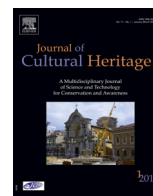




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Case study

The use of powdered bismuth in Late Gothic painting and sculpture polychromy



Tomáš Čechák^{a,1}, Tomáš Trojek^{a,2}, Radka Šefců^{b,*,3}, Štěpánka Chlumská^{b,4},
 Anna Třeštíková^{b,5}, Marek Kotrlý^{c,6}, Ivana Turková^{c,7}

^a Department of Dosimetry and Application of Ionizing Radiation, Czech Technical University in Prague, Břehová 7, 11519 Prague, Czech Republic

^b National Gallery in Prague, Staroměstské náměstí 12, 11000 Prague, Czech Republic

^c Institute of Criminalistics Prague, Bartolomějská 12, 11000 Prague, Czech Republic

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ABSTRACT

This paper presents a material study of the altarpiece in the chapel at Křivoklát (Pürglitz) Castle called Křivoklát Ark (around 1480–1490), located in Central Bohemia, Czech Republic. The Křivoklát Altarpiece is one of the most important works of Jagiellonian courtly art in Bohemia. It is decorated with polychrome sculptures and panel paintings. An initial investigation of the gilded and silvered parts of the paintings, sculptures and architectural decor of the altarpiece was undertaken using a portable X-ray fluorescence analyser. Not only the expected metallic elements gold and silver were identified, but also bismuth. This surprising result led on to a complex study of the altarpiece, focused on the layered structure and the method by which bismuth was used the paint layers under the metal-coated areas (under the gold and silver plating). The coating technique using bismuth powder in the Late Gothic period has already been described in scientific publications. However, our paper deals with a rare technique, i.e. the use of powdered bismuth in red bole and its plating with gold and silver leaf. Several micro-samples were therefore taken from carefully selected parts of the altarpiece. Only a minimum amount of sample material was taken, due to the significance of altarpiece. The samples were then analyzed with optical and electron microscopy, EDS analysis, micro-XRF, and other methods. The quantitative element mapping on the cross-section of a micro-sample with gilding showed distributions of several elements (Bi, Au, Fe, Al, Ca); this means that the presence of bismuth grains in the red layer under the gilding leaf was proven. Interdisciplinary cooperation and a combination of microscopic and spectral methods have enabled us to describe this unique late Gothic gilding technique, in which metallic bismuth was intentionally used to affect the color scheme of the coated areas in paintings and polychrome sculptures.

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1. Introduction

The untraditional use of powdered pigment based on bismuth was ascertained in the extensive investigation of one of the

best-known relics of Jagiellonian court art in Bohemia, a retable from the castle chapel of the royal castle of Křivoklát (Bohemia, around 1480–1490) [1,2]. The Retable of the Coronation of the Virgin Mary, adorning the main altar of the chapel, is a representative example of the combination of panel paintings and statues into a single unit as far as concerns both composition and content, which was typical of the decoration of late Gothic altarpiece. In the heritage fund of the Czech Lands this is one of the best-preserved examples of this type [3]. In spite of this, however, some researchers have expressed doubts about the authenticity of the existing unit, in particular with regard to the proof of fires at the chapel and the extensive repairs to and restoration of its interior, including the preserved furnishings, at the end of the 19th century and beginning of the 20th century.

There has also been repeated attention paid to the question of ascribing the authorship of the statues and paintings of the Křivoklát Retable. These were usually evaluated individually and

* Corresponding author.

E-mail addresses: tomas.cechak@jfifi.cvut.cz (T. Čechák), tomas.trojek@jfifi.cvut.cz (T. Trojek), sefcu@ngprague.cz (R. Šefců), chlumska@ngprague.cz (Š. Chlumská), trestikova@ngprague.cz (A. Třeštíková), marek.kotrlly@pcr.cz (M. Kotrlý), ivana.turkova@pcr.cz (I. Turková).

¹ Tel.: +420 224 358 132; fax: +420 224 811 074.

² Tel.: +420 224 358 237; fax: +420 224 811 074.

³ Tel.: +420 221 279 255.

⁴ Tel.: +420 224 810 835.

⁵ Tel.: +420 221 279 255.

⁶ Tel.: +420 974 824 406; fax: +420 974 824 323.

⁷ Tel.: +420 974 824 315; fax: +420 974 824 323.

were ascribed to the group of masters invited by Vladislav II to renovate the royal residence in Prague. The paintings of the retable bear visible signs of workshop praxis with evident fluctuation in the quality, while maintaining the unified framework of the whole. They are not isolated in the heritage fund of Central Bohemia, but so far there have been no reliable answers to the questions concerning individual workshop ascription (the circle of the Master of the Křivoklát Altarpiece, the Master of the Litoměřice Altarpiece) [4]. In this context, the recognition and interpretation of a less common technological procedure, such as the use of powdered bismuth as a component of the poliment for areas of metal leaf of the painting and polychromy, are very helpful, as they contribute both clear arguments for the appurtenance of individual parts of the retable to the unit as a whole, and also an important technological description of the workshop practices of the creators of the Křivoklát Retable.

Bismuth (Bi) was identified during the investigation carried out on the Křivoklát Altarpiece on the gilded and silvered areas of the painting, the statues and the architectural décor, together with the usual metallic elements—gold (Au) and silver (Ag).

