

Article

“Codex 4D” Project: Interdisciplinary Investigations on Materials and Colors of De Balneis Puteolanis (Angelica Library, Rome, Ms. 1474)

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Abstract: This paper sheds light on the manufacturing processes, techniques, and materials used in the splendid illuminations of the oldest surviving copy of De Balneis Puteolanis, preserved at the Angelica Library in Rome (Ms. 1474). The codex is one of the masterpieces of mid-13th-century Italian-Southern illumination, traditionally referred to as the commission of Manfredi, son of Frederick II. The findings reported in the article result from the interdisciplinary study conducted in 2021–2023 in the framework of “Codex 4D: journey in four dimensions into the manuscript”, a multidisciplinary project involving many competences and dealing with art-historical studies on manuscripts, diagnostic and conservative analyses, scientific dissemination, storytelling, and public engagement. The considerations we present aims at increasing the knowledge of book artefacts while respecting their extraordinary complexity; data from non-invasive diagnostic investigations (X-ray fluorescence, Vis-NIR reflectance and Raman spectroscopies, hyperspectral imaging, and multi-band imaging techniques as ultraviolet, reflectography, and thermography), carried out in situ with portable instruments on the book, have been integrated with observations resulting from the historical-artistic study, and the reading of some ancient treatises on the production and use of the pigments and dyes employed in illumination.

Keywords: manuscript; illumination; diagnostic analyses; multidisciplinary study; 4D virtual and annotated model; Web3D applications; holographic showcase; manuscript accessibility



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1. Introduction

1.1. The Manuscript as a Sum of Skills and a Vehicle of Tangible and Intangible Values

Throughout the Middle Ages, manuscripts were vehicles for the transmission of a text, in space and time [1], as well as artefacts with a specific materiality to be analysed, reconstructed, and interpreted. Their creation involved numerous actors in the various production phases (from the preparation of the parchments to their binding) but also in the same operative stage. These codices were often enriched with sumptuous illustrations and decorations, executed as a result of a specific technical preparation. The illuminations themselves, which are the focus of this article, were sometimes the result of collaboration between artists with different specialisation, skill levels, and technical maturity. It is closely connected to the training methods, which involved gradual learning and a long practical instruction. After all, it appears that the technical manuals were not widely circulated and, therefore, were insufficient in helping them to acquire the necessary skills. It is equally difficult to determine how much illuminators were influenced by motif books and

iconographical guides in their choices [2]. These very complex aspects are the subject of extensive review and are quickly mentioned only to recall the complexity of these artefacts.

Manuscripts are complex and fragile objects, the study of which inevitably involves specialists from different backgrounds in an essential and interesting dialogue, which is even richer in the case of illuminated books, such as those investigated in our project. We are talking about a particularly large and heterogeneous community due to the specificity of the illuminated books, which contain not only text but also ornamental elements and illustrations.

The study of illuminated manuscripts, therefore, requires an interdisciplinary approach involving philologists, palaeographers, codicologists, art historians, and more, as has long been unanimously recognised by the scientific community. The dialogue with scholars in diagnostic investigations on the manuscript heritage is also not as consolidated, but in constant and remarkable growth. This is also due to the progressive diffusion of increasingly advanced mobile instrumentation that avoids moving the codes from their conservation places. These analyses are useful in providing information on the techniques and the materials used by illuminators, and their *modus operandi*, and for understanding the level of specialisation of the various craftsmen involved in making books. These data, in turn, must necessarily be integrated with the results of historical-artistic, codicological, palaeographic, and textual studies to provide a complete understanding of the manuscripts in their extraordinary complexity [3].

The information, provided by diagnostic investigations on the one hand, and by technical-artistic treatises and recipe books on the other, should be integrated and linked with precise geographical and chronological contexts. This crucial connection remains one of the most demanding challenges today, due to the controversial localisation and dating of some textual sources, and the lack of broad knowledge bases, tools, and services to support the research on these topics. Consider, for example, the recent debate surrounding the discovery of a new copy of the famous *De Arte Illuminandi* (L'Aquila, Archivio di Stato, Ms. S57), which complements the only previously known copy preserved in the National Library of Naples (Ms. XII E27) [4]. As is well-known, this is the only treatise specifically dedicated to the art of illumination. The considerations that have arisen in connection with the edition of the new copy refute the high dating of the work, brought forward to the end of the 13th century, and its place in Naples, in a secular environment connected to Angevin court [5]. According to the most recent hypothesis, the treatise would have been written in Abruzzo at the end of the fourteenth century.

Regarding the creation of knowledge bases to support research, some initiatives have been trying for some time to respond to these specific needs by creating databases focused on materials and techniques. The implementation of an environment to support these studies is, for instance, one of the objectives of the DIGILAB platform of the E-RIHS infrastructure. This platform is being developed within the Humanities and Heritage Italian Open Science Cloud (H2IOSC) project, funded by the PNRR, whose embryonic form is represented by the DataSpace platform (<https://dataspace.ispc.cnr.it>, accessed on 26 April 2024) [6].

1.2. State of the Art of Manuscript Accessibility in Libraries

Italian state libraries belonging to the Ministry of Culture and, above all, to libraries with important historical collections have among their tasks to conserve and enhance their collections even if their protection, conservation, and valorisation often seem to contrast each other.

Documents such as manuscripts are usually consulted only by specialists and scholars and some of those, due to their great preciousness, are entirely excluded from consultation, unless authorised by the Institute Director.

Manuscripts and ancient books can be viewed mainly at exhibitions, but most people often have only a superficial contact with the artefacts displayed inside the museums or library display cabinets, without being able to appreciate them fully. In fact, the volume is presented in a static way, dimly lit for conservation reasons, and opened on a particular page chosen for significant content written or depicted there.

The main tools available to library users are catalogues. The online ones are today increasingly simple to use: they have different navigation modes and functions, and they provide information based on standardised description and indexing systems corresponding to the user's search needs.

The types of users who search through mediation tools used by libraries are different so that their needs are not always satisfied. In reference to what has been said, it would be necessary to study interfaces, languages, and differentiated research approaches. Similarly, the increasingly widespread digital libraries which have specific characteristics or viewing modes do not often meet the needs of all digital users.

A ligature scholar or a restorer looking for previous restorations or for chemical analysis or biological processes conducted on materials and manufacturing techniques finds that those data are ineffective in 2D digitisation and are poorly detailed or completely absent in the catalogues.

A scholar interested in the manuscript materials and structure cannot be helped only by a traditional 2D digital version of it, because he/she cannot extract the useful data and measurements. Conversely, a scholar interested in the manuscript text can benefit from consulting a 2D digital copy.

In addition, if the manuscript has palimpsest or damaged papers, even the scholar interested only in the meaning of the text may find it difficult using the digital copy. Moreover, the viewing of the artefact through tools such as Wood's lamp does not solve the problem by making the request from scholars for multi-spectral images necessary.

A manuscript or an ancient book instils history and cultural messages.

Manuscripts have always been studied for their content in the preparation of critical editions or new critical text editions. In recent years the field of their study and the consequent requests of the users have increasingly moved towards the research and data analysis of the specimen, origin, use, and reuse of the document.

The creation methods and the conservation have also been considered. In short, the entire life of the document is studied starting from the moment of its packaging and physical realisation until its arrival in the preservation institute.

The library instruments do not satisfy the different interested users or those who could be interested in the documents and data stored in them.

The recent pandemic and widespread forced closures and access limitations have pushed libraries to think even more than before about all these issues and how to expand and diversify the accessibility to their book heritage, while improving knowledge by exploiting the new digital contexts and the new horizons of technologies.

1.3. The Codex 4D Research Project: A Multidisciplinary Approach to the Study of Manuscripts

In 2021–2023, the project "Codex 4D: journey in four dimensions into the manuscript" has been developed by the Institute of Heritage Science of CNR and the University of Rome Tor Vergata, in collaboration with the Angelica and Casanatense Libraries in Rome, as a result of the financial support of Lazio Region (POR FESR Lazio 2014–2020).

This research project introduces a novel interdisciplinary approach to the study, digital representation, and narration of ancient manuscripts, beyond the mere traditional 2D digitisation of contents [7]. The codex is considered in its complexity, as a "body" made up of intangible and tangible values, with a structure and contents composed of many materials and holding a wealth of stories. It is, in fact, the result of artisanal craftsmanship and artistic skills, beliefs, deeds, and manifestation of power; it may have undergone censorship, dismemberment, and some forms of concealment. These stories are imprinted, and sometimes hidden, in its materials, which constitute a significant part of its value, as signs of the history of culture and society.

In the Codex 4D project, virtual-reality and mixed-reality environments have been created to interact with virtual models of manuscripts, to enhance the perception and understanding of both their tangible and intangible values, considering:

- (1) the form and structure;

- (2) the content and meaning;
- (3) the materials, execution techniques, and state of conservation.

The manuscripts were digitised by integrating photogrammetry and mid-wave infrared techniques to create multidimensional virtual models on which to contextualise the information referring to visible surface elements (RGB) and that referring to invisible elements (IR), hidden beneath the surface, such as preparatory drawings, pentimenti, fragments of texts buried beneath the binding, gilding, and illumination detachments.

In addition, non-invasive chemical, microbiological, and physical analyses have been carried out on both the structural elements and sheets of interest in the manuscripts, by the University of Rome Tor Vergata and by MOLAB, the E-RIHS infrastructure mobile laboratory led by CNR ISPC (<https://www.e-rihs.it/laboratori-mobili/>, accessed on 26 April 2024). Such investigations were aimed at detecting material degradation products, traces of biodeteriogens in the present or past life of the manuscript, pictorial materials, and procedures.

The results of such studies were mapped onto the 4D virtual model, in which the fourth dimension represents the stratigraphy (Figure 1). The model is semantically characterised and annotated, and the user can explore it using specific tools, investigating features starting from the surface through the different depth levels.

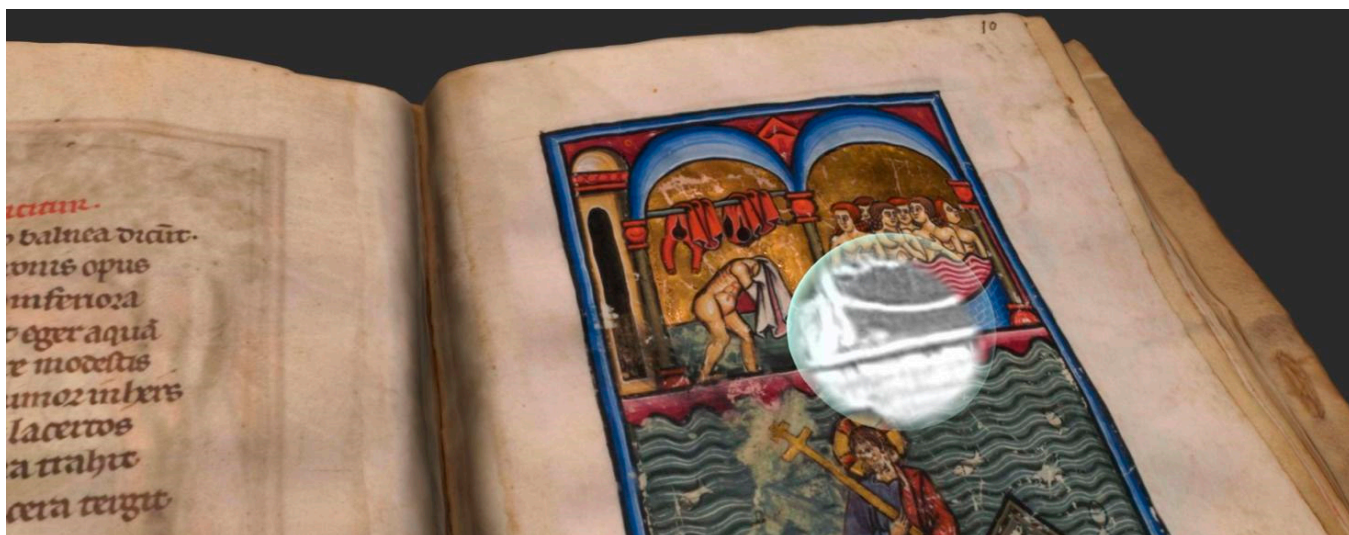


Figure 1. 4D model of ms 1474 De Balneis Puteolanis c. 13r, preserved at the Angelica library in Rome. The lens shows the hidden layers (IR) beneath the surface (RGB).

The research project has, therefore, developed along two thematic strands:

1. Innovate digitisation and documentation processes through the integration of methodologies and techniques and following a multidisciplinary approach;
2. Innovate the methods of content representation and transmission to the public, through a detailed study of users and their needs and the design of advanced digital environments.

The manuscripts investigated by the project are three, and, for each one, two or three configurations were digitised in 4D:

Ms 1474 De Balneis Puteolanis [8]: cc. 9v-10r; cc. 12v-13r; cc. 19v-20r.

Ms 459 Book of Hours [9]: closed, cc. 21v-22r; cc. 67v-68r.

Ms 1102 Divine Comedy [10]: cc. 4v-5r; cc. 55v-56r.

The results obtained help to broaden the accessibility of these exceptionally valuable assets, often difficult to enjoy and to understand. This achievement was made possible by the integration of many different competences into the team: palaeographers, codicologists, art historians, conservation scientists, physicians, chemists, biologists, 3D modellers, experts in communication and user studies, computer scientists.

In this paper, the methodologies adopted for the study of the content, materials, and execution techniques of sheet 13r of the codex De Balneis Puteolanis (ms 1474) are presented

in depth. Non-invasive diagnostic investigations consisted in X-ray fluorescence, Vis-NIR reflectance and Raman spectroscopies, hyperspectral imaging, multi-band imaging techniques as ultraviolet-induced fluorescence, reflectography, and thermography, which were carried out in situ, with portable instruments, on the book. The results were compared and supplemented with observations from an art-historical study and the reading of some ancient treatises on the production and use of pigments and dyes generally employed in illumination. The result was an understanding of the pictorial palette employed by the miniaturists of De Balneis, unexplored before, as they will be discussed in the Section 3.

1.4. State of the Art of Non-Invasive Analytical Studies of Illuminated Manuscripts

The illuminated manuscripts were investigated by means of different techniques over the years. However, being fragile and precious objects, they must necessarily be studied using non-destructive and non-invasive methods. Among them, imaging techniques, such as X-radiography [11], ultraviolet-induced luminescence (UVL) [12], and multispectral imaging (MSI) [13,14], are the most widely used for the characterisation of ancient manuscripts. More specifically, X-ray imaging techniques have been used to read ancient writing and for the in-depth investigation, thus revealing information related mainly to the book structure [11]. On the other hand, UVL and MSI have many applications in the recovery of faded or damaged texts or in the reading of palimpsests [15].

