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Determination of pigments in colour layers on walls of some selected historical buildings using optical and scanning electron microscopy

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Abstract

For successful restoration of painted walls and painted coloured finishing coats it is necessary to determine the composition of the original colour layers. Identification of the pigments used in The Cistercian Abbey of Stična and The Manor of Novo Celje was carried out using optical and scanning electron microscopy. Selected samples of wall paintings were inspected by the combined application of an optical microscope and a low-vacuum Scanning Electron Microscope to determine their colour and structural features and to identify the position of individual pigment grains. Energy dispersive spectroscopy was used to determine the elemental distribution on selected surfaces and elemental composition of individual pigments. It was found that the most abundantly used pigments were iron oxide red, cinnabar, green earth, umber, calcium carbonate white, ultramarine, yellow ochre and carbon black. These identifications have allowed us to compare the use of various pigments in buildings from different historical periods.

Keywords: Optical microscopy; Scanning electron microscopy; Energy dispersive spectroscopy; Pigments; Historical buildings

1. Introduction

The crucial point in restoration of historical objects is to preserve stylistic authenticity and, at the same time, to assure materials durability. A successful and integral long-term preservation can only be achieved through examination and understanding of all wall layers.

We selected two very important Slovenian historical monuments: The Cistercian Abbey of Stična and The Manor of Novo Celje, built at different ages and on different locations, to briefly examine all wall layers including plasters and finishing paint layers. In the present work we mainly focused on the study of pigments in the paint layers of the walls.

To provide an understanding of the composition of the materials used and the technique followed by the artist, application of several complementary analytical techniques is usually required. The study of pigments used in artwork has comprised a wide range of techniques [1–3] such as X-ray diffraction [4–7],

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particle-induced X-ray emission [8,9], Raman or Fourier-transform Raman spectroscopy [7–13], photoluminescence spectroscopy [14], Fourier transform infrared spectroscopy [6,7,10] as well as various microscopical techniques — optical microscopy [5,6,15,16], scanning electron microscopy coupled to energy dispersive X-ray spectrometry [5–8,17,18] and transmission electron microscopy [17].

The aims of the investigation presented in this paper were to develop an efficient procedure for analysis and characterization of paint layers containing pigments, to determine the origin of pigments in selected samples and to find the differences in pigments used in selected objects and/or geographical locations through history. For this purpose, the results of two microscopical techniques, that is, optical and scanning electron microscopy, were combined with information obtained from energy dispersive spectroscopy.

2. Experimental

The sampling was carried out by scraping off the wall paintings and the plasters with a scalpel. We collected representative samples of each different colour found in the wall. In the case of The Manor of Novo Celje we additionally collected pieces of "stucco lustro" consisting of gypsum and pigments.

The samples were mounted into a two-component epoxy resin and carefully ground with 800-mesh SiC grinding paper. After grinding, the surfaces were polished on a cloth using 3-μm and 1/4-μm diamond pastes.

Polished cross-sections of the samples were investigated using optical microscopy (Olympus BX60), recorded by a JVC 3-CCD video camera, and scanning electron microscopy (SEM, Jeol 5500 LV, Japan), while qualitative, quantitative and mapping analyses of selected areas of the samples were performed by energy dispersive spectroscopy (EDS, Oxford Instruments, Great Britain) using the INCA software.

The Scanning Electron Microscope (SEM) was a low-vacuum type, which offered two different modes of working, conventional, high vacuum mode and newer low-vacuum mode (pressure from 1 to 130 Pa). In this low-vacuum mode the samples need not be coated with an additional conductive film of gold or graphite. This way, we avoided possible damage of the samples. Also, such uncoated samples remained suitable for further or repeatable investigation. In the low-vacuum mode a special back-scattered electron (BSE) detector was used which provided the topographical and compositional information in one image. All SEM examinations and EDS analyses of this work were done in the low-vacuum mode using the special BSE detector with the pressure in the chamber between 10 and 22 Pa (the actual pressure was indicated on the lower left part in each SEM image), using an accelerating voltage of 20 kV. The real acquisition time for EDS qualitative and quantitative analyses was approximately 100 s, while for mapping analyses the acquisition time was between 400 and 600 s. The self-calibration of the EDS was made before testing; a cobalt standard was used for a gain calibration. No extra standards were used. EDS quantitative analyses were done considering all elemental analyses; normalised totals were used.

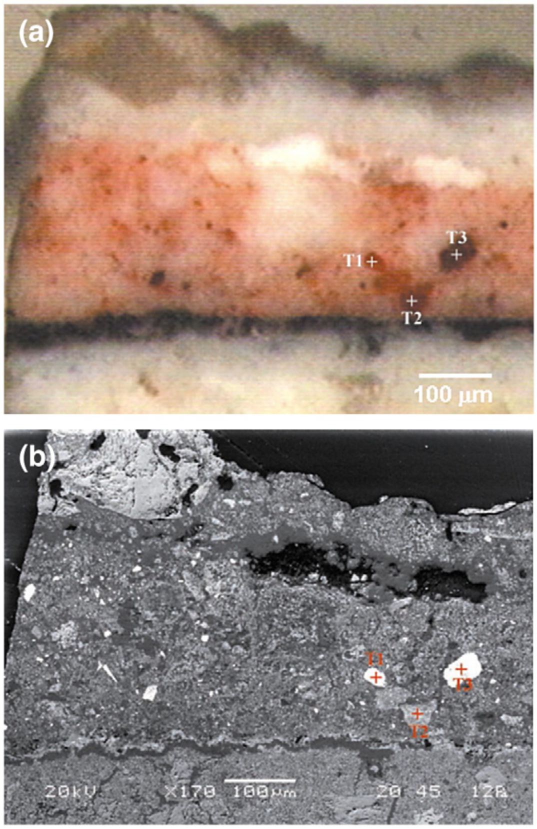

Fig. 1. (a) Optical and (b) SEM image (BSE image, working distance = 20 mm, spot size = 45) of the same area of a polished cross-section of a representative painted coat from the Cistercian Abbey of Stična.

3. Results and discussion

In order to identify the microstructure and composition of the layers in the walls, especially of the pigments, we adopted the following strategy. First we