Workshop “Metallurgy for Forging Process Design and Tool Life Improvement and XRD Forum”

2020 January 29th: TGGS (KMUTNB), Bangkok

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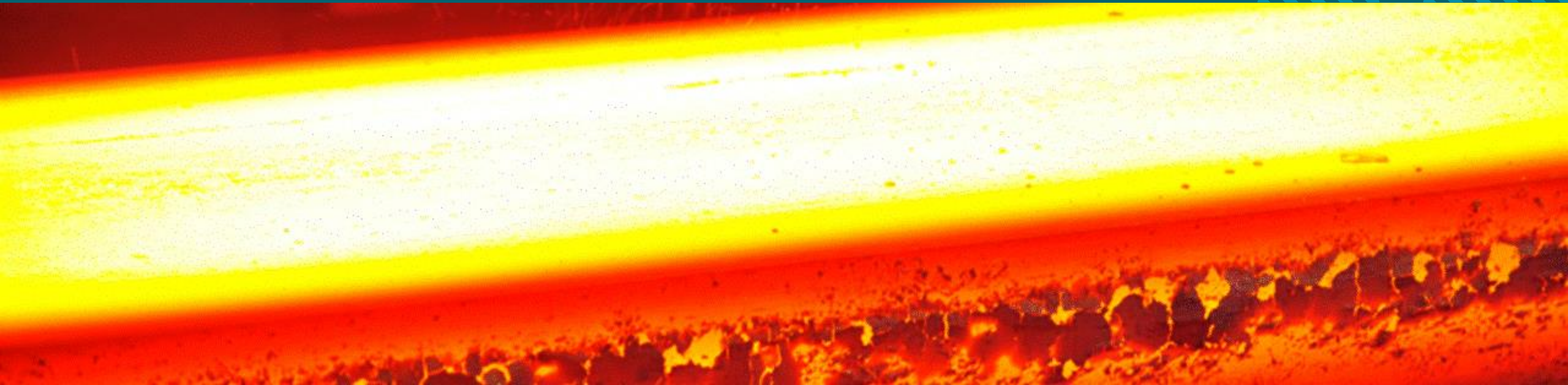
a spectris company

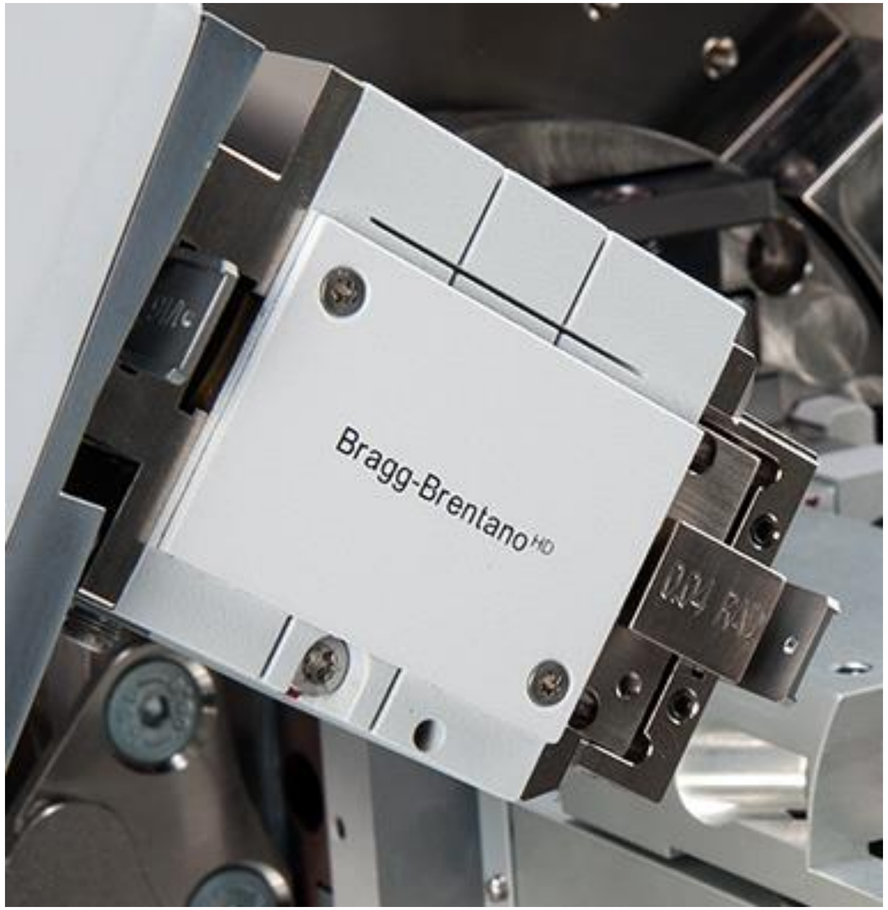
Panalytical technologies to improve signal to noise ratio; investigation of ferrous and non-ferrous alloys by XRD

XRD application specialist: Dr. Matteo Pernechele



Mirrors for Bragg-Brentano geometry

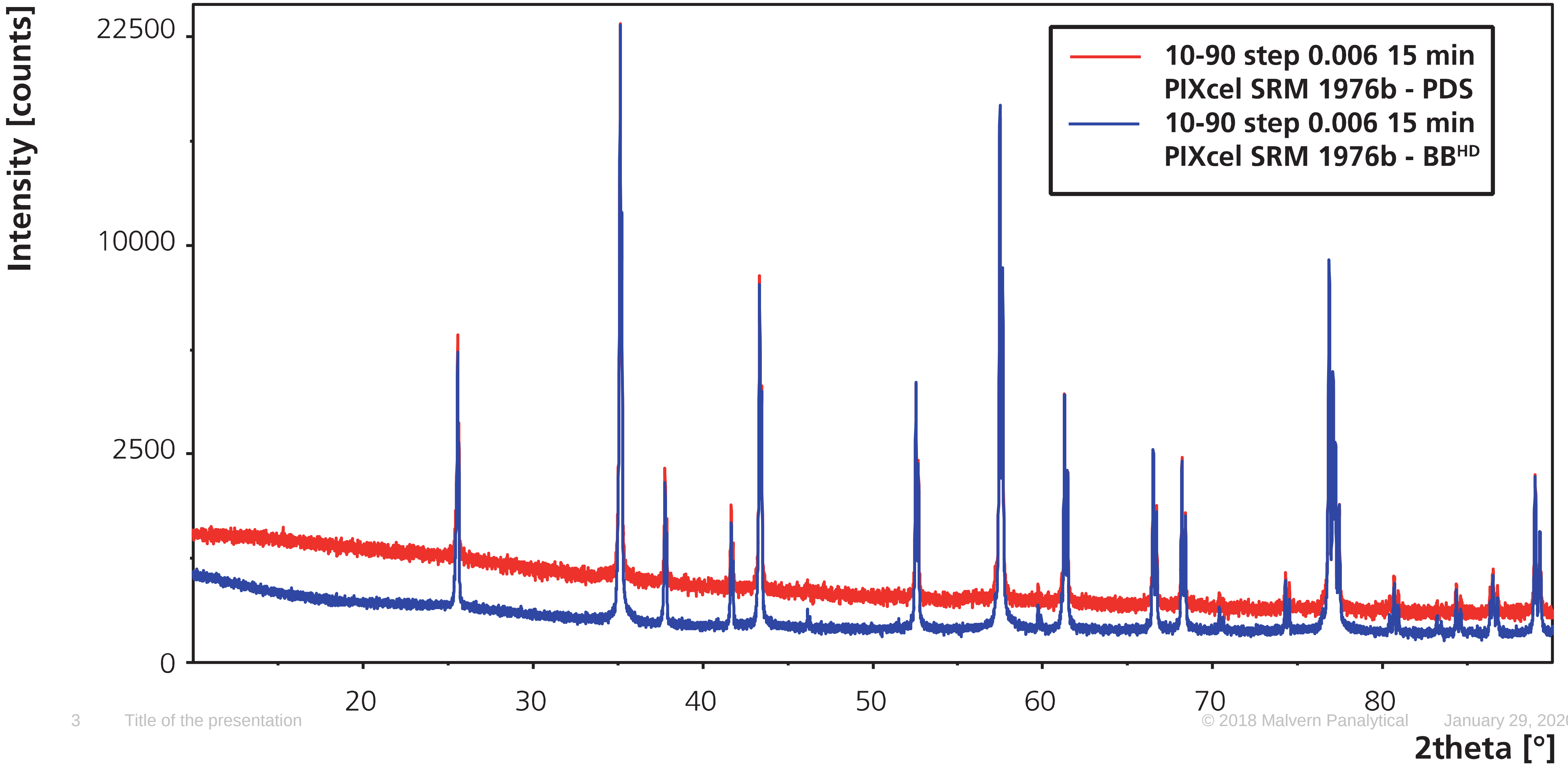
Mirrors provide a divergent beam with high spectral purity

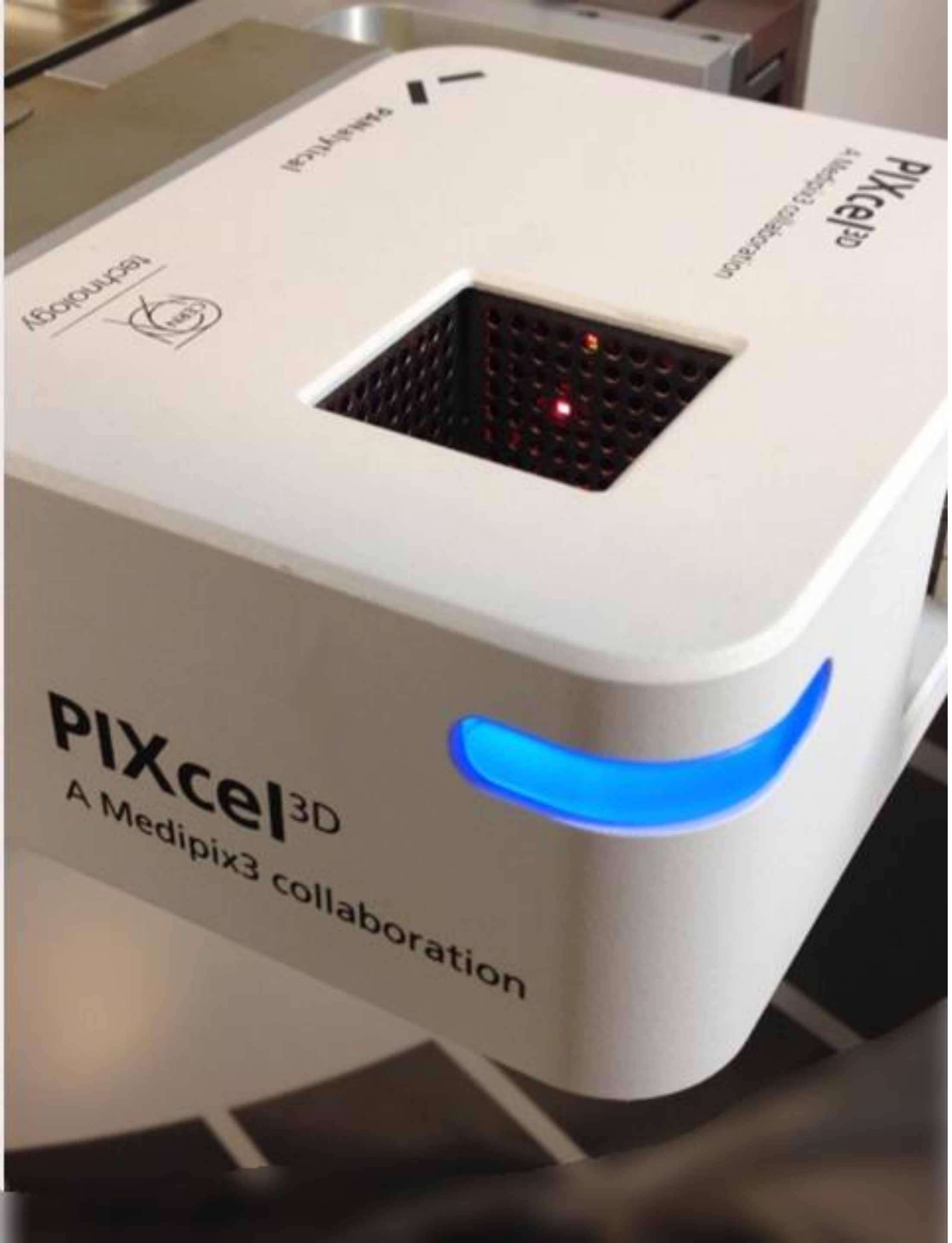


- BBHD (Bragg-Brentano High Definition) is a divergent incident beam module for high-quality Bragg-Brentano data with an energy resolution of < 450 eV (removes K!).
- Available for Cu and Co radiation
- It provides higher intensities than conventional Bragg-Brentano optics (Slit optics + K_β filter)
- It provides a significantly improved, smooth background and hence better detection limits (trace phases, amorphous components)
- Better low-angle performance than slit optics
- Reduced excitation of fluorescence

Mirrors for Bragg-Brentano geometry

Mirrors provide a divergent beam with high spectral purity





$PIXcel^{1D}$ & $PIXcel^{3D}$ Detector

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Empyrean and Aeris systems
Detector is optimized for Cr, Co, Cu radiation
Improved detection efficiency (~15% more)
Increased linearity range (0 – $25*10^6$ cps/column)
0D, 1D, 2D and 3D
55 µm x 55 µm (sharp image)
Point spread function 1 pixel (sharp image, no blur)
High dynamic range ($>10^{10}$)
Two levels energy discrimination
True photon counting
No need for recalibration

Fe bearing ore: Aeris case study

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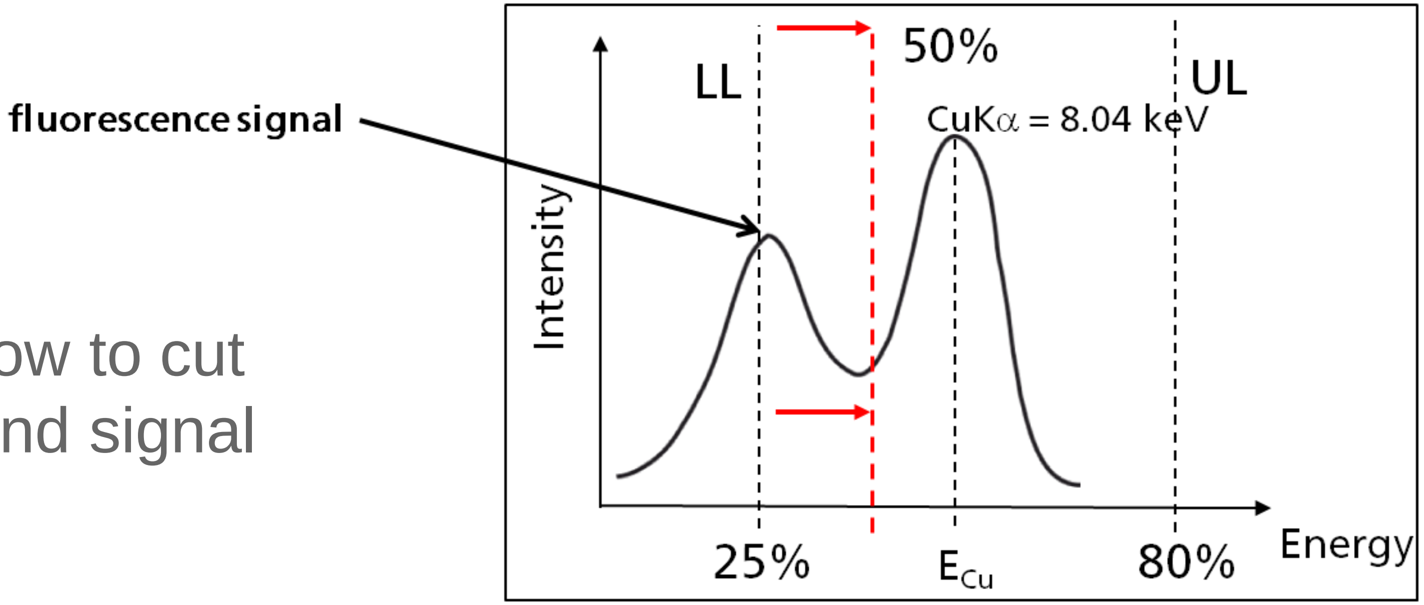
Detector PHD settings

Detectors have the capability to define an energy window for the detected pulses, controlled by the pulse height distribution (PHD) electronics.

The fluorescence-induced background can be reduced by setting the lower level closer to the energy of the used radiation.



Principle of adjusting the PHD window to cut out fluorescence induced background signal

Signal to noise

Aeris Case Study: Iron ore

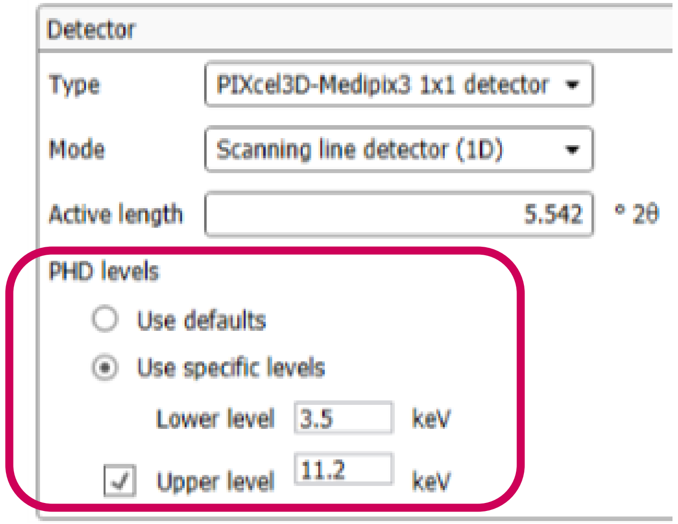
- How good are your XRD data?
- Can we detect small impurities?
- How can we optimize the instrumental setup?

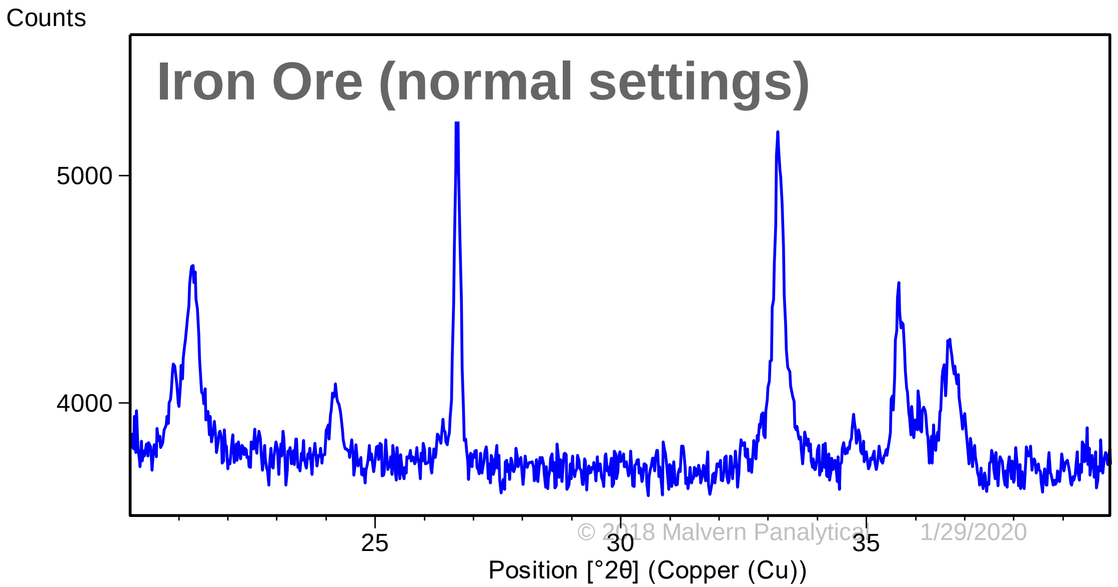
Signal to noise $$\frac{S}{N} = \frac{I - B}{3\sqrt{B}}$$

$where\ I = \text{signal}\ intensity, B = background\ intensity$

50 sec measurement with Aeris (Copper Tube)

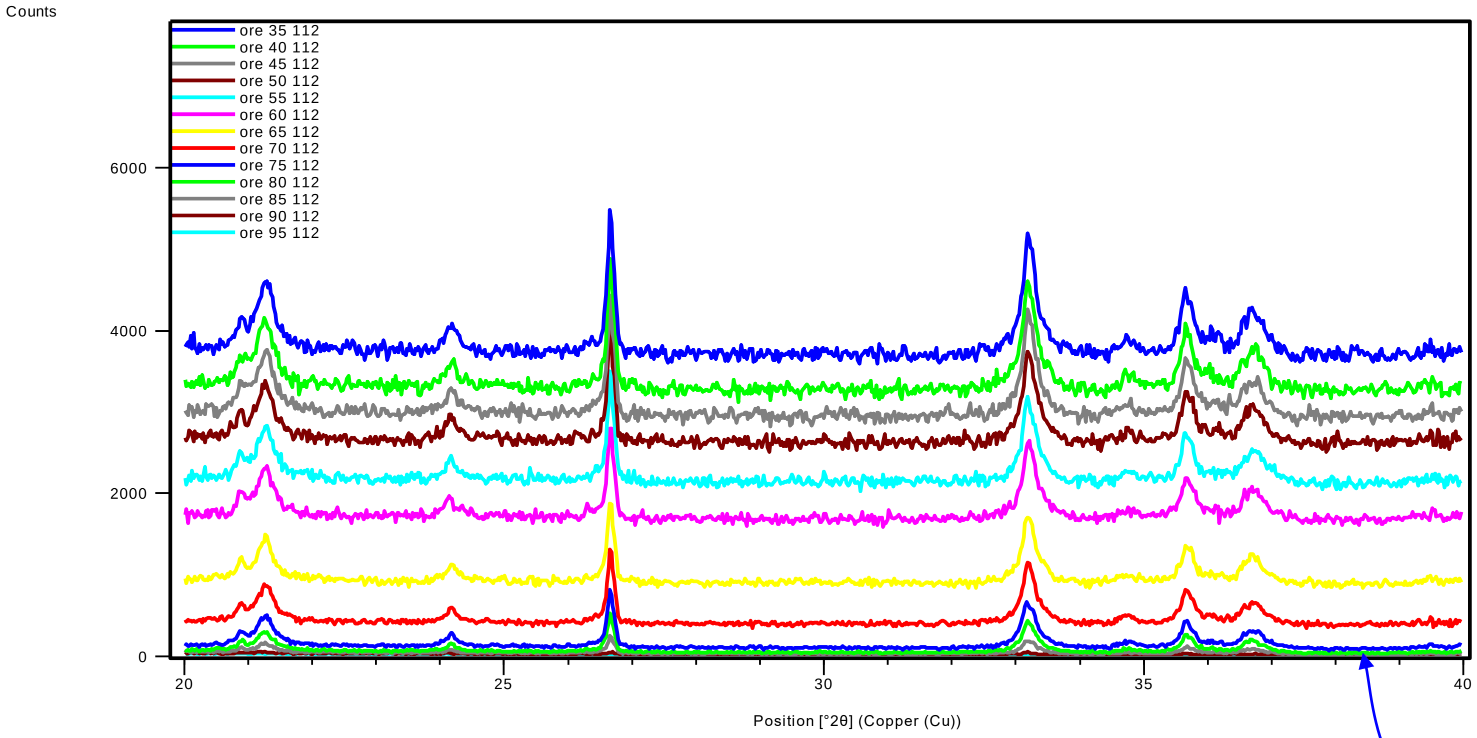
Signal to noise as a function of PIXcel Detector PHD levels

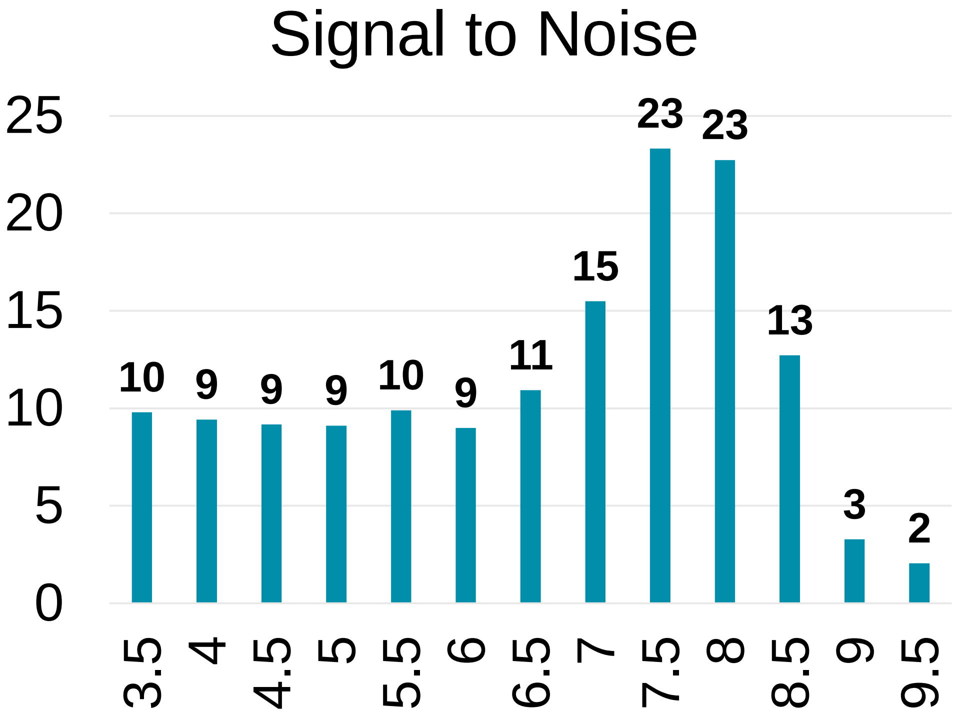




XRD scans with different PHD minimum values

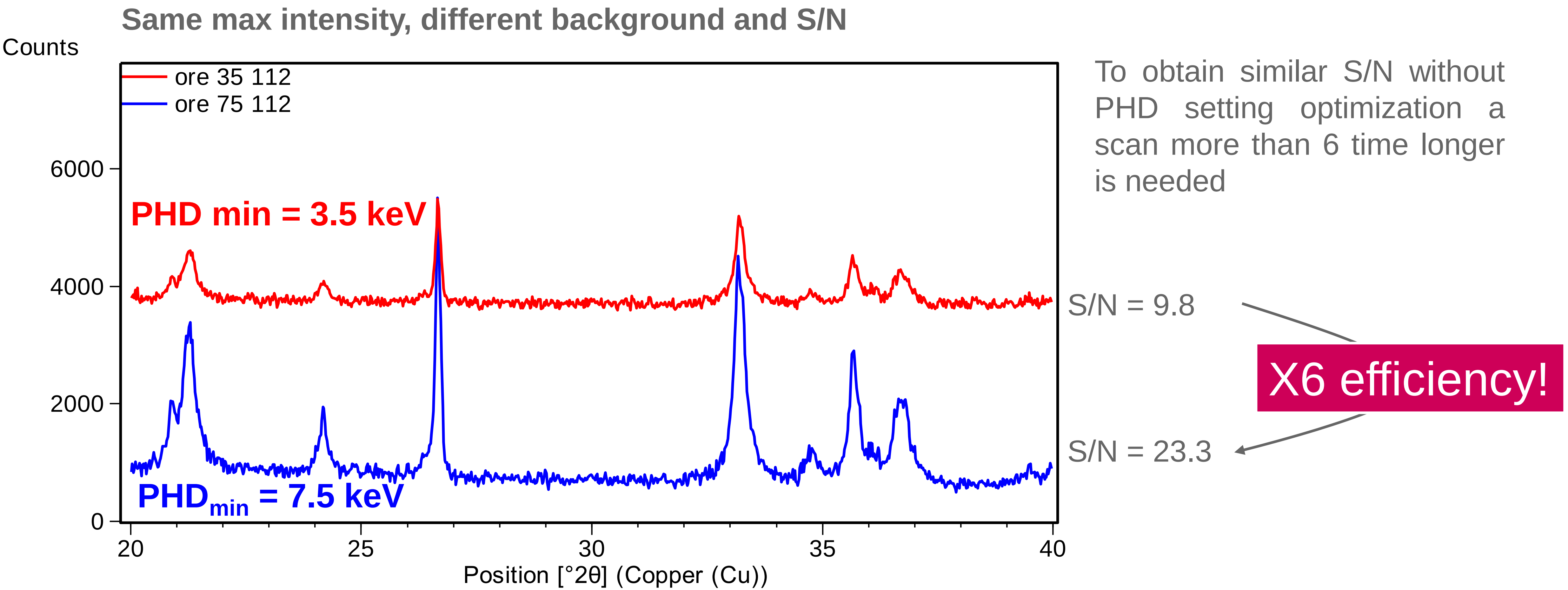
Lower signal and lower background. But S/N?





