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G. I. Katsigras Museum: In-Situ Measurements in Paintings by G. Gounaro

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Abstract George Gounaropoulos (1889-1977) was one of the early 20th century artists who introduced modern art in Greece. Following his academic studies at the School of Fine Arts in Athens, he studied and worked in Paris, where in the 1920s he developed his personal artistic style. The Municipal Art Gallery of Larissa, G.I. Katsigras Museum owns ten works by Gounaropoulos. George Katsigras (1914 – 1998) was a doctor and significant art collector who subsequently donated his collection to the Municipality of Larissa. He was a close friend of Gounaropoulos from early on which explains why the Katsigra collection contains some rare examples of the artist's early and experimental painting. Therefore, we had the opportunity to examine six oil paintings, comprising of a self- portrait from 1912, four works from the early to mid-1920s and one from around 1927-29. The paintings' study was carried out with the valuable help of new technologies. Two non-destructive methods, XRF and Raman Spectroscopy were used. The combination of those methods gave the most accurate results, capable of creating a database, that could be used to identify other unknown paintings of the artist or to authenticate paintings that do not bear his signature. The research's main objective is the reconstruction of the artist's color palette. Moreover, the in-situ study did not affect the paintings' condition. The needed measurements were easily taken, even without taking the artworks down.

Keywords XRF Spectroscopy, Raman Spectroscopy, Non Destructive Methods, G. Gounaropoulos, Pigments, Analysis

1. Introduction

In our project we undertake analytical scientific research on works by the eminent Greek modernist painter George Gounaropoulos (1889-1977). Over the last decades, conservation and scientific research have contributed significantly to the better understanding and sometimes de-coding of great works of art by old and modern masters. We believe that some interesting facts will present themselves to us during the course of this research.

The G. Gounaropoulos Museum was founded after the artist's death and following the donation of his house and studio by his late son, Ilias Gounaropoulos to the Municipality of Zographos. The "heart" of the museum is the artist's house and studio which hosts a permanent collection of over forty artworks.

George Gounaropoulos was one of the early 20th century artists who introduced modern art in Greece. Born in a Greek family in the town of Sozopolis on the Black Sea, George Gounaropoulos came to Greece with his parents and siblings in his early teens. His evident talent in painting was the only passport of the financially strained young migrant to the School of Fine Arts in Athens. His artistic training was mainly in the academic style, which was the dominant artistic approach by his professors, all of whom belonged to the so called "School of Munich" and represented the conservative wing of Greek artists. His main teachers were Georgios Roilos and Spyridon Vikatos [1].

Following his highly successful studies and after having served in the Second Balkan War and World War I, in 1919 Gounaropoulos left for Paris. Thanks to a grant by a Greek foundation he was able to live in the artistic capital of his time and to study in the best independent art academies, namely l' Académie Julian and l' Académie de la Grande Chaumière [1]. Under the influence of the modern art movements and with his Greek cultural heritage deeply embedded in his artistic expression, Gounaropoulos developed his own personal artistic style, which evolved through the years and the creation of his oeuvre.

At this stage of the project, non-distructive analysis was applied on Gounaropoulos paintings in the collection of the Municipal Art Gallery of Larissa, G.I. Katsigras Museum. George Katsigras (1914 – 1998) was a doctor and significant art collector who subsequently donated his collection to the Municipality of Larissa [2]. He was a close friend of

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Gounaropoulos from early on which explains why the Katsigra collection contains some rare examples of the artist's early and experimental painting.

2. Materials and Methodology

2.1. Materials

A brief outline of the basic characteristics of each one of the paintings that were studied follows.

The painting Self Portrait 1912 (oil on board, 27,5x17 cm) is the earliest work by Gounaropoulos that the scientists have been able to examine. Its heavy, dark color palette and the expressive gaze of the sitter are typical of the artist's academic style, as he mastered it at the School of Fine Arts in Athens [2]. The representation of the artist in a turban, the pose, and the light on the left half of the face are reminiscent of Rembrandt's Self-portrait at the easel 1660 in the Louvre. Interestingly, a reproduction of this particular Rembrandt self-portrait was always hung next to Gounaropoulos's study table. Similarly, Gounaropoulos's self-portrait was always hung next to Katsigra's desk.

