

Microanalysis of pigments in painted artworks

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Abstract

This paper summarizes the current knowledge concerning the materials analysis of painted artworks. In the introduction materials analysis is interrelated with other disciplines within a broad context of the research of cultural heritage. Current methodological and instrumental developments in the area are described with a special attention given to non-invasive analytical methods. The article also briefly deals with the relation of natural science, technology and humanities in the investigation and conservation of the fine art. In more detail historical painting techniques are discussed and paint layers are described as composed materials containing both organic and inorganic compounds in characteristic layer sequences. The aim of materials microanalysis of paints is to get both technological and materials signatures, which both could be specific for the period, region or workshop. Therefore the identification of organic and inorganic materials in paints should always be accompanied by the description of the layer stratigraphy and finding other detailed characteristics that relate to the origin of the painting. Mineralogy plays an important role in the analysis of paint layers, because the majority of historical pigments are minerals. When using the tools of mineralogical analysis, particularly the X-ray diffraction methods, one can get an idea of the process of formation and/or fabrication of pigments and its regional provenance. It also helps to identify the provenance of the painting itself. A substantial part of this paper deals with the mineralogical analysis of historical pigments. Carefully selected case studies demonstrate the usefulness of the method to solve important tasks of the origin of artworks.

Resumen

En este artículo se hace un resumen del estado actual de conocimiento del análisis de los materiales que constituyen las obras de arte pintadas. En la introducción se interrelaciona el Análisis de Materiales con otras disciplinas dentro de un amplio contexto de la investigación del Patrimonio Cultural. Se describen los actuales avances metodológicos e instrumentales en esta área, con especial atención a los métodos analíticos no invasivos. El artículo también trata brevemente la relación de las Ciencias Naturales, la Tecnología y las Humanidades en la investigación y conservación de las obras de arte. Se discuten con más detalle las técnicas pictóricas históricas y se describen las capas pictóricas como materiales compuestos, que contienen tanto compuestos orgánicos como inorgánicos en secuencias de capas características. El interés del microanálisis de los materiales de las pinturas es encontrar huellas, tanto tecnológicas como materiales, que puedan ser específicas de un período, región o taller. Por esto, la identificación de los materiales orgánicos e inorgánicos en las pinturas debe venir siempre acompañada por la descripción de la estratigrafía de las capas y el hallazgo de otras características de detalle relacionadas con el origen de las pinturas. La Mineralogía desempeña un papel importante en el análisis de las capas pictóricas, ya que la mayoría de los pigmentos históricos son minerales. Al recurrir a los instrumentos del análisis mineralógico, y en particular a los métodos de Difracción de Rayos X, podemos hacernos una idea de los procesos de formación y/o fabricación de los pigmentos y su procedencia regional. Esto también ayuda a identificar la procedencia de la misma obra pictórica. Una parte importante de este artículo se extiende sobre el análisis mineralógico de los pigmentos históricos. Se han selec-

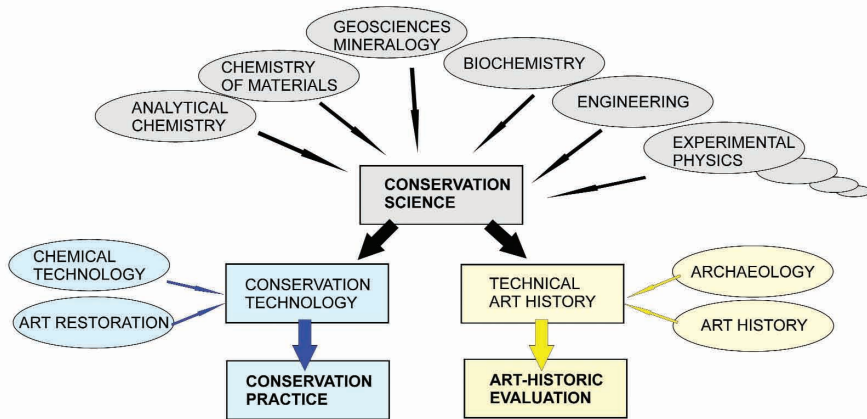


Fig. 1. Interrelation of the fields of science (in grey), technology (in blue) and humanities (in yellow) in the cultural heritage investigation and protection.

cionado a este propósito algunos casos prácticos que demuestran la utilidad de este método para resolver cuestiones importantes sobre el origen de las obras de arte.

