

# XRF and Raman Spectroscopy of Pigments and Binders in Works of Bulgarian Artists from the Collection of Krasimir Dachev

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**Abstract:** Five paintings with signatures of Anton Mitov, Boris Mitov, Yaroslav Veshin from the Dachev Collection were studied at the Centre for Archaeometry with Laboratory for Conservation and Restoration (CALCR) with X-ray fluorescence spectrometer (XRF), supplemented by Raman spectroscopy. The paintings were pre-examined under a microscope, UV, IR source, spectrophotometer and a colour analyser at the laboratory in the Institute of Ethnology and Folklore Studies with Ethnographic Museum (IEFSEM BAS) according a contract between the institute and the owner for an authentication of the collection.

**Keywords:** Anton Mitov, Boris Mitov, Yaroslav Veshin, authentication

**Ключови думи:** Антон Митов, Борис Митов, Ярослав Вешин, идентификация



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At the annual conference of Heritage.bg some preliminary observations and analyses were shared, concerning five works of old Bulgarian painters. They are part of a collection, belonging to Krasimir Dachev. More than fifty paintings are passing now through an evaluation of their authenticity. Iliya Nikolov, a restorer in the Institute of Ethnology and Folklore Studies with Ethnographic Museum, Bulgarian Academy of Science (IEFSEM BAS) is authorized with the expertise – the contract is concluded between the institute and the owner.

Initially the paintings were studied with a trinocular microscope OZL 464 and different sources of UV and IR light, then with a spectrophotometer Cary 60 UV-Vis, Agilent

and a colour analyser RGB-1002. Additional non-destructive analyses were applied to the selected areas in the Centre for Archaeometry with Laboratory for Conservation and Restoration (CALCR) with a S1 XRF Titan, Bruker and a Raman spectrometer Bravo, Bruker.

The portraits are signed by Anton Mitov (1862 – 1930), Boris Mitov (1891 – 1963), Yaroslav Veshin (1860 – 1915). These painters are educated outside Bulgaria – Anton Mitov in Italy, his son Boris mainly in Bulgaria and Paris. Yaroslav Veshin (Jaroslav František Julius Věšín) is one of those Czechs with

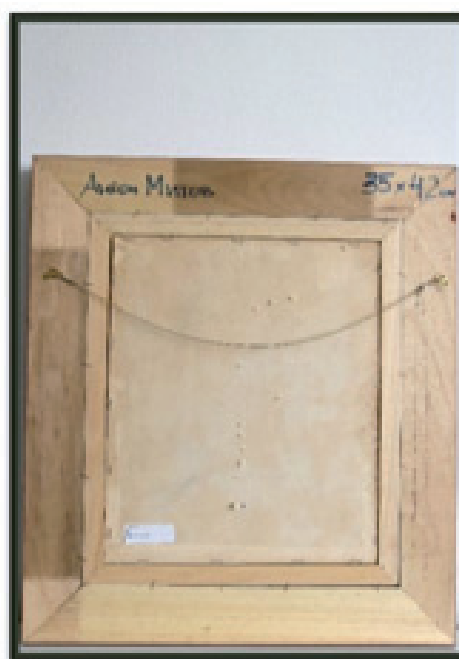
Markvichka (Ivan Mrkvička, born Jan Václav Mrkvička, 1856 – 1938), Dobruski (Václav Dobruskə, 1858 – 1916) etc. that played an important role in the Bulgarian cultural and artistic life after the liberation from Ottoman rule. They have studied in Prague and Munich<sup>1</sup>. Both Mitov, Markvichka, Veshin, being aware that even traditional religious painters should undergo an academic studies along with new modern artists<sup>2</sup>, were founders and teachers or just teachers in the school of art, developed later to National academy of art. A young state was in need for contemporaneous educational institutions.

### X-ray fluorescence spectrometry (XRF), completed with Raman spectroscopy-results and first interpretations:

The first painting is Anton Mitov's 'Shop'<sup>3</sup>, signed, dated in 1898. The technique is oil on paper. This picture was drawn "a la prima", and somewhere after 1976 it was transferred on phazer. A finishing firnis can be observed on the original varnish, so one can suppose undocumented interventions for conservation.



