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Case study

Enhancing the examination workflow for Byzantine icons: Implementation of information technology tools in a traditional context

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ABSTRACT

In the interdisciplinary domain of conservation science, a critical and selective eye is required in order to allow researchers to choose the most effective combination of analytical techniques for each project and, more importantly, to process and analyze the resulting volume of diverse data. The current essay attempts to combine a more traditional workflow for the examination of painted objects with techniques borrowed from the domain of computer science in order to yield the maximum amount of information and make that added knowledge more accessible to the researcher. The project was approached as a case study, regarding a post-Byzantine icon. Three-dimensional digitization with a laser scanning system, X-ray radiography and optical microscopy were applied for the determination of several structural characteristics of the painted surface and the icon's state of preservation. Multispectral imaging was used for the collection of surface spectral data, which were subsequently processed by means of cluster analysis in a novel approach to map the composition of the painted surface. Finally, micro-X-Ray Fluorescence (μ-XRF) was chosen as the primary source for surface pointwise elemental composition data while Fourier Transform Infrared Spectroscopy (FTIR) and Gas Chromatography coupled with Mass Spectroscopy (GC-MS) provided additional assistance in the characterization of materials based on their molecular structure. A custom platform was developed to address the issue of multilevel visualization and assessment of the data, designed to act as a tool for viewing and combining the acquired information. Via this integrated approach valuable information regarding the icon was revealed, including the verification of a prior conservation attempt and partial overpainting, the recording and quantification of the warping of the wooden panel and, finally, the identification of the constituent materials and their spatial distribution.

1. Introduction – Aim of the current study

In recent years, the systematic study of cultural heritage has led to the emergence of the conservation science domain as one of highly interdisciplinary nature. Within this scope, the focus of researchers is shifting towards the determination of more effective workflows for the holistic examination of the artifact in question and the subsequent combination of the acquired data, in order to produce concrete results. Taking into consideration the above arguments, the current essay attempts to formulate and apply such an integrated procedure for the examination of painted artifacts. The project was approached as a case study regarding a post-Byzantine icon.

The process of creating an icon in accordance with Byzantine tradition follows a well-defined protocol [1]. However, during the post-Byzantine era (16th till early 19th century) artists became increasingly liberated from the strict rules of Byzantine icon painting and experimented with materials and techniques [2]. The variety of materials used in Byzantine and post-Byzantine panel

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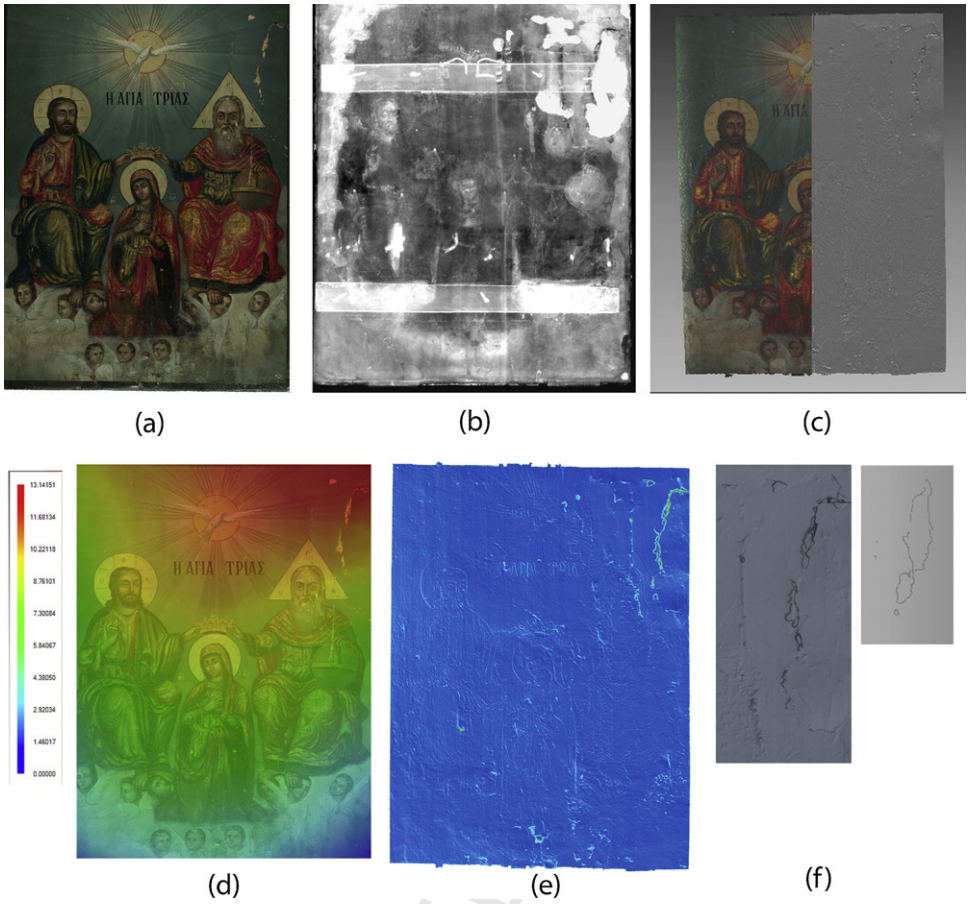

