



FEDERATION OF MYANMAR ENGINEERING SOCIETIES



Clarifying XRD and XRF : Understanding Their Role in Metallurgy and Materials Engineering

29-3-2025
(Saturday)

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Overview of Presentation Structure

1. Introduction to Material Characterization
2. Understanding XRD: Principles and Applications
3. Understanding XRF: Principles and Applications
4. Comparing XRD and XRF
5. Case Study: Practical Integration
6. X-Ray Safety
7. Conclusion



1. Introduction to Material Characterization

“Characterization describes the features of **composition** and **structure** of a material”

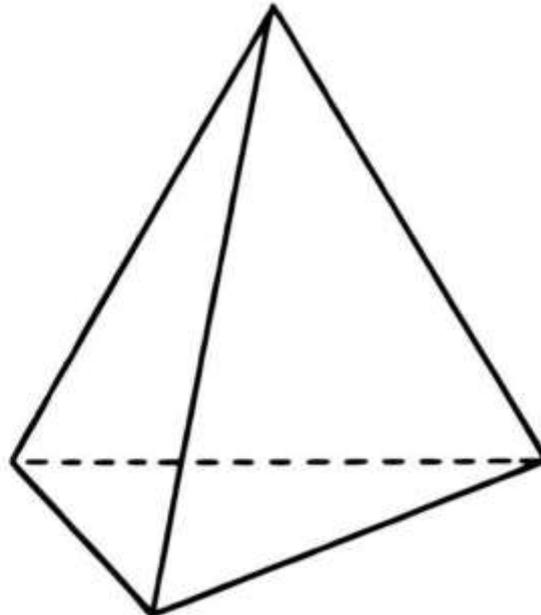
Different ways for shaping materials into useful components or changing their properties.

Processing

- method of preparing material

Structure

- arrangement of internal components
 - subatomic
 - atomic
 - microscopic
 - macroscopic (bulk)



Performance

Materials

Characterization has 2 main aspects:

- measuring the **physical and chemical properties** of materials
- measuring the **structure** of a material

Properties

- material characteristic
- response to external stimulus
- mechanical, electrical, thermal, magnetic, optical, deteriorative

Classification of Characterization based on information to be obtained

Chemical Composition

- **X-Ray Fluorescence (XRF):** Identifies and quantifies elements present in a material.
- **Energy-Dispersive X-ray Spectroscopy (EDS):** Analyzes the elemental composition of a specific region within a sample (often used in conjunction with Scanning Electron Microscopy - SEM).
- **Mass Spectrometry (MS):** Determines the mass of molecules in a sample, aiding in chemical identification.

Microstructure:

- **Scanning Electron Microscopy (SEM):** Creates high-resolution images of a material's surface, revealing its morphology and topography.
- **Transmission Electron Microscopy (TEM):** Provides even higher resolution images, allowing visualization of a material's internal structure at the atomic level.
- **X-Ray Diffraction (XRD):** Analyzes the crystal structure of a material by identifying the arrangement of atoms and molecules.

Physical and Mechanical Properties:

- **Mechanical Testing:** Measures a material's strength, stiffness, hardness, and other mechanical properties through techniques like tensile testing, compression testing, and hardness testing.
- **Thermal Analysis:** Evaluates a material's response to changes in temperature, including techniques like Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA).

Surface and Interfacial Properties:

- **Atomic Force Microscopy (AFM):** Creates high-resolution images of a surface, revealing its topography and measuring forces at the atomic level.
- **X-ray Photoelectron Spectroscopy (XPS):** Analyzes the chemical composition and electronic state of elements at a material's surface.

XRD : X-ray diffraction
XRF : X-ray fluorescence

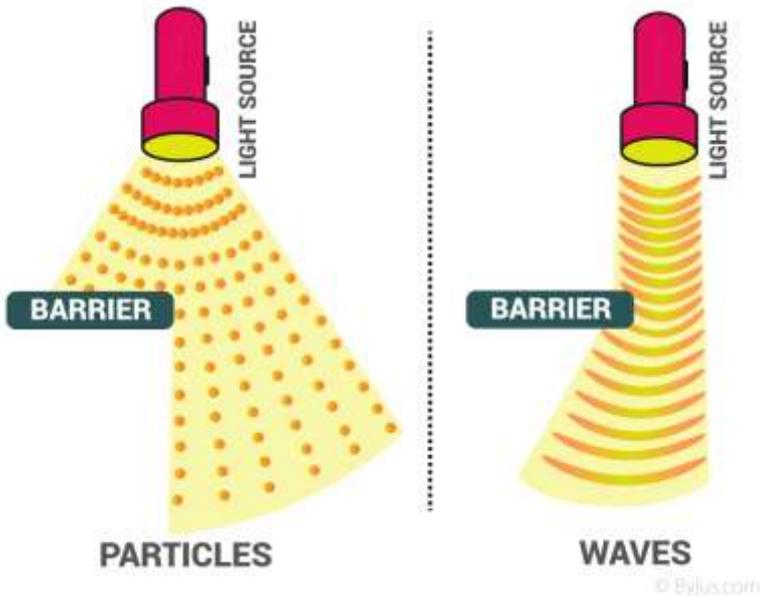
Understanding XRD: Principles and Applications



History of X-Rays

- X-rays were discovered in 1895 by the German scientist Roentgen (1845-1923), the first Nobel Prize for physics.

- X-rays



Electromagnetic wave

Dual nature (wave and particle properties)
Invisible

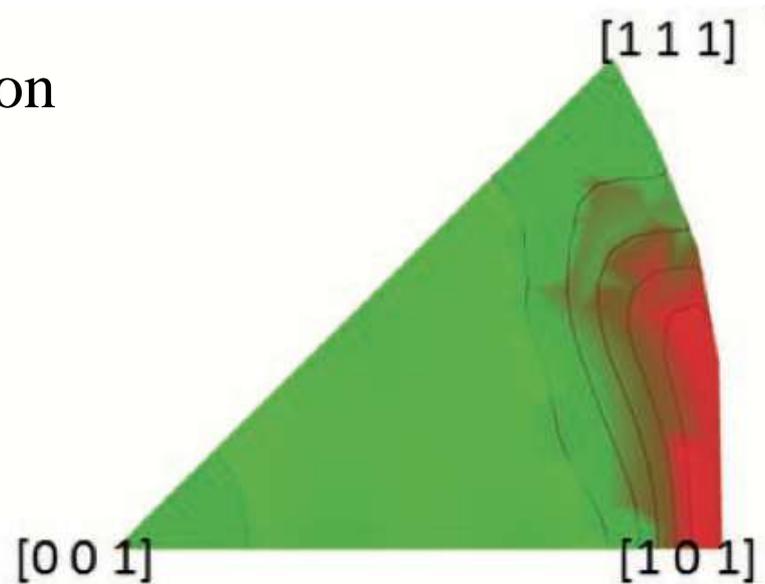
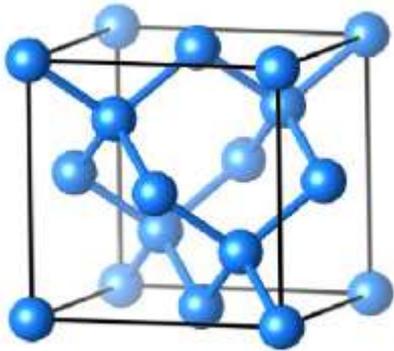
Short wavelength (0.1 nm to 10 nm)
high energy beam (good penetration)

Other electromagnetic waves —
light, radio waves and γ -rays



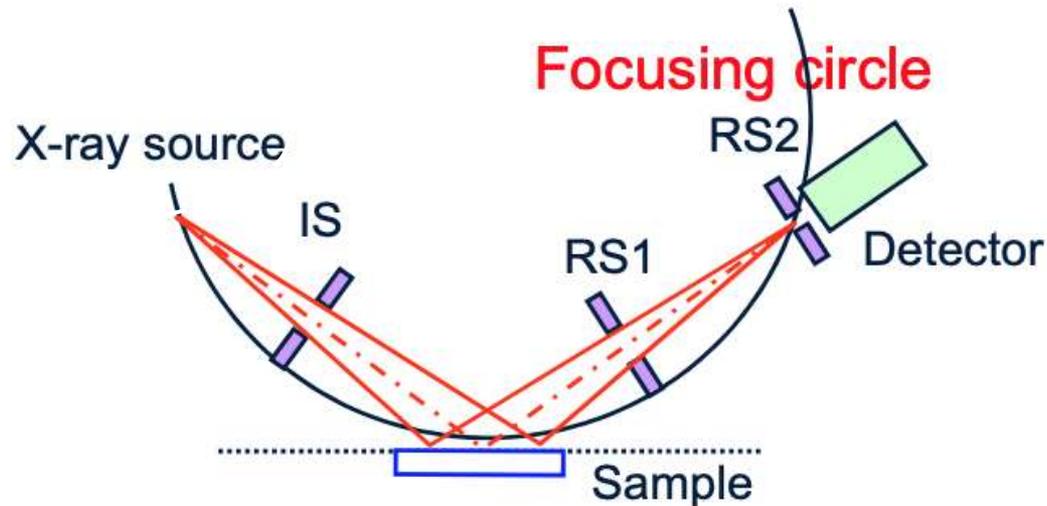
- 2012 was the 100th Anniversary of X-Ray Diffraction (XRD)
- XRD : Determining the crystal structure (e.g BCC, FCC, HCP)
Identify chemical compounds / phase (e.g Fe_2O_3 , CaCO_3)
Quantitative Phase Analysis (e.g $\text{Fe}_2\text{O}_3 = 53\%$, $\text{CaCO}_3 = 47\%$)
Crystallite Size and Microstrain

