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μ-XRPD investigations of pigments in the 17th-century panel paintings from Gdańsk and the northern region of Poland

ABSTRACT

This study was focused on identifying the components of ground and paint layers in several panel paintings which were created during the 17th century in Gdańsk (northern Poland). Due to the fragile nature of the paintings, very small samples of paint and ground layers were taken and mounted in synthetic resin, to prepare cross-sections that could be used in several nondestructive studies, such as X-ray powder micro-diffraction (μ-XRPD). White, yellow, red, blue and green layers were examined. Studies revealed that the white paint layers contained calcite, cerrusite and/or hydrocerrusite; the yellow layers contained lead tin yellow type I; blue layers contained azurite and/or lazurite. The detection of μ-Al2O3 in the red layer suggests the presence of an organic dye in a base containing aluminium. The obtained results clearly prove the importance and usefulness of X-ray powder diffraction techniques in investigations of objects of cultural heritage.

Keywords: conservation science, identification of pigments, X-ray powder micro-diffraction (μ-XRPD), analysis of cross-sections

Introduction

Proper recognition of artists' technology and techniques often requires application of a broad range of interdisciplinary research methods based on the study of written sources (treatises and manuscripts), old painting workshops, practical reconstruction of formulas, artistic experience and physical and chemical investigations [1–3]. Panel paintings by Anton Möller (1563/65–1611), Isaac van den Blocke (1589–1628) and Hermann (or Herman) Han (1580–1627/28), all of whom lived in Gdańsk (Poland), were investigated in this study.

Anton Möller was an artist from Gdańsk's Golden Age [4]. He is best known for painting biblical themes and allegorical compositions, which are often compared to the art of Flanders and the Netherlands. Möller mainly used red lake pigments in parts of garments to achieve light and shade effects.

Isaac van den Blocke painted scenes from classical mythology, the history of ancient Greece and Rome, and the Old Testament. He came from an artistic family of Dutch origin and was appointed in Gdańsk as a painter of the city and as a promoter of the town's prosperity.

Hermann Han was also an artist based in Gdańsk. His early works were devoted to morality scenes, but he is mostly known for his altar paintings with depictions of St Mary, and for his compositions related to the history of the Church, painted for the Cistercians in Pelplin and Oliwa. He was appointed as Court Painter to the Polish King [5].

At the beginning of the 17th century, Gdańsk was an important centre of textile crafts. A dozen dye manufacturers worked in the city. Some of the dyes were made by craftsmen who came from the Netherlands [6, 7]; thus it can be assumed that local workshops were the source of dyestuffs for the painters working there.

The painting techniques and materials used in the workshops of Gdańsk artists have not yet been described and are not well known. To learn about 17th-century artists' workshops in Gdańsk, several physical and chemical techniques were applied. Optical microscopy under visible and ultraviolet light enabled the study of the stratigraphy of painting layers; energy-dispersive X-ray microanalysis in a scanning electron microscope (SEM-EDX) made it possible to learn about the elemental composition, but for indisputable determination of inorganic crystalline pigments and materials, X-ray microdiffraction analysis was applied. Essential problems solved by X-ray Powder Diffraction (XRPD) phase analysis include cases where certain substances with the same or similar chemical composition occur in different crystal structures, which is often the case in investigations of objects of cultural heritage [8–10].

Laboratory X-ray powder micro-diffraction is a very effective non-destructive method for direct phase analysis of samples smaller than 1 mm containing crystal constituents, with no need for pre-treatment. It is suitable for identification of pigments in fragments of colour layers of works of art, or their cross-sections, as well as for examination of secondary degradation products [11].

