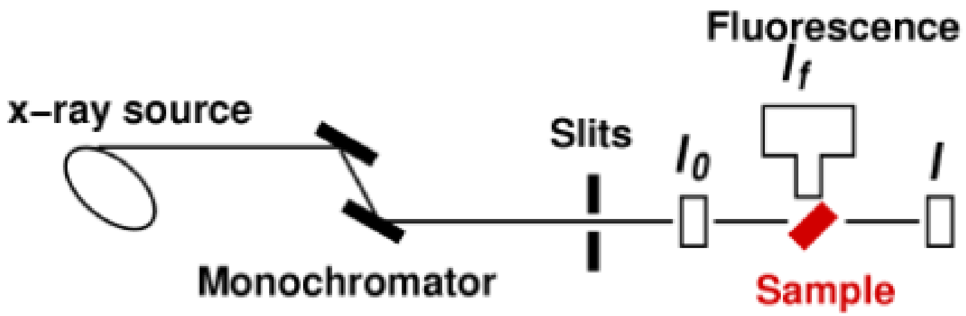


Result (2) Calculation of Cd Conc. for Rice Specimens

Specimens	Area of Production	Cd Conc. (ppm)	Dead Rate(%)	ICR/OCR (Mcts)	Peak intensity for Cd (cts/100sec)	
					Peak	BG
Embryo		-0.2451	12.2	131.8/87.7	1853	174559
Black Rice #1	Toyama	0.7567	14.9	164.3/99.3	6862	202971
Black Rice #2	Fukushima	0.1563	14.3	156.5/96.8	3860	195092
Red Rice	Unknown	0.5689	15.7	172.9/101.8	5923	209836
Akitakomachi #1	Akita	-0.0407	14.8	162.9/98.9	2875	204170
Akitakomachi #2	Iwate	0.1353	15	165.5/99.6	3755	204420
Koshihikari #1	Yamagata	0.0321	14.2	155.3/96.4	3239	196088
Koshihikari #2	Fukushima	0.5313	15.3	168.7/100.6	5735	207096
Hitomebore	Miyagi	0.4003	16.4	182.2/104.4	5080	215875

NIES Rice Flour Standards	Cd Conc. (ppm)	Dead Rate(%)	ICR/OCR (Mcts)	Peak intensity for Cd (cts/100sec)	
				Peak	BG
#1	0.023	13.2	142.8/92.0	2821	181999
#2	0.32	12.9	138.8/90.5	4604	175110
#3	1.82	12.5	134.2/88.7	11371	171787

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

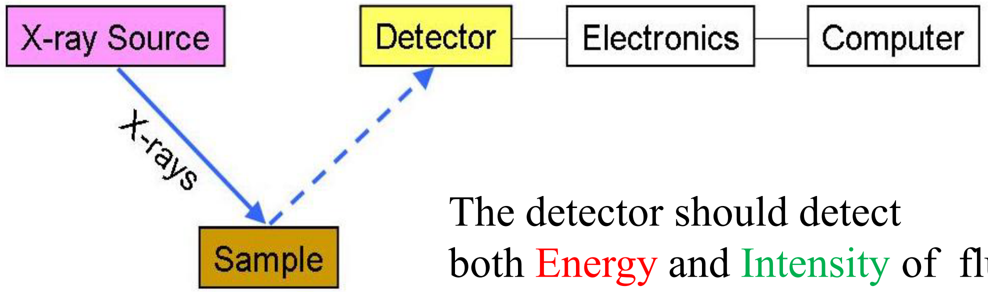
How to measure E and I.

Two methods of XRF analysis

(a) Energy dispersive spectroscopy

(b) Wavelength dispersive spectroscopy

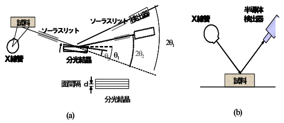
EDS



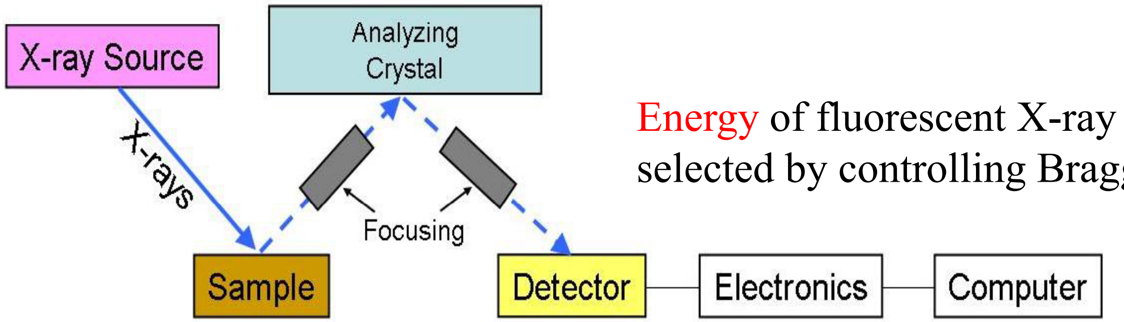
The detector should detect both Energy and Intensity of fluorescent X-ray

WDS

d-spacing

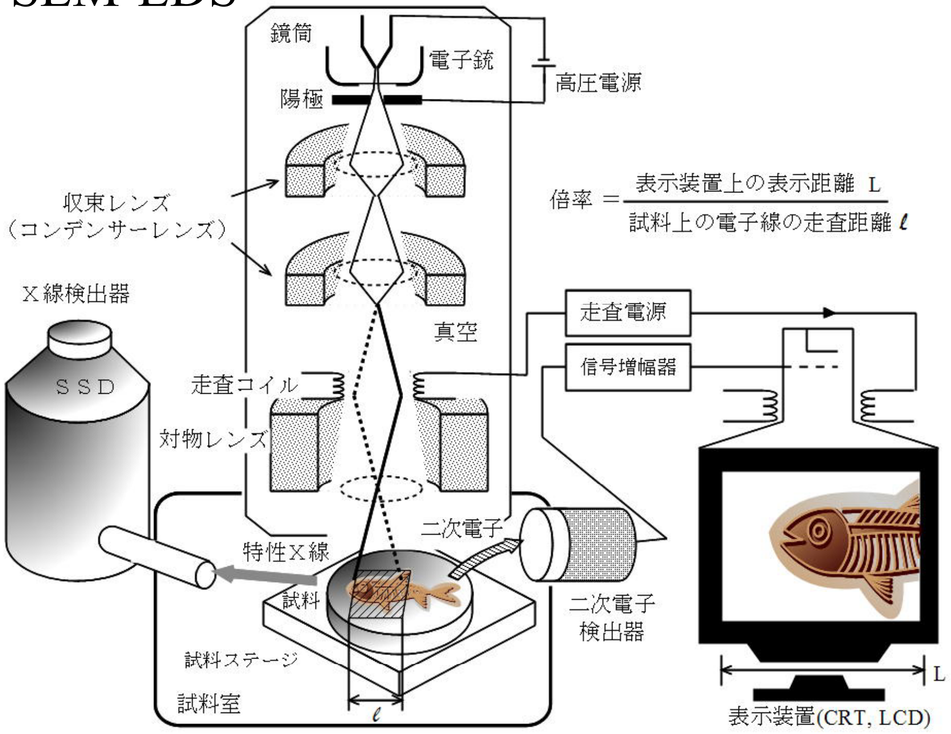


Analyzing crystal

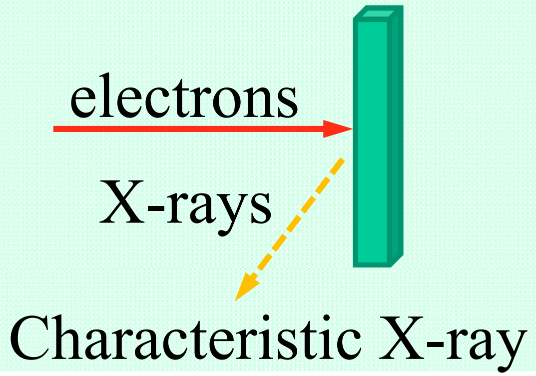


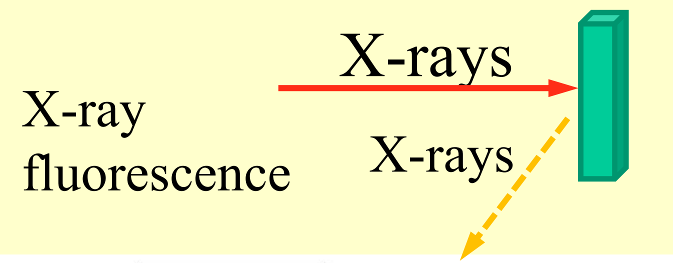
Energy of fluorescent X-ray can be selected by controlling Bragg angle.

SEM-EDS

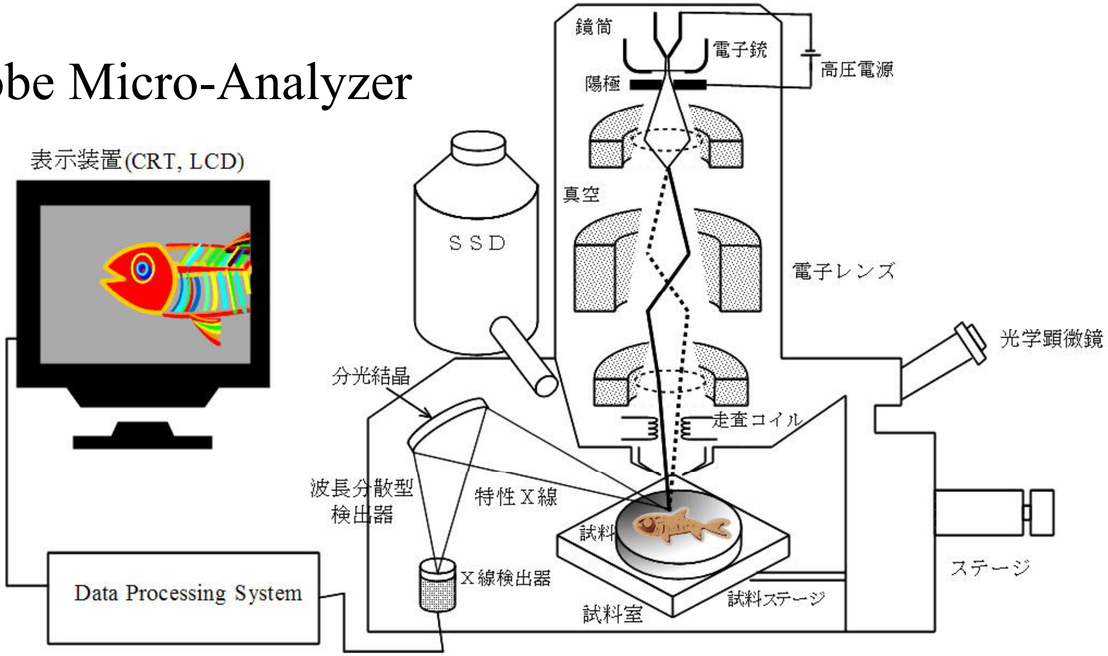


Elemental Analyses with electron





Electron Probe Micro-Analyzer (withWDS)

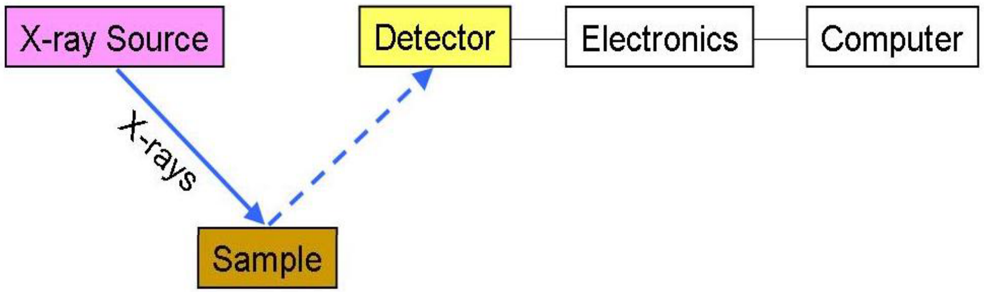


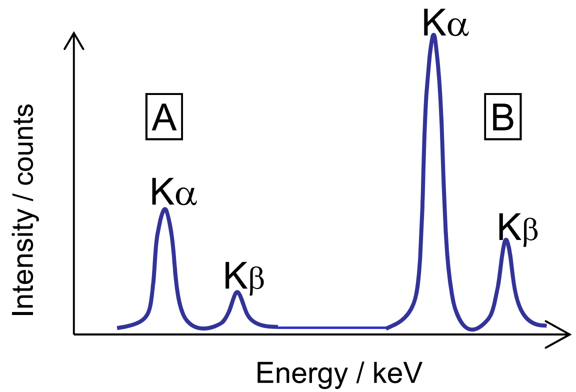
- needs vacuum condition
- heavy damage of sample

(a) Energy dispersive spectroscopy

EDS

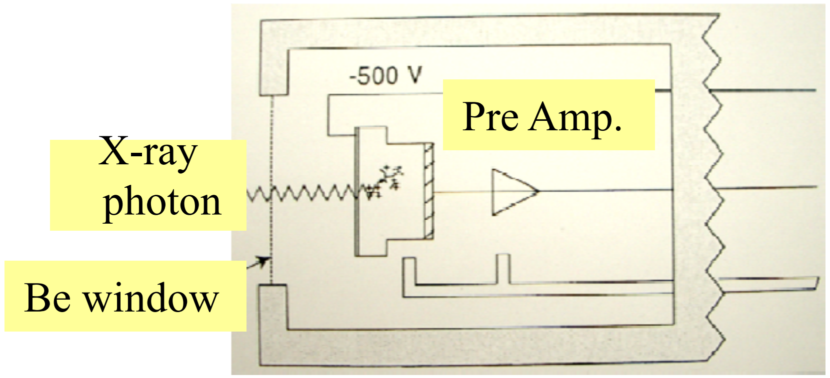
How to measure E and I.





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

→ SSD, SDD



Si(Li) detector electron-hole pair →3.85eV

ex. Fe Kα 6.400keV 6400/3.85=1662 pairs

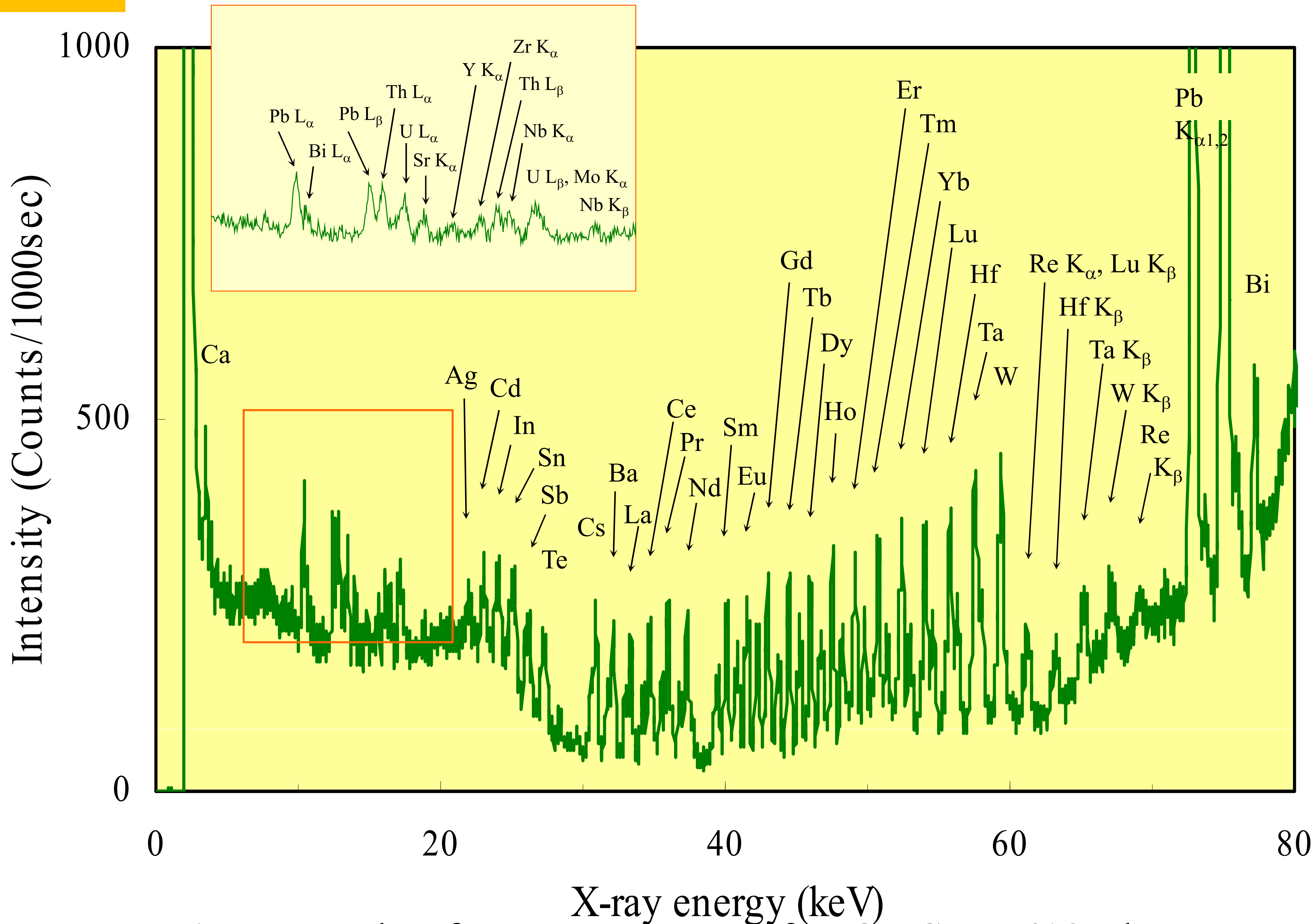
Bias voltage(-500V) cause currents flow.

Principle of Si(Li) detector → a reverse-biased silicon diode.

The charge collected at the anode is converted to a voltage by an amplifier. This results in a voltage pulse that is proportional to the number of pairs created and thus to the incident X-ray energy. The resolution is determined by the energy required to create an electron-hole pair (3.8 eV).

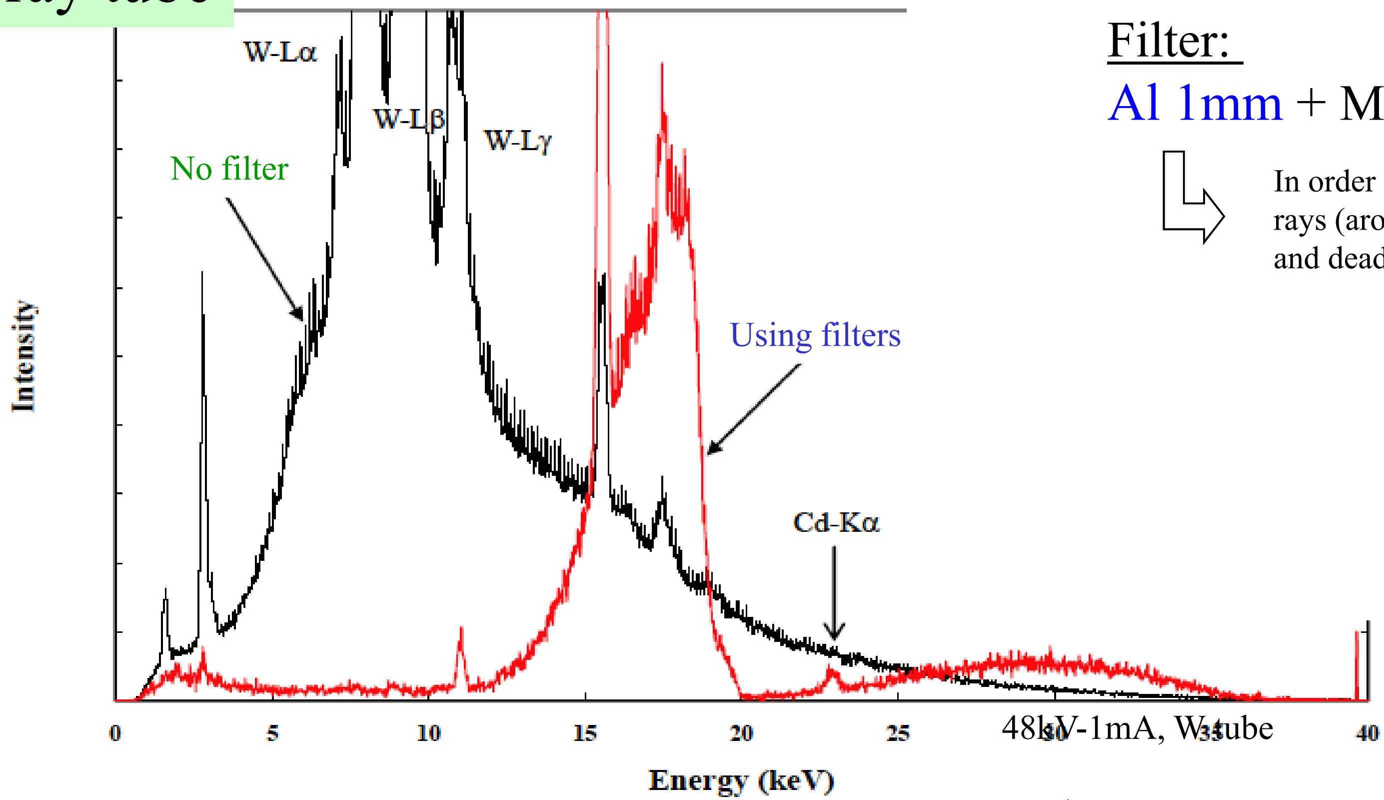
EDS

Measurement : Data = XRF spectrum



An example of XRF spectrum of NIST SRM612 glass

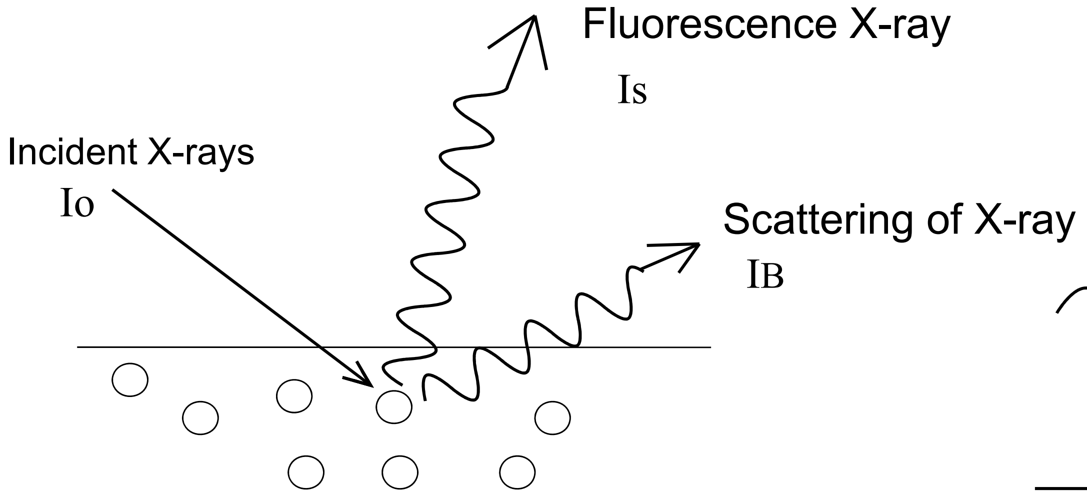
W X-ray tube

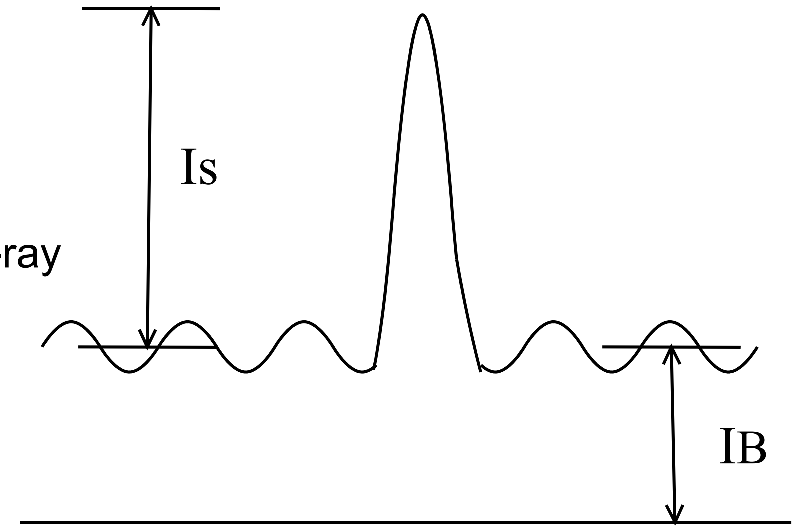


Filter:

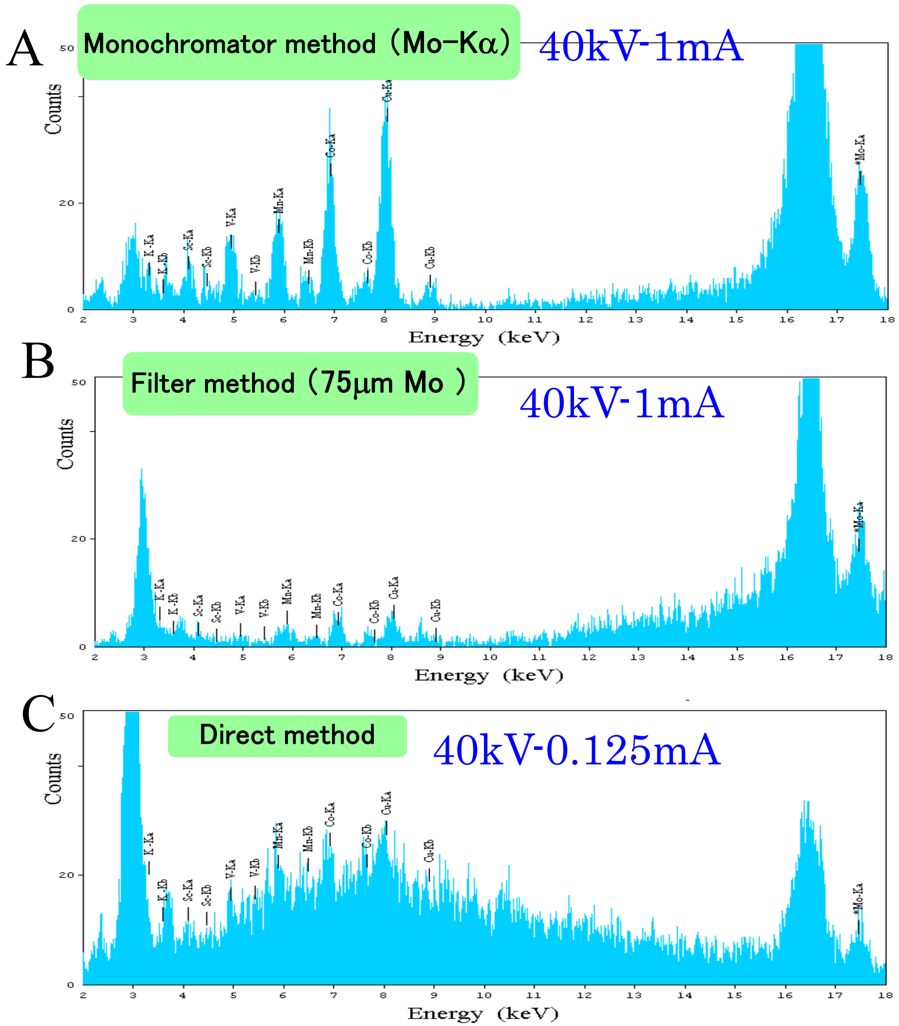
Al 1mm + Mo 0.15mm

In order to decrease low-energy X-rays (around 10 keV) from a tube, and dead rate as much as possible





Reducing influence of backgound

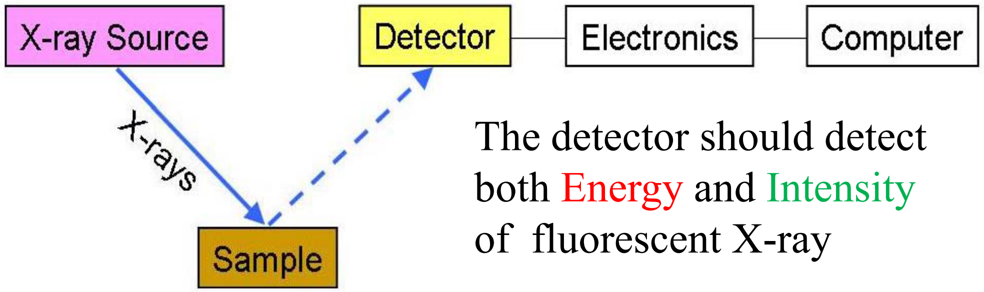


	A	B	C
P.I. (cps)	4.53	0.57	0.57
B.G (cps)	0.08	0.06	2.99
P/B	56.6	9.5	0.2
LLD/ppb	2.65	18.2	129

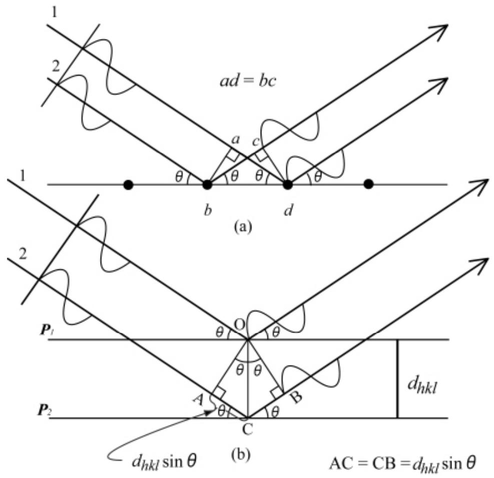
Sample : Cu, Co, Mn, V, Sc, K 0.2ppm
50μl dried up on the holder
Sample holder : Polyethylene 5μm film
X-ray tube : Mo
Measurement time : 200sec

Improving Signal/Background ratio is most important points for XRF

	Advantage	Disadvantage
EDS	High Efficiency Multi-elemental detection	Low resolution Scattering Background



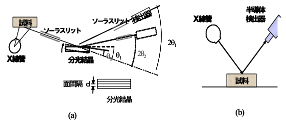
The detector should detect both Energy and Intensity of fluorescent X-ray



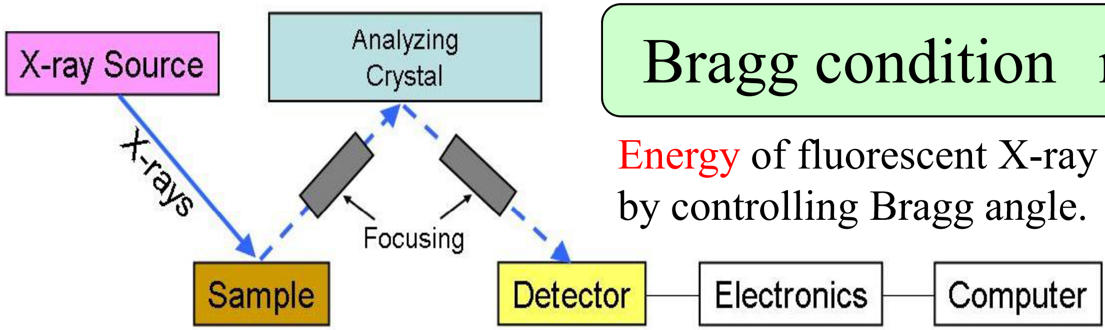
Improving energy resolution

WDS (Wave Dispersive Spectroscopy)

d-spacing



Analyzing crystal



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

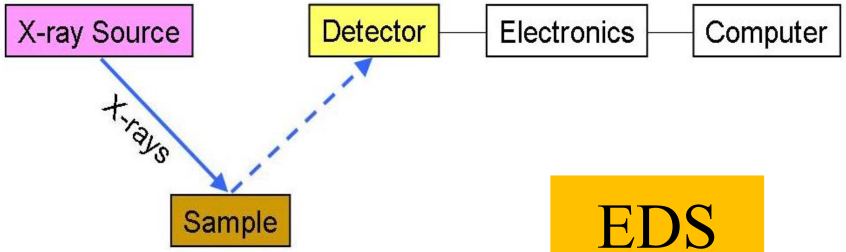
Energy of fluorescent X-ray can be selected by controlling Bragg angle.

The detector should detect Intensity of fluorescent X-ray

5.1 X-ray Fluorescence Analysis

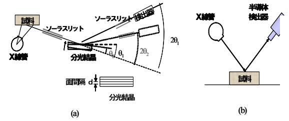
Commonly used analyzer crystal: LiF, ADP (ammonium dihydrogen phosphate), Ge, graphite, InSb, PE (*tetrakis*-(hydroxymethyl)-methane: penta-erythritol), KAP (potassium hydrogen phthalate), RbAP (rubidium hydrogen phthalate) and TlAP (thallium(I) hydrogen phthalate). In addition, synthetic multilayer is used to detect the light elements in the range Li to Mg.

material	plane	d nm	min λ nm	max λ nm	intensity	thermal expansion	durability
LiF	200	0.2014	0.053	0.379	+++++	+++	+++
LiF	220	0.1424	0.037	0.268	+++	++	+++
LiF	420	0.0901	0.024	0.169	++	++	+++
ADP	101	0.5320	0.139	1.000	+	++	++
Ge	111	0.3266	0.085	0.614	+++	+	+++
graphite	001	0.3354	0.088	0.630	++++	+	+++
InSb	111	0.3740	0.098	0.703	++++	+	+++
PE	002	0.4371	0.114	0.821	+++	+++++	+
KAP	1010	1.325	0.346	2.490	++	++	++
RbAP	1010	1.305	0.341	2.453	++	++	++
Si	111	0.3135	0.082	0.589	++	+	+++
TlAP	1010	1.295	0.338	2.434	+++	++	++
6 nm SM	-	6.00	1.566	11.276	+++	+	++

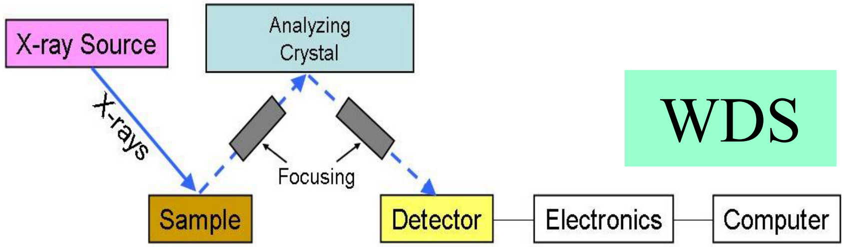


EDS

d-spacing



Analyzing crystal



WDS

	Advantage	Disadvantage
WDS	High resolution High S/B	Low efficiency needs high flux of Io
EDS	High Efficiency Multi-elemental detection	Low resolution Scattering Background

Synchrotron Radiation is ideal source of Insident X-ray

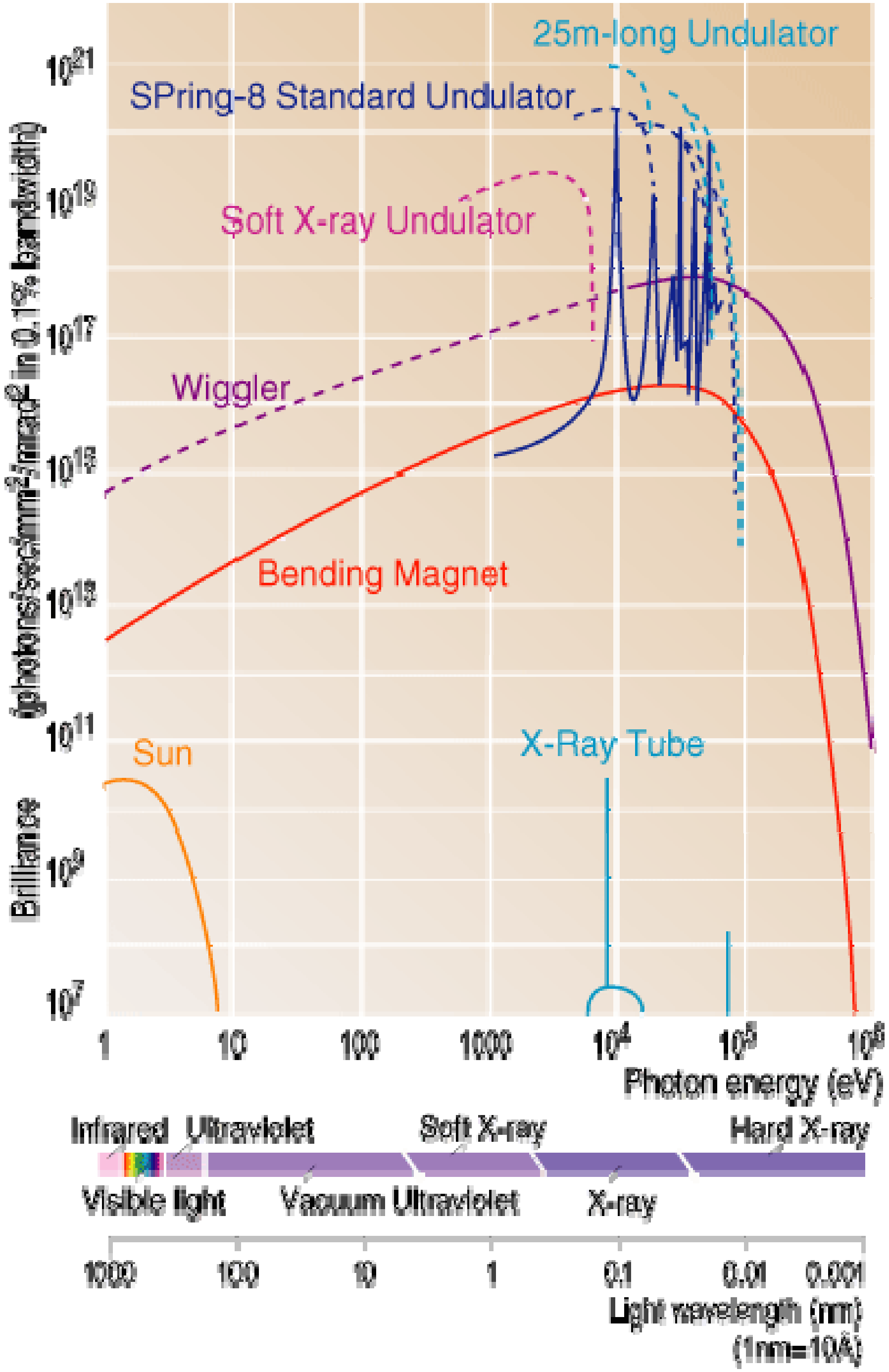
SR Propertie

1) **High Brilliance Source**
   (small size and high collimation X-ray
   strong intensity (high density) =>**signa**
   high collimation =>**micr**
   =>**total**

2) **Linear polarization**
   (p polarization + 90° arrangement) => **back**

3) **White (bending magnet), quasi-monoch**
   monochoromatic X-rays => **back**
   (monochromator) => **sele**
   (S/B o
   continuous energy scanning =>**XAF**
   (Chen

4)**High and low energy X-ray excitaiton**
   =>**hea**



Outline of the lecture

- **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

(3) Energy tunability

- Chemical state analysis by Fluorescence –XAFS

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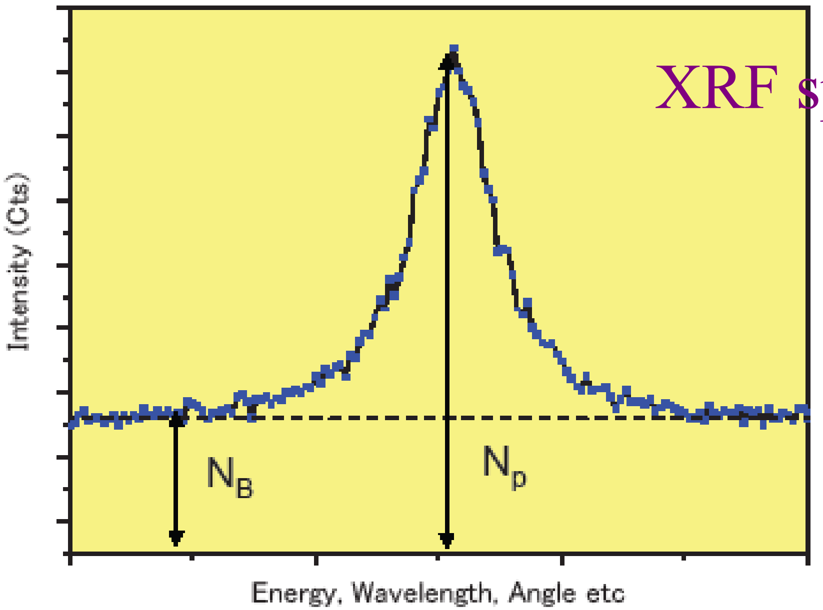
(5) Multiple X-ray analytical technique - A combination of **μ-XRF imaging, μ-XRD, XAFS and SEM**

- Conclusion

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) $(2k \sim 3.3k)$

Np increase ＝ Signal increase

→ High brilliance source ○

High flux source ○

Synchrotron Radiation

N_B decrease →

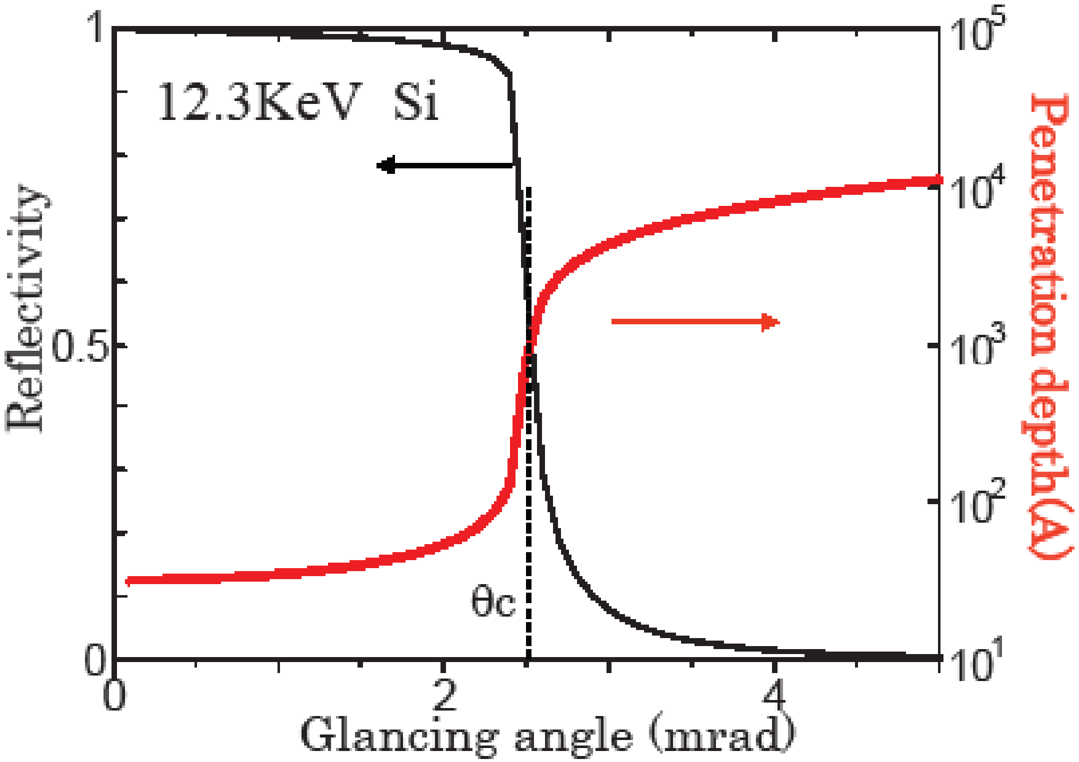
Monochromatic Excitation ○

WDX

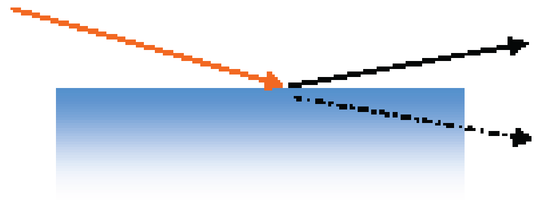
Total reflection

A solution to decrease background N_B

TXRF for Ultra Trace Element Analysis

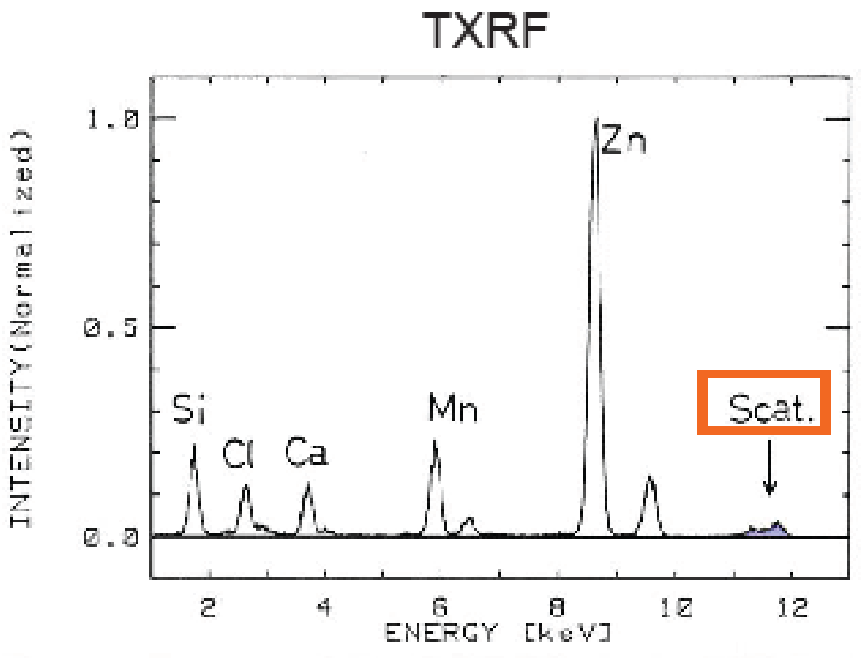


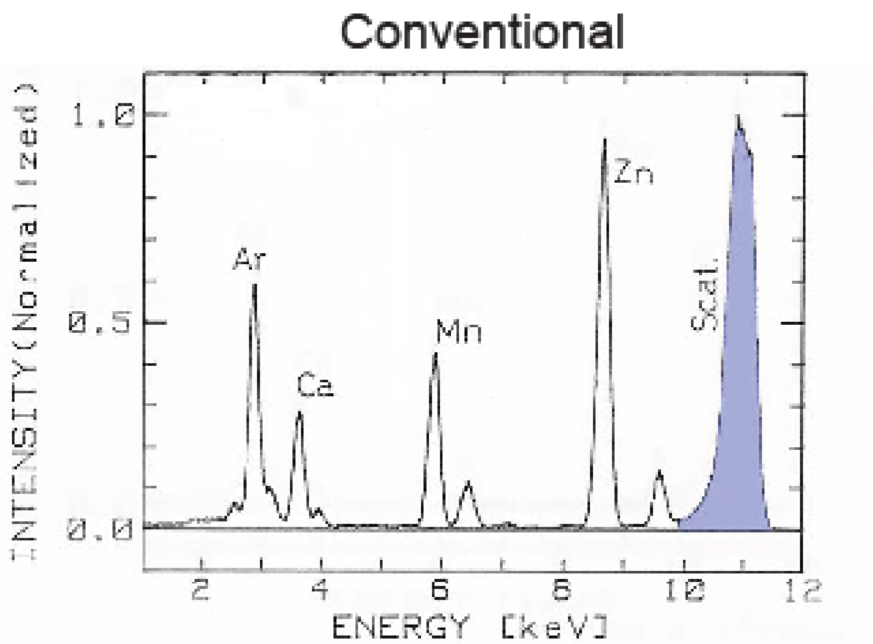
Extremely Shallow Penetration Depth

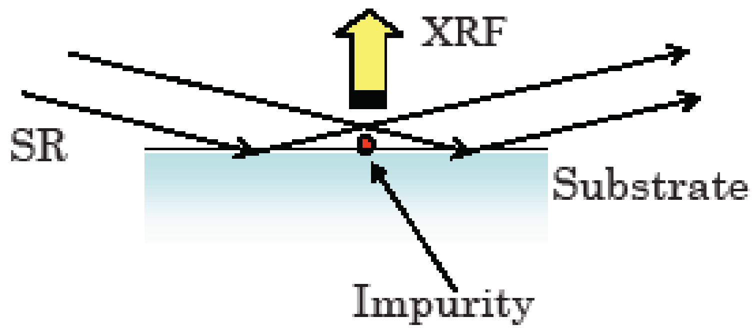


Total Reflection of X-rays at a flat and smooth surface (Si wafer, optical flat .....)