Texture/ Orientation



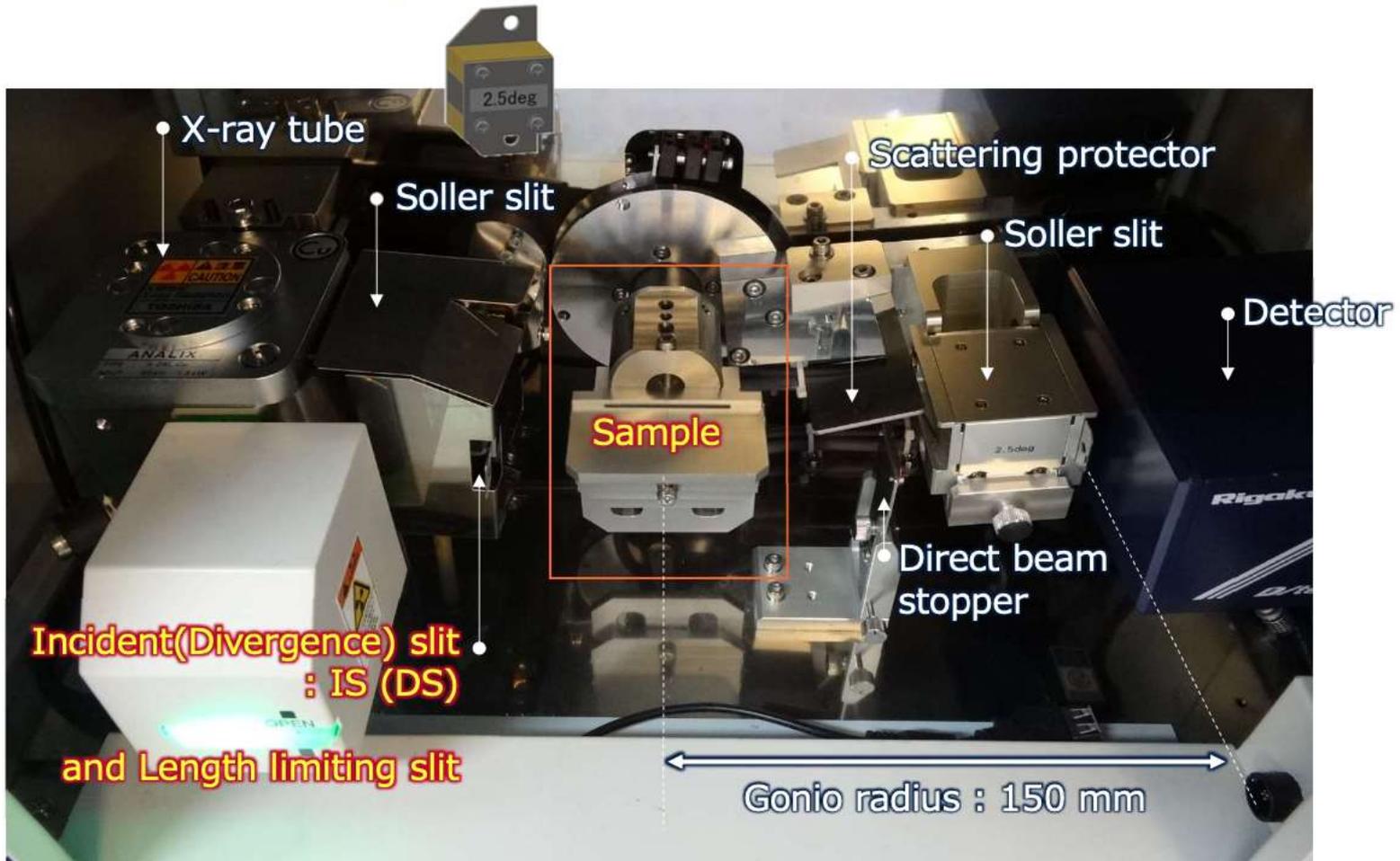
Sample types
: powder,
solid ,
liquid samples

Bragg-Brentano (BB) optics (Para Focusing optics)



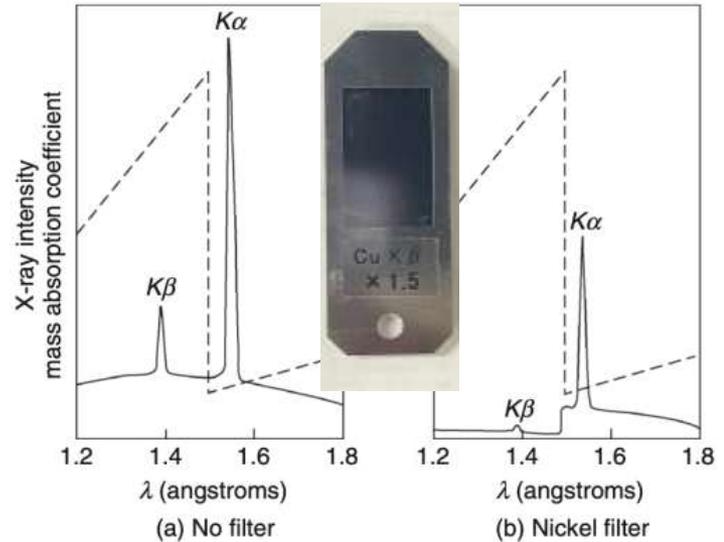
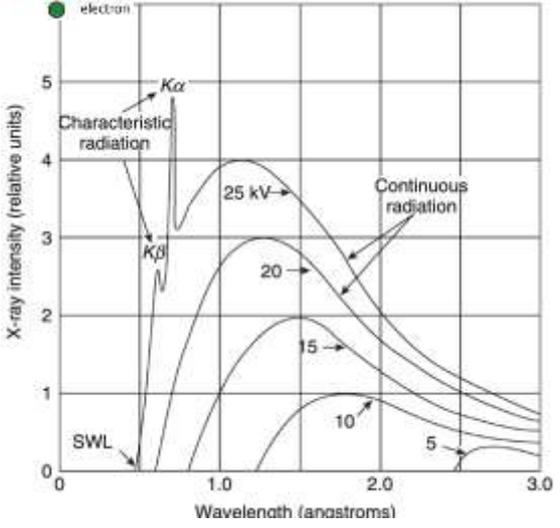
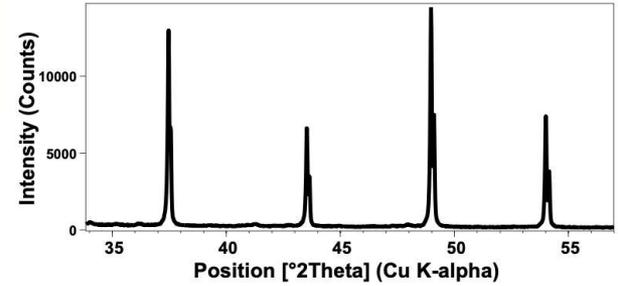
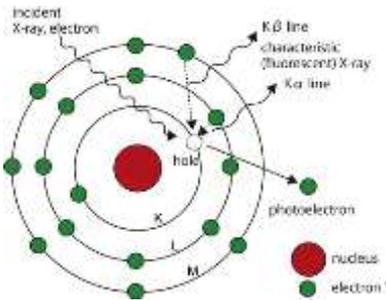
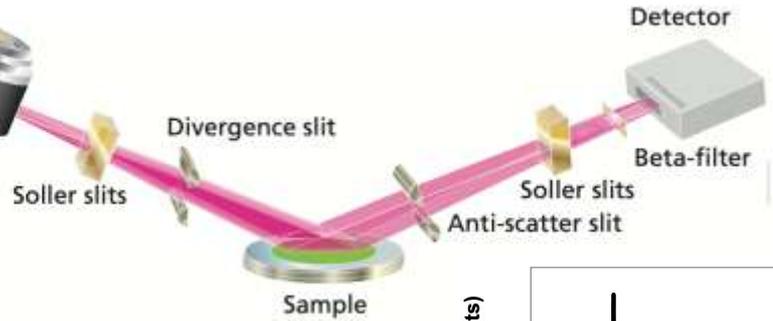
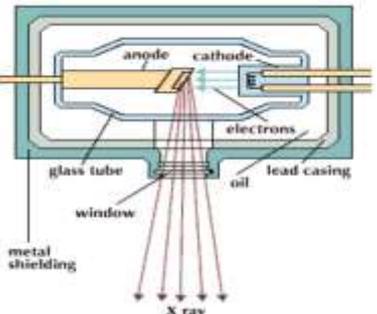
- ✓ Standard optical system with **high intensity and high resolution**
- ✓ Incident X-ray beam is divergent
- ✓ **Systematic errors**
- ✓ Basic optical system used for powder XRD

Optics of MiniFlex



The orange letters are the parts that you change as needed.

Generation of X-Rays

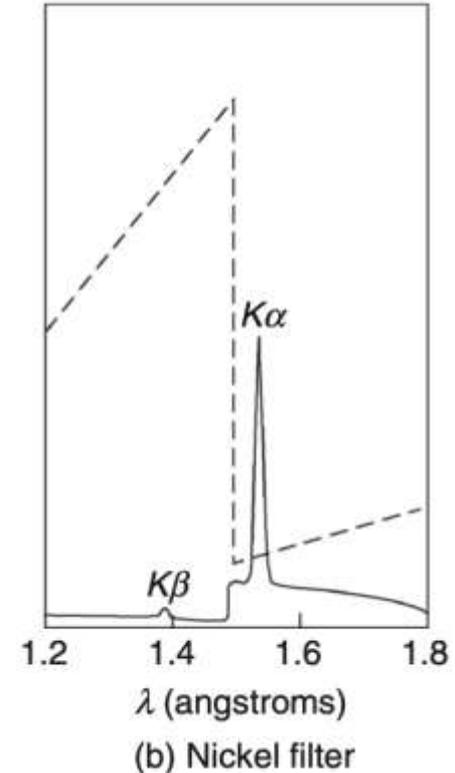
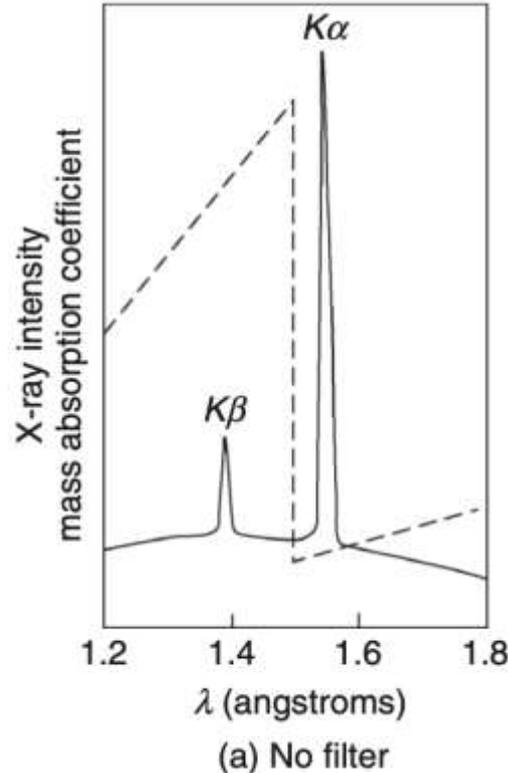


