Non-destructive Analyses of the Colour Palette, Gilding and Varnish of an Icon

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Abstract: *An icon from the region of Shumen was provided for analysis of the colour palette, the gilding and the varnish coating (supposed to be dammar or mastic) at the Centre for Archaeometry with a Laboratory for Conservation and Restoration (CALCR), University of Sofia. For this purpose selected segments on the surface were studied by non-destructive methods with instruments like: portable X-ray spectrometer Titan S1 Bruker, micro-x-ray fluorescent spectrometer Mistral M1 Bruker, infrared spectrometer with a reflection and absorption variant Alfa II Bruker, Raman spectrometer Bravo1 Bruker.*

Key words: X-ray spectrometry, Raman spectrometry, FT-IR, pigments, archaeometry
Ключови думи: рентгенофлуоресцентна спектрометрия, раманова спектрометрия, инфрачервена спектрометрия, пигменти, археометрия

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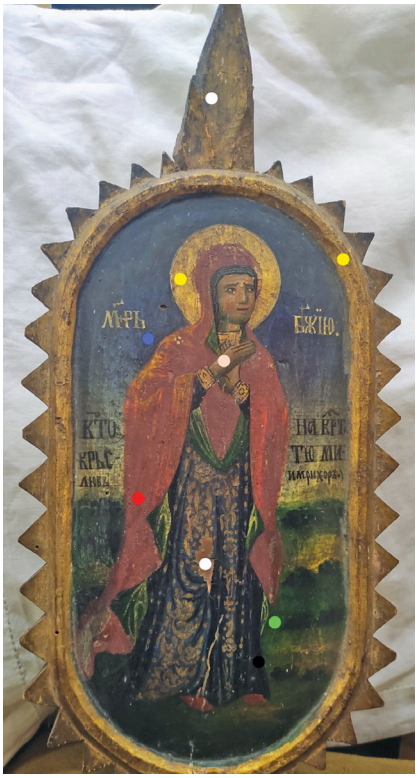
In December 2021 several artifacts were brought to the Center for Archaeometry with Laboratory for Conservation and Restoration (CALCR), Sofia University for analyses. Among them was a wooden icon with the image of the Virgin Mary from the region of Shumen. The researcher from the Regional Museum of History at Shumen, who was preparing a publication, expected to clarify some questions regarding the colour palette, the gilding and the coating, assuming traditional use of natural resins dammar, mastic.

It was not supposed to damage the artefact with invasive approaches so it was impossible to observe directly the stratigraphy of layers or to use sampling required for some techniques like gas chromatography. Only non-destructive methods have been applied, which did not violate the integrity of the object. The Center for Archaeometry with Laboratory for Conservation and Restoration (CALCR), Sofia University is well equipped for researches on artistic works and artefacts with: Portable X-ray fluorescence spectrometer Titan S1 Bruker, Micro-X-ray fluorescence spectrometer Mistral M1 Bruker, Infrared spectrometer with a reflection and absorption variant Alfa II Bruker

and Raman spectrometer Bravo Bruker[1]. Raman and FT-IR spectrometry are combined often when identifying not only pigments but primers, binders, varnishes in works of art.



Virgin Mary from lypira, 19th century, Bulgaria.
Photo: *Anelia Nikolova*

MEASUREMENTS

Selected points on the surface of the icon were measured.

First two sectors were chosen to receive an information for the gilding:

– 1. On the oval surrounding the painted area

– 2. On the halo of the Virgin Mary

For the colour palette:

– 3. blue

– 5. brown-red

– 6. black

– 7. green

– 9. colour of the hand of the figure

– 4. and 8. unpainted wood (with hope to distinguish the materials used for coating)

RESULTS, INTERPRETATION

The results of measurements of the selected sectors (points) on the icon, made with a portable X-ray fluorescent instrument Titan S1 Bruker show that the oval surrounding the painted area of the icon, as well as the halo of the Virgin Mary (respectively points 1 and 2) are gilded with gold from 19 to 21 K. Gilding is also applied to other parts of the figure and on the rays of the wooden panel (**Tab.1**).

