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Technical examination, material characterization, and restoration of the landscape painting by Mıgırdiç Givanian (1848-1906)

Pintura de paisagem de Mıgırdiç Givanian (1848-1906): exame técnico, caraterização do material e restauro

SELEN SERTAB KAYSER[1,2]
ÖZDEN ORMANCI [3*]
OĞUZ EMRE KAYSER [2,3]

1. Mimar Sinan Fine Arts University, Department of Conservation and Restoration of Artworks, Cumhuriyet Mahallesi Silahşör Caddesi No:71, Bomonti/Şişli, 34380 İstanbul, Turkey

2. Ankara Hacı Bayram Veli University, Conservation of Cultural Property PhD Program, Ankara, Turkey

3. Mimar Sinan Fine Arts University, Department of Conservation and Restoration of Cultural Property, Cumhuriyet Mahallesi Silahşör Caddesi No:71, Bomonti/Şişli, 34380 İstanbul, Turkey

ozden.ormanci@msgsu.edu.tr

Abstract

This study presents the documentation, technical examinations, material characterization, and restoration work of an oil painting on a metal plate signed by Mıgırdiç Givanian. The painting was analyzed with visible, ultraviolet and oblique light, optical microscopy, X-ray, Raman and micro-X-Ray fluorescence spectrometry. Optical microscopy provided insights into the painting technique and deteriorations. It was determined that the artist used an iron-based metal plate and pigments including lead white, calcite, vermilion, Prussian blue, hematite, carbon black, and gypsum, which were identified through Raman analysis. The XRF analysis suggested the possibility of a copper-based green pigment, lead-tin yellow, and chrome yellow. During the restoration phase, the yellowed varnish layer on the surface was cleaned, and the localized retouches on the painting surface, were removed. As a finishing application, the surface was re-varnished and retouched. This study is significant as it represents the first comprehensive work conducted on a painting signed by Givanian.

KEYWORDS
Givanian
Conservation of oil paintings
Paintings on metal support
Raman Spectroscopy
μ-XRF

Resumo

Este estudo apresenta a documentação, a caraterização dos materiais e o trabalho de restauro realizado a uma pintura a óleo sobre placa metálica, assinada por Mıgırdiç Givanian. Utilizou-se luz visível, ultravioleta e oblíqua, microscopia ótica, raios X, espetroscopia de Raman e fluorescência de micro raios X. A microscopia ótica permitiu conhecer a técnica de pintura e as deteriorações. Determinou-se, por Raman, o uso de uma placa metálica (ferro) e pigmentos, incluindo branco de chumbo, calcite, vermelhão, azul da Prússia, hematite, negro de fumo e gesso. A análise XRF sugeriu a possibilidade de um pigmento verde à base de cobre, amarelo de chumbo-estanho e amarelo de crómio. o restauro, limpou-se a da camada de verniz amarelecida da superfície e removeram-se os retoques localizados na superfície da pintura. Como acabamento, a superfície foi envernizada e retocada. Este estudo é significativo, pois representa o primeiro trabalho exaustivo efetuado sobre uma pintura assinada por Givanian.

PALAVRAS-CHAVE
Givanian
Conservação de pinturas a óleo
Pinturas em suporte metálico
Espectroscopia Raman
μ-XRF

Introduction

Mıgırdiç Givanian (Mıgırdiç Civanyan, Megerdich Jivanian)

Mıgırdiç Givanian was born in 1848 in Istanbul, Beşiktaş. His father, Hovhannes, was a respected violinist who served as a court musician during the reign of Sultan Abdülmecid. He attended elementary school at an Armenian school in Beşiktaş, where he received lessons in painting from the artist Apraham Sakayan [1]. During his early years, Mıgırdiç Givanian worked on stage set design for the theater company of the renowned playwright Hovannes Kasparyan. Between 1860 and 1870, Armenian architects, mainly the Balyan family, constructed buildings along the shores of the Bosphorus, and foreign painters were commissioned for the interior decorations of these structures. Mıgırdiç Givanian collaborated with these painters, contributing to the interior decorations of Beylerbeyi and Çırağan Palaces [1]. In 1874, Mıgırdiç Givanian took lessons at the studio of the French painter Pierre Desire Guillement located on Hammalbaşı Street in Beyoğlu [2]. He traveled to Italy and received painting education there between 1876 and 1879 [3].

Mıgırdiç Givanian not only gained renown as a painter but also became famous for his stage decorations. He created numerous set designs for the Ottoman Theatre, which was owned by Güllü Agop in Samatya. Additionally, he worked on the set decorations for Sotiraki's Grand Theatre in Galata [2].

Due to insufficient financial means to rent a gallery and organize exhibitions, Givanian often exhibited his paintings by hanging them on the walls in the streets, making sales in this unconventional way. He particularly displayed his works on walls around the Ottoman Bank in Galata or in places where hotels frequented by Russians were located, conducting sales in these areas [1].

The artist, who predominantly incorporated Istanbul themes into his paintings, depicted scenes of the Bosphorus and the Golden Horn. It is known that in his sky and sea-themed paintings, he drew inspiration from the renowned painter Ayvazovski [3]. Givanian met Ayvazovski during the latter's visit to Istanbul in 1874. Ayvazovski advised Givanian regarding paintings reminiscent of his own, saying, "Sign your canvases featuring seascapes as Ayvazovski; at least then you'll have the opportunity to sell them for a higher price" [1]. Nevertheless, Givanian consistently signed and sold his paintings with his own signature.

