Article

A Combined Non-Destructive and Micro-Destructive Approach to Solving the Forensic Problems in the Field of Cultural Heritage: Two Case Studies

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Abstract: The present paper discusses the importance of non-destructive and micro-destructive technology in forensic investigations in the field of cultural heritage. Recent technological developments and the wide availability of modern analytical instrumentation are creating new possibilities for performing scientific measurements and acquiring data directly on-site—thereby limiting, where possible, sampling activity—as well as learning about the technologies and materials that were employed in the past to create cultural assets. Information on periods, chemical composition, manufacturing techniques, etc., can be gathered more easily. Overall, the benefits of on-site forensic investigations are multiple, including the potential to increase substantially the speed and efficacy of the criminal justice system. However, such benefits are only realized when data quality is guaranteed and findings can be used as forensic evidence in court. The present paper shows data from the non-destructive and micro-destructive analysis of different artworks and objects provided by the Cosenza Carabinieri Unit for the Protection of Cultural Heritage and Anti-Counterfeiting (Calabria, Italy). In particular, two oil paintings on canvas depicting cherubs (Italian: *putti*), recovered as fragments of larger religious artworks, and two bronze belt and helmet fragments were investigated. In the first case, the research aimed to define the original pictorial layer, identify any reconstruction pictorial areas or pictorial retouching, assess the state of conservation, reconstruct the previous conservation treatments, and provide indications about the chronology of the artworks. In the second case, analysis was performed both to define the bronze chemical composition and the origin of the soil (earth) found within the objects during their recovery. For these purposes, the analytical approach involved the use of non-destructive and micro-destructive analysis as follows: infrared reflectography (IRR), ultraviolet-induced visible fluorescence (UV), X-ray fluorescence analysis (XRF), digital optical microscopy (DOM), scanning electron microscopy equipped with EDX microanalysis (SEM-EDX), and Fourier transform infrared spectroscopy (FT-IR). The results made it possible to collect valuable diagnostic information and answer questions posed by the institutions for the resolution of various doubts about forensic science and cases concerning the seizure, recovery, or return of archaeological or historical-artistic objects of cultural interest.

Keywords: cultural heritage; forensic sciences; non-destructive analysis; micro-destructive analysis

1. Introduction

The scientific approach plays an important role in forensic science and in investigations connected to cultural heritage objects. In this field, the main problem is the difficulty in analyzing samples and in some cases the unfeasibility of subjecting these specimens to a standard analytical technique. In particular, the choice of the proper analytical approach is

crucial, because artworks are unique and therefore unrepeatable. So, the best procedure is to adopt a non-destructive or micro-destructive integrated approach. This is useful when the investigated artwork or object is constituted of different materials, e.g., pigments, stone, glass, ceramics, soils, metal, etc. [1–3]. Non-destructive and minimally invasive methods are based largely on physical principles and, as a function of their specific application, can provide data on the origin and manufacture of an artwork, as well as on the raw materials used [4–8].

In addition, given the different nature of the objects which may be investigated, the integration of multi-layered and multi-spectral representations of imaging data (widely used in paintings) with the most common spectroscopic techniques used in the field of cultural heritage may help to increase the wealth of information and the resolution of various issues. Such imaging techniques, which are completely non-destructive, can make the results provided by an integrated diagnostic plan of pictorial artworks more significant. They can confirm the presence or otherwise of any anomalies, support the choice of areas to be measured by minimizing the ambiguities of information derived from a single diagnostic method to distinguish original or restoration areas, and make an important contribution in the authentication process [9]. However, basic problems and operational limitations can also be encountered in forensic science when applied to cultural heritage, especially in the following cases: (a) when different kinds of materials need authentication; (b) when "unknown" samples are analyzed and then matched to "reference" materials or databases by an objective comparison; (c) when only non-destructive investigations are required, without damaging eventually valuable artefacts; or (d) when only very small samples are available (in the case of micro-destructive sampling), which are really difficult to investigate [4,5,9–12].

This study overcomes such limitations through the adoption of a multi-analytical approach where data derived from non-destructive techniques are merged with results obtained from minimally destructive ones. Multi-analytical techniques applied in forensic sciences, therefore, can provide valuable information that: (a) facilitates the efforts of institutions in conducting the investigations; and (b) brings to light historic information that is embedded in the remains and objects of the past. Indeed, the archaeological and historical-artistic antiquities market is being constantly supplied with illegally excavated artefacts, stolen works, and forgeries. In the case of canvas paintings, fragmenting large artworks into smaller paintings to sell on the black market is a known practice. It enables people to make more profit while at the same time making the original work less recognizable. When illicit collections are seized and recovered by law enforcement officers, they are delivered to museums. As a result, inauthentic objects or artworks deprived of their context become part of the collections of public institutions [13–21].

The authenticity and previous conservative treatment of a work or object can only be ascertained through scientific analysis [22]. It is worth underlining that specific protocols have to be followed to establish the attribution, dating, and possible origin of each material cultural asset, as well as the materials that constitute it, the techniques that were used to create it, and its state of conservation at the time of recovery. The present study comprises two case studies related to cultural heritage, where an integrated analytical approach was necessary to resolve several different issues. The artworks and objects were provided by the Cosenza Carabinieri Unit for the Protection of Cultural Heritage and Anti-Counterfeiting (Calabria, Italy). Specific data (i.e., geographical locations, group identity, etc.) have not been included for security and privacy reasons.