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



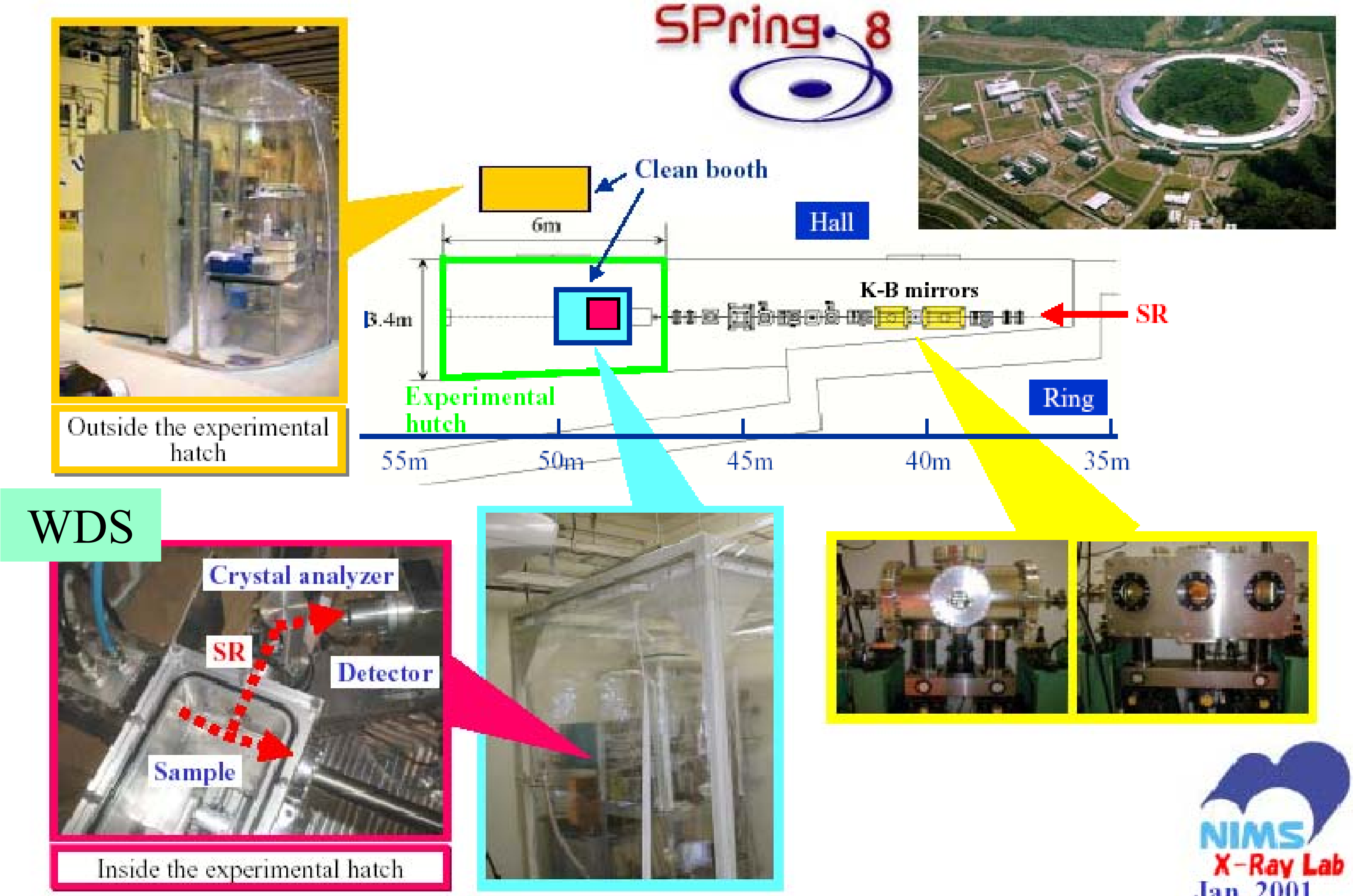




Si wafer

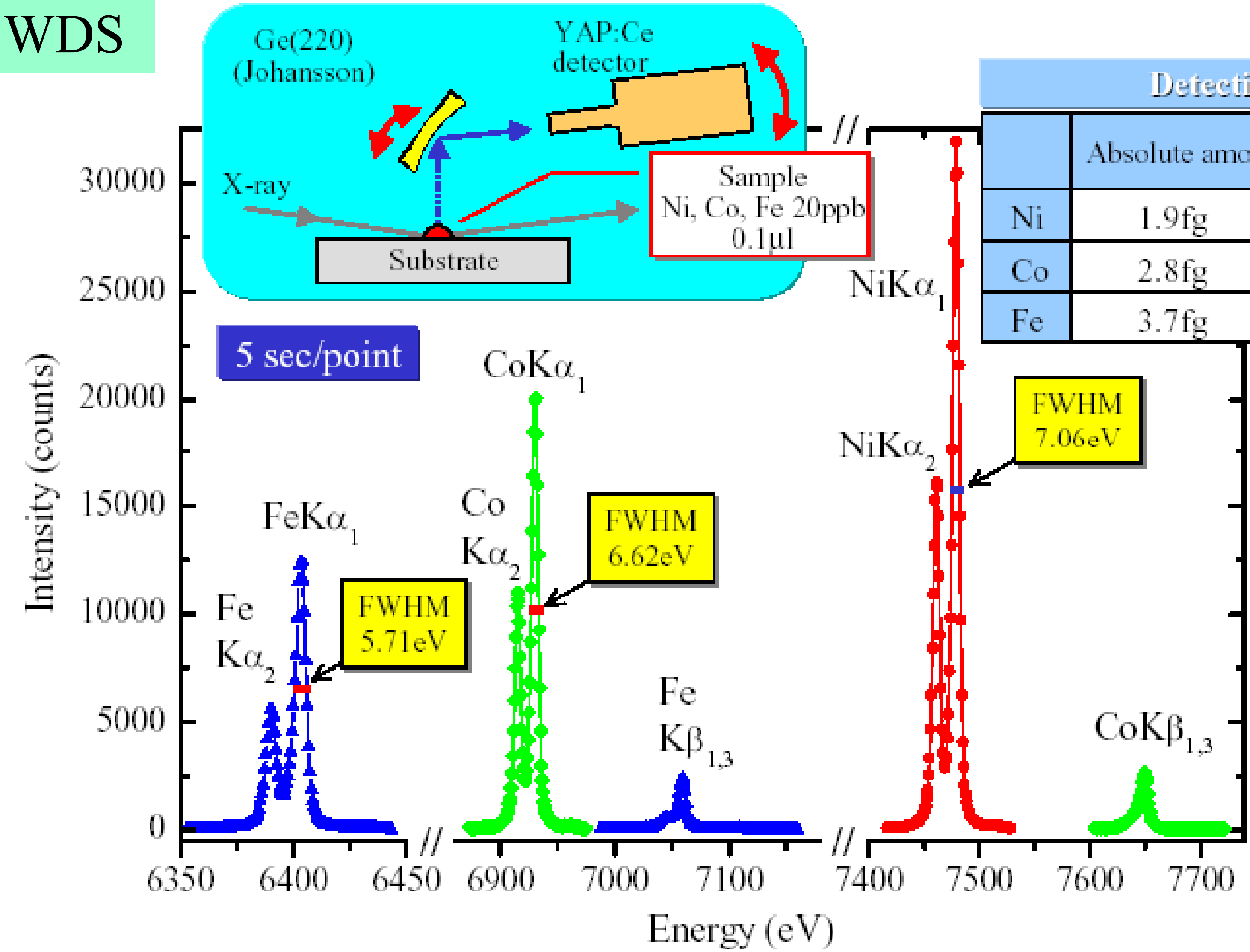
10^{15}atoms/cm^2=>10^8atoms/cm^2

TXRF Experiments at Beamline 40XU, SPring-8



WD-TXRF Spectra for Trace Elements in Micro Drop

WDS



Detection limit

	Absolute amount	Concentration of solution of 0.1μl
Ni	1.9fg	19ppt
Co	2.8fg	28ppt
Fe	3.7fg	37ppt

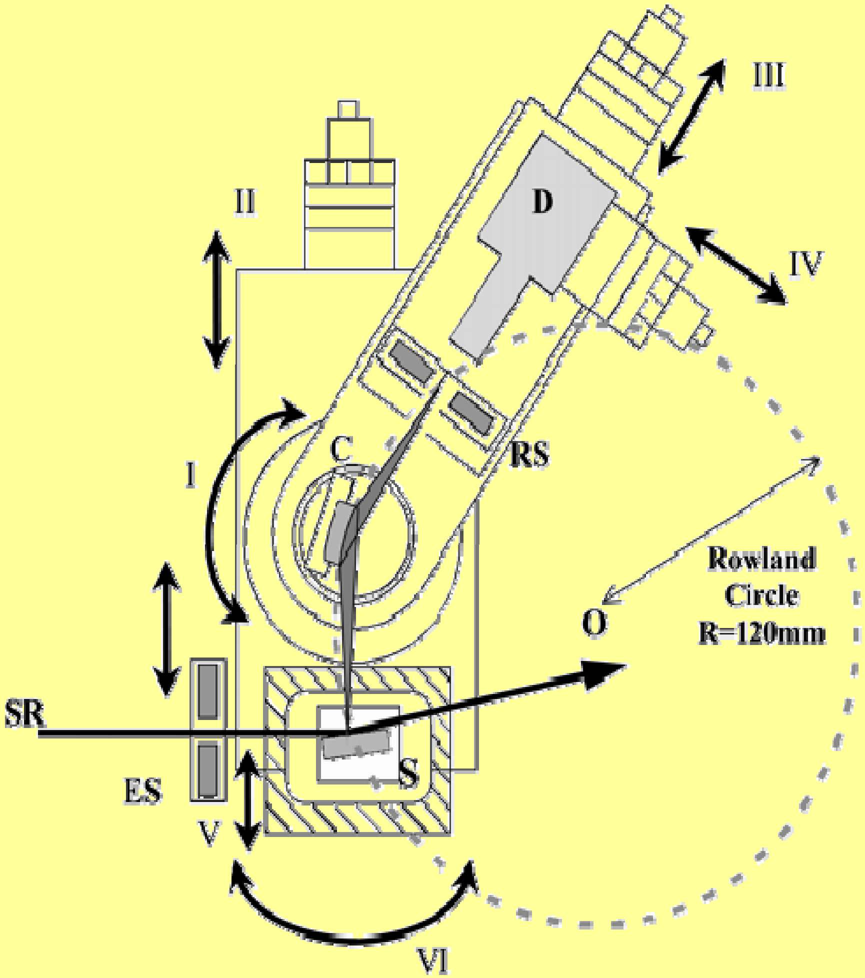
NIMS X-Ray Lab
Jan, 2001

World record of MDL by total reflection SR-XRF

WDS

$3.1x10^{-16}$g= 0.31fg

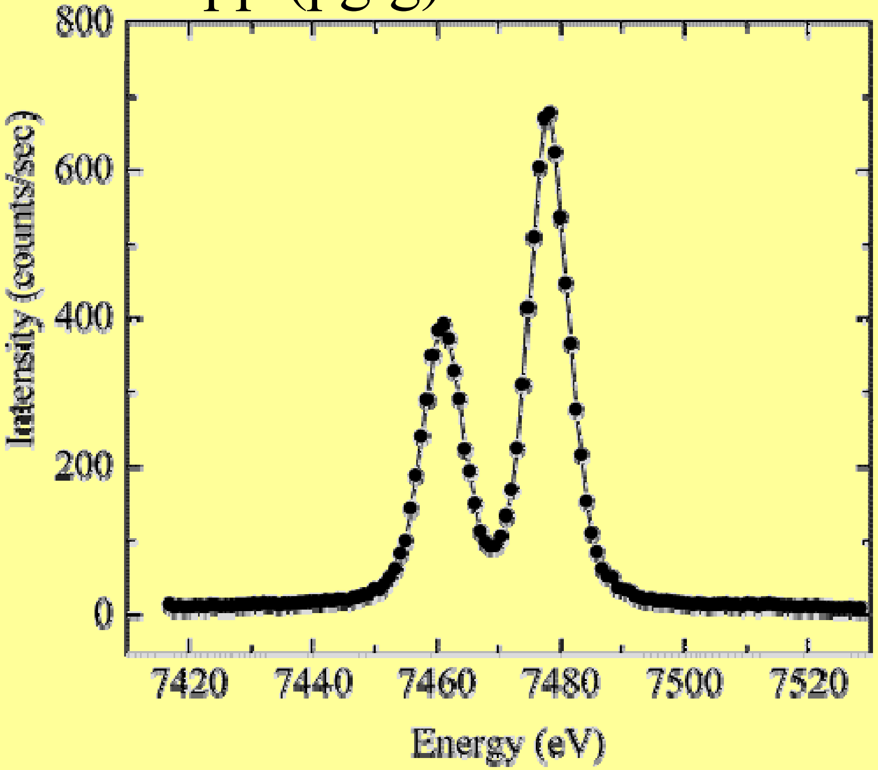
3.1ppt(pg/g)　$3x10^{6}$atom



(a) Crytal monochormator

C: Ge(220)Johansson type

D:YAP:Ce scintillation counter

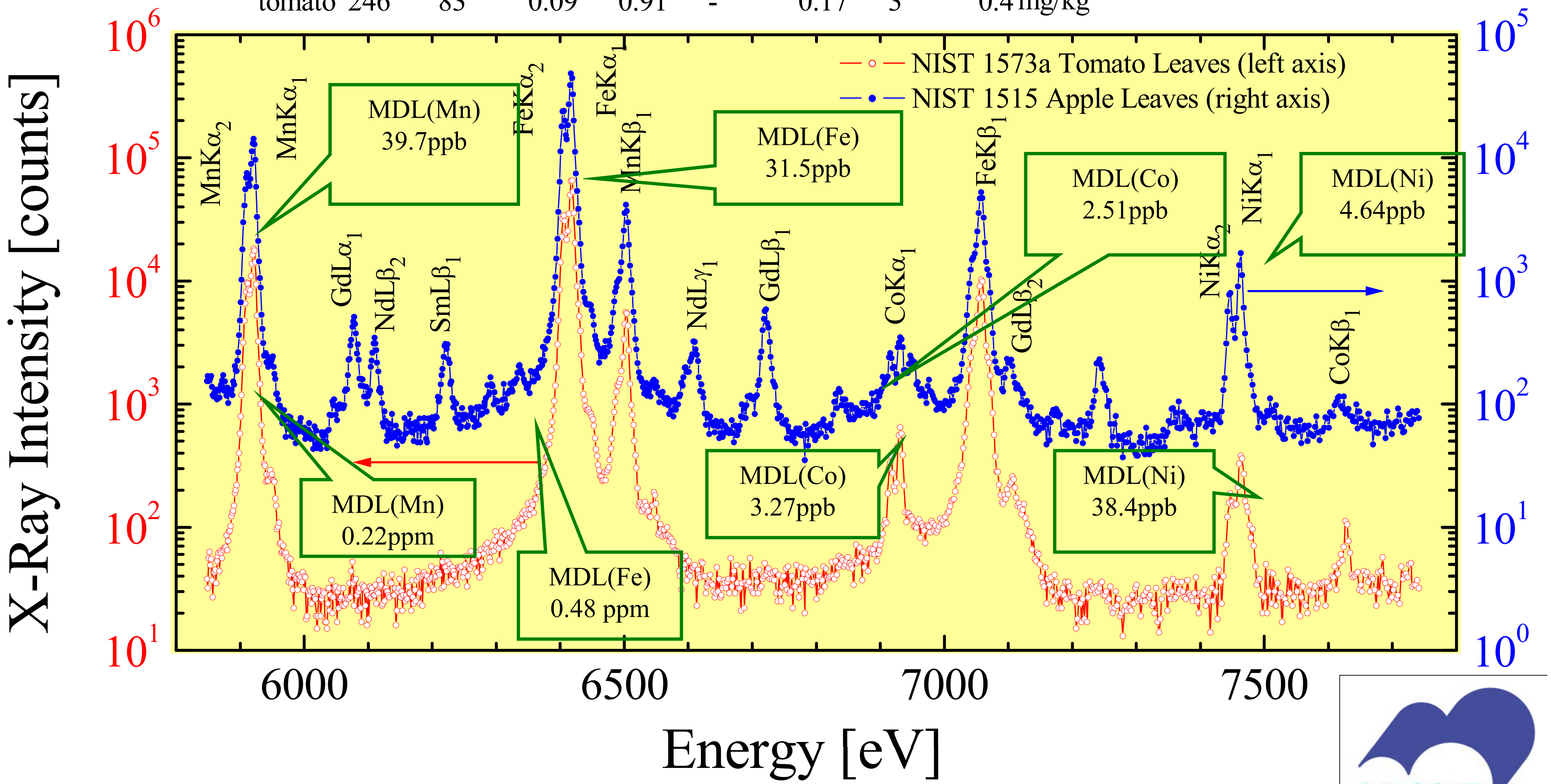


(b)XRF spectrum of 0.1ml Ni (1ng/g)solution　(20s/point)

Typical XRF Spectra Obtained by R=100 Spectrometer
Trace Metals in Apple and Tomato Leaves (NIST1573a and 1515)

	Mn	Fe	Co	Ni	Nd	Gd	Sm	Tb
apple	54	83	0.09	0.91	17	3	3	0.4 µg/g
tomato	246	83	0.09	0.91	-	0.17	3	0.4 mg/kg

1sec/point



WDS

NIMS X-Ray Lab

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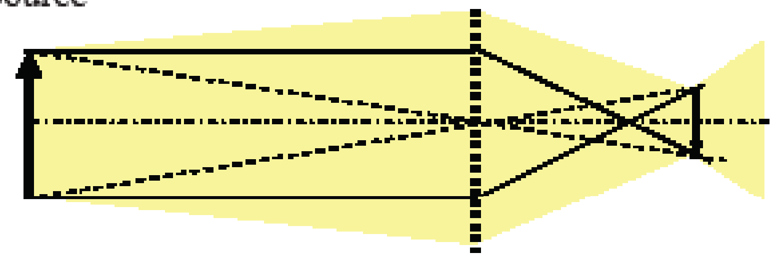
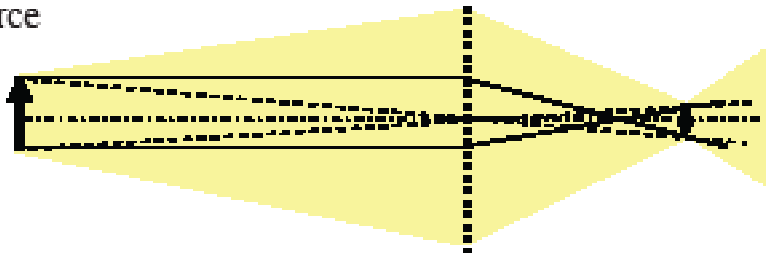
- Conclusion

SR is suitable for production of X-ray microbeam

X-ray source and X-ray microbeam





$1/a + 1/b = 1/f$ $M = b/a$

Helmhortz invariant

$y \times u = y' \times u'$

y,y' source and focus size

u,u' divergence and convergence angle

Low emittance source => small y x u

Small source size and low divergence

(3rd generation ring)

⇒Smaller focus with higher intensity

⇒micro-beam to nano-beam

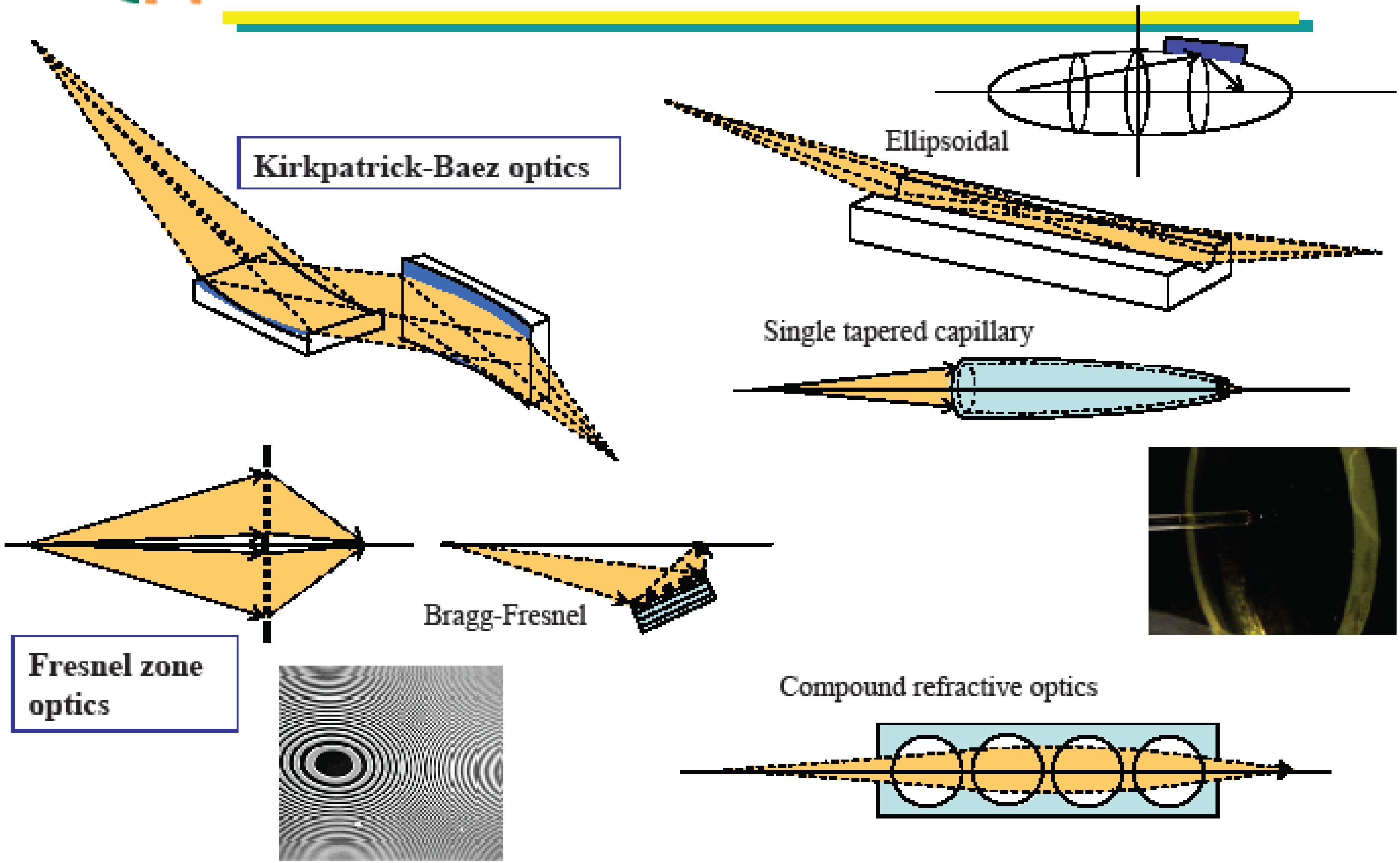
X-ray Focusing Elements

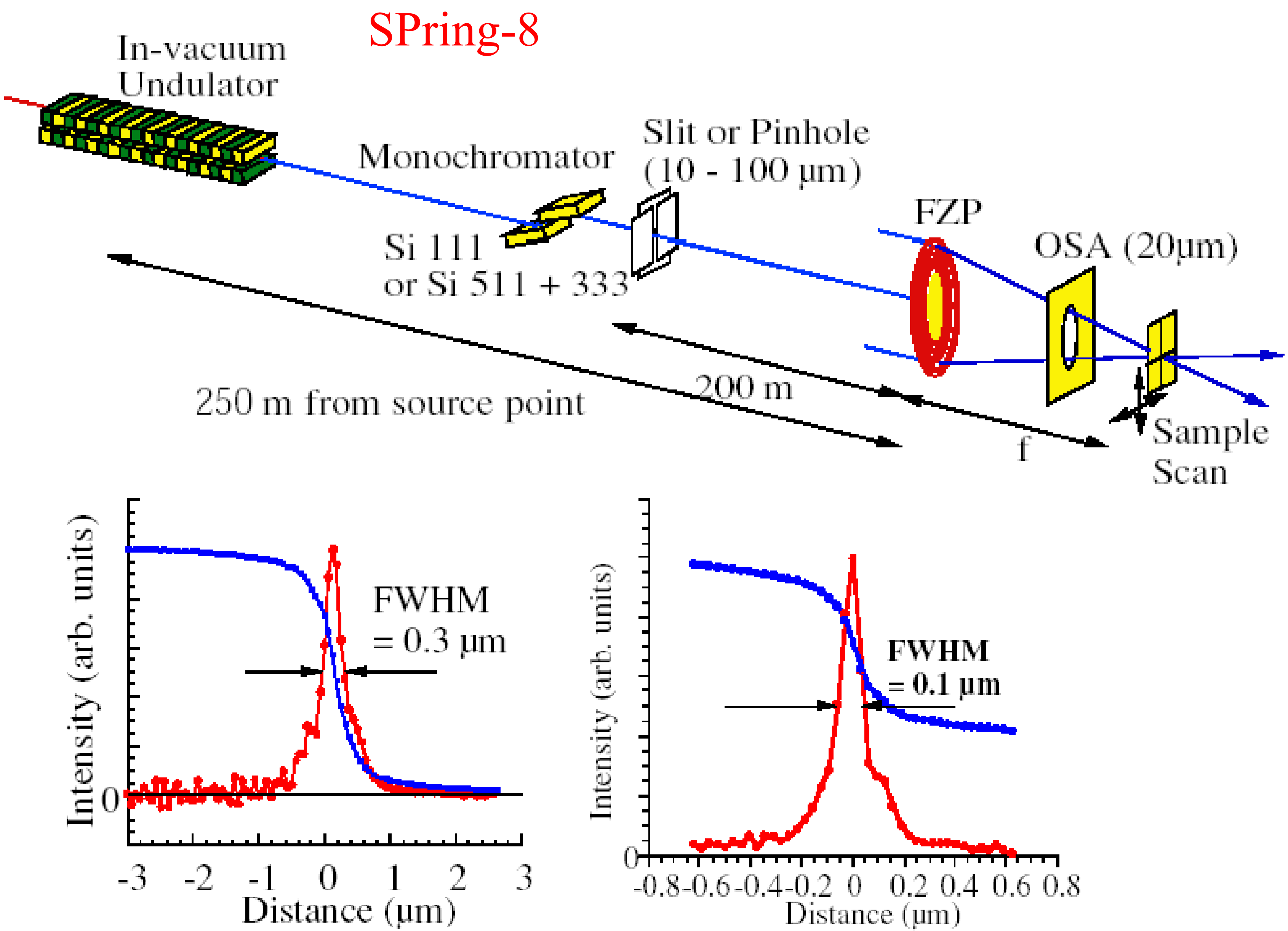
$n = 1 - \delta - i\beta \qquad \delta \sim 10^{-5}$

X-rays: electromagnetic wave with short wavelength

Reflection	Grazing incidence mirror
No chromatic aberration	spherical / aspherical
	toroidal (bent cylinder)
	elliptical, ellipsoidal
	parabolic, paraboloidal
	Capillary (single, poly)
Diffraction	Fresnel Zone plate
Energy dependence	Bragg-Fresnel lens
	Crystal (asymmetric reflection / bent crystal)
Refraction	Compound refractive lens

X-ray microbeam Optics





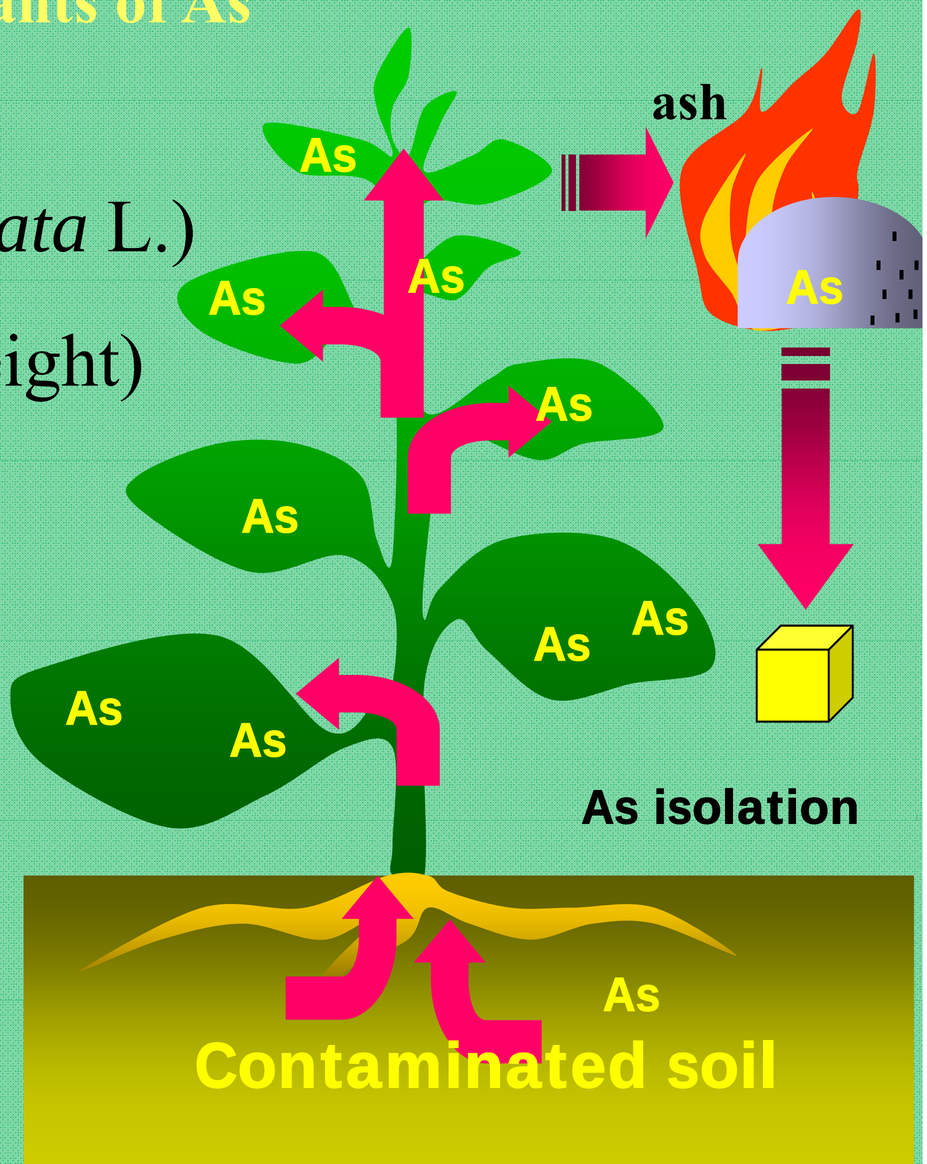
Beam profile at focal points made by FZP at 8keV

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

Study of hyperaccumulator plants of As

Chinese brake fern (*Pteris vittata* L.)

