X-ray fluorescence analysis

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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 and X-ray analysis





X-ray energy E > Binding energy Eb

Bohr model and emission of X-ray fluorescence

Principle of X-ray fluorescence (XRF) analysis

$\begin{array}{c|c} \mathsf{Energy} & \Delta \mathsf{E} & \text{characteristic to each element} \\ & & & & \\ &$

Intensity number of X-ray photons \rightarrow concentration Quantitative analysis



XRF spectrum of NIST SRM612 glass



XRF analysis

(a) Wavelength dispersive spectroscopy

(b) EDS Energy dispersive spectroscopy

©http://www.postech.ac.kr/dept/mse/axal/index.html

Principle of analyzing crystal



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 TIAP (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	++	+	+++
TIAP	1010	1.295	0.338	2.434	+++	++	++
6 nm SM	-	6.00	1.566	11.276	+++	+	++

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



Si(Li) detector electron-hole pair \rightarrow 3.85eV

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

Bias voltage(-500V) cause currents flow. 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).



Characteristics of SR and the advantages in X-ray fluorescence analysis with application examples





SR Properties and SRXRF



(1) Highly Brilliant X-ray Source





Wavelength Dispersive Technique







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



Conventional



TXRF Experiments at Beamline 40XU, SPring-8



©K. Sakurai(NIMS)

WD-TXRF Spectra for Trace Elements in Micro Drop



©K. Sakurai(NIMS)



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



(2) Parallel beam with small divergence





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

Helmhortz invariant

y x u = y' x 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

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

X-rays: electromagnetic wave with short wavelength

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

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Beam profile at focal points made by FZP at 8keV

©Y.Suzuki(2002)

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

Study of hyperaccumulator plants of As and Cd



Phytoremediation

Environmentally friendly low cost technique

Key:Use of hyperaccumulator plant

As

Cd



Arsenic Hyperaccumulator *Pteris vitteta* L. (モエジマシダ)



Cd Hyperaccumulator *Arabidopsis halleri* ssp.gemmifera (ハクサンハタザオ)



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

As hyperaccumulator Chinese brake fern (*Pteris vittata* L.) (As: *ca*. 22,000 μg/g dry weight)

Arsenic distribution and speciation in an arsenic hyperaccumulator fern by Xray 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)
Life of fern



Fertile pinna

Cultivation of fern



arsenic-contaminated soil

As level in soil : 481 μ g g⁻¹dry Term : ~3 weeks Average As level : ~720 μ g /gdry



As level* pinna : 2800 - 4500 μ g g⁻¹dry midrib of a frond : 84 - 250 μ g /g dry

* Anal. By AAS

culture medium containing As (1 ppm 4days)

Sample preparation for microbeam analysis



freeze dry of frozen



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 (1 st mirror)	250 mm	100 mm
(2 nd 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

low







Accumulation of As at Fertile with high spores along marginal parts

A section of pinna



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

M-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

(3) Energy tunability

Chemical state analysis by Fluorescence -XAFS





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Chemical State Analysis

• XAFS (X-ray Absorption Fine Structure)

- XANES

- · Chemical shift of absorption edge
- · The intensity of the white line
- EXAFS
 - Local structure
 - Coordination number
- X-ray Emission
 - Chemical state analysis
 - · Chemical shift of the K or L emission lines
 - Intensity ratio of $K\alpha$ and $K\beta$
 - Emission Spectroscopy
 - Resonant inelastic emission spectroscopy

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XAFS analysis

40-20

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

in vivo XAFS





Chemical State analysis by XANES

-Chemical Shift of X-ray Absorption edge-



As K-edge XANES analysis





Analysis of Cd Ka line

Arabidopsis halleri

Cd and Zn hyper-accumulator

and

Cd in Rice

Micro X-ray fluorescence imaging and micro X-ray absorption spectroscopy of cadmium hyper-accumulating plant, *Arabidopsis halleri* ssp. *gemmifera*, using high-energy synchrotron radiation

Journal of Analytical Atomic Spectrometry, 23, 1068-1075 (2008)

N. Fukuda, A. Hokura, N. Kitajima, Y. Terada, H. Saito, T. Abe and I. Nakai.

Arabidpsis halleri ssp. Genmifera (ハクサンハタザオ)





Arabidopsis halleri is known as a Cd and Zn hyperaccumulator, which contained more than 9000 mg/ kg Cd and Zn.