Key-words: Conservation science, materials micro-analysis, powder X-ray microdiffraction, painting technique, mineral pigments, clay minerals.

1. Introduction

Materials analysis of tangible cultural heritage is a key part of conservation science. Conservation science is a branch of natural science that is concerned with the material aspects of works of art, their deterioration and conservation. Conservation science, contrarily to conservation technology, falls to the fundamental research of materials, describes the processes of their interactions and develops new tools for their description. Technical and technological solutions are then derived from the current knowledge obtained.

Conservation science relies on measurements of physical and chemical properties. Such measurements are central to analytical chemistry, that branch of chemistry concerned with determining the qualitative and quantitative identity of a substance (Mazzeo *et al.* 2011). Recently, non-destructive analysis of cultural heritage objects represents one of major trends in analytical chemistry (Chiari 2008; Martin *et al.* 2010). Better understanding is the first necessary step for better preservation, conservation, restoration and protection and gives also deci-

ve arguments for an art-historic evaluation of works of art (Fig. 1).

It should, however, be said that without the participation of other scientific branches, a comprehensive analysis is only hardly possible – this is simply given by the diversity of materials that form cultural heritage objects (stones, paper, plaster, glass, pigments etc.). Substantial limitations of any analysis of works of art are given by the fact that no sam-

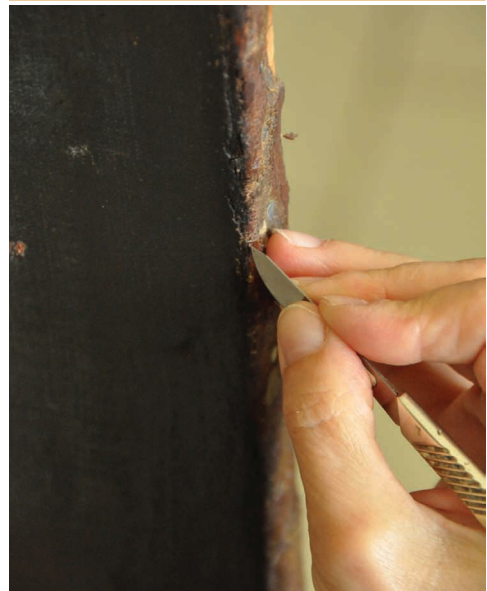


Fig. 2. Sampling. Conservators should make a compromise between representativeness of the collected sample and minimizing a risk of the painting damage

pling is usually allowed or only minute samples are possible to get. Furthermore their internal heterogeneity can be considerable (Fig. 2).

Because of these reasons in Europe in last decades, non-invasive (integrity of the object is preserved, no sampling is necessary) and non-destructive micro-analytical (sample is taken, but analyzed as is, not consumed or modified) methods were widely tested in cultural heritage field – especially in the case of paintings. This growing trend can easily be demonstrated on the increasing number of publications in top-impacted analytical journals. Current developments can be divided into two directions

- developments in physical principles and instrumentation – e.g. portable instruments (Grieten and Casadio 2010; Miliari et al. 2010) and
- developments in measuring and interpretation strategies – including unconventional approaches (Cardell et al. 2009; Palmieri et al. 2011).

2. Paints as composed materials

In cultural heritage, composed materials appear as an integral part of historic objects, artifacts and works of art of any kind. The most important fact is that their internal heterogeneity brings a crucial information related either to the technology of manufacturing, natural process of formation, or the process of secondary modification, deterioration etc. From the analytical point of view composed materials taken (if ever) in minute amounts from objects represent unconventional samples that cannot be homogenized or modified without a risk of loose of information described above.

A comprehensive methodology that includes an advanced description of internal structures and materials composition of different art objects made of composed materials is not developed yet. Close collaboration and composite action of several scientific branches is needed to achieve inevitable synergic effects routing to develop such a methodology based on using up-to-date analytical and imaging

instruments (Jonge and Vogt 2010; Yonehara et al. 2010). The necessity of an interdisciplinary approach to solve this problem is evident.

In a routine practice of the investigation of paintings, imaging and analytical methods are not yet fully interrelated. Conservators use conventional UV-Vis photographs, IR reflectography (IRR) or radiography (XR) and/or computer tomography (CT) to visually interpret technical signatures of the author visually – without any knowledge of materials used (Fig. 3). Analytical chemists, on the other hand, frequently perform “blind” analyses of materials without any knowledge of how they are organized in the layer sequence, what are their interrelations and what these “textural patterns” mean in terms of the painting technique. Materials and structural/technological signatures should be, however, studied together in a substantially higher level of understanding than is common today.