Fig. 1. a: high definition color image of the painted surface; b: X-ray radiograph of the icon (after digitally registering the four individual radiographic plates); c: 3D model of the painted surface, shown with and without color information; d: color-coded elevation map of the surface revealing the warping of the panel; e: color keyed view of the surface relief, showing the incisions outlining the figures; f: extracted outline of the crack at the upper right hand side of the surface.

painting have been the subject of a significant number of studies in order to facilitate the conservation of such artifacts and, moreover, as a means of differentiating between different artists or 'schools'. The majority of studies combine micro-FTIR and micro-Raman spectroscopy for the identification of inorganic pigment materials, Gas Chromatography or High Performance Liquid Chromatography coupled with Mass Spectrometry (GC-MS and HPLC-MS respectively) for the identification of organic materials (binders and pigments) and microscopic techniques in order to unveil the full stratigraphy of the icon [3 and references therein]. XRF spectroscopy has also proven useful for the identification of inorganic pigments, based this time on their signature elemental composition [4–6]. Infrared reflectography and UV imaging have been used in an auxiliary fashion for the preliminary examination of both pigments and varnishes [3,7,8]. Finally, structural information of the wooden support and information regarding underlying preparatory layers is usually acquired through the use of X-ray radiography [8].

In the current paper an effort is made to combine these traditional approaches with modern digitization techniques and tools from the Information Technology domain in order to form a more holistic and contemporary workflow. For the purposes of recording structural information, X-ray radiography was complemented by three-dimensional laser scanning of the painted surface, a technique applied successfully in a variety of cases regarding paintings [9,10]. Material characterisation is accomplished, on the one hand, through an entirely non-invasive approach, using multispectral photography coupled with cluster analysis in order to obtain a map of the pigment materials based on their spectral properties. The identification of possible pigments was assisted by the use of μ-XRF spectroscopy, applied in situ, for pointwise elemental data. On the other hand, techniques requiring sampling were also used. Sample cross-sections were examined by optical microscopy in order to study the icon's stratigraphy. The combined application of GC-MS and FTIR provided data regarding both organic and inorganic materials. On a final note, the possibilities of integrating the multitude of obtained data into a single platform were investigated. To this end, a custom platform was created, combining the 3D model visualisation with the available spectral and elemental data in a multilayer integrated representation.

2. Experimental

2.1. Description of the icon

The subject of this case study is a post-Byzantine icon from the region of Moschopoli (Fig. 1a), dated back to the first half of the 19th century. The icon, depicting the Coronation of the Virgin, is painted on a wooden panel (47.8 cm × 36 cm). The surface exhibits various defects while the panel itself presents substantial warping. The paint layer exhibits two different optical qualities, being more matte or more reflective in places, indicating the use of different paint media – egg and drying oil respectively, or even a mixture of both. This fact is in agreement with the testimony of the owner's family, stating that the object had undergone a conservation attempt around 1951. The extent of the areas exhibiting optical properties of a drying oil medium suggests that the icon had been

