Multi-analytical study of solid materials:

application of vibrational spectroscopy combined with X-Ray and electron microscopy methods

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Analytical methods in the study and preservation of cultural heritage

- dates back to the late 18th century but expanded exponentially since the late 20th century.

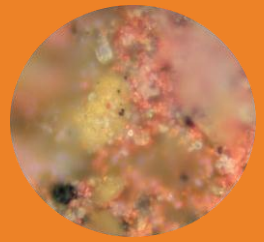
The identification of the materials in the composition of cultural valuables **enriches the information obtained from the study of historical documents** and other written sources.

This information is also of great importance for **choosing the most appropriate methodology** for their conservation and restoration.

The chemical characterization

of the used materials provides information regarding:

- their composition,
- origin
- changes that may have occurred in the fabrication process and as a result on natural aging,
- the causes of the destruction of an object,
- detection of later interventions,
- the technologies used to produce them.



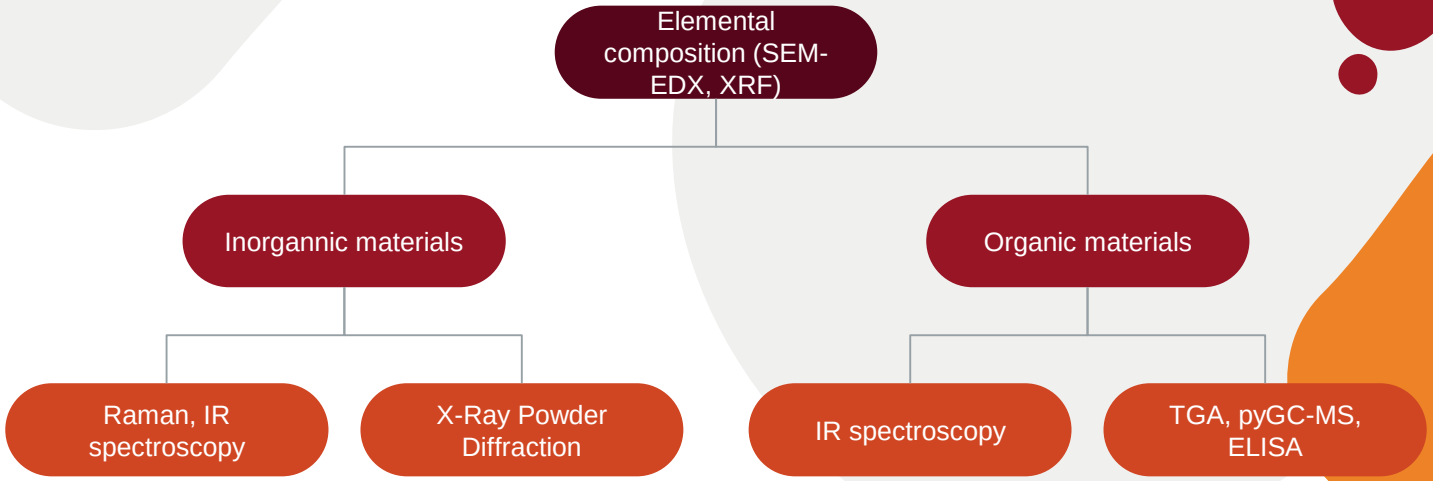
A chalenging task!

The samples and objects to be analyzed have usually a very complex composition, multilayer structure, the amounts are very small, or the sampling is impossible and requires non-invasive techniques…

…. a single method cannot provide sufficient information.

Therefore, the best strategy is to apply a multi-analytical approach.

Multi-analytical study of art and archaeology materials



Case studies

- Wall paintings in the Catholicon of Rila monastery
- Mural decoration in Thracian monuments
- Polychrome icon stand from Kurilo monastery

1

Wall paintings in Rila monastery

The Church "The Nativity of the Virgin“

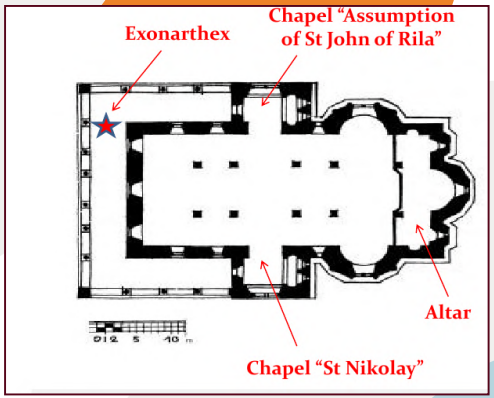
Rila monastery

History

The construction of the monastery main church (catholicon) was completed in 1837. The wall paintings in the main altar, the two side chapels “Assumption of St John of Rila” and “St Nikolay”, the nave and the exonarthex (the outer church gallery) were executed in the succeeding period of 1840-1847.

