

## ANALYTICAL INVESTIGATION OF TWO SOCIALIST REALISM PORTRAITS EXPOSED TO HIGH LEVELS OF HUMIDITY. CASE STUDIES FROM THE HISTORICAL MUSEUM OF BOSNIA AND HERZEGOVINA

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### Abstract

*This paper describes the combined use of several analytical methods to characterise the painting technology used in two socialist realism portraits of national heroes from World War II that are now housed in the Historical Museum of Bosnia and Herzegovina. Inspection under UV light has shown that there was no previous retouching or overpainting on either painting. Microchemical tests identified the type of canvas. The radiograms indicated whether pigments with lower or higher atomic masses were used and how well the ground was rubbed among the threads of the canvas. A better penetration of the ground into the canvas and layers of oil dye that were applied to both sides of Painting 1 contributed to its better protection against high humidity. TLC revealed the type of ground on both paintings as a classic chalk-glue ground. The high humidity was responsible for the occurrence of metal soaps on Painting 2, which were confirmed by FTIR. The XRF analysis was used to describe the pigment palette, trace the causes of existing damages, and facilitate retouching. The results of this integrated diagnostic approach were used to optimise the conservation and better understand the features and techniques used in the creation of Bosnian socialistic artwork.*

**Keywords:** *Painting material; Socialist realism; UV light radiography; Textile fiber microscopy; TLC; FTIR; XRF*

### Introduction

The identification of materials and techniques used in the creation of easel paintings is an essential step prior to the conceptualization of their conservation and restoration methodologies. Works created after the 19<sup>th</sup> century, when artists started deviating from the classic painting techniques and traditional materials and moving towards experimentation with new materials, are a particular challenge for conservators and restorers, as the identification of such paintings is much more complex and practically impossible if based solely on their experience with painting techniques. Today, a spectrum of scientific methods is used for the characterization of painting materials. Their choice first and foremost depends on the availability of instruments, time, financial opportunities, and the amount of sample possible to take. A successful interpretation of analytical results usually involves scientists, conservators, restorers, and art historians.

The aim of this work was to examine two socialist realism paintings of national heroes from World War II (Figs. 1 and 2). Both paintings are owned by the Historical Museum of Bosnia and Herzegovina and are located in the museum's art collection depot.

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The painting in figure 1 is mostly painted in earth tones, with heavy use of white for brightening, as well as other colours that are hard to see due to the layers of dirt that have deposited on the surface over the years. The author applied paint in layers of different thickness. Because the canvas was not big enough to properly tighten it in the working frame, after stretching the painting, the author applied ground and a layer of white on the opposite side to achieve the desired tension. Apart from that and accumulated dirt, no other shortcomings have been observed.

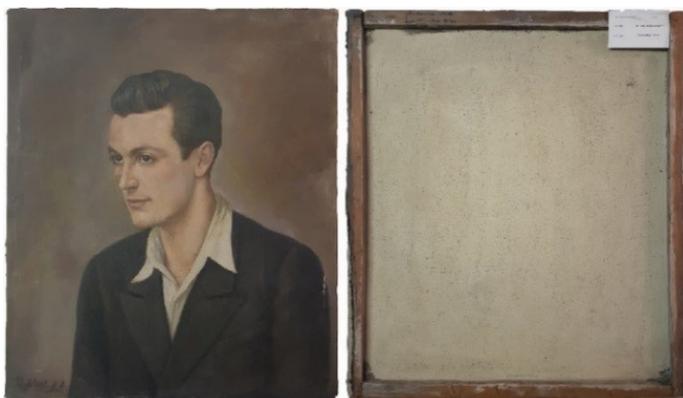


Fig. 1. "Portrait of Ante Rukavina" was made Milenko Atanacković in 1951

The painting in figure 2 was painted with thin washes, with slightly thicker layers in areas of the face, hat, and collar where brush strokes are visible. The pigment palette is modest, and the colouring is very dark. Many craquelures are visible on the painting because of exposure to high relative humidity (RH) and mechanical damages during storage, transfer, and exhibition. The biggest damage is in the upper right corner, where the ground and the paint layers are blanching and weakly linked to the canvas or primary support. This damage appeared quite quickly, in a matter of years, and required urgent intervention to prevent further loss of integral parts of the painting.



Fig. 2. "Portrait of Đuran Kovačević" was made Ljubo Lah in 1952

After the war, socialist realism was the official artistic movement in Yugoslavia; art existed in the service of politics and was considered a tool for conveying political and ideological ideas. Thus, in the period from 1948 to 1953, the government ordered portraits of national heroes to honour their sacrifice and bravery, presenting them as the embodiment of an ideal socialist man capable of victory and building a new society. The most distinguished Yugoslav painters of

the time were entrusted with the creation of these portraits. Therefore, socialist heritage represents a true treasure of Bosnian and Herzegovinian history, culture, and art [1]. Nevertheless, after the dissolution of Yugoslavia, interest in this heritage declined, so no special attention was paid to its preservation.

The aim of this work was to portray the combined use of different analytical methods for the identification of painting materials and techniques, including ultraviolet (UV) light, radiography (RTG), Fourier-transform infrared spectroscopy (FTIR), fibre microscopy, thin-layer chromatography (TLC), and X-ray fluorescence (XRF). The identification of the materials constituting an artwork along with the understanding of their interaction with the environment is valuable for discovering the artist's executive techniques, recognising previous interventions, defining the current preservation status, and determining the most appropriate conservation or restoration procedures [2].

