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X-ray Diffraction for powder sample

Rigaku Corporation
Application laboratory
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Today's topics (AM)

- Features of Rigaku TTRAXⅢ
- Basics of powder XRD
  - Feature of XRD
  - Evaluation item
- Texture analysis for bulk sample
  - Measurement and Process
- SAXS for nano-size sample
  - Principle and Optics
  - Application

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Feature of TTRAXⅢ

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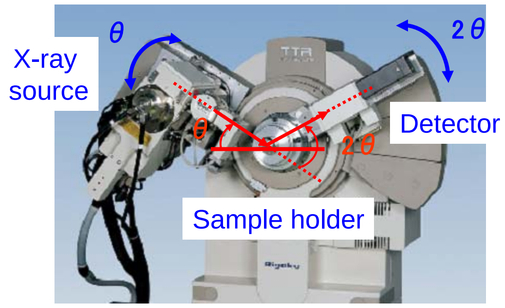
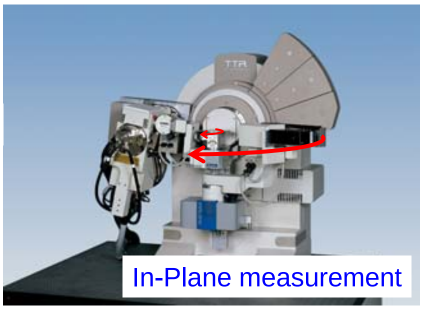
Rigaku TTRAXⅢ





(2θχ/φscan)

- Horizontal goniometer
- High power X-ray source
- Parallel beam method
- In-Plane axis

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Feature of TTRAXⅢ

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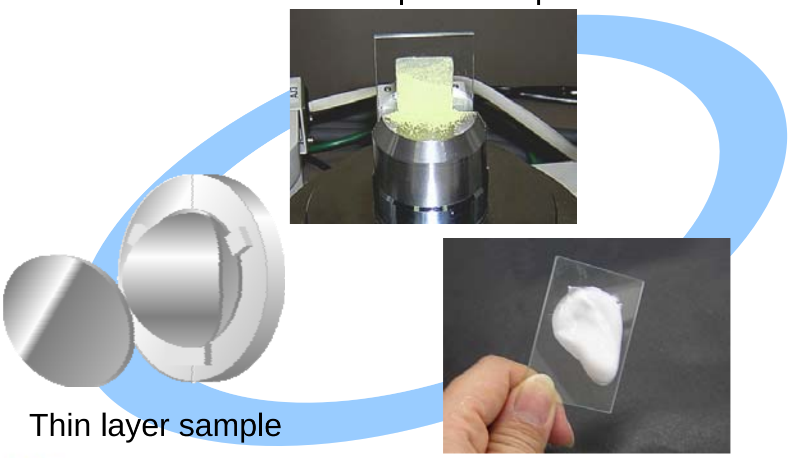
In case the sample isn't set to horizontal….

Hard-to-pack sample



Thin layer sample

Semi-liquid sample

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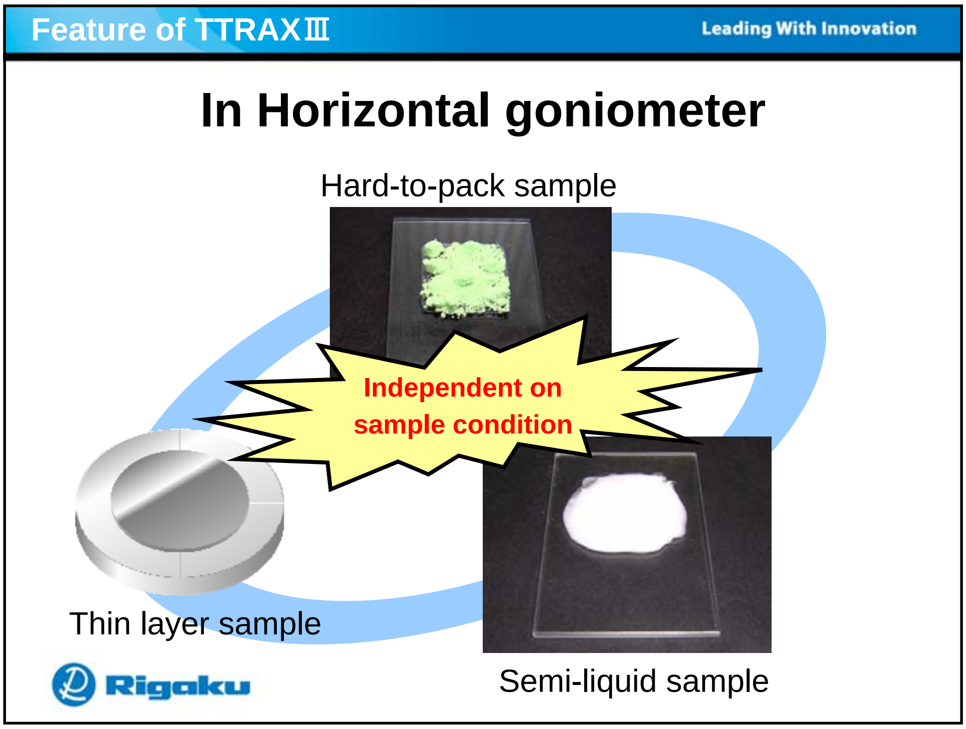
Feature of TTRAXⅢ
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In Horizontal goniometer
Hard-to-pack sample
Independent on sample condition
Thin layer sample
Semi-liquid sample
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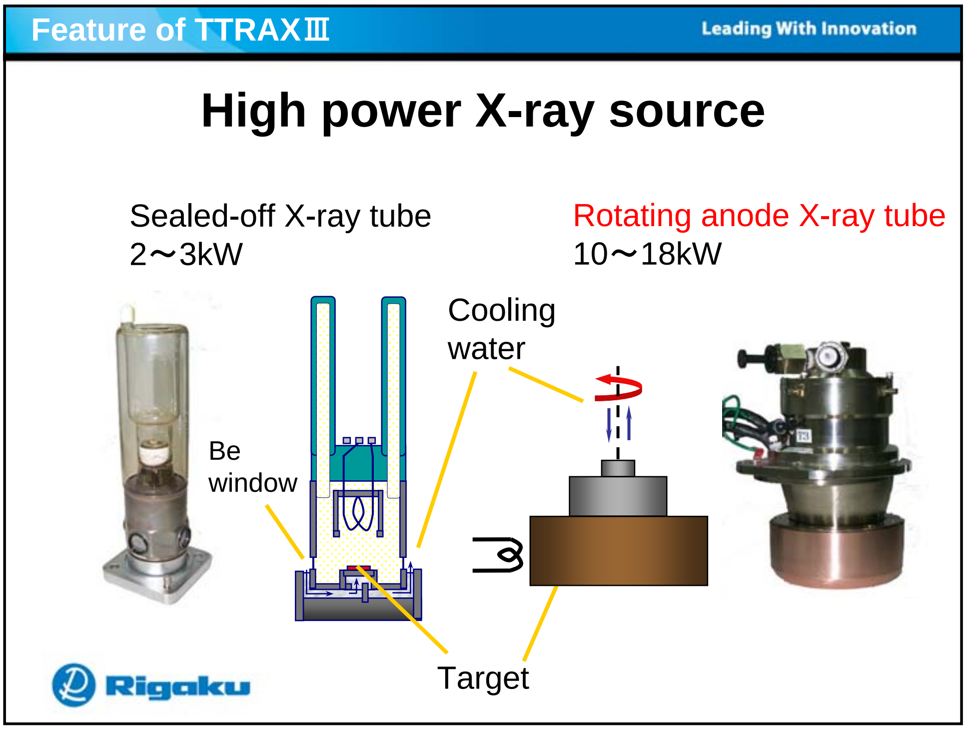
Feature of TTRAXⅢ
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High power X-ray source
Sealed-off X-ray tube
2～3kW
Rotating anode X-ray tube
10～18kW
Cooling water
Be window
Target
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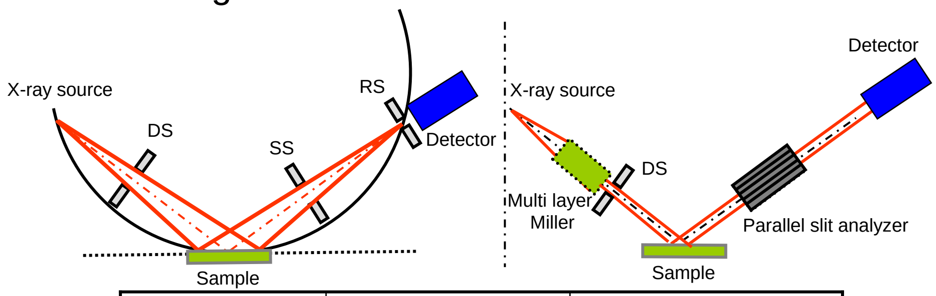
Geometry for powder sample

