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Combining XRF, Multispectral Imaging and SEM/EDS to Characterize a Contemporary Painting

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Abstract: Diagnostic analyses on a contemporary painting on canvas were performed with X-ray fluorescence (XRF), multispectral imaging and scanning electron microscope/energy dispersive spectroscopy (SEM/EDS). The results of each method provided complementary information to deepen the knowledge of the pictorial technique. Multispectral imaging provided insight into the topmost layers. XRF analysis made it possible to characterize the chemical composition of some materials and pigments used by the artist. Additional information such as that relating to canvas preparation emerged with the SEM/EDS technique. The results reveal (i) the use of pre-treated industrial canvas; (ii) the preparatory layer consists of plaster covered with a primer with titanium white, zinc and lithopone; (iii) a layer of cadmium yellow ground was inserted to give depth and three-dimensionality to the painting; (iv) the absence of underlying design; (v) the characterized pigments are all contemporary and (vi) a fixative spray covers the paint.

Keywords: XRF; multispectral imaging; SEM/EDS; contemporary painting; pigments

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1. Introduction

Advanced analytical methods and techniques are essential prerequisites in the field of cultural heritage as they provide the means to understand the objects under investigation. Through the identification of materials and processes, a deeper understanding of the craftsmanship and technology used can be developed. These analytical methods also allow one to perform authenticity studies or contribute to the development of simple diagnostic techniques necessary for practical applied conservation [1]. Depending on the information required, non-invasive techniques (i.e., those that do not require the removal of a sample from the object and that leave the object in the same state after analysis), micro-destructive techniques (i.e., those that consume or damage micro-fragments of material and may require the removal of a sample) and non-destructive techniques (i.e., those that enable a sample or a complete object to be re-analyzed for further examination) can be used [2]. Individual techniques [3,4] or a combination [5–7] of them are often used. The combination of some of these techniques generates important data even on limited objects such as hand-colored daguerreotypes [8,9].

The X-ray Fluorescence (XRF) technique is widely used for preliminary screening [10,11]. It identifies chemical elements (not compounds) by acquiring X-ray fluorescence spectra in point mode or via Macro-XRF (MA-XRF) scanning [12,13]. Scanning (MA-XRF) and hyperspectral imaging (HSI) provide more representative results than in situ point analysis or characterization of pigment micro-sections. When combined, they can be of great help in the characterization of pigments and the possibility of mapping their presence in a painting, though with more time and greater costs [14].

Multispectral imaging techniques have increasingly become part of examination and analysis methodologies. These techniques include luminescence (emitted light) imaging methods (ultraviolet-induced luminescence (UVIL); visible-induced infrared luminescence

(VIL) and visible-induced luminescence (VIVL) as well as a range of related broadband reflectance imaging methods (visible reflectance (VIS), infrared reflectance (IR) and ultraviolet reflectance (UVR)) [15,16]. They offer qualitative, non-invasive and often relatively inexpensive and portable tools for spatial localization of specific materials or material types, and the equipment, image acquisition and processing are relatively inexpensive.

Combined methods such as IR and XRF analyses were carried out on, for example, St. Jerome in the studio and St. Francis Delivering the Rule, paintings conserved in the Museo and Real Bosco di Capodimonte. There, the complementary results provide a first overview and hypothesis regarding the pictorial palette and techniques used by the artist [17]. The same methods were also used in the study of manuscripts [18].

The aim of this work is to implement a diagnostic investigation methodology with instrumentation available at the CIRCE laboratory to characterize artworks using non-destructive or micro-destructive techniques. The investigated object is a painting realized by a contemporary artist, studied to understand color palette and execution technique.

The painter is Francesca De Cola, originally from Castelvetere S/C (Avellino, Italy). She was trained as a figurative artist with an impressionist imprint. Her painting is inspired by aspects of reality. Her distinctive feature consists of her brushstrokes expanding on the canvas with strong and warm tones, treating forms creatively and non-representatively.

The painting, made on canvas with oil mixed with tempera to give more brightness, depicts a scene of daily life in Burkina Faso seen by the author during her stay in the Craft Center of Ouagadougou in 2006. It portrays two native women as they wait in line to buy groceries at the local market. It was made for a charity auction to raise funds for Burkina Faso and has since been in the private collection of one of the authors (C.S.).

The results obtained from this measurement test were then shown to the artist who validated and confirmed them. The painting was chosen for chromatic reasons as it is characterized by the presence of a few colors used in a distinct manner with a small amount of blending. They seem, indeed, to be used as a single pigment where there are no particular light or shadow effects.

2. Materials and Methods

The canvas painting is 35 × 41 cm^2 (Figure 1). It was investigated through various methodologies to obtain different and complementary information.