Architecture and fine arts

The architecture and fine arts are characteristic example of the Bulgarian National Revival (18th–19th centuries). The main monastery church presents wall paintings by the most prominent zographs of the time – Dimitar Zograph, Zahari Zograph, Kostadin Valyov, Ivan Obrazopisov and Stanislav Dospevski.



Murals in the main altar

Aim of the study

- to reconstruct the chromatic palette and clarify the technological aspects associated with the painting technique

- to expand the knowledge and documentation of the painting materials and techniques used in of the late Bulgarian Eastern Orthodox hagiography

Background

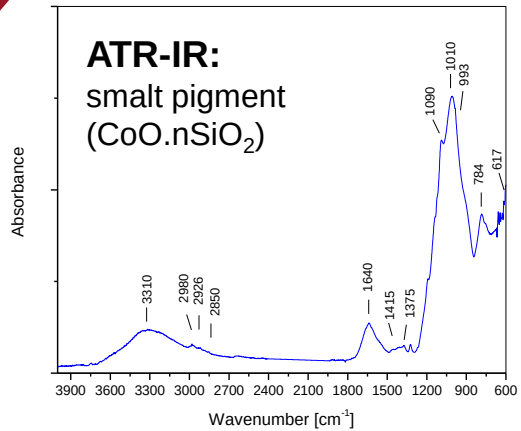
(separated in several zones of bright colors)

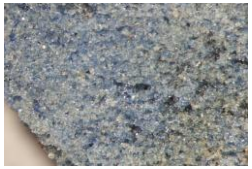
Scenes

(divided by frames painted in an orange-red color)

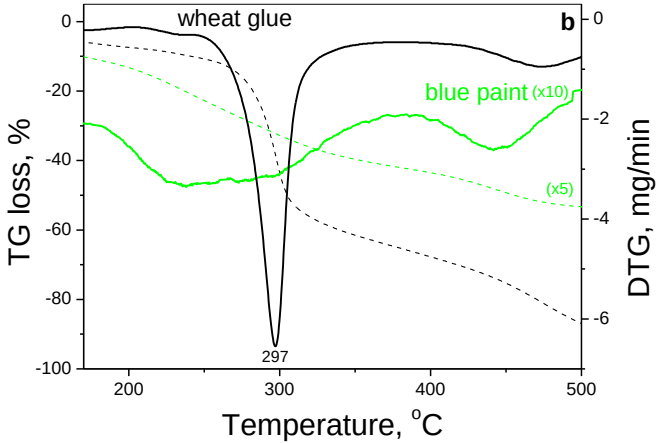
Blue from the background:

