An integrated analytical approach for the characterization of repainted wooden statues dated to the fifteenth century

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ARTICLE INFO

ABSTRACT

The present study aims to set-up an investigation integrated methodology to identify pigments and binders present in the original layers and the subsequent repainted layers that characterize two polychrome wooden statues dated to the fifteenth century. In particular a multi-analytical approach has been applied on two Ligurian Christs, the first one from San Bartolomeo parish in Zuccarello, the second from Borghetto San Niccolò (placed in Liguria region, Noethern Italy) both repainted many times during the centuries. By comparing the results of XRF analysis performed with portable instrumentation on the surfaces and on the stratigraphic sequences coming from different areas of the works of art, with the data obtained by SEM-EDS and corroborated with μ-FTIR and portable Raman spectroscopy findings, the pigments present in the different layers were identified. By μ-FTIR spectroscopy and thanks to the application of some staining tests (with Oil red and Amido black) the chemical nature of the organic binders employed was disclosed. Thanks to the presence of specific pigments, such as Prussian blue, barium sulphate, titanium oxide and some organic colorants, linked to specific historical periods, it was possible to date the layers and to reconstruct the history of the two examined statues. These detailed investigations on complex stratigraphic cross sections have been carried out as part of a conservation project and the results obtained have provided restorers with important information useful for the intervention on these statues and for their conservation.

1. Introduction

The polychrome wooden sculpture is a complex artefact because of the presence of different materials and techniques. During centuries, due to changes in style or decay, works of art such as Christ statues closely related to the cult, were often repainted. It often happened that these statues were completely repainted rather than integrated into the areas where the colour had fallen, as instead it is done today in the common practice of restoration. Repainting to renew the underlying layers could be motivated simply by a change of taste and style and this happened in particular in the case of devotional artefacts, such as the two Christ wooden statues studied in the present paper. In particular the objects of this study are two fifteenth-century Ligurian (Northern Italy) Christs, namely Christ of Zuccarello and Christ of Borghetto San Nicolò, both characterized by heavy alterations.

Our aim was to set up an analytical protocol to identify pigments and binders of the original layers and the subsequent overpaintings that characterize these polychrome wooden sculptures. The acquisition of these data could be a support not only to the activity of the restorers, who frequently have to face the removal of the over layers, but also allows to deepen the knowledge of the historical artistic context of these works of art.

The combined set of analyses applied in this paper consisted of preliminary non-invasive techniques such as portable X-ray fluorescence spectroscopy (XRF) followed by the characterisation of cross-sections, prepared for selected samples, by means of Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS) and micro Fourier Transform Infrared spectroscopy (μ-FTIR). Furthermore, in order to preliminary identify the organic binders employed, some investigations were carried out with optical microscopy using UV radiation and specific staining tests, such as Oil red and Amido black, were used to identify the chemical nature of the binders (oils or proteins). A confirmation of the nature of the binders was also obtained by μ-FTIR. Finally, portable Raman spectroscopy has been used to highlight the presence of some pigments.

It is worth to notice that the application of a multi-analytic protocol is certainly a winning strategy in the case of the identification of the chemical nature of substances, both organic and inorganic [1–9].

In this study the integrated use of all these methodologies has allowed to set up a protocol that can be applied to the study of com-

plex stratigraphies and multi-layers paintings such as those typical of the statues here examined and, more in general, in the case of heavily repainted wooden statues. In fact knowledge of the stratigraphic sequence of these heterogeneous layers is fundamental for understanding the artist's painting technique and for conservation issues.

To our knowledge in the scientific literature the papers dedicated to the studies of wooden sculptures [10–13] are significantly less numerous than works concerning the analysis of other types of works of art such as for example canvases or wooden tables.

The presence on the two examined statues of numerous over-paintings represents an analytical challenge.

Scanning electron microscopy generally employed for morphological surface investigation for example of mortars, pigments and stones, if equipped with EDS can provide elemental analysis [14]. The use of portable X-ray fluorescence spectroscopy has recently become one of the most widely employed analytical techniques in the in-situ scientific examination of works of art and certainly it is very useful in case of very complex stratigraphies [15]. XRF is commonly used for major and trace elemental analysis for pigments, stones and mortars [14,16]. Both SEM-EDS and XRF should be combined with spectroscopic techniques such as FT-IR or Raman spectroscopy in order to carry out a molecular speciation [14,17]. Furthermore FT-IR is often employed to identify the chemical composition and structure of organic pigments and binders [3,9,14]. μ-FTIR spectroscopy has been also successfully applied for the study of cross-sections [2,18,19]. Similarly a great quantity of studies has been published on the application of Raman spectroscopy for the identification of pigments and dyes [9,14].

The study carried out on the two Christs statues has also allowed a new possibility of comparison, based on the analytical data, in the classification system of the "*selva dei Cristi feriti liguri quattrocenteschi nel Ponente*", of which these two works are part, proposed in the text *"La Sacra Selva. Scultura lignea in Liguria tra XII e XVI secolo"* [20,21].

2. Materials and analytical methods

2.1. The two studied sculptures

The two statues here examined are two fifteenth-century wooden polychrome sculptures from the Ligurian area of Ponente: the Deposition of Christ of Zuccarello (SV, Savona) and the Crucified Christ of Borghetto San Nicolò (IM, Imperia).

The Christ of Zuccarello (Fig. 1a), preserved in the parish church dedicated to San Bartolomeo in the small town of Zuccarello (Liguria, Northern Italy) and dated to 1440–1460, is a sculpture of almost monumental dimensions, 167 × 42 × 26 cm, and represents a dead Christ. With a strong devotional value for the community of Zuccarello, the statue has been repainted several times, so much to hinder its reading and to render the plasticity of the original carving not very appreciable. The conservation and restoration intervention recently started, allowed the recovery of the first repainting of the work datable to the second half of the sixteenth century.

The Christ of Borghetto (Fig. 1b), coming from the homonymous village in the province of Imperia (Liguria, Northern Italy) is smaller and currently is preserved in the headquarters of the Superintendence of Genoa and the provinces of Imperia, La Spezia and Savona, in Palazzo Balbi in Genoa; the statue presents a compromised conservative state of the oldest polychromies. The dimensions are 90 × 77 × 19 cm. The work can also be dated to the fifteenth century and has been so repainted to completely alter the original carving technique.

As for the Christ of Zuccarello, 7 samples of the pictorial film (as indicated in Fig. 1a and in table 1) were taken; in this way the different parts of the statue (skin, thong, crown, hairs) and the total succession of the layers, from the original preparation to the outermost repainting, have been sampled.