Multispectral imaging was performed to reveal details about the painting surface (varnish, pigments and presence of underdrawings). The system used was a Samsung NX500 Digital Camera 28 MPX (APS-CMOS BSI) designed by Madatec Srl to acquire images from different light sources. Spotlights with 365 nm UV wavelength, in combination with some filters, allowed different techniques to be applied; in detail, images of the induced fluorescence (UVF) were obtained with a UV Band Pass filter (320–380 nm) and images of ultraviolet induced luminescence (UVIL), with two High-Pass (HP) infrared filters at 760 and 850 nm. Three HP infrared filters at 760, 850 and 950 nm; one interference at 1070 nm and infrared lamps with a rated power of 275 W were used to acquire IR images. The UV-IR cut filter (390–700 nm) was employed for visible (VIS) images. A 98% reflectance white chalk standard was placed near the painting during the acquisition of all images. The software used for the image processing was RawTherapee. It is a powerful, cross-platform and open-source raw-image-processing software released under the GNU General Public License version 3.

A USB digital microscope (Mic-Fi Digital Wi-Fi Microscope) enabled study of the morphology of the painting surface.

Points with different color samplings were analyzed using the XRF technique that enabled a determination of their elemental compositions (Figure 1). The method was applied with the handheld XRF spectrometer XSORT XHH03 produced by SPECTRO. The instrument was equipped with a Rh tube that operates at 50 kV and a current of 125 μA capable of detecting all chemical elements from Mg to U; the 10 mm^2 Si drift detector has the energy resolution of about 160 eV at the K_α line of the Mn (5.9 keV). Each spectrum

was acquired with a measurement time of 60 s (40 s using a 50 kV tube voltage and 20 s with 15 kV). Each single measurement consisted of two separate measurement cycles wherein the durations could be selected independently. In the first cycle, the voltage was set to 50 kV and was a filtered excitation. In the second additional cycle, the voltage was set to 15 kV and was an unfiltered excitation optimized for measurement conditions of light elements. Methods were constructed and calibrated using the memory of the ICAL intellectual calibration logics managed by the instrument efficiency diagnostic system. Acquisition and data analysis were carried out using XRF Analyzer CE and XRF Analyzer PRO software.

Figure 1. Painting and localization of measurement points selected for XRF analysis. Points 1 and 2 are not present because they are located on the backside of the canvas. The sampling point of the yellow background pigment is circled in black.

A targeted analysis of the painting surface was carried out using a Scanning Electron Microscope coupled with Energy Dispersive Spectroscopy (SEM/EDS). For these micro-invasive techniques, three micro samples were removed from the main areas to preserve the integrity of the artwork; two were small pieces of the canvas (Figure 2a,b) placed on the backside, while the other was an embossed pigment fragment (Figure 2c) in which a light yellow (a) and a darker yellow (b) were present. They were analyzed in high vacuum mode using the ESEM Quanta FEI 200 by FEI Company equipped with a 10 mm^2 Si drift detector. Genesis 4000 software by EDAX (Ametek®) was used for the collection and the micro-EDS data analysis. Spectra were collected for 90 s of live time with a voltage of 25 kV and amp time (the time the detector processes one X-ray count) of 51.2 µs.

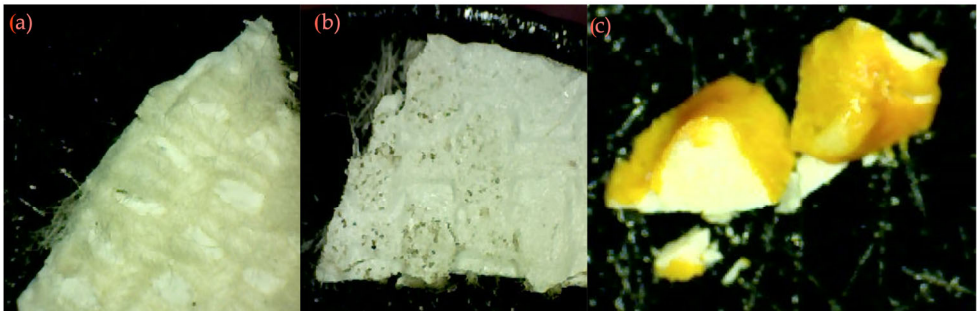

Figure 2. Microscope image of sampled fragments analyzed using SEM/EDS. (**a**) Sample 1, raw canvas. (**b**) Sample 2, preparatory layers of canvas. (**c**) Sample 3, yellow background pigment.

3. Results

3.1. Multispectral Imaging

Multispectral imaging enabled an acquisition of initial data concerning the distribution of the varnish and pigments, which appeared unevenly distributed over the entire surface of the painting.

The UVF technique revealed heterogeneously distributed blue, violet, red and brown fluorescence emitted from the upper layer of the painting (Figure 3). The blue areas correspond in the VIS image to the areas where a glossy varnish/protective film was applied (signs of spraying are evident); the violet areas correspond to the areas where white pigment was used; the red areas correspond to the spiral-shaped decorations and some shades of the background and the brown areas are distributed all over the background.

Figure 3. UVF image processed with RawTherapee software. Automatic white balance, temperature at 6500 K, blue channel value at 243 and green channel value at 90 were used.