X-ray Chromatic filter

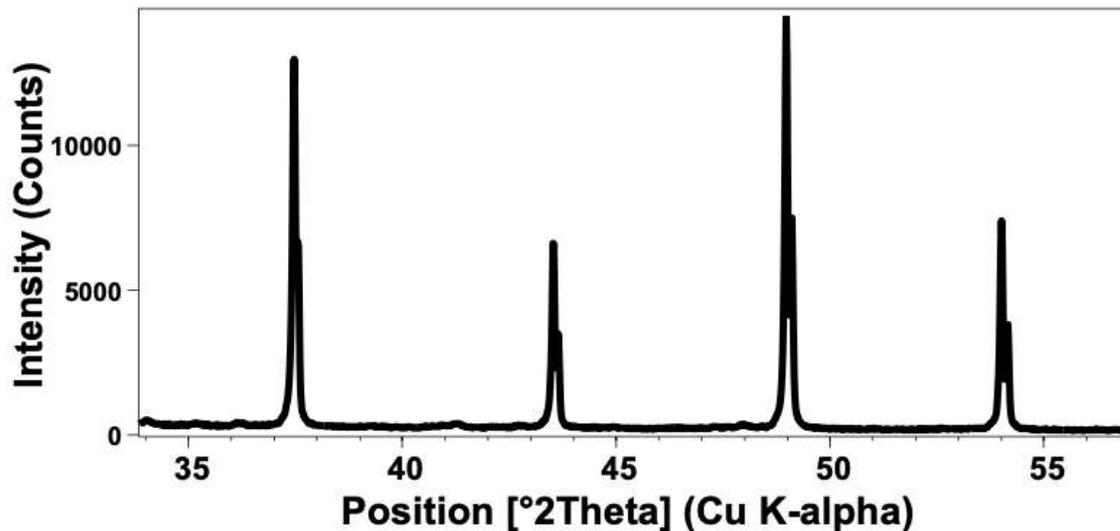
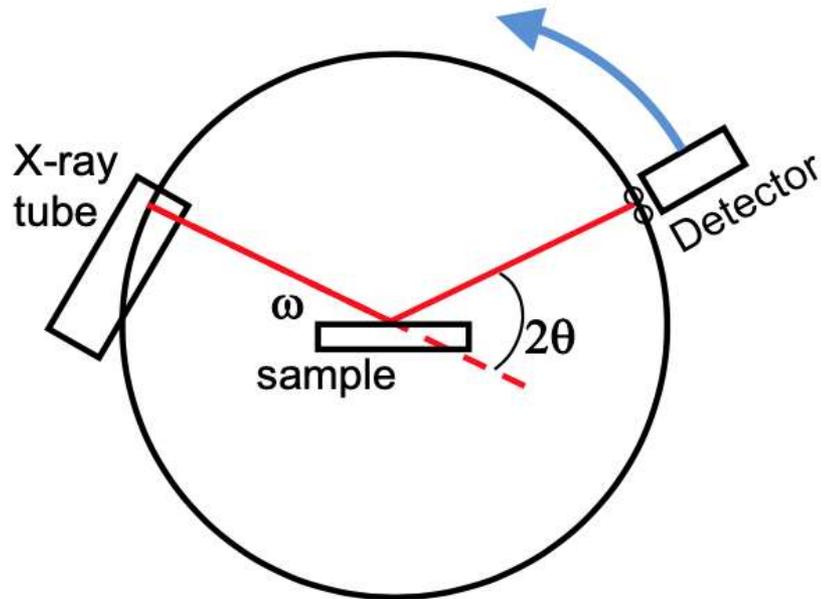
To obtain monochromatic radiation-

- Undesirable wavelength can be suppressed by passing an absorber (filter)
- The filtration is never perfect.
- Thicker the filter, better the suppression of K_{β} component but this also results in weaker K_{α} .

Target metal	Filter
Mo	Zr
Cu	Ni
Co	Fe
Fe	Mn
Cr	V



Generation of X-Rays



The detector moves in a circle around the sample

- The detector position is recorded as the angle 2θ
- The detector records the number of X-rays observed at each angle 2θ
- The X-ray intensity is usually recorded as “counts” or as “counts per second”

Incident(Divergence) slit size : IS (DS)

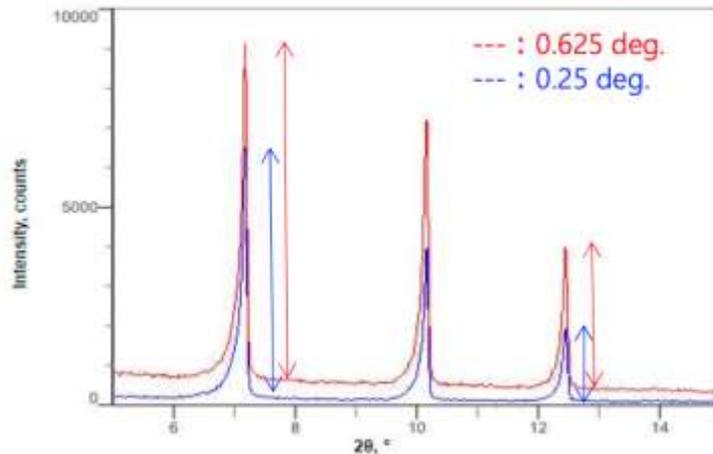


$2\theta = 5 \text{ deg}$

$2\theta = 10 \text{ deg}$

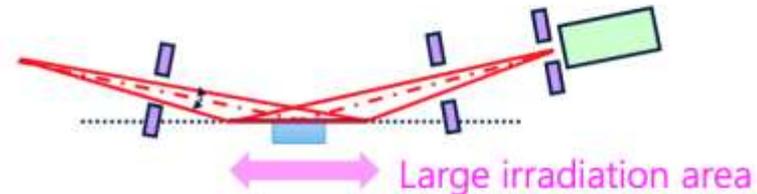
$2\theta = 20 \text{ deg}$

The beam size is 20 mm at the sample position

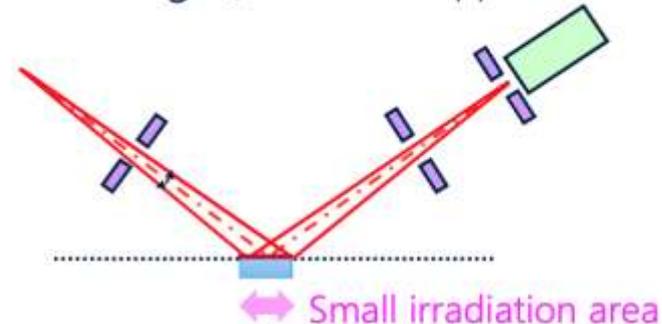


< Schematic View, DS=1.25 deg >

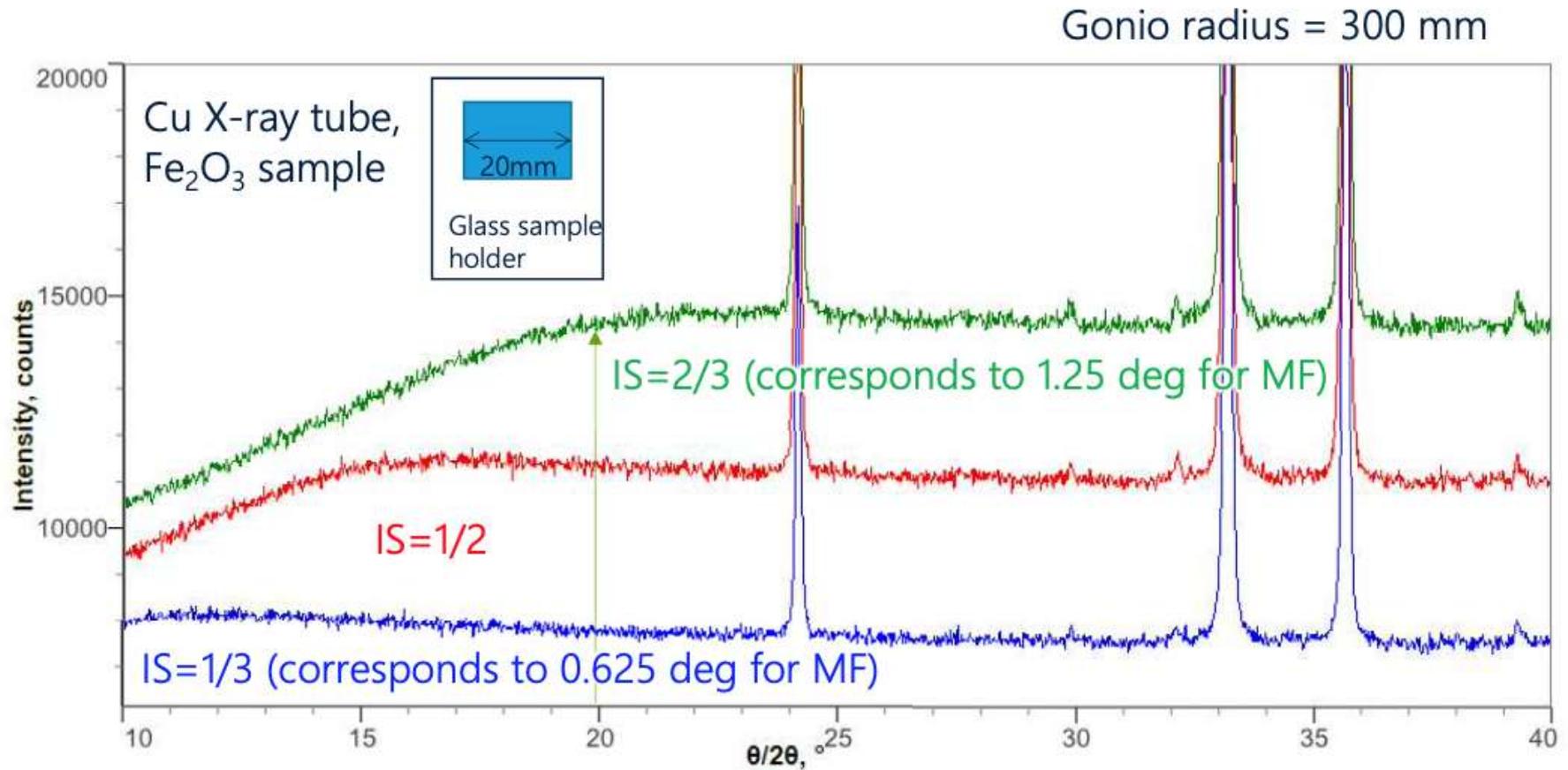
$2\theta/\theta = 5 \text{ deg}$ (Beam size : approx. 80 mm)



$2\theta/\theta = 20 \text{ deg}$ (Beam size : approx. 20 mm)



Importance of Divergence Slit Width



The horizontal beam size at the sample position is determined by the incident angle and the divergence slit size.

How to set the optimized measurement Condition

[1] Test measurement

DS(=IS) = 0.625 deg

Scanning method $2\theta/\theta$

Scan angle range 10 ~ 90°

Sampling width 0.02deg.