Figure 1. Self-Portrait c.1912

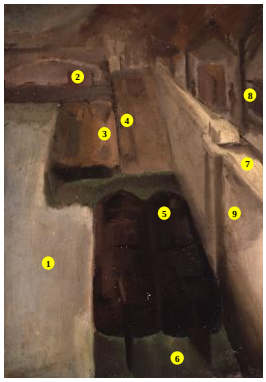

Figure 2. Barges on the Seine c.1920-1922

The paintings Barges on the Seine 1920-22 (oil on cardboard, 47x35 cm) and Bridge over the Seine 1920-22 (oil on canvas, 62x59,5 cm) are works from the artist's early years in Paris, when he experimented with the artistic paradigms of Amedeo Modigliani, Paul Cézanne and cubism. The Seine was a favorite theme among impressionist and post-impressionist artists. Gounaropoulos chooses a point of view from above but in Barges on the Seine he employs Cézanne's passage approach to the rendering of the perspective, i.e. the perspective unfolds in height and not in depth diminishing the illusion of the third dimension and emphasizing the two-dimensionality of the canvas. The geometrical composition and the neutral palette relate also to paintings by Juan Gris and Pablo Picasso from the cubist period. In Bridge over the Seine the dominant shape of the tree creates a curvilinear structure that adds a lyrical nuance to the strict geometrical composition.

Girls embroidering 1924-25 (oil on canvas, 60x80 cm) belongs to a group of works from the early 1920s in which the artist explores the geometrical rendering of the young female form and its relationship with the pictorial space, under the influence of similar works by Cézanne. The three women are depicted highly stylised and appear as three versions of the same person. The outline of their bodies forms an oval shape which encloses the melodic movements of their arms and hands and is traversed by the rhythmic curve of the cloth.

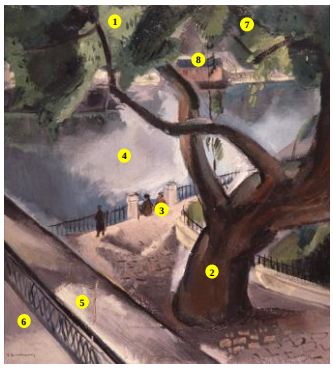

Figure 3. Bridge over the Seine c.1920-1922

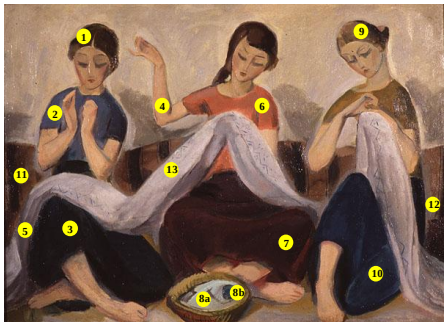

Figure 4. Girls Embroidering c. 1924-1925

The painting Fair-haired nude 1924-25 (oil on canvas, 91x64 cm) is a transitional work that illustrates the development of the artist's personal style. His palette becomes brighter and his colours very fluid, creating an impression of lightness. As a result, his sensuous, volumetric female figure becomes gradually transparent and ethereal, floating in the pictorial space as if defying gravity. This type of female representation will define the artist's mature style and will evolve further over the next decades.

Still Life c. 1927-29 (oil on canvas, 64,5x79,5 cm) is a typical Gounaropoulos painting of this genre. The translucent still life elements (basket with grapes, watermelon slice, pitcher) are interwoven with the landscape elements and the internal light that emerges from the depths of the composition, creating a luminous and poetic metaphysical ambiance.

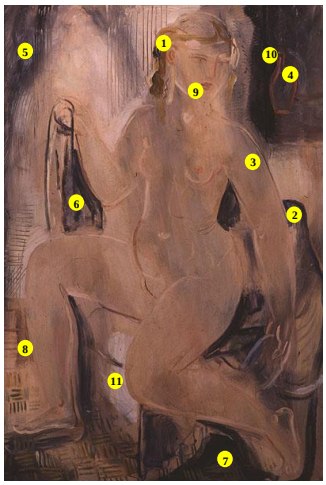

Figure 5. Fair - Haired Nude c.1924-1925

Figure 6. Still Life c.1927-1929

2.2. Methodology

In this study several non-destructive methods were applied, in order to identify the pigments on the artist's paintings and to reconstruct his color palette, as his work has only been analysed theoretically so far.

