

Tintoretto in the city of La Plata? Several investigations for the reattribution of the *Portrait of Melchior Michael* to Tintoretto

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ABSTRACT

The records of the Museo Provincial de Bellas Artes “Emilio Pettoruti” (Provincial Museum of Fine Arts of Buenos Aires "Emilio Pettoruti") indicate that a work belonging to Jacopo Comin, "Tintoretto," is part of its cultural heritage, of great value to the museum and the university city of La Plata. Over time, and perhaps due to the ambitious nature of this attribution, the original assertion was called into question. Now, taking into account a comprehensive spectroscopic analysis using Raman and FTIR-ATR techniques, in which cinnabar (HgS), lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and carbon black were determined, along with tracking the artwork and its journey to the city of La Plata, we are able to affirm the validity of the work, the Portrait of Melchior Michael, reconfirming and reattributing it to the colossal Jacopo Comin, Tintoretto.

KEYWORDS

Tintoretto; Raman spectroscopy; ATR-FTIR; pigments; attribution; art history, Portrait of Melchior Michael

1. Introduction

The effect of art on our lives manifests itself on several dimensions. This statement is widespread; studies on the benefits of stimulation for people with dementia caused by visiting museums and observing different artworks have been reported [1]. In this regard, a versatile solution for micro-profilometry based on a set of conoscopic holography sensors has been developed. The application of such an instrument allows both to touch the untouchable and unattainable artworks mainly for visually impaired people as well as for new uses of analyses, since this technique contributes to obtain new information [2,3]. A substantial art component is constituted by historical paintings. These paintings are not only significant from an artistic point of view, promoting scientific actions fostering to minimize aging due to the passage of time, but also, in many cases, due to the diversity of documentary information they may contain. More recently and focusing a diversified discipline of art scholars and computer scientist a digital classification model has been proposed. This tool is possible by training a machine learning model with a number of artists and artworks. The degree of accuracy reaches a very reasonable value [4].

In the present study we will attempt to add scientific evidence to the authentication of an artwork, the *Portrait of Melchior Michael* (Figure 1), attributed to Tintoretto. Micro-samples were taken from selected regions of the artwork, which are found to be damaged and will require future restoration. Therefore, in this work, we will mainly use micro-Raman spectroscopy with the scope of determination of the pigments and also to provide valuable information for the subsequent restoration process. In order to provide additional data for authentication, the confirmation of provenance and opinions of art experts and art historians will also be considered. This logic, which will be used in this particular example, is also analyzed in recent works from the point of view of information for the machine learning algorithms [5].



Figure 1. Portrait of Melchior Michael, attributed to Tintoretto, (dimensions 140 x 118 cm), Museo Provincial de Bellas Artes, La Plata, Argentina.

The Portrait of Melchior Michael (Figure 1) is currently at the Museo Provincial de Bellas Artes "Emilio Pettoruti" (Provincial Museum of Fine Arts of Buenos Aires "Emilio Pettoruti") located in the city of La Plata, Province of Buenos Aires, Argentina. This Museum was founded in 1922 and already in 1932 Sara Wilkinson Santamarina de Marsengo (1870-?), an Argentinean aristocrat, donated her collection of works of art, an act which was recorded in the Museum's patrimonial entry book dated December 28, 1932. One of these paintings, the mentioned *Portrait of Melchior Michael*, a Tintoretto's contemporaneous admiral of the Venetian fleet, was recorded as belonging to Jacopo Comin, "Tintoretto". This and five other paintings, featuring the signatures of Goya, Raeburn and other well-known artists that make up the collection, were acquired by Sara Wilkinson during her travels through Europe. Her arrival to Buenos Aires on the German Cap Arcona ship on Oct. 27, 1932 is documented [6]. It is known that during this trip on 6 October, 1932 Cap Arcona collided with the French cargo ship Agen in the North Sea. Agen was subsequently beached, but later was refloated and escorted into Hamburg, Germany [7].

