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ORIGINALS VS. FORGERIES: THE SIGNIFICANCE OF WHITE PIGMENTS IN ARTWORK EVALUATION

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Abstract

The study presents results obtained during an extensive project dealing with the identification of forgeries of famous Czech painters from the first half of the 20th century – Josef Čapek, Emil Filla, Josef Šíma, Václav Špála and Jan Zrzavý. In art authentication, it is essential to gather enough relevant information from scientific examination of original paintings, because this helps us determine art materials used by a particular artist in a given period. The research focused on white pigments, as they are good markers of the paintings' date of origin, especially in the period between the 1920s and the 1950s. To identify the materials, we employed non-invasive molecular analysis (Raman spectroscopy) combined with elemental analysis (X-ray fluorescence spectroscopy). Using titanium white as an example, we explored the availability and import of this pigment in Czechoslovakia. Czech painters used titanium white with anatase structure rather sparingly, even though it was available on the market at the latest in 1928 and was still used in the 1950s. Rutile has been identified in two artworks from the second half of the 1960s. In addition to traditional white pigments, lead sulphate was also present in the studied artworks. This white pigment has been detected in only a few paintings, suggesting it was not very common. In the Czech milieu, lead sulphate was found exclusively in the paintings from the 1920s and the 1930s. The results obtained through this investigation provide valuable information about the use of different pigments by individual painters. They can serve as comparative data in the process of art authentication.

***Keywords**: Forgeries; Non-invasive analysis; Raman spectroscopy; Titanium white; Lead sulfate; Czech painting*

Introduction

On the Czech art market, paintings from the first half of the 20th century are in high demand, including particularly the famous avant-garde painters such as Emil Filla (4 April 1882 – 7 October 1953), Josef Čapek (23 March 1887 – April 1945), Josef Šíma (18 March 1891 – 24 July 1971), Jan Zrzavý (5 November 1890 – 12 October 1977) and Václav Špála (24 August 1885 – 13 May 1946) (Fig. 1). These artworks reach high auction prices from hundreds to millions of euros. But the increasing demand and high value attracts forgers and there are numerous criminal cases connected with the sales of artwork counterfeits. In this situation, tools for accurate art authentications become essential, including relevant data, the knowledge and practical experience of individual artists with the technique and art materials. In addition to art-historical assessment and restoration research, scientific examination plays a key role in this process [1, 2]. Scientific research of original artworks provides fundamental data that can serve as comparative material for experts in authentication. As part of this research, various analytical techniques are applied to identify and classify the art materials.

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Fig. 1. Václav Špála, *Bouquet with tulips*, 1936 (A); Emil Filla, *Cellist*, 1930 (B); Josef Šíma, *Red Signal of Shadow*, 1967 (C); Josef Čapek, *Children in the garden*, 1928 (D); Jan Zrzavý, *Port in Brittany*, 1930 (E)

During the first half of the 20th century, new pigments were introduced and sold in the form of commercial paint tube formulations. Because the time when they were first produced is usually well known, their presence in artworks may help with dating. Synthetic organic pigments are particularly important for dating artworks, as most of them were discovered within a clearly defined time. Also, titanium white, produced in two structural modifications – anatase and rutile – is a good indicator of an artwork's date of origin. In Europe, titanium white with anatase structure was first produced in Norway. Titan Company A/S was founded in 1916, beginning the production of titanium white pigment in 1918. Because of the manufacturing process, the first pigments were composite, with anatase precipitated on barium sulphate. The production of titanium white pigments continued to develop in 1920s and in 1923 pure anatase was made [3]. In 1927, the production of titanium white began in Czechoslovakia [4]. The French company Société Bourgeois (later Lefranc Bourgeois) was the first to introduce titanium white with anatase structure in paint tubes. Soon, other companies also began to make titanium white – Société Lefranc in 1927, Winsor & Newton after 1928 and H. Schmincke & Company in early 1930s [5]. Industrial synthesis of rutile was developed in Czechoslovakia between 1930 and 1933 in *Spolek pro chemickou a hutní výrobu* (Association for chemical and metallurgical production) [4]. The process was kept secret until 1937 when it was patented. That same year, the German company *Titangesellschaft* patented its own method of rutile manufacturing, starting production in 1938 [5]. Even though the production ceased during the World War II, the pigment was available in Europe after 1945. A number of manufactures began to make it again after 1950. Production of rutile further expanded at the beginning of 1960s when the chloride process was developed, making the pigment cheaper [3]. In the United States, rutile was available in the early 1940s [6].