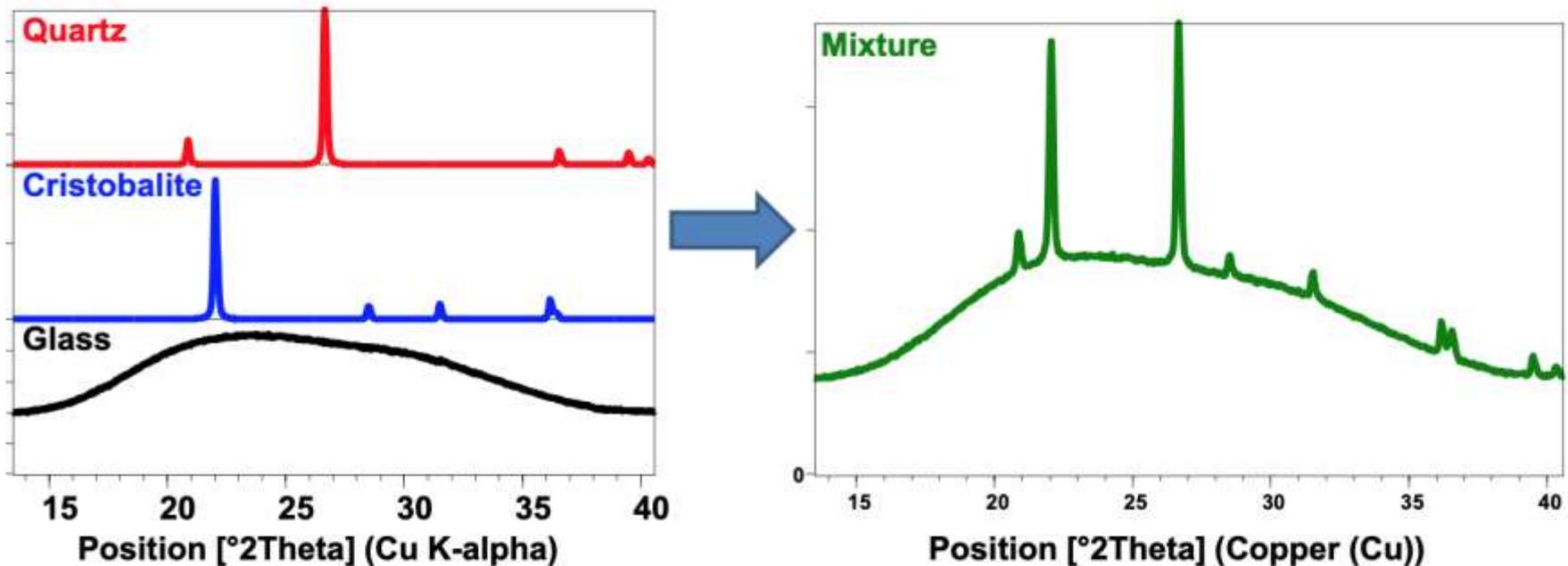
Detection mode *Standard mode*

Scan speed 40° / min

[2] Measurement for quantitative analysis

- ① When the **starting angle** of the measurement is **20 deg** in 2θ ,
DS should be **1.25 deg** considering of intensity and the beamwidth.
(Intensity will be increased to 2 times of intensity of test measurement)
- ② The sampling width should be set to "**FWHM of the main peak x 1/5-1/10**"
- ③ **Select** XRF or standard mode on **detection mode**
(when selected XRF mode, the intensity will be a half)
- ④ The scanning speed should be set so that the intensity will be to be over 10,000 counts

The diffraction pattern of a mixture is a simple sum of the diffraction patterns of each individual phase.



- From the XRD pattern you can determine:
 - What crystalline phases are in a mixture
 - How much of each crystalline phase is in the mixture (quantitative phase analysis, QPA, is covered in another tutorial)
 - If any amorphous material is present in the mixture

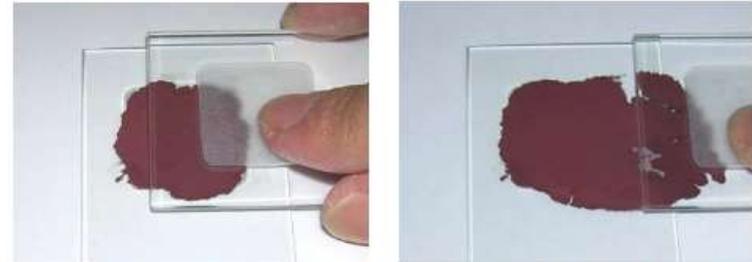
Sample Preparation

1. A glass sample holder is placed on a paper and sample is filled into sample holder



The dent side is surface.

2. Make even the surface of the sample using the backside of a glass sample holder.

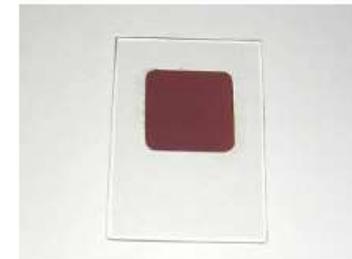


When sample powder is attached to the backside of the holder, Clean the holder before flattening the surface.

3. Repeat until the surface becomes the same height as a edge of glass sample holder.



4. Finish



Low back ground sample holder

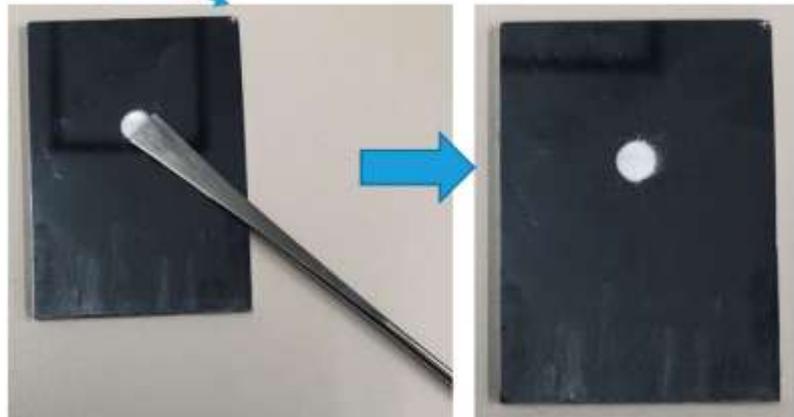
Front side



Back side



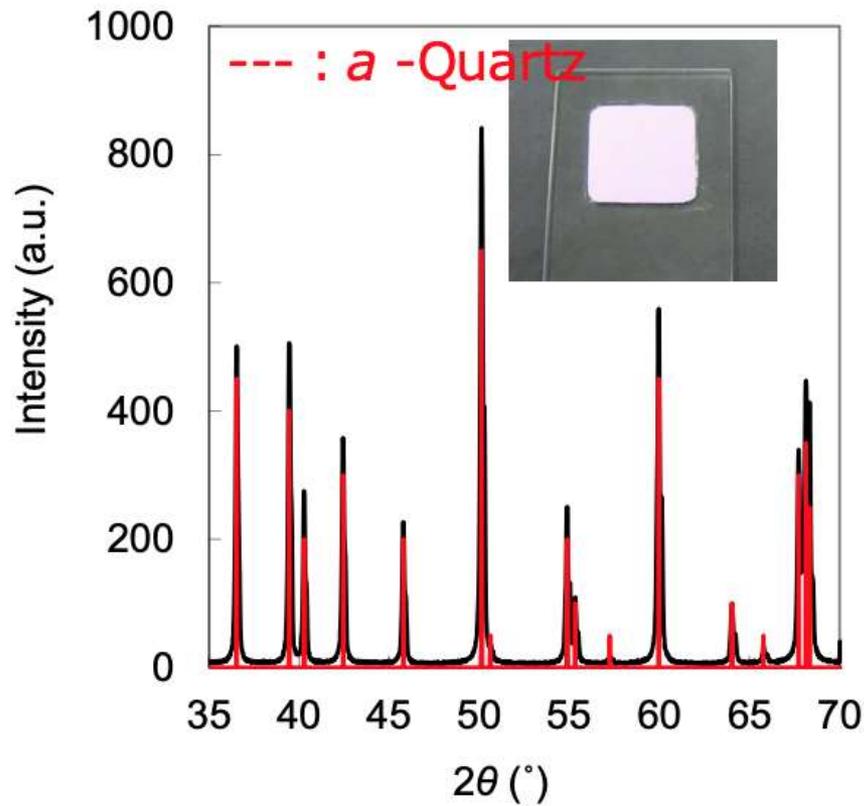
a trace of sample



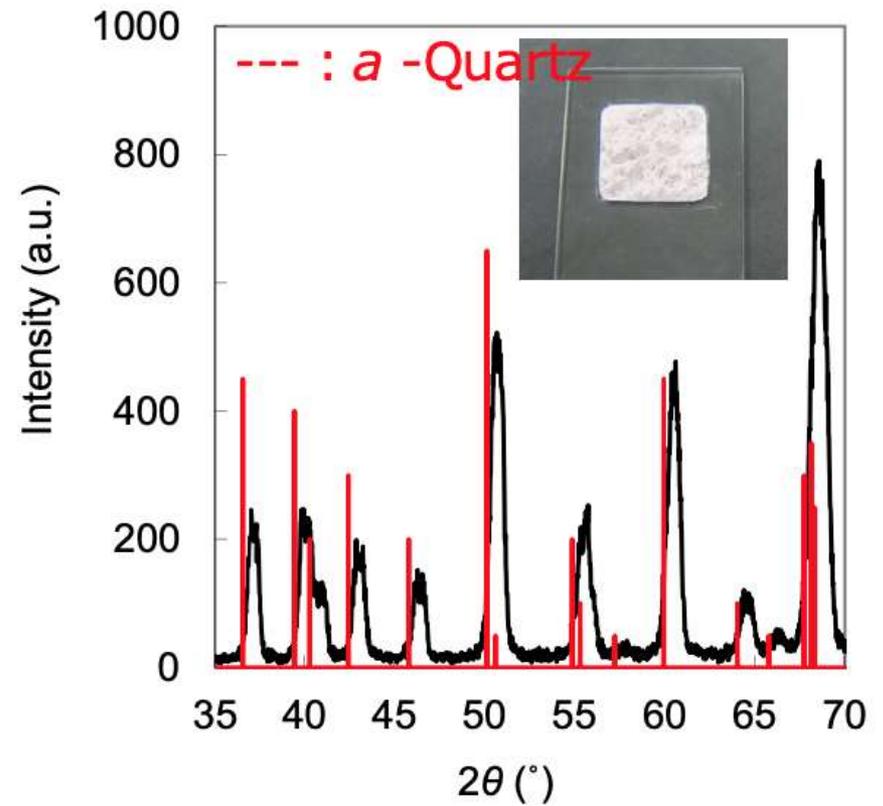
Put a small amount of sample in the small dent and use a spatula to flatten the surface.

