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ArabLab 2018

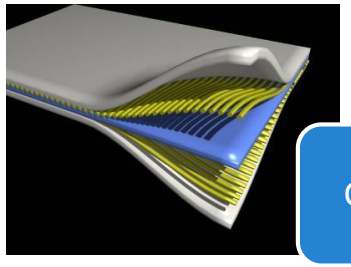
# Chemical and Structural Analysis of Materials using XRF and XRD


**Didier Bonvin, Nazih Ziade, Dr.Simon Welzmiller and Dr. Ravi Yellepeddi**

**Thermo Fisher Scientific**

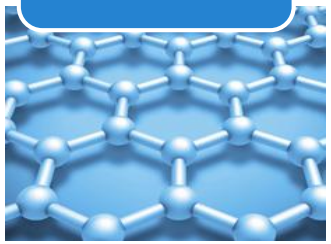
**Switzerland**

# Advanced materials in our lives

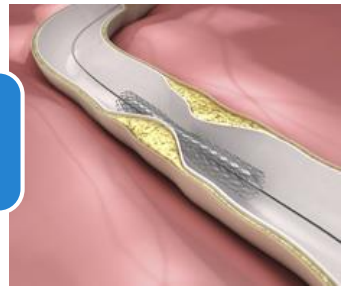


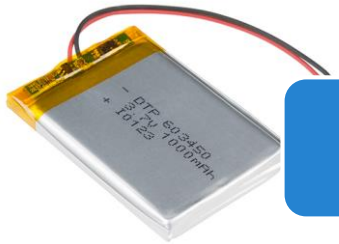
Composites

Nanomaterials



Biomaterials





Energy Materials

Polymers

Ceramic & Glass

Metals & Alloys

Electronics & Photonics





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# A variety of complementary techniques used for Chemical and Structural analysis of Materials

**SEM** **TEM** **IR**

**Multi-Modal** **RAMAN**

**XRD** **XRF**

**FT-IR** **XPS** **EDS**

**WDS** **CT**

# Enabling the Materials Development Cycle

## CHARACTERIZE

### Structure

- Electron Microscopy
- SPM
- **XRD**

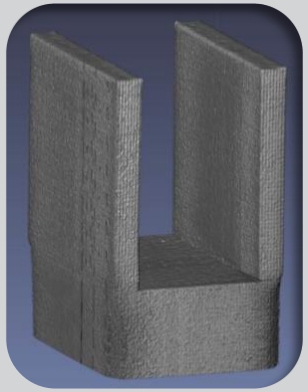
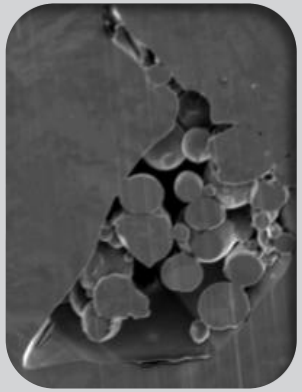
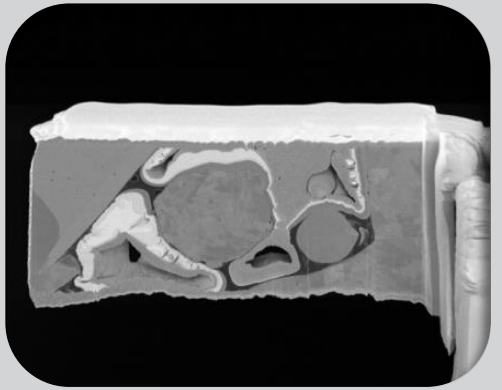
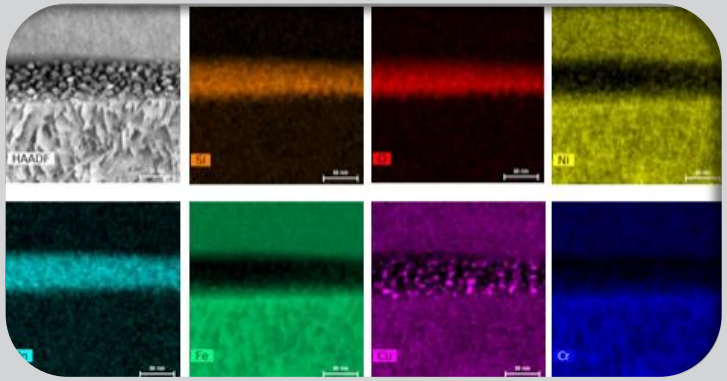
### Composition

- MS; quantitative, destructive
- EDS, **XRF (Elemental)**; XPS (surface)
- Raman; molecular, hard samples
- FTIR
- Multimodal Techniques:
  - Rheo-Raman, XPS-Raman

### Properties

- Particle size
- Thermal
- Rheological

# Materials Science Multi-Modal, Multi-Scale Workflow


**Chemical Analysis** | **Selection of Area of Interest** | **TEM prep** | **Atomic Structure**

Meter | Millimeter | Micrometer | Nanometer | Atomic


ARL QUANT'X
EDXRF Spectrometer


iXR Raman Spectrometer

**ARL PERFORM'X XRF**

DXR 2Xi Raman Imaging Microscope


Nicolet iN5 Microscope


FEI Helios G4 CX

UltraDry EDS Detector


ARL EQUINOX XRD

Thermo Scientific K-Alpha+ XPS


FEI Themis Z TEM

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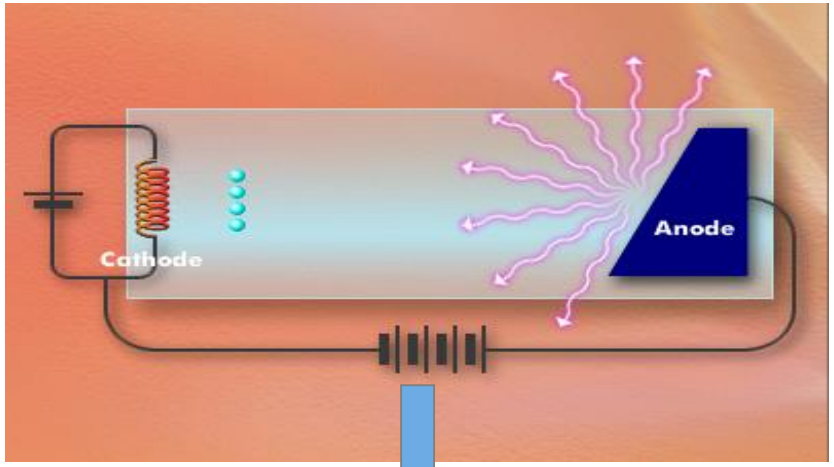
# WDXRF, EDXRF and XRD:  Elemental  and Phase analysis of a variety of materials

- *Cement and building materials*
- *Metals, Slags*
- *Petroleum, Polymers, Oils*
- *Ores and raw materials*
- *Chemicals/Pharmaceuticals*
- *Geology*
- *Environmental*
- *Food products*
- *Mining extraction*
- *Universities, central labs*
- *Thin films, magnetic media, paints*
- *Etc..*

# Wave – Matter Interaction

Reflection

**X-rays Production** : classically by excitation of external electronic level with electron beam



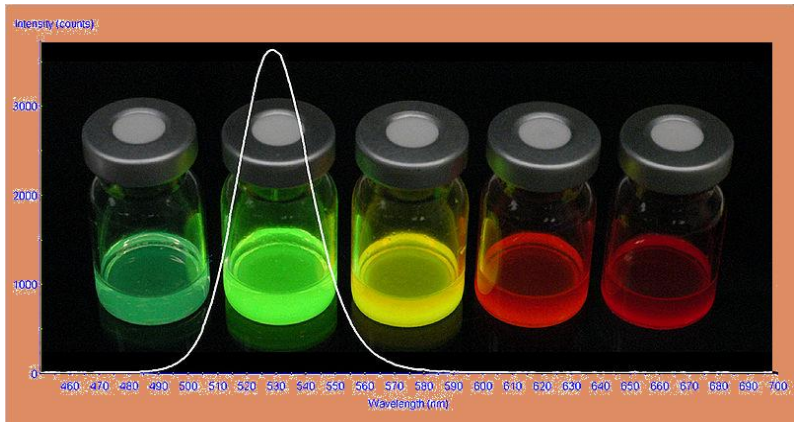

Diffusion

Imaging

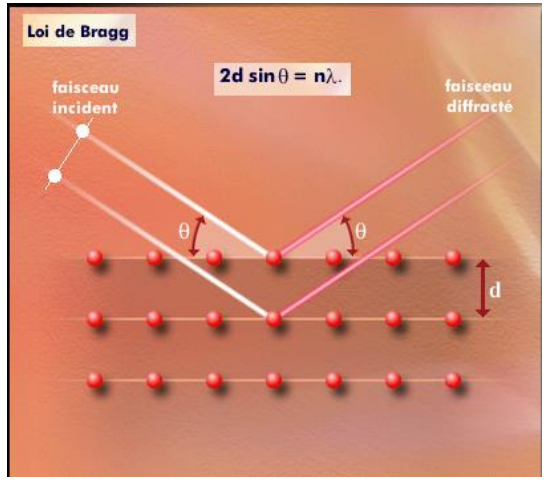

XRD

XRF

Fluorescence




Diffraction







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# Thermo Scientific XRF and XRD Product Portfolio