In the study of illuminated manuscripts, mid-wave infrared (MWIR) imaging techniques can be used to investigate all the main elements of the book, such as its structure, the constituent materials, and subsurface invisible features. In this respect, one of the main advantages offered by MWIR imaging techniques is the possibility to perform, in a relatively fast and non-destructive way, a broad-spectrum kind of analysis, thus providing information of fundamental importance for the evaluation of the book conservation state and useful also for a direct punctual/compositional analysis [16].

In the range of the punctual analysis of an illuminated manuscript with portable instruments, the combination of visible-near-infrared reflectance imaging, Raman spectroscopy, and X-ray fluorescence represents one of the most diffused approaches, to deepen the study of the constitutive materials and the painting techniques, and to evaluate the state of conservation. In particular, the identification of the colour palette and inks of the original materials, restoration products, and degradation substances of both pictorial layers and parchment are key information that can be achieved by the application of these complementary techniques [17–20].

2. Materials and Methods

2.1. De Balneis Puteolanis: Context and Value of the Codex

The manuscript 1474 held by Angelica Library is one of the best-known and sumptuous illuminated manuscripts of the Swabian period, from southern Italy. The volume is part of a body of surviving “profane” work made as real “figure books” to be intended for sovereigns or the court entourage [21]. The manuscript, on parchment, is a luxury example illustrated with great ability, as confirmed by art-historical and stylistic studies and by the diagnostic investigations carried out as part of the Codex 4D project.

The manuscript is written in Latin, and it is the oldest surviving copy of De Balneis Puteolanis, Pietro da Eboli’s poem describing the Baths of Pozzuoli and Baia and celebrating their therapeutic properties.

The dating of Pietro da Eboli’s work is controversial. According to the almost unanimous opinion of scholars, the work was composed between 1211 and 1221 and dedicated to Frederick II [22]. However, even in very recent studies, it backdating to the years 1194/5–1197 has been proposed, and the dedication to the father of Frederick II, Henry VI, has been hypothesised [8,23].

The dating of the De Balneis Puteolanis copy preserved at the Angelica Library is also controversial. The prevalent view is that the codex was made during the reign of Manfred, son of Frederick II, and can be placed between the 6th and the 7th decade of the 13th century. A piece of evidence supporting this dating is the scribe Johensis’ signature,

at the end of the dedication verses on f. 19v. The same scribe also signed two splendid, illuminated Bibles, the Vat. lat. 36 of the Vatican Library (the Manfred Bible) and the Ms. lat. 40 of the Bibliothèque Nationale de France.

The *De Balneis Puteolanis* in the Biblioteca Angelica currently consists of 18 epigrams in Latin, to which the Prologue and Dedication must be added. Structural modifications and restoration have profoundly changed its original appearance. There are numerous gaps and the arrangement of the sheets has been altered due to a completely arbitrary recovery.

The manuscript is splendidly illuminated; each composition describing and celebrating the virtues of the Baths is followed by a full-page illustration, in a parallel narrative between verse and images. The figurative cycle does not merely transpose the text into figures but enriches it with narrative, realistic and descriptive details, and topographical references. The alteration of the original fascicular sequence of the manuscript and the loss of some sheets, lead, in some cases, to an incongruence between text and image, compromising the complementarity between them.

The illustrations show very close stylistic kinships with the decorations of a group of luxury manuscripts which traditionally referred to artists, perhaps organised in a truly secular workshop, active in Naples between the 1250s and 1260s. This group of codices has been reconstructed starting from the splendid Manfredi Bible. The connections between these manuscripts are so clear as to lead some critics to assign to the same artist the illustrations of *De Balneis Puteolanis*, the most important illuminated sections of the two Bibles signed by Johensis and the ornaments of another Bible now in Paris (BNF, Ms. lat. 10428). On a substratum of clear Byzantine origin, the illuminator grafts more updated inflections of transalpine provenance, already present in the Frederick era, with suggestions of classic manners. The result is a mix of accents, and the manuscript can be interpreted as a great gift.

The sheets 13r-v being investigated features a full-page illumination of *Balneum de Ferris*. The bath stood along the shores of Lake Avernus, near the temple of Apollo, as we read in the first verses of the epigram penned in the facing sheet. The scene is divided into two parts. The top section shows the ruins of the Temple of Apollo. Two male figures can be seen looking up with wonder, as the temple collapses before their eyes. On the right side of the scene, a man unleashes the arrow of his bow to hit one of the birds sitting on the ruins. In the lower area, the illuminator depicts bathers who are immersed from the waist down in a polygonal bath. The space appears almost suffocated by their naked bodies, which are heavily marked by thick lines traced to define the belly, limbs, side, and faces, in physiognomies, movements, and poses that are replicated. On the left side of the scene, the waters flow, marked by rigidly parallel waves among which fish can be glimpsed.

2.2. Data Processing and Data Integration

2.2.1. Digitisation Campaign

The digitisation of the codes was conducted by exploiting structure from motion (SfM), a photogrammetric technique that allows obtaining a 3D reconstruction of an object from a sequence of RGB images, recorded with a standard camera from different angles around the object (one shot every 15°) [24]. To integrate the IR images into the model, the workflow adopted for the RGB images was replicated in thermal infrared: the thermal camera was moved around the object similarly to the RGB camera, so that there were corresponding and overlapping capture points. IR images were acquired by pulsed thermography in the mid-IR (spectral range 3–5 microns). Matching the RGB dataset with the IR dataset is a prerequisite for implementing the most accurate alignment possible on the virtual model. However, the images obtained by pulsed thermography do not guarantee robust feature detection and cannot be aligned via SfM to the 3D model. Therefore, for their alignment in the 3D space, consistently with the RGB set, it was necessary to introduce, prior to thermographic acquisition, a reflectographic acquisition step in MWIR without thermal stimulation, by illuminating the code with an MWIR source. This last step enabled MWIR reflectographic images with adequate contrast and feature detection to be used for 3D

processing [25]. These reflectography images were acquired in the same configuration and with the same device (thermal camera) used to record the thermographic sequences that allow virtual stratigraphic exploration at greater depth. The grip match between reflectograms and thermograms thus allowed the entire set of IR images to be oriented to the RGB model. A panel equipped with a black and white grid, auto-recognition target, and metric reference was also designed and constructed, to be placed around the codex during acquisition. Such a panel has visible patterns in both the RGB and MWIR, and is thus aimed at facilitating the orientation of the RG and IR images and scaling the model in real-world units.

The diversity of technical characteristics of the photogrammetric and thermographic acquisition tools in terms of optics, focal length, depth of field, distance to be observed from the artefact, and the need on the part of the staff engaged in digitisation to move around the manuscript made it necessary not only to calibrate all the cameras, but also to design and organise the work space and the acquisition set extremely carefully. Therefore, 3D simulations of the acquisition space and set were created prior to carrying out the work in the library (Figure 2).

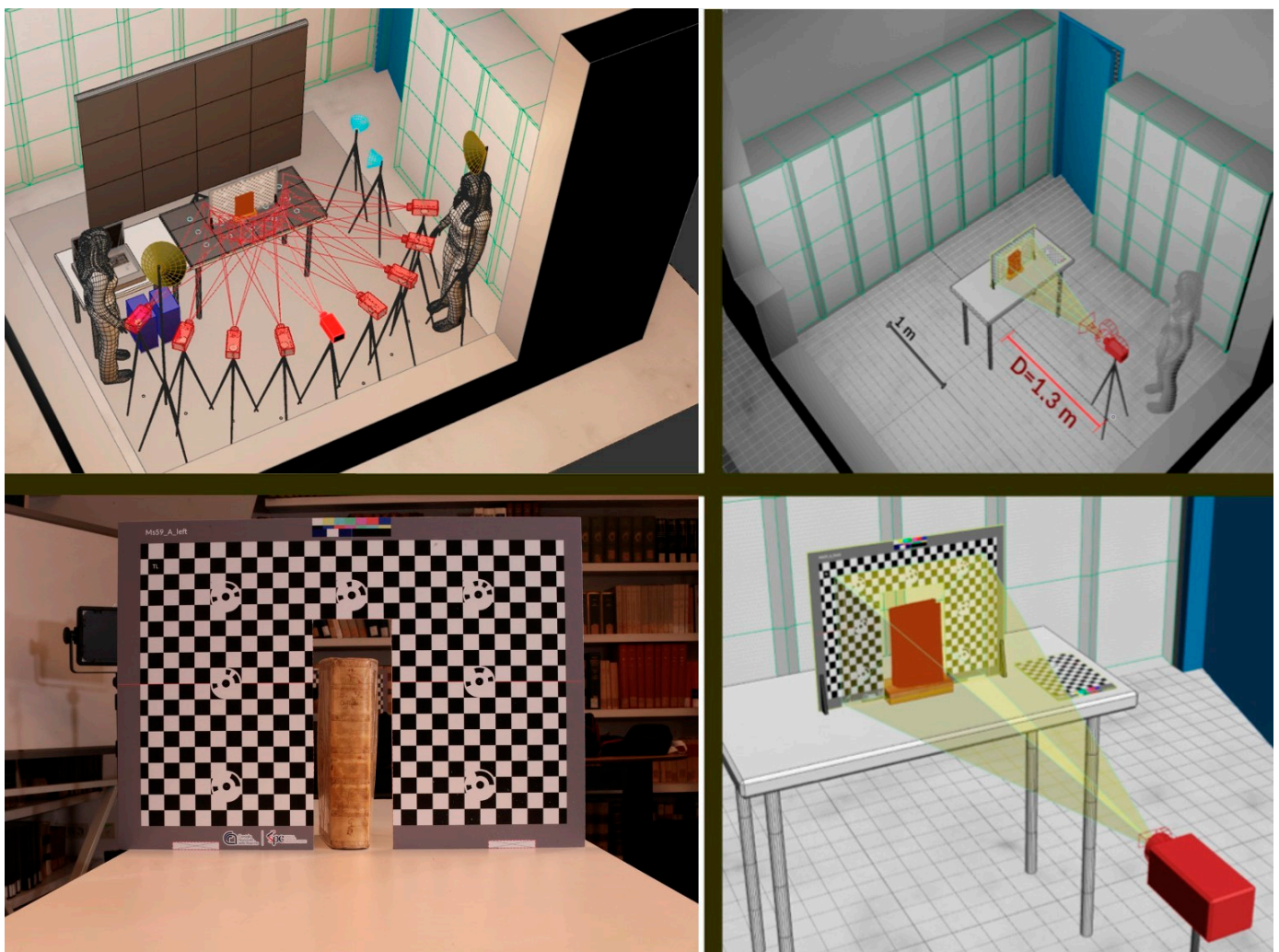


Figure 2. Acquisition set: from virtual simulation to the fulfilment at the Angelica Library.

2.2.2. IR Images Resolution Enhancement

To make feature detection possible on the IR images, Gigapixel AI software v. 5.8.0 was also used to increase the resolution of the reflectograms and thermograms, whose original resolution was 320×240 pixels, by 4 times (Figure 3). The procedure for recognising

the relative positions of the camera with respect to the object was then performed using Metashape and Reality Capture software v. 1.2.

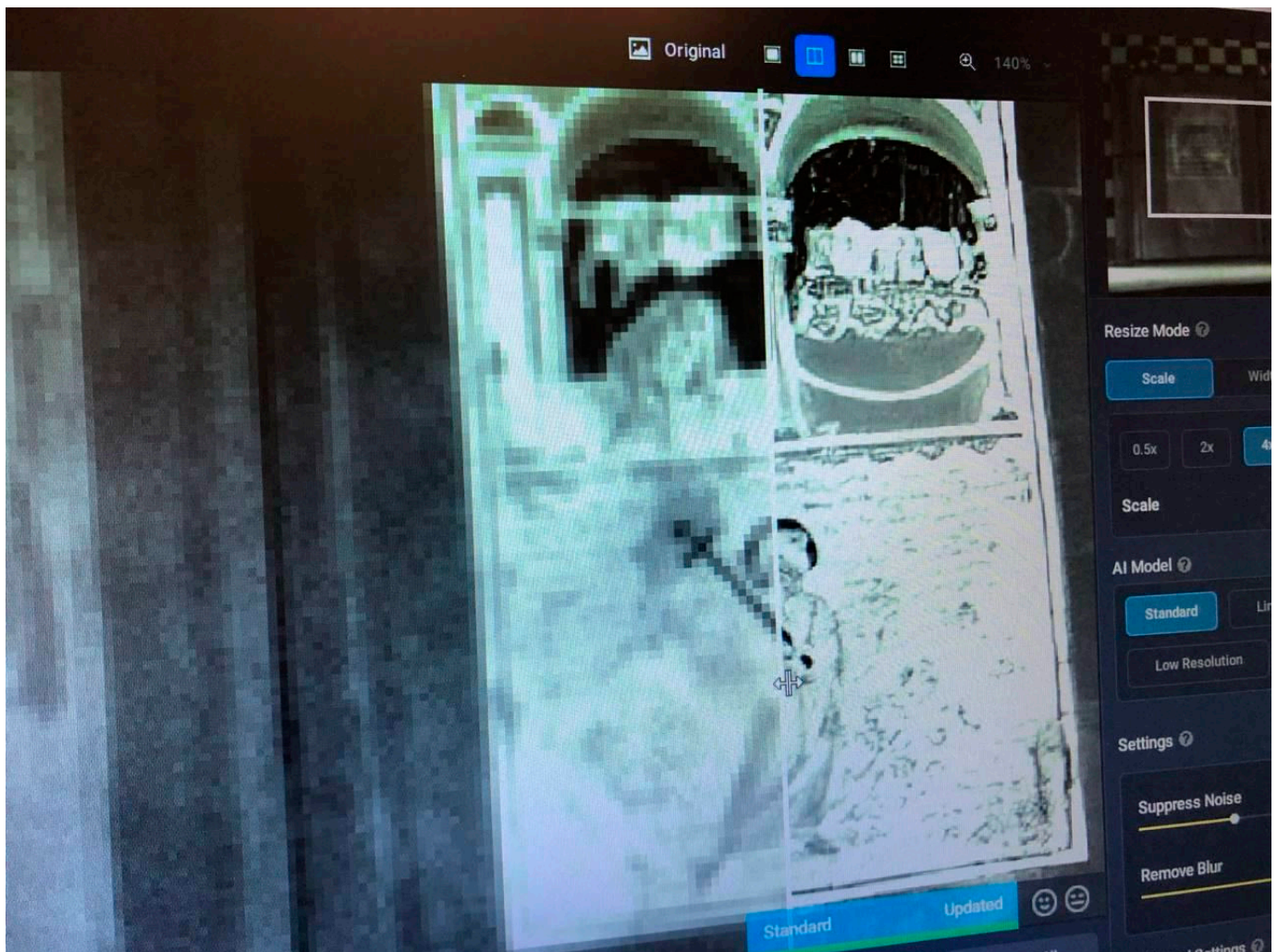


Figure 3. Resolution enhancement on a written part of De Balneis Puteolans through AI algorithm.