Lead sulphate, a rather rare pigment, can also serve as an indicator of the date of origin during the authentication process. A recipe describing its production under the name "White Precipitate of Lead" was published in 1795 [7]. It was on a list of white pigments in a treatise from 1835 [8] and until 1930s it was sold as a paint [9]. In addition to lead sulphate ($PbSO_4$), other compounds with similar structure are classified as white pigments base on lead sulphate – $PbSO_4 \cdot 4PbO$, $PbSO_4 \cdot 3PbO \cdot H_2O$, $PbSO_4 \cdot 3PbO$, $PbSO_4 \cdot 2PbO$ or $PbSO_4 \cdot PbO$ [10]. Lead sulphate is listed as C.I. Pigment white 3 and basic lead sulphate ($PbSO_4 \cdot PbO$) as C.I. Pigment white 2. In 1882, Joseph Benjamin Freeman patented a new pigment based on the mixture of lead sulphate and zinc white. In 1885, Freeman patented an improvement to the pigment consisting in the addition of barium sulphate [9, 11]. It was sold under different trade names; pure $PbSO_4$ was referred to as Fast White, Flemish white or Freeman's White Lead. However, similar names – Freeman's White or Freeman's White Lead – were also used for the combination of $PbSO_4$ and ZnO or $PbSO_4$, ZnO and $BaSO_4$ [9]. This pigment has been identified in only a few paintings, suggesting that it was far from common. Corbeil et al. investigated the use of this pigment in 55 artworks by Toronto-based painters from 1912 to 1943 [9]. The analysed artworks contained a combination of lead sulphate with zinc oxide. The authors of the study pointed out that this white pigment was identified exclusively in selected artworks dating to the limited period of 30 years. The supplier of the pigment has yet to be discovered. In 1924, a white pigment based on the mixture of lead sulphate with zinc oxide and barium sulphate was manufactured by the Forbes company. Nevertheless, this mixture was not identified in analysed artworks [12].

These white pigments give us an idea about the individual artists' practices. At the same, they can indicate an artwork's date of origin because they were used for a limited period of time. Although there were new pigments on the market, some artists were conservative and preferred materials they knew and had a good experience with. Moreover, different pigments were available in different countries. In art authentications, it is important to know which artist used which materials, a reflection of both personal preference and local availability. For this reason, we conducted a systematic investigation of artworks by prominent Czech painters active mainly in the first half of the 20th century, with part of the analysed artworks dating to the 1960s. We primarily employed non-invasive methods. Raman spectroscopy played an essential role because as a method of molecular analysis, it helps us distinguish structures with same chemical composition. Collected data will serve as a fundamental comparative material in the authentication process. Identification of the material that was not available in the expected time of the artwork's origin is clear evidence, that the work can't be original. Presence of pigment that was not used by the painter makes the artwork suspicious.

Experimental part

Almost one hundred paintings by Czech painters Josef Šíma, Josef Čapek, Jan Zrzavý, Václav Špála and Emil Filla dating from 1907 to 1968 were analysed as part of this study. The analysis was performed using non-invasive X-ray fluorescence analysis and Raman spectroscopy. Measured spots were documented via digital USB microscope.

Photomicrographic documentation

Photomicrographic documentation was performed using a digital USB microscope Dino-Lite Pro AM4113ZTFV2W, polarised visible and ultraviolet light (λ = 375nm), 1.3-megapixel, magnification 50× and 200×. The photographs were processed in the program DinoCapture 2.0 and Adobe Photoshop.

X-ray fluorescence analysis (XRF)

The X-ray fluorescence analysis was performed using a portable NITON XL3t GOLDD instrument with a mini-X-ray source using a silver anode with a maximum voltage of 50kV. Elements heavier than aluminium ($Z > 13$) were detected. An integrated large-volume silicon detector was used to determine the radiation emitted from the surface of the painting from an area with a minimum diameter of 3mm. The measured area was photographed with an integrated CCD camera. Each analysis took 120–140s. The measurements were taken without any direct contact with the artwork from a distance of no more than approximately 5 mm.

Non-invasive mobile Raman spectroscopy (RS)

A Bruker Bravo spectrometer was used for the mobile Raman spectroscopy. The instrument is equipped with a dual laser with suppressed fluorescence – Sequentially Shifted Excitation (SSE). The measurements were taken in a spectral range of 170(300)–3200cm^{-1} with a laser output < 100mW and spectral resolution of 10–12cm^{-1}. The measurements were taken from the surface of the artworks. The evaluation was performed using the Opus program. The spectra were compared with the spectral library of the Chemical-technological Laboratory of the National Gallery Prague.