- Focusing method
- Parallel Beam



	Focusing method	Parallel beam
Systematic error	1. Flat sample 2. Umbrella effect 3. Adsorption effect 4. Eccentric error	Umbrella effect
Intensity	Strong	medium

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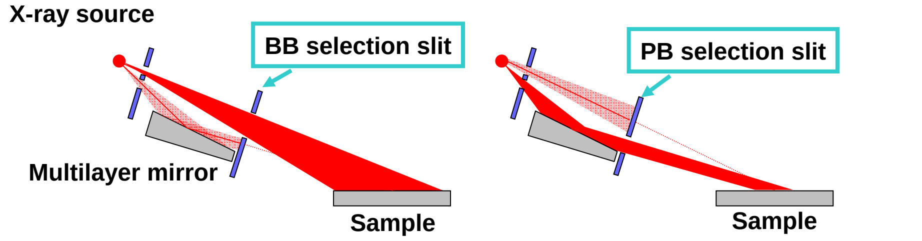
Cross Beam Optics

Rigaku patented technology

BB and PB geometries are simultaneously mounted, aligned, and selectable.



Focusing geometry (BB) **Parallel beam geometry (PB)**

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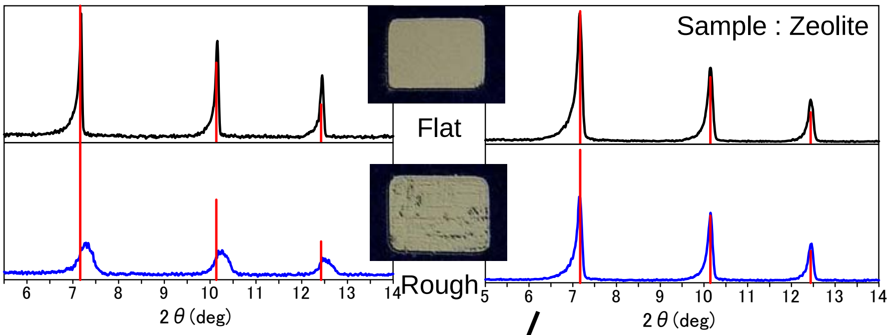
Measurement of rough sample surface

Focusing method | Parallel beam



Hold of peak shape, peak position and FWHM

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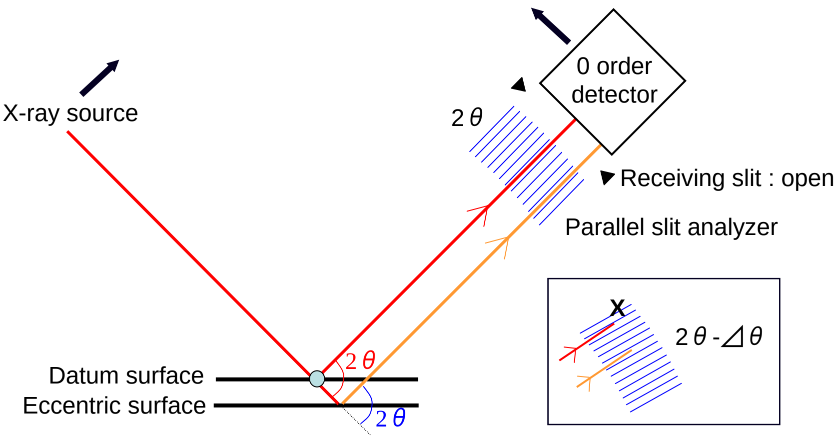
Free from Eccentric error (Parallel beam)



Basics of XRD

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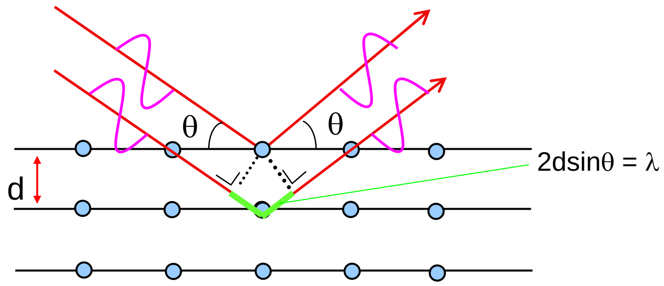
Interaction of substance and X-ray :1