2.2.3. Photogrammetric Processing of Models, RGB, and IR Texture Alignment and Optimisation

Once the RGB and IR datasets were acquired and the resolution of the thermograms was increased with AI algorithms, the photogrammetric model was reconstructed through camera orientation and the creation of a point cloud with XYZ and RGB spatial information.

A polygonal solid model (mesh) was then extracted, and photorealistic rendering was optimised through the creation of the photographic texture.

On the model it was possible to consistently superimpose all the thermograms acquired at various depth levels. For this reason, the model can be considered 4-dimensional, containing the formal-volumetric surface and stratigraphic information. Software used were Reality Capture, Metashape, 3D Studio max, and Blender.

Final models with various textures and editable orthophotos were exported in interoperable formats (.obj, .fbx, .jpg, .tiff, and .png). The models were then optimised for real-time fruition in VR and MR platforms through the following operations: (1) remeshing in Instant Mesh, (2) UV mapping and final editing in Blender, and (3) texture building in any SfM software.

2.2.4. MOLAB Analysis for the Investigation of Pigments and Pictorial Materials of the De Balneis

The analyses carried out by MOLAB were focused on sheet 13r of De Balneis Puteolans. The different types of complementary analyses were combined to achieve a comprehensive

knowledge about the nature of the pigments and preparatory layers, as well as the state of conservation of the manuscript.

The results were compared and supplemented with observations from art-historical study and the reading of some ancient treatises on the production and use of pigments and dyes generally used in illuminations. This led to a hitherto unexplored knowledge of the pictorial palette employed by the miniaturists of De Balneis, that will be presented in the Section 3.

2.3. Investigation on Pictorial Materials

2.3.1. Infrared Thermography

The set-up used in this work consists of two flash lamps Bowens Estime 3000 with an energy rating tuneable up to 3000 watt-seconds, inducing an estimated temperature increase of the order of few degrees. The component of the radiation from the sources lying in the MWIR range was cut off by filters placed in front of the sources to avoid spurious signal generated by the MWIR radiation not emitted by the sample. The employed MWIR camera is a CEDIP Jade having a 320×240 Indium Antimonide (InSb) focal plane array which is sensitive in the 3–5 μm -wavelength range. The dedicated software Altair 5.50 was employed to process a sequence of images collected with a frame rate of 150 Hz during the thermal relaxation following the absorption of the light pulse. Images collected at larger delays from the pulse show features located at larger depth. To obtain the time-dependent change of the thermographic signal to start from the zero level in all the pixels, a pixel-by-pixel subtraction of the frame obtained just before the flash pulse from the sequence of the thermograms has been performed.

2.3.2. Multi-Band Imaging

For the MBI techniques, a digital Canon EOS 7D for UVL images and a Canon EOS 400D modified through the removal of the internal ICF/AA filter for IRR acquisitions were used. Both cameras were equipped with a Canon EF-S 18–135 mm $f/2.8$ IS lens (Canon, Tokyo, Japan), and, as radiation sources, two Quantum T5D-R flashes (Quantum Instruments, Bartlett, IL, USA) were used, equipped with a QF80 Qflash UV/IR Wave Reflectors with a filter holder (Quantum Instruments, Bartlett, IL, USA). To provide a proper output and input wavelength band for each technique, different combinations of filters were used. For UVL acquisition, the objective mounted a B + W 486 UV/IR cut while the flashes were equipped with B + W 403 UV black filters. For IRR, both objective and flashes mounted B + W 093 IR filters.

2.3.3. Hyperspectral Imaging

A Portable Visible Hyper-Spectral Imaging System (VIS) by Surface Optics SOC710-VP has been used to acquire hyperspectral images. The system is a high-precision instrument that uses a low-noise, high-speed acquisition silicon-based CCD as a high-quality spectrometer in the 400–1000 nm range; it features an integrated scanning system, and image collection and analysis software. The SOC710 can record hyperspectral images at a rate of 4 megabytes of data per second (128 band elements per second at 12-bit resolution, 520 pixels per line, up to 33 lines per second). The camera, mounted on a photographic tripod, was positioned at variable distances from the surface of the codex ranging between 1.3 and 0.8 m, obtaining approximately $13 \times 17 \text{ cm}^2$ (at 1.3 m) and $10 \times 13 \text{ cm}^2$ (at 0.8 m) single frames with about 0.25 and 0.20 mm of lateral resolution. Two halogen lamps from Elinchrom (300 W) were used as illumination sources for the reflectance images, while two LED lamps (excitation wavelength at 405 nm) from Hoenle were used for the fluorescence ones. The sources were placed at 45° with respect to the surface and at the same distance as the camera from the surface.

2.3.4. Raman Spectroscopy

A portable Xantus-2TM (Rigaku, Boston, MA, USA) Raman spectrometer was used for Raman analysis; the instrument is equipped with a thermoelectrically cooled CCD and enables two excitation wavelengths to be deployed, 785 nm and 1064 nm. For both

wavelengths, the measurements were performed using laser power in the range between 30 to 70 mW and an acquisition time ranging between 5 and 10 s.

The instrument collection lens attachment was removed and replaced with a standard microscope objective (20×, WD 1.3 mm, NA 0.4, Olympus); the device was mounted on a micro-positioning stage to enable the setting of focus distance with high accuracy and reproducibility and positioned on a tripod. Cut and baseline correction were performed using OPUS software.

2.3.5. X-ray Fluorescence

A portable XRF analyser Elio (Bruker, Billerica, MA, USA) was used for XRF analysis; the instrument is equipped with an excitation Rh target X-ray tube, 10 kV–50 kV, 5 μ A–200 μ A, 4 W, a SDD detector (area 17 mm²) with CUBE technology, energy resolution < 140 eV for Mn K α , and collimator of 1 mm. The detected elements range from Na (Z = 11) (with helium purge) to U (Z = 92). The instrument is equipped with two pointing lasers (axial and focal) for the alignment and with an internal digital camera to acquire a magnified image of the analysed area, with a field of view of 10 mm \times 10 mm. The analyser is fixed on a motorised XY stage, in turn mounted on a tripod (height 43–188 cm) for 2D mapping with a travel range of 100 mm \times 100 mm. The dimensions of the measurement head are 170 mm \times 265 mm \times 170 mm (W \times D \times H), the weight 2.1 kg. The data acquisition is controlled by software ELIO package, the post-processing mapping analysis is performed by ESPRIT Reveal software.

3. Results

3.1. Thermographic Investigation

As mentioned above, pulsed thermography, being able to perform the in-depth investigation of features hidden at different depths, was applied to the study of the state of conservation of cc. 9v–10r and cc. 12v–13r of the manuscript De Balneis Puteolanis. The results were also useful to direct further complementary investigations carried out by other imaging and compositional techniques (MOLAB). For the sake of clarity, the pulse thermography configuration is based on the recording of the IR radiation emerging from the sample surface following the temperature changes caused by the absorption of a VIS light pulse and by the heat diffusion [26]. In optically semi-transparent samples, like books, the subsurface feature is directly heated by the incident light, and, if the light absorption by the surrounding areas is smaller than that of the feature, then a thermal contrast revealing the feature can be obtained in the thermogram [27]. This mechanism enables the detection and, in some cases, the characterisation of different elements of interest in ancient books (i.e., pentimenti, and detachment of the gold leaf) [28,29].

For each illumination, three different thermograms, corresponding to increasing depths, were extracted from the sequence. As an example, concerning the illumination of Figure 4a, the thermograms recorded just immediately after (Figure 4b), and 100 ms (Figure 4c), and 300 ms (Figure 4d) after the light pulse, respectively, are shown. The thermograms show the overlapping of the different pictorial layers, all of them visible in the thermogram of Figure 4a. With increasing delays, first, the most superficial dark marks of the waves disappear. At larger delays (Figure 4d), even fishes become less visible in the thermogram and only the preparatory white graphic marks of the waves remain evident. The three thermograms extracted from the sequence can be viewed on the virtual 3D model and constitute the fourth dimension.

Moreover, the thermographic results obtained on c. 10r enabled the detection of different features of interest from the artistic point of view and, mainly, were used to direct punctual investigations. Among them, one of the main important results consisted in the possibility to observe a different thermal behaviour of the gildings in the single illumination of Figure 5. In fact, the gilding in the upper part of the illumination (Figure 5a), characterised by a mirror-like appearance, presents several detachments, indicated by the arrows, while the less glossy gilding in the lower part shows a very good conservation state (Figure 5b). This difference could be due to the use of different materials, both for the

gilding and the preparatory layer, or gilding techniques. As will be shown hereafter, the Raman spectroscopy and XRF results, which are reported in the following Section 3.3.7, confirmed the different composition of the preparatory layer beneath the two gilding parts, eventually responsible for the different kind of damage observed.

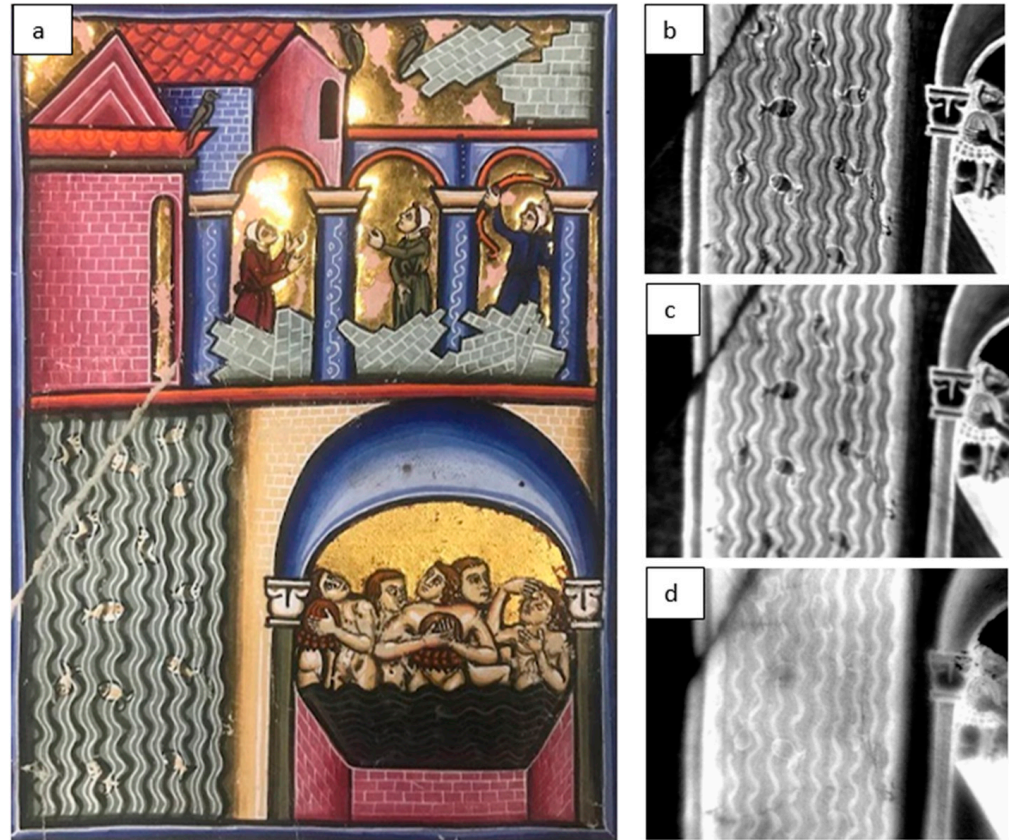


Figure 4. De Balneis Puteolanis, preserved at the Angelica library in Rome. (a) Photograph of the illumination of c. 13r and corresponding thermograms recorded just (b), 100 ms (c), and 300 ms (d) after the light pulse.

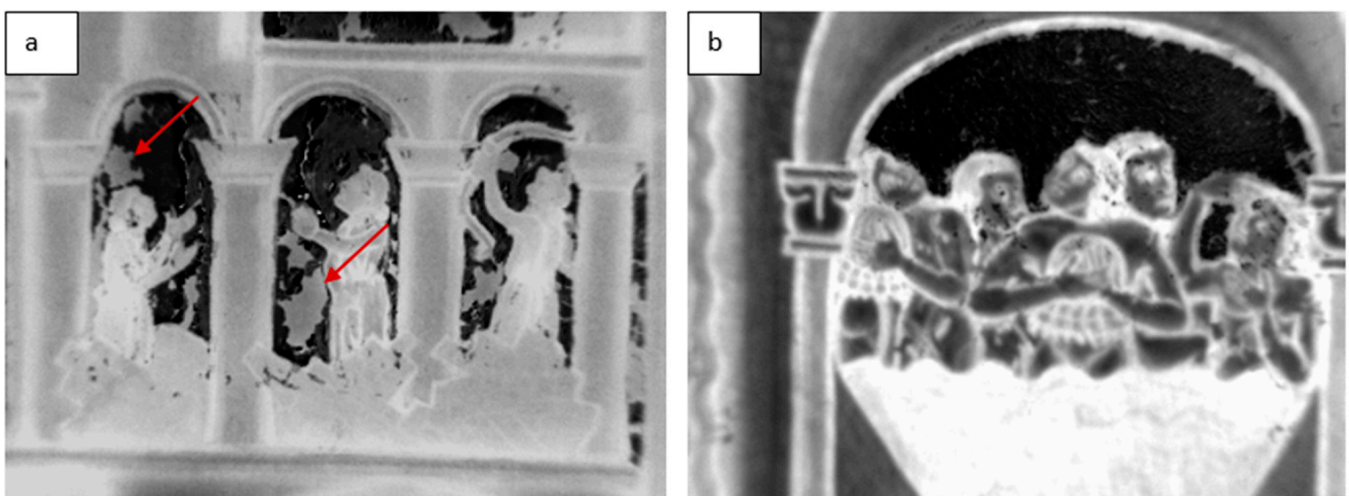


Figure 5. De Balneis Puteolanis, preserved at the Angelica library in Rome. (a) Thermogram of the upper (a) and the lower (b) parts of the illumination of c. 13r. The arrows indicate the detachments of the gold leaf that are evident only in the upper part (a).

3.2. Multi-Band Imaging

Multi-band imaging is a useful tool in manuscript investigation and conservation since it can be used to acquire data which are essential for the preliminary characterisation of the palette and the definition of the state of conservation and to guide the selection of areas to be analysed by single-spot techniques [30–33].

Ultraviolet-induced luminescence (UVL) is useful for extracting information on the presence of organic dyes (e.g., red lakes), aged organic materials such as natural resin-based paints, drying oils, or other substances of a biological nature such as fungi and moulds, which can then be localised on the surfaces.