Standard vs Optimum setup for iron samples

Renormalize scans to show same max intensities



To obtain similar S/N without PHD setting optimization a scan more than 6 time longer is needed

Comparisons with Co radiation

Aeris-Co vs Aeris-Cu

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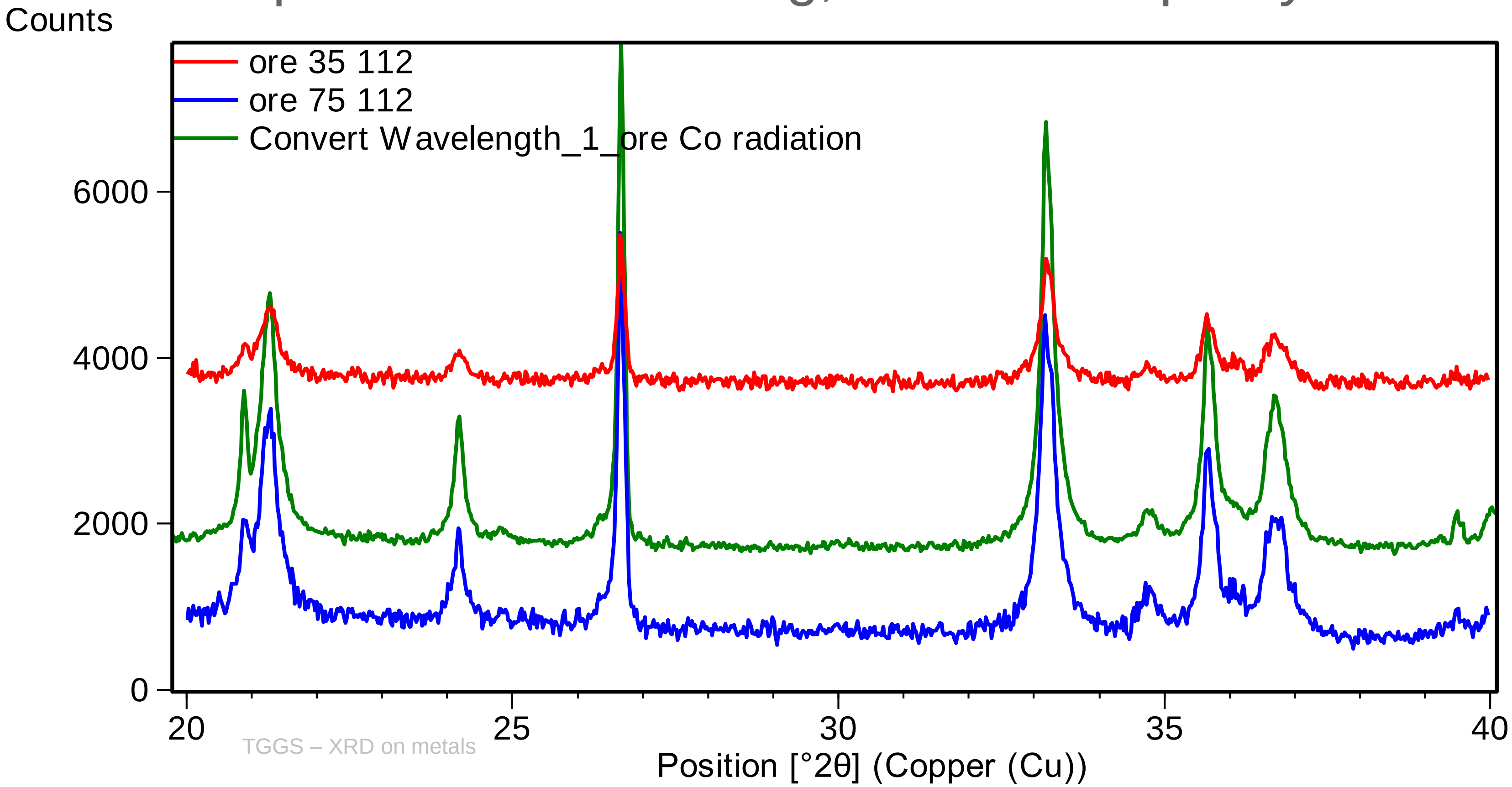
Without the energy discrimination of the PIXcel detector, a measurement of 10 minutes on Aeris-Co would take 4 hours on Aeris-Cu (same S/N).
With optimized PHD setting, same data quality can be obtained in 40 minutes.



Note:
Co radiation probes roughly x5 more volume of Cu radiation.

S/N = 9.8

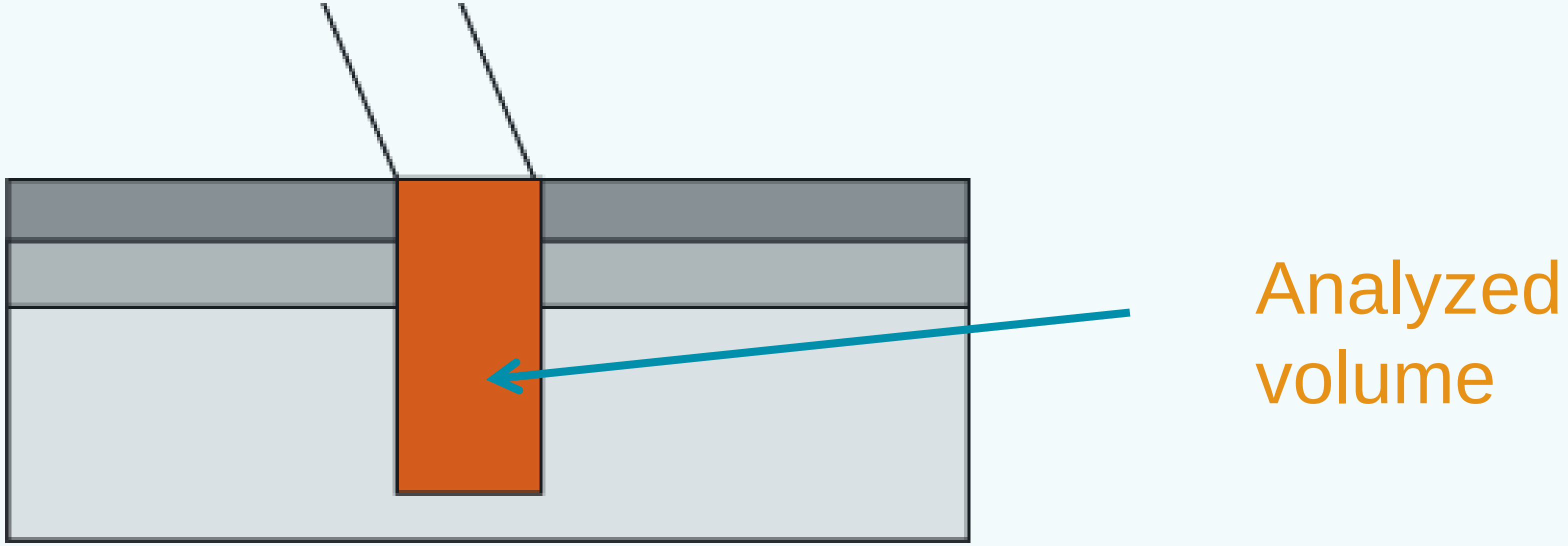
S/N= 48.4

S/N = 23.3

x 4

x 6

Penetration depth: intrinsic limit of Cu tube with steel



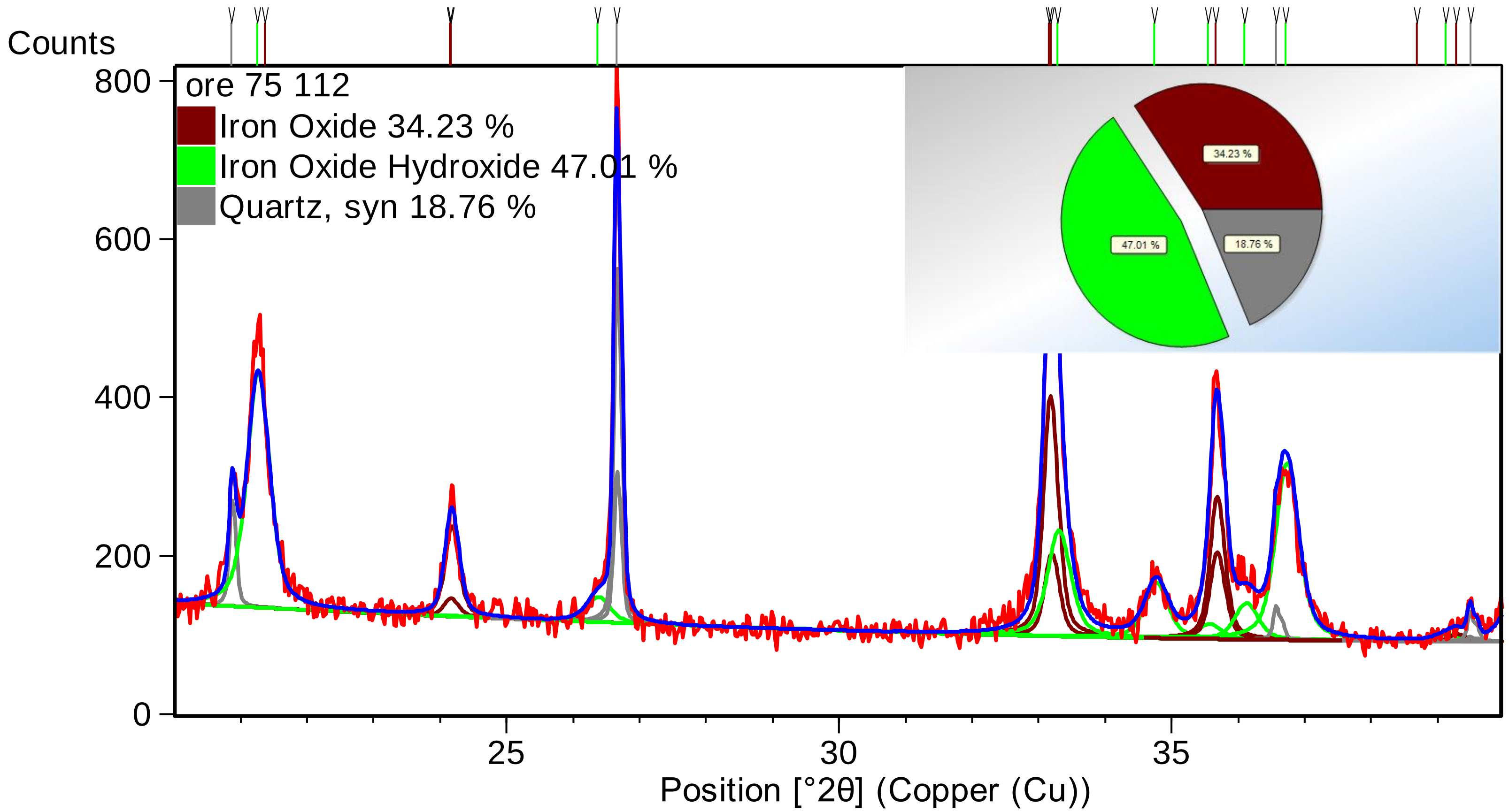
Sampling depth in steel			
X-ray source	{hkl}	°2θ	sampling depth [μm]
Co	310	161	48.5
Cu	222	137	8.8

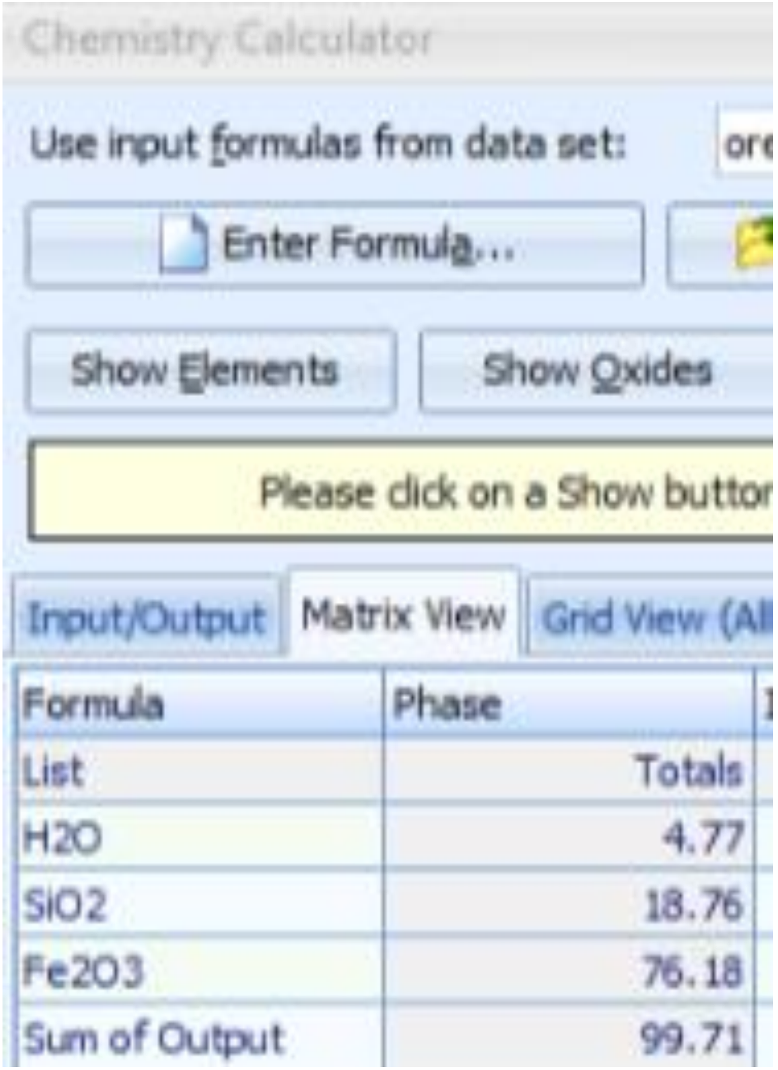
X5

Rietveld Refinement using HighScore Plus

Goethite, Hematite, Quartz.

75 wt% of Fe_2O_3





Conclusion

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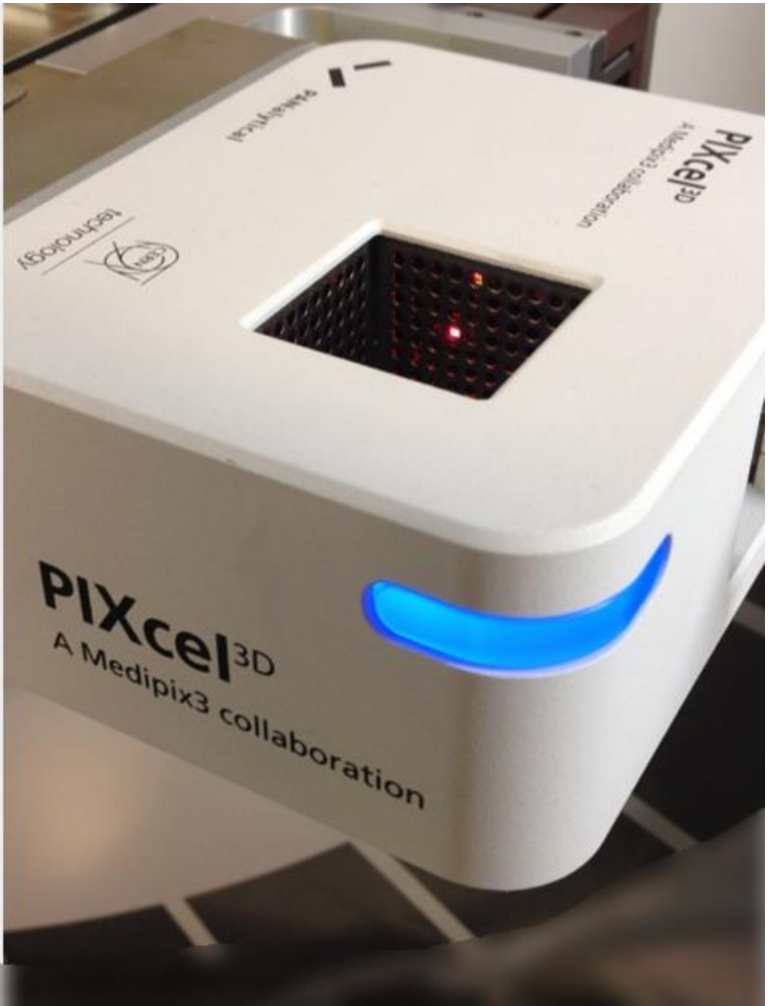

- Cobalt tube is preferable to Copper tube for analyzing iron ore and steel (Co is 2400% better)
- Panalytical PIXcel detector can filter out fluorescence radiation
- PIXcel help bridging the gap between Copper and Cobalt tube (Co is “only” 400% better)
- PIXcel is available for older model (Xpert powder) and newer models (Aeris, Empyrean)

Complete XRD analysis of steel

with Empyrean (Co tube)

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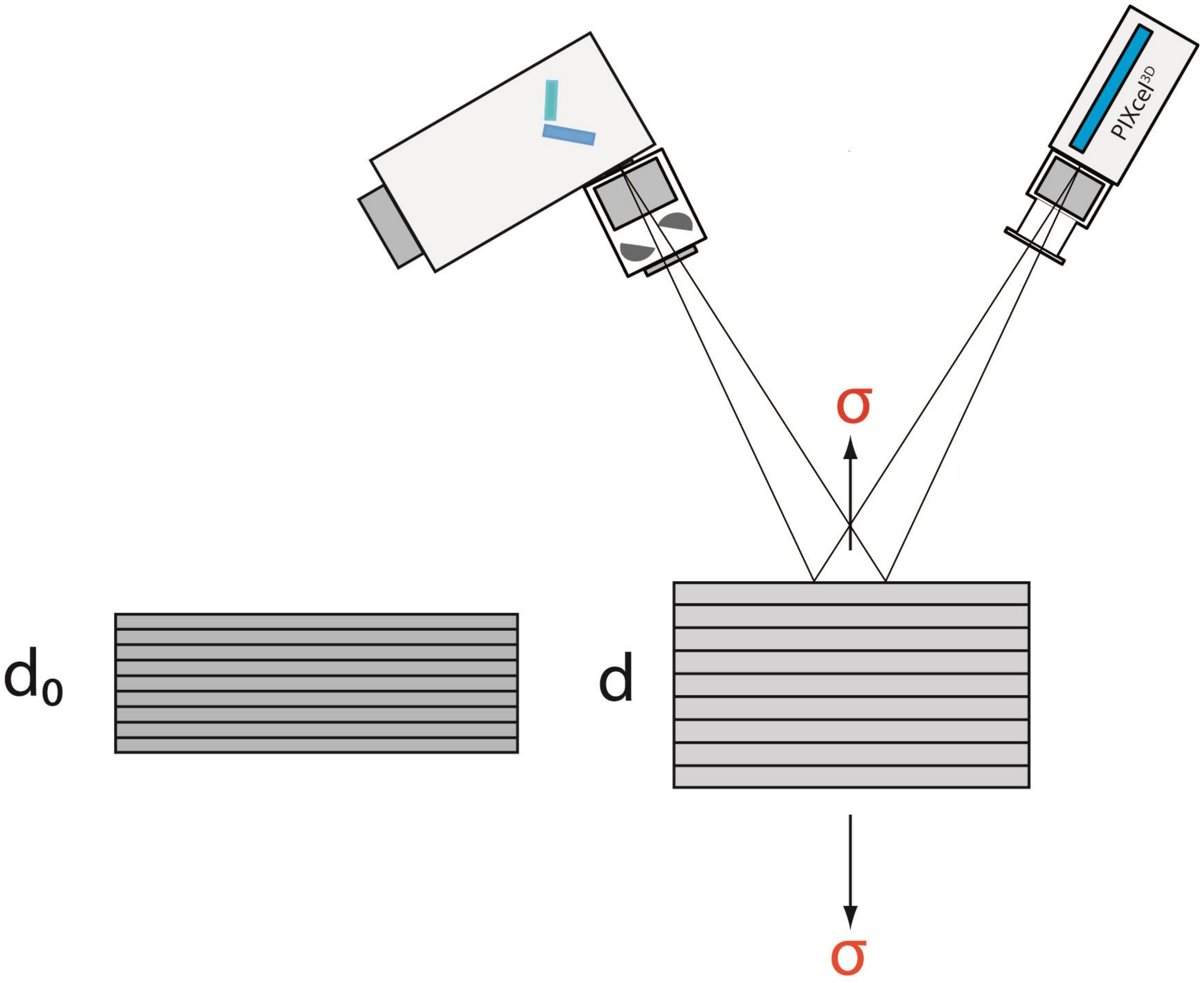
Select proper instrument for the task - Empyrean

Multi-purpose
instrument

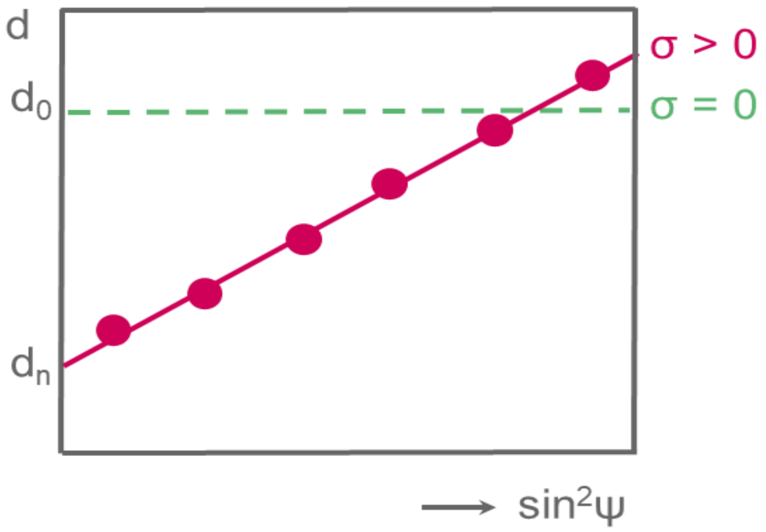
- Powder XRD
- Basic SAXS
- Omega stress
- Omega texture
- GIXRD
- Reflectometry

- *in situ* XRD
- Advanced SAXS
- Comp. tomography
- Advanced thin film metrology
- PDF
- Hard radiation
- Advanced stress/texture

Peak position → residual stress



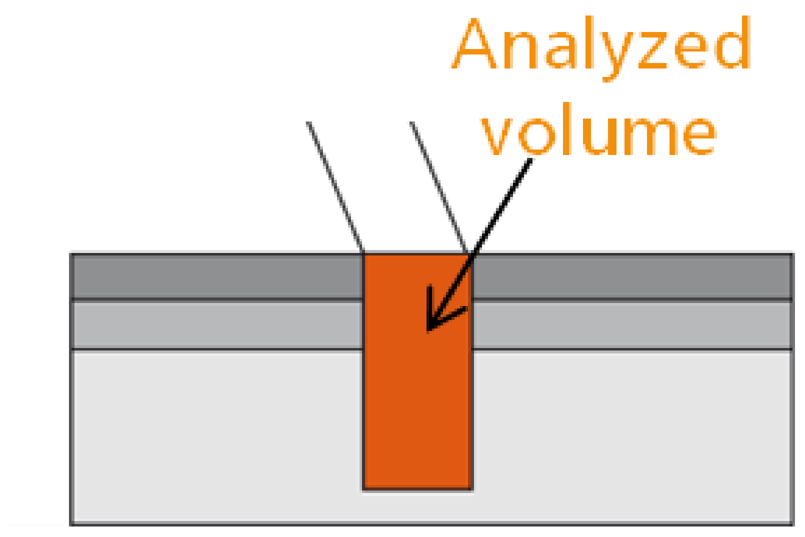
$$\varepsilon = \frac{d - d_0}{d_0} = \frac{\Delta d}{d_0} \longrightarrow \sigma = E.\varepsilon$$

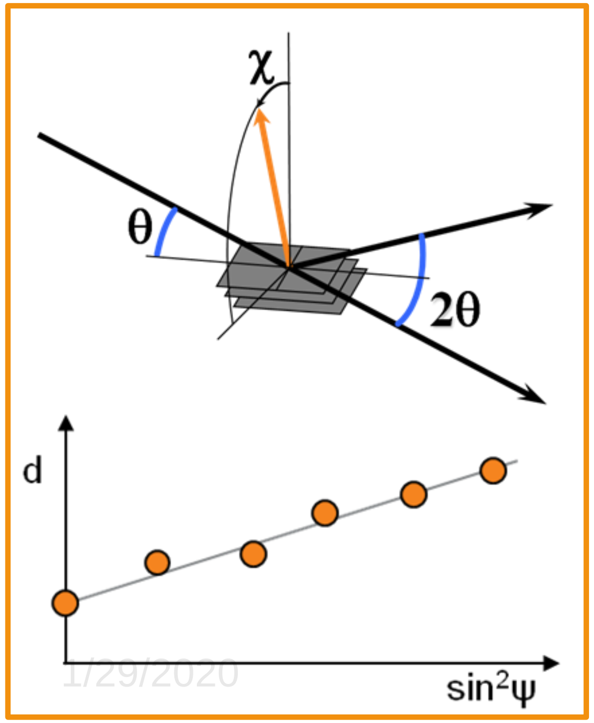


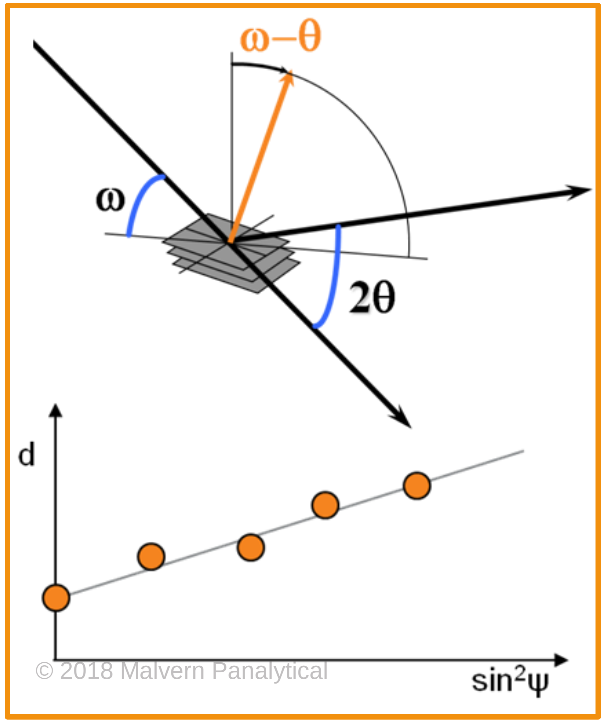
How can it be measured?

