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## Non-destructive micro-analytical differentiation of copper pigments in paint layers of works of art using laboratory-based techniques



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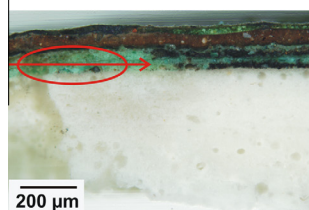
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### HIGHLIGHTS

- An analytical procedure for identification of Cu pigments in artworks is presented.
- This procedure is efficient for both mineral and verdigris-type pigments.
- It consists of detailed elemental and structural analyses and is non-destructive.
- Preliminary study of the verdigris' loss of crystallinity has been performed.

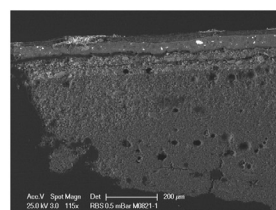
### GRAPHICAL ABSTRACT

#### Basic description (colour and stratigraphy)



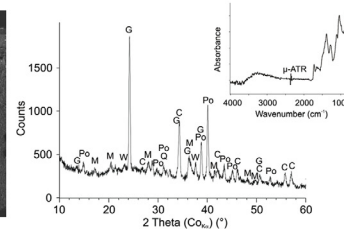
- light microscopy

#### Pigments - assessment (elemental composition)



- SEM-EDS

#### Pigments - specification (phase analysis)



- micro-IR, micro-XRD

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### ABSTRACT

An unambiguous identification of pigments in paint layers of works of art forms a substantial part of the description of a painting technique, which is essential for the evaluation of the work of art including determination of the period and/or region of its creation as well as its attribution to a workshop or an author. Copper pigments represent a significant group of materials used in historic paintings. Because of their substantial diversity and, on the other hand, similarity, their identification and differentiation is a challenging task. An analytical procedure for unambiguous determination of both mineral-type (azurite, malachite, posnjakite, atacamite, etc.) and verdigris-type (copper acetates) copper pigments in the paint layers is presented, including light microscopy under VIS and UV light, electron microscopy with elemental microanalysis, Fourier transformed infrared micro-spectroscopy (micro-FTIR), and X-ray powder micro-diffraction (micro-XRD). Micro-Raman measurements were largely hindered by fluorescence. The choice of the analytical methods meets the contemporary requirement of a detailed description of various components in heterogeneous and minute samples of paint layers without their destruction. It is beneficial to use the combination of phase sensitive methods such as micro-FTIR and micro-XRD, because it allows the identification of both mineral-type and verdigris-type copper pigments in one paint layer. In addition, preliminary results concerning the study of the loss of crystallinity of verdigris-type pigments in proteinaceous binding media and the effect of lead white and lead tin yellow as highly absorbing matrix on verdigris identification in paint layers are reported.

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## Introduction

Various copper compounds have been used as blue and green pigments and dyes since ancient times. Among copper pigments, one can find natural minerals such as malachite and azurite, their artificial analogues (the so-called verditers), compounds with ambiguous origin such as various basic copper chlorides and/or sulphates, synthetic pigments from both the ancient times (e.g. Egyptian blue) or the modern times (such as emerald or Scheele green), as well as manufactured organometallic copper substances like verdigris (copper acetates) that have been known since ancient times, or relatively new phthalocyanin [1]. With regard to the extensive variety of copper pigments, only those which can be found in European painted artworks since mediaeval times to the 18th century are subject of the present work. Their structure and chemical composition are summarised in Table 1.

Identification and distinguishing of copper pigments in paint layers is rather challenging due to their chemically close composition and similar colour, especially when non-destructive micro-analytical investigation of samples is required. Regardless of the origin of copper pigments, it is useful to divide them into two groups according to their chemical nature – mineral-type copper pigments, i.e. inorganic salts that have mineralogical analogue, and verdigris-type copper pigments, i.e. organometallic substances derived from copper acetate.

Among the mineral-type copper pigments, we can include wide-spread copper carbonates – blue azurite ( $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ) and green malachite ( $\text{Cu}_2(\text{CO}_3)(\text{OH})_2$ ), as well as less known copper chlorides and sulphates either occurring in a range of structural polymorphs with identical chemical composition (e.g. atacamite, paratacamite, clinoatacamite or bottalackite – all of them have the formula  $\text{Cu}_2\text{Cl}(\text{OH})_3$ ) or having close chemical composition, differing by the number of hydroxyl groups and/or molecules of crystalline water (e.g. brochantite,  $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ; posnjakite,  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ; langite,  $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ); or antlerite  $\text{Cu}_3\text{SO}_4(\text{OH})_4$  [2]. The palette of copper chlorides used for painting purposes is further diversified by rare pigments like cumengeite

( $\text{Pb}_{21}\text{Cu}_{20}\text{Cl}_{42}(\text{OH})_{40} \cdot 6\text{H}_2\text{O}$ ) or calumetite ( $\text{Cu}(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$ ) [3,4]. Among the rare copper pigments belong also copper phosphates and silicates like pseudomalachite ( $\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$ ) or chrysocolla ( $\text{Cu}_{2-x}\text{Al}_x(\text{H}_{2-x}\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$  ( $x < 1$ )) [2].