By using the same set for the UVF realization, the UVIL technique was performed. The emitter must be free of infrared emissions and combined with an IR filter at 850 nm. This technique enabled the authors to obtain information regarding cadmium distribution.

Figure 4 shows the white areas where cadmium was non-uniformly distributed, especially in the background of the painting and in the clothes and hair of both figures. In the visible range, these areas are characterized by the presence of yellow and red pigments. This indicates that both pigments were cadmium-based: cadmium yellow and cadmium red. Cadmium yellow was applied as a primer over the preparatory layer. Cadmium red, instead, was used to paint the clothes, such as the skirt, where the red color was unevenly distributed more intensely on the upper part than on the lower part. The artist may have intentionally painted the skirt in this way to emphasize the upper part.

Figure 4. UVIL image obtained with UV lamps and IR filter at 850 nm and processed with RawTherapee applying the automatic black/white function.

IR photography was carried out by applying several available IR filters (NB 760, 850, 950 and 1070 nm) to the digital camera. As the sensitivity to longer wavelengths increased, the sensors enabled a better perception of the reflectance produced by the preparatory layers, due to the progressive permeability of the pigments, which were increasingly transparent. Figure 5 shows the IR image at 760 nm. It enabled the authors to obtain a layered portion of the pictorial surface. The relief is clearly visible in addition to the black pigment outlining the contours of the main figures and their skin.

Figure 5. IR image (NB 760 nm) processed with RawTherapee software. Automatic punctual white balance using 98% reflectance white chalk standard was placed near the painting. Automatic b/w and contrast to 26 were selected.

Increasing the wavelength to 1070 nm (Figure 6) did not highlight the presence of a preparatory drawing, but primarily revealed the decorations of the painting that were made in embossed form. In this case, the under drawing was not executed with materials detectable in the IR band such as metal tips or ink. The black pigment used to outline the edges of the figures, the skin of the women and the artist's signature was not transparent despite the large wavelength of the filter used. It could be a carbon-based pigment capable of absorbing infrared radiation (the image data show strong contrasting characteristics [16]). The green pigment used to make some parts of the clothes and hats was partially transparent. The black circular decorations on the bottom were not transparent to the IR either.

Figure 6. IR image (NB 1070 nm used in combination with a High Pass (HP) 850 nm) processed with RawTherapee software. Automatic white balance was performed using white chalk standard with 98% reflectance.

3.2. XRF Analysis

The compositions of the preparatory layers of the painting and pigments of different colors were identified using the XRF technique [19]. The results are briefly reported in Table 1. XRF spectra of all measurement points are included as Supplementary Materials, Figures S1–S18.

Table 1. Principal chemical elements detected using the XRF technique. The color, the main chemical elements detected and the pigment/material identification are described.

Color/XRF Point	Principal Chemical Elements	Pigment/Material
White (on canvas)/2	S, Zn, Ba, (Ti?)	Lithopone (+titanium white?)
White (back canvas)/1	Ca, Fe, Sr	chalk
Yellow/3,4	S, Cd, Zn	cadmium yellow
White (painting)/14	Ti, Zn	zinc white + titanium white
Red/15	Cd, Se	cadmium red
Red spiral decorations/10	Cu	?
Green/11,12	traces of Cu	malachite?
Orange/13,19	Fe	ochre
Black/20	traces of Cu	?

Calcium (Ca), iron (Fe), zinc (Zn), strontium (Sr) and barium (Ba) were present in all measurement points and, therefore, are characteristic of the preparatory layers of the canvas.

Ca indicates chalk ($CaCO_3$), which is very commonly used for priming. Fe could be an impurity in this material. Zn and Ba constitute lithopone, a white color based on barium sulfate ($BaSO_4$) and zinc sulfide (ZnS), or mixtures of barium sulfate and zinc sulfide or zinc oxide [20]; Sr is also a common impurity in barium sulfate [21,22]. The identification of lithopone could suggest that the painting was made in the contemporary period [20]. Titanium (Ti) could be present in all measurement points as titanium white, but the overlapping of its K line with that of the Ba L line does not permit its clear identification.

To understand how the canvas was prepared, two unpainted pieces of canvas placed on the back of the artwork, close to the wooden support, were sampled and analyzed (Figure 2a,b). The first fragment had a raw side (sample 1, back of the canvas-XRF point no. 2) in which the canvas texture was visible, while the other had a white-colored side (sample 2, surface preparatory layer- XRF point no. 1). Barium was detected on both samples, but Ba-L lines were only found in sample 2, suggesting the presence of lithopone on the surface. Figure 7 shows the comparison of the XRF spectra at points 1 and 2 of the canvas. The characteristic lines L of Ba of sample 2 (spectrum brown) are clearly visible.