The purpose of this paper is to present the application and results obtained with the use of μ-XRPD in investigations of cross-sections of paint layers in samples taken from 17th-century paintings. The examined samples were taken from two of Möller's paintings: *The Tribute Money* (1601) from the Gdańsk History Museum; *Seven Acts of Charity* (1607) from St Mary's Church in Gdańsk; and from paintings attributed to Möller's workshop: *Allegory of Wealth* (ca 1600) from the National Museum in Gdańsk and *Allegory of Pride* and *Model of the World* (ca 1600) from the National Museum in Poznań. We have also examined one sample from Blocke's painting *Servilius Appius* (1608–1609) from the Main Town Hall in Gdańsk and samples from three of Han's paintings: *The Assumption of Mary* (1618) from the Cathedral in Pelplin; *The Coronation of Mary*, painted after 1624, and *The Prussian Attack on the Monastery in Oliwa* (ca 1613) from the cathedral in Oliwa. The cross-sections of the samples were prepared by embedding the samples in a small resin block (acrylic resin 'Duracryl 0' Spofa Dental – Praha) and then polishing their surface. The thickness of the paint layers in the samples embedded in the resin was in the range 60-200μm. All X-ray powder micro-diffraction measurements were performed on cross-sections.

Apart from identification of materials used by old masters, in our study we also wanted to learn about the methods used for preparing lake pigments [12] with particular reference to substrates that have been used since earliest times and to supplement the data on the types of substrates used in Gdańsk paintings in the first half of the 17^{th} century.

Experimental

Two types of μ-XRPD instrumentation can be employed in the studies of cultural heritage objects: one based on a laboratory source of X-rays and another employing synchrotron radiation (SR). The microscopic size of the primary beam which is obtained at SR sources enables characterization of each layer in complex stratigraphic samples, and nowadays such investigations, especially in analysis of paintings, are increasingly undertaken [13–15]. However, synchrotron XRPD measurements are not a routine, everyday practice, mainly due to problems with the access to the synchrotron radiation facilities. That is why in our studies we performed μ-XRPD experiments with the use of X-rays from laboratory sources.

The measurements were carried out on a X'Pert PRO MPD diffractometer, CuKα radiation, 40kV and 30 mA, a graphite monochromator and PIXCEL PSD detector. The apparatus was equipped with a collimator (output beam diameter 0.1 mm) which enabled performance of the micro-diffraction measurements. We studied a total of twelve cross-sections. For most of them we were able to obtain powder diffraction patterns good enough to be analysed. In one case we were unable to record a powder pattern suitable for XRPD analysis. Phase analysis and pigment identification were performed with the use of a PDF-4+ database [16].

Energy-dispersive X-ray microanalysis in a scanning electron microscope SEM-EDX was performed by using LEO Electron Microscopy Ltd, England, 1430 VP model, 2001, equipped with energy dispersive X-ray spectrometer – EDX Quantax 200 with XFlash 4010 detector of Bruker AXS, Germany 2008.

Results and discussion

For each investigated sample there were specific scientific problems to be solved by means of μ-XRPD technique. These problems and most interesting results are described below.

3.1. μ-XRPD results for *The Tribute Money*

In the sample taken from red area of this painting we wanted to learn whether the white ground layer consisted of chalk or gypsum, as well as what kind of lead white was present in the sample. Additional questions concerned the red pigment. The results of this study, shown in Fig. 1, indicate that calcite $CaCO_3$ (PDF 00-001-0837) and hydrocerussite $2PbCO_3Pb(OH)_2$ (PDF 04-012-2150) are the only main crystalline components of the sample.

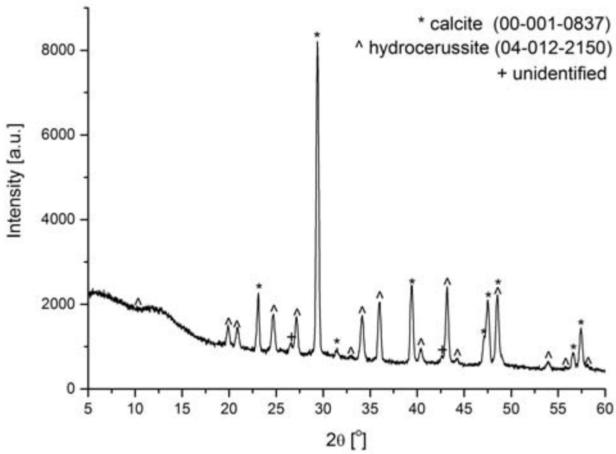

Fig. 1. Powder diffraction pattern of the red paint layer for the sample taken from the painting *The Tribute Money*