Due to the Armenian events that began in Anatolia during the reign of Abdulhamid II, Givanian had to migrate to Odessa in 1894. He lived in Russia for a total of 11 years, spending seven years in Odessa with his family and four years in St. Petersburg. The artist returned to Istanbul in 1905 but sadly passed away there in 1906 [1].

The use of metal plates as supports in paintings

The technique of painting on a metal plate support surface was commonly preferred from the mid-16th century to the late seventeenth century [4]. Especially in the Netherlands and Italy, copper was extensively used by artists for this technique during the mentioned period [5]. Examples of using metal as a support can be observed in Italy in the sixteenth century. Vasari recorded that Sebastiano del Piombo created approximately 1530 paintings on supports made of lead, silver, and copper. The technique was quickly adopted by Northern European artists in Rome and Bologna. Subsequently, it became a widely accepted technique throughout almost all of Europe [6]. The development of the engraving technique in the sixteenth century may have played a significant role in its spread, as it facilitated easier access to copper plates [5].

The rigid and smooth surface of the metal allows brushstrokes to become nearly invisible, enabling artists to work on finer details and achieve more luminous paintings [6]. Artists such as Rubens, Jan Brueghel I, Rembrandt, Diego Velasquez, Hals, Elsheimer, the Carracci, Guercino, Guido Reni, and Claude created paintings on copper in the seventeenth century [7-8]. Jan Brueghel the Elder created nearly 165 paintings on copper [6]. There are more than 2,000 works created on metal plates, with 500 of them in the collection of the Galleria degli Uffizi in Florence. These works are housed in museums across Europe and America [7].

Before the surface was used for painting, some preliminary processes were necessary. Some of these procedures included rubbing the plates with garlic to remove excess oil or roughening the surface to enhance paint adhesion. Eighteenth-century sources indicate that these processes were sometimes applied by hand [5, 8-9]. Many copper plate paintings feature a ground layer composed of lead white or earth pigments mixed with linseed oil [10]. However, there are paintings where the natural color of the copper plate is incorporated as part of the artwork, and therefore, no ground layer is applied [5].

Surfaces obtained from metal plates are not absorbent. Despite the thin paint layer, the lack of oil absorption allows the colors to retain their saturation. When combined with the smoothness of the surface, this characteristic results in vibrant and glossy paintings [11].

Tin or tin-coated iron, silver, zinc, aluminum, and steel have also been used as support surfaces in painting [8].

In paintings on metal plates, it is not possible to investigate the stratigraphy of the painting. The presence of metal on the support surface hinders the ability to conduct destructive analysis. Hence, it is vital to utilize non-destructive analytical techniques in the examination of the artwork [7].

This study focuses on the investigation and restoration of Givanian's landscape painting, as well as the identification of the plate used as a support and the pigments used in the painting. The oil painting signed "Givanian" is created on a metal plate measuring 51.5 × 36.0 cm (Figure 1). The date of creation of the artwork, which is currently housed in a private collection, is not specified.

