How to Analyze Materials

A PRACTICAL GUIDE FOR POWDER DIFFRACTION

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International Centre for Diffraction Data

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CERT NR. 11409.1

To All Readers

This is a practical guide. We assume that the reader has access to a laboratory diffractometer, analysis software, and an ICDD database.

We do not cover the theory of phase analysis nor do we explain the algorithms in the applied software and databases.

Information on theory and algorithms can be found in ICDD documents, such as technical bulletins (6), publication articles (>1,000), and tutorials (>40) located on our website: www.icdd.com.

We do not specify the software; ICDD databases work with over 40 known software packages. We have included "hints" on how you can evaluate whether the software package is working properly in your analyses.

Overview

- The vast majority of materials are crystalline solids made of periodic arrays of atoms.

- Crystalline solids, when exposed to monochromatic X-rays will diffract according to the principles of Bragg's law. This is the principle behind single crystal crystallographic analysis and powder diffraction analysis.

- In powder diffraction analyses, a random oriented, finely ground powder is required for multi-phase identification and quantitation.
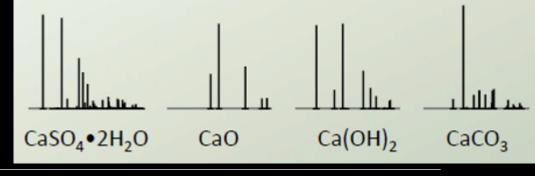
Note: Electrons and neutrons can also be used in diffraction analyses as they have the same critical wavelengths required by diffraction physics.
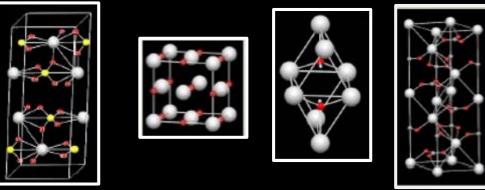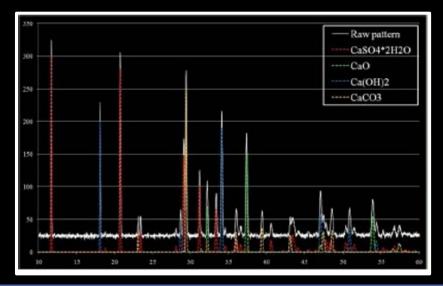
Why It Works

$CaSO_4 \cdot 2H_2O$ CaO $Ca(OH)_2$ $CaCO_3$

- Each crystalline component phase of an unknown specimen produces its own powder diffraction pattern.

- These patterns arise from the crystal structures of the component phases.

- The pattern for multi-component mixture consists of the weighted sum of the individual patterns for each component in the mixture.

Raw pattern
CaSO4*2H2O
CaO
Ca(OH)2
CaCO3

Basic Requirements

1. Good Data
2. Good Analysis Software
3. Good Reference Database

Obtaining Good Data

Elements of Good Data

High signal to noise ratio

Good counting statistics

Randomly oriented powders

Data available in electronic format for processing

To obtain a randomly oriented powder and achieve good counting statistics, the particle size needs to be below 1 micron.

In practice this rarely occurs and is a root cause of many, if not most, problems in powder diffraction analysis. The more your powder deviates from the ideal size and distribution, the more chance you have for errors in phase identification and quantitative analysis.
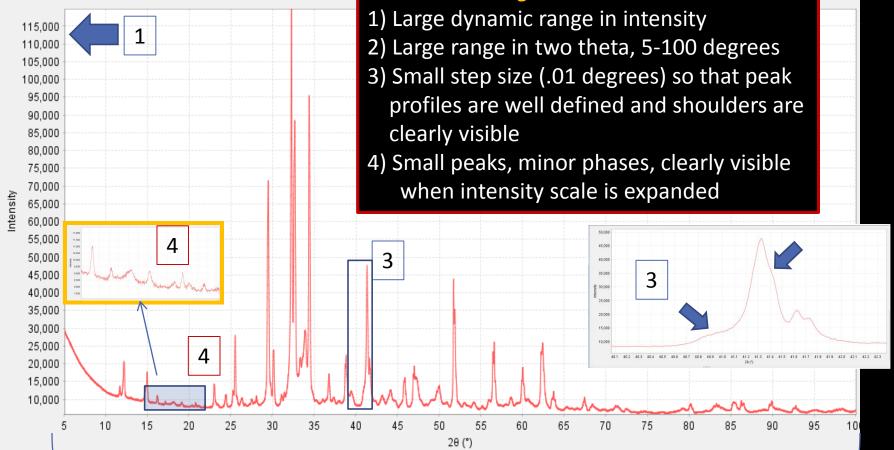
Good Data