Cultural heritage objects can be categorized according to technological signatures. Using this clue, easel and wall paintings together



Fig. 3. Use of infrared reflectography (IRR) and X-ray radiography (XR) to visualize internal structure of the painting or, like in this case, to uncover an original painting completely over-painted by another painting (adopted from Hradil et al. 2006).

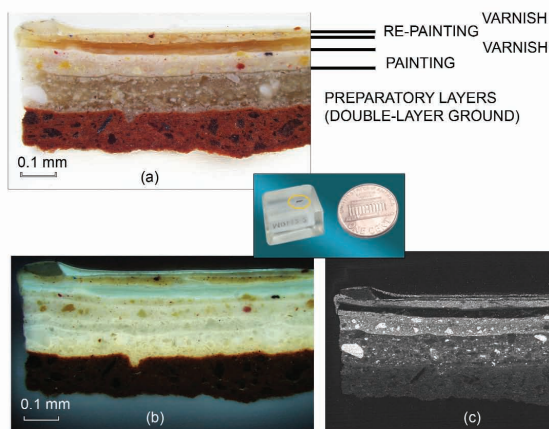


Fig. 4. Simplified description of the layer stratigraphy in cross-section of the painting fragment embedded in polyester resin (in the middle) as visible in white (a) and UV (b) lights and in backscattered electrons (c)

with polychrome sculptures, for example, belong to one single group – all these objects are classified as fine art (not applied art) and contain color (painting) layers applied in logical sequences following similar technological rules (Fig. 4). This group of painted artworks will only be considered in the following text.

Paint layers represent composed mixtures of organic and inorganic compounds (pigments and their binders) of very different properties, which are further composed to characteristic layer sequences; the description of this internal structure of paints together with the identification of organic binders (glue, egg yolk, whole egg, linseed oil etc.) is relevant for interpreting of historical painting technique with period and regional specificity.

In the traditional European paintings, the technological principles were held relatively strictly. The layer sequence starts with ground layers that served as a coating material to prepare the surface of a wooden panel or canvas. By their color, they were also closely related to the techniques and materials in the subsequent painting. Different types of (under)drawings and/or priming (*“imprimatura”*) belong also to the so-called preparatory layers.

Then the sequences of paint layers follow. Each the painting sequence is usually finished by varnish based e.g. on egg white, natural oils and resins and, later on, on synthetic acrylates. Original painting sequence can very frequently be over-painted by later re-paints.

In the European fine art, one of the first famous manuals of technical experiences, material preparations and painting itself, is the early renaissance work by Cennino Cennini issued first in 1437 (*Cennino 1978*). A very good review of treatises and ‘recipe-books’ from the 12th to the 18th centuries is given by



Fig. 5. Degradation and color change of minium (Pb_3O_4). In the environment of dissociated carbonic acid minium disproportionates as follows: Pb_3O_4 (orange minium) + $2H_2CO_3 \rightarrow PbO_2$ (brown-black plattnerite) + $2PbCO_3$ (white cerussite) + $2H_2O$; this process of darkening is showed on the example of Pre-Romanesque murals in Slovakia (a), where some blackened parts of figures (b) were later retouched by carbon black (c) – not further respecting the original coloring.

