Instrumentation and Measurements

XRD (X-Ray Diffraction)
Presentation of ThermoFisher X-ray part (very quick)

- Interaction X-ray and matter (no maths, good for digestion)

Some real XRD examples:
- Texture/Stress Combination on Equinox 6000
- Phase transition at (not very) high temperature on Equinox 3000
- Combined XRD/XRF on Equinox 100
- Dynamic studies on Equinox 100

XRD basics
- Texture
- Stress
- Thin Layer
- Powder

XRD setup: Some important parameters defining an instrument
Our leading scientific products, services and workflow solutions

The world leader in serving science

Analytical precision and diagnostic excellence

Accelerating discovery research

Inspiring meaningful genetic analysis

One-stop access for scientific products and services

Instrument and enterprise services

Invitrogen

Applied Biosystems

Thermo Scientific

Thermo Fisher Scientific
We take pride in our Mission: We enable our customers to make the world healthier, cleaner and safer.
We help our customers accelerate innovation and enhance productivity, underpinned by quality. Our customer value proposition:
<table>
<thead>
<tr>
<th>Pharma and Biotech</th>
<th>Applied Markets</th>
<th>Life Sciences</th>
<th>Healthcare</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clinical Trial</td>
<td>Mass Spectrometry</td>
<td>Cell Culture</td>
<td>Pathology</td>
</tr>
<tr>
<td>Manufacturing</td>
<td>Chromatography</td>
<td>Human Health</td>
<td>Transplant</td>
</tr>
<tr>
<td>Formulation</td>
<td>Lab Equipment</td>
<td>Reproductive</td>
<td>Diagnosis</td>
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<tr>
<td>API</td>
<td>Scientific Supplies</td>
<td>Mass Specimenary</td>
<td>Infectious</td>
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<tr>
<td>Bioproduction</td>
<td>Consumables</td>
<td>Reproductive</td>
<td>Clinical</td>
</tr>
<tr>
<td></td>
<td>Lab Equipment</td>
<td></td>
<td>Immunodiagnostic</td>
</tr>
</tbody>
</table>

Unsurpassed and evolving portfolio mix
**XRF**: Elemental analysis

Performace in WDXRF

**ARL OPTIM’X**: Surprising performance

**ARL PERFORM’X**: High performance sequential XRF

**ARL EQUINOX Series**
- Benchtop XRD
- Advanced research XRD

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

**EDXRF**

**XRD**: Analysis of structure, crystallography phases or compounds

**ARL 9600 Series**
- Integrated XRF-XRD

**ARL EQUINOX Series**
- Stand-alone powder XRD
- Integrated XRF and XRD

Thermo Scientific XRF and XRD Product Portfolio: Strong And Complementary Technologies
Key Figures

Staff seniority average: 10 years
PhD, Engineers and Technicians
Staff 2015: 20 employees 80% technically qualified

Creation: 1974 of INEL SAS

Resources

Components and electronic cards design & integration
Installation & After Sales Service for instrumentation
X-Ray diffraction systems assembling
Mechanical parts design & Metrology
Informatics tools development & assistance
Research & Development, technical assistance

All technical and human resources are situated in our headquarter in France:

Thermo Fisher Scientific – XRD Research

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+33 (0)2 3880 4545
44410 ARTENAY, France
Z.A. C.D. 675
When a photon does encounter an atomic particle, it transfers energy to the particle. The energy may be reemitted back the way it came (reflected), scattered in a different direction, or transmitted forward into the material.
The energy of photons used for optical spectroscopic measurements of various quanta.

E<sub>Hz</sub>: exahertz (10<sup>18</sup>)
Y<sub>HZ</sub>: yottahertz (10<sup>24</sup>)
Z<sub>HZ</sub>: zettahertz (10<sup>21</sup>)
X-rays Production: classically by excitation of external electronic level with electron beam.
**X-Ray Diffraction basics (1/3)**

- Planes of atoms act like a diffraction grating.
- Constructive & destructive interference lead to peaks in scattered intensity.
- Values of \( \lambda \) & \( d \) determine \( 2\theta \).
- Bragg's law: \( n \lambda = 2d \sin \theta \)
- Where:
  - \( n \) = order of radiation
  - \( \lambda \) = wavelength of radiation
  - \( 2d \) = lattice spacing of crystallites in the powder sample
  - \( \theta \) = Bragg angle

...
With XRD we measure distances... nothing more.