SEM-EDX: O, Si, K, S, Fe, As, Co, and Ni

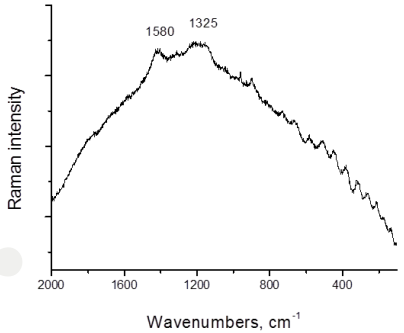




XRD: did not reveal any particular crystalline phase



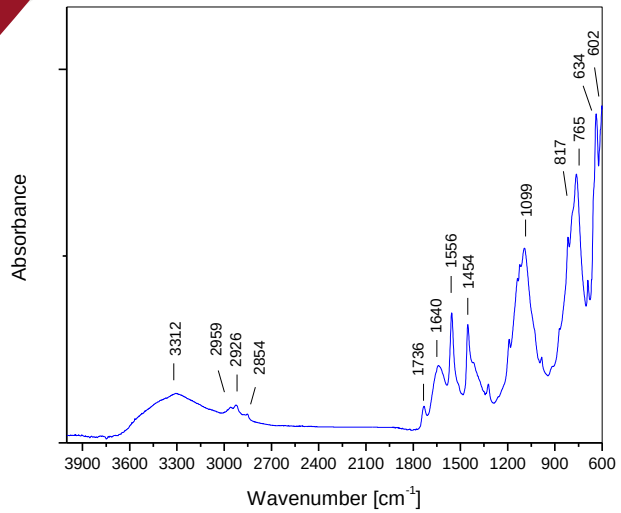
TGA: Carbo-hydrate binder



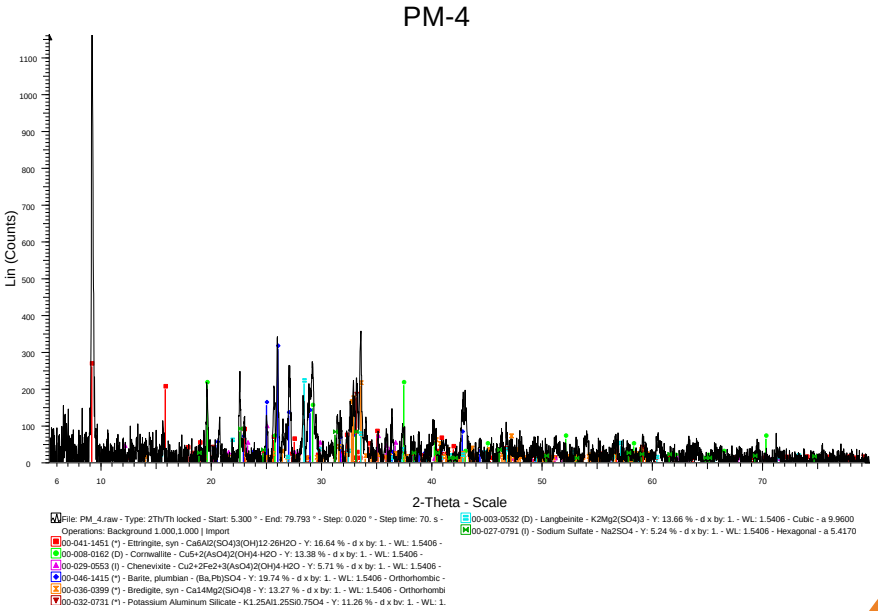
Raman spectroscopy:
Black underlayer of cabrbon black and calcite

Green from the background:

SEM-EDX: O, K, S, Ca, As, Cu, Ba, Cl



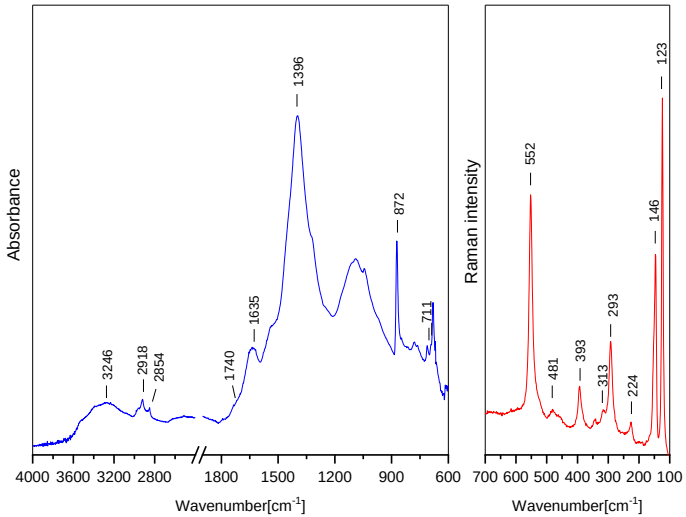
ATR-IR: Emerald green $Cu(CH_3COO)_2.3Cu(AsO_2)_2$ and egg binder



XRD: As-containing minerals cornwallite and chenevixite, sulfate minerals, silicate minerals

Red-orange from frames:

SEM-EDX: Pb, O, S, Fe, Ca, K



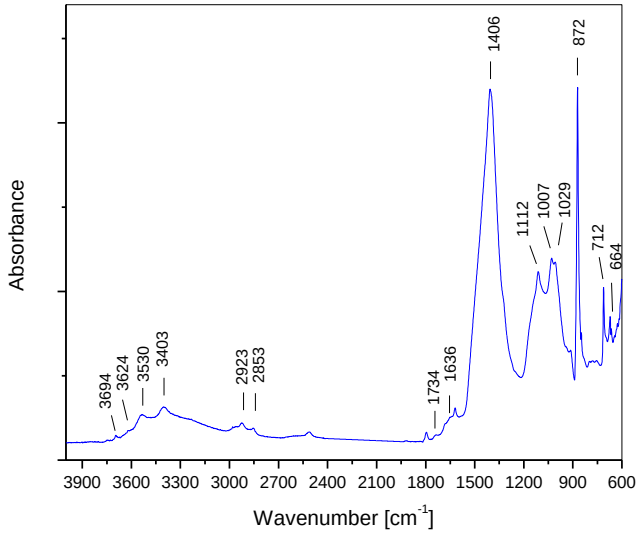
ATR-IR: calcite ($CaCO_3$), binder (egg)
Raman: red lead (Pb_3O_4), hematite (Fe_3O_4)

XRD: calcite, gypsum, quartz, hematite

TGA: binder (egg)

Red from the garments:

SEM-EDX: O, Ca, Si, S, Fe, Al, Mg, and K



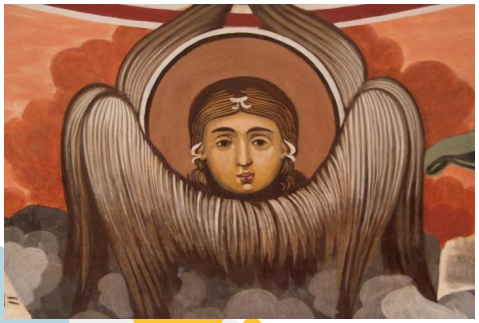
ATR-IR: calcite ($CaCO_3$), gypsum (Ca_2SO_4), binder (egg)

XRD: gypsum, anhidrite, quartz, cristobalite, lepidocrocite FeO(OH)

Summary

1. **Pigments in the background**
   mainly (modern) synthetic pigments - smalt, emerald green, chrome yellow and vermillion mixed with calcite
2. **Pigmen ts in the garments and figures**
   natural pigments - yellow ochre, green earth and sienna, red lead and hematite – in the frames dividing the scenes
3. **Painting technique**
   the murals were executed by the traditional egg tempera technique, with only exception of the smalt paint of the background where carbohydrate glue is present as binder.
4. **Preservation state**
   no severe damage was found; minor alterations of the pigments, the binders are in stable condition

Murals in the nave



The murals in the church nave by Dimitar Zograph and Zahari Zograph in 1844.

Background

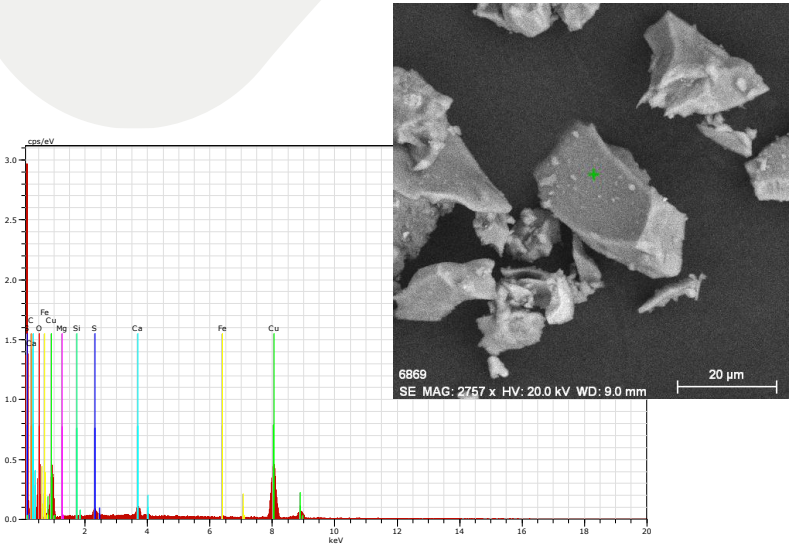
(blue sky and landscape motives)

