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### Original study Archiving Cultural Objects in the 21st Century

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#### Abstract

Recent developments in three-dimensional technologies and measurement instrumentation combined with multimedia databases offer today new possibilities for the integrated and complete description of Cultural Heritage Objects (CHO). In this work, we present an attempt to develop a database for archaeological ceramic and glass artifacts, where in addition to digitized two-dimensional images and three-dimensional reconstructions, description, typological characteristics and historical information for each artifact will also include point-wise surface data, forming a GIS-like<sup>1</sup> environment for CHO. This information will contribute significantly to the comparative study of artifacts, provenance studies, determination of weathering, authentication and detection of forgery, inspection of past restorations, and ultimately, their preservation.

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#### 1. Introduction

The advent of new technologies in digitization and digital reconstruction as well as their applications revolutionized the way information is stored, archived, retrieved and presented. Their impact on the registration, documentation, dissemination, presentation and ultimately, preservation of Cultural Heritage (CH) could be enormous. In addition to the visual recording (two-dimensional (2D) and three-dimensional (3D) imaging), systematic recording of the physical and chemical characteristics, typological description and historical information of CHO led to the first CH databases, mainly for research purposes.

The digitization of the CHO in two dimensions, using film or digital photography, and the storage of the 2D representation alongside the description of the CHO enriched the content and made it more appealing to the general public. A presentation in the form of a digital catalog, where images

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are combined with historical excerpts, has already become a standard in promoting private collections and museums. On the other hand, physical and chemical characteristics are interesting only to a limited number of researchers. When the digital catalogs describe CHO to a greater extend and go deeper into scientific facts, they can also be used for educational purposes and typological research [1,2].

Multimedia brought a new era with virtual worlds. The relatively simple catalogs, enriched with video and graphics, transformed the static presentations to virtual museums, while multimedia databases offer now a multitude of information formats. Still, even today, this wealth of information remains to a great extend bound to a 2D world. The latest great advances in 3D technologies offer today new opportunities to record the CH in high precision and detail, and to present it in an attractive way. The typical "do not touch" caution, becomes now a bold "please touch and examine".

It is not only the new imaging methods that help in the documentation and preservation of CH, but innovations in instrumentation provide with more accurate, point-wise measurements of physicochemical characteristics and mechanical properties of objects. Combination of such measurements with 3D imaging and mapping techniques give rise to novel ways to register and present information that can revolution-

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<sup>&</sup>lt;sup>1</sup> GIS stands for Geographical Information System. Such a system usually involves the detailed description of a part of the earth's surface in particular layers of information formed in a database.

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ize once again the recording of CH: recording will be integrated and complete since we now have the ability to describe, digitally store, and retrieve CHOs not only macroscopically, but also in a point-size manner that enables the virtual reconstruction in every conceivable detail. The impact that such a reconstruction will have on the scientific research as well as the dissemination of knowledge and the attraction of public interest is profound.

An attempt, to this end, is made in the Cultural and Educational Technology Institute (CETI), with the collaboration of its Archaeometry and Multimedia Laboratories, aiming to the development of a multimedia database for archaeological ceramic and glass artifacts. The database includes detailed 2D images and 3D representations of archaeological ceramic findings accompanied with morphological descriptions and historical and scientific data such as dating, mechanical properties and stoichiometric analysis data. Where appropriate and possible these measurements are mapped on the 3D representation to form a GIS-like environment for each CHO. This way, the user-researcher will be able to examine CHOs from every aspect, avoiding at the same time to impose possible strain to the actual artifact. The main advantage of such integrated recording is that CHOs are stored and remain digitally available indefinitely in time and space.

The main contribution of our idea in the world of CH is the 3D recording and mapping of physicochemical properties in the form of a GIS-like system for every CHO, while the majority of existing databases are bound to a 2D world.

#### 2. The database

The design of a cultural database requires the solution of several problems that can be divided into three main categories:

- *Precise definition* of the "problem" (theoretical concept), that is isolation of the various classes and objects into abstractions and definition of the connections or relationships between them. This is the least technical of the three categories but the most essential, since decisions made at this stage have to be followed to the end.
- Database *implementation*, using one or more available tools. A common solution to this issue is the use of a relational database model, which operates by defining the

various classes into "table entities", which are linked to each other according to relationships guided by the classes.

• The *end-user aspect*: the target group must be defined in terms of demands and level of knowledge; the user interface must be friendly enough, while rich in terms of available options, so that the users can form various kinds of queries or combinations of queries to submit to the system. We have decided to develop two different interfaces, one for the ordinary users (general public) and another for the researchers.