In the case of the Christ of Borghetto, because of the smaller dimensions of the statue, it was possible to withdraw, in order to have the complete stratigraphy and to sample the different areas (skin,
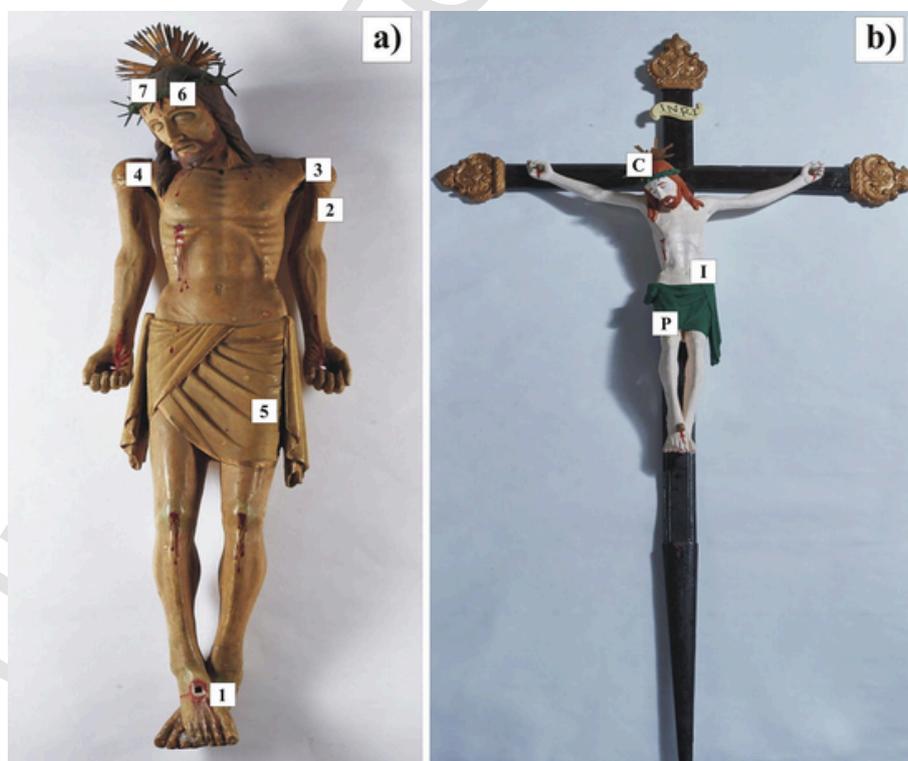

Fig. 1. The two examined wooden statues: a) Christ from Zuccarello; b) Christ from Borghetto San Nicolò.

Table 1
Analysed samples collected from the two statues.

Christ of Zuccarello		Christ of Borghetto San Nicolò	
Sample	Description	Sample	Description
1	skin, right foot	I: I1, I2	skin, right side
2	skin, left arm		
3	skin (see point 3 in Fig. 1)		
4	right shoulder		
5, 5.1	thong, left flap	P: P1, P2	thong
6	crown of thorns		
7	hairs	C: C1, C2, C3, C4	hairs

thong and hairs), only 3 samples (Fig. 1b and table 1). For both statues it was taken the maximum numbers of samples allowed by the superintendence. The problem of layers decohesion, especially the older ones, made it practically impossible to take a single sample that presents the complete succession of the layers and for this reason in some cases more than one fragment was taken for each sample (table 1).

2.2. Analytical methods

2.2.1. Optical microscopy observations

In order to prepare the cross-sections, the samples were embedded in Technovit ® 4004 thermosetting resin, by Kulzer company, inside silicone sample containers resistant to the resin dilution solvent.

The observations carried out on the stratigraphic cross-sections of the samples taken from the Christ of Zuccarello and the Christ of Borghetto, were performed with an optical microscope (Nikon Labophot) at 40, 100 and 200 enlargements, in reflected visible light and in UV light (Mercury Lamp- Power Supply – HBO 50).

2.2.2. Oil red and Amido black tests

Oil red and Amido black tests were used in order to carry out a preliminary identification of the nature of the binders [22–25]. Oil red is a lysochrome diazo-dye (also known as Oil Red O) used for staining of neutral triglycerides and lipids while Amdio black (also known as acid black1) is also a diazo-dye and is a protein-staining reagent commonly used for the enhancement of proteins. The method is based on the preferential absorption of a dye by a given substrate due to a chemical affinity between them. The procedure consists in applying, for a certain time, the specific dye for the substance to be detected on the sample cross-section [22]. Then a washing step follows (using demineralized water and 30% ethanol) to eliminate the excess of the dye that has infiltrated but not fixed. Since the dye Oil red should be fixed to the substrate only in the presence of particular acid groups typical of oils and resins, giving a red color, it would allow to highlight the presence of this kind of binders. Amido black is a general protein stain since it reacts with proteins resulting in a dark blue to black staining.

In addition to the presence of oil, colouring with Oil red could provide data on its aging and distribution in the sample. The aging process of the oils in fact is faster on the surface where the binder is exposed to the air, and is therefore subject to greater oxidation, while it is slower in depth where it is protected by the upper layers. Therefore, if within the stratigraphy it is found a colour graduation that turns from pink to a more intense red, this should be an indication of the drying process of the oil that started from the surface, where there is a less marked response to colouring, and is not yet completed in depth.

2.2.3. XRF analysis

The instrument used for the analysis was a Spectro xSORT portable XRF spectrometer. Measurement parameters were as follow: current in-

tensity: 50μA; voltage: 40 KV; acquisition time: 60 s; spot diameter: 9 mm.

Measurements were carried out following what is specified by UNI-Normal 10705 "Analisi per la fluorescenza a raggi X con strumentazione portatile" (May 2007) and 10945 "*Beni Culturali: caratterizzazione degli strati pittorici. Generalità sulle tecniche analitiche impiegate*".

2.2.4. Fourier transform infrared spectroscopy (FT-IR)

The analyses were carried out by μ-ATR FT-IR system using a Nicolet iN10 MX instrument equipped with an infrared microscope, from Thermo Scientific. 128 scans were applied for the spectra acquisition and the investigated range was 400–4000 cm^{-1}.

2.2.5. Scanning electron microscopy coupled with energy dispersive X-ray analysis

The samples were analysed by SEM-EDS to obtain qualitative/semi-quantitative information on the chemical composition according to procedures already set-up [26]. The instrument was a Hitachi TM1000 equipped with an energy dispersive X-ray spectrometer (Oxford Instruments SwiftED). The spectra were directly acquired on the cross-sections since no metal coating was required in this case to analyze non-conductive samples.

2.2.6. Raman spectroscopy

Raman spectra were acquired by a BWTek i-Raman EX device, equipped with a fiber optic probe and a 1064 nm Nd-YAG laser source. All the measurements were performed directly on the statues surfaces. A spectral range between 100 and 2500 cm^{-1} was investigated with a resolution of about 4 cm^{-1}, while the laser power was tuned between 40 and 120 mW according to the sample characteristics. In order to acquire spectra with a good signal to noise ratio, the latter were obtained as the sum of 10 or 20 accumulations, depending on the sample response.

3. Results and discussion

3.1. The Christ of Zuccarello: pigments and inerts

As regards Christ of Zuccarello, through the use of a portable XRF instrumentation an initial mapping was carried out on the statue surface. It is worth remarking that, being the penetration depth of X-ray source of few μm, the analysis will reflect not only the contribution coming from the outermost layer, but also that from the underling layers including the preparatory layer [27].

In particular on the outermost layers lead, titanium, barium, calcium, sulphur and iron were detected (as it is shown in Fig. 1s). These elements, in agreement with the literature [28–30] could be related to the use of lead white, titanium dioxide, barium sulphate, calcium sulphate and iron oxides.

XRF is not enough specific to guarantee molecular identification and as a consequence in order to achieve the unambiguous identification of the species, combined approaches have to be followed. As attested in numerous studies reported in the literature, SEM- EDS, that in the present study has been applied on cross sections samples, permits the identification of the different components present thanks to the possibility to carry out analyses on the singles particles allowing to confirm some hypotheses [30]. In Fig. 1s some example of SEM-EDS single particles analyses putting in evidence the presence of the species here discussed are reported. Furthermore XRF and SEM-EDS measurements should be corroborated with μ-FTIR analyses, as reported in different examples in this text.

Lead white (2PbCO$_3$·Pb(OH)$_2$) is the most important of all lead pigments historically used and oftenly the presence of lead could be related to the use of white lead [31]. Titanium dioxide white pigments are the products of twentieth-century technology [32]. The survey car-

ried out by XRF suggests with certainty that at least the last repainting layer was made after 1920, when titanium white was introduced on the market. In fact during the 1920s many plants were established worldwide and many types of pigments based on titanium oxide were introduced during this decade [32].

As regards barium sulphate it was first suggested as an artists' pigment about in 1782, but the major introduction of both natural and synthetic materials into commerce probably took place in the period 1810 to 1820 [33].

