A Multi-analytical Study of a 20th Century Oil Painting of King Farouk at The Egyptian Agricultural Museum

دراسة متعددة التحاليل للوحة زيتية من القرن العشرين للملك فاروق بالمتحف الزراعي المصري

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Abstract

The main objective of the present study is to characterize the structure and material of the paint layers used in an oil painting from the 20th century, a life-sized canvas painting of the Egyptian King Farouk, dated back to the first half of the 20thcentury (1940-1950)by the Egyptian painter Muhammad Hassan (1892-1961), displayed in the Heritage Collection Museum at the Egyptian Agricultural Museums in Dokki, Giza. Different techniques were utilized to better understand the materials used before the conservation process. USB digital microscope, Gas Chromatography-Mass Spectrometry (GC-MS), Micro-Raman Spectroscopy (MRS), and Scanning Electron Microscopy with Energy Dispersive X-ray Spectroscopy (SEM-EDX) were used. The results revealed that (i) a linen canvas support, pre-treated with a sizing layer of animal glue, was used; (ii) the ground layer consisted of lead white mixed with animal glue as an Adhesive; (iii) the identified pigments were celadonite, viridian, lemon yellow, lithopone, and ivory black, mixed with linseed oil as a binding medium;(iv)no varnish layer was found. Finally, these results highlighted the materials and techniques of the modern Egyptian oil painting school during the 20thcentury. Therefore, the most suitable methods of restoration and conservation were utilized.

Keywords: 20th century oil painting, Analytical technique, Conservation, SEM-EDX, GC-MS, MRS.

الملخص

يتمثّل الهدف الرئيس من هذه الدراسة في دراسة المواد الملونة وخصائصها وطبقات التصوير المستخدمة في لوحة زيتية من القرن العشرين، وهي لوحة على كانفاس بالحجم الطبيعي للملك المصري فاروق، يعود تاريخها إلى النصف الأول من القرن العشرين (1940-1950م) للرسام المصري محمد حسن (1892-1961م)، معروضة بمتحف المقتنيات التراثية داخل المتحف الزراعي المصري بالدقي، الجيزة. تم استخدام تقنيات مختلفة لفهم المواد المستخدمة بشكل أفضل، تمهيدًا لترميمها وصيانتها. تم استخدام المجهر الرقمي USB، ومطياف ميكرو رامان (MRS)، والميكروسكوب الإلكتروني الماسح مع وحدة تشتيت طاقة الأشعة السينية (SEM-EDX) والكروماتوغرافي الغازي مع مطياف الكتلة (GC-MS). وقد بينت النتائج: (1) استخدام قماش الكتان كحامل للوحة، وقد تمت معالجته مسبقًا بطبقة من الغراء الحيواني؛ (2) تتكون أرضية التحضير من الرصاص الأبيض الممزوج بالغراء الحيواني كمادة لاصقة؛ (3) المساحيق اللونية المستخدمة هي الأخضر الأرضي، أكسيد الكروم، الأصفر الليموني، الليثيبون واسود العاج ممزوجين مع زيت بذر الكتان كوسيط (4) لا توجد طبقة ورنيش على سطح اللوحة. أخيراً، فقد سلطت هذه النتائج الضوء على مواد وتقنيات المدرسة المصرية الحديثة في التصوير الزيتي خلال القرن العشرين ومن ثم اختيار أفضل الطرق للعلاج والحفظ.

الكلمات الدالة: لوحة زيتية من القرن العشرين، التقنية التحليلية، ترميم وصيانة، SEM-EDX، GC-MS، MRS.

1. Introduction

The 20thcentury witnessed a major transformation in the arts. Painters became free from traditional constraints and employed new materials and techniques. Oil painting, in particular, underwent a period of profound experimentation as artists sought to expand the expressive potential of the medium. One major area of innovation was the use of pigments and medium for experimentation towards new techniques and visual forms[1,2].In the mid-20thcentury, artists were affected by the newly produced synthetic materials in the art market, such as manufactured oil paints, which changed dramatically with the invention of metal tubes introduced into the art market[3].Additionally, toxic inorganic pigments were replaced by benign – and often cheaper – organic dyes to address issues of health and safety, cost control, and compliance with environmental legislation[4,5].

Various vegetable oils were used in these new paint formulations. In addition to traditional drying oils (linseed oil, walnut oil, and poppy seed), other drying, semi-drying, and non-drying fatty binders were used, perhaps as inexpensive and readily available alternatives to walnut and poppy oil. Examples included safflower[6,7]. Additives were also chosen to provide good stability for pigments. However, modern oil paints revealed higher problems in stability, such as insufficient drying, efflorescence, the appearance of drying cracks, phase separation in the coating, and water sensitivity, as confirmed by the physicochemical studies on modern oil paints and paintings[8].

Commonly used methods for pigment identification, such as SEM-EDX and XRD, are suitable methods for identifying inorganic pigments. GC–MS is the most used technique for the identification of drying oils in paintings[9,10].Moreover, MRS is a

[1]Van den Berg, K. J., Bonaduce, I., Burnstock, A., Ormsby, B., Scharff, M., Carlyle, L., ... & Keune, K.*Conservation of modern oil paintings*. 2019: Springer.

[2]Izzo, F. C., Ferriani, B., Van den Berg, K. J., Van Keulen, H., & Zendri, E. *20th century artists' oil paints: the case of the Olii by Lucio Fontana.* Journal of Cultural Heritage, 2014. 15(5): p. 557-563.

[3] Izzo, F.C., *20th century artists' oil paints: a chemical-physical survey.* 2011.

[4] Boon, J., *Molecular aspects of mobile and stationary phases in ageing tempera and oil paint films in Early Italian Paintings*. in *Techniques and Analysis Symposium*. 1997.

[5]Van Den Berg, J.D., K.J. Van Den Berg, and J.J. Boon. *Chemical changes in curing and ageing oil paints*. in *Triennial meeting (12th), Lyon, 29 August-3 September 1999: preprints. Vol. 1*.

[6]Mills, J. and R. White, *Organic chemistry of museum objects*. 2012: Routledge.

[7]Lomax, S.Q. and T. Learner, *A review of the classes, structures, and methods of analysis of synthetic organic pigments.* Journal of the American Institute for conservation, 2006. 45(2): p. 107-125

[8]Sivester, G., Burnstock, A., Megens, L., Learner, T., Chiari, G., & van den Berg, K. J. , A cause of water-*sensitivity in modern oil paint films: the formation of magnesium sulphate.* Studies in Conservation, 2014. 59(1): p. 38-51.

[9]Colombini, M. P., Andreotti, A., Bonaduce, I., Modugno, F., & Ribechini, E. *Analytical strategies for characterizing organic paint media using gas chromatography/mass spectrometry.* Accounts of chemical research, 2010. **43**(6): p. 715-727.

noninvasive method for the identification of inorganic pigments or natural organic lake pigments and dyestuffs[11]. It performs well for modern organic pigments as a basic database and identification protocol [12] . Particularly in the 20thcentury, analytical techniques and methods applied to the study of artworks have constantly advanced in the service of art by the identification of artists' materials and heritage conservation[13].

By reconstructing using historically appropriate materials, it was revealed why materials were prepared in a certain way. It is also possible to know the effect of the paintformulation on the structure and composition of the painting, such as the role of pigments in curing and aging processes, as derived from several analytical studies on oil paints. This also can serve as reference samples to compare the results of analyses and to help interpret analytical results[14].The current work presents a preliminary study on Easel painting characterized by the multi-techniques approachto explore the materials and to draw technique in the works of the painter Mohammed Hassan (1892-1961),an Egyptian painter who participated in the arts movement in Egypt, after studying the fine arts. He was called a professor of portraiture as he was interested in the academic school.He also devoted his efforts to the creation of the Agricultural Museum in Dokki and the Museum of Civilization in Gezira[15,16].