The obtained results are valuable since this work represents the first comprehensive research on the technical characteristics of socialist realism art in Bosnia and Herzegovina. To the authors' knowledge, there is no scientific literature on the material characterization of socialist realism art in Bosnia and Herzegovina and other countries of the former Yugoslavia.

## Experimental part

### *Samples*

These two portraits had been exposed to very high humidity for a long period of time. The damaged condition of these paintings required urgent conservation intervention. An analytical examination before attempting artefact conservation is relevant in order to plan the best practices of intervention. The diagnostic work conducted was focused on the characterization of painting materials and followed the sampling map presented in figure 3.

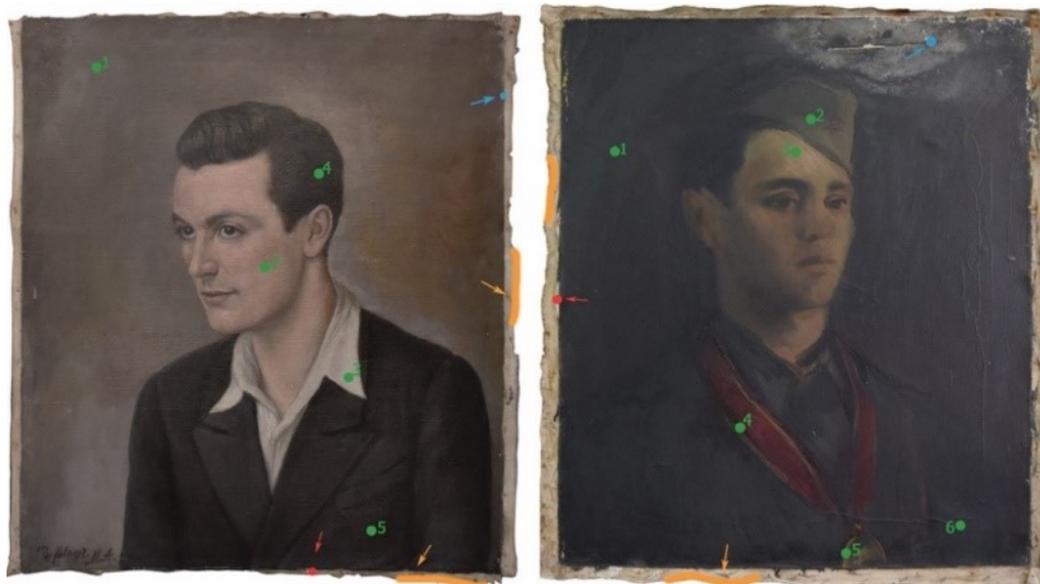


Fig. 3. Sampling map for A) *painting 1* and B) *painting 2*  
 ● Fibres ● TLC ● FTIR ● XRF

### *Instruments and methods*

#### *UV light*

The inspection under UV light was done in a dark room using a UV lamp ( $\lambda = 366$  nm). The obtained results were recorded by a digital camera without the use of filters.

#### *Radiography*

For radiography purposes, a digital device called the *Opera G500C (General Medical Merate)* was used as a source of radiation. The size of the used film was 24 x 30 cm. The focus of the x-ray tube was ca. 100 cm removed during imaging: 2.5 mAs and 40 kV for *painting 1* and 3 mAs and 42 kV for *painting 2*. Since the painted layers on the canvas are very thin by radiography standards (several mm) – lower penetrance energies with a richer RTG photon beam had to be used. This so-called soft radiation, enables a better display of details. Cassettes or phosphor plates on which 'latent' images are formed and later transformed to a digital image via digitizer were used for recording information obtained after radiating the artefacts with x-rays. For evaluating the obtained results, the software *SE Media Viewer, Version 4.0.2.0 (AGFA Health Care)*, was used. The obtained images were processed and interpreted based on the differentiation of grey shades with functions such as brightness and contrast, distance, zoom, positive and negative, and cropping.

#### *Textile Fibre Microscopy*

For the purpose of identification of the primary support, preliminary inspection was performed using a digital USB microscope, *Dino-Lite AM7915MZTL – EDGE*, after which a few warp and weft threads up to 3cm in length were taken from its edges. Before the disintegration of threads from the canvas support, the same methodology was used to prepare reference cotton and linen threads. In the fibre identification process, samples are investigated at a minimum of 100x magnification and often stained to accentuate morphological features. Warp and weft threads were treated as separate samples. The disintegration of threads was performed using the TAPPI T401 [3] method. Complete disintegration of more resistant samples was achieved with the addition of 1% NaOH and 0.05 N HCl solutions, as described in the TAPPI method. This procedure also removed the leftovers of binder, fillers, and other materials that could have interfered with the analysis. Graff C and Herzberg reagents for fibre colouring were added to thread samples for easier identification. The reagents were prepared according to the aforementioned TAPPI standard. The prepared samples were observed under the *Olympus Microscope Digital Camera DP12* microscope [4].