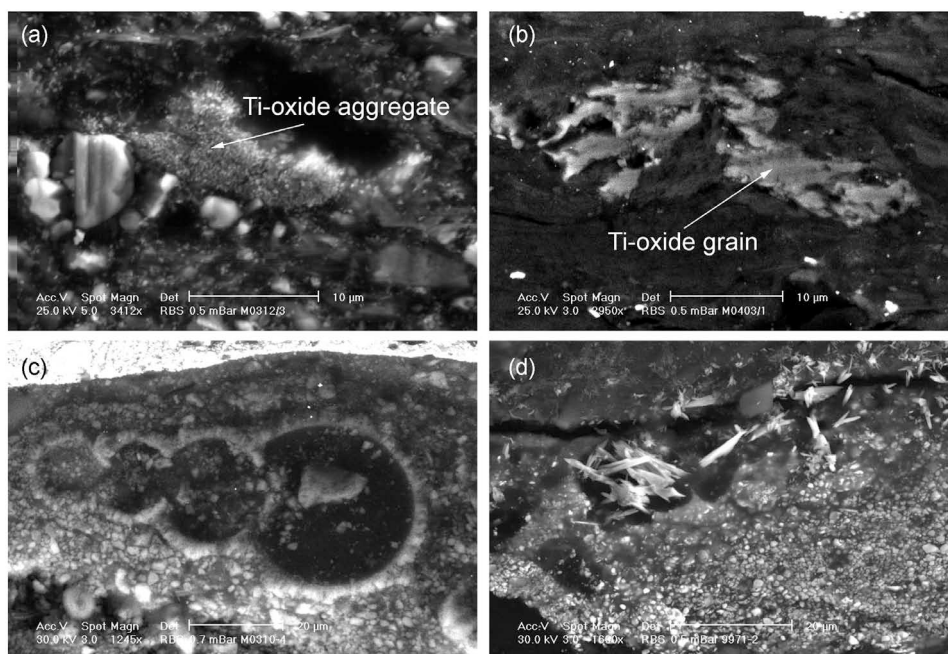


Fig. 6. Grain size and morphology is related to the origin of minerals. Aggregate of small uniform particles of synthetic titanium white (anatase – TiO_2) used in modern paints since 1920 (a) vs. weathered grain of natural anatase in the same scale as a common admixture in clay-based pigments used since the pre-history (b); microfossils indicating a natural origin of the chalk (limestone) used instead of artificially prepared calcium carbonate or carbonatized lime (c); sharp and elongated crystals of neo-formed salts in porous space of color layers as an example of secondary deterioration process (d).

Merrifield (1967). Then, further works on painting techniques with a general scope should be mentioned, e.g. *Eastlake (1960)*, *Laurie (1967)*, *Berger (1973)*.

To properly interpret the painting technique is thus not only needed to identify materials but also to locate them in the layer sequence (*Rosi et al. 2011*). Heterogeneity of the source materials from which the paint layers are made is further important for understanding their provenance and/or properties and thus it should not be lost or overlooked during the analysis. To properly interpret these source materials in the context of their use in the history combining knowledge of analytical chemistry and geosciences is needed.

On the other hand, the description of secondary-developed textures – e.g. corrosion and weathering rims, surface layers etc. is relevant for better understanding of deterioration processes and virtual reconstruction of original colors (*Fig. 5*). A description of zones of degradation and explaining deterioration processes

is another popular field of recent investigations of works of art (*Monico et al. 2011*).

3. Microanalysis of pigments

3.1. Mineral and synthetic pigments

Pigments in color layers of paintings are either natural (mineral) applied simply after mere mechanical pre-treatment and separation not-affecting their chemical or phase composition (e.g. malachite, azurite, celadonite, cinnabar, orpiment etc.), or manufactured - prepared by chemical reactions from substantially different raw materials (e.g. smalt, lead white, verdigris).

In a relatively lower extent, also organic pigments are prepared from organic dyes by precipitation on inorganic substrate (e.g. red organic lakes). Gradually, a lot of mineral pigments have been substituted by their artificial analogues (e.g. artificial ultramarine, artificial orpiment, vermilion etc.), however, on the other hand, some of them survived until

CONTENT OF MINERALS (wt.%)	Reference samples / deposits			Samples of red "bole" grounds of paintings				
	Hořelec (CZ)	unknown (IT)	Kronach (D)	M0627	JSII	M0036	M0366	J1006
	Bk type	Bs type	C type					
Kaolinite	60	44	40	70	74	87	39	40
Hematite	20	20	10	12	18	8	10	10
Anatase	7	5	1	7	6	3	10	2
Smectite	—	29	—	—	—	—	26	—
Quartz	3	0,5	44	9	—	—	4	44
Goyazite	4	1	—	—	1	1	—	—
Calcite	—	—	—	2	—	—	—	—
Siderite	—	—	—	—	—	1	—	—
Illite	<0,5	—	5	—	—	—	—	4
Gypsum	—	1	—	—	—	—	—	—
Cristobalite	—	—	—	—	—	—	11	—
ATTRIBUTION TO TYPE				Bk	Bk	Bk	Bs	C

table 1. Comparison of mineralogical composition of five selected red clay-based grounds of paintings from the Czech collections and their attribution to three different source materials from historical mining deposits – Horenc in the Czech Republic (Bk), Kronach in northern Bavaria (C) and yet unknown locality in northern Italy (Bs)

the present days (e.g. clay-based pigments – “earths”). During the 19th century industrial production of new synthetic pigments (e.g. zinc white, synthetic alizarine etc.) has started. Fundamental works on pigment origin, preparation, use and identification are given e.g. by Feller (1986), Roy (1993), Fitzhugh (1997) and Berrie (2007).

