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Analytical studies of the Alexandrovo Thracian tomb wall paintings

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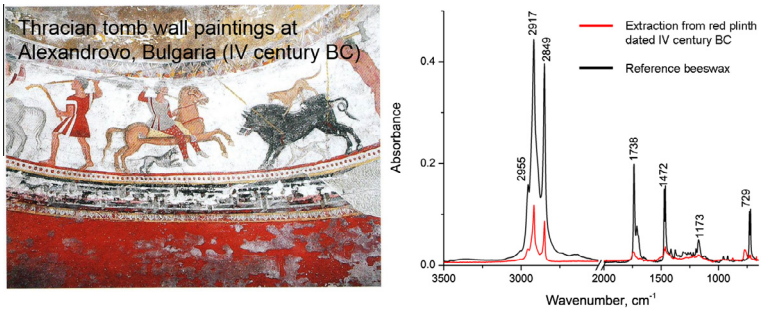
HIGHLIGHTS

- DSC, FTIR, HRTEM and EDS analysis of archaeological samples.
- Beeswax used as a binding agent in Thracian tomb wall paintings in the 4th century BC.
- Presence of Au, TiO_2 and CeO_2 nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

A profound study of samples obtained from Thracian tomb wall paintings at Alexandrovo, Bulgaria (dating back to the fourth century BC) were carried out by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR) and Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR FTIR), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS). The current work provides a glimpse of the ingenious construction and painting techniques used in Thracian tomb at Alexandrovo. The results suggest that beeswax was used as a paint binder and also revealed presence of various nano-materials.

Introduction

The scientific analysis of an artwork can provide knowledge about the techniques and materials used during a specific time period and assist discovering forgeries or later repainting. The detailed knowledge of the materials composition of an artwork is an important prerequisite to carry out research in the field of art science or archaeology and to establish the proper procedures for conservation and restoration. However, a single analytical technique cannot provide complete information about the materials and techniques used in the artwork and usually complementary methods of examination and analysis have to be carried out in parallel.

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The ancient Thracian tomb at Alexandrovo, Bulgaria (dated to the fourth century BC) [1] is considered as one of the most significant recent discoveries since there are very few sites with mural decoration known from this period. It holds important historical, cultural and scientific information about the religion and life of the ancient Thracians as well as about the construction and painting techniques used back then [2]. Although objects and burial remains were missing, the architecture and wall paintings are in their original state as they were made in antiquity without any conservation treatments. The interior of the tomb was originally decorated in the past. The main elements of the decoration are figurative frieze with hunting scenes which, fortunately, are completely intact (Fig. 1). At the time of discovery, part of the decoration was found fallen down and broken into pieces of different sizes. After collecting samples for analysis, only a passive conservation was carried out [3].

A life-size copy of the tomb, made in stone and having the same wall paintings, was built in a modern museum center of Thracian Art in the Eastern Rhodopes and displayed to the audience in order to ensure preservation of the original tomb.

The petrological study revealed that the tomb was made of riodacitic vitroclastic tuff stone. [3].

It is known that wax-based painting technique was used by ancient artists [4–8]. However, the composition, the way of preparation and the application of ancient wax-based paints remains subject to debate [9]. A previously reported investigation of the Thracian tomb at Alexandrovo provided preliminary information about the cross-sectional morphology of the murals [3] It was found that the paint layer was deposited on plaster made of pure slaked lime as a binder and river sand as inorganic filler. The composition of the inorganic filler is similar to the tuft – stone widespread in the Eastern Rhodopes. There are grains of quartz, sanidine, plagioclase, biotite, and amphibol [3]. The drawing was applied on the fresh wet plaster typical for the *fresco* technique which is the most frequently used technique in the Thracian wall paintings [2,4]. Due to the wetness of the plaster, an unavoidable diffusion of $Ca(HO)_2$ through the color layer took place. In the course of drying a process of carbonation occurs leading to the formation of transparent protective crust on the surface sealing the color layer [4,5].

The aim of this study is to give sufficient information about the elemental composition of the wall painting and particularly to prove the usage of beeswax in the painting techniques used by the Thracians tribes inhabited the eastern Balkan Peninsula.

Fig. 1. Fragment of the decoration in the burial chamber: hunting scene, ornamental frieze, yellow plinth (uppermost), black plinth (in the middle) and red plinth (underneath). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Experimental

Red plinth sample from ornamental frieze (Fig. 1) was analyzed by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), Attenuated Total Reflectance Fourier transform infrared spectroscopy (ATR FTIR), scanning electron microscopy (SEM), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS).

The sampling method consists of two steps: firstly, the top surface protective layer of $CaCO_3$ was removed with scalpel knife in order to expose the clean surface of the paint.

The actual sample taken for analysis was prepared by scraping off the red color layer. This was carefully executed in order to avoid contamination from the plaster substrate. The obtained powder sample was divided into four parts for DSC, FTIR, HR-TEM and EDS analyses.

Differential scanning calorimetry (DSC) analysis was carried out using a SETSYS-2400 Evolution TG-DSC apparatus (SETARAM, France) under the following conditions: temperature interval: from room temperature to 200 °C, temperature heating rate of 10 °C min^{-1} and static air atmosphere. Individual samples (~8.5 mg) were placed in platinum pans. Data processing was performed by specializing CALISTO software for thermal analyses.

The FTIR and ATR-FTIR spectra were recorded on Bruker Tensor 27 FT spectrometer at a resolution of 2 cm^{-1} and 64 scans. The samples were measured in solid state (KBr pellet) and for ATR technique they were directly applied on a ZnSe crystal.

It is quite challenging task to analyze the composition of the paint binder since the quantity of the investigated samples is very small. The binder of the sample was extracted with chloroform. Commercially available spectral quality chloroform was used as solvent. After having been kept for two days at room temperature, the extracted solution was applied with micropipette on a ZnSe crystal. The chloroform was then evaporated in a draught of hot air. In this way, very thin (almost invisible) film of binder was obtained on the surface of ZnSe crystal.

To provide detailed morphological and compositional information about the studied sample at micro and nano-scale HR-TEM (LaB6) JEOL 2100 is employed. The system is equipped with high-resolution Gatan digital camera providing resolution of 0.2 Å which makes possible detailed observation of the crystal lattice, obtaining diffraction pattern and accurate measurement of the lattice d-spacing with the help of Digital Micrograph software. In scanning transmission electron microscopy (STEM) mode, dark field (HAADF/Z-contrast) detector is used to provide excellent compositional contrast. EDS system Oxford Instruments equipped with a large-area 80 mm^2 SDD (Silicon Drift Detector) X-Max^N 80 T is employed to study the elemental composition in Point&ID, LineScans, layered and elemental mapping modes. To analyze the EDS data, the latest version of AZtecTEM software is utilized.

For HR-TEM analysis, the samples were grinded and after preparing a water suspension, a drop of about 8 μL was put on the TEM grid and dried.

Results and discussion

Analysis of the paint binder by DSC and FTIR

The previous study indicated that the paint binder might contain beeswax [3]. In order to confirm this hypothesis, DSC and FTIR analyses were carried out. Both methods have been used to identify waxes and they appear to be very suitable techniques for such investigation. [7,10–16].

The beeswax is translucent solid substance that melts easily. Standard melting point analysis only partially describes the