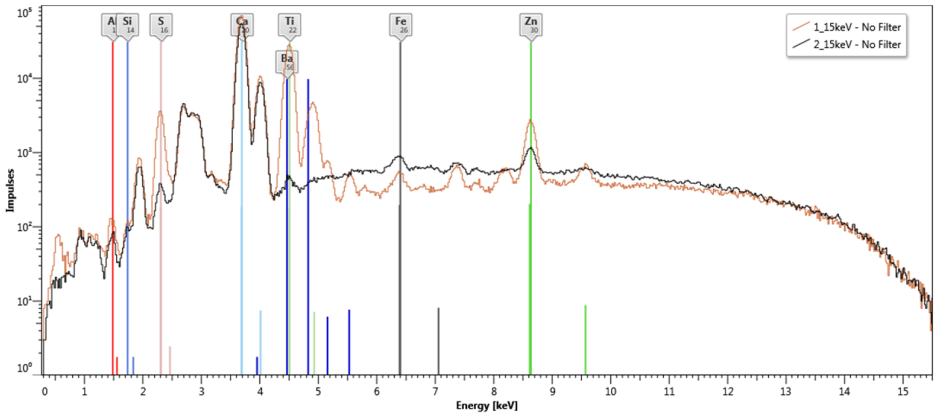

Figure 7. Comparison of XRF spectra no. 1 (in brown) and 2 (in black) from 0 to 15 kV. The presence of the characteristic L lines of barium at point 1 is clearly visible.

The different shades of the yellow background of the painting (Figure 1) were investigated. At some points, the cadmium yellow pigment was present as S, Cd and Zn (cadmium sulphide CdS, usually combined with zinc oxide ZnO). at other points (no. 5, 6 and 8), it was not possible to characterize the yellow as it does not consist of dominant inorganic elements; in fact, only the peaks of the elements of the preparatory layer were present in the spectrum. The white color was characterized by Zn and Ti so, it could be a zinc white mixed with titanium white.

Cd was also detected in the red areas together with selenium (Se), identifying the pigment as cadmium red (CdSe). The darker shades of the red color, used for some of the background decorations, show the addition of a pigment/material containing copper (Cu).

The green and black pigments did not present dominant characteristic elements through XRF analysis but only trace elements. For example, in the green and black pigments, traces of Cu were detected. The intense green (point 11 in Figure 1) could be malachite. The lighter shades (point 12 in Figure 1) were probably obtained by adding a mixture of zinc white and titanium white to the green pigment to make it lighter.

The black pigment could not be identified because it is composed of chemical elements that are undetectable using XRF analysis.

The orange pigment is characterized by Zn and Ti and traces of Fe, suggesting the presence of an ochre mixed with titanium white and zinc white.

3.3. SEM/EDS

SEM/EDS analysis was used to obtain more information on the canvas and its preparatory layer and yellow background pigment (yellow-A and dark yellow-B) as only these parts could be sampled.

Sample 1 (raw canvas, Figure 2a), sample 2 (white side of canvas, Figure 2b) and sample 3 (yellow background pigment, Figure 2c) were analyzed using a backscattered electron detector to take advantage of atomic number contrast; the brightness in a BSE image of a sample containing various phases of different composition is a function of the mean atomic number.

The resulting image of sample 1 (Figure 8a) clearly shows the weave of the fabric consisting of a high amount of carbon (C) and oxygen (O). The lighter parts consist of Ca and C, hence the chalk (calcium carbonate). It was used in the canvas preparation process. Table 2 repots cps (i.e., count per second) of the main characteristic lines (K or L) of the detected elements using EDS analysis. All SEM/EDS spectra are included in the Supplementary Materials, Figures S19–S25.

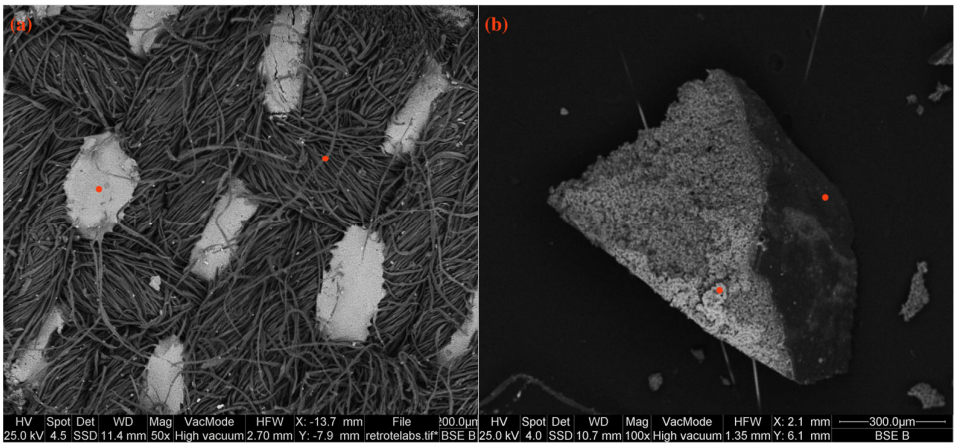

Figure 8. SEM images showing the images of (**a**) sample 1 (backside of the canvas) and (**b**) pigment fragment of the yellow background (sample 3). Red dots indicate the areas analyzed using EDS corresponding to the results in Table 2.