XRF imaging of a leaf of A. halleri ssp. Gemmifera.



μ -XRF imaging of a trichome taken from a leaf.





X-ray Energy : 37 keV Beam size : $3 \mu m \times 3 \mu m$ Measurement points : 59 point × 226 point measurement time : 0.5 s/ point

Trichomes are epidermal hairs present at the surface of leaves of *A*. *halleri*, and their functions are thought to be an exudation of various molecules.

Brown Rice

Cd 1 ppm solution was added to the soil.



Beam size : 50 μ m × 50 μ m

Measurement points : 101×41 points

Cd was in the whole tissue, but Zn was localized in the embryo.

Summary

 μ-XRF imaging technique utilizing SR can monitor time dependent process of arsenic transfer in a leaf tissue of hyperaccumulator fern.

• It is possible to visualize arsenic transfer from root to marginal part of leaf within 30min after feeding.

•Cell level element analysis and chemical state analysis of Cd in the plant is possible

Prospect of microbeam analysis

Microbeam \rightarrow 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





Opt. microscope

Iron mapping in a part of a nucleus

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



Photon Factory BL-12C



19el-SSD

 $\Theta c < 0.3^{\circ}$

Heating behavior of titania nanosheet by TXRF-XAFS



Ti K-edge XANES spectra as a function of temperature



(4)High energy X-ray

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) \rightarrow

Overlapping of heavy elements L lines with light elements K lines Sample porcelain, Source: Mo K α X-ray 40 kV-40 mA, time:1000sec



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

L line for all elements 20 keV >Above 20 keV \rightarrow K line only \rightarrow suitable for analysis of elements heavier than Rh K α (= 20.17 keV)

Advantage of high energy XRF

- High sensitive analysis of trace heavy elements by excitation of K-shell electrons of heavy elements
- Low absorption effect and high penetration depth
- Application field of high energy XRF
 Heavy elements (Lanthanoid elements, U, Nb, Zr, Hf, W, Cd, Hg etc.) are important in industry
 (high-Tech materials) , environmental science, geochemistry, archaeology, forensic science for provenance analyses.

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 mm²

Experimental setup for high energy XRF



XRF spectrum of NIST SRM612 glass: 61 trace elements in 50ppm level(*scattering)


XRF spectrum of a standard sample (rock: granite JG1) excited at 116keV for 1000sec.

MDL for JG1 sample								
Contents/ ppm		I _{peak}	I _{back}	MDL/ppm				
Fe	2.02 ^{a)}	1557	366	0.097 ^{a)}				
Rb	181	577	281	30.8				
Sr	184	719	258	19.2				
Zr ^{b)}	108	395	293.5	54.7				
Cs	10.2	280	181	4.2				
Ba	462	7205	354.5	3.8				
La	23	535	355.5	7.2				
Ce	46.6	520	86	3.0				
Nd	20	862	154.5	1.1				
Sm	5.1	136	45	1.1				
Gd	3.7	108	42.5	1.1				
Dy	4.6	110	41	1.3				
Er	1.7	86	51.5	1.1				
Yb	2.7	125	61	1.0				
Hf	3.5	268	98.5	0.6				
W	1.7	737	199.5	0.1				



Application field of high energy XRF

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

Analysis of trace heavy elements.

Principle of Provenance Analysis of China Ware

Raw material \rightarrow Porcelain Stone Trace element composition tells the locality





Provenance analysis of Old-Kutani China wares based on the information of heavy elements composition obtained by high energy XRF

 \diamond Kutani china wares were first produced in the late 17th century in the Kaga Province in Japan. In 1710, however, after half a century of continuous production, the kiln was suddenly closed.

◆Pottery from this early period is known as Old Kutani, which is extremely precious. However, there is a possibility that the Old Kutani might come from Arita, another famous production place of porcelain since 17th century in Japan.

◆Identification of Old Kutani and Arita is an important and mysterious problem in Japanese art history. This is the first nondestructive analysis of museum grade samples of Old Kutani.