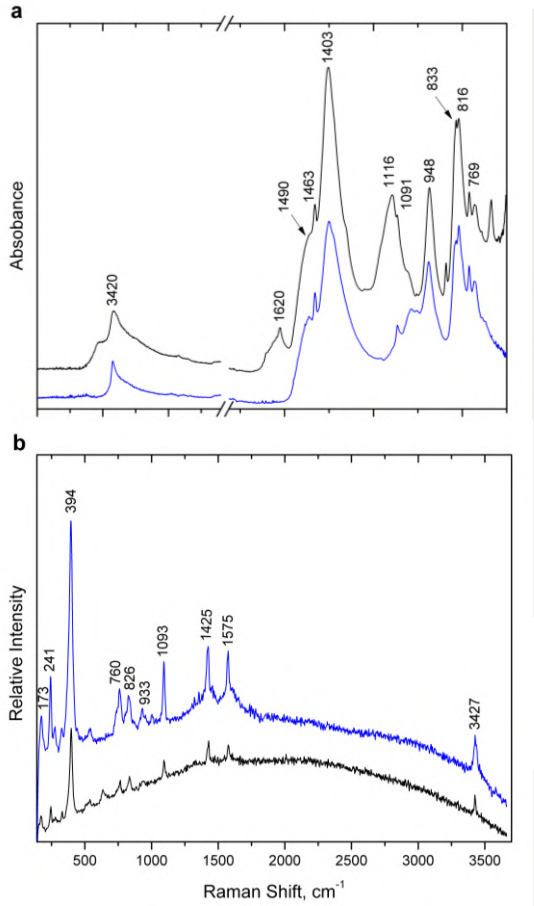
Scenes

(divided by frames painted in an orange-red color)

Blue from the hoods of the saints:

SEM-EDX: Cu as primary metal element and Mg, S, Ca, Si, and Fe as secondary elements



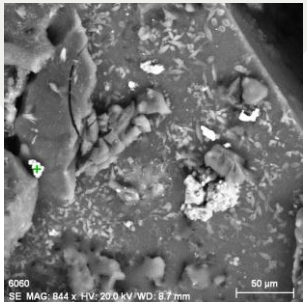


ATR-IR: azurite ($2CuCO_3.Cu(OH)_2$ and gypsum in the sample; reference azurite – in blue

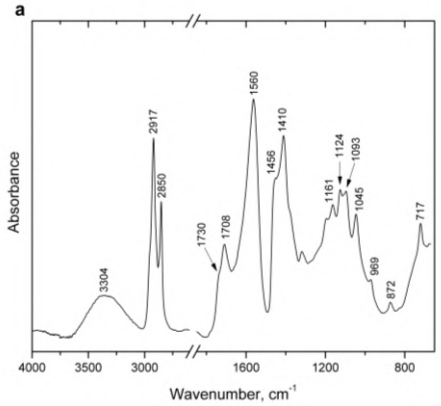
Raman spectroscopy: Blue grain in the sample - azurite ($2CuCO_3.Cu(OH)_2$; reference azurite – in blue

Mordant in the gilded saint haloes:

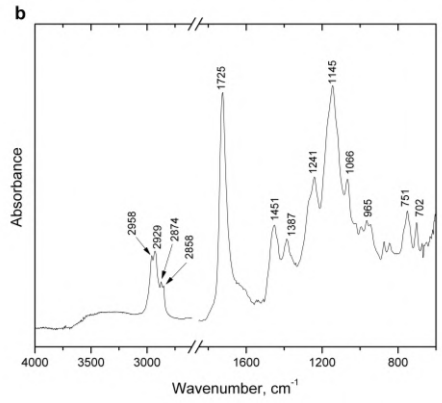
SEM-EDX: S, Na, Ca, K, Mg, Zn, and Pb



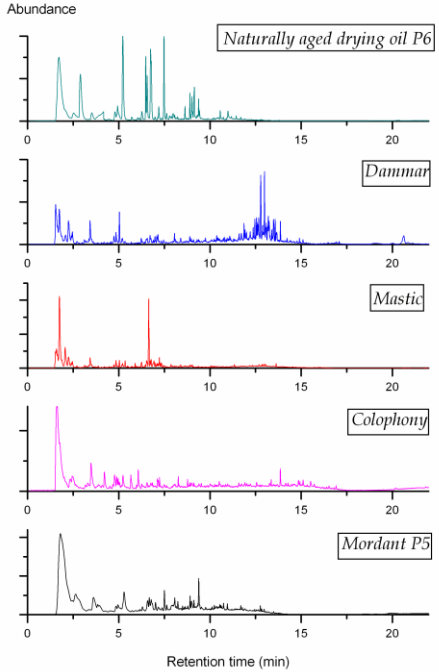
Based on BSE imaging and subsequent SEM-EDX analysis in point several small particles of Pb-contaning material were identified within the sample.