Table 2. Cps of main characteristic lines (K or L) of the detected elements using EDS analysis of sample fragments.

Code	C	O	Na	Mg	Al	Si	S	Cl	K	Ca	Ti	Fe	Zn	Cd	Ba
Sample 1-white area	517	207	33	24	27	34	36	35	24	416	/	8	/	/	/
Sample 1-tissue	195	98	6	/	/	8	13	13	11	21	/	/	/	/	/
Sample 3-white area	84	91	/	/	/	/	/	/	/	477	/	/	/	/	/
Sample 3-B	815	103	76	/	30	77	25	33	24	63	/	/	/	/	/
Sample 3-A	622	117	/	11	15	51	30	11	15	74	/	4	24	22	/
Sample 2_1 *	268	290	/	33	55	/	420	/	37	243	350	25	59	/	339
Sample2_2	608	128	/	/	/	/	83	/	/	60	168	/	42	/	/
Sample2_3	258	270	75	36	98	117	81	74	55	331	26	22	/	/	/

* This sample also contains Sr (47 cps).

In sample 2, wherein some EDS points were collected (Figure 9), the particles consisted of elements such as S, Ti, Zn and Ba that belong to the white pigments used in the painting and ground layers, namely titanium dioxide and barium sulphate and zinc oxide or lithopone.

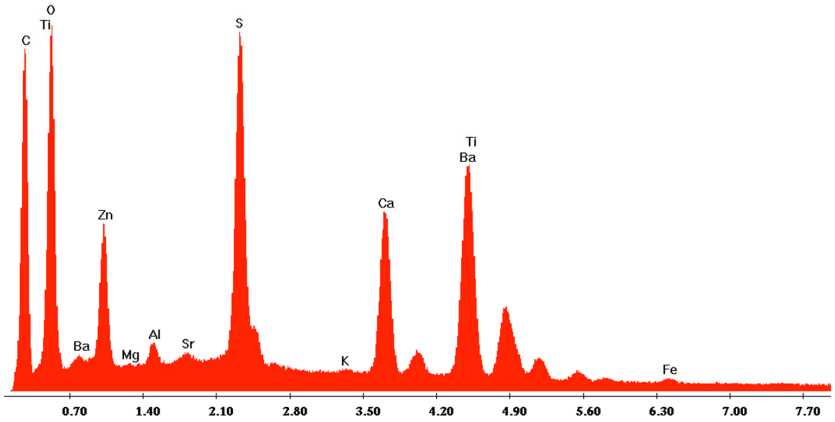

Figure 9. SEM/EDS spectra of sample 2_1. The characteristic lines of all elements detected are labelled.

The pigment fragment of the yellow background (sample 3) is shown in Figure 8b. The lighter parts consist of Ca, C and O. Therefore, as a technique for the preparatory layer, the artist used chalk.

The yellow pigment is characterized by the presence of cadmium and zinc.

The dark yellow pigment is characterized by the presence of traces of sodium, silicon, aluminum, calcium, potassium, and sulfur. No characteristic pigment appears with this technique. However, further investigation (e.g., Raman, XRD and FT-IR techniques) is needed to better understand the composition of this area.

4. Discussion

The multi-analytical approach implemented enabled the acquisition of relevant data on the constituent materials and techniques used. The work presented here is a verification test to validate the diagnostic methods and techniques used. It shows how the results of the various techniques corroborate or complement the information even if the paintings are contemporary and were made with industrial products.

UV and UVIL fluorescence provided details on the gloss varnish and the distribution of some pigments. The unevenly applied gloss varnish spray is clearly visible in blue (Figure 3) where small droplets are easily visible. The combination of the information obtained from the two techniques (UV and UVIL) with that from the XRF technique (point mode) enabled some pigments to be mapped.

The areas with purple fluorescence (UV), that possess a white color in the visible range, are related to zinc white mixed with titanium white, elements detected via XRF measurements.

The white areas visible in the UVIL corresponding to a brown color in the UV (yellow in the VIS) were analyzed with XRF. The pigment was catalogued as cadmium yellow due to the presence of CdS. In Figure 10, two points of the yellow background and canvas were compared: point 18 corresponding to the white area, point 17 to the non-white area and point 1 to canvas without pictorial layers (see points in Figure 1).

The presence of cadmium was only detected in point 18 and not in point 17. This shows that Cd is present in the light areas.

The areas with a red fluorescence (UV), those relating to the red spiral decorations and some areas of the background (VIS) were further investigated. Initially, it was thought that these areas consisted of cadmium red, but this was not confirmed through the UVIL image (Figure 4), given the absence of white in those areas, or according to the the XRF measurements, which did not show the presence of Se in those areas but only of Cd due to the yellow base. Therefore, by combining this information, it was possible to map these pigments using only a few measurement points.

