



MASARYK UNIVERSITY
FACULTY OF SCIENCE
DEPARTMENT OF CHEMISTRY

Prof. RNDr. Viktor Kanický, DrSc.
Kamenice 753/5, 625 00 Brno,
Czech Republic
phone 549 49 4774, fax 549 49 2494,
e-mail: viktork@chemi.muni.cz

Charles University in Prague
Faculty of Science
RNDr. Roman Skála, Ph.D.,
Chairman of the committee
for the defence of the dissertation
Albertov 6
128 43 PRAHA 2

Ph.D. Thesis Evaluation Report
RNDR. ZDEŇKA ČERMÁKOVÁ, G.G. (GIA)
MINERALOGICAL ANALYSIS OF HISTORICAL PAINTINGS

1. Thesis contents

Submitted Ph.D. thesis contains text of 56 pages and five published articles. The thesis, written in English, is introduced with acknowledgements and abstracts in Czech and English. After **Introduction**, consisting of motivation and aims of work, **State of the art**, **Experimental**, **Results and Discussion**, **Conclusion**, and **References** follow. **Appendix** comprises reprints of 3 articles and 2 manuscripts. At the time of peer review of the thesis both articles have been issued.

2. Thesis parts and chapters evaluation

Aim of work

The dissertation work is devoted to study of historical mineral painting pigments important for the authorship designation and the provenance determination in a geological and art-historical sense. Microanalytical methods are employed for study of pigments and their in tiny microsamples. Pigments degradation due external and internal influencing factors is also investigated using model samples and elucidation of degradation pathways is proposed.

Aim of work is defined precisely and with a deep knowledge of issues.

State of the art

Principles of physicochemical analytical methods employed for microanalysis of layers are well described in connection with specific features of artwork specimen. Both micro analysis and mineralogical analysis are discussed as complementary methods for identification of pigments in artworks, investigation of their provenance, historical





period, and degradation. The work contains an introduction to the issue of identification of pigments used in paintings. A brief overview of both natural and synthetic mineral pigments employed in fine art is presented including historical development. Pigments investigated in this work were selected with the aim to study: *i)* provenance and/or authorship; *ii)* tendency of degradation; and *iii)* undescribed analytical identification in microsamples. For these purposes, the following pigments were examined: vivianite, fluorite naturally irradiated fluorite (antozonite), crocoite, orpiment and cooper-based pigments.

The current state of the issue is described in detail and with knowledge of the context. There is clearly excellent know-how in mineralogy, restoration of artworks and instrumental analysis.

Experimental

In the experimental part mineralogical samples as well as artworks' microsamples are summarized. Procedures of laboratory preparation of synthetic vivianite for monitoring of degradation, production of hoganite and vivianite model samples, and experiments with vivianite are described. A detailed description of analytical instruments and methods used, namely optical microscopy, portable X-ray fluorescence, scanning electron microscopy – energy dispersive spectroscopy, X-ray diffraction and X-ray micro-diffraction, Raman spectroscopy, Fourier-transform infrared spectroscopy in transmission and reflection mode (including micro-), Mössbauer spectroscopy and UV-Vis spectroscopy (reflectance) is provided including operating conditions set for particular samples.

Description of sample preparation and examination as well as a list of used instruments indicates a wide range of author's experimental skills. The number of involved laboratories and analytical instruments indicates excellent organization skills and sophisticated research strategy.

Results and Discussion

This section summarizes results presented in five papers published in peer-reviewed international journals, which are recorded in Thomson-Reuters Web of Science database. Microanalysis of paint layers of artworks with the aim to identify correctly rare pigments like vivianite, fluorite and crocoite for provenance/authorship and dating is examined and applied successfully. Microanalysis is also used for study of copper based pigments. In spite of their chemical similarity, their specific features and precise description presented in this work makes it possible to distinguish particular minerals and provenance determination. Pigment degradation and changes induced by both external and internal agents are studied with special attention to hoganite and vivianite.