This data set was collected by a laboratory diffractometer
The specimen was a finely ground cement, prepared to a fine dust by use of an attrition mill, and placed in a cavity mount

What makes it good data?
1) Large dynamic range in intensity
2) Large range in two theta, 5-100 degrees
3) Small step size (.01 degrees) so that peak profiles are well defined and shoulders are clearly visible
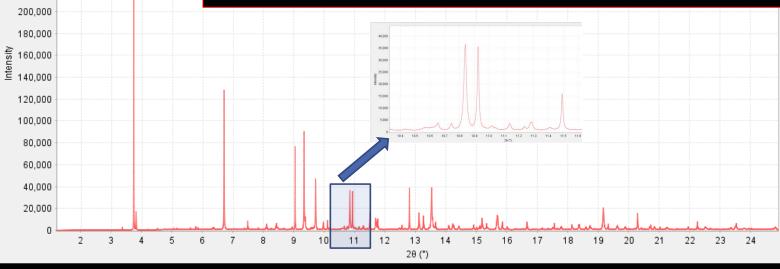4) Small peaks, minor phases, clearly visible when intensity scale is expanded

Better Data

This data set was collected at a synchrotron. The specimen was a finely ground vitamin pill mounted in a capillary.

What makes this better data?
— The data set has a large dynamic intensity range.
— The high peak profile resolution resolves most overlapping peaks, a step size of 0.01 degrees was used.
— Excellent counting statistics are achieved in minutes versus hours for a laboratory diffractometer

This data is fundamentally better than the previous slide since the exceptional peak resolution eliminates most peak overlap, producing accurate intensities without the need for mathematical deconvolution.

Hints – Good Data

Examine your signal to noise

Know your instrument resolution – measure it using NIST SRM 660b or NIST SRM 640d

Reduce particle size to 1-10 microns
- mortar & pestle, cryo-mill or attrition mill

Measure your particle size
- Use a sieve or...
- measure with laser light scattering or…
- use a microscope

Good Analysis Software

Elements of Good Analysis Software

Does the software find all the peaks present in a diffraction pattern? The software needs to be able to distinguish between low intensity peaks and noisy background.

Can the software distinguish between sharp and broad peaks – if not, you may have problems identifying nanomaterials and/or amorphous materials.

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Finding Peaks – an Important Step

Most commercial software uses 4-5 programs to calculate a peak position. These programs are often compiled together in a batch analysis step so that the user does all five steps in rapid sequential order with a single input command.

Import data

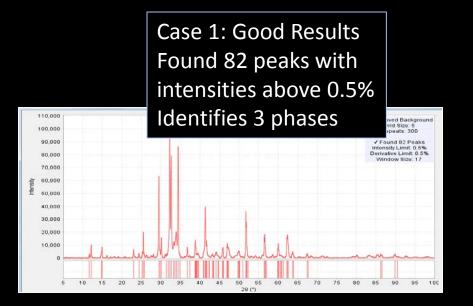Calculate background

Smooth data (if required)
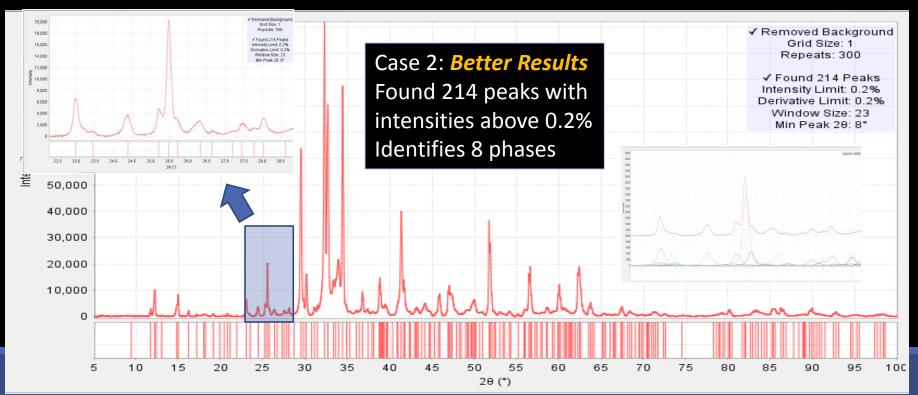
Remove alpha 2 (if required)

Identify Peaks

It is always important to analyze the output since these algorithms can often be tuned and optimized for various types of samples. Read the program help files to see if you can optimize the results for your specific analysis.