## EDXRF

**ARL QUANT'X-**
Top performance EDXRF

**Portable Niton**

## WDXRF

**ARL PERFORM'X**
High Performance sequential XRF

**ARL OPTIM'X:** Surprising performance in WDXRF

**XRF: Elemental analysis**

## Integrated XRF and XRD

**ARL 9900 Series**
Integrated XRF-XRD

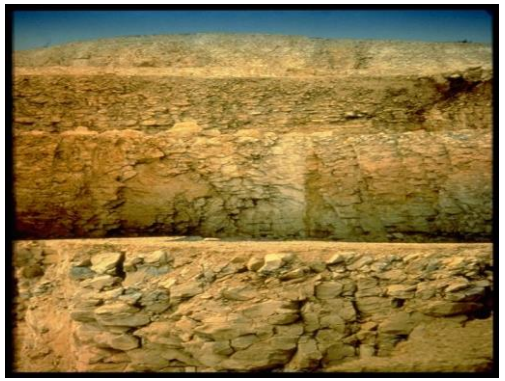
## Powder XRD

**Equinox 6000:** High performance Powder XRD

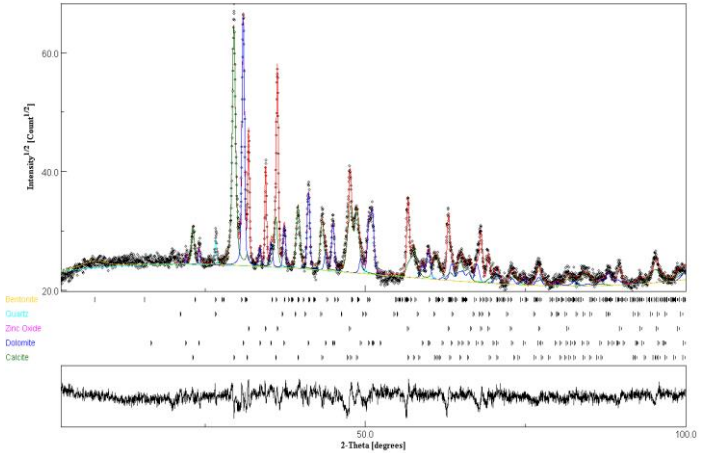
**Equinox 100 & 1000**
Benchtop XRD

**XRD: Analysis of**
**Structure-crystallography**
**Phase or compound**

# Geology/Mining/Core drilling: Laboratory and Field XRD




Calcite, Quartz, Dolomite,Bauxite..




## The problem

Geological exploration, mineral processing and raw material screening for industrial production require identification and quantification of specific phases of economic interest in addition to their chemistry

## The analysis

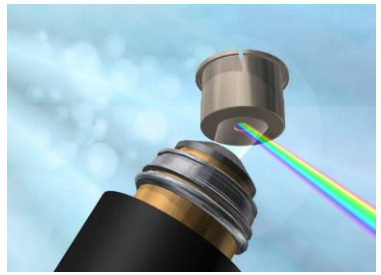
Use a Powder XRD to characterize the mineral content of any ore body and total geochemical analysis including other techniques such as XRF and FTIR.

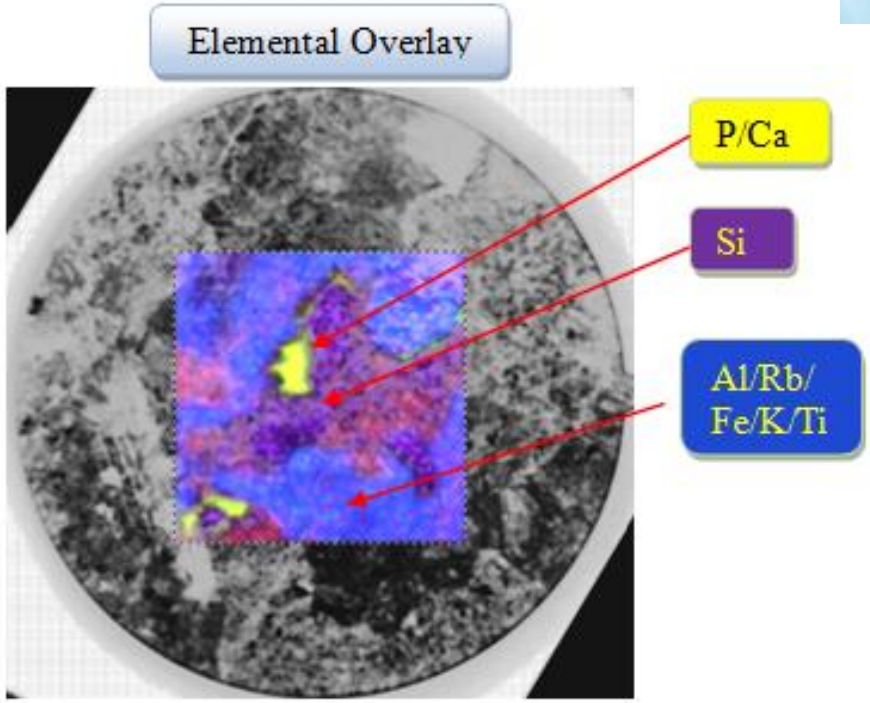
EQUINOX 100 bench-top (transportable) for field applications and EQUINOX 1000/3000 for Geochemical labs

## The solution

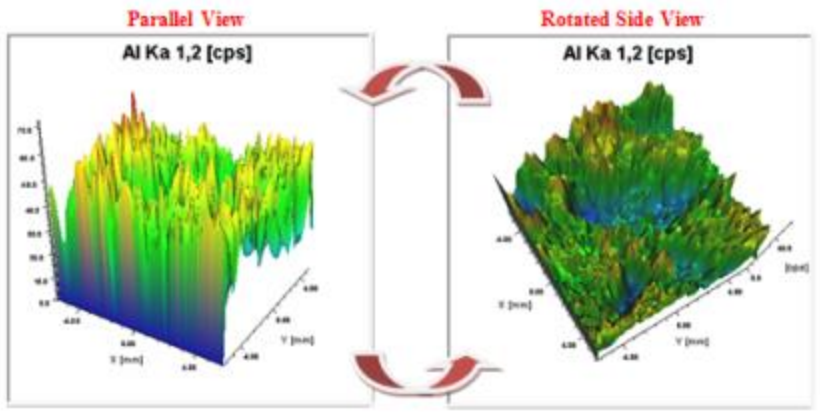
- Complete Mineralogical/Phase analysis in Bauxite, Alumina and other aluminum bearing minerals in few seconds to minutes using Position Sensitive Detector
- Qualitative and Quantitative Phase analysis using Rietveld programs
- High throughput with large 30-position sample loader and unattended batch operation

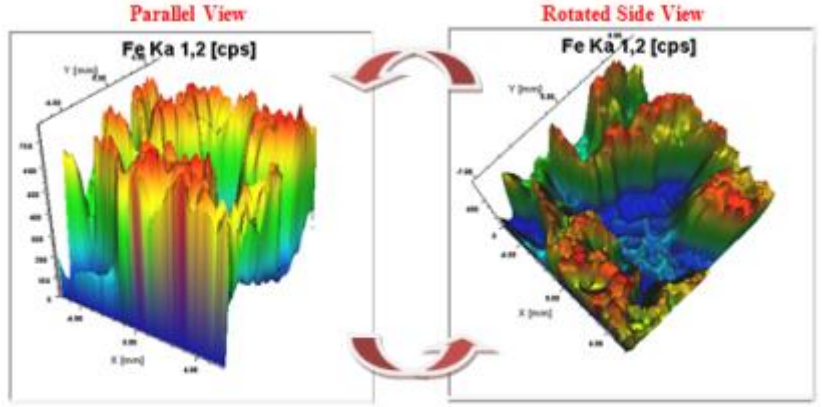
# Feldspar example: Elemental Mapping using XRF