Results and discussion

Titanium white

Elemental analysis is not sufficient for the distinction between the two structures of titanium white (TiO_2) – *anatase* and *rutile*, but they can be clearly identified via non-invasive Raman spectroscopy. Anatase is characterized by intensive Raman band at ~ 141cm^{-1} and other less intensive bands at ~ 393, 513 and 636cm^{-1} (Fig. 2).

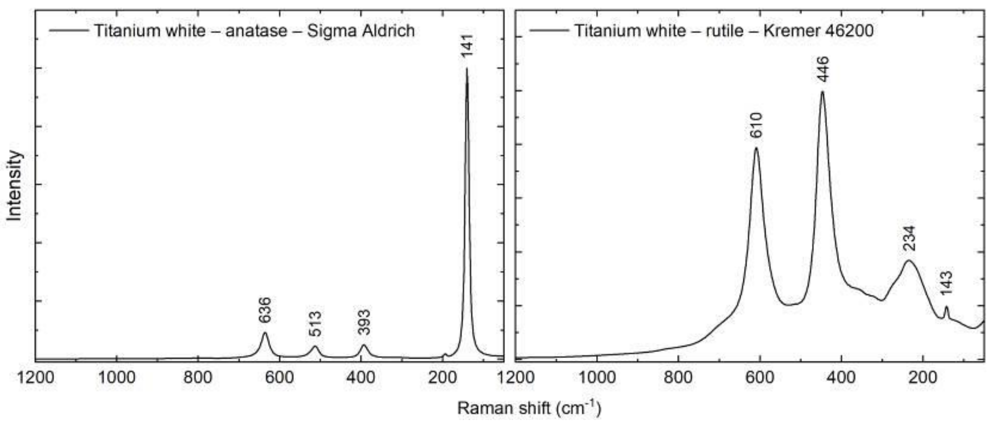

Fig. 2. Raman spectra of titanium white structures – anatase and rutile

Although the spectral range of the instrument used is limited on the side of shorter wavelengths (the measurement starts at 170cm^{-1}) and the main band is not displayed on the spectra, the other bands are clearly visible for unambiguous identification (Fig. 3). Rutile is characterized by intense bands at 234, 446 and 610cm^{-1}.

No titanium white was found in the paintings by Václav Špála created between 1923 and 1940. This may be caused by the painter's conservatism – he used the same art materials throughout his career. Other painters used titanium white to a limited extent (Fig. 4). The oldest artworks where anatase structure was identified were two paintings by Josef Čapek *Children in the garden* (1928, 44×50cm, oil on canvas, National Gallery Prague, inv. no. O 3451) and *Snowy Village* (1928, 45.5×52cm, oil on canvas, National Gallery Prague, inv. no. O 3775) from 1928. Its presence indicates that Czech painters were able to buy this new pigment just a few years after it was first produced.