#### *TLC*

To determine the binder in the ground, TLC was performed using a method described by *S. Gocan* [5]. Glue solutions and glue-chalk gesso were used as reference samples. Samples of rabbit skin, animal skin, and bone glue were prepared as 6% (w/v) water solutions heated at 80°C. Part of the glue samples were separated so that a mixture of Bologna chalk and zinc white pigment (2:1) could be added. A classic glue-chalk gesso made according to instructions from *M. Kraigher-Hozo* [6]. A layer of glue solution was added to the pieces of cotton canvas, followed by two layers of ground with appropriate gesso. After the ground dried, appropriate amounts of samples were scraped off the canvas (0.12g for *painting 1* and 0.23 g for *painting 2*). The hydrolysates were prepared by heating the samples and reference materials in 6 M HCl for 12 hours at 105–110°C. The reference samples and the specimens were applied on activated TLC glass plates (20×20cm) coated with silica gel G 60 and placed into the mobile phase of the following composition: chloroform: 17% NH<sub>3</sub> = 4: 4: 2 (v/v/v). The plates were left for 1.5–2 h to develop, allowed to dry, sprayed with 0.2% ninhydrin solution (in acetone), and heated at 110°C for 5 min. Rf values were determined for reference samples and both specimens.

#### *FTIR*

A minor amount was taken from the surface of the paint and ground to a fine powder. Infrared spectra were collected on a *Perkin Elmer BX FTIR* using KBr pellets in the transmission mode.

### *XRF*

The elemental composition of the pigments was determined using a portable XRF spectrometer (*Olympus, Vanta, C Series*) with the following characteristics: excitation source: (Rh W): 8 – 40 kV; primary beam filtration: 8-position auto-selected filter per beam per mode; detector: silicon drift detector. The instrument was calibrated using a selection of pure elements, oxides, and other certified reference materials. It allows for rapid multilayer analysis of complex materials. According to the technical sheet taken from the manufacturer's website, this instrument can detect chemical elements from P ( $Z = 15$ ) to U ( $Z = 92$ ). For the XRF analysis, five representative spots were selected for *painting 1* and six spots for *painting 2* (Fig. 3).

## Results and discussion

### *UV Light*

The detection of materials (natural varnish, certain pigments) and alterations (presence of yeast and mould, retouching, copies, additionally added signatures) with a UV lamp was based on the fact that different materials may exhibit different colours and intensities of fluorescence, while they look identical when observed in day-light conditions. This diagnostic method can reveal the presence of old varnish layers and determine whether there are retouched or newly repainted areas [7]. After the examination with UV light, it was determined that neither of the paintings had had subsequent interventions in the form of retouching. Unlike *painting 2*, *painting 1* did not show any fluorescence. According to *D. Measday* [8], dammar and mastic varnishes show quite an intense greenish fluorescence after 20 years, which suggests a natural resin. In this way, an unequally applied layer of natural resin varnish was detected on *painting 2* (Fig. 4). It is also highly improbable that it was coated with a layer of synthetic varnish, as it was not in wide-scale use in the art of that period.



Fig. 4. Inspected under with an UV lamp indicates a presence of dammar varnish on *painting 2*

The bright grey to yellowish discolouration on the surface of *painting 2* was suspected to be the product of fungal or yeast colonies' metabolism or colour, which had developed as a

consequence of the painting's exposure to conditions where microorganism growth is sustainable. New or light growth can be detected by UV light, which causes the mould to appear luminescent. In easel paintings, the support and the sizing materials may be easily degraded by microorganisms since these materials include cellulose and proteins, which are nutritive for fungi and moulds [9]. However, the inspection under visible and UV light did not show changes that would suggest the appearance of microorganisms on cellulose materials (wood and canvas). All visible changes can be found on coloured and ground layers that are no longer closely bonded with the support. These changes are irreversible and manifest themselves as the missing parts of the dye and ground layers and as stains on the surface of the painting. Damage caused by bacteria or fungi that is not visible to the eye appears grey in the ultraviolet [10]. However, characteristic luminescence was not detected in this case. *P. Bosch-Roig* and *P. Sanmartín* [11] state that zinc oxide has been found to exert fungicidal activity and is used to great advantage in preventing the growth of fungi and bacteria in paints [12]. For that reason, paintings where zinc white was used generally do not show problems due to infestation and biodeterioration as long as they are exhibited or stored under appropriate conditions. Detection of ZnO would indicate that fungi or mould were not the cause of changes on the coloured surface of *painting 2* and that another cause must be sought.

### **Radiography**

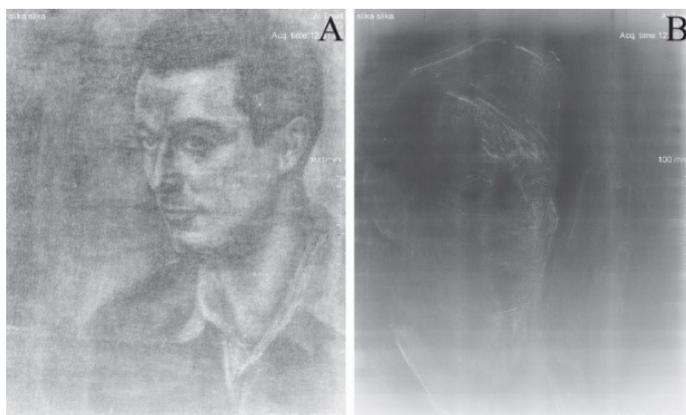
The paintings were exposed to X-rays, which have the ability to penetrate materials in a non-destructive and non-invasive manner and reveal features not apparent under visible and UV light, but that can be important for studying the technical characteristics and overall condition of the works. The X-radiograph showed that there are no artist pentimenti or copies, which means that the artists did not change the original concept in the process of painting.

