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Differentiation between anonymous paintings of the 17th and the early 18th century by composition of clay-based grounds

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ABSTRACT

Numerous anonymous paintings are preserved in depositories of European galleries. The reasons why they are not being shown to the public differ, but one of them is their doubtful attribution and relative dating. There is a large amount of unsigned paintings of varying artistic quality and also lots of copies of unknown provenance. We have found out that mineralogical analysis based on X-ray powder micro-diffraction measurements is able to provide exact parameters for the classification of earthy ground layers of paintings into well-defined types. In the period of the 17th and the early 18th century, these types were regionally specific, because various coloured clay-based materials became popular thanks to significant changes in the painting technology. They gradually substituted previously used white chalk and/or gypsum (gesso). Within comparative research performed on paintings from Czech collections, we were able to distinguish those of Italian and those of Central-European provenance. We have defined five types of grounds that differ in clay minerals' structures (presence of expandable and interstratified structures, various crystallinity indices etc.) and their relative contents, and, in addition, in characteristic elemental ratios and admixtures, either natural or artificial.

1. Introduction

Up to the modern times, internal structure and sequence of individual layers of the painting were defined by very strict rules. Any important change of technology was gradual, and always preserved strong relations between materials, technique and style. The use of different materials in different periods and regions was, besides the tradition, further influenced by their sources and their efficient availability, as well as by the level of technological knowledge of their treatment. Everybody knows that the employed materials somehow correspond to the provenance of the painting itself, but there is still an entire lack of exact parameters usable as appropriate fingerprints. A description of these fingerprints is a necessary first step along with the elaboration of their measurement methodology; only then the recognition can be established.

The construction of historical paintings and wooden polychrome sculptures has always been the same – on the support of choice (wood or canvas), a ground layer is usually applied to flatten its surface. A thin insulation layer separates this ground from subsequent colour layers that eventually include a preparatory drawing and/or priming (imprimitura) followed by consequent layers of paint. In the traditional European art, several types of grounds appear on panel and easel paintings – white gypsum-based or chalk-based (from Byzantium to Gothic period), and colour clay-based (typically in Baroque) (Stols-Witlox, 2012). While white or grey chalk-based grounds had persisted in Central Europe to the 2nd half of the 16th century and the early 17th century, in the same period of time, artists in Italian (such as, e.g., Carravaggio) and Franco-Flemish environments (such as, e.g., Van Dyck or Nicolas Poussin) have already started using clay-based (earthy) grounds (Duval, 1994; Bergeon and Martin, 1994; Roy, 1999). The gradual change of technology and composition of ground layers has started in Italy in the 16th century – as a first step, a slight tinting of the white priming layer appeared; then, clay-based materials combined with other pigments partially or fully substituted the white gypsum (*gesso*) or chalk materials previously used for grounds in Middle Ages and Renaissance (Dunkerton and Spring, 1998). The colouring of white *gesso* using many different pigments followed by the dominancy of earthy pigments in grounds has already been described on a wide set of paintings. The major problem of all previous classifications is, however, that they were based only on visual observations combined with the knowledge of elemental composition, which does not lead to the distinguishing of signs of origin and to the differentiation of materials added later on during further treatment (additional colourants, calcination etc.) (Martin, 2008). The gradual change from white to mid-tone and, subsequently, from mid-tone to dark colours was realised by additions of lead-tin yellow, cinnabar, charcoal black, and also red lake, azurite and (especially) earthy pigments. The change in composition of earthy pigments has never been studied despite its important

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relation to the material's provenance and technological properties of the layer (colour, adhesive power, swelling). Technological experiments with composition of clay-based grounds continued during the 17th century (Stols-Witlox, 2012). Although the bloom of the painting on coloured grounds is the most important change of the technique in the 16th century, it has been studied only a little. The significance of this transition is immense, as one hundred years later, the clay-based grounds are predominant in the whole Europe (Hradil et al., 2003).

Conventional approach to the analysis of minute paint micro-samples (less than 1 mm large and heterogeneous) usually includes their embedding in synthetic resin and polishing to obtain their cross-section. These micro-sections are considered as "standard" samples, as the layer stratigraphy can be described on them and further analyses can be performed on individual layers. In some cases, there is enough of the material taken from the painting and more than one fragment is available – thus, some of them can be measured without any pre-treatment. Due to the heterogeneity of these untreated fragments, only their bottom (= ground) and top layers can be measured. Routinely, description of the sample by the means of optical microscopy is followed by semi-quantitative elemental analysis (e.g. by scanning electron microscopy coupled with energy dispersive spectroscopy – SEM/EDS or micro X-ray fluorescence – μ-XRF), and by spectroscopic analyses of pigments and binders by Raman and infrared microspectroscopy (μ-Raman, μ-FTIR). None of these methods leads to the distinguishing of clay minerals in earthy pigments due to their variable chemical composition further affected by numerous admixtures, structural similarities, low Raman scattering of clay minerals together with high fluorescence caused by Fe-rich admixtures commonly preventing obtainment of their Raman spectra (Košařová et al., 2013). As a result, only admixtures are positively identified, e.g. iron oxides (hematite, goethite), which act as chromophores in the mixture, but they do not lead us to the provenance of the material (Benquerenca et al., 2009; Iordanidisa et al., 2011; Damiani et al., 2014). To identify clay minerals, it is necessary to apply X-ray micro-diffraction (μ-XRD). In this field of study, this method is still unconventional, although we have already published its advantages and limitations (Švarcová et al., 2010). In our previous paper, we have also discussed that the laboratory μ-XRD gives results comparable with synchrotron μ-XRD, therefore, they can be obtained in standard laboratory conditions (Švarcová et al., 2011).