The designer of a cultural database should also consider the possible limitations imposed either by the involved data or by the used database/archiving system. At present, our database supports multimedia content and multi-languagepolytonic text for textual data. Specifically, for the multilanguage-polytonic text requirements the chosen solution was the usage of Unicode fonts (although occasional problems are expected to occur, since Unicode [3] is not yet widely accepted). For enhanced flexibility in database management and data "warehousing" the adopted solution was to keep the multimedia content in separate external files, and include only file names in the database. We believe that this will be sufficient for the first stage of our implementation.

When dealing with archaeological objects there are two basic categories of data:

- *Cultural*: Comprises external characteristics of objects, such as the type of the object, its dimensions, etc., as well as historical and social information.
- *Technological*: Include information related to the chemical, mineralogical and physical properties of the material, archaeological dating information, etc.

A summary of the characteristics included in the database is given in Table 1. Each of the categories extends to an open list of sub-categories, with each sub-category being an open list of a variable length of elements (datasets).

#### 3. Presentation of a 3D CH multimedia database

A combination of different technologies was recruited in order to achieve the best possible acquisition of detailed data and interaction level between the user and the database, within a 3D environment distributed over a network.

Internet has been acknowledged as one of the most challenging platforms for programming. The Java programming

Table 1
Data types in the database

Dua types in the database	
Cultural data	Technological data
Object type (lycithos, pithos, etc)	Archaeological dating (measurement method, results)
Provenance (e.g., Corinthian)	Chemical content (elemental)
Historical era (e.g., Neolithic)	Mineralogical content (composition)
Morphological characteristics shape, size, color, decoration, etc.)	Physical properties (porosity, hardness, plasticity, strength, etc.)
Present condition (in fragments, a whole, etc.)	Surface traits (color, pigments, inks, texture, etc.)
Restoration and Conservation work	Structure–Microstructure
Excavation data	Other characteristics (e.g. firing temperature, vessel content, etc.)
Ownership museum, private collection, etc.)	Erosion and environmental effects (patina, cracks, etc.)

language is based on the power of global networks and the idea that the same software should run on different platforms and operating systems. A Java application can be easily delivered over the Internet or over any other network. Thus, it is considered as a powerful programming platform to evolve an application based on the "thin client–thick server" software engineering architecture.

In the late 1960s and 1970s, research on a number of fronts formed the basis of virtual reality as it appears today (e.g., projection-based VR [4,5], head-mounted displays [6,7]). In the mid-1980s, the different technologies that enabled the development of virtual reality converged to create the first true VR systems. The term "Virtual Reality" was originated at 1989 by Jaron Lanier, the founder of VPL Research, defining it as "a computer generated, interactive, 3D environment in which a person is immersed." Since then, virtual reality has captured the public imagination and lots of work has been done to explore the possibilities of virtual reality in new areas of application such as medicine, chemistry, scientific visualization.

Virtual reality is more than just interacting with 3D worlds. By offering presence simulation to users as an interface metaphor, it allows operators to perform tasks on remote real worlds, computer generated worlds or any combination of both. The simulated world does not necessarily have to obey to natural laws of behaviour. Such a statement makes nearly every area of human activity a candidate for a virtual reality application.

The Virtual Reality Modeling Language (VRML) and Java provide a standardized, portable and platform independent way to render dynamic, interactive 3D scenes across the Internet. Integrating two powerful and portable software languages provides interactive 3D graphics plus complete programming capabilities plus network access [8–11]. The Web is being extended to three spatial dimensions thanks to VRML, a dynamic 3D scene description language that can include embedded behaviors and camera animation. A rich set of graphics primitives provides with a file format, which can be used to describe a wide variety of 3D scenes and objects. The VRML specification is an International Standards Organization (ISO) specification [12].

Java adds complete programming capabilities and network access, making VRML fully functional and portable. This is a powerful new combination, especially as ongoing research shows that VRML combined with Java provide with extensive support for building large-scale virtual environments [13]. However, there were two major limitations in VRML 1.0:

- Lack of support for dynamic scene animation, and;
- No traditional programming language constructs.

Difficult issues regarding real-time animation in VRML 1.0 included entity behaviors, user–entity interaction and entity coordination. VRML 2.0 development tackled these issues directly, using event-driven ROUTEs to connect 3D nodes and fields to behavior-driven sensors and timing. If Java or JavaScript are to be supported in a VRML browser, they must conform to the formal interface specified in the specification [12] Annexes B and C, respectively. Major browsers now support both. Using Java is the most powerful way for 3D scene authors to explore the many possibilities provided by VRML [13].

