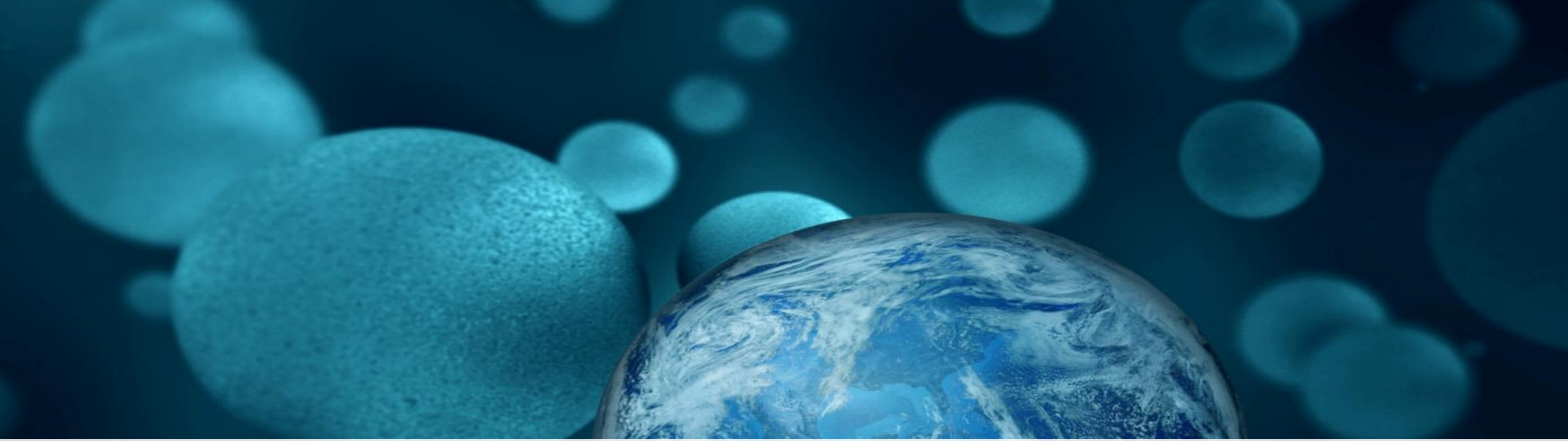


ThermoFisher SCIENTIFIC

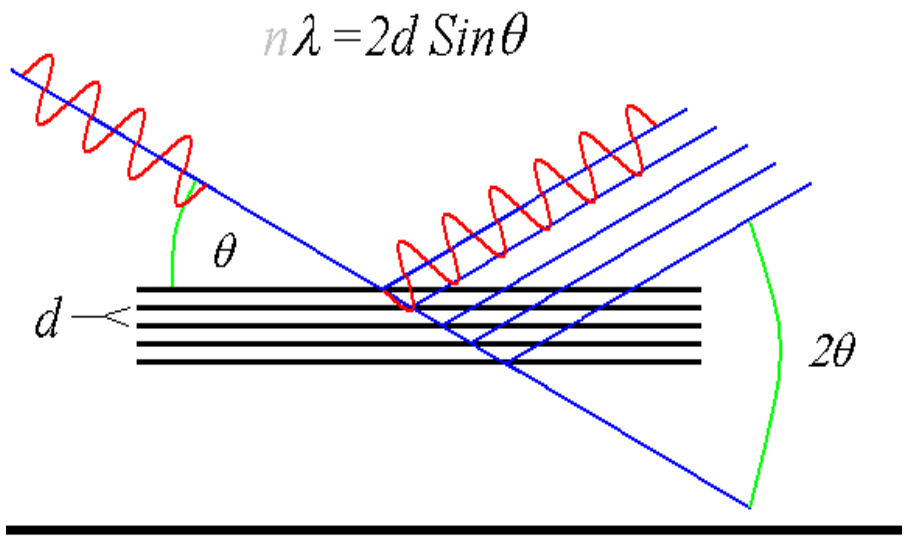
ARL EQUINOX XRD

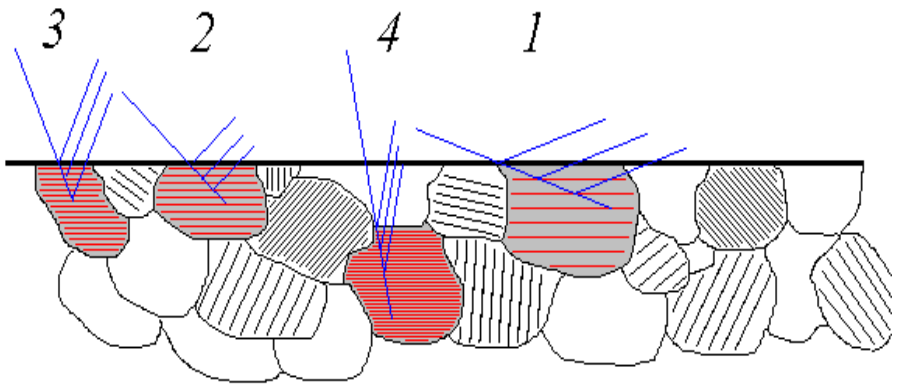
Real-Time X-ray Diffraction Solutions for Industrial and Research Applications

***Sofia,* October 2016**

Dr. Christophe Fontugne
Global application Manager

X-Ray Diffraction basics (1/3)





- Planes of atoms act like a diffraction grating
- Constructive & destructive interference lead to peaks in scattered intensity
- Example of 4 compounds/minerals each with different crystallographic orientations
- Values of λ & d determines 2θ

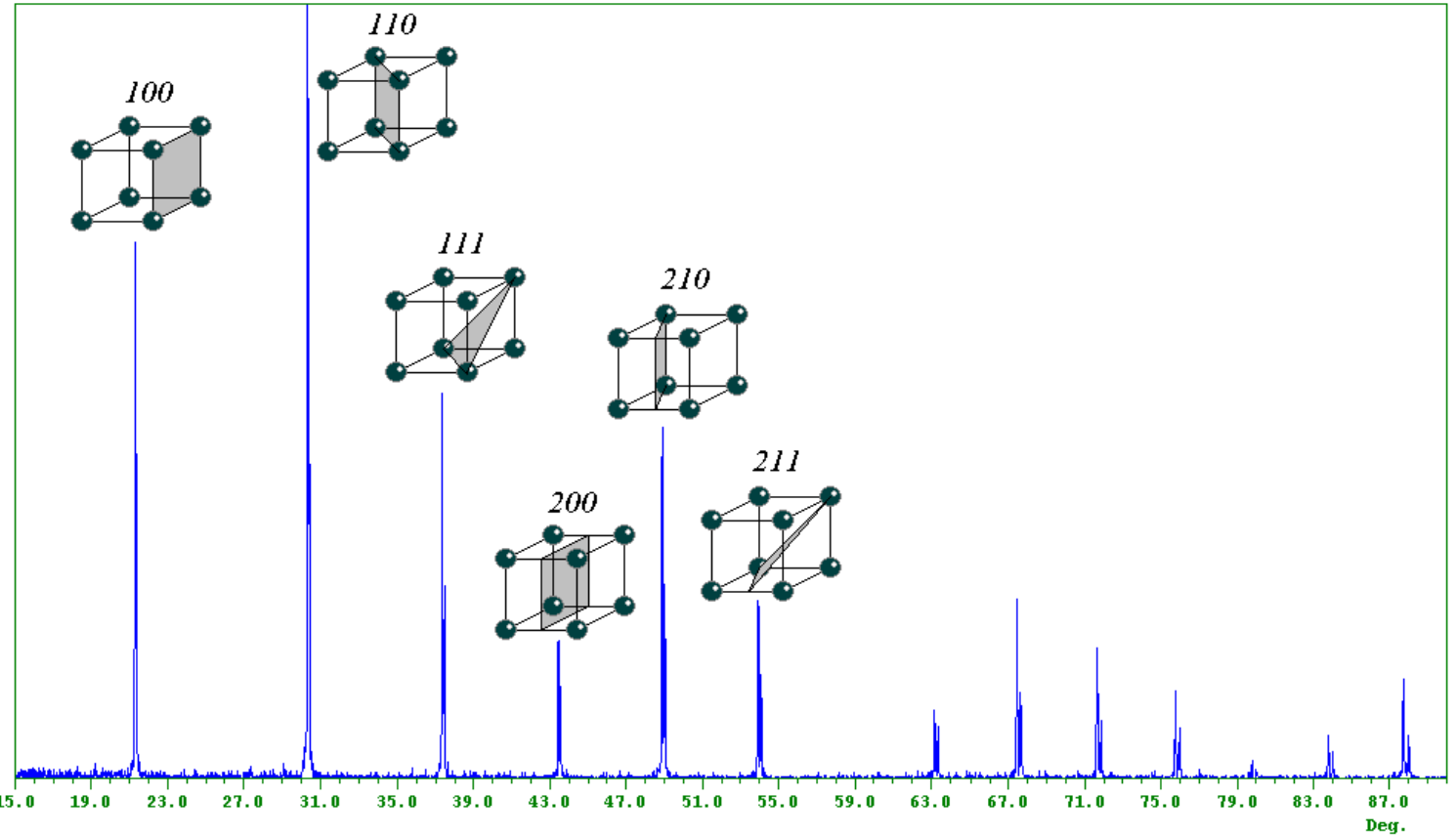
Bragg's law : $n\lambda = 2d \sin\theta$

- Where
- n = order of radiation
- λ= wavelength of radiation
- 2d = latice spacing of crystallites in the powder sample for XRD
- θ = Bragg angle

X-Ray Diffraction basics (2/3)

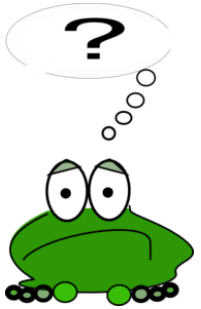
Peak position→d-spacings

Peak intensity→nature and atomic positions in planes



With XRD we measure distances...
… nothing more

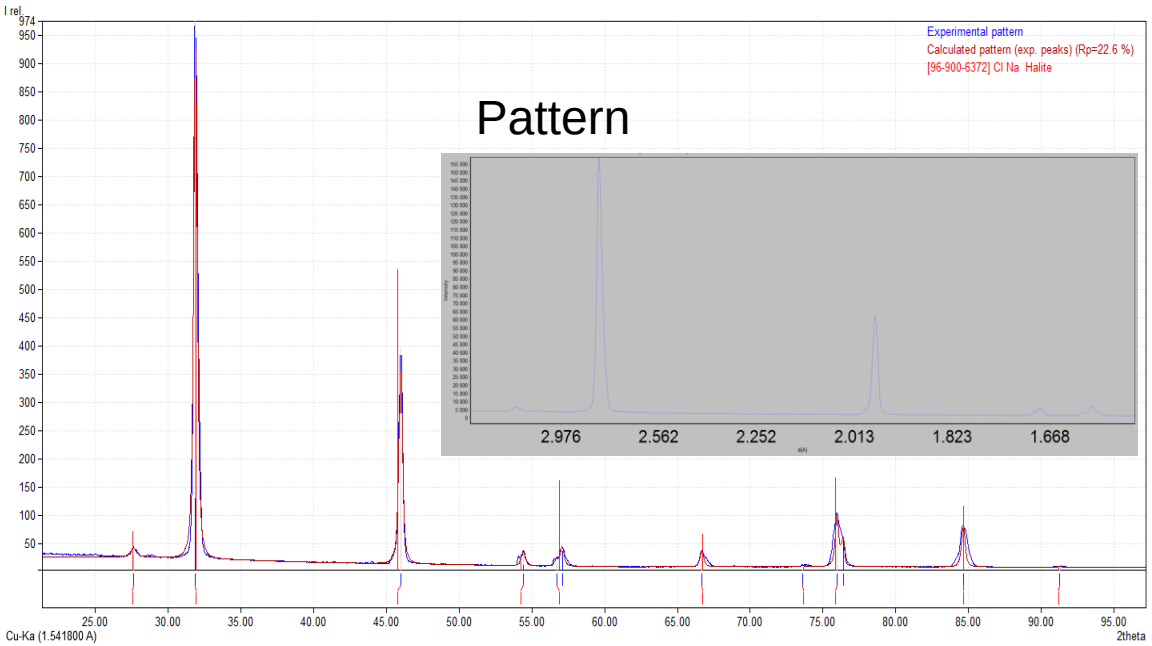
Chemical composition
Phases
Structure
…..



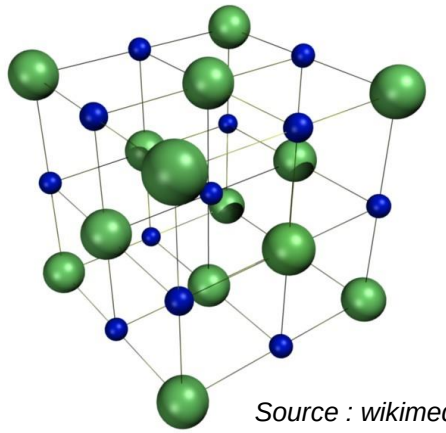
X-Ray Diffraction basics (3/3)

DATABASE

Without a Database we can not do much...



DATABASE



Source : wikimedia

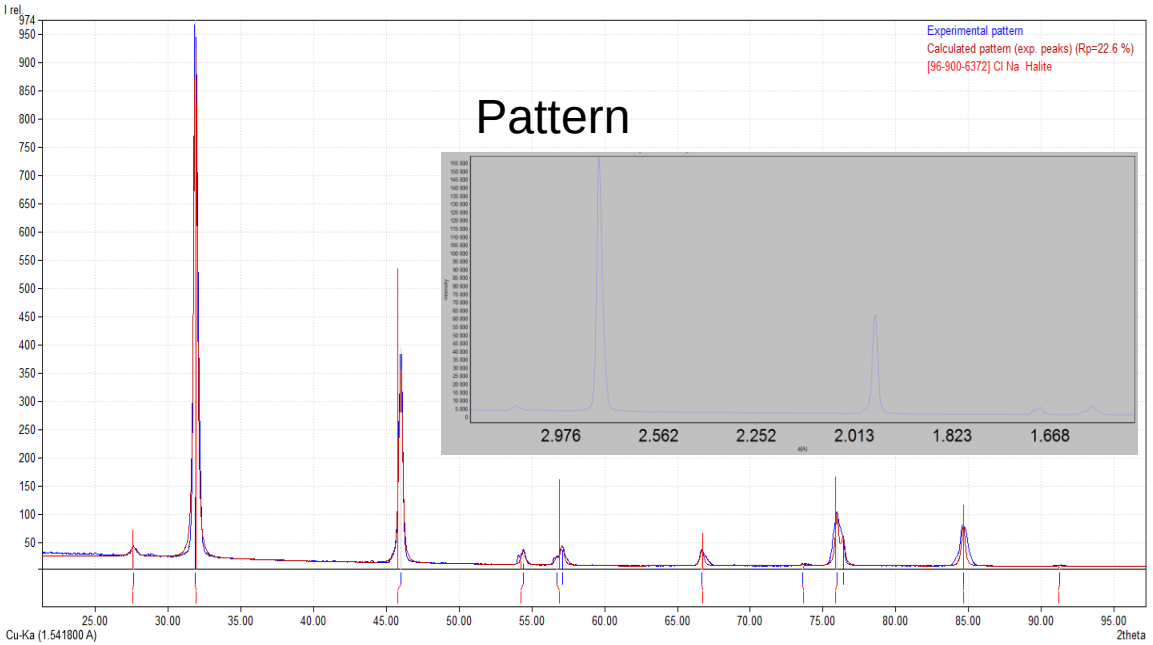
Halite (NaCl)...