The first case study considers two fragments of oil on canvas paintings from a private collection, both of which depict *putti* (from the Latin *putus*, meaning little man). These have been common figures in the visual arts from the earliest times. Loosely connected to the notions of both angelic spirits and romantic love, and once depicted as winged youths, by the time of the Renaissance they had devolved into little more than chubby infants, sometimes winged, sometimes not, sometimes mischievous with bow and arrow, and sometimes witnesses to heavenly scenes [23]. The main objective behind the diagnostic

investigations conducted into these artworks was to identify the pigments used on the red-brown ground and pictorial layers to establish approximately when and how the two canvas fragments were created. This would make it possible to trace the original executive context, to compare the fragments, and to compare them with other fragments attributable to the same original painting, which had been stolen and cut into smaller pieces for the illegal market; and to verify any documented restoration interventions and remakes. Moreover, diagnostic imaging can guarantee correct stylistic readability of the figurative subjects, as requested by institutions for investigative purposes.

The second case study considers three bronze fragments from two belts and a helmet that were completely deprived of their context, so any useful information about style, date, and origin, was lacking. The alloys and chemical and mineralogical composition of the soils (i.e., earth) found inside the objects were studied. By comparing these data, valuable information, such as that related to the production period and the area of recovery (i.e., whether these were compatible with an archaeological find or whether the objects were imitations or had been intentionally tampered with), could be obtained, as requested by the institution that was in charge of the investigations. To extract the maximum amount of information and data, both non-destructive in situ and micro-destructive analytical techniques were used. This involved infrared reflectography (IRR), ultraviolet fluorescence (UVF), X-ray fluorescence (XRF), digital optical microscopy (DOM), scanning electron microscopy equipped with EDS microanalysis (SEM-EDX), and Fourier transform infrared spectroscopy (FT-IR). Several issues were thereby resolved and valuable information was given to the Cosenza Carabinieri Unit for the Protection of Cultural Heritage and Anti-Counterfeiting. The investigations showed the reliability of the multi-methodical approach in forensic sciences when applied to cultural heritage.

2. Materials and Methods

Five artworks were investigated (two fragments of paintings and three bronze objects) using both in situ and laboratory investigations. Details about the items and the analytical techniques are described in Table 1. The data from the findings are discussed according to type. Case study 1 comprises the painting fragments and Case study 2 the bronze objects.

Table 1. Investigated samples, description, and techniques employed.

	Object ID	Brief Description	Techniques Employed
Case study 1	Painting 1	cut-out of oil on canvas	IRR, XRF, UV, DOM
	Painting 2	cut-out of oil on canvas	IRR, XRF, UV, DOM
Case study 2	F1	fragment of a bronze belt	SEM-EDX, XRF, FT-IR, DOM
	F2	fragment of a bronze belt	SEM-EDX, XRF, FT-IR, DOM
	H1	fragment of a bronze helmet	SEM-EDX, XRF, FT-IR, DOM

2.1. Case Study 1: Paintings

Case study 1 comprises two cut-outs from oil on canvas paintings (Table 1), both depicting three *putti* and stylistically attributable to the XVIII century. Painting 1 (Figure 1A,B) was 35 cm × 30 cm and Painting 2 (Figure 1C,D) 75 cm × 60 cm.

From a macroscopic point of view, both paintings have a lining that was attached to to a non-original wooden frame after the theft and following subsequent cutting of the original painting into pieces. In addition, Painting 2 presents some blistering on the left side. This runs longitudinally because of the incorrect adhesion of the original canvas to the new lining support. In both cases, visual inspection made it possible to observe on the reverse of the fragments the cuts of the original canvas along the edges of the frame (Figure 1). To analyze the original pictorial layer, identify any repainting or pictorial integration, and assess the state of conservation, an integrated and totally non-invasive analytical approach was applied.

Figure 1. Front and back of the two fragments of oil paintings on canvas, attributable to the XVIII century: (**A**–**D**) Painting 1 (size: 35 cm × 30 cm); (**D**,**E**) Painting 2 (size: 75 cm × 60 cm). The degradation revealed during the first condition report is described in the legend. Details (**C**,**G**) show along the edges of the frame the cuts of the original canvas, attached to the lining canvas; (**D**) evidence of the original craquelure and use of a *risparmio* techniques, leaving the red-brown ground layer visible; (**F**) back of the lining canvas with an evident curved patch (red dashed line); and (**H**) wide blistering on Painting 2 highlighted by raking light observation.

A DINOLITE AM4113TFVW portable digital optical microscope (DOM), was used preliminarily to observe the painting surfaces in visible light at 50 and 200 magnifications. It has the following technical characteristics: resolution, 1.3 megapixels; magnification, 10×-50×; 200×; illumination, 4 UV light-emitting diodes (LEDs) with 400 nm + emission; 4 built-in white LEDs; a color CMOS sensor; manual calibration; and a measurement accuracy of approximately ±3 µm.

