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Complementary Use of Raman and µ-XRF Spectroscopy for Non-destructive Characterization of an Oil Painting by Turkish Painter İbrahim Çallı

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Abstract: The aim of the present work was to investigate the pigments used in oil painting "in the park" created in the first half of the 20th century, by Turkish painter and academician İbrahim Çallı (1882-1960). The non-destructive analyses were performed with a combination of µ-XRF and Raman Microscopy. Obtained results revealed following pigments on the investigated painting: Zinc white (ZnO), zinc yellow ($K_2O{\cdot}4ZnCrO_4{\cdot}3H_2O$), chrome yellow ($PbCrO_4$), strontium yellow ($SrCrO_4$), ultramarine ($Na_7Al_6Si_6O_{24}S_3$), prussian blue ($Fe_7C_{18}N_{18}$), hematite ($\alpha$-$Fe_2O_3$), cadmium red (CdSe), barite ($BaSO_4$), and carbon black. There is a great lack of knowledge about the materials used in Turkish painting and this non-destructive study provides the first systematic investigation into Çallı's palette.

Keywords: Micro-Raman, micro-XRF, pigment characterization, non-destructive analyses, Turkish painting.

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INTRODUCTION

There was a widespread assumption that art and technology were notions opposite to each other. However, during the recent years, a great awareness has been created across several disciplines that modern science and technology are crucial for a better insight into art and cultural heritage(1,2). The characterization of pigments on artworks is the major interest by reason of providing detailed historical and technological information. The identification of the chemical composition and degradation products of the pigments used, provide a remarkable contribution to the conservation method to be employed(3,4). This would also allow the detection of forgeries by the detection of anachronistic pigments due to well establishing chronology of most pigments(5). However, pigment analysis can be a challenging problem because of the extremely limited sampling of works of art. In such cases, the non-destructive techniques, which can be applied on the object itself, is obviously mostly desirable. In a detailed analysis of the different possible techniques for pigment analysis, it is reported that Raman microscopy is the best single technique for this purpose due to its specificity, sensitivity, spatial resolution, and providing spectra which are free from interference by the surrounding materials(6–9). Many authors have previously reported Raman studies of oil painting mainly focused on the palette composition and pigment admixtures and in some cases on the degradation of pigments(10–17). However, to the best of our knowledge it is not very likely to find scientific data on the Turkish paintings, except a work investigating a Feyhaman Duran painting, the contemporary of İbrahim Çallı(18).

In parallel with the westernization policies of the Ottoman Empire, a new style of art entered to Ottoman visual culture. The most important event regarding the history of Turkish painting was the foundation of Sanayi-i Nefise Mektebi (1882) in İstanbul (today, Mimar Sinan Fine Arts University), which was founded by Osman Hamdi Bey who

received education of painting in Paris. A group of young artists who graduated from the Academy of Fine Arts went to study abroad after the Second Constitutional Revolution. They returned to the empire with the beginning of World War I in 1914 and despite training in academic style, they started painting with an impressionistic palette. This younger generation rebelled against the academism of their teachers and introduced a new concept of painting to Turkey(19–21). İbrahim Çallı (1882-1960) is one of best known member of the group and has a more active position than the others. He is considered to be the pioneer of the Impressionist trend in Turkey, such that the group is also known as the “Çallı Generation”(20,21).

The paper here presented intends to display the analytical characterization results of the Çallı’s pigment palette which he used on the painting “in the park” (75 cm x 60 cm). It is understood from the artist's signature that the painting was created before 1934, when the surname law came out. Raman and µ-XRF spectrometers were used with the aim of characterizing the pigments used. For the first time in this study, an oil painting by a Turkish painter was analyzed non-destructively considering the importance of the painting and it is also crucial to state that, this work is the first to investigate a Çallı painting, regarding the pigment palette.

