Combining microscopic and macroscopic X-ray fluorescence and X-ray powder diffraction mapping for highly specific imaging of degradation phenomena in historical paintings

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Cultural heritage (CH) artefacts such as paintings, stained glass windows and (illuminated) manuscripts are examples of complex macroscopic objects consisting of a multitude of different materials, in close proximity to or in intimate contact with one another. Given sufficient time and a number of external stimuli (such as impinging UV and visual light, variable relative levels of humidity or of reactive volatile species from the ambient atmosphere) these react with one another and form secondary products. When such spontaneous chemical reactions negatively influence the mechanical properties of the artefact (or part thereof) at the macro-level or significantly change one of its relevant properties (color, surface texture, …), they become noticeable. Understanding the mechanisms and principal factors that trigger or determine the speed of these alteration reactions is very relevant for both preventive and corrective art conservation.

To gain such insights, employing a combination of analytical methods that allow to extract information on the chemical constituents of the degraded surface of CH artefacts at different length scales and with relevant chemical specificity, has been proved to be very effective. Preferably (but not all) such methods are non-invasive, i.e. do not cause damage to the CH artefacts being studied. At the macro-scale, i.e., the length scale of the CH artefacts in their totality (cm to m), various forms of hyperspectral imaging can be used. Macroscopic X-ray fluorescence (MA-XRF) and diffraction (MA-XRPD) are non-invasive imaging methods with intermediate to high chemical specificity that are very suitable for examining the surface of CH artefacts, either to obtain information on the original materials used to construct the artefacts or on any surface alteration that took place during the artefact’s history. MA-XRF and MA-XRPD scanners can be constructed using X-ray tube sources.

Large scale particle accelerators such as synchrotron facilities are able to generate X-ray beams of sub-micrometer dimensions. With these, it is possible to study heritage materials at the nanometer to micrometer level. Methods such as (sub)microscopic X-ray fluorescence, X-ray absorption spectroscopy and X-ray diffraction, either used sequentially or simultaneously, allow to study minute samples of CH artefacts, complementing the information obtained by macro-level investigations and allowing to formulate hypotheses on the manufacturing technology the artefacts and/or degradation mechanisms that have modified their surface.

As a first example of the combined use of micro- and macro-level chemical imaging methods, (a) the study of metal-based inks used to write Egyptian papyri. Red and black inks inscribed on 12 ancient Egyptian papyrus fragments belonging to the Papyrus Carlsberg Collection (Copenhagen), deriving from the Tebtunis temple library in Fayum, Egypt were analyzed using synchrotron-based 2D elemental and phase mapping. From the XRF maps, information can be extracted on the ingredients used to prepare the inks while XRD allowed to identify the secondary Pb compounds that formed in situ.

As a second example, the degradation of the pigments present on the ceiling of Upper Basilica of St. Francis in Assisi, Italy will be discussed. Part of these 13th century frescos, painted by Cimabue, Giotto and their studios, collapsed during an earthquake in 1997, making unique sample materials available for analysis. More specifically, the use of micro- and macrolevel XRF and XRPD will be discussed to study the degradation/ blackening of pigments such as lead white, vermilion and azurite. As common triggering factor for the alteration over a period of ca 700 years, the presence of oxidizing Cl-compounds is strongly suspected.

A third example involves the use of micro- and macro-level XRF and XRPD for the study of the pigments and their degradation behavior in Rembrandt’s masterpiece ‘The Nightwatch’, a large oil on canvas from the 17th C owned by the City of Amsterdam that is part of the collection of the Rijksmuseum. Especially the MA-XPRD maps of the white (lead-rich) areas of the paint reveals information on the manner in which Rembrandt intentionally altered the rheological properties of the paint by adding specific chemical agents to it.

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