ATR-IR: metal carboxylates and resin in the mordant (a) and naturally aged drying oil (b)



Pyrolysis GC-MS: drying oil with dammar resin



Summary

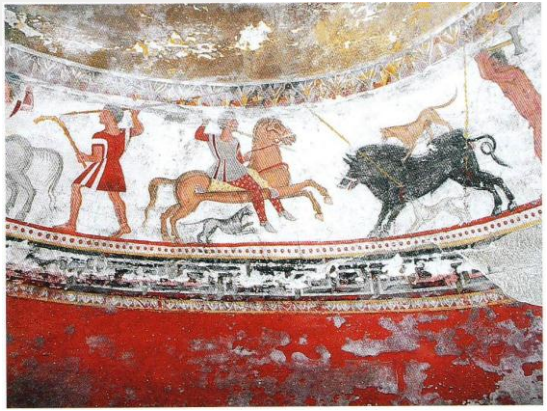
1. **Pigments in the background**
   smalt with carbohydrate binder, painted on white underlayer; green earths.
2. **Pigmen ts in the garments and figures**
   natural earth pigments; red lead; azurite - a specific feature of Zahari Zograph's works in the church
3. **Painting technique**
   egg tempera technique, except for the smalt paint which is mixed with a carbohydrate binder.
4. **Preservation state**
   no severe damage was found; minor alterations of the pigments; calcium oxalate as degradation product of the binder

2

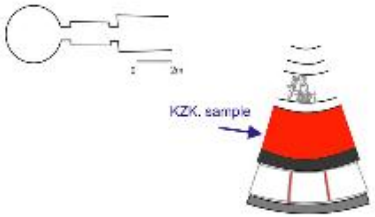
Mural decoration in Thracian monuments

Alexandrovo, Kazanlak, Sevtopolis, Dolno Lukovo, Helvecia

Thracian wall painted monuments (4-3 century BC)

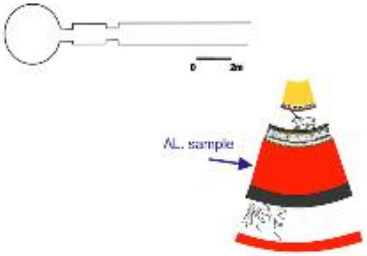


Hunting scene in the burial chamber of Alexandrovo tomb



Kazanlak tomb

(a.)



Alexandrovo tomb

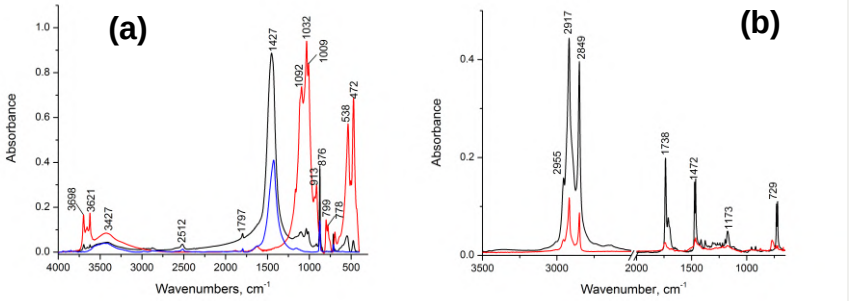
(b.)

Sevtopolis wall paintings

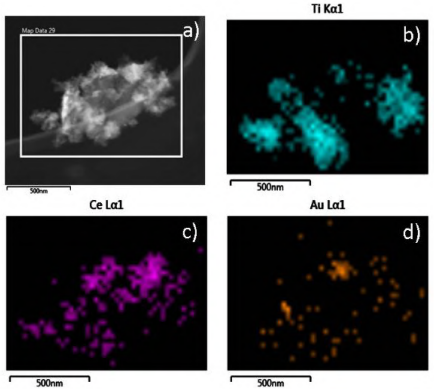
(c.)