**Figure 1.** Anton Mitov, 'Shop'. Recto  
**Фигура 1.** Антон Митов, „Шоп“ – лице

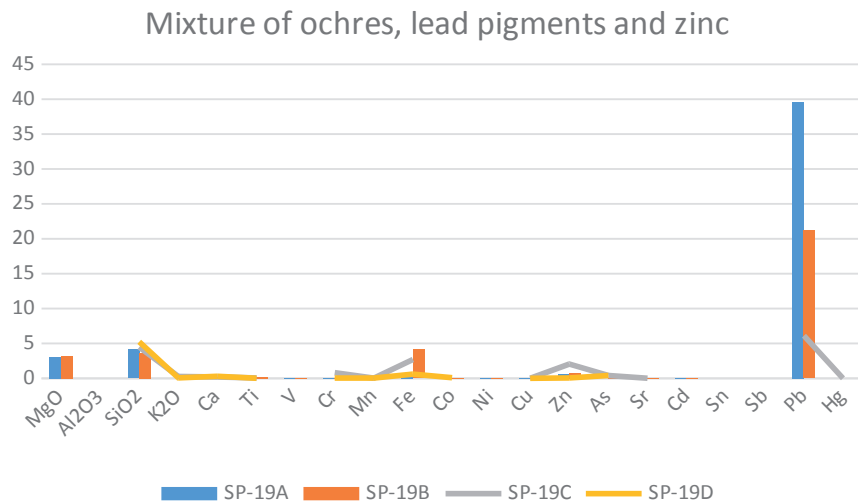


**Figure 2.** Anton Mitov, 'Shop'. Verso  
**Фигура 2.** Антон Митов, „Шоп“ – гръб

<sup>1</sup> Dinova-Ruseva 2004: 2-8.

<sup>2</sup> Ivanova 2003: 178.

<sup>3</sup> All of the photos here were taken by Iliya Nikolov.



**Figure 3.** XRF, Anton Mitov, ‘Shop’  
**Фигура 3.** Рентгено-флуоресцентен анализ – „Шоп“

SP-19A. earth iron oxide pigments (ochre, Sienna) and lead white 2  $\text{PbCO}_3 \cdot \text{Pb(OH)}_2$ , and  $\text{PbCO}_3$  (background)

SP-19B. Pompeian red /red ochre/ or Sienna and minium  $\text{Pb}_3\text{O}_4$  (signature)

SP-19C. Prussian blue  $\text{C}_{18}\text{Fe}_7\text{N}_{18}$  or ultramarine  $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_2\text{S}_3$  /or indigo  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ?/ with zinc yellow /potassium chromate  $\text{K}_2\text{O} \cdot 4 \text{ZnCrO}_4 \cdot 3 \text{H}_2\text{O}$ /, lead white or yellow? (green - shoulder)

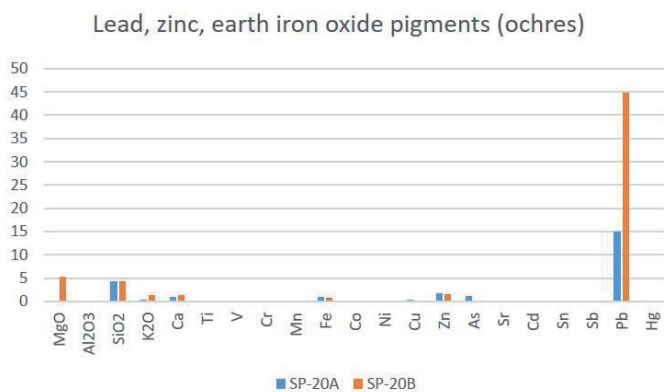
SP-19D. prussian blue  $\text{C}_{18}\text{Fe}_7\text{N}_{18}$  or ultramarine  $\text{Na}_7\text{Al}_6\text{Si}_6\text{O}_2\text{S}_3$  /or indigo  $\text{C}_{16}\text{H}_{10}\text{N}_2\text{O}_2$ ?/ and lead pigment (blue – shoulder)

Three paintings, attributed to Boris Mitov, were analysed:

Boris Mitov, ‘Iliya Iurgev – the owner of the patisserie *Old Sofia*’, signed, dated in 1923. Oil on canvas, 48/58.