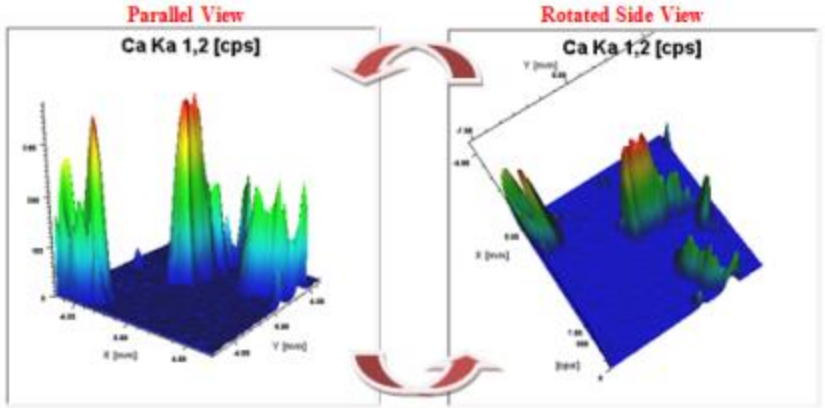


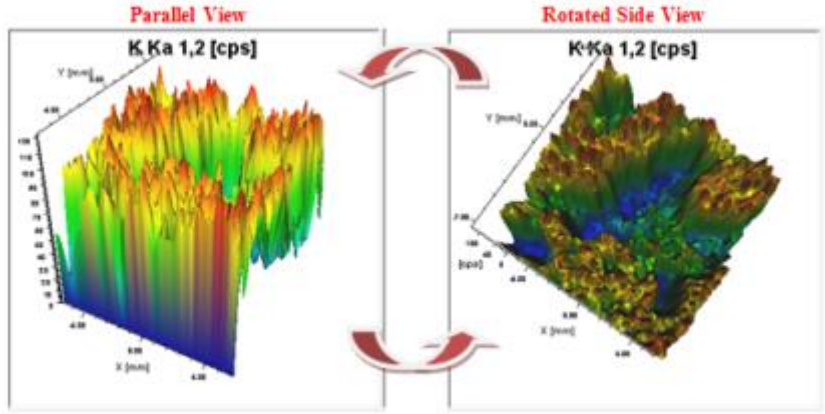



# Feldspar: XRF Data to represent the distribution of elements within the mineral sample

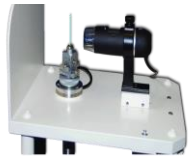


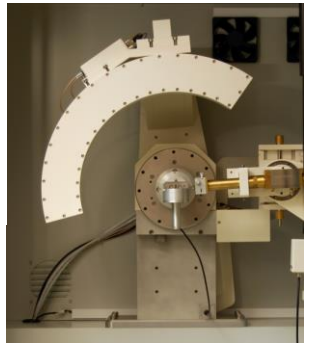



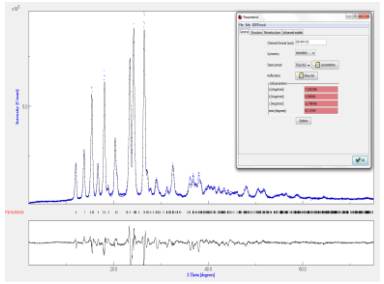



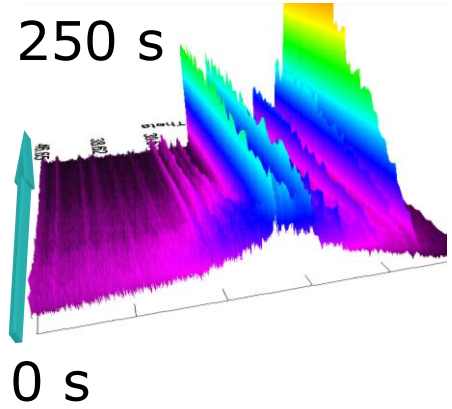



# Crystallinity, Polymorphism and Structural finger printing of Pharmaceutical Products by XRD








## Indication of a Problem

Crystal structure of the active molecule in pharmaceutical products is an important information for the synthesis and application of new formulations. Rapid screening for polymorphism, crystallinity, stability and reproducibility of the formulations are routinely carried out by XRD.

## Analyze the Problem

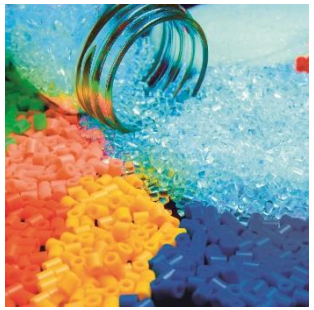
Very fast identification and screening of pharma products using EQUINOX 100 XRD can be done to establish various structural parameters and characteristics in real time. Depending on the nature of the sample and quantity, both transmission and reflection mode XRD can be done.

## Solve the Problem

*Study and obtain the following information in few seconds to minutes:*

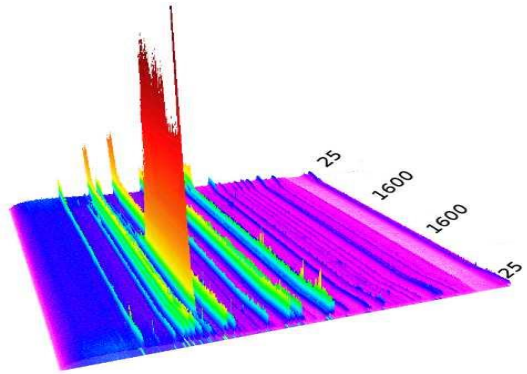
- *Time-dependent crystallization*
- *%Crystallinity vs Amorphous*
- *Polymorphism and their stability*
- *Crystallite size and bio-availability*
- *Reactivity to temperature and environment*

# Dynamic studies of materials: Real-time structural changes captured by XRD



Equinox 3000 +
HTK16 (Anton Paar

Phase transition at high temperature
5s per pattern with multilayer mirror




## Indication of a Problem

Materials undergo structural changes as they are heated, treated and/or stressed. Their reactivity and stability in controlled environment are also important for their manufacturability and scaling-up from research to production.

Real-time changes need to be captured for optimization and efficiency of the process

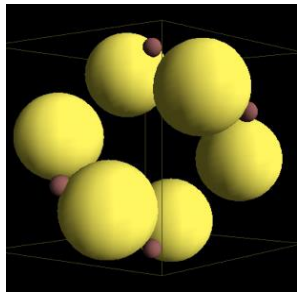
## Analyze the Problem

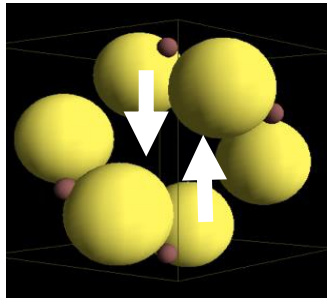
Whether it is the crystallization of pharmaceutical products or transformation of an amorphous material into crystalline or vice versa, real-time dynamic monitoring of their specific phases is required and XRD can be used to track such reactions and dynamics.

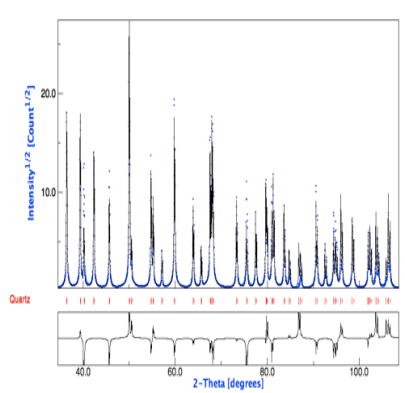
## Solve the Problem

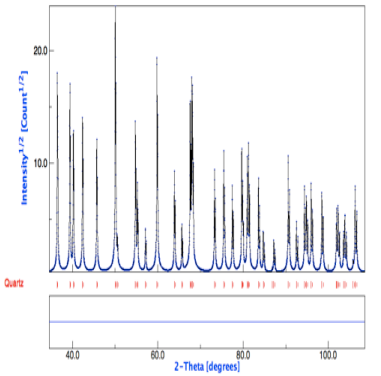
EQUINOX XRD technology is based on real-time simultaneous detection of full pattern in few seconds to minutes and this enables dynamic studies of materials most efficiently. Even the bench-top EQUINOX 100/1000 can be used with different options to study reactivity and kinetics of such materials in real time.

# Structural simulations, molecular modeling and XRD pattern






## Indication of a Problem

Material Research Scientists need to simulate and model the appropriate molecular structure to ensure the expected properties when the material is synthesized. Structure refinement of new or applied materials is a pre-requisite for their optimization.