While azurite has been used as a predominant blue pigment in European mediaeval painting up to the 17th century (beside considerably more expensive ultramarine), malachite has been employed, in the same period of time, to a lesser extent because of the easy availability of other green pigments, such as verdigris or green earth. They both almost disappeared in the 19th century, being substituted by cheaper blue and green industrially produced pigments [1,2]. The atacamite-type pigments have been most frequently identified in wall paintings and in remainders of polychromes on stone or ceramic [3,5–7], which is probably closely related to the fact that they are often corrosion products of another copper pigment alteration caused by salt attack. The occurrence of copper sulphates in painted artworks is reported quite sporadically. Posnjakite (together with malachite) was found on several wall paintings as well as panel painting from the 15–16th century [3,5]. Some of the authors, who found brochantite in the works of art from the 19th century [8,9], suppose its intentional application. Other copper pigments are quite rare; chrysocolla has been found e.g. in the 13th century wall paintings [10].

Besides the mineral-type copper pigments, verdigris-type pigments derived from copper acetate represent important bluish green pigments that have been used since antiquity till the 19th century [11], being used in egg or glue tempera and usually mixed with lead–tin yellow or lead white on Gothic panel paintings and illuminations, or on easel paintings of the 15th to the 17th century applied with oil [12]. Verdigris-type pigments were of artificial origin; they were produced in the wine-growing regions, because the remains of the wine production were used for their preparation. The term verdigris has a loose definition, however, it usually refers to copper acetates, which can be generally divided into two groups – neutral and basic. Neutral copper acetate of the formula  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$  crystallizing in the monoclinic crystal system has a distinctive blue–green colour. The chemical composition of basic copper acetates (or basic verdigris) seems to be a more critical issue. Scott and Kühn [2,11] reported five various chemical formulas of basic copper acetates which could be available in the history, however, these substances were not synthesised as phase pure entities and thus reliable reference data are not available for their unambiguous identification. The only one exception is basic copper acetate with a formula of  $\text{Cu}(\text{CH}_3\text{COO})_2[\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$  (can be written also as  $\text{Cu}_2(\text{CH}_3\text{COO})(\text{OH})_3 \cdot 2\text{H}_2\text{O}$ ), whose crystal structure was determined and diffraction pattern and infrared spectra reported [13]. The knowledge about the remaining basic copper acetates is very poor. Since they are all crystalline substances, it is often pointed out that powder X-ray diffraction (XRD) should be the preferred method for identification and differentiation of copper acetates [2,11].

It is apparent that proper identification and differentiation of copper pigments occurring in a range of chemically close substances is not a trivial task, especially, if the micro-samples of paint layers should remain unchanged by the analysis. This requirement of non-destructivity arises from the attempt to minimise invasion into the works of art. The number and amount of the sampling should be limited to a minimum extent while still satisfactory for the following analysis, and the micro-samples of paint layers should be maintained and archived for later examination, e.g. for comparison studies of painting technique or for evaluation of the conservation treatment. Besides the non-destructivity, the space resolution of analytical techniques is another limitation. Samples of paint layers are usually smaller than 1 mm and they exhibit considerable inner heterogeneity, which requires employment of various analytical methods. Finally, further requirement is the

**Table 1**  
Historic copper pigments and their corrosion products: chemical composition and structure.

Pigment	Chemical composition	Structure
<i>Copper acetates</i>		
Verdigris basic (the only one with determined crystal structure)	$\text{Cu}(\text{CH}_3\text{COO})_2[\text{Cu}(\text{OH})_2]_3 \cdot 2\text{H}_2\text{O}$	Monoclinic
Verdigris neutral (hoganite)	$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$	Monoclinic
<i>Copper carbonates</i>		
Azurite	$\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$	Monoclinic
Malachite	$\text{Cu}_2(\text{CO}_3)(\text{OH})_2$	Monoclinic
<i>Copper chlorides</i>		
Atacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Orthorhombic
Bottalackite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Monoclinic
Calumetite	$\text{Cu}(\text{OH},\text{Cl})_2 \cdot 2\text{H}_2\text{O}$	Orthorhombic
Clinoatacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Monoclinic
Cumengeite	$\text{Pb}_{21}\text{Cu}_{20}\text{Cl}_{42}(\text{OH})_{40} \cdot 6\text{H}_2\text{O}$	Tetragonal
Paratacamite	$\text{Cu}_2\text{Cl}(\text{OH})_3$	Trigonal
<i>Copper phosphates</i>		
Pseudomalachite	$\text{Cu}_5(\text{PO}_4)_2(\text{OH})_4$	Monoclinic
<i>Copper silicates</i>		
Chrysocolla	$\text{Cu}_{2-x}\text{Al}_x(\text{H}_{2-x}\text{Si}_2\text{O}_5)(\text{OH})_4 \cdot n\text{H}_2\text{O}$ ( $x < 1$ )	Orthorhombic
<i>Copper sulphates</i>		
Antlerite	$\text{Cu}_3\text{SO}_4(\text{OH})_4$	Orthorhombic
Brochantite	$\text{Cu}_4\text{SO}_4(\text{OH})_6$	Monoclinic
Langite	$\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$	Monoclinic
Posnjakite	$\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$	Monoclinic

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