#### 4. VRML and Java interfacing

The VRML 97 standard does not support the development of shared multi-user worlds. Developers may implement the lacking multi-user and network support in the current standard by means of the Java interfaces without necessitating the definition of non-standard extensions to VRML. Although the current VRML standard does not provide explicit support for the development of multi-user worlds, it does, however, provide the developer with two Java programming interfaces which allow for the implementation of multi-user capabilities:

Java via VRML's Script node and External Authoring Interface [12–18]:

- Java via VRML's Script node is well specified and multiple compliant browsers exist. Sometimes is referred to as the JavaScript Authoring Interface (JSAI);
- *External Authoring Interface (EAI)*. Rather than provide Java connectivity from "inside" the VRML scene via the Script node, the EAI defines a Java or JavaScript interface for external applets which communicate from an "external" HTML web browser [19]. EAI applets can pass messages to and receive from VRML scenes embedded in an HTML page. The primary benefit of the EAI is the ability for direct communications between the encapsulating HTML browser and the embedded VRML browser. The EAI provides an interface between the VRML world and a Java applet residing on the same page loaded in the Web browser. The EAI now allows for four types of access into the VRML scene:
  - access the functionality of the Browser Interface;
  - send events to eventIns of nodes in the scene;
  - read last value sent from eventOuts of nodes;
  - receive notification when events are sent from eventOuts in the scene.

The EAI thus provides all the functionality of the JSAI although being somewhat more difficult to program.

In the context of multi-user client/server VRML applications, we decided to adopt the EAI, since an applet, executing at the client, can provide with both the networking capabilities of Java and the access to the internal workings of the VRML world through the EAI [14].

A few years ago, Sun released the Java3D class library for 3D graphics programming [20]. Java3D is an API, providing a programming interface for 3D that is analogous to the Abstract Window Toolkit (AWT) for 2D graphics. Java3D programs are saved as Java byte codes, not as a modeling format.

All interfaces are well matched, well specified, openly available and portable to most platforms on the Internet.



Fig. 1. Representation, at work, of technologies that provide with surface and geometry data; (A) 3D laser scanner for surface geometry (0.1 mm resolution), (B) point chemical composition with a  $\mu$ -XRF system (0.1 mm resolution).

VRML scenes in combination with Java can serve as the building blocks of cyberspace. Building large-scale internet-worked worlds now appears possible. Using VRML and Java, practical experience and continued success will move the field of virtual reality past speculative fiction and isolated islands of research onto desktops anywhere, creating the next-generation Web [13].

## 5. Presentation of a CH multimedia database using virtual reality (VR)

One of the most successful applications of VR is in the representation of historical and cultural heritage. The main reason for this success is that in many cases the represented data do no longer exist or are partially destroyed and cannot be viewed in any other way. In addition, the usual photographic (2D) representation often imposes the requirement to present many pictures of an object (taken from a number of different points of view) so as to be able to give viewers a complete description.

In order to implement a system that is able to deliver the virtual reality content of a multimedia database and to use a universal format compatible with most internet browsers, the obvious choice [21], today, is to adopt Virtual Reality Mo-

deling Language (VRML) [22]. VRML is a well established solution, with ISO approval and the ability to run in many different Internet browsers. VRML appears to be even more applicable as its file format is supported by many state-of-the-art 3D applications in such a degree that importing and exporting from one application to the other is a process of a few mouse-clicks. This file format is fully compatible with the software and hardware CETI is using for the acquisition of 3D geometry and point-wise surface information from the artifacts. Fig. 1 shows the 3D scanning and data acquisition procedures.

The innovation of the proposed scheme is that there is no other multimedia database of cultural heritage with 3D data that can be accessed through the internet and also be able to provide with specific object data according to the viewer's point of view. A block diagram of the proposed system is depicted in Fig. 2. The block diagram of the work being carried out by the system is depicted in Fig. 3.

The usage of the system can be summarized within a three-stage interaction procedure:

• At the first stage, the user is prompted to access the database search engine in order to locate an object or a family of objects matching desired search criteria. The database generates a report of all matching records and prompts the user to select one from the list.



Fig. 2. The architecture of the VRML presentation system.



Fig. 3. The three-stages system interaction procedure.

- At the second stage, the user gets specific information concerning the selected object and a 3D representation through VRML language.
- At the third stage, the user interacts with the 3D representation of the object, by turning, zooming, and panning, and by clicking on the surface of the object the database reports specific surface information (such as erosion or specific element density and other measurements stored in the database).

More technically, a client implemented within a Java applet is used to forward user's requests (queries) to a server application via a TCP packet socket connection. The server application is responsible for constructing a SQL command, which will be forwarded to the multimedia database server. Once again, the server application will collect the data and forward them back to the applet where they will be presented to the user in a typical 2D environment of text fields.

The External Authoring Interface (EAI) is the core to the interactive communication between the VRML world and the Java applet. EAI allows a Java applet to control the contents of the VRML window. Of course, this requires that both VRML window and Java applet are embedded in the same HTML page. Having those two worlds merged, a powerful platform is delivered. A platform, where high complexity real time 3D graphics coexist with 2D user interface and parallel supported by database connectivity and distributed application issues.

