Invited Lecture

Imaging of pigments and alteration products at the surface of paintings by Johannes Vermeer using macroscopic X-ray powder diffraction scanning (MA-XRPD)

Frederik Vanmeert, Silvia Centeno, John Delaney, Kate Dooley, Koen Janssens, Katrien Keune, Anna Krekeler, Dorothy Mahon, Elke Oberthaler, Sabine Penot, Carol Pottasch, Abbie Vandivere, Ige Verslype, Steven de Meyer, Annelies van Loon

Rijksmuseum

f.vanmeert@rijksmuseum.nl

Cultural heritage objects possess immense material and immaterial value, serving as open windows into humankind's past. Through them, we can grasp how man perceived and depicted the world as it was centuries ago. Many of the questions concerning cultural heritage objects that are addressed with analytical techniques revolve around three main topics: (i) how the object was created, (ii) its current condition, and (iii) how it can be better preserved for future generations. For this, a detailed chemical characterization of the materials present within cultural heritage objects is crucial. These materials may have been originally used by the artists, were added in later stage or have formed spontaneously over time. X-ray powder diffraction (XRPD) is a powerful tool for addressing these questions as it provides precise identification and quantification of the different crystalline materials present. Furthermore, it offers detailed structural information as well as texture analysis providing important clues into various production methods [1]. The focus of this presentation will be on recent research utilizing a mobile macroscopic X-ray powder diffraction (MA-XRPD) instrument capable of scanning the surface (typically in the dm2 range) of oil paintings in order to visualize the distribution of the different crystalline materials present in the top layers. Over the past year(s), we used this non-invasive technique for the detailed study of 18 paintings attributed to Johannes Vermeer (1632 - 1675) encompassing an extensive part of his oeuvre spanning his entire career. From the study of Girl with a Pearl Earring (Mauritshuis, NL), it already became evident that in order to create the smooth transition from bright skin tones to the shadowed cheek of the Girls face, Vermeer made use of distinct types of the pigment lead white, a synthetic pigment consisting of basic lead carbonate, hydrocerussite ($2PbCO_3.Pb(OH)_2$, HC) and neutral lead carbonate, cerussite ($PbCO_3$, C) [2], each with their own optical and handling properties. These different lead white types could be distinguished and visualized within the painting with MA-XRPD based on the mass fraction ratio of hydrocerussite and cerussite [HC/(HC+C)]. Vermeer's deliberate choice of pigments to achieve subtle optical effects is further shown in his extensive use of the vivid and costly blue pigment ultramarine, derived from the rare semiprecious stone lapis lazuli. Vermeer widely employed this pigment not only to the create vibrant blue tones known from works such as The Milkmaid (Rijksmuseum, NL), but also mixed it with other pigments to produce different greens, whites and blacks [3]. While MA-XRPD is able to directly identify the mineral lazurite [$(Na,Ca)_8(AlSiO_4)6(SO_4,S,Cl)_2$)] responsible for ultramarine's blue color, it also provides information about various accessory minerals present within the purified pigment, such as quartz, diopside, sodalite, sanidine and nepheline, consistent with impurities associated with Afghan ultramarine [4]. The highly specific and quantitative information obtained with MA-XRPD on 18 works by Vermeer allowed us to discern time-dependent changes in his use of lead white and his choice of ultramarine quality, while also revealing evidence of their chemical (in)stability over time. With this research we are able to further map the evolutions within Vermeer's artistic practice and provide additional clues for dating his works.

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