Single {hkl} methods (ω-stress, χ-stress)

- the position of a single reflection (usually > 100 °2θ) is measured at different ψ & φ.
- **χ-stress :** sample is tilted using a cradle
- **ω-stress** : the goniometer is tilted with respect to the horizontal sample
- positive and/or negative tilts (both directions only required for shear stresses)

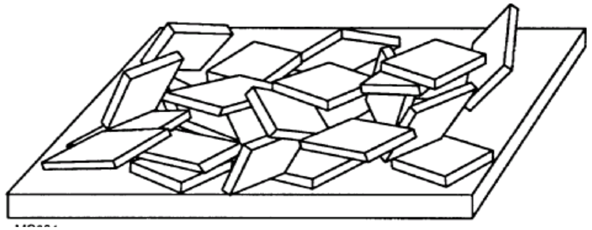




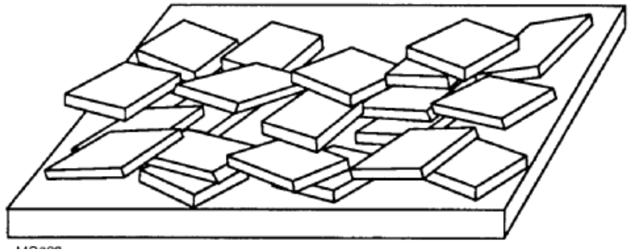


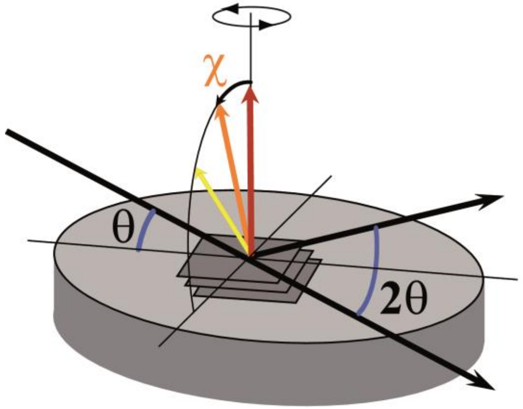
Peak intensity → preferred orientation/texture

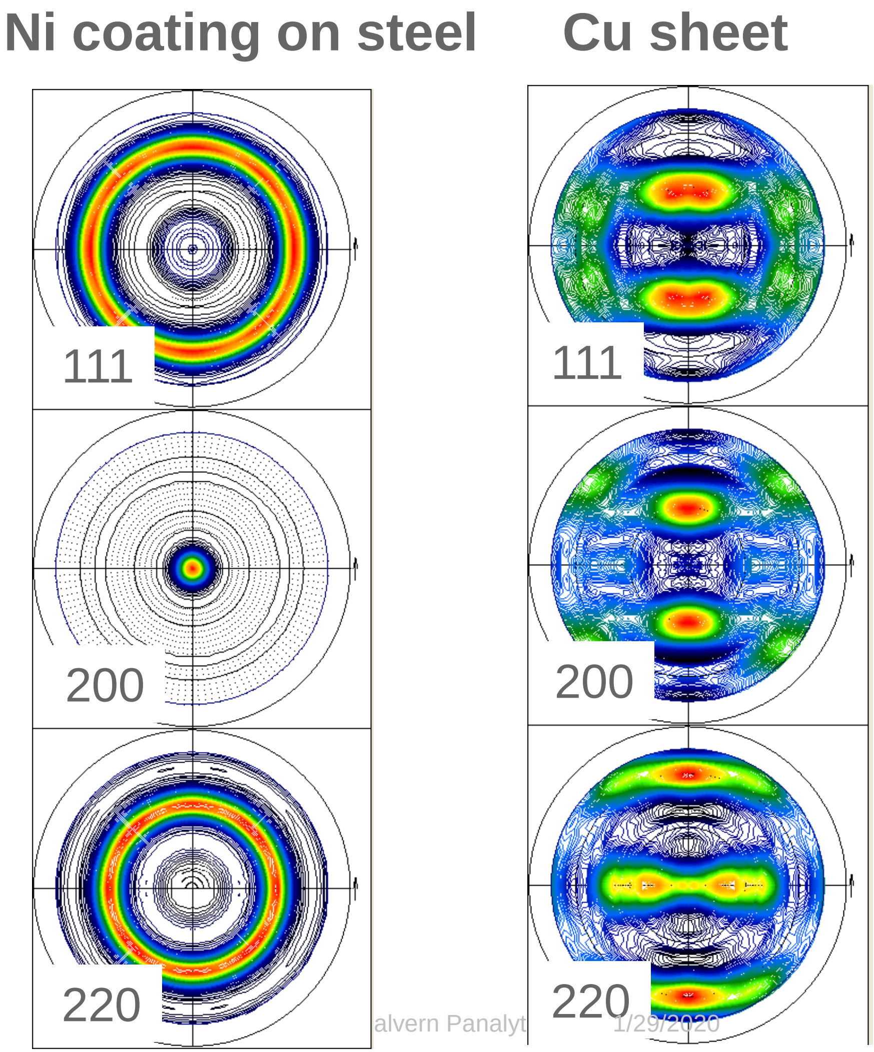
Random orientation



Preferred orientation



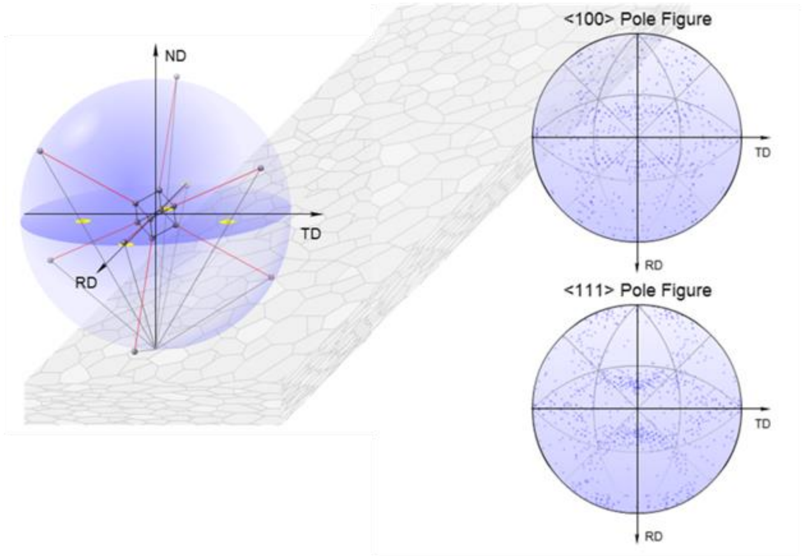




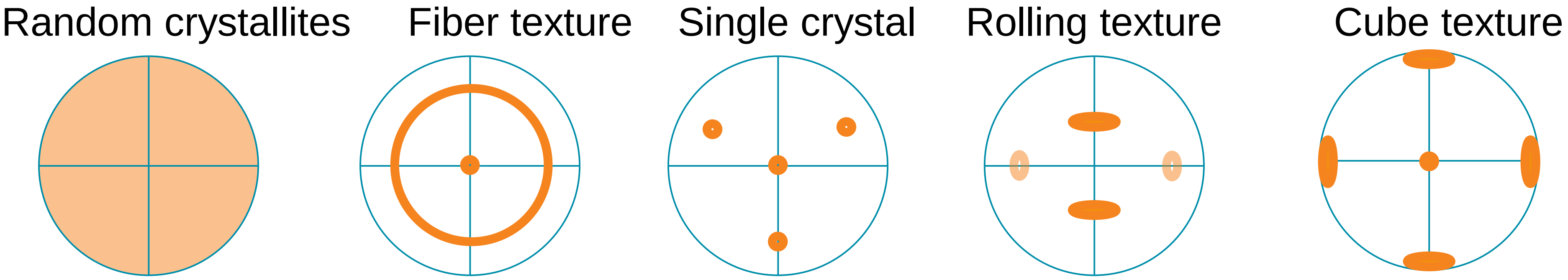
Texture – General information

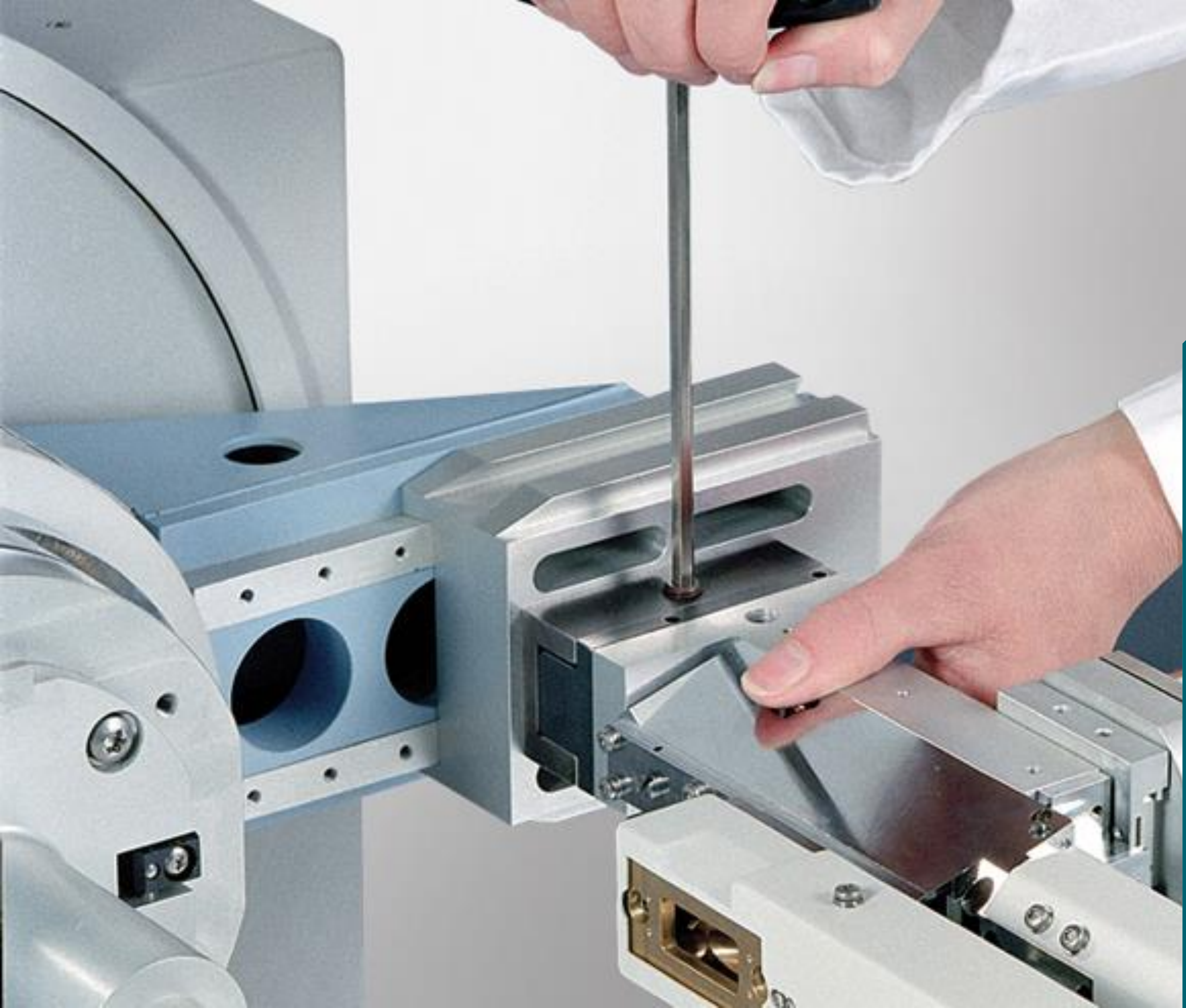
Depending on the texture in the material the sum of all crystallites will produce specific features characteristic for a certain type of texture

A good texture analysis is only possible if sufficient particle statistics are present (spot size >> average grain size)



- Examples of typical texture types and schematics of characteristic pole figures





How difficult are XRD advance techniques?

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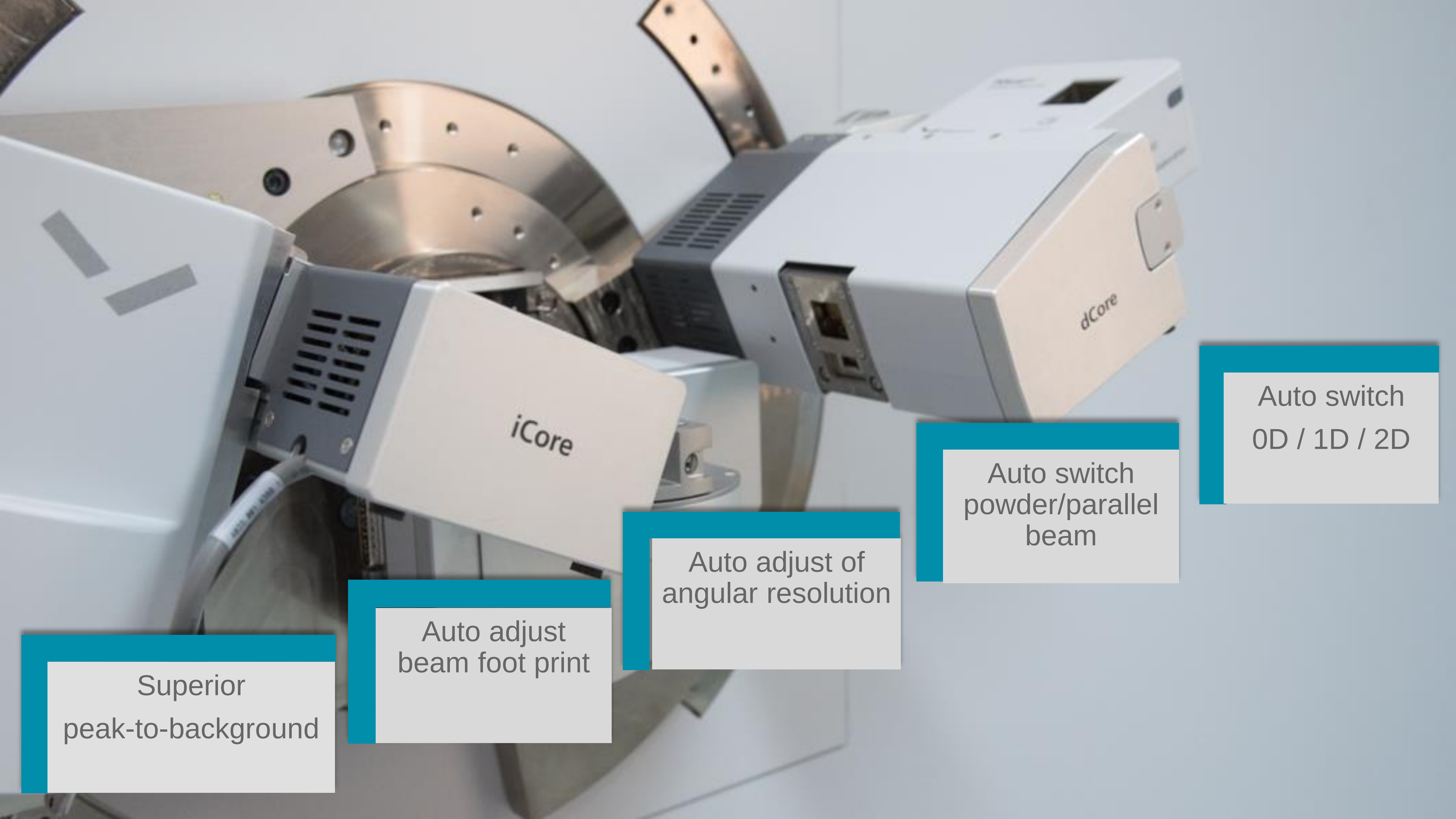


Superior
peak-to-background

Auto adjust
beam foot print

Auto adjust of
angular resolution

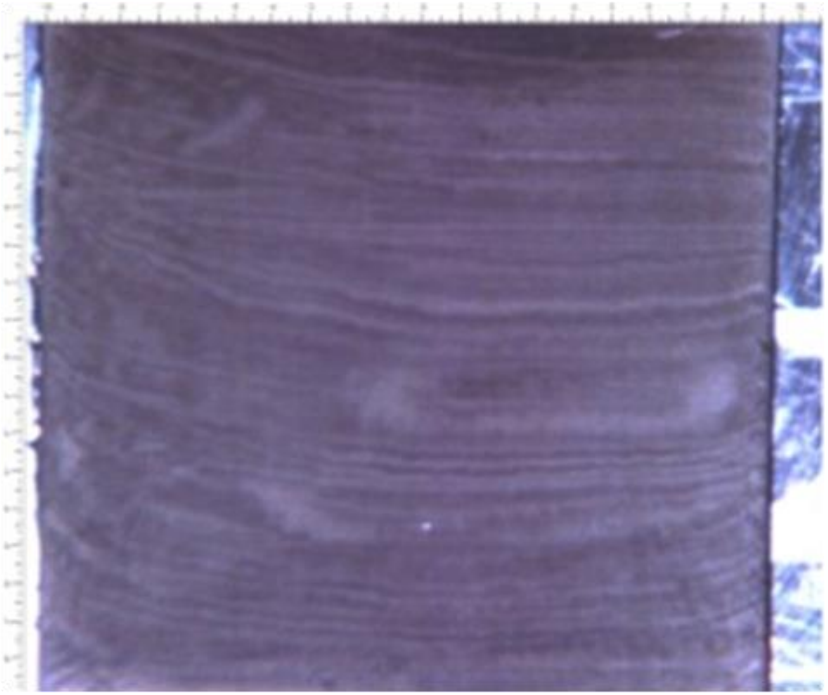
Auto switch
powder/parallel
beam

Auto switch
0D / 1D / 2D

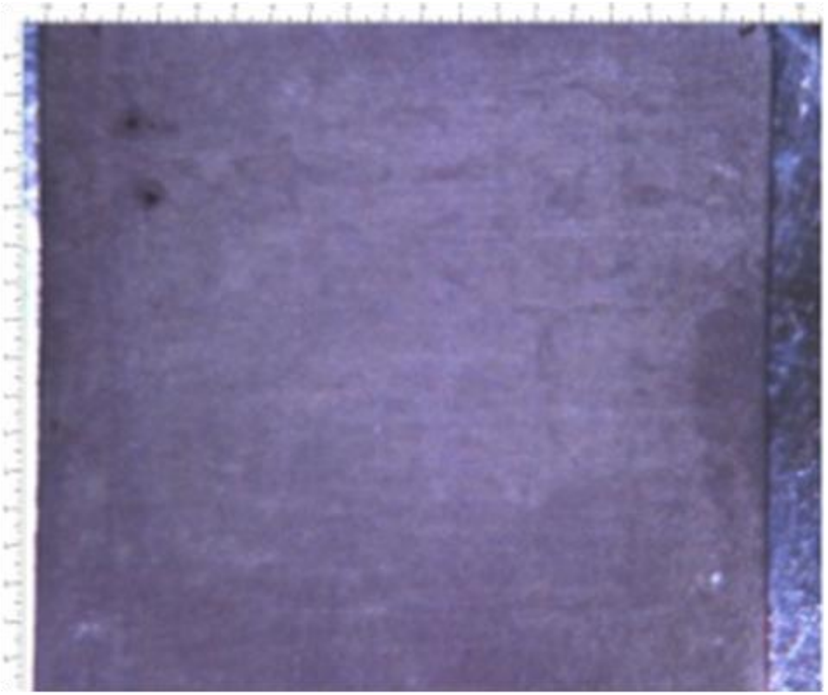
2 Steel Samples: before and after tempering

XRD Analyses using Empyrean:

- phase composition (retained austenite), crystallinity, texture and residual stress.

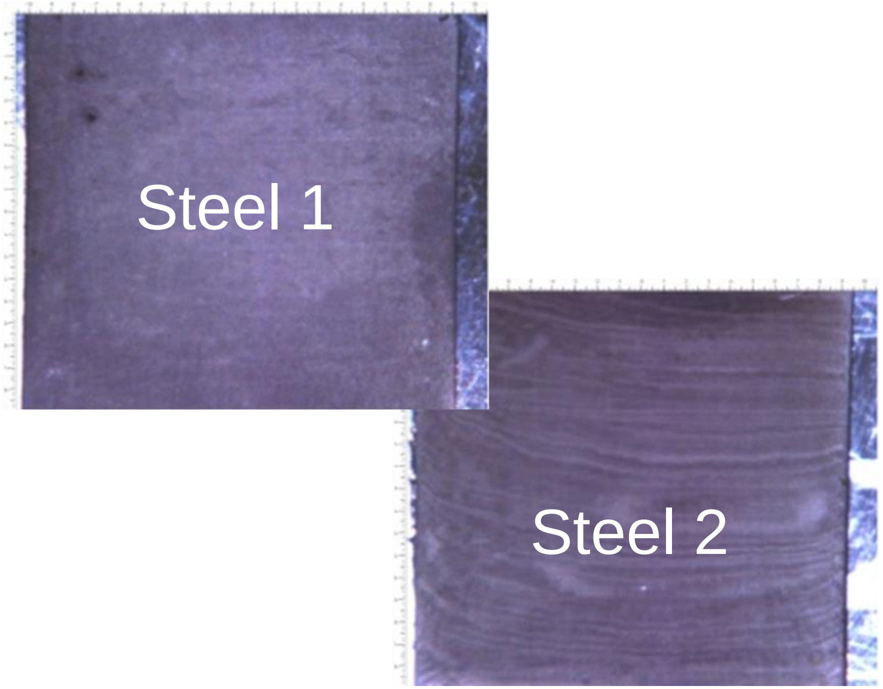


Sample-1



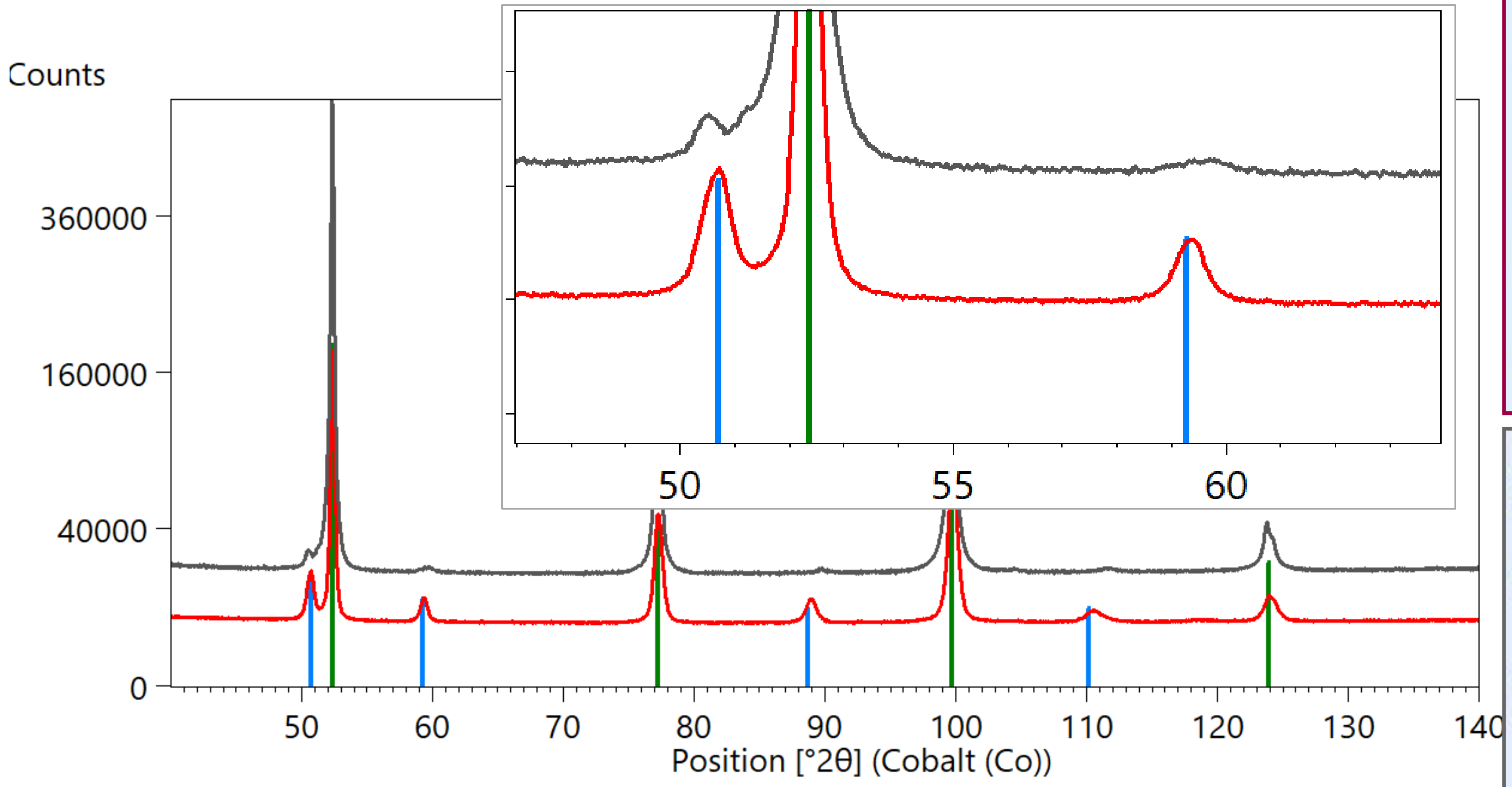
Sample-2

What can we learn using XRD?



- Phase composition
- Crystallite size
- Residual stress
- Texture

Phase composition (peak position & intensity)



Austenite (Fe, FCC)
Ferrite/Martensite (Fe, BCC)

12 min per sample

Sample -1

Retained Austenite Volume %: 10.1

No of Austenite peaks : 5
No of Ferrite peaks : 4

----------- WARNINGS -----------
Texture Austenite (>10%) : Yes
Texture Ferrite (>10%) : No
Low Austenite (<1%) : No

Compliance with ASTM E975 norm: No

Sample -2

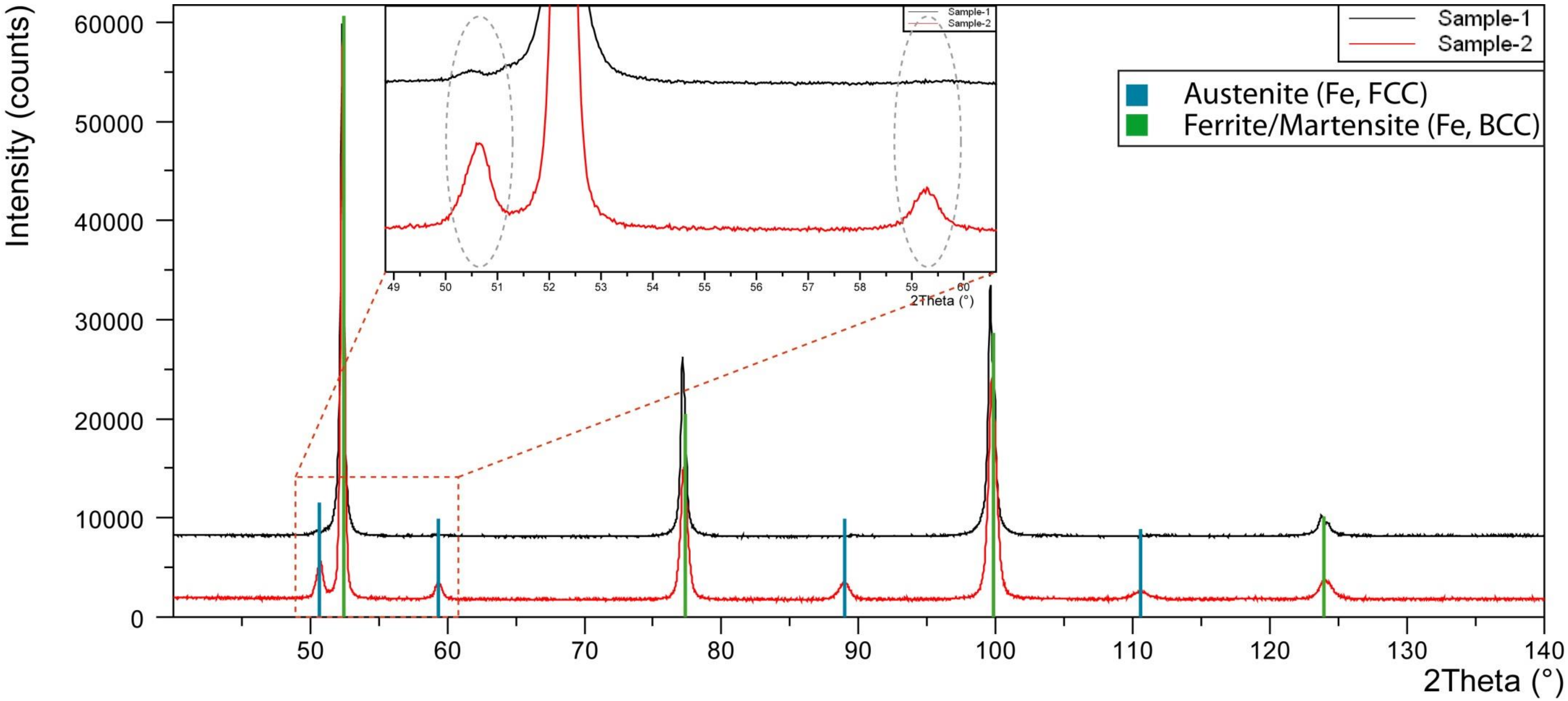
Retained Austenite Volume %: 0.7

No of Austenite peaks : 5
No of Ferrite peaks : 4

----------- WARNINGS -----------
Texture Austenite (>10%) : Yes
Texture Ferrite (>10%) : No
Low Austenite (<1%) : Yes