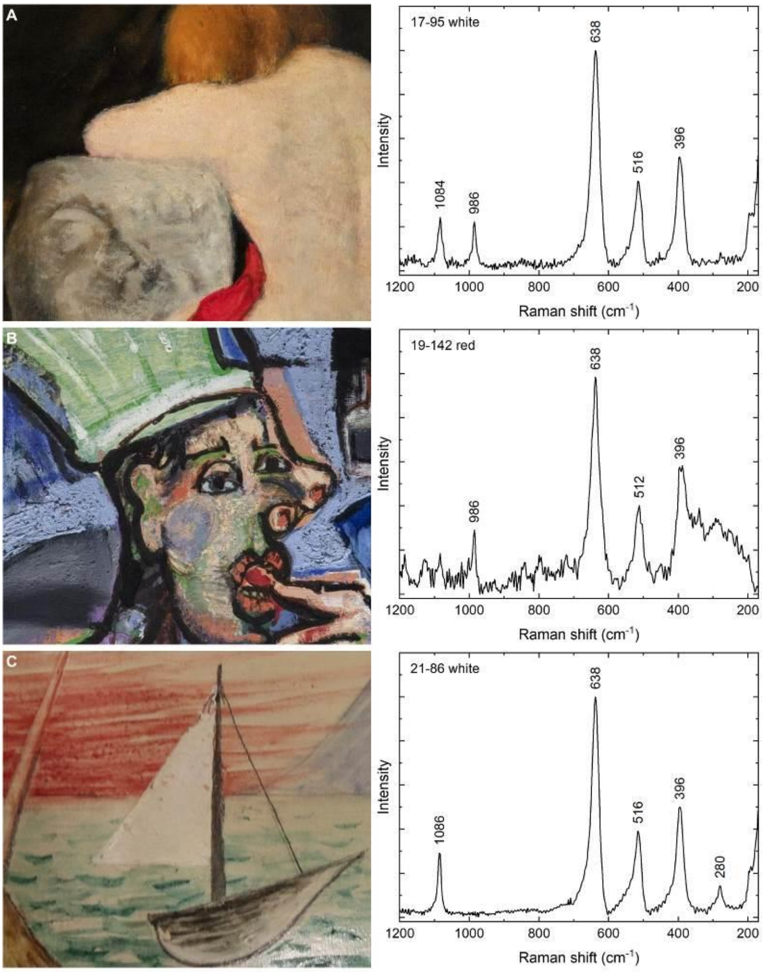

Fig. 3. Deatils of measured areas on the paintings where anatase was identified and corresponding Raman spectra: Josef Šíma, *Silent shadow* (A), Emil Filla, *Cook (Alchemist)* (B), Jan Zrzavý, *Ocean landscape* (C); besides anatase, calcium carbonate (characteristic bands ~1085 and 280cm^{-1}) was identified in paintings by Josef Šíma nad Jan Zrzavý and barium sulphate (characteristic band ~986cm^{-1}) in paintings by Josef Šíma and Emil Filla

This also corresponds with the pigment's presence in other artworks described in the professional literature, with *Shirt Front and Fork* by Jean (Hans) Arp (c. 1924, Australian National Gallery), *Yellow Hickory Leaves with Daisy* by Georgia O'Keeffe (1928, Stieglitz Collection, Art Institute of Chicago) and *Silver Sun* by Arthur Dove (1929, Stieglitz Collection, Art Institute of Chicago) being the earliest [3, 5]. In 1930s, no titanium white was identified in paintings by Josef Čapek. Nevertheless, anatase was presumably available in Czechoslovakia during this period, as it was identified in several paintings by Josef Šíma from 1933 to 1939 – *Sea* (1933, 65.5×90.5cm, oil on canvas, National Gallery Prague, inv. no. O 12931), *Reminiscence of Illiad* (1934, 58×120cm, oil on canvas, National Gallery Prague, inv. no. O 8522), *Silent shadow* (1936, 100×70cm, oil on canvas, National Gallery Prague, inv. no. O 17158) and *Landscape* (1939, 58.5×120.5cm, oil on canvas, National Gallery Prague, inv. no. O 5947). The number of analysed artworks from later periods was limited but in the 1940s, anatase was identified in painting *People of Deucalion* (1943, 60.5×81cm, oil on canvas, National Gallery Prague, inv. no. O 4031) by Josef Šíma but also those by Emil Filla – *Cook*

(Alchemist) (1948, 73×92cm, oil on canvas, National Gallery Prague, inv. no. O 13937) and *Still Life with fruit and bouquet* (1949, 33×41.5cm, oil on canvas, National Gallery Prague, inv. no. O 11503).

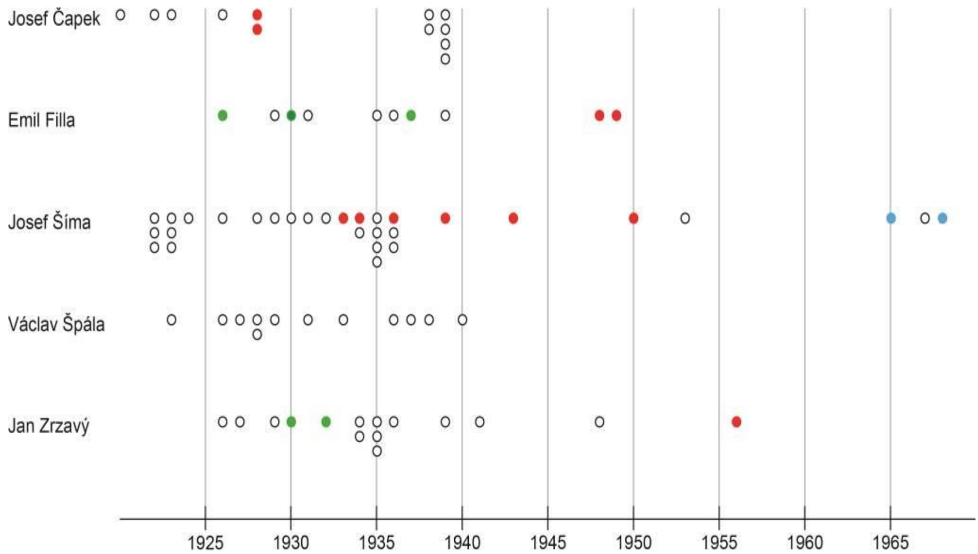

Fig. 4. Overview of analysed artworks; paintings containing anatase are marked in red, rutile in blue and lead sulphate in green