Infrared reflectography (IRR) is a well-known and non-invasive technique based on wideband imaging in the near-infrared (NIR) range. It makes it possible to look beneath the visible layers of paint [24–26] and to detect, where present, whether any underdrawing has been carried out with carbonaceous matter and possibly the technique that was employed to transfer it onto the preparation layer, such as tracing of the cardboard, "*spolvero*", or the use of a grid. The technique also makes it possible to reveal hidden pictorial layers and to highlight undocumented previous restoration interventions and/or remakes that could not be identified with the naked eye or UV light because of the high fluorescence of the superficial varnished layers.

Visible fluorescence induced by UV radiation is a useful tool for obtaining details that are not visible to the naked eye. Calibrated UV-induced visible fluorescence analysis, with specially filtered UV sources, enabled us to study the surface of the paintings and evaluate their state of conservation; to identify the possible existence of inhomogeneity on the surfaces due to the presence of non-original materials; and to reveal faded substances or other traces of possible interventions at later stages. This could help us to identify the original materials employed and to carry out a qualitative mapping of different chemical substances present on the objects' surfaces. We were able to establish whether recent

restoration procedures or alterations to the polychrome surfaces had been carried out and to differentiate between new and old pigments on the pictorial layers [27].

The UV and IR multispectral images were acquired using a digital camera with a charge-coupled device (CCD) photographic sensor—the MADATEC 28.2 MP multispectral system. The UVF-induced visible fluorescence acquisitions were obtained with a UV-IR cut filter and filtered LED sources with an emission peak centered at 365 nm. The IR images were acquired using filters centered at 850 nm and 950 nm, homogeneously illuminating the surfaces using halogen lamps.

Portable X-ray fluorescence (XRF) spectroscopy was used to identify, at the elemental scale, the composition of certain representative painted areas, in terms of major and minor constituents. XRF spectra were collected through an AMPTEK XRF spectrometer. This consists of a miniature X-ray tube system Mini-X—Amptek, which includes the X-ray tube (max voltage of 40 kV, max current of 0.2 mA, target Rh, collimator 1 or 2 mm), the power supply, the control electronics and the USB communication for remote control; a Silicon Drift Detector (X-123SDD—Amptek) with a 125 to 140 eV FWHM @ 5.9 keV Mn Kα line Energy Resolution (depends on peaking time and temperature); 1 keV to 40 keV Detection range of energy; max rate of counts to 5.6×10^5 cps and software for acquiring and processing the XRF spectra. The primary beam and detector axis formed an angle of 0 and 40 degrees, respectively, perpendicular to the sample surface. The measurement parameters for both case studies were as follows: tube voltage 35 kV; current 80 μA, and acquisition time 60 s. No filter was applied between the X-ray tube and the sample; and the distance between sample and detector was around 1 cm. The setup parameters were selected to ensure a good spectral signal and an optimal signal to noise ratio (SNR).

2.2. Case Study 2: Bronze Objects

Three samples were examined (Table 1, Figure 2): fragments from two belts (i.e., F1 and F2), and one from a helmet (i.e., H1).
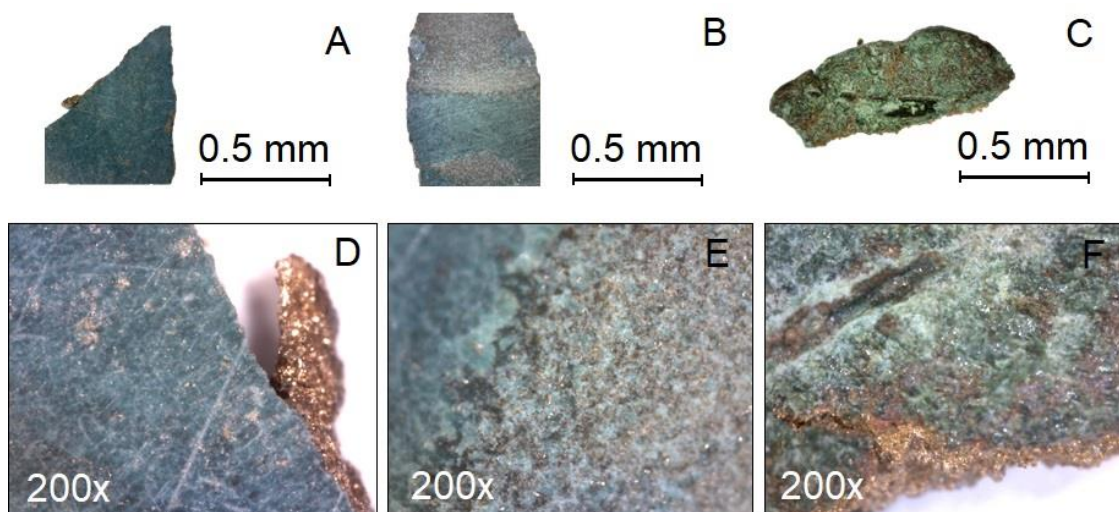

Figure 2. (**A**,**D**) F1 Fragments; (**B**,**E**) F2 fragments; (**C**,**F**) H1 fragments.

Preliminary investigations were carried out to identify the alloy and the composition of the patinas. A study was then carried out on the soils that were present in the fragments upon their recovery.