Bragg's condition of diffraction

- The conditions for a reflected (diffracted) beam are given by the relation

$2d\sin\theta = n\lambda$ ***Bragg's equation***



d : Interplanar spacing
θ : Bragg angle
λ : X-ray wavelength
n : 1,2,3···

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Basics of XRD

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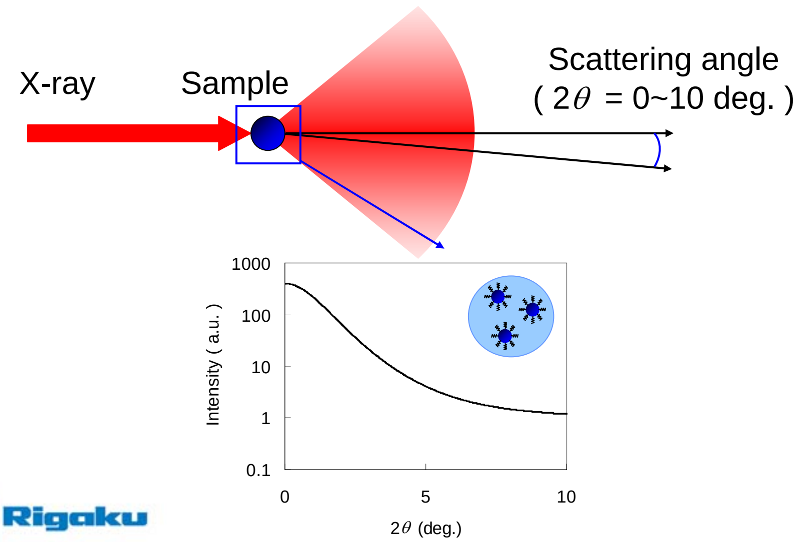
Interaction of substance and X-ray :2

X-ray diffuse scattering



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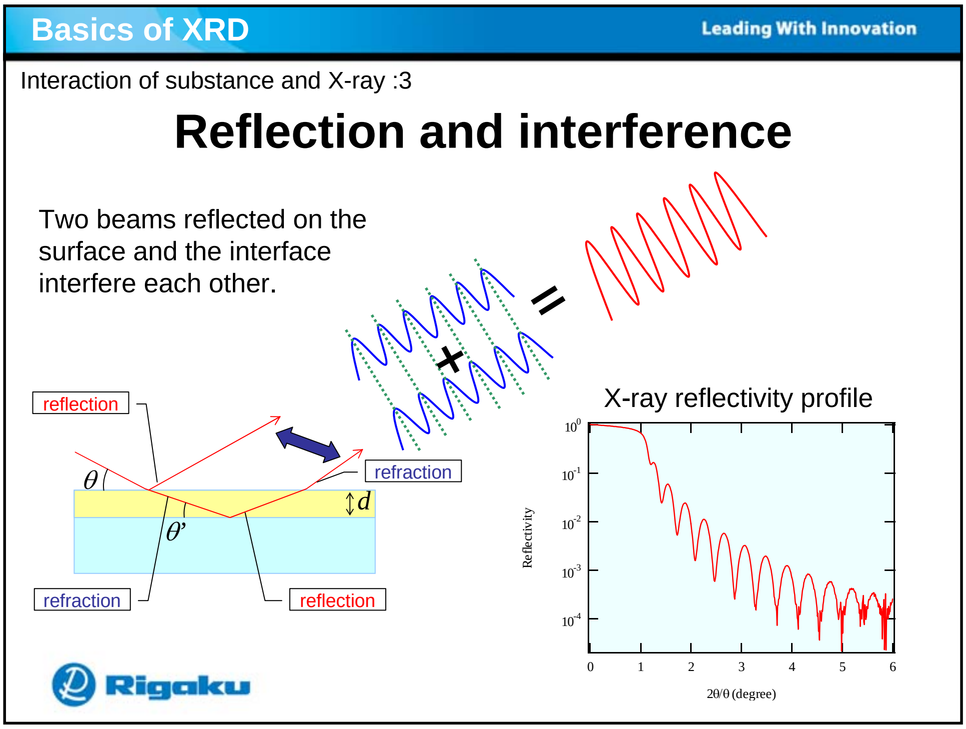
Basics of XRD
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Interaction of substance and X-ray :3
Reflection and interference
Two beams reflected on the surface and the interface interfere each other.
reflection
refraction
refraction
reflection
θ
θ'
d
X-ray reflectivity profile
Reflectivity
2θ/θ (degree)
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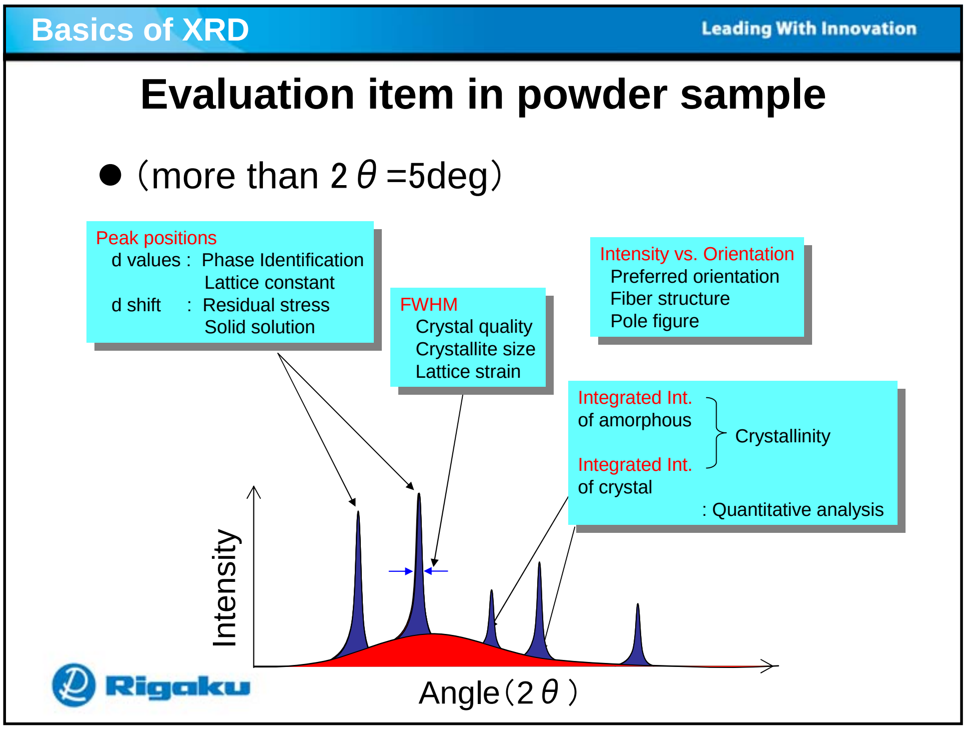
Basics of XRD
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Evaluation item in powder sample
● (more than 2θ =5deg)
Peak positions
d values : Phase Identification
Lattice constant
d shift : Residual stress
Solid solution
FWHM
Crystal quality
Crystallite size
Lattice strain
Intensity vs. Orientation
Preferred orientation
Fiber structure
Pole figure
Integrated Int. of amorphous
Integrated Int. of crystal
Crystallinity
: Quantitative analysis
Intensity
Angle (2θ)
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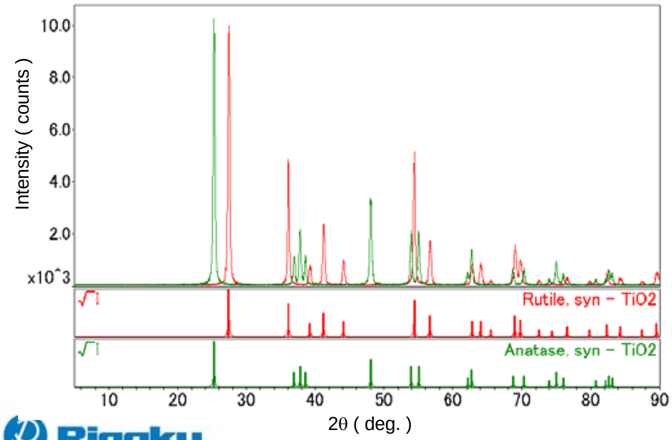
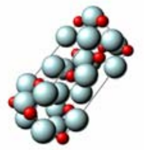
Phase Identification in X-ray diffraction