(As: *ca.* 22,000 µg /g dry weight)



Arsenic distribution and speciation in an arsenic hyperaccumulator fern by X-ray spectrometry utilizing a synchrotron radiation source

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)

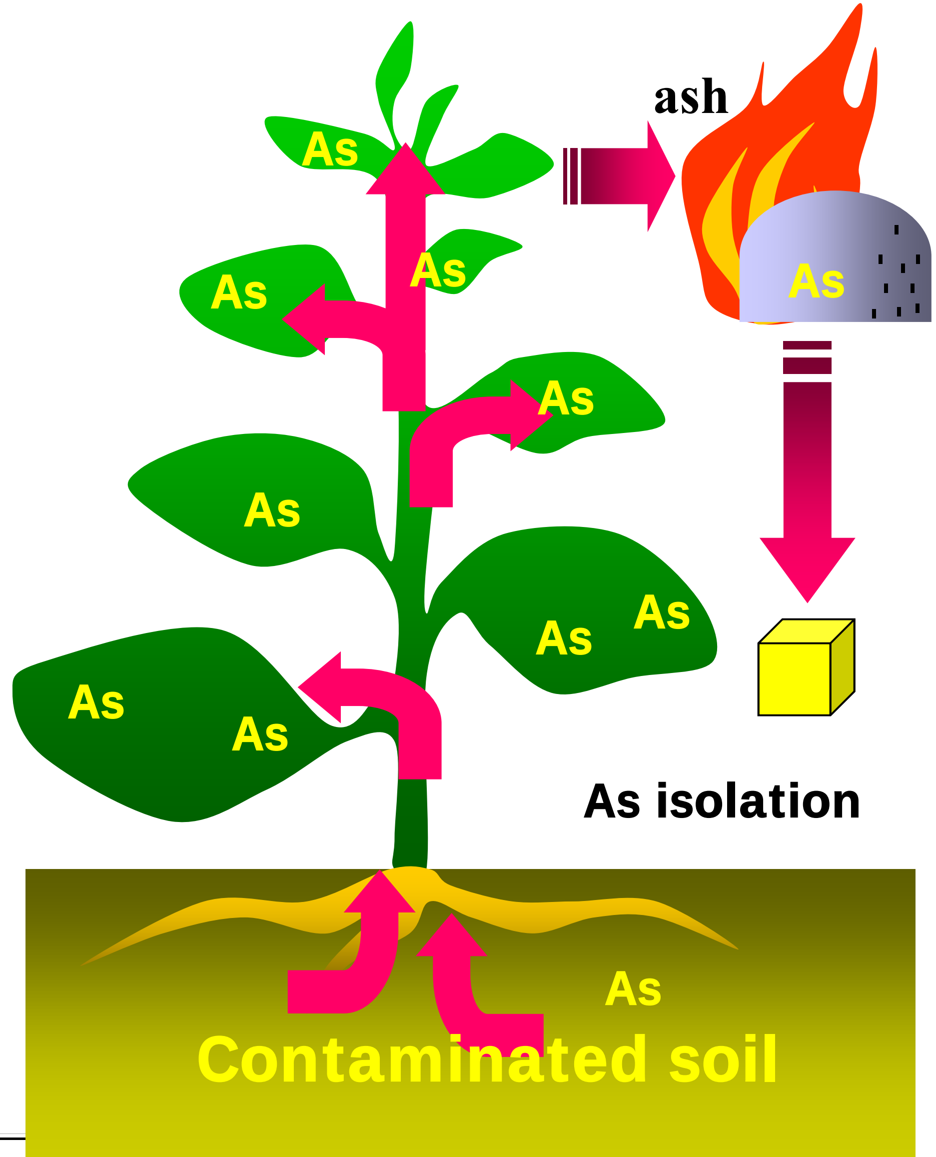
Phytoremediation

plant / remediate

Green technology by plant

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

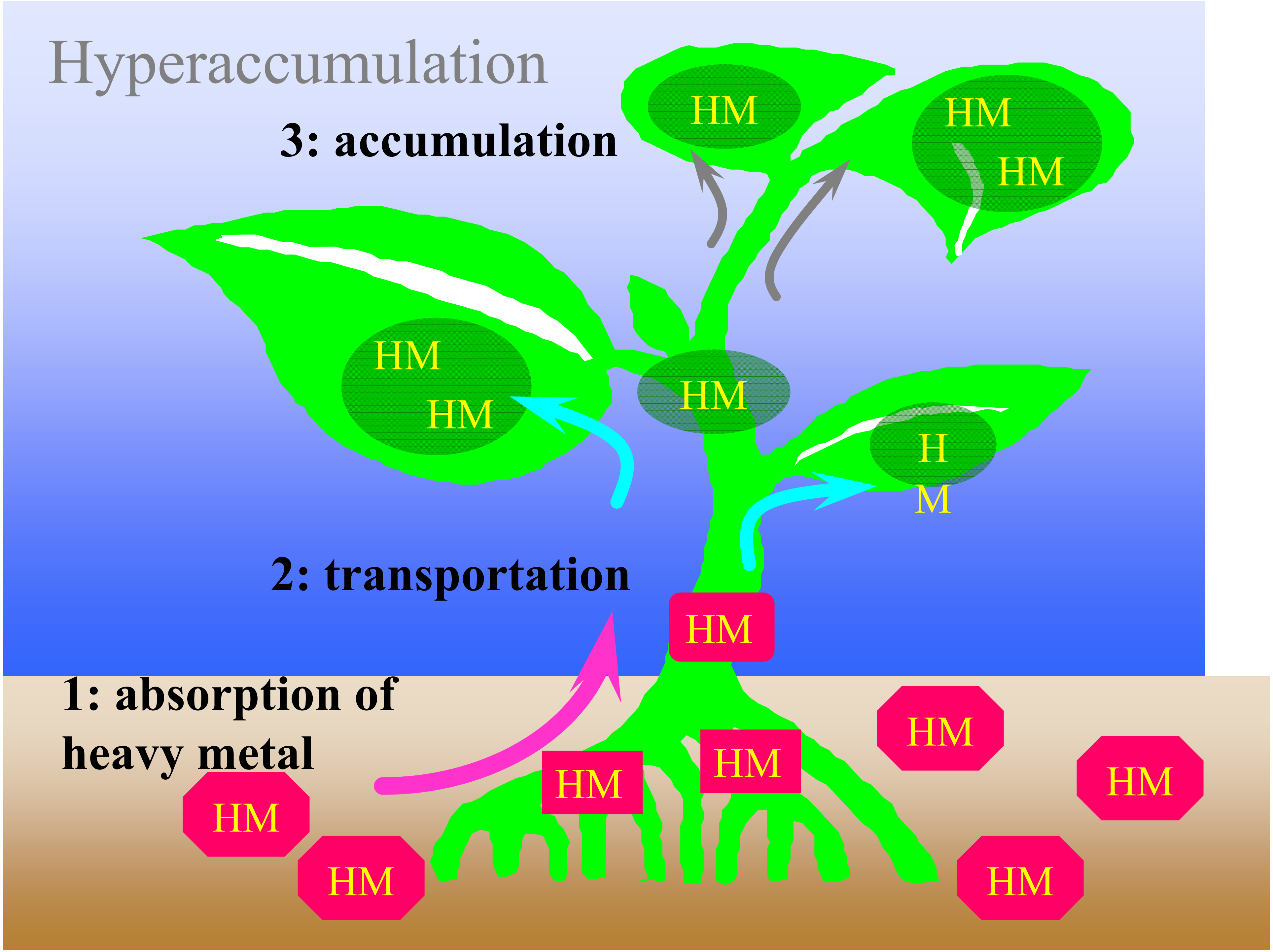
Some specific kinds of plants are known to be heavy metal hyperaccumulator



Element	conc./ ppm	plant
As*1	22,630	*Pteris vittata L.*（モエジマシダ）
Cd	11,000	*Athyrium yokoscense*（ヘビノネゴザ）
Pb	34,500	*Brassica juncea*（カラシナ）

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

Application Example
Chinese brake fern (*Pteris vittata* L.)


Hyperaccumulation
3: accumulation
HM
HM
HM
HM
HM
HM
H
M
2: transportation
HM
1: absorption of
heavy metal
HM
HM
HM
HM
HM
HM
HM

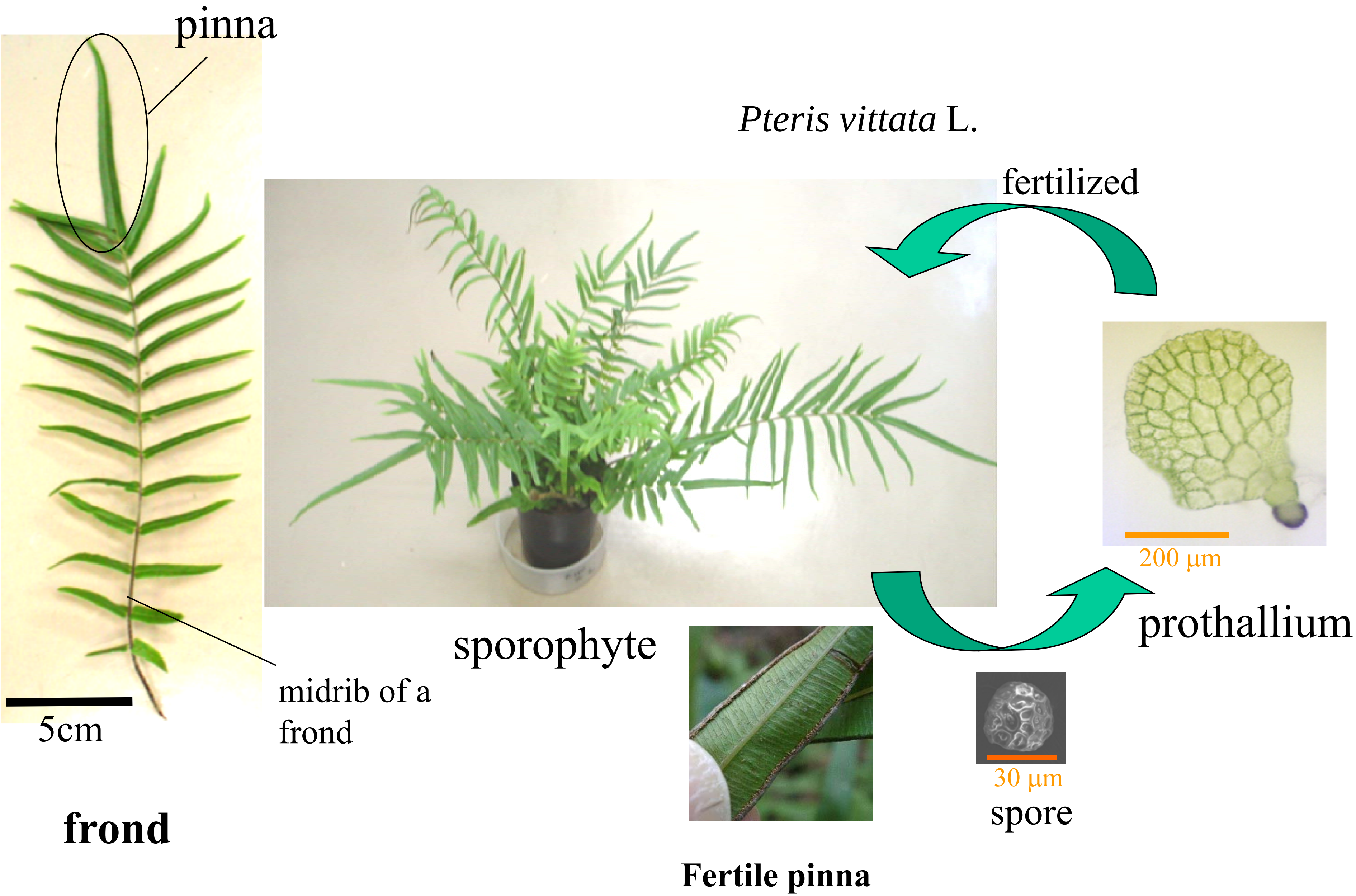
Application of SR X-ray analyses

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

- In vivo chemical state analysis of metals in the plant
  → X-ray absorption fine structure (XAFS) analysis

- Chemical state analysis in cell level
  → μ-XANES

Life of fern


pinna
Pteris vittata L.
fertilized
200 μm
prothallium
sporophyte
5cm
midrib of a frond
30 μm
spore
frond
Fertile pinna

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)

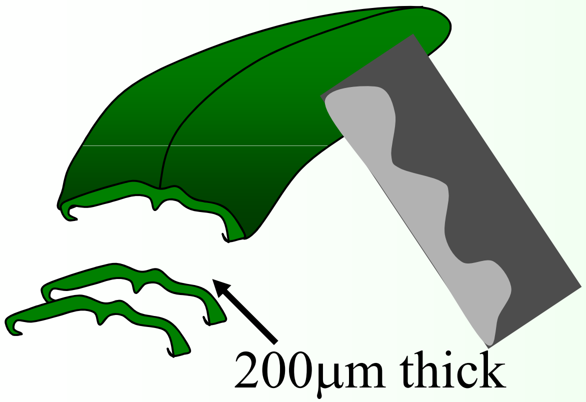
As level*

pinna：2800 - 4500 μg g^{-1}dry

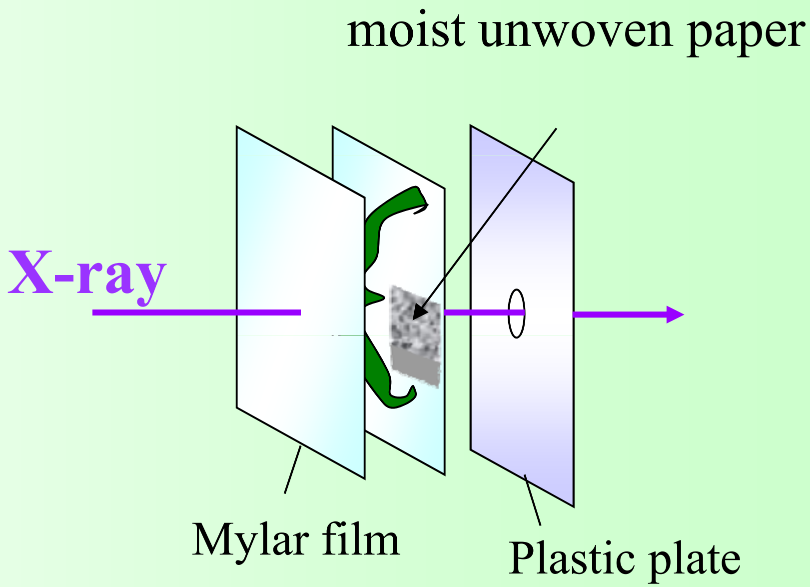
midrib of a frond：84 - 250 μg /g dry

* Anal. By AAS

Sample preparation for microbeam analysis



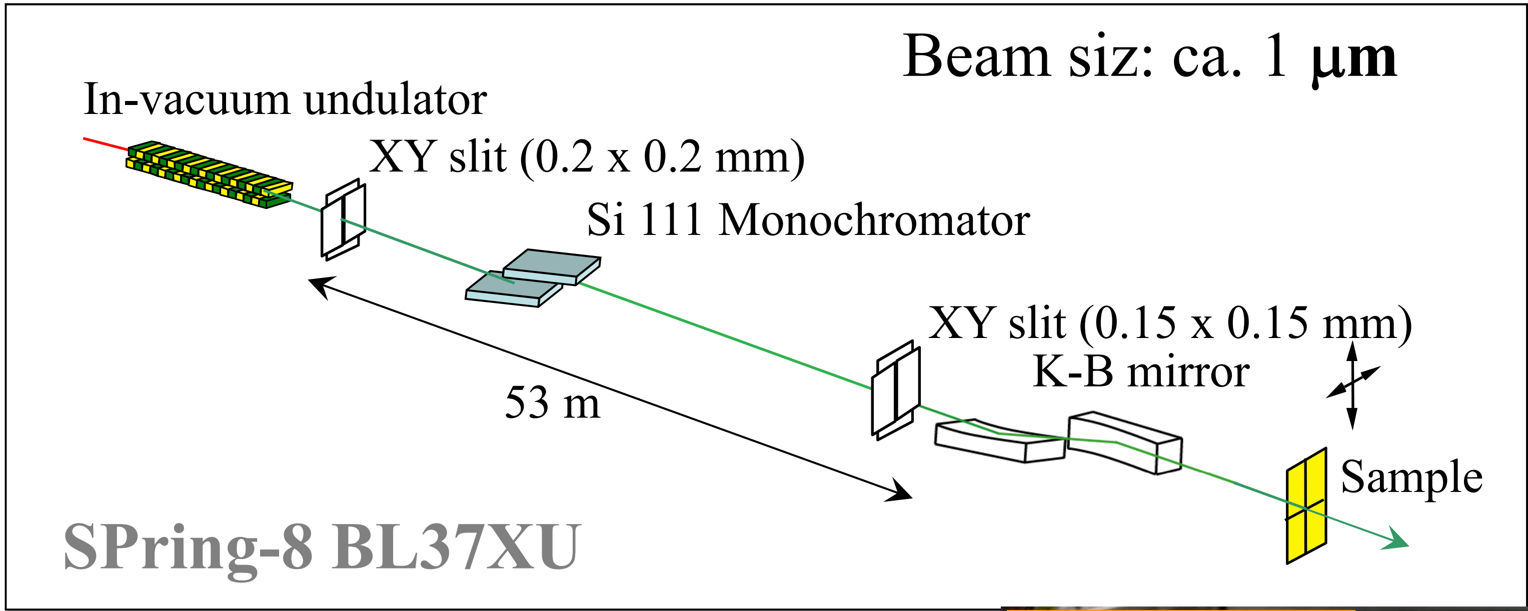
vertical slicer (Model HS-1, JASCO Co.)



freeze dry of frozen

μ-XRF, μ-XANES

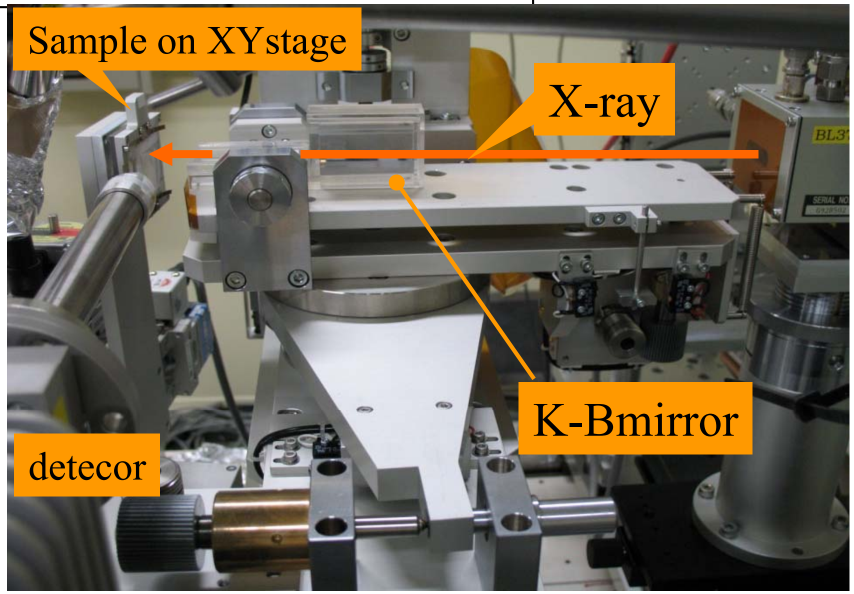
X-ray energy
As: 12.8keV
Cd: 37.0keV



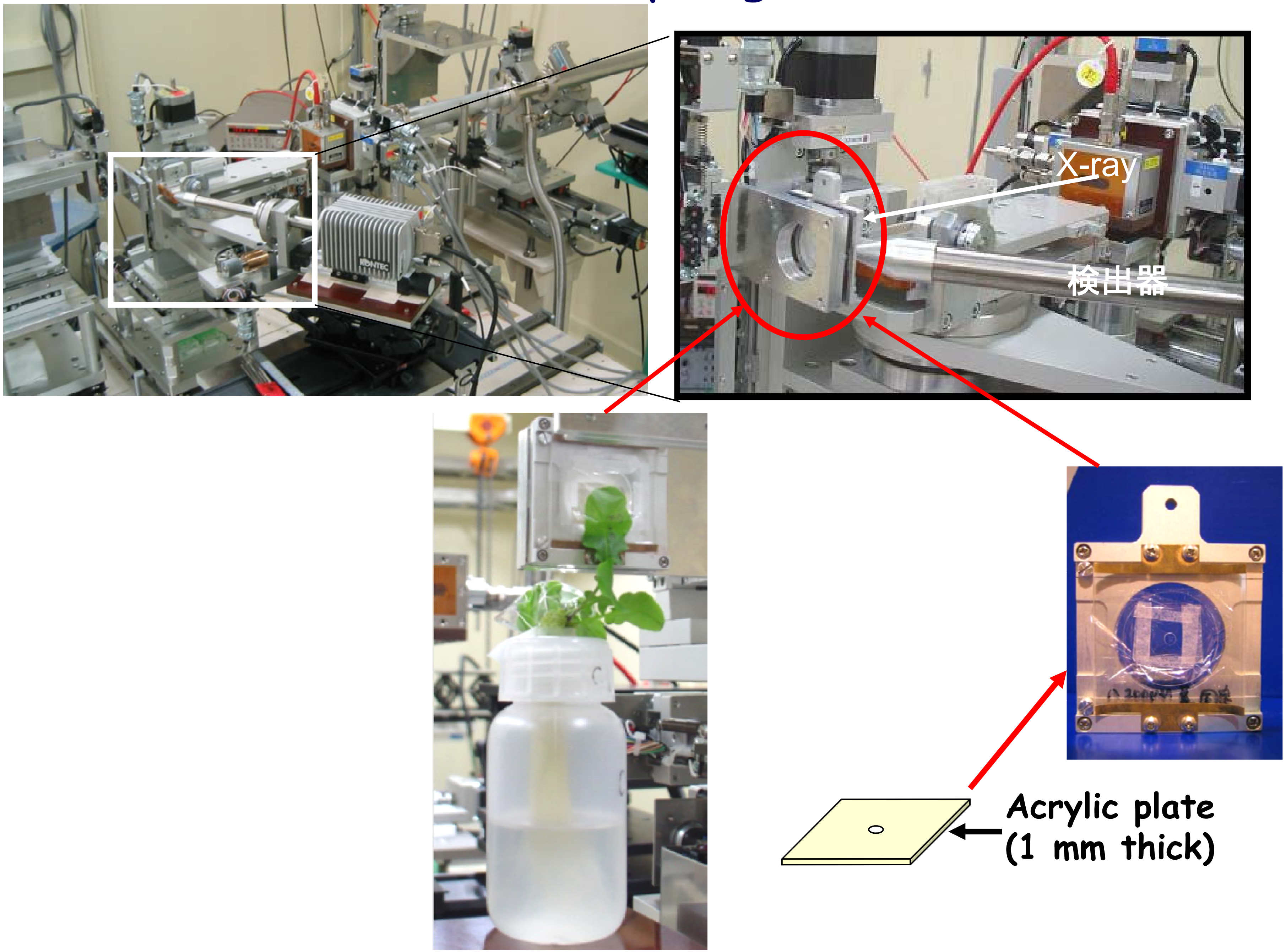
- BEAMLINE DESCRIPTION -
The light source : In-vacuum type undulator
(Period length : 32 mm, the number of period : 140)
Monochromator : Double-crystal monochromator
located 43 m from the source