A portable XRF spectrometer (see the above-mentioned description) and SEM-EDX analysis were used to study each object. The latter was performed on the surface of the samples to obtain information about the micromorphology and chemical composition (in terms of major elements). The study was conducted using a Hitachi TM4000 scanning electron microscope, equipped with a STEM detector and the AztecOne Energy Dispersive

Spectrometry (EDS) System from Oxford Instruments. Analyses were carried out using an acceleration voltage of 5 kV, 10 kV, and 15 kV, under high vacuum conditions.

A portable digital optical microscope (see the above-mentioned description) was also used to observe the bronze surfaces.

Finally, an FT-IR analysis was conducted on the soils recovered from the internal parts of the fragments to establish whether the finds had been displaced. It was performed using a Perkin Elmer Spectrum 100 spectrophotometer equipped with an attenuated total reflectance (ATR) accessory. Infrared spectra were recorded in ATR mode, in the range of 500–4000 cm^{-1}, 32 scans, at a resolution of 4 cm^{-1}.

3. Results and Discussion

3.1. Case Study 1: Paintings

3.1.1. Microscopic Observation

The original pictorial surfaces, the area of pictorial integrations (localized through an initial observation under UV LEDs), the applied protective layer, the surface morphology, the overlap between continuous layers, and the characteristic craquelure were preliminarily examined and documented using a portable digital microscope. The following were observed in Painting 1: (a) the original brown pictorial layer was compromised of severe thinning; (b) the original canvas and a trace of reddish ground layer in correspondence with a color lacuna; (c) a pink-reddish pictorial layer along the craquelure fractures with minimal retouching; and (d) a UVF image confirmed contours of thin retouchings and the presence of recent protective and minimal residues of an older varnish (Figure 3A–D). In the case of Painting 2 (Figure 3E–H), there was also an area where the original pictorial layers were covered by a non-original protective layer and more recent pictorial retouching (both observable under UV LED sources). The darker portions (brown) were attributable to residues of the original protective layers (solubilized and not completely removed before the application of the current thick layer of varnish, as shown in Figure 3E,F). Figure 3G shows retouching on the original surface. It was highlighted under UV LEDs (the dark area in Figure 3H); a blue-white fluorescence of the thick protective layer was also documented.
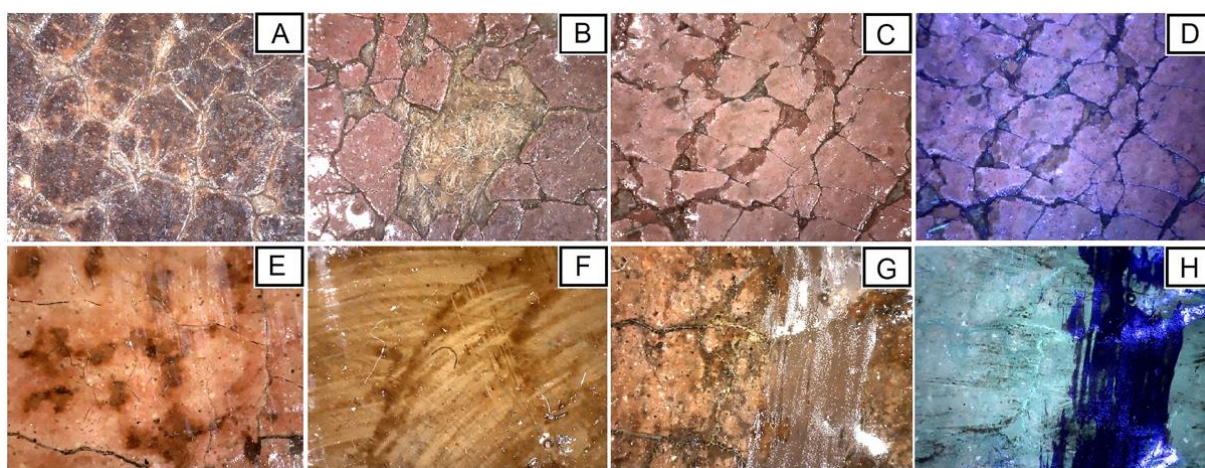

Figure 3. Digital optical microscopy images on selected areas of Painting 1 (**A**–**D**) and Painting 2 (**E**–**H**). (**A**,**B**): areas of the original painting, where the reddish-brown ground is also evident in some portions affected by thinning, and the original canvas is visible in correspondence of a lacunae; (**C**): the large fractures of the craquelure are retouched with thin pictorial integrations evident even under UVF (**D**); (**E**,**F**): original painting with traces of both original and non-original superficial protective varnish. In particular, the darker portions (brown) in (**F**) are attributable to residues of the original protective layer (solubilized and not completely removed before the application of the current thick layer of protective varnish); (**G**,**H**): area showing both original and non-original pictorial brushstrokes. The repainting visible on the right side of both images is accentuated above all in H through the use of UV (dark area).

In both paintings, preliminary observations using the optical microscope revealed several previous restorations. These substantially altered the correct reading of the original pictorial surfaces, as confirmed by the following multispectral investigations.