Role of Heavy Elements

Good fingerprint elements

- Cosmic abundances of the heavy elements with atomic number larger than 26 (Fe) are small compared with the lighter elements.
- They exhibit characteristic distribution in earth, for the heavy elements such as rare earth and U often posses large ionic radii and high oxidation states.
- The trace elements often substitute for major elements, whose manner is largely affected by the nature of the elements such as the ionic radii, oxidation state as well as the PTC condition.

→ High energy SR-XRF analysis



Kutani

Raw Material

Samples

Fragments of porcelain excavated at each old kiln of Kaga, Arita, and Fukuyama.
Kutani: 121 Arita: 57 Fukuyama: 10
Museum grade samples which are thought to be original: 6







XRF spectrum of fragments of china ware excavated from Old Kutani kiln







Material History

A latent record of information stored in a substance tells its origin and history

Every substance was produced in the past. The law of causality determines the chemical state of a substance.

During the formation and existence of a substance, the information of its material history is recorded in the substance in various forms such as the concentration, distribution, and chemical state of the trace elements as well as chemical composition, structure, isotope ratio of the major elements.

Application of the material history: Information of the material history can be used in various scientific fields

- Archaeology, forensic analysis, geology, geochemisty \rightarrow To reveal the past based on the material history.
- **Biological sciences**: life history, migration history, environmental problems
- Industrial application: prediction of source material, production method and patent related problems
- Environmental science: monitoring of environmental change→industrial, biological, and social activities etc.

Highly sensitive nondestructive X-ray analyses utilizing SR are most suitable techniques to reveal the material history of the sample.



Forensic application

S&W Gunshot Residue



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)





Date: July 25, 1998

Place: Festival Site at Sonobe, Wakayama Pref. JAPAN Acute Arsenic intoxication : Death 4

Injured 63

Material evidence around the crime Arsenic oxides:

- in the curry
- adhered to a paper cup found at the festival site, dumping ground
- on a plastic container found in the kitchen of a woman whose husband used arsenic oxide in his job as a professional exterminator of white ants
- five samples of arsenic sized from around their house

Requests and Solution

• Analysis of Bi,Sb,Sn in ppm level in the sample of 0.01mg in less than three weeks

X-ray fluorescence analysis utilizing 116keV X-rays from SR (New approach) → Heavy element analysis by K-line X-rays allow good separation of the peaks of the elements in the XRF spectrum without any interference of light elements.

Problems

• In total, police seized eight kinds of arsenic oxide samples as evidence but there was no proof connecting them. Especially the amount of the sample (ca.0.01mg) adhered to the plastic container was too small to be analyzed by any conventional analytical techniques at the National Scientific Criminal Investigation.

Priciple of identification :material history of arsenic trioxide →heavey elements impurity: Sb,Bi Sn,Mo





Experimental Results and Interpretation

- Characteristic features of being common in the appraisal samples
 - •Existence of Mo only in the appraisal samples
 - •Sn and Sb exist in nearly equal amount level while the Bi level is 2 or 3 times higher than the Sn and Sb levels
- The probability of the coincidence
 = Mo × Sn × Sb × Bi
- Conclusion

The eight samples all arsenic trioxide from the same source

- → Public Prosecutor's Office.
- \rightarrow This crime in now under justice.

(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



SPring-8 BL37XU

X-ray: 12.8 keV Beam size : 1.8 μ m × 2.8 μ m Step size : 2.0 μ m × 3.0 μ m Meas. time : 0.1 s/point Detector : SDD



SR-µ-XRF & SEM-EDS

strengite FePO₄·7H₂O jarosite KFe₃(SO₄)₂(OH)₆



SR-µ-XRF & SEM-EDS



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
<i>d </i> Å	I / I ₀	<i>d</i> / Å	I / I ₀	hkl d / A I / I	hkl $d / A I / I_0$
		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 FePO₄·7H₂O
PDF No. 33-667
** jarosite KFe₃(SO₄)₂(OH)₆ PDF No. 22-827





As


As accumulation mechanism



Conclusion

Limitation of the SR-XRF

- 1. Microbeam analysis
 - i) the thickness of the sample should be in the order of beam size
 - \rightarrow 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 \rightarrow from cell level to sculpture, paintings
 - in situ, in vivo, in air at any temperature
- 6. Information
 - concentration: major(%), minor, trace(ppm) elements $C \sim Na \sim U$ 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