a b

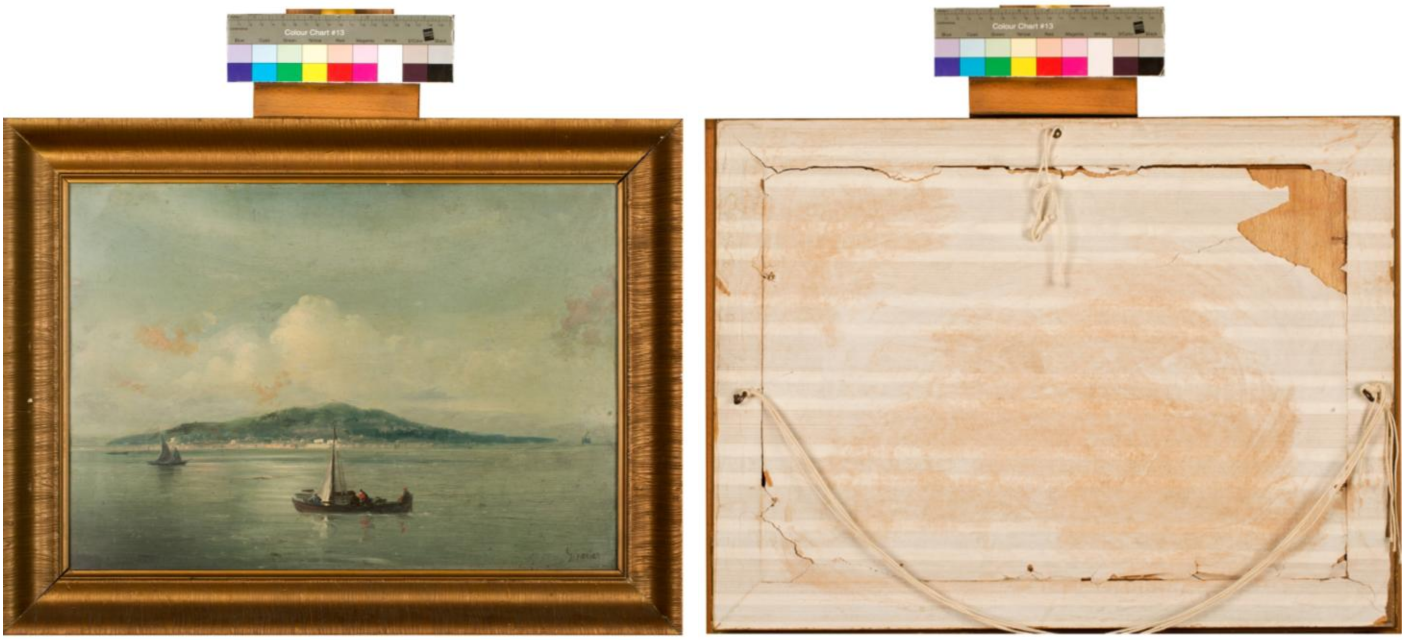

Figure 1. Givanian's landscape painting: *a)* front and *b)* back surface photographs taken under visible light of the painting (f/18, 1/160).

Analytical techniques

Visible light photography

All photographs were taken with Canon EOS 5D Mark III camera under a high-intensity LED light source equipped with 98 white LEDs (5000K) and 8 UV LEDs.

Microscopy

Microscopy examinations were performed with a Zeiss Microsystems Opmi Pico Camera microscope and processed using Zeiss ZEN imaging software.

Ultraviolet light (UV)

The UV lamp we used is a standalone lamp, specifically the CTS Art Lux 5L/5LW.

X-ray analysis

X-ray images were acquired using a Radiolight apparatus (GILARDONI, Italy) with the current set to 3 mA and the voltage adjusted to 50–55 kV.

Raman spectroscopy

The Raman microscopy observations were conducted using a Bruker SENTERRA Dispersive Raman spectrometer. The investigation utilized 20× magnification objectives to precisely direct the 785 nm laser beam onto the samples. The laser power used for irradiation, ranging from 1 to 50 mW, and the duration of exposure were modified during the course of the investigation. The analysis was conducted directly on the painting, utilizing a TE-cooled CCD detector to record the signals.

Micro-X-ray fluorescence spectroscopy (μ-XRF)

The elemental characterization of the metal plate was conducted. In cases where additional support was required for Raman analysis, supplementary XRF analyses were also performed. The analyses were performed using a Bruker ARTAX micro-X-Ray Fluorescence spectrometer (μXRF) equipped with a molybdenum source. The spectrometer operated with an electric accelerating potential of 40 kV and a current of 600 μA. The video camera, along with the motorized X-Y-Z stage, facilitated the process of focusing and searching for specific points of interest.

Painting characterization

Throught visible light it was possible to verify that the metal plate is backed by a wooden support. The reverse side of the painting is entirely covered with paper. There are visible retouches indicating color changes on the surface. Areas with extensive retouching can also be perceived under visible light (Figure 1). Additionally, dark-colored pinpoint formations have been observed on the paint layer. The artist's signature is in the lower right corner of the painting (Figure 2a).

Detail photographs were taken to examine the dark-colored pinpoint formations on the surface of the artwork (Figure 2a-d). Inspection revealed that these were not dirt deposits, but rather deteriorations resulting from metal corrosion on the oil paint surface.

The areas exhibiting color change were examined under a digital microscope. Microscopic images of these areas are shown in Figure 3. During the restoration process, the support metal plate was detached from the wooden plate it was adhered to in order to address surface deformations. The microscopic image of the corrosion observed on the reverse side is presented in Figure 3e-f. The paint layer was also examined with an optical microscope. As a result of the examinations, it was determined that the colors were mixed with each other

(Figure 4a-b). Looking at the microscope images of the support plate in Figure 4c-d, traces of etching can be seen on the ground. It is thought that this is due to a technique used in metal plate paintings to increase the adhesion of the paint to the surface.

Figure 2. Detail of: *a)* signature of the painter; *b-d)* deteriorated areas.