Neither minium nor iron red was identified, indicating the possible presence of an organic red dye which does not exhibit a diffraction pattern. This might be a kind of amorphous red lake [17,18]. The absence of gypsum indicates that the lake pigment was not precipitated in gypsum. The major element detected in the red layer by SEM-EDX analysis is aluminium. This result indicates the use of aluminum hydroxide as the substrate for red dye. The red layer consists of red, blue and white particles. In the second measurement performed for the same sample the X-ray beam was focused on the blue and white pigments in the paint layer. The aim was identification of the type of lead white and identification of blue pigment which was applied. In this case we have detected hydrocerussite $2PbCO_3Pb(OH)_2$ (PDF 00-001-0687) and calcite $CaCO_3$ (PDF 00-001-0837). On the basis of the obtained XRPD pattern we were not able to precisely identify the blue pigment. However, in this pattern a high background with broad maxima are observed. The results of identification of the red layer by SEM-EDX analysis are: C, O, Al, Si, Cl, K, Ca, Fe, Co, As, Pb. The presence of Si, K, Co indicates that the amorphous blue pigment – smalt was used by the painter in this layer. In 17th century the painters mixed red lake pigments with different blue ones in order to obtain the purple hue. In the *Tribute Money* Möller probably used red lake pigment with smalt and a bit of white lead.

3.2. µ-XRPD results for *Servilius Appius*

In the next study we investigated a cross-section of the sample taken from the painting by Isaac van den Blocke, *Servilius Appius* (1608).

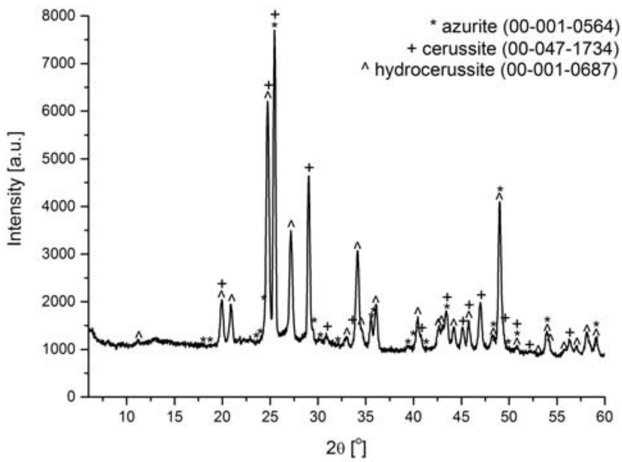

Fig. 2. Powder diffraction pattern of the blue paint layer for the sample taken from the painting *Servilius Appius*

The results depicted in Fig. 2 show that in this sample there are two different types of lead white: hydrocerussite – $2PbCO_3Pb(OH)_2$ (PDF 00-001-0687) and cerrusite – $PbCO_3$ (PDF 00-047-1734). In the diffraction pattern there are also maxima which pertain to azurite $2CuCO_3Cu(OH)_2$ (PDF 00-001-0564). These maxima overlap with those pertaining to cerussite and hydrocerussite; however, their intensities suggest that azurite is present in the sample.

In the studies described above we performed µ-XRPD measurements focussing the beam on whole paint layers, each of which is in fact built of a few thin layers corresponding to a different colour. In the case of the samples taken from Anton Möller's picture *Seven Acts of Charity* the paint layers of different colours were thick enough to measure two of them independently in the same sample.

