Bulgarian Chemical Communications, Volume 56, Special Issue C (pp.142-147) 2024 DOI: 10.34049/bcc.56.C.SI-19

Multidisciplinary analysis of two pictures by D. Dobrovich – a preliminary report

A. A. Nikolova[1, 2], I. B. Nikolov[3], D. V. Lesigyarski[1, 2], B. K. Zlateva[2, 4*]

[1]*National Institute of Geophysics, Geodesy and Geography, Bulgarian Academy of Sciences, Acad. G. Bonchev blvd., bl. 3, Sofia-1113, Bulgaria*

[2]*Center of Archaeometry with Laboratory of Conservation and Restoration, Faculty of History, Sofia University "St. Kl. Ohridski", 35, Galichica Str., Sofia-1164, Bulgaria*

[3] *Institute of Ethnology and Folklore Studies with Ethnographic Museum, Bulgarian Academy of Sciences, 6A Moskovska Str., Sofia-1000, Bulgaria*

[4]*Faculty of Pharmacy and Chemistry, Sofia University "St. Kl. Ohridski", 1, J. Bourchier Blvd., Sofia-1164,* Bulgaria

Received: September 17, 2024: Revised: September 27, 2024

In this work, we are presenting a preliminary study of the pigments used in two paintings by Dimitar Dobrovich: "Children playing with soap bubbles," oil on canvas, and "Roma. Girl with a Jar", oil on canvas. They were analyzed non-destructively by means of X-ray fluorescence (p-XRF) and Raman spectrometry. Chemical analysis of the used pigments and the obtained analytical results show a very rich palette, including cinnabar, ochre, lead white, lead yellow, minium, realgar/orpiment, gold, etc.

The interest in the technical-technological features of these paintings aims to determine the specific issues for conservation and restoration purposes. This particular task is part of a larger study of more than 70 paintings from the private collection of Mr. Miroslav Dachev, subject of multidisciplinary analyses for autentification.

Keywords: Dimitar Dobrovich, p-XRF, Raman spectroscopy, pigments

INTRODUCTION

Dimitar Dobrovich was born in 1816 in Sliven, Ottoman Empire (nowadays Bulgaria). He was the first painter of Bulgarian origin to have an academic education. The reconstruction of his biography is a matter of discussions because a lot of information for his Greek and Italian periods is missing or is not systemized yet. In his educational background we can notice the school in Sliven with Athos monks teaching in Greek, several schools in Istanbul, among them one in Kurucheshme in which at the time he met Sava Dobroplodni, Gavril Krastevich, Georgi Rakovski, etc. In 1834–1837 he studied at the Phanar Greek Orthodox College. In 1837 or later (1838) he moved to Athens and here were his first serious steps in the fine arts with Theophil Hansen, an architect; then at the Polytechnion or the School of Arts (1844-1848) his teachers were Filippos and Georgios Margaritis, the French Pierre Bonirote and the Italian Raffaello Ceccoli. Dimitar Dobrovich won awards at the annual expositions and competitions of the School and some of his paintings were part of the first collection of the Art gallery of Athens. So he was considered to be a Greek painter. In 1848, Dobrovich moved to Rome to continue at the Accademia di San Luca thanks to a grant given to him by king Otto I or, moreover, by Alexandros Ionidis according to Lysandros Kaftantzoglou, a famous neoclassical architect and director of the Polytechnion at the time when the fine arts were introduced in the education. At the Eternal city he took part in the change of the regime defending the new Roman republic (1848). Afterwards he received a citizenship in Rome as a Greek national. He returned to Bulgaria in 1893 and organized an exhibition at the National assembly with his original works and copies of famous Italian paintings. He died suddenly in 1905 in his hometown.