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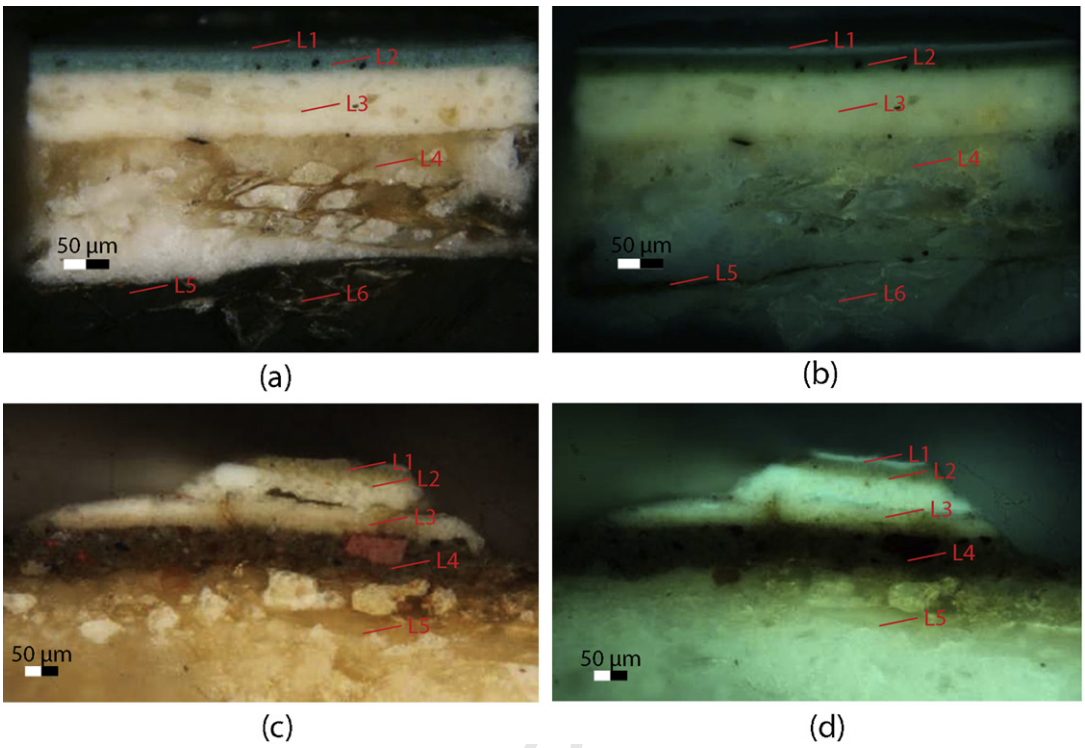

Fig. 2. Stratigraphic analysis under ×20 magnification of (a) sample TRI.D3 under visible light conditions, (b) sample TRI.D3 sample under UV light conditions, (c) sample TRI.D9 under visible light conditions, (d) sample TRI.D9 under UV light conditions. A full description of the constituting layers can be found in Section 3.2 Stratigraphy.

considerably overpainted during the conservation procedure (the entire area of the sky, the halos and partly the figures themselves).

2.2. Non-invasive analysis

The digitisation of the icon was performed with a colour point laser scanner system, able to simultaneously record both the geometry and the colour of each point on the object's surface (Arius 3D Foundation Model 100). The scanning process required 43 scans to be completed and resulted in a final 3D model composing of 32,639,543 colour points. The chosen X-ray system was a portable Yxlon Smart 160E/0.4 (31 kV, 6 mA, 85 cm from the object's surface, 60 s exposition, Kodak Industrex AA400 film). A total of four radiographs were obtained in order to cover the entire surface. Multispectral imaging was conducted using the MUSIS MS multispectral recording system, capable of acquiring images in seven wavelength bands, ranging from 300 nm to 1000 nm, with an interval of 100 nm. In addition to the reflectance images in the visible and infrared areas of the spectrum, one more image depicting the fluorescence of the different surface materials under ultraviolet light was acquired. Finally, a micro-XRF system (SPECTRO AI direct tube excited XRF system with Mo tube, 150 μm nominal spot diameter, 45 kV, 0.5 mA, 150 s measurement time) was employed to acquire 44 measurements directly from the panel's surface (non-invasively). The penetration depth of X-Ray radiation can be considered approximately 100 μm for most matrices, meaning that the elemental composition at each sampling point corresponds to the bulk composition of all layers penetrated by X-Rays (paint layer and underlying preparatory layers).

