Chemical and Structural Analysis of Materials using XRF and XRD

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Switzerland

ArabLab 2018
Advanced materials in our lives

- Nanomaterials
- Composites
- Biomaterials
- Polymers
- Energy Materials
- Ceramic & Glass
- Metals & Alloys
- Electronics & Photonics
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

<table>
<thead>
<tr>
<th>Chemical Analysis</th>
<th>Selection of Area of Interest</th>
<th>TEM prep</th>
<th>Atomic Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>iXR Raman Spectrometer</td>
<td>ARL PERFORM’X XRF</td>
<td>DXR 2Xi Raman Imaging Microscope</td>
<td>FEI Helios G4 CX</td>
</tr>
<tr>
<td>ARL QUANT’X EDXRF Spectrometer</td>
<td>ARL EQUINOX XRD</td>
<td>Thermo Scientific K-Alpha+ XPS</td>
<td>FEI Themis Z TEM</td>
</tr>
</tbody>
</table>

UltraDry EDS Detector
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

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

- Reflection
- Imaging
- Diffusion
- XRD
- Diffraction
- XRF
- Fluorescence

Radiographic picture by Röntgen in 1895

Laue de Bragg
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

**Integrated XRF and XRD**
- ARL 9900 Series Integrated XRF-XRD

**Powder XRD**
- Equinox 6000: High performance Powder XRD
- Equinox 100 & 1000 Benchtop XRD

**XRF: Elemental analysis**

**XRD: Analysis of Structure-crystallography Phase or compound**
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 fingerprinting of Pharmaceutical Products by XRD

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.

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

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

Solve the Problem
Dynamic studies of materials: Real-time structural changes captured by XRD

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.

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.
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.

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.

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.
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.

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.

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

1. Clay Minerals
   - Quartz

2. Limestone
   - Dolomite

3. Iron ores
   - Aluminum oxides

4. Kiln Feed

5. Hot meal
   - Langbeinite

6. Free lime
   - Clinker phases
   - Periclase

7. Additives:
   - Gypsum phases
   - Slag
   - Fly ash
   - Pozzolan
   - Limestone

8. Cements
XRF and XRD Applications in Mining and Mineral Extraction processes

1. FeTiO₃, TiO₂, ZrSiO₄, Fe₂O₃, Fe₃O₄, FeO etc.

2. ZrSiO₄, TiO₂

3. Minerals in tailings
IRON and STEEL Process: Chemical and Phase Analysis by XRF and XRD

Raw Materials Processing

1. Fe₂O₃
   Fe₃O₄
   FeO

2. CaCO₃

Processing

3. Cast iron
   Fe₃C
   Fe-metallic

4. Slags
   CaO (free lime in slags)

Steel Making

5. Fe-metallic
   FeO
   Fe total

Steel Processing

1. Raw Materials Processing
2. Steel Making
3. Hot Rolling Mill
4. Cold Rolling Mill
5. Steel Processing
INTEGRATED XRF-XRD Instruments for Process Control and Industrial Materials

X-Ray Fluorescence

X-Ray Diffractometry
Example of combined analysis: XRF results first

XRF data
Example of combined analysis for process control: Chemistry and Mineralogy

XRF data

XRD data
Materials Analysis: Structure-Property studies

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)

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
17-7 Stainless Steel

<table>
<thead>
<tr>
<th>Elements</th>
<th>Conc%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>72.25</td>
</tr>
<tr>
<td>Cr</td>
<td>17.92</td>
</tr>
<tr>
<td>Ni</td>
<td>7.700</td>
</tr>
<tr>
<td>Mn</td>
<td>2.130</td>
</tr>
<tr>
<td>Mg</td>
<td>&lt;2e</td>
</tr>
</tbody>
</table>
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.

### UniQuant Spot Analysis of a stainless steel

<table>
<thead>
<tr>
<th>Element</th>
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<tr>
<td>Fe</td>
<td>56.56</td>
</tr>
<tr>
<td>Cr</td>
<td>16.50</td>
</tr>
<tr>
<td>Mg</td>
<td>21.08</td>
</tr>
<tr>
<td>Ni</td>
<td>4.290</td>
</tr>
<tr>
<td>Mn</td>
<td>1.560</td>
</tr>
</tbody>
</table>
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

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

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