In 1950s, anatase was found in *Portrait of Božena Němcová* (1950, 100×81cm, oil on canvas, National Gallery Prague, inv. no. O 4546) by Josef Šíma and *Ocean landscape* (1956, 23.8×36.4cm, oil on canvas, National Gallery Prague, inv. no. O 15238) by Jan Zrzavý. Rutile has been identified in two painting by Josef Šíma – *Vista* (1965, 89×116cm, oil on canvas, National Gallery Prague, inv. no. O 12291, Fig. 5) and *Red Signal of Shadow* (1968, 60×73cm, oil on canvas, National Gallery Prague, inv. no. O 12292). This may be connected with the new manufacturing process that made the production cheaper and the pigment more available. Limited use of rutile was documented in paintings from 1948 [5], but it is possible that the pigment was not sold in Czechoslovakia in this period.

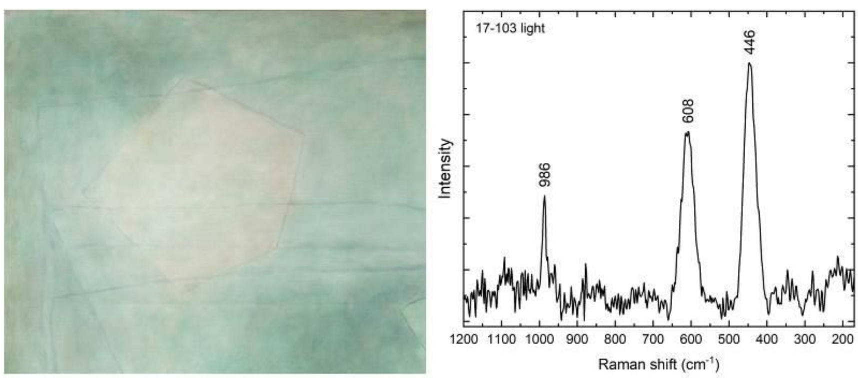

Fig. 5. Deatil of measured area on the painting by Josef Šíma, *Vista* where rutile and barium sulphate (Characteristic band ~986cm^{-1}) were identified and corresponding Raman spectrum

White pigments based on Lead sulphate

White pigments based on lead sulphate were another subject of inquiry. As stated in the introduction, there are several structures of lead sulphate pigments. Our investigation focused mainly on the pure lead sulphate ($PbSO_4$) or basic lead sulphate ($PbSO_4 \cdot PbO$) and their combination with zinc white (ZnO) or barium sulphate ($BaSO_4$). All these compounds can be distinguished by their Raman spectra (Fig. 6).

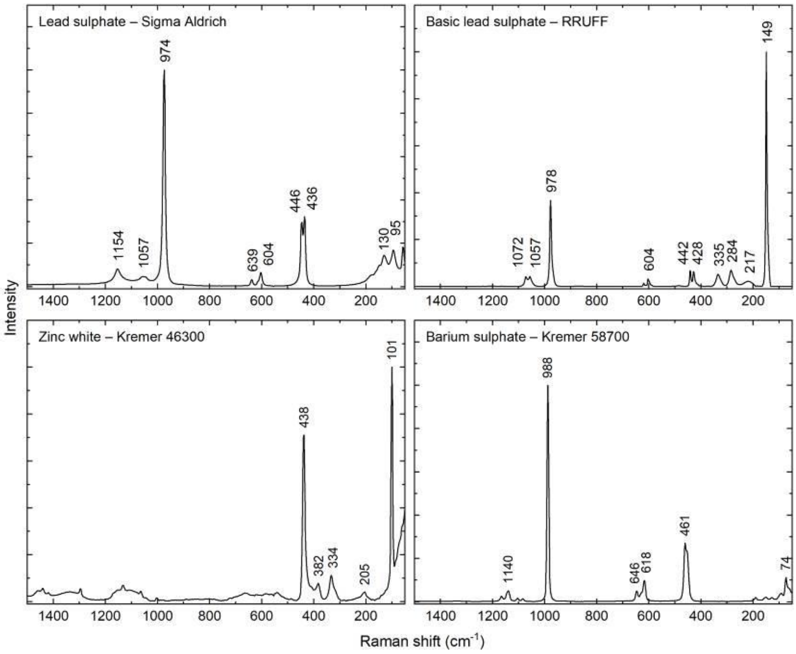

Fig. 6. Raman spectra of selected white pigments – lead sulphate, basic lead sulphate, zinc white and barium sulphate [13]