Table Details of focusing optics by K-B mirror

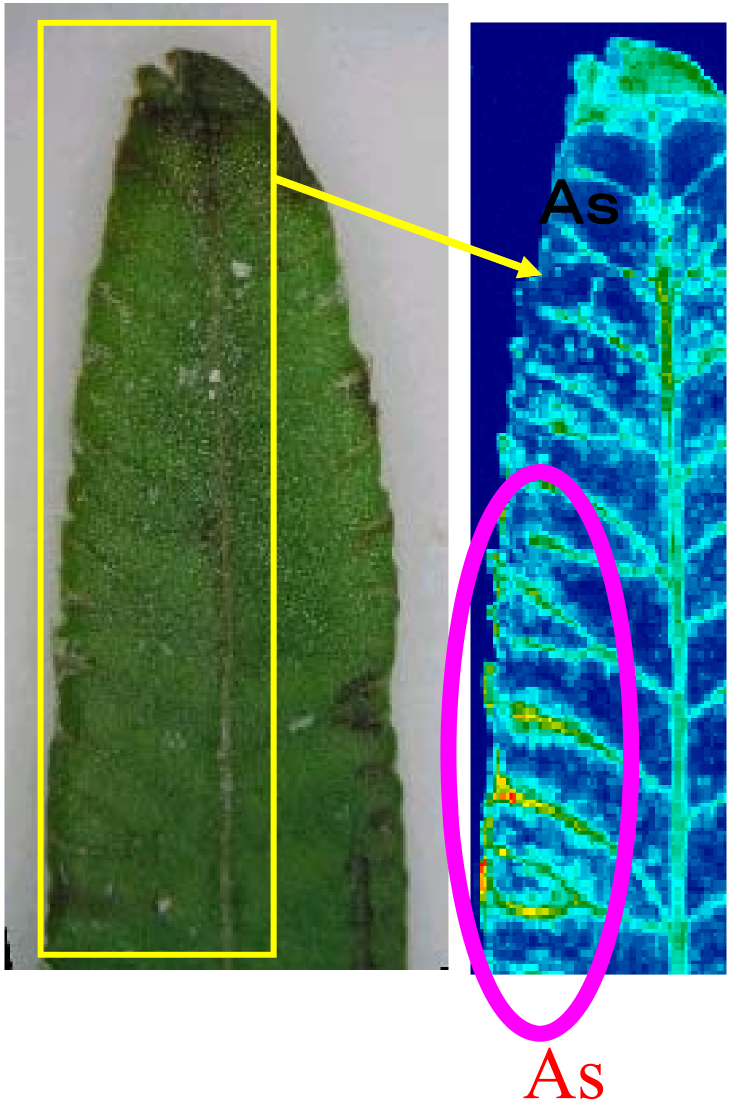
	37 keV[1]	12.8 keV
Material	fused quartz	fused quartz
Surface	platinum coated	platinum coated
Focal length (1st mirror)	250 mm	100 mm
(2nd mirror)	100 mm	50 mm
Average glancing angle	0.8 mrad	2.8 mrad

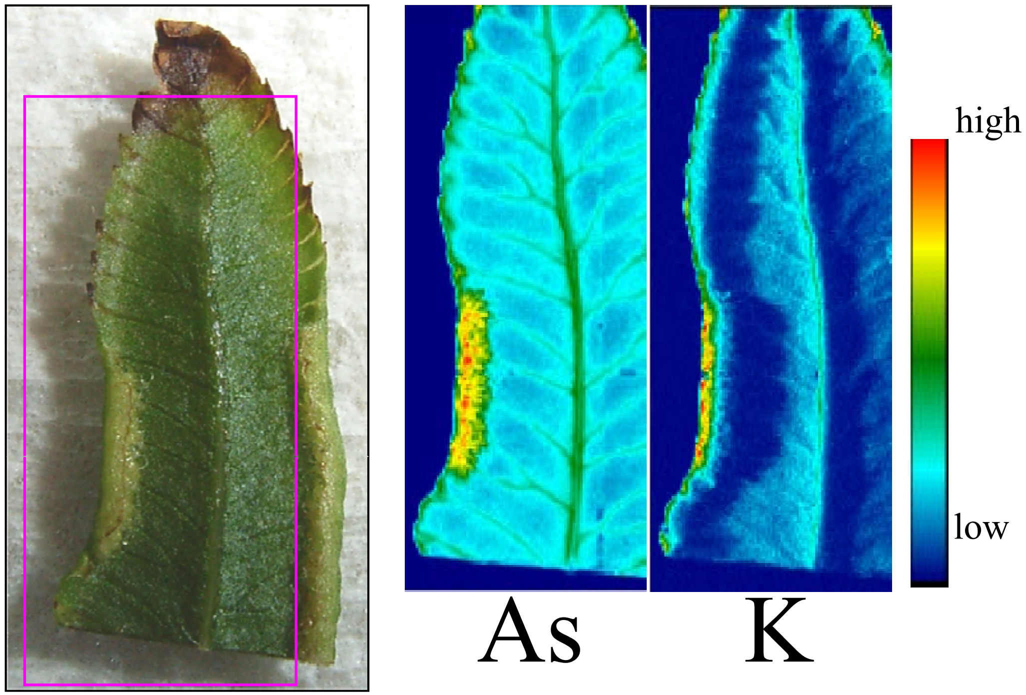


Instrument ~Spring-8 BL37XU~



XRF imaging for As, K, and Ca of pinnae

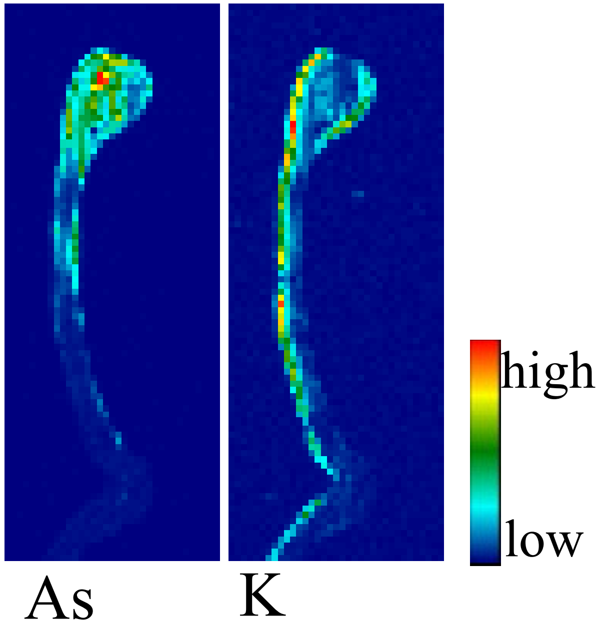


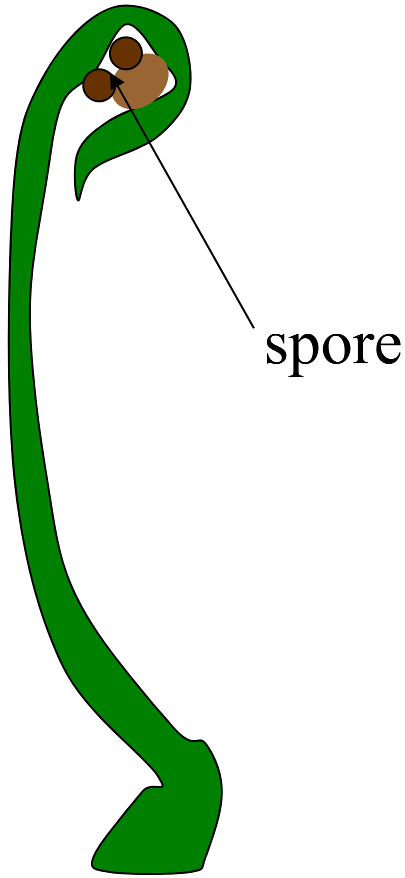


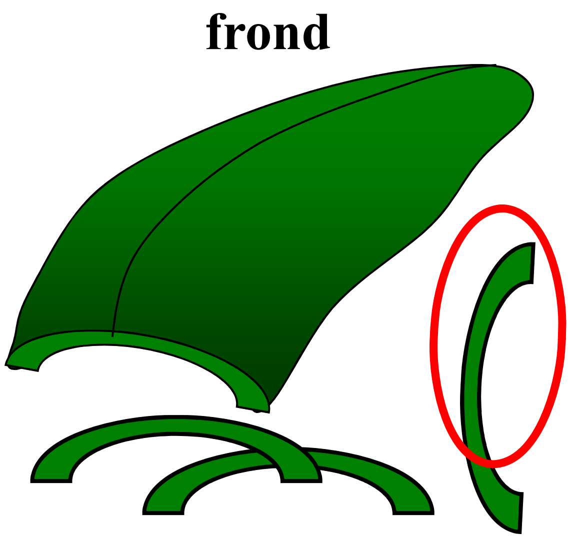
high
low

Accumulation of As at Fertile with spores along marginal parts

A section of pinna







X-ray Energy : **14.999 keV**

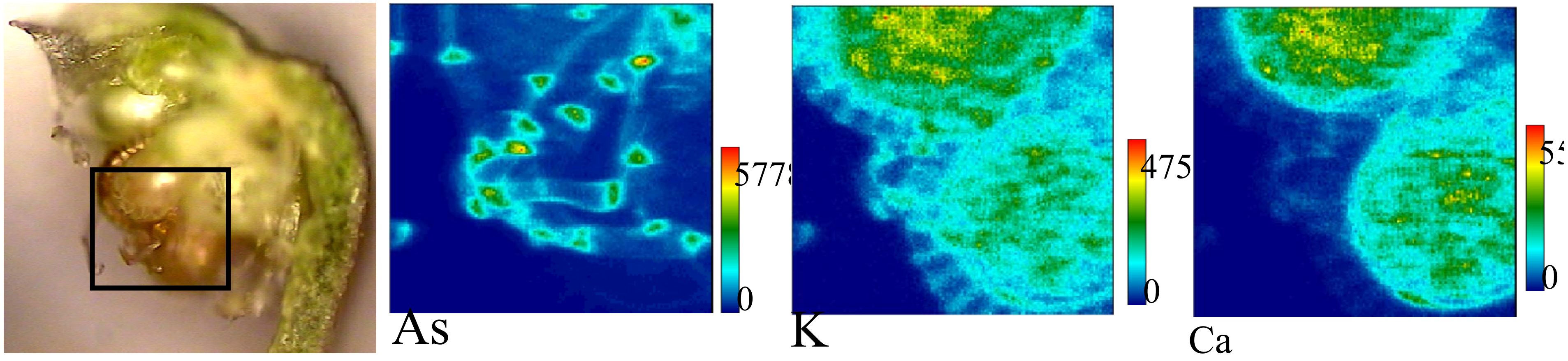
Beam size : **50 µm × 50 µm**

Step number : **35 point × 90 point**

measurement time : **1 sec/point**

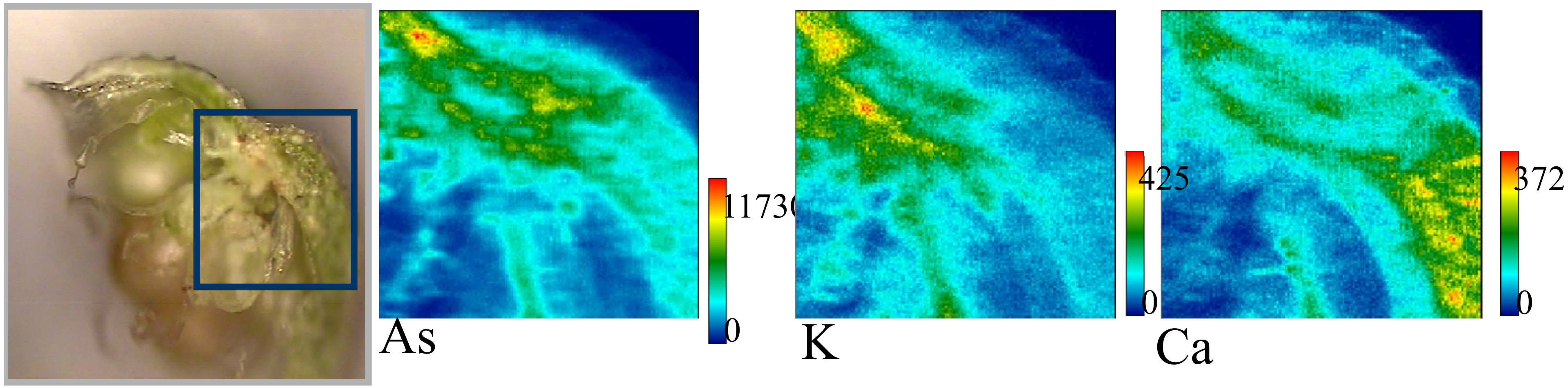
X-ray Energy : 12.8 keV
Beam size : 1.5 μm × 1.5 μm
Exposure time : 0.2 sec. / point
Point : 150 point × 150 point

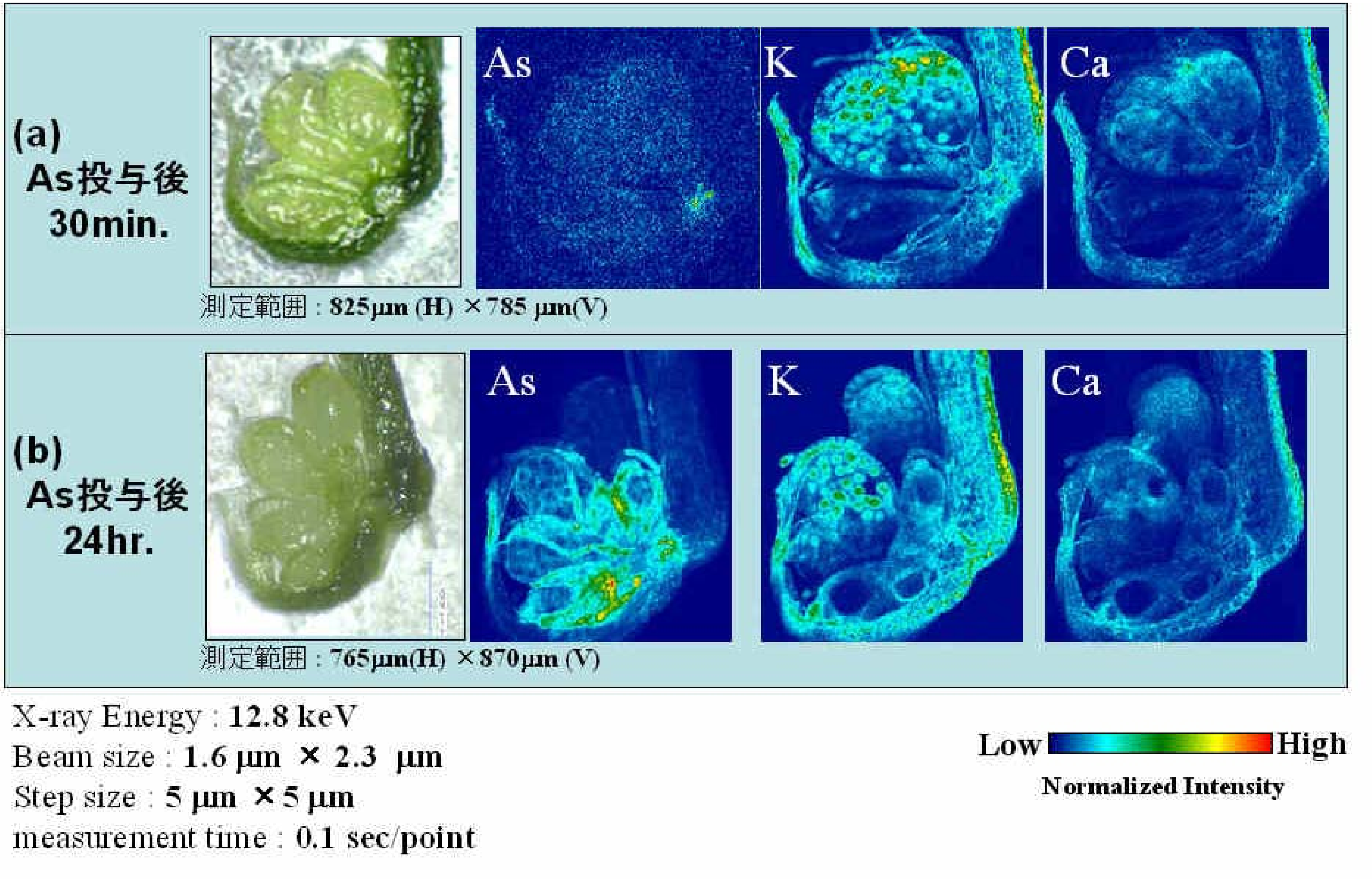
μ−XRF imaging at SPring-8



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





μ-XRF imaging of leaf at (a)30min and (b)24 hr after arsenic feeding.

Time dependent observation of arsenic transfer in leaf tissue of hyperaccumulator fern

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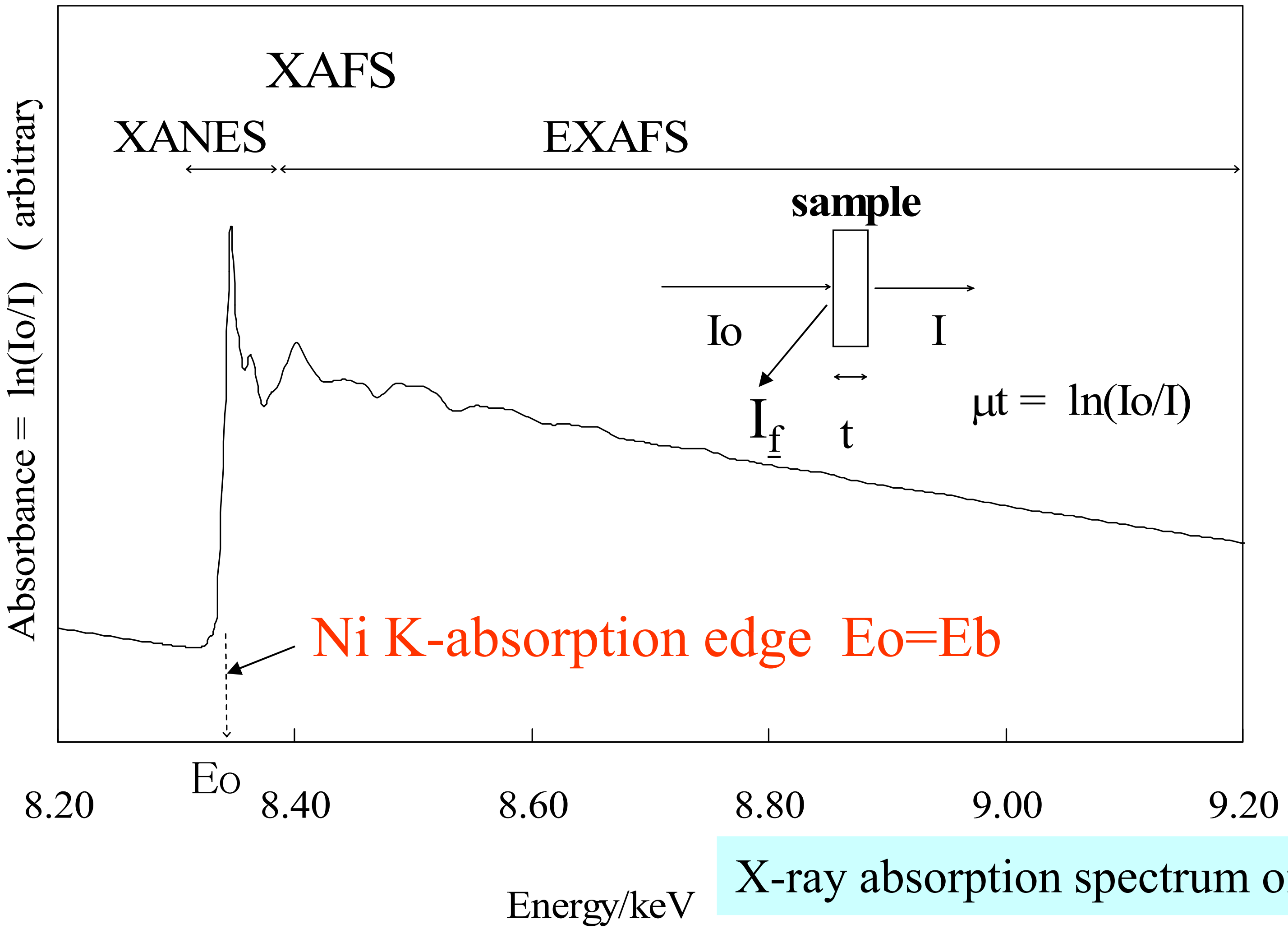
(5) Multiple X-ray analytical technique - A combination of **μ-XRF imaging, μ-XRD, XAFS and SEM**

・Conclusion

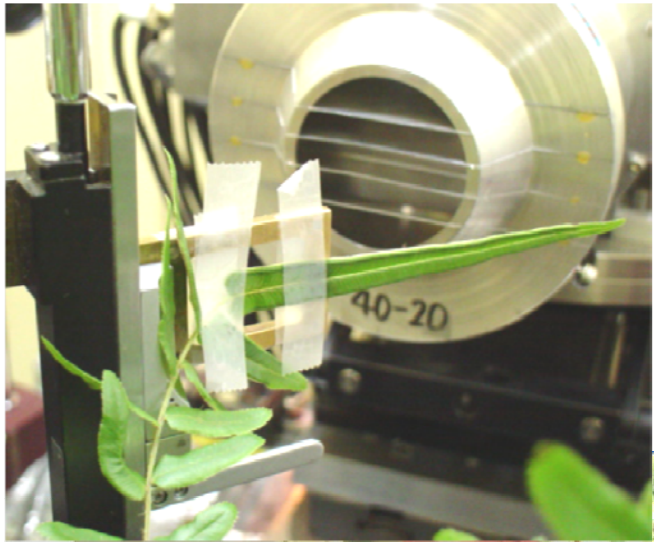


X-ray absorption spectrum of $LiNiO_2$

XANES: X-ray absorption near edge structure
electronic state, oxidation number

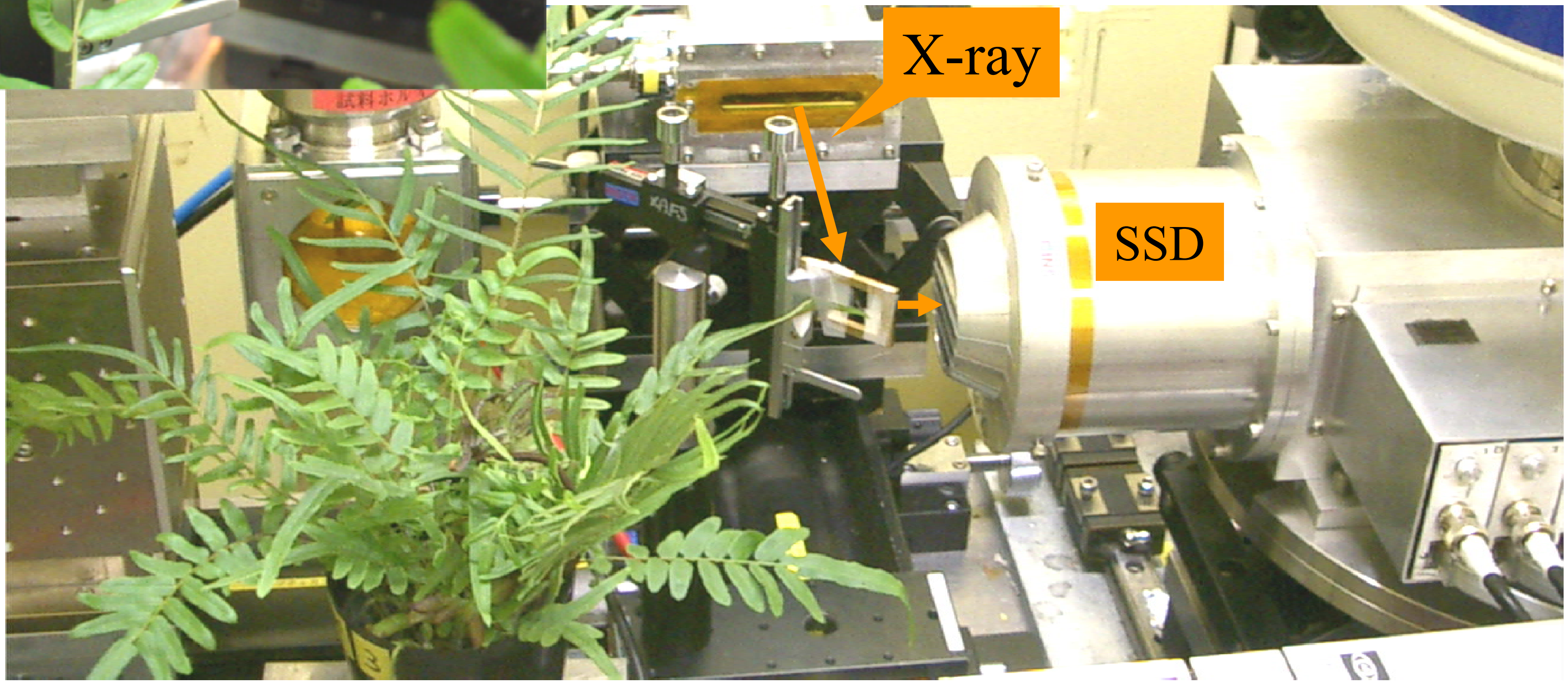
EXAFS: Extended X-ray absorption fine structure
local structure (atomic distance and coordination No.)