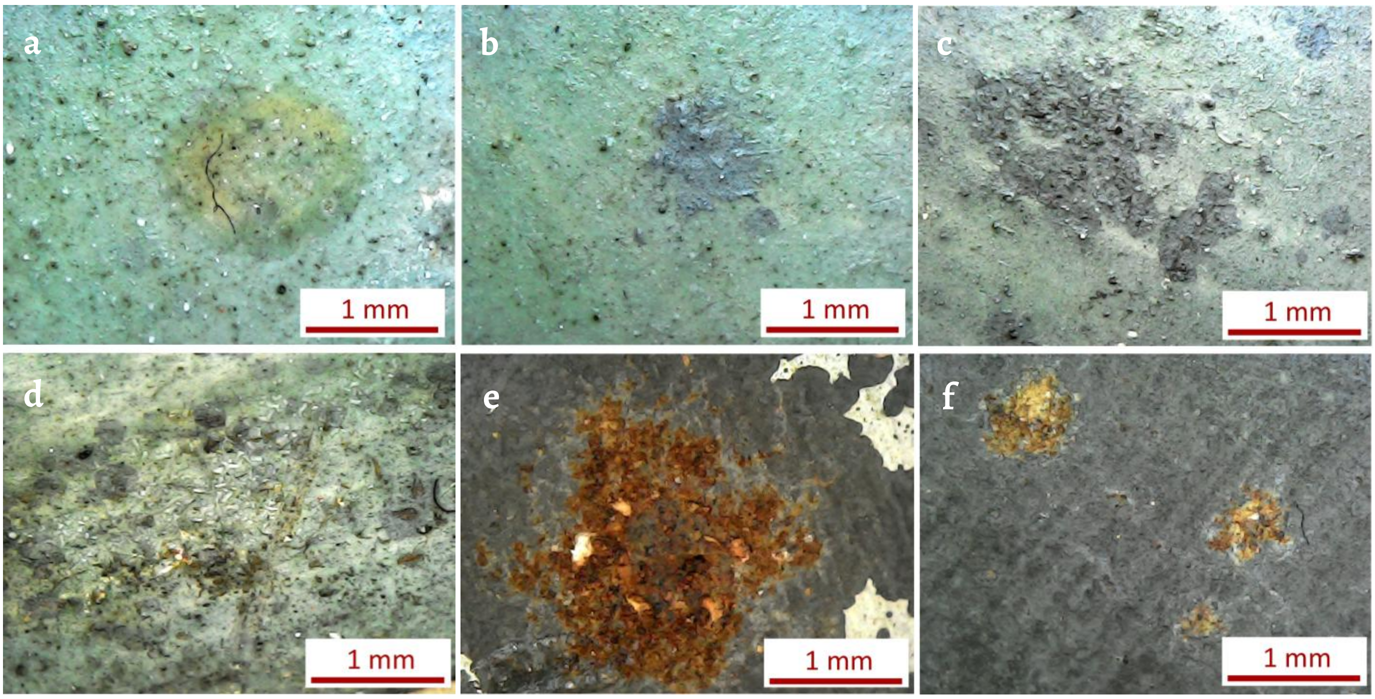

Figure 3. Corrosion observed on the metal surface: *a-d)* frontal views; *e-f)* back surface views.

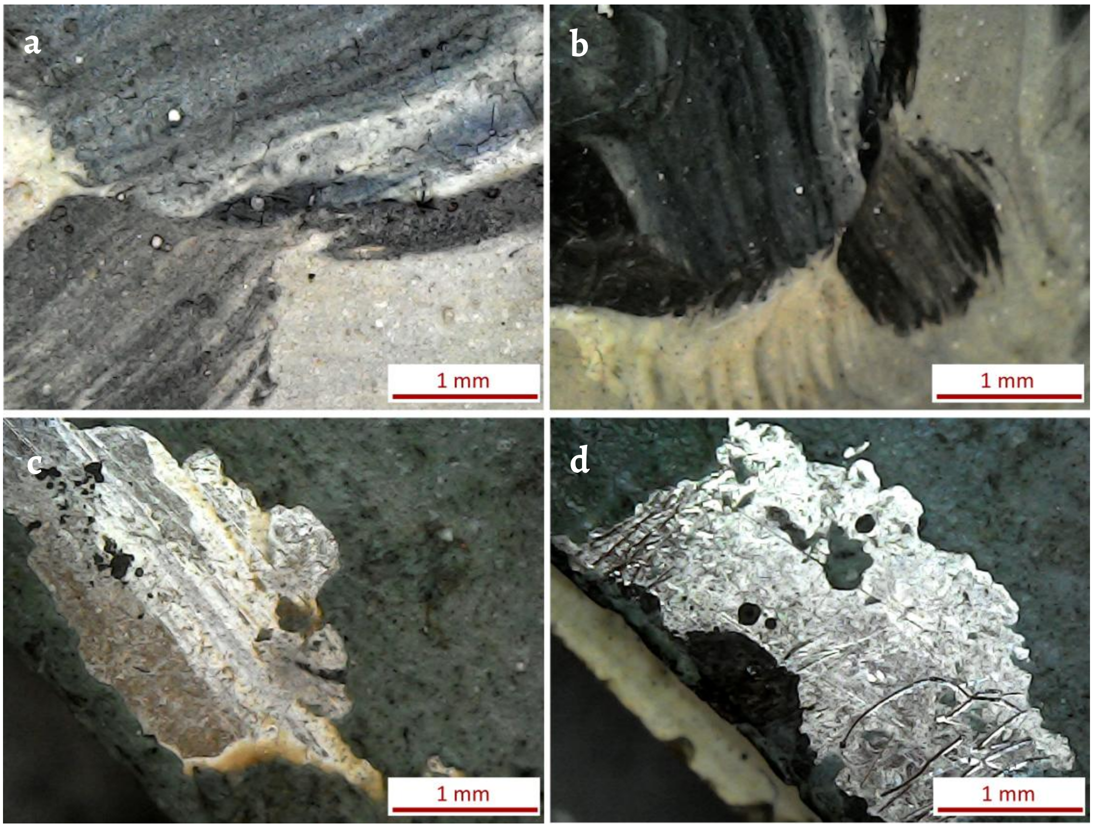

Figure 4. Optical microscopy of the: *a-b)* paint layer; *c-d)* metal plate seen on the surface when the wooden frame is removed.

Figure 5. Painting under ultraviolet light.