3.1.2. Multispectral Imaging Investigations

Figure 4 compares the IRR and UVF images of Painting 1 and Painting 2. The IRR investigation did not reveal any traces of *pentimenti*, carbonaceous underdrawings, or underlying pictorial brushstrokes corresponding with the original area of the paintings, nor traces of the original frame or tensioning. This last aspect further confirms that the fragments were extracted from large artworks and that they were not close to the original frame.
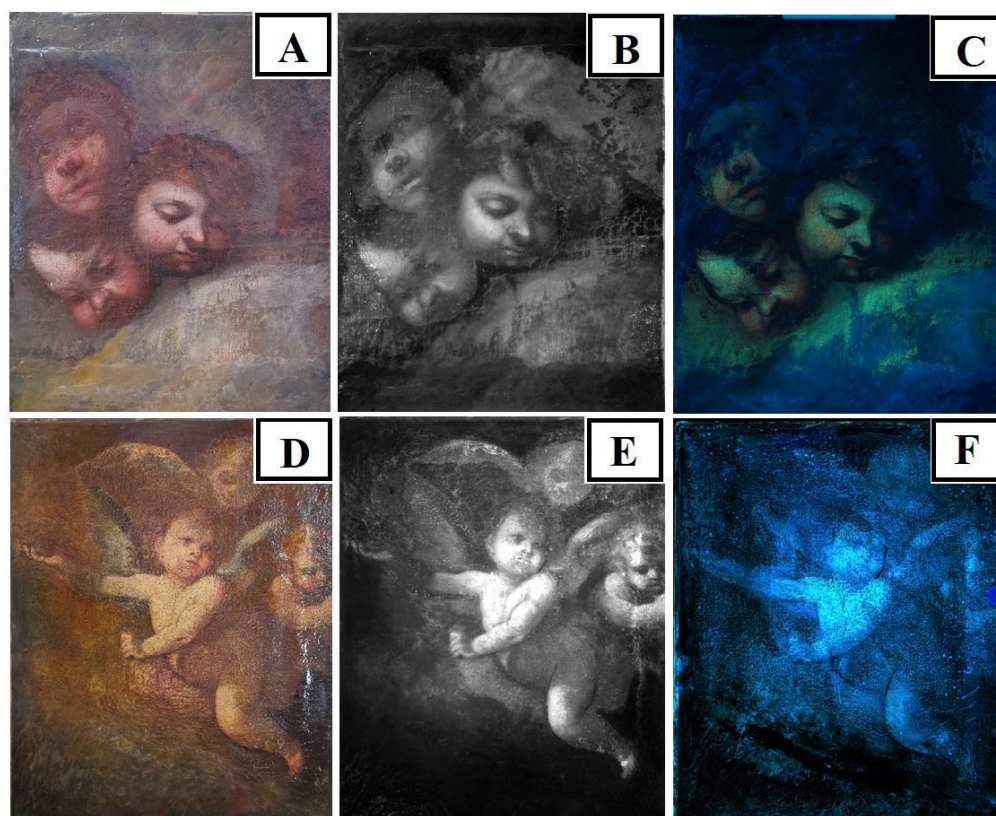

Figure 4. Photograph of Painting 1 and Painting 2 (**A,D**) and related 950 nm IR (**B,E**) and UV (**C,F**) images. In the IR images, the areas affected by repainting appear to be of a darker grey tone than the original pictorial layer of the same color in the visible range. The same pictorial areas appear devoid of visible fluorescence under a UV source (dark areas), confirming the mapping of pictorial retouchings overlapped onto the original surfaces.

In the case of Painting 1 (Figure 4A–C), the results suggest the presence of superficial retouching or pictorial integrations identifiable as dark grey in the IR images and as darker areas in the spectral response of the protective varnish under UV.

The dark areas did not show any UVF, highlighting the extensive areas of reconstruction (in the upper and lower bands) and the retouching of certain details (in the original portion of the work). Ultraviolet fluorescence observation made it possible to differentiate the original portion of the *putto*'s face, which was of a higher quality than the part of the face attributable to subsequent restoration procedures.

The bright whitish fluorescence response of the flesh tones and clouds, limited to the original portions, is typically attributable to lead white in oil medium [27], the identification of which was confirmed by the chemical analysis reported below. In addition, in the IR

range, the perimeter of the original portion of the painting was visible in the central part of the current support.

The upper and lower areas showed a different IR spectral response. In particular, greater IR absorption was observed, detectable by the darker shade of grey in the reflecto-graphic image. This suggests that those areas indicate a remake, partially superimposed on the original painted area due to the resizing of the initial fragment [28].

In Painting 2, the greater IR absorption (darker areas) suggests pictorial retouching of the original painting.

Pictorial brushstrokes and remakes prevail in the brown background. This was probably necessary to harmonize the original area to the new support, both aesthetically and dimensionally. Indeed, the original pictorial surfaces are characterized by lower absorption in IR compared with the repainted area, the tones of which have darker gray tones than the original layers.

Moreover, in the case of Painting 2, the images obtained by UVF (Figure 4D,E) highlight the presence of a surface layer of protective paint characterized by a bluish response (typical of an aged synthetic paint). This varnished layer makes it less possible to observe the behavior under UV of the underlying pictorial layer. Small differences are observable between the varnish applied to the original pictorial layer (limited to figurative subjects) and the brown remade layer (in the lower and upper bands of the painting).

In the lower portion, the absence of fluorescence is observable, corresponding with an area that lacks the original support and it is of interest also because of the integration of the preparation layer (see the back of canvas support in Figure 1). The perimeter of this area corresponds with the anomaly observable on the back of the support.

