

## Combination of X-ray powder diffraction with other techniques

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X-ray Powder Diffraction (XRPD) is a powerful tool for the characterization of ordered materials. In recent decades, the availability of brilliant X-ray synchrotron sources allowed solving and refining crystal structures by powder diffraction in an almost routine fashion [1] and the study of dynamical evolution of crystal structures [2]. The basic limitations of XRPD originate from the interference nature of the diffraction process itself, thus limiting detection selectivity and sensitivity and requiring ordered samples. Moreover powder diffraction suffers of peak superposition problems with a reduction of information amount with respect to single crystal diffraction. For these reasons, many “real world” materials (catalysts, dyes, drugs for instance) containing disordered moieties and/or amorphous or liquid-like phases or showing surface- or defect-related phenomena constitute a problem for their characterization using XRPD only. **Energetic** features (reaction heats), **surface** properties, information on gas, liquids **non-periodic** systems in general, **adsorbates** can not be studied by XRPD only. **Chemical selectivity** (Al. vs. Si, Fe vs. Co etc.), except in the case of resonant diffraction experiment (indeed difficult and limited to sample containing heavy atoms in sufficient amount) is very limited. In these cases, other techniques can provide useful complementary information.

**Electron microscopy** techniques (*SEM*, *TEM*) can be used for studying the crystallite size, the morphology but also for structure solution (when exploiting the *Electron Diffraction setup*) employing nanocrystals instead of using typical micron-sized crystals [3]. **Spectroscopy** techniques have wide complementarities and applications in combination with XRPD. Solid-state Nuclear magnetic resonance (*SS-NMR*) can be used to obtain important information (number of independent atoms, coordination of the atoms) for structure solution and can investigate defect states and amorphous states [4]. *Raman* spectroscopy can give information on surface effects, disordered/light atoms, information at the interaction level and has the very positive feature of being a flexible instrumentation, making it particularly apt for combination at in situ conditions [5]. *Infrared* spectroscopy can give hints on adsorbed species, surface properties, hydration species. *EXAFS* can give information at the short range scale (i.e. coordination and distances) also on amorphous samples [6]. *Mass Spectroscopy* allows gas identification and quantification [7]. Other techniques widely used are *thermo gravimetric/Differential scanning calorimetry (TG/DCS)* [8] for thermal stability, water and volatile species quantification, *Dynamic light scattering (DLS)* [9] for particle size distribution in solution and suspension, *Small Angle X-ray scattering (SAXS)* for low ordered materials and soft matter, depending on the studied system.

The techniques can be combined in different fashions, i.e. statically and separated, or at in situ conditions but separated or at in situ and in simultaneous setup. The first is the more simple approach, apt to study static samples. The latter is the more challenging setup, that offer the possibility of obtaining an exhaustive characterization of transformations occurring into the sample. X-ray Powder diffraction (XRPD) beamlines at the various synchrotron facilities are presented. In particular, the available experimental setup are described together with some applications. The applicability of powder diffraction in static (structural solution and refinement) and dynamic (in situ approach) experiments is discussed with particular details to the available non-ambient conditions that can be reached (low and high temperature and or pressure, photo-induced modifications). The possibilities and limitations of the techniques are described.

Detailed description of the setup and examples of applications [7,10] are given for in situ simultaneous Raman/XRPD combination.

## References

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