2. Materials and Methods

2.1.Case Study Painting and Samples

The subject of the case study painting is King FarouqPainting(Fig. 1 A,B) by the Egyptian painter Mohammed Hassan (1892-1961) (Fig. 1 C),preserved in the Heritage Collections Museumat the Egyptian Agricultural Museums. The painting depicts King Farouk (1920-1965) at the end of his reign, in the royal suit, standing and holding his sword, and wearing his medals.He wears a white glove and a red Ottoman fez over his head.

[10]Elsayed, Y., *Identification of oil media in five canvas paintings at the Agricultural Museum in Egypt.* J. of Faculty of Archaeology (Qena), 2015. **10**: p. 60-92.

[11]Smith, G.D. and R.J. Clark, *Raman microscopy in art history and conservation science.* Studies in Conservation, 2001. **46**(sup1): p. 92-106.

[12]Vandenabeele, P., Moens, L., Edwards, H. G., & Dams, R.*Raman spectroscopic database of azo pigments and application to modern art st*udies. Journal of Raman spectroscopy, 2000. 31(6): p. 509-517.

[13] Fremout, W. and S. Saverwyns, *Identification of synthetic organic pigments: the role of a comprehensive digital Raman spectral library.* Journal of Raman spectroscopy, 2012. **43**(11): p. 1536-1544.

[14] Van den Berg, J., *Analytical chemical studies on traditional oil paints.* Amsterdam: University of Amsterdam, 2002.

[15] Al-Sharouni, S., *Museum in a book* 1ed. Egypt: Alshrok House Vol. 1. 1998, p 35.

[16]Alrubaie, S., *Introduction to the contemporary art in Arab land,* Author House 2014, p: 44

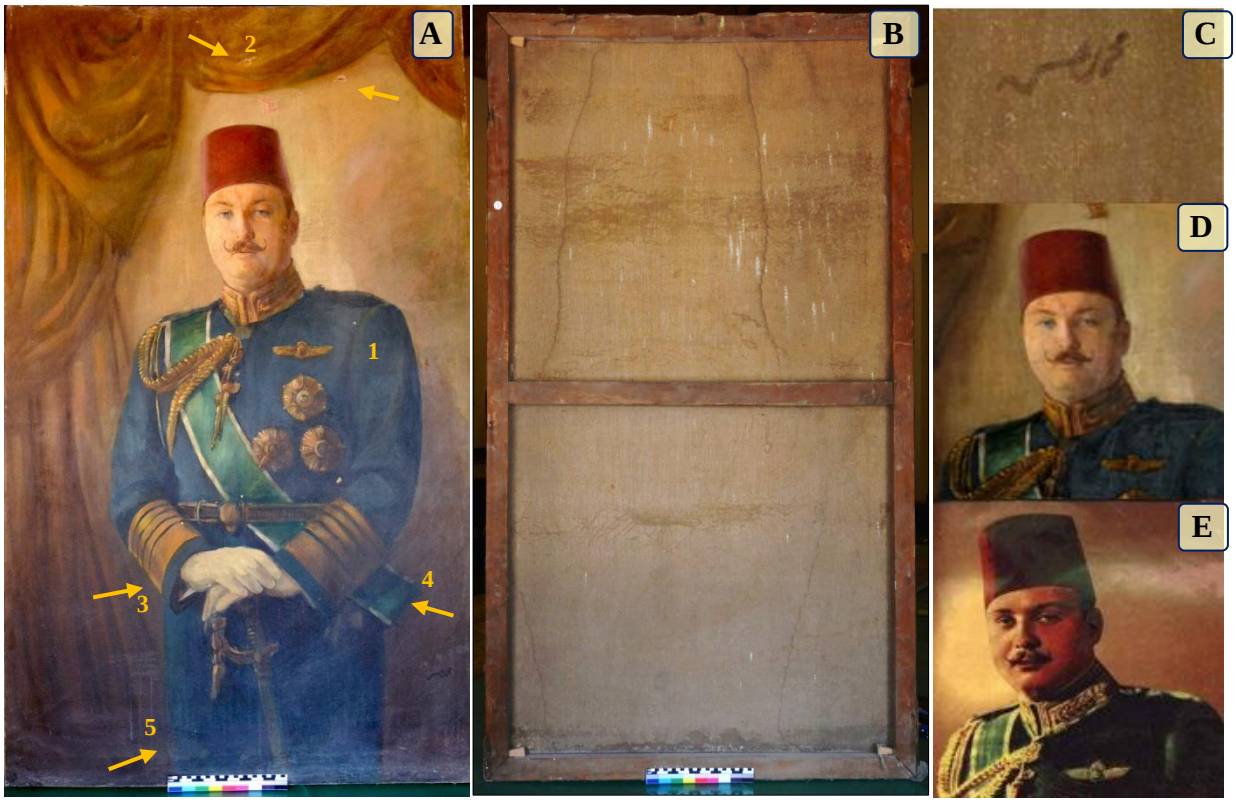

Fig. 1 The case study of King Farouq Painting, **A.** front, **B.** back, **C.** Mohammed Hassan'ssignature, **D.** Portrait of King Farouk,**E.** Photographic picture of King Farouk from the archive at the end of his reign.

The case study object was painted with oil on a canvas. Its size is 103 x 172 cm, excluding the frame. By comparing an archive portrait of King Farouk (Fig. 1 D, E) and his portrait in the case study painting, in terms of appearance, facial features, as well as suit and medals that he wears, as his outfit indicates a certain period of life[17], we find that it dates to the end of his rule and the artist's life during this period (1892-1961).Therefore, the painting can be dated to the first half of the 20th century(1940-1950). Six micro samples were collected for testing, avoiding structural and aesthetic damage to the artwork (Fig. 1 A). They were collected by scrapping off approximately 1 mg of the paint layers in different color spots to identify the pigments, medium, and ground layer. It was necessary to perform micro-sampling to obtain a fragment containing all the layers forming the work of art. This micro-sample or cross-section, once embedded in resin, can be easily used as a base to perform many investigations and analyses (Fig. 3 A, f)[18].

2.2.Technical investigation

2.2.1. USB microscopy

A handheld USB digital microscope (ROHS, M8704-1000, China) with magnifications of 100x and 1000x was utilized to study the painting surface's

[17] McLeave, H., *The Last Pharaoh: Farouk of Egypt*, 1970., p:87.

[18]Derrick, M., Souza, L., Kieslich, T., Florsheim, H., & Stulik, D. *Embedding paint cross-section samples in polyester resins: Problems and solutions.* Journal of the American Institute for Conservation, *1994*, 33(3), 227-245.

morphology. A cross-section was made for analyses to identify the artistic materials[19]. It was used in small magnification (up to 500×). The USB digital microscope is a simple and cost-effective method for getting microscopic colored images with fair magnification, especially since there is no possibility for other non-invasive techniques.

2.2.2. GC-MS

Small amounts (0.05–0.10 mg)of a collected sample were prepared to extract methyl ester of fatty acids, according to Rossell et al.[20].GC - MS analysis of the chemical composition of your samples was performed using Trace GC 1310- TSQ 9000 mass spectrometer (Thermo Scientific, Austin, TX, USA) with a direct capillary column TG - 5MS 30 m x 0.25 mm x 0.25 um film thickness). The column oven temperature was initially held at 50 °C and then increased by 5 °C/ min to250 °C held for 2 min. increased to the final temperature of 300 °C by 30 °C / min and held for 2 min. The injector and MS transfer line temperatures were kept at 270 and 260 °C, respectively; helium was used as a carrier gas at a constant flow rate of 1 ml/min. Spectra were collected, and their components were identified by comparing their mass spectra and retention times with those in the WILEY 09 and NIST 14 mass spectral databases[21].