Chemical composition

Phases

Structure

Peak position-d-spacings

Peak intensity-nature and atomic positions in planes

With XRD we measure distances... nothing more.

Chemical composition

Phases

Structure

Peak position-d-spacings

Peak intensity-nature and atomic positions in planes
• Should give this pattern

• Halite (NaCl)...

Source: Wikimedia

DATABASE

Without a Database we can not do much.
One important issue with XRD is isomorphism.

A complementary technique sensitive to chemistry is helpful (XRF).

Ag$_2$Sb has the same structure as NaCl.

This is one real issue with XRD.
THIN LAYER (GIXRD)
What is called thin layer

Layer 1

Issue 1

To control penetration depth of X-Rays

Issue 2

Speed: if layer is really thin (few nm) is really thin

Issue 3

Often quality of signal is poor due to a lack of crystallinity

Issue 4

(epitaxial layer is really high required and dynamic detector sometimes required)

Substrate

GIXRD (or thin layer) is used to see the first few nm to 1µm of sample

Layer 0r 6000

Layer attachment or Equinox 5000 and Ω and Z are required (thin layer)
Bump spacing: information on thickness

Bump decay: information on roughness (angstrom scale)

XRR (X-Ray Reflectometry)

5nm Nb layer

10nm Ni layer

Unique feature for a desktop instrument

Difficult:

Thin is easy (less than 300 nm) thick is very difficult.

Information obtained 1/2
Stack of 128 W/Si layers on Silicon substrate

SI = 2.2nm
W = 1.1nm
Diffraction of course

4µm Ni layer on Iron
Au on TbPC2

What is Epitaxie?

Thin layer but with nearly same structure as a single crystal.
STRESS
A simple cubic structure is always the same. 

\[ n \alpha = 2d_hk l \sin(\theta hkl) \]

What is (residual) stress?
Some violence

Sample larger than before

Sample smaller than before

DEFORMATION

Side View

Top View

Stress
\[ d_1 < d < d_2 \text{ & } d_3 \]

\[ d_2 = d_3 \text{ in case of uniaxial stress} \]

\[ d_1 > d > d_2 \text{ & } d_3 \]
Texture measurement using Precix robotic system.
TEXTURE
What is called texture?

Preferred orientation / texture

Powder or random texture

Texture means classically deviation from random texture.
And many other things.
The Instrument is designed to retrieve the information we are looking for. It allows to measure and quantify physical parameters (length, weight, power, energy, time) that are looking for. It allows to measure and quantify the information we retrieve, which is designed to retrieve the information we need.
X-ray diffraction setup

Environment

Elastic coherent interaction:
- reflectometry: investigation on thin film for measuring thickness, roughness and density
- diffraction: investigation on phases
- absorption: imaging and radiography
- reflecctionmetry: investigation on thin film for measuring thickness, roughness and density

Incoherent elastic interaction:
- diffusion by a rough surface or crystalline defects

In instrumental configuration, adapted according to:
- type of measurement
- type of sample
- accuracy of the result

Instrumental configuration 2D or 3D
- powder, bulk, fibres
- small angle measurements
- grazing measurements
- small angle measurements

Detection

Sample

Optic

X-ray Source

Performances depend on the instrumental function

X-ray diffraction setup
A light emission characterized by:
- spectral range
- solid angle
- intensity
- dimension and shape of the source

Optimizing the characteristics of a source allows to focus on a given interaction.