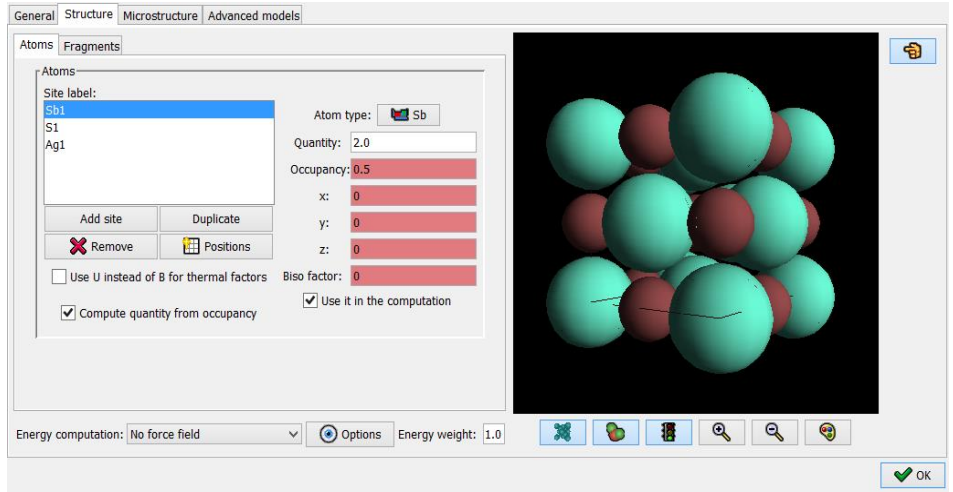
… should give this pattern

ThermoFisher SCIENTIFIC

One important issue with XRD : isomorphism

This is one real issue with XRD





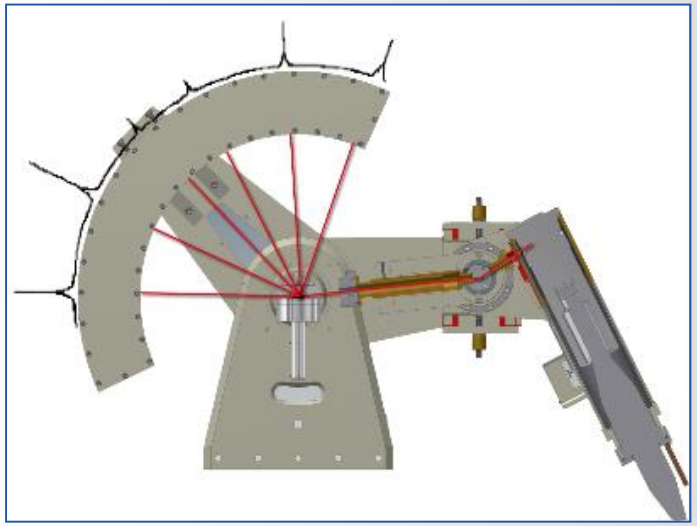
AgS_2Sb has the same structure as NaCl !!!

A complementary technique sensitive to chemistry is helpful

From simple bench-top XRD to more flexible platforms

It is a real time XRD system based on a curved detector

• Working principle



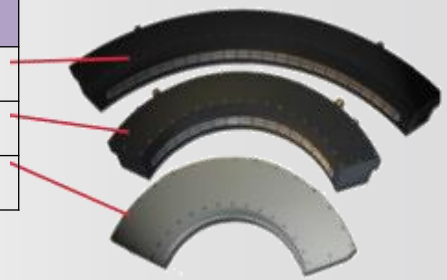
Curved detectors principle

The EQUINOX diffractometers use the curved detectors principle, namely real time acquisition across a wide acquisition range.

- No motorization required (no wear, accuracy)
- Asymmetric acquisition mode: for a single θ sample incidence you can see all diffraction peaks on the detector

• Version

	Detection angular Range	Curvature (mm)
CPS590	90° 2θ	500
CPS120	120° 2θ	250
CPS180	110° 2θ	180



Analysis Speed & Resolution

No mechanical movement and no maintenance

Full diffraction pattern in few minutes

We have 2 Desktop XRD instruments in our portfolio.

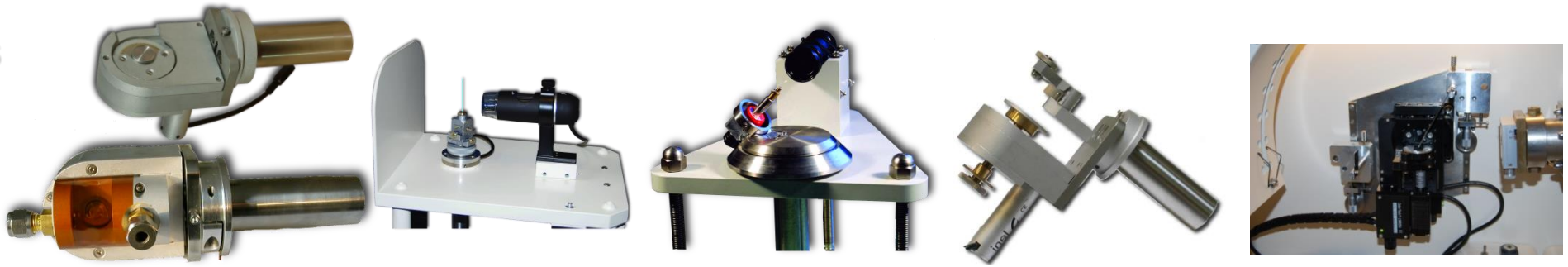
Equinox 100

- Equinox 100 is based on latest micro-source technology
- Very high photon density, low power source
- Smart Optics™ (Multilayer mirror optics)
- Low power requirements, no external cooling
- Can work on battery if needed (car battery)

Equinox 1000

- Equinox 1000 is a full-size instrument made compact
- 3kW generator, no power limitation
- Standard X-Ray tubes
- Water cooling required

Various Sample holders



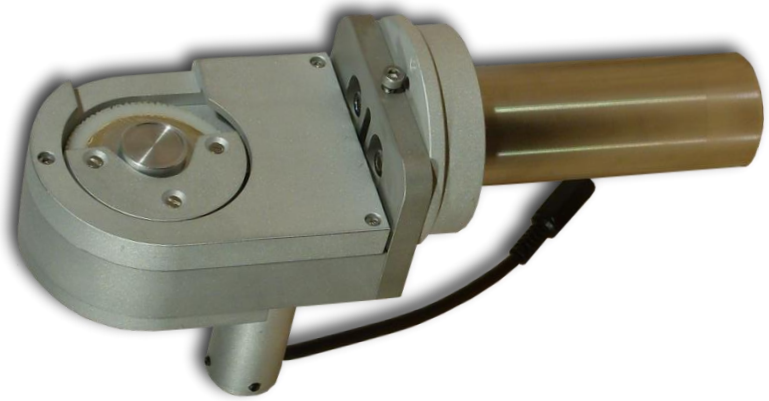
Description

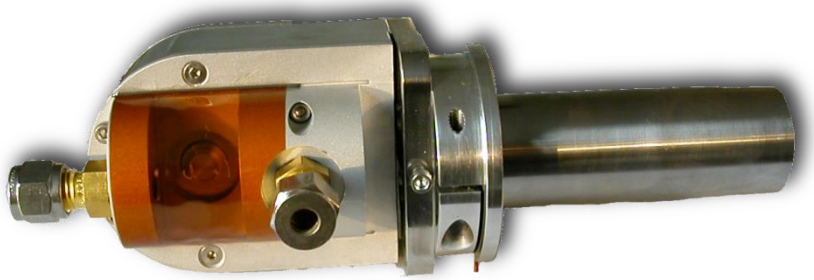
- **Desktop (680 x 582 x 524mm)**
- **Lightweight 75 Kg**
- **Easy to install, run and maintain**
- **No Alignment needed**
- **MicroSource coupled Smart Optics™**
- **No external cooling**
- **No external gas supply**
- **Standard electric plug**
- **<200W Total power consumption**
- **6 Positions auto-sampler (optional)**
- **Thin layer attachment (optional)**
- **Only 1 LAN cable for communication**

Technical aspects

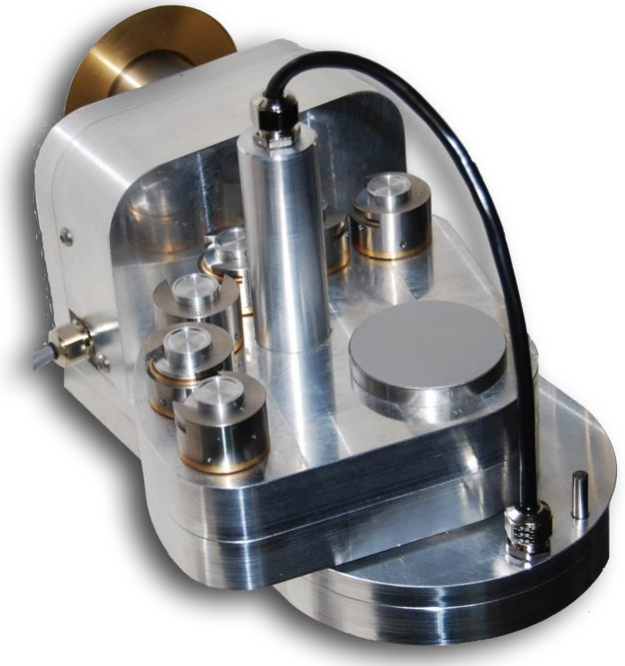
- X-Ray µSource : 50W with thermostatic regulation
- Multilayer mirror
- Latest CPS180 Real time detector
- Slit assembly
- Spinning sample holder
- Software under Windows 7
- Accessories (calibration powder, reference sample holder...)