Preliminary indications about the state of conservation of the present illumination have been provided by UVL images which reveal the presence of discontinuities and abrasions in the paint film (Figure 6a). Moreover, UVL fluorescence emissions highlighted the presence of lead-based white pigment used for the details of the ruins and the flesh tones of the men, characterised by a yellowish emission (Figure 6b), as well as the evidence of a weak pinkish emission in red areas to be probably related to red lake (Figure 6c).



Figure 6. De Balneis Puteolanis, preserved at the Angelica library in Rome. (a) UVL image; (b) detail of the architecture and flesh tones obtained with a lead white; and (c) detail of the pinkish emission linked to the possible presence of red lake.

In the infrared false-colour image (IRFC) shown in Figure 7, the blue areas appear uniform in tone, indicating the presence of the same pigment throughout the illumination, and, in particular, the reddish tone may suggest the presence of ultramarine blue. Even

for the red areas, which show a yellowish tone in IRFC, the possible use of mixtures of different red pigments as red lakes, red ochre, and vermilion can be preliminarily inferred.



Figure 7. De Balneis Puteolanis, preserved at the Angelica library in Rome. IRFC image.

3.3. Detected Materials and Techniques

The measurement points and the results obtained for each point are shown in Figure 8 and Table 1, respectively. A multianalytical approach has been adopted with the aim of integrating every single result achieved by the complementary techniques; the overall interpretation of the data is shown in Table 1.



Figure 8. De Balneis Puteolanis, preserved at the Angelica library in Rome. Picture of the illumination with indication of point measurement locations.

Table 1. Point measurements with results based on cross data obtained with different analytical techniques (Raman spectroscopy, XRF, UV-VIS-NIR reflectance spectroscopy, and hyperspectral imaging). It must be specified that not all points were measured with all the analytical techniques.

Description	Nr	Results
Parchment	26	Ca, Cl, S, K, Fe: elements ascribed to the preparation process of the animal skin
	48	Protein signals, probably lipid signals
White	6	Lead white
	31	Lead white
	37	Lead white
	42	Lead white
Purple	5	Animal-derived anthraquinonic lake, lead white
	25	Animal-derived anthraquinonic lake, lead white
	29	Animal-derived anthraquinonic lake, lead white
Brown	7	Iron oxides, lead-based pigment, vermilion
	8	Iron oxides and hydroxides, lead-based pigment
	40	Iron oxides, lead-based pigment
Red	17	Vermilion, possible use of an organic dye and lead-based pigment
	18	Vermilion, possible use of organic dye and a lead-based pigment
	27	Vermilion, lead-based pigment
	28	Animal-derived anthraquinonic lake
	30	Vermilion, lead-based pigment
	32	Animal-derived anthraquinonic lake, lead white
	39	Lead-based pigment, animal-derived anthraquinonic lake
	41	Lead-based pigment, animal-derived anthraquinonic lake
Blue	1	Ultramarine blue, lead white
	12	Ultramarine blue, lead white
	13	Ultramarine blue, lead white
	14	Ultramarine blue, lead white
	15	Ultramarine blue
	16	Ultramarine blue, possible use of a black pigment
	35	Ultramarine blue
	46	Ultramarine blue, lead white
	50	Ultramarine blue
51	Ultramarine blue	
Green	3	Vergaut, possible use of green copper-based pigment as glazing
	4	Vergaut, possible use of green copper-based pigment as glazing
	19	Copper-based green pigment, lead white
	20	Vergaut, possible use of green copper-based pigment as glazing
	24	Copper-based green pigment, lead-based pigment
	43	Copper-based green pigment, lead-based pigment
	44	Copper-based green pigment, lead-based pigment
49	Copper-based green pigment	
Yellow	2	Lead-based pigment, vermilion used as shade, possible presence of unidentified pigment(s)
	36	Lead-based pigment, possible presence of unidentified pigment(s)
	47	Lead-based pigment, possible presence of unidentified pigment(s)
Flesh tone	9	Lead white, unidentified pigment (s)
	10	Possibly lead white, unidentified pigment (s)
	34	Lead-based pigment, vermilion
Gold	11	Gold leaf
	23	Gold leaf
Pink preparation layer of gold leaf	21	Vermilion, anhydrite, and gypsum.
Red preparation layer of gold leaf	38	Vermilion, red lead, anhydrite, and gypsum
Lacuna on the preparation layer of gold leaf	22	Vermilion, anhydrite, and gypsum (residues of the preparation layer of gold leaf)
	33	Vermilion and gypsum (residues of the preparation layer of gold leaf)
	45	vermilion, anhydrite, gypsum (residues of the preparation layer of gold leaf)

3.3.1. Parchment

The preliminary step of the analyses comprised the characterisation of the parchment outside the painted areas (points 26 and 48). The XRF punctual spectrum (Figure 9) highlighted a strong presence of calcium, ascribed to the dehairing and the whitening processes of the animal skin (especially considering that sheets 12v-13r show the hair side of parchment and are more yellowish, with hair follicles) [20,34,35], besides minor amounts of chlorine, sulphur, and potassium, used in the conservation processes of the animal skin [20,35], and iron, possibly due to the contamination of the inks [20,35], as

clearly visible in the optical image reported in Figure 9. The NIR reflectance spectroscopy (Figure S1) showed the presence of protein signals, and possible evidence of lipids. Due to an intense fluorescence background, the punctual Raman spectroscopy did not provide any relevant results.

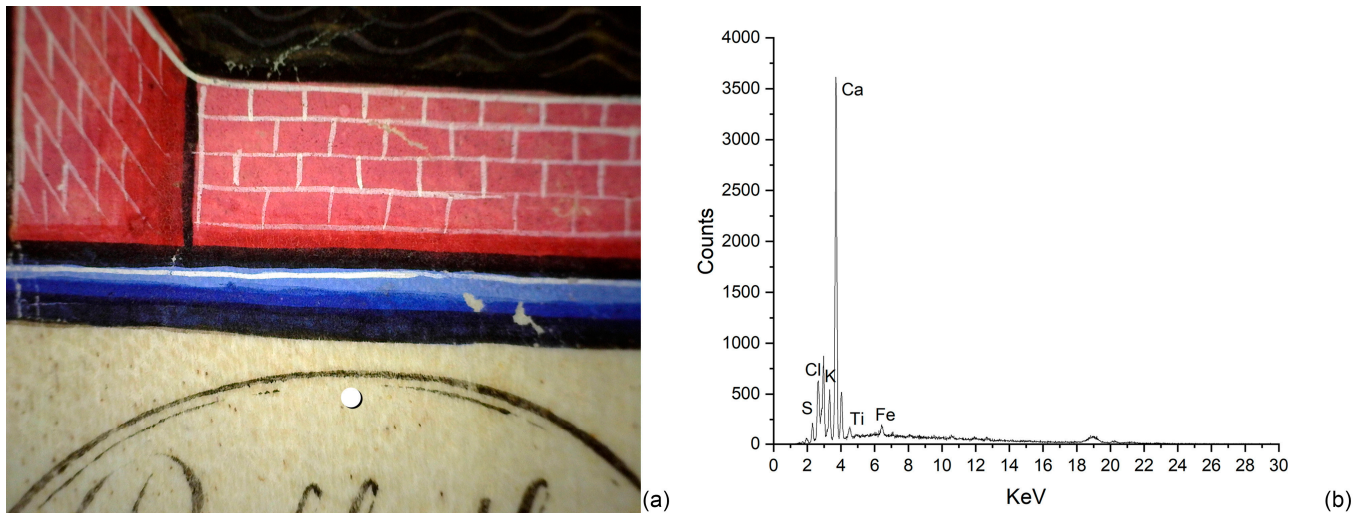


Figure 9. Optical image (a) and XRF spectrum (b) of the parchment (point 26). The white dot in (a) indicates the measurement position.

3.3.2. White

The white areas concern the white portions of the ruins of the Temple of Apollo (between the green bricks, in the triangular roof, the capitals, and decorations of the columns), the waves of the sea, and some details of the men. The only white pigment used in these portions is lead white, as demonstrated by the Raman (Figure 10) and NIR reflectance spectroscopy (Figure S2). Hyperspectral images (Figure 11) provide additional information: lead white has also clearly been used in mixture with other pigments in the red- or green-coloured areas to obtain lighter tones.

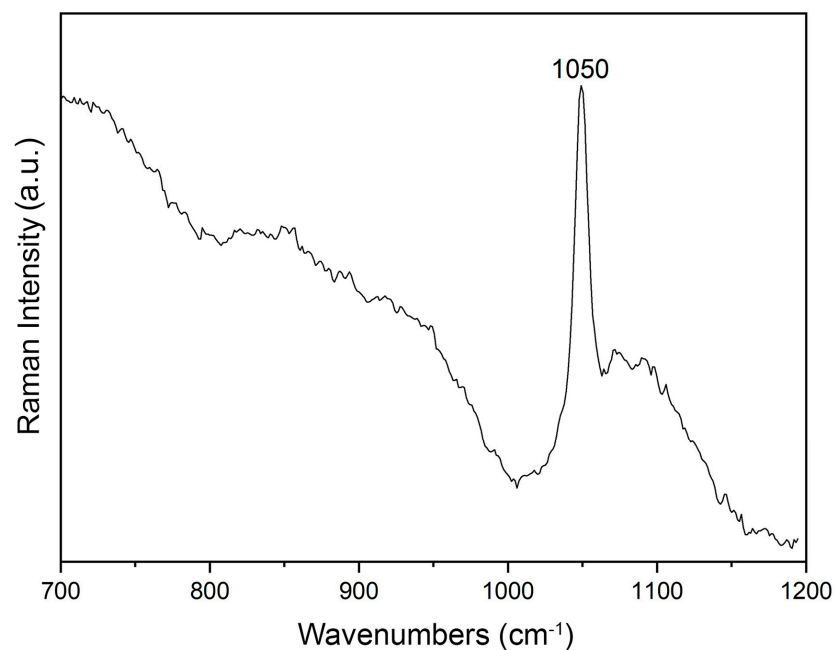


Figure 10. Raman spectrum collected on point 6. The Raman band visible at 1050 cm⁻¹ is attributed to the stretching mode of lead white carbonate group [36].

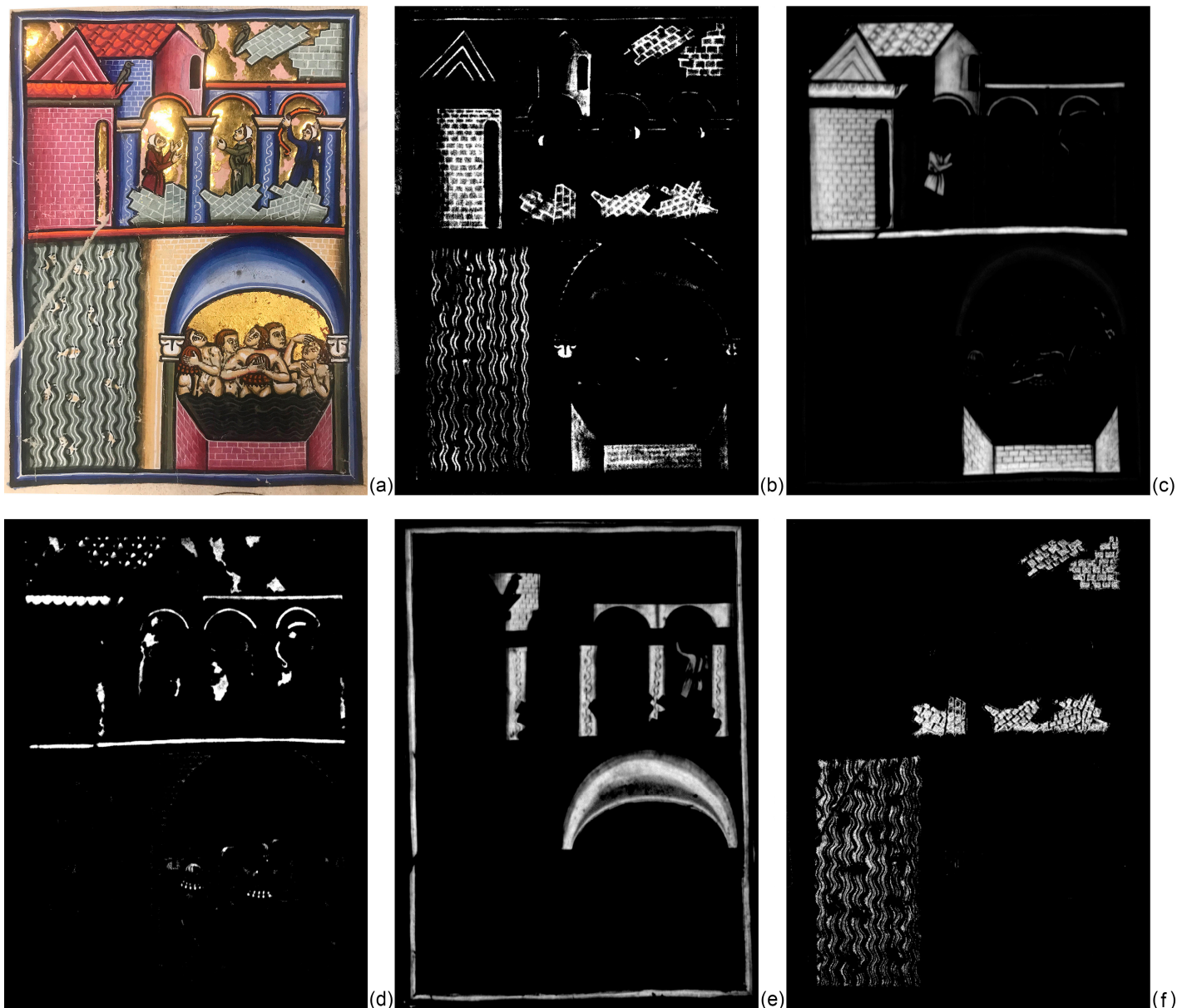


Figure 11. Picture of the illumination (a) and hyperspectral maps of lead white (b), red lake (c), vermilion (d), ultramarine blue (e), and copper-based pigment (f).

3.3.3. Red, Purple, and Brown

The red, purple, and brown areas have been obtained with different colours used in mixture or individually. Hyperspectral imaging (Figure 11) shows the use of red organic lake, also confirmed by UV-vis-NIR spectroscopy (Figure 12); it is mostly used in the ruins of the Temple of Apollo in mixture with lead white, as supported by the presence of lead in XRF spectra (Figure S3), with the intent of lightening the purple nuances.

Combining the information achieved with punctual analysis and hyperspectral imaging, the outstanding ability of the artist on using up to three red pigments in small painted areas has been highlighted: red lake for the red shadows of the bodies (Figure 11c); iron oxides and hydroxides, probably related to the use of ochre pigment(s), for the brown portions of the hair (Figure 13 and Figure S4); and vermilion for the red tones of the hair (Figure 11d). The hyperspectral maps also show the combination of red lake and vermilion for the tiles of the roof, using red lake for the main margins and vermilion for the tiny

details (Figure 11c,d). The red lake is assumed to be an animal-derived anthraquinonic lake as shown in the UV-vis-NIR reflectance spectra [37].