As already underlined XRF analysis allows the identification of the elements present in the entire thickness, without distinguishing between the various levels of repainting. As a consequence the results at this stage did not prove to be exhaustive.

It was therefore attempted to carry out XRF measurements on uncovered layers by the opening of some unveiling slots (as shown in Fig. 2 and in particular in Fig. 2g), in order to partially overcome the limits of applicability of this technique. These slots have a widht of 2 cm and allow, thanks to the pregressive unveiling of the layers (each layer corresponds to an area of about 2×2 cm^2), to put in evidende the sequence of the repaintings. In this way it is possible to obtain a sequence of XRF spectra each of them on a deeper layer progressively proceeding towards the older ones. For example in Fig. 2g the spectrum obtained on layer 3 (the second on the right side of the slot) shows the presence of Pb, Ca, S, Fe, Si and Sr. Ca and S are due to gypsum as confirmed by FT-IR analysis reported in Fig. 2f (see the following discussion on cross sections analysis). Fe, Si and Sr are probably linked to the presence of some iron based pigment such as an ochre.

XRF analysis, in some cases, was useful for highlighting some elements not evidenced by SEM-EDS since XRF was performed on wider areas. On the other hand, SEM-EDS can be performed also on single particles (some examples of single particles analyses are reported in Fig. 2s).

In order to investigate the composition of the individual layers and due to the complex stratigraphy of the samples examined (in some cases about 20 successive layers were identified in an alternation of preparatory layers and pictorial films), the analysis was carried out, as already mentioned, using SEM-EDS on the cross sections prepared.

Some of the most interesting results obtained combining the different techniques employed are presented and illustrated below and in particular it is discussed in detail the case of 4 samples from the Christ of Zuccarello (sample 1 from the skin, samples 5 and 5.1 from the thong, sample 6 from the crown of thorns and sample 7 from the hairs).

In Fig. 2a-d the cross sections of sample 1, taken from the right foot of the Christ of Zuccarello, as they have been observed by optical microscopy, are shown. The stratigraphy is complex and presents numerous heterogeneous layers. An ancient original polychromy is present, coeval with the realization of the support, consisting of a preparatory layer of considerable thickness (2, Fig. 2a) and an extremely thin pictorial film (3, Fig. 2a), surmounted by a finishing layer (4, Fig. 2a) applied after the underlying layer had already been cracked, as demonstrated by the partial penetration of the binder. Then there are different re-paintings. The preparatory layer (2) has a thickness of 165 μ-m and, as evidenced also by XRF analysis acquired on the slot corresponding to layer 3 (the analysis as we have specified before, includes also the underlying layer due to the penetration of X-ray radiation, i.e. layer 2), is formed by a mixture of white lead and gypsum (an XRF spectrum has been acquired also on the slot corresponding to layer 2, in Fig. 2g placed to the right of the slot corresponding to layer 3, and S, Ca and Pb have been evidenced for this layer, too). EDS spectrum on layer 3 (Fig. 2e) shows the signls due to S, Ca and Pb. The presence of Fe in the XRF spectrum (Fig. 2g), as already discussed, is due to a iron-based pigment, probably an ochre [34]. In the EDS spectrum registered on layer 3 (Fig. 2e) iron was not evidenced while its presence was disclosed thanks to single particles analysis.

So the original polychromy (layer 3 in Fig. 2e) contains a lead compound (probably white lead) and gypsum, in accordance with the technique used at the time. The presence of gypsum has been highlighted also by FT-IR as shown in Fig. 2f, where the spectrum acquired on layer 3 is compared with the spectrum acquired on a reference spectrum of gypsum. Together with gypsum signals, other peaks are present at 1673, 1543 and 1445 cm^{-1} due to an organic binder of proteinaceous origin. The first two signals are due to amide I and amide II [35–36] while the third one by some authors is indicated as amide III [35] even if according to other authors it is at slightly lower wavenumbers [37–38].

Coming to the outermost layer 18, SEM-EDS spectrum reported in Fig. 2e show the signals due to Ba, Pb, S and Ca. However it is remarkable to underline that on each sample some EDS measurements (at least 3) have been carried out and an average semi-quantitative composition has been obtained; in case of layer 18 also Ti and Zn (this in very small quantity), have been disclosed (the average percentage chemical composition determined is reported in the inset of Fig. 2e while in Fig. 3s a spectrum obtained performing a single particle analysis and showing also the presence of Zn and Ti is shown together with the corresponding semi-quantitative analysis).

In the literature BaSO$_4$ has been sometimes evidenced on the base of SEM–EDS analysis [29]. In our case this specie has been confirmed by FT-IR spectrum (Fig. 2h) where the signals due to BaSO$_4$ at 1168 and 1076 cm^{-1} are clearly present [39] together with an absorption at 1400 cm^{-1} that can be due to lead white even if calcite could also be present because of the characteristic feature at 870 cm^{-1} [39,40]. As mentioned before barium sulphate was introduced in the second half of the eighteenth century while the presence of titanium white dates to the last repainting after 1920. White zinc was introduced at the end of the eighteenth century and spread above starting from 1830.

The signals at 1729 cm^{-1}, 2920 and 2854 cm^{-1} (Fig. 2h) are due to a binder of oleic nature [35,39] while the signal at 1515 cm^{-1} could indicate the presence of lead soaps showing at this wavenumber the carboxylate anti-symmetric stretching mode [41].

In Fig. 3a and 3c the cross sections of the two samples 5 and 5.1, taken from the thong of Christ of Zuccarello are reported. Also in these two cases the stratigraphy is complex and numerous heterogeneous layers are observable. An ancient layer is present, coeval with the realization of the support, consisting of a preparatory layer of considerable thickness (2, Fig. 3a) (analogous at what observed for sample 1 and having the same composition) and an extremely thin pictorial film (3, Fig. 3a), surmounted by a finishing layer (4, Fig. 3a). Some re-paintings follow including layer 7 and layer 11. In particular layer 7 corresponds to the first repainting and represents the innermost layer brought to light after the removal of the most recent layers (Fig. 4a). In this layer Pb, Ca, S and Cu have been observed by SEM-EDS analysis (not reported). A copper based pigment has been probably used but the low quality of the micro FT-IR spectrum didn't allowed to identify it. During the statue restoration, after the removal of the outermost layers a decoration with red and green lines appeared as it is shown in Fig. 4a (a copper pigment was probably used for the green). Some Raman spectra (Fig. 4b) have been acquired with a portable instrument on the different areas of the unveiling slot as shown in Fig. 4a. In this way the presence of cinnabar (signals at 252, 287, 344 cm^{-1} [42]), used for the red lines, has been highlighet for layer 7 (Fig. 4b). The spectrum acquired on layer 7 shows also the signal at 1050 cm^{-1} due to hydrocerussite [42,43]. In the same figure Raman spectrum acquired on layer 11 is reported and the signals due to hydrocerussite at 1050 cm^{-1} and to gypsum at 1019 cm^{-1} are present.