2.2.3. SEM-EDX

The identification of deterioration phenomena is one of the sampling targets. Therefore, the study used SEM-EDX (JEOL JSM-6510 LV, JEOL Ltd., Japan, ACCEL_20KV, MAG 4300, SIGNAL SEI, WD10mm) at Mansoura University. SEM-EDX analyses were implemented at low vacuum without coating. SEM-EDX is the most common technique used for investigation and analysis in the field of art conservation[22,23].

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[19]Keune, K. and J.J. Boon, *Imaging secondary ion mass spectrometry of a paint cross section taken from an early Netherlandish painting by Rogier van der Weyden. Analytical Chemistry*, 2004. 76(5): p. 1374-1385.

[20]Rossell, J., B. King, and M.J. Downes, *Detection of adulteration.* Journal of the American Oil Chemists' Society, 1983. **60**(2Part2): p. 333-339.

[21]Abd El-Kareem, M. S., Rabbih, M. A. E. F., Selim, E. T. M., Elsherbiny, E. A. E. M., & El-Khateeb, A. Y., *Application of GC/EIMS in combination with semi-empirical calculations for identification and investigation of some volatile components in basil essential oil.* International Journal of Analytical Mass Spectrometry and Chromatography, 2016. 4(1): p. 14-25.

[22]Bruni, S., Guglielmi, V., Della Foglia, E., Castoldi, M., & Gianni, G. B.,*A non-destructive spectroscopic study of the decoration of archaeological pottery: from matt-painted bichrome ceramic sherds (southern Italy, VIII-VII BC) to an intact Etruscan cinerary urn.*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2018. **191**: p. 88-97.

[23] Darchuk, L., Tsybrii, Z., Worobiec, A., Vázquez, C., Palacios, O. M., Stefaniak, *Argentinean prehistoric pigments' study by combined SEM/EDX and molecular spectroscopy.*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2010. **75**(5): p. 1398-1402.

2.2.4. MRS

A non-destructive characterization of painting materials was carried out by MRS to identify the characteristic bands of minerals[24]. The types of bonds were detected using a Confocal Raman microscope (Jasco NRS-4500, Tokyo, Japan) at the range of 200–2000 cm-1. For both Raman data acquisition and processing, Jasco spectroscopy suite software was used. Micro-Raman spectroscopy has several advantages that make it the key choice for combined analytical procedures, and a particular advantage in quantitative studies is the linear relationship between species concentration and band intensity[25].

3. Results and Discussion

3.1. Visual and microscopic results

Identifying the components of the case study painting is the first step to better understand the materials and techniques of painting used by the painter and to detect the potentialdegradation phenomena[26].The results revealed that the case study painting was painted with oils on a canvas support. The accumulation of dirt particles on the surface of the painting greatly contributes to its deterioration. Both dirt particles and degradation products badly affect the perception of important surface properties, such as gloss or color, and may additionally distract from the intended experience (Fig 2. A). The appearance of the front side of the painting is typical of a traditional oil technique and gives no indication of tears, holes, or defects in its construction except in the lower half of the painting. There were randomly distributed raised rings of medium paint. Partial sheen was observed; it differed from the rest of the painting's appearance, resulting from previous retouching of this entire area (Fig 2. B).

Cracks, flaks, missing paints, and losses were also observed, especially on the edges of the stretcher. The painting layer had a few long cracks across the surface. At the back of the painting, the canvas support had many signs of decay and deterioration, such as dust, stain spots, and friability (Fig 2. C-G). The canvas was woven in the plain 1/1 technique (Fig. 3 C, D), observed by a USB microscope. Additionally, SEM micrographs confirmed the canvas weaving technique and revealed that the fiber type was linen (Fig 4 A, B). The distinctive composition of the canvas (warp and weft) appeared on the paint layer.

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[24]Lau, D., Villis, C., Furman, S., & Livett, M.*Multispectral and hyperspectral image analysis of elemental and micro-Raman maps of cross-sections from a 16th century painting. Analytica chimica acta, 2008. 610(1): p. 15-24.*

[25] Schulte, F., Brzezinka, K. W., Lutzenberger, K., Stege, H., & Panne, U.*Raman spectroscopy of synthetic organic pigments used in 20th century works of art.* Journal of Raman Spectroscopy: An International Journal for Original Work in all Aspects of Raman Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh Scattering, 2008. **39**(10): p. 1455-1463.

[26] Burnstock, A. and K.J. van den Berg, *Twentieth century oil paint. The interface between science and conservation and the challenges for modern oil paint research.* Issues in contemporary oil paint, 2014: p. 1-19.

USB digital microscopy revealed typical stratigraphy from cross-section examination, as illustrated in (Fig 3 E-G), that the layered composition of the painting understudy consisted of a textile support composed usually of stretched on a rigid wooden frame, a glue size, a thin ground, and a paint layer and with no varnish layer. This is what many artists of the 20thand 21stcenturies are accustomed to (unvarnished oil paintings). It exposes oil paintings to many problems[27]. Overall, the paint surface is flat and smooth, and the paint surface has no varnish, and is rich in texture (Fig 4C).

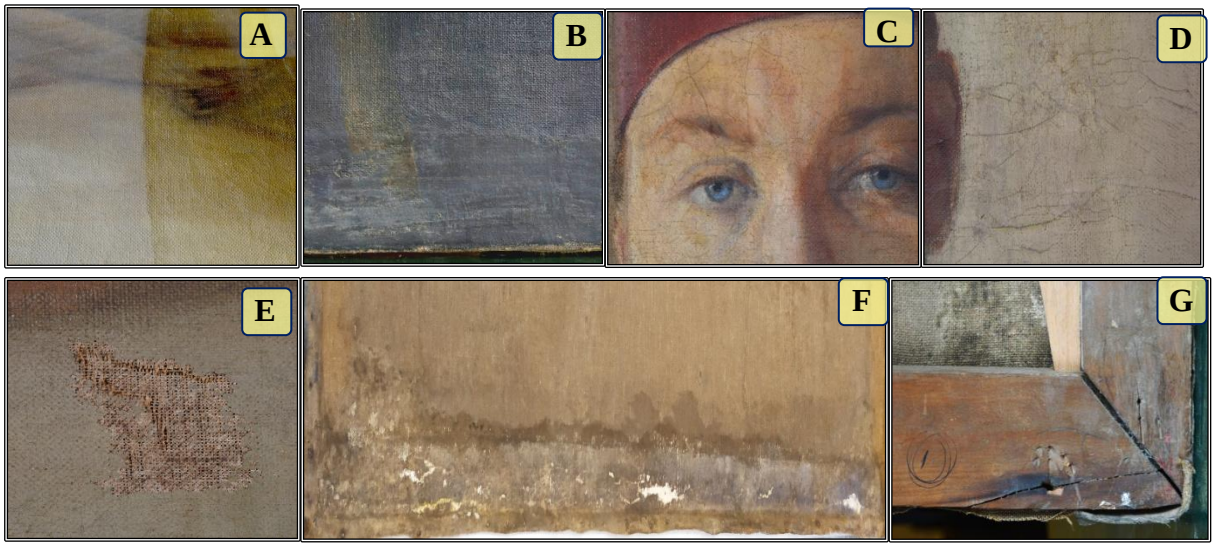

Fig 2. Visual examination of King Farouq Painting shows **A.** Dirt particles, **B.** Fault old retouching**, C., D., E.** Cracks, macro cracks, flakes, peeling and missing paint area, **F.** Stains and fragile, **G**. Weakness of wooden frame.