Case 1: Good Results
Found 82 peaks with intensities above 0.5%
Identifies 3 phases

If your software finds more peaks, chances are you will identify more materials. In case #1, the peak intensity threshold was set too high and in case #2 >100 *additional* peaks were found above background. In case #1, the three highest concentration materials were found. In case #2, 5 *additional* phases in concentrations below 5 weight percent were found.

Case 2: **Better Results**
Found 214 peaks with intensities above 0.2%
Identifies 8 phases

Hints – Good Analysis Software

Test your software!

Prepare a specimen(s) with known concentrations of ingredients.*
Does your software find all the peaks? Does it find low intensity peaks? Broad peaks? Peak shoulders?

At the ICDD, we often use Centrum vitamin pills for testing purposes. The ingredients are listed on the label and concentrations can be calculated. These pills are sold throughout the world in pharmacies. Most Centrum vitamins contain a mixture of vitamins and minerals both in low and high concentrations. If you want to test the software's ability to detect weak peaks and peaks near background levels make sure you have a low concentration material in your test sample.

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A Good Database

Elements of a Good Database

Identifications are made by matches to reference data. If the reference data are of poor quality, the match will be poor quality. If the database is not comprehensive, then materials will not be identified _or_ they will be misidentified producing false positive results.
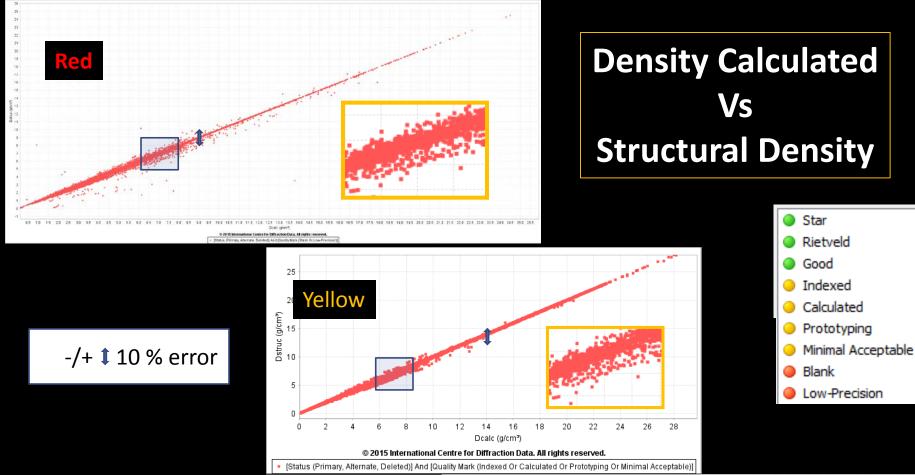
1. The data in the database should have an evaluated and assigned quality that relates to the reliability and accuracy of the reference.

2. The database should be organized in a way that facilitates the identification process.
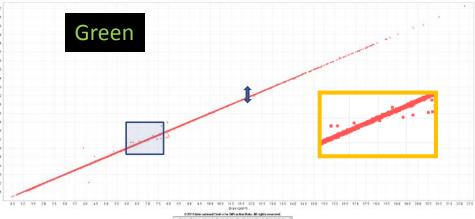
3. The database should be comprehensive – containing all known materials, in all forms of solid state matter (i.e. crystalline, non crystalline, nano crystalline, amorphous).

Density Calculated Vs Structural Density

Red

Yellow

-/+ ⇕ 10 % error

Green

Star
Rietveld
Good
Indexed
Calculated
Prototyping
Minimal Acceptable
Blank
Low-Precision

Missing or misplaced atoms cause displacements off the slope of one. The missing density (atoms) effect peak intensities and scaling factors use in phase identification and quantitative analysis. The highest quality references (green) should be used whenever possible for best analytical results.