By μ--FTIR analysis on layer 11 (Fig. 3g) it was possible to identify the presence of ferric ferrocyanide because of to the characteristic stretching of CN group at about 2083 cm^{-1}. Ferric ferrocyanide corresponds to the pigment commercially known as Prussian blue [44]
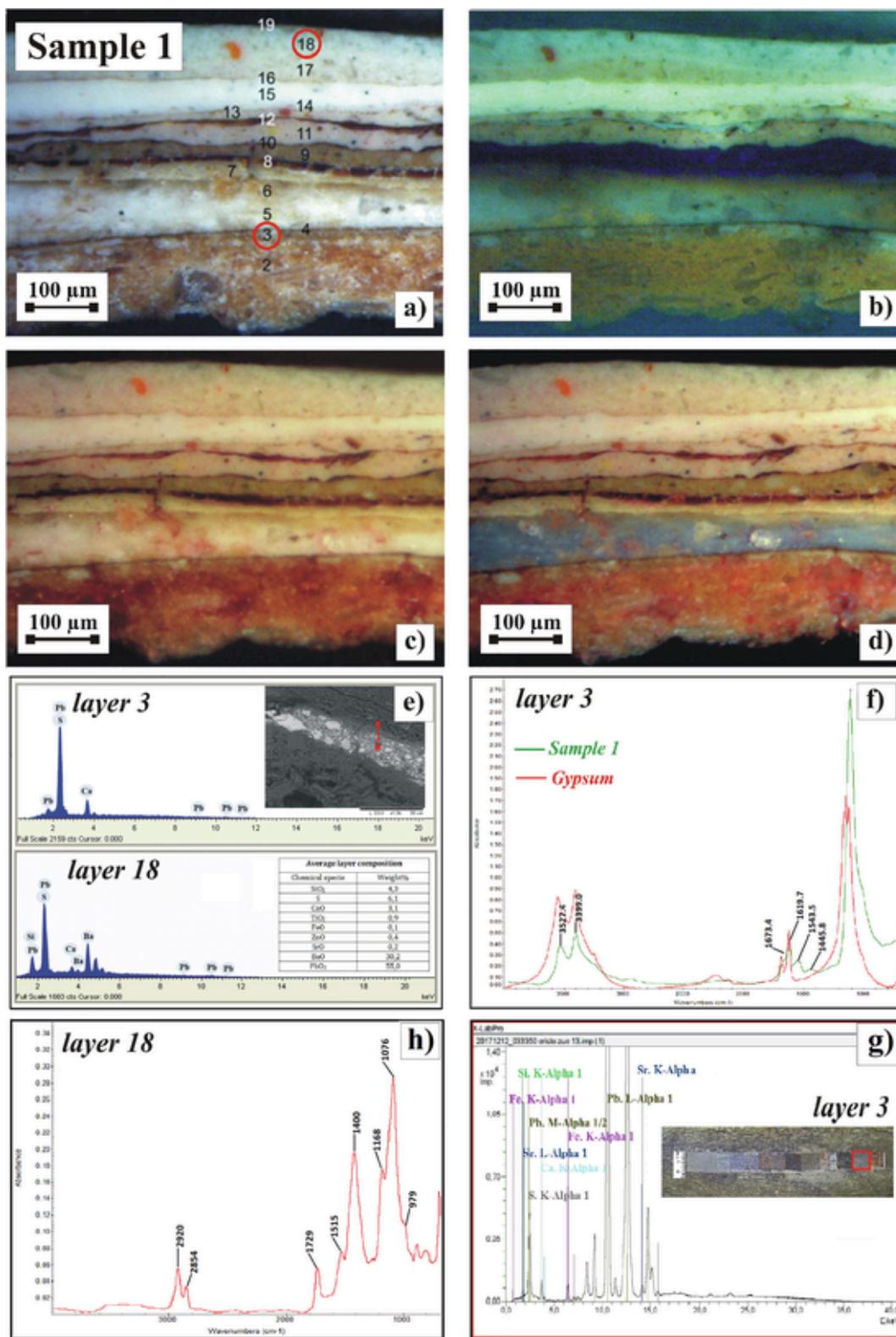
Fig. 2. Cross section of sample 1 from the Christ of Zuccarello a); Uv fluorescence image b); images of the cross section after the application of Oil red c) and Amido black d); EDS spectra on two selected layers (in the inset it is reported the average chemical composition, obtained examining different areas of layer 18 e); FT-IR spectrum on layer 3f); an unveiling area on the statue surface and the XRF spectrum acquired on layer 3 g); FT-IR spectrum on layer 18 h). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

that was widely distributed since the early 1700s and was one of the most commonly used blue pigments until about 1970 [45]. The signals at 1780, 2925 and 2861 cm^{-1} are due to a binder of oleic nature [35,39].

Fe, the element confirming the presence of Prussian blue, in this layer has been clearly highlighted by XRF analysis while in the corresponding SEM-EDS spectrum the signal due to Fe was quite weak;
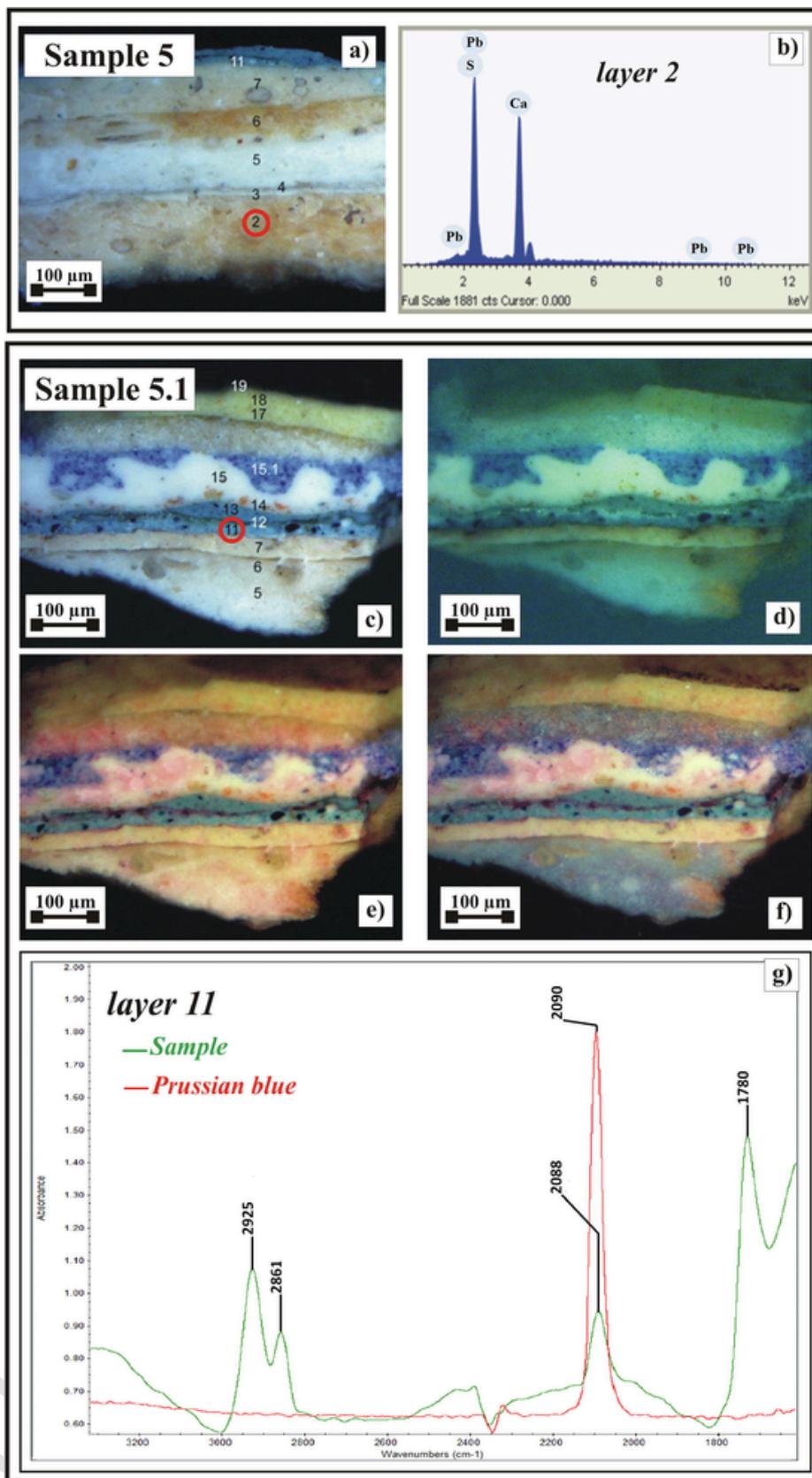
Fig. 3. Cross section of sample 5 from the Christ of Zuccarello a) and EDS spectrum on layer 2b); cross section c), Uv fluorescence image d) and images of the cross section after the application of Oil Red e) and Amido Black f) of sample 5.1; EDS spectrum of layer 11 g). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
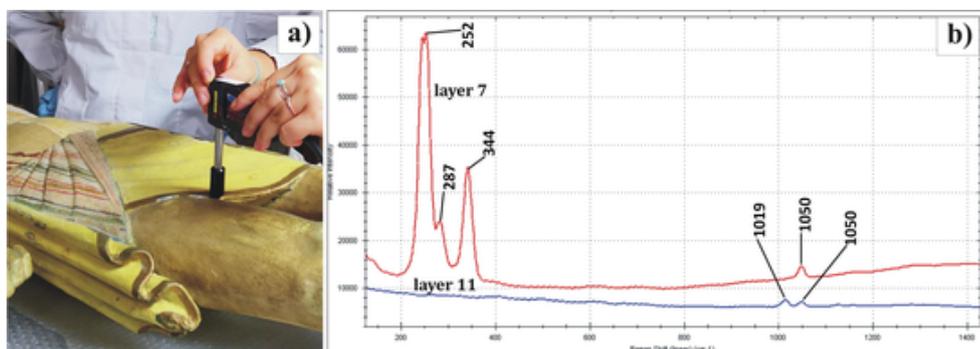
Fig. 4. An image of Christ of Zuccarello where inner layers have been brought to light after the removal of the most recent repaintings a); Raman spectra acquired on selected spot of the unveiling area corresponding to layer 7 and layer 11 of the thong.