In both paintings, although the IR images indicate clearly the presence of a thick layer of altered protective varnish, it was possible to obtain a better reading of the illustrations and painted figures.

3.1.3. XRF Analysis

The XRF analysis performed on the original pictorial surfaces allowed us to identify, for both paintings, the typically pure pigments or mixtures that were used in the XVIII century (Figure 5) [29]:

- Lead white $[(PbCO_3)_2 \cdot Pb(OH)_2]$, a natural pigment used since ancient times. This was found both in a mixture in the pictorial layers and in the ground (deducible from the high counts of lead in the dark areas of the pictorial surface and the response obtained in all XRF spectra);
- Vermillion (mercury sulfide, or HgS) has also been used since ancient times. We identified small amounts of it in the mixture for the preparation of the flesh tones, in the red portion, and in the ground or thin primer (probably present in a mixture in very small quantities in the reddish-brown preparation layer, where it was visible even when under the microscope; see Figure 3 and Painting 1 in particular);
- Ochres (iron oxides/hydroxides with clays) are pigments associated with impurities of potassium and manganese oxides typical of natural earth [29]. They are used for brown ground and mixed in red and brown pictorial layers.

A copper-based pigment was detected in Painting 2. The elemental analysis did not allow the unequivocal identification of a blue chromophore; however the simultaneous presence of a high count of copper lines and the high IR absorption of this pictorial layer suggested the use of azurite ($2CuCO_3 \bullet Cu(OH)_2$), a mineral that has been used as a blue pigment since ancient times.

The results obtained by XRF analysis were supported by the evidence provided by the previously discussed diagnostic imaging investigations (DOM, UVF and IRR). Uniform spectral responses showed that the above-mentioned pigments were used for both paintings. This confirmed that the pigment *palettes* were typical of the historical period (i.e., the XVIII century).
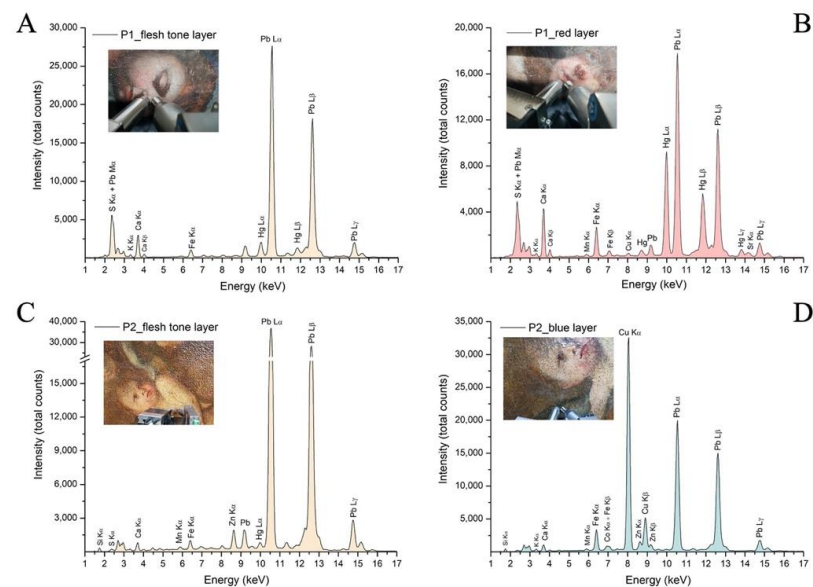
Figure 5. XRF spectra of Painting 1 (**A**,**B**) and Painting 2 (**C**,**D**). It is important to note that the measurements refer to original areas; however, in the case of Painting 2, it was not possible to avoid thin retouching along the craquelure lines, which resulted in the presence of minimal zinc counts in the XRF spectra.

3.2. Case Study 2: Bronze Objects

3.2.1. Microscopic Observation

Observations at high magnification confirmed the similarities between the two belt fragments from the morphological point of view (Figure 2D,E). The acquired images show in both cases a thin green-grey patina that, in the *lacunae*, allows the surface of the metal alloy to be seen directly. In particular, for the F2 fragment, a dark green layer with a smooth and shiny surface is apparent. This layer is growing on the first one and shows a more inhomogeneous and "powdery" appearance.

The images of the helmet fragment (Figure 2F) show a different formation of patinas on the bronze surface. The first dark red layer may be attributed to the formation of a lower layer of copper oxide (cuprite) on which blue-green layers of copper compounds (perhaps chlorides and/or carbonates) began to grow under the conservation conditions [30].

3.2.2. XRF Analysis

X-ray fluorescence investigations in the case of finds made of metallic materials allow the qualitative and, under certain conditions, semi-quantitative analysis of the chemical elements in the alloy and elements present on the surface (artificial patinas) induced by ongoing or past corrosion processes. The analysis of both the alloy and the patina can provide useful information in the case of artificial processes for the falsification of typical corrosion patinas, characteristic of archaeological bronzes or more generally of ancient metal finds.