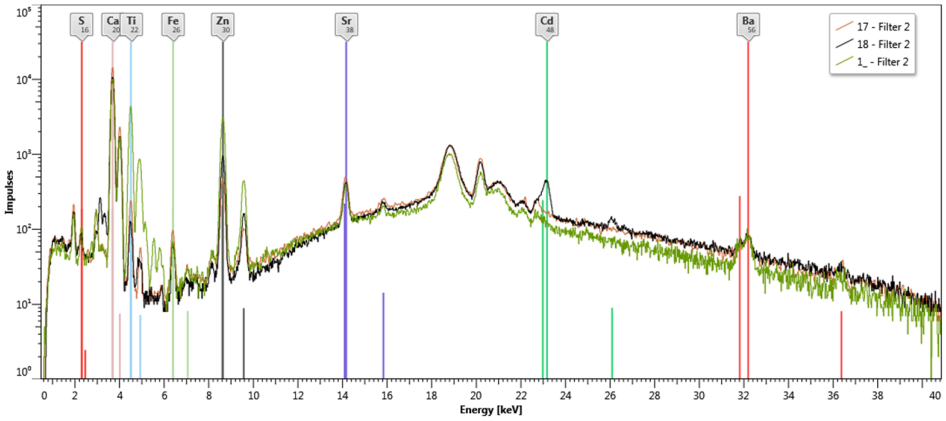

Figure 10. XRF spectra of measuring points 17 (orange), 18 (black) and 1 (green). The characteristic lines of all elements detected were highlighted. Rhodium and argon were excluded.

The IR image shows that the preparatory layer has no underdrawings. Combined with EDAX analysis, it provided information on the technique used by the artist to prepare the background of the painting and plaster relief technique. The XRF technique allowed the authors, where possible, to characterize the artist's palette. However, more and clearer information was obtained by combining this with SEM/EDS analysis. Only with the EDS technique was it possible to detect the presence of titanium white in the preparatory layer that was not easily identifiable with the XRF technique; in fact, in this layer, the characteristic L lines of Ba overlap with the characteristic K lines of Ti. This result allowed the authors to characterize the preparatory layers made up of the canvas (layer 1 in Figure 11); it was prepared with a layer of chalk (layer 2 in Figure 11, gypsum has been excluded due to the absence of sulfur) and covered by priming with titanium white, zinc and lithopone (layer 3 in Figure 11). The shape and constituents of these three layers show that the canvas was made according to an industrial procedure. Then, the artist prepared the industrial canvas with the plaster relief technique (layer 4 in Figure 11) covered with a yellow ground (layer 5 in Figure 11) to create depth and three-dimensionality to the painting and applied the pigment (i.e., cadmium yellow in an uneven way, layer 6 in Figure 11).

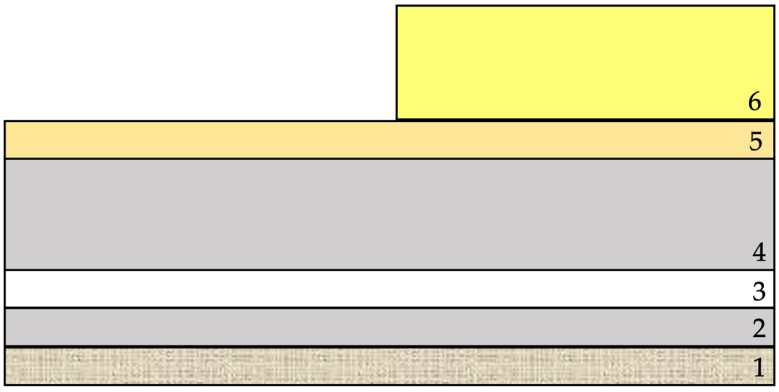

Figure 11. Layout of the preparatory layer of the painting.

The characteristic elements of the preparatory layer are present in all XRF measurements. Only a careful analysis of the spectra enabled the authors to identify the inorganic pigments. The red of the decorations, the yellow of the background, the black and the green must be further investigated as they have not been identified exhaustively with the available techniques.

In the 19th century, several new inorganic pigments expanded the range of technically useful dyes, including chromium oxide green, cadmium yellow, zinc white, ultramarine blue, iron oxide red and metallic bronzes (Cu/Zn). Other synthetic inorganic pigments

appeared on the market in the 20th century: titanium dioxide, cadmium red, iron oxide yellow, iron oxide black, bismuth vanadate and mica-based effect pigments [23]. The presence of some of them in the analyzed painting confirms that the period of production is post-20th century.

The author of the painting was sought out and found, who described her painting technique, validating our results. The artist confirmed the use of pre-treated industrial canvas and the absence of a preparatory drawing. She used a preparatory layer consisting of chalk and rabbit glue. To generate greater depth and three-dimensionality, the chalk was applied with a small knife by hand. The plaster was first painted with a bright yellow and then covered with cadmium yellow. To recall the desert's sand, the background was shaded with brown pigment. Finally, the painting was varnished with a fixative spray. She also confirmed the use of the pigments identified in the analysis.