Summarizing, the following technologies have been used in this implementation:

- a Java-enabled Web browser (standard, client-side);
- a VRML97 compliant browser plug-in;
- a Java applet running in the Web browser (downloaded from the Web server to the client);
- a Java server application (executing on the Web server). Fig. 4 is an illustration of the technologies involved in the



Fig. 4. Interaction of different technologies.

current development. The combination of these technologies

gives the ability to the end user to run the client on any Operating System platform. Java is highly supported by Internet browsers and of course VRML plug-ins are freely available over the Internet [23].

The user interacts with the object by a complete freedom of movements (rotation, zooming, panning, etc.). Selection of a specific area (region of interest) is done by selecting a rectangular region on the 3D object. With the EAI, the position of the region of interest is transferred to the client applet. The applet forwards the information in the format of a streamed string to the server. The server is now responsible for querying the database. Results are retrieved from the multimedia database, averaged over the selected region and sent back to the client. Apart from the technological data, the server supplies the client with a filename path, which the client uses to download a more detailed 2D image of the region of interest. This image is also presented to the user. Fig. 5 shows a screen-shot of the web application, which is under development [24].

In a second phase, the interface will be enhanced with 2D charts of technological data and its functionality will be improved with full control of the VRML world within the applet (preselected viewpoints, preselected-highlighted regions-of-interest, enhanced navigational interface, etc.). Furthermore, issues related with 3D data and image compression as well as network security issues currently under investigation will be embodied. Considered technologies include JPEG2000, MPEG4 3D, and future VRML revisions (2002). They are expected to lead in lower volumes of data transmission and higher speeds of interaction, which will address the most important network issues related with information retrieval in similar systems.

#### 6. Conclusions

A multimedia database with real (digitized), realistic (reconstructions) and interactive 3D representations of objects was developed for archaeological ceramic and glass artifacts. The database contains historical, morphological and analytical data for the recorded artifacts alongside their 3D digital images and representations. The researcher/user has access to the entire information related to an artifact and can interact with its 3D representation by turning, zooming, and panning. In addition, the interested user can retrieve specific local surface data (elemental composition, pigment, etc.) by click-



Fig. 5. Screenshot of the web application. The architecture of the VRML presentation system.

ing on the surface of the object, thus taking advantage of the recent developments in measurement instrumentation that contribute significantly to the integrated documentation of cultural objects. The database makes use of the "thin client—thick server" approach, implemented on a Java platform. External Authoring Interface enables communication with the VRML interface in the client side.

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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 ( $\mu$ -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.

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#### 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

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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 painting have been the subject of a significant number of studies in

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(c)



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.

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 ( $47.8 \text{ cm} \times 36 \text{ cm}$ ). 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 considerably overpainted during the conservation procedure (the entire area of the sky, the halos and partly the figures themselves).





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.

#### 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<sup>-1</sup>, with a resolution of 4 cm<sup>-1</sup>. 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<sup>-1</sup> up to 150 °C, isothermal 1 min, 7 °C min<sup>-1</sup> 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<sup>-1</sup>

#### 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 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

#### 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

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 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.

#### 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)	РЬ	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

#### 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 -  $47 \mu m$ ). 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  $-5 \mu m$ ). 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  $\mu$ m) and a finely grained layer (D3.L3 - 30  $\mu$ m). 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.

These results were used as a guide in the interpretation of the elemental composition data, acquired by the  $\mu$ -XRF analysis. Data from sampling locations exhibiting no overpainting were assessed first, in order to determine the materials of the original





**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.

composition. As mentioned above (Section 3.2) the original paint layer has an average thickness of 47  $\mu$ m, thus allowing the X-rays to penetrate the original priming layer as well. The combined thickness of the overpainting layers is between 85–195  $\mu$ m. Therefore, in sampling locations corresponding to overpainted areas the X-ray signal of the original composition is minimal. Additionally, 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







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.

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 noninvasive course of analysis. The blue pigment was identified as Prussian blue, thanks to a very weak but characteristic band at 2094 cm<sup>-1</sup>. The only signals assigned to the binding medium

#### 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 Calcite	Original varnish layer Coarsely grained priming layer
Lithopone + calcite Prussian blue Linseed oil	Blue pigment of the sky region Binding media of blue pigment

indicate the presence of an aged oil: CH stretching bands at  $2927 \text{ cm}^{-1}$  and  $2853 \text{ cm}^{-1}$  and C=O stretch at  $1722 \text{ cm}^{-1}$  and 1709 cm<sup>-1</sup>. 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 lavers of sample TRI.D3 as well as Sample TRI.D4 (original varnish laver). Analysis of laver 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.

#### 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  $\mu$ -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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