**Figure 4.** Boris Mitov, ‘Iliya Iurgev – owner of the patisserie *Old Sofia*’  
**Фигура 4.** Борис Митов, „Илия Юргев – собственик на сладкарница *Стара София*“



**Figure 5.** XRF, ‘Iliya Iurgev – owner of the patisserie *Old Sofia*’  
**Фигура 5.** Рентгено-флуоресцентен анализ – „Илия Юргев – собственик на сладкарница *Стара София*“

SP-20A. earth iron oxide (caput mortum?), lead, zinc pigment /Raman spectroscopy – charcoal?/ (signature – grey and violet)

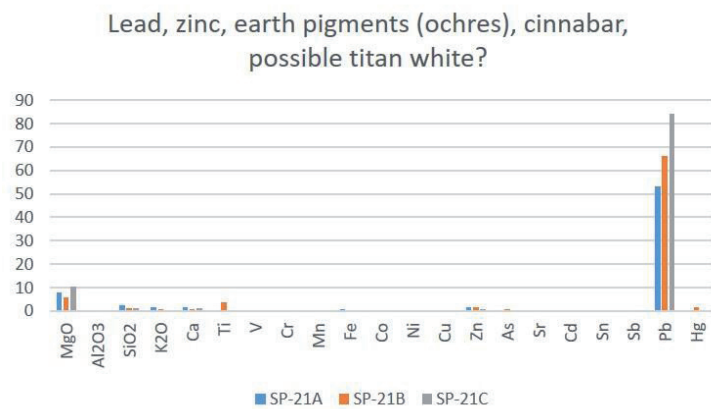
SP-20B. earth iron oxide (caput mortum?), green earth  $\text{K}[(\text{Al}, \text{FeIII}), (\text{FeII}, \text{Mg}) (\text{AlSi}_3, \text{Si}_4) \text{O}_{10} (\text{OH})_2]$ , lead, zinc pigment /Raman spectroscopy – charcoal?/ (mixture of grey and violet with ochre)

There is no significant difference between the palette, used for the signature, and the picture's background.

Boris Mitov, 'Portrait of a man with a fez', signed, dated 1898. Oil on canvas, 50/60.



**Figure 6.** Boris Mitov, 'Portrait of a man with a fez'  
**Фигура 6.** Борис Митов, „Портрет на мъж с фес“



**Figure 7.** XRF, Boris Mitov, 'Portrait of a man with a fez'

**Фигура 7.** Рентгено-флуоресцентен анализ – Борис Митов, „Портрет на мъж с фес“

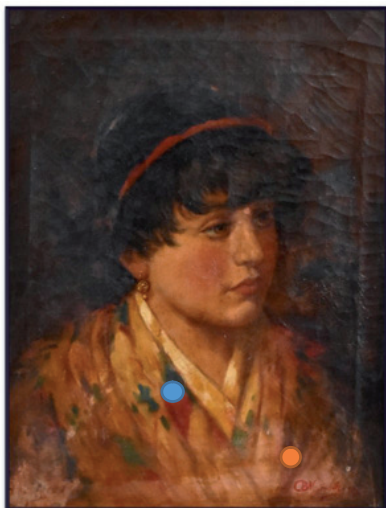
SP-21A. ochres or other earth iron oxide, lead, zinc pigments /Raman – charcoal?/ (signature and background)

SP-21B. ochres or other earth iron oxide pigment, minium  $Pb_3O_4$ , titan white?, zinc white  $ZnO$ , cinnabar  $HgS$  /confirmed with Raman spectroscopy too/ (fez)