Compliance with ASTM E975 norm: No

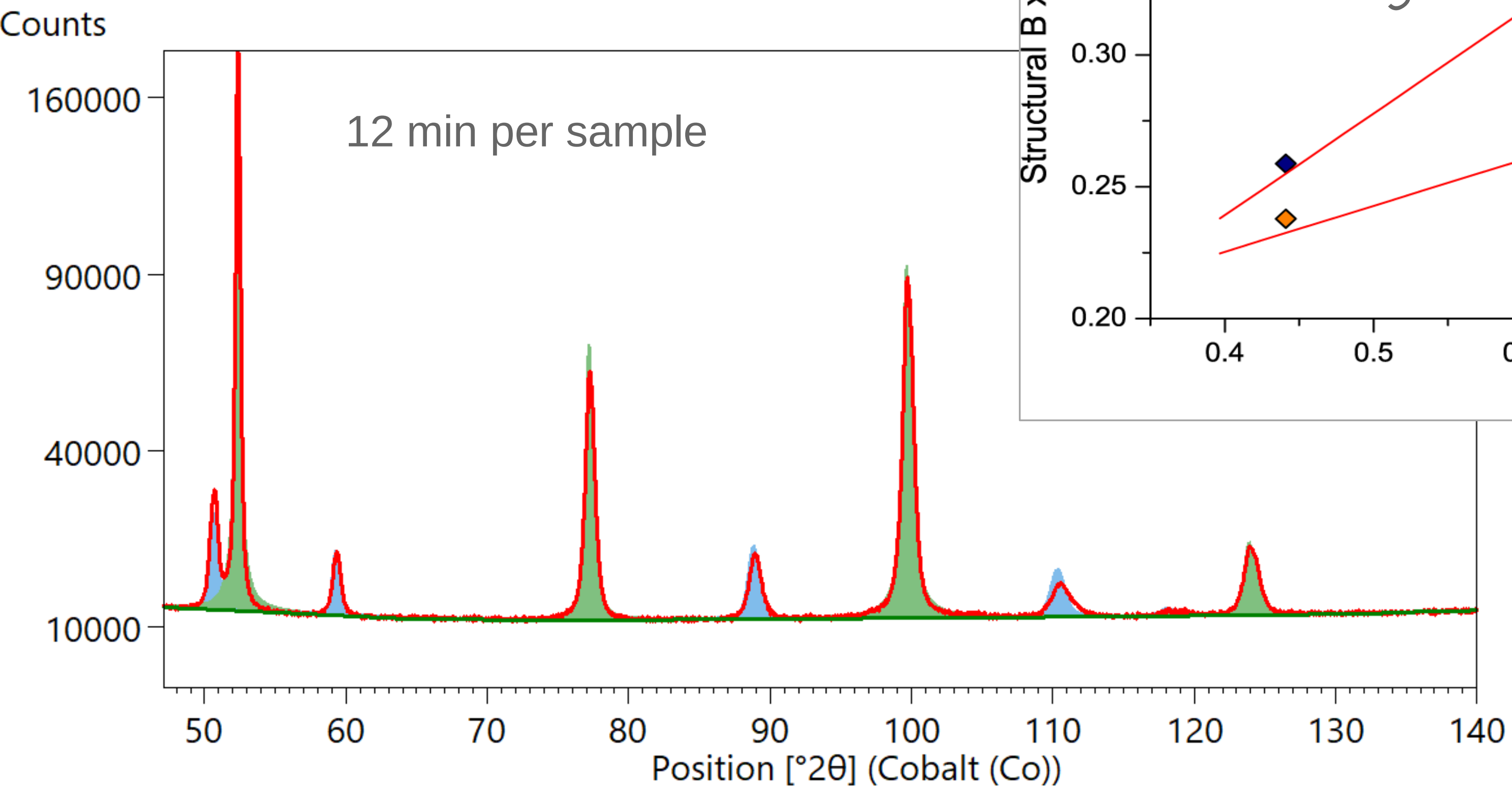
Results – Phase ID

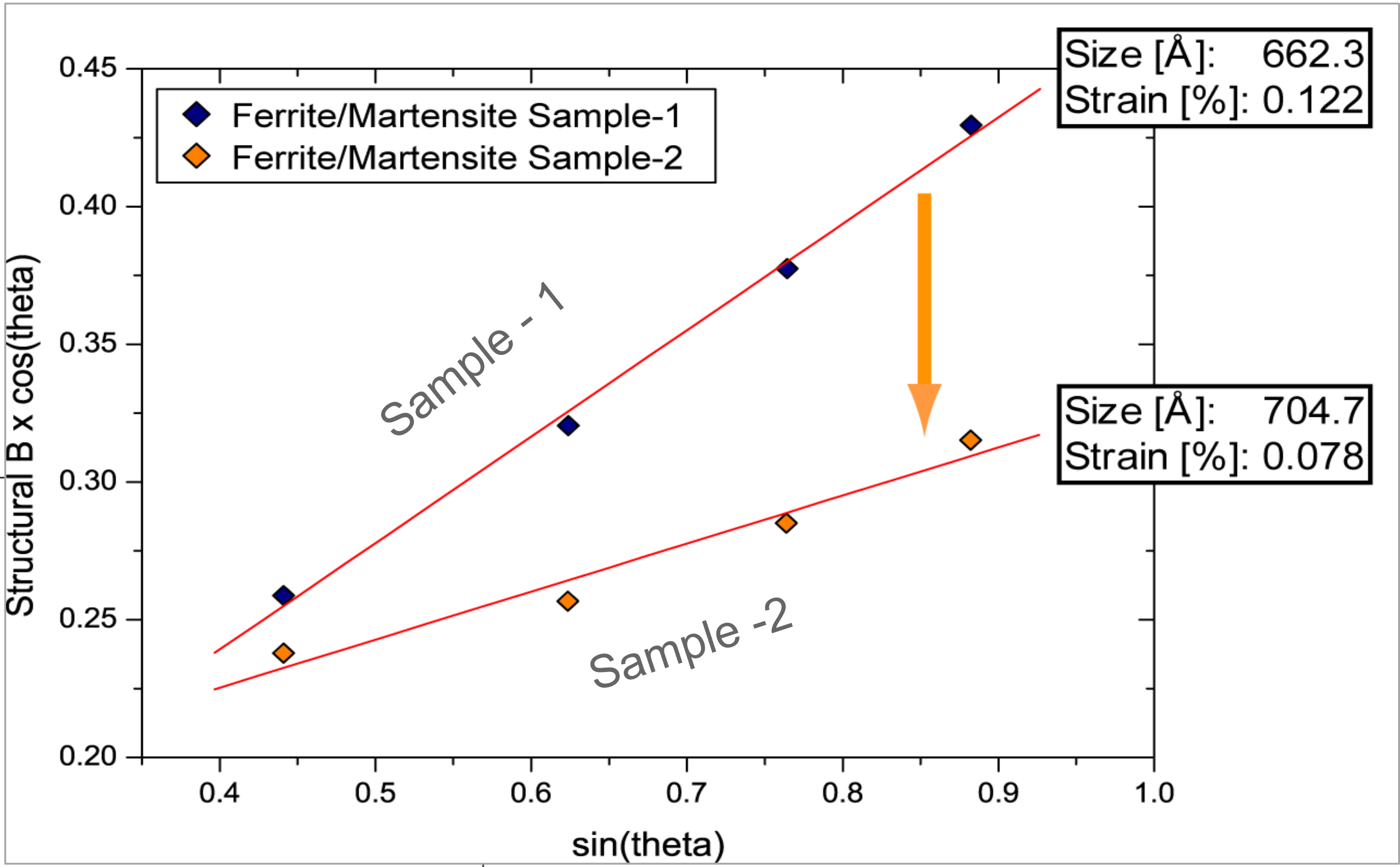


Sample-2 showing a significantly higher Austenite signal than Sample-1

Crystallite size and strain

From peak broadening



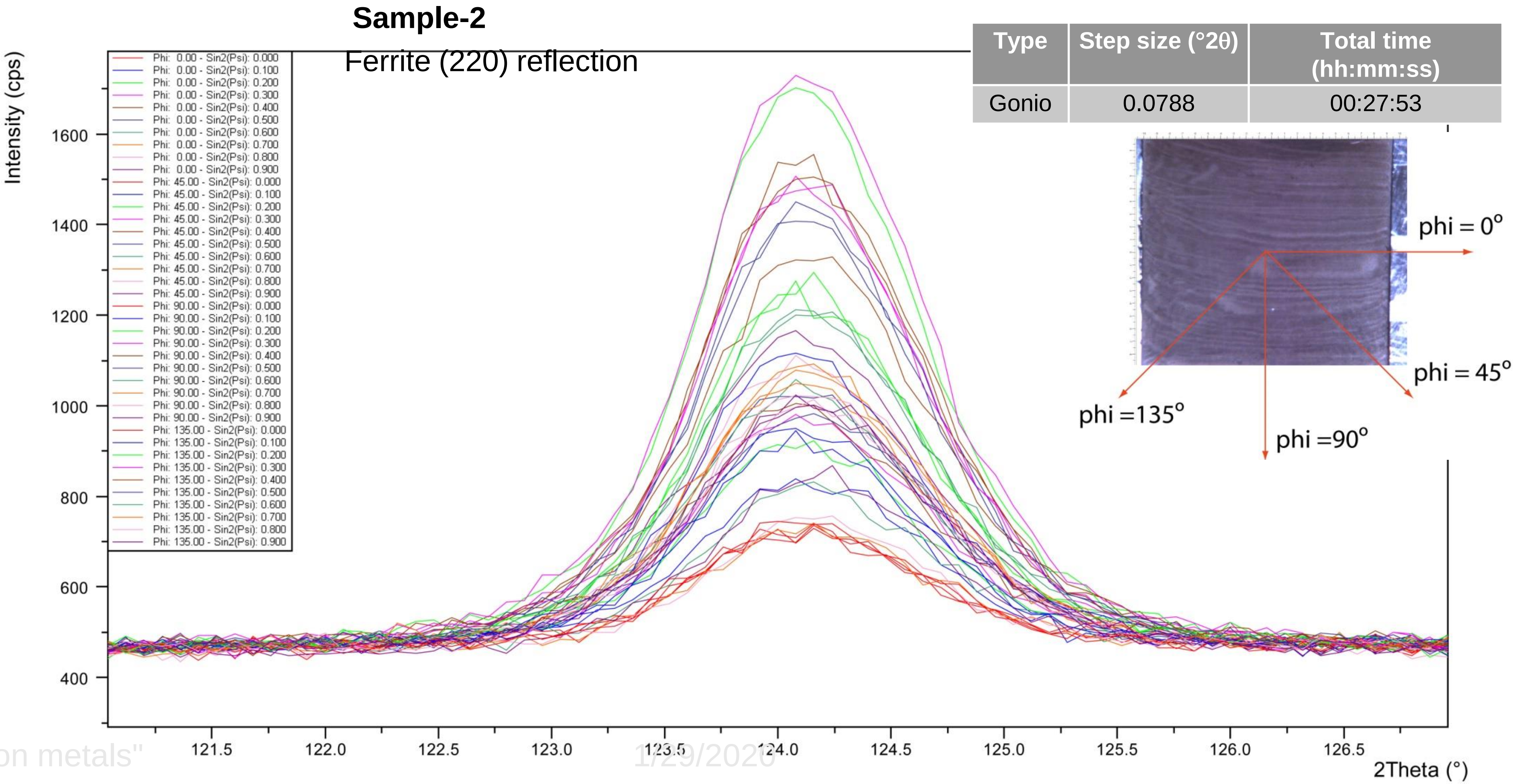


Results – Residual stress

Full tensor residual stress measurements classical χ-stress approach.

Hence the sample was tilted in χ and measured in all sample 4 directions.

Type	Step size (°2θ)	Total time (hh:mm:ss)
Gonio	0.0788	00:27:53



Residual stress (peak position at different tilts)

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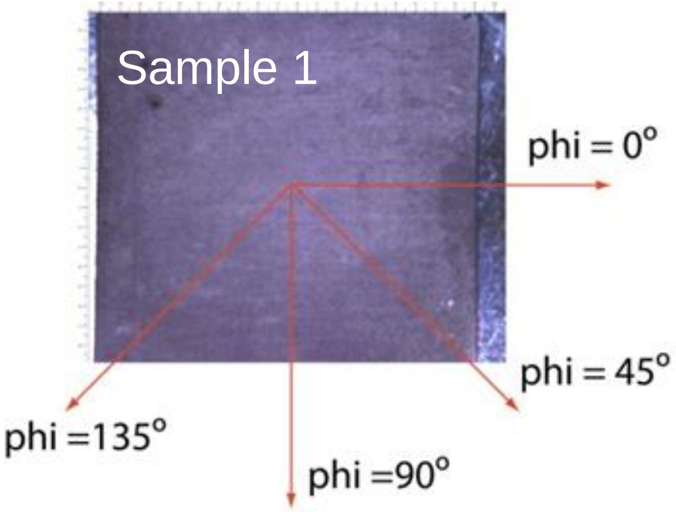
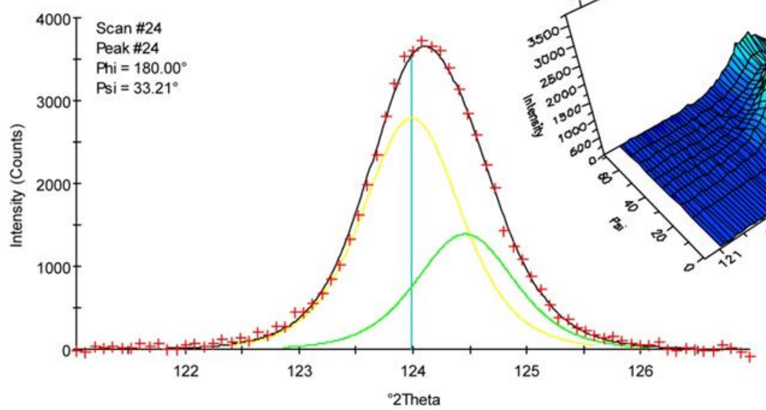
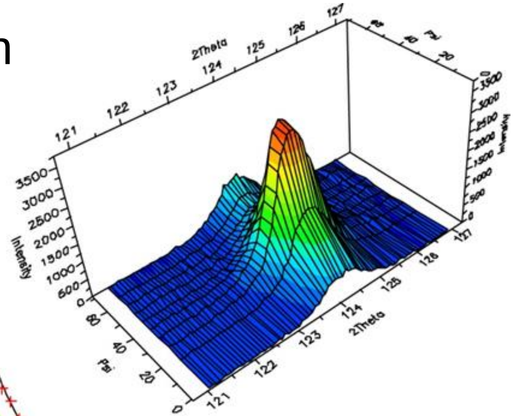
Ferrite (220) reflection



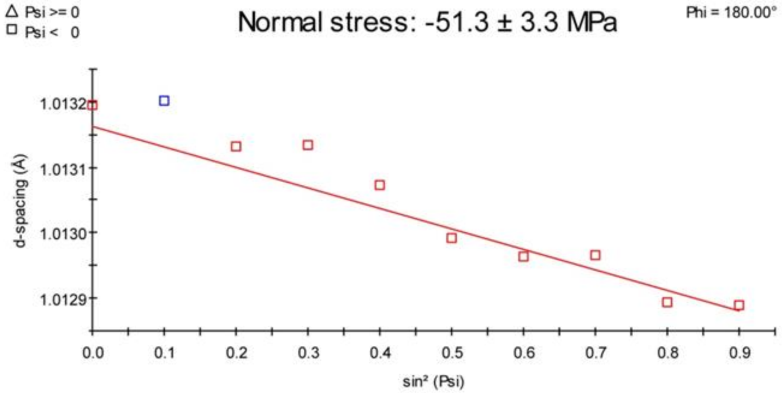
σ_{11} = -51 MPa



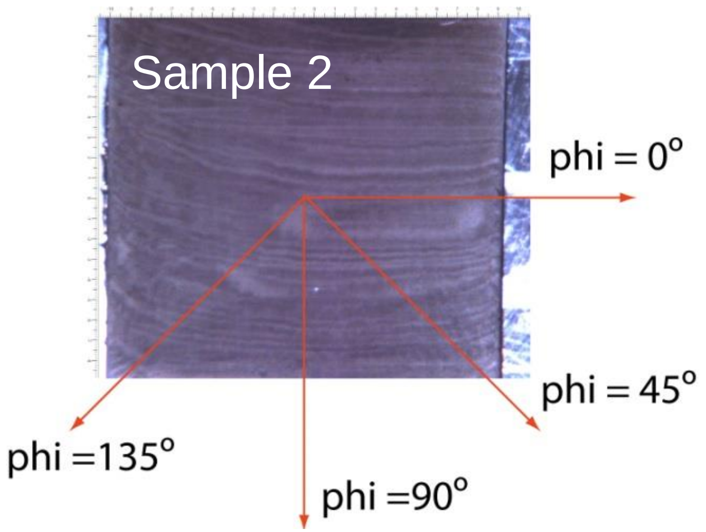


σ_{22} = 0 MPa

$$\sigma_{ij} = \begin{bmatrix} -51 & -5 & 0 \\ -5 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$



Residual stress (peak position at different tilts)

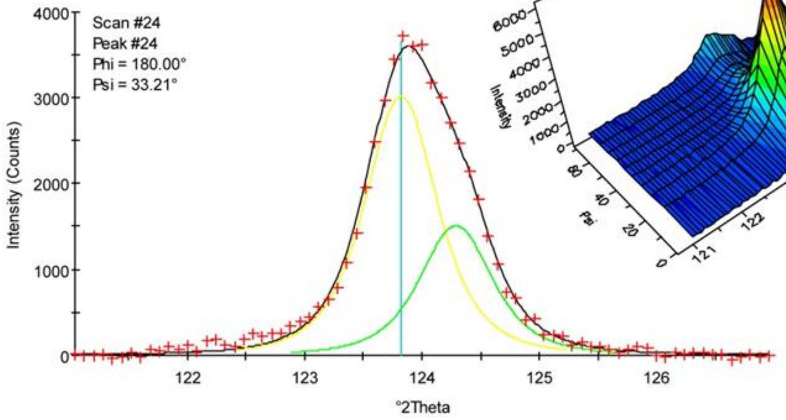


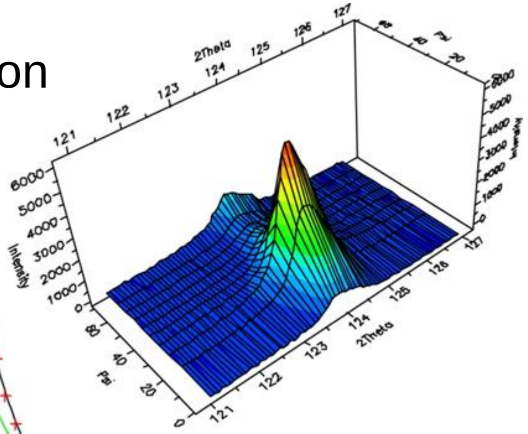
σ_{11} = -34 MPa

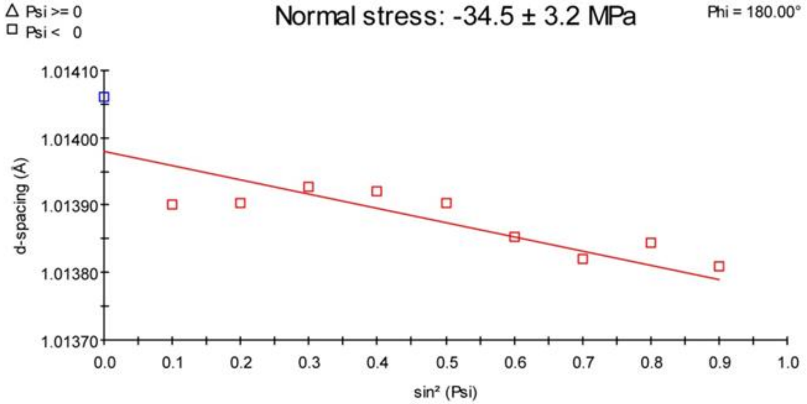
σ_{22} = 0 MPa

$$\sigma_{ij} = \begin{bmatrix} -34 & 13 & 0 \\ 13 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

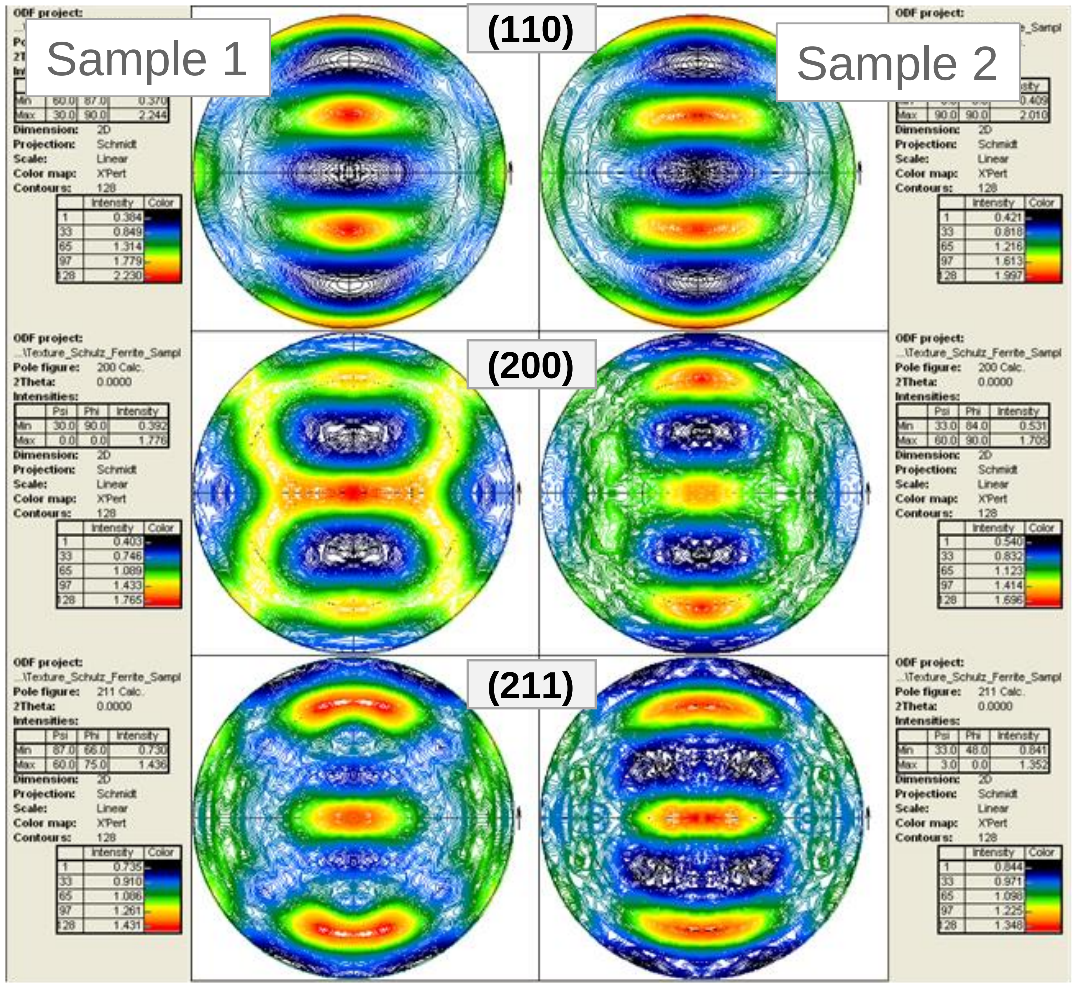
Ferrite (220) reflection







Texture (peak intensity at different tilts)



Pole figures of the {110}, {200}, and {211} reflections of Ferrite were measured .

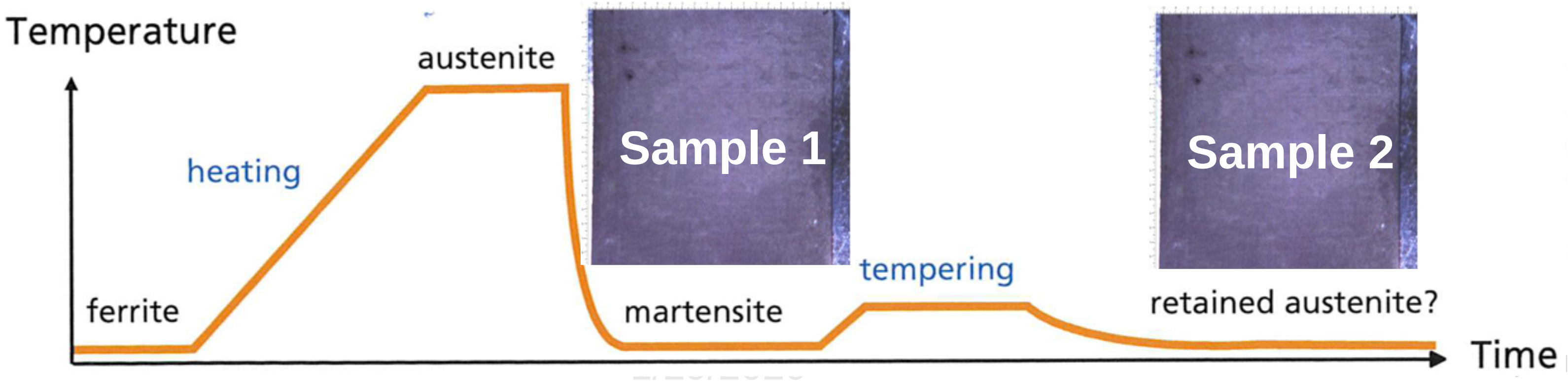
Very similar pole figures: rolling texture.

Sample-1 stronger preferential orientation (supported by the K-factors)

Sample-1		Sample-2	
{hkl}	K-factor	{hkl}	K-factor
110	0.38	110	0.40
200	**1.78**	200	**1.48**
211	1.36	211	1.29

Results summary

	Phase composition		Crystallite size		Texture			Residual stress	
	Ferrite [wt%]	Austenite [wt%]	size [nm]	strain [%]	type	K-factors		σ_{11} [MPa]	σ_{22} [MPa]
Sample-1	89.9	10.1	F: 66	0.11	rolling texture	(111) (200) (220)	0.38 1.78 1.36	-51	0
Sample-2	99.3	0.7	F: 70	0.08	rolling texture	(111) (200) (220)	0.40 1.48 1.29	-34	0



Conclusions

- Panalytical Empyrean diffractometer provide a wide range of techniques for the characterization of metals and alloys
- As a non-destructive, bulk technique XRD (vs SEM, TEM, EBSD)
- Panalytical Empyrean represents a fast and complete solution for metal analysis. phase composition, crystallinity, texture and residual stress.
- In combination with dedicated software packages most of these analysis can even be automated

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Fluorescence

Sample Fluorescence

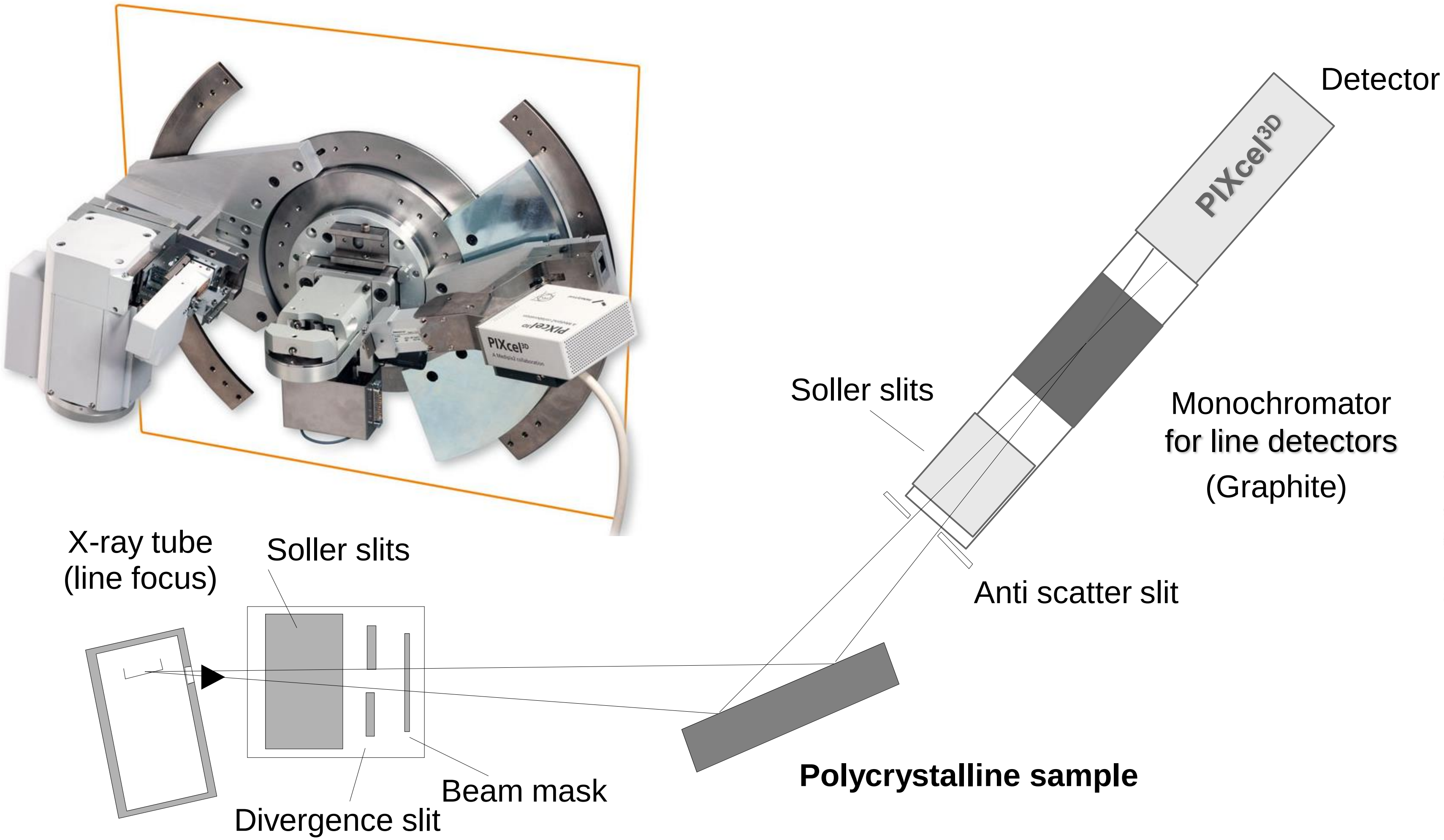
- Incident X-ray photons excite electrons in certain elements in the sample, which results in the emission of the characteristic X-ray radiation of the respective elements.