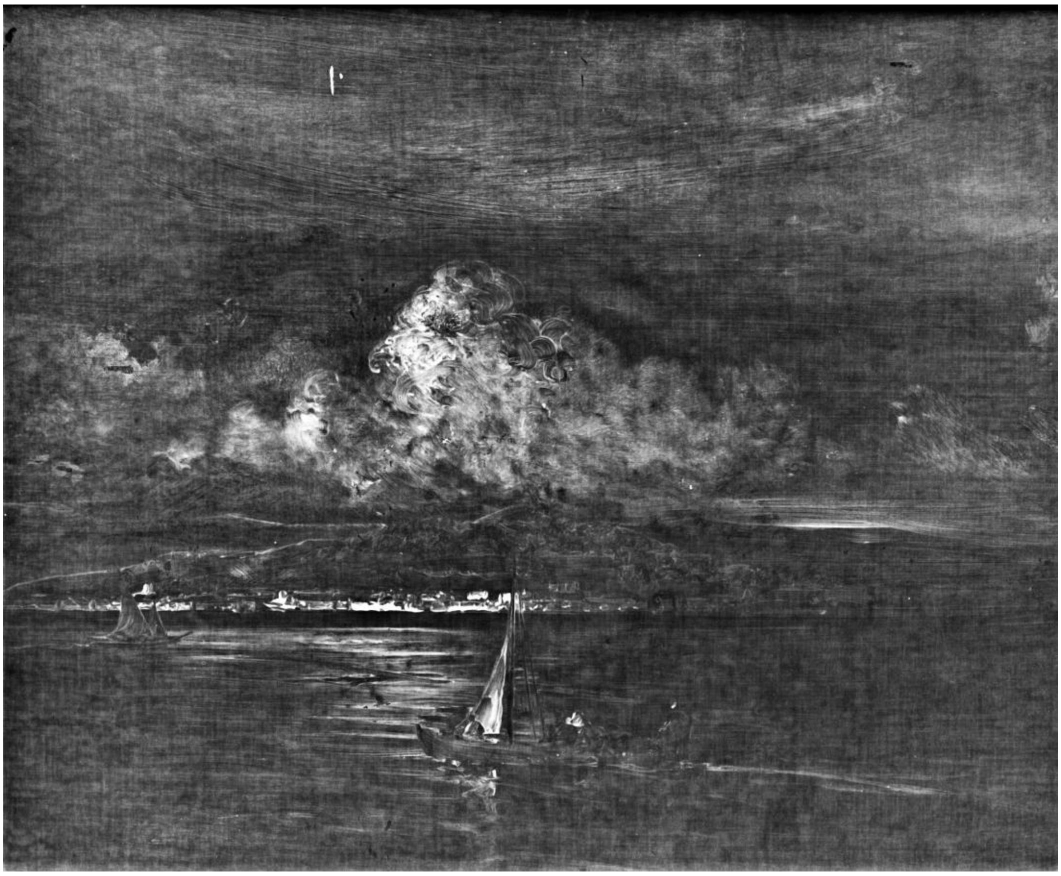

Figure 6. Painting under X-ray radiation.

When the painting is analyzed under ultraviolet (UV) light, it is thought that the layer giving green reflection to the surface is the varnish layer (Figure 5). In addition, when viewed under UV light, irregular brushstrokes and retouching areas can be seen on the paint layer. The large dark-colored area on the right edge and the small dark-colored areas scattered throughout the painting indicate previously retouched areas.

As it is well known, high-Z elements exhibit more secondary electron emission than low-Z elements when exposed to high-energy x-rays [12-13]. Pigments that contain elements with high atomic numbers, such as lead, exhibit strong x-ray absorption properties, effectively blocking the passage of x-rays through the painting. Hence, pigments that contain lead would exhibit a white appearance on the produced radiograph. Conversely, numerous other pigments, particularly those containing elements with low atomic numbers, such as carbon, are highly transparent to x-rays [14]. Therefore, it is possible to say that lead white was used in almost the entire painted area, as seen in Figure 6.

The XRF analyses conducted on the metal plate, the support of the painting, revealed the presence of Fe, Sn, and Pb (Figure 7).

The XRF study revealed Pb signals at every analyzed point, strongly indicating that the artist likely used lead white (composed of $2PbCO_3{\cdot}Pb(OH)_2$) as the ground layer. This conclusion is based on the consistent detection of lead signals across various locations of the painted surface, suggesting the intentional application of this pigment. Lead white, which was one of the most prominent white pigments used beginning with the Roman period and continuing beyond, was frequently used in paintings as a preparative layer or base [15]. In addition, it was commonly utilized for the purpose of producing opacity in the body color in order to provide further brilliance to other colors. This method is a characteristic that is present in a great number of impressionist works. In addition, this pigment was frequently utilized in order to significantly improve the drying capabilities of paintings [15].

