INDEXING AND SOLVING CRYSTAL STRUCTURES FROM POWDER DIFFRACTION DATA USING THE BRUKER-AXS SUITE AND EASILY ACCESSIBLE FREE SOFTWARE. A PRAGMATIST'S VIEW.

Robert Papoular, Atomic Energy and Alternative Energies Commission, France

e-mail: robert.papoular@cea.fr

Pioneered about 25 years ago from high-resolution synchrotron powder diffraction data, ab initio structure solution from X-ray powder data has made tremendous progresses due to both instrumental and software achievements. The days when the use of powder diffraction was restricted to fingerprint identification are long over.

Whilst there is no possible competition between the (tens of) thousands of Bragg reflections that can be collected on a single crystal diffractometer and the meager hundreds or less ones measurable in a powder diffractogram, single crystal are not always available and we have to make do with the accessible powder samples.

By pushing high-resolution to the limit at prominent synchrotron beamlines, Bragg peak overlap is brought down to a minimum and noise effects minimized (provided that the sample does not die in the X-ray beam). There is no black magic in further pushing up the limit of the ever increasing large-sized crystals being solved. This is achieved by injecting chemical knowledge (via restraints and constraints) to the observed XRPD data. In the case of organic materials or pharmaceuticals, this is done primarily by introducing a flexible or rigid model for some of the molecular blocks which automatically incorporates the connectivity of the chemical moieties involved. For an inorganic material such as a metallic oxide, modeling the crystal structures using tetrahedra, octahedra or both achieves a similar goal, and as in the previous organic case substantially reduces the number of effective variables. This war has long been won resulting in the development of the ubiquitous DASH, EXPO, FOX, XLENS + TALP software.

The next war front is to try to achieve similar successes for the new generation of laboratory instruments from a benchtop D2 Phaser (e.g., equipped with a LYNXEYE detector) to an SXD Prospector working in powder diffraction mode with a 2D APEX II CCD detector. The aim of the game is now to get data which are as synchrotron-like as possible. The first step is to get rid experimentally or numerically of the extraneous Cu $K\alpha_2$ contribution to the powder diffractograms usually present at a lab source. This first step results in an effective monochromatic beam so much more suitable for indexing. The second step is to remove as much as possible of the noise on the measured data by making use of a carefully measured resolution function on a NIST Standard Reference Material [SRM] such as Al$_2$O$_3$. The resulting Full Width at Half-Maximum [FWHM] $v.s.$ 2$\Theta$ reflects how much (careful) smoothing is justified at any portion of the measured diffractogram. A third and last essential step relates to optimizing the minimum 2$\Theta$ (largest $d$) and maximal 2$\Theta$ (smallest $d$). Regarding the latter, two figures should be kept in mind: Assuming Cu $K\alpha$ radiation, Bragg peaks should at least be observed down to $d = 2$ Å resolution ($2\Theta \approx 45^\circ$) for successful indexing and up to $d = 1$ Å (atomic) resolution to be able to apply Direct Methods successfully using one of the only two successful available free software for powder data that allow for it: EXPO (C. Giacovazzo et al., Bari) and XLENS (J. Rius et al., Barcelona).

In this talk, the points mentioned in the last paragraph will be illustrated using data collected on a D2 Phaser and a Prospector / APEX II (used in powder mode) [Northwestern University], as well as on a D8 Advance diffractometer [University of Ioannina].

This talk would not have been possible without the expertise and the datasets obtained from Peter Mueller (MIT, Boston), Bruce Noll (Bruker AXS, Madison), Nathan Henderson (Bruker AXS, Madison), Amy Sarjeant (now at CCDC, Piscataway) and Nikolaos Kourkoumelis (University of Ioannina).