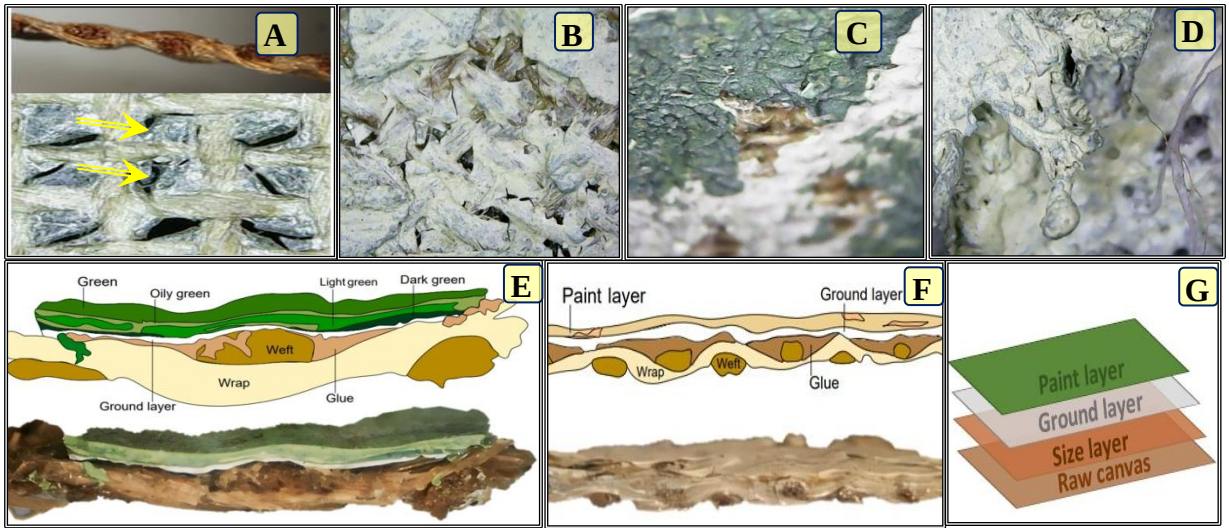

Fig 3: USB digital micrographs: **A.**Linen canvas and sizing coat, **B.,C**. Flakes, peeling, missing paint area and fragility of ground and paint layer, **D.** Wrinkling in the paint layer**, E., F., G.**A cross-section of the painting

[27] Burnstock, A. and K.J. van den Berg, *Twentieth century oil paint. The interface between science and conservation and the challenges for modern oil paint research.* 2014, p.1-19.

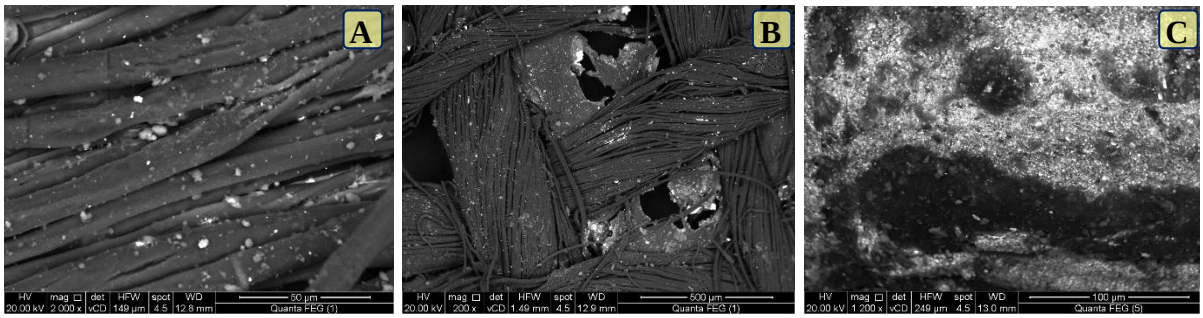

Fig 4: SEM micrographs of the painting: **A.** Linen canvas, **B.** Sizing layer, **C.** Fragility of ground and paint layer

3.2.GC-MS

The result of GC-MS analysis of the extracted oil from the samples is shown in (Fig5). GC-MS analysis showed saturated and unsaturated fatty acids. (P) palmitic acid and (S) stearic acid were the most abundant saturated acids, while oleic, linoleic, and linolenic were the most abundant unsaturated acids[28].traces of fatty, (Sub) subric, and (A) azelaic acids indicated that oxidation occurred.

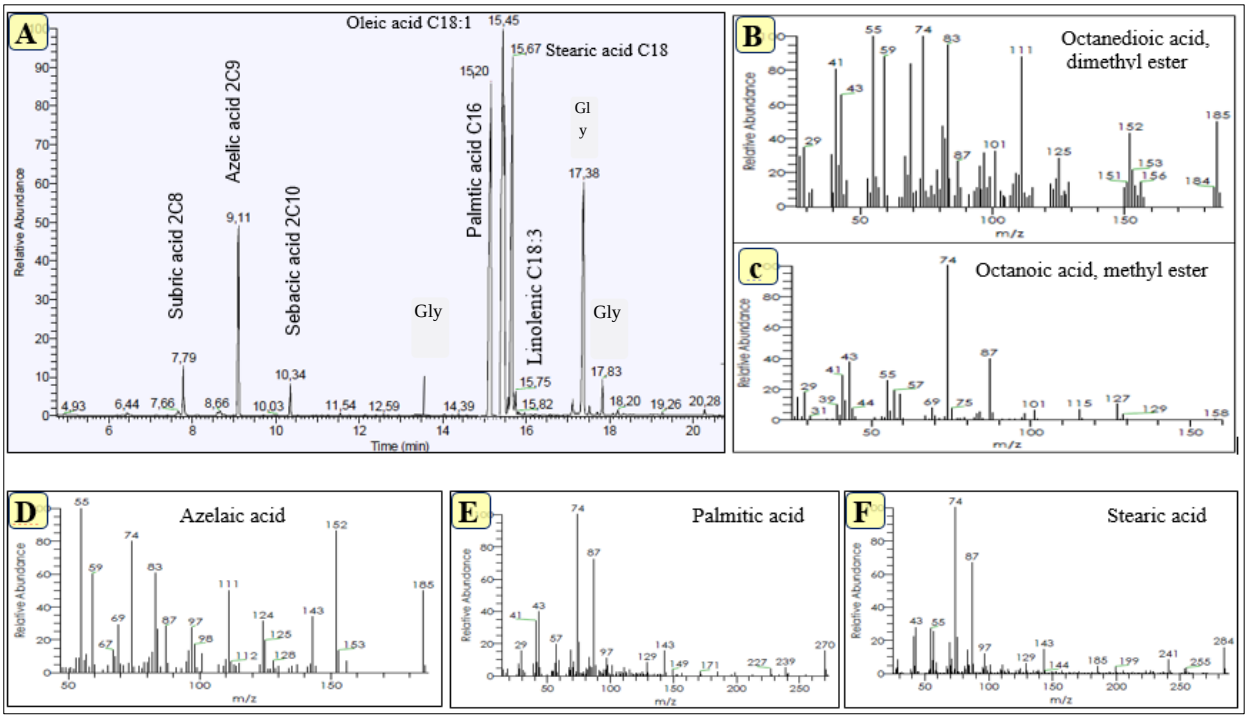

Fig. 5: **A.** GC-MS spectrum of the drying oil, **B, C, D, F.** Mass spectra of Octadecanoic acids, Azelaic, Palmitic, and Stearic acids, respectively

The analytical results of the GC-MS procedure were finally expressed in terms of molar ratios. The characteristic parameters that are commonly used to characterize the molar ratios are P/S, A/P, Sub/ A, and O/S. The molar ratios used in this research are as follows[29,30]:

[28]Mohie, M.A. and G.M. Sultan, *Analytical study and structural treatment for a thin panel pain*ting. Pigment & Resin Technology, 2021. 50(2): p. 104-112.