Dimitar Dobrovich spent the majority of his life abroad, and his works were influenced by Italian Romanticism, but he also painted icons in Orthodox tradition and religious subjects. He achieved great heights in the realm of portraiture [1]. He made also many replicas of Italian Renaissance masterpieces. Nowadays, the majority of his works are not accessible for Bulgarian art historians except those brought by him in the country and kept at the National Art Gallery, Sliven Art Gallery, which was named after him, and in private collections (not only in Bulgaria). Many of his paintings were sold at tenders and auctions under somebody else's name [2, 3]. The so described situation makes every study of his works a valuable contribution to the knowledge of his life and art as in our case.

* To whom all correspondence should be sent:
E-mail: *ahbz@chem.uni-sofia.bg*

Two paintings of Dimitar Dobrovich were submitted for examination, technological attribution, and conservation to the laboratory of the Institute for Ethnology and Folklore Studies with the Ethnographic Museum at the Bulgarian Academy of Sciences in 2023, along with more than 70 other paintings from the private collection of Miroslav Dachev. The contract between him and the scientific institution concerns the examination and authorization of the collection. Our previous investigation by XRF, Raman spectroscopy, and microscopic analysis showed that some of the works have been manipulated (our unpublished data).

The recognition process often involves expertise from art historians able to do detailed research and comparisons with famous works from this author and period. This can also include analysis of brushes (strokes and texture), coatings, composition of works, and materials used. If the work is signed or tagged, this can provide key information about authorship. Through the examinations, signatures are verified. Forgers must have a high level of craftsmanship in order to be unrecognizable from the original. The lack of documentation, disputes about the real author of the work or its authenticity, or insufficient documentation to support its provenance, author, or value, a damaged or inadequately restored piece of art, poor storage, or insufficient expertise can cause difficulties for attestation. Chemical and technical analyses of the paintings are essential to determine the composition of the materials used in the works of art and to detect possible restorations, repairs, overpainting, or forgeries. Nondestructive methods such as XRF and Raman spectrometry are widely used for analyses of the objects of cultural heritage, such as manuscripts [4, 5], ceramics [6, 7], paintings [8, 9], and other materials. Techniques such as FT-IR, XRD [11], and LA-ICP-MS are also applied [12].

The current research and conservation activities aim to ensure the reinforcement of the polychromies and the primer and to perform a reasonable reconstruction of several details as well. The necessity for doublage and restorations is due to the vulnerability of these works of art and especially the state of emergency of the original primer, which poses problems.

MATERIALS AND METHODS

Materials

In this study we are presenting the preliminary results of the pigments used for the analyzed areas in two works by Dimitar Dobrovich: "Children playing with soap bubbles," 46/36 cm, executed in oil technique on canvas, shown in Fig. 1, and "Roma. Girl with a jar", oil on canvas, presented in Fig. 2.

Methods

The portable XRF (p-XRF) instrument used for this study was a Bruker Titan S1 spectrometer equipped with a Fast Silicon Drift Detector (SDD) cooled by Peltier elements and a resolution of the order of 160 eV FWHM at 6 KeV. The excitation source of this instrument was a Rh-target X-ray tube, 4W, 40 kV, with a spot size of 3 mm^2 and a five-position automatic filter change.

To collect the Raman spectra of the analyzed paints, a handheld instrument called the Bruker Bravo was used. A dual laser excitation was applied at wavelengths of 785 nm and 814 nm during each measurement, resulting in spectra ranging from 300 to 3200 cm^{-1}. Fluorescence caused by the laser excitation of the material is often an obstacle in processing the raw Raman spectra trying to identify the substance analyzed. To mitigate the fluorescence when using the Bravo Bruker instrument, a patented sequentially shifted excitation method (SSETM) is applied, which results in spectra with higher resolution and sensitivity.

In order to obtain more precise information about the pigments used by the painter, areas with different coloring were selected for the analysis. These areas were analyzed by the two techniques described above. The selected areas are described in Table 1 and are pointed out in Figs. 1 and 2.