2.3. Invasive analysis

A total of seven samples were collected (Table 1). The sampling procedure was conducted using a Zeiss Axion Plan 5.X 0.1HD microscope with a Canon EOS 400D camera. For the further examination of the samples two microscopic setups were used: a Leica Leitz DMRB microscope with a Canon EOS 5D Mark II camera and, finally, a Keyence VHX–500FD digital microscope. The samples were examined under both visible and UV light conditions. The μ-FTIR analysis was conducted with a Perkin Elmer system constituted by a Paragon 1000 PC FTIR Spectrometer and an i-SERIES FTIR microscope. The system was used in transmission mode. The scanning region was 4000–500 cm^{-1}, with a resolution of 4 cm^{-1}. A total of five free samples were prepared from layers L1, L2, L3, L4 and L6 of sample TRI.D3 (Fig. 2a, b) using a diamond head (High Pressure Diamond Optics). The resulting spectra were compared with reference spectra from the IRUG and Sadtler databases. The equipment used for the GC-MS analysis was a Perkin Elmer Clarus 500 GC coupled with a MS (electron impact 70 eV, ion source temperature 230 °C, interface temperature 280 °C). Prior to GC-MS analysis, the samples were submitted to derivatisation (transesterification to the corresponding methyl esters) using methanol (30 μL) and MethPrepII (Altech, USA; 10 μL). The resulting solutions were first placed in an ultrasonic bath for 5 minutes and subsequently in a sand bath at 60 °C for 2 hours. Chromatographic separation was performed on a Perkin Elmer Elite 5ms column (stationary phase: 5% phenyl - 95% methylpolysiloxane, internal diameter: 0.25 mm, film thickness: 0.25 μm, length: 30 m). The temperature program used was as follows: initial temperature 100 °C, 0.5 min isothermal, 15 °C min^{-1} up to 150 °C, isothermal 1 min, 7 °C min^{-1} up to 300 °C, isothermal 20 min. The injector was set to spitless mode, at 280 °C and with a helium gas flow-rate of 1.2 mL min^{-1}

3. Results

3.1. Structural information

X-ray radiography (Fig. 1b) unveiled elements of the original painted layer, thus verifying the presence of partial overpainting. In the original composition the halo of the figure of The Holy Father

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Table 1
Invasive analysis sampling locations description.

Sample No.	Sample name	Sampling location	Apparent material layers
1	TRI.D2	Internal surface of crack	Paper film or similar material
2	TRI.D3	Surface abrasion near crack	Overpainting layers, stucco, original varnish
3	TRI.D4	Original icon layers	Original varnish
4	TRI.D6	Black border of the icon	Black and blue overpainting pigments, stucco, original varnish
5	TRI.D7	Surface abrasion near crack	Blue overpainting pigment, stucco, original varnish
6	TRI.D8	Beard of the Holy Father	Overpainting varnish, overpainting pigments, stucco, original varnish, original painted layer, original preparatory layer
7	TRI.D9	Forehead of the Holy Father	Overpainting varnish, overpainting pigments, stucco, original varnish

Table 2
Cluster analysis results. Each cluster is assigned to a certain pigment or mixture of pigments according to the areas of the painted surface that its reconstructed image overlaps with.

Fuzzy clustering results		k-means clustering results	
Cluster No.	Corresponding material	Cluster No.	Corresponding material
1	Faint yellow pigment, overpainting	1	Red pigment, overpainting
2	Red pigment, original composition	2	Red + Yellow pigment, original composition
3	Green pigment, original composition	3	Blue + White pigment (lighter, more white pigment), overpainting
4	Yellow pigment, overpainting	4	Red pigment, original composition
5	White pigment, overpainting	5	Green pigment, original composition
6	Blue pigment, overpainting	6	Blue pigment, overpainting
7	Red pigment, overpainting	7	Faint yellow pigment, overpainting
8	White pigment, original composition	8	White pigment, overpainting
9	Green pigment, overpainting	9	White pigment + flesh tones, original composition
		10	Green pigment, overpainting
		11	Yellow pigment, overpainting
		12	Blue + White pigment (darker, less white pigment), overpainting

is of round shape, in contrast with its present triangular shape. This triangular shape, reminiscent of the Papal Tiara (latin: 'Triregnum'), is a western iconographic element more commonly used in Italian rather than Byzantine religious art [11]. The preparatory design of the composition seems to be incised onto the surface, a technique indeed common to that era [1,11].