After scanning the icon along the central part of its surface with the Mistral M1 micro-X-ray fluorescence spectrometer Bruker an almost uniform distribution of lead Pb and mercury Hg is revealed. One possible explanation involves the application of red pigments under the gilding – namely cinnabar HgS, or a mixture of cinnabar and minium PbS04, or another lead pigment like lead white Pb (CO3) 2.2Pb (OH) 2 and even Parisian yellow PbCrO4. Thus, a visual effect is achieved – a shade of gilding. Otherwise, it can be a sign for undocumented restoration, retouching.

The spread of minium can be seen in Raman spectra too for all the chosen points in the range of 544, 546, 548 cm-1. For the area of the halo – maybe a mixture of minium and cinnabar (463 and 372 cm-1).

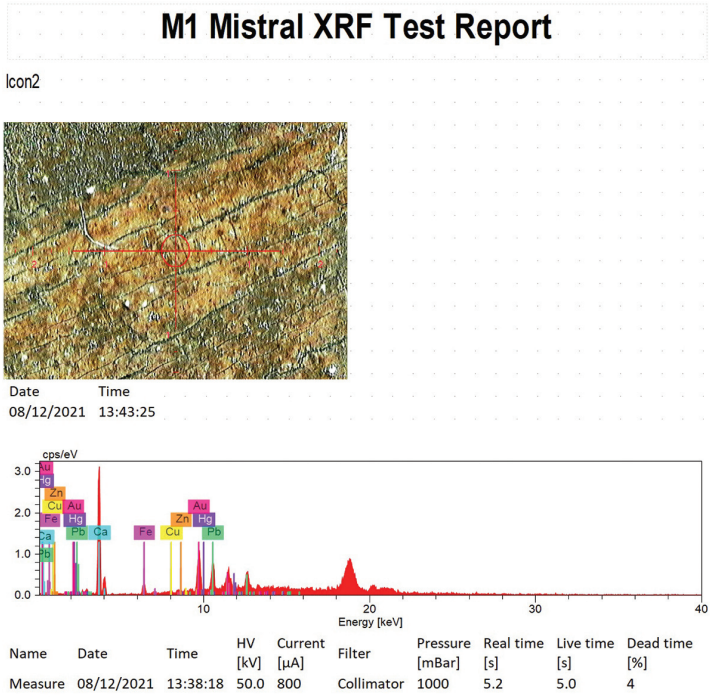
The Raman spectra readings by a Raman library point to another interesting side of the gilding technique. Results from the nimbus match with 69 % probability the mineral Idrialite C22H14 (780 nm) – a hydrocarbon associated often with cinnabar, metacinnabarite and realgar in nature. Like in the case of the black pigment, the presence of carbon is confirmed with the identification of graphite C. The Valentinite (514 nm) is the source of the antimony white pigment Sb203 the receipt of which was published in 1919 but it can be a doubtful identification. The first spectrogram detects a 57 % probability of amber (785 nm) content and jodargyte AgI (514 nm). In the other spectrogram from the gilded area we can find with the highest probability the amber, then jodargyte AgI, etc., so one can accept that a mixtion or an amber based mixture (mastic, amber etc.) was used as a mordant for the gold[2].

Table 1. Portable XRF Bruker S1 Titan – gilding

		Cr	Fe	Cu	Zn	Pd	Au
Gold 1	21.0 K Gold	0.18	2.33	0.66	1.01	1.44	87.69
Gold 2	19.6 K Gold	0.2	3.87		0.98	3.4	81.77

[1] CALCR is equipped with the first three instruments due to the Heritage.bg project.

[2] *Sandu, de S´a, Pereira* 2011.



n/a	No.	Date	Time	M.Time/s	Ca c/%	Fe c/%	Cu c/%	Zn c/%	Pb c/%	Hg c/%	Au c/%
	1	08/12/2021	13:35:19	5	8.20	0.38	0.00	0.00	91.02	0.20	0.20
	2	08/12/2021	13:35:30	5	2.33	0.25	0.00	0.00	94.01	3.35	0.06
	3	08/12/2021	13:35:41	5	18.22	0.00	0.00	0.00	77.70	3.96	0.12
	4	08/12/2021	13:35:51	5	6.50	0.45	0.00	0.00	87.62	5.37	0.05
	5	08/12/2021	13:36:02	5	24.13	0.18	0.00	0.00	70.33	5.35	0.00
	6	08/12/2021	13:36:13	5	6.97	0.46	0.00	0.00	87.17	5.22	0.18
	7	08/12/2021	13:36:24	5	19.44	0.85	0.00	0.00	75.39	4.32	0.00
	8	08/12/2021	13:36:34	5	33.00	0.69	0.00	0.15	62.09	4.07	0.00
	9	08/12/2021	13:36:46	5	27.16	1.36	18.07	0.00	52.37	1.04	0.00