RESULTS AND DISCUSSION

In Table 1 the analytical data for the elemental compositions of the analyzed areas on both works of D. Dobrovich (Figs. 1, 2) based on p-XRF (in weight %) is presented. Four measurements were performed on each spot, and then a standard deviation was calculated. The selected areas (Figs. 1, 2) were measured with a hand-held Raman spectrometer as well and all of the results are combined in Table 2.

Fig. 1. Children playing with soap bubbles (analyzed areas): 1a – Green curtain; 1b – Shoulder (natural body color); 1c – Red cover tissue; 1d – Another shoulder (white cloth); 1e – Dark hair; 1f – Reddish-brown cover; 1g – Blue-grayish background; 1h – Canvas (new).

Fig. 2. Roma. Girl with a jar (analyzed areas): 2a – Blue sky; 2b – Forehead (natural body color); 2c – Yellow-orange color of the sky; 2d – A hand on a jar; 2e – White cloth; 2f – Red sleeve; 2g – Vegetation; 2h – Blue dress, 2i – Lips; 2j – Brown hair; 2k – Brown-orange ribbon; 2l – Brown-orange color of the dress; 2m – Canvas; 2n – A possible overpainting on the shoulder.

Interpretation of the analytical results

Taking into account both elemental composition and Raman spectra, the following preliminary assumptions about the pigments used in the investigated paintings of Dimitar Dobrovich can be made:

1a. The green curtain was probably painted with a mixture of Lead yellow chromate $PbCrO_4$, (a mineral crocoite in nature) (Raman - 361 cm^{-1} s, 941 cm^{-1} m) [12, 13] and Prussian blue [15].

1b. Lead yellow chromate $PbCrO_4$, or another chrome based pigment, Lead white: Hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$, Cerussite $PbCO_3$ for the natural body color of the shoulder.

1c. Red cover: Realgar/Orpiment As_2S_3, (Raman – 353 cm^{-1}vs, 356 cm^{-1}vs(sh)) [12], Minium Pb_3O_4, Lead yellow chromate $PbCrO_4$, Ochre (Hematite Fe_2O_3, Goethite α-FeOOH) (Fig. 3a)

1d. Another shoulder, white cloth – almost 100% Lead white Hydrocerussite $2PbCO_3{\cdot}Pb(OH)_2$, Cerussite $PbCO_3$ (Raman bands at 1370 and 1052 cm^{-1}) [14].

1e. Dark hair: Realgar/Orpiment As_2S_3, Goethite, α-FeOOH (Goethite bands at 552, 485, 387 cm^{-1}, Hematite, 1330 cm^{-1}) [14].

1f, 1g. A reddish-brown cover and a greyish background: Realgar/Orpiment As_2S_3, possible Lead yellow chromate $PbCrO_4$ in different proportions. Prussian blue is very probable in the sample 1g.

1h. New canvas: Lead white (once mentioned, the formulae will not be repeated further in the text), Zinc white ZnO, Titanium white TiO_2.

2a. Blue sky: Lead white, a blue pigment most probably Prussian blue [12].

2b. Front head – almost 100% Lead white, Lead yellow chromate and Massicot yellow (PbO).

2c. Yellow-orange color of the sky Lead yellow chromate, Massicot yellow, also iron oxide mineral (Goethite or Lepidocrocite) and with a high probability – Shannonite which is an oxidized form of Cerussite.

2d. Hand on the jar: Lead white or Litharge, Ochre (most probably lepidocrocite), Shannonite.

2e. White cloth: almost 100% Lead white, Lead yellow chromate (Fig. 3b).

2f. Red sleeve – maybe the most interesting result, a mixture of Cinnabar, Realgar, Minium Pb_3O_4), Gold, and Lead Yellow chromate. According to the XRF data, the Au content is 6.713%, which means that most probably colloid gold was used along with the other components to achieve the red color (Fig. 3c).

2g. Vegetation: Lead white, Crocoite, Ochre (Hematite).