Further on, X-radiographs may also provide data on the canvas weave and the ground. Painting materials consisting of elements with higher atomic numbers have a greater ability to absorb X-rays, whereas elements with lower atomic numbers produce lighter radiographic images and block the X-rays [13, 14]. The radiogram of *painting 1* (Fig. 5A) is quite bright because the artist used a lot of white pigment, particularly in a layer of white oil paint, which he applied over the entire reverse side of the canvas support. At the time the painting was created, lead white was not in use due to its toxicity. In the second half of the 19<sup>th</sup> century, it was replaced by zinc white [15] and mixed with titanium white to achieve better properties. High-quality titanium white pigment was possible only after 1957 [16]. Therefore, zinc white (Zn atomic number: 30) was probably used as a white pigment, which has a high X-ray absorbance, resulting in a fairly bright radiogram of *painting 1*.

The radiogram of *painting 1*, also clearly shows the structure of the canvas fibres. The natural fibres are almost transparent to X-rays, but because the hollows in the weave become filled with ground, the material shows up on the photographic plate in the negative, revealing the intricacies of the weave and each lump and twist in the thread [14]. That is true for *painting 1*, since the ground was well rubbed among the threads of its canvas. Chalk (CaCO<sub>3</sub>) and plaster (CaSO<sub>4</sub>), made up of atoms with smaller atomic masses that transmit light, are used as fillers in the ground, making the structure of the canvas clearly visible on the radiogram.

The *painting 2* radiogram (Fig. 5B) is dark because pigments of higher atomic masses were used, resulting in a lack of strong contrast. *D. Oliveira et al.* [17] state that the pigments with Fe ( $Z = 26$ ), such as ochre and other earth pigments, do not absorb a lot of X-rays, so the radiogram is quite dark. The partisan cap, the face, and the red ribbon are the brightest parts of the *painting 2* radiogram. The structure of the fibres is more difficult to see, probably also because the ground had not been so thoroughly rubbed among the threads of the canvas as in *painting 1*. According to *G. Buli* [18], ground that does not penetrate well into the threads, as is the case with industrial canvases, and stays above the surface of the canvas gives significantly weaker protection from humidity. This explains why *painting 2* was more damaged, even though both paintings were exposed to high RH. Apart from the difference in the ground, it is important to

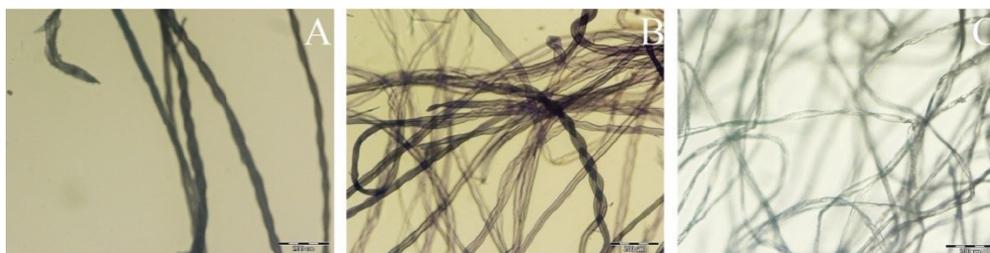
note that layers of ground and oil dye applied also from the backs of the canvas in *painting 1* contributed to its better preservation state.



**Fig. 5.** Radiography images of A) *painting 1* and B) *painting 2*

### ***Textile Fiber Microscopy***

Based on the visual inspection with a DinoLite digital microscope, it seems that the warp and weft were made from the same material. Further identification steps were undertaken to document the type of fibre used as well as to make informed decisions about future treatment, exhibition, and storage. Warp and weft samples (Fig. 6) were compared to reference samples (Fig. 7) and literary data (Fig. 8).



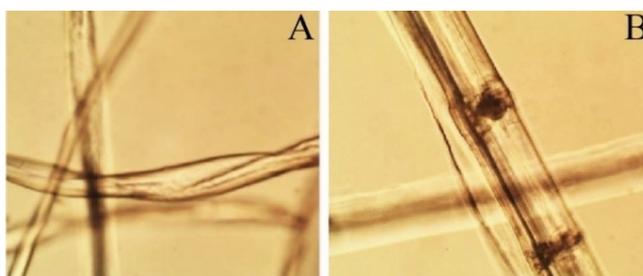
**Fig. 6.** Fibres of *painting 1* stained with Herzberg (A) and Graff C reagent (B) and *painting 2* without staining reagents (C)



**Fig. 7.** Reference fibres of A) cotton and B) flax fibres at a magnification  $\times 200$

The fibre samples were stained with Graff C and Herzberg reagents that not only accentuate the fibre morphology but also stain a range of colours depending on the degree of

cellulose and lignin present in the fibre. Fibres with high cellulose content stain red as opposed to lignin-rich fibres that stain yellow [3], but the colour can vary in raw and processed fibres of the same type [19]. Interestingly, the various chloro-iodine stains, such as Herzberg, which stain cellulose red, violet, or blue, and lignocellulose yellow, seldom act on old and desiccated fibre except at nodes or points of fracture. However, even the coloration of all fibres within each sample, as well as their morphological characteristics that are key to their identification, have confirmed that the analysed canvasses were made from the same type of fibre. The weft and warp of both paintings were made from cotton. The fibres were recognised based on the twists along the length and their ribbon-like appearance and thick walls, as described by *C. McBride* [13] and *I. Markova* [20]. Further on, cotton fibres can be easily distinguished from linen fibres that resemble bamboo sticks due to their characteristic nodes or cross-markings and striation markings along the length between the nodes. The lumen of linen fibres looks like a narrow line, which significantly differs from cotton fibres' hollow, tube-like, and cross-sectional shapes [20].