3.3. μ-XRPD results for *Seven Acts of Charity*

From the first measurement of the sample taken from the red part of the painting, we wanted to learn what the ground layer was composed of. The results shown in Fig. 3 clearly indicate that ground layer consists of calcite $CaCO_3$ (PDF 00-001-0837) along with two types of lead white.

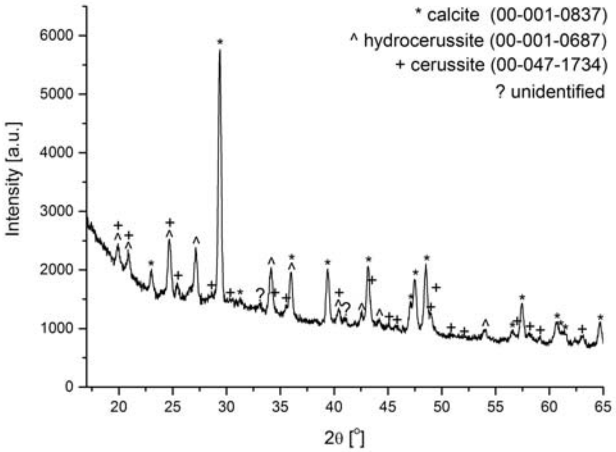

Fig. 3. Powder diffraction pattern of the ground for the sample taken from the painting *Seven Acts of Charity*

In the second study of this sample the X-ray beam was focussed on the red layer.

The results are depicted in Fig. 4. The main crystalline component of the red layer is γ-Al_2O_3 (PDF 00-001-1308).

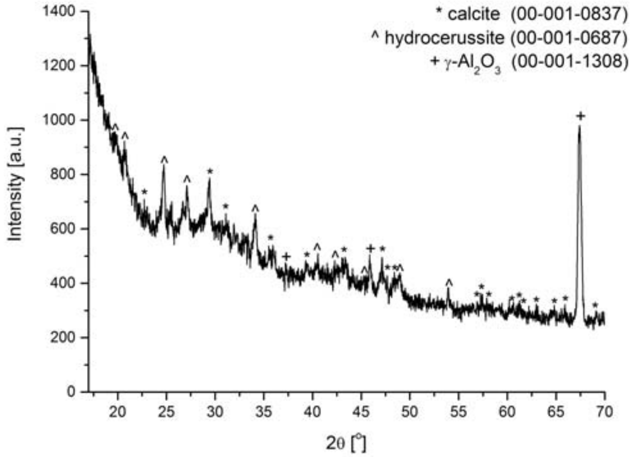

Fig. 4. Powder diffraction pattern of the red paint layer for the sample taken from the painting *Seven Acts of Charity* (point no 4)

Because the diameter of the beam is wider than the thickness of the red paint layer, in the diffraction pattern, one can see also the maxima from calcite and hydrocerussite. Similarly to the red layer in the sample taken from *The Tribute Money*, neither red crystalline pigment was identified, indicating the use of a red dye by the master. The presence of γ-Al_2O_3 suggests that the substrate used during the preparation of the red lake is aluminium-based. However, the obtained diffraction data do not correspond to any of the various crystalline aluminium (oxy) hydroxides, such as gibbsite $Al(OH)_3$ or boehmite γ-AlO(OH) [12]. At this stage of the analysis, it was difficult to determine why there was no maxima from aluminium hydroxide, which, according to documentary sources, was usually the substrate for organic red dyes.

For a sample taken from the same painting, but from the blue parts, two μ-XRPD measurements were performed. In the first one the X-ray beam was focussed on the lower border of the blue paint layer. In the powder diffraction pattern we observed diffraction maxima characteristic for azurite $2CuCO_3Cu(OH)_2$ (PDF 00-001-0564), hydrocerussite $2PbCO_3Pb(OH)_2$ (PDF 00-001-0687), and calcite $CaCO_3$ (PDF 00-001-0837).

