

REFLEX QPA

Reflex QPA allows you to determine the relative proportion of different phases, including both inorganic as well as organic systems, in a mixture based on powder diffraction data. It is a widely used analytical method for phase characterization in various industries.

Quantitative phase analysis (QPA)¹ refers to the determination of relative amounts of different phases in multi-phase samples. X-ray powder diffraction is perhaps the most powerful method of obtaining quantitative phase information from multi-component mixtures in the fields of science and engineering for materials research. It is also an important tool for quality and process control in the industry. The power of the method lies in its simplicity and speed. Its applications include the characterization of pharmaceuticals, corrosion products, intermetallics, and contaminants, as well as forensic analysis, mineral assays, and fiber analysis.

WHAT DOES REFLEX QPA DO?

Reflex QPA has been developed to determine the relative amounts of different phases in a mixture by means of a powder diffraction pattern of the mixture.

In Reflex QPA, the pure component phases that comprise the mixture may be represented by:

1. Crystal structures (The Rietveld method^{2,3,4})

The experimental diffraction pattern is characterized as the superposition of powder diffraction patterns simulated from the crystal structures of the component phases. Pattern, sample, lattice, and structural parameters for each phase are refinable during a calculation.

2. Experimental powder diffraction patterns

Reflex QPA supports the use of the standardless method and the internal standard method. For each phase, parameters associated with line shift corrections may be refined.

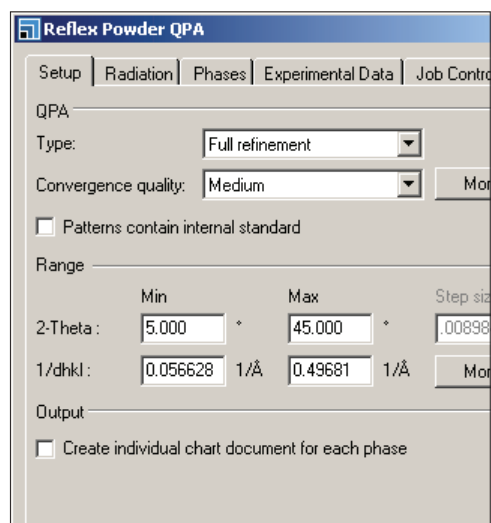


Figure 1: The Materials Studio user interface displaying the Reflex QPA control panel.

The standardless method^{5,6} assumes that all the patterns are recorded under an identical experimental setup. For the internal standard method^{7,8}, a fixed weight fraction of a standard material is added to all pure component phases as well as the mixture phase before their powder diffraction patterns are recorded.

3. A combination of scenarios of 1 and 2

This approach combines the standardless QPA method using crystal structures as input (the Rietveld method) with the standardless QPA method using experimental powder patterns as input.

THE MATERIALS STUDIO ADVANTAGE

Reflex QPA is part of Materials Studio®'s Reflex product, providing a seamless integration with other modules in Reflex (Powder Diffraction, Powder Indexing, and Powder Refinement) and Reflex Plus for a full crystal structure determination. Experimental powder diffraction patterns are readily visualized using the Materials Visualizer. Materials Studio's integrated model building and editing tools enable you to construct, visualize, and manipulate molecular fragments in the asymmetric unit of a crystal structure representing for systems such as drugs, pigments, metal oxides, and zeolites.

Results generated by Reflex QPA can be analyzed using Materials Studio's spreadsheet-like study table environment. The study table provides an easy association of the crystal structure or experimental powder diffraction pattern for each pure component phase with its estimated contribution in the mixture phase (e.g. integrated intensity, intensity fraction, weight fraction). It also offers powerful sorting and plotting functionality. Chart documents containing the decomposition of the input

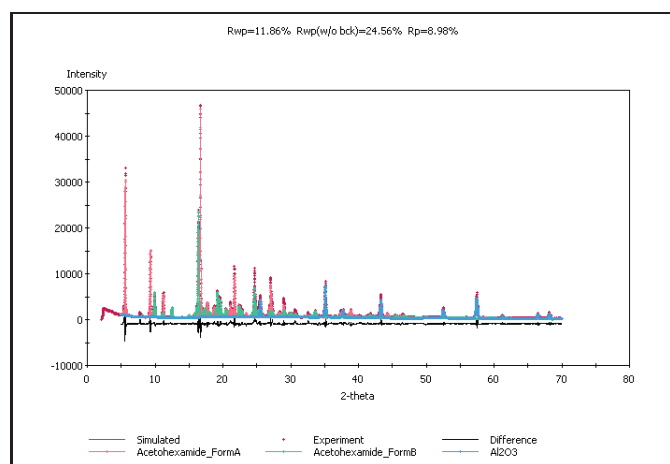


Figure 2: A decomposition of input experimental powder diffraction pattern of the phase mixture in terms of the patterns of all the individual component phases.