The 3D laser scanning process produced a base model of an extremely high level of detail. The detailed relief of the painted surface allowed the extraction of the outlines of the more significant cracks and the measurement of their dimensions and depth (Fig. 1c, f). The incisions of the preparatory design that were observed on the X-ray radiographs were also visible on the 3D model surface (Fig. 1e). Finally, the most important result from the examination of the 3D model was the verification and quantification of the warping of the wooden panel. The contour measurement feature offered by the RapidForm 2006 software was used to plot a color-coded elevation map of the surface (Fig. 1d). The resulting representation shows the direction of warping while it allows the measurement of

Table 3
Indicative material characterization results from the non-invasive path of analysis.

Material	Signature element for characterization [13]	Corresponding layer/Use
Gypsum	Ca, S	Original priming material
Calcite	Ca	Priming material (original or overpainting)
Gold leaf	Au	Original gilding layer
Lithopone	Ba, Zn, S	Priming layer of the overpainting
Lead white	Pb	White pigment, original material
Titanium white	Ti	White pigment, overpainting
Orpiment + Lead white	As, Pb	Yellow highlights, original material
Barium yellow (Lemon yellow)	Ba, Cr	Yellow of the halo regions, overpainting
Chromium yellow	Pb, Cr	Yellow pigment, overpainting
Prussian blue	Fe (in conjunction with FTIR data for disambiguation)	Blue pigment of the sky region, overpainting
Cinnabar	Hg, S	Red pigment, original material
Madder	Organic pigment, recognized by characteristic UV fluorescence	Red pigment, overpainting
Red lead (Minium)	Pb	Red pigment, inconclusive results regarding whether it belongs to original or overpainted layer
Viridian green	Cr	Green pigment, original material
Paris green + Chromium yellow	Cu, As + Pb, Cr	Green pigment mixture, overpainting
Cinnabar + Lead white	Hg, S + Pb	Flesh tones, original material
Umber	Fe, Mn	Flesh tones, overpainting

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a height difference of 13.14 mm between the top right and bottom right hand corner of the surface. The height difference between the top left and bottom left side corner was approximately 8.8 mm.

3.2. Stratigraphy

Sample TRI.D9 (Fig. 2c, d) comprises of the total number of layers of both the original painting and overpainting. The original priming material (D9.L5 - 188 μm) appears homogenous and exhibits good cohesion with the original paint layer (D9.L4 - 47 μm). The layers of the overpainting follow, appearing thinner and evenly applied (priming: D9.L3 - 50 μm, paint layer: D9.L2 - 30 μm, varnish: D9.L1 - 5 μm). Sample TRI.D3 (Fig. 2a, b) represents only the overpainting layers and the original varnish layer. The original varnish (D3.L6 - 60 μm) shows craquelure and is quite thick. A dark colored layer (D3.L5 - 5 μm), not visible in the examination of the previous sample, is attributed to contaminants deposited on the original surface. In this case, the priming of the overpainting appears to consist of two distinct materials, a more coarsely grained layer (D3.L4 - 130 μm) and a finely grained layer (D3.L3 - 30 μm). The overpainting restorer probably applied the materials in a different manner depending on the condition of the underlying original surface. The pigment and varnish layers (D3.L2 and D3.L1 respectively) have approximately the same thickness with the corresponding ones in sample TRI.D9.

3.3. Material characterization through non-invasive analysis

The data acquired from the multispectral analysis consisted of the icon's image recorded under visible light (original RGB data), six spectral band reflectograms (corresponding to the wavelength regions of 400–500 nm, 500–600 nm, 600–700 nm, 700–800 nm, 800–900 nm and 900–1000 nm), a False Color Infrared representation of the icon (created by exchanging the R-channel data of the visible color image with the reflectogram of the 900–1000 nm region) and, finally, the UV fluorescence image recorded using a 370 nm lamp. The grayscale values (0–255) of each pixel from the IR reflectograms and the RGB color information of the other recorded images represent the spectral characteristics of each corresponding point on the painted surface. Thus, each point of the painting can be described by a vector of N = 15 dimensions (Fig. 3a). The vector data were subjected to cluster analysis, using both the k-means and fuzzy clustering algorithms [12] offered by the Mathworks' MatLab software platform, in order to group the pixels according to their similarity (minimizing the Eucledian distance in N-dimensional space). Finally, the members of each cluster were assigned back to their corresponding pixels is order to reconstruct the image of each cluster on the painted surface.