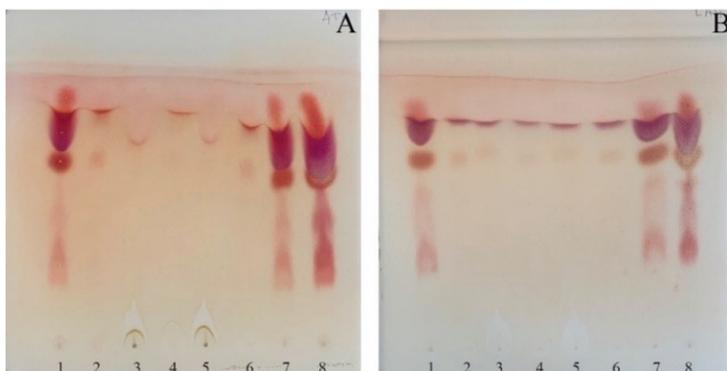


**Fig. 8.** Microscopic appearance of A) cotton and B) flax fibres at magnification  $\times 500$  [13]

Until the 20th century, cotton was not commonly used as a support for easel paintings. Compared to linen, cotton canvas is cheaper, and the strength of its fibre is considered to be weaker [13]. After the end of World War II, the options for textile support for painters were limited, to say the least. *C. Young and A. Katlan* [21] state that cotton canvas was more available in the first years after the war. Linen has been mass-produced only since the 1970s. This data suggests that in the period in which the paintings were made, cotton canvas was much more readily available. However, some technicians are warning that cotton canvas is not a good choice for glue-chalk ground, given its extreme sensitivity to high humidity, which leads to craquelure formation [22]. This is the reason why craquelures appeared in *painting 2*. Humidity influenced the dimensional reactions of ground and canvas to a much lesser degree in *painting 1*, as explained in Section *Radiography*.

### **TLC**

Thin-layer chromatography was used as a preliminary method for testing of ground contents. Ground samples from the paintings were compared with reference samples, that is rabbit skin, and other animal skin and bone glue hydrolysates, as well as glue-chalk grounds based on these glues. Method optimization showed that in order to achieve good results, a min 0.5 g preparation sample is required, and sample hydrolysates need to be further concentrated by evaporation. Upon interpretation of results, it was concluded that the binder for *paintings 1 and 2* was protein-based, also known as a classic chalk-glue ground. The aggravating factors during analysis were: sample mass and interfering substances, such as pigments, oil, fillers and similar (Fig. 9).



**Fig. 9.** TLC chromatograms of:

- A) painting 1** - bands: (1) rabbit skin glue; (2) sample from the paint; (3) ground with rabbit skin glue; (4) sample from the paint; (5) ground with skin glue; (6) ground with bone glue; (7) skin glue; (8) bone glue.  
**B) painting 2** - bands: (1) bone glue; (2) ground with bone glue; (3) sample from the paint; (4) ground with rabbit skin glue; (5) sample from the paint; (6) ground with skin glue; (7) rabbit skin glue, (8) skin glue