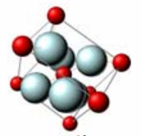
- The powder diffraction pattern is characteristic of the substance
- The diffraction pattern indicates the state of chemical combination





Anatase
(Photocatalyst etc)

TiO2



Rutile
(Cosmetic etc)

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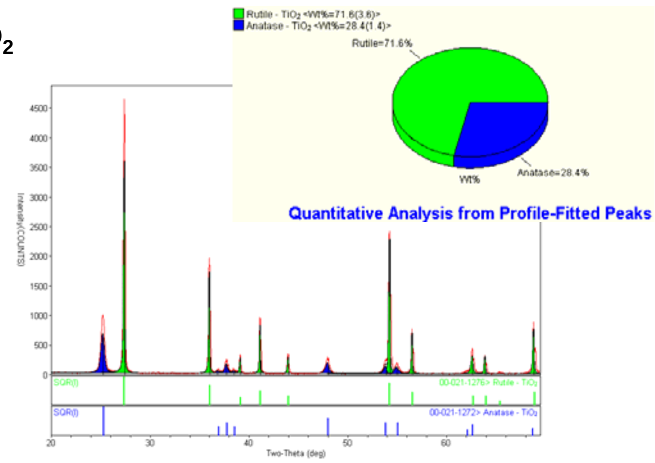
Quantitative analysis(RIR method)

The concentration of each phase is calculated by integrated intensity and RIR value

Polymorphs of TiO_2
Rutile (RIR:3.40)
Anatase (RIR:3.30)
Brookite

Preparation
Rutile:Anatase=3:1

Result
Rutile: 71.6wt%
Anatase: 28.4wt%



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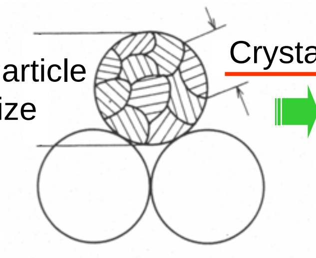
Crystallite size

Polycrystal

There is one or multiple crystalline in one particle.

Small angle X-ray scattering ⇦ Particle size



Crystallite size ⇨ The width of diffracted line
- ・Scherrer method
- ・Hall method

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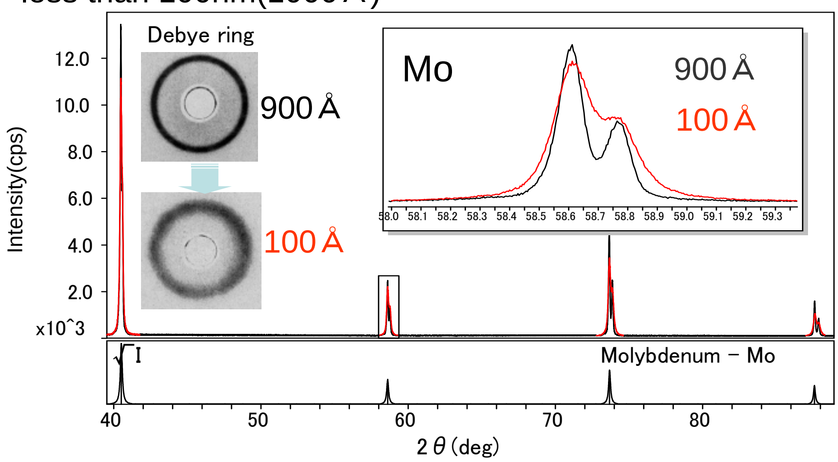
Crystallite size -Mo-

The width of diffracted line broaden in crystallite size less than 100nm(1000Å)



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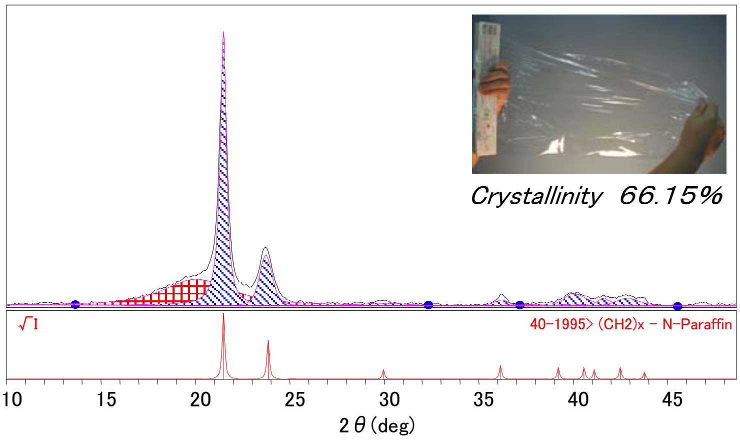
Basics of XRD Leading With Innovation

Crystallinity

Plastic wrap



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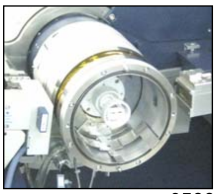
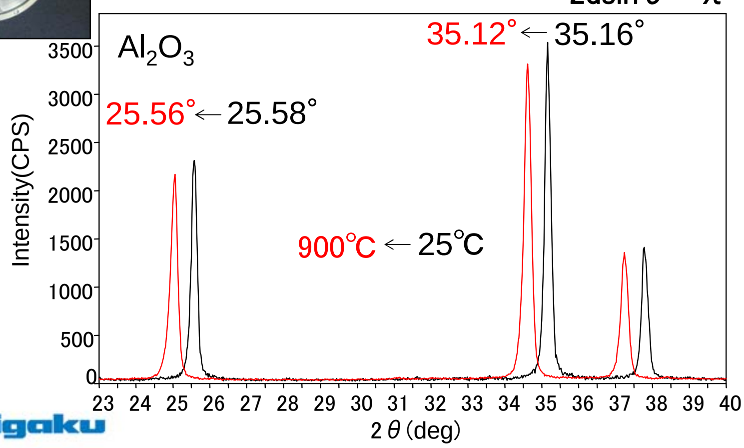
Change of lattice constant