In the second measurement the X-ray beam was focussed on the middle of the blue paint layer. Analysis of the obtained powder diffraction pattern shown in Fig. 5 suggests that there are two blue pigments in the sample: azurite $2CuCO_3Cu(OH)_2$ (PDF 04-013-7672) and lazurite $Na_6Ca_2Al_6Si_6O_{24}(SO_4)$ (PDF 04-012-9627) with a small admixture of hydrocerussite $2PbCO_3Pb(OH)_2$ (PDF 00-001-0687) and calcite $CaCO_3$ (PDF 00-001-0837).

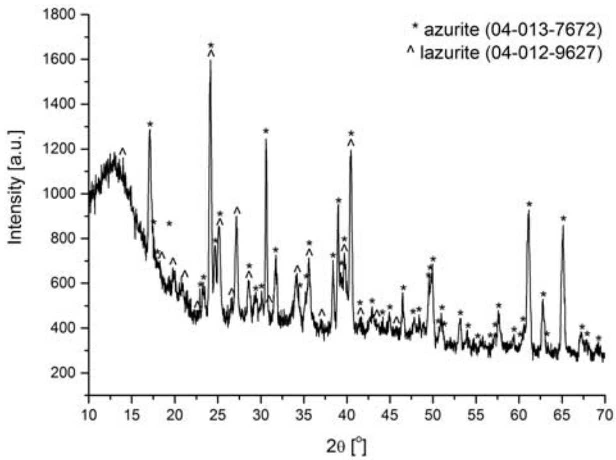

Fig. 5. Powder diffraction pattern of the blue paint layer for the sample taken from the painting *Seven Acts of Charity* (point no 7)

We may conclude that Anton Möller used azurite and ultramarine – one of the most expensive pigments in those times. Ultramarine was obtained from lapis lazuli, mined in Afghanistan, whose main constituent was mineral lazurite. Azurite, which was imported from Hungary, become costly and difficult to obtain after the conquest of Hungary by Ottoman Empire in 1526 [19].

3.4. μ-XRPD results for *Coronation of the Blessed Virgin Mary*

In the sample taken from the blue part of this painting, we wanted to identify the blue pigment. The results indicate that Hermann Han used azurite, but the μ-XRPD data were ambiguous and this result is not completely convincing.

In the investigations of yellow paint layer in the sample taken from Hermann Han's *Coronation of the Blessed Virgin Mary*, lead tin yellow type I (Pb_2SnO_4) was detected. The maxima of hydrocerussite were also present in the diffraction pattern. The results are shown in Fig. 6.

3.5. μ-XRPD results for *Allegory of Pride and for Model of the World*

We also analysed the blue paint layer in the samples taken from *Allegory of Pride* by an unknown painter who worked in Gdańsk in the same period. In this case, azurite was certainly used by the master.

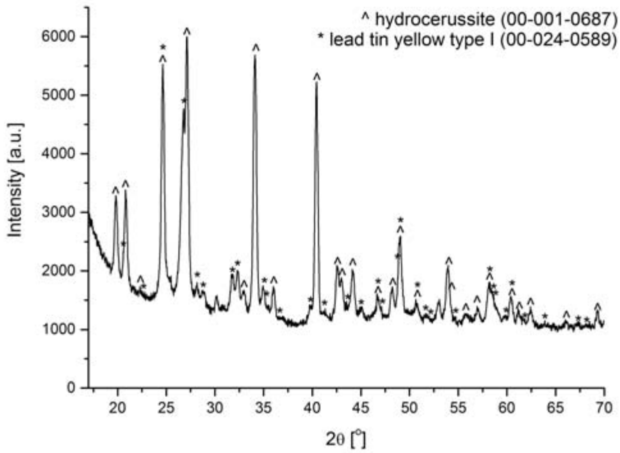

Fig. 6. Powder diffraction pattern of the yellow paint layer for the sample taken from the painting *Coronation of the Blessed Virgin Mary* from the cathedral in Oliwa

Most difficult to identify in the whole study were the green pigments, which we tried to identify in the painting *Model of the World*. Even though we performed several μ-XRPD measurements focussing the X-ray beam on different points of the green paint layer, we detected only calcite with an admixture of SiO_2. One of the obtained XRPD patterns shown in Fig. 7 exhibits a high level of background. It may suggest that an amorphous compound (or a mixture of amorphous, or poorly crystallized compounds) is present in the sample.