SSRT : spinning sample holder



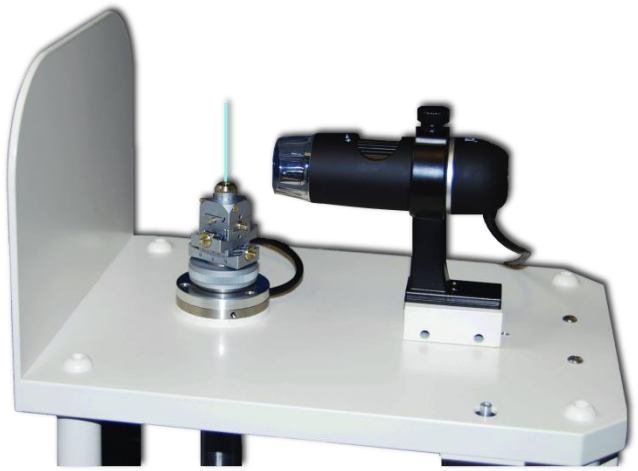


Controlled atmosphere sample spinner



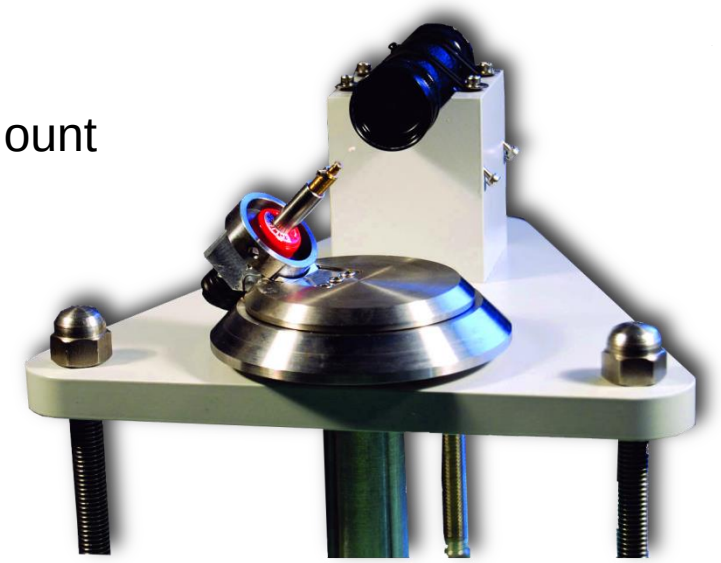
Sample changer :
6 Positions

Equinox 100 : Transmission

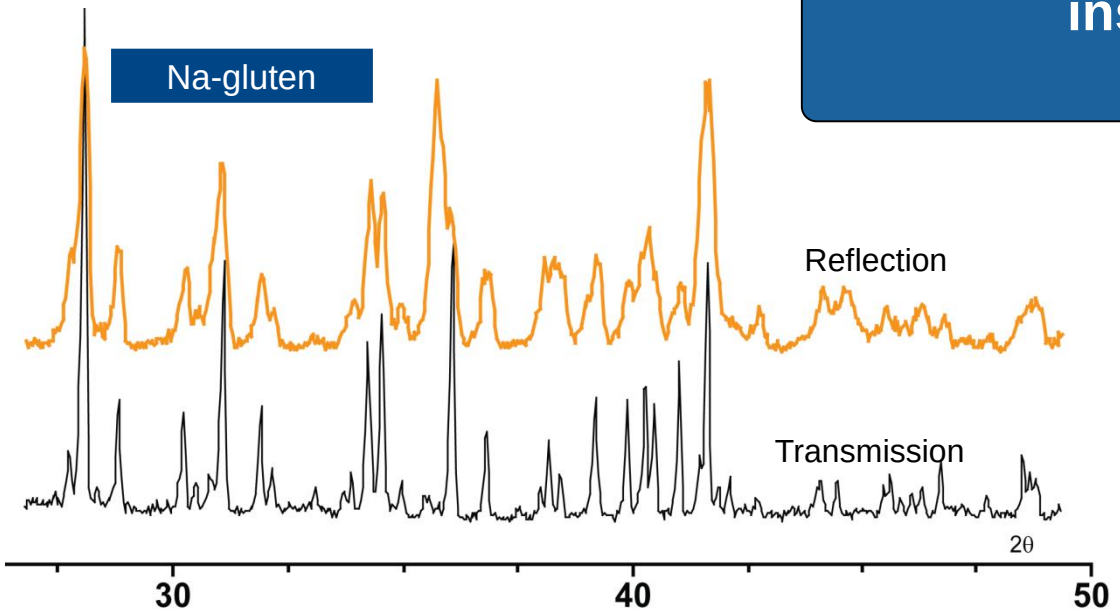


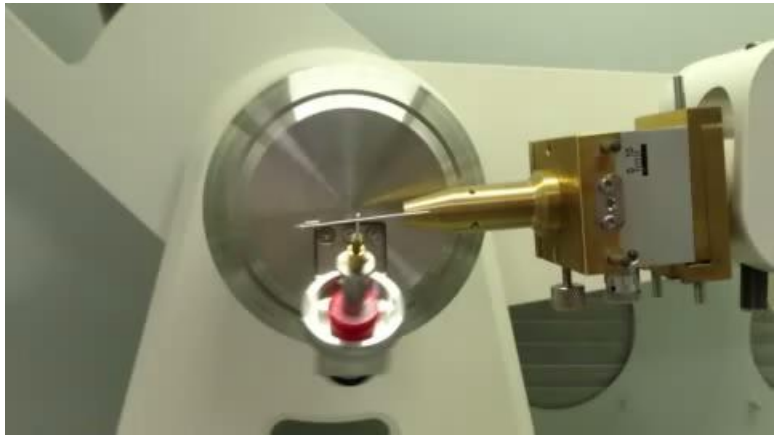
Capillaries

Gandolfi Mount



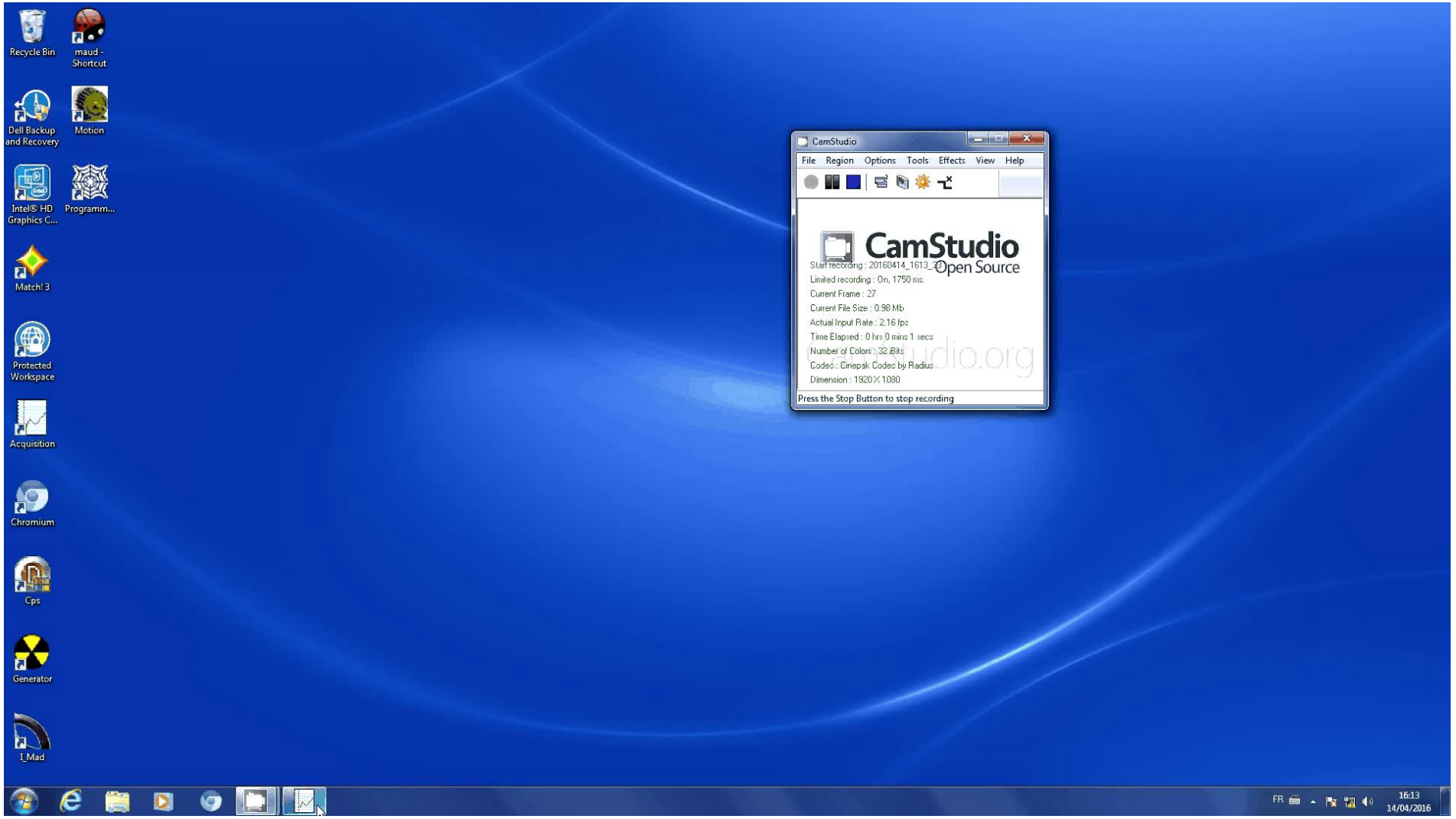
Unique feature for a desktop instrument



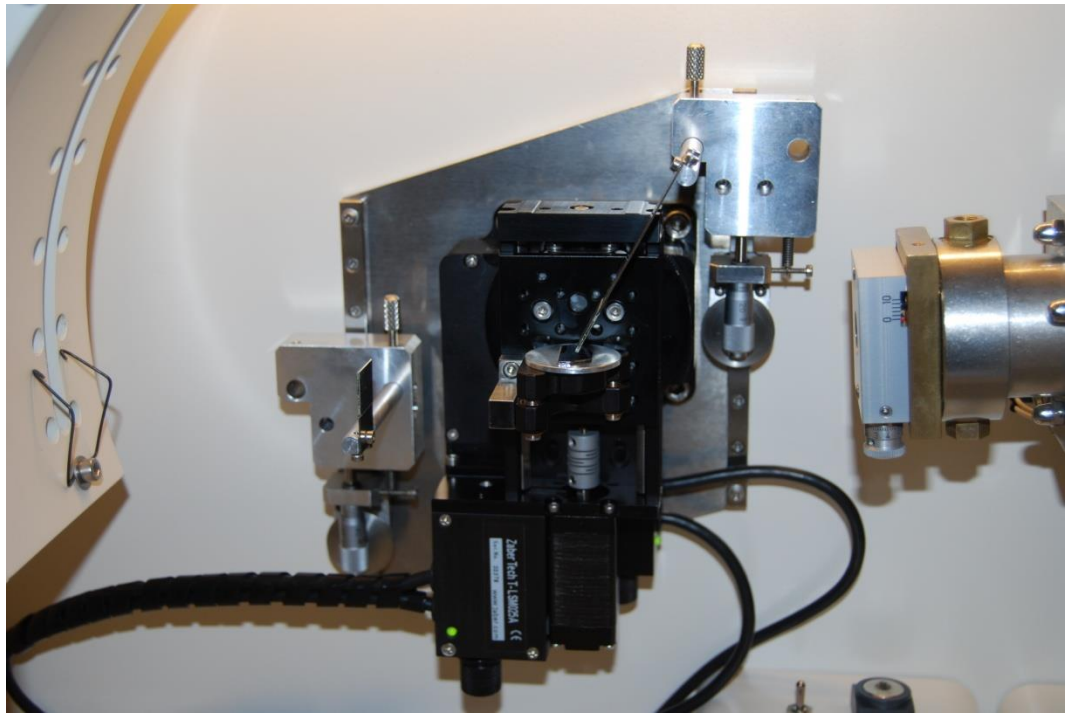


ThermoFisher SCIENTIFIC

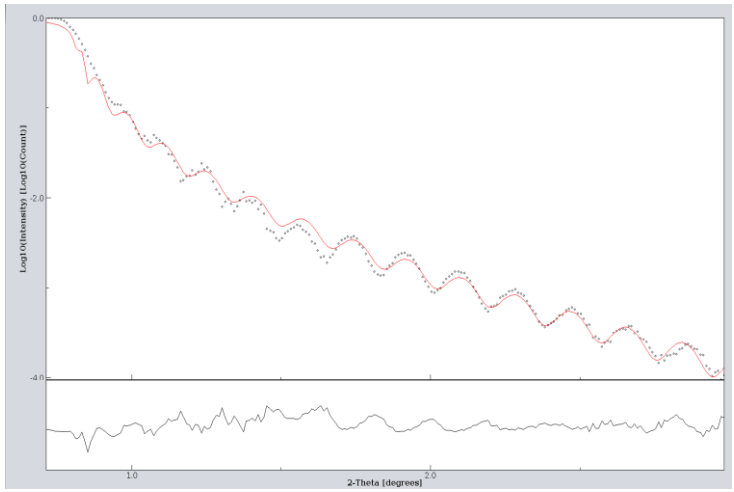
Equinox 100 : Example 1 Y2O3 powder



Equinox 100 : Thin Layer - GIXRD



Thin layer : GIXRD – XRR
Bulk Samples
Uniaxial stress (omega scan)

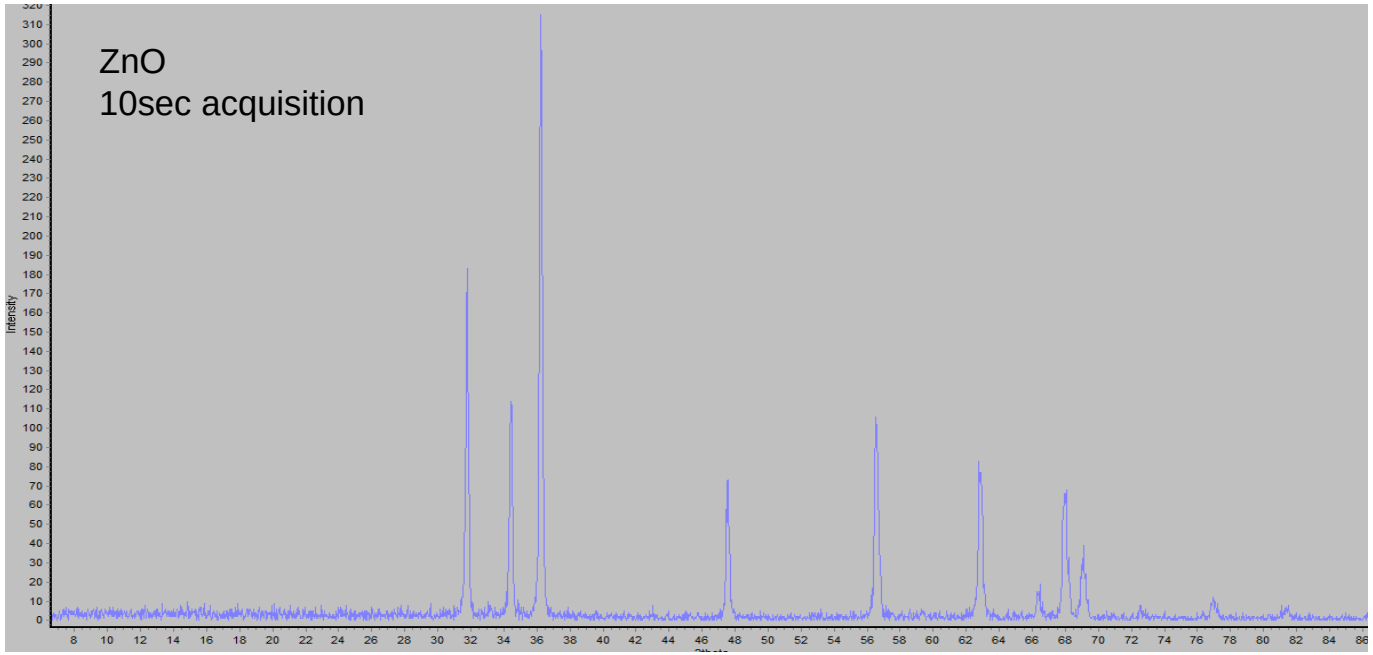


X-Ray Reflectivity curve
5nm Nb layer

Unique feature for a desktop instrument

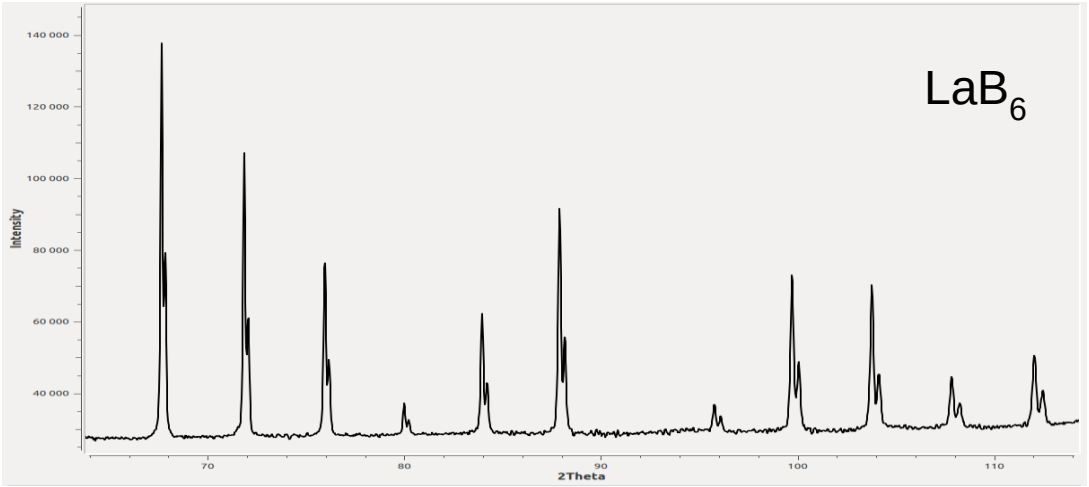
Equinox 100 : Performance (Sensitivity and Resolution)

Peak/Background equivalent to high power XRD



Equinox 100' sensitivity enables fast measurement times even with its low X-ray power