Monitoring the change of lattice constant in real time

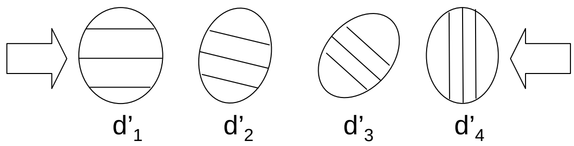
→<u>in situ</u> measurement

$2d\sin\theta = \lambda$

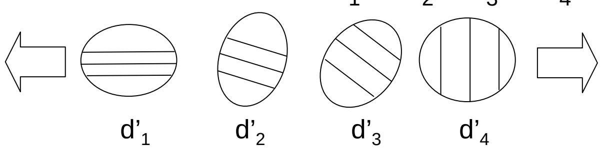


Stress and interplanar spacing

Compressive stress $d'_1 > d'_2 > d'_3 > d'_4$



Tensile stress $d'_1 < d'_2 < d'_3 < d'_4$



Bragg's condition of diffraction

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

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Basics of XRD
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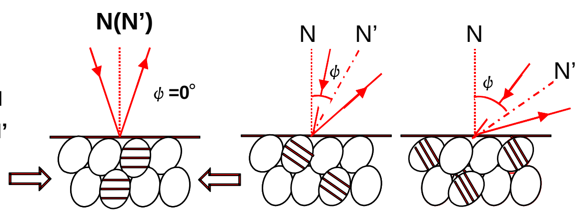
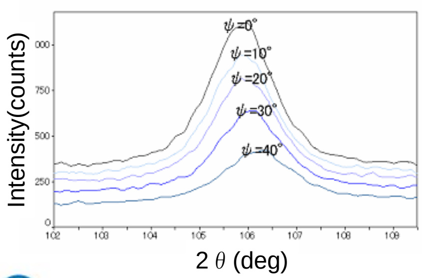
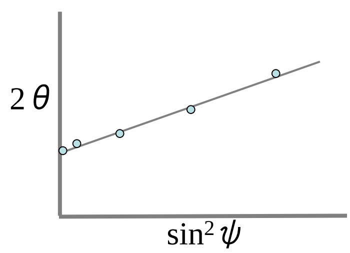
Peak shift and sin$^2\psi$ diagram

Normal line of sample surface :N

Normal line of lattice plane :N'







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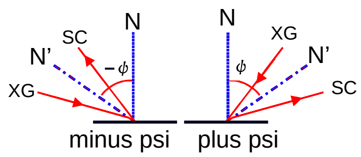
Calculation of stress value

$$\sigma \text{(stress value)} = K \cdot \frac{\Delta 2\theta}{\Delta \sin^2\psi}$$

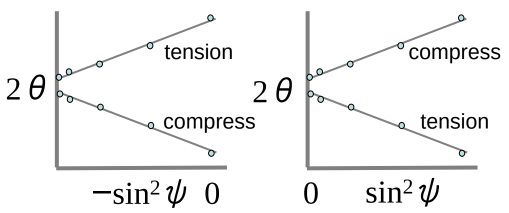
Slope of $\sin^2\psi$ diagram

$$K \text{(stress constant)} = \frac{-E}{2(1+\nu)} \cdot \cot\theta_0 \cdot \frac{\pi}{180}$$

Material-specific value
{E: young's modulus, ν: poisson ratio,
θ_0: diffraction angle in stress free condition}



Iso-inclination method(Fixed Psi)



Basics of XRD
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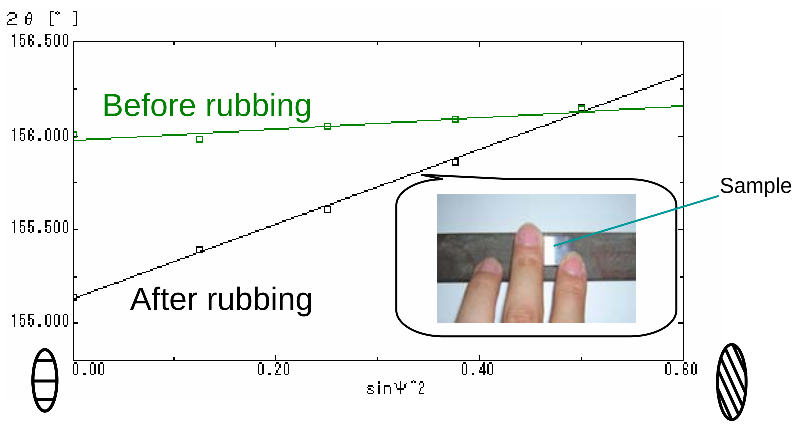
Measurement of residual stress

- Iron plate



Texture evaluation and pole figure analysis for bulk sample

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Texture and substance

Nonoriented sample : brick, concrete, (powder)

Oriented sample : aluminium foil,
iron plate
plastic bottle

Single crystal : silicon wafer, diamond, quartz

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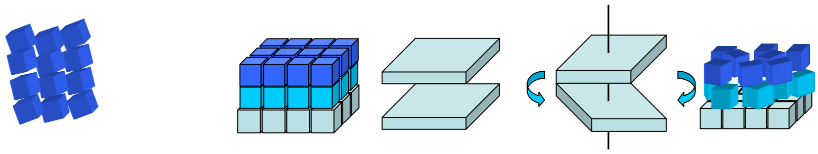
What is oriented sample?

The condition that a lattice plane faces to the same direction



Metal orientation (rolled sample)	Approximate equivalent to single crystal (Epitaxial film)	Uni-axial orientation (fiber orientation)

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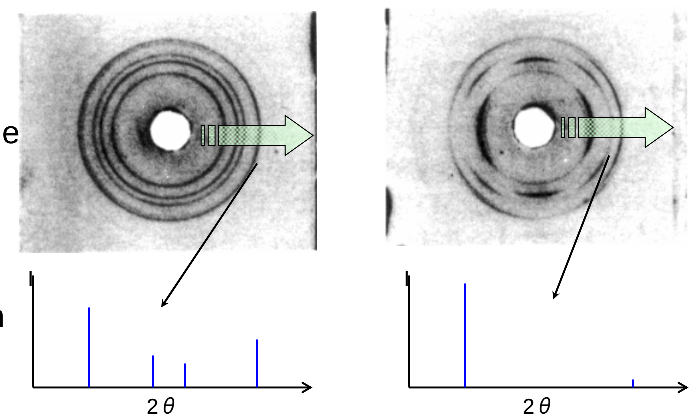
2D image and 2 θ -I diffraction pattern

nonoriented | oriented

2D image

Diffraction pattern



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Texture evaluation

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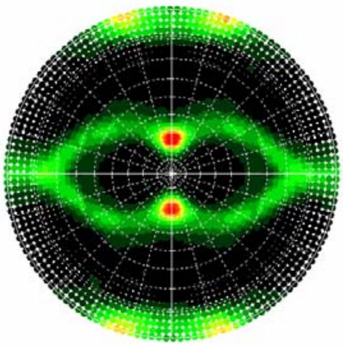
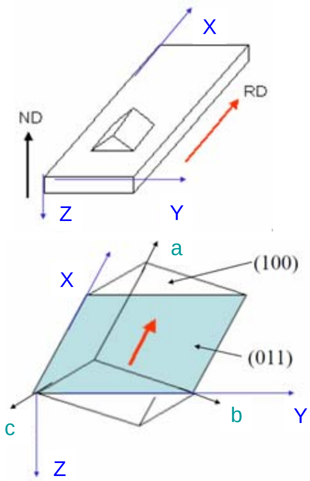
What is the purpose of texture?

