Applied Radiation and Isotopes 95 (2015) 8–12

Contents lists available at ScienceDirect

Applied Radiation and Isotopes

journal homepage: www.elsevier.com/locate/apradiso

Investigation of the panel painting of St Anne with the Virgin Mary and the Child Jesus using analytical and imaging methods

R. Šefců [a], Š. Chlumská [a], A. Třeštíková [a], T. Trojek [b,*], L. Dragounová [b]

[a] National Gallery in Prague, Staroměstské nám. 12, 11000 Prague, Czech Republic
[b] Czech Technical University in Prague, Department of Dosimetry and Application of Ionizing Radiation, Břehová 7, 11519 Prague, Czech Republic

HIGHLIGHTS

- Purple fluorite has been identified in shadows of white draperies in the painting.
- Simple depth profiling technique with XRF analysis was successfully applied.
- Authorship of the Master of the Litoměřice Altarpiece has been proven.

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form
18 July 2014
Accepted 29 September 2014
Available online 8 October 2014

Keywords:
Non-invasive analysis
X-ray fluorescence
Late Gothic
Panel painting
Pigments
Master of the Litoměřice Altarpiece

ABSTRACT

This paper presents an investigation of a panel painting depicting St Anne with the Virgin Mary and the Child Jesus that dates back to the beginning of the 16th century. This work is attributed to the Master of the Litoměřice Altarpiece, who was the most important painter in the time period of the Jagiellonian dynasty in Bohemia (the historical name of a part of the Czech Republic). At present, the painting is deposited in the collections of the National Gallery in Prague.

The aims of this study were to carry out a systematic collection of sufficient data to make correct interpretations of the materials that were used, to compare the results with the technique of the Master of the Litoměřice Altarpiece, and in this way to prove his authorship.

In the analyses of the material compositions, emphasis was placed on non-destructive and non-invasive methods, e.g. X-ray fluorescence microanalysis, which was performed using a device with lateral resolution of 20 μm. Further applied methods were X-ray radiography, Infrared Reflectography, photographic documentation in visible and ultraviolet light, Scanning Electron Microscopy–Energy Dispersive Spectroscopy, Infrared microspectroscopy with Fourier transformation, and microscopic analysis.

1. Introduction

Various analytical techniques are applied in the study of art and archeological objects. It is a particularly difficult task to make analyses of medieval panel paintings and to interpret the results, because the paintings consist of several layers that usually include a ground, an under-drawing, under-paintings, paint layers, and a varnish. In addition, mixtures of pigments were usually used. Conventional recent procedures for obtaining information on the depth distribution of the paint layers include taking a micro-sample from a selected point on the painting, preparing it for micro-optical analysis, and making measurements using Scanning Electron Microscopy–Energy Dispersive Spectroscopy (SEM–EDS), (Chaplin et al., 2010). The main advantage of this procedure is the possibility to recognize pigments and layers that are present, and also to determine their thicknesses. The disadvantages are related to the fact that it is sometimes difficult or even impossible to take samples. Where this is the case, non-invasive methods are very beneficial. Investigations of complex tasks of this kind usually require a combination of methods. The most important methods are X-ray fluorescence analysis (Musílek et al., 2012; Uhlir et al., 2008; Szökefalvi-Nagy et al., 2004), proton induced X-ray emission (Neelmeijer et al., 2000), Raman spectroscopy (Deneckere et al., 2012; Sawczak et al., 2009), Fourier transform infrared spectroscopy (FT-IR) (Vahur et al., 2010), and X-ray diffraction (Eveno et al., 2011).

This paper summarizes the results of an investigation of the panel painting of St Anne with the Virgin Mary and the Child Jesus, National Gallery in Prague, inventory no. DO 4102, see Fig. 1.

* Correspondence to: Czech Technical University in Prague, Břehová 7, 11519 Praha 1, Czech Republic. Tel.: +420 224 358 256; fax: +420 224 811 074.
E-mail address: tomas.trojek@fjfi.cvut.cz (T. Trojek).