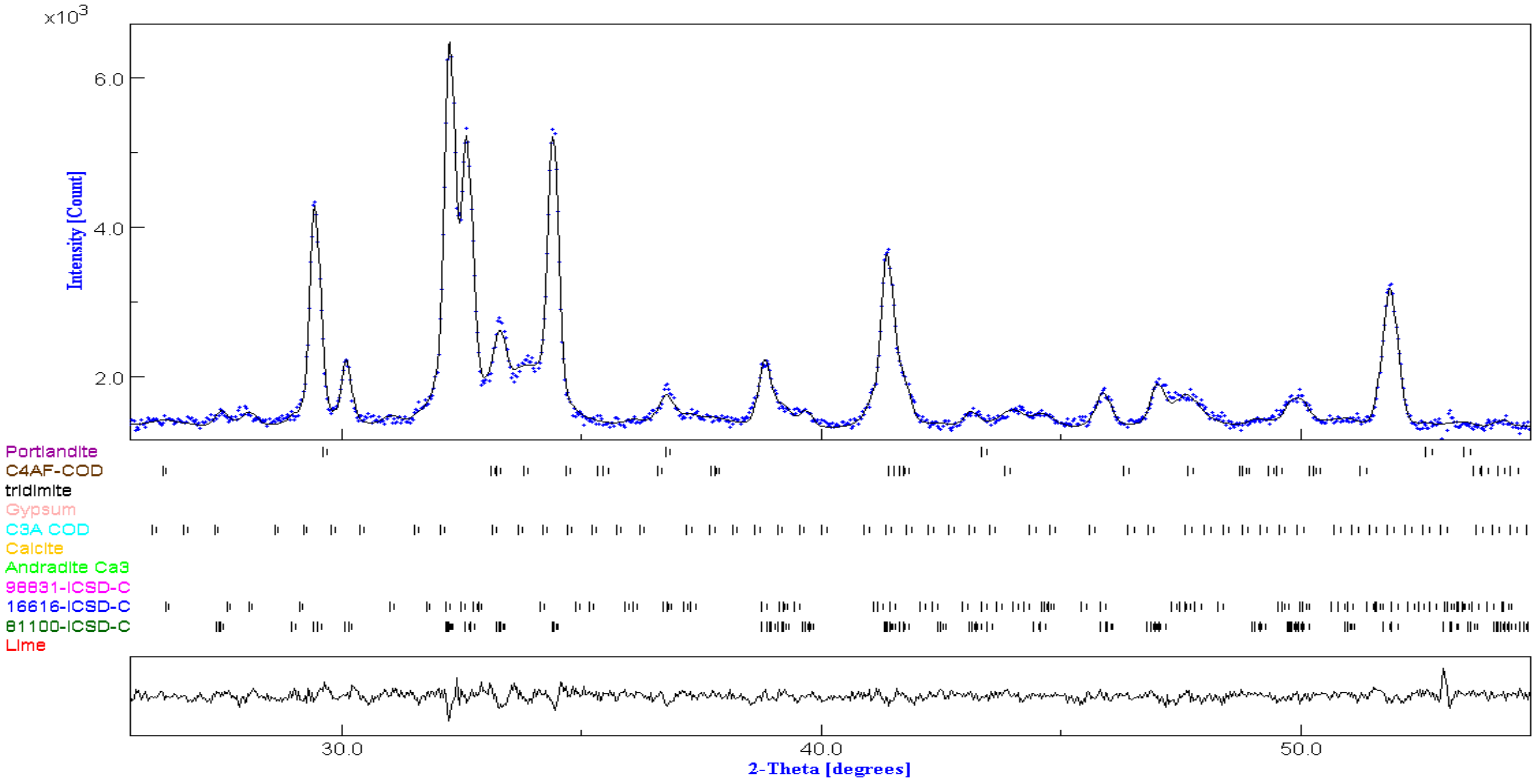
Equinox 100 resolution comparable to any standard XRD



Routine measurements on powders :

- Phase identification / quantification
- **Quality control**
- Full Rietveld refinement (Quantitative analysis...)
- Easy to use, high-throughput, thanks to short acquisition time

Equinox 100 : Rietveld refinement on Clinker

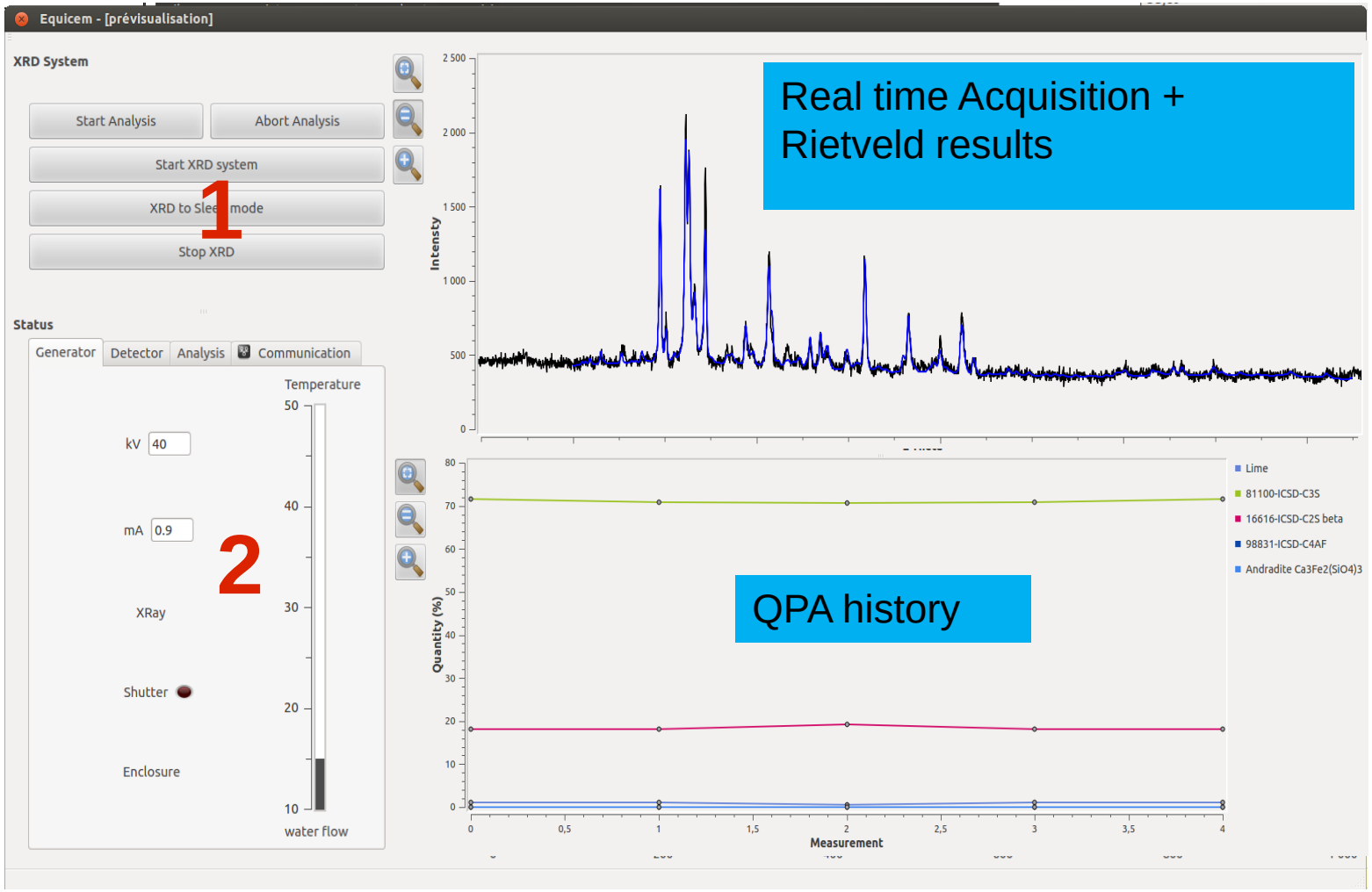


Equinox100 standard, 15 minutes for 110°

EquiCem : Wizard based QC QPA automatic rietveld analysis software

Simple Graphical User Interface

Live Displays



Rietveld analysis Results – Equinox 100

	Equinox-100
Anode Tube	Cu
Power	40W
Repeats	12
Time per repeat	300s
Rietveld Analysis	
C3S	67+/-0.45
C2S	19+/-0.49
C3A_c	0.9+/-0.08
C3A_o	8.7+/-0.20
Free lime (NiO)	**1.25+/-0.09**
Anhydrite	1.01+/-0.13

Precision test 12 runs :

12 repeated scans of the same cement material doped with NiO (to represent free lime)

300s counting time Repeatability of the Rietveld analysis

Equinox 1000: The Only Bench-Top XRD with high power

Description

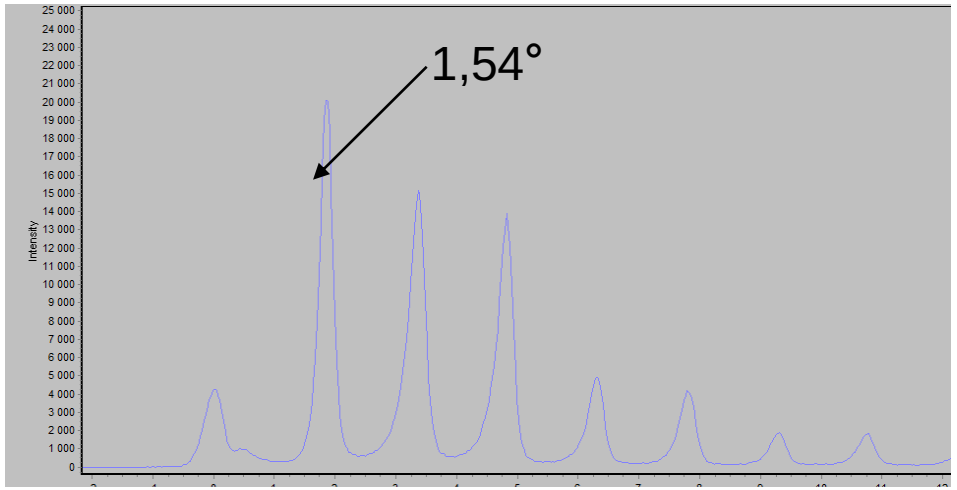
- **Bench top, but 180kg**
- **Compact : 996 x 715 x 750 mm**
- **3kW Generator (no limitation)**
- **Standard X-Ray tube**
- **CPS180 like Equinox 100**
- **External water cooling required**
- **No Alignment needed**

The only benchtop XRD without power limitation available

ThermoFisher SCIENTIFIC

Equinox 1000: Standard Power XRD on a bench-top with much faster analysis times

- Higher resolution than EQ100
- Real Generator (3 kW) (miniflex is 600W)
- Pure Kα1 with Ge(111) monochromator (not possible with competitor benchtop systems)
- Even SAXS
- Sample changer : 30 positions



Equinox 1000 Configuration

X-Ray tubes : Copper or Cobalt

Cobalt : Iron containing samples, Organics

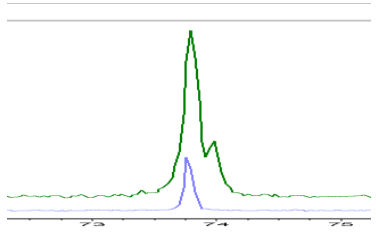
Copper : most widely used

Germanium (111), graphite or SiamX (option)

Germanium : pure Kα,1 high resolution, "pure patterns", low intensity

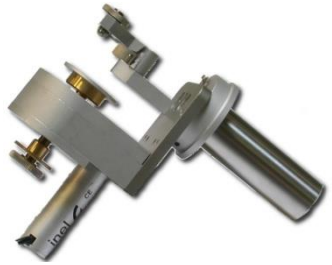
Graphite : high intensity at low cost (5 times faster than Ge), about same speed as Equinox 100

SiamX : both monochromators in same housing



Sample holder : SSRT, or SSRZ bulk sample holder, Thin layer, transmission...