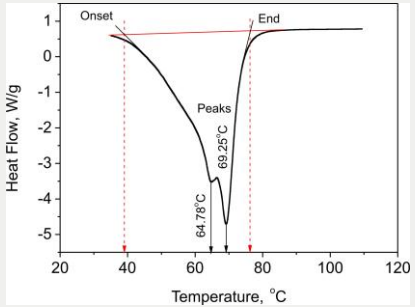
Red paint characterization:

FTIR (a): red plinth sample (black line); standard $CaCO_3$ (blue line) and standard red ochre (red line);
ATR-FTIR (b): extracted sample from the red plinth (red line) and reference beeswax (black line)

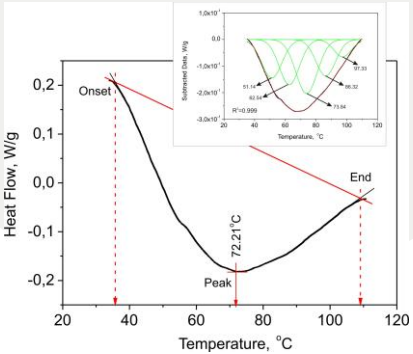


SEM-EDX: main elements in the red plinth - Ca, O, Fe, Si, Mg; less than 1 weight (wt)% - Al, Ti, Ce, Au, K, S, P





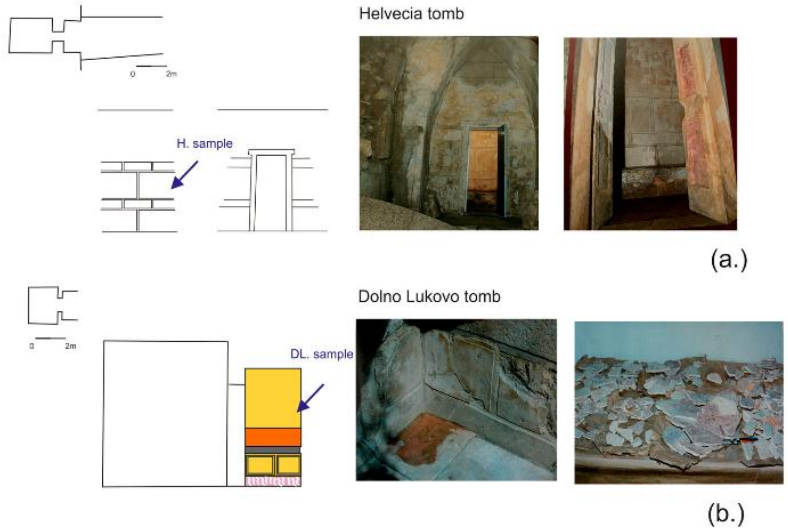
DSC: reference beeswax

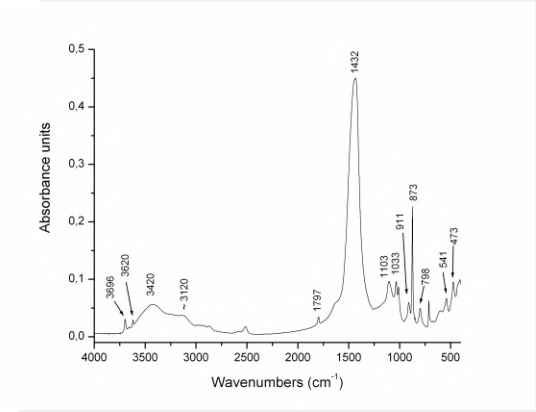


DSC: beeswax in the red paint from Alexandrovo

Yellow paint characterization:

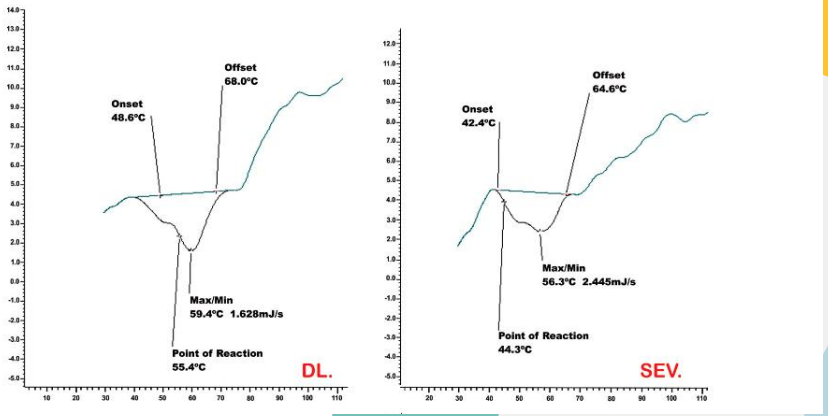
FTIR: yellow ochre in the yellow paint sample from Dolno Lukovo tomb