Natural and artificial pigments differ in content of various admixtures, variable grain size and crystallinity. These properties affect the opacity and color fastness of the pigment (Fig. 6).

The knowledge about when and how the historical pigments were being replaced by the synthetic ones contributes to the dating of paint layers. Mineralogical analysis describing the process of the formation of individual mineral pigments in nature helps to indicate the regional provenance of painting materials by comparing them with materials from reference sources (Table 1).

Modifications of the pigments structures, different admixtures and contaminations of the product could also be related with different fabrication processes and thus with different workshops. To assign the authorship of anonymous paintings the materials analysis should always be combined with the description of artistic style within comparative studies.

3.2. Methodology

Complete fingerprint of each painter can be folded from the material composition of colors (materials fingerprint), the method of their preparation, mixing and spreading in layers (technological fingerprint) and artistic expression (style fingerprint). The first two fingerprints provide extra information about the region and the period of artwork origin.

Obtaining a complete fingerprint today requires costly transportation of the painting for a long distances and extensive sampling - otherwise the evaluation is highly subjective and it results in the growing of the trade with forgeries. The costs of analyses, the transport of works of art, insurance costs, etc., which are usually too high for regional museums, churches and other owners, have their share on the growing interest in non-invasive analytical techniques. Despite a significant boom in this field in last years, it must be said that without sampling the description of author's fingerprint will always be only partial (Fig. 7).

Once samples are taken from the prestigious works of art, they become a part of a physical archive and may not be lost or consumed during their analysis. Therefore, the main effort is directed to analyze a small amount

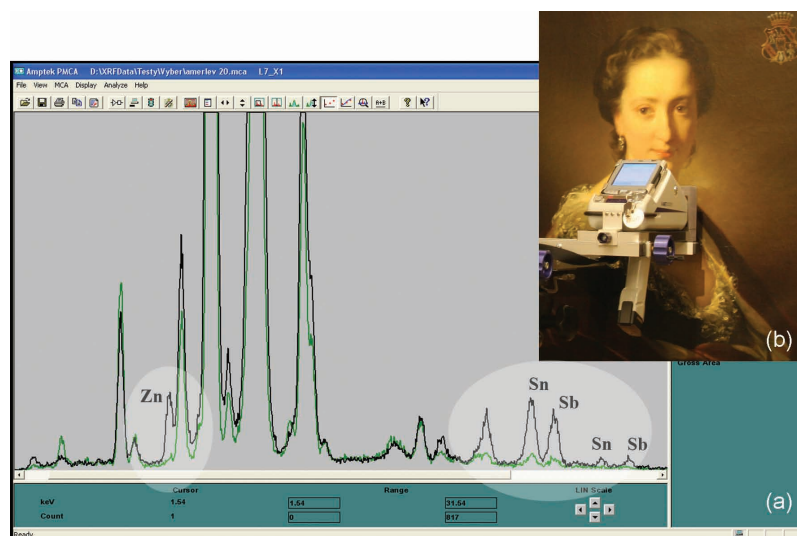


Fig. 7. X-ray fluorescence spectra (a) obtained by non-invasive punctual measurement by hand-held equipment (b). Use of mixed Pb-Sb-Sn yellow (i.e. $Pb_2SbSnO_{6.5}$) instead of pure Naples yellow (i.e. bindheimite - $Pb_2Sb_2O_7$) is here indicated by a joint occurrence of Sb and Sn in yellow color together with Zn - zinc white (ZnO); use of this uncommon pigment is one of author's fingerprint of the 19th century painter Friedrich von Amerling.

of a sample by the most methods in a non-destructive way to obtain maximum information without any loss of material. Sample pre-treatment has to be minimized and, if applied, it has to be acceptable for most or, ideally, all techniques which are necessary for complete examination of the sample. This implies testing of particular methods, namely their detection limits, accuracy, and correctness of measurements because they can differ significantly from those of the standard procedures.