The confirmation of the attribution of the present work to the colossal Tintoretto will also have as a correlate to enhance the cultural heritage of the Pettoruti Museum and the city of La

Plata. It should be noted that an artwork of Tintoretto similar to the one analyzed in this paper, *Bildnis eines weißbartigen Mannes*, 1570, is in a prominent part of the Museum of Art History of Vienna (Kunsthistorisches Museum Wien). It is interestingly that in the year 2013 at the Victoria and Albert Museum in London, a new painting was attributed to Tintoretto. Until then, *The Embarkation of St Helena in the Holy Land* was assigned to Andrea Schiavone, a Venetian artist of Croatian origins, a contemporary of Tintoretto. According to its curator Ana Benedetti “the style, with its broken brushwork and a palette of cool greys offset by white, ochre and carmine, is typical of early work by Tintoretto” [8]. Another dimension to be taken into account is not only the availability of the found pigments but also their relative cost at that time. For this reason the documentation linked to the 16th century pigment trade, both in Venice and in areas relatively close to the Mediterranean Sea will be also taken into account [9–11]. With all this background, with the existing documentation, with the analysis of the work and with the determination of the pigments used for the preparation of the painting under study, including ostensible retouching performed, the attribution of the painting to Jacopo Comin, the great "Tintoretto" (1518–1594), whose evolutionary objective was to combine the drawing of Michelangelo and the colors of Titian, will be established.

2. Experimental part

Micro-samples were carefully extracted from several areas shown in Figure 2. The characteristic of selected points is that they suffered from some aging damage and that they constitute sectors that shall be adequately restored with the help of the results obtained.

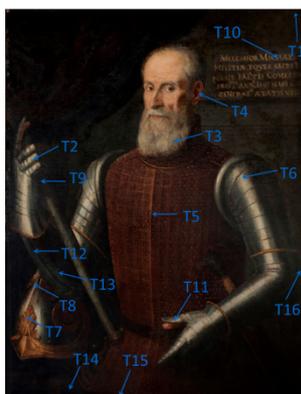


Figure 2. Virtual map of the Portrait of Melchior Michael located at the Museo Provincial de Bellas Artes, La Plata. The arrows followed by identification's numbers indicate the points where the samples were taken.

Raman spectra for the solid samples were measured at room temperature with a Horiba Jobin Yvon T64000 triple monochromator Raman spectrometer in subtractive mode with a confocal microscope and cryogenic CCD detection. The samples were mounted on a computer motorized XYZ mapping stage. The Ar⁺ and Kr⁺ laser lines at 514.5 and 647.1 nm, respectively, were alternative used for the excitation of the samples. Several different spots from each sample were measured under the same experimental conditions. The Raman wavenumbers were calibrated with Si wafers or CCl₄ contained in a sealed glass tube, using the bands at 520.7 and 459.0 cm⁻¹, respectively. The LabSpec 5.45.09 software program was employed to acquire and process the Raman spectra.

ATR-FTIR spectra were obtained with a 6700 Thermo Scientific Nicolet FTIR spectrometer equipped with a Smart iTX Optical Base ATR accessory containing a diamond crystal, in the 4000-400 cm⁻¹ spectral region. The resolution was 4 cm⁻¹ and the number of scans was 64.

3. Result and discussion

The samples extracted from the regions indicated in Figure 2 were analyzed by micro-Raman, taking between 5 and 10 spectra per sample from different spots, in order to analyze possible heterogeneities. Some selected samples were further analyzed by ATR-FTIR. The identity of the samples was determined by comparing the measured spectra with those reported in different databases and scientific literature. A complete list of the obtained spectroscopic data is presented in Table S1 of the Supplementary Material, while some selected results are described below. At this point it is important to highlight the difference between the two spectroscopic methods used in this work. Raman spectra were taken over areas of approximately 1 μ², while ATR spectra were performed over macroscopic portions of the samples. For this reason, it was possible to detect individual components in the first case, while mixtures of compounds and materials were detected in the ATR spectra. On the other hand, while the ATR spectrum detects the majority components, in the Raman spectra

minority components can be selectively intensified, particularly pigments, for example through the resonant or pre-resonant Raman effect.