### FTIR

After determining that the pulverisation and blanching of the coloured layer in *painting 2* are not the result of microorganism action, the next suspect was the appearance of metallic soaps. The painted layer at this spot was soft, cracked, and unstable, with crater-like holes up to 1 mm. Therefore, the sample was taken from the place where the damage occurred (Fig. 3B, sample a). Many metals and reactive metal compounds, such as oxides, hydroxides, and salts, easily react with fatty acids in oil-based paints and form metal carboxylates. Zinc soaps received significant attention due to their harmful effects on paintings dated from the 19<sup>th</sup> century onward, which corresponds to the widespread use of ZnO as a white pigment. Commonly used oil mediums, including linseed oil, contain various fatty acids that can react, giving Zn soaps. The transformation of an acid into a salt is easily detectable by the FTIR spectroscopy method based on the changes in the characteristic asymmetric and symmetric carboxyl group frequencies [23–25]. The soaps of primary importance for this research, zinc palmitate and/or zinc stearate, having nearly identical spectra (C18 and C16), were usually simultaneously detected as sources of degradation. The general appearance of the spectrum (Fig. 10A) revealed broad bands and the presence of free fatty acids from linseed oil and zinc soaps in the form of zinc palmitate and/or stearate. The attribution of specific frequencies of metal soaps in the real sample is based on the data of the synthesised carboxylates, taking into account that the real sample is not an ideal one [26]. The crystal structures of zinc aliphatic carboxylate salts of different chain lengths were determined by diffraction techniques [27, 28]. In all structures, Zn with coordination number four and  $sp^3$  hybrid orbitals builds a tetrahedral arrangement of  $[ZnO_4]$  bonds from two carboxylates *via a* bidentate bridging structure. In the carboxylate absorption region, a pair of  $\nu_{as}$  (COO) and  $\nu_{sym}$  (COO) found at 1544 and 1399  $cm^{-1}$ , confirmed the presence of Zn carboxylate. In addition,  $\Delta\nu$  value (145  $cm^{-1}$ ) which indicates the separation between asymmetric and symmetric carboxylate stretching, revealed a higher structural symmetry characteristic of Zn soaps [29]. The value of  $\nu_{as}(COO^-)$  suggested partial crystallinity of Zn soaps [30]. In the region of C-H stretching,  $\nu_{as}(CH_2)$  and symmetric stretching appeared at 2925 and 2852  $cm^{-1}$  respectively, while the methylene bending vibrations  $\delta(CH_2)$  were found at 1459  $cm^{-1}$ . The intensity of  $CH_2$  bending frequency supports an aliphatic long chain. Based on the lack of C=C-H vibration close to 3000 $cm^{-1}$ , there is no evidence of unsaturated carboxylates, e.g., Zn azelate. The presence of a small amount of free fatty acids and esters in the sample was confirmed by absorption at 1716 (shoulder) and 1736  $cm^{-1}$ , respectively. The strong absorption centred at about 3400  $cm^{-1}$  was attributed to OH stretching vibrations from free acids; moreover, the width of the band indicated the presence of hydrogen bonds between free carboxyl groups. Along with this absorption, the

band at  $1625\text{ cm}^{-1}$  revealed the presence of H-O-H bending, which is either crystal water from Zn soap or originates from moisture. Currently, the main 'culprit' of metallic soap synthesis is considered to be the transport of fatty acids and ions through the paint film via water. This transport occurs naturally during the drying and ageing of the oil medium. Some theories indicate that this phenomenon may be related to the characteristics of the material and the artist's technique, but also to the exposure of the object to high RH [31]. *C. Romano et al.* [30] also believe that increased RH accelerates the hydrolysis of the coloured film, i.e., the release of fatty acids that become available for reaction with metal ions ( $\text{Zn}^{2+}$ ) from pigments, thus building metal soaps. Exposure of *painting 2* to high RH for a long time probably accelerated the process of the formation of metallic soaps and the onset of degradation.

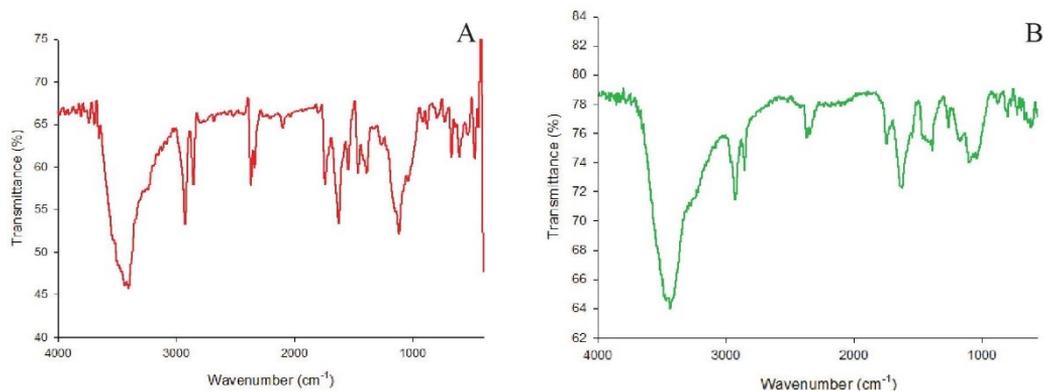


Fig. 10. IR spectra of A) Zn soap from *painting 2*;  
B) sample of *painting 1* with characteristic carbonate, sulfate vibrations and ester vibrations

In order to identify the chemical composition of the filler in the ground layer, minute amounts of the samples (Fig. 3A and 3B: sample b) were taken. In the spectrum of *painting 1* (Fig. 10B), the characteristic vibrations of calcium carbonate and gypsum were found.  $\text{CO}_3^{2-}$  as a planar molecule showed three IR active vibrational modes: asymmetric  $\nu_3$  at  $1385\text{ cm}^{-1}$ , out of plane  $\nu_2$  at  $873\text{ cm}^{-1}$  and  $\nu_4$  plane bending at  $722\text{ cm}^{-1}$ . The presence of the highly symmetric tetrahedral  $\text{SO}_4^{2-}$  molecule was proven on the basis of the asymmetric  $\nu_3(\text{S-O})$  stretching at  $1098\text{ cm}^{-1}$  and the "umbrella" bending motion of four oxygen atoms in  $\text{SO}_4^{2-}$  molecule at  $666\text{ cm}^{-1}$  [32]. Strong and broad absorptions centred about  $3430$  and  $1620\text{ cm}^{-1}$  correspond to the stretching frequency and H-O-H bending of water molecules, respectively. Corresponding bands for carbonate in the sample of *painting 2* were found at  $1385$  and  $722\text{ cm}^{-1}$ , asymmetric stretching of the S-O appeared at  $1096\text{ cm}^{-1}$  while the „umbrella" motion is very poorly differentiated. Both spectra of samples (*paintings 1 and 2*) confirmed that Bolognese chalk (chalk + gypsum) was used as filler.