For lead sulphate, the most intensive characteristic band is at ~ 974cm^{-1}, less intensive bands at ~ 436 and 446cm^{-1} and minor bands at ~ 95, 130, 604, 639, 1057 and 1154cm^{-1}. Basic lead sulphate is characterized by main Raman bands at ~ 149 and ~ 978cm^{-1}. Mobile Raman spectrometer with spectral range from 170cm^{-1} does not allow to observe all the main bands, but the individual forms of lead sulphate can be distinguished based on bands between ~ 428–446cm^{-1} where there is a slight shift in the position for individual structures. Zinc white is characterized by intense band at ~ 438cm^{-1} and other bands at ~ 101, 205, 334, 382cm^{-1}. Barium sulphate can be identified based on the presence of intense band at ~ 988 cm^{-1} and less distinctive bands at ~ 74, 461, 618, 646 and 1140cm^{-1}. It was not always possible to identify all compounds of interest by means of non-invasive Raman spectroscopy. In some cases, zinc was identified using elemental X-ray fluorescence analysis, but Raman spectroscopy did not confirm the presence of zinc white due to the higher fluorescence in the measured area. It was relevant to observe the presence of zinc white and barium sulphate, as they were an integral part of some pigments based on lead sulphate. *Corbeil et al.* [9] points out that it is important to monitor the ratio of lead and zinc, because in commercially produced white pigments sold under the name Freeman's white, this ratio was constant. If the artist mixed lead sulphate with zinc white on the palette, the ratio would be variable.

In the Czech artworks examined, lead sulphate was primarily identified in paintings by Jan Zrzavý and Emil Filla from the period between 1920 and 1937 (Table 1). Almost all these paintings contain a combination of lead sulphate and zinc white. In paintings by Emil Filla, minor amount of barium was identified as well. Barium sulphate wasn't confirmed by Raman spectroscopy so the presence of other barium compounds cannot be excluded.

Table 1. Results of RS and XRF analysis from areas where lead sulphate was identified

Position	RS	Chemical formula	XRF
Jan Zrzavý, Port in Brittany (1930)			
blue sky	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Ca, Cr, Co, Sn (Al, Si)
	zinc white	ZnO	
	chalk	$CaCO_3$	
purple background	lead sulphate	$PbSO_4$	**Zn, Pb**, S, P, Ca, Co, As (Al)
	chalk	$CaCO_3$	
	cobalt violet light	$Co_3(AsO_4)_2$	
green-blue roof	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Ca, Cr (Al, Si)
	zinc white	ZnO	
	chalk	$CaCO_3$	
purple wall	lead sulphate	$PbSO_4$	**Zn, Pb**, S, P, Ca, Co, As (Al)
	chalk	$CaCO_3$	
pink house	lead sulphate	$PbSO_4$	**Zn, Pb**, S (Si, Ca)
	zinc white	ZnO	
green vegetation	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Ca, Cr
	chalk	$CaCO_3$	
blue boat	lead sulphate	$PbSO_4$	**Zn, Pb**, Al, S, Co, Sn (Ca)
	zinc white	ZnO	
white sail	lead sulphate	$PbSO_4$	**Zn, Pb**, S
	zinc white	ZnO	
purple house	lead sulphate	$PbSO_4$	-
	zinc white	ZnO	
dark purple house	lead sulphate	$PbSO_4$	-
	chalk	$CaCO_3$	
	cobalt violet dark	$Co_3(PO_4)_2$	
Jan Zrzavý, Thoulinguet (1932)			
white	lead sulphate	$PbSO_4$	**Zn, Pb**, S (Ca, Cr, Co, Sn)
	zinc white	ZnO	
grey terrain	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Ca, (Cr)
	zinc white	ZnO	
	chalk	$CaCO_3$	
Emil Filla, Still Life (1926)			
white blue	lead sulphate	$PbSO_4$	**Zn, Pb**, S, (P, Cl, Ca, Cr, Mn, Fe)
	zinc white	ZnO	
	Prussian blue	$Fe[Fe^{3+}Fe^{2+}(CN)_6]$	
	ultramarine	$Na_{8-10}Al_6Si_6O_{24}S_{2-4}$	
blue	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Cr, Co (Al, P, Cl, Ca, Fe, Ba)
	zinc white	ZnO	
	Prussian blue	$Fe[Fe^{3+}Fe^{2+}(CN)_6]$	
dark blue	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Cr, Co (Al, Ca)
	zinc white	ZnO	
	Prussian blue	$Fe[Fe^{3+}Fe^{2+}(CN)_6]$	
	vermilion	HgS	
white	lead sulphate	$PbSO_4$	**Zn, Pb**, S (P, Cl, Ca, Cr)
	zinc white	ZnO	
Emil Filla, Cellist (1930)			
white	lead sulphate	$PbSO_4$	**Zn, Pb**, S (Cl, Ca, Fe, Sr, Ba)
green	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Cr (Si, Cl, K, Ca, Ba)
blue	lead sulphate	$PbSO_4$	**Zn, Pb**, S, Co (Cl, Ca, Fe)
Emil Filla, White Night (1937)			
green background	lead sulphate	$PbSO_4$	**Zn, Pb**, S (Ca, Cr, Co, Cd, Ba)

Using Raman spectroscopy, only lead sulphate and no basic lead sulphate and other structures were found. Zinc white was sometimes only identified via XRF (Fig. 7).