this is due to the fact that the pigment has a high colouring power and probably in the areas investigated by SEM-EDS its quantity was lower (by XRF a larger portion of sample has been investigated).

In Fig. 5a the stratigraphy of sample 6 taken from the crown of thorns of the Christ of Zuccarello is reported. The original polychrome, layer 3, appears to consist mainly of gypsum, as confirmed by the FT-IR spectrum, and a copper based pigment, perhaps malachite (Cu is present in Fig. 5e) not identified by FT-IR. The presence of chlorine can be due to atacamite (copper chloride) that often is present together with malachite. The presence of P in the SEM-EDS spectrum could be due a black based pigment (perhaps charcoal); nevertheless the black colour of the layer could be associated to the darkening of the copper based pigment.

The chemical analysis of layer 11 (Fig. 5e) reveals magnesium, aluminum, silicon, phosphorus, sulfur, chlorine, potassium, calcium, manganese, iron and lead. Because of the presence of all these elements and the brown colour, a pigment similar to a terra d'ombra could have been used. It is worht to note that lead in the EDS spectra reported in layers 7 and 11 has been detected in low concentration but enough to be revealed by the instrument. This element has been better highlighted through EDS single particle analysis.

Layer 15 (Fig. 5e) contains aluminum, silicon, sulfur, potassium, calcium, titanium and traces of chromium, not found anywhere else, that could be attributed to a modern green pigment. The presence of titanium white would postpone this layer after 1920.

3.2. The Christ of Borghetto and the comparison between the two statues: pigments and inerts

Given the reduced size of the statue and because of the considerable number of layers present, for the Christ of Borghetto it was not possible to proceed with the opening of unveiling slots of the dimensions required by the portable XRF instrument.

Below in the text we discuss the case of two samples from the Christ of Borghetto (sample P from the thong, Fig. 6; sample C from the hairs, Fig. 7). As regards the average composition of the preparatory layer of sample P, it is quite similar to what has been observed for the Christ of Zuccarello (in both cases white lead and gypsum as attested by SEM-EDS analyses corroborated with FT-IR data). It is worth to notice that sample P of Fig. 6a corresponds to fragment P1 of table 1 and the stratigraphy in this case is not complete but ends with layer 14.

The outermost re-painted layer of the thong has been realized using a bright dark green (see Fig. 1b) that , from the point of view of the compositional analysis, has shown the presence of titanium together with high quantity of chloride (Fig. 4sa). The complete stratigraphy of the thong has been obtained on fragment P2 (table 1) and is shown in Fig. 8 where the outermost layer correspond to layer 23. In order to try to disclose the chemical nature of this green pigment a Raman spectrum has been acquired (Fig. 8a) by a portable instrument, directly

on a selected area of the thong (evidenced with a red spot in Fig. 8c). In the Raman spectrum a peak due to barium sulphate is observable at 987 cm^{-1} [43]. Even if barium has not been evidenced in layer 23 by SEM-EDS, it was disclosed in layer 21 (Fig. 4sb); so the presence of BaSO$_4$ signal could be due to a contamination or to the laser penetration in the underlying layer. Furthermore numerous peaks that could be attributed to a synthetic organic colorant are present (and in particular the bands at 1321, 1394 and 1592 cm^{-1}). Some classes of synthetic colorants containing azo-groups show peaks in the range 1200–1600 cm^{-1} [46]. The presence of chlorine might also be of help for the pigment identification: some yellow modern organic colorants contain chlorine as substituent such as chlorine-nitro aniline or chlorine-nitro anilide [47] that could be mixed with a blue colorant to obtain green. Comparing the spectrum reported in Fig. 8a with the numerous spectra reported in the literature for modern organic pigments, a good accordance has been found between some of the signals and the azo type colorant PY97 (Clariant is the supplier) [46]. It is also worth to notice that PY97 has chloride as a substituent in the molecule and Cl has been highlighted in layer 23 by SEM-EDS (see Fig. 4sa).

Some signals of lower intensities remained however unassigned in the Raman spectrum. Another class of pigments that could have been used is that formed by phthalocyanines consisting of complexes in which a copper atom is linked to phthalonitrile molecules. The pigment is a blue with a great colouring power, remarkable tone brilliance and exceptional light stability. It is known that by chlorinating this pigment, greenish blue (Cyan), turquoise and finally very bright green are obtained. Since their introduction in the XX century (and precisely in 1936 [50]) blue and green phthalocyanines are among the most used pigments. Among these PG7 and PG36 green colorant [48,49,50] and also copper phatalocyanine CuPc [51] show signals in the same spectral range as our sample but a more precise identification is not possible (some of the spectra of other green colorants belonging to the same group are not published, at least to our knowledge).

It is worth to note that in our case the presence of copper was disclosed in layer 21 (Fig. 4sb) together with barium and chlorine while iron, silicon, titanium and chlorine were revealed in layer 23 (Fig. 4sa). As a consequence what is observable is a mixed contribution of the two layers 21 and 23. As already mentioned this could be due to laser source penetration in the underlying layers. It has to be remarked that a portable instrument has been used in this case allowing the acquisition of the signals only on the surface of the statue. Furthermore it is important to remember that an unambiguous identification by means of a portable Raman spectrometer can be sometimes challenging due to the high fluorescence that partly can mask the signal coming from the pigments.