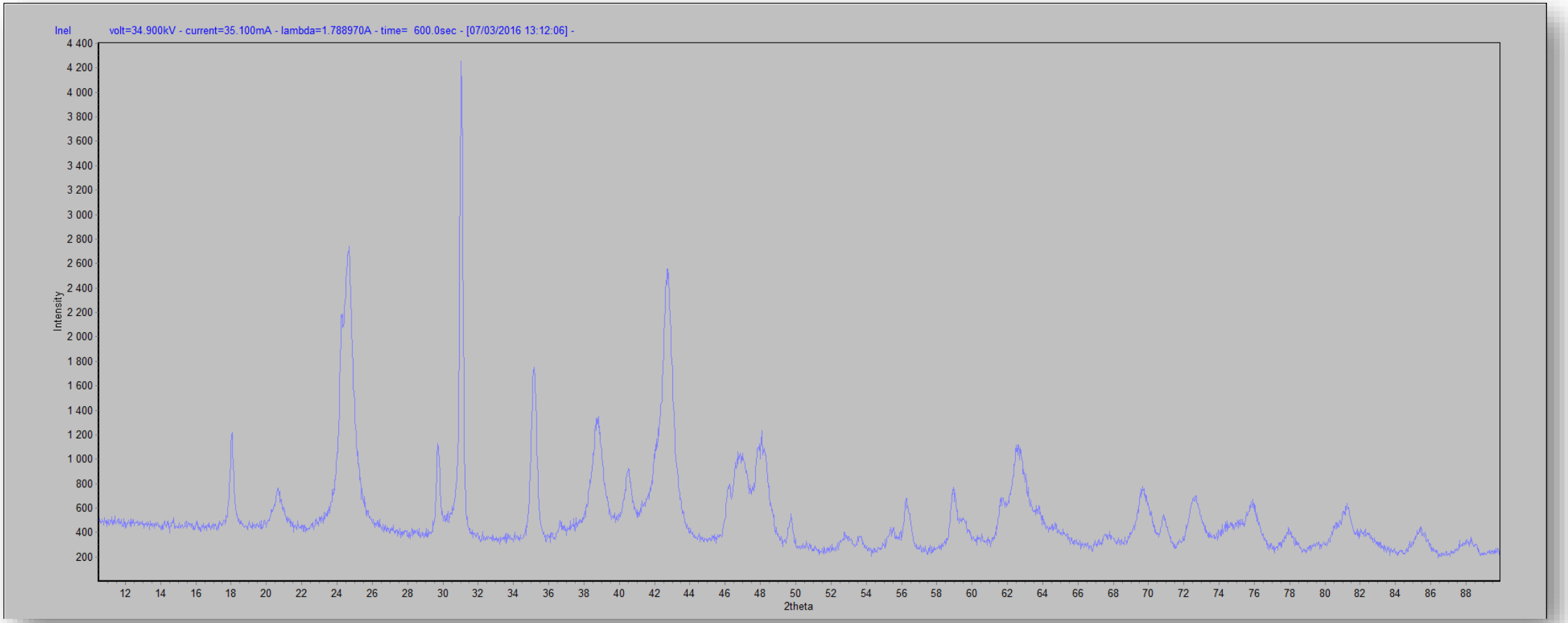
SSRT : spinning sample holder



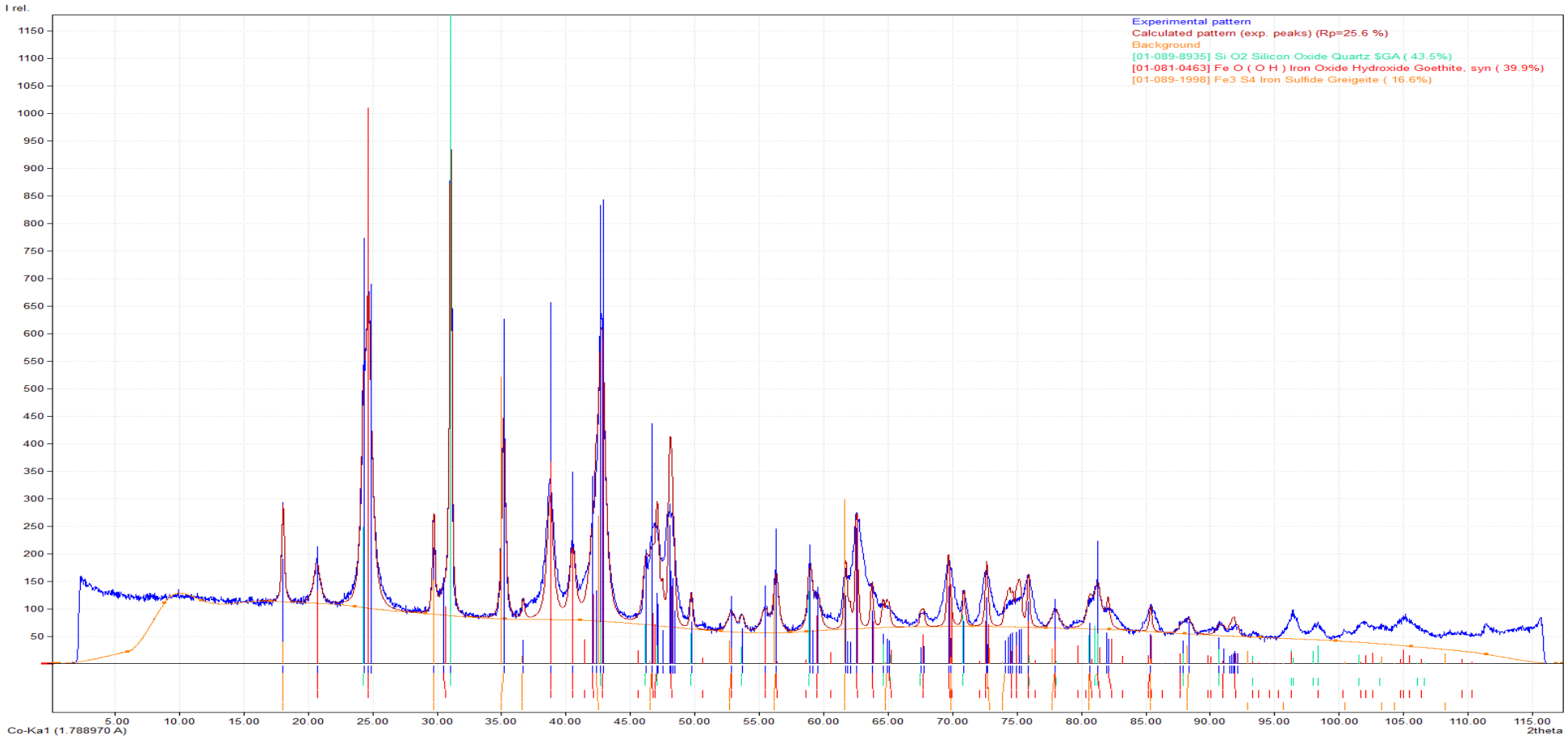
SSRZ : spinning sample holder

Sample spinner under controlled atmosphere

Geological sample : recorded 10min on Equinox 1000, with Graphite monochromator



Search / Match results : 40% Goethite (FeOH), 16%iron sulfide, 44% Quartz



Routine measurements on powders

- **Phase identification / quantification**
- Quality control (graphite monochromator preferred)
- XRR / GIXRD (with Ge monochromator)
- Rietveld refinement (Quantitative analysis...)

ARL Equinox 3000 / 3500

Most sold versatile research grade XRD in our product portfolio

ThermoFisher SCIENTIFIC

Equinox 3000 / 3500

- **State of the art Powder XRD**
- **Versatility is the key word**
- **CPS120 detector (Equinox 3000)**
- **Or CPS590 (Equinox 3500) for high resolution system**

Similarities with previous Equinox systems

- Asymmetrical working mode (fixed incidence)
- Monochromatic primary beam
- No movements during acquisition
- Type of X-Ray generator
- Real time detection
- Powder diffractometer
- Ready for dynamic studies
- Ready for thin layer analysis

Equinox 3500

Different from desktop : versatility

- Wavelength : From Cr to Mo (for experts)
- Transmission with focusing Mirror (good optimization)
- Bigger sample size
- Bigger angular range (manual rotation)
- Temperature up to 2400°C
- More sample holders (humidity, DSC stage, diamond anvil etc....)
- Bigger optional motorized sample handling

Advanced measurements on polycrystalline samples

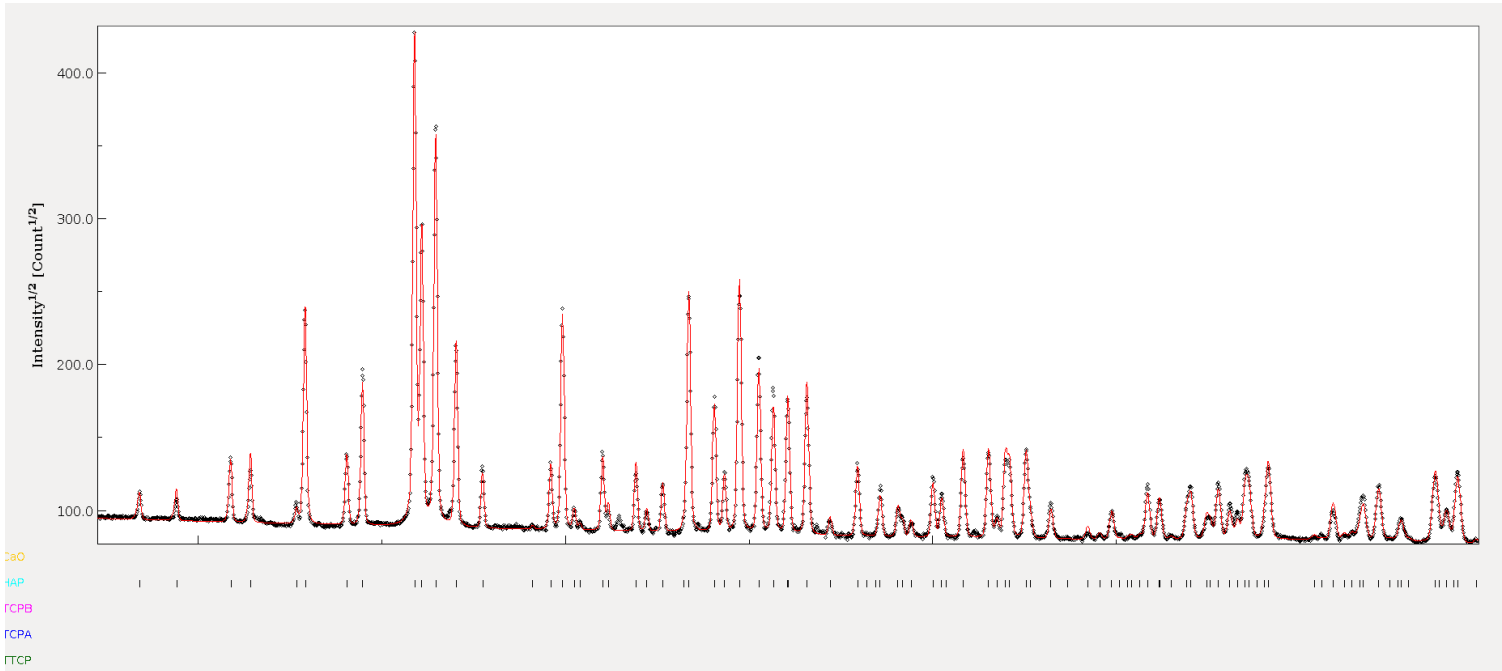
- Phase identification / quantification
- Research grade studies including Cell refinement (optional software)
- **High resolution static and dynamic studies**
- **Precise Rietveld analysis**
- SAXS capabilities (slightly below 1°)
- Thin layer/low quantity powders thinly spread
- Rugged -very low service cost
- Much more versatile from a mechanical point of view : Arms motorization, optics like mirrors, easier wavelength change etc....

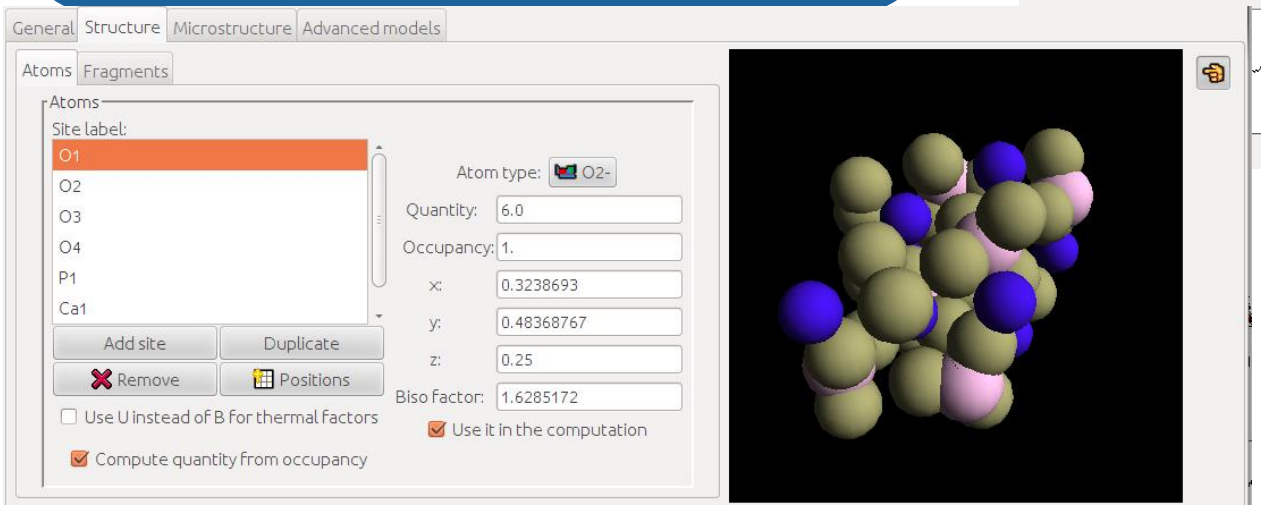
Equinox 3000 Example for research application: Structure refinement

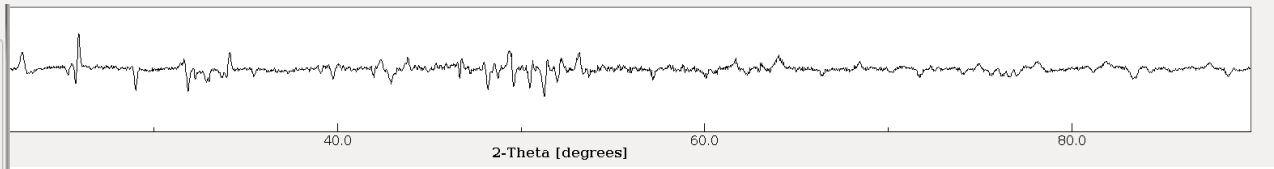
HAP (hydroxylapathite) sample : used in biomedical applications (bio-compatible prosthetic)

Recorded in transmission mode on Equinox 3000, Ge monochromator

Structure refined using MAUD software



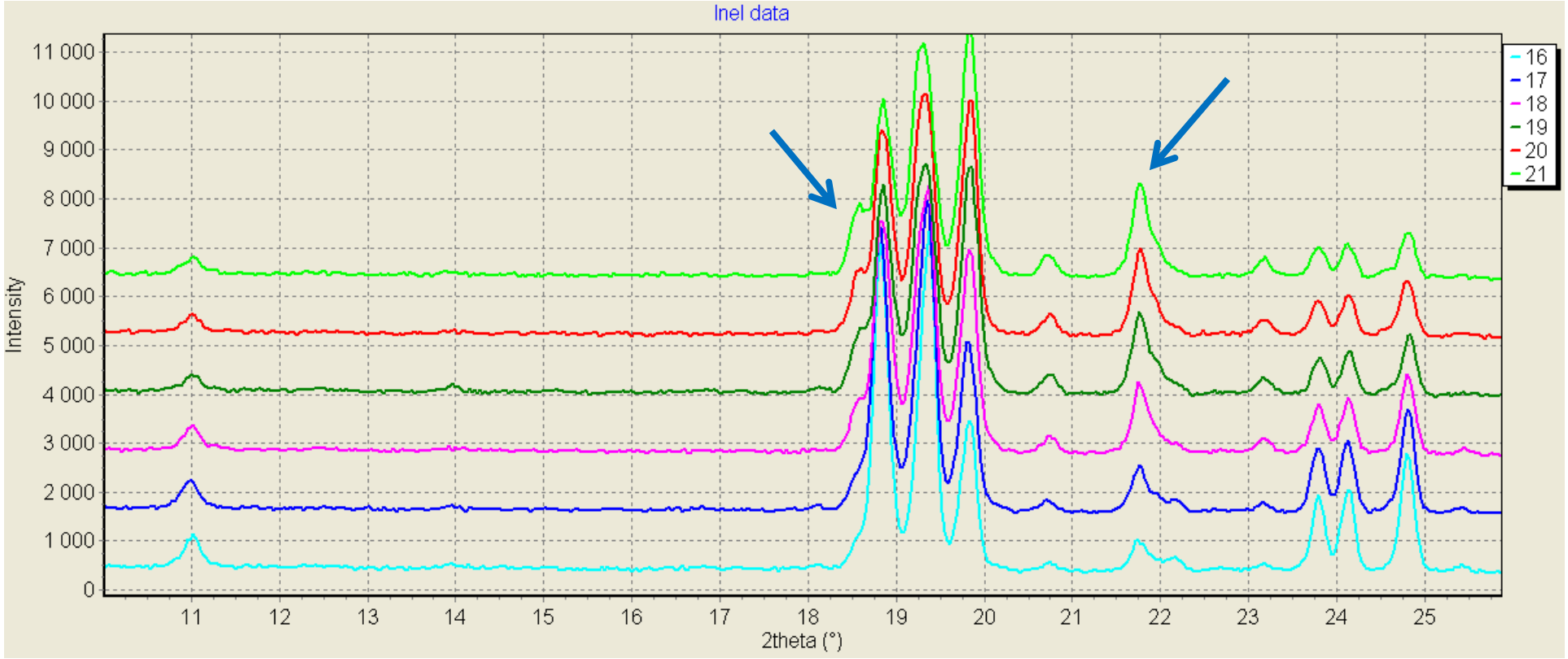




ThermoFisher SCIENTIFIC

Diffractograms

On the graph below, are represented diffractograms recorded for each sample. We can clearly evidence an increase of STPP 1 with the index (blue arrows).