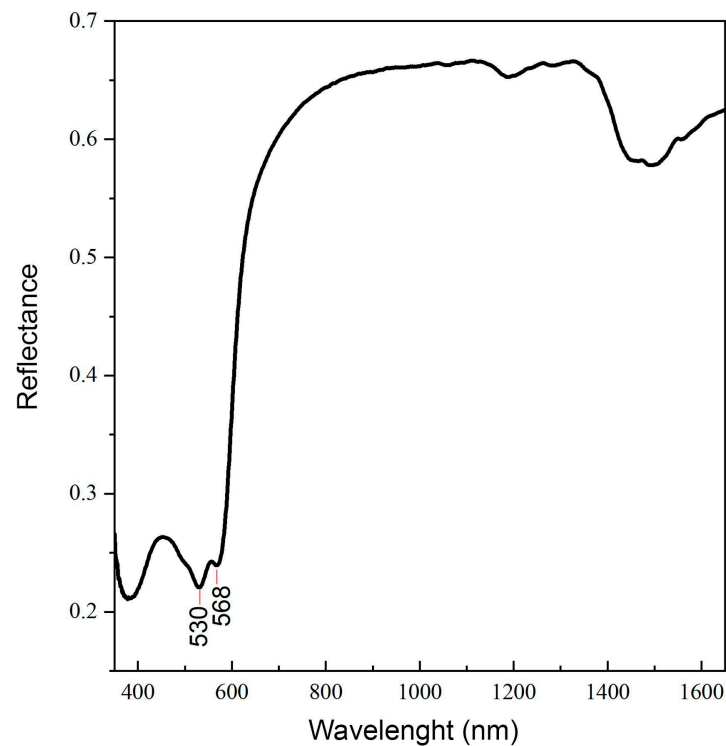


Figure 12. Reflectance spectrum of point 5. In the spectrum are identified the signals of an animal-derived anthraquinonic lake and lead white.

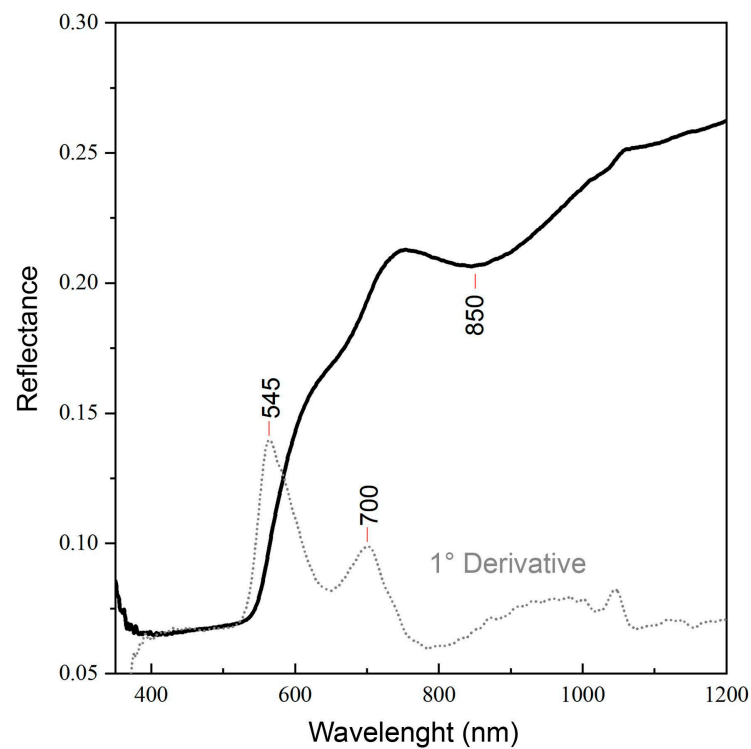


Figure 13. Reflectance spectrum of point 40. In the spectrum (and its first derivative), the signals of iron oxides and hydroxides are identified, suggesting the use of ochre pigments.

3.3.4. Blue

The only pigment used for the blue portions is ultramarine, as suggested by IRFC images, and then supported by both Raman spectroscopy (Figure 14) and UV-vis-NIR reflectance spectroscopy (Figure S5). Hyperspectral maps (Figure 11) show a distribution of this pigment in the ruins of the Temple of Apollo, in a blue robe and in the frame of the illumination. The blue arch in the lower part of the illumination has been produced by mixing ultramarine with a progressively increasing lead white amount to obtain a remarkable range of blue shades, from deeply dark to light blue. As shown in the optical image reported in Figure 15, in the upper part of the arch, an unidentified black pigment has probably been added to obtain a very dark hue.

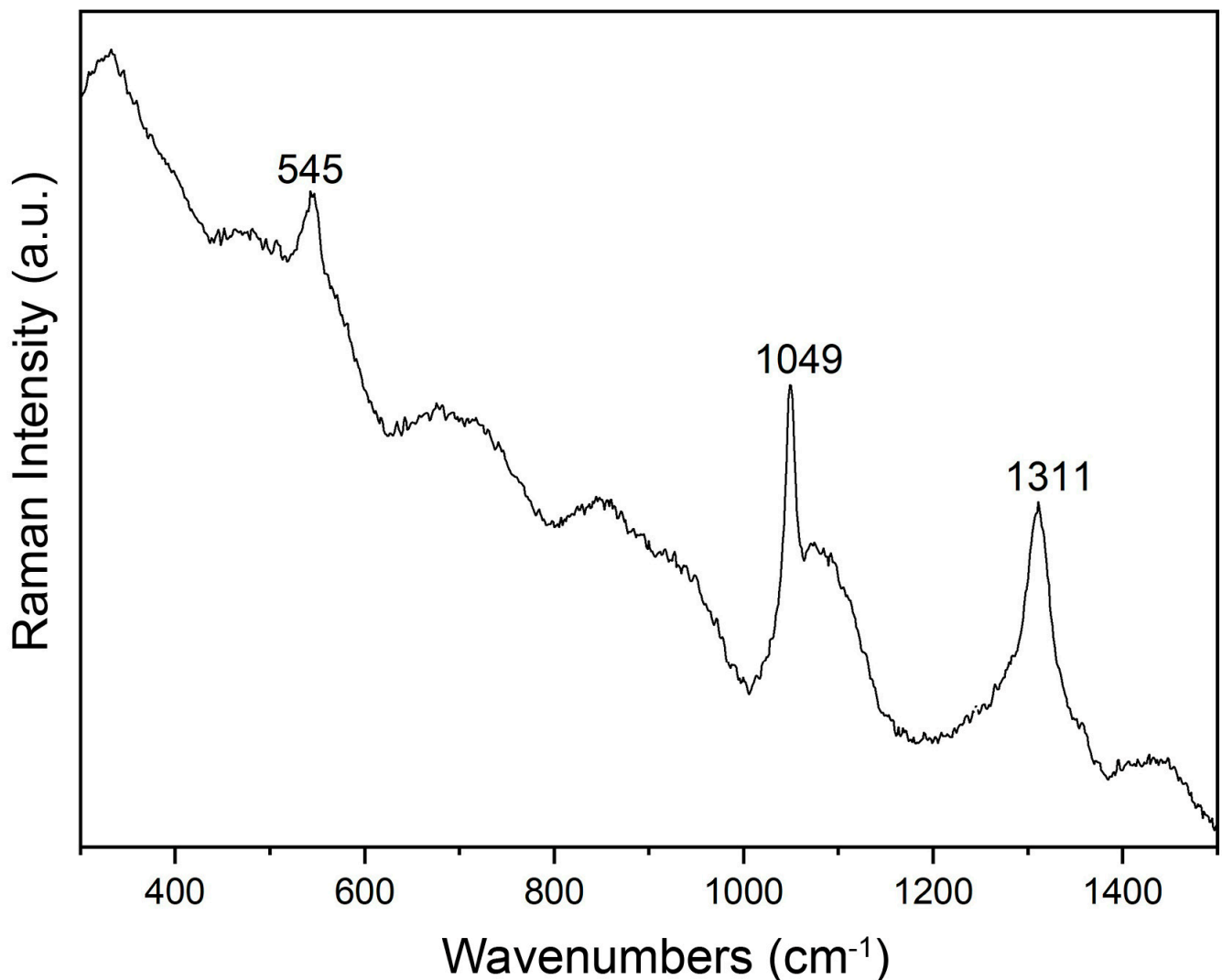


Figure 14. Raman spectrum of the blue arch (point 13). The Raman band at 545 cm^{-1} is ascribed to ultramarine blue, and the 1049 cm^{-1} Raman band is ascribed to lead white. The band observed at 1311 cm^{-1} is attributed to a luminescence phenomenon associated with the use of a 785 nm excitation laser for the analysis of ultramarine blue.

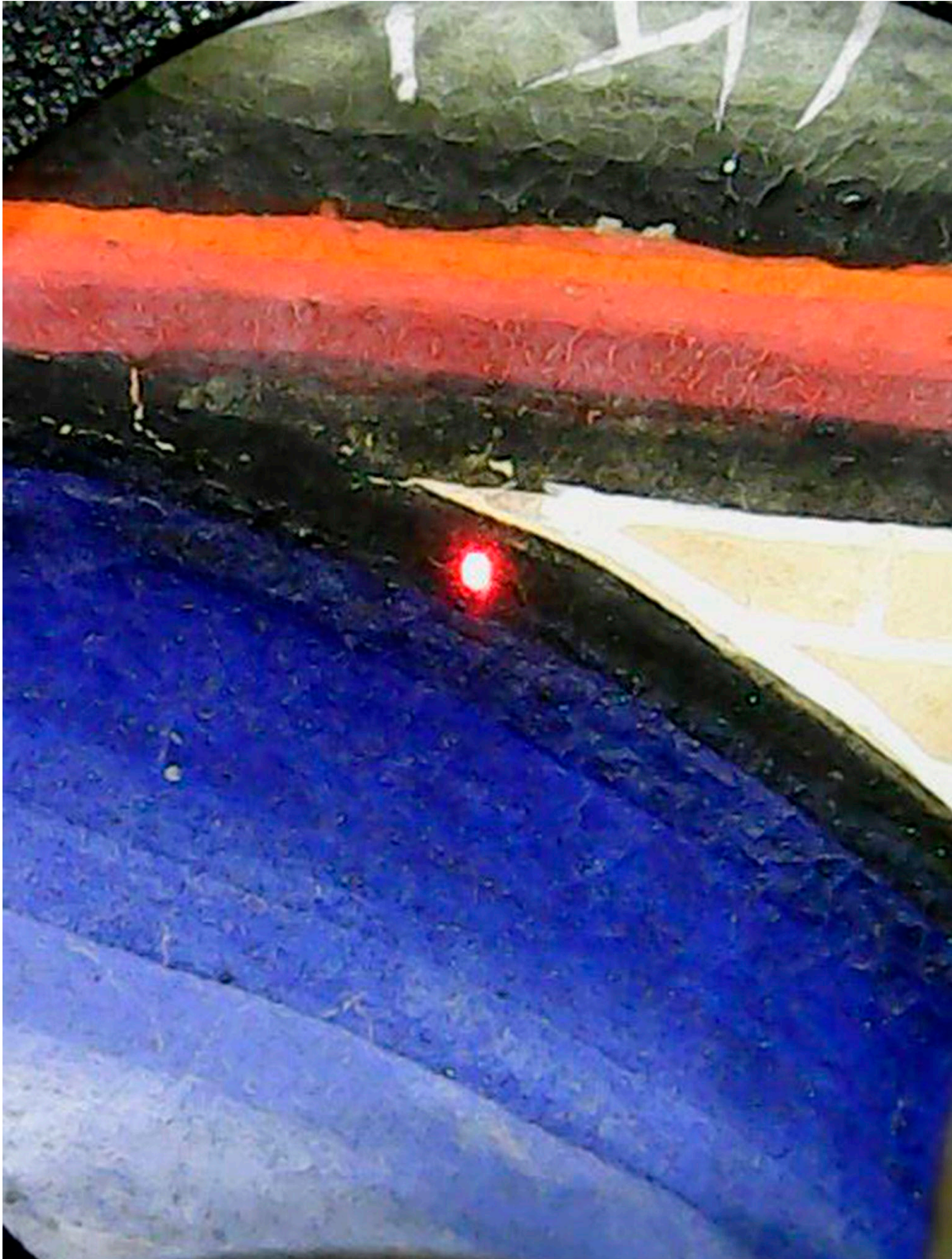


Figure 15. Optical image of the upper part of the arch. The red dot indicates the XRF measurement position (point 16).

Natural ultramarine is obtained by crushing and grinding the lapis lazuli rock and selectively extracting the blue mineral lazurite, which is responsible for the blue colour. As reported by M. Gonzalez-Cabrera et al. in 2020 [38], natural lazurite occurs in association with other minerals like calcite, pyrite, diopside, wollastonite, forsterite, phlogopite,

muscovite, and other sodalite group members such as nosean and haüyne depending on the geographical origin of the rock.

The most famous traditional method to purify lazurite as reported in Cennino Cennini's [39] is a lengthy extraction process. Sophisticated extraction procedures are documented starting from the end of the 13th and the beginning of the 14th century [40]. Early evidence is found in Ms. 1075 (*Scripta Colorum*) of the State Library of Lucca [41]. In *De Arte Illuminandi* [4], the description of the system is more synthetic and reflects a traditional and simple system, closer to the precepts contained in two 13th-century treatises for the illuminators: the *Liber de coloribus qui ponuntur in carta* [42], and the *Liber colorum secundum magistrum Bernardum* [43].

In 1828, a synthetic version of the ultramarine blue pigment was first obtained by means of a chemical process involving both calcination and oxidation steps [38].

The Raman spectra acquired in the blue areas of the illumination exhibit the Raman fingerprint of ultramarine blue at 549 cm^{-1} that can be assigned to the symmetric stretching mode of the $\text{S}3^-$ ions in a sodium alumino-silicate matrix [44]. However, a further strong band at around 1311 cm^{-1} is consistently present in all Raman spectra acquired, that does not correspond to the Raman features of lazurite. In the literature, it is reported that a strong luminescence signature occurs in the range between 1200 and 2000 cm^{-1} of the Raman spectra when using a 785 nm excitation wavelength [38,44]; the luminescence effect is wavelength-dependent since, using other excitation sources in the visible range (633 , 514 , and 488 nm), only the diagnostic Raman features of ultramarine are visible.