XAFS analysis

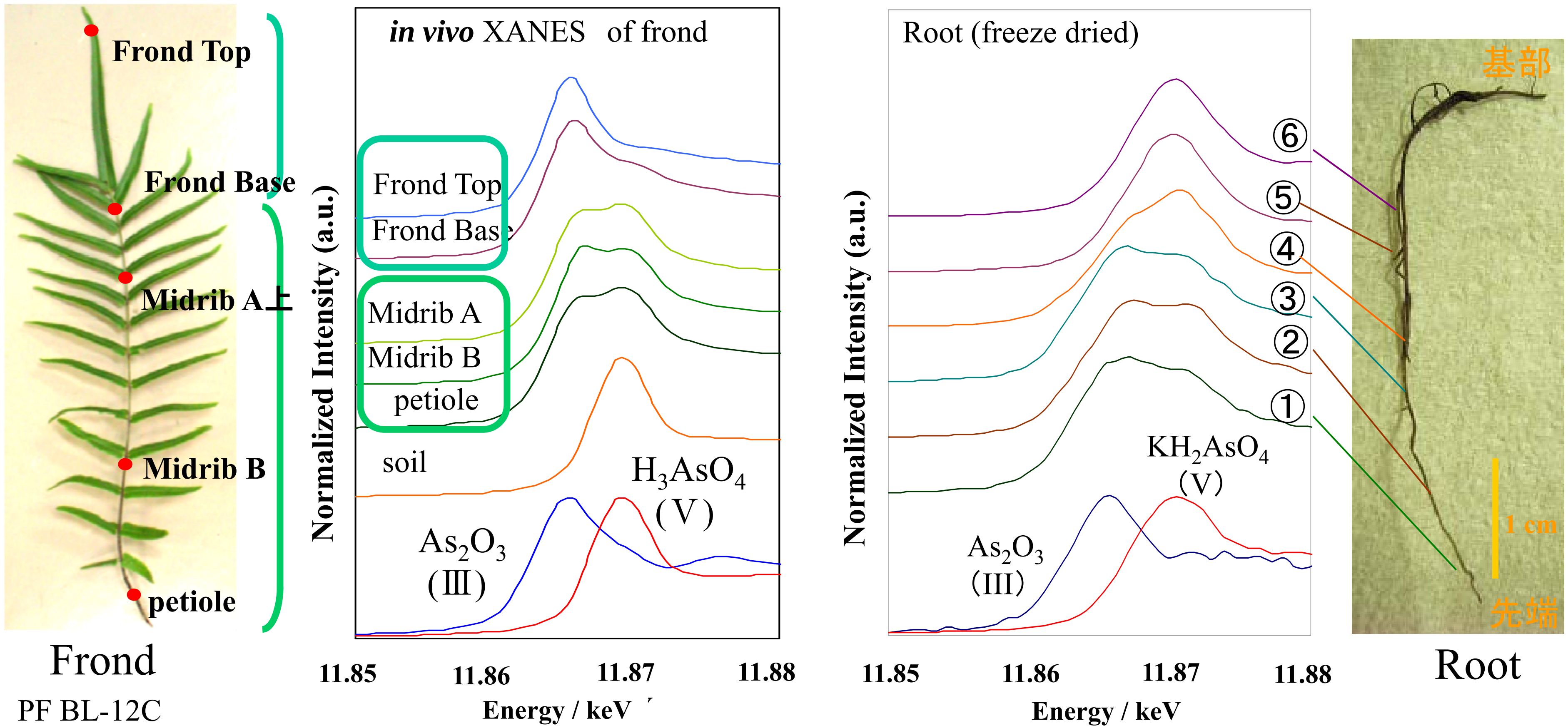


KEK PF BL12C
As K-edge (11.863 keV)
Si(111) double crystal
Fluorescence mode
19elements-SSD

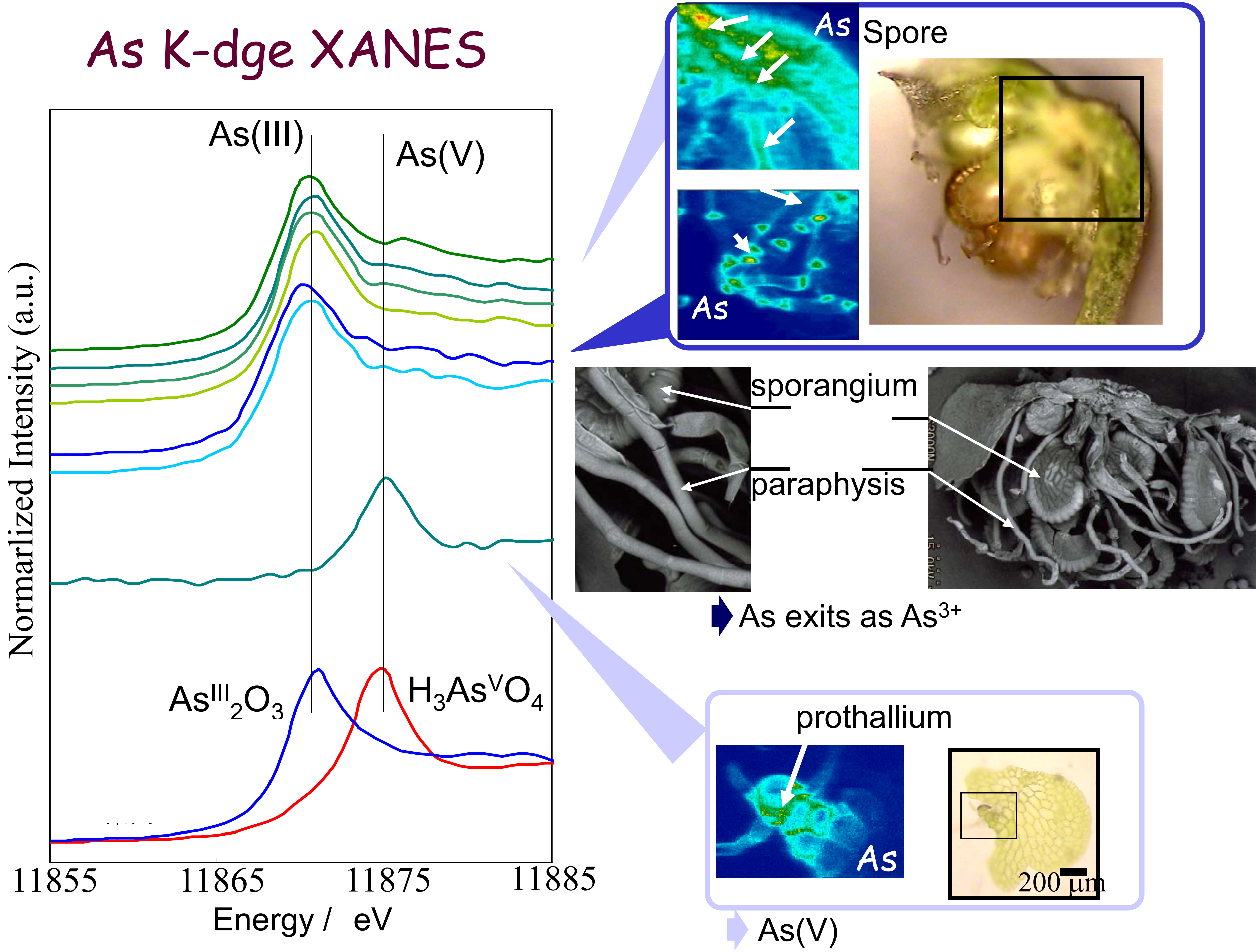
in vivo XAFS



As K-edge XANES analysis

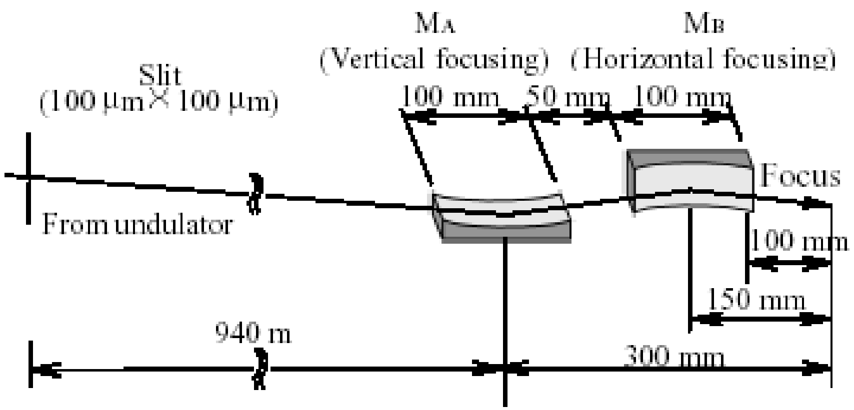


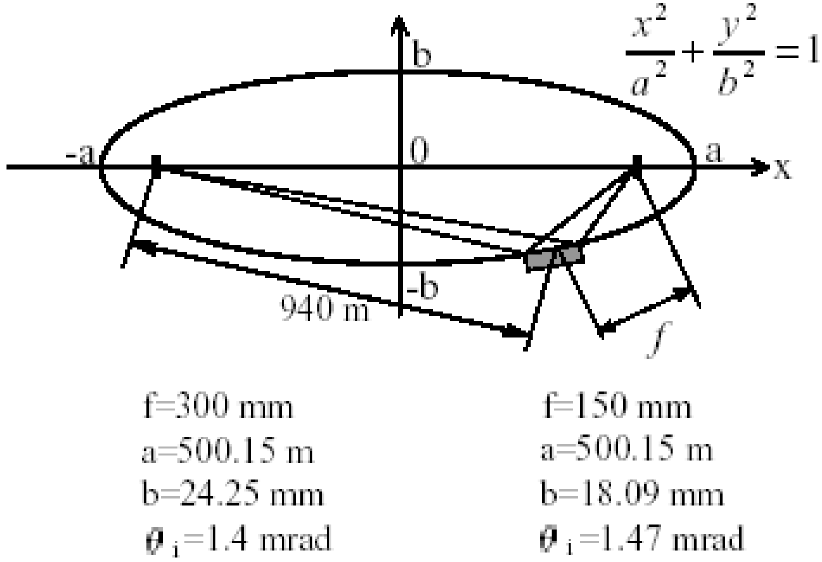
As K-dge XANES



Prospect of microbeam analysis

Microbeam → Nanobeam



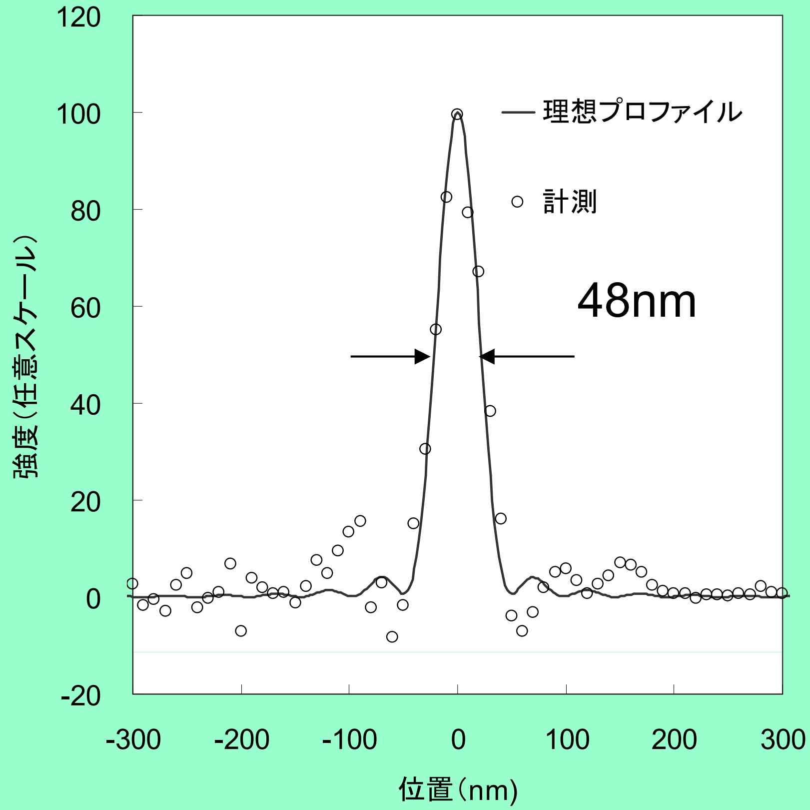


Nano-beam focusing system at SPring-8

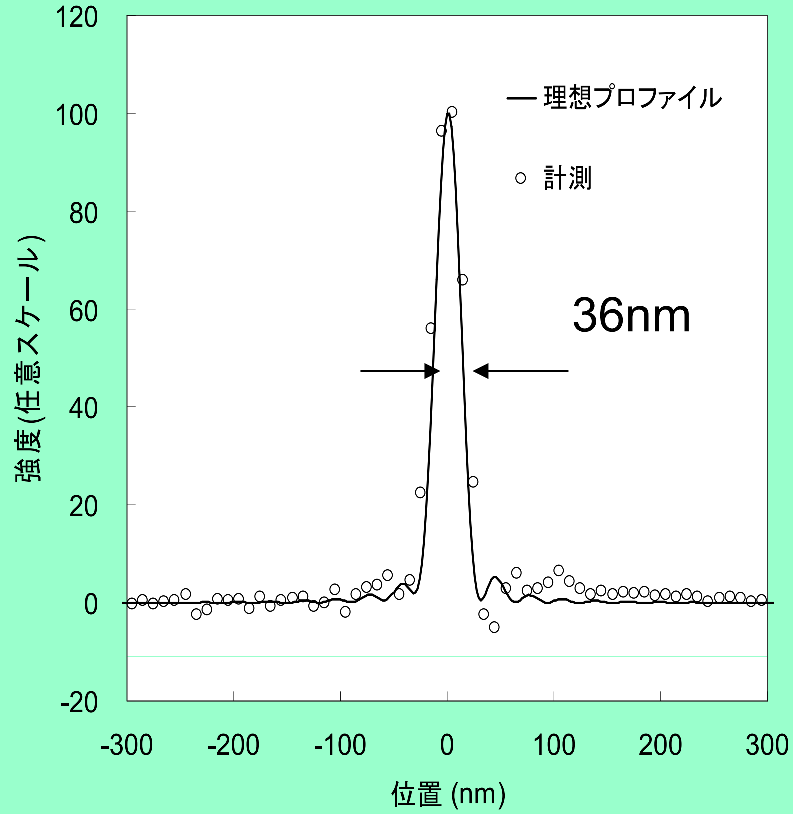
(left) Hig precision K-B mirror

(right) Optical parameters of elliptical mirror

Yamauchi et al.（Osaka Univ.)

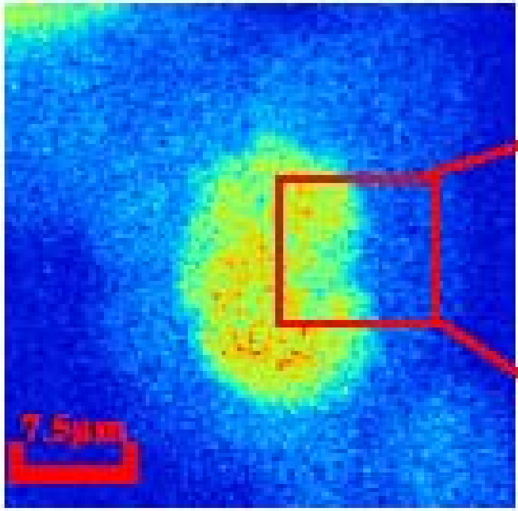


(a)vertical

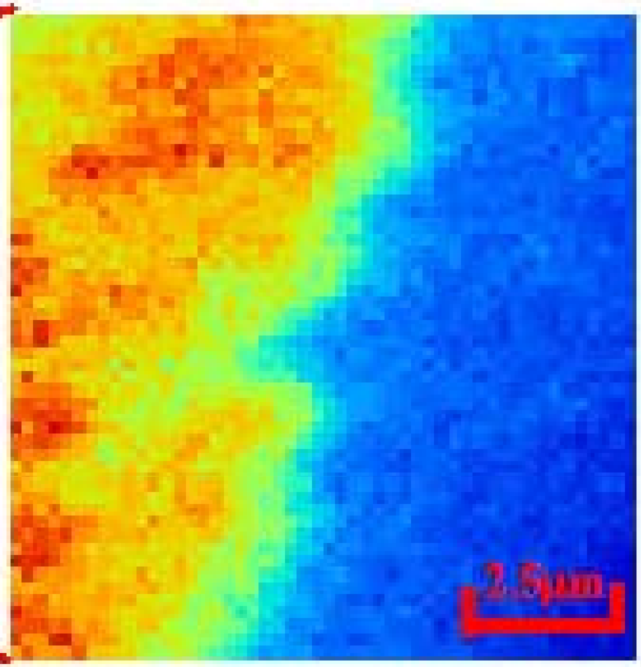


(b)horizontal

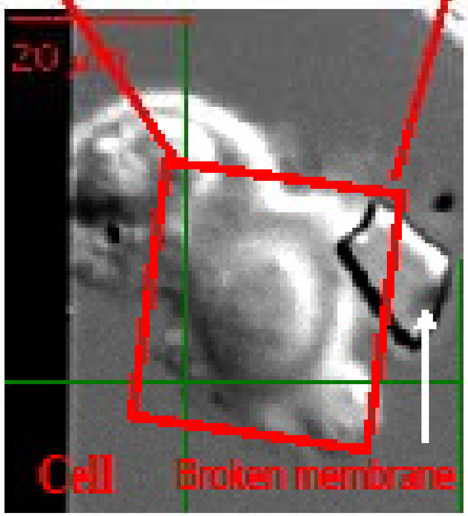
Beam profile



Full image of cell as iron mapping



Iron mapping in a part of a nucleus



Opt. microscope

Experimental condition of the iron mapping

Sample	Human cell
X-ray Energy	15keV
Beam size	200nm x 200nm
Scanning pitch	200nm/pixel
Scan area	10µm x 10µm

Organelle level analysis

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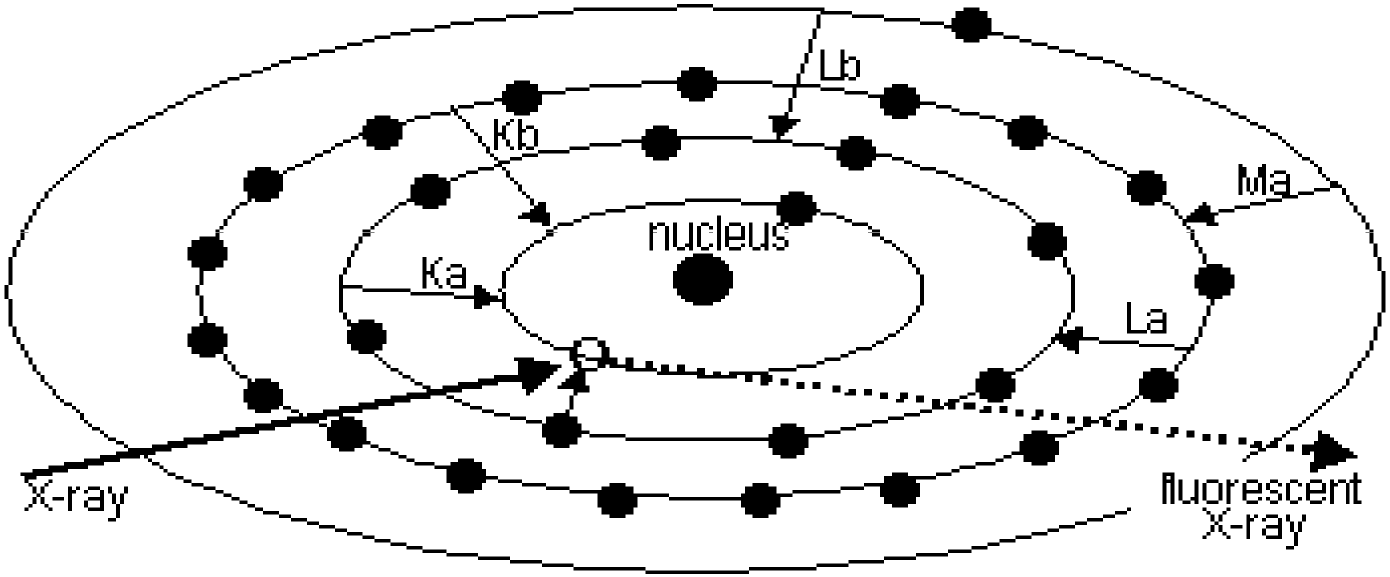
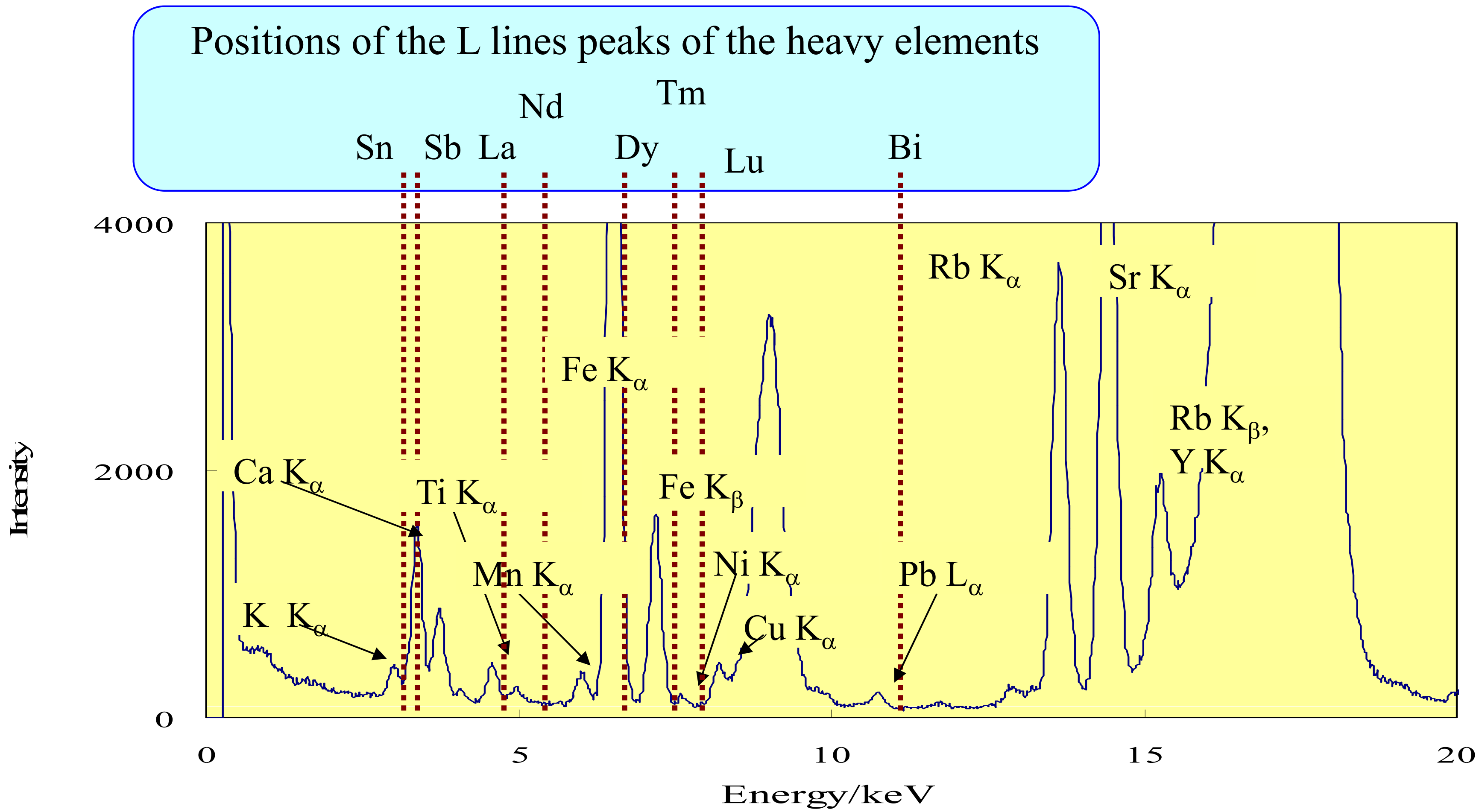
High energy SR-XRF