Results

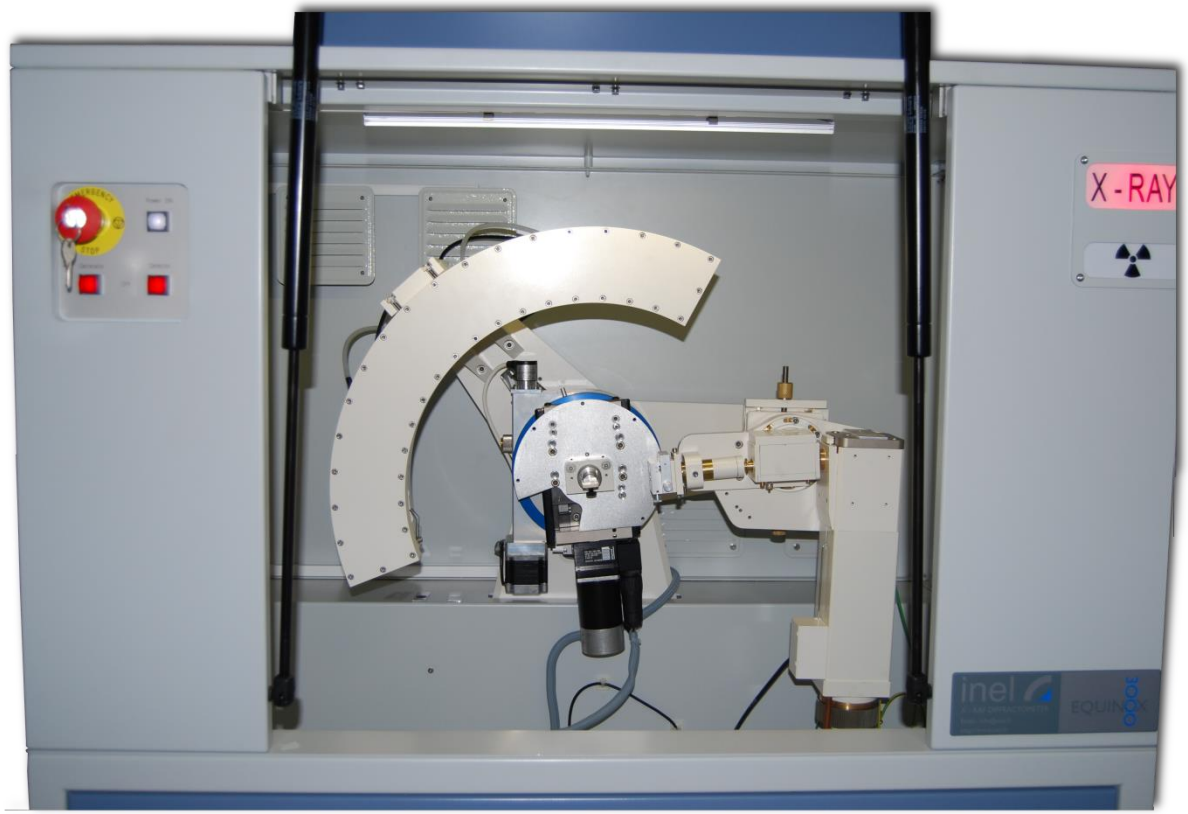
Quantitative analysis has been performed by using the Rietveld method, on10 min acquisition runs.

Good reproducibilité, and good agreement with other techniques (chemistry)

Expérience					moyenne					
		STPP I	STPP II		STPP I		STPP II			
Echantillons		Na5 O10 P3	Na5 O10 P3	Na5 P3O10,6H2O	Na5 O10 P3		Na5 O10 P3		Na5 P3O10,6H2O	
		740378	721083	760054	740378		721083		760054	
16	a	17,6	82,4	0,0	17,67	0,21	82,33	0,21	0,00	
	b	17,9	82,1	0,0						
	c	17,5	82,5	0,0						
17	a	25,9	70,7	3,4	25,90	0,20	70,73	0,35	3,03	0,32
	b	25,7	70,4	2,9						
	c	26,1	71,1	2,8						
18	a	40,8	57,0	2,2	40,90	0,17	56,93	0,31	2,17	0,58
	b	40,8	57,2	2,0						
	c	41,1	56,6	2,3						
19	a	50,6	46,1	3,3	51,35	0,54	45,23	0,60	3,43	0,13
	b	51,3	45,1	3,6						
	c	51,7	44,9	3,4						
	d	51,8	44,8	3,4						
20	a	51,2	46,3	2,5	51,17	0,45	46,57	0,38	2,27	0,25
	b	51,6	46,4	2,0						
	c	50,7	47,0	2,3						
21	a	60,7	37,4	1,9	60,20	0,56	37,93	0,50	1,87	0,15
	b	60,3	38,0	1,7						
	c	59,6	38,4	2,0						

Multilayer mirror optic

Runs with Anton Paar XRK900 reaction chamber



Photovoltaic Application

(Solar Cell)

(CH3NH3)PbI3

Structural change Vs

temperature.

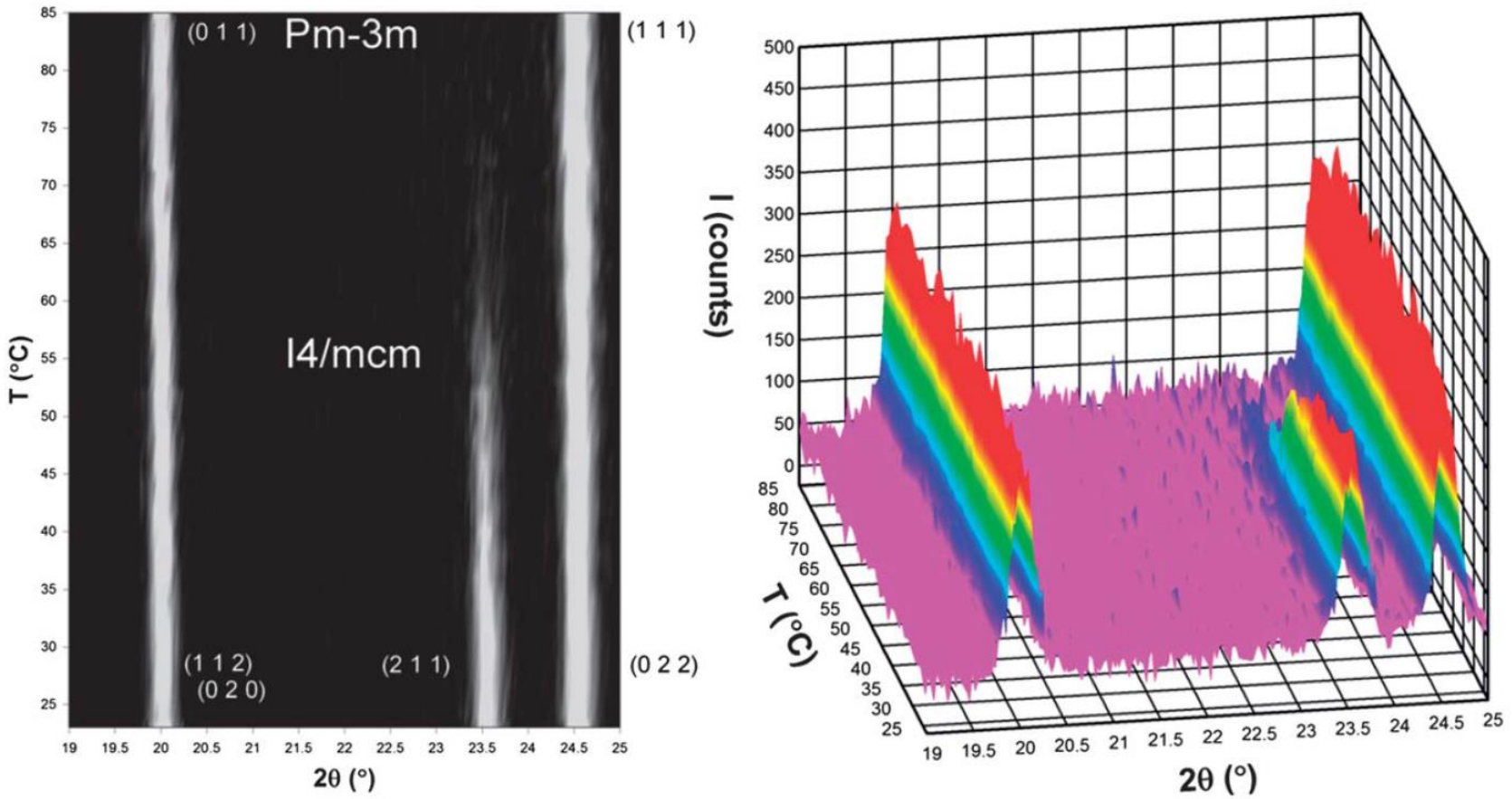
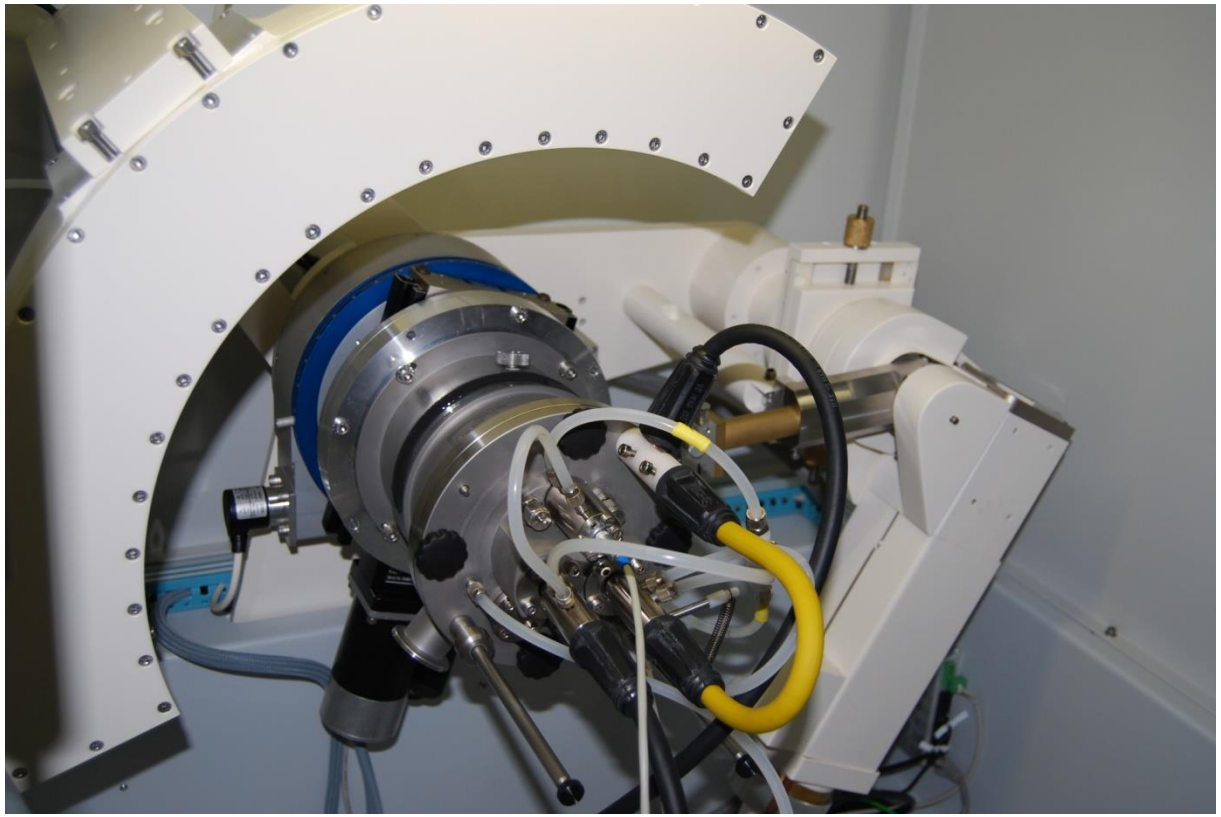


Fig. 5 Expanded areas of the two and three dimension powder X-ray diffraction patterns, which show the gradual disappearance of the 211 reflection associated with the tetragonal supercell.