The authors ascribe this feature to the presence in the lazurite powder of diopside impurities containing some transition metals. This is highly relevant since the luminescence features acquired with a 785 nm excitation wavelength, which correspond to the laser used in this study, are indicative of the natural origin of the ultramarine blue pigments. Moreover, the luminescence pattern can also indicate a different geological provenance, as supported in [44] where Kremer ultramarine pigments with different origins (Afghanistan and Chile) were analysed with a 785 nm excitation wavelength. Interestingly, the luminescence pattern observed in this illumination shows a quite good agreement with that of Kremer pigments originated from Afghanistan; on the contrary, the Raman pattern of the Kremer powders originated from Chile exhibit a higher number of luminescence bands with no agreement with the spectra acquired in the present illumination. This outcome supports the evidence that the ultramarine used in mediaeval manuscripts is more likely to come from Afghanistan [39,44].

The use of natural precious lapis lazuli in each blue area of the illumination strongly underlines and confirms the priceless value of this art object.

3.3.5. Green

Two kinds of green pigments have been detected in the illumination. The waves and the ruins of the upper part show a strong content of copper in the XRF spectra (Figure 16), indicating the use of a copper-based green pigment, as confirmed by the UV-vis-NIR reflectance spectra (Figure S6). The presence of lead in the XRF spectra suggests the mixture of the pigment with a variable amount of lead white. The literature on mediaeval illumination pigments indicates the traditional use of verdigris [45]; however, no analytical evidence has been achieved about the presence of this pigment in the present illumination. The second kind of green pigment was identified in the columns of the lower part of the illumination, in the man's green robe and in the birds. The Raman spectra (Figure 17) clearly exhibit the presence of a mixture of blue pigment indigo (549 , 1311 , and 1573 cm^{-1}), with the yellow pigment orpiment (290 , 311 , and 356 cm^{-1}). This mixture is known as "vergaut" which is a quite common pigment used in illuminated manuscripts and described in mediaeval technical literature [4,19,39,42,43]. The presence of lead in the XRF spectra (Figure S7) and a weak band at 1051 cm^{-1} in the Raman patterns (Figure 17) suggest the presence of lead white in mixture with vergaut.

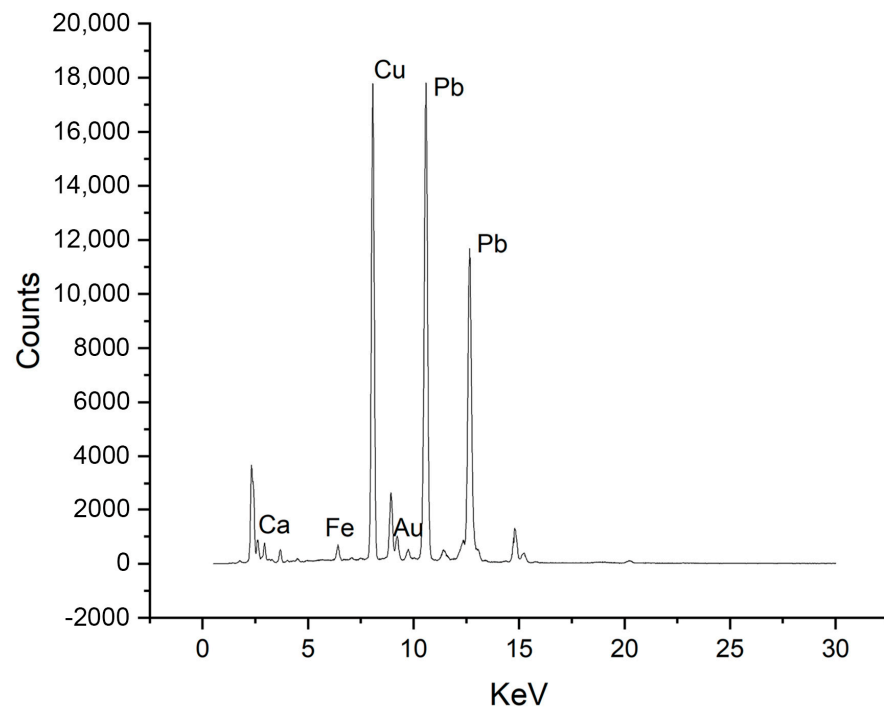


Figure 16. XRF spectrum acquired on the green architecture in the upper part of the illumination (point 19). The intense peak of copper (Cu) suggests the presence of a copper-based green pigment. The peaks of lead (Pb) are associated with the presence of lead white.

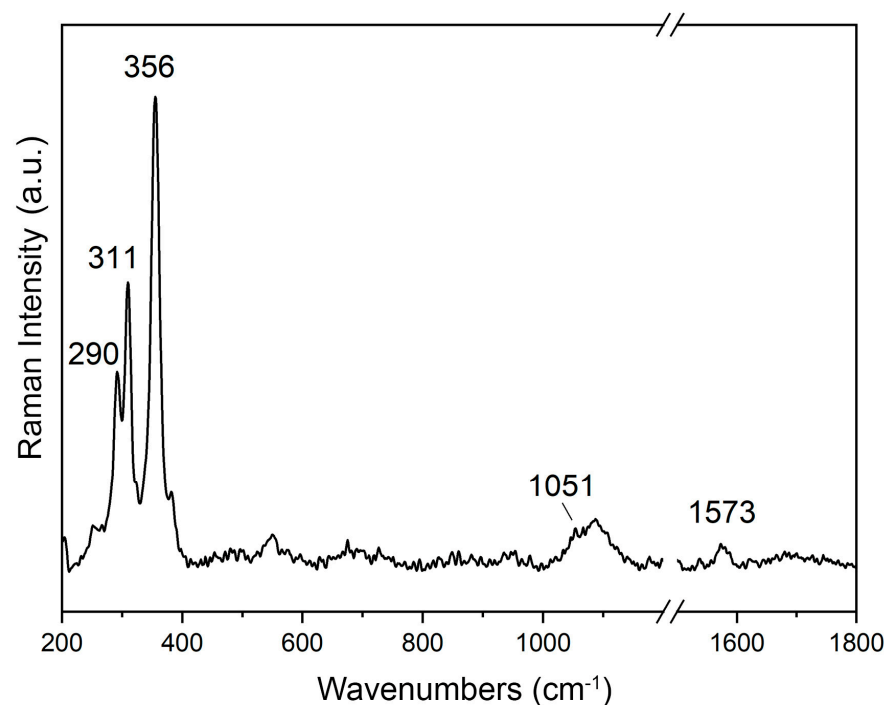


Figure 17. Raman spectrum collected on the green column (point 4). The spectrum highlights the presence of the pigment vergaut, a mixture of orpiment (Raman bands at 290, 311, and 356 cm^{-1}), and indigo (549 and 1573 cm^{-1}). The Raman band at 1051 cm^{-1} is ascribed to lead white.

Interestingly, a glazing made by a copper-based green pigment has been detected over the areas painted with vergaut, as clearly shown in the optical image of the columns of the lower part of the illumination (Figure S7).

3.3.6. Flesh Tones and Yellow

All the flesh tones and yellow areas are characterised by the presence of lead as the main element in the XRF spectra (Figure S8). Only in the two measurement points related to the flesh tones has lead been unequivocally ascribed to lead white (Figure 18). In the columns of the lower part of the illumination, vermilion has been used for the dark yellow shades.

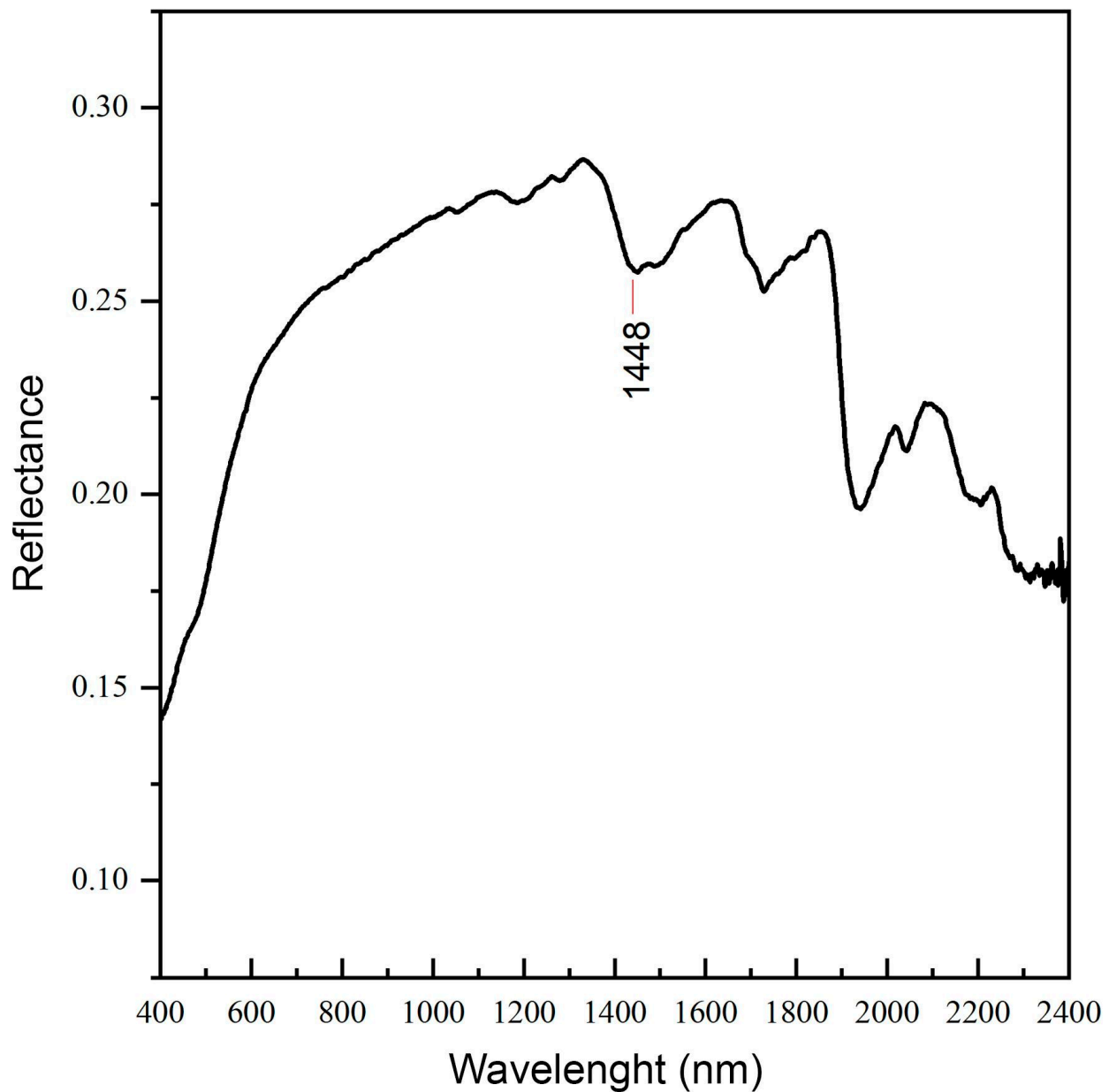


Figure 18. Reflectance spectrum collected on point 9. In the spectrum, the signal of lead white can be identified [46].

Nonetheless, for both colours, the chromophore pigment has not been identified.

3.3.7. Gilding

A peculiar aspect concerns the golden areas of the illumination, both in the lower and upper parts, which cover a large part of the surface. Gold leaf has been used (Figure 19), and, interestingly, two different preparation layers have been detected under the leaf.

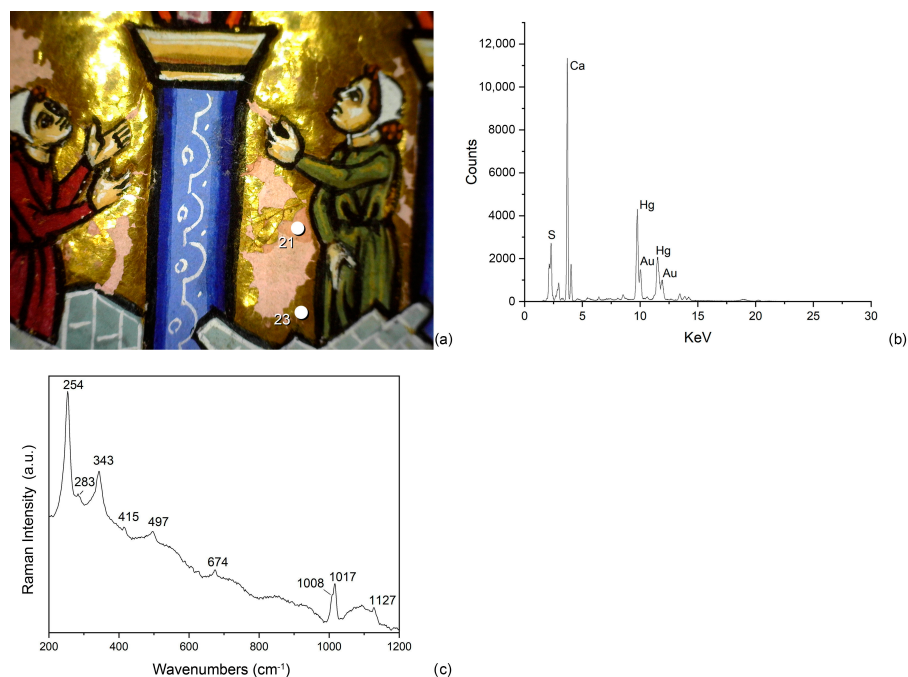


Figure 19. Optical image of the illumination where gilding and the pink preparation layer are visible (a); XRF spectrum acquired on the gilding (point 23) (b), and Raman spectrum collected on the pink preparation layer (point 21) (c). The white dots in (a) indicate the XRF and Raman measurements locations. The presence of gold (Au) in the XRF spectrum suggests the use of gold leaf. The peaks of mercury (Hg) are related to the presence of vermilion in the preparation layer under the leaf (b). In the Raman spectrum, the bands of vermilion (254 and 343 cm^{-1}), gypsum (1008 cm^{-1}), and anhydrite (1017 cm^{-1}) can be distinguished. The Raman bands at 415, 497, 674, and 1127 cm^{-1} can be ascribed to both gypsum and anhydrite (c).

The presence of relevant lacunae in the golden areas, both in the upper and lower parts of the illumination, allows directly exploring the composition of the preparation layers, which exhibit a pink colour in the upper part and a dark red hue in the lower part. Raman spectroscopy highlighted that both layers are characterised by the presence of vermilion, gypsum, and anhydrite with different relative amounts (Figures 19c and 20); interestingly, in the dark red preparation layer, red lead was also detected. In the areas where the preparation layer of the upper portion of the illumination is missing, and thus the parchment emerges, the same compounds of the preparation layer are found as residues.

