Micro-Electron Diffraction Applications in The Structural Analysis of Metal-Organic Frameworks and Amorphous Phases Prepared by Mechanochemistry

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Micro-electron diffraction (micro-ED) is a recently developed technique suitable for the structural analysis of materials from individual micro- or nano-sized powder crystallites. ELDICO SCIENTIFIC's studies on amorphous phases (by X-ray powder diffraction) of quininium aspirinate [1], a drug-drug salt synthesized by neat mechanochemistry, led to the astonishing discovery of a few crystallites (around 2 um size), with sufficient crystalline order to afford the determination of a unit cell, among a majority of amorphous, non- diffracting crystallites. Quininium aspirinate is known to yield amorphous phases by neat ball milling or neat manual grinding the reactants in a mortar with pestle [1]. The latter products are known to recrystallize upon storage for around two years, although the phase transition timeframe has not been studied in detail. This work reports a novel use of micro- ED to screen for poorly crystalline seeds of the crystalline phase that will potentially grow from the bulk amorphous, which could prove very valuable for the full characterization of pharmaceuticals potentially formulated as amorphous, and other technologically important organic materials and their polymorphs. This work will also show X-ray powder diffraction measurements and Williamson-Hall graphs investigating the recrystallization process inside sealed glass jars, wherein amorphous quininium aspirinate is exposed to air only, and to solvent vapors such as N,N-dimethylformamide, hexane, and acetonitrile. All these vapors remarkably accelerate the recrystallization kinetics, from months to hours. Trends in size and strain parameters of the crystalline phases will be also shown.

Examples of crystal structure determination (including H positions) directly from powder crystallites of three metal-organic frameworks will be included. In these cases, laboratory X- ray powder diffraction data using Bragg-Brentano optics has shown strong preferred orientation effects in low angle diffraction peaks, rendering intensity data practically not usable for structural analysis beyond the determination of plausible unit cells and space group symmetries.

References

[1]- N. Harris, J. Benedict, D. A. Dickie and S. Pagola, Acta Cryst. (2021) C77, 566–576.