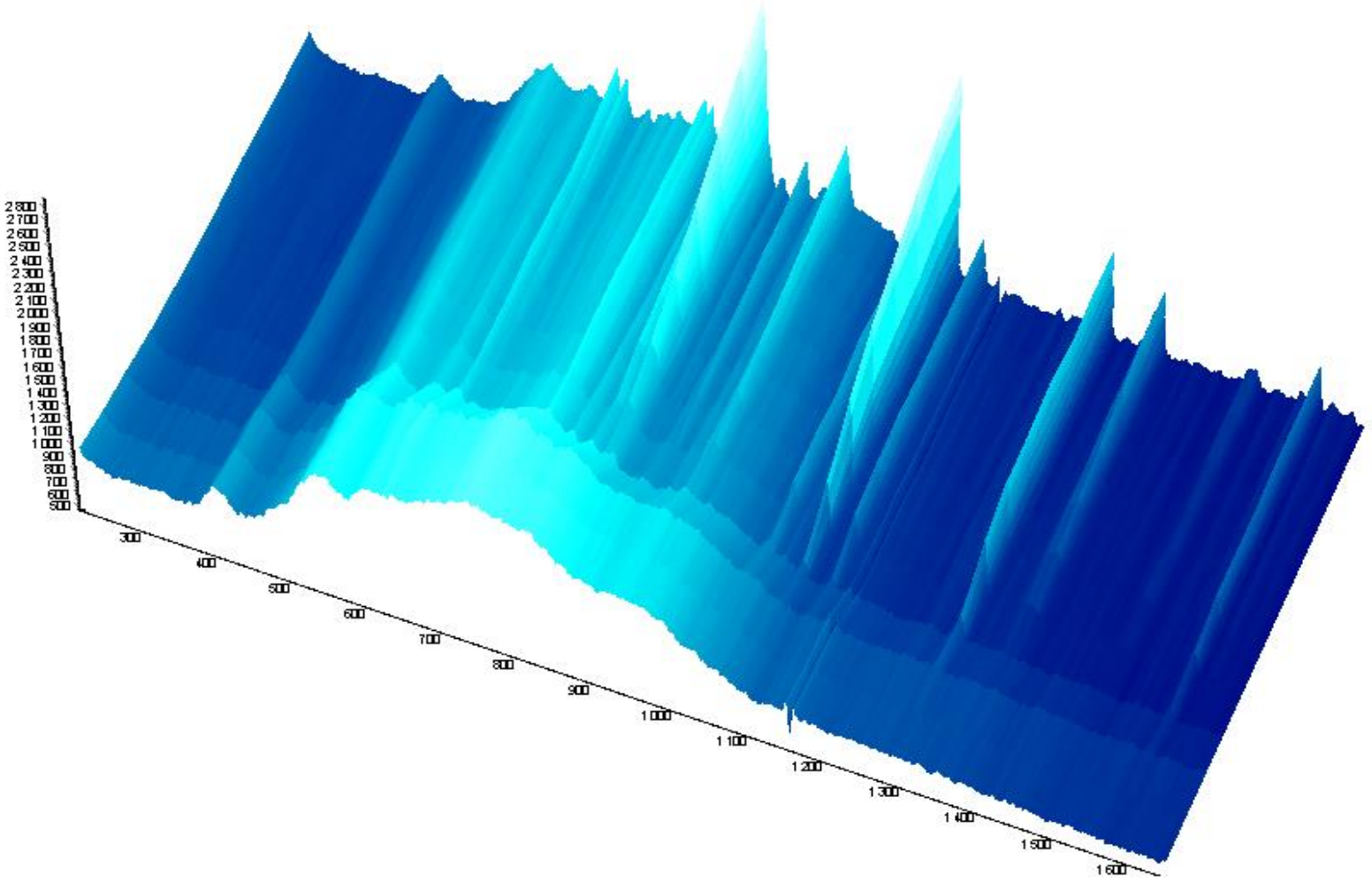
J. Mater. Chem., A 2013 , 1, 5628

Buehler HDK1.4

Automatic sample dilatation correction



Glass crystallization at high temperature

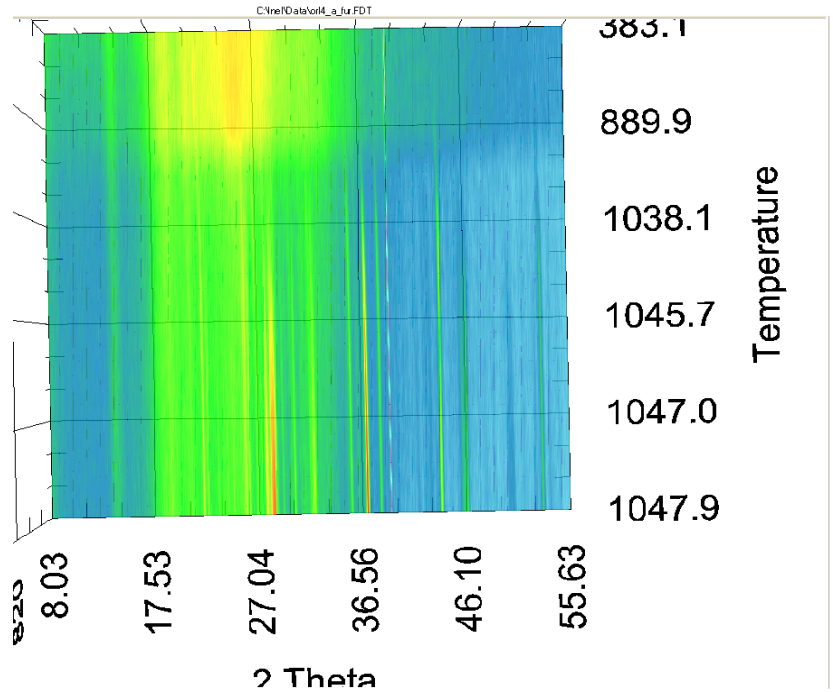


CONDITIONS :

power : 38kV – 38mA,

Furnace : FUR1200

acquisition: 3min



ThermoFisher SCIENTIFIC

State of the art powder diffractometer : <0.045° fwhm peaks can be recorded with CPS 590 detectors in real time (Equinox 3500).

Equinox 3500

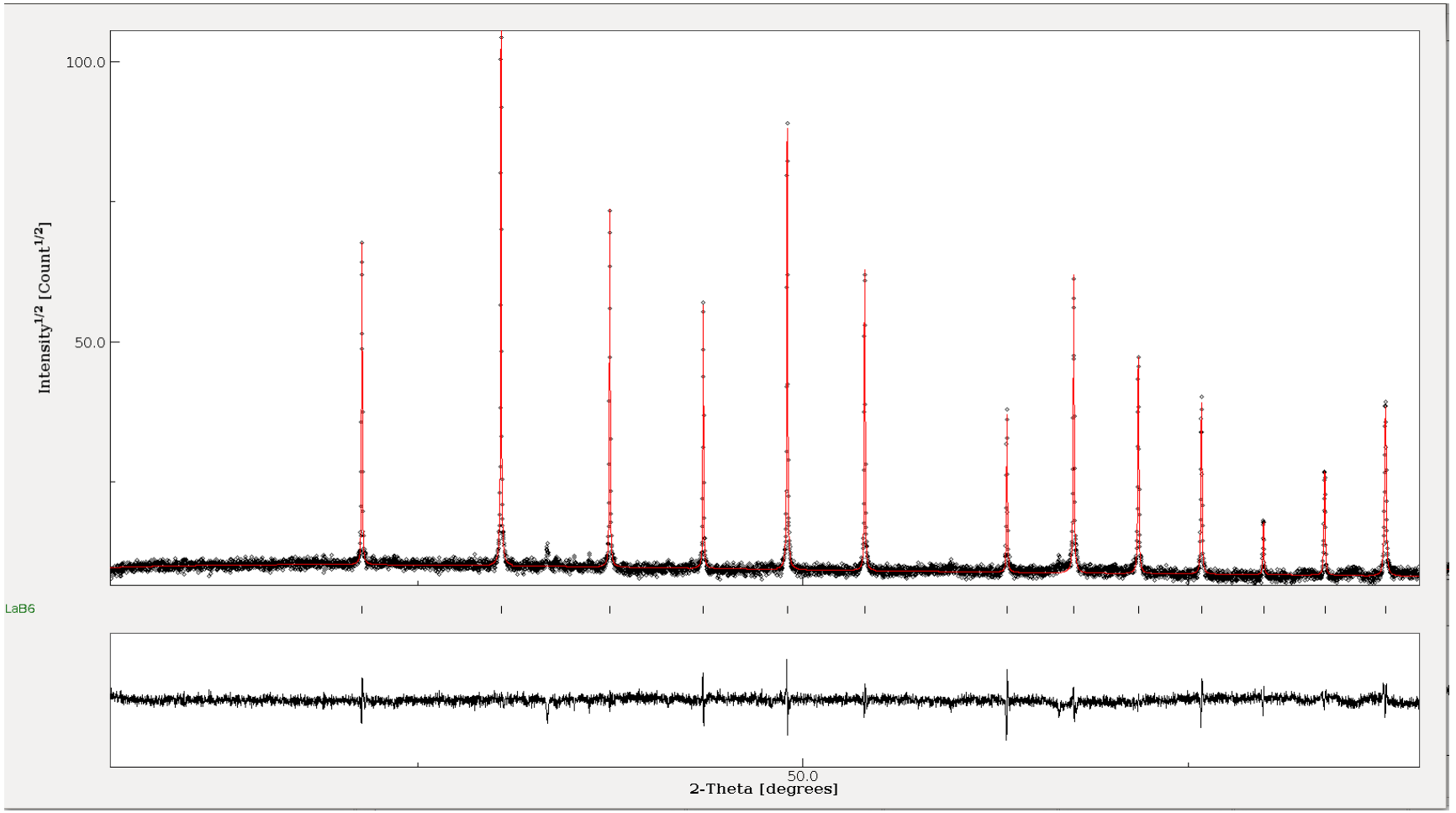
Equinox 3500 : High resolution work

LaB6 powder sample

Recorded in reflexion mode on Equinox 3500 (Ge monochromator)

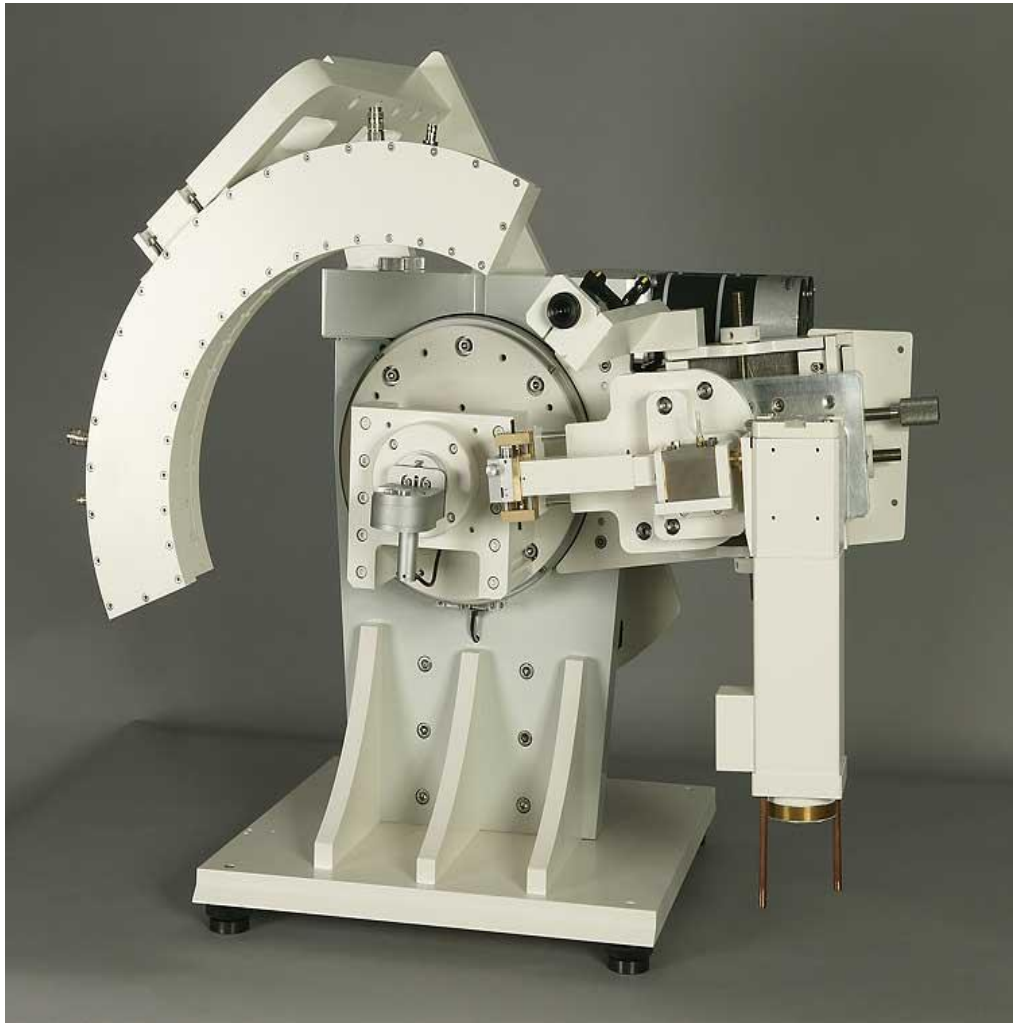
Instrumental function refinement using MAUD software

FWHM : <0.04° between 30 to 50° 2θ



For increased versatility, we developed a range of XRD goniometers. They are of course equipped with CPS detectors.

- Motorized Ω and 2θ (as θ/θ or θ/2θ)
- CPS 120 for Equinox 5000
- CPS 590 for Equinox 5500
- Point detector « compatible »



Equinox 5000 is an Equinox 3000 for the experts....

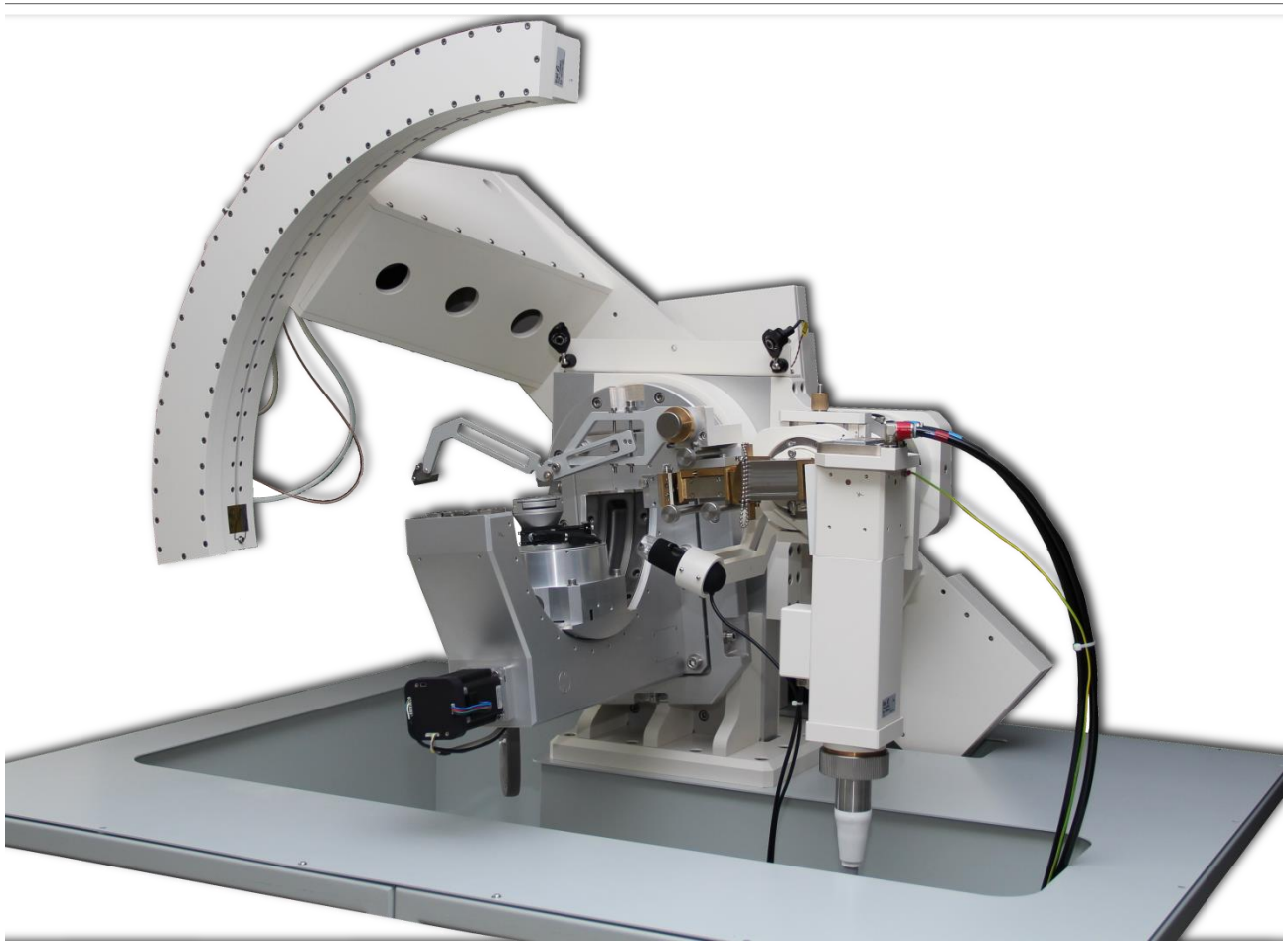
… or for central analysis labs (lots of different configuration made easy)

- Same use as the Equinox 3000
- Increased angular range without manual intervention of user (>160° seen in tenders)
- Switch from symmetrical (-60 to 60°) mode to standard mode (0 to 120°) by means of a motion (2 Theta)
- Detector calibration easier
- Changing incidence, omega scans
- Thin layer option much cheaper : omega stage is already there.