Which plane is faced to Rolling direction and Normal direction?





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Texture evaluation

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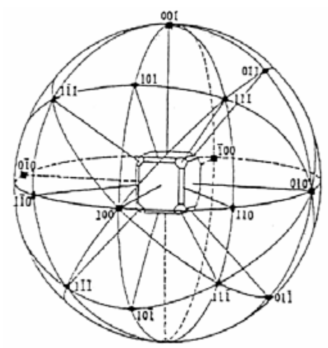
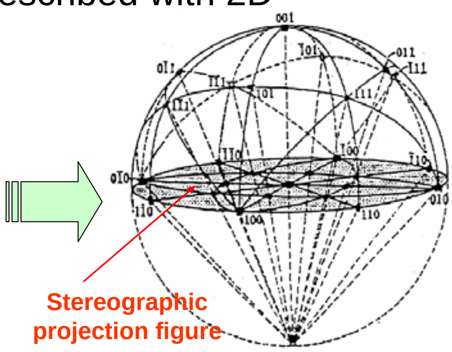
Spherical projection method and Stereographic projection method

3D is described with 2D





Spherical projection method

Stereographic projection method

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Texture evaluation

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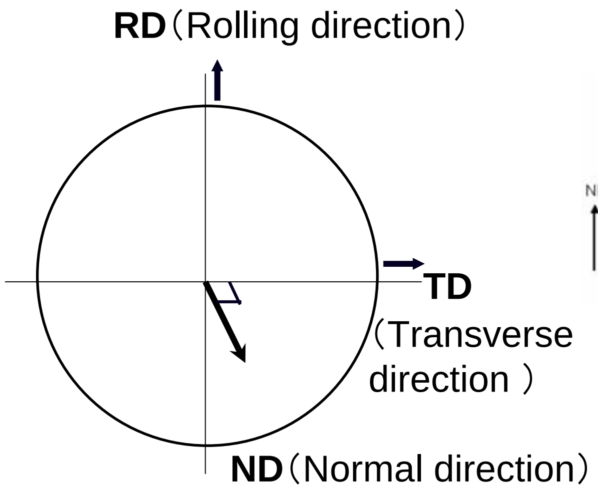
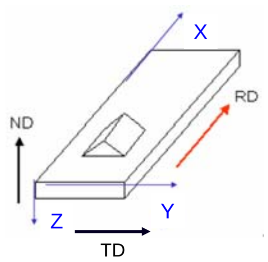
Pole figure





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Texture evaluation

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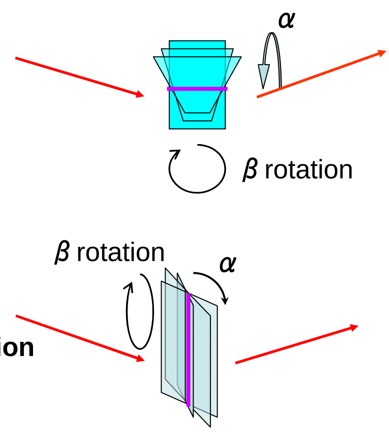
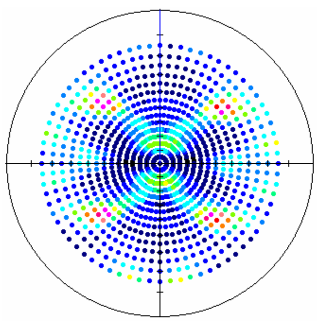
Sample behavior in Reflection method and Transmission method

Reflection method

Transmission method



Beta rotation at each alpha angle
Alpha:5deg step
(ex.15→20･･･85→90deg)
Beta: 5deg step
(ex.0→5･･･355→360deg/ α angle)



Sample is moved centering around purple line

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Texture evaluation

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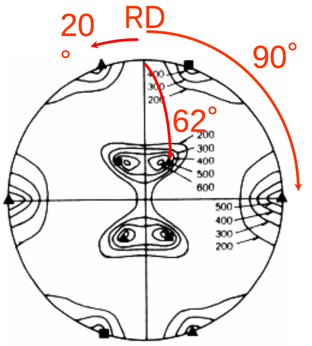
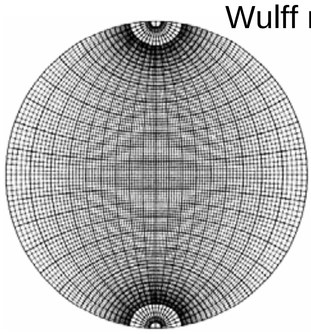
Orientation analysis :step1

Pole figure of (111) in rolled Cu-Zn(70-30)



Wulff net.



The angle between RD and each pole is estimated with Wulff net.

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Texture evaluation

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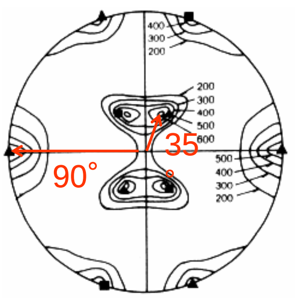
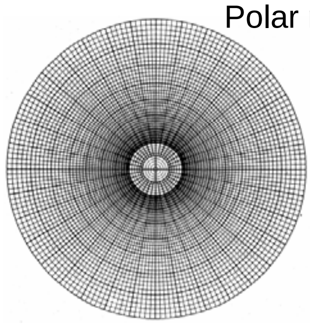
Orientation analysis :step2



Polar net



The angle between ND and each pole is estimated with Polar net.

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Texture evaluation
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Orientation analysis :step3

Angle between plane in ($h_1k_1l_1$) and ($h_2k_2l_2$) of cubic crystal

($h_1k_1l_1$)	($h_2k_2l_2$)				
	100	110	111	210	211
100	0 90				
110	45 90	0 60 90			
111	54.7	35.3 90	0 70.5 109.5		
210	26.6 63.4 90	18.4 50.8 71.5	39.2 75.0	0 36.9 53.1	
211	35.3 65.9	30 54.7 73.2 90	19.5 61.9 90	24.1 43.1 56.8	0 33.6 48.2

ND (arrow: 111 row – 110 column)
RD (arrow: 211 row – 111 column)

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Texture evaluation
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Orientation analysis :step4

Angle between plane of cubic

(111)(110)=35.5, 90° → ND

(111)(211)=19.5, 61.9, 90° → RD

Rotate standard (110) projection of cubic crystal 35degree clockwise.