From the analysis carried out to date, it was possible to verify that the fragments from the two belts are characterized by a very similar chemical composition and the same intensity values of the characteristic peaks of the chemical elements: copper and tin (the major elements), and silicon, iron, nickel, lead, and arsenic (minor or trace elements). The helmet fragment has a high lead content in the matrix of the bronze alloy, which consists mainly of copper and tin. In addition, silicon, titanium, and iron were identified as minor or trace elements. These may have been derived from the ore deposits that were exploited for bronze production [31].

The XRF spectra for each fragment are shown in Figure 6. They were acquired using the same measurement conditions and reported using the same numerical scale, so they can be directly comparable.
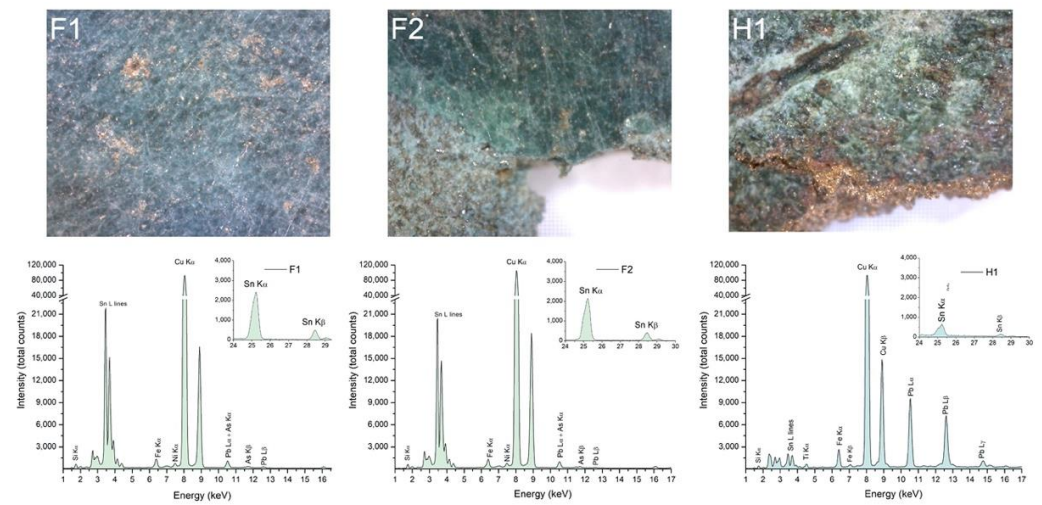
Figure 6. Images of the three bronze fragments at high magnification, acquired using a digital optical microscope and corresponding XRF spectra.

3.2.3. SEM-EDX Analysis

Further semi-quantitative analysis was performed on the outer surface of the metal fragments (Table 2). The acquired results provided the percentages of the identified chemical elements on alloy-burial environment interaction products.

Table 2. Semi-quantitative analyses by SEM-EDS on the metal fragment surface.

F1 Fragment Element (Weight %)	1	2	3
Aluminum	2.5	1.6	1.4
Silicon	5.9	4.2	4.1
Phosphorus	0.8	0.8	0.7
Iron	2.2	2.0	2.2
Copper	4.2	5.0	4.5
Tin	84.4	86.5	87.1
F2 Fragment Element (Weight %)	1	2	3
Aluminum	0.6	0.9	14.7
Silicon	4.5	5.3	4.2
Phosphorus	0.7	0.5	0.5
Iron	2.0	1.8	1.8
Copper	7.6	8.6	6.1
Tin	84.5	82.9	72.7
H1 Fragments Element (Weight %)	1	2	3
Aluminum	0.9	0.7	0.9
Silicon	7.1	7.1	7.4
Calcium	0.6	-	-
Iron	2.6	-	-
Copper	25.4	25.7	29.3
Tin	37.8	40.3	38.1
Lead	25.6	26.3	24.2

The superficial layers of the two belt fragments were similar in composition (i.e., both had a high tin content, followed by a copper content of around 5%). As has been noted, the helmet fragment differed because lead was present (which was also highlighted in the XRF analysis). It, too, had a high tin content (around 40%) and copper (around 25%). The high

tin content in each of the samples may have been the result of a decuprification process or the selective dissolution of copper that causes the replacement of metal in corroded products [32,33]. Further, it could be linked to the so-called tinned surfaces (when molten tin is applied to bronze) and layers of both the η (eta) and the Σ (epsilon) phases, which develop by interdiffusion between the bronze and the molten tin, create layered structures in the following sequence: surface tin, eta phase, epsilon phase, and substrate bronze [34]. In addition, the presence of elements such as aluminum and silicon may be due to their migration from the soil to the porous external layers of the samples [35]. A remarkable feature that all the samples have in common is the absence of chlorine among the corrosion products. This may be linked to the microenvironmental conditions. The absence in this area of chlorine compounds suggests that the copper present is cuprite or, in the first two samples, copper phosphates (which is associated, e.g., with decomposing buried bones and other organic or inorganic phosphorus-containing materials) [36,37].

Further analysis would be necessary to evaluate whether the distribution of chemical elements was attributable to the patina (the result of interaction with the burial environment) or the original composition of the alloy. This information could be useful when attempting to verify the expected production period, which may be hypothesized in terms of archaeological or stylistic phases.