2. Proven examples of the use of bismuth

Metallic bismuth was used to imitate silver as a cheaper substitute for this or in a mixture with tin known as shell or mussel silver. The first mentions of the mining and obtaining of metallic bismuth come from Agricola (*De Re Metallica Libri XII*, ed. 1556) [5]. Bismuth is also mentioned by Valentine Boltz von Rufach in a historical recipe-book (*Illuminierbuch*, published in Frankfurt in 1549), the author calls it *argentum musicum* and discusses it in connection with book illustration and calligraphy (preparation of inks at the turn of the 15th and 16th centuries) [6]. The metallic bismuth was used to imitate silver on artistic craft objects of small size, dated to the 16th century [7].

Modern material investigation has truly shown the use of bismuth as gray powdered pigments in the work of illuminators in several manuscripts [8–11]. It was also confirmed by research into the paintings of Italian Masters, as emerges from the recent findings in the analysis of the paintings of Fra' Bartolommeo and Raphael Santi [12,13]. The gray bismuth powder was used as a dispersed pigment in the paint layer on the ground, resulting in a grey coloring. Bismuth use is also evident on the background of the reliefs on the inner sides of the movable wings of the late Gothic Retable from the Monastery in Estavayer-le-Lac in modern-day Switzerland from the twenties of the 16th century [14].

The above-mentioned examples of the technological use of bismuth differ, however, from the technological procedure of the creators of the paintings and polychromy of the carvings of the Křivoklát Retable, because on the Křivoklát Retable powdered bismuth was found under the gold and silver leaf in the layer of poliment.

Only the use of bismuth mixed with red earth and red lake in the mordant layer beneath God the Father's gilded halo on the Coronation of the Virgin by the Master of Cappenberg (Westphalia, around 1520) from the National Gallery in London is related to a technique probably comparable to that used on the Křivoklát Retable [13].

3. Experimental

The survey of the Křivoklát Retable started with non-invasive analytical methods: photography in visible light (VIS), macro-photography, infrared reflectography (IRR) and X-ray fluorescence [14–17].

3.1. Non-invasive methods

Macro-photographic documentation was performed with the USB microscope Dino-Lite Pro AM413ZT, polarized light, 1.3 megapixel, magnification 50×, 200×. The photos were processed in the program Dino-Capture 2.0 version 1.3.9.

Infrared reflectography was carried out using a Sony DSC-F828, filter F-PRO B+W, HOYA 58 mm, Infrared R72.

Non-invasive element analyses were carried out using portable X-ray fluorescence (XRF), Niton XL3t Thermo Scientific. This XRF system includes an X-ray tube with a silver target and it was operated at a voltage of 35 kV. The diameter of the investigated area was approximately 3 mm. The time for one analysis was 20–30 s.

3.2. Sampling and analytical methods

Micro-samples were taken for analysis from the throne of the God the Father. The micro-sample was fixed in methyl methacrylate resin (Clarocit). After hardening the cross-sections the section was gradually dry-ground and polished (Silicon carbide SiC).

Consideration of the stratigraphy was carried out on an Eclipse 600 Nikon polarizing microscope in reflected and intersecting light, on a dark field and after excitation by UV light, Hg discharge lamp, UV filter 330–380 nm and 450–490 nm. Morphological traits of individual pigments on prepared sections were examined in intersecting polarized light in parallel (PPL) and crossed (XPL) nicols. Usual magnification was 200–1000×.

Standard analysis of the element composition on the sections was carried out on a scanning electron microscope with an energy-dispersing detector (SEM/EDX) on the instrument A LYRA3 TESCAN analysis unit equipped with a Si (Li) X-ray detector. The analysis took place in a high vacuum, acceleration voltage 20 kV, BSE detector. The quantitative element mapping was performed with an EDS Bruker Quantax, ESPRIT software. The polished cross-section was prepared by applying a graphite coating.

Micro X-ray fluorescence analyses were performed with an EAGLE 3 equipped with Cathode material Rh, focus 50 μm, voltage 40 kV, current 30 mA, measured in a vacuum.

4. Results and discussion

With regard to the above-mentioned tasks of the comprehensive investigation of the Retable an important aim was the acquiring of knowledge about the nature and extent of the use of bismuth. Information was gradually collected and evaluated on its structure and type of use in layers of painting and polychromy. Using XRF analysis it was possible to map out in a non-invasive manner the entire extent of its occurrence. A total of 249 points were measured on the retable, of which 78 spectra from gilded and silvered areas were obtained (Fig. 1).

On the paintings on the external sides of the movable wings – on the halos of the figures of the saints (St Sigmund, St Wenceslas, St Vitus and St Vojtěch) and on parts of their clothing, including the surface of the tinned relief – the gilding is executed on mordant. There is also mordant gilding and silvering on the paintings of the Marian Cycle on the inner sides of the movable wings – again on parts of the clothing (viz. the Adoration, robe of the Black King), the plating of the tinned reliefs and on smaller gilded areas of the paintings such as the caskets and goblets (also the Adoration). On the statues in the center of the Retable – the altar case – there is mordant gilding on the hair of the kneeling Virgin Mary and on the hair of the angels. On all these surfaces, plated on mordant, there was demonstrated by XRF analysis, apart from the appropriate metal foil, gold (Au) and silver (Ag), also the presence of lead

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