Figure 3 depicts the Raman spectrum corresponding to a micro-sample taken from the T1 position. It is originated by vibrational modes (1590 and 1352 cm^{-1}) of carbon black, by comparison with the spectra reported in the literature [12]. The Raman spectrum of a particular point of sample T13, named T13-b, is also shown in the Figure. The difference between both spectra is that T13-b contains not only carbon black but also Cu-phthalocyanine green (see below). The most intense bands of this last Cu-compound under the current experimental conditions appear also in the spectrum T13-b at 1530 , 1208 and 680 cm^{-1} (see below in Figure 10 the Raman spectrum of Cu-phthalocyanine green from T13-a, registered without other components) and compare fairly well with those reported in the literature [13].

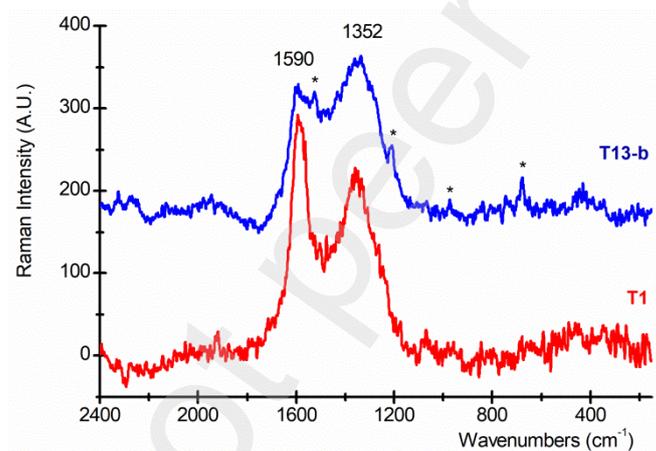


Figure 3. Raman spectra (excitation wavelength: 647.1 nm ; $50\times$ objective (0.75NA)) of T1 (bottom, red-trace, acquisition time: 30 s ; 8 accumulations) and T13-b (top, blue-trace, acquisition time: 60 s ; 4 accumulations) samples assigned to carbon black (the presence of bands belonging to Cu-phthalocyanine green, marked with asterisks, is also observed in the spectrum T13-b).

The carbon black vibrational bands at 1590 and 1352 cm^{-1} of T1 presents relative intensity values of 290 and 223 and full width at half maxima of approximately 78 and 194 cm^{-1} , respectively. This set of data agrees with the characteristics of graphite with a high degree of graphitization [14]. In the impressive paper dealing on the Tintoretto's painting "Wedding feast at Cana" black pigments are mentioned [15]. Other authors report also on the probably

use of black charcoal on this piece of art [16]. Carbon in its graphite variety has also listed in an extended collection of pigment vibrational data [13].

Figure 4 shows the ATR spectra of the samples collected from the T2 and T3 position (Figure 2). These spectra compare fairly well with the *INR00009* file reported in the literature by the Infrared & Raman User Group [17] for the IR spectrum of Dammar resin (CAS number 9000-16-2) or Hiroe or pale East India Singapore resin, whose name is due to the fact that the resin is obtained from the Dipterocarpaceae family of trees, which grow in India and Southeast Asia. Its triterpenoid composition originates its photochemical and chemical activity, aging and yellowing processes, mainly significant in connection with the artworks' preservation. A study of the varnish problem in old paintings was discussed in the literature. It is known that pine resin in oil paint was detected as a medium for glazing in the work of Girolamo da Carpi, "The Adoration of the Kings", achieved in the period 1545–50. The use of resins in other paintings belonging to the XVII and XVIII century was also reported [18]. However, it was not until the XIX century that the use of these kinds of resin-based media has been widespread used as additives to oil paint. In a publication of E. René de la Rie, the use of dammar resin is reported to have been dated 1829 by the German apothecary F. Lucanus [19]. An ATR spectrum very similar to the one reported here was found in the study of "Wedding Feast at Cana" by Jacopo Tintoretto [15].