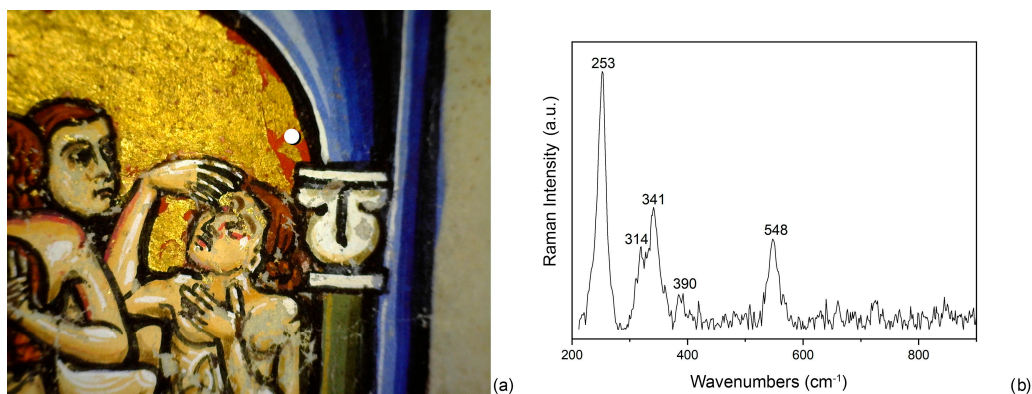


Figure 20. Optical image displaying the gilding of the lower part of the illumination, along with its lacunae (a) and Raman spectrum collected on the pink preparation layer (point 38) (b). The white dot in (a) indicates the Raman measurements location. The Raman bands at 253 and 341 cm^{-1} are ascribed to vermilion; the Raman bands at 314, 390, and 548 cm^{-1} are ascribed to red lead.

3.4. Some Technical-Artistic Observations between Diagnostic Investigations and Mediaeval Treatises

The analytical investigation campaign allows us to add a few more pieces to our knowledge of the materials and techniques used to make the illuminations of *De Balneis Puteolanis*. Although the analysis was carried out systematically on a single sheet, the results provide some food for thought and allow us to reread and enrich the scholars' observations, based, until now, only on the visual evaluation of the codex [22]. These initial considerations, which can be further developed in the future, confirm the artist's remarkable technical ability, his prowess, and the preciousness of the manuscript. It would be useful to extend the investigations to other illuminated sheets of the sumptuous manuscript to assess their technical-executive uniformity.

The gilding technique deserves first consideration. As we have seen, the investigations highlighted two different preparation layers and the exclusive use of gold leaf in both sections of the full-page illumination (Figure 8). The analysis of the preparatory layer, therefore, seems to exclude the use of the red bole, which had been hypothesised based on observation with the naked eye of the lacunae.

The use of the bole in the preparation layer seems to spread in the Western world in the 13th century and found a theoretical formulation in late-13th-century technical treatises for illuminators [42,43], in *De Arte Illuminandi* [4], and later sources. Its use is attested in the southern Italian area, in a cultural context close to the *De Balneis Puteolanis*, in the sumptuous Pontifical kept in the Diocesan Museum of Salerno [47–49]. As investigations of the sumptuous Salerno manuscript have confirmed, however, bole was only used for the gilding of illuminations datable to the second phase of execution, to be placed between the late 13th and early 14th century [50,51]. This manuscript is incomplete and shows more executive phases. This makes it very useful because it reveals valuable insights into the production processes and working methods adopted by the end-of-the-13th-century illuminators.

In *De Balneis Puteolanis*, the support for fixing the gold leaf is not composed of bole as hypothesised by scholars based on visual analysis. In the overlapping scenes of the *Balneum de Ferris*, two different preparations composed of vermilion, gypsum, and anhydrite, in different relative quantities, were used. Red lead has been added to the lower preparation, giving it a deep red tone. The choice made in *De Balneis Puteolanis* does not seem to have a special place in technical-artistic recipe books, not even in sources that dedicate numerous recipes to gilding, such as the *Liber colorum secundum magistrum Bernardum*, from the end of the 13th century [43], which contains ten rules for gilding. A reference to the use of cinnabar and red lead for the preparation layer of gilding is contained in the first book of *De Diversis Artibus* by the monk Theophilus, from the end of the 12th century, [5,52]. A full reading of recipe XXIX reveals, however, that it deals with the materials and the procedure to be followed to apply gold powder in illuminations. Powdered gold appears to have been used by the illuminator to colour other illustrations in the Poem, such as in the large tunic of the female figure in the *Balneum Sulfutara* (f. 4r). It is well-known that this technique was widespread in the Gothic illuminations of the transalpine world and was employed in the group of manuscripts of southern Italian origin grouped around the *Manfred Bible*, whose close affinities with the *De Balneis Puteolanis* have been noted above [22].

As the results of the diagnostic investigations reveal, the illuminator of the *De Balneis Puteolanis* has great technical maturity in preparing a colour using pigments of different types, which he uses individually or mixes to obtain different shades. The artist's skill and expressive richness are evident in the colouristic rendering of the architectural elements in the scene, as well as in the treatment of the flesh tones. In this regard, note the ability to shade the volumes and define the anatomical features of the figures with highlights, skilfully using lead white as the main element mixed with vermilion or lacquers of animal origin and other unidentified ochre pigments.

Once again, the artist adopts an executive practice that finds its closest theoretical reference in *De diversis artibus* by the German monk Theophilus. The falls in colour allow us to observe the preparatory layer of flesh colour, which is even more evident in

other, more damaged illustrations (e.g., ff. 4r, and 18r). The *De Arte Illuminandi*, and other technical treatises of the 13th century transmit a different practice involving using a uniform layer of green colour on which a flesh colour was applied, allowing the basic preparatory layer to emerge for building shadows. Once again, an example of these two distinct practices is offered by the sumptuous Pontifical of Salerno, that allows us to follow the actual stages by which illuminators drew and painted their images, and the material and technical processes.

These brief and limited observations may be extended in the future, in the hope of carrying out diagnostic analysis campaigns on other manuscripts from the southern Italian area of the Swabian and early Angevin periods. This would make it possible to extend the knowledge base, offering historians of illuminated manuscripts new elements useful for reconstructing the artists' *modus operandi*, the executive practices, and the materials used.

3.5. Outcomes and Digital Applications for Diverse Audiences

Several outputs were developed in the Codex 4D project, that differ in (a) type of users, (b) context of use, and (c) type of experience, and, therefore, adopting different communication styles:

- A multimedia web site (<https://codex4d.it/>, accessed on 26 April 2024) designed for in-depth educational and scientific purposes, in which the Codex 4D project, the methodologies and technologies employed, and the results of the research are recounted;
- An online virtual-reality environment (Web App), designed for the scientific visualisation and analytical exploration of the manuscript 4D model, intended for more expert users;
- A holographic showcase designed as a mixed-reality installation for museum and library audiences, in which research data are translated into an emotional narrative through a dramatic and engaging style.

3.5.1. The Web Site

From a communicative point of view, the project purpose was to shape a direct multidisciplinary experience with manuscripts.

The Codex 4D website (<https://codex4d.it>, accessed on 26 April 2024) has educational as well as scholarly value. It offers a wide variety of sections that allow users to embark on a narrative and multimedia journey, characterised by simple interactivity and aimed at a broad audience interested in learning about the context of ancient manuscripts.

The main sections of the site are as follows:

- (1) Project—The objectives and, from an educational perspective, all the survey and documentation methodologies and technologies used in the project are explained with a special focus on integration methods. The composition of the working group is also presented;
- (2) Collection—The codices are introduced and contextualised, with the possibility, for each one, to directly access the complete description, and the photo-gallery of all the sheets. For each manuscript, it is also possible to access the Web App and start the 4D exploration of the codex model, in its various configurations;
- (3) Narrated Glossary—The basic knowledge is provided to embark on the journey through the materials and stages of manuscript making (Figure 21);
- (4) Results—The outcomes of the projects, such as digital applications, deliverables, and scientific publications, are presented.

codex4d

PROJECT COLLECTION **NARRATED GLOSSARY** RESULTS EN

Home / Narrated glossary

NARRATED GLOSSARY

The narrated glossary provides the basic knowledge to undertake the journey through the manuscript, facilitating the understanding of terms and concepts that may not always be obvious. This glossary is not merely a list of definitions. On the contrary, it follows a structured logic that focuses on the materials, techniques, processes and skills needed to create a codex. It uses simple language, without claiming to be exhaustive.

Media preparation steps, writing substances, dyes and tools

Gold

Colours

Inks and pens

Paper

Parchment

Stages of book production and decoration

Collation

Folio design

Writing

Decoration

Binding

<https://codex4d.it/en/narrated-glossary/>

(a)

codex4d

PROJECT COLLECTION **NARRATED GLOSSARY** RESULTS EN

Home / Narrated glossary / Parchment

NARRATED GLOSSARY

Media preparation steps, writing substances, dyes and tools

gold

colours

inks and pens

paper

parchment

< Pigments >

When painting miniatures, the pigments used were mainly of mineral origin. These included: for the colour blue, lapis lazuli and azurite, the latter being much less precious; malachite for green; cinnabar and especially minium (hence the term 'miniature') for red and orpiment for yellow. One pigment of animal origin is purple, obtained from a mollusc. A similar purplish red can also be obtained from lichens.

Cinnabar, Europeana

Azurite, General Catalogue of the Cultural Heritage

Malachite, General Catalogue of the Cultural Heritage

(b)

Figure 21. Narrated glossary: (a) main interface; and (b) pigment section.

3.5.2. The Web App

An advanced Web3D environment is dedicated to the interactive visualisation and scientific analysis of manuscripts and the questioning of contextualised information (annotations or semantic descriptors) in four dimensions. The main target is an audience predisposed to thorough study and discussion.

The environment is based on the ATON open-source framework developed by the CNR ISPC [53,54].

Tools have been implemented allowing the user to choose to explore specific configurations and sheets of the manuscript, explore stratigraphic layers through a detection lens switching from superficial RGB to IR images, take measurements, move the lighting in the scene to better highlight specific details, and open or create annotations related to mapped information on specific points of interest. A video demo of the Web App can be seen here: <https://tube.rsi.cnr.it/w/jZi6XWdHcqMBeYZo52SKTf>, accessed on 20 April 2024.

The Web App can be accessed through a double profile (Figure 22):

- public, allowing only the exploration of existing contents;
- editor (through authentication), which can modify and create new contents.

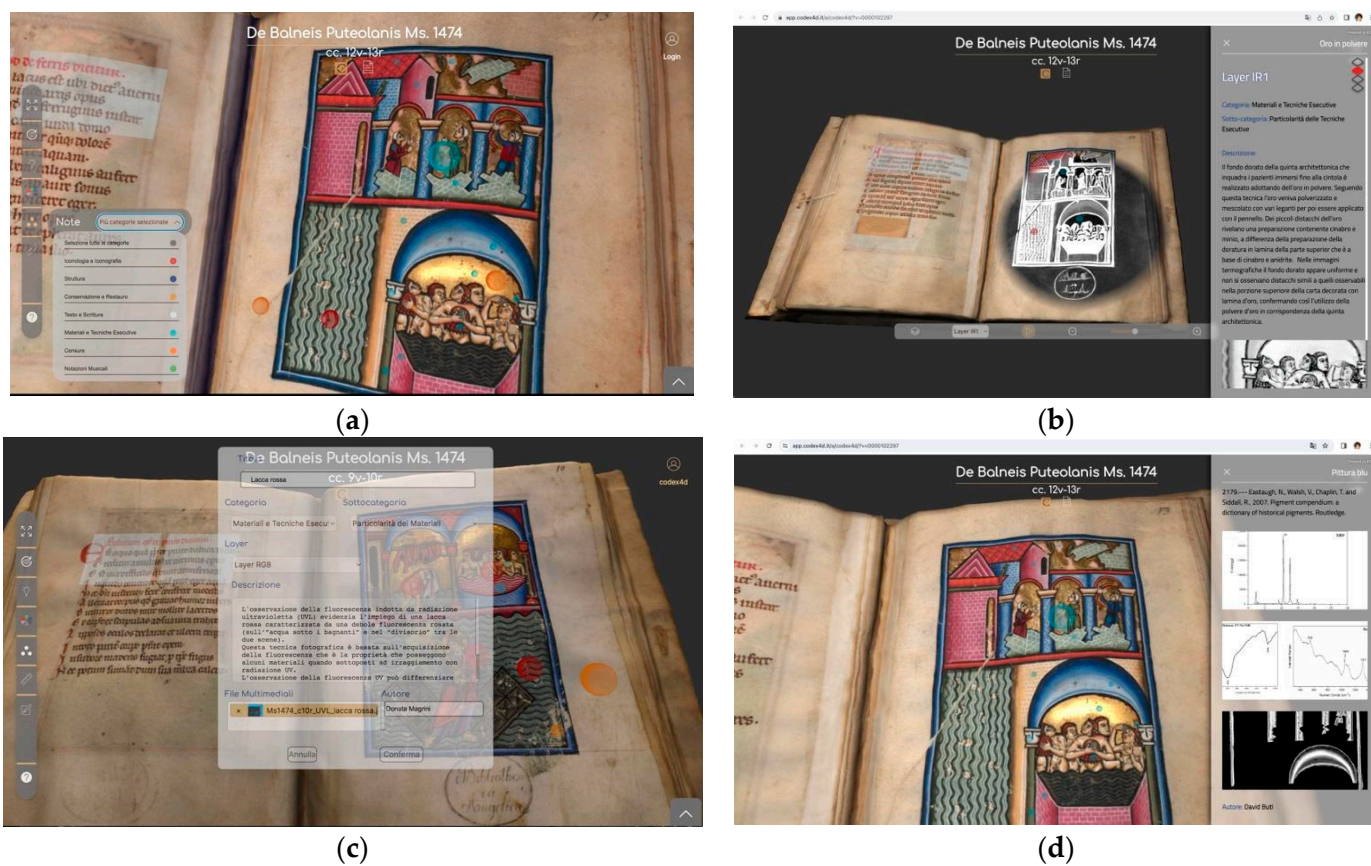


Figure 22. Tools and services developed in the Web App, ms 1474: (a) interface to filter annotations to be visualised on the 4D model; (b) annotation referred to gilding state of conservation, as revealed by thermography; (c) interface to create an annotation in the editor profile; and (d) annotation referred to the blue paint of the dome in the illumination in low register.

To organise the large amount and variety of processed content along orderly editorial lines, it was necessary to organise it into categories and subcategories (Figure 23). Such a structure is useful for editors creating new content, but also for end users who can easily focus on what they are interested in, filtering information related to the 4D model at will.

Categories	Subcategories	
Iconography and Iconology	Description	Characters and Symbols
	Dating and Attribution	Ideological Message
	Style	Sources and Traditions
	Visual Comparisons	Reconsiderations
	Ornamental Elements	Subsequent Modifications
Materials and Execution Techniques	Particularities of Materials	Particularities of Execution Techniques
Structure	Size	Re-use Elements
	Binding	Structure Particularities
	Layout	
Conservation and Restoration	Restoration	Physical Evidence
	Biological Evidence	Theft And Subtraction
	Chemical Evidence	Damage
Text and Writing	Transcription,	Translation
	Particularities of Writing	Notes
	Subsequent Amendments	
Censorship	Text Censures	Damage Censures
Musical Annotation		

Figure 23. Categories and subcategories created to manage a huge amount and variety of contents in the Codex 4D project.