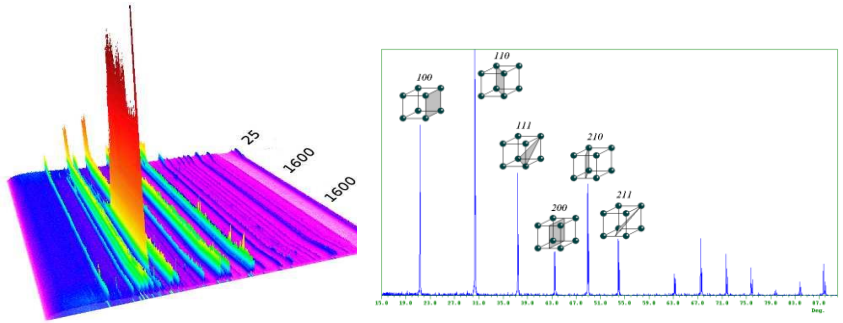
## Analyze the Problem

From the initial chemical composition and atomic coordinates, scientists need to build a crystallographic model and iterate or refine the structure until it matches closely with the expected molecular bonding/structure.

## Solve the Problem

XRD is the fastest and most reliable technique for studying structure-property relationship and elucidate materials as a function of their final state. Rietveld programs (quantitative structural determination) are used in conjunction with XRD and EQUINOX XRD + MAUD programs are designed for such scientists.

# Materials Science Research – Batteries & Fuel Cells - Spectroscopy


## The problem

Graphite, Lithium Ion and other battery manufacturers need to ensure highest conductivity or charge density of the materials used. These properties are structure or orientation dependent and a consistent crystal structure or alignment of conducting lattices is essential to increase yield and efficiency.

## The analysis

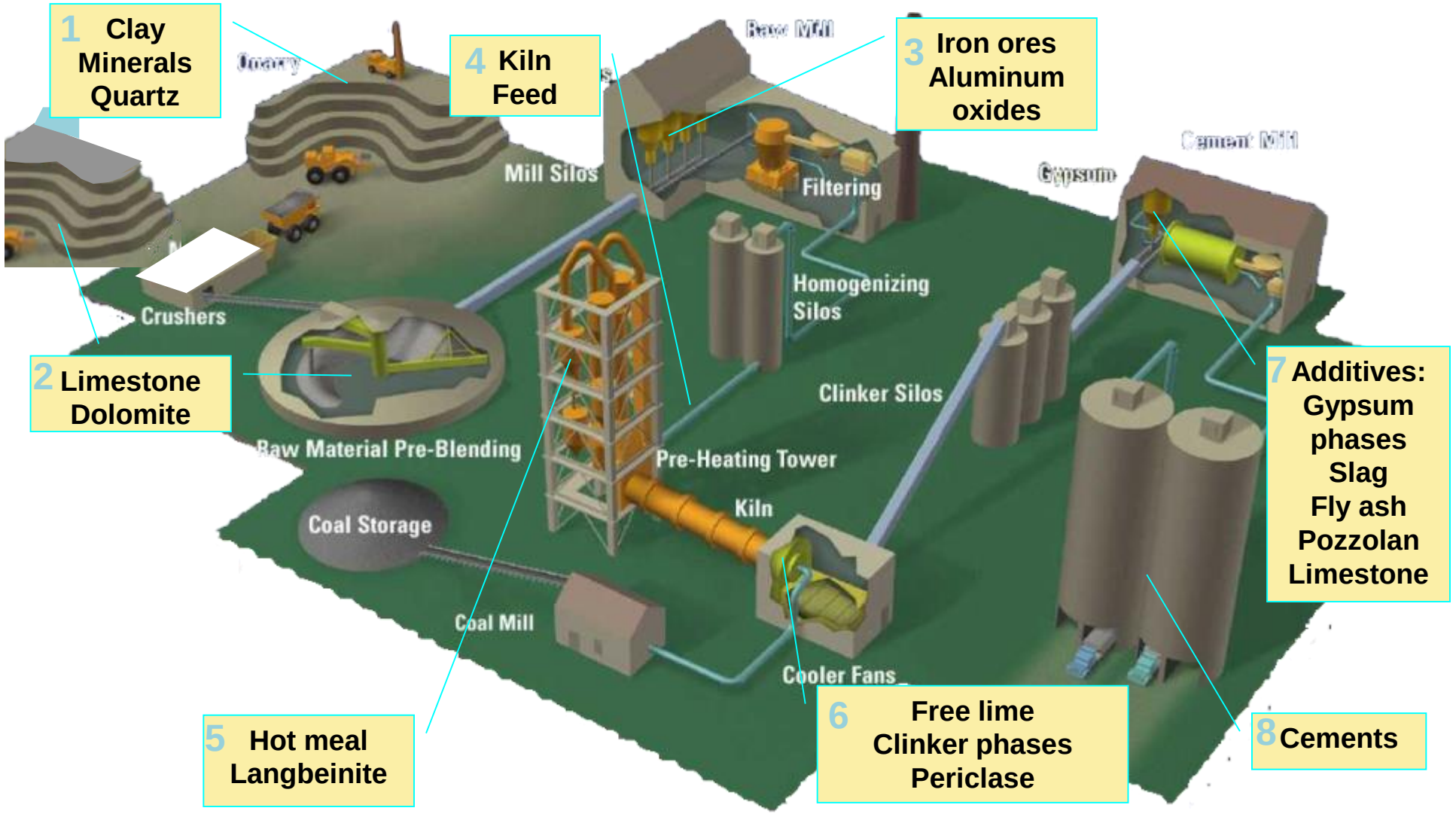
Use the X-ray Diffraction system to check for the appropriate crystal structure, amorphous versus crystallinity, specific orientation characteristics with diffraction pattern (linewidth, intensity ratio of different reflections) and thickness/homogeneity and density of thin films or layers

## The solution

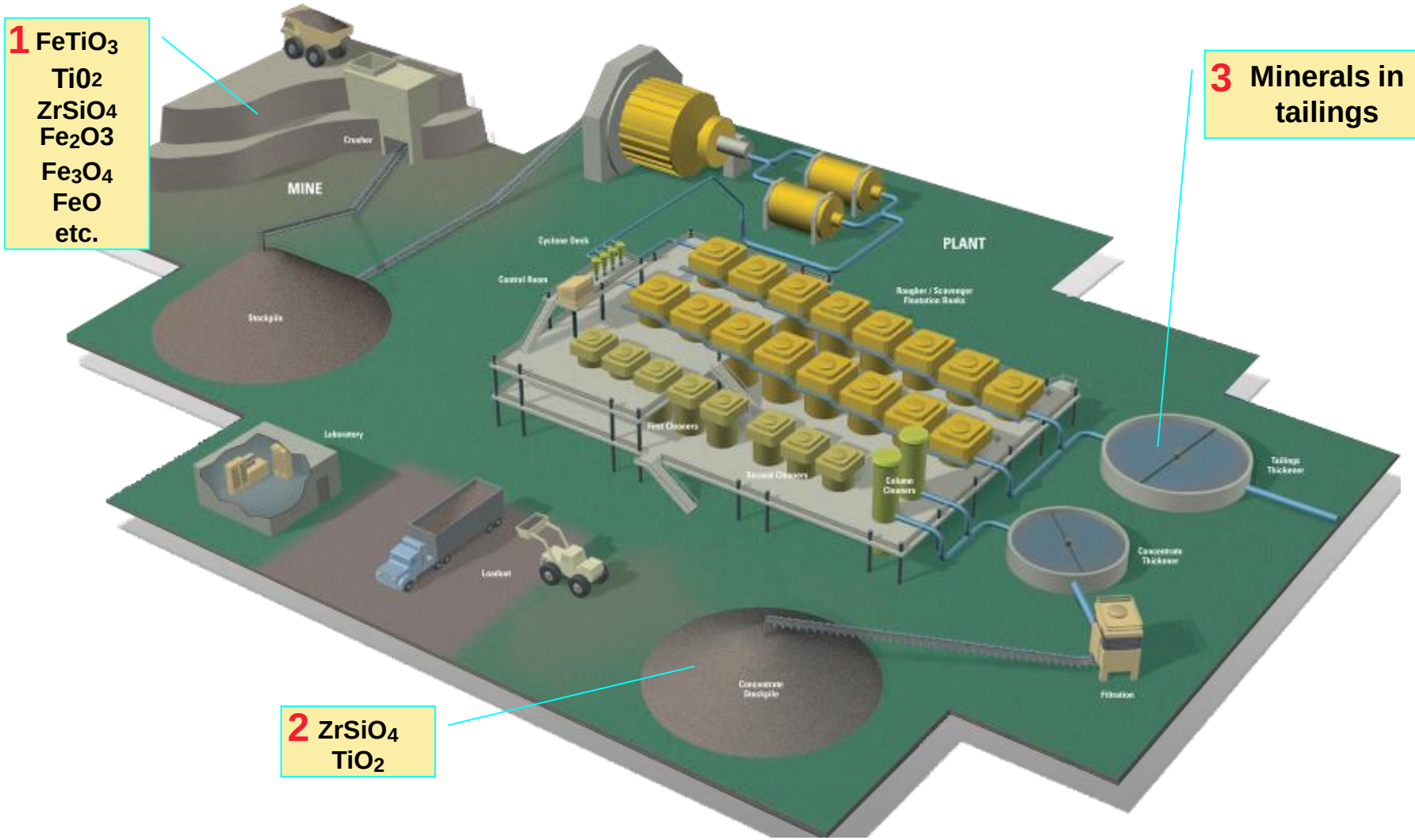
Use XRD to determine

- % Crystallinity versus Amorphous content of the active material to optimize the process
- Identify and Quantify specific polymorphic structures of interest to increase the yield
- Structural stability and repeatability in real-time to enhance lifetime
- Thickness, surface roughness and density of layers or coatings