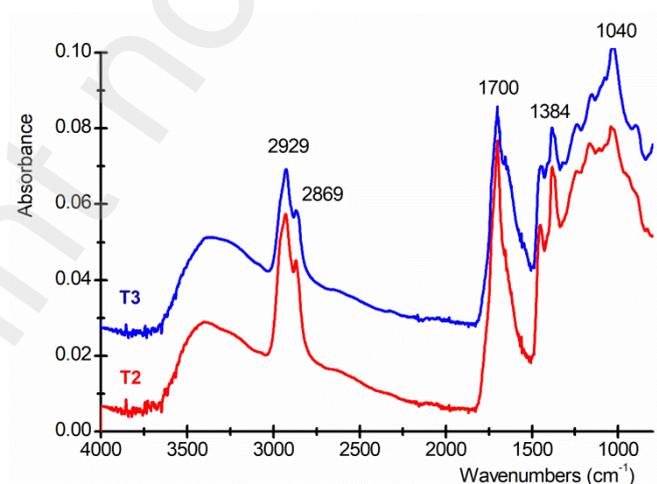


Figure 4. ATR-FTIR spectra of T2 (bottom, red-trace) and T3 (top, blue-trace) samples (4 cm⁻¹ resolution; 64 scans), attributed to the varnish.

Figure 5 depicts the Raman spectra of T4 and T5 samples (see Figure 2). The band at 1048 cm^{-1} , corresponding to the totally symmetric stretching of CO_3^{2-} $\nu_1(A'_1)$, is indicative of the presence of a lead carbonate. On the other hand, the ATR spectrum of sample T5 (Figure S1) reveals the exclusive presence of lead white (basic lead carbonate, $2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$) [20], which agrees with what has been reported in other pieces of Tintoretto [15]. Due to the fact that different colors are observed in the two areas (T4 and T5), it can be inferred that lead white was mixed with other pigments [13].

In connection with lead white, special attention to the well-known blackening process was devoted. However, the blackening process, i.e. the formation of PbS (black) by the reaction of PbCO_3 with hydrogen disulphide (H_2S) is blocked by the presence of varnishes, which obstruct the contact of the reactants [21]. The process of blackening by formation of PbS was really observed in our study of the Tucumán Flag. The central inscription invoking to Bernabé Aráoz, was originally made with crocoite (PbCrO_4). A black color was mainly observed in places in where, due to the passage of time, the original inscription had been removed [22].

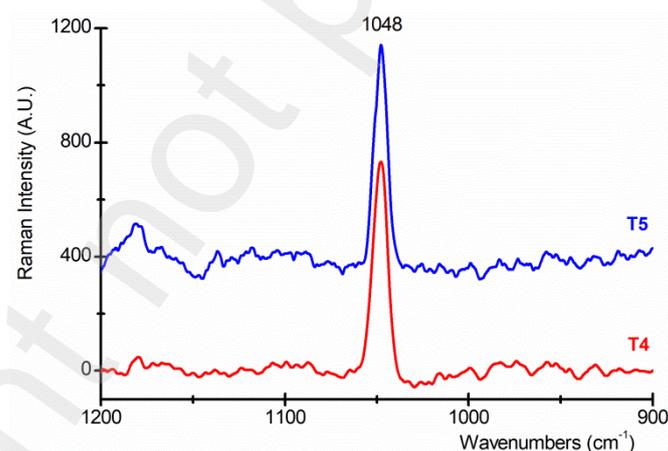


Figure 5. Raman spectra (excitation wavelength: 514.5 nm; 50× objective (0.75NA)) of T4 (bottom, red-trace, acquisition time: 10 s; 32 accumulations) and T5 (top, blue-trace, acquisition time: 5 s; 64 accumulations) samples corresponding to lead white.

Sample T6 contains Cu-Phthalocyanine blue, as evidenced by the Raman spectrum depicted in Figure 6, which corresponds to the reported Raman spectrum of this pigment [23]. It is

worth mentioning that the synthesis of phthalocyanine was first reported in the first half of the XX century, which implies that this pigment was added subsequently to the execution of the painting under study [24]. It is really not necessary to be an art specialist to observe, through the not very neat brushstrokes, the affectation to the original work through the use of Cu-phthalocyanine in some sectors of the painting.