MATERIALS AND METHODS

All the studies were performed non-destructively using the facilities of Central Research Laboratory (MerLab), functioning under Materials Research Center for Cultural Property and Artworks in Mimar Sinan Fine Arts University, İstanbul, Turkey.

For elemental characterization, a Bruker ARTAX 800 micro X-Ray Fluorescence spectrometer (µ-XRF) with molybdenum source, at an electric accelerating potential of 40 kV and a current of 600 µA was used. The measuring head which consists of a central unit containing a Peltier-cooled silicon drift detector, the laser spot and the CCD camera, allowed us to focused on the different spots of the sample. Each spectrum was collected during 60s and evaluated by ARTAX software.

Raman microscopy measurements were made with a Bruker SENTERRA Dispersive Raman spectrometer, which is equipped with an Olympus confocal microscope mounted onto a crane (Figure 1). In this study, 20x and 50x magnification objectives were employed to focus the 785 nm laser beam onto the samples. The irradiating laser power (1-50 mW) and the exposure time has been changed during the study. The analysis were performed directly on the painting, and the signals recorded by a TE-cooled CCD detector. The band intensities are defined as vw: very weak; w: weak; m: medium; s: strong; sh: shoulder throughout the text.

Since, the analyses were based on the use of non-destructive techniques, no samples were removed from the painting. After the visual inspections on the artwork, the colors and points to be analyzed were selected considering their homogeneity and the analytical reproducibility, and they were shown in Figure 2.

Figure 1. The raman spectrometer, which was used in this study, equipped with a confocal microscope mounted onto a crane.

Figure 2.İbrahim Çallı's oil painting "in the park" (75 cm x 60 cm) and the points from which Raman and XRF spectra were collected.

RESULTS AND DISCUSSION

As shown in Figure 3, paint layers were applied directly onto the rough surface of a wooden panel support, no preparation layer was laid on.

Figure 3. Photograph showing the Wooden panel support.

XRF analysis of the Spot 1 shows three elements which can be related to white color: zinc and lead. On the other hand, Raman analyses were carried out from a significant number of points and only one measurement yield a useful Raman spectrum (Figure 4) since zinc white is a poor Raman scatter(22). This spectrum confirmed the application of zinc white with the characteristic bands at 99, 320 and 435 cm^{-1}(23). However, white paint is likely a mixture of lead white and zinc white.

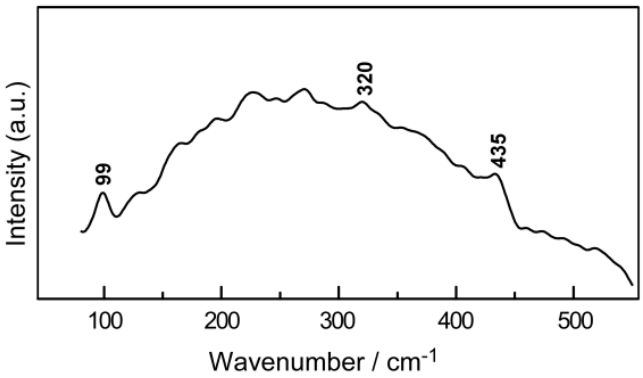

Figure 4. Raman spectrum of the white color (Spot 1).

Figure 5 shows the Raman spectrum of the green color, Spot 6. The green pigment was detected to be not a green chromophore but a mixture of Prussian blue $[Fe_4[Fe(CN)_6]_3 \cdot xH_2O]$ and chrome yellow ($PbCrO_4$). The intense peak at 2153 cm^{-1} and weaker bands at 2091, 534, and 277 cm^{-1} clearly indicate the presence of blue, while the band at 841 cm^{-1}, due to CrO_4^{2-} stretching, is assigned to chrome yellow(3,24,25). Prussian blue is reported as a compatible pigment which can be used in mixtures with lead chromate to produce green color and many studies have shown its predominant application as a blue pigment used to achieve green hues(22,24,26–28). Furthermore, the spectrum shows a band at 987 cm^{-1} which is

caused by barium sulfate ($BaSO_4$) and its presence may be related to Prussian blue since barium sulfate is reported to be detected in Prussian blue widely(29). It may also be intentionally added as an extender or a white pigment. The analysis of XRF spectra confirmed these findings and revealed the presence of Zn, Fe, Cr, Ba, Pb, and S. In addition to these elements Ca, which may be suggesting the application of a small amount of calcite ($CaCO_3$), was also detected.