[29]Mills, J. and R. White, *Organic chemistry of museum objects*. P: 55.

- P/S: (C16/C18) ratio was used to identify traditional drying oils. This evaluation was based on saturated fatty acids, such as palmitic and stearic. The P/S ratio was0.97, which confirmed the use of linseed oil as a medium.

- A/P: (2C9/C16) the ratio distinguishes between drying oils and egg lipids: A/P<0.3 for egg and A/P>.6 for oils. It can be used to measure the oxidation in the fatty material because azelaic acid and other diacids arise from the oxidation of unsaturated fatty acids found in the oil. This ratio is influenced by manyagents,e.g. the presence of pigments and driers, the pre-heating during preparation, and the rate of oxidation, degradation, and polymerization of the paint layer. The value of the A/P ratio was0.6, which confirmed that the media were oil and numerous dicarboxylic acids, e.g. azelaic and suberic acids, the compounds of the unsaturated fatty acids[31,32].

-Sub/A: (2C8/2C9) refers to the pre-heating processes in oil preparation. If the value of Sub/A is above 0.4, it may refer to the presence of a heat-bodied oil, not raw oil. The result of this ratio was 0.8, which might refer to pre-heated oil, i.e., the pre-polymerization of the medium material[33].

-O/S: oleic (C18:1)/stearic (C18:0) expresses the maturity of the oil and is considered an index of oxidation. The O/S value of old films is usually around 0.1-0.2, as the oleic content is very low. However, the result of the O/S value of 0.9 showed a high amount of oleic acid, confirming the young age of the painting layer and the minor reaction of autoxidation[34]. Oil films are evaluated by their fatty acid values compared to the literature. Several peaks related to glycerol derivatives (Gly) and numerous oxidized octadecanoic acids were produced by the oxidative scission of unsaturated fatty acids (Fig 5B-D).

3.3.SEM-EDX

SEM-EDX results are presented in (Fig. 6) and (Table 1).In sample 1(the ground layer)(Fig. 6A), a fair proportion of lead was detected. The presence of lead is generally attributed to some type of lead-containing pigment, such as white lead. The obtained

[30]Cappitelli, F., *THM-GCMS and FTIR for the study of binding media in Yellow Islands by Jackson Pollock and Break Point by Fiona Banner.* Journal of Analytical and Applied Pyrolysis, 2004. **71**(1): p. 405-415.

[31]La Nasa, J., Zanaboni, M., Uldanck, D., Degano, I., Modugno, F., Kutzke, H.& Colombini, M. P. , *Novel application of liquid chromatography/mass spectrometry for the characterization of drying oils in art: elucidation on the composition of original paint materials used by Edvard Munch (1863–1944).* Analytica Chimica Acta, 2015. **896**: p. 177-189.

[32]SCHILLING, M.R. and H.P. KHANJIAN, *GAS CHROMATOGRAPHIC ANALYSIS OF AMINO ACIDS AS ETHYL CHLOROFORMATE DERIVATIVES.* 1996.

[33]Castellá, F., Pérez-Estebanez, M., Mazurek, J., Monkes, P., Learner, T., Niello, J. F., ... & Marte, F. , *A multi-analytical approach for the characterization of modern white paints used for Argentine concrete art paintings during 1940–1960.*Talanta, 2020. **208**: p. 120472.

[34]Bayliss, S., van den Berg, K. J., Burnstock, A., de Groot, S., van Keulen, H., & Sawicka, A., *An investigation into the separation and migration of oil in paintings by Erik Oldenhof.* Microchemical Journal, 2016. **124**: p. 974-982.

spectra revealed the presence of lead due to lead white[35]. The results confirmed the presence of hydro cerussite $2PbCO_3 \cdot Pb(OH)_2$, which was commonly used as a ground layer, one of the oldest synthesized pigments, and the most used white pigment until the late 19th century. Fe could be an impurity in this material[36]. The result of sample 2 (dark green sample) (Fig. 6B) revealed a low signal of Mg, suggesting the presence of celadonite (green earth) $K[(Al,Fe_3C),(Fe_2C,Mg)](AlSi_3,Si_4)O_{10}(OH)2$[37], demonstrating the trend Si > Al > Mg.

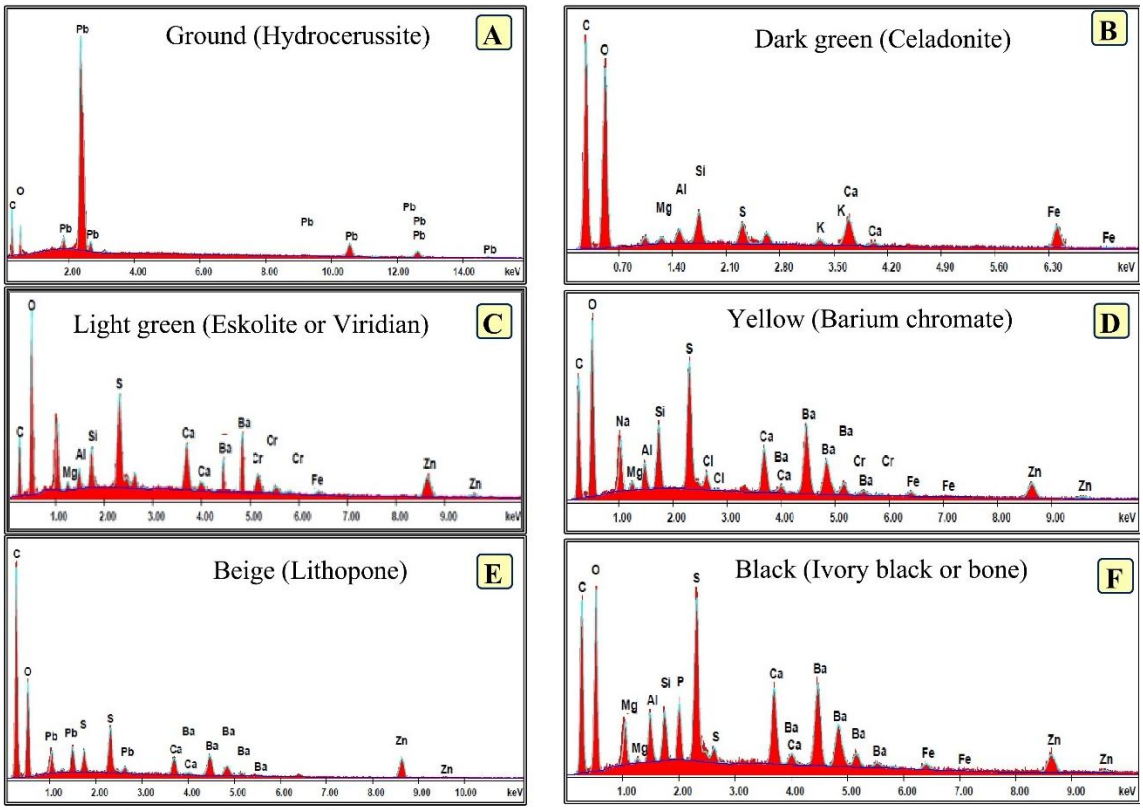

Fig 6. EDX results of the 6 collected samples

Table (1) SEM-EDX results of the 6 collected samples and the suggested used materials

No	Samples	Detected elements	Suggested used pigments
1	Ground	C, O, Pb	Pb (lead white)
2	Dark green	C, O, Mg, Al, Si, S, Ca, K, Fe	Mg, Al, Si,S, Ca, K, and Fe (celadonite)
3	Light green	C, O, Cr, Ba, Mg, Al, Si, S, Ca, Zn	Cr (lemon yellow) or viridian, Ba (Pyrite), Zn (zinc white) + Al, Si,S, Ca (celadonite)

[35]Paradisi, A., Sodo, A., Artioli, D., Botti, A., Cavezzali, D., Giovagnoli, A., ... & Ricci, M. A. *Domus Aurea, the 'Sala dellemaschere': Chemical and spectroscopic investigations on the fresco paintings.* Archaeometry, 2012. **54**(6): p. 1060-1075.