3.2.4. FT-IR Analysis

The soil samples were comprised of small amounts of incoherent material that had adhered to the walls of the fragments themselves. Fourier transform IR analysis was carried out because this requires only a few milligrams of material. As Figure 7 shows, the spectra of the two different soils, i.e., the soil from the belt and helmet fragments, overlap perfectly, which indicates a probable homogeneity of composition. The IR spectra revealed both absorption bands of silicates [38,39]. However, through the FTIR analysis, it was not possible to give a specific indication of the silicate minerals present in the analyzed soils since the absorption peaks are common to several silicate minerals having similar molecular structures [38]. In particular, the main absorptions of IR radiation were found between the following wavelength ranges: $1250/1000 \text{ cm}^{-1}$, which is associated with the asymmetrical stretching vibration of the Si-O-Si bond; $820/760 \text{ cm}^{-1}$, which is associated with the Si-O symmetrical stretching vibration; $705/685 \text{ cm}^{-1}$, which is associated with the Si-O symmetrical bending vibration; $545/435 \text{ cm}^{-1}$, which is associated with the out of the plane bending vibrations of the O-Si-O bond. However, despite the limitations of the IR technique in identifying exactly the mineralogical composition of soil samples (it should be used in combination with other techniques [38]), it allowed a homogeneity of composition to be established which seems to confirm the hypotheses of the same provenance between the two types of finds.
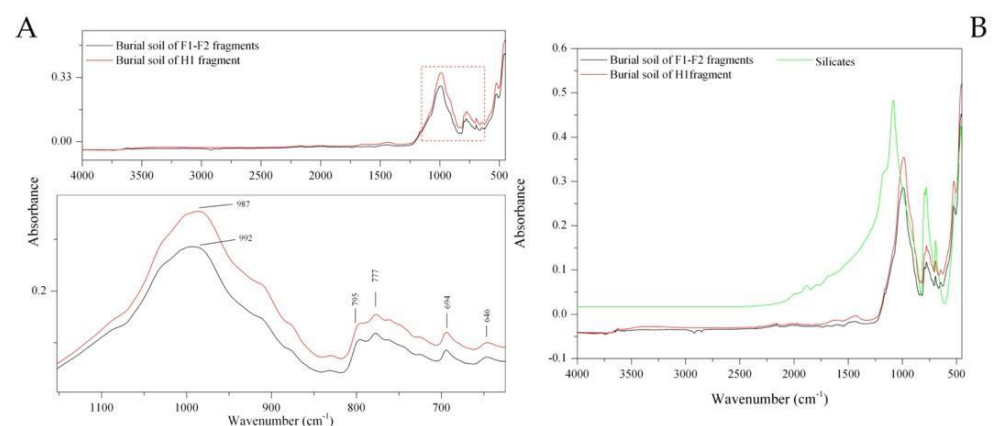

Figure 7. (**A**) IR spectra of the two burial soils compared with silicate absorption bands (**B**).

4. Conclusions

The present study highlighted the supporting role that a non-invasive or minimally invasive scientific analysis can play in providing the archaeological or historical artistic context of seized finds. Detailed information on the paintings and the bronze items delivered by the Cosenza Carabinieri Unit for the Protection of Cultural Heritage and Anti-Counterfeiting (Calabria, Italy), was not available, because forensic investigations were ongoing. The investigations described therein were therefore aimed at assisting the process.

Preliminary observations of the paintings were carried out (both with the naked eye and with microscopic techniques), to verify the state of conservation and the methods used to anchor the original fragments to the new supports (i.e., canvas lining and wooden frames). Both items had clearly been cut from larger paintings. No evidence of tensioning or any fingerprints from the original frame was initially evident. Infrared reflectography and UVF confirmed the absence of *pentimenti*, showing large areas of pictorial integration.

Wide surface retouchings were observed. These were probably designed to make the colors and aesthetics of the fragments uniform and to fill the *lacunae* derived from their resizing and poorly conserved state. X-ray fluorescence investigations provided information on chemical elements and suggested the presence of inorganic chromophores on the original painted surfaces: i.e., lead white, vermillion, natural earth pigments, while in the case of Painting 2, a copper-based pigment in the layers of blue.

Chemical analysis and microscopic observations confirmed the presence of a red-brown preparation (which artists began to use from the XVII century) in the ground. All the pigments identified in the two painting have been used since ancient times, and the absence of synthetic pigments in the original areas of the canvases suggests that both works are pre-XIX century.

The entire set of spectroscopic and multispectral data therefore confirm the authenticity of the seized fragments and consequently the authenticity of the large stolen canvas paintings from which they were cut.

Finally, preliminary results acquired through surface analysis of the bronze objects allowed us to confirm that the two belt fragments have a similar composition. They therefore probably belong to a series of metal objects produced with the same alloy. The helmet fragment showed a different composition from the belt fragments. Further analysis of the distribution of chemical elements from the core to the outer surface would be needed to verify the various layers of corrosion products and the original composition of the core alloy. The burial soils showed the same characteristics, thus indicating that the metal objects may have come from a similar location and had not been displaced.

The two case studies in the present research illustrate the importance of specific analytical and diagnostic protocols when examining objects recovered from seizures and thefts if their provenance and the manufacturing techniques involved in their production are to be established. Only then can we answer questions posed by institutions regarding the authenticity and archaeological/historical/artistic context of objects that may have been lost as a result of crimes committed against Cultural Heritage and later recovered.

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