experimental powder diffraction pattern of the phase mixture in terms of the patterns of the component phases can be embedded in the study table.

Structural information, diffraction data, and chart documents can be readily exported to and imported from other PC applications—allowing easy sharing of the results with colleagues and an easy incorporation into documents created by standard word processor, spreadsheet, and presentation packages. In addition, high quality images can be easily produced.

HOW DOES REFLEX QPA WORK?

In QPA from crystal structures, usually referred to as the Rietveld method, the pure component phases are represented by their crystal structures. The diffraction pattern of the mixture is decomposed into the superposition of powder diffraction patterns simulated from these crystal structures. During a QPA calculation, in addition to the intensity coefficients, all the user-specified refinement parameters (including pattern, sample, lattice, and structural parameters) of the simulated intensity may be refined to optimize the agreement between the diffraction pattern of the mixture phase and the superposition of the simulated intensities from the pure phase crystal structures. This approach combines the determination of the weight fractions with a Rietveld refinement of all pure phase crystal structures.

In QPA from powder patterns, the pure phases are represented by their experimental powder diffraction patterns. Reflex QPA supports the use of the standardless method as well as the internal standard method.

The standardless method relies on the pure component phase powder diffraction patterns being recorded under identical experimental conditions. To calculate weight fractions, the scattering intensities of the pure patterns are related directly to the mixture intensities. Parameters associated with line shift corrections caused by a variety of experimental aberrations are refinable during a QPA calculation.

The internal standard method involves adding a fixed weight fraction of a standard material with a distinctive powder pattern, often corundum, to all the pure phases and the phase mixture. The scattering contribution of the standard serves as a reference, allowing the intensities of the pure phase powder patterns to be related to that of the mixture, and thus relating to the weight fractions. The presence of a common internal standard provides a means to correct for varying experimental conditions, sample adsorption, and matrix effects. Internal standard QPA requires an extra preparation step - all the experimental powder patterns need to be normalized such that the scattering intensity contribution from the standard is the same for all the patterns.

The internal standard method proceeds in two steps. In the first step, the intensity of the standard contribution in each phase is determined and the pattern intensity is rescaled such that the scattering intensity contribution from the standard is the same for all the patterns. In the second step, a quantitative phase analysis is performed using the scaled phase mixture and pure phase powder patterns.

It's even possible to combine the use of crystal structures and experimental powder patterns for representing the component phases within a single QPA calculation. For this to work, one or more calibration phases must be present to relate the diffraction intensities from the pure phase experimental powder diffraction patterns and the simulated intensities calculated from the crystal structures. The calibration phase is a pure phase for which both the crystal structure and the experimental powder diffraction pattern are included to the calculation. Once the relationship between the two intensity scales is estimated, the simulated intensities generated from the crystal structures can now be used together with the experimental powder patterns for the other phases, so as to evaluate the weight fractions.

HOW REFLEX QPA BENEFITS YOU

Reflex QPA offers a comprehensive collection of state-of-the-art algorithms for phase analysis. The flexible representations of pure component phases facilitate materials characterization in many different industries, which may be impossible otherwise due to lack of knowledge of, for example, the structural models.

Reflex QPA can be applied to both organic and inorganic systems. The amorphous content can be estimated by means of the internal standard method. Addition of an internal standard to both the pure component phases and unknown samples eliminates instrumental and matrix effects, and allows for unconstrained analyses to be conducted by direct fitting of experimental powder patterns to each phase in the sample. Corrections for preferred orientation effects are available through the Rietveld method. A combination of standard patterns is fitted to observed patterns using least-squares minimization, thereby reducing user intervention and bias.

Reflex QPA provides researchers with a fast pathway for the application of computational techniques to solve real industrial problems.

