

The painting technique of Macedonian painters:

Py/GC/MS and GC/MS based techniques for the analysis of organic materials used by Dicho Zograph workshop

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Introduction

Dimitar Krstev (1819-1872), known in Macedonian sacred art as Dicho Zograph, is one of the most prominent and productive 19th century Macedonian iconographer. During the mid of the 19th century, he and his co-workers painted nearly 2000 religious paintings (wall paintings, icons, reliquaries and pennants) in many orthodox churches and monasteries in today's Republic of Macedonia and the neighbouring countries. Despite the numerous works left, scientific analysis of the materials used by his productive 19th c. workshop is lacking.

The present work comprises characterization of the 19th century painting materials used by Dicho Zograph in the wall painting from our sacral monuments: "St. George the Victorious"-v.Rajčica, "St. Paul"- v. Tresonče, "St Ilija"- v. Stenče and "St George"- v. Lazaropole.

Analytical Approach

In order to unequivocally determine the organic materials used as binding media, Pyrolysis Gas Chromatography–Mass Spectrometry (Py/GC/MS) and Chromatography–Mass Spectrometry (GC/MS) were carried out on 11 selected samples.

Micro-Raman spectroscopy was used to emphasize the pallets of pigments which were applied in the wall paintings in all of these churches.

Py/GC/MS. A few µg of the samples admixed with 2 µL of hexamethyldisilazane were inserted into a quartz tube and analysed by means of a Pyroprobe CDS Analytical Inc. 5000 Series coupled on line with the injection port of a 6890N GC System Gas Chromatograph coupled with a 5973 Mass Selective Detector (Agilent Technologies) single quadrupole mass spectrometer, equipped with split/splitless injector.

GC/MS. The analyses was carried out with a 6890N GC System Gas Chromatograph (Agilent Technologies) coupled with a 5975 Mass Selective Detector single quadrupole mass spectrometer, equipped with a PTV injector.

Micro-Raman spectroscopy. Measurements were performed with LabRam 300 (Horiba Jobin-Yvon) Raman spectrometer equipped with two lasers: He-Ne laser and doubled Nd:YAG laser. A microscope with x10, x50 and x100 magnification was used. The backscattered light was dispersed by using the 1800 g/mm grating and is detected on a CCD detector (pixel 1024x256).

Results

Py/GC/MS analysis

Py/GC/MS was performed on two samples from different churches showing preliminary information about organic materials used in the paintings.

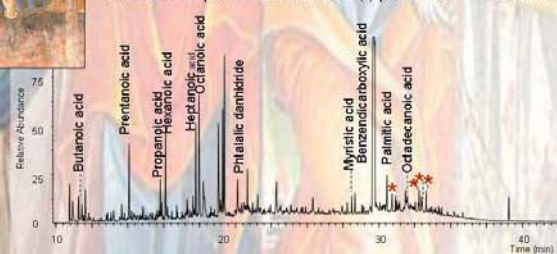
The results obtained from Py/GC/MS suggested that proteinaceous and lipidic materials as well as diterpenoid and synthetic resins are present in the samples while the presence of saccharide materials could be excluded (Table 1).

Table 1. Summary of results from the Py/GC/MS analysis

Sample	Lipid material	Proteinaceous materials	Saccharide materials	Phthalate derivatives	PAH
T1/Blue	No	Egg, Animal glue, Casein	No	No	No
St5/Blue	Yes	Egg, Animal glue	No	Yes	Yes



Figure 1. Pyrogram of the sample St5/Blue from minute 10 to 40. Identified compounds are indicated. (*) peaks identified as PAH.



Pigment analysis by micro-Raman spectroscopy

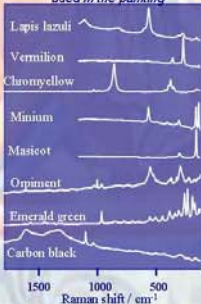
The analysis confirmed that Dicho Zograph and his workshop have used a huge palette of pigments. 18 different pigments were identified:

Traditional pigments used from antiquity (malachite, azurite, green earth, orpiment, calcite, carbon black, lead red, lazurite),

synthetic pigments, dating from 19th – 20th century (Mars yellow, chrome yellow, Mars red, Prussian blue, Emerald green).

Interestingly, **verdigris**, mentioned in Dicho's painter's Manual as the main green pigment used in sacral paintings, has not been identified in any of the churches under study.

Raman spectra of some pigments used in the painting



Markers of a **pinaceous resin** (dehydro-abietic acid together with dihydroabietic acid and 7-oxo dehydroabietic acids) can be identified with a consistent content in five of the samples (Table 2).

Several compounds, having mass spectra showing some common features with those from pine resin markers, are also present, suggesting the use of a **modified pine resin**.

