Fingerprinting Natural Ultramarine in 15th-17th century Netherlandish paintings

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In order to create a painting, an artist must carefully select his painting materials and especially those materials that convey color to the painting. In the 15th-17th century, most colored pigments were inorganic in nature, many of them powdered minerals. Painters' pigments comprise commonly available materials such as earth colours and bone black, but also rare ones such as the red pigment vermillion/cinnabar or the blue pigment ultramarine.

The most expensive pigment of many historical periods is without any doubt natural ultramarine, sometimes referred to by its mineral names lazurite or lapis lazuli [1]. Lazurite is an alumino-silicate mineral containing zeolite cages in which sulphur polyanions are present that give it its characteristic blue colour. In the 15-17th century, natural ultramarine was a material more expensive than gold. It derived its scarcity and high price from the fact that the only known mines of natural ultramarine were located in a remote northeastern Afghan province called Badakhshan. In the 15-17th century, most natural ultramarine was transported along the silk road and reached Europe via Venice [2]. What was traded in this manner were either large lumps of the blue/white lazurite-rich rocks (that also contain other minerals) or already (partially) purified lazurite powder. In Venice and other locations in Europe, by means of the application of various crushing and particle selection techniques [3], the purity of the blue pigment was then improved, creating different grades of ultramarine of widely different price.

By means of Macroscopic X-ray powder diffraction (MA-XRPD), it is possible to record the distribution of crystalline materials in historical paintings and thus to identify which inorganic pigments were employed by an artist to create a specific work of art. In recent years, this method has been employed by our group to identify the inorganic pigments present in masterworks by artists such as Vincent Van Gogh [4] (19th century), Johannes Vermeer [5] (17th century) and Jan Van Eyck [6] (15th century).

Of particular usefulness for highly specific pigment mapping of oil paintings is reflection mode MA-XRPD. Although dependent on the diffraction characteristics of the pigments studied and on the measurement conditions, in this mode, the detection limit of scanning MA-XRPD is of the order of 2-5%. Next to allowing for a direct identification of the pigment mixtures that constitute the paint of a particular hue, this ability to detect and identify minor components in a complex mixture makes it also possible to employ MA-XRPD to record fingerprints of specific pigments and highlight art historically relevant differences between pigment subtypes. For example, in Vermeer's *Girl with the Pearl Earring*, it was possible to establish that Vermeer used at least two distinctly different subtypes of lead white to paint the Girl's face: one hydrocerussite-rich ($2PbCO_3.Pb(OH)_2$) to paint the lighter/highlighted facial areas and another, poorer in hydrocerussite and richer in cerussite ($PbCO_3$) which is used in the shadow areas [5,7].

Since natural ultramarine pigment powder is invariably prepared by purification of (heat-)crushed lazurite-rich Afghan rocks, the resulting powder not only contains microcrystals of the blue mineral lazurite, but also of its accessory minerals such as albite, sodalite, diopside, pyrite, quartz, sanidine etc. Some of these share the structure and overall chemical composition of the blue alumino-silicate mineral while others are quite different. All these accessory minerals, however, lack the intense blue color of lazurite and thus alter the color intensity and tone of the blue pigment when they are (too) abundantly present.

Through MA-XRPD mapping of blue areas of a series of Netherlandish paintings by well-known 15th and 17th century artists from various museums in Belgium and the Netherlands, we have made a non-exhaustive survey of the pattern of accessory minerals present in 15th and 17th century natural ultramarine. The aim of the survey was to answer questions such as: (a) does the fingerprinting pattern of the accessory mineral change with time? (b) and if so, does it change gradually or erratically? and (c) is the pattern significantly affected by the application of the purification methods? In the presentation, preliminary answers to some of these questions will be discussed by means of examples from the oeuvre of 15th-17th century artists Petrus Christus, Albrecht Bouts, Jan Steen and Johannes Vermeer.

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