- If this emitted radiation is close to the Cu Kα, it will be detected!

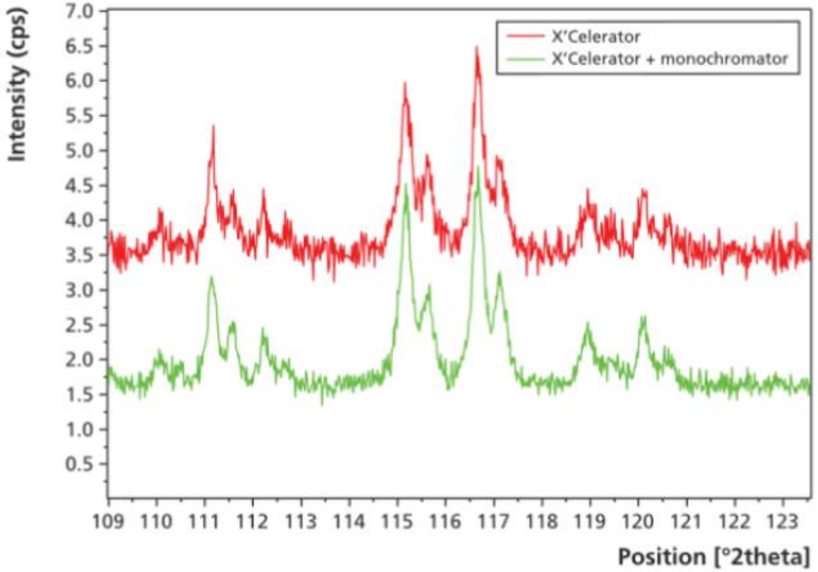
- During this process the incoming photon is absorbed. This process results in a significant reduction of the penetration depth in fluorescent samples.

- This radiation will not effect peak position or intensity; it will only increase the background.

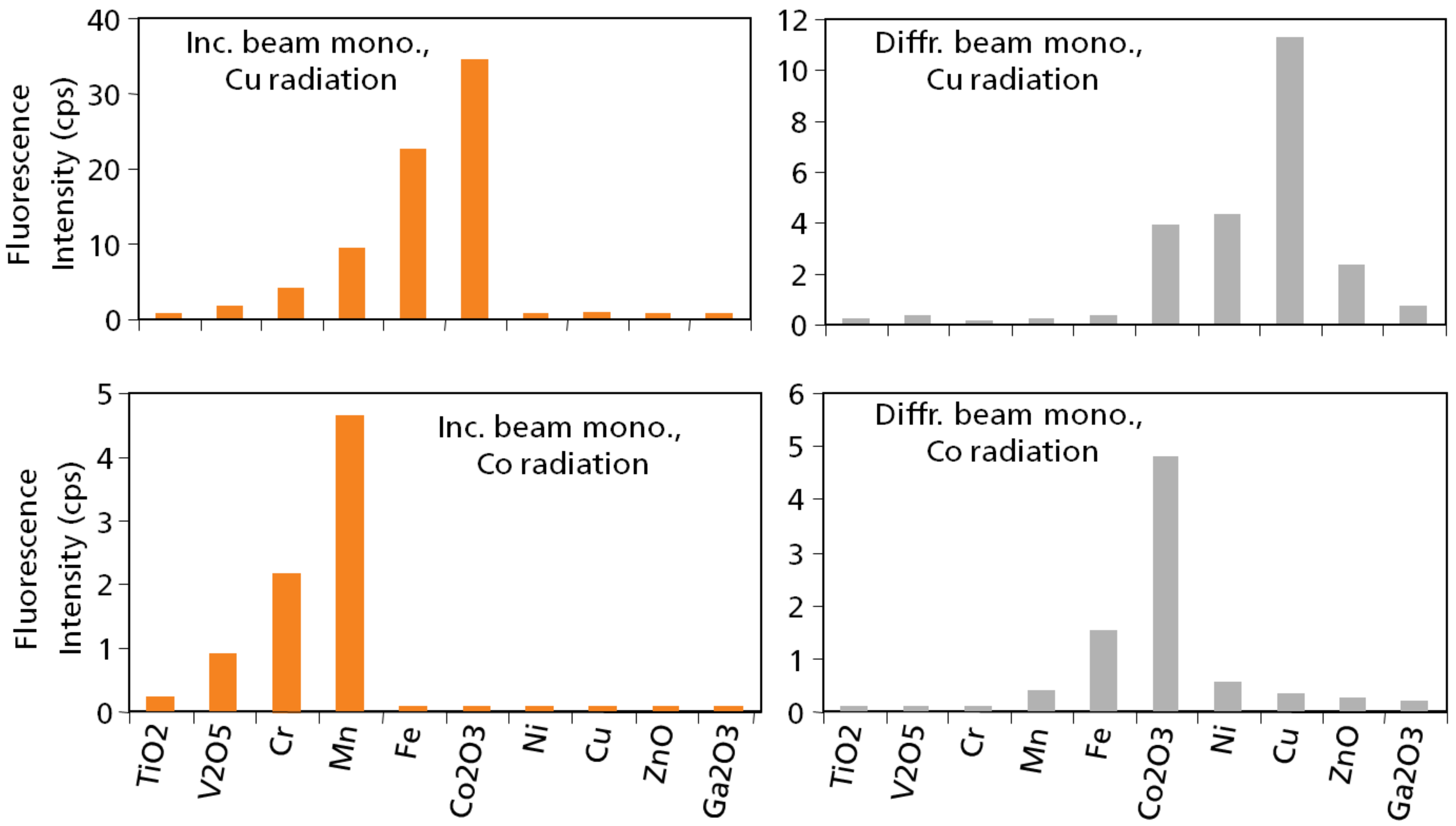
Diffracted Beam Monochromator for line detectors



Cathode material for Li battery: $LiNi_{0.33}Co_{0.33}Mn_{0.33}O_2$

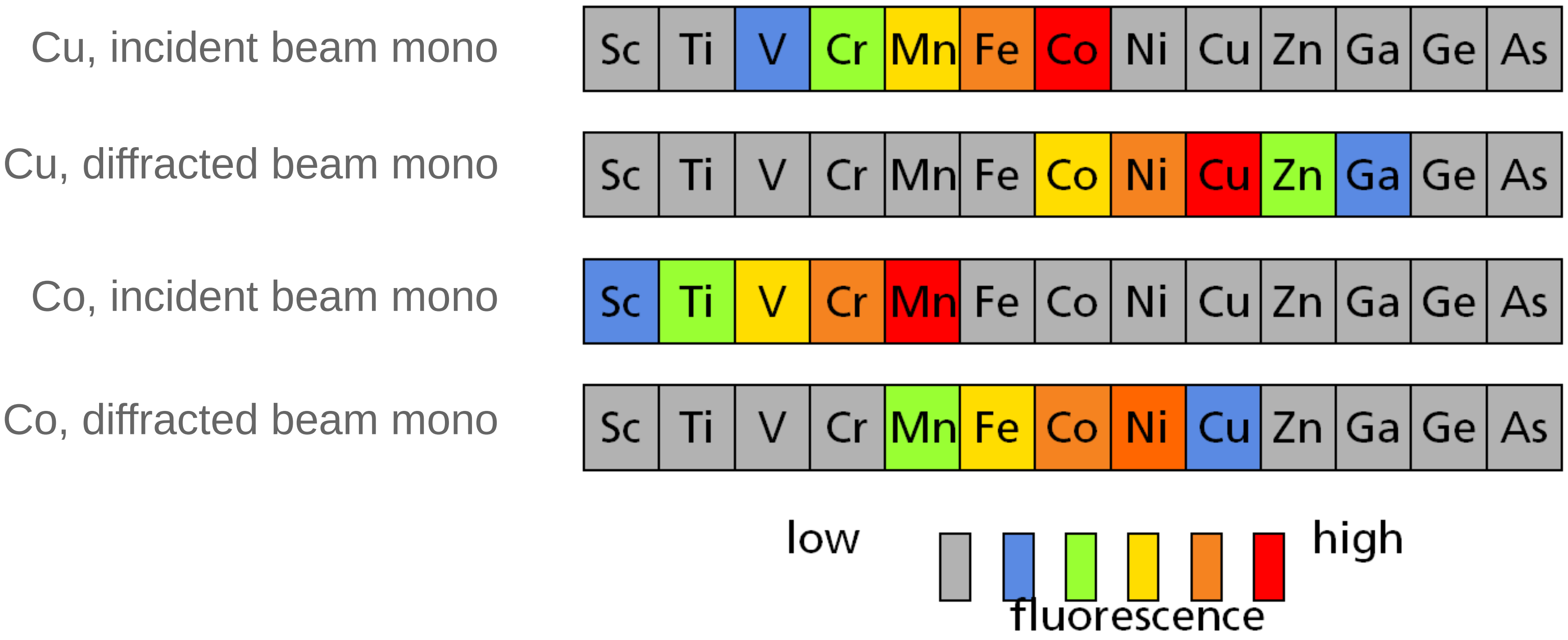


Effect of Monochromators on Fluorescent Intensity

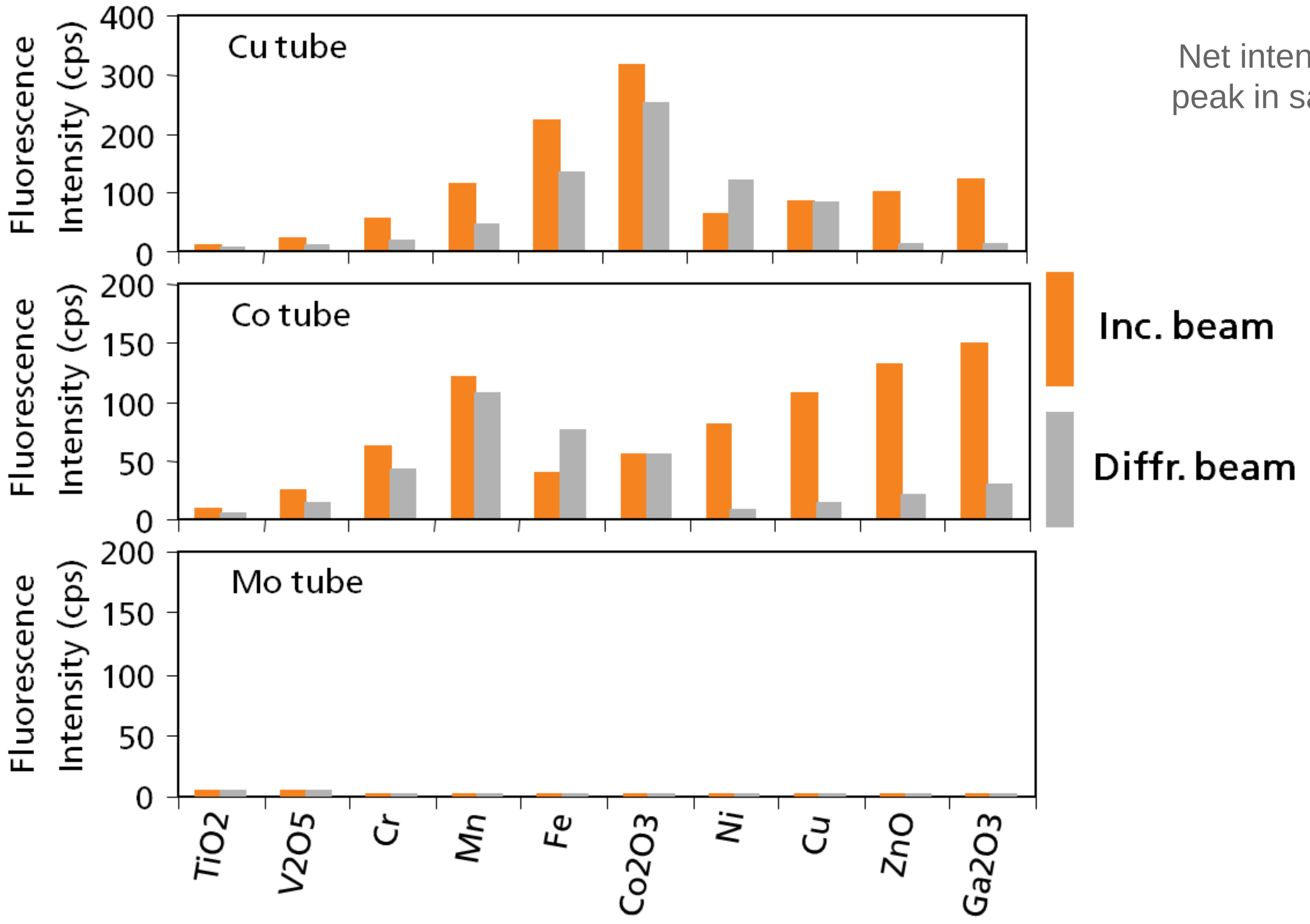


Rules of Thumb - Monochromators

Monochromators help to reduce the range of problematic elements



Effect of β-filters on fluorescent Intensity



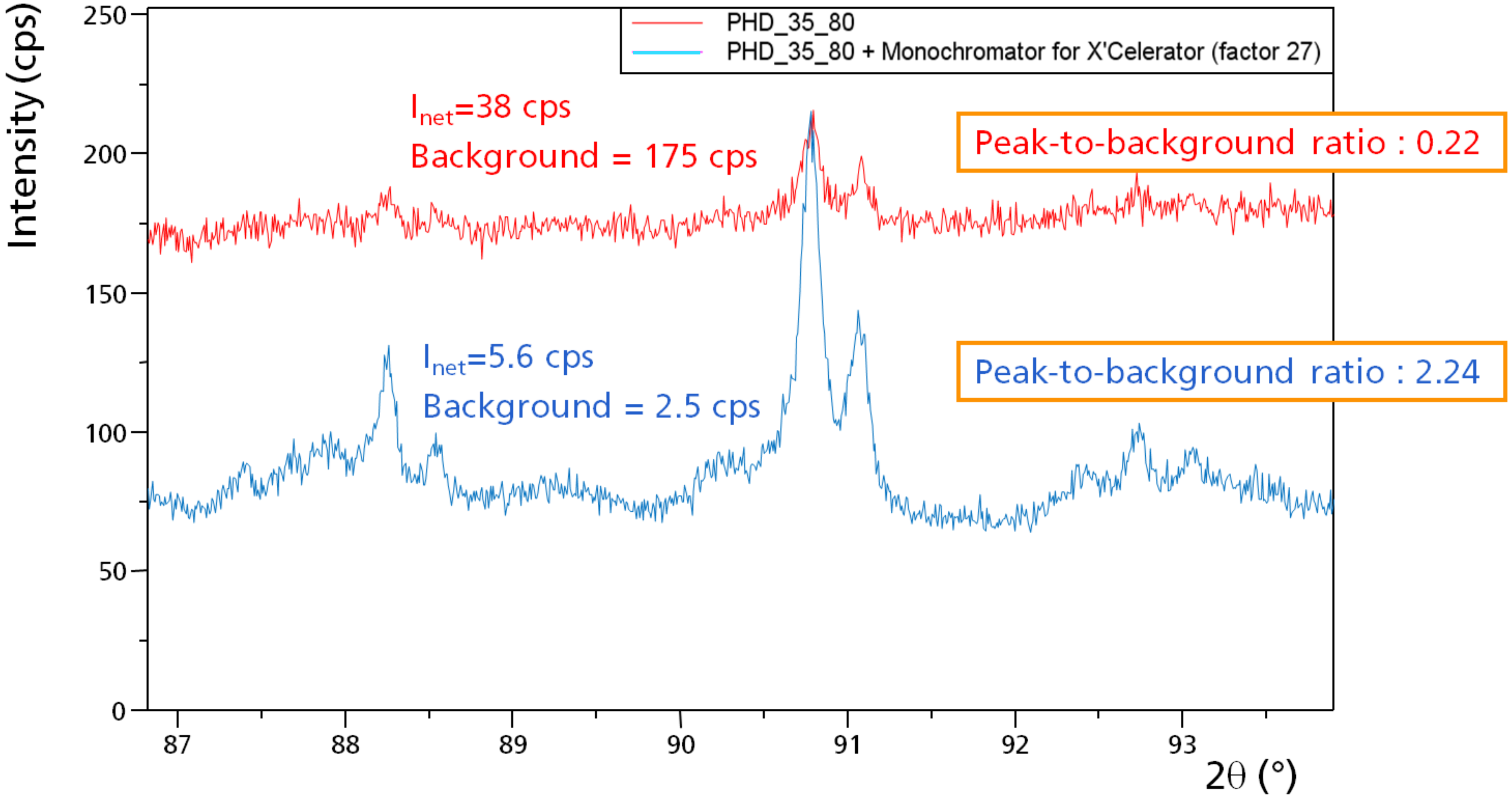
Net intensity of main peak in sample 7 (Ni):

2598 cps

1350 cps

794 cps

Effect of Monochromator



Rules of Thumb – X-ray Sources

- For not too complex patterns, Mo radiation is a valuable alternative
- When going from Cu to Co radiation:
  - *The peak intensities drop by a factor of about 3*
  - *Exception Fe and Co samples: there the intensity rises by a factor of 3!*
- Effect of varying penetration depth when absorption edges of elements in the sample are close to the characteristic radiation

Extra slides

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Building X-Rays tube is in our blood

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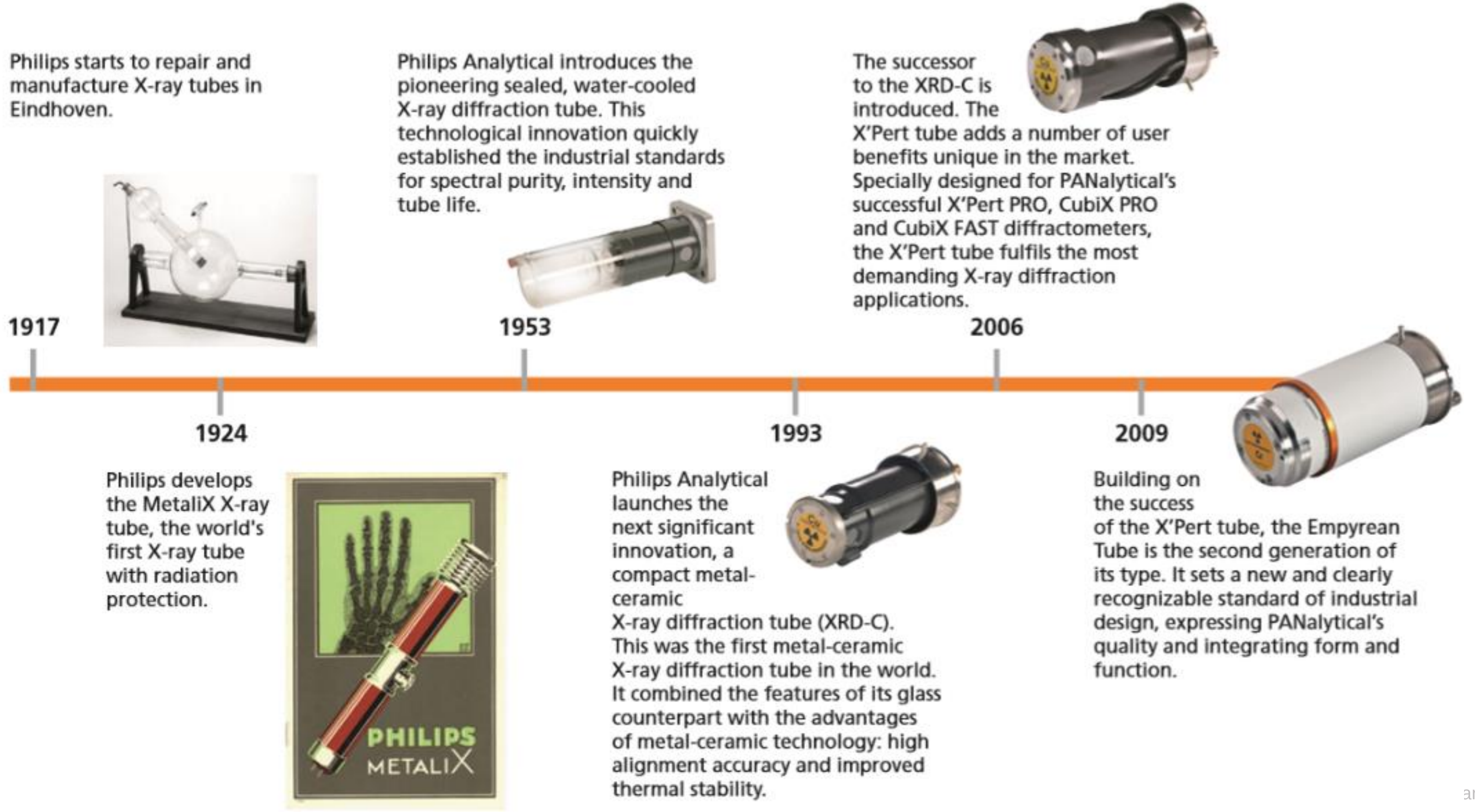
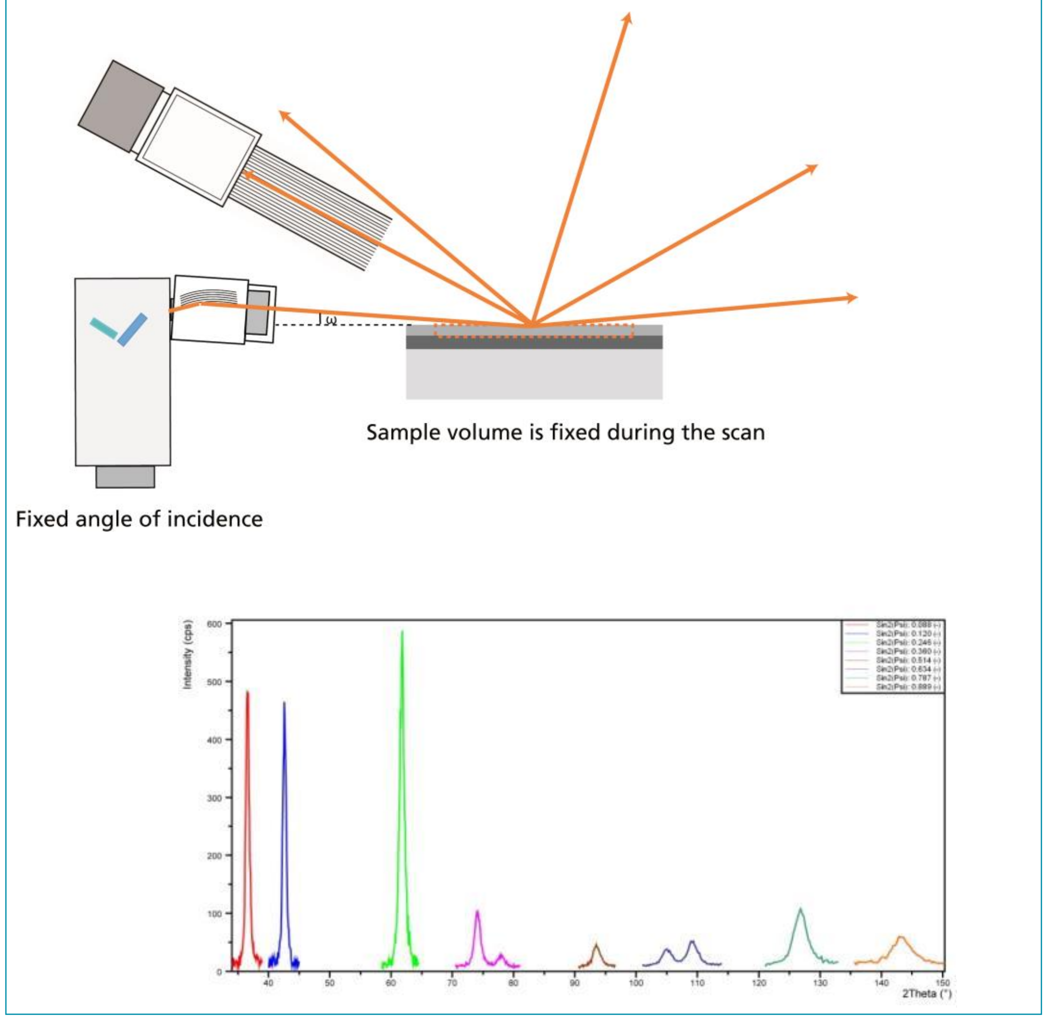
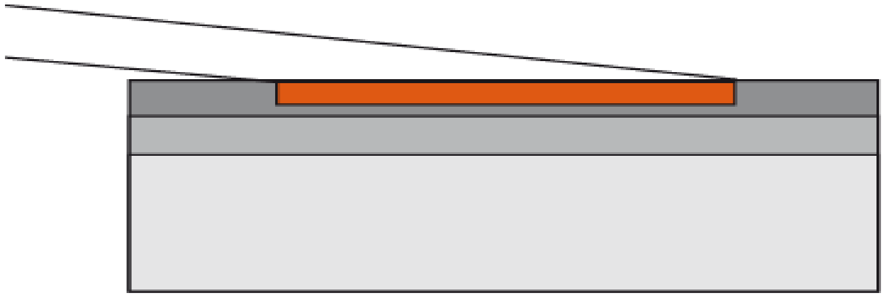


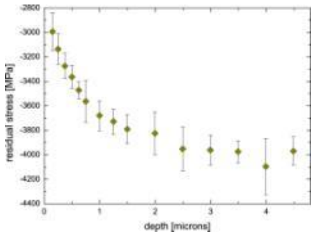
Grazing incidence (GI) XRD

- GI-XRD is based on the relationship between the angle of incidence (ω) and the penetration depth of the X-ray beam
- Penetration depth can be controlled
- Constant volume during one measurement
- Sensitive to compositional variations and stress gradients within bulk materials, single layers and layer sequences
- **Preferred approach for the analysis of thin layers and coatings**