2h. Blue of the dress: Lead white, Prussian blue, Carbon black also possible (Raman bands at 1350 and 1600 cm^{-1}).

2i. Lips: Lead white, Cerussite, Orpiment, and Ochre mineral (most likely Hematite).

2j. Brown hair: Crocoite, Ochre (Goethite), Massicot and Minium.

2k. Orange-Brown ribbon: Lead white, Minium, and Ochre (Goethite).

2l. Brown-Orange dress: Lead white, Crocoite, Minium, and Ochre (Goethite).

2m. Canvas: Lead white, Ochre (Goethite).

2n. Probable overpainting on the shoulder – body color. Missing XRF measurement, just Raman spectrum – Lead white, Crocoite, Cerussite, and Shannonite Pb_2OCO_3 (Fig. 3d).

As the analytical data show, the lead pigments were widely used by the painter, probably for the primer too. In 2023, it was reported that there was a presence of new lead oxide pigments like Plumbonacrite and Shannonite (see also 1n) in Leonardo da Vinci`s famous paintings: Mona Lisa, a sample from the base layers with Shannonite being detected for the first time in such an art work; and Last Supper, a mural in the Convent of Santa Maria delle Grazie in Milan, where Leonardo used oil on the wall and the Shannonite and Plumbonakrite were found in the samples from the primer. Shannonite is orthorhombic and probably turns to Hydrocerussite in the presence of oil. In nature its use was not mentioned by Leonardo in his records, just the Massicot and Litharge [16]. If this lead mineral is confirmed by FT-IR or other methods for the analyzed spot 2n, it does not prove the overpainting. However, the area under question should be further examined, combining appropriate techniques.

Table 1. Elemental concentrations (weight %) determined by the p-XRF measurements.