The results, summarized in Table 2, show the possibilities offered by spectral data analysis in comprehending the distribution of materials in the painted surface. In the case of k-means clustering each pixel is assigned to one unique cluster whereas in fuzzy clustering each pixel is described by a degree of belonging to each of the clusters [12]. Consequently, a k-means cluster may correspond not only to a specific pigment but also to a mixture of different materials. In fuzzy clustering, on the other hand, each cluster corresponds to a unique pigment and the pigment mixture of each point/pixel may be deduced by combining the clusters this pixel belongs to. As long as it is always taken into account that k-means clusters correspond not only to pure pigments but mixtures as well they can offer a more convenient way of representing the spatial distribution of different materials on the painted surface (Fig. 3b). Finally, by examining the overlap of each cluster with areas attributed to either the original composition or the overpainting (determined by their different optical properties and the information from the radiographs) the cluster may be assigned to one of the two cases.

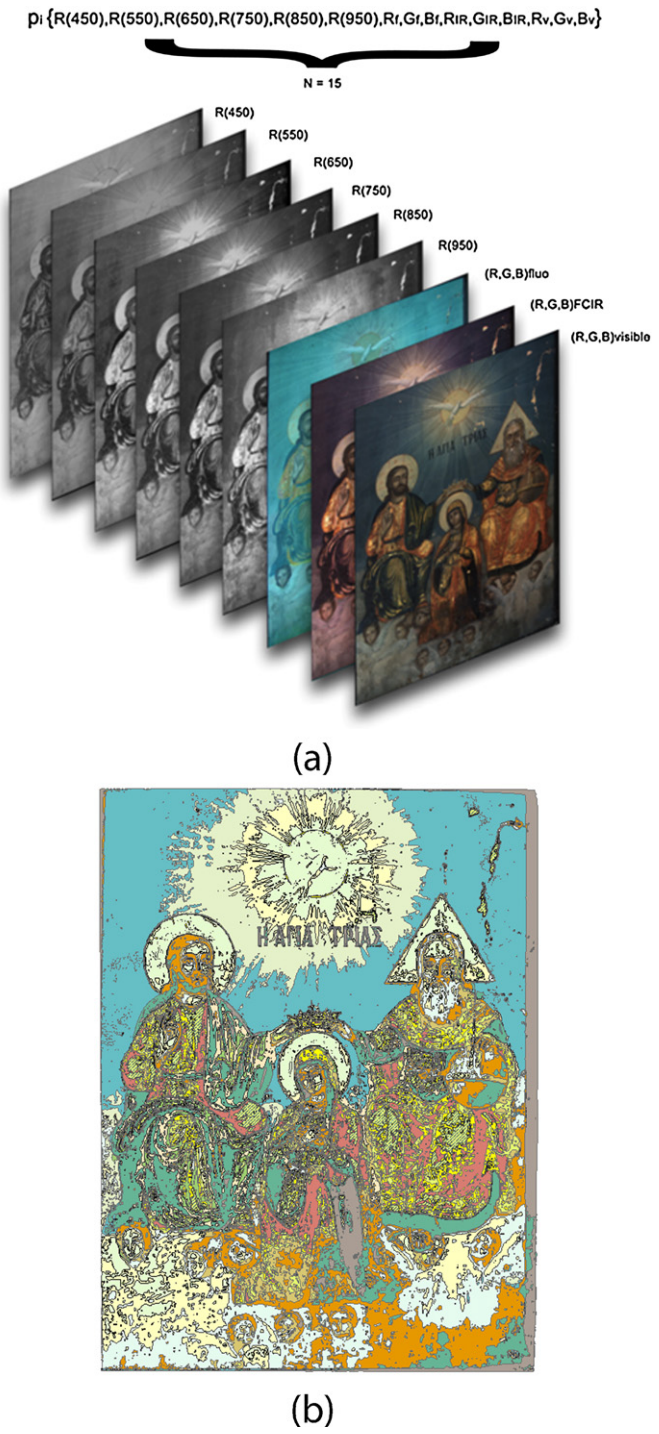

Fig. 3. a: construction of the 15-dimensional vector data representing the painted surface; b: the resulting map of k-means clusters (Table 2) representing the spatial distribution of different materials and mixtures.