The analytical techniques used were X-ray Fluoresence along with Raman Spectroscopy and Optical Microscopy, which were performed in-situ. [6]

To detect the chemical elements in percentages and in traces the portable Thermoscientific X-MET-8000 Expert XRF analyser was used, equipped with a 50KV mini W-Target X-Ray Tube and a Single Collimatorof 6mm diameter. In order to acquisit the data, a built-in software was used and measurements were saved, as Unicode ASCII file format is compatible for further analysis with specialized software. Due to the nature of research a cross-check calibration was applied with pigments of known XRF spectrum, supplementary to the built-in shutter calibration. [3]. In total 70 measurements were carried out with XRF technique and the colors studied were: Green, blue, yellow, red, pink, brown, black, and white.

Figure 7. In-situ XRF experimental work in paintings

Regarding the Raman analysis measurements were taken at the same points so as to identify the chemical composition of each pigment, by using a portable Rock-Hound Delta Nu Raman Spectometer, equipped with a near-infrared 785nm laser source, adjusted to 8 cm^{-1} resolution and a spectrum range of 200 cm^{-1} to 2000 cm^{-1} was used. To ensure the correct Raman shift measurements and operation, calibration tests were conducted using the specific palette of pigments Checker. Scientific software SpectraGryph was used to analyse the spectra and then, identification of the chemical compositions was achieved through cross-referencing them to the international pigments databases, Clark (UCL) [5], Checker (Italy) [4].

All measured Raman spectra, before the main process of pigment identification were subjected to a pre-processing procedure such as baseline correction, Savitzky - Golay smoothing and normalization [8].

Last but not least optical microscopy was conducted with the contribution of flash light type LED black lights FL-100/200 with UV-A intensity and UV wavelength. To ensure the right operation at the required UV intensity, the microscope had been first checked and a photometer specially designed to measure the UV irradiance from 320-400 nm with a peak at 365 nm was chosen.

3. Results and Discussion

In figures 1-6 are shown with yellow dots all the sampling points for each color hue. Following, is presented a table with all summarized results of XRF analysis and pigments identified by Raman spectroscopy. In figures 8 -, representative Raman spectrums for different color along with reference spectrums, are shown. [7].

The analysis of all paintings with a portable XRF revealed elements which turned up to be rather helpful in order to identify the specific pigments. The presence of Titanium (Ti) led to Titanium White, Zinc (Zn) to Zinc White and Lead (Pb) to Lead White. Interestingly though G. Gounaropoulos seems to have used Titanium White only on the painting Self Portrait which is his oldest painting. During and after his stay in Paris, he depicts white color by using White Lead and White Zinc. (Figure 9) Most certain these two pigments,

judging by the large percentages that XRF revealed, were also used by the artist to prepare the paintings' substrate. In some cases, it was noticed that Lead White was mixed either with Cadmium Red to depict pink color or with Cadmium Yellow to depict light yellow. So, their use was to enlighten the colors. Aluminum (Al) and Silicon (Si) led to Ultramarine pigment regarding Blue color (Figure 8), respectively Cadmium (Cd) referred to Cadmium Red as well to Cadmium Yellow.