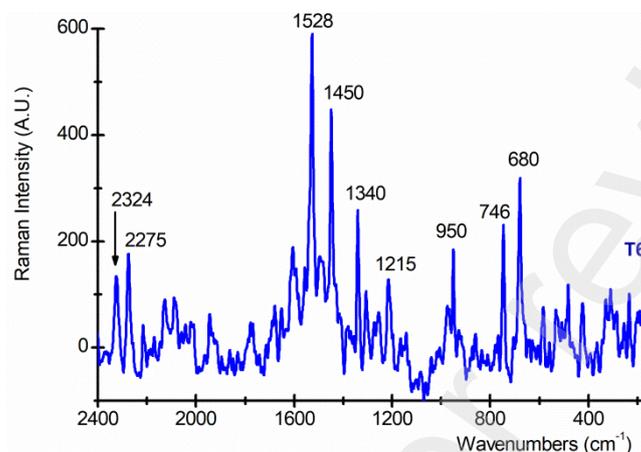


Figure 6. Raman spectrum of T6 sample (excitation wavelength: 647.1 nm; 50× objective (0.75NA); acquisition time: 60 s; 16 accumulations) attributed to Cu-phthalocyanine blue.

Figure 7 presents the ATR-FTIR spectrum of T7 sample. Its Raman counterpart can be appreciated in Figure 8. The apparent inconsistency of both results obtained for the Melchior Michael's helmet, the ATR results are attributed mainly to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) whereas the Raman results are due to presence of calcium carbonate, can be explained taken into account that the micro Raman results belong to a rather punctual sample while the ATR-FTIR corresponds mainly to an extended area. Figure 7 also shows IR bands at 2920 and 2849 cm^{-1} , presumably corresponding to aliphatic CH_2 stretching modes. Thus, the whole vibrational spectra, calcite, gypsum and organic components can be determined from the helmet. It is known that gypsum can be formed through a sulfation process. The presence of SO_2 in the wet air can react with calcite to give gypsum [25]. The relative size of both species is also different. The higher volume of gypsum can originate stress in the structure and fragment separation. It is worth to be again mentioned, that this point, T7, was selected due to observed imperfections in the painting.

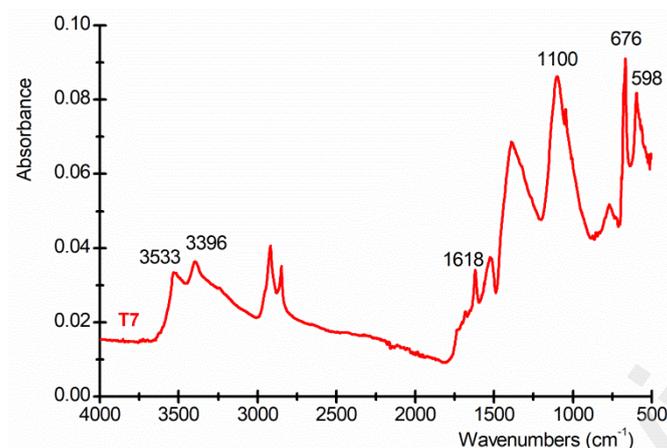


Figure 7. ATR-FTIR spectrum of T7 sample (4 cm^{-1} resolution; 64 scans) attributed to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

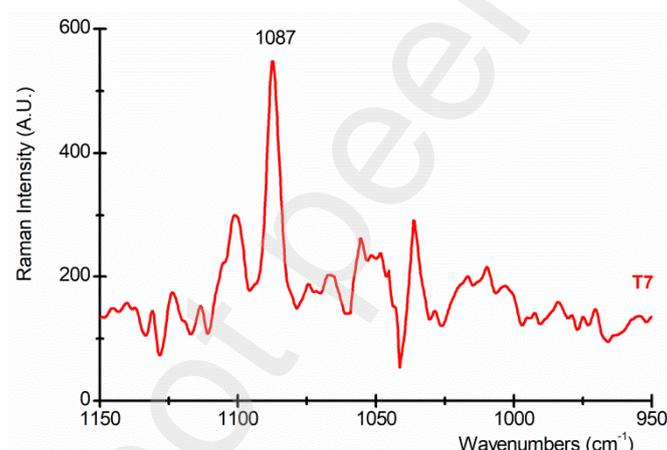


Figure 8. Raman spectra of T7 (excitation wavelength: 514.5 nm ; $50\times$ objective (0.75NA); acquisition time: 10 s ; 16 accumulations) attributed to CaCO_3 .