5. Conclusions

Three diagnostic techniques in the field of cultural heritage were used to characterize a contemporary painting, depicting a scene from daily life in the Burkina Faso, painted by Italian artist Francesca De Cola. The combination of different methods was very helpful to provide details on the materials and execution technique used by the artist. UVF, UVIL and IR techniques were applied with a digital camera, special filters and light sources. The UVF image identified the areas of the painting where a glossy protective spray varnish and some pigments are present. The UVIL image showed the distribution of the cadmium yellow and cadmium red pigment in the background of the painting and in the clothes of the two figures. The application is not homogeneous but alternated by another unidentified light-yellow pigment. The IR image was helpful in revealing the areas made using a copper-based pigment (such as a green pigment that could be malachite), the use of a black pigment and decorations made in relief. XRF analysis, performed in point mode, was helpful in identifying some pigments and the composition of the preparatory layers. The latter were also investigated using the SEM/EDS technique, which clarified the use of an industrial canvas pre-treated with plaster and white pigment based on titanium and lithopone. In addition, the plaster relief technique was used.

Individual techniques and their combination proved to be suitable for the study of this contemporary painting, even if some pigments need further investigation.

This investigation offers a starting point for the development of a multi-analytical diagnostic methodology that the following research group intends to offer.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/qubs7020013/s1. Figure S1. XRF spectrum of measuring points 3 (yellow); Figure S2. XRF spectrum of measuring points 4 (yellow); Figure S3. XRF spectrum of measuring points 5 (yellow); Figure S4. XRF spectrum of measuring points 6 (yellow); Figure S5. XRF spectrum of measuring points 7 (green); Figure S6. XRF spectrum of measuring points 8 (yellow); Figure S7. XRF spectrum of measuring points 9 (yellow); Figure S8. XRF spectrum of measuring points 10 (green/yellow); Figure S9. XRF spectrum of measuring points 11 (green); Figure S10. XRF spectrum of measuring points 12 (green); Figure S11. XRF spectrum of measuring points 13 (orange); Figure S12. XRF spectrum of measuring points 14 (white); Figure S13. XRF spectrum of measuring points 15 (red); Figure S14. XRF spectrum of measuring points 16 (green); Figure S15. XRF spectrum of measuring points 19 (orange); Figure S16. XRF spectrum of measuring points 20 (black); Figure S17. XRF spectrum of measuring points 1 (backside); Figure S18. XRF spectra of measuring points 17 (orange spectrum) and 18 (black spectrum); Figure S19. SEM/EDS spectra of white area of sample 3; Figure S20. SEM/EDS spectra of dark yellow (B) area of sample 3; Figure S21. SEM/EDS spectra of yellow area (A) of sample 3; Figure S22. SEM/EDS spectra of tissue-sample 1; Figure S23. SEM/EDS spectra of white area-sample 1; Figure S24. SEM/EDS spectra of point2-sample 2; Figure S25. SEM/EDS spectra of point3-sample 2.

Author Contributions: Conceptualization, J.B., E.S. and C.S.; methodology and software, J.B. and E.S.; validation, C.S. and A.D.; formal analysis, J.B. and E.S.; investigation, J.B., E.S. and C.S.; resources, J.B., E.S. and C.S.; data curation, J.B. and E.S.; writing—original draft preparation, J.B. and E.S.;