[36]Manzano, E., et al., *A combination of invasive and non-invasive techniques for the study of the palette and painting structure of a copy of Raphael's Transfiguration of Christ.* Heritage Science, 2021. **9**: p. 1-14.

[37]O'Hanlon, G., *Green Earth Pigments in Art—Uses, Properties and Colors.*

4	Yellow	C, O, Mg, Al, Si,S, Ca, Cr, Ba, Zn	Ba+Cr (barium chromate), Zn (zinc white), and/or Mg, Al, Si, S, Ca (celadonite)
5	Beige	C, O, S, Ca, Pb, Ba, and Zn	Zn+Ba+S (lithopone), Pb (lead white), Ca (chalk)
6	Black	C, O, S, Ca, P, Ba, Si, Mg, and Zn	Ca+P+Mg (ivory black) bone black, Ca (chalk), Zn (zinc white)

The results of sample 3 (light green)(Fig. 6C)revealed the presence of Cr, which might relate to green Esko lite CR_2O_3(chromium oxide) green or viridian with some impurities of Si, Mg, Cl, Ca, Zn, and Ba, suggesting the presence of celadonite, zincate and/or barite, used as a white coloring pigment for lightening the green pigment[38].The results of sample 4 (yellow)(Fig. 6D)revealed the presence of barium chromate due to the presence of Ba and Cr[39], and the presence of Mg, Al, and Si illustrated the identification of celadonite. From the 19th century onwards, it was called by various names, such as lemon yellow, ultramarine, yellow, and strontian yellow[40].

The spectrum of the beige sample (sample 5) (Fig.6E) showed a high intensity of sulfur (S) and barium (Ba). It might refer to barite ($BaSO_4$). Zn, Ba, and S might refer to lithopone ($BaSO_4$.ZnS) or mixtures of barium sulfate and zinc sulfide or zinc oxide pigments that were commonly used as coloring agents for beige and grayish-white pigments in different shadows. The identification of lithopone might ensure that the painter made this painting in the contemporary period, and the traces from Cr confirmed the addition of a little lemon yellow to obtain the beige shadow.

As first evidence, SEM–EDX results of the black sample (sample 6)(Fig. 6F)showed Ca, P, and Mg, which implied the bone black or ivory black($C+Ca_3(PO_4)_2$)with traces of lithopone elements (Ba, S, and Zn).They indicated that the painter used a mixture of pigments for the degree of the black suit to get the dark grey color[41].

3.4.MRS

SEM-EDX results were not sufficient to confirm the components of pigments; therefore, another method was used to verify the results, which clearly highlighted the necessity of applying additional screening techniques to overcome these limitations[42]. MRS results of the samples (Fig. 7) revealed the features in the range 200-1200/2000cm^{-1}(Table 2) as follows:

[38] Gražėnaitė, E., *Inorganic green pigments: investigation of historical and synthesis of novel pigments by sol-gel method*. 2018, Vilniaus universitetas.

[39]Eastaugh, N., *Pigment compendium: a dictionary of historical pigments*, 2007: Routledge.

[40]Kühn, H. and M. Curran, *Chrome yellow and other chromate pigments*, in *Artists' pigments; A handbook of their history and characteristics*. 1986. p. 187-217.

[41]Martins, A., Coddington, J., Van der Snickt, G., van Driel, B., McGlinchey, C., Dahlberg, D., & Dik,J.*Noninvasive analysis using macro X-ray fluorescence mapping (MA-XRF) and multivariate curve resolution-alternating least square (MCR-ALS).* Heritage Science, 2016. **4**(1).

[42]Sara, B., Austin, N., Anna, C., Valentina, C., Hervé, V., Caroline, T.,& Daniela, C.*Multianalytical study of historical luminescent lithopone for the detection of impurities and trace metal ions*: p. 6049-6056.

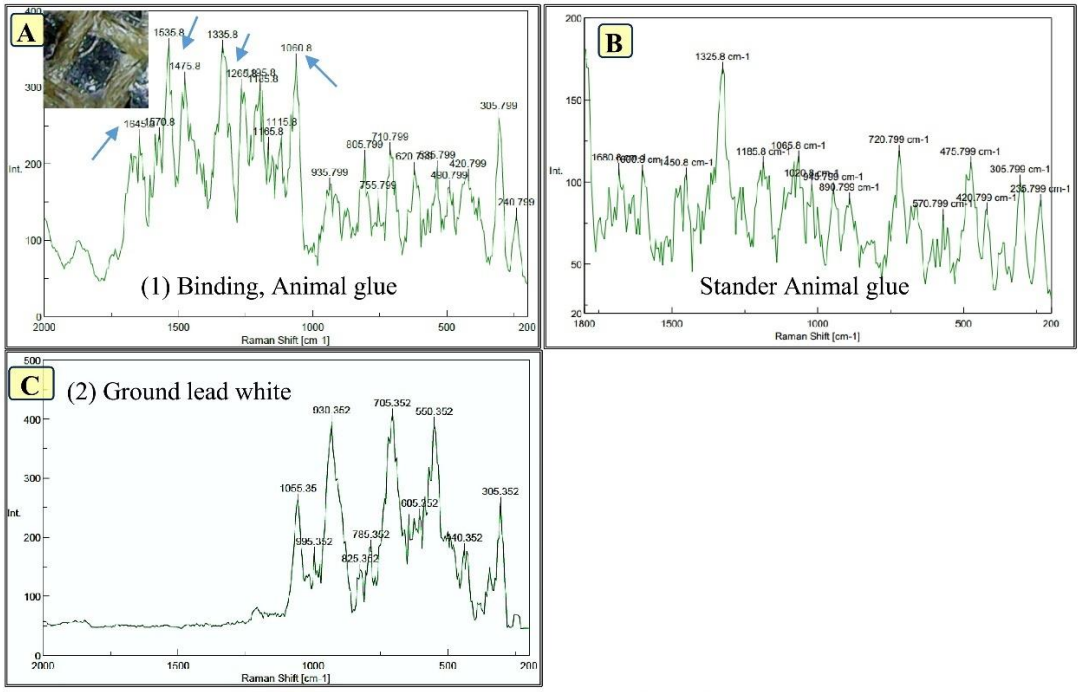

Fig. 7 MRS spectra of the ground layer sample; **A. c**ollected animal glue spectrum, **B.** standard animal glue spectrum, **C.** lead white

Table 2. Characteristic Raman wavenumbers of analyses samples, chemical composition, and main references

N	Samples	Name and composition	Wave numbers cm^{-1}	References
1	Binding	Animal glue (Gelatin)	305- 420-535-799-805-895-935-1060-1265- 1335-1175-1475-1645	[43]
2	Ground	Hydrocerussite, $2PbCO_3 \cdot Pb(OH)_2$	440-605-995-1055	[44]
3	Media	Linseed oil	285,455,565,690,797,845,890,1060, 1265,1480,1655,1730	[45]
4	Dark green	Celadonite, K (Ca, Mg, Fe_2 (Fe_3Al)[Si_4O_{10}]($OH)_2$)	225-290-410-420-535-605-675-799-900	[46]
5	Light green	Viridian (chrome oxide) CR_2O_3	230-300-360-425-570-675-870	[47]

[43]Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., & Van Hooydonk, G., Analysis *with micro-Raman spectroscopy of natural organic binding media and varnishes used in art.*, p. 261-274.