RD is $[1\bar{1}2]$

This texture is (110)$[1\bar{1}2]$. (hkl)[*uvw*]=h**u*+k**v*+l**w*=0

ND RD

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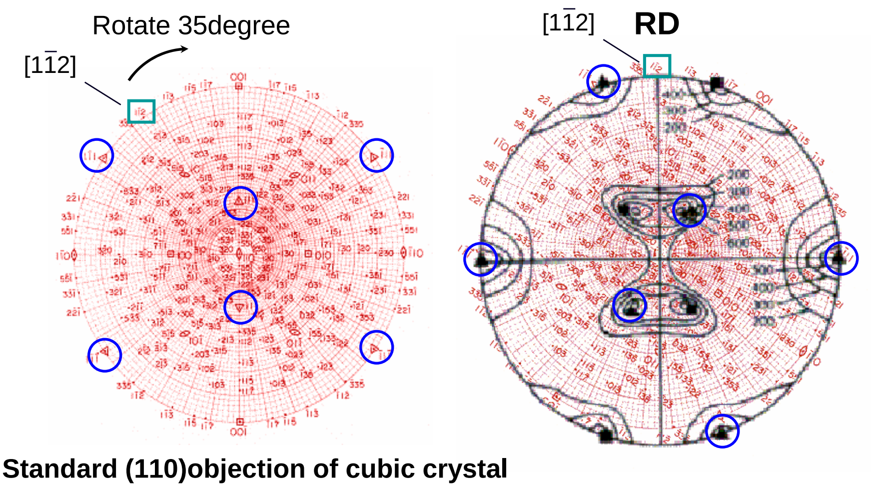
Process by stereographic objection figure



Standard (110)objection of cubic crystal

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Small angle X-ray scattering for nano-size sample

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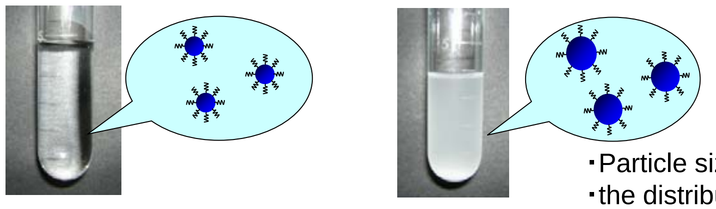
Purpose of SAXS

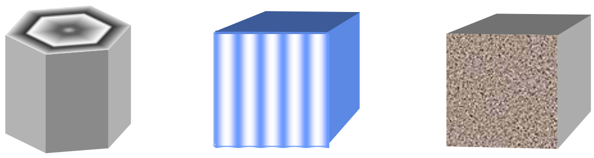
Small Angle X-ray Scattering

- Particle size estimation (X-ray scattering)



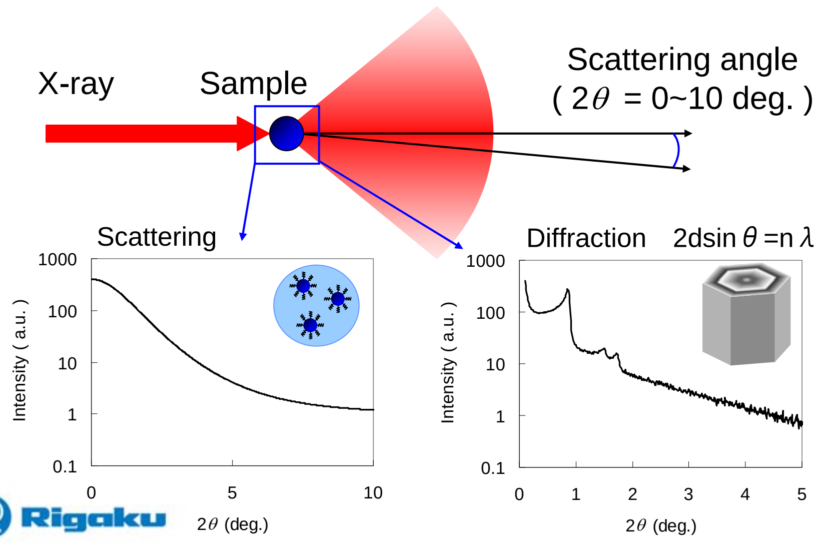
・Particle size
・the distribution

- Phase identification (X-ray diffraction)



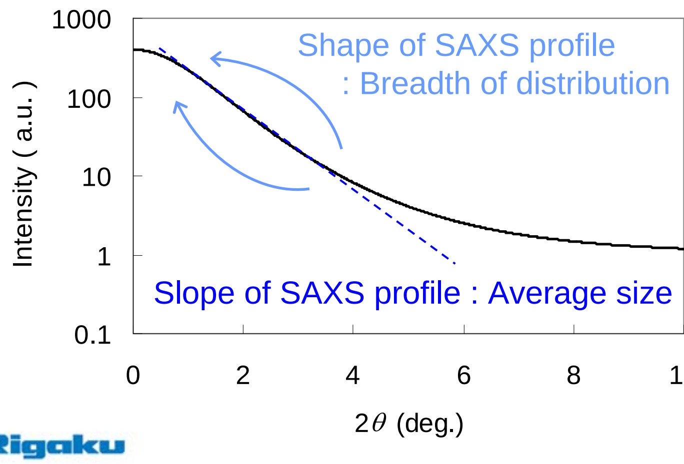
・molecular structure

Principle of SAXS



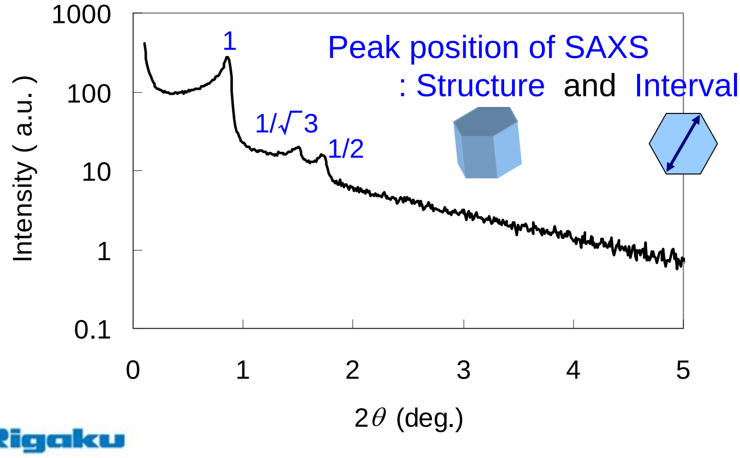
Particle information

- Particle size and particle distribution

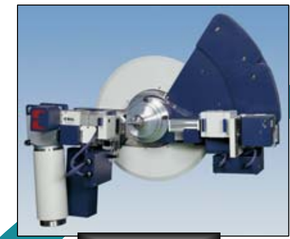


Phase information

- Long-period structure

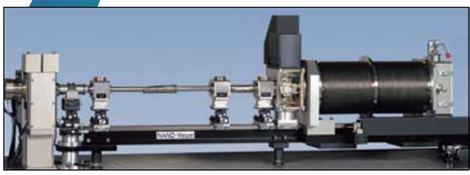


Instrument for SAXS



UltimaⅣ

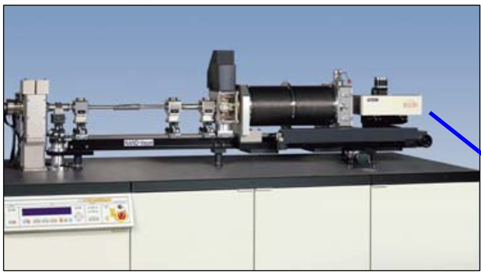
TTRAX III



NANO-Viewer

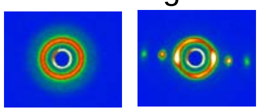
Point focus optics

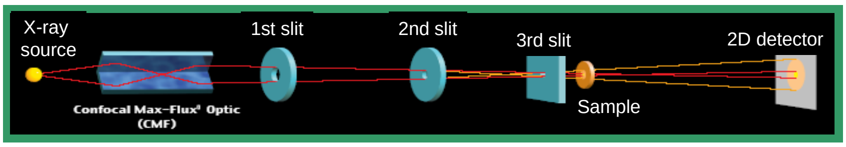
- **NANO-Viewer (2D-SAXS System)**



Semiconductor
2D detector Pilatus100k

2D image

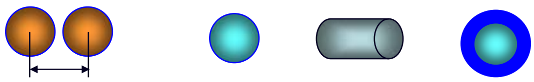




3slits optics

NANO-Solver

- Automatic particle size & distribution estimation !