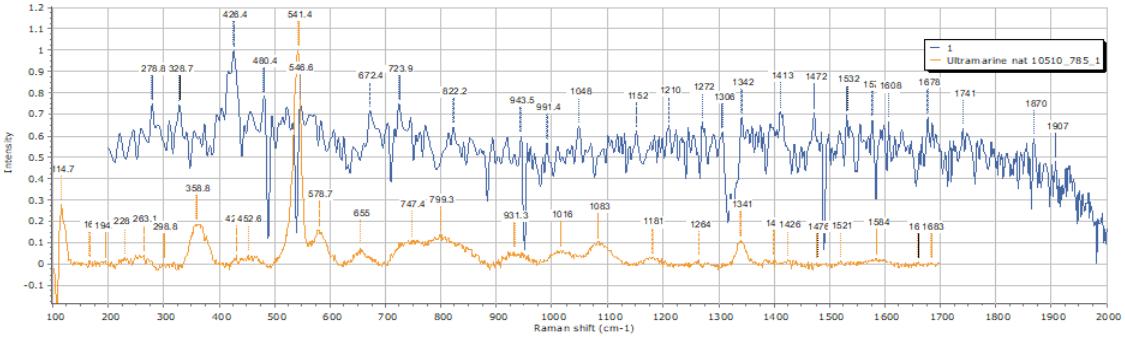

Figure 8. Raman spectrum Blue of Self-Portrait identified as Ultramarine

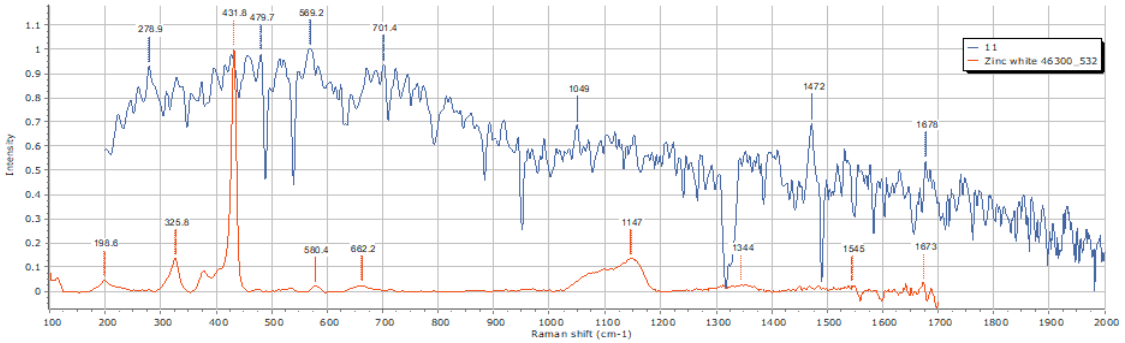

Figure 9. Raman spectrum White of Fair - Haired Nude identified as Zinc White

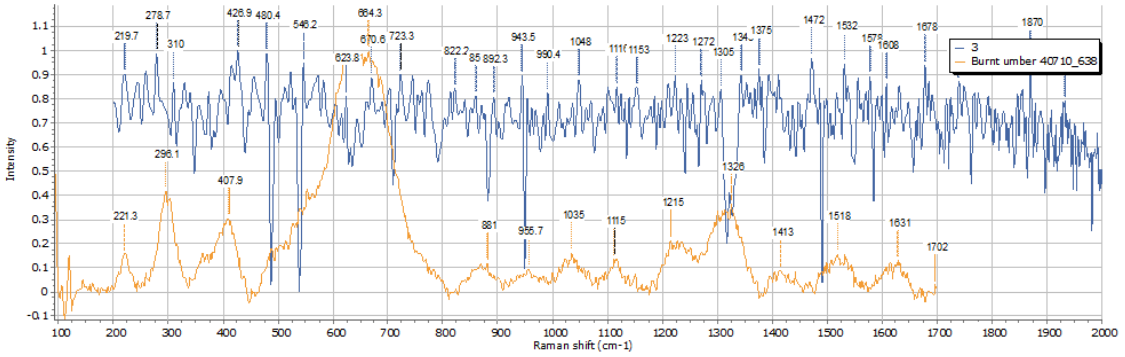

Figure 10. Raman spectrum brown of Barges on the Seine identified as Burnt umber

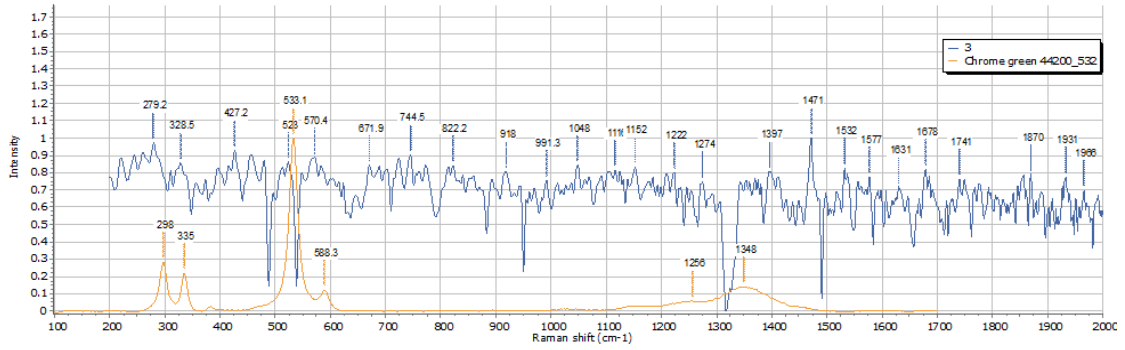

Figure 11. Raman spectrum green of Girls Embroidering identified as Chrome green

Table 1. Summarized Results by XRF and Raman Spectroscopies of the six paintings

Colour Hue	Elements by XRF	Pigment identified by Raman Spectroscopy
Self Portrait c.1912		
Light Blue	Pb, Zn, Ti, Si, S	Ultramarine (583, 364, 1036cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Titanium white TiO_2 (449, 614, 236cm^{-1})
Purple / Blue	Pb, Si, Zn, Ti, Al	Ultramarine (583, 364, 1036cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Red lead Pb_3O_4 (120cm^{-1})
Light Yellow	Pb, Ti, Zn, V, Si	Titanium white (449, 614, 236cm^{-1}) TiO_2 + Yellow ochre (405cm^{-1})
Ochre dark yellow	Pb, Ti, Zn, Cr, Fe	Yellow ochre (405cm^{-1}) Fe2O3.H_2O
Red/Orange	Pb, Ti, Zn, V, Si	Cadmium red (296,200,136cm^{-1}) CdSe + Yellow ochre (405cm^{-1})
Pink skin	Pb, Zn, Ti, S, V	Titanium white (449, 614, 236cm^{-1}) TiO_2 + Cadmium red (296,200,136cm^{-1}) CdSe
Moustache	Pb, Ti, Si, Zn, Al	Ultramarine (583, 364, 1036cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Carbon black (1332, 1576 cm^{-1})
White Collar	Pb, Zn, Ti, Si, V	Titanium white (449, 614, 236cm^{-1}) TiO_2