# XRF-XRD APPLICATIONS IN CEMENT INDUSTRY



# XRF and XRD Applications in Mining and Mineral Extraction processes



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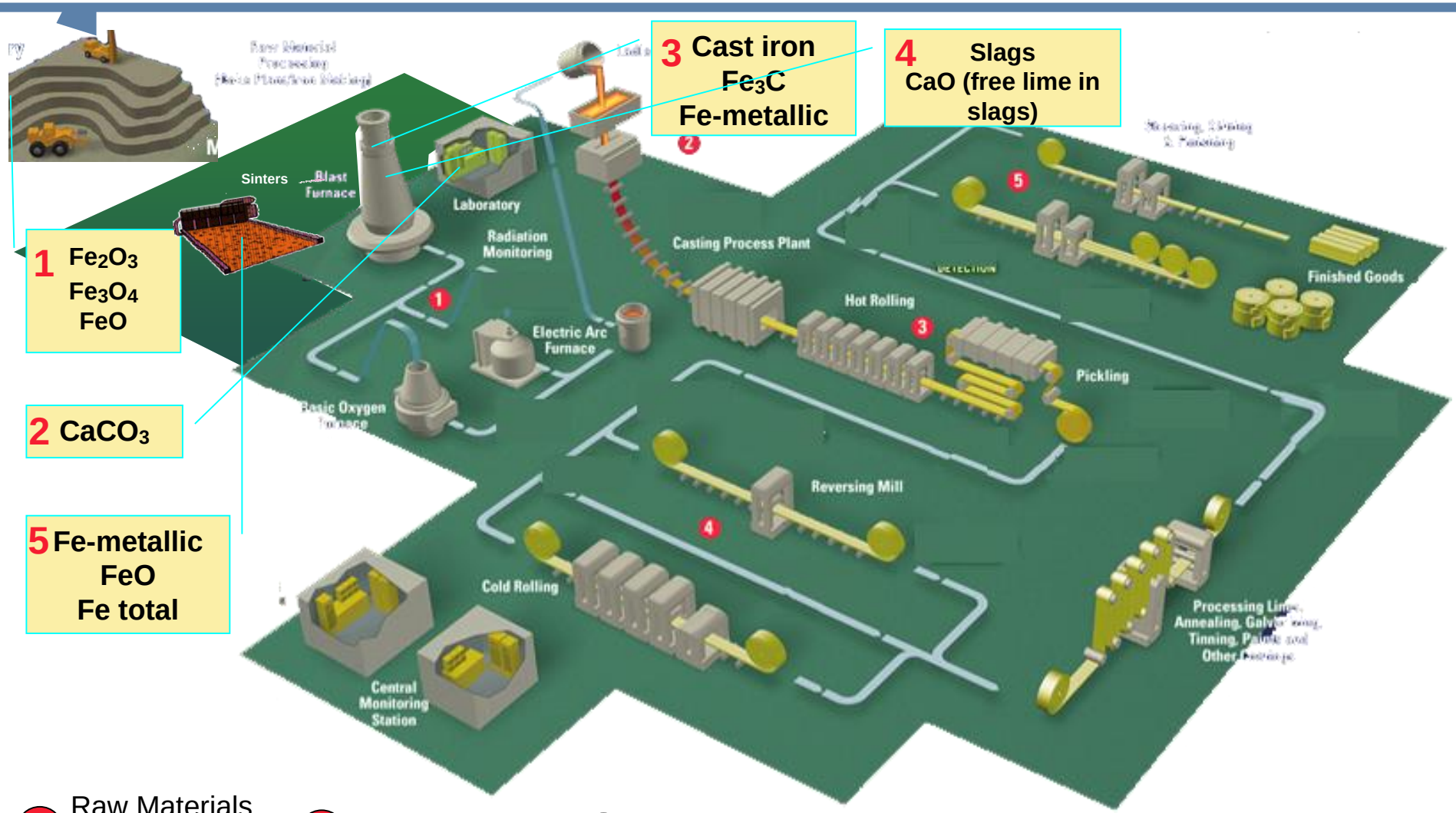
# IRON and STEEL Process: Chemical and Phase Analysis by XRF and XRD




1 Raw Materials Processing  2 Steel Making  3 Hot Rolling Mill  4 Cold Rolling Mill  5 Steel Processing



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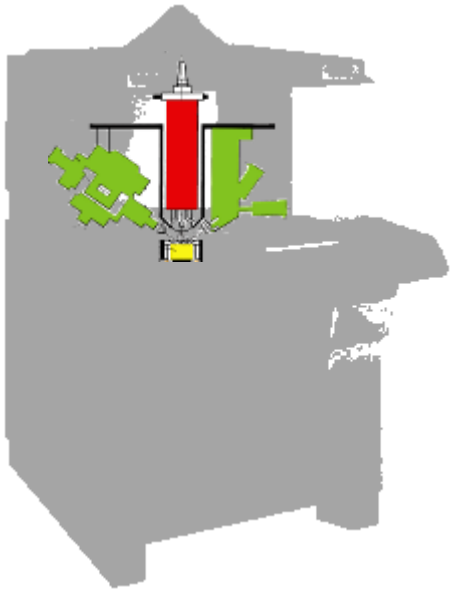
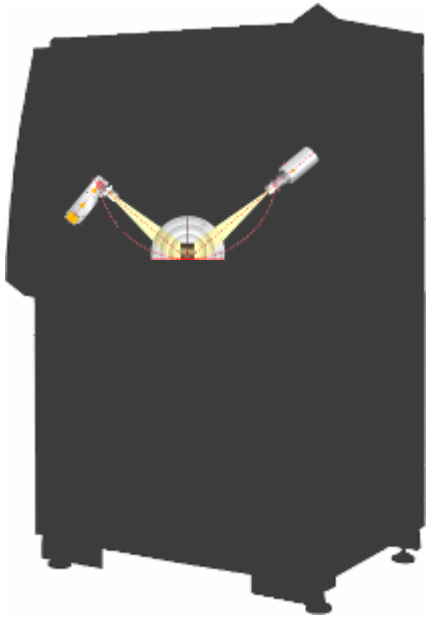
# INTEGRATED XRF-XRD Instruments for Process Control and Industrial Materials