The Raman spectra of T8, T10, T11 and T15 samples are shown in Figure 9. Three bands at 341 , 282 , and the most intense at 251 cm^{-1} are present in the spectra, originated by the red pigment cinnabar (HgS). The tonality observed for these 4 surfaces agrees with the results found. The spectroscopic detail of cinnabar, with a trigonal twofold-coordinate structure, is based on close-packed helical chains and a low D_3 symmetry. The symmetry assignment for the three experimentally determined vibrations is 341 cm^{-1} , E; 282 cm^{-1} , E and 251 cm^{-1} , A_1 [26]. These vibrational modes are all active in the D_3 symmetry. Regarding its stability, unlike several binary compounds of Zn, Cd and Hg, with S, Se and Te, HgS is the only one

that presents the change to a zinc-blende phase (meta-cinnabar) at high temperatures ($335^{\circ}\pm 10^{\circ}\text{C}$) in air atmosphere. This behavior ensures a good property for the permanence of the color in the pigment [27].

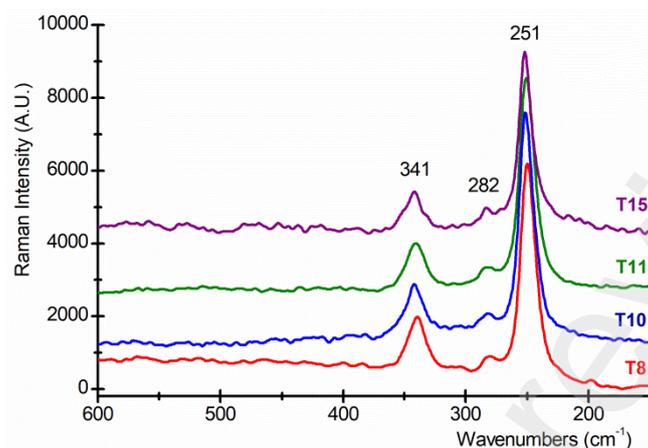


Figure 9. Raman spectra of, from bottom to top: T8 (red-trace), T10 (blue-trace), T11 (green-trace) and T15 (violet-trace) samples (excitation wavelength: 647.1 nm; 50× objective (0.75NA); acquisition time: 10 s; 8 accumulations), evidencing the presence of cinnabar (HgS).

Figure 10 shows the Raman spectrum of T13-a sample, with bands at 1530, 1439, 1386, 1333, 1277, 1208, 1079, 972, 950, 812, 782, 770, 750, 736, 719, 700, 680, 638, 584, 541, 525, 505, 468, 354, 287, 261, 220, 194 and 141 cm^{-1} . This set of signals compare fairly well with the Raman spectrum of Cu-phthalocyanine green, according with relevant antecedents in the literature [28]. Furthermore, a resonance Raman behavior was found by comparison of our data with the *ROD00115* file reported in the literature by the Infrared & Raman User Group [17]. Special care should be taken into account for the attribution to the green (the chlorine substituted phthalocyanine) or blue Cu-phthalocyanine [29]. The difference in both vibrational spectra is precisely observed in the C–Cl stretching vibration region and, of course, in the case that it has been recorded, in the C–H stretching vibration region. The Cu-phthalocyanine green pigment was also founded in some regions of T13 sample, (see for example T13-b Raman spectrum in Figure 3), mixed with carbon black. These spectra, which reveal the presence of a compound prepared for the first time in the 20th century, and the visible intervention of the work in this region, suggest a clear retouching of the painting.

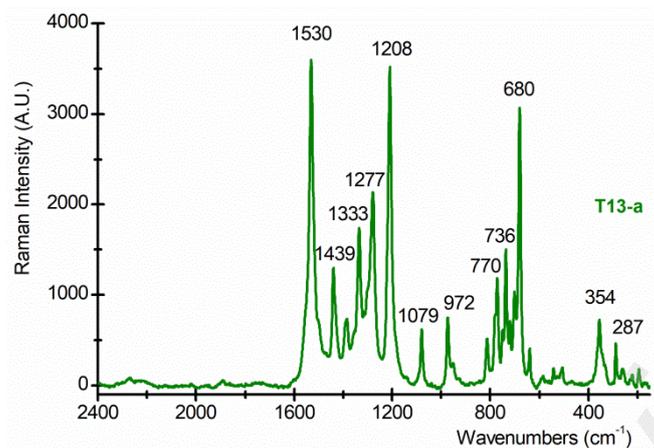


Figure 10. Raman spectra of T13-a sample (excitation wavelength: 647.1 nm; 50× objective (0.75NA); acquisition time: 60 s; 16 accumulations), corresponding to Cu-Phthalocyanine green.