Highest energy

Bi Kα 76.35 E_b=90.57

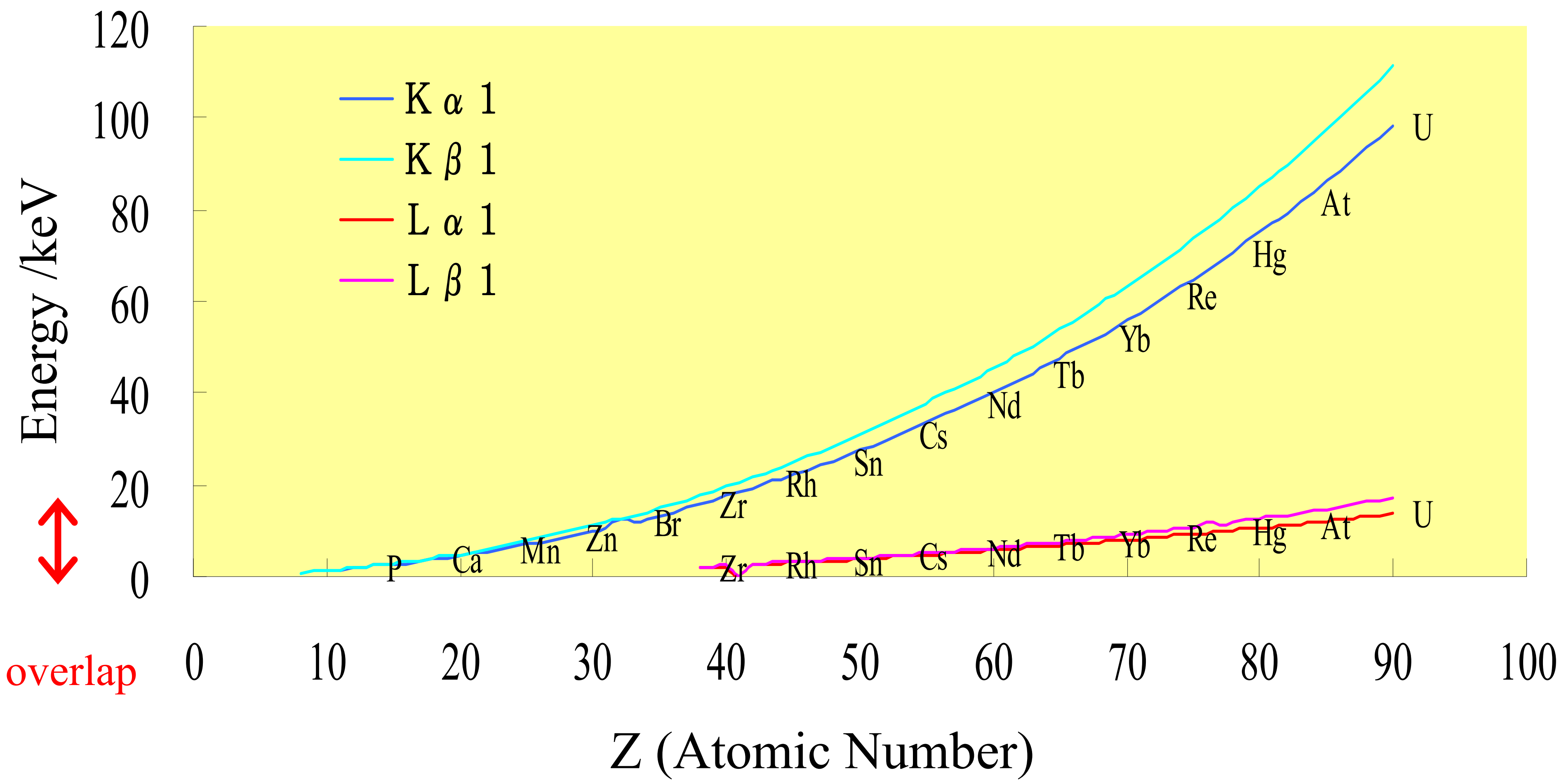
U Kα 97.17 E_b=115.66keV



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



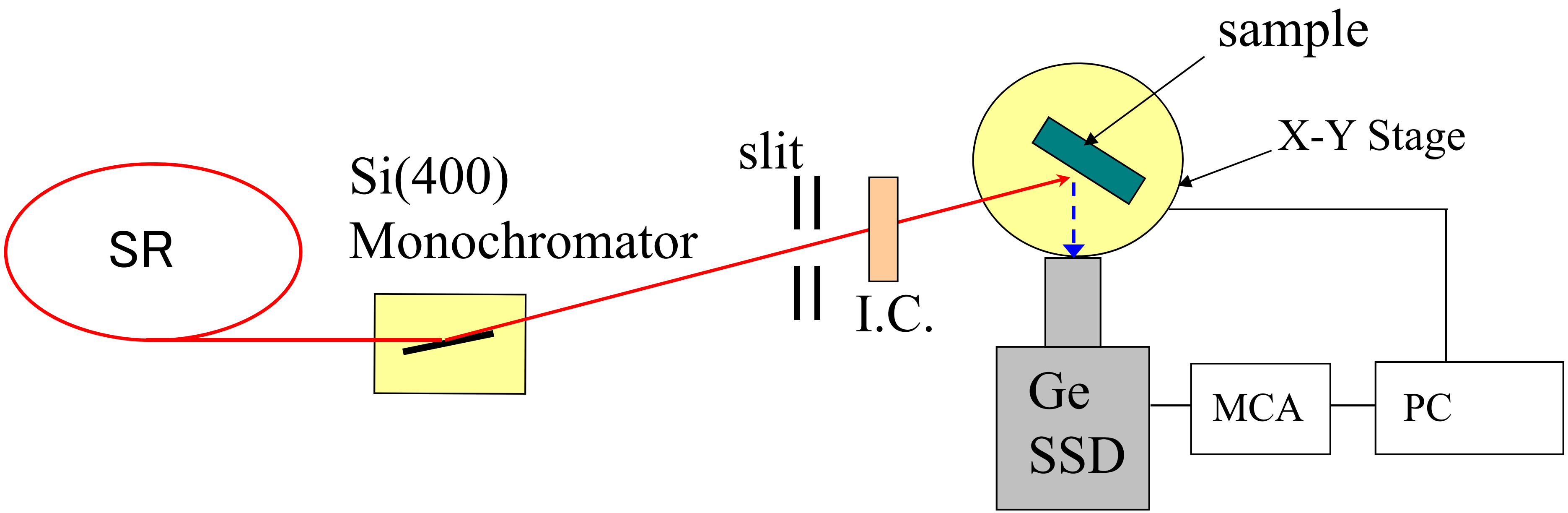
X-ray fluorescence energies of K & L lines v.s. atomic number

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)

BL08W （for High-energy inelastic scattering experiments)

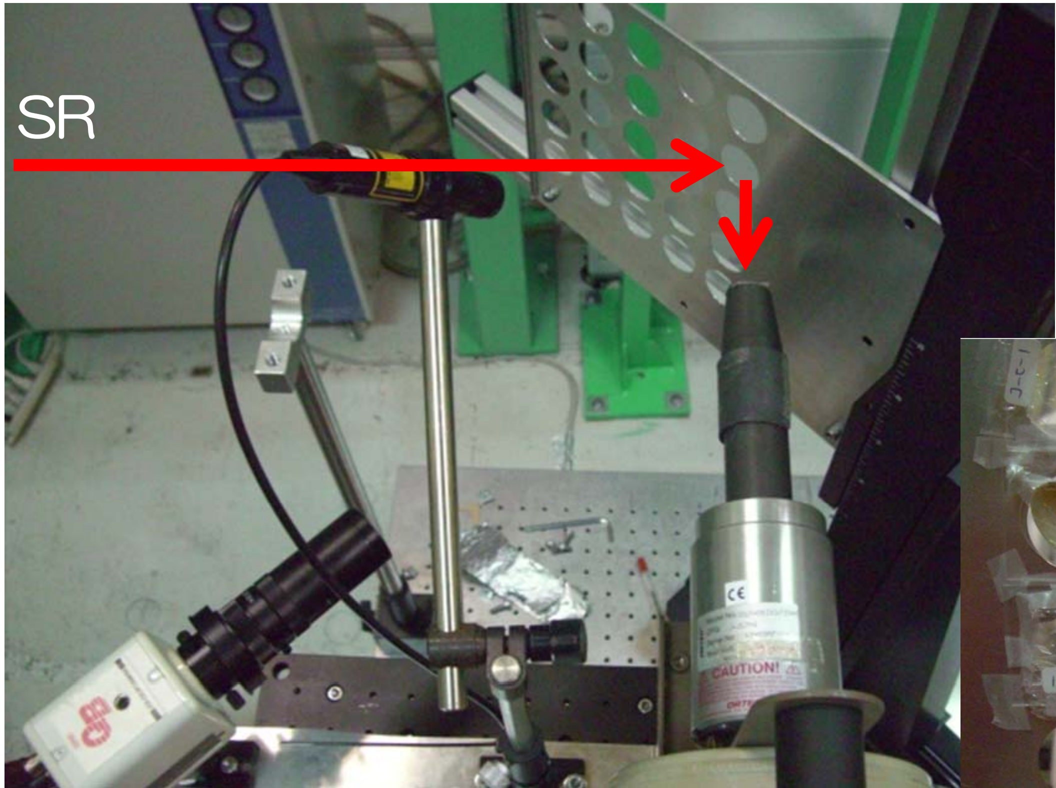


Eliptical multipole wiggler (Gap:160～25.5 mm)
Excitation energy:116 keV (100-150 keV)
Beam size : 1～0.1 mm^2

Experimental setup for high energy XRF

HE-SR-XRF at @SPring-8 BL08W

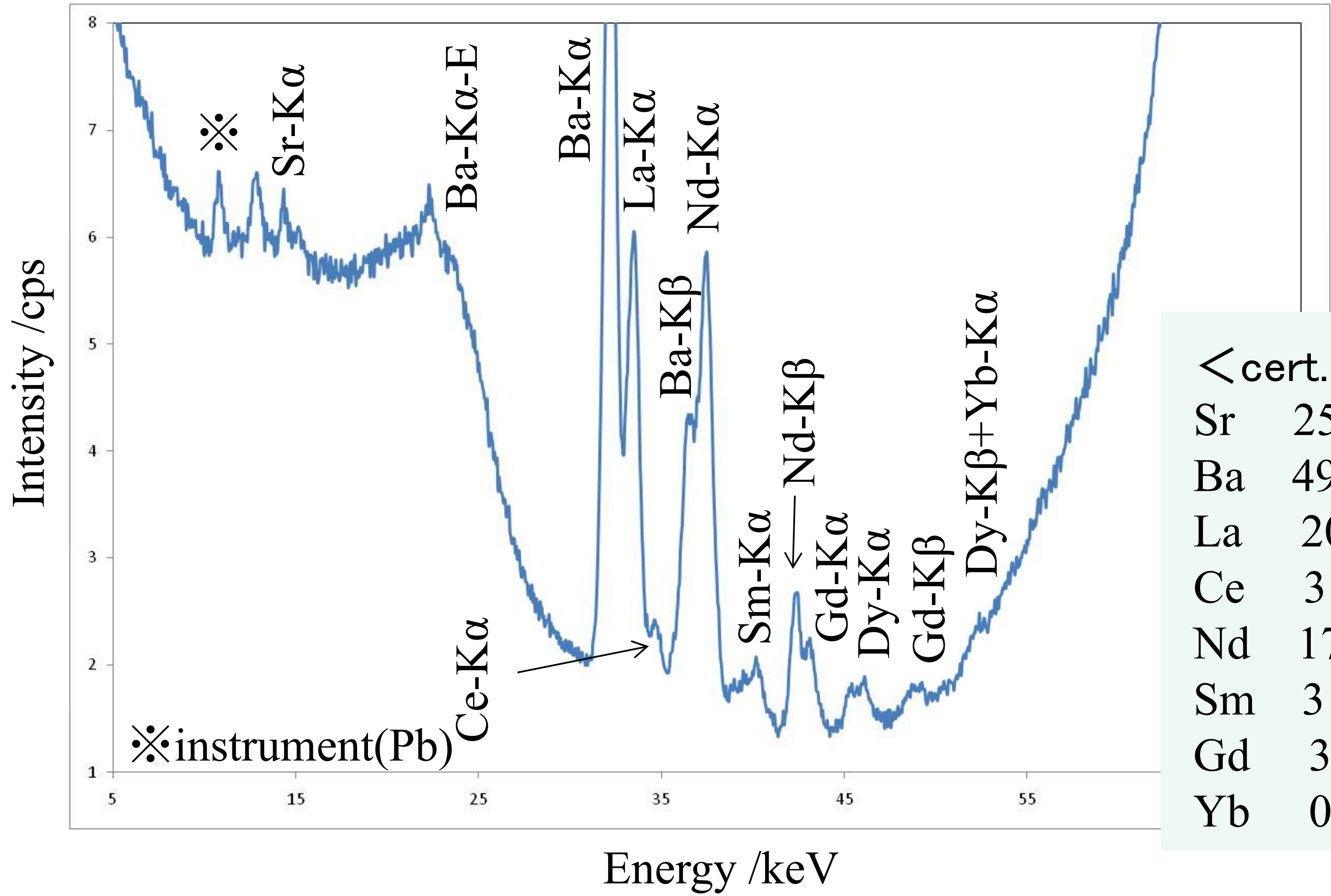
25 samples



Detector

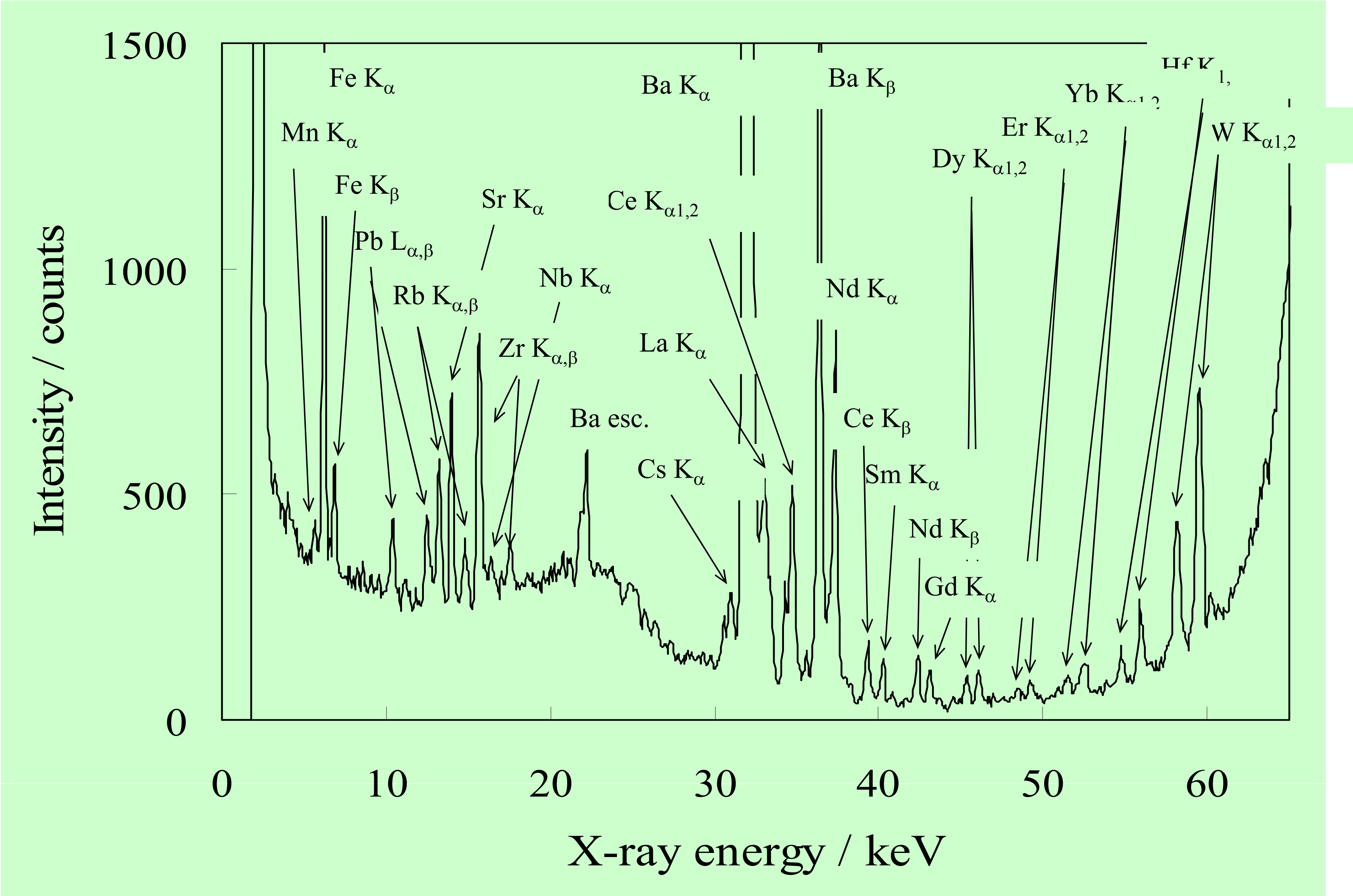
Slit 200 μm×200 μm、meas. Time 600～2000 sec

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



XRF spectrum of a standard sample (rock: granite JG1)

excited at 116keV for 1000sec.

Outline of the lecture

- **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

(3) Energy tunability

- Chemical state analysis by Fluorescence –XAFS

(4) High energy X-ray

(5) Multiple X-ray analytical technique -
A combination of **μ-XRF imaging, μ-XRD, XAFS and SEM**

- Conclusion

Application field of HE(high energy)-SR-XRF

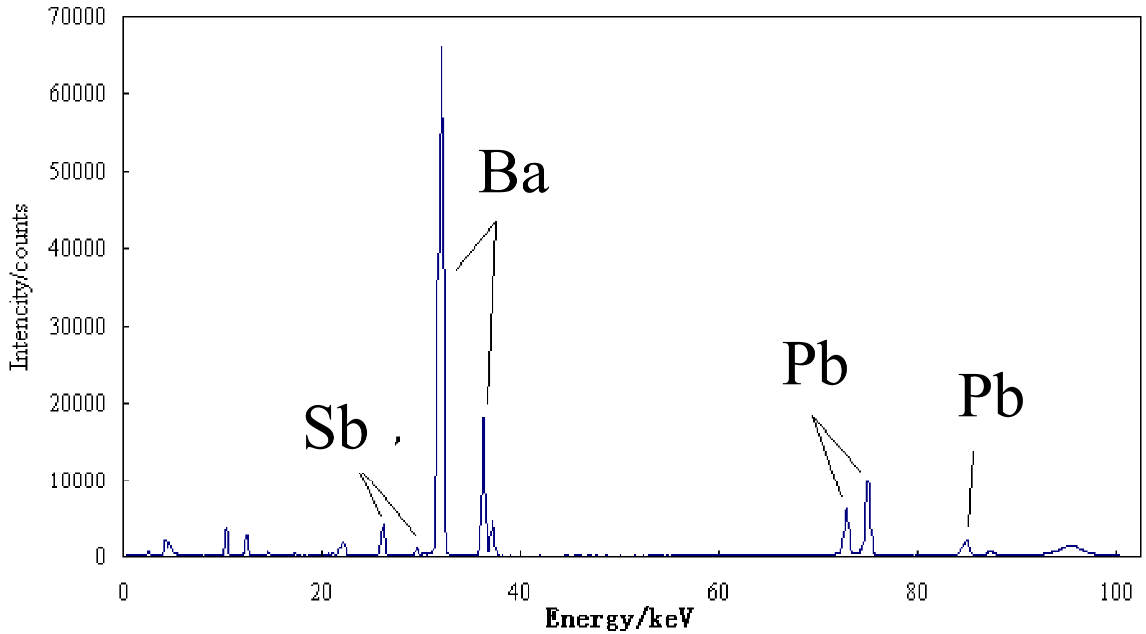
Analysis of trace heavy elements.

- Archaeology : nondestructive provenance analysis
- Forensic analysis
- Industrial chemical analysis of high-Tech materials
- Geochemistry

Forensic application

S&W Gunshot Residue

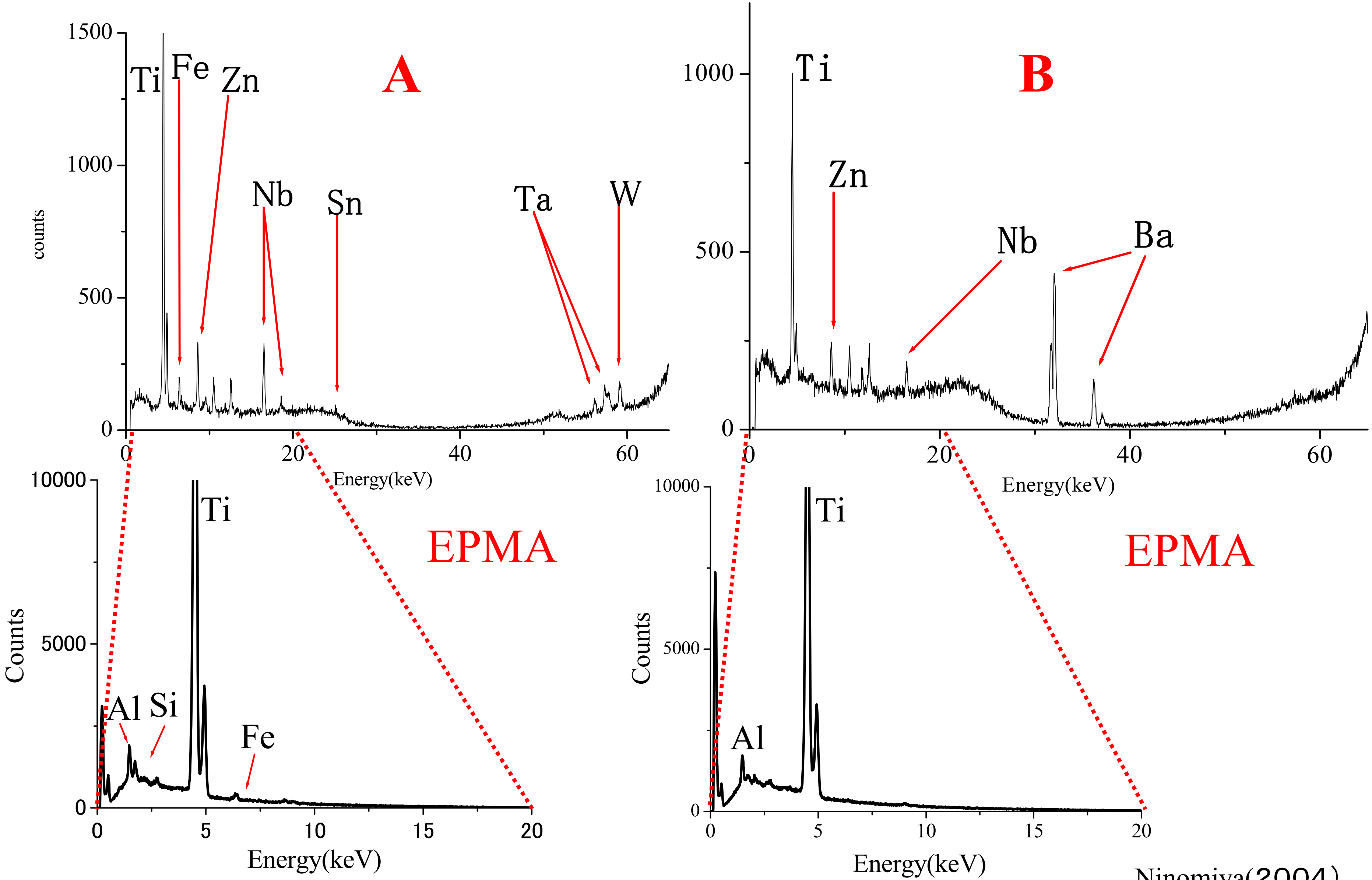
Characteristic element: Ba,Sb, Pb



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)

(5) Multiple X-ray analytical technique

A combination of μ-XRF imaging, m-XRD,XAFS and SEM

Chemical speciation of arsenic-accumulating mineral in a sedimentary iron deposit by synchrotron radiation multiple X-ray analytical techniques

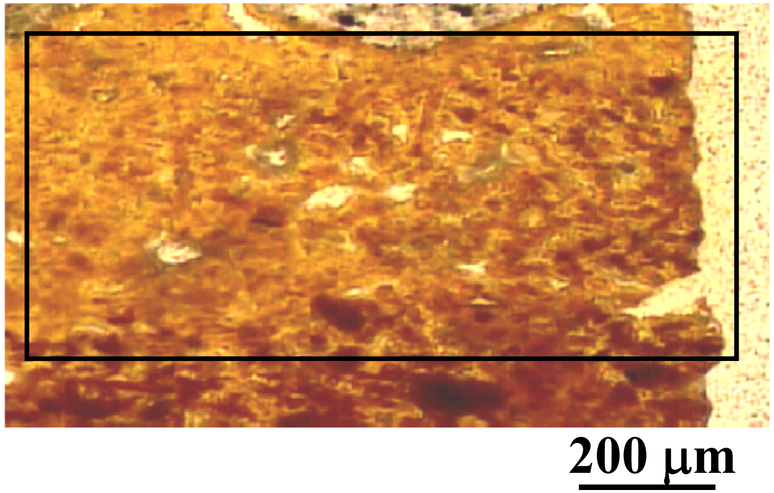
S.ENDO,Y.TERADA,Y.KATO,I.NAKAI
Environ.Sci.Technol.2008,42,7152.

Comprehensive characterization of As(V)-bearing iron minerals from the Gunma iron deposit by

Sample the Gunma iron deposit of quaternary age

SR-μ-XRF XRF imaging

As depositing sediments



SPring-8 BL37XU

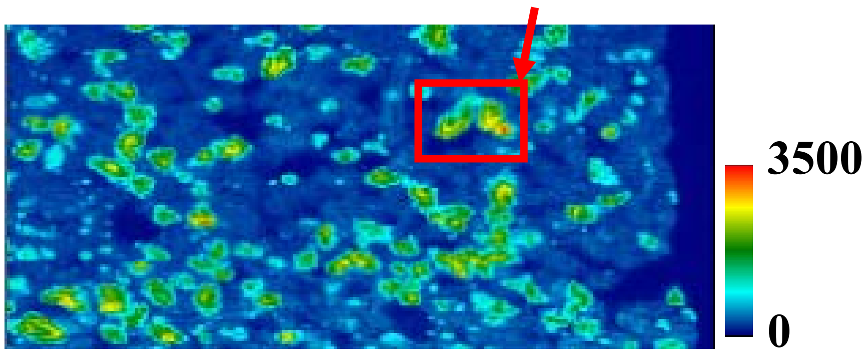
X-ray: **12.8 keV**

Beam size : 1.8 μm × 2.8 μm

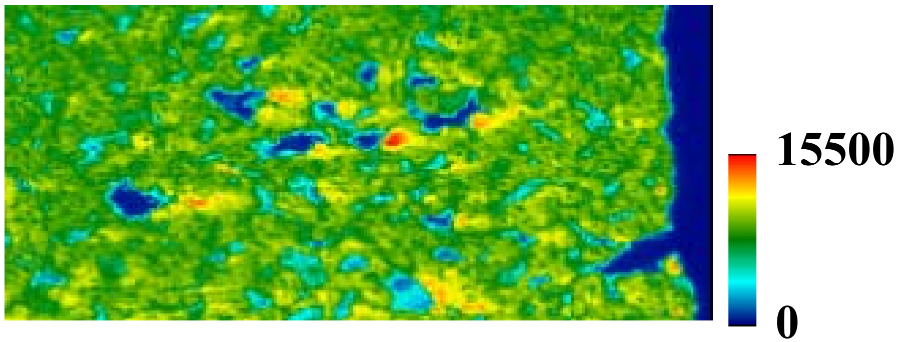
Step size : 2.0 μm × 3.0 μm

Meas. time : 0.1 s/point

Detector : SDD



As



Fe

strengite $FePO_4 \cdot 7H_2O$?

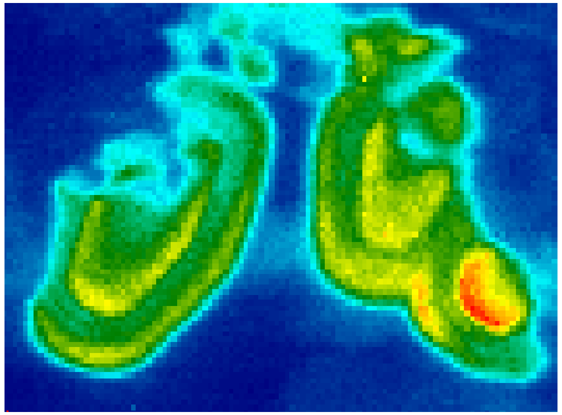
jarosite $KFe_3(SO_4)_2(OH)_6$?

goethite FeOOH?