These results were used as a guide in the interpretation of the elemental composition data, acquired by the μ–XRF analysis. Data from sampling locations exhibiting no overpainting were assessed first, in order to determine the materials of the original composition. As mentioned above (Section 3.2) the original paint layer has an average thickness of 47 μm, thus allowing the X-rays to penetrate the original priming layer as well. The combined thickness of the overpainting layers is between 85–195 μm. Therefore, in sampling locations corresponding to overpainted areas the X-ray signal of the original composition is minimal. Additionally,

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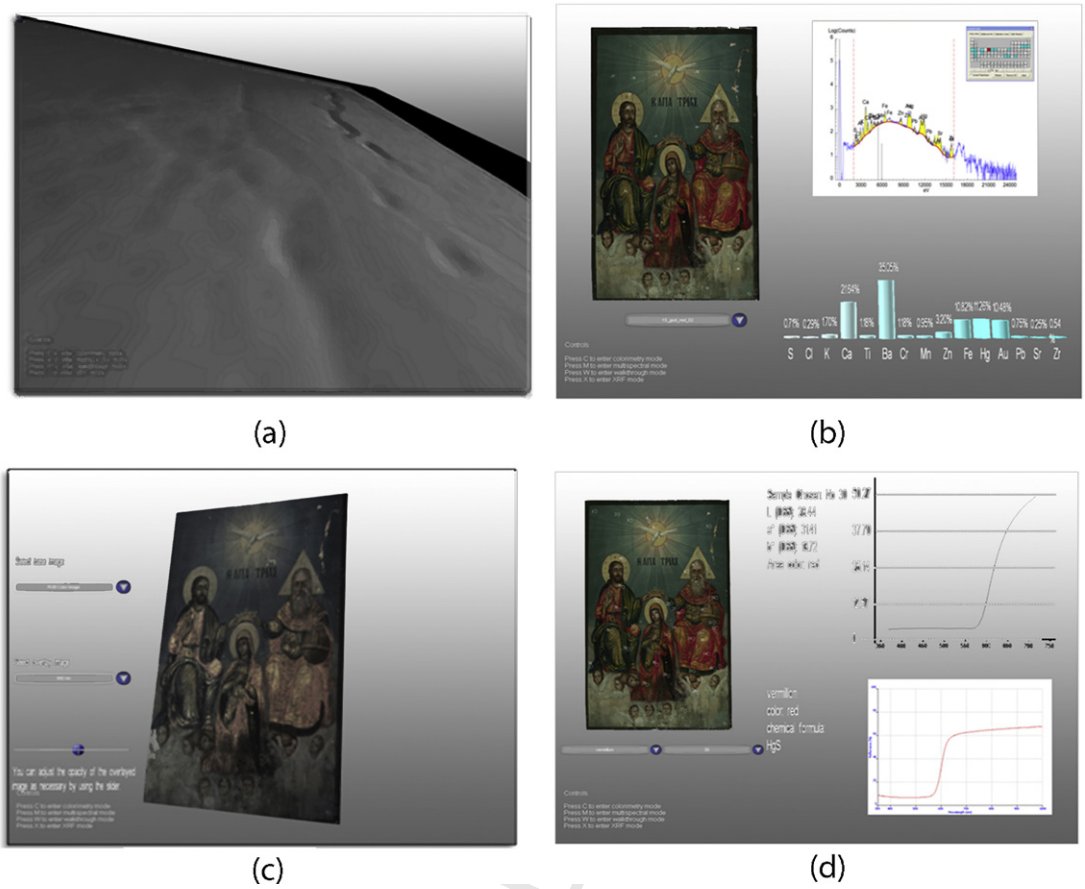

Fig. 4. Sample images from the operation of the custom information visualization platform: a: 3D model examination mode; b: elemental composition examination mode; c: multispectral data examination mode; d: comparison of acquired spectral data with reference spectra.

the previously acquired information regarding the original materials could be used to identify the residual elemental profile of underlying original layers if necessary. The elements detected at each sampling location were compared with the signature elements of different pigments [13]. Disambiguation between possible pigments was achieved by taking into account the color of the corresponding area and which of the pigments would have been available within the two different time-frames of the original composition (first half of 19th century) and the overpainting (around 1951). Moreover, the material distribution map acquired through cluster analysis was used to correlate data from different sampling locations across the painted surface. The critical simultaneous assessment of all the above information allowed for a relatively definitive identification of the different pigments and materials (Table 3).