Comprehensive Data Collections
- classified and edited by experts

The ICDD databases are organized into 48 collections consisting of subfiles and subclasses. This organization system allows the user to quickly use the appropriate chemistry or application for the analysis and eliminates false positive results.

PDF-4+ 2015   365,877 Entries
PDF-4/Organics 2016   501,964 Entries

Edited subfiles, unique to the Powder Diffraction File

31 Subfiles
17 Subclasses
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48 Collections

Chemistry
Minerals
Metals & Alloys

Application
Forensic
Cements

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Hints – A Good Database

Databases need to stay modern. If you want to reproduce old results use an old database. If you want to have better results, that reflects improvements in instrumentation and data quality, use a more modern database.

All fields grow with time. While many basic minerals have been known for over 100 years, ~1000 new minerals entries are published each year. Many of the new references (~80%) are higher quality determinations of previously identified minerals. The overall quality of the reference data improves with time, resulting in more phases being determined more accurately.

New fields emerge and require new references. Modulated structures, thermoelectrics, and hydrogen storage materials have had rapid growth in the past 5 years.

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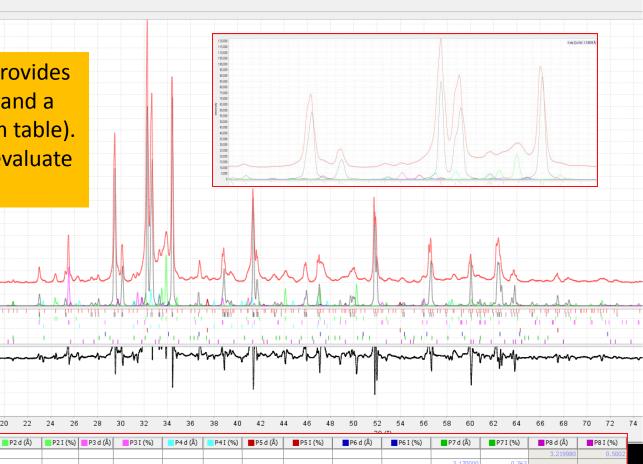11409.1

Putting It All Together

Good Data + Good Software + Good Database = Best Results
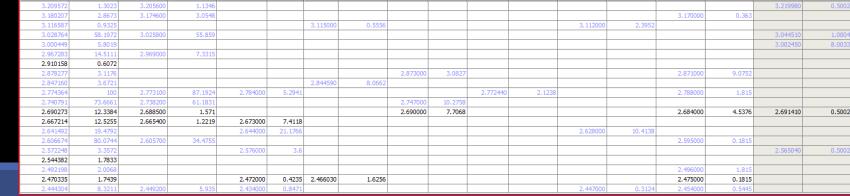
Most analysis software provides a visual match (top plot) and a numerical match (bottom table). Both should be used to evaluate your results.

Elements of a Good Result

In the previous example, the quality of the specimen data and the high quality of the reference data means that the d-spacings (peaks) were matched to four significant figures (see table) with the significance to a thousand of an Ångstrom or ten thousand of a nanometer! This is the power of powder diffraction.

This precision is used to match the hundreds of d-spacings in the pattern to an 8 component mixture. Such complex mixtures are found in everyday applications such as geological sampling, analysis of concretes and cements, and formulation analyses of pharmaceuticals.

The use of poor data, poor software, or a bad database places limitations on the precision of the technique and the ability to analyze complex patterns into the individual components. The inability to deconvolute peaks and their intensities also effects quantitative phase analysis which depends on accurate measurements of intensities and the ability to accurately deconvolute intensities in areas where there is peak overlap.

How to Evaluate a Good Result

1) Use your eyes – Does the solution appear to match the experimental data? Use plots, magnify the axes, and look carefully at the fit.

2) Use numerical data – Nearly all commercial software will provide numerical tables of experimental d-spacing, intensities versus d-spacing, and intensities of the matched components.

3) Use vendor provided "scoring" – All commercial software sorts matches by a scoring algorithm. Usually this is a composite score based on factors such as d-spacing, intensity match, missing lines (lowers score), number of matched lines (increases score) etc. It is always advisable to read the help files to understand the scoring method.

4) Use common sense and your senses – Do the results suggest physical properties, colors, crystal habits of the components that you can observe in the specimen? Do your results match your customers' expectations based on the source, history, and processing of the sample?

Thank you for viewing our tutorial.
Additional tutorials are available at the ICDD website.

www.icdd.com

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