Cravat	Pb, Si, Ti, Al, Zn	Ultramarine (583, 364, 1036 cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Carbon black (1332, 1576 cm^{-1})
Bridge over the Seine c.1920-1922		
Light Green	Pb, Cr, Ir, As, Si	Chrome green (538,301, 340 cm^{-1}) Cr_2O_3
Brown	Pb, Zn, Fe, Si, As	Burnt Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Red	Pb, Ti, As, Ir, Cd	Cadmium red (296,200,136cm^{-1}) (CdSe)
Light Blue / Grey	Pb, As, Ir, Si, Cd	Lead white (1050, 413, 1372 cm^{-1}) 2PbCoPb (OH) + Ultramarine natural (583, 364, 1036 cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$
White	Pb, As, Ir, Cd, Si	Lead white (1050, 413, 1372 cm^{-1}) ($2PbCO_3$ Pb (OH_2)
Grey / Purple	Pb, Zn, As, Ir, Si	Carbon black (1332, 1576 cm^{-1}) + Lead white (1050, 413, 1372 cm^{-1}) ($2PbCO_3$ Pb (OH_2)
Dark Green	Pb, Cr, Si, As, Al	Chrome green (538,301,340 cm^{-1}) Cr_2O_3
Dark Blue	Pb, Ir, As, Cd, Fe	Ultramarine natural (538, 364, 1036 cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$
Yellow / Beige	Pb, As, Ir, Cd, Fe	Cadmium Yellow (353 cm^{-1}) CdS
Barges on the Seine 1920-1922		
White / Grey	Pb, As, Zn, Cr, Ir	Carbon black (1332, 1576 cm^{-1}) + Lead white (1050, 413, 1372 cm^{-1}) ($2PbCO_3$.$Pb(OH)_2$
Red	Pb, As, Zn, Fe, Ir	Cadmium red (296,200,136cm^{-1}) CdS
Brown / Orange	Pb, Fe, Zn, As, Ir	Burnt Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Brown	Pb, Zn, As, Fe, Ir	Van dyke brown (1600, 1378 cm^{-1}) Fe2O3 (·H2O) + MnO2 (n H2O)
Green	Pb, Cr, Zn, As, Fe	Chrome green (538,301,340 cm^{-1}) Cr_2O_3
White / Yellow	Pb, Zn, As, Ir, Cd	Lead white (1050, 413, 1372 cm^{-1}) ($2PbCO_3$.$Pb(OH)_2$ + Cadmium Yellow (353 cm^{-1}) CdS