FEATURES

Setup

- The initial crystal structures can easily be imported from other sources or created using the Crystal Builder within the Materials Visualizer.
- Read in a variety of diffractometer file formats, including 3CAM, Bruker, Galactic SPC, GSAS raw, ICDD PD3, ILL, JCAMP, PAnalytical XRDML, Philips, Scintag, and Stoe.
- Allows for different radiation sources with multiple wavelengths and user-defined polarization.
- Ability to pre-process experimental data, for example via background subtractions, data smoothing, scaling, and $K\alpha_2$ stripping.
- No limit on the number of pure component phases.
- Crystal structures or experimental powder diffraction patterns for the pure component phases are stored in a spreadsheet-like study table.
- Multiple default settings allow for simple operations, or advanced users can adjust individual simulation parameters as necessary.

- For pure component phases represented by crystal structures, pattern, lattice, sample, and structural parameters are refinable. For the pattern parameters, a versatile range of peak profiles is provided, including Gaussian, Lorentz, Mod. Lorentz#1, Mod. Lorentz#2, Pseudo-Voigt, Pseudo-Voigt, Person VII, Thompson-Cox-Hasting, David-Voigt and Tomandl pseudo-Voigt. Choice of asymmetry correction consists of Rietveld, Howard, Berar-Baldinozzi, and Finger-Cox-Jephcoat. For the sample parameters, sample and instrument broadening effects are simulated. Isotropic and anisotropic temperature factors can be accounted for, as well as the effects of preferred orientation. The structural parameters include rotational, translational, and torsional degrees of freedom for any molecular fragment in the unit cell.
- For pure component phases represented by experimental powder diffraction patterns, parameters associated with line shift corrections may be refined.
- Ability to propagate the refinement settings from one pure phase component document to any or all of the others in the input study table.
- The background contribution of the mixture experimental powder diffraction pattern can be fitted as part of a QPA calculation.

CALCULATION FEATURES

- Ability to treat both organic and inorganic systems.
- Pure component phases can be represented by (1) crystal structures, (2) experimental powder diffraction patterns, or (3) the mixture of (1) and (2).
- Ability to determine the scaling factor required for normalizing the powder diffraction patterns with respect to the internal standard.
- Full refinement calculates the relative contents of a number of specified pure phases in a given mixture from the powder diffraction pattern of the mixture, performing a Rietveld refinement of the input parameters through a specified number of iterations and obtaining the weight fraction for each component phase.

- Refine weights calculates the relative contents of a number of specified pure phases in a given mixture from the powder diffraction pattern of the mixture, but does not refine any of the input parameters. The effect is the same as performing a full refinement calculation with all the refinement options turned off.
- Calculate integrated intensity, intensity fraction, and weight fraction for each component phase.

Running Jobs

- All Reflex QPA jobs are run in the background freeing up the Materials Studio client for other research.
- All Reflex QPA jobs can be submitted to local or remote compute servers.

Results

- Calculated integrated intensity, intensity fraction, and weight fraction for each component phase as well as a chart document containing the calculated powder diffraction patterns for the pure phases and its estimated contributions to the mixture pattern are stored in a study table.
- Parameter settings are automatically saved for each simulation.

Analysis

- Analysis is carried out with the help of spreadsheet-like study tables.
- Each atomic structures or experimental powder diffraction patterns for any given pure component phase is embedded in the study table, allowing for independent viewing using the 3D Viewer tools in the Materials Visualizer.
- Chart documents showing the contribution of each potential phase to the experimental mixture pattern can be analyzed with the Chart Viewer tools in the Materials Visualizer.
- A user specified subset can be filtered out from a study table into a new table.
- Flexible graph plotting enables plotting properties against each other, and plotting to a selected subset.

- All or part of a study table can be copied and pasted into Microsoft Excel® and Microsoft Word®.
- Structures and chart documents can be exported to bitmap files, and also be printed on grayscale or color PostScript printers.

SYSTEM DETAILS

Operated through the Materials Visualizer on Windows® 2000 and XP, Reflex QPA calculations can be executed on Windows® 2000, Windows 2003 Server, Windows XP, SGI IRIX, Red Hat Linux (Intel IA32, EM64T, and compatibles), and SuSe Linux (Intel IA32, EM64T, and compatibles) operating systems.

To learn more about Materials Studio, go to accelrys.com/materials-studio

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