Nevertheless combination of different techniques such as Raman spectroscopy and elemental compositional analysis, in our opinion have allowed to advance some conceivable assignments.
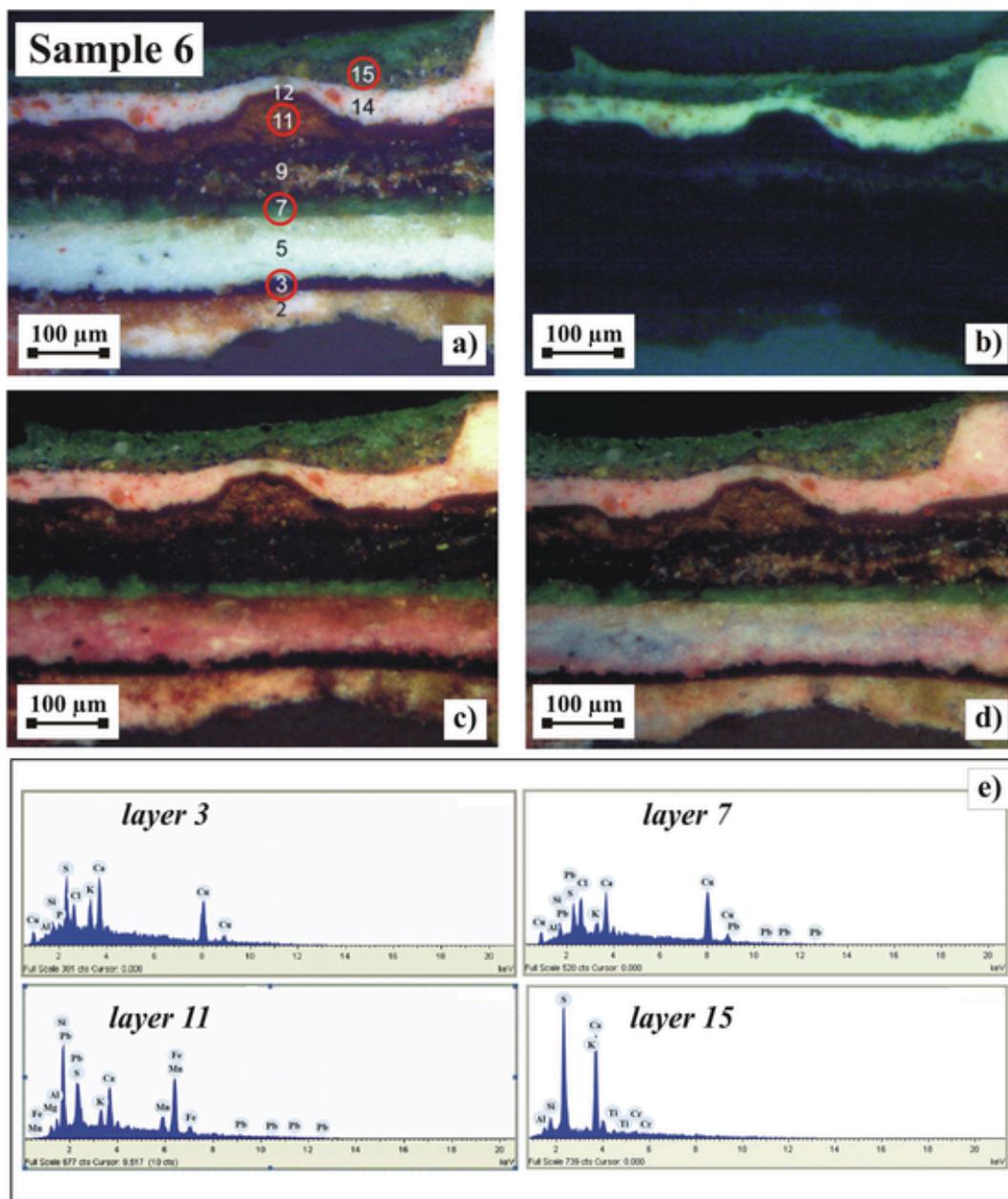
Fig. 5. Cross section of sample 6 from the Christ of Zuccarello a), Uv fluorescence image b) and images of the cross section after the application of Oil red c) and Amido black d); EDS spectra on some selected layers e). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
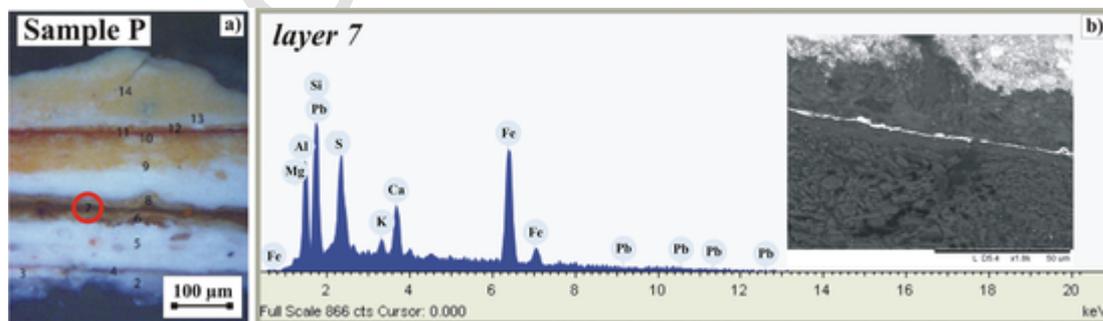

Fig. 6. Cross section of sample P from the Christ of Borghetto a); EDS spectrum of layer 7 and in the inset the SEM image where the layer is clearly visible b).
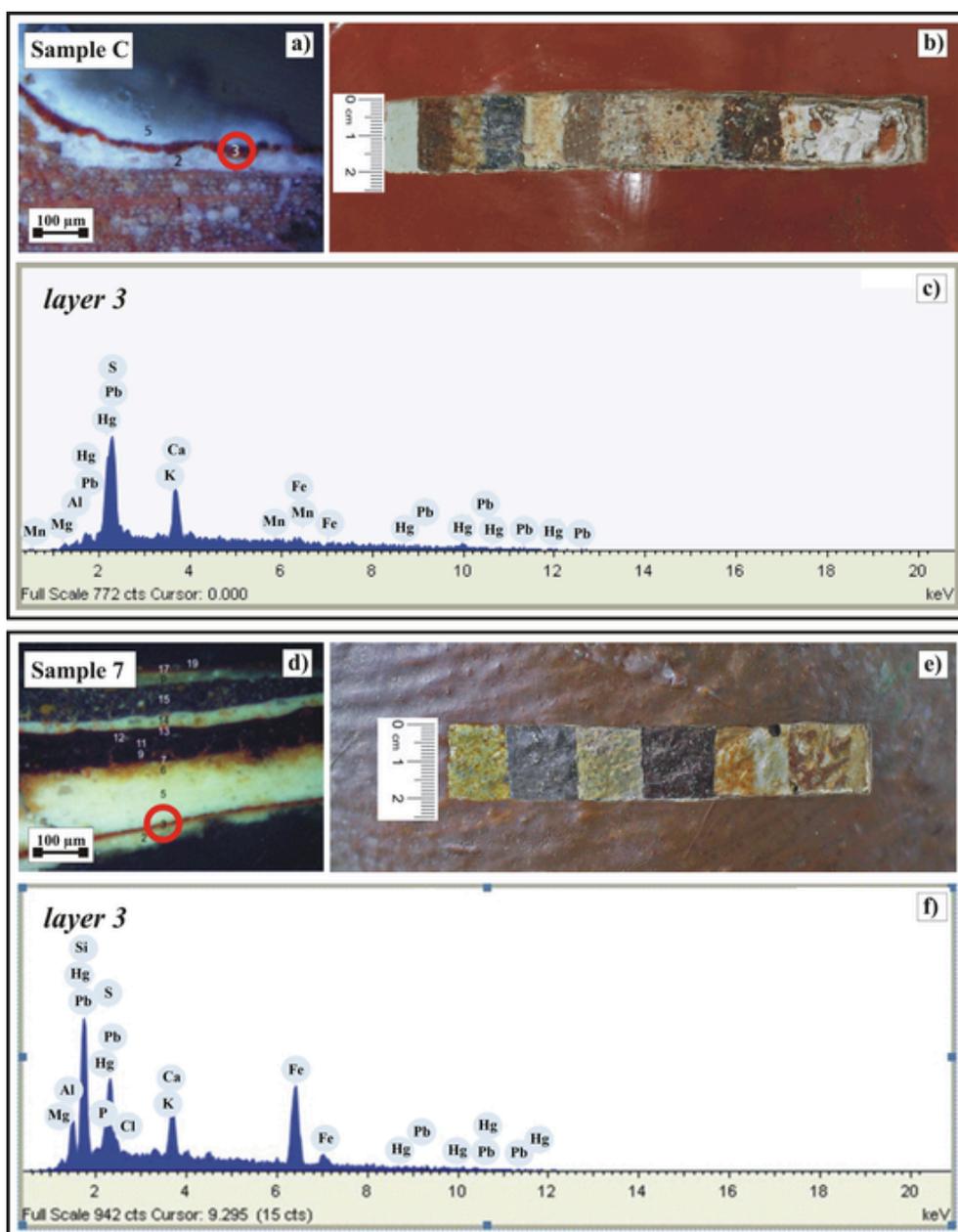
Fig. 7. Cross section of samples from the hairs of the two statues (a and d); EDS spectra of the original painting of the two statues (c and f); unveiling areas on the surface of the two statues in correspondence of the hairs.