In addition to the inorganic components, the presence of ester functional groups of fatty acids was revealed in *painting 1*. Esters showed three characteristic frequencies: carbonyl  $\text{C=O}$  stretching found at  $1742\text{ cm}^{-1}$  and two ester C-O bonds. The C-C-O and O-C-C stretching, including the C-C stretching of atoms on the left and right places of ester oxygen, were found at  $1259$  and  $1035\text{ cm}^{-1}$ . In the sample from *painting 2* (Fig. 3B: sample b), there is no evidence for the ester  $\text{C=O}$  group.

### XRF

The XRF analysis was performed to conduct an elementary analysis of the pigments and fillers used in the creation of both paintings. Results of visual inspections and other analytical methods, as well as data from the history of pigment and painting techniques, were all taken into account during the interpretation of the results. Pigments are usually identified for several

purposes: to describe their historical use, to trace the causes of existing damages, and to facilitate retouching. Based on the XRF analysis, a tentative list of inorganic pigments (Tables 1 and 2) and fillers was proposed for both paintings.

**Table 1.** Pigment palette used for *painting 1*

Colour	Measurement spots	Detected elements		Identified pigments
White	1, 2, 3, 4, 5	Zn, Ti, in trace: Pb	Zinc white / Titan white	ZnO + TiO <sub>2</sub>
Yellow	1, 2, 3, 4, 5	Zn, Cr, K Fe, in trace V	Zinc yellow Yellow ochre	K <sub>2</sub> O x 4ZnCrO <sub>4</sub> x 3H <sub>2</sub> O Al <sub>2</sub> O <sub>3</sub> - 2SiO <sub>2</sub> x 2H <sub>2</sub> O + Fe <sub>2</sub> O <sub>3</sub> x 3H <sub>2</sub> O
Red	2	Fe, in trace: Hg, Se, V	Red ochre	Fe <sub>2</sub> O <sub>3</sub> + clay + silicates
Brown	1, 2, 3, 4, 5	Fe, in traces: Mn	Umbr	Fe(OH) <sub>2</sub> + MnO <sub>2</sub> + SiO <sub>2</sub>
Green	1, 2, 3, 4, 5	Fe, K, in trace: V	Green earth	K[(Al,Fe <sup>3+</sup> ),(Fe <sup>2+</sup> , Mg](AlSi <sub>3</sub> Si <sub>4</sub> )O <sub>10</sub> (OH) <sub>2</sub>
Black	1, 2, 3, 4, 5	Ca, P	Bone black	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + CaCO <sub>3</sub> + C

**Table 2.** Pigment palette used for *painting 2*

Colour	Measurement spots	Detected elements		Identified pigments
White	1,2,3,4,5,6	Zn, Ti, in trace: Pb	Zinc white / Titanium white	ZnO + TiO <sub>2</sub> ,
Yellow	1, 2, 3, 4, 5, 6	Fe, in traces: As, V Pb, Cr	Yellow ochre Chrome yellow	Al <sub>2</sub> O <sub>3</sub> x 2SiO <sub>2</sub> x 2H <sub>2</sub> O x Fe <sub>2</sub> O <sub>3</sub> x 3H <sub>2</sub> O PbCrO <sub>4</sub> x PbSO <sub>4</sub>
Red	2, 3, 4	Fe, in traces: Hg, Se V	Red ochre	Fe <sub>2</sub> O <sub>3</sub> + clay + silicates
Brown	6	Fe, in traces: M, V	Umbr	Fe <sub>2</sub> O <sub>3</sub> + MnO <sub>2</sub> + SiO <sub>2</sub>
Green	1, 2, 3, 4, 5, 6	Fe, K, in trace: V	Green earth	K[(Al,Fe <sup>3+</sup> ),(Fe <sup>2+</sup> , Mg](AlSi <sub>3</sub> Si <sub>4</sub> )O <sub>10</sub> (OH) <sub>2</sub> Cr <sub>2</sub> O <sub>3</sub> x 2H <sub>2</sub> O
	1	Cr	Viridian	
Black	1, 2, 3, 4, 5, 6	P, Ca	Bone black	Ca <sub>3</sub> (PO <sub>4</sub> ) <sub>2</sub> + CaCO <sub>3</sub> + C

### Fillers

In *painting 1*, as well as in *painting 2*, all measurement spots revealed high concentrations of Ca and S, which can be attributed to the ground layer consisting of chalk (CaCO<sub>3</sub>) and gypsum (CaSO<sub>4</sub>) as fillers, Bologna chalk (detected by the FTIR), animal glue as the binder (as shown by the TLC), and white pigment. It can be concluded that both painters prepared the canvas with a classic chalk primer (gesso). Since XRF cannot identify Ba, the high content of S could originate from BaSO<sub>4</sub> [33], often found in the ground layer but also as an ingredient in factory-prepared pigments. Its presence is indicated by the detection of Sr in all measuring points on *painting 1*; the combination of S, Ba, and Sr is usually associated with BaSO<sub>4</sub> as filler. Sr is an impurity originating from raw barite or lithopone [34]. According to *E. Franceschi and F. Locardi* [35], the detection of Sr could also be used as a marker for the presence of gypsum.