N	*Color*	*Si*	*Ti*	*V*	*Cr*	*Fe*
1a	Green	1.61±0.08	1.48±0.09	0.544±0.039	**6.47±0.42**	**4.74±0.45**
1b	Body color	<0.002	<0.001	<0.002	<0.002	<0.001
1c	Red	1.92±0.09	0.19±0.01	<0.002	0.14±0.01	**12.85±1.21**
1d	White	<0.002	<0.001	<0.002	0.19±0.01	0.83±0.08
1e	Dark hair	1.99±0.10	0.17±0.01	0.044±0.03	0.09±0.01	**11.10±1.04**
1f	Reddish-brown	1.31±0.06	0.12±0.01	<0.002	0.17±0.01	**7.03±0.66**
1g	Blue-grayish	<0.002	0.13±0.01	0.040±0.03	0.17±0.01	**2.88±0.27**
1h	-	**8.19±0.41**	**4.47±0.28**	1.393±0.100	0.39±0.02	**6.91±0.65**
2a	Blue	1.67±0.08	**2.18±0.13**	<0.002	0.09±0.01	0.91±0.09
2b	Body color	<0.002	<0.001	<0.002	0.12±0.01	0.85±0.08
2c	Yellow-orange	<0.002	0.46±0.03	<0.002	0.17±0.01	1.02±0.10
2d	Body color	1.79±0.09	**1.59±0.10**	0.305±0.022	0.10±0.01	1.29±0.12
2e	White	<0.002	<0.001	<0.002	0.12±0.01	0.71±0.07
2f	Red	<0.002	<0.001	<0.002	0.09±0.01	0.54±0.05
2g	Dark green	2.42±0.12	0.33±0.02	0.122±0.009	0.07±0.01	**10.19±0.96**
2h	Blue	1.54±0.08	0.32±0.02	0.094±0.007	0.12±0.01	**2.15±0.20**
2i	Red	1.75±0.08	0.17±0.01	0.040±0.003	0.07±0.01	1.31±0.12
2j	Brown	2.85±0.11	0.66±0.04	0.247±0.018	0.07±0.01	**13.13±1.23**
2k	Brown-orange	1.60±0.07	0.41±0.03	0.158±0.011	0.07±0.01	1.41±0.13
2l	Brown-orange	1.98±0.10	0.77±0.05	0.331±0.024	0.06±0.01	**8.02±0.75**
2m	-	<0.002	**2.67±0.17**	1.040±0.075	0.07±0.01	0.69±0.06
N	*Color*	*Ni*	*Zn*	*As*	*Hg*	*Pb*
1a	Green	0.111±0.009	<0.001	<0.001	<0.002	81.43±0.54
1b	Body color	<0.001	<0.001	<0.001	0.01	**96.96±0.65**
1c	Red	0.138±0.011	<0.001	**5.33±0.50**	<0.002	70.66±0.47
1d	White	<0.001	0.076±0.006	<0.001	<0.002	**98.02±0.65**
1e	Dark hair	0.138±0.011	<0.001	**3.00±0.28**	<0.002	78.38±0.52
1f	Reddish-brown	0.081±0.006	<0.001	**17.35±1.61**	<0.002	54.58±0.37
1g	Blue-grayish	0.118±0.009	<0.001	**7.03±0.65**	<0.002	78.93±0.53
1h	-	0.395±0.030	**0.41±0.03**	<0.001	<0.002	59.30±0.40
2a	Blue	<0.001	**0.312±0.03**	<0.001	<0.002	**94.26±0.63**
2b	Body color	<0.001	<0.001	<0.001	<0.002	**98.22±0.66**
2c	Yellow-orange	<0.001	<0.001	<0.001	<0.002	**96.92±0.64**
2d	Body color	<0.001	<0.001	<0.001	<0.002	**93.56±0.62**
2e	White	<0.001	<0.001	<0.001	<0.002	**99.16±0.66**
2f	Red	<0.001	<0.001	**19.77±1.84**	**14.43±1.32**	18.12±0.12
2g	Dark green	0.059±0.005	<0.001	<0.001	0.01	86.04±0.57
2h	Blue	0.222±0.017	0.09±0.01	<0.001	<0.002	**93.43±0.62**
2i	Red	0.054±0.004	<0.001	**6.57±0.61**	0.25±0.02	82.71±0.55
2j	Brown	0.057±0.004	<0.001	<0.001	0.02±0.01	80.57±0.54
2k	Brown-orange	<0.001	<0.001	<0.001	<0.002	**95.84±0.63**
2l	Brown-orange	0.054±0.004	<0.001	<0.001	<0.002	87.32±0.58
2m	-	<0.001	<0.001	<0.001	<0.002	**95.02±0.63**

Table 2. Summary of the Raman bands determined for the analyzed paintings and the possible pigments used according to these data (for elemental concentrations see Table 1).

Sample description	*Measured Raman bands (cm^{-1})*	*Possible pigments detected (formula and some reference characteristic bands in parentheses)*
1a Green curtain	366; 472; 587; 809; 884; 942; 1014; 1071; 1869; 2093; 2150	Crocoite ($PbCrO_4$; 366, 825); Massicot yellow PbO (809) Prussian blue; ($FeIII_4[FeII(CN)_6]_3$; 585; 2090, 2155)
1b Shoulder (natural body color)	368; 472; 590; 880; 947; 1051	Crocoite ($PbCrO_4$; 366, 825); Lead white ($2PbCO_3 \cdot Pb(OH)_2$; 1050)
1c Red cover tissue	351; 594; 878; 968; 1157; 1329; 1444; 1856; 1901; 2026; 2835; 2926; 3072	Realgar (α-As_4S_4; 340); Orpiment (As_2S3_3; 379) Minium (Pb_3O_4; 390, 550); Goethite (α-FeOOH; 299, 387, 480, 549)
1d Another shoulder (white cloth)	332; 396; 613; 925; 1050; 1304; 1370	Cerussite ($PbCO_3$; 1052, 1370); Crocoite ($PbCrO_4$; 366, 825) Lead white ($2PbCO_3 \cdot Pb(OH)_2$; 1050)
1e Dark hair	337; 382; 467; 533; 887; 1007; 1335; 1377	Realgar (α-As_4S_4; 340); Orpiment (As_2S3_3; 379) Goethite (α-FeOOH; 299, 387, 480, 549); Hematite (Fe_2O_3) 411, 496, 610, 1330)