There are three reasons why it is important to investigate ground layers in detail: (i) they are usually thicker than individual colour layers and thus the chance of their correct measurement is greatly improved, (ii) they usually cover the whole support of the painting, therefore, there is no need for extensive sampling – only one micro-sample of the painting is sufficient and representative enough for the study of the ground, and (iii) they can come from regional sources, because the consumption of this material was relatively higher and thus the price became a very important factor; in case of clay materials, there were numerous deposits with regional importance that provided material of sufficient quality. Some of them have been mentioned already in very old historical sources (Da Costa, 1757) and known by their local names, such as, e.g., Bohemian or Tokay bole etc. On the other hand, the composition of ground layers refers to periods, regions or, eventually, workshops, but not to the artists themselves, because usually they had not done these preparations in person. Based on the here-described analyses, the anonymous paintings can be attributed to regions and periods, but not to the individual painters (who also commonly travelled). The aim of this study is to provide specific and distinguishing features related to the provenance of materials used for the grounds in the 17th to the early 18th century paintings from the collections in the Czech Republic. We have tried to obtain these parameters repeatedly and we have improved the methodology of their measurement. As a conclusion, we aspired to be able to decide if these parameters are usable for correct assignment of anonymous paintings and if these new methodical approaches can be recommended for their general use in other similar comparative studies.

2. Materials and methods

2.1. List of paintings and samples

Within our study, micro-samples from thirty 17th to early 18th century canvas paintings from Czech collections have been analysed by combination of micro-analytical methods. The selection of paintings

Table 1a
List of analysed canvas paintings from the Czech collections with known (either Bohemian or Italian) provenance.

Code	Artwork, place	Artist	Period of creation	Region of creation	Analysed as
M0627	Painting from the Calvary Cycle, Franciscan monastery, Kadaň, CZ	Anonymous	18th C	Bohemia	Cross-section
M0036	St. Teresia, Church of Our Lady Victorious, Prague, CZ	Jan Bedřich Hess (?-1673)	1680	Bohemia	Cross-section
J0904	Crowning with Thorn IV., St. Nicholas Church, Lesser Town, Prague, CZ	Karel Škréta (1610–1674)	1673–1674	Bohemia	Fragment
J1020	St. Charles Borromeo attend the plague-stricken in Milan, National Gallery in Prague, CZ	Karel Škréta (1610–1674)	1647	Bohemia	Fragment
M0731	Portrait of the painter of miniatures, National Gallery in Prague, CZ	Karel Škréta (1610–1674)	1635	Bohemia	Fragment
J1006	Portrait of a horse called Flery, with groom, National Heritage Institute, Regional Office in České Budějovice (Budweiss), Hluboká Chateau, CZ	J.G. de Hamilton (1672–1737)	1705 or 1707	South Bohemia	Fragment
J1007	Portrait of an unknown black horse, National Heritage Institute, Regional Office in České Budějovice (Budweiss), Hluboká Chateau, CZ	J.G. de Hamilton (1672–1737)	1723	South Bohemia	Fragment
M0410	Madonna with child (copy of Madonna of Klatovy), private owner	Anonymous	18th C	South Bohemia	Fragment
J0919	Leto and Peasants, National Heritage Institute, Regional Office in Kroměříž, Vizovice Chateau, CZ	Stefano Magnasco (1635–1673)	17th C	Italy	Fragment/cross-section
J0734	Still Life with watermelons, grapes, peaches, figs, and two pigeons, National Heritage Institute, Regional Office in Brno, Rájec nad Svitavou Chateau, CZ	Jakob van de Kerckhoven or Giacomo da Castello (1637 1712)	17th C	Italy	Fragment
M0514	Landscape with a staffage National Gallery in Prague, CZ	Anonymous Italian painter	17/18th C	Italy	Fragment/cross-section
J1116	Tityos (Prometheus) Art Gallery in Ostrava, CZ	Giovanni Battista Langetti (1635–1676)	17th C	Italy	Fragment
J0920	Philosopher, National Heritage Institute, Regional Office in České Budějovice (Budweiss), Chateau Náměšť nad Oslavou, CZ	Giovanni Battista Langetti (1635–1676)	17th C	Italy	Cross-section
M0365	Tomyris with the head of Kyros, Ministery of Culture, Prague, CZ	Anonymous Italian painter	2nd half of the 17th C	Italy	Fragment