### White pigments

The detection of Zn and Ti on all measuring spots of both paintings indicates heavy usage of white pigment, which itself is a combination of ZnO and TiO<sub>2</sub>. According to *B. Driel et al.* [36], mixtures of titanium and zinc were very popular in the mid-20th century. *H. Kühn* [12] states that many paint manufacturers mix those two pigments to get the ideal white colour for oil paintings. He also points out that many manufacturers add ZnO to pigments other than white, mixing it with almost all oil paints to brighten them but also for its antimicrobial properties. The low concentration of Pb (in all measurement spots on both paintings) may originate from an added drying agent rather than from the lead white pigment. Lead white nearly disappeared after World War II [36], but manufacturers of industrial paints often add some lead to zinc white oil paint to accelerate its drying process [37].

### Green pigments

Fe and K were also detected on all measuring spots on *paintings 1 and 2*. They constitute green earth, which was mixed with zinc yellow and applied as a layer of imprimatura on *painting 1*. The dark olive green imprimatura on *painting 2*, applied across the whole surface of the canvas,

is made from a mixture of green earth and black bone. To paint the background (measuring point 1) of *painting 2*, some viridian was added (as indicated by the presence of Cr and Pb) to the mixture of green earth, black bone, and yellow ochre.

Vanadium, often found in samples of earth pigments, has been detected in all measuring spots on both paintings. Considering the high concentrations of Fe in both paintings, the presence of V indicates that Fe can be attributed to the use of earthy pigments (green earth, ochres, and umbra).

#### *Yellow pigments*

Cr, Zn, and K were also detected in all measuring spots on *painting 1*, and their combination points to zinc yellow ( $K_2O \times 4ZnCrO_4 \times 3H_2O$ ) used in the imprimatura layer. Yellow ochre is a pigment frequently used by painters to create a skin tone (mixed with zinc white as well as red ochre, earth green, and bone black). It was also used for this purpose in the analysed paintings, as indicated by the presence of Fe (measuring spot 2 on *painting 1* and measuring spot 3 on *painting 2*), which constitutes yellow ochre. The golden medal on *painting 2* (measuring spot 5) was also painted with yellow ochre. Furthermore, chrome yellow, as indicated by the presence of Pb and Cr, was used in this painting (in mixture with green earth, bone black, zinc white, and yellow ochre) to paint the hat (measuring spot 2) and suit of the national hero (measuring spots 4 and 6). Traces of As were also detected on tree measuring spots (3, 4, 5) on *painting 1* and four (1, 2, 4, and 6) on *painting 2*. According to literature [38],  $As_2S_3$  is found in yellow ochre with orange tones. However, as it is also used as an insecticide on cotton, it could come from the textile carrier [39].

#### *Red pigments*

On both paintings, red ochre ( $Fe_2O_3$  + clay + silicates in different ratios) was most likely added to yellow ochre and zinc white to achieve the pinkish tone of the skin. On *painting 2*, the red ribbon and the stars on the hat were also most likely painted with red ochre. However, red ochre is indistinguishable from yellow ochre (also used to emphasise details on the five-pointed star) on XRF, so a more precise detection of Fe pigments requires further analyses. The low Hg and Se concentrations in multiple measurement spots suggest that cinnabar ( $HgS$ , Se) may have been added to red  $Fe_2O_3$  to achieve a brighter tone [40].

#### *Brown pigment*

On *painting 1*, umbra was confirmed by the detection of Fe and Mn. Umbra differs from other earth pigments, which all have Fe, by its content of manganese oxide and hydroxide [36]. The author abundantly mixed this pigment with other pigments, particularly white and black. Umbra was also detected on measuring spot 6 of *painting 2*, which indicates that umbra was used to paint the suit of the national hero (together with other pigments).

#### *Black pigment*

In *paintings 1 and 2*, bone black was identified based on the presence of Ca and P [41, 42] on all measuring spots on *painting 2* (as a layer of the imprimatura, in mixture with green earth) and on the darkest measuring spots of *painting 1*: hair (measuring spot 4) and suit (measuring spot 5).

## Conclusions

The characterization of the two paintings was conducted using different, mostly complementary analytical methods ranging from inspections under UV light, microchemical tests, TLC, radiography, FTIR, and XRF. The methodology proved suitable not only to reveal the paintings' stratigraphy but also to trace the sources of the deterioration.

This is the first recorded diagnostic work on the painting techniques of socialist realism art in Bosnia and Herzegovina. Both artists used cotton canvas as support, protein-based binders, and pigments mostly based on earth tones, but also modern pigments identified based on the presence of Cr. The obtained results were useful not only in gaining a better understanding of the painting techniques but also in analysing the damage caused by exposure to high humidity and even the direct action of water. This is particularly visible on *painting 2*, given the appearance of craquelures, bright grey to yellowish discoloration, and metal soaps on its surface. *Painting 1* was less deteriorated due to a better penetration of the ground into the canvas threads and the application of oil dye on both sides.

Ultimately, the obtained results and the limited data available in the literature were utilised to expand the scientific background on the materials and techniques used by socialistic realism artists and to fill the knowledge gap on this emerging topic. The proposed methodology can be used and preferably supplemented with more non-destructive analyses to characterise materials, trace damage sources, and tailor the conservation work on paintings accordingly.

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