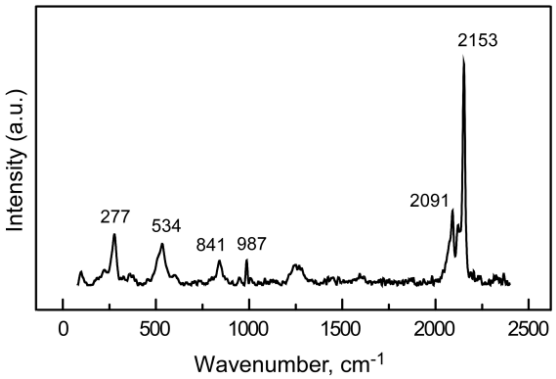

Figure 5. Raman spectrum of the green color (Spot 6).

Regarding the yellow color (Spot 4), characteristic Raman bands of zinc yellow at 114 (vw), 162 (vw), 346 (m), 358 (sh), 412 (vw), 776(vw), 874 (vs), 894 (sh), 942 (m) cm^{-1} were detected (Figure 6) (25,27,30). Zinc yellow was first synthesized in about 1800 cm^{-1} but it has not been used as a pigment until the second half of the 19th century. The basic zinc chromate has the composition $4Zn(OH)_2{\cdot}ZnCrO_4$, while most modern yellows are of the $K_2O{\cdot}4ZnCrO_4{\cdot}3H_2O$ composition(31–33). In this study, detection of K in XRF spectrum of the yellow color, indicating the application of a pigment having zinc potassium chromate hydrate composition. Besides these elements mentioned above, the XRF analysis revealed the presence of Sr, Pb, Fe, Ba, and S in Spot 4. The high amount of Sr detected in yellow area can be considered as an important clue indicating the application of strontium yellow (Strontium chromate, $SrCrO_4$) pigment, although it was not detected in the Raman spectra. The presence of Pb, Fe, Ba and S may not be unambiguously related to the yellow pigment, rather may be indicating the underlayer pigment, which we believe is a mixture of Prussian blue and chrome yellow as it is identified on Spot 6.

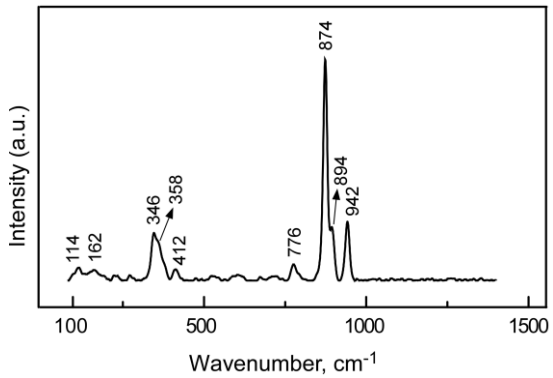

Figure 6. Raman spectrum of the yellow color (Spot 4).

As for the blue, the Raman spectra performed on the Spot 5 showed the use of ultramarine blue, which is a three-dimensional aluminosilicate complex with a sodalite structure containing sodium ions and sulfur groups ($(Na,Ca)_8(AlSiO_4)_6(O,S,SO_4)_{1\text{-}2}$) (3,25,32). The Raman spectra of the ultramarine blue obtained have bands at 268 (vw) 375 (w), 549 (vs), 584 (sh), 1096 (vw), cm^{-1} as shown in Figure 7(34–36). The elements regarding the underlying green color, Fe, Pb, Cr, Ba and S, were also detected in XRF spectra.

