

Exploring the Chemistry of Artworks with X-ray eyes

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X-ray based methods of analysis are eminently suited for material characterization and chemical imaging of painted works of art and related cultural heritage (CH) artefacts. This can be realized by using X-rays generated in compact, laboratory sources and by means of powerful X-ray beams produced at synchrotron facilities. A comprehensive review of the possibilities of these methods for studying the chemical compounds present in painted works of art was recently published [1]. These can be employed for various purposes, e.g.,

- revisualization of overpainted representations, revealing early stages of the creative process or intentional alterations of the composition done during the lifetime of the artwork;
- (highly specific) identification of the pigment types used and the pigment subtypes present, providing opportunities to study the provenance and authenticity of works of art; and
- identification of the nature and distribution of secondary products, formed on the paint surface by spontaneous degradation of the original painting materials.

In this contribution, amongst others, the following recent case studies will be discussed:

- (a) multiscale XRPD imaging of the spontaneous degradation of the pigments of the 13th vault paintings by Cimabue and Giotto in the Basilica of St. Francis in Assisi, IT [2];
- (b) 3D elemental analysis by XRF tomography of minute paint samples from Rembrandt's 17th c. masterpiece *The Nightwatch* (NL) to better understand his paint formulation [3] and
- (c) investigating of the exact nature of innovative purple pigments in works by Robert Delaunay, a prominent Parisian (F) early 20th C. fauvist artist [4].

[1] L. Monico, K. Janssens et al., Advanced X-ray techniques to study the alteration of pigments in paintings. *Il Nuovo Cimento* 2025; *La Revista del Nuovo Cimento* 48 (2025) 315-434.

[2] E. Avranovich et al., Multi-Scale X-ray Imaging of the Pigment Discoloration Processes Triggered by Chlorine Compounds in the Upper Basilica of Saint Francis of Assisi. *Molecules* 2023; 28: 6106.

[3] F.T.H. Broers et al. Correlated x-ray fluorescence and ptychographic nanotomography on Rembrandt's *The Night Watch* reveals unknown lead "layer", *Sci. Adv.* 2023; 9: eadj9394.

[4] V. Gonzalez et al., Structure–Optical Properties Relationships in Cobalt-Based Purple Pigments Used by Robert Delaunay. *J. Am. Chem. Soc.* 2025; 147: 2587–2596.