n/a	No.	Date	Time	M.Time/s	Ca c/%	Fe c/%	Cu c/%	Zn c/%	Pb c/%	Hg c/%	Au c/%
	10	08/12/2021	13:36:56	5	2.45	0.35	2.94	0.00	94.26	0.00	0.00
	11	08/12/2021	13:37:08	5	14.95	0.67	0.00	0.00	79.22	4.76	0.40
	12	08/12/2021	13:37:19	5	25.05	1.38	0.50	0.00	71.98	0.62	0.47
	13	08/12/2021	13:37:31	5	5.16	0.45	0.00	0.00	89.64	4.62	0.14
	14	08/12/2021	13:37:43	5	7.60	0.52	0.00	0.00	91.47	0.30	0.11
	15	08/12/2021	13:37:54	5	4.83	0.51	0.00	0.00	94.29	0.24	0.14
	16	08/12/2021	13:38:06	5	10.00	0.40	0.00	0.00	89.05	0.38	0.17
	16	08/12/2021	13:38:18	5	86.63	1.62	0.42	0.27	4.50	0.82	5.75

The results obtained by the portable XRF show a significant amount of calcium in all examined sectors, with the highest values in unpainted areas (points 4 and 8), and for the pigments supposed to be of organic origin – black and blue (7 and 3), followed by 5 – red-brown and almost equal values for 6 – green and 9 – from the hand. Aluminum is present in smaller quantities again in all samples, but the amount in the areas without painting is higher. Potassium values are significant only in sample 4 from which we hoped, together with sample 8, to distinguish the varnish and the binder in comparison with the information from the painted area and the gilding. We suppose that calcium and aluminum, as well as potassium are indicators of the primer with some clay impurities. According to the literature, it is usually an inert material that will serve as a substrate for the next layers in combination with an organic binder. Often these are: gypsum in three forms – unburned (CaSO4.2H2O), anhydrous (CaSO4) or burned (CaSO4. ½H2O /), ground limestone, chalk CaCO3 (calcium carbonate) and CaO (calcium oxide). In a preparation layer one can find a pigment too – white or not. A lead white (Pb (CO3) 2.2Pb (OH) 2) and a zinc white (ZnO) are most commonly used as a substrate under the painting[3].

Primers can be detected also using the FT-IR. The literary sources mention that the water from the gypsum (1008, 1145-1250 cm-1) can be recognized between 3470-3394 cm-1, and it fits our results for almost all measured segments on the icon surface[4]. With the Raman instrument a gypsum is identified for the blue area – 1007 cm-1[5].

We cannot confirm a presence of chalk with typical peaks in the absorption regime in the range of 1420, 874, 713 cm-1 and of calcium carbonate – 1408, 872 cm-1 in the ground layer.

The natural terpenoid resins mastic as well as dammar can be recognized in the obtained

[3] *Mafredas* 2017: 8, 9.
[4] *Medhat, Ali, Abdel-Ghani* 2015, 157.
[5] *Konstantas, Karapanagiotis, Boyatzis* 2021: 7, Table 2.

peak bands from the FT-IR instrument, as well as other organic components, such as oils, used in painting. From the literary sources organic materials and oil binders are expressed in the range of 2942, 2864, 1736, 1685 cm-1. Embedding resins absorption band is 1727, 1285, 745 cm-1, for dammar – 1703/1704, 1455, 1382 cm-1[6]. Dammar varnish mixed with turpentine was measured with infrared instrument – it matches our measurements for 2922/2923 cm-1 and 1030/1031 cm-1. Binders are also animal protein adhesives – gelatin, casein, egg yolk or white etc. The characteristic absorption bands related to Amide I and II of egg binder are respectively at 1645 and 1540 cm-1, egg ester band is at 1742 cm-1[7] – our results lack of clear indications for a presence of an egg protein.

According to the results from the portable XRF Titan S1 Bruker the colour palette is composed mainly of inorganic pigments – Fe, Zn, Al, Ca, Hg, Cu, Cr, Ni, Mn, Sn, Ba, in different proportions in order to achieve the desired color and hue. The nuances can be obtained by mixing the pigments too[8].

