X-Ray Diffraction and Crystal Structure
X-ray diffraction (XRD) is one of the most important non-destructive tools to analyse all kinds of matter - ranging from fluids, to powders and crystals. From research to production and engineering, XRD is an indispensable method for structural materials characterization and quality control which makes use of the Debye-Scherrer method. This technique uses X-ray (or neutron) diffraction on powder or microcrystalline samples, where ideally every possible crystalline orientation is represented equally. The resulting orientational averaging causes the three dimensional reciprocal space that is studied in single crystal diffraction to be projected onto a single dimension. One describes the three dimensional space with reciprocal axes $x^*, y^*$ and $z^*$ or alternatively in spherical coordinates $q$, $\varphi^*$, $\chi^*$. The Debye-Scherrer method averages over $\varphi^*$ and $\chi^*$ and only $q$ remains as an important measurable quantity. To eliminate effects of texturing and to achieve true randomness one rotates the sample orientation. In the so-called diffractogram the diffracted intensity is shown as function either of the scattering angle $2\theta$ or as a function of the scattering vector $q$ which makes it independent of the used X-ray wavelength. The diffractogram is like a unique “fingerprint” of materials. This method gives laboratories the ability to quickly analyze unknown materials and characterize them in such fields as metallurgy, mineralogy, forensic science, archeology and the biological and pharmaceutic sciences. Identification is performed by comparison of the diffractogram to known standards or to international databases.
F-S=S-RS=150mm
DS=1.25° (0.625°)
SS=1.25°
RS=0.3mm
X-Ray Diffraction (XRD) and Crystal Structure: Required Knowledge

- Bragg’s relation for X-ray scattering
- Max von Laue and Bragg method
- Debye-Scherrer technique
- Crystal lattice and reciprocal space
- Lattice parameters
- Identification of compounds
- Powder Diffraction File (PDF)
- Cambridge Structural Database (CSD)
- Electron density determination
- Principles of a Bragg spectrometer
- X-ray tube and X-ray production
- X-ray optics, slits, Soller slits, X-ray reflexion
- Wavelength discrimination
- X-ray detectors
- Sample preparation
- Compare with Neutron Diffraction
- Application of the XRD method to different other fields
X-Ray Diffraction and Crystal Structure: Tasks and Goals

- Set-up
- Produce
- Set-up
- Determine
- Determine
- Determine energy
- Determine the
- Measure energy
- Determine
- Compare energy

**WARNINGS**
- Be careful.
- Shut down
- Never touch
- Remove source after measurement
The RIGAKU MINIFLEX II X-ray diffractometer

Phase identification

Powder X-ray diffraction

Phase Identification
- Rutile (TiO₂)
- Anatase (TiO₂)
- Hematite (Fe₂O₃)

Quantitative analysis
- ZnO: 65%
- MgO: 35%

Crystal structure
- Dimetric/Hexagonal

Diffraction pattern matching
Goniometer & optics (incident)
- X-ray tube
- 5° soller slit
- Divergence slit
- Sample stage
- Shutter

Goniometer & optics (receiving)
- SS 1.25°
- Scintillation counter
- 5° Soller slit
- RS 0.3 mm
- Ni Kβ filter

Options
- Specimen Rotation Attachment
- Auto Sample Changer (ASC-6)
  - No alignment required
Vitamins are another group of materials commonly tested with XRD. The wrong polymorph of a vitamin is usually inert and provides no benefit to the consumer. For example, the B vitamin pantothenic acid has two polymorphs, one of which is inert. The data in Figure 2 is from a B-complex vitamin supplement. Using XRD it is possible to identify each component, and whether the correct polymorph is present to ensure proper potency.

**Measured XRD pattern of a B-complex vitamin supplement**
Simulated XRD patterns of cocaine-maltose mixtures

Simulated diffraction patterns of cocaine and maltose are displayed along with the peak positions of the International Centre for Diffraction Data (ICDD) standard. Two mixtures, 50% cocaine / 50% maltose and 10% cocaine / 90% maltose, show the qualitative differences in the XRD pattern as the components are varied. Qualitative identification is based on the presence of the unique diffraction lines for each substance, the "X-ray fingerprint." In addition, a quantitative determination can be made for each component by measuring its peak intensity and comparing it to the intensities measured from one or more samples of known concentration.
General XRD phase/composition identification analysis

General X-ray diffraction phase/composition identification will distinguish the major, minor, and trace compounds present in a sample. The data usually includes mineral (common) name of the substance, chemical formula, crystalline system, and reference pattern number from the ICDD International database. A summary table of analysis results and diffraction plot with reference pattern markers for visual comparison is shown below.

<table>
<thead>
<tr>
<th>Minor phases</th>
<th>Minor phases</th>
<th>Trace phases</th>
</tr>
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<tbody>
<tr>
<td><strong>Anhydrite</strong>, CaSO4 - orthorhombic ICDD # 72-0916</td>
<td><strong>Calcite</strong>, syn CaCO3 - rhombohedral ICDD # 05-0586</td>
<td><strong>Portlandite</strong>, syn, Ca(OH)2 - hexagonal ICDD # 44-1181</td>
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<tr>
<td><strong>Gypsum</strong>, syn CaSO4.2H2O - monoclinic ICDD # 33-031</td>
<td><strong>Brucite</strong>, Mg(OH)2 - hexagonal ICDD # 74-2220</td>
<td><strong>Quartz</strong>, SiO2 - hexagonal ICDD # 64-0312</td>
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