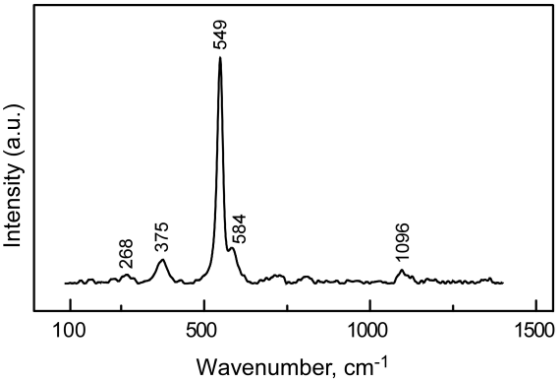

Figure 7. Raman spectrum of the blue color (Spot 5).

The Raman analysis of the black color (Spot 2) have given the spectra of a carbon-based black pigment distinguished by two broad bands at around 1320 and 1580 cm^{-1} as shown in Figure 8 (37,38). On the other hand, the detection of Ca and P in XRF spectra, can be associated with the presence of bone black.

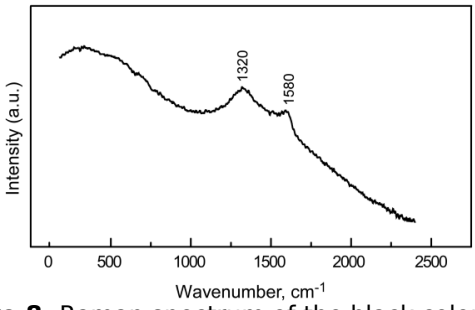

Figure 8. Raman spectrum of the black color (Spot 2).

For the red color (Spot 3), no useful Raman spectra could be collected. However, the detection of key elements such as Cd and Se in XRF spectrum was a clear indication of the presence of cadmium red pigment (CdSe) and allowed us to distinguish the pigment used from that of any other red pigments (Figure 9). It is also worth noting that the result is emphasized the importance of complementary using of the Raman and XRF techniques for identification purposes.

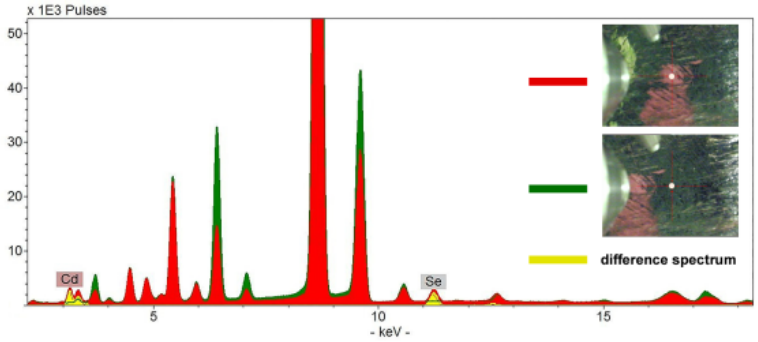

Figure 9. XRF spectra collected from the red and green colors and the difference spectrum.

As regards to artist signature (Spot 7), the color was identified as a mixture of pigments and obtained by adding carbon-based black pigment to hematite (α-Fe_2O_3) to produce a brown hue. Figure 10 shows the Raman spectrum and the bands at 230 (m-s), 297 (vs), 413 (m-s), 504 (w-m), 617 (m), 676 (w), 801 (vw) cm^{-1} were assigned to the presence of hematite, whereas those at 1318 and 1601 cm^{-1} were assigned to carbon-based black pigment (37–40). In addition, besides the elements arising from the under layer, Cd and Se were also detected in XRF spectrum. Thus, the analysis revealed that the occurrence of this brown pigment used for signature consisting of a mixture of at least three different pigment which are hematite, carbon black and cadmium red.