1. For the black pigment (point 7 on the Virgin Mary`s clothes) the results collected with the portable XRF are Ca, Pb, Al. Probably it`s charcoal or another carbon black pigment according to the literary data, although in our measurement there is no carbon C. But the reading of the Raman spectra confirms this practice identifying with more than 75-89 % probability the presence of graphite C (780 nm, 513 nm), 35 % of Idrialite C22H14 (780 nm), then again Amber (780 nm) with 30 % match.

Table 2. Portable XRF Titan S1 Bruker – pigments

	Al2O3	K2O	CaO	Ti	Mn	Fe	Ni	Cu	Zn	As	Sn	Au	Hg	Pb
Blue 3	1.2388	0.3430	**5.2230**	0.0344	0.0050	0.1229	0.0215	< LOD	0.0050	0.5571	0.0792	< LOD	0.0293	**7.2559**
Wood 4	**1.8858**	**1.7984**	**10.301**	0.0935	0.0082	0.25	< LOD	0.0071	0.0044	0.0033	0.0341	0.0031	0.0093	0.0195
Red 5	**1.7662**	0.2471	3.5973	0.0421	0.0065	0.1712	0.0653	< LOD	0.0543	**1.2822**	0.1585	**0.0127**	**3.8468**	**17.9064**
Green 6	0.8601	0.3206	2.5316	**2.988**	0.0195	0.1718	**5.131**	**5.131**	< LOD	**2.5695**	< LOD	0.0046	0.1693	2.3172
Black 7	1.0299	0.3881	**6.2339**	0.0843	0.0108	0.1863	< LOD	0.0121	0.0028	0.2299	< LOD	0.0061	0.0716	2.5502
Wood 8	**2.1638**	0.5401	**6.4866**	0.0486	0.0101	0.1368	< LOD	0.0029	0.0044	0.0031	< LOD	< LOD	< LOD	0.0385
Hand 9	**1.684**	0.1705	2.5375	0.0522	0.0081	0.1486	0.2313	0.1463	0.0795	**4.3441**	0.1927	< LOD	0.9808	**68.9147**

*For 5 and 9 the portable XRF detected Cr – 0.0142 и 0.0157 %, and for 9 only Co – 0.0051 %.

2. The Amber is expressed as well in the Raman band of the blue pigment (point 3, upper part of the icon). The most common elements, detected by the portable XRF, are Pb, Ca, Al. Iron and copper are not in quantities supposing a Prussian blue or a copper mineral such as azurite, Egyptian blue. Traces of cobalt are found only in the colour of the hand (point 9). Although sodium is not reflected in the result, it can be assumed that a pigment based on lazurite or Persian blue, ultramarine [(Na, Ca) 8 (AlSiO4) 6 (SO4.S, Cl) 2 was used. Lapis lazuli is a very expensive, rare mineral found in 3 natural forms – hauyne (Na, Ca) Al6Si6O24 (SO4) 1-2, sodaliteNa8 (Al6Si6O24) Cl2 and noselite Na8Al6Si6O24 (S04)], with impurities such as calcite (CaCO3)[9]. A synthetic ultramarine also became widely available for artists since it`s invention in 19th c. Another possibility is indigo C16H10N2O2, woad and this one seems to be confirmed by the Raman spectrometry with 1616 s and 1463 m cm-1 peaks. The presence of lead can be explained by an impurity or by the application of lead white 2PbCO3 · Pb (OH) 2 under the painted layer also confirmed by the Raman measurement with a characteristic peak – 1052 cm-1.

3. Portable XRF finds in the Red pigment (point 5) elements like Pb, Hg, Ca, Al, As, Au.

[6] *Prati, Volpi, Fontana, Galletti, Giorgini, Mazzeo, Mazzocchetti, Samori, Scuitto, Tagliavini* 2018: 8, fig. 4.
[7] *Prati, Volpi, Fontana, Galletti, Giorgini, Mazzeo, Mazzocchetti, Samori, Scuitto, Tagliavini* 2018: 9.
[8] *Mekaj, Civici* 2019: 222-229.
[9] *Tauson, Goettlinger, Sapoznikov, Mangold, Lustenberg* 2012: 133.