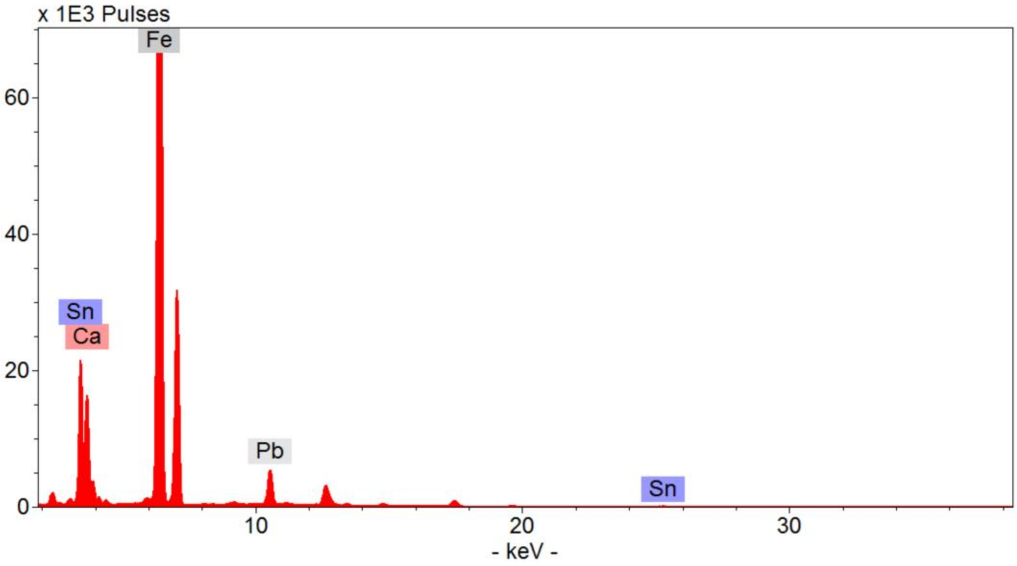

Figure 7. XRF spectrum of the metal plate.

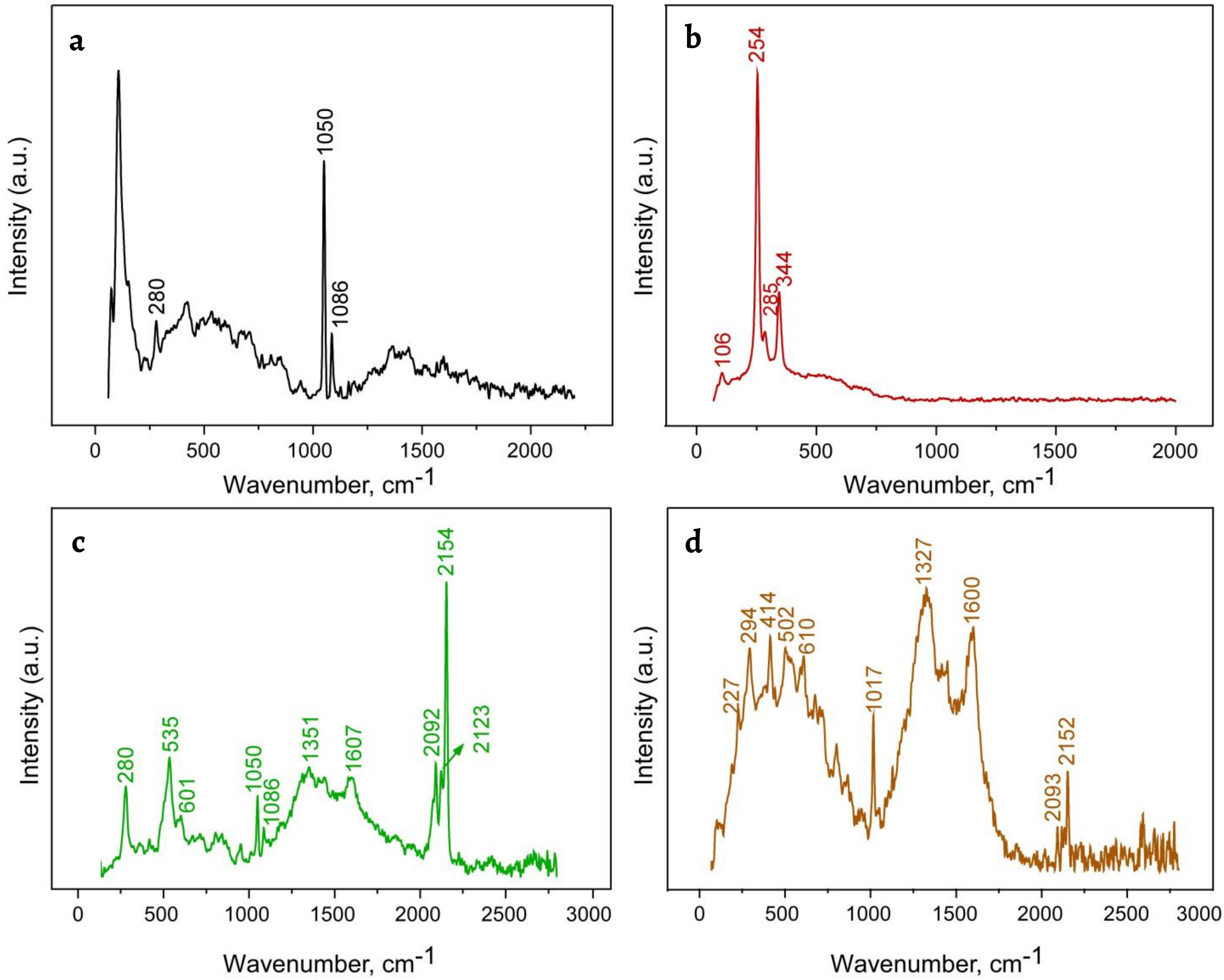

Figure 8. Raman spectra of the paints: *a)* white; *b)* red; *c)* green; *d)* brown.