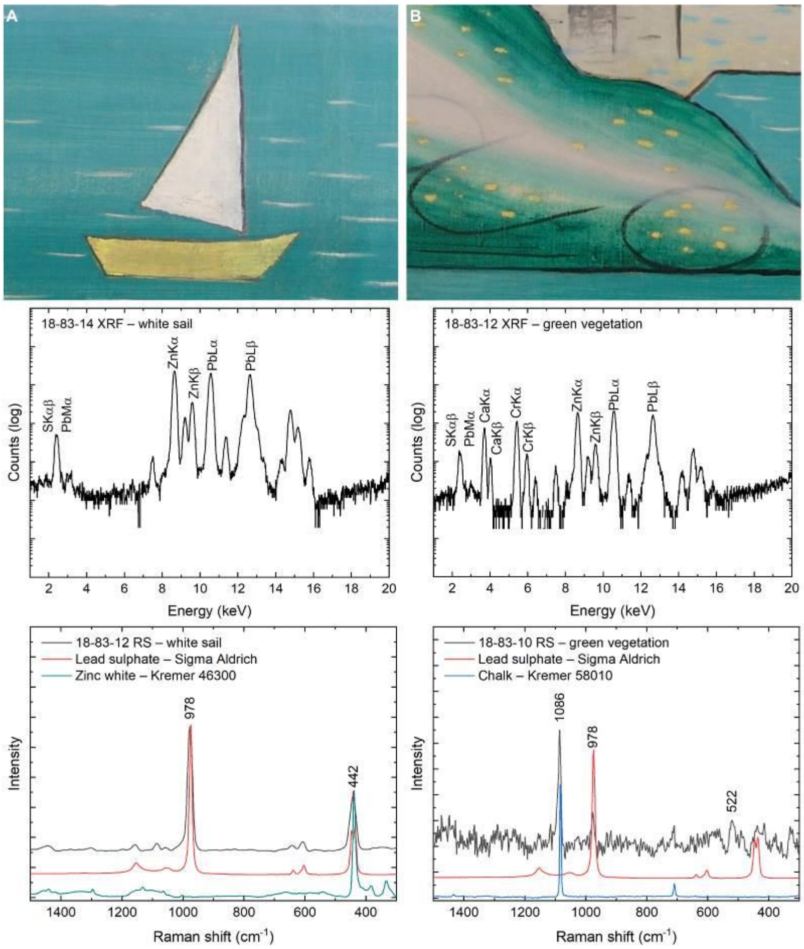

Fig. 7. Details of measured areas on the painting by Jan Zrzavý, *Thoulinguet* and corresponding XRF and Raman spectra

Lead sulphate with zinc white was confirmed in Jan Zrzavý's paintings *Port in Brittany* (1930, 60.5×92.5cm, oil on canvas, National Gallery Prague, inv. no. O 9370) and *Thoulinguet* (1932, 66×101cm, oil on canvas, National Gallery Prague, inv. no. O 13491). In the case of the former, the pigment was identified in almost all the analysed areas throughout the painting. It is therefore possible, that it was used as a basic white pigment and mixed with other colour pigments applied in paint layers. The combination of lead sulphate and zinc white was also found in Emil Filla's *Still Life* (1926, 65×75cm, oil on canvas, National Gallery Prague, inv. no. O 8370), *Cellist* (1930, 145.5×97.5cm, oil on canvas, National Gallery Prague, inv. no. O 11494; Fig. 8) and *White night* (1937, 114×146.5cm, oil on canvas, National Gallery Prague, inv. no. O 9627). The ratio of lead and zinc was not calculated due to the presence of other lead-based pigments in the analysed areas (e.g. lead white – 2 $PbCO_3 \cdot Pb(OH)_2$ or red lead – Pb_3O_4). Moreover, the non-invasive analysis does not show in which layer the individual pigment is present, and so it is possible that pure zinc white was used in another paint layer. For all these reasons, the calculated ratio may be misleading.