http://dx.doi.org/10.1016/j.apradiso.2014.09.019
0969-8043/

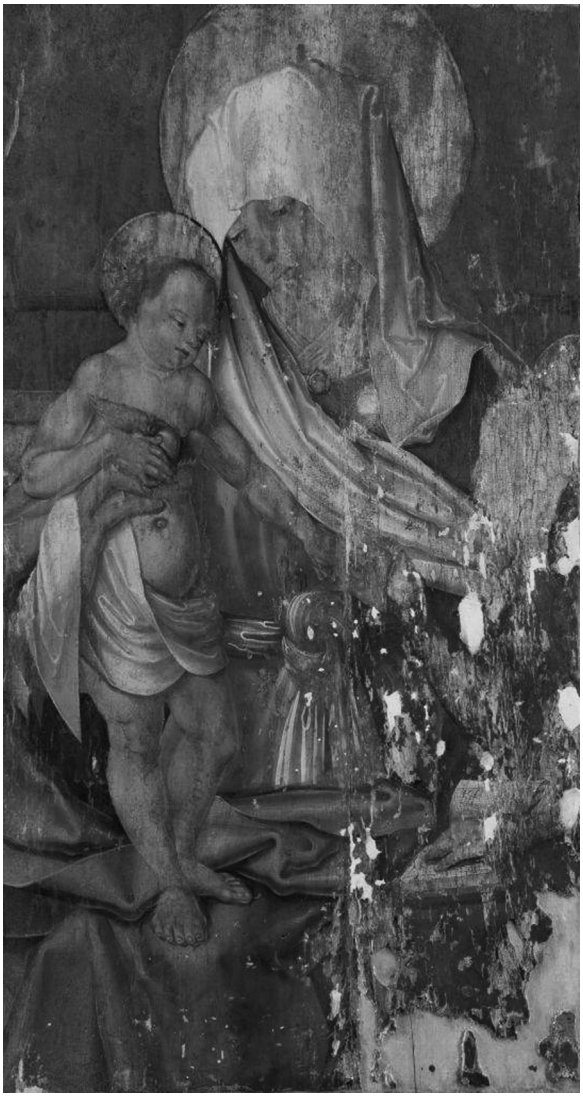

Fig. 1. Master of the Litoměřice Altarpiece, Panel painting of St Anne with the Virgin Mary and the Child Jesus, National Gallery in Prague. Photograph© 2014 National Gallery in Prague.

Modern non-invasive imaging and analytical methods (especially X-ray fluorescence analysis) were applied, and were intentionally combined with surveys of the colored layers performed with conventional procedures. A combination of the two modalities corresponds to recent trends in materials research, and it was also successful in our investigation. Information on the material composition of the paint layers, and of the ground was of practical significance, as it formed the basis for the restoration of this panel painting. It also made it possible to verify the attribution of the painting to the Master of the Litoměřice Altarpiece (Kotková, 2007).

The panel painting of St Anne with the Virgin Mary and the Child Jesus was painted with egg tempera with an admixture of oil on lime wood (69.5 cm × 39 cm). The stratigraphy that was performed proved that there was a traditional late Gothic layered structure that includes a ground, an under-drawing, under-paintings, and subsequent application of the colored layers. The painting was repeatedly repaired in former times because the wooden support was damaged by a ligniperdous insect, which probably caused local destruction of the wood. The original painting was damaged by new repairs which included crude overpaints that distorted the original painting style. A complex survey was therefore essential to enable the subsequent restoration work to retrieve the original painting.

The oeuvre of the Master of the Litoměřice Altarpiece, who was a prominent artist in time period of the Jagiellonian dynasty in Bohemia, includes almost 30 panel painting (mainly fragments of retables), (Pešina, 1973). His painting technique and the painting technique of his workshop had already been studied within the attributed oeuvre, and has been documented in detail. Specific characteristics typical for all his works have been identified (Chlumská et al., 2012). The aim of the recent investigation of the painting of St Anne with the Virgin Mary and the Child Jesus was to demonstrate the same specific character, and thereby to prove the attribution to the Master of the Litoměřice Altarpiece and his workshop. However, the analyses of the material composition were limited by the condition of the painting, which looks rather like a torso. The number of micro-samples that were taken was therefore reduced to a minimum, and most of the analyses were performed non-invasively.

2. Experimental

The survey of the panel painting started with X-ray radiography, photography in visible light and ultraviolet radiation, and infrared reflectography (IRR). Macro-photos of fragments were also taken. Because of the condition of the painting, just 5 micro-samples were prepared in the form of cross-sections. These cross-sections enabled the stratigraphy of the painting layers to be evaluated, and the composition of the pigments, dyes and binders to be determined using microscopy analysis, SEM-EDS, Raman spectroscopy, and FT-IR.

Due to the limited number of micro-samples, 40 additional analyses were performed non-invasively using X-ray fluorescence microanalysis (μXRF) at the Czech Technical University in Prague (Trojek and Hložek, 2012). The μXRF system consisted of a semiconductor Si–PiN detector (Amptek X-123 X-ray detector system, dimensions 6 mm^2 × 0.5 mm, Be window – 25 μm), a molybdenum X-ray tube equipped with polycapillary focusing optics (XOS, X-Beam: Powerflux PF), and a positioning system. The geometry arrangement was 90°/45°. The detector was located 10 mm from the analyzed spot. The X-ray tube was operated at a maximum voltage of 50 kV and a maximum current of 1 mA. The diameter of the focal spot was about 20 μm at a distance of 4 mm from the end cap of the polycapillary optics. The time for one analysis was 2–3 min.

A complex evaluation of this heterogeneous system of paint layers could only be made by combining the selected methods. The μXRF results were compared with information obtained through analyses of the micro-samples. The database gathering the results of the analysis of the Master of the Litoměřice Altarpiece and his workshop became an important corrective.

3. Results and discussion

The acquired μXRF spectra were evaluated with the AXIL code, and the net count rates and the net count rate ratios, which quantified the content of a given element, were determined for selected X-ray lines. This data enabled us to draw several conclusions even though the count rates and the count rate ratios are also influenced by the layered structure of the painting, and also despite surface and matrix effects.

Calcium was identified with μXRF in all the spectra, because it is present in the ground layer as natural chalk ($CaCO_3$). A comparison with the results of the analyses of the micro-samples provided an explanation for the high amount of Ca in the shadows of the white draperies of St Anna and Jesus, see Fig. 2. The reason is the presence