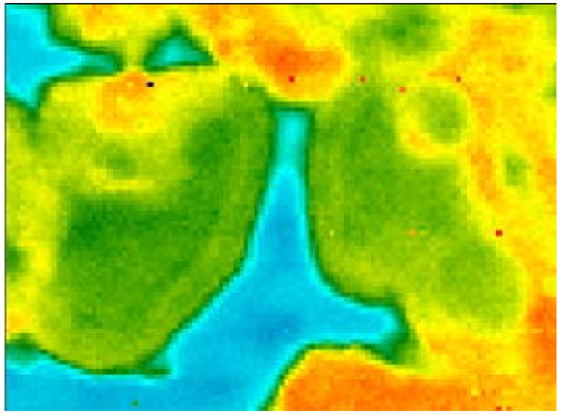
Purpose: which mineral accumulate arsenic?

SR-μ-XRF & SEM-EDS

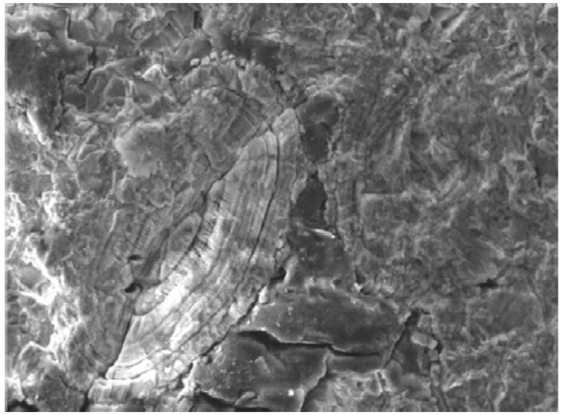
strengite $FePO_4 \cdot 7H_2O$
jarosite $KFe_3(SO_4)_2(OH)_6$



As 1800 0



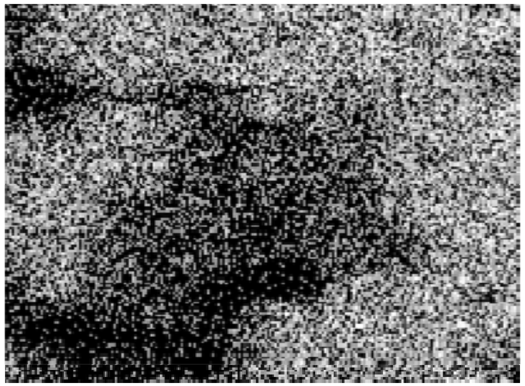
Fe 11000 0



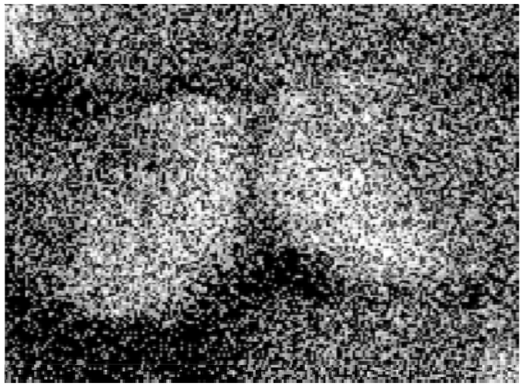
SEM image **20 μm**

Beam size: 1.8 μm×2.8 μm
Step size : 1.0 μm×1.0 μm

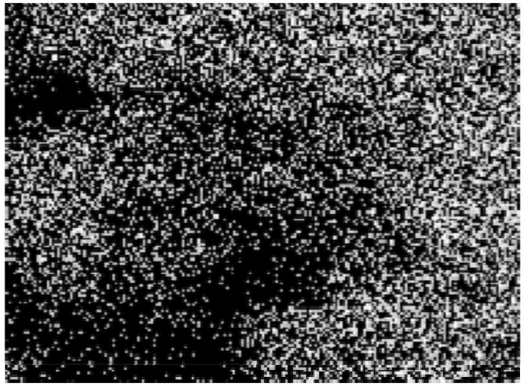
As at the region with peculiar concentric morphology



S (SEM-EDS)



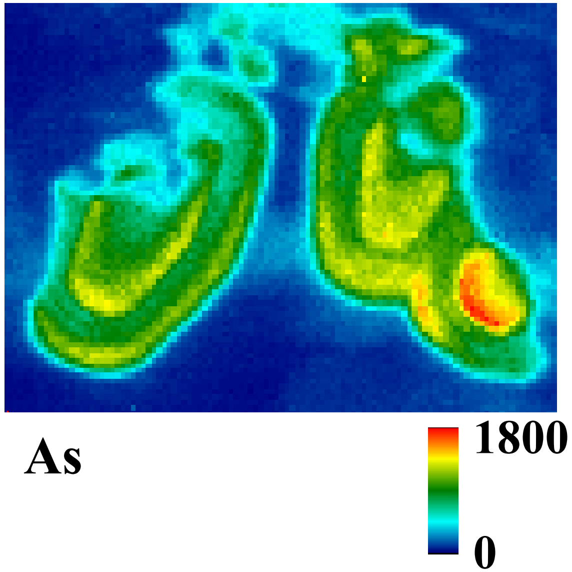
P (SEM-EDS)

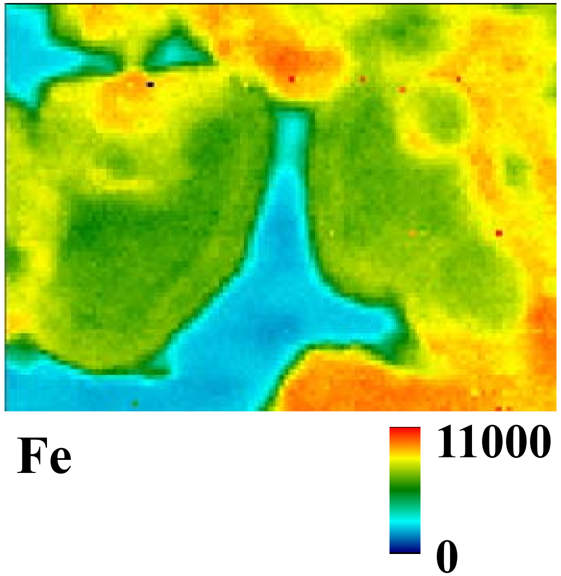


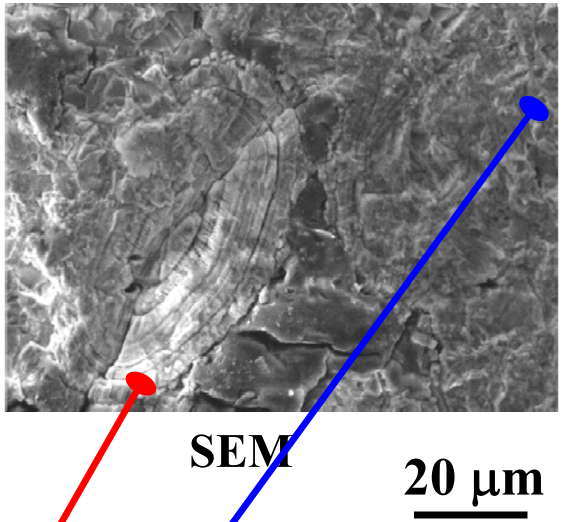
K (SEM-EDS)

Positive correlation between As and P, negative for S and K

SR-μ-XRF & SEM-EDS



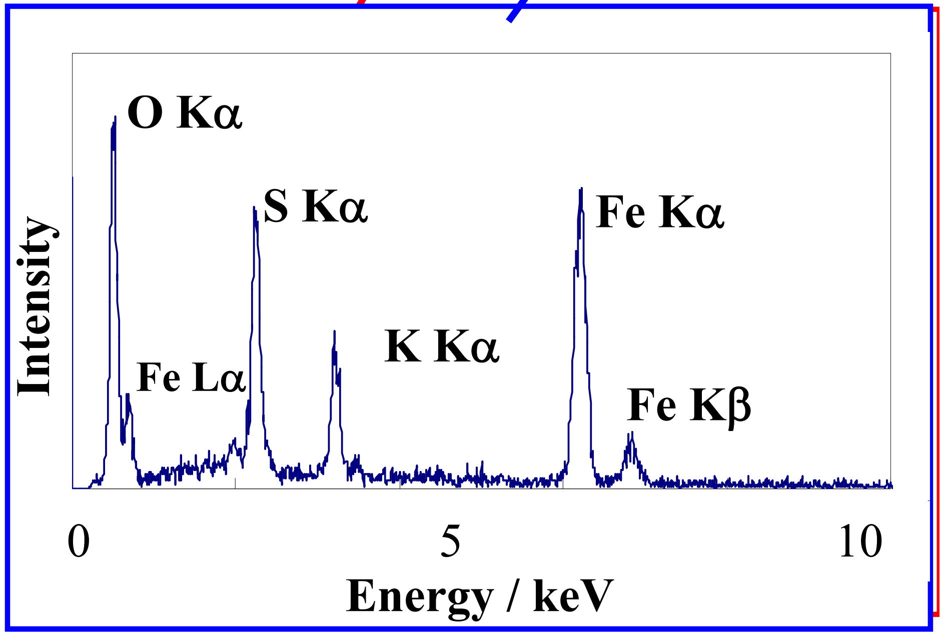




Beam size: 1.8 μm × 2.8 μm
Step size : 1.0 μm × 1.0 μm

Localization of As.

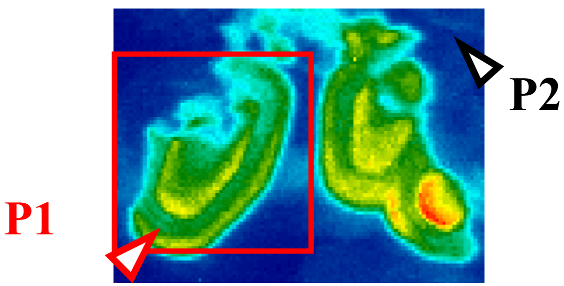
strengite $FePO_4 \cdot 7H_2O$
jarosite $KFe_3(SO_4)_2(OH)_6$



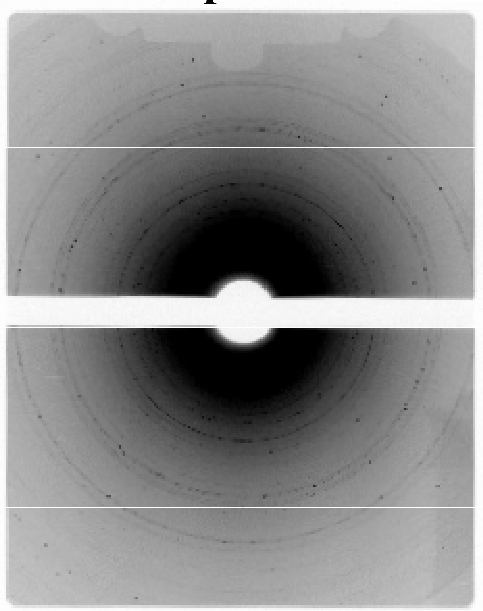
SEM-EDS spectrum

XRD

X-ray : 12.8 keV
Beam size : 50 μm × 50 μm
Meas.time **: 12 min. / sample**
IP (Imaging Plate)



XRD point



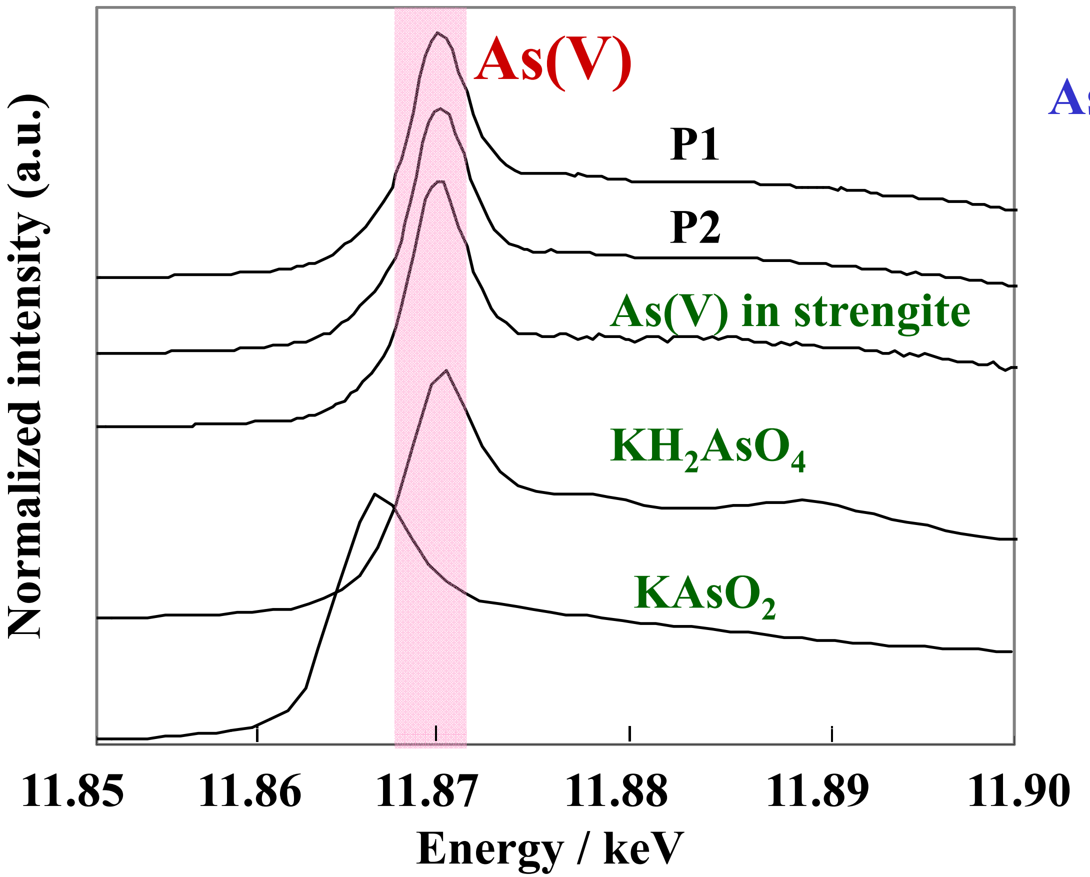
XRD pattern (P1)

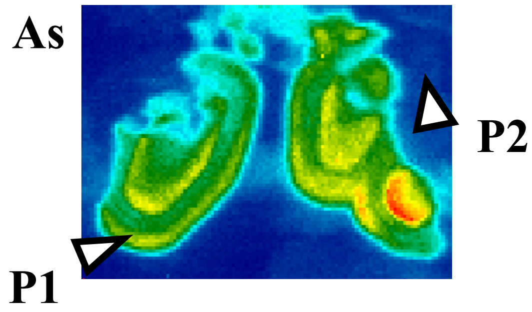
P1		P2		strengite			jarosite		
d / Å	I / I_0	*d* / Å	I / I_0	*hkl*	*d* / Å	I / I_0	*hkl*	*d* / Å	I / I_0
		5.93	32				101	5.93	45
		5.75	14				003	5.72	25
5.49	55			111	5.509	60			
		5.10	56				102	5.09	70
4.95	43			020	4.954	30			
4.37	100			201	4.383	85			
4.00	22			211	3.996	45			
				121	3.959	13			
				112	3.719	25			
		3.63	32				110	3.65	40
3.27	21			221	3.281	17			
3.12	53	3.11	72	122	3.114	100	201	3.11	75
		3.07	100				113	3.08	100
2.99	16			311	3.002	45			
2.95	19	2.97	12	131	2.949	45	202	2.965	15
		2.88	8				006	2.861	30
				231	2.631	11			
2.56	45	2.55	20	132	2.546	50	204	2.542	30

*** strengite $FePO_4 \cdot 7H_2O$ PDF No. 33-667**
**** jarosite $KFe_3(SO_4)_2(OH)_6$ PDF No. 22-827**

μ-XANES

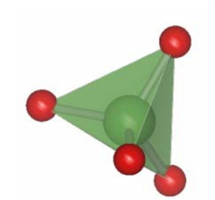
As K-edge XANES spectra
measured by 2μm X-ray beam





XANES points

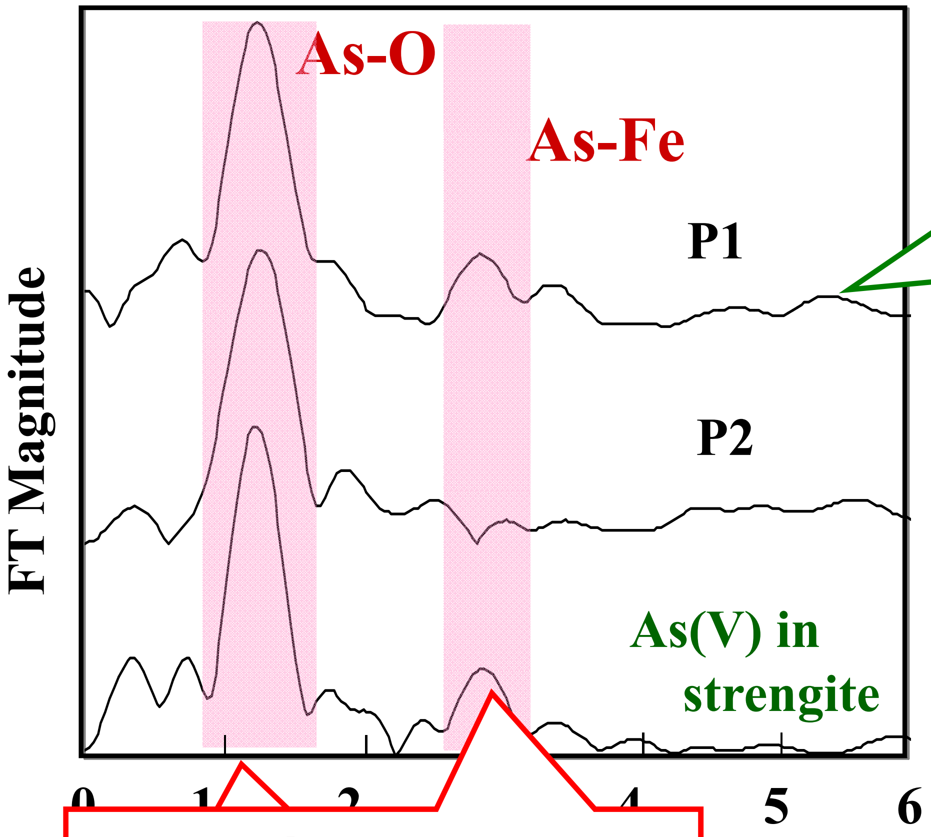
As exists as As(V) in the sample
(AsO_4^{3-}, $HAsO_4^{2-}$)

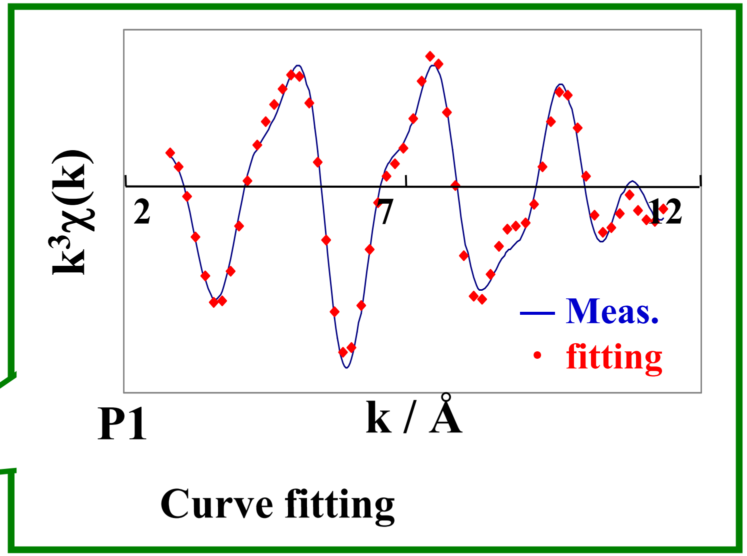


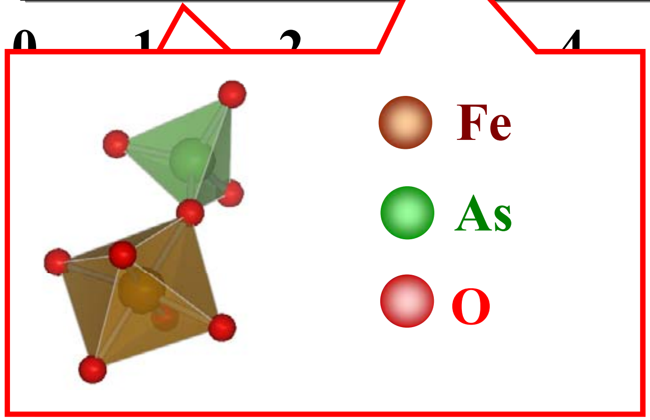
AsO_4^{3-}

strengite ($FePO_4 \cdot 2H_2O$)

μ-EXAFS







strengite FePO4·7H2O

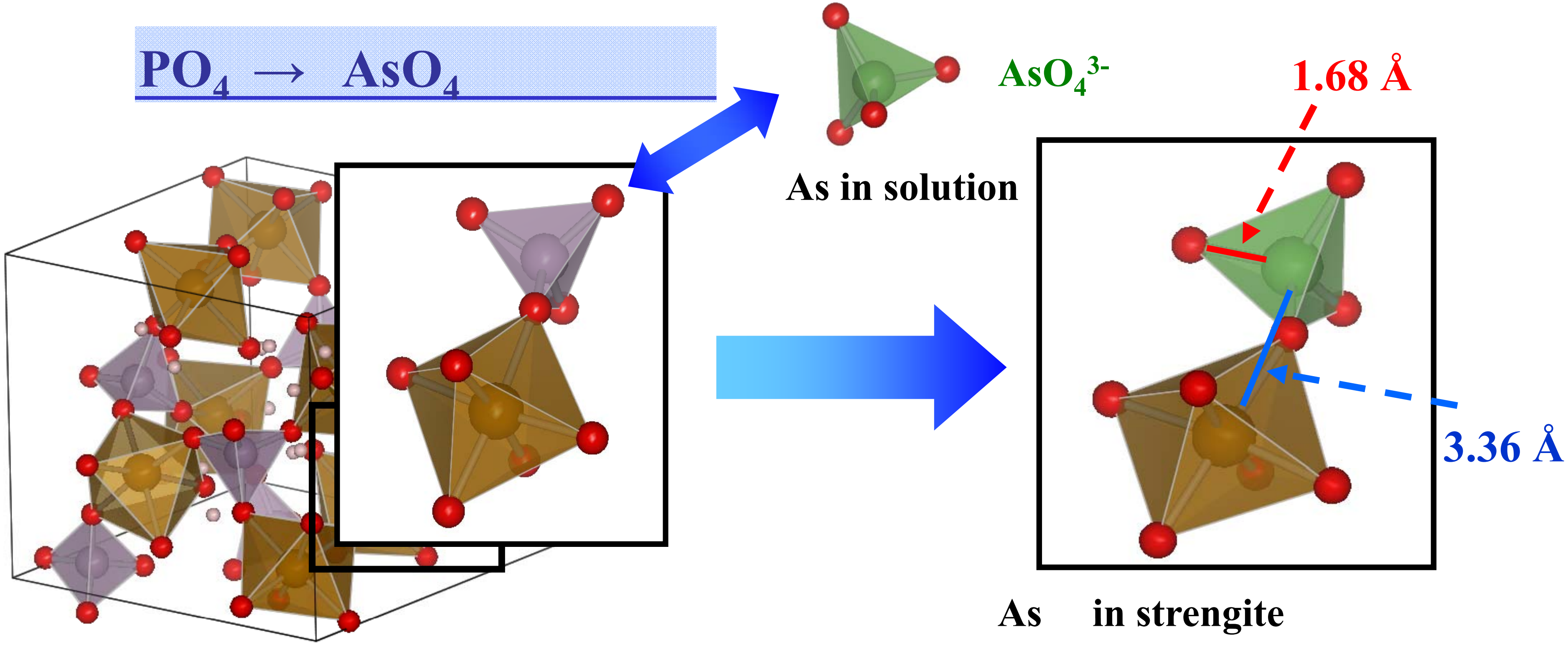
EXAFS

	Atom	r / Å	CN
P1	O	1.68	4.0
	Fe	3.36	4.0
P2	O	1.69	4.0
As(V) in strengite	O	1.68	4.0
	Fe	3.35	4.0

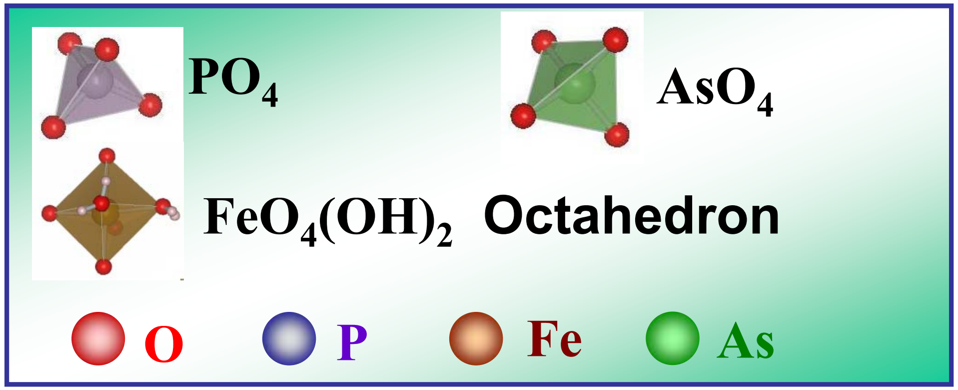
$As \rightarrow AsO_4$

AsO_4 tetrahedra-Fe(III)octahedra

As accumulation mechanism



Crystal structure of strengite ($FePO_4 \cdot 2H_2O$)



PO_4 tetrahedra in **strengite ($FePO_4 \cdot 2H_2O$)** is substituted by AsO_4 teterahedra

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