Flat and Uneven Sample Surface

Flat sample surface



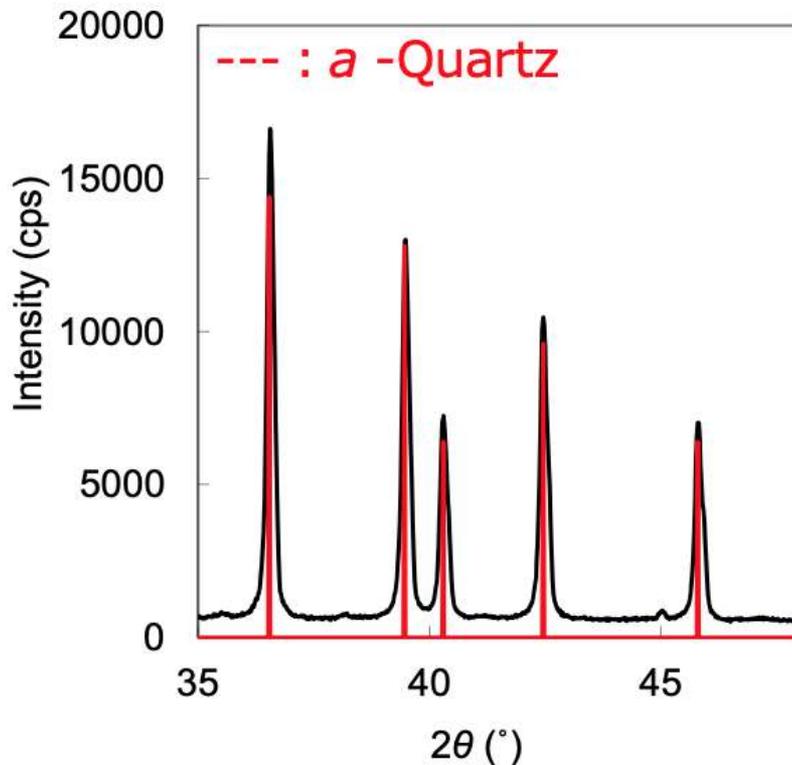
Uneven sample surface



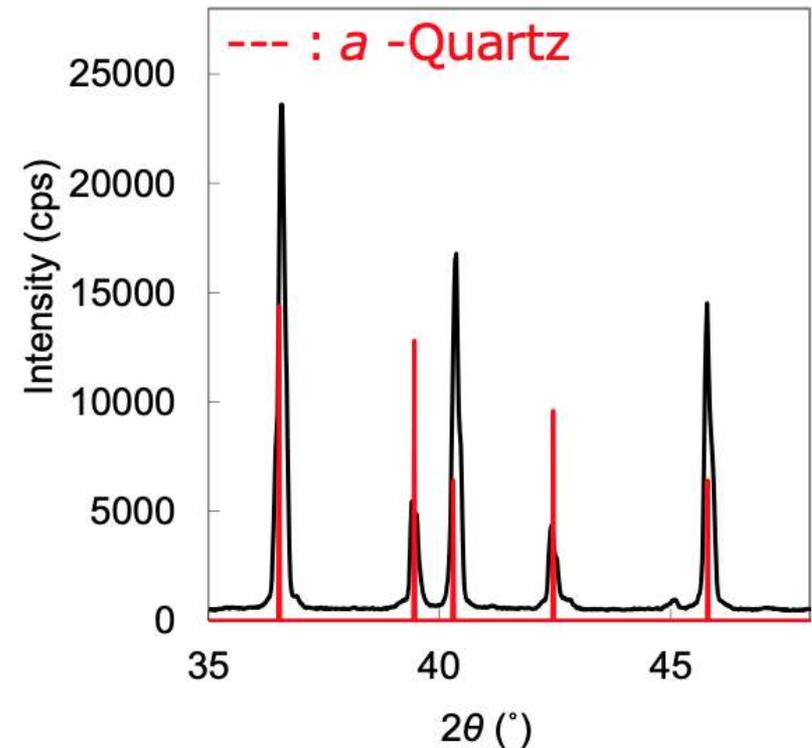
Fine and Coarse Crystallite Sample

- Relation between crystallite size and X-ray diffraction peak

fine crystallite (10 μm)



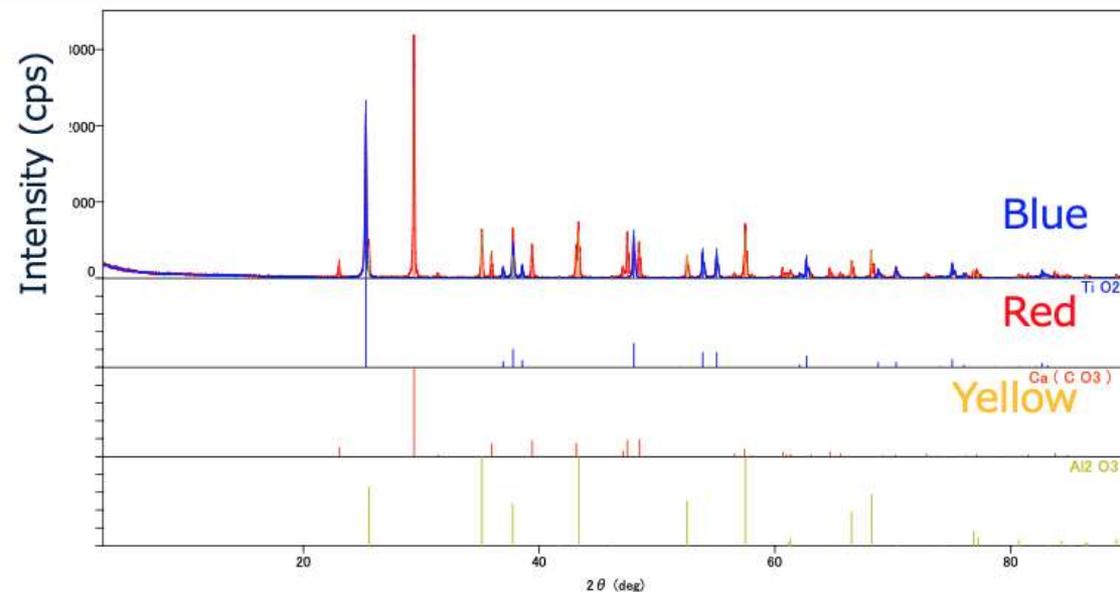
Coarse crystallite (100 μm)



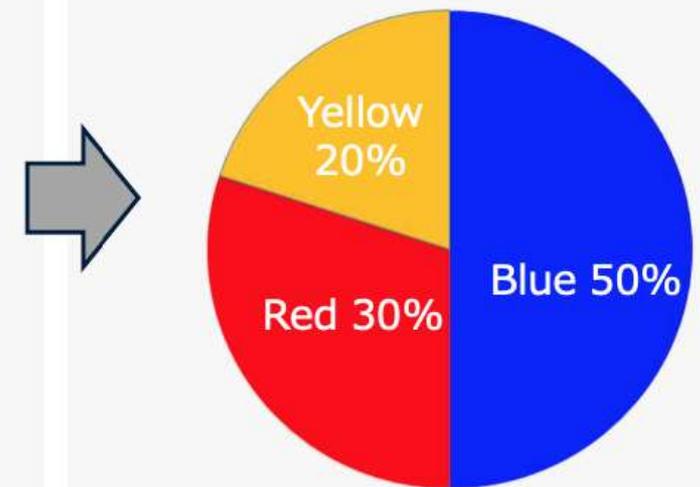
Quantitative analysis

The amount ratio of crystal phase in the sample is obtained from integrated intensity of X-ray diffraction profile.

Integrated intensity ratio of each phase



Amount ratio of crystal phase



RIR, d-I pattern decomposition, and Rietveld method

Method		Weight fraction
RIR method	Simplified analysis based on the RIR described in the database	Calculated based on the RIR and integral intensity of the highest peak of each phase
WPPF – d-I pattern decomposition	The lattice parameters and profile function parameters are refined individually.	Calculated based on the RIR and integral intensity of the highest peak of each phase
WPPF – Rietveld analysis	All crystal structural parameters are refined.	Calculated based on the scale factor and RIR of each phase.

RIR method

The weight ratio can be calculated from the integrated intensity of the highest peak and RIR(Reference Intensity Ratio) values.

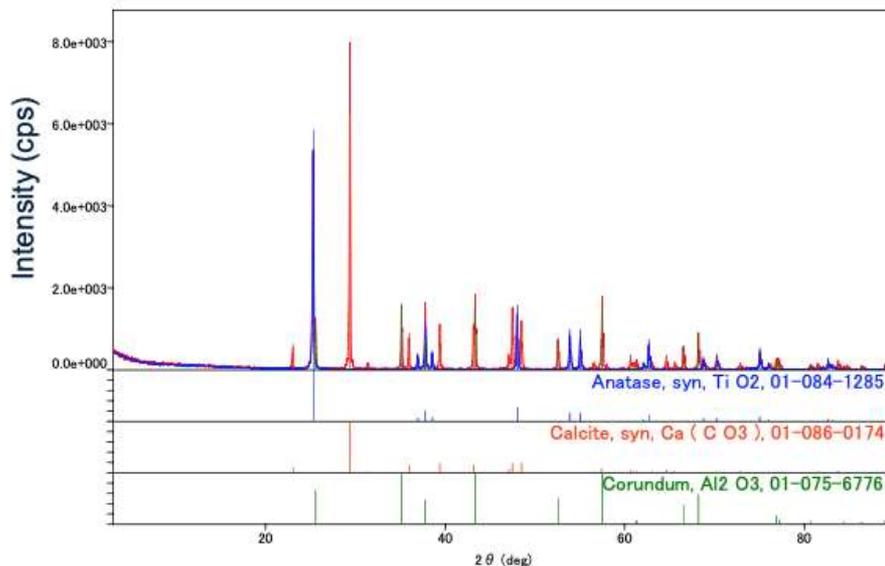
RIR values is estimated by intensity ration between Al_2O_3 and substance.