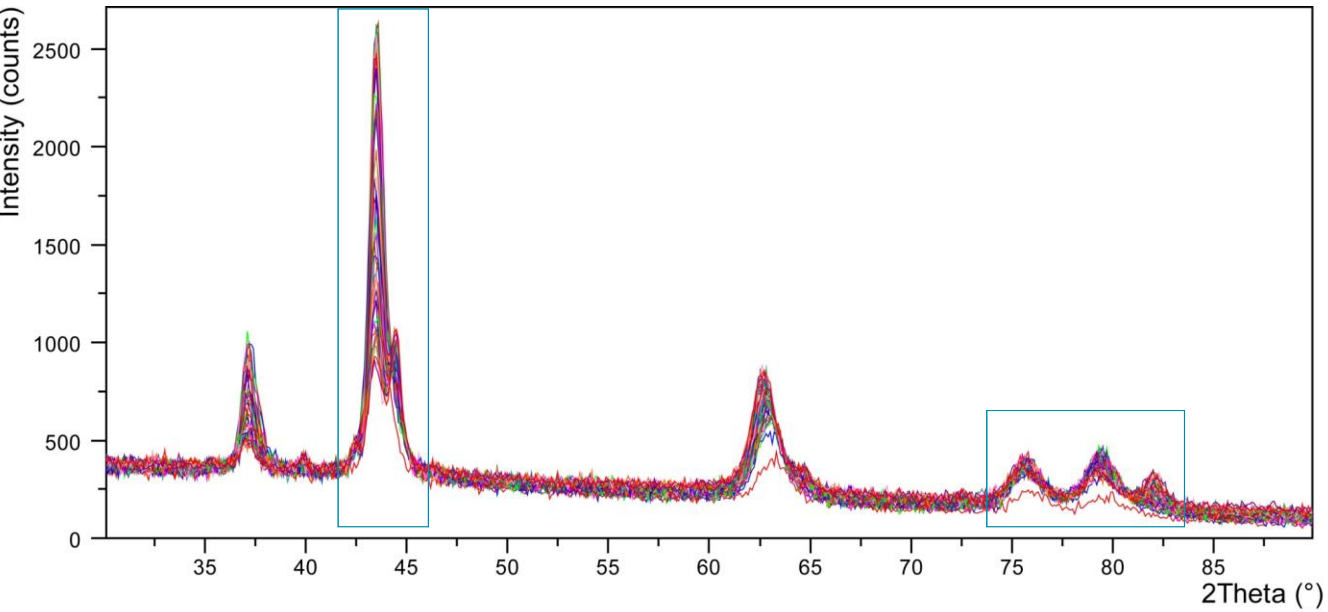


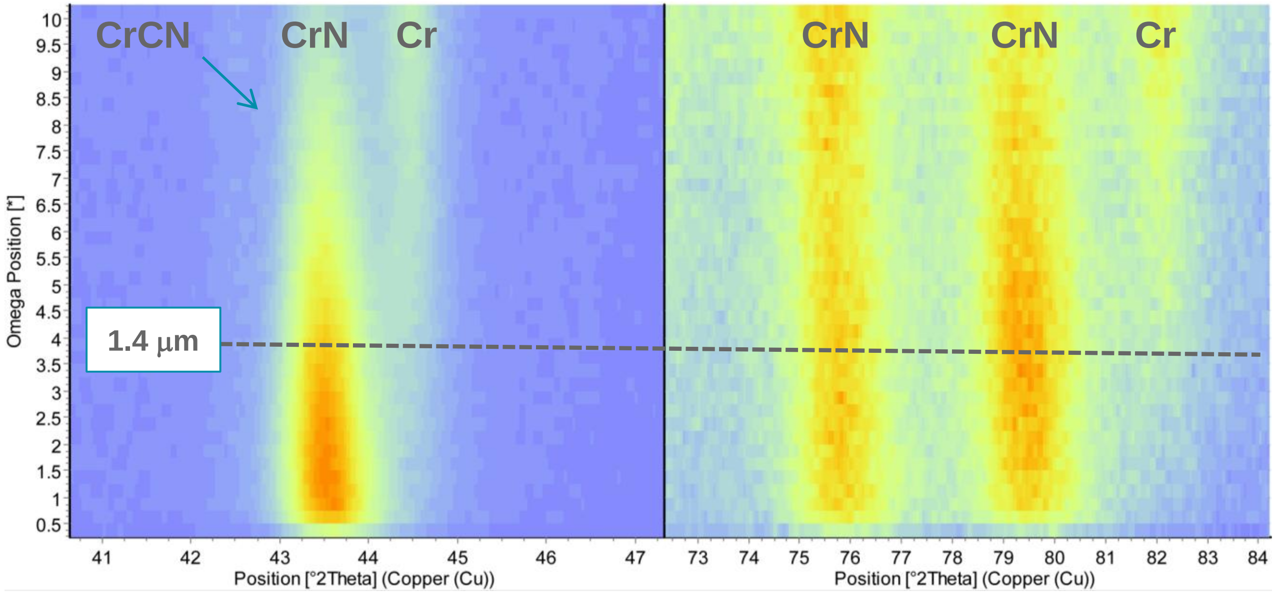
Analyzed volume





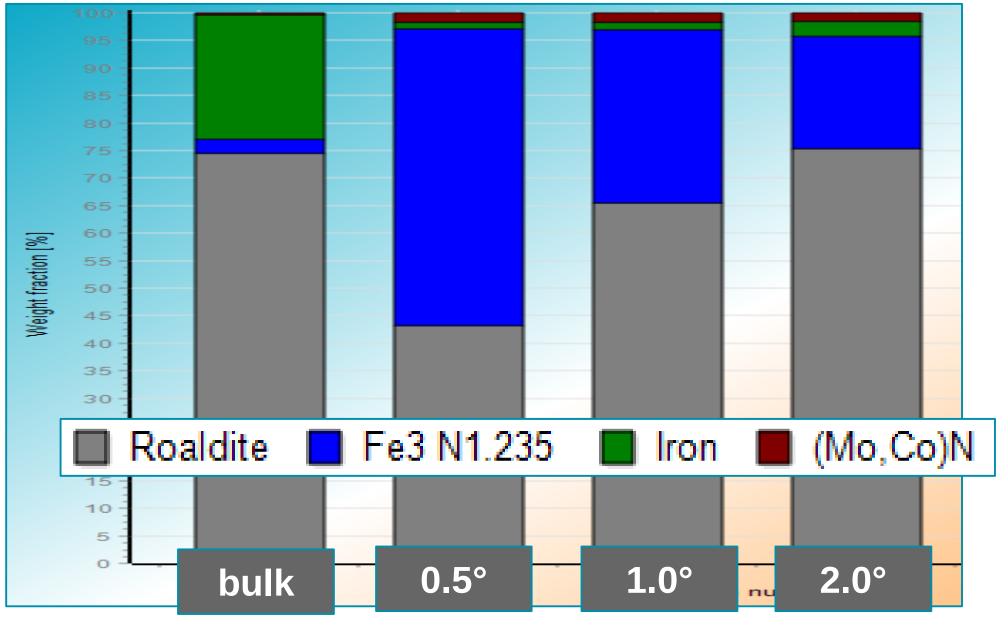
Grazing incidence (GI) XRD – phase profiling



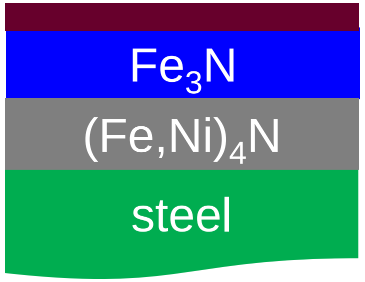


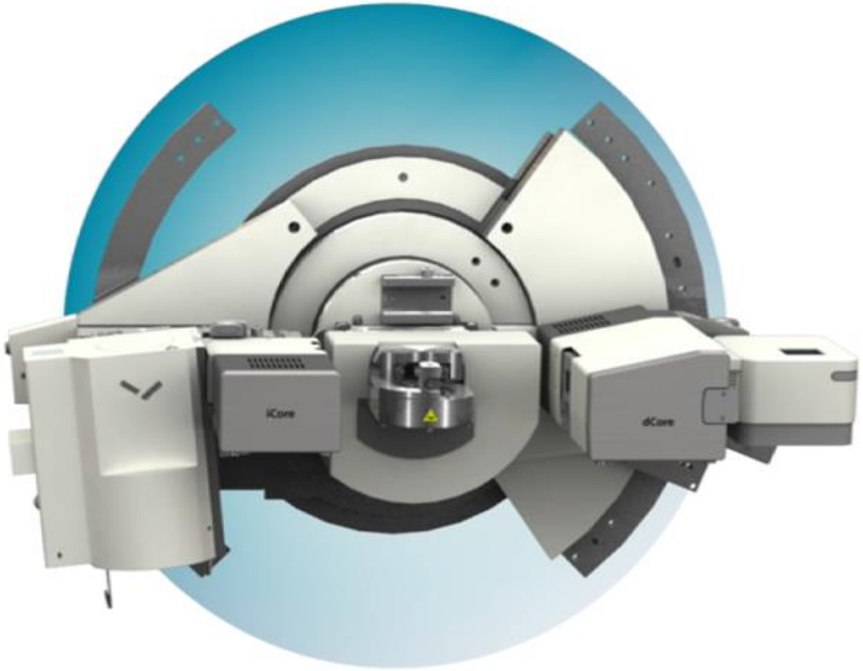
- Using the GI approach phase variations in phase composition can be mapped with increasing depth.
- For that full 2θ scans at different ω-angles are collected
- The example shows a CrN layer that on a Cr-CrCN layer with a transition at 1.4 μm.

Empyrean with multiCore optics



depth





Phase composition

Tabletop or floor-standing diffractometer?

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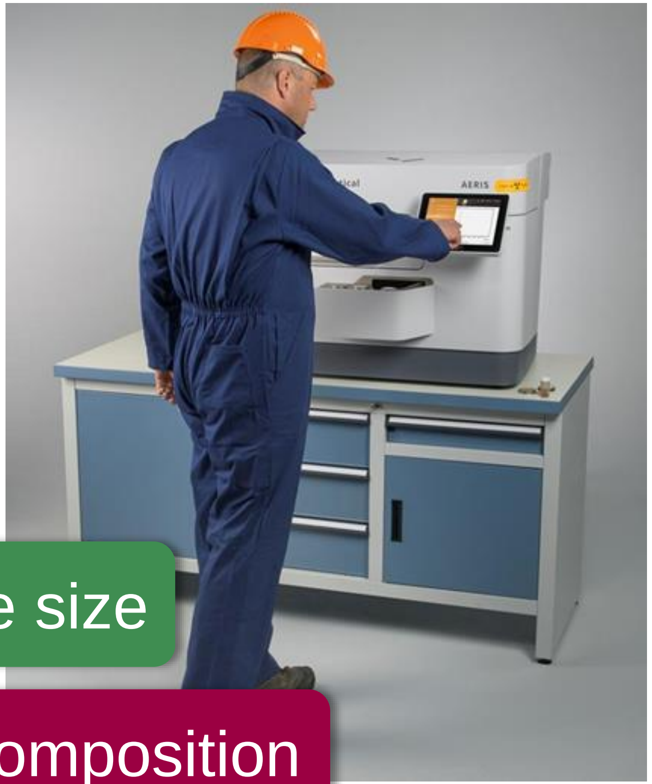


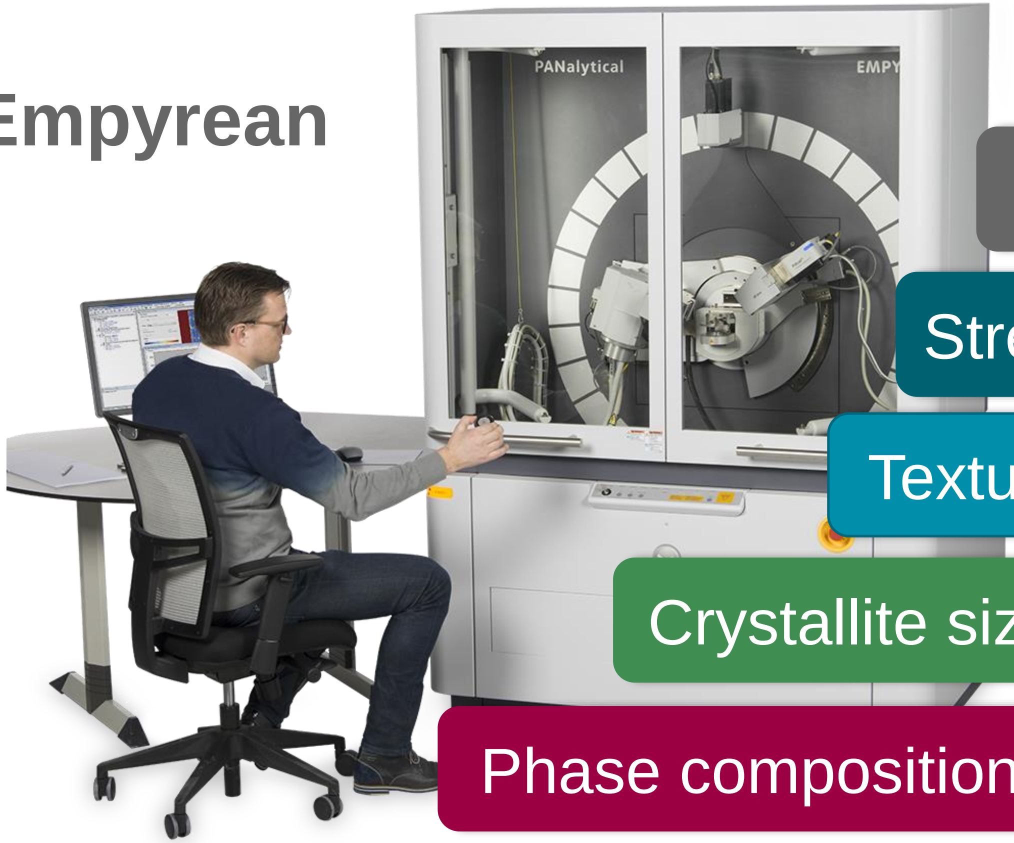
Crystallite size

Phase composition

Aeris

or

Empyrean



...

Stress

Texture

Crystallite size

Phase composition

The Aeris Benchtop XRD

Ease of use – crucial in industry

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Step 1 – Place your sample

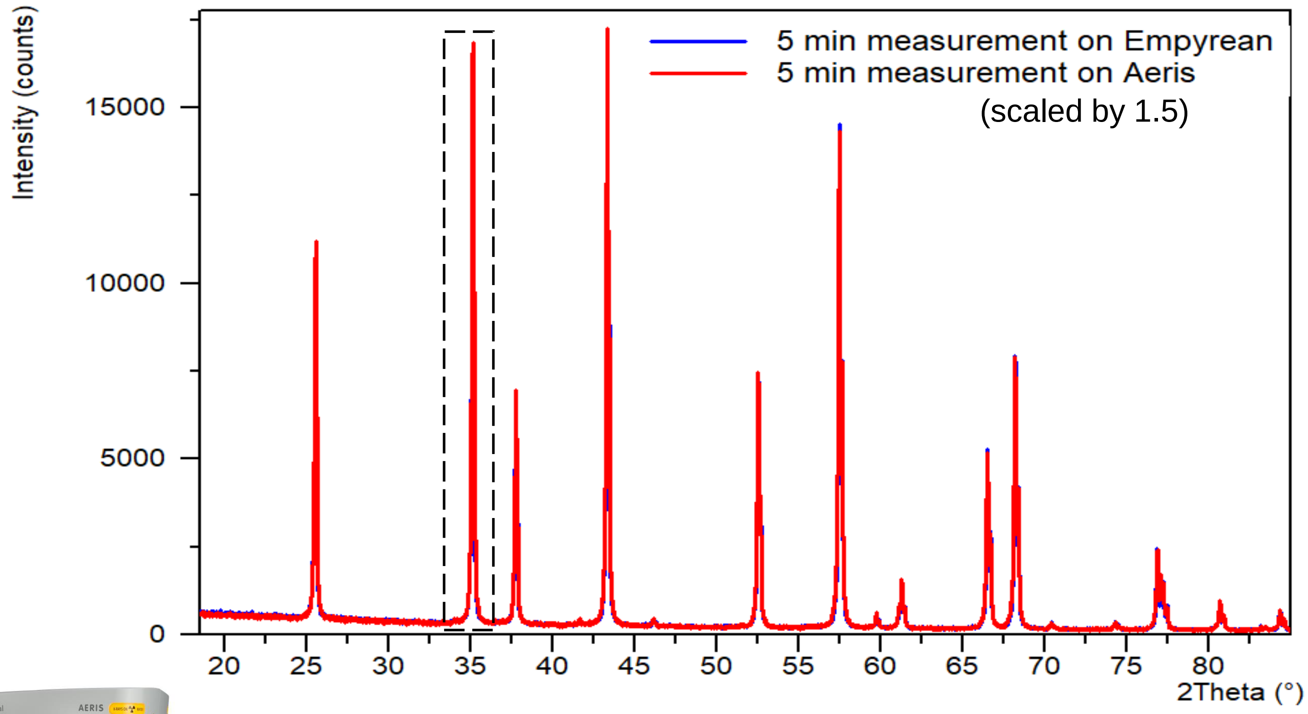
Step 2 – Choose measurement program

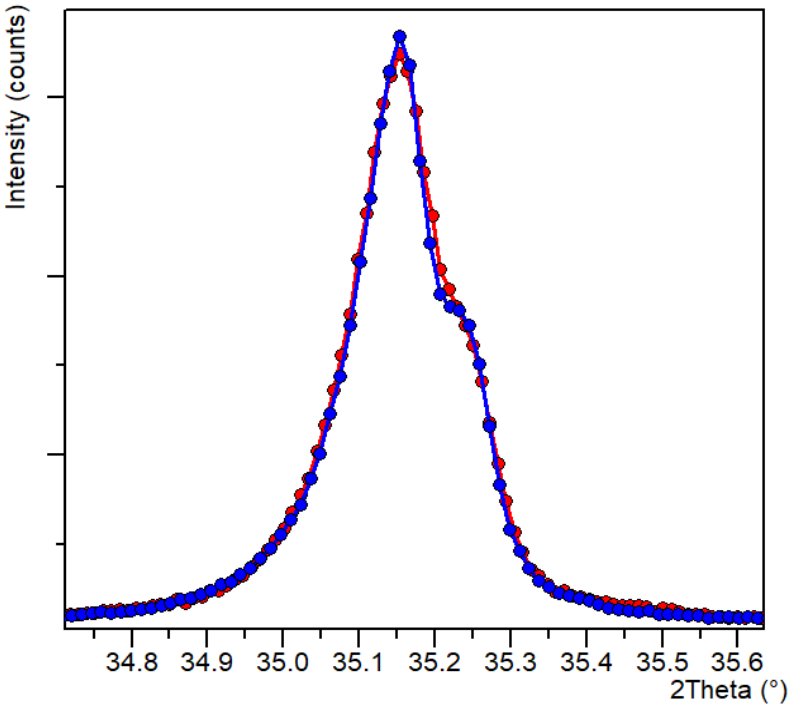
Step 3 – Enter sample information

Step 4 – Results

Bridging the gap to full-power lab diffractometer

NIST Al_2O_3

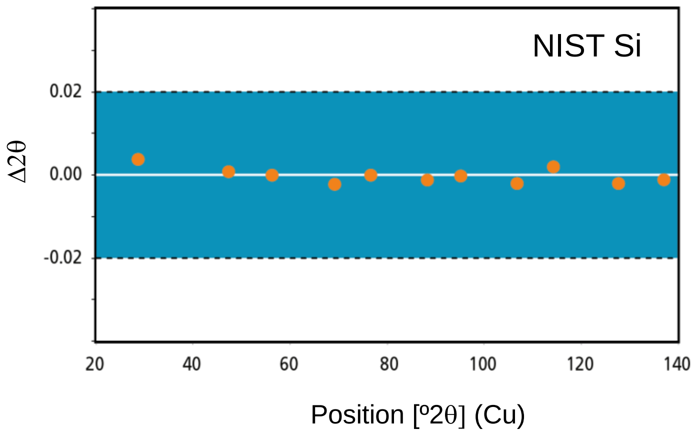




Average analyses time
is **5 - 10 minutes per sample**

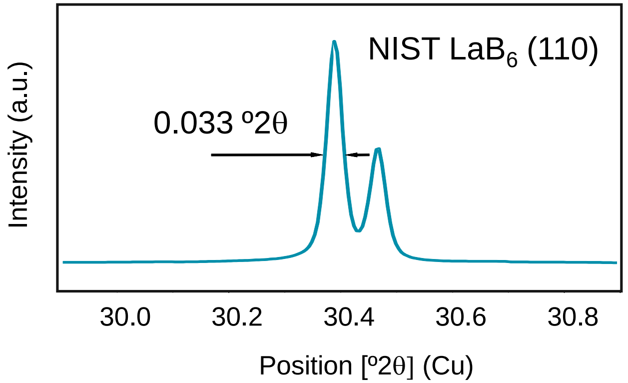
Bridging the gap to full-power lab diffractometer

Linearity

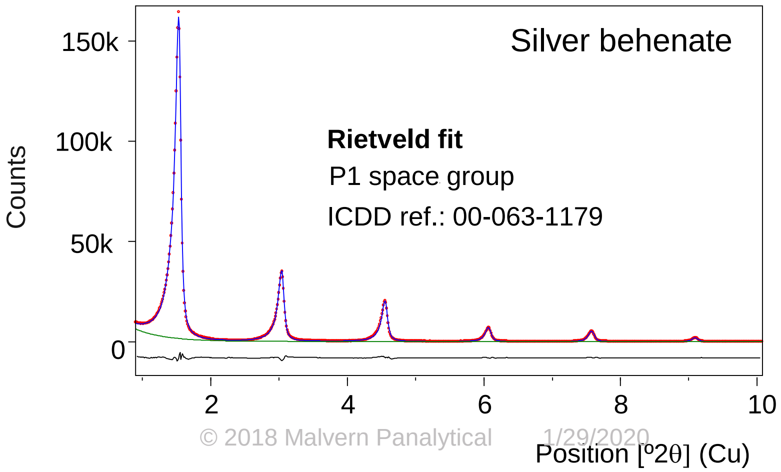


Aeris delivers best-in-class data quality

Resolution



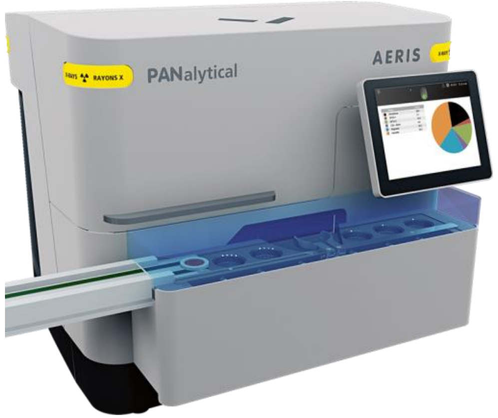
Low angle performance

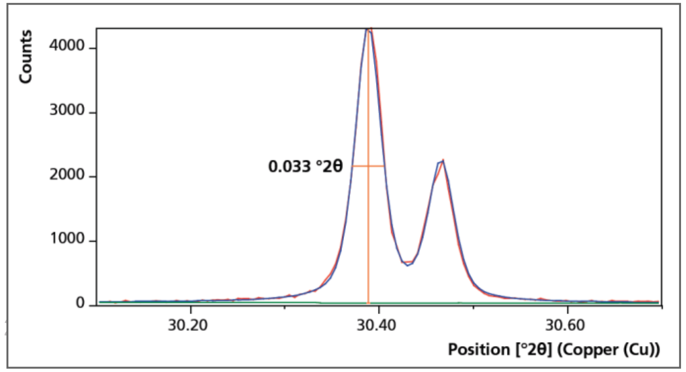


Conclusions

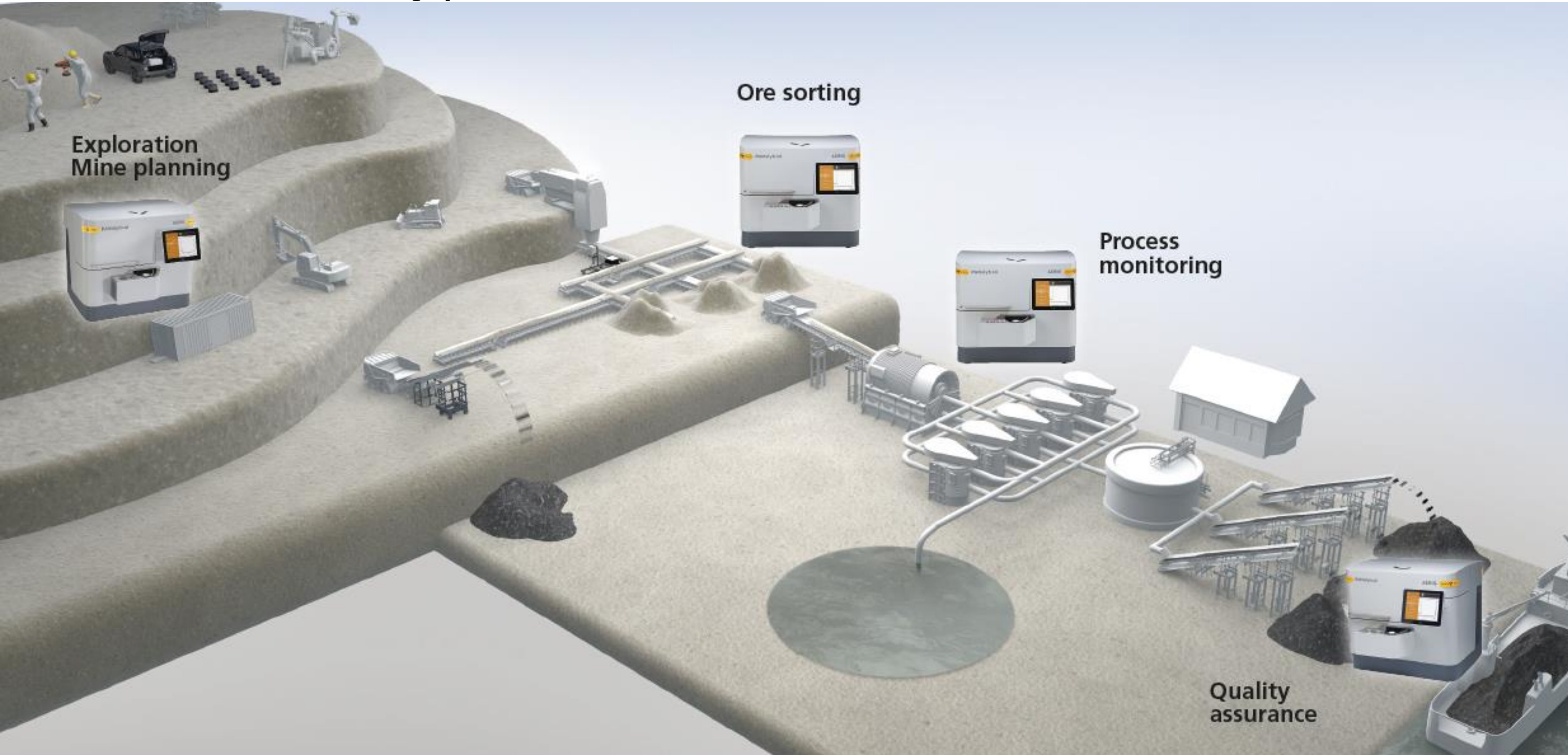
- **Aeris is…**
  - **…very intuitive in its use**
  - **…flexible wherever in your process you need it**
  - **…automatable**

- **Aeris has…**
  - **…a low cost of ownership**
    - Lifetime tube
    - Limited infrastructural needs
    - No chiller
    - No gases
    - Small footprint
  - **… a performance comparable to a full size XRD**
    - Speed / intensity
    - Resolution
    - Linearity

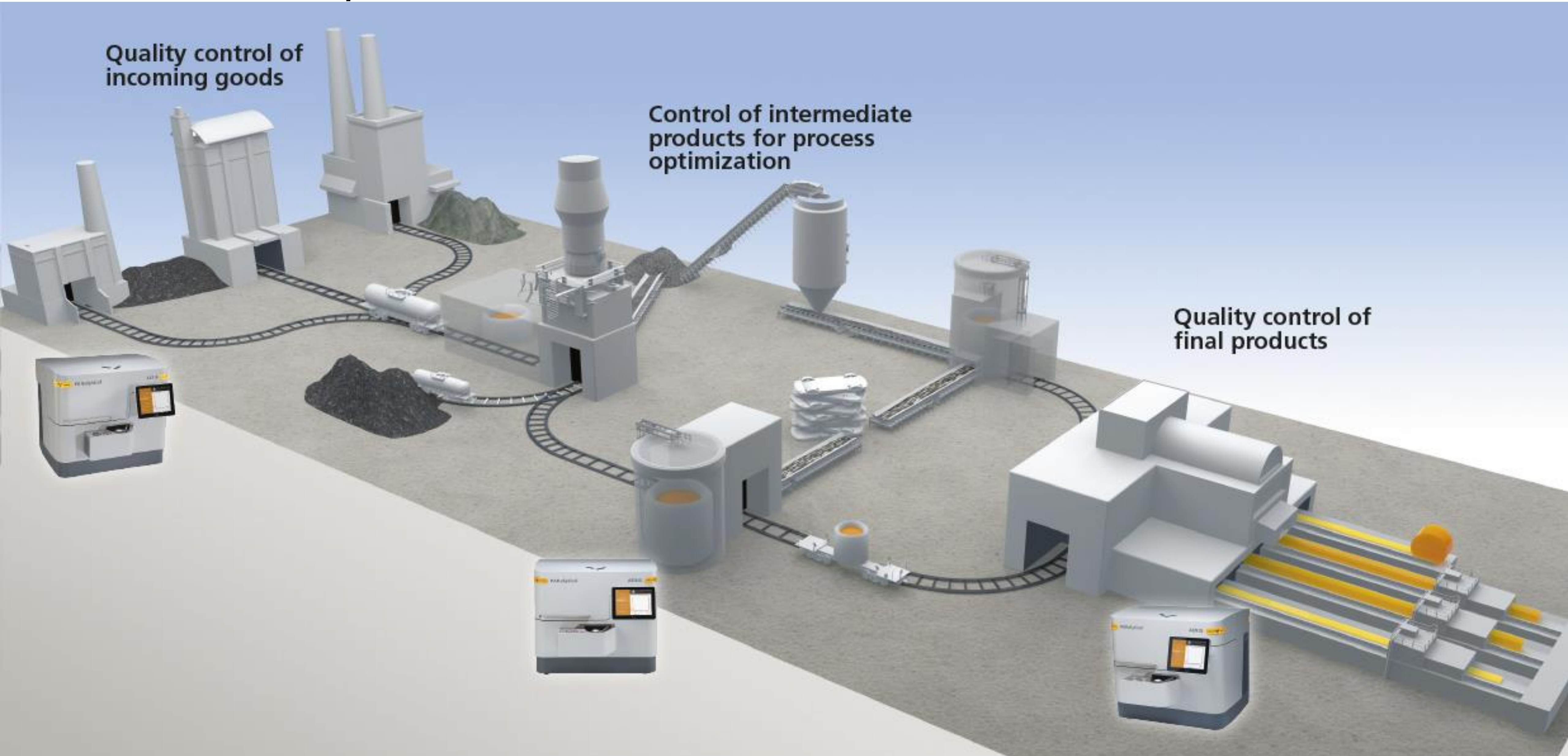




XRD in the mining process



XRD in metal production



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The new Empyrean

The intelligent diffractometer

- New MultiCore Optics
  - Fully automated X-ray optics
  - Swap between many applications
  - Increase sample throughput
  - Optimize resolution and intensity automatically