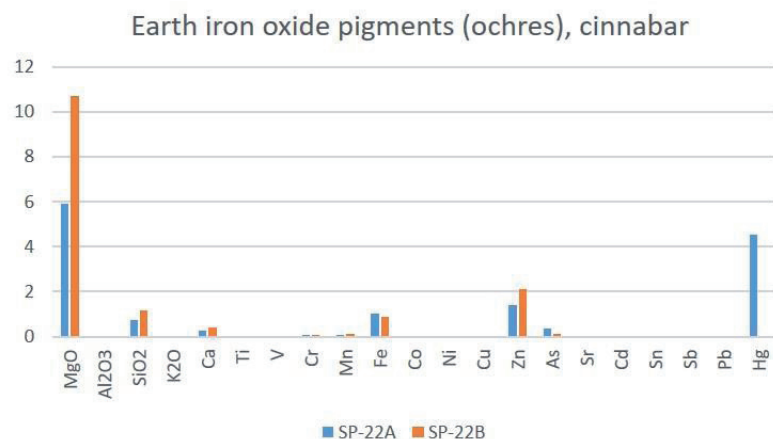
SP-21C. ochres or other earth iron oxide pigment, lead white  $2 PbCO_3 \cdot Pb(OH)_2$  and  $PbCO_3$  (white cloth)

Only the appearance of titan (rutile – a pigment?) poses questions.

1. Boris Mitov, 'Portrait of a woman', signed, dated in 1898. Oil on canvas, 36/45.



**Figure 8.** Boris Mitov, 'Portrait of a woman'  
**Фигура 8.** Борис Митов, „Портрет на жена“



**Figure 9.** XRF, Boris Mitov, 'Portrait of a woman'  
**Фигура 9.** Рентгено-флуоресцентен анализ – Борис Митов, „Портрет на жена“

SP-22A. cinnabar  $HgS$ , ochre /or burnt Sienna?/, zinc white  $ZnO$ ? (red of the scarf)

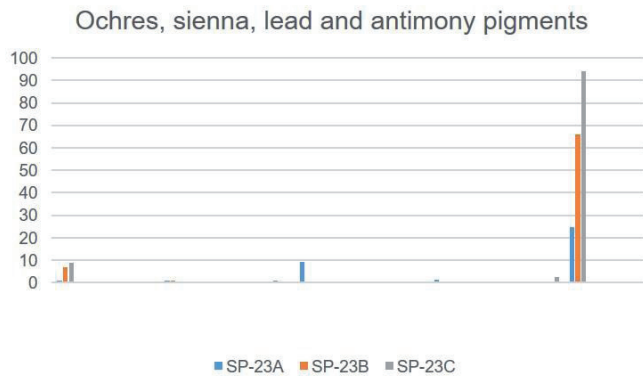
SP-22B. similar, but without cinnabar and with more  $MgO$  /Sienna or the signal may come from the colours of the scarf/? (red of the signature)

Apparently the picture was signed later. A comparison between the XRF results from the red of the scarf and of the signature does not really prove this. After the microscopic study, the interventions with a black paint and a new layer of varnish (firnis) were observed. The translucency of the hue gives impression for the use of alizarin – a red dye with chemical formula  $C_{14}H_8O_4$ , but it cannot be detected with these instruments. Often it's combined with other red colours for an optical effect, and this can be the case here according the chemical results.

**5. Yaroslav Veshin, 'Naked male body'. Oil on canvas.**



**Figure 10.** Yaroslav Veshin, 'Naked male body'  
**Фигура 10.** Ярослав Вешин, „Голо мъжко тяло“



**Figure 11.** XRF, Yaroslav Veshin, 'Naked male body'  
**Фигура 11.** Рентгено-флуоресцентен анализ – Ярослав Вешин, „Голо мъжко тяло“

SP-23A. burnt Sienna or Pompeian red and minium  $Pb_3O_4$  (signature)  
 Sp-23B. ochre, Sienna?, yellow lead antimonate  $Pb_2Sb_2O_7$  (Naples yellow) and lead white 2  $PbCO_3 \cdot Pb(OH)_2$  and  $PbCO_3$  /Raman spectrometer – cinnabar?/ (skin colour – reddish)  
 SP-23C. similar mixture and minium  $Pb_3O_4$  /Raman spectrometer – does not find cinnabar, but lead white and maybe copper?/ (skin colour)