<table>
<thead>
<tr>
<th>Point or Linear</th>
<th>Linear</th>
<th>Point or Linear</th>
<th>Linear</th>
<th>Spectral Range</th>
<th>Resolution Improvement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Small</td>
<td>Small</td>
<td>Small</td>
<td>Small</td>
<td>Large</td>
<td>Small or Large</td>
</tr>
<tr>
<td>Focusing</td>
<td>Very small</td>
<td>Focusing</td>
<td>Very small</td>
<td>Large (60°)</td>
<td>Few degrees</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Monochromatic</td>
<td>Molybdenum</td>
<td>Monochromatic</td>
<td>Large</td>
<td>Large</td>
</tr>
<tr>
<td>Diffusion</td>
<td>Reflection</td>
<td>Diffraction</td>
<td>Imaging</td>
<td>Fluorescence</td>
<td></td>
</tr>
</tbody>
</table>

This is achieved by using appropriate optics (1D, 2D, monochromator, mirror, collimator, slits ...).
An optic is characterized by:

- mosaicity
- spectral
- resolution
- beam size
- capture angle
- range

Focusing vs. Divergence:

- Convergent beam
- Kirkpatrick Baez
- Single collimation
- Pin-hole
- Channel-cut
- Flat Cu or Fe Si
- Flat graphite
- F1 and K1
Effect of optic: comparison between high resolution and high flux
Effect of wavelength on the mixture of minerals.
Function detection

0D Detection:
Acquisition is done stepwise
2θ and statistics are time dependent

1D Detection:
Acquisition is done in snapshots
Statistics is time dependent

2D Detection:
Acquisition is done in snapshots
Texture information but point beam required
Statistics is time dependent
Existing Instruments and Applications
ARL Equinox 100: A bench-top XRD for routine XRD—Performance with Convenience

Description

- Desktop (680 x 582 x 524mm)
- Lightweight 75 Kg
- Easy to install, run and maintain
- Light weight 75 Kg
- Only 1 LAN cable for communication
- Thin layer attachment (optional)
- 6 Positions auto-sampler (optional)
- <200W Total power consumption
- Standard electric plug
- No external gas supply
- No external cooling
- MicroSource coupled Smart Optics™
- No Alignment needed
- Desk top (680 x 582 x 524mm)
Equinox 100: Powder sample holders

Sample changer: 6 Positions

SSRT: Spinning sample holder

Capillaries

Gas reaction at room temperature
Slightly radioactive (alpha particles)
Air sensitive samples

Clays: Slow adapted to labs

Organic samples

Gandolfi Mount

Proprietary & Confidential

Equinox 100: Powder sample holders
Equinox 100 resolution comparable to any standard XRD

Peak/Background equivalent to high power XRD
Unique feature for a desktop instrument
5 minutes acquisitions cycled over 2 hours.

AI2S3 oxidation in air (used in explosive)
Complete experiment takes about 2 hours.
XRD/XRF combination inside an Equinox 100

Oxidation layer on steel belt

No phase containing manganese is obviously identified with XRD, but with XRF we evidence manganese.
SOLSA project: bulk sample mapping at mm scale

Data fusion: merging imaging-XRD-XRF data

In order to perform correlation mapping sample holder on E100

bulk sample mapping at mm scale
Multilayer mirror optic

Runs with Anton Paar XRK900 reaction

chamber
Structural change vs. temperature.

Photovoltaic Application

J. Mater. Chem. A 2013, 1, 5628
Automatic sample dilatation correction

Buehler HDK 4
Glass crystallization at high temperature

**CONDITIONS:**
- Power: 38kV - 38mA
- Furnace: FUR1200
- Acquisition: 3min
How do we see that with XRD?

Possible hot domed stage

CPS120

collision between detector and X with

Compatible with CPS590 (risk of)

Stress analysis software (Diffstress)

Texture analysis software (Labotex)

Motorized elevator

X/Y stage for mapping

Equinox 6000
Random texture (i.e., no texture)

Random Aluminum standard texture

`Probability (mrd)`

1.00

1.10

1.20

1.30

1.40

1.50

1.60

1.70

1.80

1.90

2.00

2.10`
If sample is textured, relative intensities of peaks will change depending on sample orientation vs beam.
Just a thought.

If we process the sample hard enough to get texture, don't we create also stress? If we have stress do we possibly have also texture?
Tilted because of about 600 MPa applied stress during process.

Lots of information.

Data processing with MAUD.