Routinely used laboratory methods for instant investigation of fragments of paints and their cross-sections are light microscopy (LM) and scanning electron microscopy coupled with energy dispersive spectrometry (SEM-EDS). They provide preliminary information about the morphology, stratigraphy, and elemental composition of paints. The semi-quantitative elemental analysis can further be improved by quantitative and trace elements analysis via particle induced X-ray emission (PIXE) and/or scanning electron microscopy coupled with wavelength dispersive spectrometry SEM-WDS (Schreiner et al., 2007).

Focusing on the identification of inorganic crystal phases, X-ray diffraction-based techniques (XRD) are very effective tools for their indisputable determination (Svarcová et al. 2010), besides more frequently used spectroscopic methods

such as Raman and/or infrared spectroscopy (Vandenabeele et al. 2007, Bacci et al. 2001). The main disadvantage of Raman spectroscopy in the mineralogical analysis of paints is a high risk of undesirable fluorescence promoted either by organic stuff (binders, sealing compounds etc.) and/or other fine-grained materials such as, for example, clays (Fig. 8).

X-ray diffraction, contrarily to Raman spectroscopy, enables indisputable identification of crystal phases, including double salts, hydrates, and unstable materials, using a huge number of reference patterns available in an array of databases. Furthermore, XRD can be used for quantification of phases in mixtures.

Implementation of mono or poly-capillary systems into the conventional diffractometers enables analysis of small volume samples or even their selected parts without any destructive pre-treatment (Svarcová et al. 2010). Introduction of X-ray microdiffraction into material characterization was made possible by synchrotron radiation sources, which are noted for high intensity X-ray beams enabling collection of diffraction data from small areas (typically of the order of 0.001– 0.1 mm) in a reasonable time (Dooryhée et al. 2005). Laboratory equipments for routine powder X-ray microdiffraction have become more frequent in last years and, as we already proved, the resulting data are generally

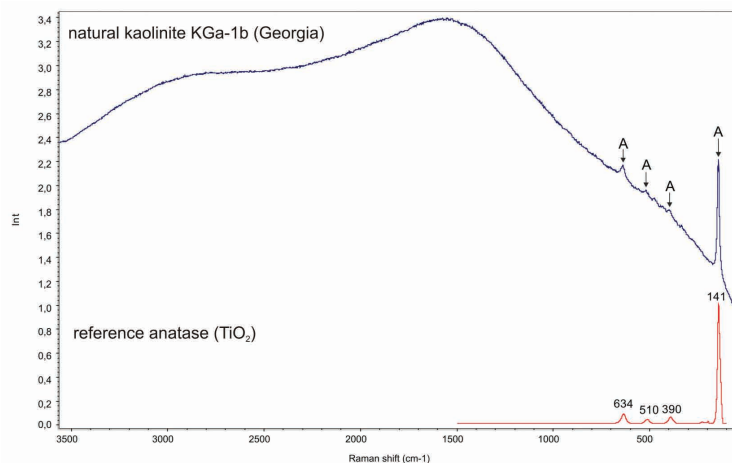


Fig. 8. Raman spectra of natural kaolinite from Georgia (U.S.A.), where only the peaks of admixed anatase (A) are clearly distinguishable; without additional information this spectra could be misinterpreted as titanium white (adopted from Kosarová, 2011).

comparable with those obtained on synchrotron-based microdiffraction (Svarcová et al. 2011a). In our workplace, for example, PANalytical X'Pert PRO diffractometer is used, equipped with a conventional X-ray tube (CoK α radiation, 40 kV, 30 mA, point focus), a glass collimating mono-capillary with an exit diameter of 0.1 mm, and a multichannel position-sensitive detector (X'Celerator) with an anti-scatter shield (Fig. 9).

3.3. Case studies

The authors have been dealing with mineralogical analysis of pigments systematically for many years and have published its results on regular basis.

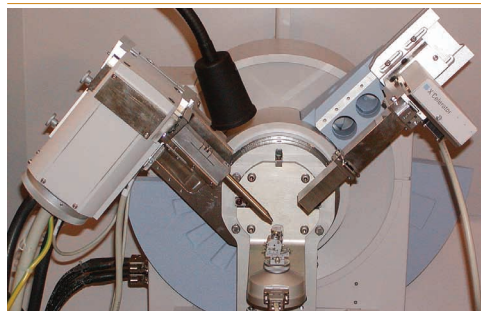


Fig. 9. Powder X-ray diffraction equipment at the Institute of Inorganic Chemistry of the AS CR in Rez, Czech Republic.