The presence of more lead and less mercury is probably achieved with cinnabar HgS and a lead pigment like minium PbS04, perhaps mixed, because the cinnabar is the most expensive red pigment. Another interpretation is that the lead comes from lead white pigment or yellow lead chromate. Chromium is found only in this area and point 9 – the hand of the Virgin Mary. The presence of arsenic also may suggest realgar As4S4, although this mineral is so unstable that cinnabar has been more preferred since the Middle Ages[10]. The Raman library finds the 78 % match with Metacinnabar (785 nm), 74 % Cinnabar, Cobaltite (780 nm).

4. The XRF for the Green (point 6) demonstrates equal values of Cu, Ni, followed by Ti, As, Ca, Pb. The pigment is based on copper and we would consider a more common green or blue pigment such as malachite Cu2CO3 (OH) 2, azurite Cu 3 (CO 3) 2 (OH) 2 if the results were not so complex. Due to the arsenic As or titanium Ti, the suggestions can be extended to the copper arsenite CuHAsO3, olivine, Cu2 (As04) OH? as well as the nickel-antimony titanium yellow rutile or titanium yellow NiO · Sb 2 O 3 · 20 TiO 2. The Raman results are similar to those, obtained for the black pigment.

5. The colour of the hand (point 9) contains nearly 70 % Pb. The highest amount of As was also measured by a portable XRF. The amount of Ca is similar to the green, of Al too. Chromium, available only in samples 5 and 9, in addition to lead white, may indicate the presence of yellow lead chromate PbCrO4, and arsenic – the common yellow pigment orpiment As2S3.

The questions of the researcher from the Regional Historical Museum of Shumen were motivated partly by dating issues. She supposes an earlier date of the icon, but it cannot be confirmed if the coating is made from dammar resin or a yellow lead chromate and a Prussian blue are used in the colour palette[11]. So the icon should be produced not earlier than 19th c. and moreover in its second half. And if in this case the stylistic observations and the epigraphic data seem to be enough for orientation in the time frame, there are difficult cases for which the analyses could be decisive or very helpful.

Thus, the instrumental techniques combined with microscopic study can be used not only for analysing the pigments, binders, primers and coating, but also for dating purposes, for authentification or to distinguish the conservation and restoration interventions.

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Prussian blue, expressed by two basic chemical formulas, KFe [Fe (CN) 6] and Fe4 [Fe [CN6] 3, was invented in 1704, has been produced and used since 1724. Yellow pigments containing lead chromate (VI) PbCrO4 or lead chromate sulphate PbCrO4.xPbSO4 in nature are associated with the rare mineral crocoite PbCrO4, identified in 1766, synthesized in 1804 and used mainly from the second half of the 19th century. Recipes for green as an admixture of yellow lead chromate or Parisian yellow with Prussian blue, sometimes mixed with BaSO4 barite and CaSO4.2H2O gypsum, appeared in 1869.

Attempts to reduce lead paints began in the 19th century, and lead white was largely replaced by the less toxic titanium or zinc white pigment.

Dammar resin has been extensively used for the production of painting varnish since the 19th c. Mastic resin is in use since ancient times.

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Недеструктивни анализи на цветовата палитра, позлатата и лаковото покритие на икона

Анелия Николова, Бойка Златева, Деян Лесигярски

В ЦАЛКР беше изследвана икона с портативен рентгенофлуоресцентен спектрометър, микро-рентгенофлуоресцентен спектрометър, инфрачервен спектрометър, раманов спектрометър на Bruker.

Беше установено, че златото в позлатата е с чистота от 19 до 21 К. Вероятно е подложен микстион /кехлибар, мастикс и др./, както и цинобър, миниум или оловен жълт хромат.

Предполагаме, че грундът е гипс или креда в комбинация с пигмент – оловна бяла, възможно и цинкова, а лаковото покритие – растително масло с дамара.

Черният пигмент вероятно е въглен, синият – индиго, червеният – цинобър и миниум с оловна бяла или жълт оловен хромат, реалгар. Зеленият пигмент се основава на медта, а заради арсена и титана подходящи възможности са медният арсенит или оливин, както и титанова жълта. В телесния цвят са измерени най-много олово и арсен, има и хром, което предполага оловна бяла, но и жълт оловен хромат, и орпимент.