Toward a Fully Automatic Structural and Chemical Quantitative Analysis by X-ray

Luca Lutterotti
Department of Industrial Engineering, University of Trento
via Sommarive, 9
Trento, Italy

X-rays are quite a versatile tool to perform several kinds of complementary analyses, from diffraction (XRD) to focus on crystallographic and structural characteristics of our samples to fluorescence (XRF) for elemental analyses or more exotic techniques like EXAFS or XANES.

XRD and XRF are two techniques widely present in most modern research and industrial labs to obtain some basic fundamental information as phase content and chemical information. We are also observing an increasing demand and offer for automatic characterisations tools as well as more portable instrumentation to be used on the field.

One example is the mining industry for which an accurate quantification of the mineralogical content and their composition is fundamental along the entire course from the exploration to the processing of material waste. In this kind of applications, an automatic and rapid processing of the collected data is paramount important.
In our laboratory, we have developed two new analysis methods based on the Rietveld approach to help reach such goals: a Full Pattern Search-Match (FPSM) and a fully combined XRD-XRF analysis.

FPSM is based on an iterative Rietveld quantitative analysis using a large database of crystal structures as input. In each iteration, the search-match ranks the structures using a specific Figure of Merit and adds the new best fitting one to the Rietveld fit until no more phases can improve it significantly. To perform all iterations and Rietveld fits needed in a reasonable time, a very fast and automatic Rietveld quantification algorithm has been implemented. We will show some examples to illustrate the strengths and the weaknesses of the method. What is undoubtable, is that the efficacy of the method is directly proportional to the quality and completeness of the database of crystal structures used.

The combined XRD and XRF analysis was developed instead to improve the accuracy of the chemical and phases quantification. It is well known that an accurate XRF elemental quantification requires the knowledge of the matrix, but not in term of elements content, but phase composition to correctly compute the absorption attenuation for all the different lines energies. The XRD may provide this information. At the same time the knowledge of the chemical composition may help the phase identification in the search-match as well as the phases quantification by constraining the overall elemental content. The combination of the two techniques is usually only done to validate the results at the end, or the chemical composition is used as input for the search-match. Very few attempts have been made for a better integration and almost all of them didn't reach the mainstream. What we are proposing is a fully combined approach in which we use a unique generalised sample description in term of crystallographic phases, each one with its own elemental composition, to fit simultaneously both the XRD and XRF patterns/spectra. Using a phases description of the sample also for the XRF fundamental parameter fitting allows in principle an exact computation of the matrix absorption. At the same time, the more accurate elemental composition will end up in a more accurate phases quantification by the XRD fitting. Some examples will be shown to illustrate how this method can provide better info about our samples.

Next target is to merge these two methodologies in a unique package to automatize the entire process from the raw experimental data to the final chemical and structural results.