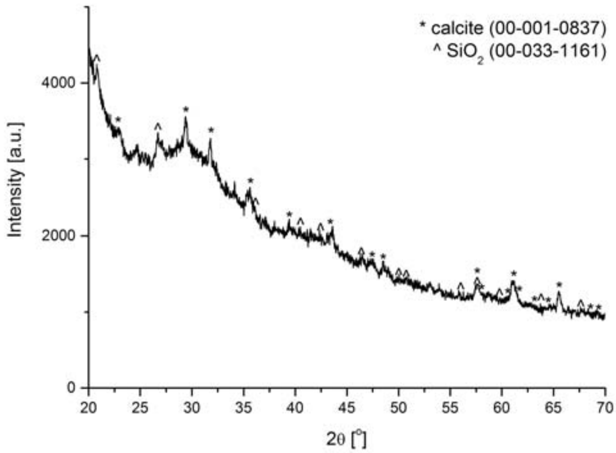

Fig. 7. Powder diffraction pattern of the green paint layer for the sample taken from the painting *Model of the World*

Among the green pigments used in the 17th century, crystalline malachite $CuCO_3 \cdot Cu(OH)_2$, verdigris (a mixture of copper acetates and hydroxyacetates), copper resinate (for which there is no data in the PDF database) and some other pigments can be mentioned [20]. We prepared a powder sample from a paint layer produced in the lab containing copper resinate and performed an XRPD measurement on it. In the obtained pattern there were some broad maxima characteristic for an amorphous phase. This result may suggest that the master used a copper resinate as a green pigment. This pigment was identified by other authors in paintings by Johannes Vermeer and Arnold Böcklin, who worked in the 17th and 18th centuries, respectively [21]. Apart from copper resinate, other weak crystalline or amorphous green pigments should be taken into consideration and the sample should be studied with the use of X-rays from synchrotron sources or by other analytical methods.

Conclusions

In this paper we have demonstrated that the chemical composition of grounds and pigments used by 17th-century masters in several panel paintings created in Gdańsk (northern Poland) can be identified by means of the μ-XRPD technique based on laboratory source of X-rays. It is worth mentioning that XRPD is one of the best methods to identify chemical compounds with similar elemental composition. Thanks to this feature we were able to identify two kinds of lead white: cerrusite and hydrocerrusite (certain identification of lead white pigment is an important indication for the attribution of paintings) [22]. In the case of yellow paint, we identified lead tin yellow type I. Old masters used two types of this pigment: type I (Pb_2SnO_4) and type II ($PbSnO_3$) [23, 24]. Their powder diffraction patterns are different and each can be easily detected by XRPD. In the blue paint layers we identified azurite and ultramarine. Interestingly, thanks to the μ-XRPD technique, we were able to identify two different blue pigments used by the master in the same blue paint layer. Moreover, the results obtained for *The Tribute Money* suggest that smalt or another amorphous blue pigment was used by the master. The investigations of red paint layer excluded the presence of crystalline red pigments, which suggests that red lakes were used in the paintings. In the case of *Seven Acts of Charity*, μ-XRPD revealed aluminium oxide Al_2O_3, whereas from the reaction between alkali and alum, aluminium hydroxide – $Al(OH)_3$, should be obtained. In practice, it is difficult to characterise this substrate, partly because it is amorphous and highly variable. The presence of Al_2O_3 in the sample will be the subject of further studies on the production and chemical characterisation of dyestuffs. Nevertheless, obtained XRPD results enriched the knowledge concerning the painting materials used by 17th-century masters in Gdańsk.

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