The analysis was conducted on the white particles found on the white clouds and the sails of the boat, revealing the presence of two substances: calcium carbonate and lead white, identified respectively by the Raman bands (Figure 8a) at 280 (weak – w) and 1086 (medium – m) cm^{-1} for calcium carbonate [16] and 1050 cm^{-1} (very strong – vs) for lead white [17].

In the red paint of the human figures on the boat as well as in the reflected shadow of the boat on the water, cinnabar was characterized by distinct bands at 254 (vs), 285 (shoulder – sh), and 344 (m) cm^{-1}, as seen in Figure 8b [18-20]. Cinnabar is a mineral composed of mercury (II) sulfide (HgS), which has a soft red color. However, it is common for impurities such as bitumen and clay particles to be found in cinnabar [21]. Cinnabar, in its natural state, has been employed as a coloring agent since ancient times, while vermilion, the artificial variant, has been recognized since the eighth century [22]. In the nineteenth century, both vermilion and cinnabar were accessible, allowing Givanian to potentially utilize either one or both of these substances. However, the absence of any impurity-related constituent in the XRF study indicates that the pigment employed is most probably vermilion.

Prussian blue was identified using micro-Raman spectroscopy of the blue and dark green brushstrokes, with Raman bands at 280 (m), 2092 (m), 2123 (sh), and 2155 (vs) cm^{-1} as shown in Figure 8c [23-27]. This suggests Givanian used a pigment combination to obtain the dark green color tone. Although no pigments were found in the Raman analyses that would produce a green color when mixed with blue, the XRF analysis conducted specifically on the green area detected Pb and Sn elements, suggesting the possible presence of lead-tin yellow, while the Cr peak indicates the potential presence of chrome yellow (Table 1). Additionally, the detection of a Cu peak suggests that a copper-based pigment might have been added to the mixture to achieve the green tone. These interpretations are based on the detected elements, and the exact composition cannot be confirmed definitively. Alongside these pigments, lead white (1050 cm^{-1}) [17], calcite [16] (1086 cm^{-1}), and amorphous carbon (1351, 1607 cm^{-1}) [28-31] were detected in the Raman spectrum of the green color (Figure 8c).

Raman analysis of the dark brown lines on the boat figure revealed a blend of pigments. This mixture involves combining hematite (α-Fe_2O_3) with a carbon-based black pigment to achieve the desired brown hue. The distinctive bands observed at 227, 294, 414, 502, and 610 cm^{-1} in the Raman spectrum (Figure 8d) indicate the presence of hematite [31-33]. Meanwhile, the bands at 1318 and 1601 cm^{-1} are associated with the carbon-based black pigment [28-31]. Additionally, the strong peak observed at 1017 cm^{-1} corresponds to $\nu 1$ symmetric stretch vibrational modes of SO_4 tetrahedra in anhydrite (calcium sulfate, $CaSO_4$), the dehydrated form of gypsum [34-35]. The peaks at 2093 and 2152 cm^{-1}, on the other hand, are attributed to Prussian blue, which is thought to originate from the blue pigment utilized in depicting the sea [20-21].

Table 1. Characterization of the pigments (Raman and XRF results) by color and associated literature is provided.

Color	Raman (cm^{-1})	µ-XRF	References
White	Calcite ($CaCO_3$): 280, 1086 (ν_1CO_3) Lead White ($2PbCO_3{\cdot}Pb(OH)_2$): 1050 (ν_sCO_3)	-	[16-17]
Red	Vermilion (HgS): 254, 285 (δS−Hg−S), 344 (ν_s(Hg−S))	Hg, Pb, S, Ca	[18-20]
Brown	Hematite (Fe_2O_3): 227 (ν_sFeO), 294, 414, 610 (δ_sFeO) Carbon Black: 1327 (νC-C), 1600 (C=C) Gypsum ($CaSO_4$): 1017 (ν_sSO_4), Prussian Blue ($Fe_4[Fe(CN)_6]_3$): 2093, 2152 (νC≡N)	-	[23-35]
Blue	Prussian Blue: 280 (Fe-CN-Fe), 2092, 2123, 2155 (νC≡N)	-	[23-27]
Green	Prussian Blue: 280, 2092, 2123, 2154 Carbon Black: 1351, 1607 Calcite: 1086 Lead White: 1050	Pb, Fe, Ca, Sn, Cr	[16-17, 23-31]
Black (signature)	Carbon Black: 1351, 1578 Lead White: 1052	-	[17, 28-31]