[44]Burgio, L., A. Cesaratto, and A. Derbyshire, *Comparison of English portrait miniatures using Raman microscopy and other techniques.* Journal of Raman Spectroscopy, 2012. **43**(11): p. 1713-1721.

[45]Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., & Van Hooydonk, G. ,p. 261-274

[46]Ospitali, F., Bersani, D., Di Lonardo, G., &Lottici, P. P.*'Green earths': vibrational and elemental characterization of glauconites, celadonites and historical pigments.* Journal of Raman Spectroscopy, 2008. **39**(8): p. 1066-1073.

[47]Burgio, L. and R.J. Clark, *Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation.*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2001. **57**(7): p. 1491-1521.

6	Yellow	Lemon yellow $BaCrO_4$	240-305-425-449-725-799-880-940	[48]
7	Beige	Lithopone $BaSO_4.ZnS$	352-425-475-555-700	[49]
8	Black	Ivory black ($Ca_3(PO_4)_2$+$Mg_3(PO_4)_2$+ $CaCO_3$+C)	1335-1585	[50'51]

-Ground layer:

MRS allows the identification of natural organic materials in artifacts[52], especially the binding media in paintings[53,54]. The Raman spectra of the studied binding materials showed a high fluorescence continuum, which was subtracted (Fig. 7A and Table 2).

The analysis of the micro-samples demonstrated that lead white and animal glue were used as the ground layer. Band intensity in the 800–1000 cm^{-1} region for gelatin could be confirmed. Animal glue is the generic term for gelatin[55].

The protein glue showed (C=O) amide I (~1645cm^{-1}) and CH2 scissors (~1475cm^{-1}).The (NH+CN),an amide III, band centered near 1265$cm^{-1}$and aromatic cyclic respiration peak (~1060cm^{-1}) in these spectra. Between 800 and 900 cm^{-1}, the characteristic bands of amino acid tyrosine residues appeared. These bands might arise from the degradation process that the link underwent over time[56].

[48] Alia, J., H. Edwards, and F. *Garcia-Navarro, FT-Raman and powder XRD analysis of the Ba (SO4) x (CrO4) 1− x solid solution.*Talanta, 1999. 50(2): p. 391-400.

[49] Burgio, L. and R.J. Clark, *Library of FT-Raman spectra of pigments, minerals, pigment media and varnishes, and supplement to existing library of Raman spectra of pigments with visible excitation.*Spectrochimica Acta Part A, p. 1491-1521.

[50]Lluveras-Tenorio, A., et al., *A multi-analytical characterization of artists' carbon-based black pigments.* Journal of Thermal Analysis and Calorimetry, 2019. **138**: p. 3287-3299.

[51] Coccato, A., Jehlicka, J., Moens, L., & Vandenabeele, Ra*man spectroscopy for the investigation of carbon-based black pigments.* Journal of Raman Spectroscopy, 2015. **46**(10): p. 1003-1015.

[52]Wehling, B., Vandenabeele, P., Moens, L., Klockenkämper, R., von Bohlen, A., Van Hooydonk, G., & De Reu, In*vestigation of pigments in medieval manuscripts by micro Raman spectroscopy and total reflection X-ray fluorescence spectrometry*. Microchimica Acta, 1999. 130: p. 253-260.

[53]Vandenabeele, P., Vandenabeele, P., Wehling, B., Moens, L., Edwards, H., De Reu, M., & Van Hooydonk,G.*Analysis with micro-Raman spectroscopy of natural organic binding media and varnishes used in art.*, p. 261-274.

[54]Chua, L., Head, K., Thomas, P., & Stuart, B.*FTIR and Raman microscopy of organic binders and extraneous organic materials on painted ceremonial objects from the Highlands of Papua New Guinea.* Microchemical Journal, 2017. **134**: p. 246-256.

[55] Nevin, A., Osticioli, I., Anglos, D., Burnstock, A., Cather, S., & Castellucci, E. *The analysis of naturally and artificially aged protein-based paint media using Raman spectroscopy combined with Principal Component Analysis.* Journal of Raman Spectroscopy, 2008. **39**(8): p. 993-1000.

[56]Lin-Vien, D., Colthup, N. B., Fateley, W. G., &Grasselli, J. G.., *The handbook of infrared and Raman characteristic frequencies of organic molecules.* Elsevier, 1991, p: 87.

The Raman spectra collected from the white areas showed a characteristically vibrational mode at 1050 cm^{-1} attributed to lead white[57](Fig. 7B). Lead white has been the most widely used white in historical painting because it is very flexible, is easy to apply, and has good opacity[58]. Additionally, painters have preferred it when preparing the ground layer.

-Paint layer

Raman spectra of different fatty acid media and characteristic Raman wavenumbers of analysis samples are shown in (Table 2 and Fig8), respectively.

The peak of drying oils (Fig. 8A) is shown at ca. 1265 cm^{-1}, which is associated with the in-plane CH deformation of cis. Di-alkyl ethylene and the peak at ca. 1655 cm^{-1}, which is associated with the stretching vibration of a cis. C=C. The peak at 1745 cm^{-1} is associated with C=O stretching, revealing information about the number of saturated bonds in the sample. The relative intensities of linolenic acid at 1655 and 1265 cm^{-1} peaks confirmed that linseed oil, which was commonly used as a medium, combined with pigments, in oil paints during the 20th century.

The composition of the dark green sample (Fig. 8B) could be determined by means of MRS. Resonance phenomena could be important in the MRS study of celadonite: with argon ion laser excitation, the bands at 459 and 960 cm^{-1} are stronger, while for higher excitation wavenumbers, the band at 394 cm^{-1} is more evident. Lower wavenumbers of the band at about 545 $cm^{-1}$are observed. The Raman spectrum showed a strong and broadband at 535 cm^{-1} and 799 cm^{-1}[59,60].

As for light green, the recorded Raman bands (Fig. 8C) at 570, 425, and 290 cm^{-1}were attributed to the hydrated oxide, and those at 360, 300, and 230 cm^{-1} to the anhydrous one. It seems that the pigment was viridian, which is a mixture of anhydrous and hydrated chromium oxides. Viridian, a hydrated chromium (III) oxide, was synthesized in the first half of the 19th century[61,62]. Raman confirmed that the

[57] Castriota, M., Cosco, V., Barone, T., De Santo, G., Carafa, P., &Cazzanelli, E.*Micro-Raman characterizations of Pompei'smortars.* Journal of Raman Spectroscopy: An International Journal for Original Work in all Aspects of Raman Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh Scattering, 2008. **39**(2): p. 295-301.

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[60]Gražėnaitė, E., *Inorganic green pigments: investigation of historical and synthesis of novel pigments by sol-gel method*. P: 42.

[61]Castro, K., Pérez-Alonso, M., Rodríguez-Laso, M. D., Fernández, L. A., & Madariaga, J. M.., *On-line FT-Raman and dispersive Raman spectra database of artists' materials (e-VISART database).* Analytical and Bioanalytical Chemistry, 2005. **382**: p. 248-258.

[62]Halac, E. B., Reinoso, M., Luda, M., & Marte, F.*Raman mapping analysis of pigments from Proas Iluminadas by Quinquela Martín.* Journal of cultural heritage, 2012. **13**(4): p. 469-473.

light green pigment used by the artist was viridian and not eskolite. The characteristic Raman bands of the yellow pigment chromospheres and the spectral assignments were made in accordance with the literature[63,64]. (Fig. 8D) revealed the presence of barium chromate, and Raman spectra showed features in the region 850–950 cm^{-1}, allowing a complete differentiation between these pigments.