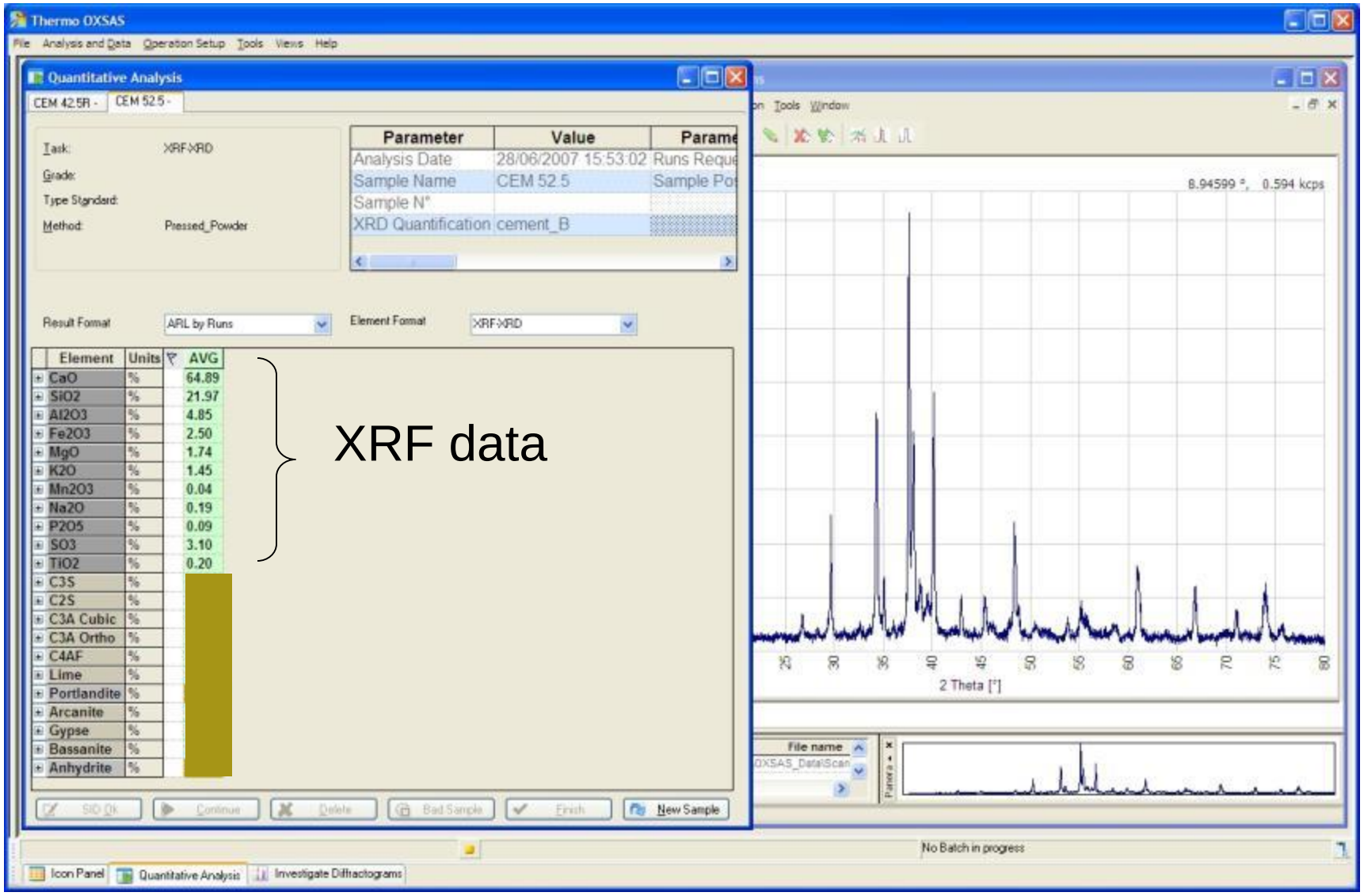


X-Ray Fluorescence

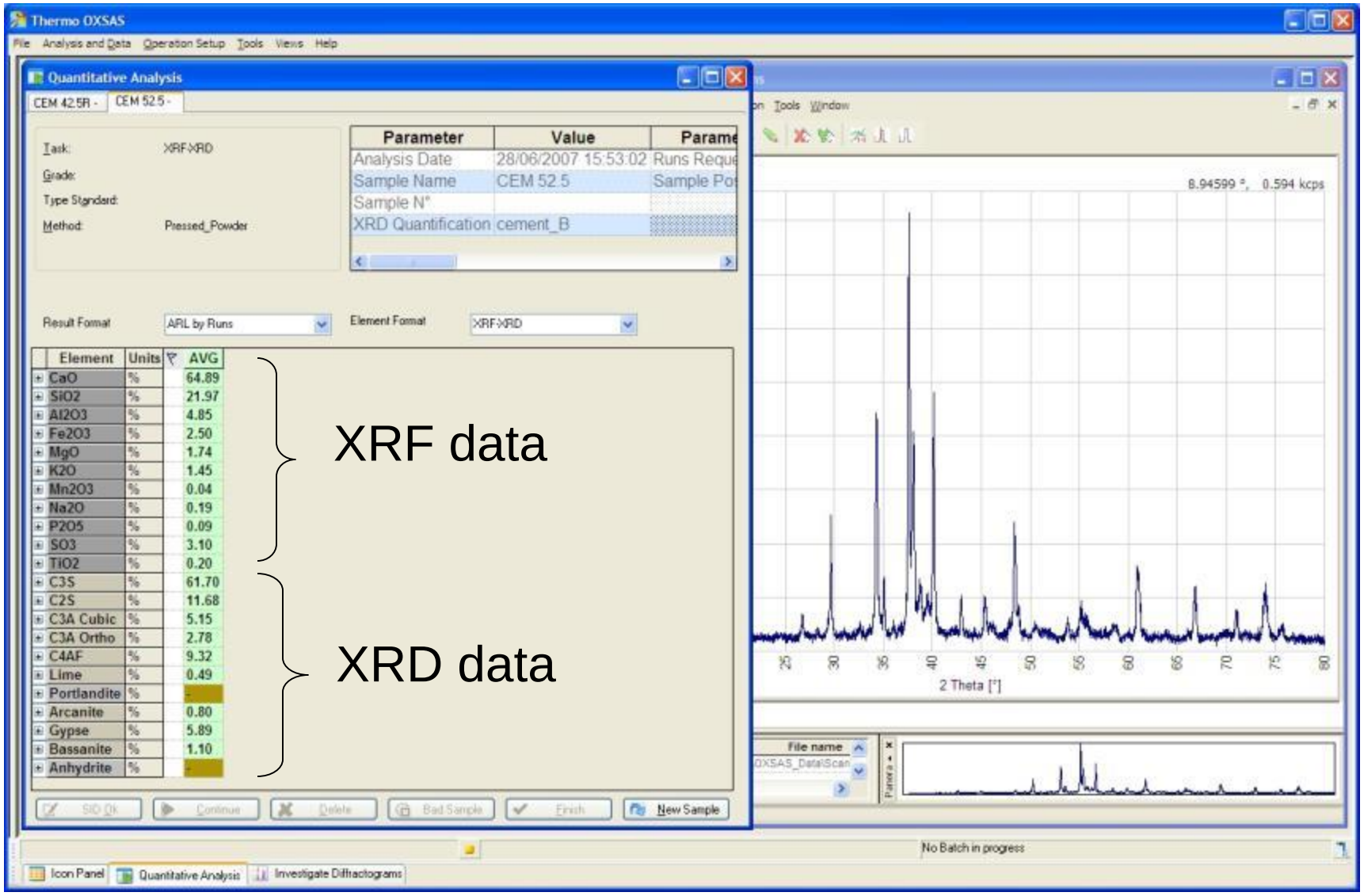


X-Ray Diffractometry

# Example of combined analysis: XRF results first



# Example of combined analysis for process control: Chemistry and Mineralogy



## What is your need to Analyze?

- Mineralogy/Phases/Compounds
- Polymorphs
- Coatings/Layers/Thin Films
- Crystallinity versus Amorphous %
- Quantitative Phase Analysis
- Phase Transitions
- Dynamic studies/Reactivity
- Preferred Orientations (Texture)
- Residual Stress
- Structure Refinement
- SAXS (Small Angle X-ray Scattering)

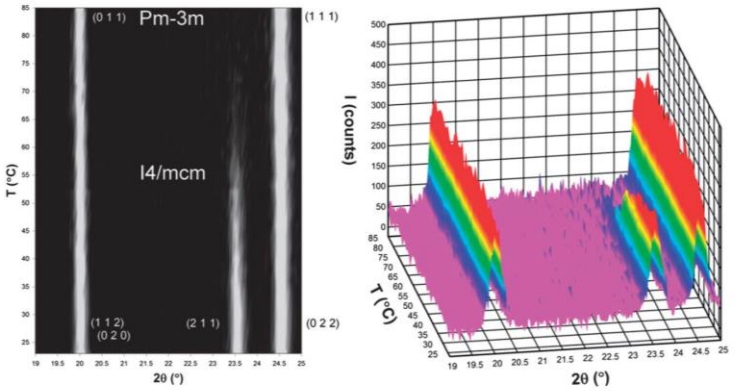
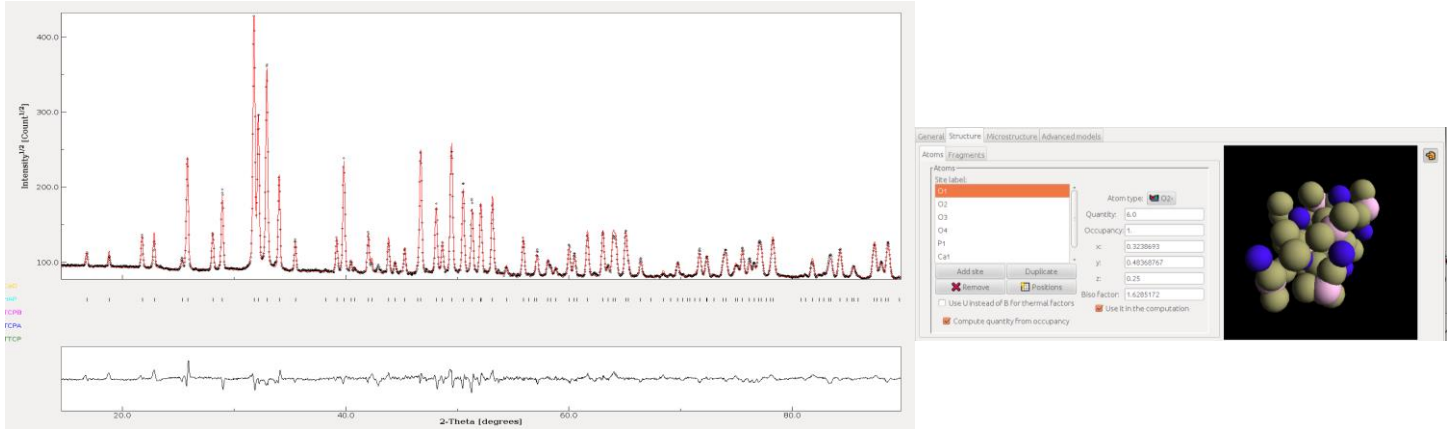



Fig. 5 Expanded areas of the two and three dimension powder X-ray diffraction patterns, which show the gradual disappearance of the 211 reflection associated with the tetragonal supercell.