Substance : A, B, C

RIR value : R_A, R_B, R_C

Weight ratio : W_A, W_B, W_C

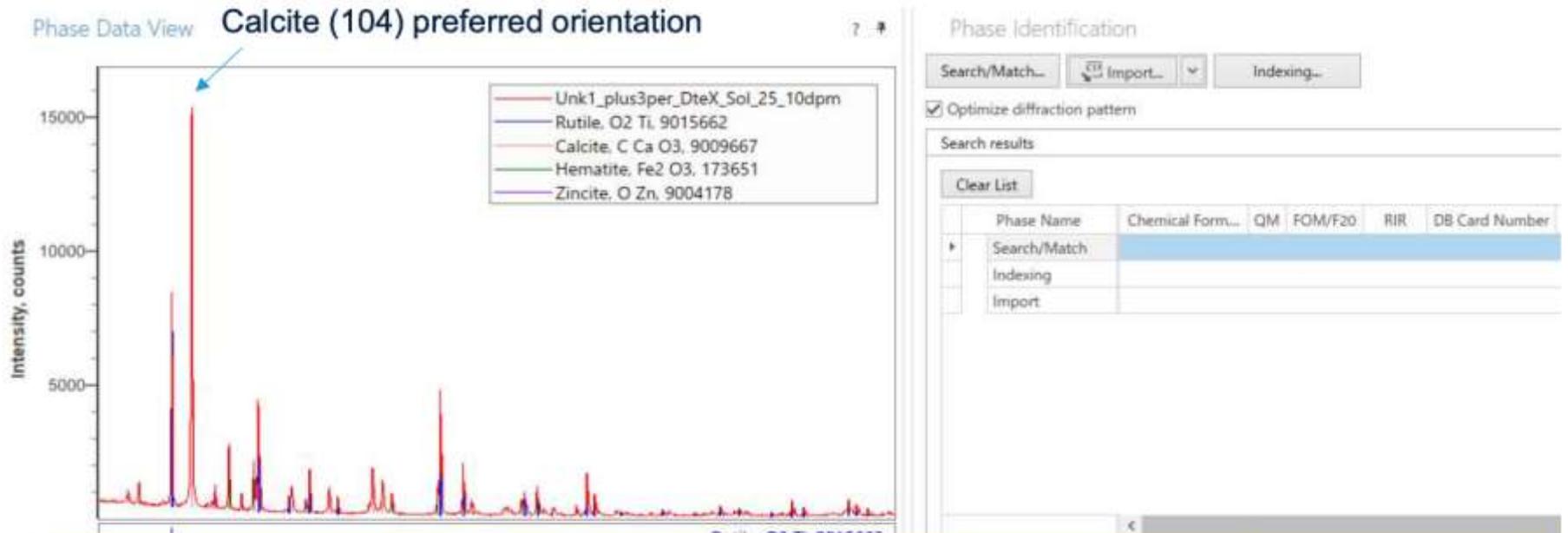
$$\frac{I_A}{R_A} : \frac{I_B}{R_B} : \frac{I_C}{R_C} = W_A : W_B : W_C$$



Substance	Integrated Intensity(cps · deg)	RIR values R_i
TiO ₂	736	4.99
CaCO ₃	883	3.22
Al ₂ O ₃	190	1.05

Substance	Wi (I/R)	Quantitative value(%)
TiO ₂	147	24.5
CaCO ₃	274	45.5
Al ₂ O ₃	181	30.0

Comparisons of quantitative methods



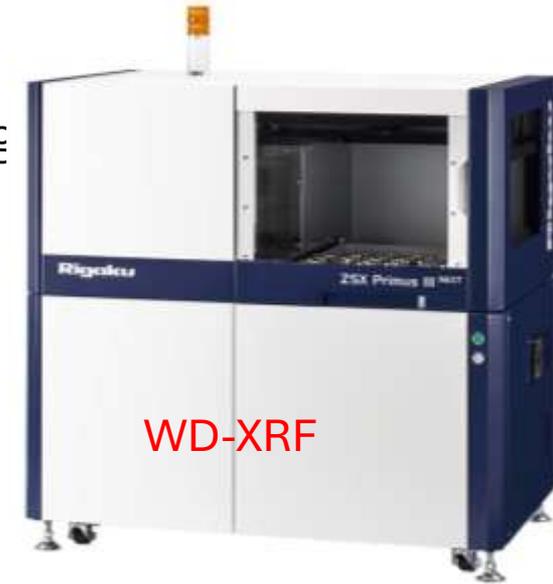
Crystal phase		Weighted value [mass%]	RIR	WPPF D-I pattern decomposition	WPPF Rietveld
Rutile	TiO ₂	37.3	24.78(13)	32.47(11)	37.22(3)
Calcite	CaCO ₃	43.7	61.12(17)	48.35(11)	44.28(4)
Hematite	Fe ₂ O ₃	14.7	11.04(9)	14.63(10)	14.03(6)
Zincite	ZnO	4.3	3.06(13)	4.56(6)	4.48(4)

3. Understanding XRF: Principles and Applications

- XRF determines **presence** and **quantities** of chemical **elements (chemical composition of materials)**.
=23%, Fe = 73%

e.g

ED-XRF



WD-XRF

- XRF - two major branches

- X-ray fluorescence (XRF) spectrometers

- (i) Wavelength dispersive spectroscopy (**WDS**)

- (ii) Energy dispersive spectroscopy (**EDS**)

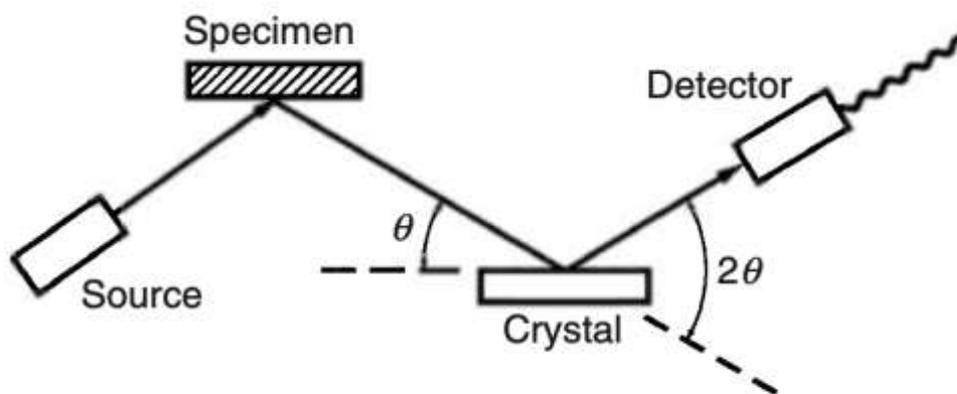
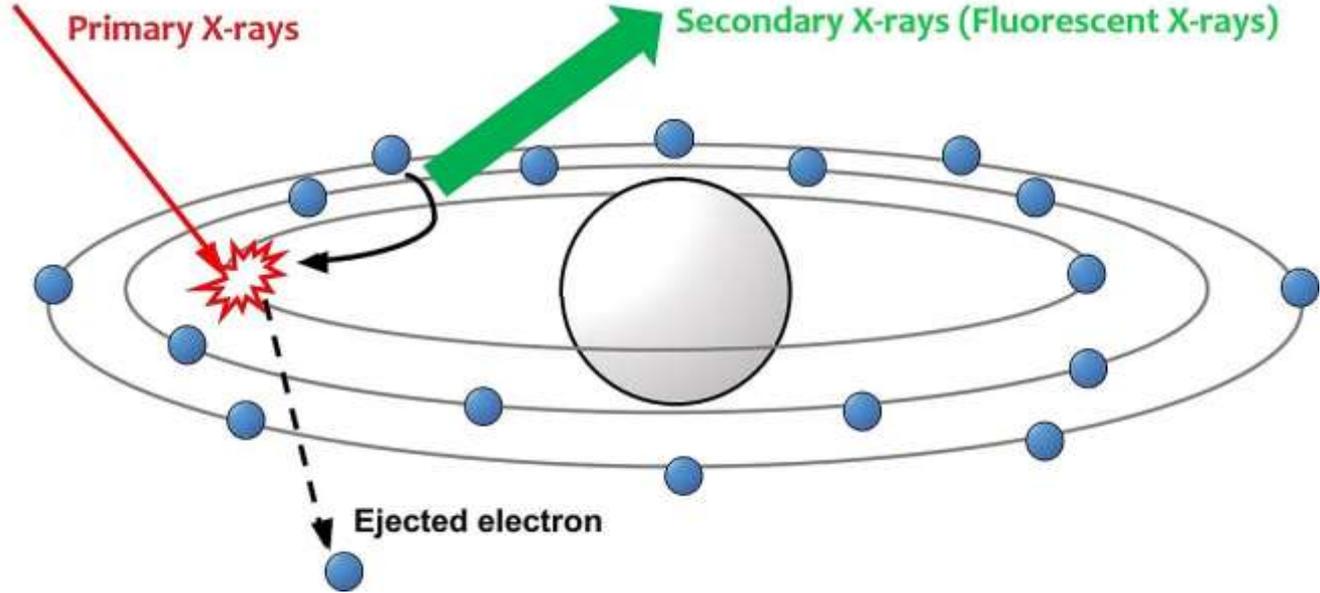
EDS Micro-analyzers in electron microscopes