A peculiarity of the Christ of Borghetto thong (sample P) is represented by the fact that a gold leaf was used in layer 7 (Fig. 6) over a layer containing white lead. The same thing has been observed for layer 11.

It is worth to note that the hairs in the two statues (sample C for Borghetto and sample 7 for Zuccarello), as regards the original pictorial layer contain the same mixture of pigments (Fig. 7) and SEM-EDS reveals the presence of Mg, Al, Si, P, S, Pb, Cl, K, Ca Fe and low quantity of Hg even if in the case of Borghetto, Mn was also present with a lower quantity of Fe with respect to Zuccarello. As a consequence for the hairs in both cases white lead, gypsum, cinnabar and iron oxide were employed. White lead and gypsum have been evidenced by FT-IR spectra; cinnabar has been disclosed for Zuccarello by Raman spec-

troscopy confirming the usage of this pigment in the more ancient layers.

In Table 2 it is reported a comparison between the two statues as for the skin chemical composition detected by SEM-EDS. In both cases a light shade has been employed and the main constituent is lead followed by calcium and sulphur.

In Tables 3 and 4 a list of the main elements/pigments highlighted in the two statues by means of the measurement carried out and useful for dating some of the examined layers, is summed up (the different pigments/elements highlighted have been already discussed in the text). In the first column the re-painting layers are reported as they have been identified by the restorers [21] (for example layer 3 belong to the original polychromy, layer 7 to the first re-painting and layer 11 to the third re-painting). This allowed the reconstruction of the history of the two Christs that, as mentioned in the introduction, because of their high religious value, during the centuries have been heavily re-
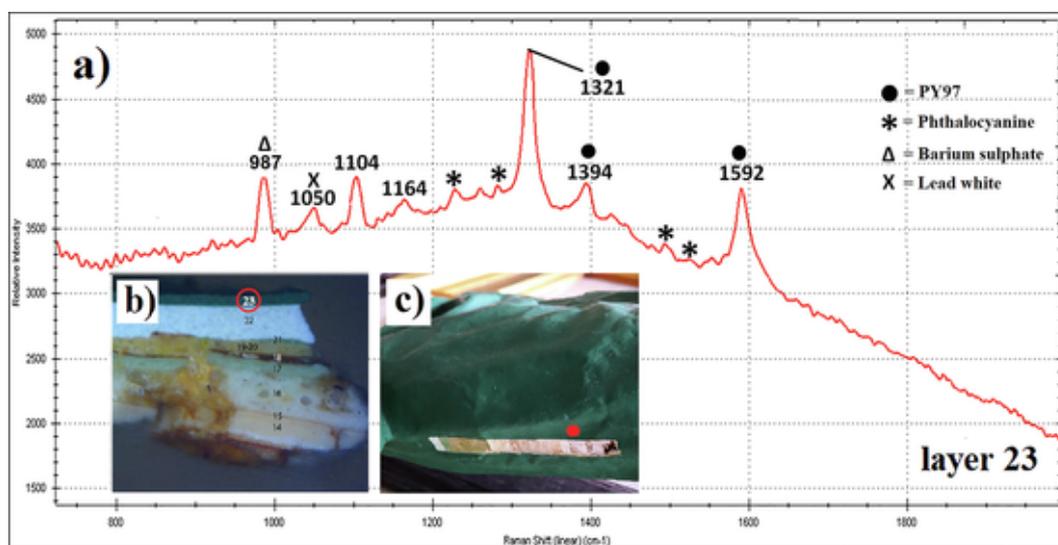
Fig. 8. Raman spectrum a) acquired on the outermost layer, corresponding to layer 23 of sample P, of Christ of Borghetto; b) cross section of sample P where layer 23 is highlighted; c) the selected area where the Raman spectrum has been acquired indicated with a red spot. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 2
Average chemical composition of skin areas as detected by SEM-EDS.

Skin chemical composition	Christ of Zuccarello	Christ of Borghetto
S	2,8%	1,9%
CaO	10,7%	11,6%
PbO_2	82,4%	83,6%

Table 3
Dating pigments for the Christ of Zuccarello in the different pictorial layers corresponding to the different repaintings of the statue (for example the original layer contains the layers 1, 2 and 3 evidenced in the cross sections) together with the techniques used for the identification (if only the elements have been identified the corresponding compound has been reported in brackets).

Christ of Zuccarello			
Succession of pictorial layers	Historical period	Pigments	Analytical techniques
original	1440–1460	Ti (lead white), Hg (cinnabar)	XRF, SEM-EDS
first	XVI century	cinnabar	Raman
second	XVII century	–	
third-fourth	XVIII century	Prussian blue	μ-FT-IR
fifth	from 1830 to 1865	barium sulphate	SEM-EDS, XRF, FT-IR
sixth	after 1920	Ti (titanium white)	XRF, SEM-EDS

Table 4
Dating pigments for the Christ of Borghetto in the different pictorial layers corresponding to the different repaintings of the statue (for example the original layer contains the layers 1, 2 and 3 evidenced in the cross sections) together with the techniques used for the identification (if only the elements have been identified the corresponding compound has been reported in brackets).

Christ of Borghetto			
Succession of pictorial layers	Historical period	Pigments	Analytical techniques
original	1470	Pb (lead white), Hg (cinnabar)	XRF, SEM-EDS
first	from XVI to XVII century	Au (gold leaf), Hg (cinnabar)	XRF, SEM-EDS
second	from XVI to XVII century	Au (gold leaf)	XRF, SEM-EDS
third		–	
fourth		–	
fifth		–	
sixth	after 1830	Ba, S (barium sulphate)	XRF, SEM-EDS
seventh	after 1920	Ti (titanium white), modern organic pigments (phtalocyanine and azo-type molecules)	XRF, SEM-EDS, Raman

painted. It is worth noting that for the Christ of Zuccarello six painting layers have been highlighted while for the Christ of Borghetto seven layers have been found by the conservators. In both cases the last repainting dates back to the first decades of the 20th century as attested by the presence of titanium white.

3.3. Consideration on the nature of the binders

In addition to the observations on cross-sections in visible light by optical microscopy (Fig. 2a, 3a and 5a), the observations by UV fluorescence (Fig. 2b, 3b and 5b) turned out to be quite interesting and made it possible to put forward some hypotheses on the origin of organic substances employed as binders.

The fluorescence colour depends on the characteristics of the optical microscope employed and in this specific case a yellow fluorescence could indicate the use of oily substances while a blue fluorescence the use of animal proteins. The green fluorescence is typical of proteins such as egg or casein, the white one of synthetic resins and the orange-yellow one of natural resins. If blue and yellow fluorescence were present in the same layer this could indicate a mixed technique.