As a result of the editor profile, the virtual-reality environment is being used not only as the final output of a research work but as a real tool for investigation, as a shared laboratory for the analysis, interpretation, and integration of data, updatable over time by the scientific community.

3.5.3. The Holographic Showcase

The 4D models and content that emerged from the surveys are also used inside a holographic museum showcase, based on the Pepper's Ghost technique [55,56]. The holographic showcase is designed as a mixed-reality environment; it works as a small theatre, equipped with lights and directing software that offers the possibility of activating multimedia events within it, interactively. The showcase introduces a dramaturgical storytelling: a narrator character, played by an actress filmed in green screen, lives in the illuminations, and tells that world from the inside. She is as small as the illuminated figures and performs actions or activates tools to enhance the reading and understanding of the codex (Figure 24a). In this way, the Codex 4D project aims not only to increase the scientific knowledge of the manuscript, but also to push the languages of scientific communication into new experimental terrain to attract and intrigue new audiences.

In the holographic showcase, the 4D model is again enriched with annotations dealing with the iconography, iconology, materials and techniques, and state of conservation (Figure 24b), which the user can explore by just moving his/her hand on the model, through simple gestures. Motion capture is managed by the Leap Motion sensor [57] and contributes to raising the user's curiosity and engagement (Figure 24c,d).

The Codex 4D holographic showcase was presented to the public for the first time at the exhibition "Languages of Heritage Science: from Micro to Macro", at the Genoa Science Festival (Villa Principe, 20 October–1 November 2022).



(a)



(b)



(c)



(d)

Figure 24. Holographic showcase at the Angelica Library in Rome, 2023–2024: (a) character telling stories; (b) annotation visualised in the holographic showcase related to blue pigment; (c) gesture-based interaction; and (d) exploration through stratigraphy (IR images).

On that occasion, a survey was conducted to evaluate the experience and impact of the showcase on the public, represented mainly by high school and university students, families, experts, and individual and group visitors [58].

Therefore, the contents have been enriched for the new exhibition set up at the Angelica Library in Rome, from 10 November 2023 to 8 February 2024 (Figure 24).

A movie demo of the holographic showcase can be seen here: <https://tube.rsi.cnr.it/w/uSjwd7sKQiy3y8D4TSNfhj>, accessed on 20 April 2024.

4. Discussion

The Value of the Codex Project from the Library's Perspective

The Angelica Library was founded in 1604. It is the oldest public library in Rome and one of the first in Europe, along with the Ambrosiana Library in Milan and the Bodleian Library in Oxford.

The library preserves a heritage of approximately 200,000 volumes, including circa 100,000 ancient, printed editions, including precious incunables, geographical maps, prints, and drawings.

Its manuscript collection consisting of approximately 3000 volumes originated from the convent of Sant'Agostino, considered the manuscript original nucleus donated by Roman nobles or by the friars themselves.

Furthermore, it has been enriched throughout the years with donations and acquisitions since the collection left by the founder Angelo Rocca (1546–1620). The collection has been enriched due to the purchase of the very rich library of Cardinal Domenico Passionei (1682–1761) which enriches Angelica's assets and from which some of the oldest precious manuscripts originated, such as the *De Balneis Puteolanis* from the mid-13th century (Ms. 1474) and a *Divine Comedy* with an estimated date of circa 1340 (Ms. 1102), both with admirable illuminations.

The participation of the Angelica Library as a partner in Codex 4D meant having the chance to experiment with innovative solutions to access the library heritage to view the document in a new dimension. From now on, it is possible, for example, to take real measurements on the pages or to have previously unknown information available for users, such as chemical, physical, or biological information such as the composition of minerals used in illuminations, the differences in gilding techniques, and the use of colours.

At the same time, in the field of valorisation, the methodologies and technologies used have made it possible to obtain a virtual code representation useful to approaching a greater and less expert audience through new exhibition methods that do not create problems from a conservative point of view.

In any case, without the involved authorities' material and human support, it would not have been possible to carry out this project.

The Angelica Library has been very active in organising and providing adequate spaces for surveys, actively participating in the material choice at each stage of the project, and indicating the achievable purposes.

After an initial research phase within the conspicuous heritage of the Angelica Library possessing the optimal physical characteristics in terms of size, conservation, and binding, with interesting contents for the public and peculiar characteristics such as the presence of illuminations, gold gilding leaf, or other interesting elements, the most famous Angelica Library manuscript was chosen: Ms. 1474.

The code, which contains Pietro da Eboli's work "*De Balneis Puteolorum et Baiarum*", has an exceptional value not only for the importance of the text and the quality and workmanship of the code, but also because it is the best precious example of one of the most important historical funds of the library belonging to Cardinal Domenico Passionei. Therefore, it is even excluded from scholars and guided tours; usually only a copy, avoiding the original version, is shown.

This code was chosen due to the deepening knowledge of the most studied manuscripts rich in bibliography trying to find out information relating to elements no longer visible or hidden in the structure of the manuscript, from the chemical to the physical or biological nature of the materials.

The investigations carried out on it have made it possible to go beyond just the digitisation of book assets and to investigate it with innovative but non-invasive tools and

technologies that have brought new data and, therefore, a new knowledge of the artefact, avoiding the predominance of one discipline over another.

These data were then collected, edited, and made available through new models designed for a wider audience and different groups made up of book scholars, illumination scholars, philologists, art historians, restorers, chemists, and biologists, but also simple visitors or university and school groups participating in educational visits.

Different types of users can now use the data obtained through the Angelica Library website under the headings “Catalogues” and “Digital Resources” where the link has been inserted to the Codex 4D project. In addition, through the link, the Ms. 1474 record is also available, along with its full digitisation plus the 4D model of some of its configurations and sheets.

Moreover, the Codex 4D project site is considered as a “further cataloguing tool” available along with the library’s traditional catalogues.

In the manuscript record, it is also possible to view a bibliography section which refers to further information available on ManusOnline (MOL), the database that includes the description, and, if available, the full and/or partial digitisation manuscripts preserved in public, ecclesiastical, and private Italian libraries managed by the Central Institute for the Union Catalogue of Italian Libraries and Bibliographic Information (Istituto Centrale per il Catalogo Unico delle biblioteche italiane e per le informazioni bibliografiche—ICCU).

Similarly, the MOL record will include the link to the Codex 4D record to make the two systems communicate with each other, providing users with a double search channel. Codex 4D widens the research fields and data provided by the library so far through its traditional tools and it is also designed to be used, above all, by those looking for information on iconology, iconography, conservation, restoration, techniques, making illuminations, etc.

In addition, these data were not previously available to users or scarcely found now; it will be improved whenever knowledge progresses with further studies and research.

Additionally, the information available on Codex 4D was available in the Institute in a different way, also through the holographic showcase used in the three-month stay with valuable feedback in the various organised guided tours. The holographic showcase and the exposed manuscript display case proved to be stimulating for the less specialised audience visitors to go deeply into it.

The different object perception and the possibility of being able to carry out interactive actions has produced a more engaging learning experience and a deeper knowledge.

At the end of the project, the library must now consider how to make it sustainable in the long term considering which purposes and aspects to privilege.

The website is certainly the most interesting library tool because it allows you to reflect on the creation of differentiated interfaces, languages, and various research tools for users. Therefore, improving and perfecting the tool would help to carry out investigations on documents. In addition, it is impossible to create a type of survey on every document in the library because it is neither practicable nor sustainable, requiring time but also the long-term availability of adequate and safe spaces, especially for XRF surveys which also require specific workplace safety conditions.

The choice of a classic digitisation is more practicable and sustainable, which has the merit of increasing the accessibility to the material regardless of the user’s presence at the storage location. The library can allow some documents to be studied and reproduced in their entirety and not just in some parts. Consequently, 2D digitalisation can be carried out by starting from those codes which have been studied less but contain increasingly requested documentary and historical materials using the most in-depth analysis techniques on some chosen and selected documents with peculiar characteristics or prestige. It would, therefore, be interesting to continue with the study, in the meantime, of the entire manuscript of De Balneis to investigate each illumination and have, for each part of the manuscript, a 4D model available. At the same time, to fully exploit its potential, it would

be useful to have a permanent minor-dimension holographic showcase to be placed in the library's reserved area for educational visits.

The holographic display case set in the reading room where users consult the volumes can only be managed for a limited period or during exhibitions; in the long term, it could clash with the reader's needs and the room dimensions. It would also be interesting to try to involve other similar types of libraries in the project by co-operating in the creation of a single space in which users can, for example, find all the multiple precious specimens from each Institute or a series of similar documents to be compared.

5. Conclusions

The results of complementary diagnostic investigations provide further elements in the story of the magnificent copy of *De Balneis Puteolanis*. Its sumptuousness on the one hand and its extraordinary quality on the other are confirmed by the profusion of gold, the use of ultramarine blue, the skillful use of different pigments for the reds, and, more generally, a much richer and more sophisticated palette than could be assumed from a mere visual evaluation (see Table 1).

The characterisation of the palette, and the extraordinary technical abilities of the illuminator, confirmed by analytical analysis, are emblematic. They tell the story of a luxury manuscript, produced in a prestigious *atelier* to satisfy a very cultured and sophisticated customer.

It would be essential to study other illustrated manuscripts traditionally attributed to the same cultural area in order to reconstruct assonances and dissonances in the choice of materials and execution techniques. This could add new elements to the complex debate on the production environments of illuminated manuscripts, the artists involved in their decoration, and the other actors involved in their production. Scholars wonder where, by whom, and at whose behest the masterpieces of 13th-century southern Italian illumination, culturally related to our Codex, were executed [21]. Locating the areas of production, delineating the personalities of the artists, and identifying possible patrons are the great challenges of research.

Our research cannot answer these questions, but it can confirm the existence of a production environment in which artists of great technical skill worked with precious materials to produce an illuminated book for a court or its entourage.

The Codex 4D project conforms to two types of user stories:

- (1) A researcher who has carried out a series of interdisciplinary studies on an illuminated manuscript, digitising it in 2D and 3D and collecting art-historical data related to the symbolic contents (texts and images) and data derived from the diagnostic investigation, related to the materials, execution techniques, and state of preservation. The large dataset composed of different types of information, referring to both the general context and punctual characteristics of the manuscript, need to be organised in a coherent way and made accessible through a digital environment that makes it possible not only to store and consult them, but also to annotate, edit, and further implement them in the future.

The researcher will have 2D and 3D digital environments useful for both scientific and experiential enjoyment. He will be able to upload his datasets to a database organised according to a semantic approach in which information is being structured into categories and subcategories.

Through a 3D Web App, he/she can visualise and stratigraphically explore the virtual model of the manuscript, on which information pertinent to the visible and invisible layers are annotated and contextualised, with the possibility of filtering and querying it selectively.

The Web App can be accessed as a "general user", for visualisation purposes only, or in "accredited editor" mode for integrating new content or editing it.

- (2) A visitor who approaches a manuscript in a museum showcase can enjoy and experience its meanings, stories, and personages through a dramatic storytelling; he/she can discover materials and execution techniques, easily interacting with the stratigraphic layers of the 4D model opening annotations. The experience is collective, and

a discussion and an exchange of active/passive roles in the system control, even a challenge in the interpretation of the content, developed within the group. Gamification techniques applied to the holographic showcase can enhance the involvement in, understanding of, and, therefore, accessibility to manuscripts in museums.

Therefore, primary actors of the Codex 4D project are art historians, codicologists, palaeographers, illumination experts, conservation scientists, restorers, library and archives workers, museum workers, teachers, and students.

Of course, some preconditions are needed to allow such an implementation:

- The ability to conduct 3D digitisation and stratigraphic analyses in libraries;
- The ability to operate with portable instruments for digitisation and diagnostics campaigns;
- The digitisation carried out according to certain criteria and requirements, to consistently integrate information on a multi-level virtual model;
- The construction of the triangulated digital model (mesh) according to the units of measurement, positioning, and orientation in 3D space that follow strict criteria and rules;
- An adequate resolution of the model and textures;
- An adequate organisation of the dataset for data ingestion into the database, according to a well-defined information architecture;
- The interoperability of formats and FAIR principles;
- The simplicity of interfaces to encourage easy and pleasant use;
- The usefulness, reliability, and attractiveness of storytelling;
- The periodic updating of the software framework.

In the future, we hope to be able to integrate other services such as automatic ancient handwriting transcription, automatic translations, and text-to-speech services.

A further occasion of development and tool integration is represented by the H2IOSC project (Humanities and Heritage Italian Open Science Cloud) [59], funded by the Italian National Recovery and Resilience Plan, using European resources. In this context, the Digilab platform is under development, consisting of a powerful digital platform, part of the E-RIHS infrastructure, based on the open science principle and designed to store and semantically explore cultural heritage research datasets through a wide variety of services and tools. In this context, a pilot on illuminated manuscripts is implemented that gives us the occasion to evolve the results obtained through the Codex 4D project.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/heritage7060131/s1>, Figure S1. Reflectance spectrum collected on the parchment (point 48). The spectrum is dominated by protein signals in the NIR region. The signals in the range between 2250 and 2350 nm could be ascribed to lipids; Figure S2. Reflectance spectrum collected on point 6. The spectrum displays the signal of lead white; Figure S3. XRF spectrum collected on point 5. The presence of lead peaks (Pb) suggests the use of lead white in mixture with the red organic lake. The latest was identified with hyperspectral imaging (Figure 11c) and UV-vis-NIR spectroscopy (Figure 12); Figure S4. XRF spectrum collected on point 7. The relatively high intensity of iron peaks (Fe) suggests the use of ochre(s) to obtain the brown hue observed on the hair of the bathers; Figure S5. Reflectance spectrum of point 35. The spectrum displays the signal of ultramarine blue; Figure S6. Reflectance spectrum acquired on point 19. The spectrum exhibits the signals of a copper-based green pigment and lead white; Figure S7. Optical image that focuses on the green column present in the lower part of the illumination, with indication of the XRF measurements locations (a); XRF spectra collected on the darker (b) and lighter (c) green colour of the column (points 3 and 4). In both spectra, the peaks of arsenic (As) and lead (Pb) are ascribed to the presence of vergaut and lead white, respectively. The peak of copper, that is particularly intense in the spectrum in (b), suggests the presence of a copper-based pigment used as glazing; Figure S8. Optical images of the yellow architecture (a) and the bathers (b) in the lower part of the illumination, with indication of the XRF measurements location; XRF spectra of points 47 and 9 (c).

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