The mineralogical analysis provides e.g. indicators which make it possible to discern provenance of various earthy pigments (containing clay minerals) found in microsamples

(Hradil et al. 2003 and 2011).

Based on distinguishing of structural modification of bindheimite (Pb₂Sb₂O₇) by Sn and identification of its accompanying minerals one can trace back procedures and raw materials to produce various types of lead-based yellows (Hradil et al. 2007).

Experimental mineralogical research has led to the novel description of the crystal structure of basic copper acetate (verdigris) – a pigment used by painters since the Middle Ages (Svarcová et al. 2011b).

Practically no attention has been paid in literature to description of clay structures in the traditional painting pigments. Most articles on analyses of paintings are happy with the statement that the painting contains an earthy pigment, iron ochre or red clay, without further specifying their compositions. Meanwhile, there is a significant diversity of such materials in terms of natural processes of their formation.

European Medieval paintings often contain intensely-colored materials, originally coming from surface layers of just uncovered polymetallic ore deposits, where clay minerals were practically missing and for which the technical term “earth” should not be even used. On the other hand, these raw materials often contained specific admixtures of metals (e.g. Pb, As or Zn), which may help to identify their origin.

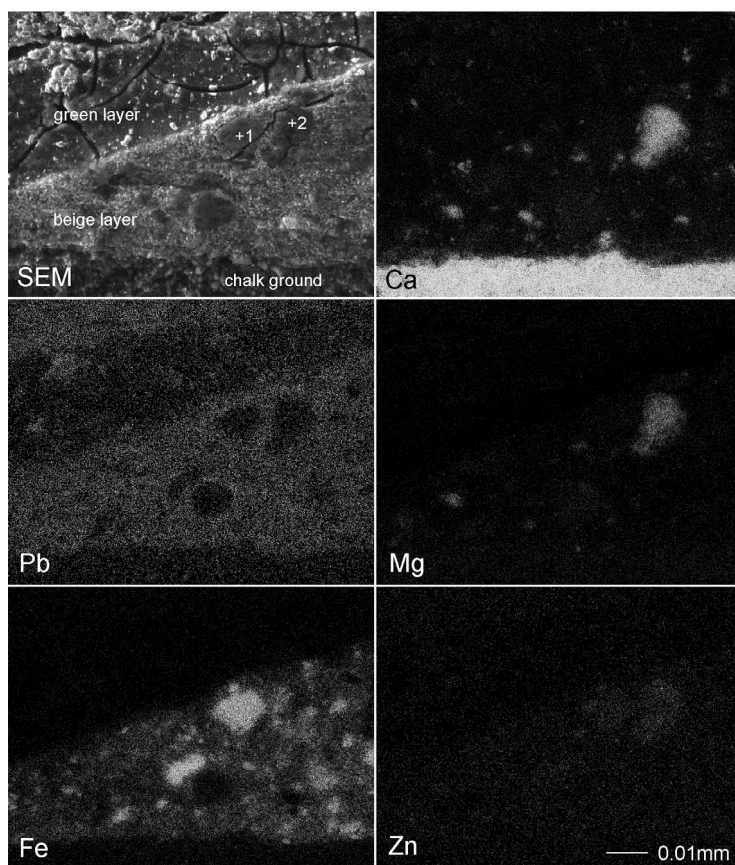


Fig. 10. X-ray intensity maps of selected elements in the original beige layer of the background, toned by red grains (Altarpiece of Matejovce, right wing); X-ray intensities correspond to relative concentrations of individual elements within the measured area, but the concentration maxima indicated by the highest intensity are different for each element (Ca maximum 100 wt%, Fe maximum 60 wt%, Mg maximum 45 wt%, Pb maximum 100 wt%, Zn maximum 5 wt%); grain +1 represents iron oxides with some admixtures of Zn-bearing minerals, and grain +2 is Zn-dolomite.

Within detailed mineralogical research of selected Gothic altarpieces in Northern Slovakia and Lesser Poland it was, for example, found that the original iron red contains goethite, hematite, calcite, and Zn-dolomite. Zinc containing dolomite represents a fingerprint indicating that the source material was mined in the oxidation zone of the carbonate-hosted Zn–Pb ore deposit near Cracow, Poland, which has been active since the 12th century. Thus one could conclude that works of the so-called Master of Matejovce altarpiece workshop can be recognized not only by their conservative style known as the ‘Cracow school’ of painting but also by very characteristic materials features indicating the author’s preference to use pigments from regional

sources, differently to other workshops of the same period and place (Hradil *et al.* 2008) (Fig. 10).