Obviously fluorescence observations provide only general indications. Nevertheless, this approach allows to carry out a preliminary investigation on the nature of the binders particularly in the case of complex systems such as those studied in the present work. It must also be considered that the materials may have undergone alterations due to aging or interactions with restoration materials, which make their reading even more complex. In Fig. 2b, for example, the light blue fluorescence could be due to the presence of a protein binder.

On the Christ of Zuccarello samples a staining with Oil red was performed for the identification of oleo-resinous binders and with Amido black for those of protein nature. Both these reagents have application in the field of forensic sciences. Oil red has been used as fingermark visualization reagent for staining fatty acids, lipoproteins and triglycerides [24–25] and stains fatty acids in red. Amido black is a diazo dye recommended for the enhancement of blood contaminated fingerprints [23] and stains proteins blue-black.

To our knowledge the only application known so far in the field of identification of fatty acids and proteins as organic binders, is reported in Matteini et al. [22] and there are no other applications published in the scientific international literature. This analysis in our opinion is advantageous since makes it possible to formulate some hypotheses and localize in a heterogeneous sample, as can be the complex stratigraphy of a wooden sculpture, the organic substances present. Thanks to the simplicity of the methodology it can be suggested as a preliminary screening before a more in depth investigation by micro FT-IR.

After the reaction with the two dyes Oil red and Amido black (Fig. 2c and 2d), for layers 5 and 6, forming a very thick white preparatory layer, the presence of a protein binder (blue colour) has been evidenced. Both layer 3 and layer18, for which a proteinaceous (for layer 3, Fig. 2f) and aoleic binder (for layer 18, Fig. 2h) were evidenced by FT-IR (see paragraph 3.1), were too thin and as a consequence did not give rise to colouring.

From Fig. 3e and 3f it can be observed how layers 5 and 6 of sample 5.1 contain both an oil binder (red colour in Fig. 3e) and a binder of proteinaceous nature (blue colour in Fig. 3f); this has been confirmed by the FT-IR spectrum (see Fig. 9) showing the signals due to an oil at 1730, 2922 and 2855 cm^{-1} and to a protein at 1642 and 1529 cm^{-1} [35–36,39]; at 1390 cm^{-1} the signal due to lead white is also present. Layer 14, 15 of sample 5.1 contain probably an oil as binder (red color in Fig. 3e). Layer 11, that on the base of FT-IR spec-

trum contained an oil as binder (Fig. 3g), shows a pale red colour in Fig. 3e.

From Fig. 5c and 5d it is evident how layer 5 contains an oil as binder (red colour in Fig. 5c) together with a protein (pale blue in Fig. 5d).

In conclusion this method based on such simple colouring tests could be complementary to μ--FTIR that is much hard-working because of the high number of layers. So the test could be preliminary to decide on which layers acquire FT-IR spectra. Furthermore the advantage, compared to classical chemical analysis such as GC–MS, is to highlight the stratigraphic distribution within the single layers. In fact GC–MS analysis [52] provides results referring to the entire sample under examination, but if this has a heterogeneous composition the information provided is just global. However, through these tests it is possible to determine only the class to which a compound belongs and not the specific compound. Moreover, the situation is made even more complex by the fact that the constituent materials, especially those of organic nature, over time have undergone numerous transformations that have changed their nature and consequently the reactivity to colours. Furthermore many substances, sometimes similar to the original ones, could have been introduced with restoration interventions, causing considerable interference.

4. Conclusions

The data acquired in the present paper by a multi analytical approach on the complex stratigraphy of the examined wooden statues first of all have allowed to disclose the chemical composition and in some cases to identify the molecular species which constitute pigments and binders. The diagnostic approach used, based on the complementary use of spectroscopic techniques (SEM-EDS, XRF, μ-FT-IR and portable Raman spectroscopy) proved to be effective in the characterization of the polychromies of the two Christ statues, for both preparatory layers and pigments and could be applied to study other works
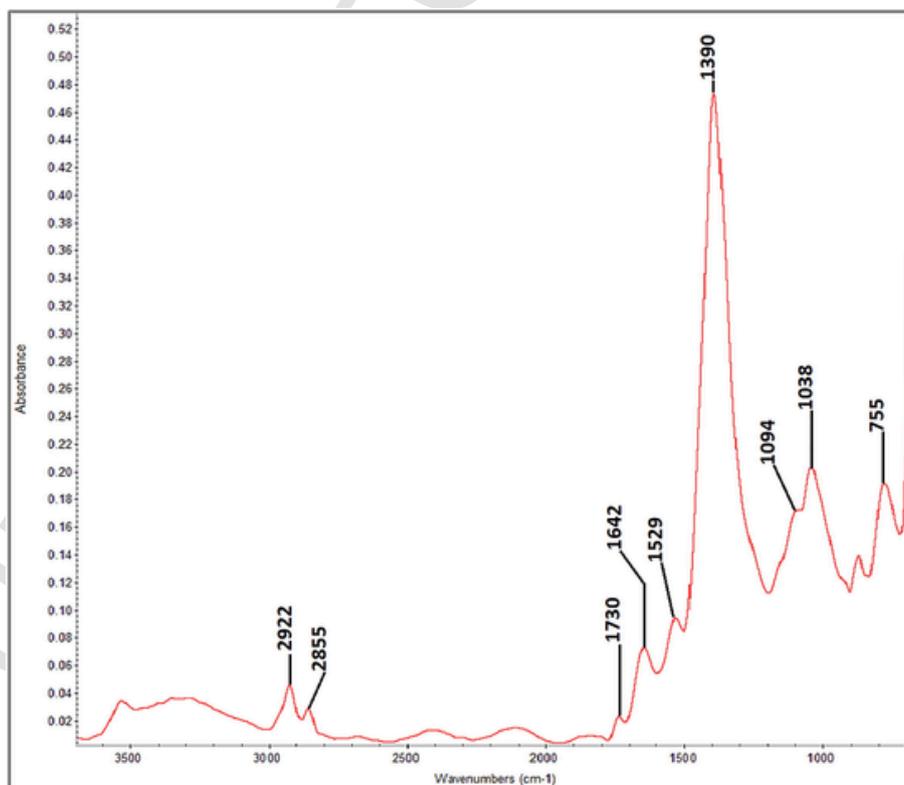

Fig. 9. FT-IR spectrum acquired on layer 5–6 of sample 5.1 from the Christ of Zuccarello and showing the signals due to an oil at 1730, 2922 and 2855 cm^{-1} and to a protein binder at 1642 and 1529 cm^{-1}; at 1390 cm^{-1} the signal due to lead white is also present.

of art of the same type. In particular it has been possible to disentangle the very complex situation present in the stratigraphy which in the case of the examined statues includes up to more than 20 layers. In the light of the results obtained it has been evidenced that the techniques used for the two Christs, for both preparation and pictorial films, are very similar.

The preliminary analysis of the binders combining UV fluorescence, Oil red and Amido black tests, with µ-FT-IR on cross sections, allows to give an overview on the use of the binders during the different historical period allowing to examine each single layer of the stratigraphy.

The discovery of some pigments (such as cinnabar, white lead, Prussian blue, barium sulphate or titanium oxide) has allowed to date the layers, obtaining unique information, which compared with other elements such as historical-artistic studies and archival research, could contribute to disclose the history of these works of art. Furthermore, the information on pigments and binders, in addition to provide historical and artistic elements, are of help in the practical activity of the restorer, who often has to face the removal of the external repainting when a complex stratigraphy is present. At this purpose the knowledge of the chemical nature of the substances present on these so heterogeneous layers is fundamental.

CRediT authorship contribution statement

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.microc.2020.105072.

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