- X-ray tube— power 0.5–3kW

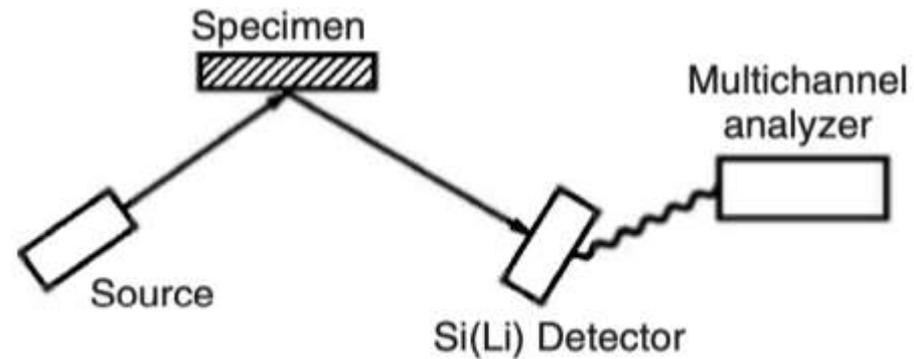
- voltage of 30–50kV



Principles of XRF



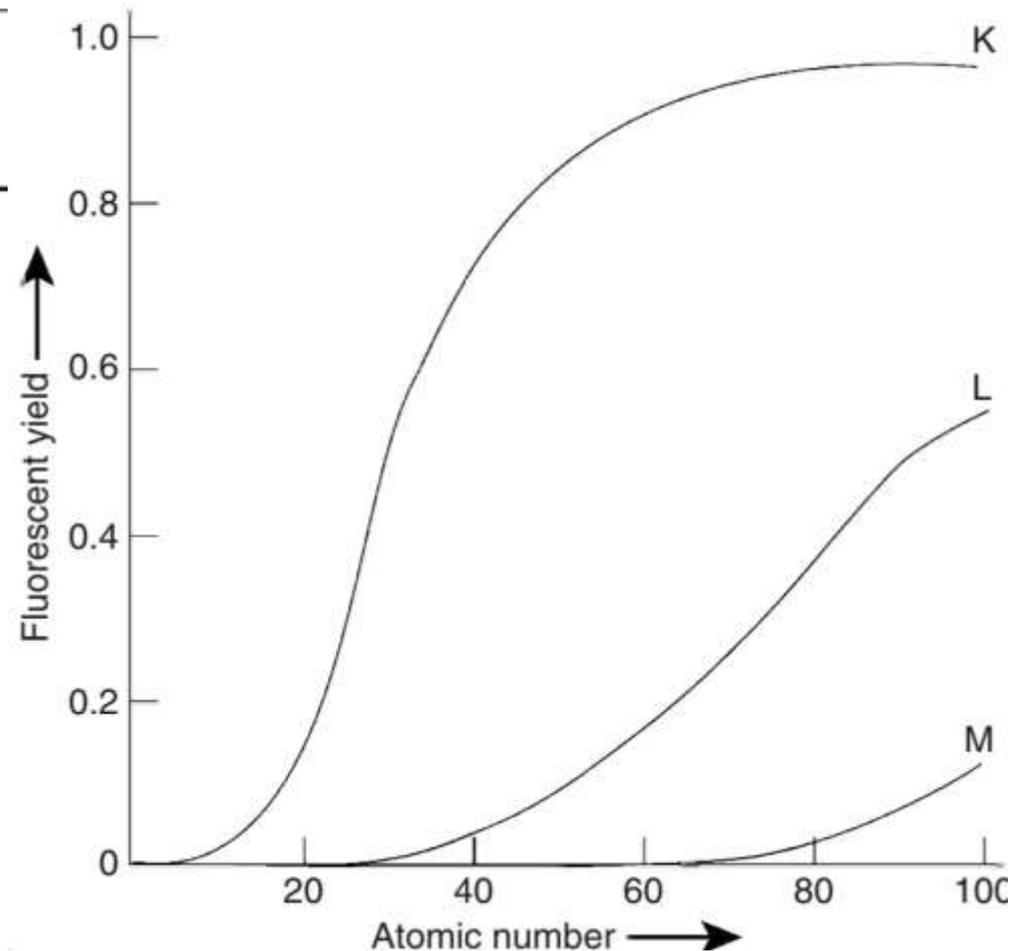
(a) WDXRF



(b) EDXRF

Fluorescent yield of elements

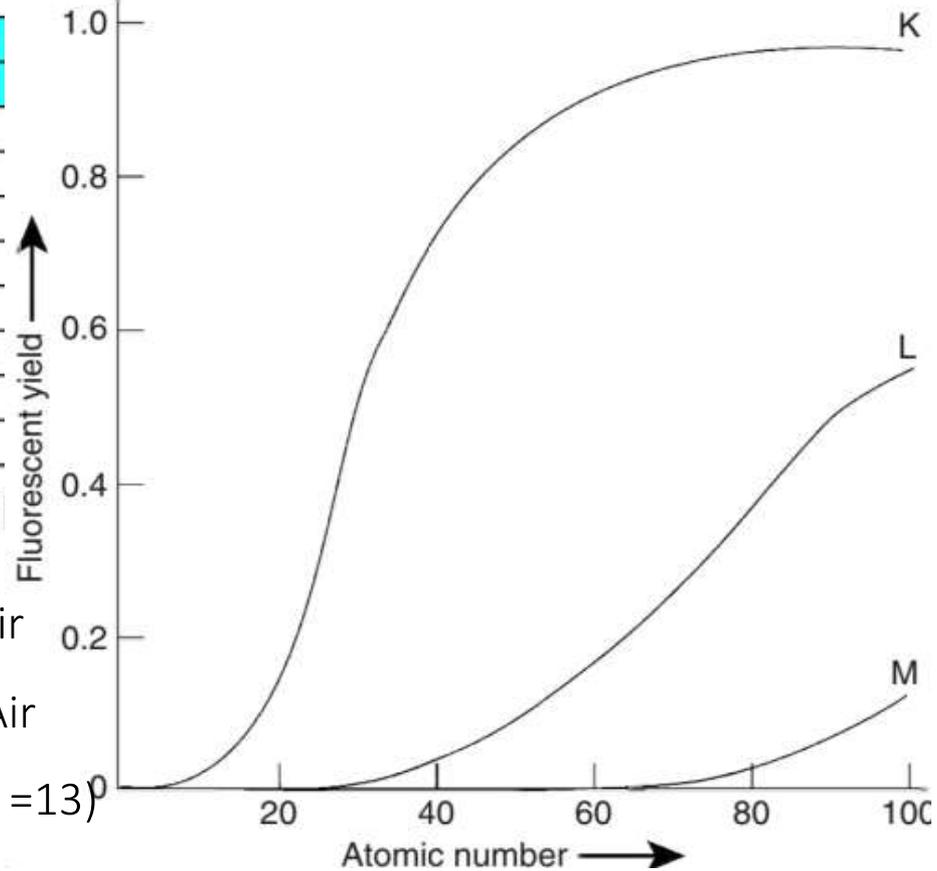
Atomic	Element	ω_K
4	Be	0.00045
5	B	0.00101
6	C	0.00198
7	N	0.00351
8	O	0.00579
9	F	0.00901
10	Ne	0.0134
11	Na	0.0192
12	Mg	0.0265



Analyzing crystal types in WDXRF

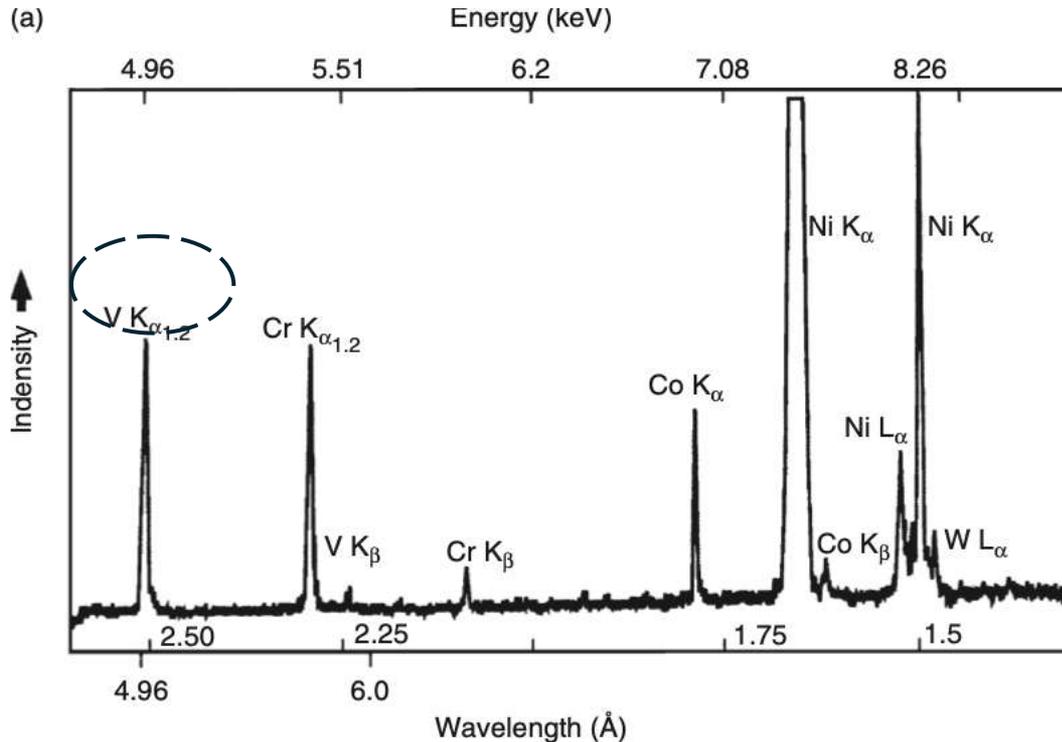
Atomic N.	4	5	6	7	8	9	11	12	13	14	15	16	17	19	20	22	23	24	25	26	27	28	29	30	33	- 60	
K Line	Be	B	C	N	O	F	Na	Mg	Al	Si	P	S	Cl	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	- Nd	
L Line														48Cd	56Ba								74W	82Pb			
LiF(200)																											
LiF(220)																											
LiF(420)																											
PETH																											
GeH																											
RX25																											
RX35																											
RX40																											
RX45																											
RX61																											
RX61F																											
RX75																											
RX85																											

Excellent
 Available



XRF working atm – vacuum, helium, air
 Best sensitivity : Vacuum > Helium > Air
 Atomic number (C=6) (Na=11) (Al =13)

Characteristic X-ray wavelengths and energies of selected elements.



Atomic number	Element	$K\alpha_1$	
		λ (Å)	E (keV)
23	V	2.504	4.952
24	Cr	2.290	5.415
25	Mn	2.102	5.899
26	Fe	1.936	6.404
27	Co	1.789	6.930
28	Ni	1.658	7.478
29	Cu	1.541	8.048
30	Zn	1.435	8.639

Sample condition for XRF

Powders:

Grinding (<400 mesh if possible) can minimise scatter affects due to particle size,
Pressing (hydraulically or manually) compacts more of the sample into the analysis area, and ensures uniform density.

Solids:

Polishing surfaces will also minimise scatter affects.
Flat samples are optimal for quantitative results.

Liquids:

Samples **should be** fresh when analysed and analysed with short analysis time if sample is evaporative.
Sample **should not** stratify (divided into groups or formed into layers) during analysis.
Sample **should not** contain precipitants/solids.

4. Comparing XRD and XRF

	XRF (X-ray Fluorescence)	XRD (X-ray Diffraction)
Purpose	Elemental composition analysis	Crystallographic structure analysis
Type of Information	Qualitative and quantitative elemental composition	Qualitative and quantitative (crystalline) phase composition, crystal structure, lattice parameters, amorphous content.
Sample requirement	Both crystalline and amorphous materials	Primarily for crystalline materials
Output	Spectrum shows peaks of each element's characteristic X-rays	Diffraction pattern of intensity vs. 2θ angle
Common use cases	Mining, environmental analysis, metal alloys, forensics	Materials science, geology, chemistry, pharmaceuticals

CHALLENGES IN DETECTING LIGHT ELEMENTS : XRF faces difficulties analyzing low atomic number elements like lithium and beryllium.



WDXRF	EDXRD
Good energy resolution	Poor energy resolution
Higher detection limit (100 ppm)	Lower detection limit (1000 ppm)
Long analysis time	Fast analysis
Expensive	Cheaper
Early 1950s	Early 1970s
Structurally complicate/bulk	structurally simple/compact
wider range of elemental analysis than EDS	

Applications of XRF vs. XRD

XRD applications

- **Materials science:** XRD is used to characterize new materials, assess their phase purity, and understand the relationship between their properties and crystal structures.
- **Polymers:** XRD helps determine crystallinity in polymers and phase transitions.
- **Ceramics:** XRD is used to determine additive stability in ceramics during processing.
- **Geology:** XRD is used to identify minerals and analyze rock formations, helping geologists understand the conditions under which rocks formed.
- **Environmental:** XRD is capable of determining asbestos and respirable silica in health and environmental monitoring.