3.4. Material characterization through invasive analysis

The results of the invasive analysis are summarized in Table 4. FTIR analysis was conducted on sample TRI.D3 in order to obtain more information regarding the layers of the overpainting. The detection of lithopone verifies the results reached by the non-invasive course of analysis. The blue pigment was identified as Prussian blue, thanks to a very weak but characteristic band at 2094 cm^{-1}. The only signals assigned to the binding medium indicate the presence of an aged oil: CH stretching bands at 2927 cm^{-1} and 2853 cm^{-1} and C = O stretch at 1722 cm^{-1} and 1709 cm^{-1}. Due to the lack of amide I and amide II bands there is no clear evidence for the presence of egg, the typical binding medium used in icons.

The samples subjected to GC-MS analysis correspond to several layers of sample TRI.D3 as well as Sample TRI.D4 (original varnish layer). Analysis of layer TRI.D3-L2 (pigment) showed an azelate/palmitate ratio of approximately 1.0, which could be indicating the presence of a drying oil medium. The palmitate/stearate ratio of approximately 2.1 is within the upper range of typical values for linseed oil. No markers for egg (typically cholesterol and its oxidation products) were found in this sample. This, however, is no definite proof of the absence of egg since these markers are particularly sensitive to degradation or ageing [14]. Additional analysis of the protein fraction (peptide and aminoacid analysis) might be able to yield more information regarding the presence or absence of egg. However, it was not possible to conduct further analysis due to the very small size of the samples. The results from both TRI.D3–L5 and TRI.D4 point to the use of Venice turpentine as the original varnish. The identification of epimanool, larixol and larixyl acetate in the chromatogram, achieved by comparison of the GC-MS analysis of the sample with that of reference material from the Rathgen Research Laboratory, and by comparison with the mass spectra from the NIST database, indicates the use of resin from trees of the *Larix* species, from which Venice turpentine is obtained.

Table 4
Material characterization results from the invasive path of analysis, regarding the original varnish layer and the layers of the overpainting.

Material	Corresponding layer/Use
Venice turpentine	Original varnish layer
Calcite	Coarsely grained priming layer
Lithopone + calcite	Finely grained priming layer
Prussian blue	Blue pigment of the sky region
Linseed oil	Binding media of blue pigment

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3.5. Information assessment and visualization

The diversity of the acquired data and the arisen need for their simultaneous assessment underlined the necessity for a multilevel approach regarding visualization and processing. An experimental custom platform was created, allowing the user to fully interact with the 3D model while integrating the results of the spectral and μ–XRF analysis. The software was developed using the Quest 3D 4 engine. The data, excluding the 3D model, are stored in an external Microsoft Access 2003 database. The software includes three modes of operation (Fig. 4). The 3D model examination mode allows the user to manipulate a detailed model of the icon, examine it under customizable lighting conditions and conduct dimensional measurements. In the elemental composition examination mode the user can view the XRF spectra and elemental composition data from any chosen μ–XRF sampling point. The multispectral data examination mode offers the possibility to view and compare any pair of two acquired spectral images. Moreover, this mode allows the user to view the reflectance spectra from any point of the painted surface and compare them to reference spectra of pigments from the Fiber–Optics Reflectance Spectroscopy Database (Institute of Applied Physics, National Research Council of Italy). The resulting software makes the data readily accessible to users, within a unified platform and through a simple interface environment, useful for those unfamiliar with database management. The platform can easily adapt to accommodate data from other similar objects with just some minor adjustments (change of base 3D model, update of database entries). On the downside, this approach does not offer any advanced processing capabilities, such as user-defined queries or statistical assessment of the data.

4. Conclusions and discussion

The current case study serves to show the potential of integrating tools from the information technology domain into the traditional workflow for the examination of painted objects. Statistical analysis applied to spectral data, when combined with μ-XRF elemental analysis, has proven a useful tool for the preliminary assessment and partial identification of the materials constituting the painted surface. The results reached through this path can be used as a guide for the planning of the invasive analysis (targeted choice of sampling locations, questions regarding the verification of the presence of certain materials). Even though μ-XRF can only offer elemental composition results (rendering material identification not definitive) in the case of certain materials (lithopone, calcite, Prussian blue) the results of the non-invasive path were fully confirmed by the subsequent invasive analysis. Additional sampling in areas with different pigments could help verify the remaining hypotheses. Moreover, 3D laser scanning emerged as an exquisite technique for recording the artifact in question but also for assisting in its scientific examination. The results acquired from the 3D model could not have otherwise been obtained by traditional means. Finally, the attempt for a multilayer visualization of the available scientific data proved useful in assisting the course of analysis. The developed platform was successful in uniting a multitude of diverse datasets in an approachable and functional way.

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