All the paintings in which lead sulphate was identified were created predominantly in the 1930s. Because zinc white was also detected in the same paintings, we may assume that the artists used commercially produced Freeman's White (mixture of lead sulphate and zinc white).

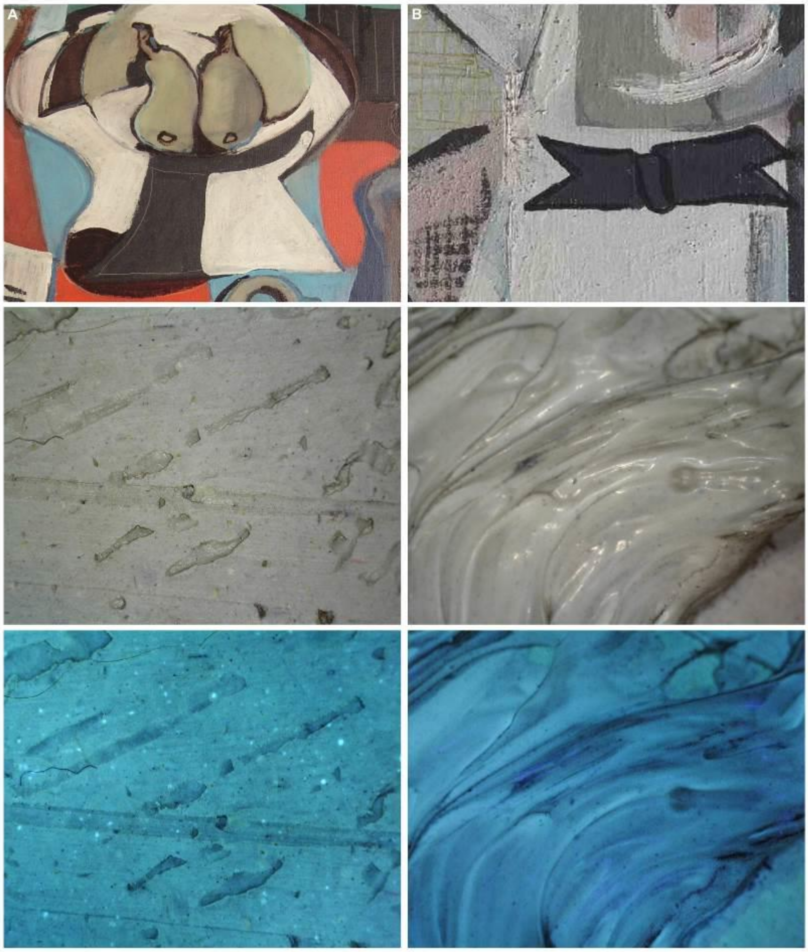

Fig. 8. Details of paintings by Emil Filla and photomicrographs in VIS and UV light of areas where lead sulphate with zinc white were identified: *Still Life* (A), *Cellist* (B)

Only small amount of barium was identified in several paintings. The use of the improved variety of Freeman's white is therefore unlikely. As part of the following survey, micro-samples will be taken from areas of interest to determine the location of different white pigments within the individual paint layers. We will also monitor the presence of other structures of white pigments based on lead sulphate. The ratio of individual components will be calculated to assess whether the painters used Freeman's white or mixed the pigments on the palette.

Conclusions

As part of the extensive scientific examination of artworks by prominent Czech painters active mainly in the first half of the 20th century, titanium white with anatase structure in several paintings from the period between 1928 and 1956 was identified. Collected data showed that this pigment was available in Czechoslovakia from the end of the 1920s onward and artists still used in the 1950s. The research also shed light on the individual artists' preferred practices. Some of these artists used the white pigment shortly after it was introduced on the market, while others did not embrace it until the 1940s or 1950s. None of the painters used titanium white as their only white pigment; lead white and zinc white were also popular during this period. Rutile was detected in two paintings from 1965 and 1968; it was not present in any of the earlier paintings.

White pigments based on lead sulphate were relatively rare. They were identified exclusively in paintings from the 1920s and 1930s. For this reason, they may serve as a marker for authentication of artworks from this period. To confirm this premise, more artworks by different artists from this period will be analysed during the follow-up investigation. The research will also be extended to include the analysis on micro-samples, helping us to better assess the presence and quantity of pigments in individual paint layers. Acquired data concerning the use of lead sulphate pigments in Czech paintings are in correspondence with previously published studies.

The results obtained from this investigation give an overview of how and when Czech painters used both forms of titanium white and white pigments based on lead sulphate. This may serve as an essential comparative material during the art authentication process. The research will be further extended to include works by other painters active predominantly in the period between the 1920s and 1960s.

Acknowledgments

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