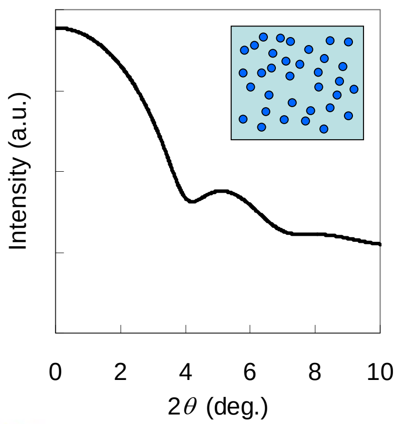


Closely particle   sphere   cylinder   Core/shell

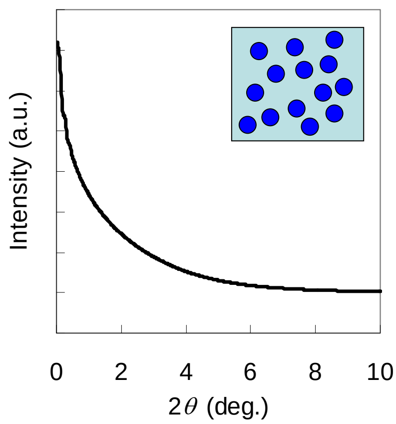
Rigaku

Relations of size and profiles

- Size : 3nm



- Size : 60nm

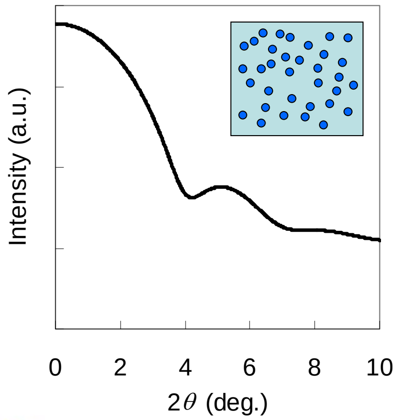


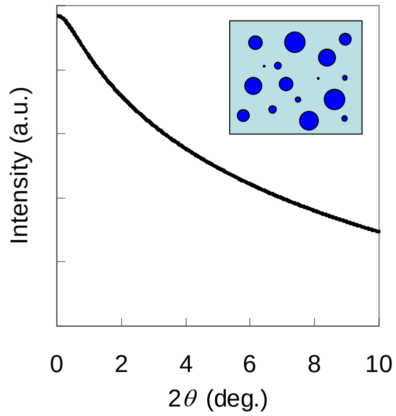
Normalized dispersion : 10 %

Rigaku

Relations of dispersion and profiles

- Dispersion : 10 %
- Dispersion : 90 %





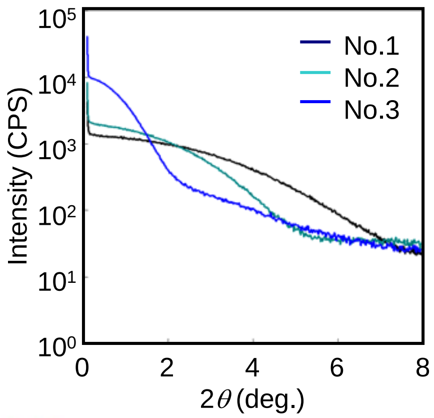
Average diameter : 3 nm

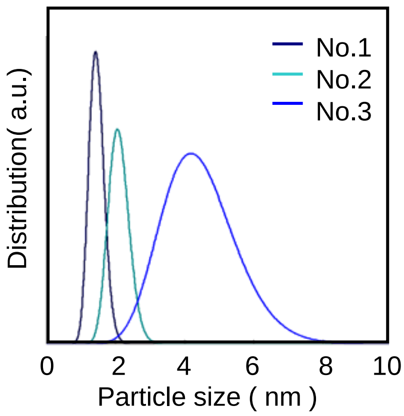
Applications of SAXS

Particle size estimation
(transmission mode)

SAXS profiles and size distribution

- Au nanoparticles



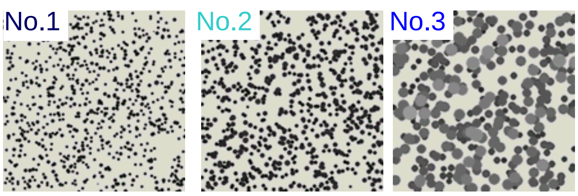


Rigaku

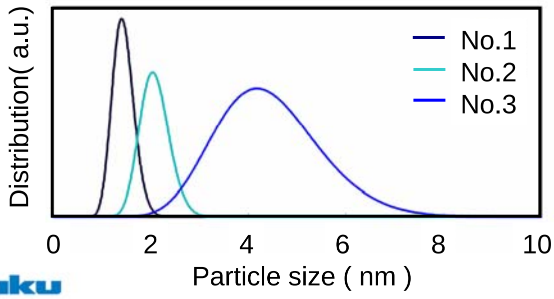
Small angle X-ray scattering
Leading With Innovation

Comparison of TEM image

TEM image



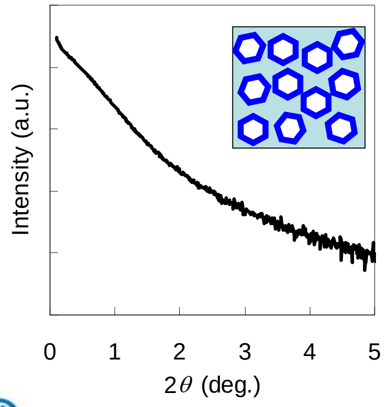
SAXS

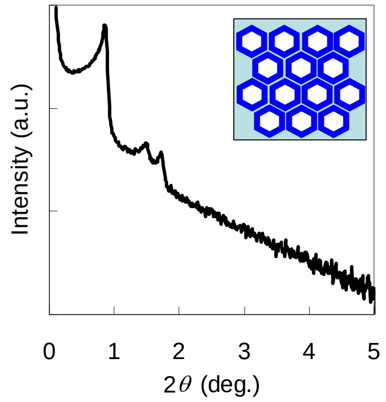


Rigaku

Nano size of porous silica

- Mesoporous silica





Rigaku