FTIR: yellow paint sample: calcite ($CaCO_3$) and yellow ochre ($FeO(OH)$)

DSC: beeswax in the yellow paint



Summary

1. **Pigments**
   Natural earth pigments (ochres), calcite and carbon black (amorphous carbon)
2. **Organic components**
   waxing (using either pure wax or a mixture with other organic components) – most probably applied as a final step of producing polished plaster
3. **Painting technique**
   drawing was applied on the fresh wet plaster typical for the fresco technique
4. **Preservation state**
   when excavated, the monuments were in different states of preservation

3

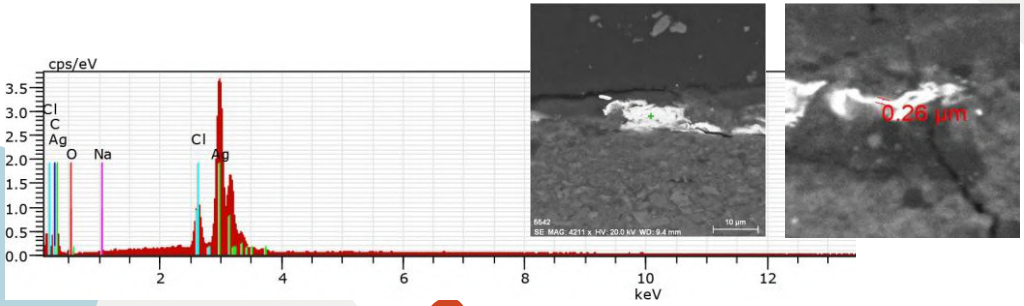
Polychrome icon stand from Kurilo monastery

19th century painted wooden icon stand

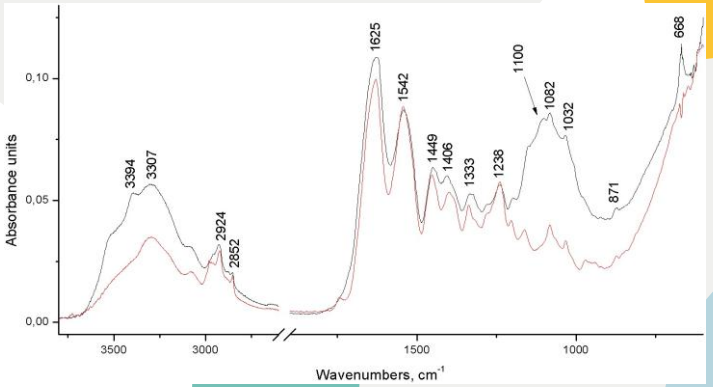
Metal coating of the columns:

The silver was coated with a transparent yellow layer most likely in attempt to mimic the appearance of gold.

SEM-EDX: The elemental analysis showed that the metal used was silver. The thickness of the leaf was measured at 7000X magnification and was found to be around 260 nm.



ATR-IR: the yellow coating over the silver (black) with a reference spectrum of animal glue (red)



Summary

1. **Materials**
   Natural earth the elemental composition and the approximate thickness of the silver leaf; the binder of the yellow coating applied over the silvered areas
2. **Open questions**
   what colorant was used for achieving the yellow tint of the silver leaf coating
3. **Hypothesis**
   It is likely that the icon stand has been painted by the same artist (or workshop) that painted the icons on the iconostasis in the church of the Kurilo monastery.

Conclusions

The multi-analytical study allowed reconstruction of the chromatic palette and painting techniques based on the identification of the used pigments, binders, varnishes and organic dyes. They also provided important information for the preservation state of the materials and the necessary restoration treatment.

Thanks!

Any questions?

You can find me at deni@orgchm.bas.bg

Credits

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ФОНД НАУЧНИ ИЗСЛЕДВАНИЯ
МИНИСТЕРСТВО НА ОБРАЗОВАНИЕТО И НАУКАТА

1869