- Improved ease of use
  - Component recognition
  - Predefined programs
  - Smart PreFIX concept

Select proper instrument for the task - Empyrean

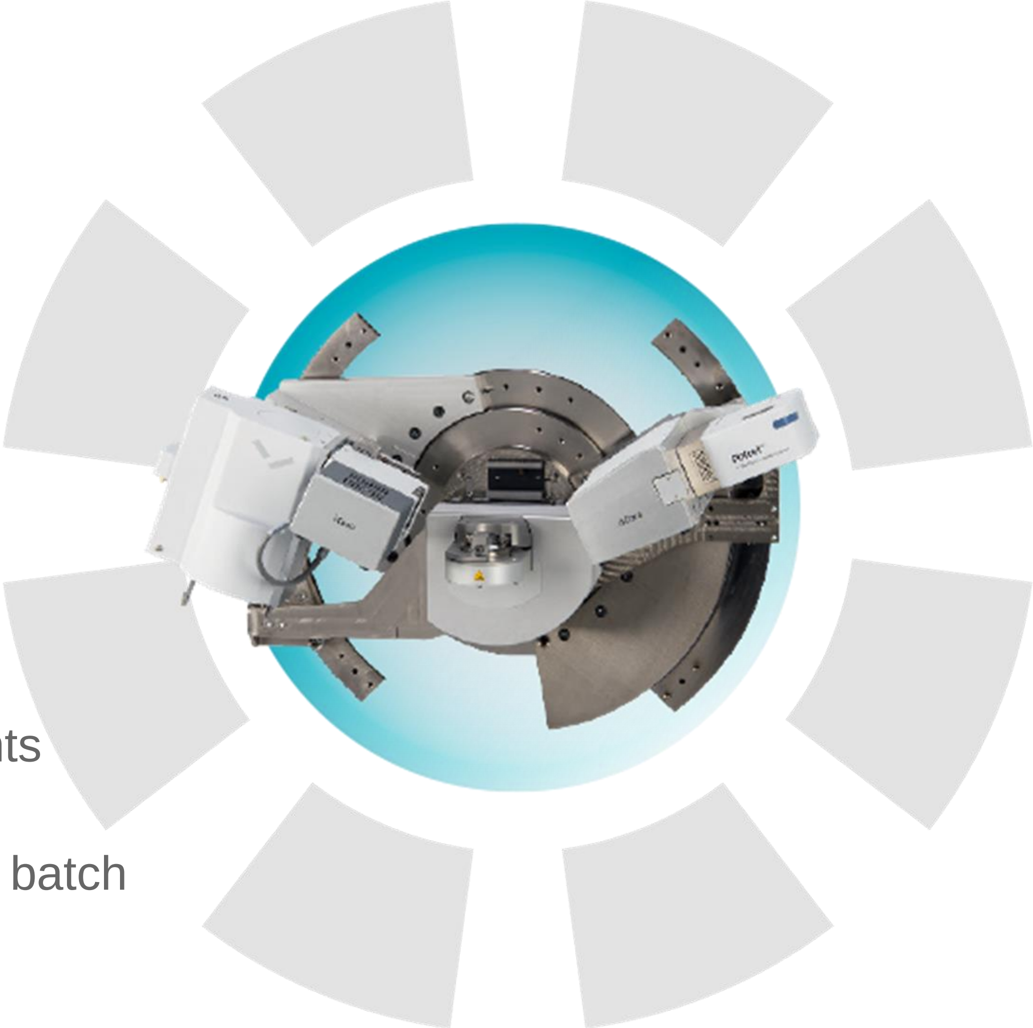
Multi-purpose instrument

- Powder XRD
- Basic SAXS
- Omega stress
- Omega texture
- GIXRD
- Reflectometry

- *in situ* XRD
- Advanced SAXS
- Comp. tomography
- Advanced thin film metrology
- PDF
- Hard radiation
- Advanced stress/texture

The Empyrean Series III – MultiCore Optics

iCore and dCore



Incident (iCore) & Diffracted (dCore) beam modules

- perform the largest variety of X-ray diffraction measurements automatically, with excellent data quality
- Seamless combination of different experiment types in one batch
- maximize utilization of the system