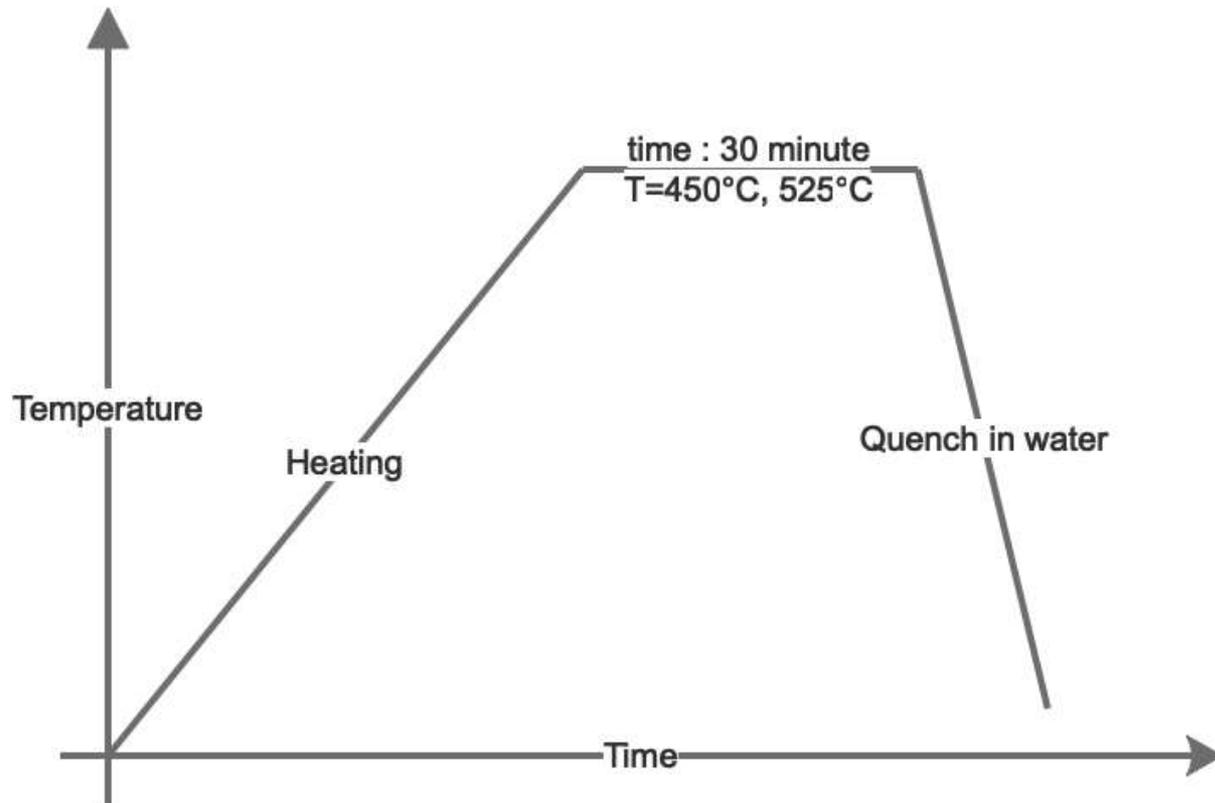
XRF applications

XRF is commonly used in industries such as mining, environmental monitoring, metallurgy, and quality control for rapid elemental analysis.

- **Mining and exploration:** XRF is used to determine full chemical analysis of **ores and minerals for metal content**, helping geologists assess the economic **potential of deposits**.
- **Environmental analysis:** XRF is used to identify and quantify contaminants in soils, sediments, and water, **including heavy metals** like lead, arsenic, and mercury.
- **Metallurgy:** XRF is extensively used in metal production to **ensure alloy composition and quality**.
- **Art and archaeology:** XRF is employed for non-invasive analysis of **historical artifacts, paintings, and ceramics** to determine their elemental composition.

5. Case Study: Integrating XRD and XRF for Alloy Development

- Objective : Investigation of Mg soluble in aluminium alloy.
- Tools : XRD for phase identification, XRF for elemental verification
- Process : Solution treatment of aluminium alloy at 450°C and 525 ° C.



XRD results for 525 °C

Al - 92.8 %
 $a=b=c = 4.052\text{\AA}$
 $\alpha = \beta = \gamma = 90^\circ$

Al_2Mg_7 - 7.2 %
 $a = 4.05\text{\AA}$, $b = 9.46\text{\AA}$, $c = 7.22\text{\AA}$
 $\alpha = \beta = \gamma = 90^\circ$

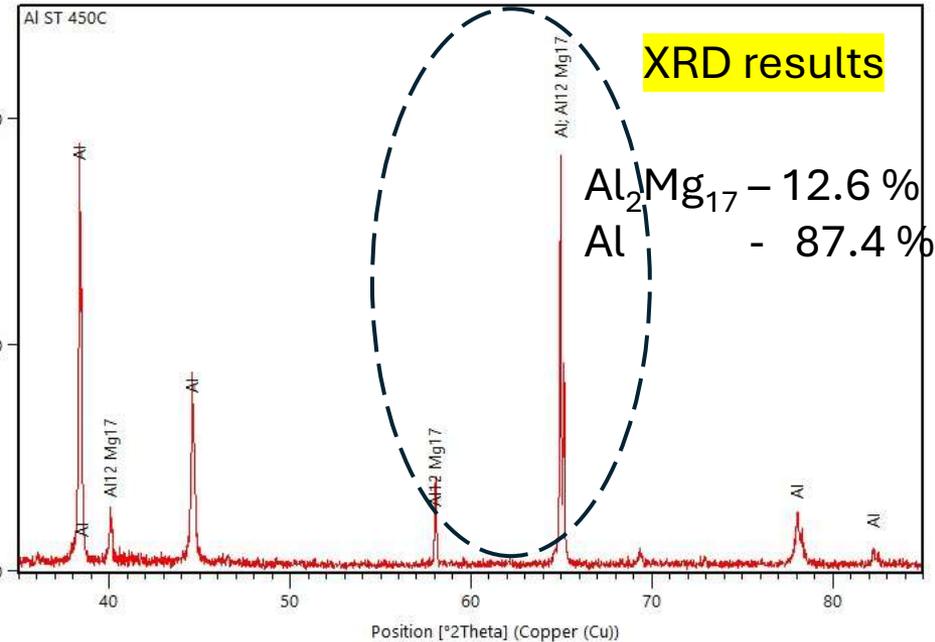
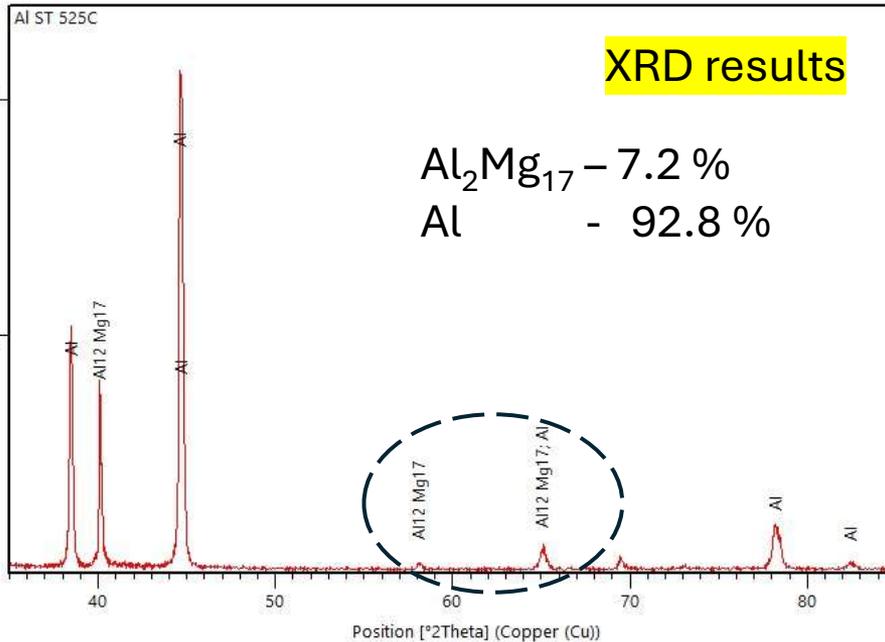
Analysis type EZ Scan XRF results
 Analysis date 2024- 3- 1 21:51
 Sample name Al_6xxx

No.	Component	Unit	Result
1	Mg	mass%	0.6046
2	Al	mass%	98.0906
3	Si	mass%	0.7344
4	Cr	mass%	0.1177
5	Fe	mass%	0.1655
6	Cu	mass%	0.2323

XRD results for 450 °C

Al - 87.4 %
 $a=b=c = 4.058\text{\AA}$
 $\alpha = \beta = \gamma = 90^\circ$

Al_2Mg_7 - 7.2 %
 $a = 4.08\text{\AA}$, $b = 9.47\text{\AA}$, $c = 7.2\text{\AA}$
 $\alpha = \beta = \gamma = 90^\circ$



6. X-Ray Safety

RADIATION

- All kinds of radiation exists in and around us at all times. The question arises what effect radiation has on us.
- A lot of radiation types are harmless, but the more energetic radiation is dangerous.
- WARNING X-RAYS ARE DANGEROUS!!!
- THEY CAN CAUSE SERIOUS PERSONAL INJURY IF SAFETY INSTRUCTIONS AND RECOMMENDATIONS ARE NOT FULLY CARRIED OUT
- They destroy and damage human tissue (burning, damage of the cell genetic material, which can cause cancer)

EFFECTS ON THE HUMAN BODY

The overall effects on the human body depending on the total dose received are of course very important.

Total body exposure	Effect on human body	Chances of survival
100 Sv	Damage to central nerve system	No chance/Only few hours
10 Sv	Damage to stomach, guts, bone marrow Little	<50% Change in blood composition
1 Sv	Change in Blood composition	Reasonable, >50%
0.1 Sv	no physical damage	Complete recovery after about 6 weeks

7. Conclusion

XRF and XRD are **both powerful techniques** that offer unique insights into materials.

XRF excels in providing **quick and accurate elemental analysis**, while **XRD** is essential for understanding the **crystalline structure and phase composition of materials**.

Each technique has its strengths, and they are **often used together** for comprehensive material characterization in research and industry.

References

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Thanks for your attention!