Grey Wall building	Pb, As, Ir, Cd, Fe	Carbon black (1332, 1576 cm^{-1}) + Lead white (1050, 413, 1372 cm^{-1}) ($2PbCO_3$.$Pb(OH)_2$
Grey Wall barges	Pb, As, Zn, Ir, Cd	Carbon black (1332, 1576 cm^{-1}) + Zinc white (435, 330, 1150 cm^{-1}) ($2PbCO_3$.$Pb(OH)_2$
Girls Embroidering c.1924-1925		
Brown Hair	Fe, Pb, Zn, Si, P	Burnt Sienna (293, 224, 406 cm^{-1}) SiO2+Al2O3+Fe2O3
Blue	Pb, Ir, As, Cd, Fe	Smalt (1093, 550, 190 cm^{-1}) (Pb) CoO.nSiO_2
Green	Pb, Cr, Fe, Zn, Ir	Chrome green (538,301,340 cm^{-1}) Cr_2O_3
Pink	Pb, Zn, As, Ir, Fe	Cadmium Red (296,200,136cm^{-1}) + Lead White (1050, 413, 1372 cm^{-1}) $2PbCO_3$.$Pb(OH)_2$
Grey	Pb, Zn, As, Ir, Si	Zinc White (435, 330, 1150cm^{-1}) ZnO + Carbon black (1332, 1576 cm^{-1})
Orange	Pb, Zn, Cd, As, Ti	Cadmium orange CdS
Bordeaux	Pb, Zn, Cd, Ti, As	Cadmium Red (296,200,136cm^{-1}) CdSe
Light Blue	Pb, Zn, As, Ir, Fe	Smalt (1093, 550, 190 cm^{-1}) (Pb)CoO.nSiO_2 + Lead white (1050, 413, 1372 cm^{-1}) $2PbCO_3$.$Pb(OH)_2$
Yellow	Pb, Fe, As, Ir, Cd	Massicot (146 cm^{-1}) (PbO)
Light Brown	Pb, Zn, Fe, As, Ir	Burnt Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Dark Brown	Pb, Zn, Fe, As, Ir	Van dyke brown (1600, 1378 cm^{-1}) Fe2O3 (·H2O) + MnO2 (n H2O) + Carbon black (1332, 1576 cm^{-1})
Fair-haired nude c.1924-1925		
Yellow	Zn, Fe, Si, Pb, Ti	Yellow ochre (405 cm^{-1}) ($Fe_2O_3H_20$)
Blue	Zn, Si, Pb, S, Fe Zn, Si, Al, Pb, S	Prussian blue (276, 538 cm^{-1}) (Fe_4{Fe (CN)6}3 Ultramarine natural (583, 364, 1036cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$