Equinox 6000

- 4 Circle Goniometer
- **Texture analysis** : all pole figures in 1 experiment
- High resolution system
- Stress analysis
- All kind of studies on polycrystalline sample

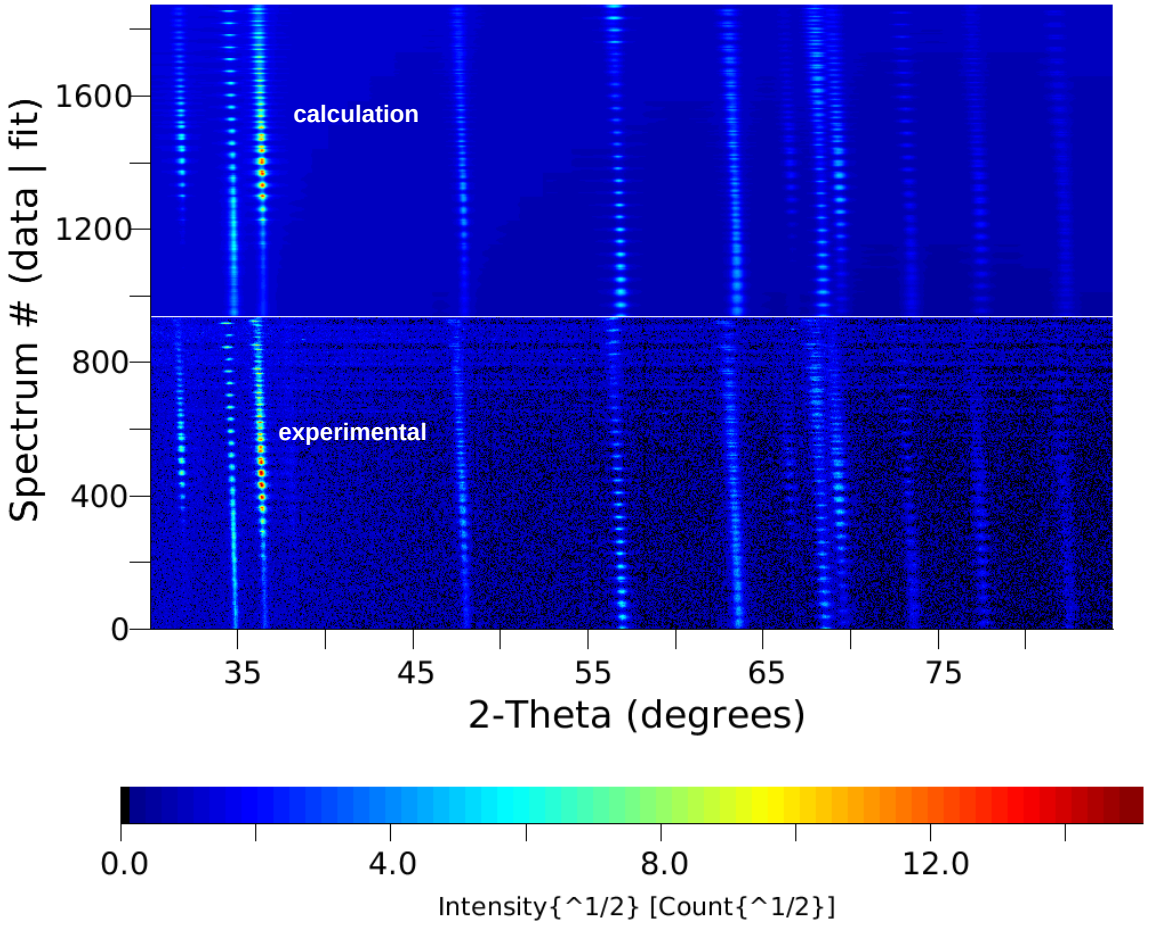
Equinox 6000 : description



- X/Y stage for mapping
- Motorized elevator
- Texture analysis software (Labotex)
- Stress analysis software (Diffstress)
- Compatible with CPS590 (risk of collision between detector and χ with CPS120)
- Possible hot domed stage

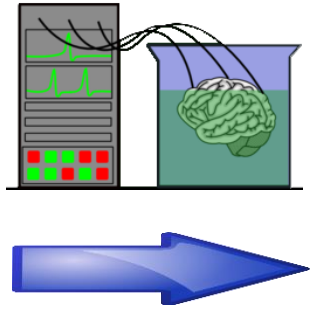
Exists also in horizontal version

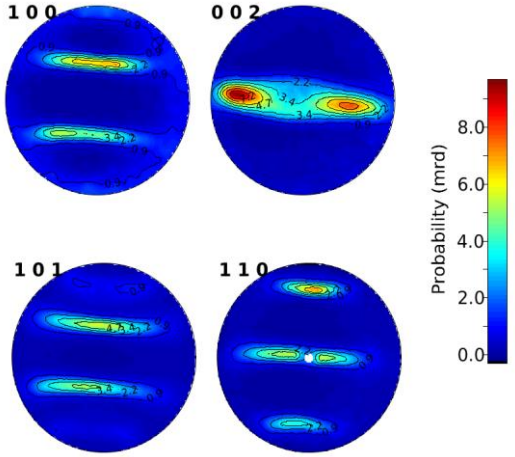
Equinox 6000 : Combined texture/stress example



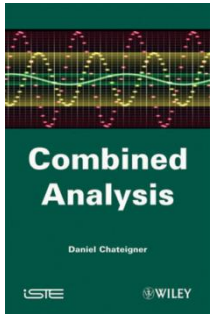
Tilted because of about 600MPa applied stress during process

Data processing with MAUD





Large detector → Lots of information



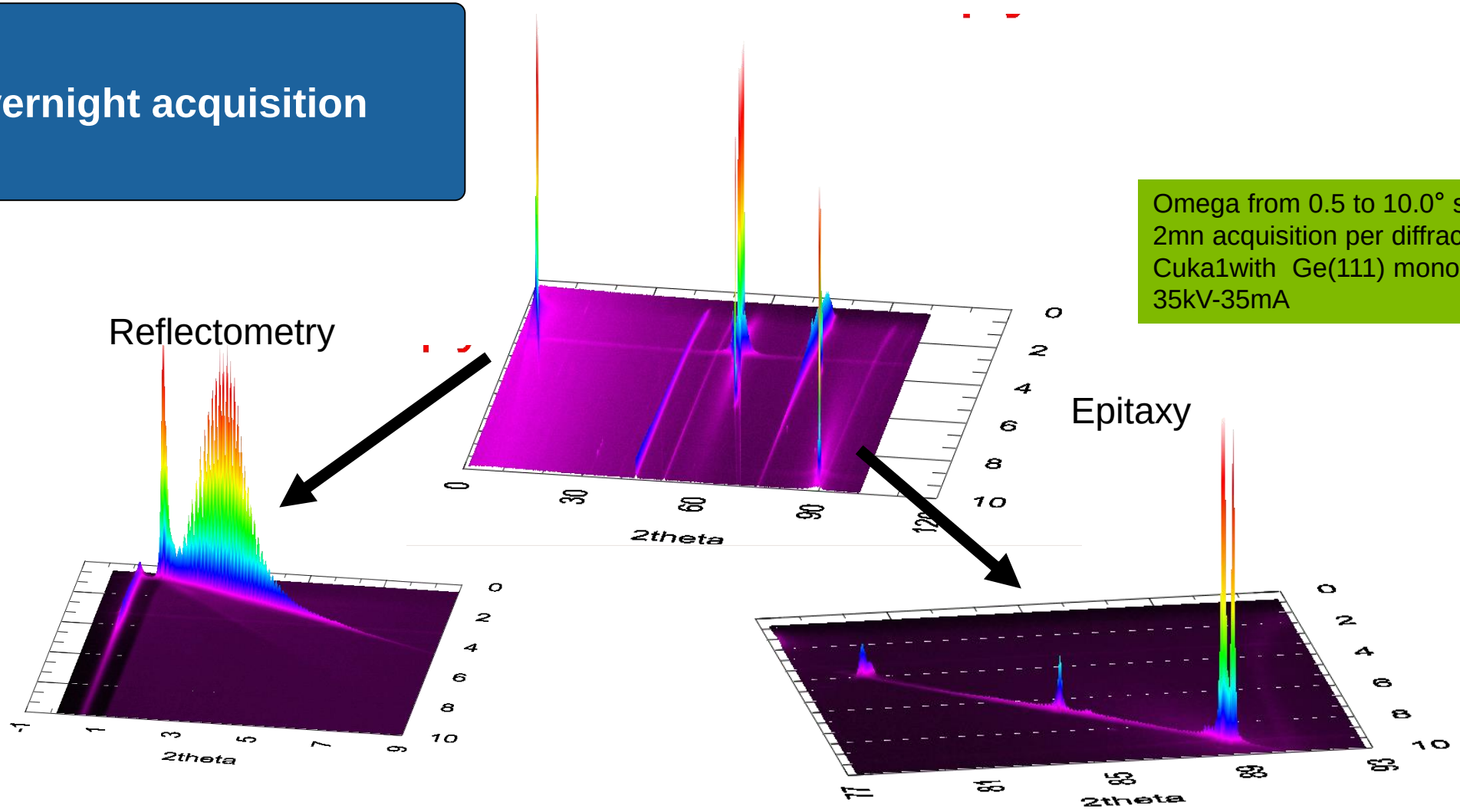
ISBN: 978-1-84821-198-8

Overnight acquisition

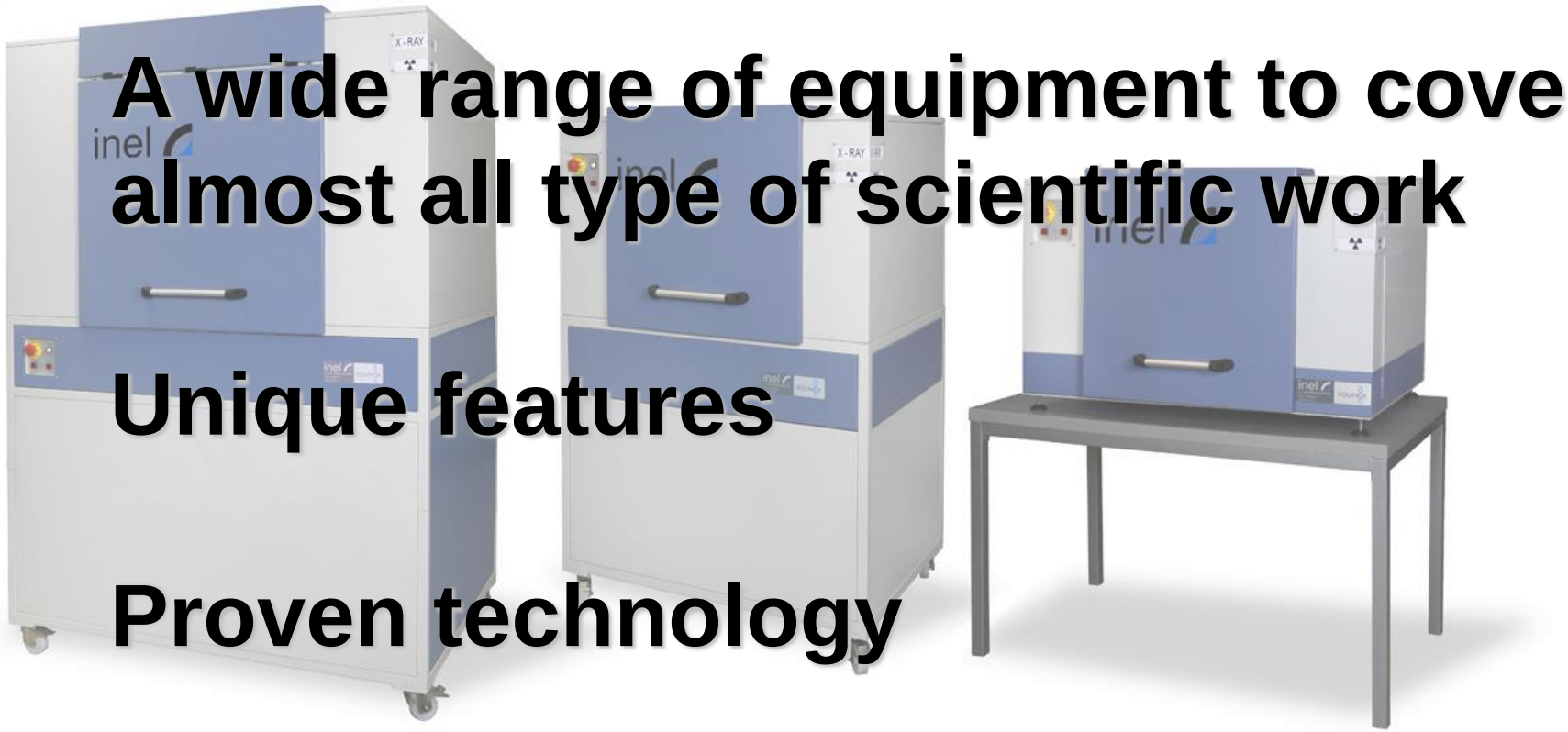
Omega from 0.5 to 10.0° step 0.05
2mn acquisition per diffractogram
Cuka1with Ge(111) monochromator
35kV-35mA

Reflectometry

Epitaxy



ARL EQUINOX



A wide range of equipment to cover almost all type of scientific work

Unique features

Proven technology

Equinox XRD Portfolio for Industrial and Research Applications

Applications	Equinox 100	Equinox 1000	Equinox 3000	Equinox 5000	Equinox 6000
Phase identification and quantification			√	√	√
Quality Control		√	√	√	√
Rietveld programs	√	√	√	√	√
High and Low temperature measurements	X	X	√	√	
Grazing incidence option	X	X			√
High Resolution measurements	X	X		√	√
θ/2θ Geometry	X	X	X	√	√
Texture analysis	X	X	X	X	√
Residual stress measurements	X	X	X	X	√

INDUSTRIAL

RESEARCH

XRD Portfolio Summary

Applications	Equinox 100	Equinox 1000	Equinox 3000/3500	Equinox 5000/5500	Equinox 6000
Phase ID and QPA	OK	OK	Ideal	Ideal	OK
Quality Control	Ideal	OK (Ge), ideal (Graphite)	OK	Too much	Too much
High / low Temperature	No	No	Ideal	Ideal	OK
GIXRD / XRR	Possible	Possible	OK	Ideal	OK (too much)
High resolution	No	No	Yes	Yes	Yes
Stress measurements	No	No	Possible	Possible	Ideal
Texture	No	No	Possible	Possible	Ideal

Thank you for your attention