writing—review and editing, C.S. and A.D.; supervision, C.S. and A.D. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Adriaens, A. Non-destructive analysis and testing of museum objects: An overview of 5 years of research. *Spectrochim. Acta Part B At Spectrosc.* **2005**, *60*, 1503–1516. [CrossRef]
2. Macchia, A.; Biribicchi, C.; Rivaroli, L.; Aureli, H.; Cerafogli, E.; Colasanti, I.A.; Carnazza, P.; Demasi, G.; La Russa, M.F. Combined use of non-invasive and micro-invasive analytical investigations to understand the state of conservation and the causes of degradation of I tesori del mare (1901) by Plinio Nomellini. *Methods Protoc.* **2022**, *5*, 52. [CrossRef] [PubMed]
3. Mazzinghi, A. XRF analyses for the study of painting technique and degradation on frescoes by Beato Angelico: First results. *Il Nuovo Cim. C* **2014**, *37*, 253–262.
4. Brocchieri, J.; Scialla, E.; Manzone, A.; Graziano, G.O.; D'Onofrio, A.; Sabbarese, C. An analytical characterization of different gilding techniques on artworks from the Royal Palace (Caserta, Italy). *J. Cult. Herit.* **2022**, *57*, 213–225. [CrossRef]
5. Sawczak, M.; Kamińska, A.; Rabczuk, G.; Ferretti, M.; Jendrzejewski, R.; Śliwiński, G. Complementary use of the Raman and XRF techniques for non-destructive analysis of historical paint layers. *App. Surf. Sci.* **2009**, *255*, 5542–5545. [CrossRef]
6. Janssens, K.; Van der Snickt, G.; Vanmeert, F.; Legrand, S.; Nuyts, G.; Alfeld, M.; Monico, L.; Anaf, W.; De Nolf, W.; Vermeulen, M.; et al. Non-invasive and non-destructive examination of artistic pigments, paints, and paintings by means of X-ray methods. *Anal. Chem. Cult. Herit.* **2017**, *374*, 77–128. [CrossRef]
7. Neri, E.; Alfeld, M.; Nasr, N.; de Viguerie, L.; Walter, P. Unveiling the paint stratigraphy and technique of Roman African polychrome statues. *Archaeol. Anthropol. Sci.* **2022**, *14*, 118. [CrossRef]
8. Kozachuk, M.S.; Avilés, M.O.; Martin, R.R.; Potts, B.; Sham, T.-K.; Lagugné-Labarthet, F. Imaging the Surface of a Hand-Colored 19th Century Daguerreotype. *Appl. Spectrosc.* **2018**, *72*, 1215–1224. [CrossRef]
9. Quintero Balbas, D.; Cattaneo, B.; Cagnini, A.; Belluzzo, P.; Innocenti, S.; Rossi, S.; Fontana, R.; Striova, J. The Colors of the Butterfly Wings: Non-Invasive Microanalytical Studies of Hand-Coloring Materials in 19th-Century Daguerreotypes. *Heritage* **2022**, *5*, 4306–4324. [CrossRef]
10. Alfeld, M.; De Viguerie, L. Recent developments in spectroscopic imaging techniques for historical paintings-a review. *Spectrochim. Acta Part B At. Spectrosc.* **2017**, *136*, 81–105. [CrossRef]
11. Musílek, L.; Čechák, T.; Trojek, T. X-ray fluorescence in investigations of cultural relics and archaeological finds. *Appl. Radiat. Isot.* **2012**, *70*, 1193–1202. [CrossRef] [PubMed]
12. Dos Santos, H.C.; Caliri, C.; Pappalardo, L.; Catalano, R.; Orlando, A.; Rizzo, F.; Romano, F.P. Real-time MA-XRF imaging spectroscopy of the Virgin with the Child painted by Antonello de Saliba in 1497. *Microchem. J.* **2018**, *140*, 96–104. [CrossRef]
13. Trojek, T.; Trojkova, D. Several approaches to the investigation of paintings with the use of portable X-ray fluorescence analysis. *Rad. Phys. Chem.* **2015**, *116*, 321–325. [CrossRef]
14. Brocchieri, J.; de Viguerie, L.; Sabbarese, C.; Boyer, M. Combination of noninvasive imaging techniques to characterize pigments in Buddhist thangka paintings. *X-Ray Spectrom.* **2021**, *50*, 320–331. [CrossRef]
15. Dyer, J.; Verri, G.; Cupitt, J. *Multispectral Imaging in Reflectance and Photo-Induced Luminescence Modes: A User Manual*; The British Museum: London, UK, 2013.
16. Paolo, A.; Triolo, M. *Manuale Pratico di Documentazione e Diagnostica per Immagine per i BB.CC*; Il Prato: Prato, Italy, 2020.
17. Scialla, E.; Improda, P.; Brocchieri, J.; Cardinali, M.; Cerasuolo, A.; Rullo, A.; Zezza, A.; Sabbarese, C. Study of 'Cona degli Ordini' by Colantonio with IR and XRF analyses. *Heritage* **2023**, *6*, 1785–1803. [CrossRef]
18. Miguel, C.; Bottura-Scardina, S.; Bottaini, C.; Valadas, S.; Candeias, A.; Bilou, F. The Power of Combining MA-XRF, Infrared Reflectography and Digital Microscopy to Unveil the Production of the 16th Century Illuminated Charter of Évora: What May Be Hidden under a Painted Surface? *Heritage* **2022**, *5*, 286–296. [CrossRef]
19. Larsen, R.; Coluzzi, N.; Cosentino, A. Free xrf spectroscopy database of pigments checker. *Int. J. Conserv. Sci.* **2016**, *7*, 659–668.
20. Bellei, S.; Nevin, A.; Cesaratto, A.; Capogrosso, V.; Vezin, H.; Tokarski, C.; Valentini, G.; Comelli, D. Multianalytical study of historical luminescent lithopone for the detection of impurities and trace metal ions. *Anal. Chem.* **2015**, *87*, 6049–6056. [CrossRef]

21. Martins, A.; Albertson, C.; McGlinchey, C.; Dik, J. Piet Mondrian's Broadway Boogie Woogie: Non invasive analysis using macro X-ray fluorescence mapping (MA-XRF) and multivariate curve resolution-alternating least square (MCR-ALS). *Herit. Sci.* **2016**, *4*, 22. [CrossRef]
22. Lizun, D.; Kurkiewicz, T.; Szczupak, B. Technical examination of Liu Kang's Paris and Shanghai painting supports (1929–1937). *Herit. Sci.* **2021**, *9*, 37. [CrossRef]
23. Pfaff, G. The world of inorganic pigments. *ChemTexts* **2022**, *8*, 15. [CrossRef]