The **A/P ratio (A/P > 1)** of some of the samples points to the presence of a **drying oil**. The absence of oleic acid in all the samples indicates that oil is already well aged.

The presence of a drying oil together with **phthalate derivatives**, mainly 1,2-Benzendicarboxylic acid, seems to indicate the use of an **alchidic resin** in some of the samples.

long chain hydroxycarboxylic fatty acids, particularly, hydroxy-sebacic acid and both isomers of 9,10-dihydroxy octadecanoic acid are detected in some samples. Hydroxysebacic acid has been recently related to the ageing of **alchidic resins**.

GC/MS analysis OF THE LIPID-RESINOUS FRACTION



Figure 2. Total ion chromatogram of the lipid-resinous fraction of sample St4/Red.

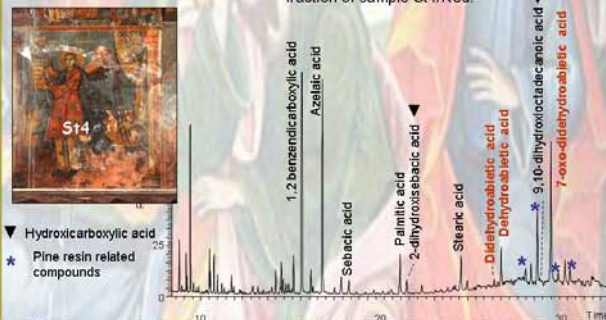


Table 2. Summary of the main compounds and materials identified in the chromatogram of the lipid-resinous fraction of the samples.

Church	Sample	Lipid material	Drying oil	Pine resin markers	Related pine resin compounds	Phthalate derivatives	Long chain hydroxycarboxylic acids
StPP	T8/Red	Yes	No	No	No	No	No
	T13/Black	No	No	No	No	No	No
	R3/Black	Yes	Yes	No	No	Yes	Yes
StI	St4/Red	Yes	Yes	Yes	Yes	Yes	Yes
	St5/Blue	Yes	Yes	Yes	Yes	Yes	Yes
	St6/Green	No	No	Yes	Yes	No	No
StG	SLP2/Red	Yes	Yes	Yes	Yes	No	No
	NLP14/Red	Yes	Yes	No	No	No	Yes
	LP1/Red	Yes	n.l.	Yes	Yes	No	No

GC/MS analysis OF AMINOACIDIC FRACTION

GC/MS analysis allowed to confirm that proteinaceous materials are present in almost all the samples

In the church "St. Peter and Paul" (where restoration processes have never been reported) only proteinaceous materials could be found. Therefore, proteinaceous material seems to be the original binding media used by the painter

The PCA score plot (Fig. 3) shows that some samples are located in the **egg** cluster, while others are located in the **animal glue** one. The position of some samples between the clusters of egg and animal glue, suggests a **mixture of egg and animal glue**.

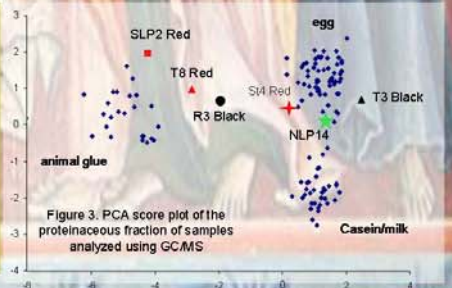


Figure 3. PCA score plot of the proteinaceous fraction of samples analyzed using GC/MS

Conclusions

In conclusion, the painting technique of the churches studied has been established. Binding media analysis showed a rich use of organic material in the painting. Some of the materials identified could be considered original from the painter and some of them were in agreement with the restoration processes undergone in the churches.

Results highlighted that Dicho's Hermeneia painting technique was based mainly on the use of proteins, though seldom linseed oil was also utilised. Interestingly, results also evidenced the restoration processes undergone by the churches and the materials used for restoration purposes such as the use of a modified pine resin as a superficial coating. The presence of a drying oil together with benzendicarboxylic acids and hydroxyl sebacic acid, a profile ascribable to an alchidic resin.

In this study total 16 pigment species were identified by using micro Raman spectroscopy. The Raman spectra confirmed that Dicho Zograph has used a huge artistic palette. Some of the pigments are traditional ones such as vermilion, azurite, green earth, orpiment, calcite, carbon black, lead red and red/yellow ochre, but Raman spectra also revealed that he has used synthetic pigments such as Prussian blue, Ultramarine blue, Emerald green and synthetic iron pigments, Mars red and Mars yellow.

The results reported in this work are not only the first scientific study on the painting technique of the Dicho Zograph's wall paintings, but showed that the palette and painting techniques of Macedonian painters of the 19th century were much more reach than those historically reported.