ABSTRACT

Historical painted works of art have a very complex inner structure. The period painting technique led to the execution of a ground layer followed by several layers of underpainting and a top paint layer, over which a layer of glaze has been applied to increase the resistance to external wear. Each of these colour layers is composed of a dye or a pigment (or their mixture) bound by organic binder. Throughout the history, pigments were commonly prepared from minerals, either extracted from natural deposits or created artificially. In these heterogeneous layers containing both inorganic and organic components, undesirable degradation changes either driven by processes taking place directly in the colour layer or influenced by external agents may occur. Mineralogical approach, which focuses primarily on the structure of studied pigments, helps in the clarification of the occurring processes, in the determination of conditions leading to degradation as well as in the identification of original/degradation phases. Furthermore, it can be profitably applied in the micro-analysis of mineral pigments present in tiny micro-samples obtained from works of art, contributes to the artwork's provenance/authorship studies and the determination of regional provenance of the employed mineral pigments.

This Ph.D. thesis focuses on the micro-analysis of rare mineral pigments vivianite, naturally irradiated fluorite – antozonite and crocoite, and also deals with their significance for provenance studies; the micro-analysis has been also performed on a large group of copper-based pigments. In addition, the thesis deals with the degradation processes caused by internal/external agents with special attention to hoganite, vivianite and orpiment.

A structural study of mineralogical samples of blue vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$) and its naturally occurring degradation products led to the application of the results on micro-samples – a suitable combination of structural methods for the identification of vivianite in colour layer was found to be X-ray micro-diffraction with micro-infrared spectroscopy in micro-attenuated total reflectance mode. Vivianite is rare pigment and has been used only by certain authors, e.g. in the Dutch painting of the 17^{th} and 18^{th} century. This thesis describes the identification of vivianite in seven paintings by Jean George de Hamilton, which was one of the factors confirming his authorship. The comparison of elemental composition and grain morphology of vivianite pigment with mineralogical and model samples indicated its sedimentary origin. The study of mineralogical samples of antozonite (heavily naturally irradiated dark violet to black CaF_2) showed that the higher is its structural damage, the broader are the diffraction lines in its diffraction pattern and the darker is its colour. On the other hand, the reported increase of the unit cell volume is not in direct proportion to the level of structural damage. A characteristic Raman spectrum of antozonite is presented thanks to which it can be easily micro-analytically detected, as shown on micro-samples of the altar painting from Italian Court in Kutná Hora created in 1497. Taking into account the limited period of antozonite's extraction, its presence may prove the expected date of execution of the studied work of art. The dating may be supported also by the identification of extremely rare yellow-orange pigment crocoite ($PbCrO_4$). It was found in unique wall paintings in the church of St. Gallus in Kuřívody, thus contributing to their dating to the end of the 13^{th} century. Copper-based pigments form a large group of chemically similar phases. In this thesis, their micro-analysis in paint layer leading to the identification of both mineral-type and verdigris-type pigments has been elaborated.

Degradation caused by internal agents, i.e. the chemical composition of the colour layer, has been studied using model experiments with neutral verdigris (mineralogically hoganite), which loses its structure in combination with proteinaceous binders. Its detection in the colour layer has been further complicated by frequent presence of highly diffracting pigments. The degradation caused by external agents has been studied on vivianite. The experiments showed that vivianite is prone to degradation both under increased temperatures from 70°C on (studied by high-temperature X-ray diffraction and Mössbauer spectroscopy, the colour change has been verified on model relining – a restoration/conservation treatment during which a new canvas is ironed to the back of the painting's old one) and under increased humidity. Finally, a degradation pathway of orpiment in wall paintings has been theoretically proposed; it will be experimentally verified in the following research.