MultiCore Optics

iCore and dCore

Phase ID and Quantification

X-ray Reflectometry

Residual Stress

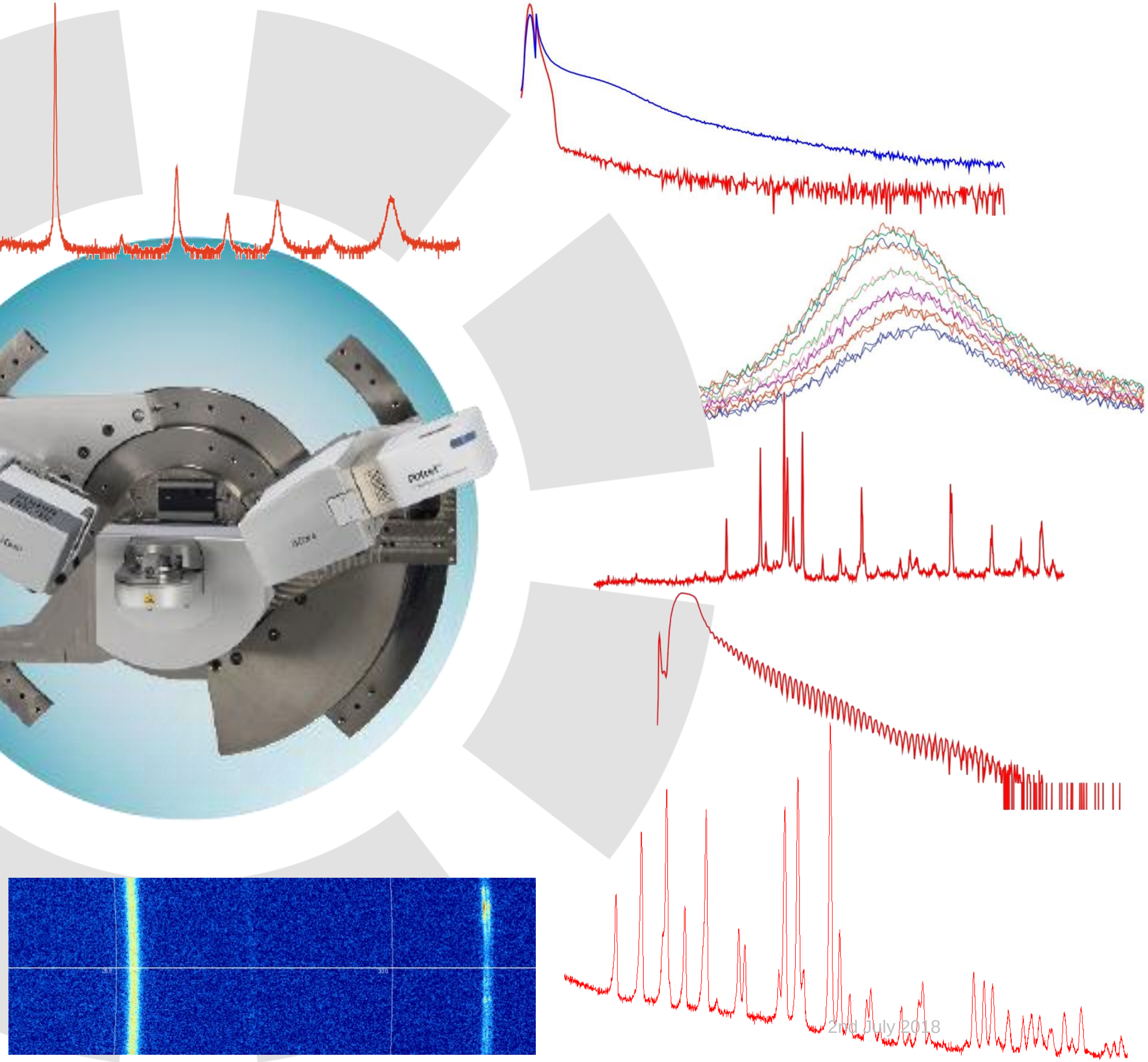
2D XRD

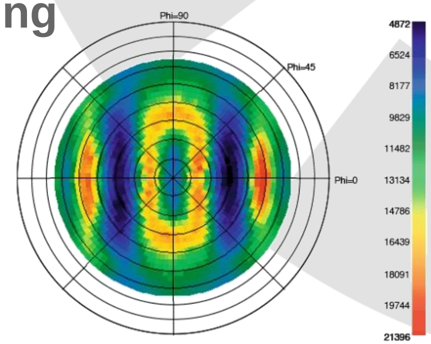
Transmission XRD

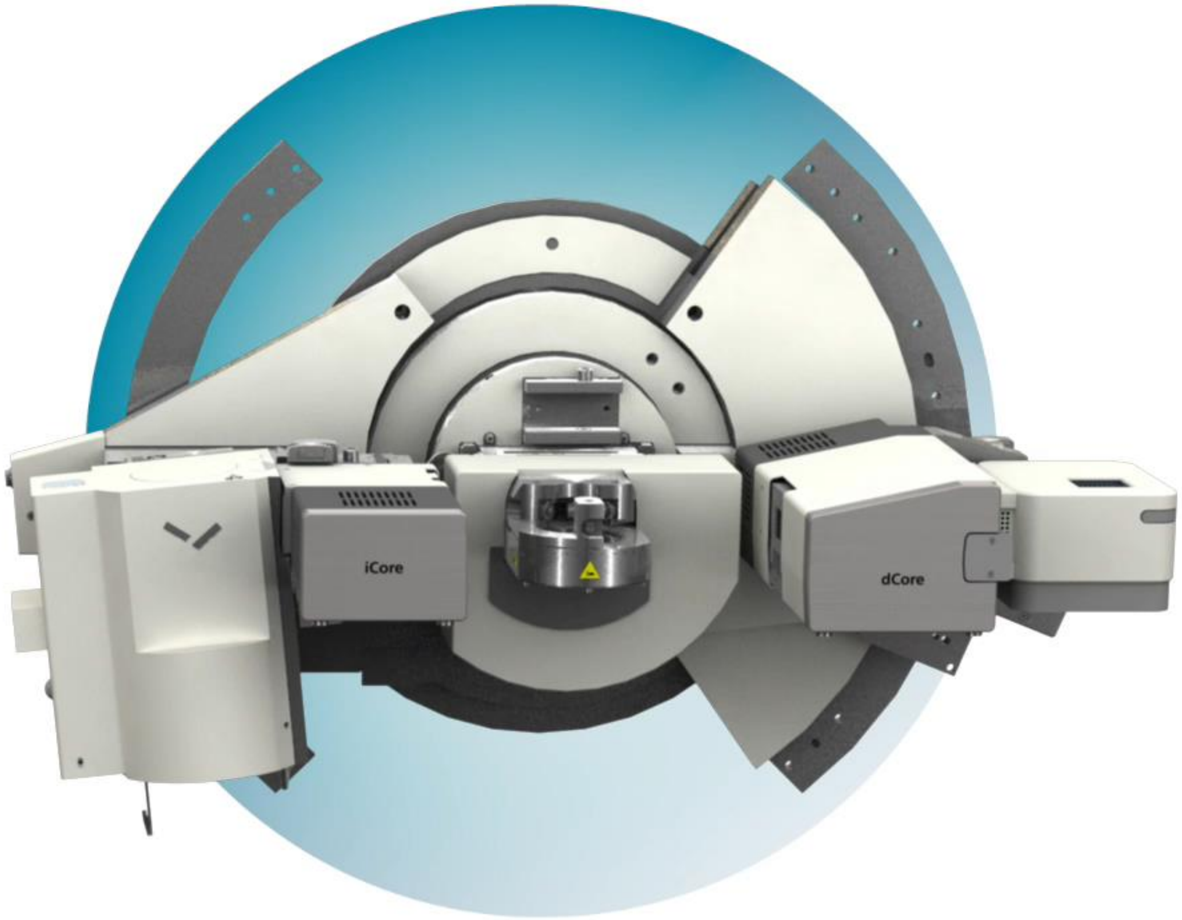
Pole figures

Small-angle X-ray scattering

Grazing Incidence XRD



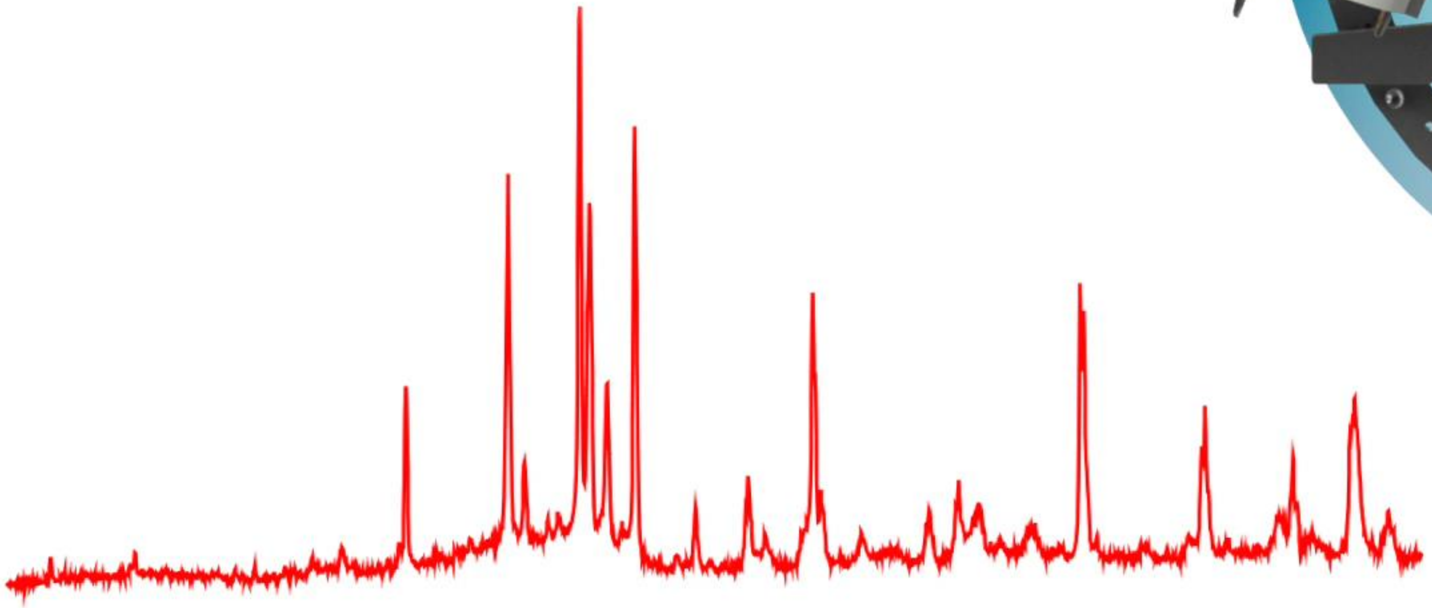


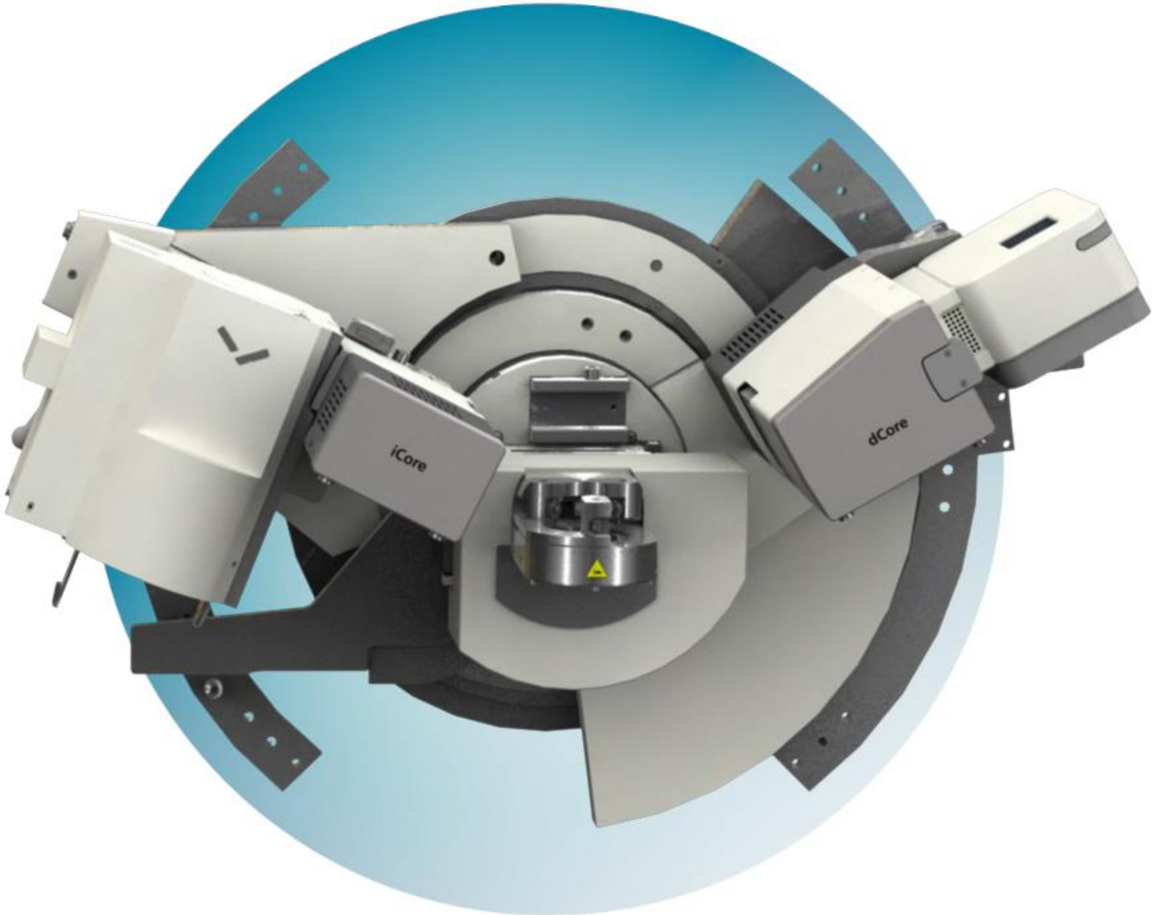

iCore
dCore

MultiCore Optics

iCore and dCore

Phase ID and Quantification

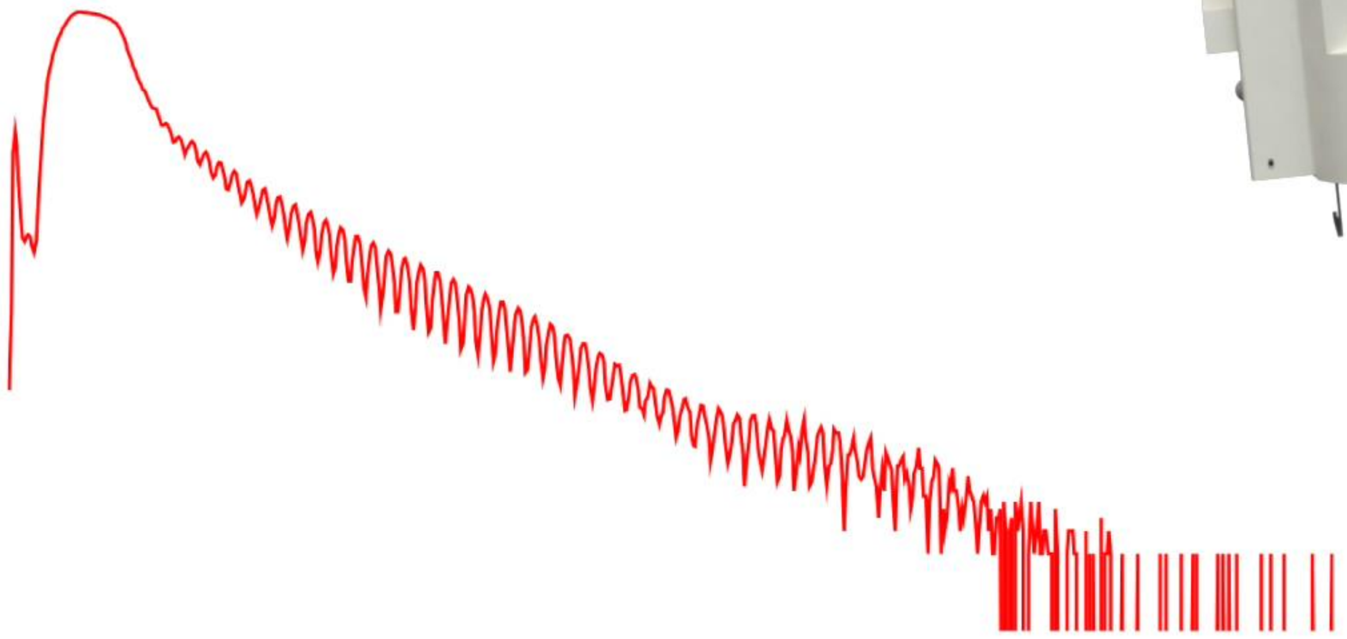


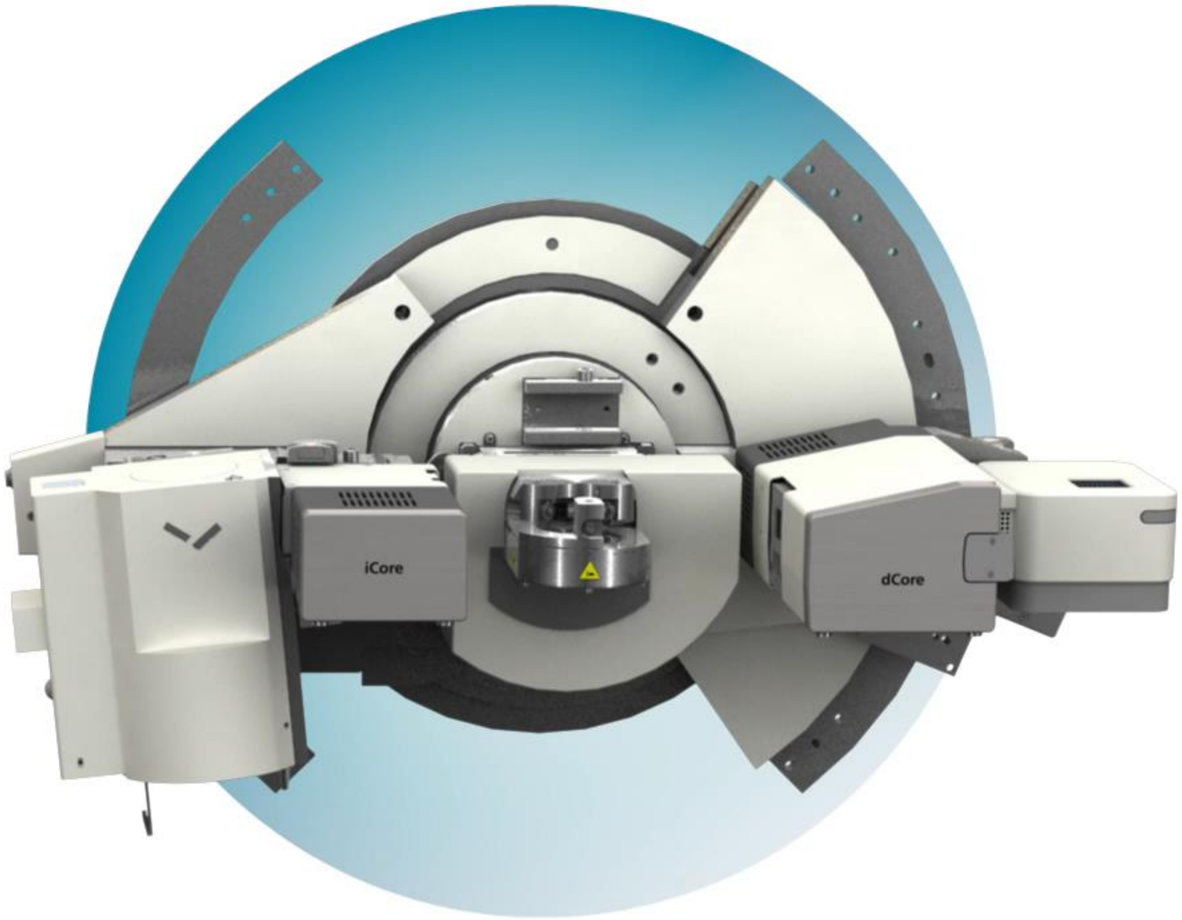


MultiCore Optics

iCore and dCore

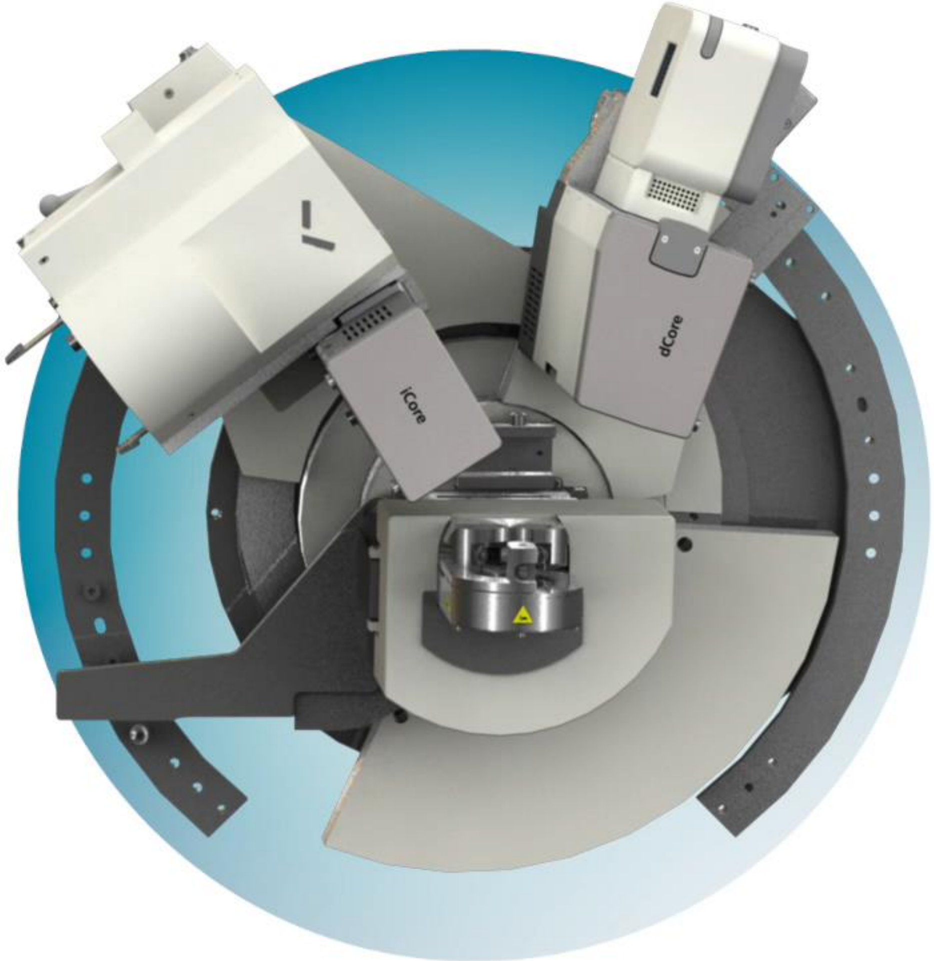
X-Ray Reflectometry

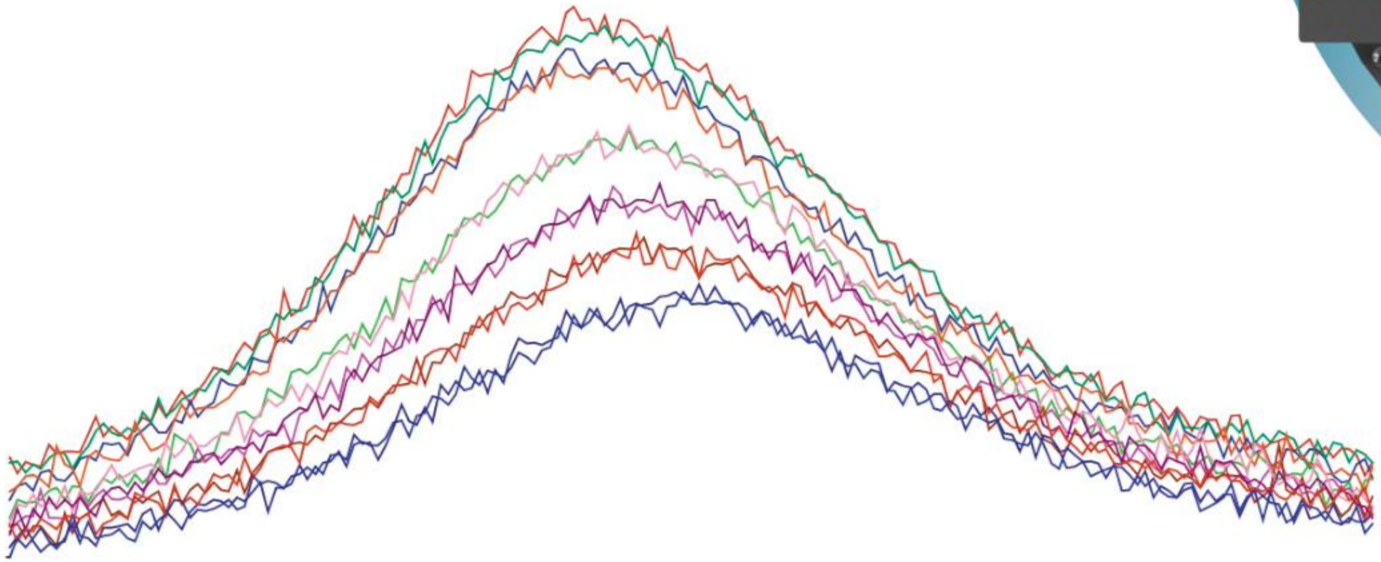




MultiCore Optics
iCore and dCore

Residual Stress

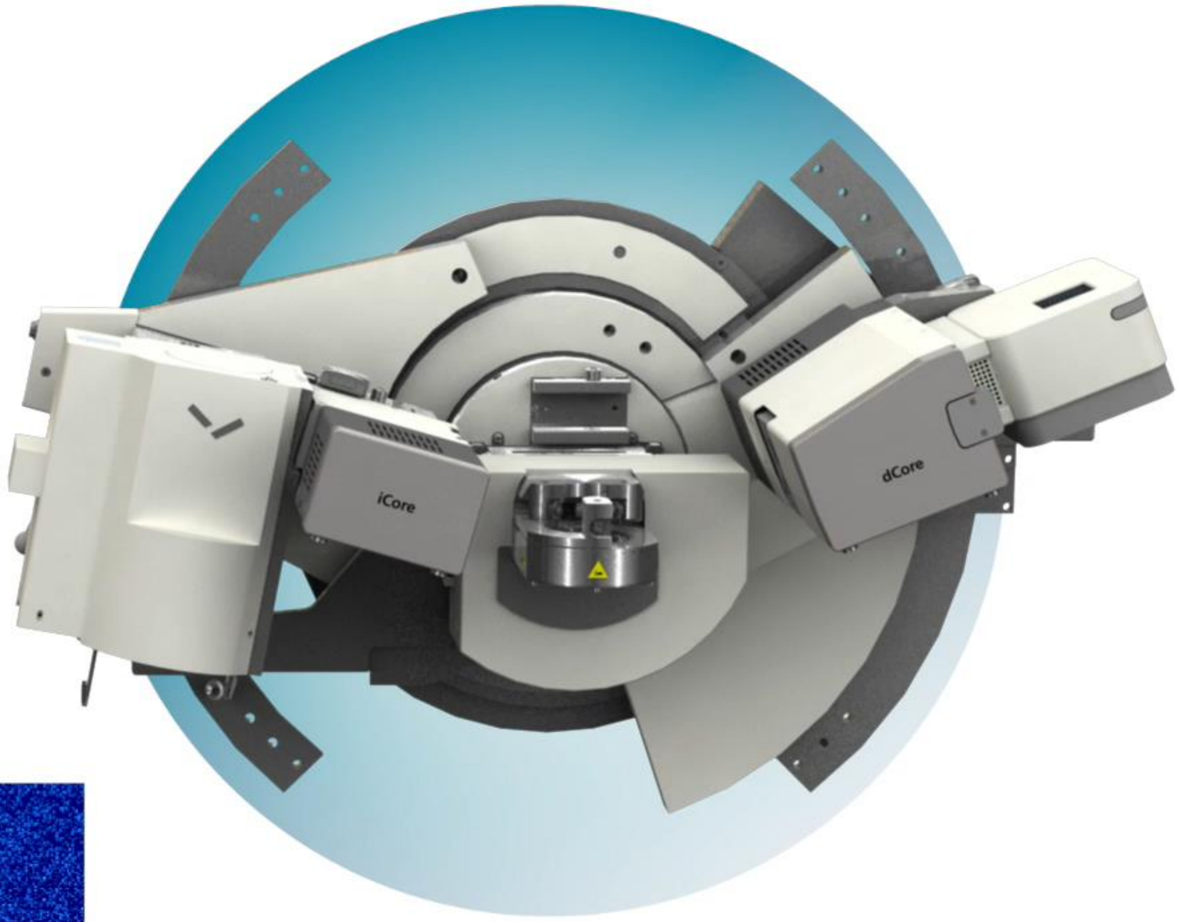


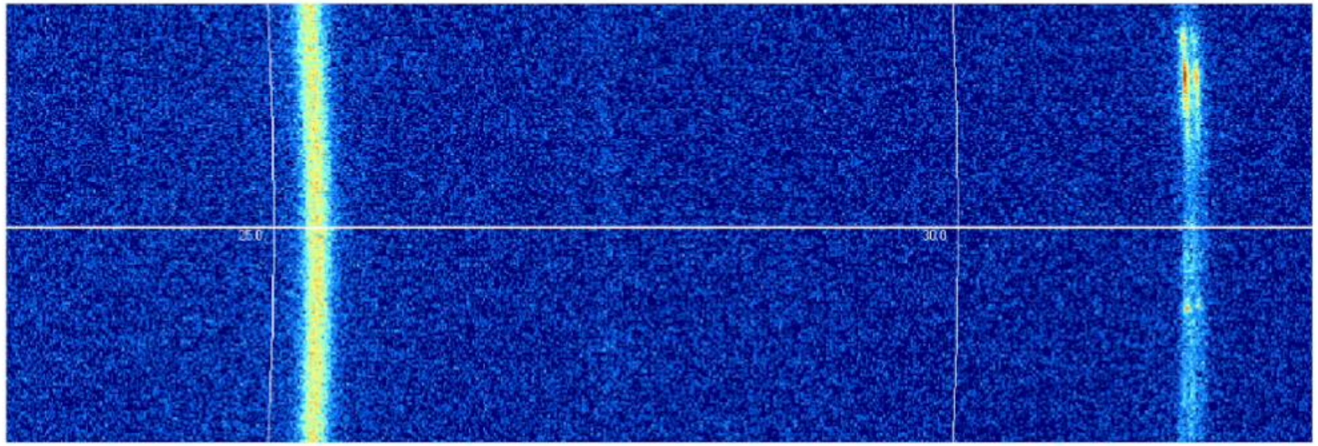


MultiCore Optics

iCore and dCore

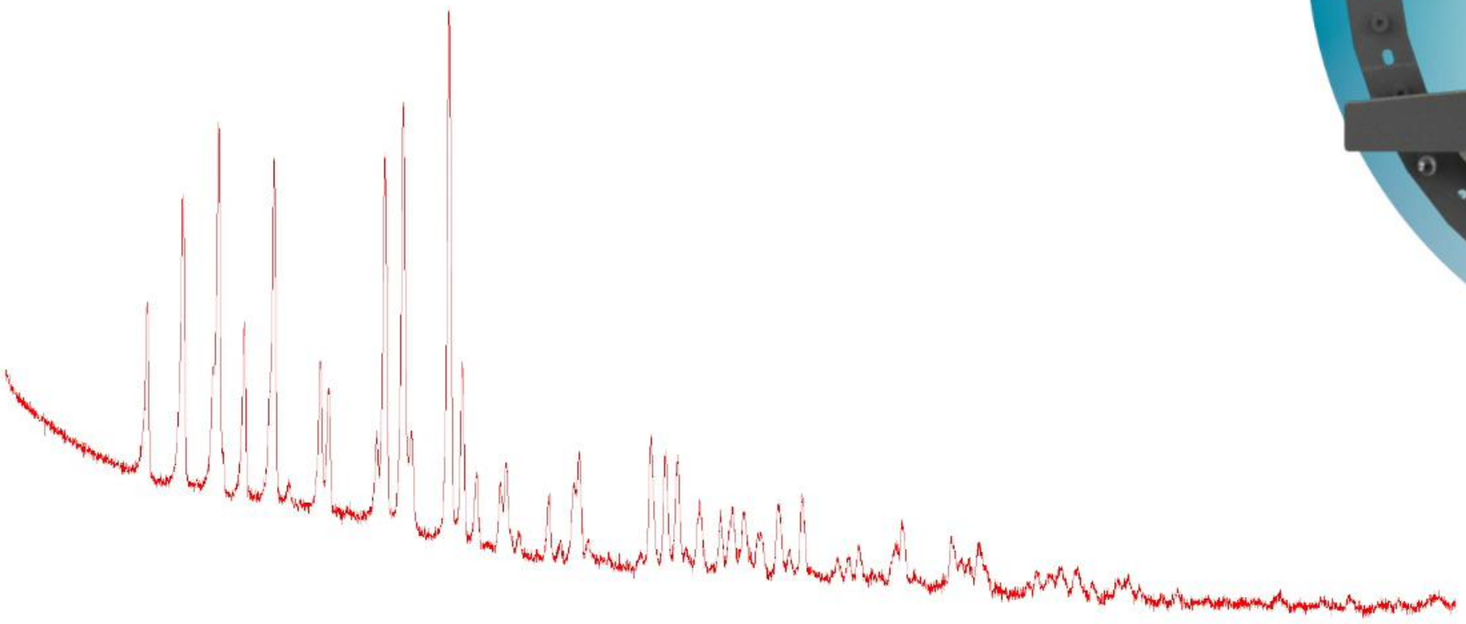
2D XRD

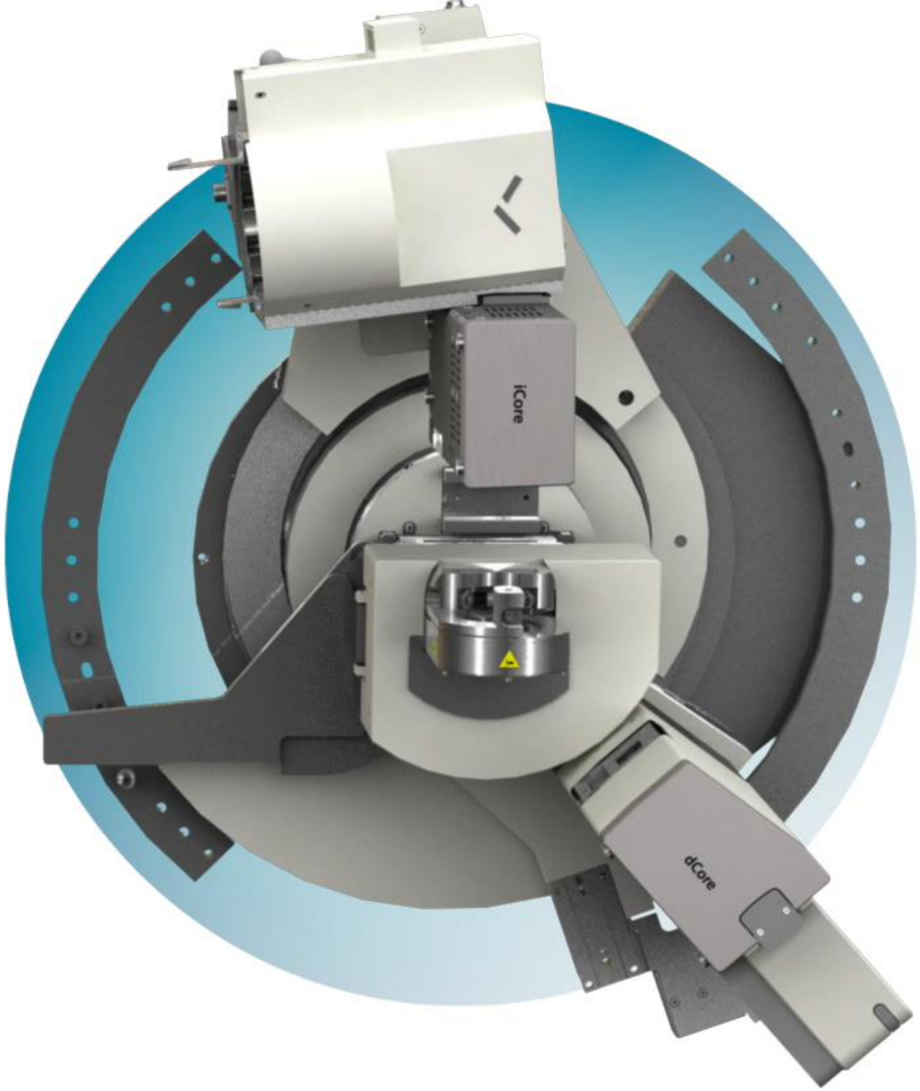




MultiCore Optics
iCore and dCore

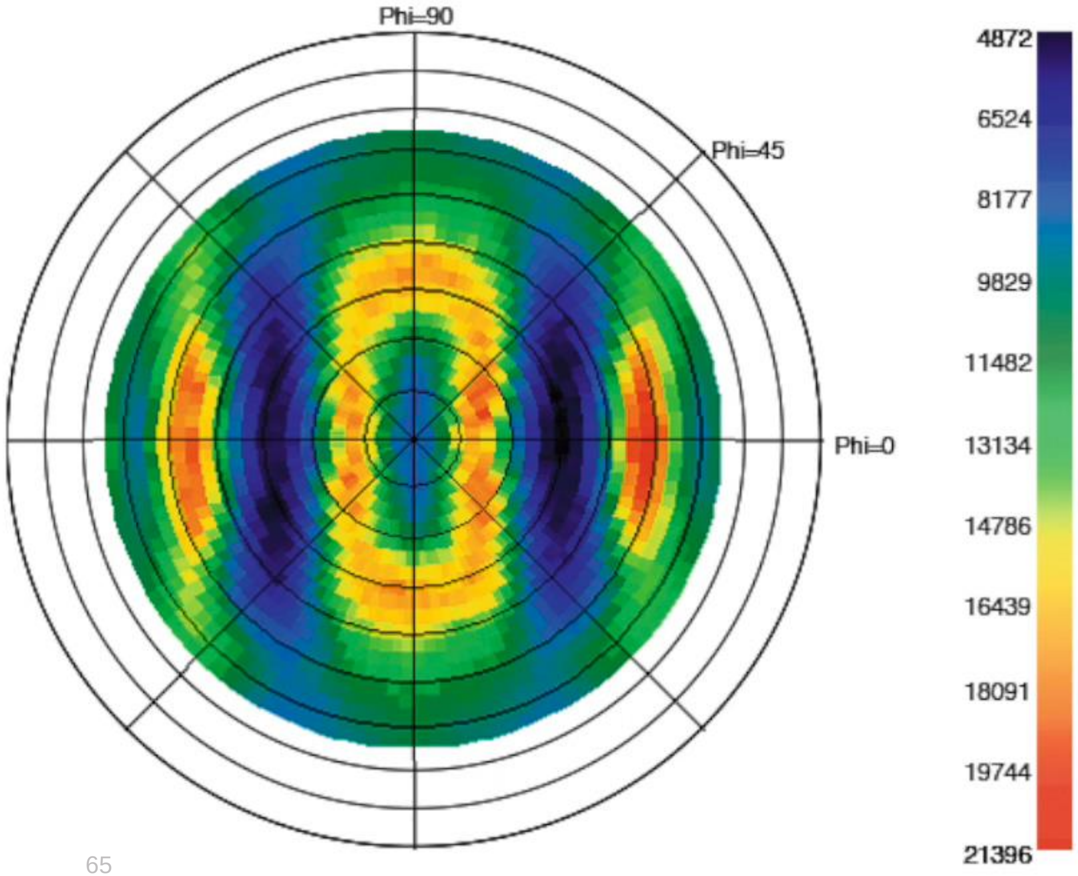
Transmision XRD

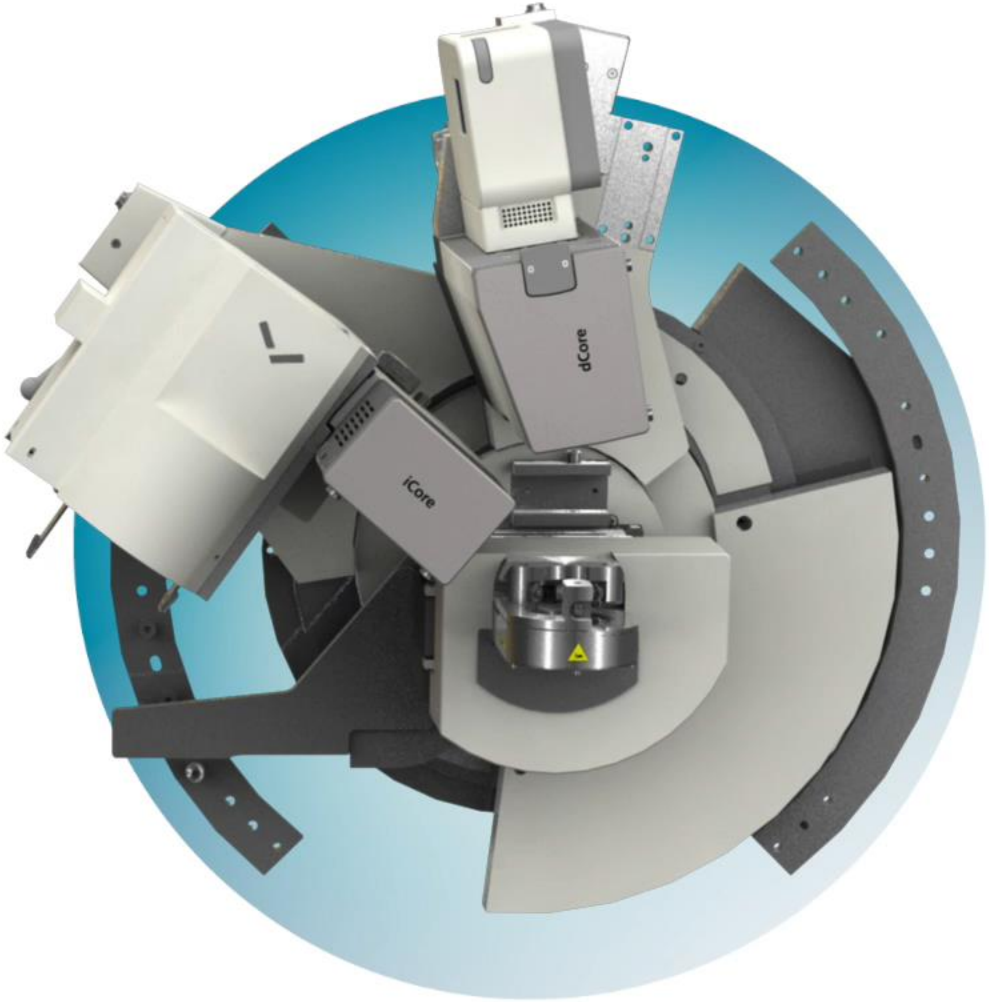




MultiCore Optics
iCore and dCore

Pole figures

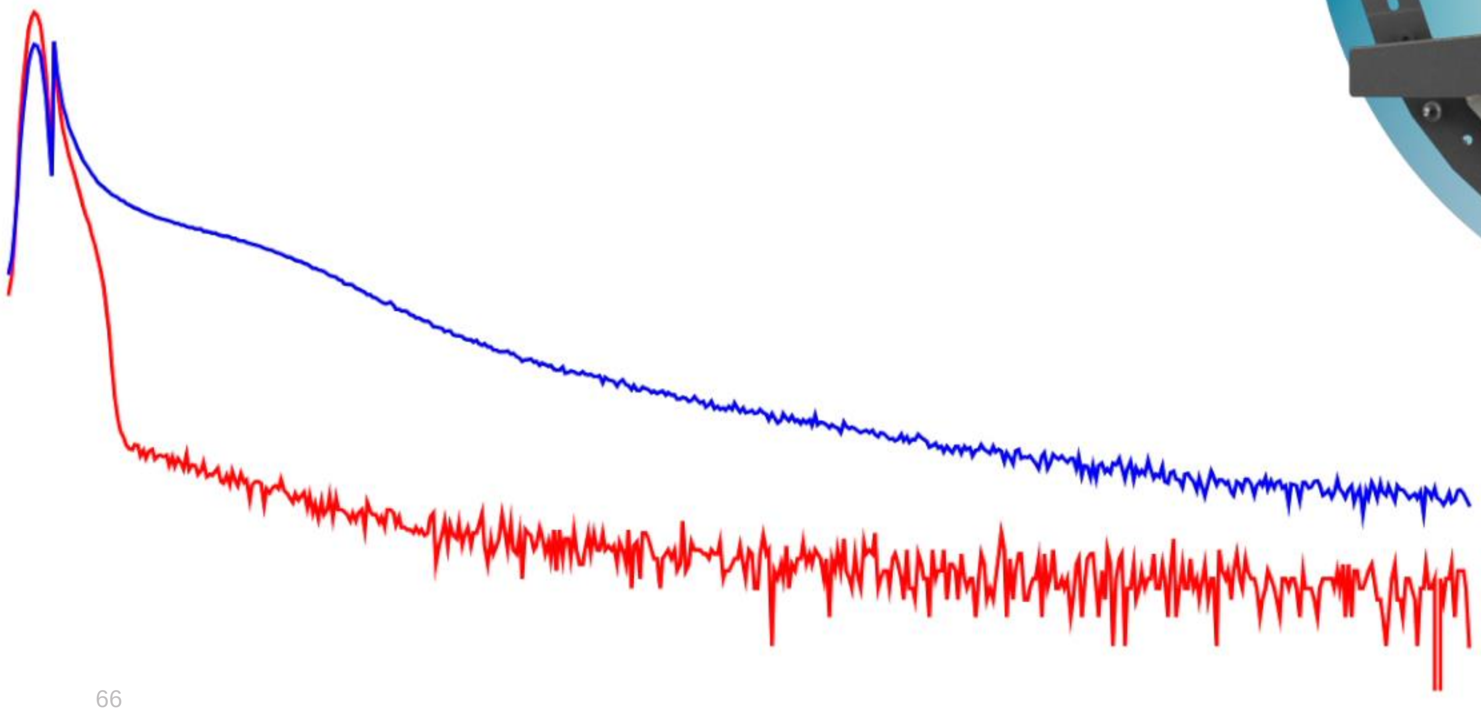


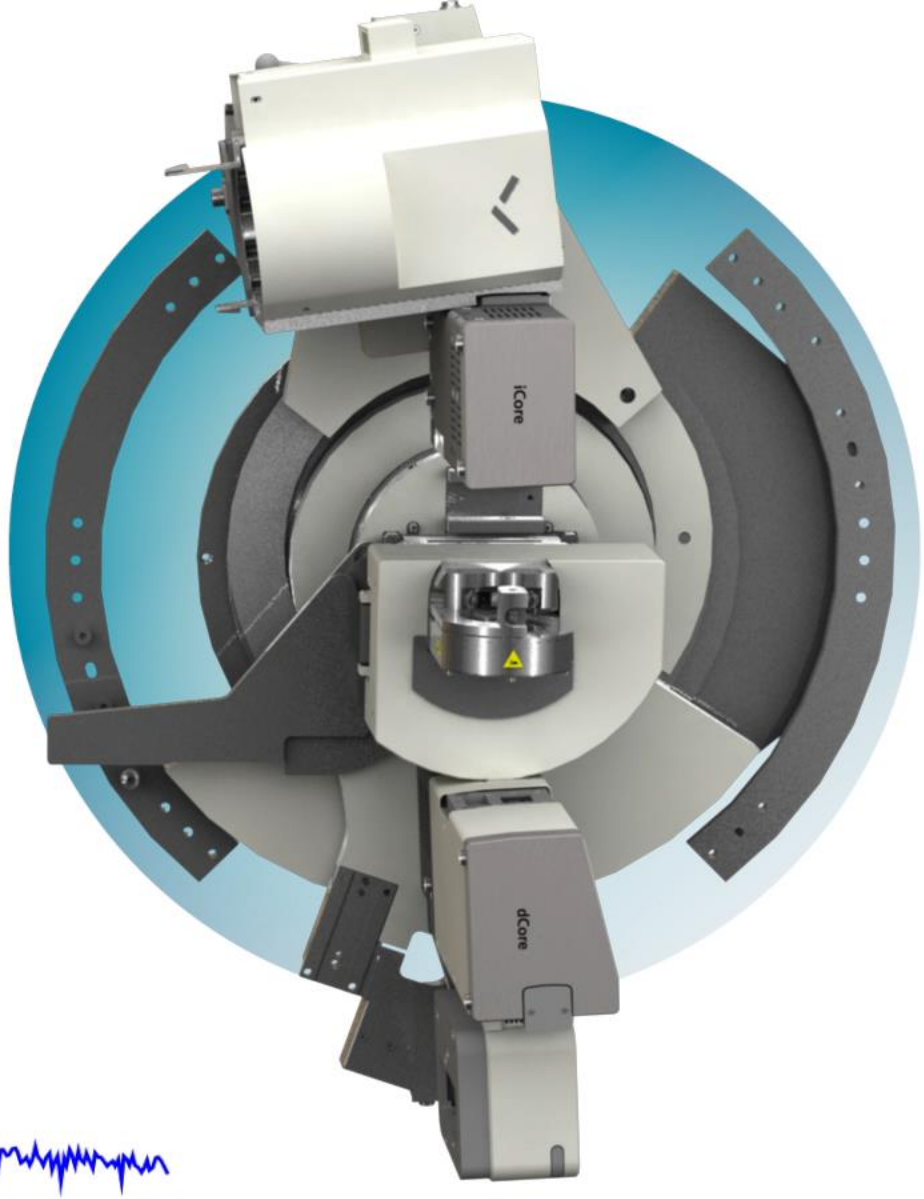


MultiCore Optics

iCore and dCore

Small-angle X-ray scattering





XRD for metals and hard metals

- Traditionally XRD analysis for this type of materials evolves around the following applications:

• **Phase analysis**	identifying and quantifying the various metallic phases and differentiating their different modifications
• **Line profile analysis**	determining crystallite size and micro-strain inside the allowing information about crystallization during processes and presence of defects inside the crystal structures
• **Grazing incidence XRD**	determining depth dependent variations (phase composition/residual stress)
• **Residual stress analysis**	quantifying the amount and regime (compressive, tensile, shear) of residual stress
• **Texture analysis**	quantifying preferential orientation of crystallites induced by processes to estimate anisotropy
• **Micro-diffraction**	determining lateral variations in phase composition, stress and texture
• **Non-ambient analysis**	determining behavior and phase transitions under non-ambient conditions
• Potential other applications:	**Computed tomography** and **reflectometry**

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