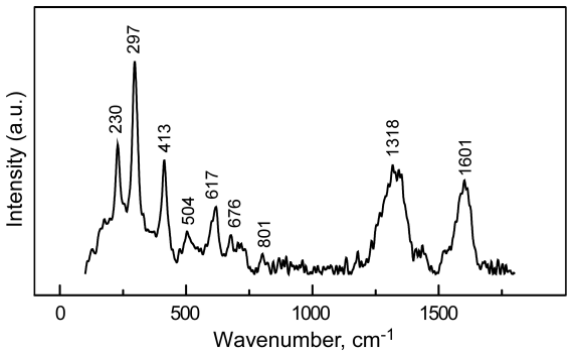

Figure 10. Raman spectrum of the brown signature (Spot 7).

There is another point to take into consideration that zinc was almost always detected in the colors analyzed. It is reported in the literature that treatises from the late medieval period recommended zinc sulfate, also known as zinc vitriol or white vitriol, as driers for varnishes and paints(41,42). The significant amount of zinc detected in this study was most probably incorporated in the form of zinc sulfate which like powdered glass. The detection of sulfur by XRF corroborates the idea of the usage of white vitriol. However, the addition of zinc may also be suggested its addition by manufacturers as a lightening agent(43).

An overview of the study, the measured points and results, is given in Table 1.

Table 1. Overview of the measured points, colors, analysis results, identified pigments, and chemical compositions.

Measuring Point	Color	μ-XRF Results (net peak area values in decreasing order)	Raman peaks (cm^{-1})	Chemical Composition	References
1	White	Zn, Pb, Fe, Cr, Ca, Ba, K, S	Zinc white: 99(w), 320(vw), 435(vw)	ZnO	(3,25)
2	Black	Zn, Pb, Fe, Ca, Cr, Ba, K, S, P	Carbon-based black: 1320(br), 1580(br)	carbon-based black	(37-40)
3	Red	Zn, Cr, Fe, Ba, Pb, Se, Cd, Ca, Sr, S	-	CdSe	
4	Yellow	Zn, Cr, K, Sr, Pb, Fe, S, Ba	Zinc yellow: 114(vw), 162(vw), 346(w-m), 358(sh), 412(vw), 776(w), 874(vs), 894(sh), 942(m)	$K_2O{\cdot}4ZnCrO_4{\cdot}3H_2O$ and $SrCrO_4$ (?)	(25,27,30)
5	Blue	Zn, Fe, Cr, Pb, Ca, Ba, S, K, Sr, Si	Ultramarine: 268(vw), 375(w), 549(vs), 584(sh), 1096(vw)	$Na_7Al_6Si_6O_{24}S_3$	(34-36)
6	Green	Zn, Pb, Ca, Ba, Cr, Fe, Sr, S	Prussian blue: 277(w-m), 534(w-m), 2091(m), 2153(vs) Chrome yellow: 841(w), Barite: 987(w)	$Fe_7C_{18}N_{18}$ $PbCrO_4$ $BaSO_4$	(24,25)
7	Signature (Brown)	Zn, Fe, Cr, Ca, Ba, Pb, Cd, Sr, S, Se	Hematite: 230(m-s), 297(vs), 413(m-s), 504(w-m), 617(m), 676(w), 801(vw) Carbon-based black: 1318(br), 1601(br)	α-Fe_2O_3,CdSe, and carbon-based black	(37-40)

CONCLUSIONS

The results of the present study once again emphasize the great potential of the complementary use of μ-XRF and Raman spectroscopy and the pigments used by İbrahim Çallı were successfully determined. The painter's palette includes zinc white, zinc yellow, chrome yellow, strontium yellow, ultramarine, Prussian blue, hematite, cadmium red, barite, and carbon-based black pigments.

The knowledge of his palette plays an substantial contribution to the knowledge of the pigments used in 20th century Turkish painting. In addition, one of the most important characteristic of this work was to be the first to investigate a Turkish painting non-destructively. Nevertheless, Çallı's paintings will continue to be analyzed to create an extensive database.

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