In conclusion a general review of these first observations and results:

	MgO	Al2O3	SiO2	K2O	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Sr	Cd	Sn	Sb	Pb	Hg
SP-19A	3.098	< LOD	4.1415		0.1902	0.1619	0.0105	0.0395	0.0315	0.1942	0.0155	0.0168	0.0212	0.6447	< LOD	0.0148	0.0999			39.6158	
SP-19B	3.151		3.5986	0.0144	0.248	0.1829	0.0156	0.0258	0.0949	4.1165	0.0181	0.0531	0.0908	0.7456	0.0084	0.0159	0.0424			21.1889	
SP-19C			4.467	0.2649	0.1946	0.0548		0.8111	0.027	2.7016			0.0068	2.0436	0.4047	0.013				6.1117	0.0088
SP-19D			5.2349	0.0675	0.2963	0.0179		0.0314	0.0332	0.6014	0.0843		0.0041	0.0536	0.4084					2.5515	
SP-20A			4.2829	0.3747	0.9501	0.1376	0.0197	0.0668	0.009	0.9218			0.3481	1.8246	1.1022					14.9969	0.0135
SP-20B	5.2262		4.339	1.3451	1.3451	0.2351	0.0084	0.0907	0.0199	0.73	< LOD	0.0089	0.0221	1.6418	< LOD					44.8859	< LOD
SP-21A	7.7475		2.6766	1.7421	1.7421	0.3444	0.0186	0.1753	0.0242	0.7618	< LOD	< LOD	0.2302	1.5017	0.1603					53.361	< LOD
SP-21B	5.9624		1.1205	0.9044	0.9044	3.78	0.1931	0.3837	0.0753	0.3201	0.0786	< LOD	0.1623	1.6287	0.936					65.9918	1.4736
SP-21C	10.5142		1.2405		1.163	0.0805		0.2043		0.2427		0.013	0.1743	0.9685	0.3273		0.09			84.0364	
SP-22A	5.9121		0.726		0.2657	0.0422		0.0809	0.0942	1.0362	< LOD	< LOD	0.0331	1.3855	0.3755		0.0407				4.5271
SP-22B	10.6802		1.1667		0.4186	< LOD		0.0862	0.1266	0.8679	0.0114	0.0122	0.0078	2.1302	0.1259		0.0512				< LOD
SP-23A	0.7509			0.4147	0.7786	0.1211	0.0167	0.0168	0.9483	9.3257			0.0244	0.0994	1.2902	0.011				24.6637	0.0428
SP-23B	6.6709		0.5145		0.9674	0.0771		0.0771	0.0177	0.343		< LOD	0.0286	0.0298	0.3192	0.0121	0.0518	0.0294	0.3242	65.9681	0.139
SP-23C	8.7334		0.4731		< LOD	0.1203		0.1203	0.0244	0.2226		0.004	0.0383	0.0206	< LOD	0.0102	0.12	0.0536	2.6672	94.1813	< LOD

**Figure 12.** XRF results for all the samples  
**Фигура 12.** Рентгено-флуоресцентен анализ на всички проби

The XRF measurements reveal that all the painters were using ochres or another iron oxide pigments (Siennas – MgO is well presented), mixed with lead and sometimes with zinc pigments. Lead can be connected to the underpainting layer, as well as other whites. Titan was detected for the red fez in a painting, attributed to Boris Mitov, and dated in 1898. Its appearance here precedes the mass production of titan white and its predominance over other white pigments (after 1919), but the pigments were available before their mass production in 20<sup>th</sup> century. A mixture of titan white and zinc white can be supposed for a primer, a gesso. The result seems curious just because this sample contains maybe a lead white too, along with the red pigments – sienna, minium?, cinnabar.