Although it is difficult to identify lithopone ($BaSO_4$.ZnS) by Raman spectroscopy because its weak characteristic band centered at 342 cm^{-1} assigned to zinc sulfide usually overlaps with the bands of other existing pigments, lithopone has characteristic Raman bands of barium sulfate (240,305,425,449,725,799,880,940 and 988 cm−1), as shown in (Fig.8E). However, Franquelo et al.[65] reported that in Raman spectra of complex heterogeneous samples, white barium, and zinc sulfide bands typically overlap with bands from other components[66].

For archaeological research purposes, the use of MRS can provide more information that may clarify the type of carbon black. MRS played an important role in the identification of graphitic/ carbonaceous material[67]. The differentiation between ivory/ bone black and the other carbon-based black pigments is reasonable by MRS due to the band at ca. 960 cm^{-1}(phosphate stretching)[68]. This band intensity varied in comparison to the carbon bands but was successfully identified[69]. Ivory black was clearly identifiable in black sample 6 by the presence of the phosphate band[70,71]

[63] Correia, A. M., Clark, R. J., Ribeiro, M. I., & Duarte, M. L.*Pigment study by Raman microscopy of 23 paintings by the Portuguese artist Henrique Pousão (1859–1884).* Journal of Raman Spectroscopy: An International Journal for Original Work in all Aspects of Raman Spectroscopy, Including Higher Order Processes, and also Brillouin and Rayleigh Scattering, 2007. **38**(11): p. 1390-1405.

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[65]Franquelo, M. L., Duran, A., Herrera, L. K., De Haro, M. J., & Perez-Rodriguez, J. L.*Comparison between micro-Raman and micro-FTIR spectroscopy techniques for the characterization of pigments from Southern Spain Cultural Heritage.* Journal of Molecular structure, 2009. **924**: p. 404-412.

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[67]Oberlin, A., *Carbonization and graphitization.* Carbon, 1984. **22**(6): p. 521-541.

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measured with a band at 1585 cm^{-1} (Fig. 8F). The results of the Raman identification (with 532-nm excitation) of the ivory black pigment of animal origin agreed with the results of SEM-EDX that showed the presence of calcium and phosphorus.

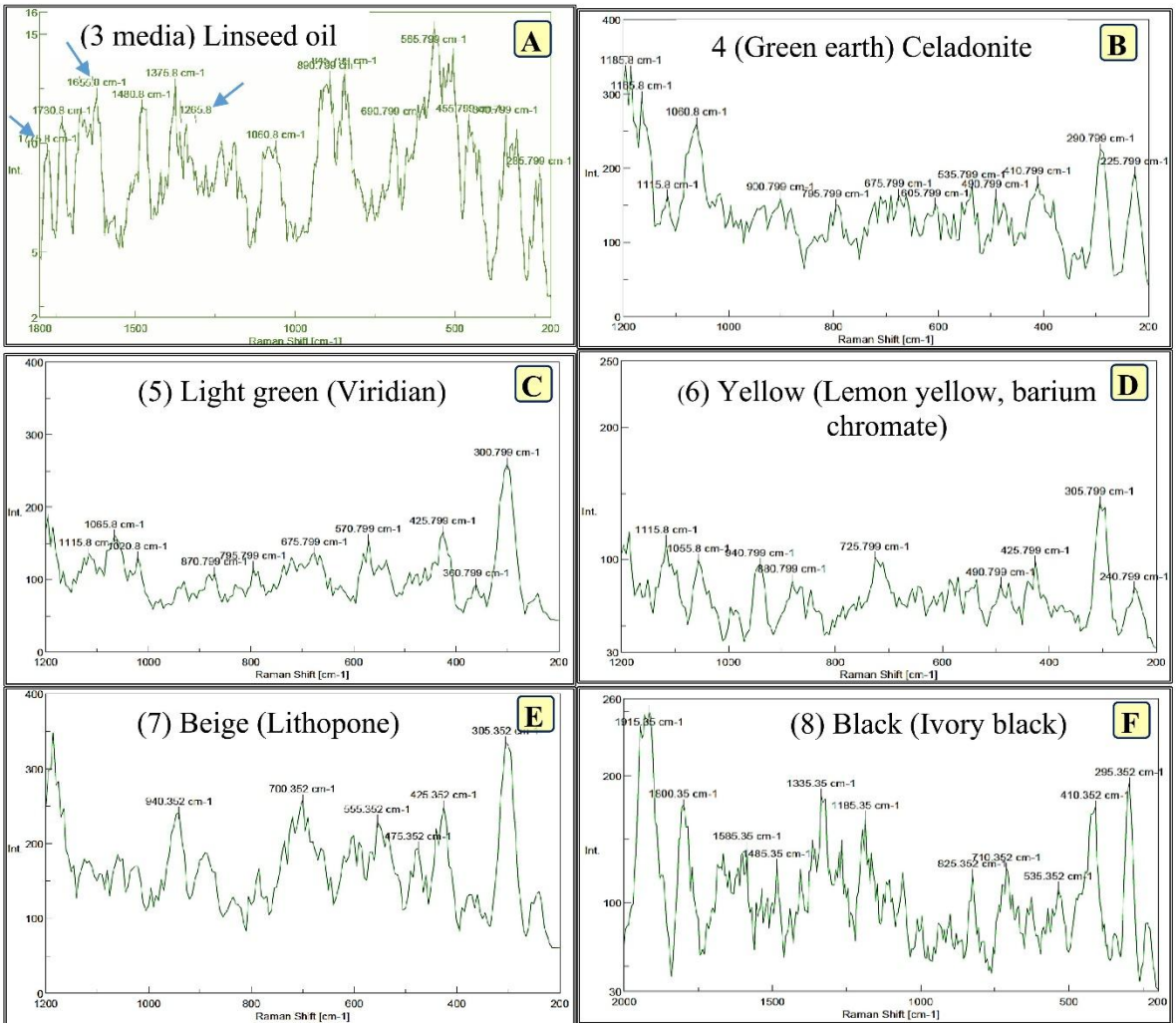

Fig. 8 MRS spectra of the collected paint samples

4. Conclusion

This research was carried out to evaluate the methodological approach that enables the characterization of materials and techniques used in20th-centuryoil paintings. Some of the identified pigments and mediums were chronologically consistent with 20th-century art history. The combination of different approaches was very helpful in providing details about the materials and execution techniques used by the artist. Examination of cross-section samples allowed the study of the pigment materials. Furthermore, MRS analysis allowed a better understanding of the painting technique.

[71]Edwards, H. G. M., Farwell, D. W., Holder, J. M., & Lawson, E. E.*Fourier-transform Raman spectra of ivory III: identification of mammalian specimens.*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 1997. **53**(13): p. 2403-2409.

MRS is clearly advantageous due to the size of samples (micro sample), simple preparation, and the possibility of subsequent analysis, such as SEM/EDX. It enabled the specification of the debatable presence of lead white and celadonite. It can easily identify the pigments that couldn't be identified by SEM–EDX, e.g.,Zn, Ba, and ivory black. However, MRS can't detect all the components of the samples, and it is possible to obtain only a single-pigment spectrum in the presence of strongly scattered pigments (e.g., lemon yellow). Therefore, it is always recommended to complement Raman analysis with other techniques.

GC-MS proved to be an excellent method for identifying the oils based on P/S ratios. It revealed the presence of linseed oil used as a medium oil in paint samples. It is recommended to be used in identifying the media used in the 20th century, either natural or synthetic. Finally, the sharing of findings on original paintings should be strongly encouraged, as creating a database of the 20th-centuryartists' materials is an essential step in the process of determining the authenticity of ancient and modern paintings.

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*painted bichrome ceramic sherds (southern Italy, VIII-VII BC) to an intact Etruscan cinerary urn.*Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2018. **191**: p. 88-97.

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