4. Conclusion

Melchior Michael was an admiral of the Venetian navy, procurator of San Marco, and a central political and military figure for the Republic of Venice. He died in 1572 (although his tomb was erected in 1570) and the present artwork was conceived by Tintoretto (1518-1594) around the year 1565 when Melchior Michael was appointed Admiral of the city's fleet. Tintoretto made portraits of Venetian nobles and bourgeois such as the Portrait of a Venetian Gentleman (ca. 1555, National Gallery of Ireland) and the Portrait of a White-Bearded Man (ca. 1570, Kunsthistorisches Museum of Wien), Figure 11. Additionally, he made numerous portraits of procurators, and in his commissioned work, there is at least one documented portrait by Melchior Michael between 1562-1563, which is close to the completion date of the portrait when the admiral was seventy-six years old [30].



Figure 11. Portrait of a Venetian Gentleman, ca. 1555 (116 x 80 cm), National Gallery of Ireland and Bildnis eines weißbärtigen Mannes (Portrait of a White-Bearded Man), ca. 1570 (92.4 x 59.5 cm), Kunsthistorisches Museum, Wien.

The connection between Tintoretto's artwork and Argentina, specifically the Pettoruti Museum in La Plata, is well-documented. In 1932, Sara Wilkinson donated a collection of paintings to the museum. The size, type, motives, and documentation of these paintings align with the original attribution of them being one of them attributed to Tintoretto. However, later they were reclassified as "school works" by Pettoruti [31].

Further investigation delves into the previous owners of the artwork. It is recorded that the piece under study was exhibited at the grand Venetian Art Exhibition held in London in 1894, under the presidency of the Duke of Westminster. It was also part of the notable collection of Leon Zomzée, which was auctioned off in Brussels in 1904. The piece was commented on by Edgar Alfred Baes, a renowned Belgian art historian, and described by Francesco Zanzotto as belonging to the Venetian Pérsico-Garriera collection in 1861 [32].

Additionally, the portrait bears similarities to various engravings depicting the features of Melchior Michael, created between 1568 and 1601. This indicates common sources for these images. The oval portrait of the admiral, an engraving printed by Natale Bonifacio Da Sebenico around 1568 and preserved in the British Museum, closely resembles the painting in the expression of the face and details of the doublet and shoulder pads [33].

Regarding the ongoing research, the spectroscopic results are also supported by the mentioned historical sources and the iconological analysis of the artwork. Thus, experimental tests have allowed for the analysis of several pigments used in the painting attributed to Melchior Michael: cinnabar (HgS), lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), calcite (CaCO_3), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), and carbon black. The correlation between the pigments used in the painting

and those reported for Tintoretto's work is significant. A varnish found in other paintings of Tintoretto was also detected in this study. Moreover, it has been determined that the noticeable areas of intrusion were a result of synthetic pigments introduced during the 20th century: Cu-phthalocyanine blue and Cu-phthalocyanine green.

In conclusion, based on the data presented here, we strongly support the attribution of the painting to Tintoretto, which is housed in the Museo Provincial de Bellas Artes “Emilio Pettoruti” in the city of La Plata.

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Rosana M. Romano: Methodology, Formal analysis, Investigation, Visualization, Writing- Reviewing and Editing. **Julieta Pellizzari:** Investigation (Sample extraction). **Federico L. Ruvitusso:** Resources, Writing - Original Draft. **Gino Pietrodangelo:** Investigation (Raman). **A. Lorena Picone:** Investigation (ATR). **Carlos O. Della Védova:** Conceptualization, Formal analysis, Writing - Original Draft, Writing- Reviewing and Editing, Supervision, Funding acquisition.

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Highlights

A Portrait of Melchior Michael painted by the colossal Tintoretto is in the city of La Plata, Argentina.

Spectroscopic techniques were used to validate its attribution from the analytical point of view.

The detail of its arrival in La Plata also reveals the origin of the work of art.