Experiments are well documented with support of photographs, images, spectra and diffraction patterns. Experiments are well planned and outcomes are logically explained.

Conclusion

This section contains significant number of valuable outcomes. It has been found that micro-ATR micro-FT-IR is suitable for the analysis of vivianite layers in cross-section. Consequently, vivianite has been identified in 7 paintings of Jean George de Hamilton and therefore, this pigment is suitable for authorship ascription. In the context of this study, the comparative elemental investigation of mineralogical samples and artwork microsamples has been performed and together with grain morphology observation indicated sedimentary origin of the vivianite pigment in the de Hamilton's paintings. X-ray micro-diffraction of antozonite has been evaluated and Raman spectroscopy has





been indicated as advantageous for identification of the period of the artwork origin due to restricted historical epoch of antozonite extraction. The identification of extremely rare and in literature only once reported mineral pigment crocoite in wall paintings in St. Gallus church in Kuřivody was helpful in dating of those paintings. A micro-analytical procedure of Cu-based pigments identification in paint layer has been developed and tested on artwork micro-samples. Concerning degradation studies, a loss of hoganite crystallinity in proteinaceous binders and vivianite sensitivity to elevated temperature have been observed based on laboratory experiments. Finally, a potential degradation pathway of orpiment in the presence of lead-based pigments in wall paintings has been theoretically proposed.

The dissertation brings a large number of new observations, significant results and conclusions relevant to the field of interest.

3. General comments

3.1. Adequacy of the thesis title and matching with thesis content

Title and content of submitted thesis are corresponding.

3.2. Objective and importance of the work

Objective of the submitted thesis is consistent with the restoration practice and research, and internationally at a high professional level. This research is very essential.

3.3. Methodology

Methodology comprises specific preparation of artwork and synthetic specimens and the use of advanced instrumental methods of physico-chemical analysis. Employed methodology is adequate to the solved problem.

3.4. Design, structure of thesis and presentation of the research subject.

The structure of thesis is logical, coherent, and transparent, and corresponds to the solved issues.

3.5. Used equipment

Used equipment is adequate to studied topic.

3.6. Presentation of results, discussion and applicability

Results are presented in text, photographs, spectra and diffractograms and are discussed extensively in context with published outcomes. Important practical conclusions are made.

3.7. Update of references and adequacy

Cited references are up-to-date and relevant to thesis topic.

4. Conclusions

*Submitted dissertation work brings novelties in the field. Five papers have been published in international renowned journals **Spectrochimica Acta Part A** and **Journal of Raman Spectroscopy**. This brings the evidence of high quality of exerted experimental and theoretical research.*





5. Recommendation

5.1. *The submitted thesis is **excellent** in its present form.*

5.2. *I deeply recommend submitted Ph.D. dissertation of RNDr. Zdeňka Čermáková, G.G. (GIA) for defence, I propose evaluation of dissertation "**excellent**", i.e. "**A**" and after successful defending of the dissertation I suggest to submit proposal to the Dean of the Faculty of Science, UK, that RNDr. Zdeňka Čermáková, G.G. (GIA) be awarded the scientific degree of*

DOCTOR OF PHILOSOPHY (PH.D.) IN GEOLOGY

according to the Higher Education Act no. 111/1998. Coll.

Questions

- Besides assessing the artistic nature and features of the painter, is the identification of one mineral pigment (e.g. vivianite) sufficient for attribution of authorship?
- Is it possible that a counterfeiter may be provided with the painting supplies and material corresponding to historical period of the original and relevant mineral deposit? I.e. artificially aged organic materials, degraded mineral pigments etc.? If so, which methods have to be used to detect the counterfeit?
- What is the role of trace elements and isotopes in age and site provenance/ authorship/ counterfeit identification?

In Brno, 14th February 2015

prof. RNDr. Viktor Kanický, DrSc.