The small amount of zinc pigments seem to be characteristic mainly for Boris Mitov's three paintings. The zinc pigment was not found only in the picture of Yaroslav Veshin, a lead pigments were missing in the samples from the female portrait and in fact it's palette and style are different from the other male portraits by Boris Mitov. Interestingly, he was Fernand Cormon's student in France from 1911 and one can suggest that this work might be from his French period, but it's dated earlier. Boris Mitov's style is academic and more realistic, formed first of all under his father's and Markvichka's influence (actually the academic approach penetrated Bulgarian artistic life with the previous generation of so called Bulgarian renaissance painters Christo Tzokev, Stanislav Dospevski, Nikolay Pavlovich, Dimitar Dobrovich), then under Cormon's direction, but also under the influence of the innovative

academism of Nikolay Raynov. All these facts doesn't exclude the exercises and imitations in a process of learning and searching of Boris Mitov's own style<sup>4</sup>. So, a shade of suspicion in terms of authenticity falls only on this female portrait, moreover a new layers of a black painting and a varnish are observed. For the red colour a presence of alizarin was supposed. These instrumental approaches were not being able to confirm that, they have detected cinnabar. The combination of both for a transparency and a vivid hue of the red colour is not excluded. In addition such dyes are photosensitive and it's good to add them to more stable paints.

For the portrait by Anton Mitov an undocumented conservation is supposed.

A Raman spectroscopy was used as a complementary technique to the XRF. It detected a probable use of charcoal several times. For the skin colour in the male image, depicted by Yaroslav Veshin, minium was used for the reddish shade, mixed most probably with lead white and Naples yellow. Some indications for application of amber in the varnish, especially for the first generation of painters after the liberation from the Ottoman rule<sup>5</sup>, should be crosschecked with another instrumental techniques – FTIR, just like all the selected areas. With FTIR one can obtain more information for the binders too.

These instrumental approaches are limited in determining the exact pigments, colours and hues, so they will be verified further with colour analyzer according standards.

Aknowledgements: This study was made possible due to the equipment, acquired thanks to Heritage.bg and INFRAMAT projects.

<sup>4</sup> *Karlukovska* 1992: 47-52.

<sup>5</sup> The occurrence of amber and copal varnishes does not seem so rare. In Bulgaria existed a long tradition in the religious art and maybe the secular art was impacted by these old techniques. The amber and the copal varnishes are common for European artists too, and some receipts are preserved (*Blockx* 1881:88-90).

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**Рентгено-флуоресцентен анализ  
и Раманова спектроскопия на пигменти  
и свързатели в картини на български художници  
от колекцията на Красимир Дачев**

**Илия Николов, Бойка Златева, Анелия Николова,  
Деян Лесигярски**

В Центъра по археометрия с лаборатория по консервация и реставрация (ЦАЛКР) с неструктивни методи бяха изследвани пет картини с подписи на Антон Митов, Борис Митов, Ярослав Вешин от колекцията на Красимир Дачев – рентгено-флуоресцентен анализ, допълнен от Раманова спектроскопия. Картините бяха предварително разгледани под микроскоп, UV, ИЧ източник, спектрофотометър и цветови анализатор в Института за етнология и фолклористика с Етнографски музей на Българската академия на науките (ИЕФЕМ-БАН) за установяване на автентичност по договор между института и собственика. Резултатите свидетелстват за използване на оловни, цинкови и земни пигменти (охри, сиена) с две изключения – цинковите бои липсват при Вешин, а в женския портрет, приписван на Борис Митов, няма оловни. В червения цвят на шала на изобразената жена, предполагаемо изпълнен с ализарин (C<sub>14</sub>H<sub>8</sub>O<sub>4</sub>), се открива живак, а Рамановият спектрометър разпознава наличие на цинобър (HgS). Наблюдавани са грубо надживописване с тъмна боя и допълнително лаково покритие. Възможно е подписът да е поставен по-късно, но от химичните анализи не е получено ясно потвърждение. Картината на Антон Митов по-скоро е автентична, но вероятно са извършени недокументирани консервационни намеси, тъй като подложката е била сменена с фазер (след 1976?) и е положен фирнис над старото лаково покритие.

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