Journal of Cultural Heritage xxx (2017) xxx–xxx

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Original article

Stratigraphic EM-EDS, XRF, Raman and FT-IR analysis of multilayer paintings from the Main Altar of the St. James Church in Levoča (Slovakia)

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ARTICLE INFO

Article history:
Received 15 December 2017
Accepted 6 March 2018
Available online xxx

Keywords:
Gothic panel
Painting
Stratigraphy
Pigment
Binding
Glaze

ABSTRACT

A total of 25 inorganic (painting pigment and substrate) and organic components (binding and glaze) have been identified in the Main Altar of the St. James Church – the highest Gothic altar of the World. Micro-sampling of the first wood panel depicting Christ in the Garden of Gethsemane, the third one depicting Christ Crowned with Thorns and the fourth one named Ecce Homo was performed to reveal the stratigraphy of the color paintings. Chalk, cinnabar, lead-tin yellow, cerussite (lead white), malachite, azurite, an iron oxide, and fluorite have been identified using optical microscopy, X-ray fluorescence (XRF), scanning electron microscopy combined with energy-dispersive spectroscopy (SEM-EDS), Raman spectroscopy and Fourier-transform infrared spectroscopy (FT-IR). Green pigment consists of hydrous copper sulfates (probably posnjakite mixed with woodwardite) and carbonates represented by fragmental and spherulitic malachite. Infrared spectroscopy confirmed the linseed oil mixed with egg albumen as the main binding constituent of color paintings, whereas animal glue was used in ground layers. The red glazing consisted of krapplak dissolved in oil, whereas the green glaze was composed by Verdigris (copper acetate) dissolved in the Venetian turpentine. Some samples contained remnants of shellac. The composition of inorganic pigments, including the exotic deep-purple fluorite unknown in the central European realm, points to combined local and remote pigment sources, thus indicating flourishing trade connections within medieval Europe after cessation of Turkish invasions in the early 16th Century.

1. Introduction

Investigation of historical artifacts and artworks using complementary spectroscopic destructive and non-destructive methods is an integral part of pre-conservation reconnaissance study, which further determines the technology and the extent of restoration. Based on this research, failures and defects can be detected, their origins can be deciphered, and proper conservation methods can be proposed. Optimal environmental conditions can be set up after restoration to avoid further degradation. Also an age of historical artifacts can be estimated from the presence or absence of specific pigments and chronology of subsequent modifications can be deciphered from the stratigraphy of multilayered pigments.

Analyses of historical artifacts have some limitations resulting from the need to avoid their damage. Routinely used techniques, such as optical and scanning electron microscopy supplemented with X-ray elemental microanalysis (SEM-EDS), are sometimes insufficient for pigment identification [1]. Hence, these methods must be supplemented by Raman and Fourier-transform infrared spectrometry that are effective tools for the identification of inorganic compounds and organic binding materials, respectively, in microscopic scales and layered materials [2–8]. Hand-held Raman, XRF, and infrared instruments have an advantage of the non-destructive in-situ analysis without the need for micro-sampling or transport of the investigated artwork. Stratigraphic analyses, however, require micro-sampling and special preparation of the sampled material to reveal the structure of multilayer painting. The combination of non-destructive spectrometric methods applied in-situ together with those applied to micro-samples in a laboratory

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https://doi.org/10.1016/j.culher.2018.03.006
1296-2074/

was used in the investigation of the Main Altar from the church of St. James in the town of Levoča, which belongs to the vintage pieces of Gothic artwork in Europe.

2. Experimental

2.1. Materials

There is a total of 14 gothic altars in the church of St. James in the town of Levoča (Eastern Slovakia) granted free royal town privileges ("*civitas nostra regalis*") by Charles Robert of Anjou in 1323 [9]. The main altar created in the early 16th Century is the highest gothic altar in the World (18.6 × 6.7 m). Its wooden relief is embellished with polychrome (gold, blue, red) decorations, whereas lateral wings are covered by paintings featuring those of Lucas Cranach and Hans Leonard Schäufelein (Fig. 1). The altarpiece with sculpture decoration was created by Master Pavol and his workshop in 1508. Panel paintings depicting scenes from the Passion cycle were probably made after 1514 by Master Hans T. and his workshop [10,11]. The polychrome and gilding were completed in 1517, as it is indicated by the evidence found in the chronicle of *Fraternitas Corporis Christi* (Brotherhood of Corpus Christi) and the *Diario* of Conrad Sperfogel – the mayor of Levoča town [12,13].

The upper row of the panel paintings shows Jesus in the Garden of Gethsemane (the scene is a mirror image of the Cranach's woodcut named Christ on the Mount of Olives), The Flagellation (almost exact copy of Cranach's Flagellation), Christ Crowned with Thorns, and Ecce Homo (almost exact copy of Cranach's woodcut of the same name). The lower row shows Christ in front of Pilate (scene and figural composition made after Cranach's woodcut Pilate Washing His Hands), Christ Falling under the Cross (an almost exact copy of Cranach's Christ Carrying the Cross), The Crucifixion and The Resurrection (after two scenes from the Passion cycle by Hans Schäufelein published in "*Speculum passionis domini Jesu Christi*" in 1507 by Ulrich Pinder [12]). Compared to originals, the painter made only minor changes in composition and details.