Table 2. Continued

1f Reddish-brown cover	344; 768; 1243; 1565; 1655; 1683; 1775; 1822; 1969; 2039;	Realgar (α-As_4S_4; 340) Lepidocrocite (γ-FeOOH; 301, 349, 378, 528, 653)
1g Blue-grayish background	342; 391; 441; 469; 598; 625; 810; 834; 1046; 1089; 1230; 1257; 1302; 2091; 2155	Crocoite ($PbCrO_4$; 366, 825); Massicot yellow PbO (809) Prussian blue; ($FeIII_4[FeII (CN)_6]_3$; 585; 2090, 2155)
2a Blue sky	543; 601; 684; 1049; 1292; 1448; 1538; 2089; 2153	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Prussian blue ($FeIII_4[FeII (CN)_6]_3$; 585; 2090, 2155)
2b Forehead (natural body color)	343; 398; 621; 844; 866; 1237; 1301; 1445; 1952; 2862	Crocoite ($PbCrO_4$; 366, 825); Massicot yellow PbO (809) Cerussite ($PbCO_3$; 1052, 1370)
2c Yellow-orange color of the sky	312; 339; 379; 400; 448; 476; 521; 752; 804	Crocoite ($PbCrO_4$; 366, 825); Massicot yellow PbO (809) Goethite (α-FeOOH; 299, 387, 480, 549) Lepidocrocite (γ-FeOOH; 301, 349, 378, 528, 653) Shannonite ($Pb_2O(CO_3)$; 332, 358, 404, 464, 656, 676, 697, 1035, 1049)
2d A hand on a jar	341; 448; 685; 774; 983; 1047; 1082; 1445; 1540; 1608	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050) Lepidocrocite (γ-FeOOH; 301, 349, 378, 528, 653) Shannonite ($Pb_2O(CO_3)$; 332, 358, 404, 464, 656, 676, 697, 1035, 1049)
2e White cloth	344; 392; 459; 658; 835; 986; 1050; 1752; 1797; 1951; 1986	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Crocoite ($PbCrO_4$; 366, 825) Cerussite ($PbCO_3$; 1052, 1370)
2f Red sleeve	340; 369; 387; 552; 834; 986; 1115; 1463; 1965	Cinnabar (HgS; 342, 353); Realgar (α-As_4S_4; 340) Minium (Pb_3O_4; 390, 550); Crocoite ($PbCrO_4$; 366, 825)
2g Vegetation	426; 493; 796; 819; 988; 1050; 1188; 1208; 1336; 1410; 2153; 2462	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Crocoite ($PbCrO_4$; 366, 825); Hematite (Fe_2O_3) 411, 496, 610, 1330)
2h Blue dress	357; 547; 684; 739; 776; 843; 1050; 1288; 1337; 1449; 1537; 1605; 1618; 1733; 2152	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Prussian blue ($FeIII_4[FeII (CN)_6]_3$; 585; 2090, 2155); Carbon black (C; 1350, 1600)
2i Lips	397; 426; 459; 493; 796; 872; 988; 1050; 1139; 1188; 1208; 1297; 1315; 1343; 1362; 1384; 1426; 1447; 1585; 1603; 1659; 1735; 1818; 1864	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Cerussite ($PbCO_3$; 1052, 1370) Orpiment (As_2S_3; 380); Hematite (Fe_2O_3) 411, 496, 610, 1330)
2j Brown hair	346; 384; 419; 467; 502; 582; 811; 985; 1004; 1250; 1275; 1349; 1395; 1446; 1487; 1678; 1810; 1833; 1910; 2024	Crocoite ($PbCrO_4$; 366, 825); Goethite (α-FeOOH; 299, 387, 480, 549) Massicot yellow PbO (809); Minium (Pb_3O_4; 390, 550)
2k Brow-orange ribbon	398; 453; 986; 1052; 1917; 1954; 2112	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Minium (Pb_3O_4; 390, 550) Goethite (α-FeOOH; 299, 387, 480, 549)
2l Brown-orange color of the dress	336; 393; 493; 770; 839; 983; 1050; 1365; 1557; 1682; 1708; 2862	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Crocoite ($PbCrO_4$; 366, 825) Minium (Pb_3O_4; 390, 550); Goethite (α-FeOOH; 299, 387, 480, 549)
2n Possible overpainting on the shoulder	346; 458; 563; 659; 846; 912; 987; 1051; 1250; 1292; 1352; 1440; 1566; 1673; 1864; 1926; 1944; 1953; 1971; 1990; 2083; 3072	Lead white ($2PbCO_3{\cdot}Pb(OH)_2$; 1050); Crocoite ($PbCrO_4$; 366, 825) Cerussite ($PbCO_3$; 1052, 1370) Shannonite ($Pb_2O(CO_3)$; 332, 358, 404, 464, 656, 676, 697, 1035, 1049)

