FULL PATTERN DECOMPOSITION

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The structure determination maze

The problems to be overcome in structure determination from powder diffraction data are twofold:

1) **the basic phase problem**, which is central to all crystallographic structure analyses, whether the data be from a single-crystal or a powder diffraction experiment

2) **the reflection overlap problem**, which is specific to powder diffraction data

No single approach to these two problems has emerged as the optimal one. The best approach always depends upon the nature and complexity of the material under investigation, and the quality of the diffraction data

**The whole process can be viewed as finding a practicable path through a maze of possibilities**
The structure determination process is a sequential one

That is, each step depends upon the previous one being correct

A mistake made early on in the procedure can make all subsequent steps useless
When the positions of the reflections are known, their intensities can be estimated. Two methods can produce a set of extracted intensities suitable for attempting a structure solution. Both derived from the Rietveld method:

**LE BAIL (1988)**
The process of using iteratively the Rietveld decomposition formula, combined with a *full profile fitting* procedure

**PAWLEY (1981)**
Removing the crystal structure refinement and adding the refinement of the individual intensity for every expected Bragg peak
The intensities estimation is best done with a whole profile fit, where a peak shape is assigned to each reflection and its intensity is either refined (Pawley method) or adjusted in an iterative procedure (Le Bail method) to fit the measured data.

This approach to the determination of the reflection intensities can be described as a model-free Rietveld refinement, where the intensities of the reflections rather than the atomic coordinates are optimized.
Profile fitting

The background is described by a polynomial

The peak shape is described by some appropriate analytical functions (gaussian, lorentzian, pearson VII….)

The FWHM, peak asymmetry, etc, are described with analytical functions, variable with $2\theta$

During the profile fitting the refinable parameters are: unit cell, $2\theta$ zero, background, shape function, FWHM, asymmetry
The individual reflection intensities can be used as input to the traditional structure solution methods

\[ \rho_{xyz} = \frac{1}{V} \sum_{hkl} F_{hkl} \exp\left\{ -2\pi i (hx + ky + lz) \right\} \]

The structure factor \( F_{hkl} \) sums the result of scattering from all of the atoms in the unit cell from the \((hkl)\) planes, to form a diffraction peak

\[ F_{hkl} = |F_{hkl}| \exp(2\pi i \phi_{hkl}) \]

\[ I_{hkl} \propto |F_{hkl}|^2 \]

lost in a XRD experiment
If the extracted intensities are to be used as input to the structure solution program, something has to be done about the overlapping reflections.

Single Crystal Diffraction

This information is distributed in a 3D space.

Powder Diffraction

The 3D diffraction data are “compressed” into one-dimension.
As a consequence

Overlap

Considerable overlap of peaks leading to severe ambiguities in extracting the intensities $I_{hkl}$ of individual diffraction maxima.
The experimental diffraction profile must be decomposed into single peaks in order to extract the integrated intensities corresponding to each hkl reflection.

The area under each peak gives the integrated intensity $I_{hkl}$ ($I_{hkl} \propto |F_{hkl}|^2$) value associated to each diffraction effect (hkl reflection).
Other problems

Background
not always easy to be correctly defined

Preferred orientation
The crystallites are not always randomly oriented. This behaviour modifies the real ratios of the experimental integrated intensities

If the scattering power is weak (light atoms) the experimental resolution is very far from being atomic
The quantity of information present in a powder diffraction experiment is the same as in the single crystal. The difficulty is in the possibility to recover the complete and correct information. The experimental structure factor moduli are generally determined with errors of about 40% when good quality laboratory X-ray data are used. The success of powder TRADITIONAL structural solution methods depends on the extraction step: the more reliable the extracted integrated intensity values, the larger the success probability of solving the structure.
Treatment of overlapping

Usually, the intensity of a peak resulting from several overlapping reflections is simply divided equally over the contributing reflections.

This is known as equipartitioning

Although this approach necessarily yields a number of incorrect intensities, it has proven to be sufficient for structure solution in many cases.

For the more difficult cases, more sophisticated approaches can be used.
The random decomposition approach in EXPO

For each group of severely overlapping reflections, a random partition of the integrated intensities is performed.

To activate the random procedure (Altomare et al., 2001) in order to improve the quality of the extracted structure factor moduli values. $p$ is the coefficient for the reflection overlapping definition ($2\theta_i - 2\theta_{i-1} \leq p\text{FWHM}_{i-1}$. Default $p$ value is 0.5)
The random decomposition approach: the main steps

An EXPO default run extracts the intensities \((I_h)\) via Le Bail algorithm

Groups of severely overlapping reflections are defined

the total integrated intensity of the group is partitioned according to:

\[
I'_h = \sum_h I_h \ast \left( \frac{r_h}{\sum_k r_k} \right)
\]

\(r_h\) is a random number associated with the reflection \(h\), \(I'_h\) is consequently a random integrated intensity value
The random decomposition approach: the main steps

The profile discrepancy factor is calculated to evaluate the efficiency of the random decomposition process:

$$R'_p = \sum_j (Y'_{oj} - SY'_c)^2$$

If $R'_p \leq R_p$, the $I'_h$ are accepted as trial integrated intensities and the $R_p$ value of the cluster is updated.

The procedure is cyclically repeated.

The $I'_h$ set having the minimum $R'_p$ is saved and used in the phasing step.
AGREEMENT FACTOR
to estimate behaviour and efficiency of the
decomposition process

On the profile:

\[
R_p = \frac{\sum_i \left| y_{oss}(i) - y_{calc}(i) \right|}{\sum_i y_{oss}(i)}
\]

The summations go over the total number of profile points

**Assesses the quality of the fit between observed and calculated profiles**

Low \( R_p \) value is necessary and not sufficient condition for a reliable extraction
The Le Bail method: limit

If two reflections strongly or completely overlap, the Le Bail approach assigns equal starting intensity values to the reflections.

The Le Bail method: advantage

Is very sensitive to the starting intensity values.

The Le Bail method can exploit some prior information in the intensity-recycled extraction process, eventually available during the solution process.
The presence of Pseudo symmetry

In a default run of EXPO, the statistical analysis of the normalized structure factors is performed to eventually reveal the presence of pseudo, to recognize the percentage and the type.
The Le Bail method can exploit some prior information in the extraction process, eventually available during the solution process.

It may benefit from the following information:
The Le Bail method can exploit some prior information in the extraction process, eventually available during the solution process. It may benefit from the following information:

The localization of a structure fragment.
The use of the information which become available during the structure solution process, reduces the tendency of the Le Bail formula to equiportion the intensity of a group of strongly overlapping reflections and improves (on average) the accuracy of the decomposition process and than of the total structural solution process.
EXPO Profile Decomposition and Intensity Extraction: an application

Experimental pattern

The pattern is divided into intervals. A single peak is also singled out.

Background estimation

Profile fitting and pattern decomposition via Le Bail method

Integrated intensity values calculation
Conclusions

Crystal structure solution by powder diffraction data is not a trivial task and is still a challenge in many cases.

A preliminary and critical point is represented by the decomposition of the experimental diffraction pattern into single integrated intensity values.

Great experimental, methodological and computing progress has been reached and implemented in many available software.
We invite contributions of papers that, while discussing the followed computational, methodological, and/or experimental strategies, point out the essential and advanced contribution of powder diffraction in identifying the unknown crystal structure of a compound.

Keywords: Structure solution methods, Qualitative analysis, Quantitative analysis, Structure refinement, Structure determination.
THANK YOU FOR YOUR ATTENTION