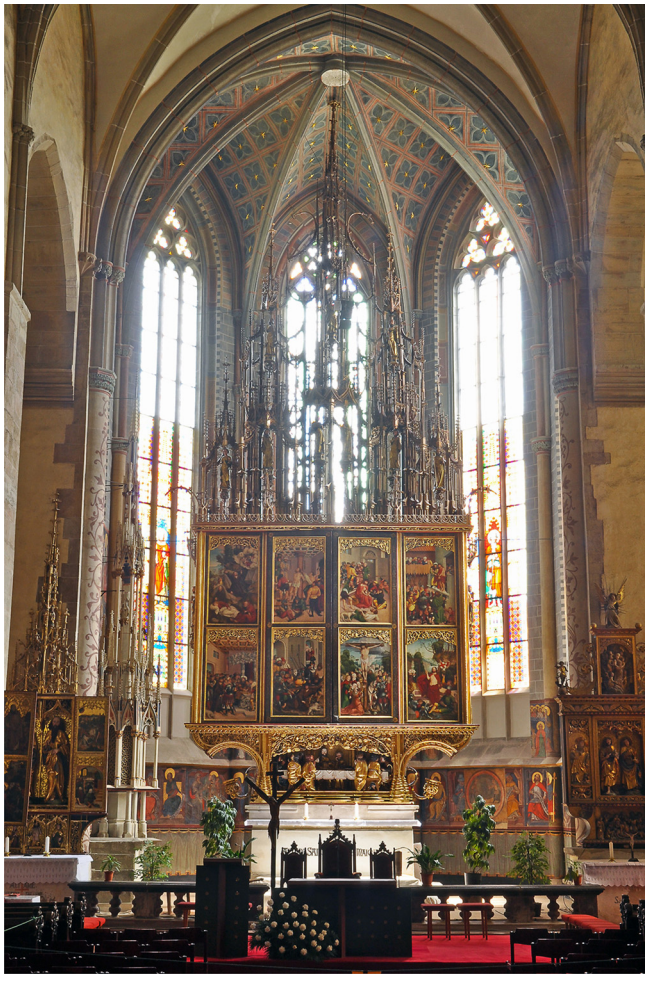

Fig. 1. Overall view of the main altar with lateral wings in the St. James Church of Levoča.

2.2. Methods

As part of the last restoration, a new survey carried out in the spring of 2014 was focused on the current condition of panel paintings. At the outset, non-destructive infrared reflectography and XRF spectrometry were performed using hand-held portable devices. Sites suitable for micro-sampling were selected based on the evaluation of preliminary data (Fig. 2). Samples studied are fragments, up to 2 mm in size. The fragments were immersed in acrylic resin (ClaroCit, Denmark or Spofacryl–Spofadental, Czech Republic), cut after hardening perpendicular to the layering and polished with water- and oil-free abrasives to avoid dissolution of soluble substances.

Documentation of polished mounts was made in reflected visible light using a Carl Zeiss Jena POL optical microscope coupled with a Canon EOS 700 camera. Gold-coated polished mounts have been subject to a standard analysis of elemental composition using the scanning electron microscope coupled with energy dispersive analyzer (SEM-EDS), whereas uncoated mounts were investigated using Raman and Fourier-transform infrared (FT-IR) spectroscopy.

Following the detailed documentation of polished mounts in back-scattered electrons at different magnifications, qualitative SEM-EDS elemental analyses were made in each layer. The number of analyses depended on the sample heterogeneity. Initial measurements were conducted at smaller magnifications (< 500×) to decipher compositions of ground painting and individual layers along the entire cross-section. Individual pigment grains were then analyzed at a 1200–1800× magnification, using a 5–10 μm electron beam diameter, which prevented, at least partially, the contamination from the surrounding binder.

Some minerals (fluorite, spherical malachite) were identified using SEM-EDS combined with optical microscopy of the powder pigment attached either on the C-tape or immersed in acrylic resin (Cargille Melmount, UK). For FT-IR analysis, the multilayer samples were pressed with overnight dried KBr powder (Acros Organics, Belgium) into a conventional disk, 13 mm in diameter, using a Die Kit (PIKE Technologies, USA) and an H-62 vacuum press (Trystom, Czech Republic) with 50–60 kN pressure applied for 2 minutes [14].

Vibrational spectrometry is established as a sensitive and spatially refined method to characterize various inorganic and organic pigments. Point Raman analyses were complemented by areal mapping with a ~2 μm lateral resolution to characterize the stratigraphy of pigment layers. The Raman micro-spectrometry was supplemented by FT-IR analyses, albeit with a smaller lateral resolution (~5 μm). The detailed stratigraphic analysis enabled recognition of internal structure of paint layers and possible secondary interventions.

The following analytical devices have been employed:

- a handheld XRF X MET 5100 analyzer, type XMDS 2677 (Oxford Instruments, UK) with silicon drift detector (SDD) and 45 kV X-ray tube for *in-situ*, non-destructive qualitative analysis of elements ranging between Mg and U;
- a JEOL JSM-6060 LA scanning electron microscope (JEOL, Japan) operating in low-vacuum (15 Pa) mode and accelerating voltage

Please cite this article in press as: J. Želinská, et al., Stratigraphic EM-EDS, XRF, Raman and FT-IR analysis of multilayer paintings from the Main Altar of the St. James Church in Levoča (Slovakia), Journal of Cultural Heritage (2017), https://doi.org/10.1016/j.culher.2018.03.006