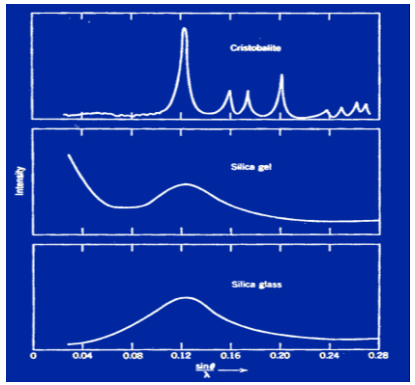
Photovoltaic Application (Solar Cell) (CH3NH3)PbI3 Structural change Vs temperature.

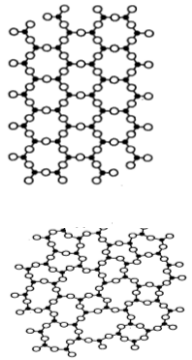


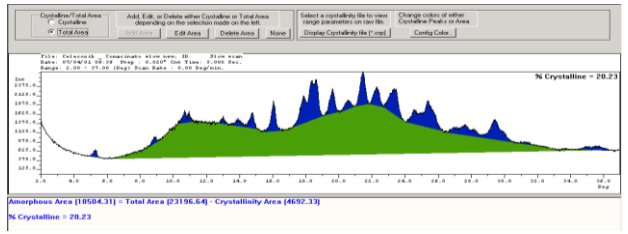

HAP (hydroxylapathite) sample : used in biomedical applications (bio- compatible prosthetic)- Structure refinement

## Which Information do you want to obtain?

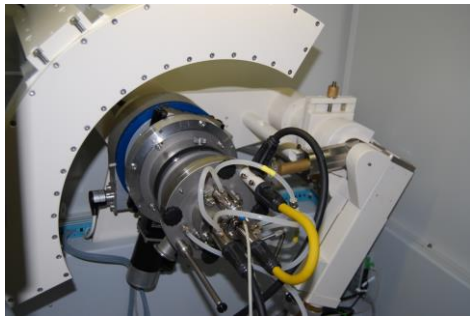
- Phase identification and quantification
- Crystallite size
- Structural changes or stability vs Temp
- Crystalline to Amorphous transition & vice-versa
- Thin films/layers-density, structure, roughness
- Polymorphs and their ratio
- Pole figures and texture

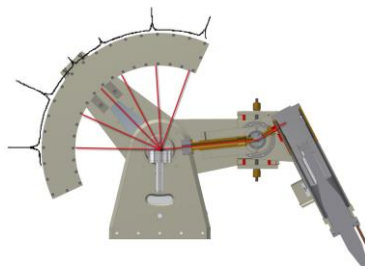


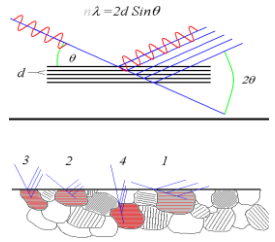



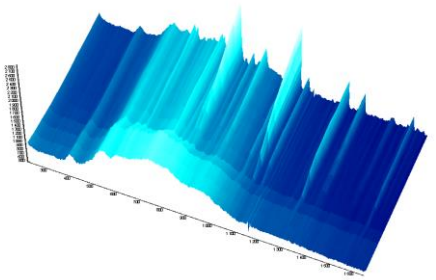


From Quartz to Glass







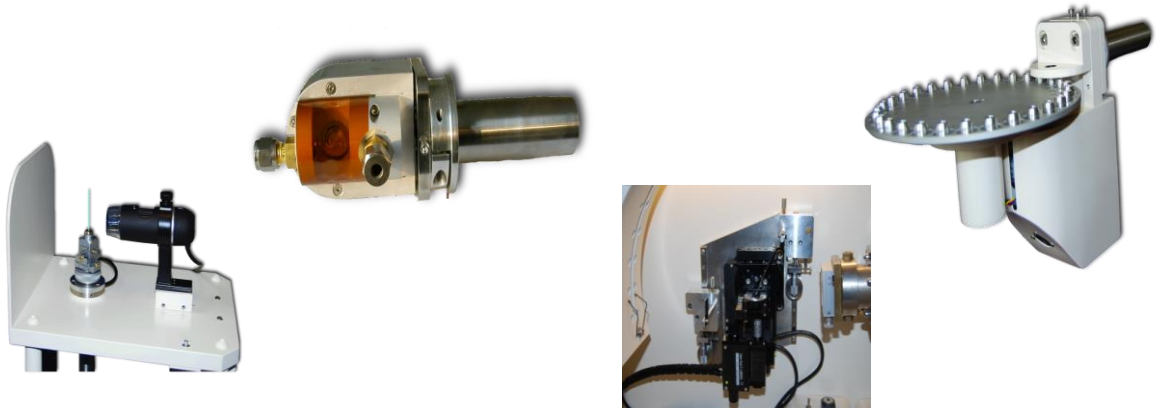



Structural changes at high temperatures

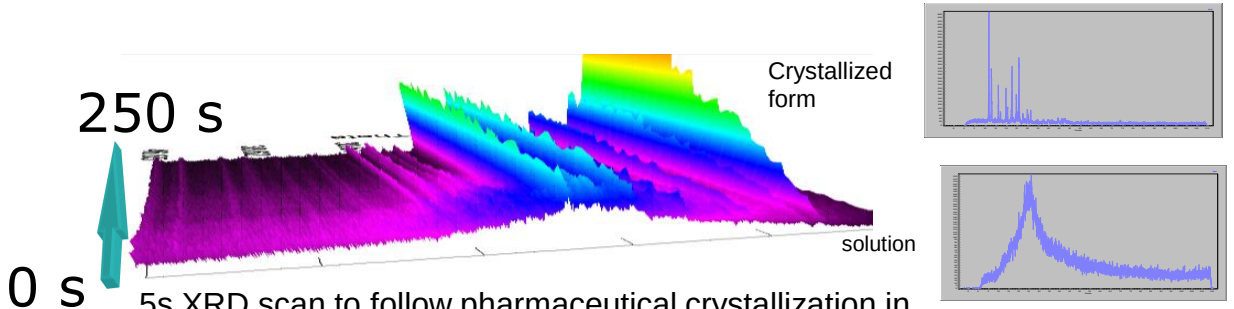
# Type and Nature of samples

What is the typical sample size, sample type, how many per hour/per day, what dynamic changes?

- Small area or large area sample?
- Sensitive/Reactive samples?
- Grains, Small quantities (few mg) or bulk material, thin films/coatings?
- Throughput requirements? (no of samples per hour or per day)
- Static or dynamic measurements? Temperature, Stress, Environment changes?
- Need to collect full XRD pattern in few seconds for rapid screening of dynamic changes of structure?