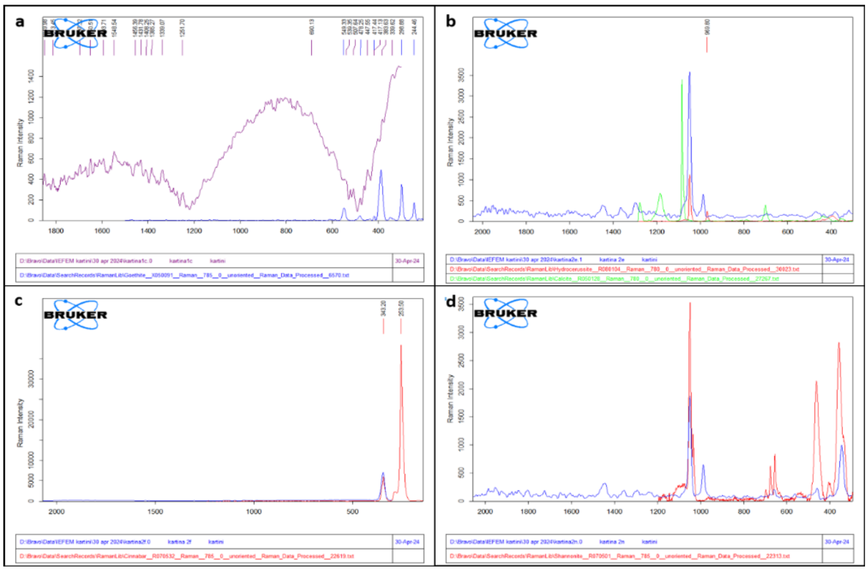

Fig. 3. Raman spectra of: **a.** 1c. Goethite; **b.** 2e. Lead white, hydrocerussite; **c.** 2f. Cinnabar; **d.** 2n. Lead white, hydrocerussite or shannonite? (probable overpainting)

CONCLUSIONS

In this study, a preliminary report is given about the two investigated paintings of Dimitar Dobrovich based on p-XRF and Raman spectrometry results. The future analysis, including FT-IR, LA-ICP-MS, filming by UV-VIS and IR cameras, radiography (only for the work "Children Playing with Soap Bubbles" due to the paintings' sizes), color measurement, and art historian expertise, is in progress. The main conclusions can be summarized as follows:

1. The palette is rich. The pigments are mainly inorganic, and the author has mixed them to achieve different colors and hues.
2. The lead pigments were widely used. We detect the presence of the two crystalline phases of the Lead white: Cerussite, $PbCO_3$, and Hydrocerussite, $Pb_3(CO_3)2(OH)_2$. The probable presence of Shannonite $Pb_2O(CO_3)$ should be confirmed. The spot 2n needs more analyses to identify the pigments used for the body color and to prove or not the possibility of overpainting.
3. One can suppose a Lead white base layer with indications for Zinc white and Tin white. Zink white was often used with Tin white, but it started to be used more often in the last decades of the 19th century.
4. The XRF does not support the use of any copper-based pigments, like Verdigris or others.