Colour Hue	Elements by XRF	Pigment identified by Raman Spectroscopy
Pink	Zn, Pb, Fe, Si, Ta	Red lead (120 cm^{-1}) (Pb_3O_4) + Zinc White (435, 330, 1150cm^{-1}) (ZnO)
Purple	Zn, Pb, Fe, Si, S, Pd	Red ochre (225, 290, 405 cm^{-1}) Fe_2O_3
Orange	Zn, Si, Fe, Al, Pb	Mars Orange (224, 291 cm^{-1}) Fe_2O_3
Green	Zn, Cr, Fe, Pb, Si	Chrome Green (538,301,340 cm^{-1}) Cr_2O_3
Brown	Zn, Pb, Si, Fe, As	Burnt Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Red	Zn, Pb, As, Si, Ti	Red lead (120 cm^{-1}) Pb_3O_4
Black	Zn, Si, Al, Pb, Fe	Carbon black (1332, 1576 cm^{-1}
White	Zn, Fe, Pb, S, Si	Zink White (583, 364, 1036 cm^{-1}) ZnO
Still life c 1925-1926		
Black	Zn, Fe, Si, Al, Co	Ivory black (1348, 1585 cm^{-1})
Brown	Zn, Al, Fe, Si, Co	Burnt Umber Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Light Blue	Zn, Fe, P, Cr, Si	Ultramarine (583, 364, 1036 cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Zinc white (ZnO)
Bordeaux	Zn, Pb, Si, Fe, Hf	Burnt Umber SiO2+Al2O3+Fe2O3+Fe3O4
White	Zn, Si, Al, Pb, Fe	Zinc White (583, 364, 1036 cm^{-1}) ZnO
Purple	Zn, Si, Al, Pb, Fe	Ultramarine (583, 364, 1036cm^{-1}) $Na_7Al_6Si_6O_{24}S_3$ + Burnt Umber SiO2+Al2O3+Fe2O3+Fe3O4
Pink	Zn, Si, Fe, Al, Pb	Zinc White ZnO + + Burnt Umber (649, 296, 410 cm^{-1}) SiO2+Al2O3+Fe2O3+Fe3O4
Yellow	Zn, Fe, Ti, Si, S	Titanium White (449, 614, 236cm^{-1}) TiO_2 +Yellow ochre (405cm^{-1}) $Fe_2O_3\,3H_2O$
Green	Zn, Cr, Si, Fe, Pb	Chrome green (538,301,340 cm^{-1}) Cr_2O_3

The element of (Fe) led to Yellow Ochre, a pigment which seems typical of the artist when it comes to depict yellow color. For brown color which is a color being used extensively by the artist on all of his paintings, the strong presence of Iron (Fe), in such high percentages led to Burnt Umber. (Figure 10) This pigment was mostly used for brown, without meaning that other pigments such as Burnt Sienna and Van dyke brown have not been traced on this research. G. Gounaropoulos to depict Pink color used different combinations, by mixing red pigments with white pigments. What remains the same on all his paintings is his preference for Chrome Green, regarding green color. (Figure 11) The element of Cr was very powerful during the analysis. The study did not reveal any other green pigment. All pigments mentioned above were also identified by Raman Spectroscopy. Both techniques came to the same results, that is why the findings are so reliable.

Through the conducted study some specific peaks rather strong constantly appeared almost on every painting. Peak 279cm^{-1} was identified as Egmode spectal signature of Hematite and peak 1472cm^{-1} as Alizarin Purple ($C_{14}H_8O_4$).

The use of optical microscope revealed that in figure one some pigments have been fluroised. Originally the figure's moustache, hair and scarf had been purple and blue-black. Furthermore, around the moustache there had been facial hair, faded away over time.

4. Conclusions

The presence study aimed at the pigment identification of six paintings of the well-known artist G. Gounaropoulos at the Municipal Art Gallery of Larissa, in the G.I. Katsigras Museum. Moreover, the reproduction of the artist's palette has also been the subject of the research.

Summarizing the results, G.Gounaropoulos has used in the particular paintings Titanium White, Lead White and Zinc White for white color, Chrome Green for green, Ultramarine, Smalt and Prussian Blue for blue, Burnt Umber, Burnt Sienna and Van dyke Brown for brown, Cadmium Red, Red Ochre and Red Lead for Red color, Cadmium Orange in order to depict orange, Yellow Ochre and Cadmium Yellow for Yellow, Ivory Black and Carbon Black for Black, Grey consisted of Carbon Black and Zinc White, Purple of Ultramarine Natural and Burnt Umber. Finally, Pink was made of either Titanium White and Cadmium Red or Lead White and Cadmium Red or Zinc White and Red Lead.

G. Gounaropoulos' colorful palette can be used to give answers looked for, by art historians and collectors interested in cultural heritage.

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