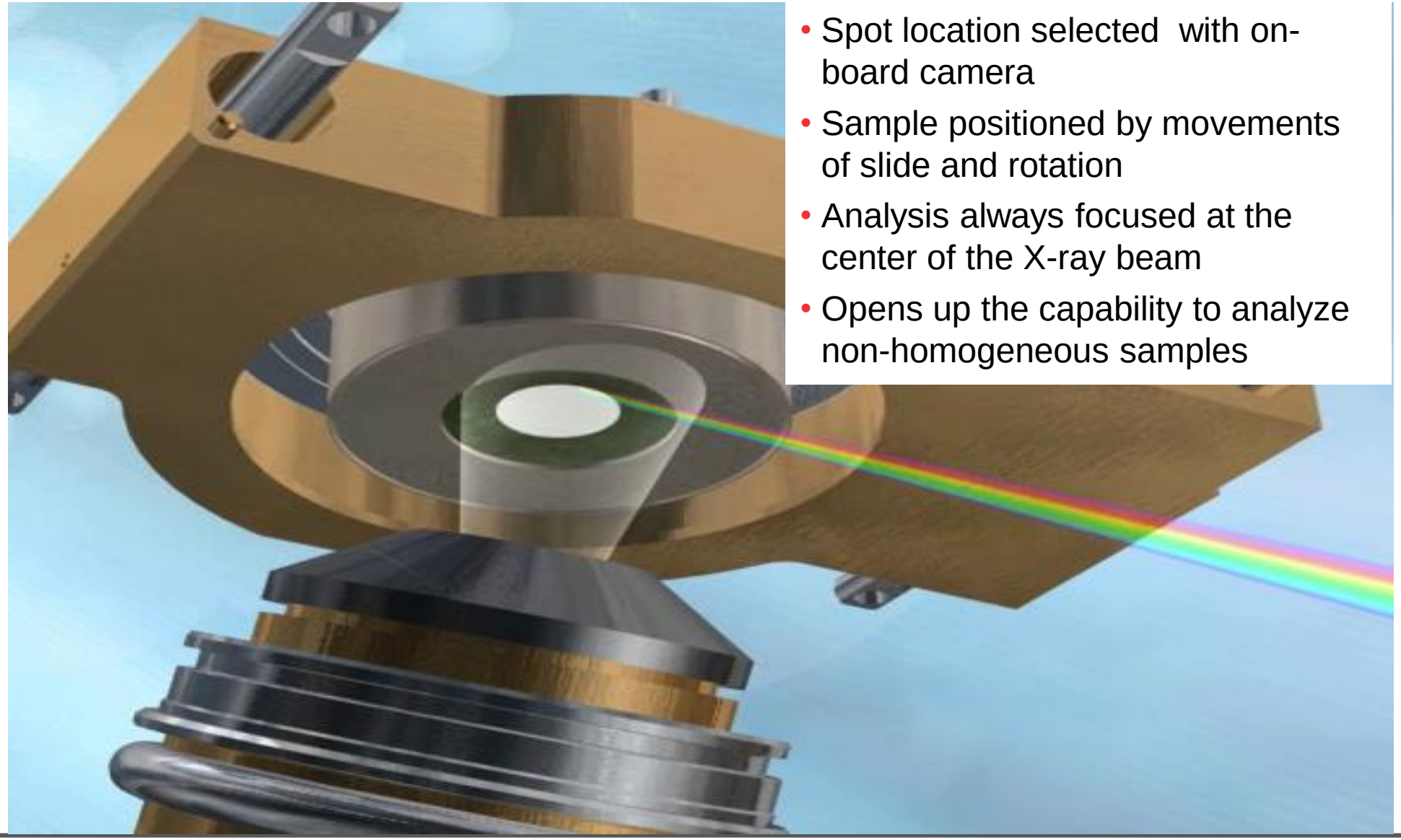


Different sample types handled with specific sample stages: Capillary stage, Controlled environment chamber, thin film stage, Multi-sample changer for batch mode




5s XRD scan to follow pharmaceutical crystallization in real time from solution to solid state

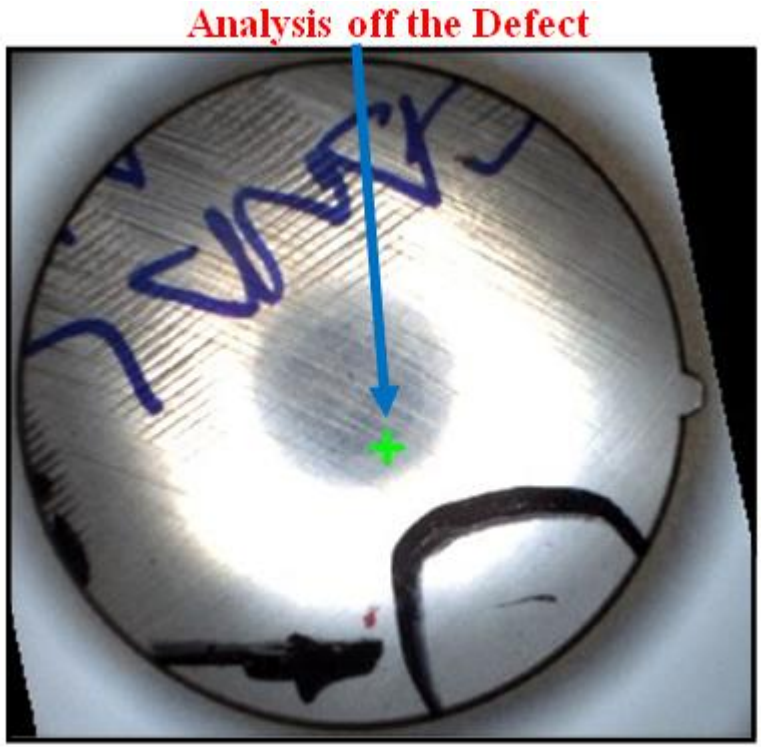
# Small Spot Analysis



- Spot location selected  with on-board camera
- Sample positioned by movements of slide and rotation
- Analysis always focused at the center of the X-ray beam
- Opens up the capability to analyze non-homogeneous samples

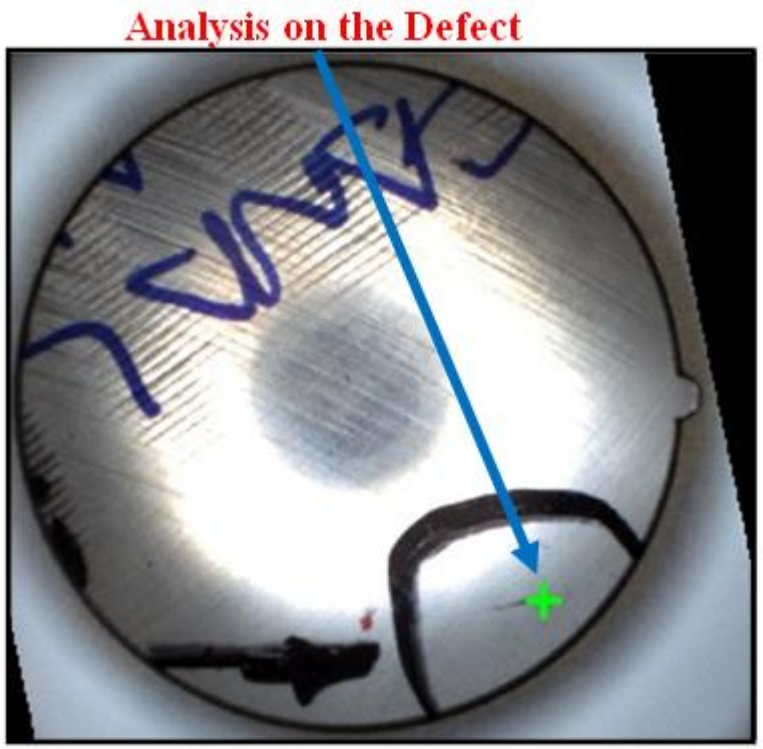
# UniQuant Spot Analysis of a stainless steel

17-7 Stainless Steel




| Elements | Conc% |
|---|---|
| Fe | 72.25 |
| Cr | 17.92 |
| Ni | 7.700 |
| Mn | 2.130 |
| Mg | <2e |

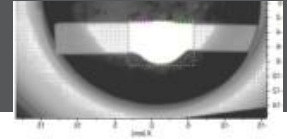
# UniQuant Spot Analysis of a stainless steel




| Elements | Conc% |
|---|---|
| Fe | 56.56 |
| Cr | 16.50 |
| Mg | 21.08 |
| Ni | 4.290 |
| Mn | 1.560 |

- Mg is detected as being the major component of this macro inclusion
- The analyst can then check for the source of this Mg and correct the process
  - Probably from refractories
- Fe, Cr, Ni and Mn are also detected because defect is smaller than 0.5mm and the goniometer sees the steel around the defect

# Mapping over a welded section



- The XRF mapping exhibits the elemental distribution over the welded section, notably for Manganese:
  - not present in the left plate
  - Homogeneously present in the right plate
  - Heterogeneously distributed in the welded zone
- Cr concentration is uniform over the 3 zones

ARL PERFORM'X – 0.5mm spot – 0.25mm steps

# The widest range of analytical methods to drive deeper materials insights

| Electron Microscopy | XPS | EDS | Raman | FTIR | XRF | XRD | Rheometry | UV-Vis |
|---|---|---|---|---|---|---|---|---|
| Multiscale imaging & analysis of various materials | Surface analysis quantitative chemical state | Elemental imaging at high spatial resolution | Chemical compound identification<br><br>Identification of both organic and inorganic materials | Chemical compound identification<br><br>Identification of organic materials in bulk state | Bulk state elemental composition | Structural crystallinity and composition | Characterization of fluid properties and other complex materials | Quantitative measurement of reflection or transmission properties of a material |









**A full spectrum of analytical tools that enable customers to advance their research, product development, and quality control capabilities**