In the case of mineral pigments, which were formed by weathering or other alteration of silicate rocks, the decisive factor is the correct identification of clay structures and their closely associated phases, e.g. iron oxides. The main reason why such information is often missing is particularly the limited availability of material from the painting, which reduces the possibility to apply standard procedures for clay investigation – separation and orientation of particles, exchange of interlayer cations etc. (Moore and Reynolds 1997).

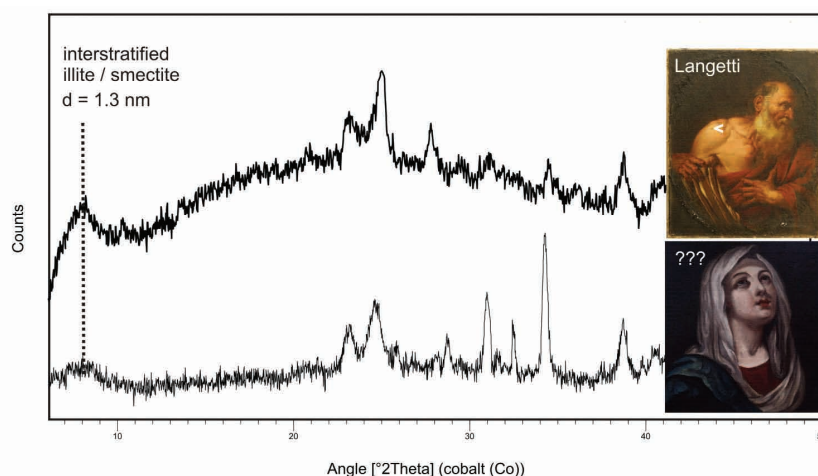


Fig. 11. Interstratified illite / smectite indicated by interplanar distance of ca 1.31 nm at the diffraction pattern of reference Italian 17th century painting by G.B. Langetti and on one anonymous painting; this clay fingerprint together with almost the same mineralogical composition of the ground helped to locate the anonymous painting to the region of northern Italy.

Completely unaddressed remains the issue of reaction of expandable clay structures in the painting layer with humidity and organic binders, which result in organo-clay complexes, both in painting and preparatory layers. However, their stability in the painting may be very significant from the viewpoint of preservation of the paintings. The only organo-clay historical pigment, which has been carefully investigated, is the so-called Maya blue – a very stable complex of palygorskite and natural indigo (Doménech *et al.* 2009; Giustetto *et al.* 2011). This pigment, however, has not been found in European paintings.

Results of last investigations demonstrated how a correct description of basal diffractions of clay minerals in the low-angle region leads to a direct determination of provenance of anonymous 17th century paintings (Hradil *et al.* 2010), or, how the source locality of the white earth (kaolin) used in the preparatory layer of Bohemian Gothic murals can be indicated by a calculation of the kaolinite crystallinity index (Svarcová *et al.* 2011a). Wide range of other examples could be given.

4. Conclusion

An estimated 90% of tangible cultural heritage is not studied by modern scientific methods. Often (and often unnecessarily) only the famous works of art in famous galleries are subjected to detailed investigations.

Is this correct? As mentioned in this paper,

the way to reduce this disparity is the current development of non-invasive analytical techniques that allow obtaining exact data in situ, even in distant places - regional galleries, rural churches, etc.

In the restoration/conservation practice the aimless collection of analytical data still prevails over the targeted analyses. Each expertise in the field of cultural heritage requires its make-to-measure methodology reflecting the diversity of materials as well as variety of tasks. When applying this approach, targeted mineralogical analysis of paint layers could directly lead to dating and to determining the provenance of anonymous works of art.

Often we also hear the opinion that artworks must first to be preserved and then (when enough money is left) discovered and explored. But is it not rather the opposite? Material properties we do not keep forever, they decompose sooner or later, and we can only slow down this process. But they were created for our inspiration and knowledge, which is not a subject of any further decay. First of all, this knowledge itself is a substantial part of our cultural heritage. And a respect to the knowledge is something what we often lack.

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