Acknowledgement: *The equipment of the Conservation laboratory of Institute of Ethnology and Folklore Studies with Ethnographic Museum, Bulgarian Academy of Sciences, and the Center of Archaeometry with Laboratory of Conservation and Restoration, Faculty of History, Sofia University, is supported by the INFRAMAT and Heritage BG projects. The portable Raman spectrometer Bravo, Bruker was provided to the Center of Archaeometry with Laboratory of Restoration and Conservation thanks to the INFRAMAT project (Contract DO1-172/28.07.22).*

REFERENCES

1. Encyclopedia of Fine Arts in Bulgaria, Volume I, Sofia, BSA.
2. P. Ioannou, In:19th century romanticism. the Life and Art of Dimitar Dobrovich 1816-1905, 236.
3. R. Marinska. The romanticist Dimitar Dobrovich (1816-1905), NBU, 2016.
4. S. Mosca, T. Frizzi, M. Pontone, R. Alberti, L. Bombelli, V. Capogrosso, A. Nevin, G. Valentini, D. Comelli, *Microch. J.*, **124**, 775 (2016).
5. K. Manukyan, B. Guerin, E. Stech, A. Aprahamian, M. Wiescher, D. Gura, Z. Schultzc, *Anal. Methods,* **8**, 7696 (2016).
6. M. Sepúlveda, S. Gutierrez, M. Campos-Vallette, E. Clavijo, P. Walter, J. J. Cárcamo1, *J. Chil. Chem. Soc.,* **58**, 3 (2013).
7. A. Pirovska. PhD Thesis, Sofia Univ. Sofia, 2024.
8. V. Walters, J. de Paula, R. Bard, R. Bard, G. González-Montiel, C. Ochoa, T. Matheson, J. Olson, A. Nguyen, D. Ile, A. Hicks, E. Gushtyuk, M. Foronda, E. Álvarez, M. Ontiveros, *J. Arch. Sci.: Reports,* **43,** 103442, (2022).
9. Lj. Damjanović, M. Gajić-Kvaščev, J. Đurđević, V. Andrić, M. Marić-Stojanović, T. Lazić, S. Nikolić, *Rad. Phys. Chem.,* **115**, 135 (2015).
10. S. Serafima, O. G. Duliu, M.-M. Manea, A.-V. Bojar, C. Costea, D.Birgaoanu, O.-Cl. Barbu, *Rom. Rep. Phys.,* **71**, 201 (2019).
11. B. Wagner, L. Kępa, M. Donten, B. Wrzosek, G. Z. Żukowska, A. Lewandowska, *Microchem. J.,* **146**, 279 (2019).
12. L. Burgio, R. Clark, *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy*, **57**, 7 (2001).
13. I. Bell, R. Clark, P. Gibbs, *Spectrochimica Acta Part A*, **53**, 2159 (1997).
14. M. Bouchard, D.C. Smith., *Spectrochim. Acta Part A: Molecular and Biomolecular Spectroscopy,* **59**, 2247 (2003).
15. L. Verger, O. Dargaud, M. Chassé, N. Trcera, G. Rousse, L. Cormier, *J. of Cult. Herit.*, **30**, 26 (2018)
16. V. Gonzalez, G. Wallez, E. Ravaud, M. Eveno, I. Fazlic, T. Fabris, A. Nevin, T. Calligaro, M. Menu, V. Delieuvin, M. Cotte*, J. Am. Chem. Soc.,* **145**, 23205 (2023).