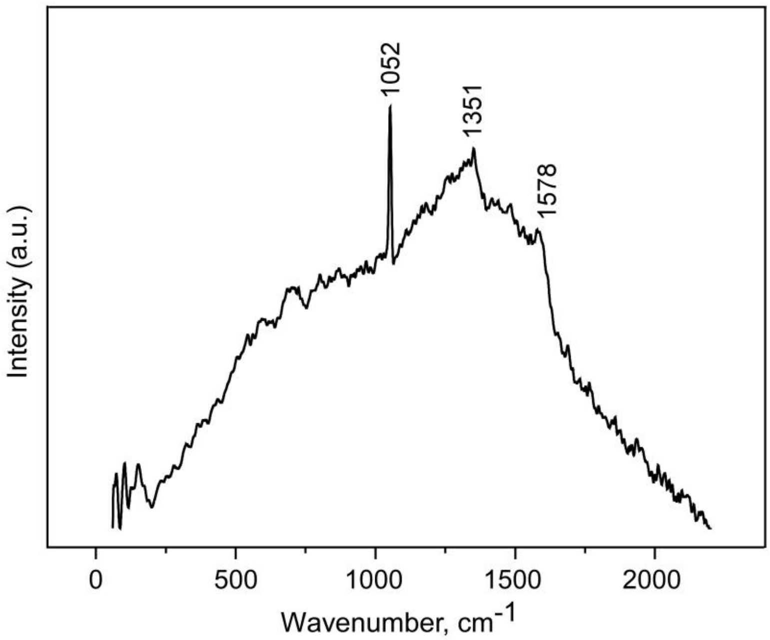

Figure 9. Raman spectrum of the signature.

Regarding the pigments used in the artist's signature, the peaks observed at 1351 and 1578 cm^{-1} in the Raman spectrum (Figure 9) indicate the presence of carbon black pigment [28-31]. Additionally, the peak at 1052 cm^{-1}, signifying lead white, has also been identified, as seen consistently across almost all spectra [17].

Painting restoration

Before starting cleaning on the paint layer, tests were carried out to determine the solubility. Firstly, Triammonium Citrate (TAC) 0.2, 0.5 and 1 % were cleaned in different color areas in order to remove dirt deposits, but no result was obtained. Therefore, varnish cleaning was started and Cremonesi test was used for this application. The Cremonesi test is a cleaning test based on mixtures of ligroin-acetone and ligroin-ethanol in different ratios. It is obtained by adding the polar solvent to the non-polar solvent in an increasing ratio to increase the polarity of the solvent mixture. It has a wide solubility area. It helps to determine the solubility level of varnish and overpaintings on the surface and to measure the resistance and sensitivity of the paint on the substrate to the solvent to be used [8]. As a result of the tests, it was decided to clean the varnish layer on the painting surface with LA6 (40 % Ligroin and 60 % acetone mixture) in the Cremonesi test.

As a result of examinations under visible light and UV light, it was determined that the pink area was retouched (Figure 1). In addition, the solubility parameters, observed during the cleaning applications, showed that it was oil paint. In the parameters where the retouching became soluble, the original oil paint was also dissolved. Because the retouch was not removed from the surface in order not to damage the original layer, it was retouched with chromatic selection technique with retouching paints (Maimeri Restauro varnish colors) over varnish. In the chromatic selection technique, the colors used in the palette are used in pure form without mixing with each other and the colors are applied in lines. In this way, when colors come side by side, they create an illusion of perception with the effect of vibration, making the color appear as a whole. While it is possible to see the colors applied in lines individually when viewed up close, they create a unity with the painting surface without being noticed from a distance [36]. The aim of the technique is to create a recognizable boundary between the artist and the restorer by respecting the work of art.

Figure 10. The final state of the artwork, following the restoration process: *a)* front and *b)* back.

The pink-colored clouds on the left side of the painting are thought to be retouching (Figure 10). However, the retouched areas show a dark reflection under ultraviolet light. Since no dark reflection was observed when the areas with clouds were examined under ultraviolet light (Figure 5), it was decided that this area was not retouched.

The final state of the artwork, following the restoration process, is shown in Figure 10.

Conclusion

The study included the technical evaluation, material characterization, and restoration of Mıgırdiç Givanian's landscape painting, which was created using the oil painting technique on a metal plate.

In this context, photographs were taken under visible light, oblique light, and UV light, which revealed the varnish layer and retouches. OM examinations determined that the observed deteriorations in the painting were caused by metal corrosion, that paints were used in mixtures, and that the metal surface was abraded to allow the paint layer to adhere. X-ray radiography was also performed on the painting and it was confirmed that lead white was used across almost the entire painted area. The analyses of the support and paint layers revealed that the painting was created on an iron-based metal plate, and the pigment palette used by the artist consists of lead white, calcite, vermilion, Prussian blue, hematite, carbon black, and gypsum, which were identified through Raman analysis. In addition, the elements detected in the XRF analysis led us to consider the possibility of a copper-based green pigment, lead-tin yellow, and chrome yellow. These results were obtained through the complementary use of Raman spectroscopy and μ-XRF, once again demonstrating the necessity of this combined approach.

Prior to initiating the cleaning process on the paint layer, solubility tests were performed. Although Triammonium Citrate (TAC) solutions were applied to various color areas, they proved ineffective. As a result, varnish removal was undertaken using the Cremonesi test, with the final decision being to use LA6 (a mixture of 40 % Ligroin and 60 % acetone) for cleaning. Following this, the restoration process involved cleaning the surface of the painting, removing the yellowed varnish layer and old retouches, re-varnishing the surface, and applying new retouches using chromatic selection technique over the fresh varnish.

Acknowledgements
The authors would like to thank Cengiz Erdamar for allowing the investigation of the precious painting belonging to his collection. The authors are also grateful to Assist. Prof. Dr. Halit Canol, former director of the Central Laboratory at Mimar Sinan Fine Arts University, for enabling the use of the laboratory facilities during the analyses.

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RECEIVED: 2024.7.22
REVISED: 2024.10.27
ACCEPTED: 2024.11.3
ONLINE: 2025.4.29