Journal of Cultural Heritage 62 (2023) 72–77

Contents lists available at ScienceDirect

Journal of Cultural Heritage

journal homepage: www.elsevier.com/locate/culher

VSI: LACONA XIII

Evaluating the integration of Thermal Quasi-Reflectography in manuscript imaging diagnostic protocols to improve non-invasive materials investigation

Dafne Cimino[a], Giacomo Marchioro[b], Paolo De Paolis[b], Claudia Daffara[a,*]

[a] *Department of Computer Science, University of Verona, Ca' Vignal 2, Strada Le Grazie 15, 37134 Verona, Italy*
[b] *Department of Cultures and Civilizations, University of Verona, Viale Università 4, 37129 Verona, Italy*

A R T I C L E I N F O

Article history:
Received 31 January 2023
Accepted 28 April 2023
Available online 24 May 2023

Keywords:
Thermal Quasi-Reflectography (TQR)
Mid infrared imaging
Materials characterisation
Integrated approach
Imaging protocol
Manuscripts

A B S T R A C T

Multispectral imaging techniques applied to book heritage are useful to scholars to obtain information on the materials under investigation. The novel introduction of Thermal Quasi-Reflectography (TQR) technique, operating in the medium wave infrared (MWIR) spectral range, can flank conventional diagnostic techniques such as UV-based methods and IR imaging techniques in the 850–1700 nm range on manuscript acquisition. As proof of concept, this work investigates the application of TQR on the Ms. XL (38) palimpsest, known as *Vergilius Veronensis*, of the Biblioteca Capitolare of Verona. While investigating the manuscript with full-field imaging technique, this work focuses its application to improve the mapping of conservation materials. The manuscript contains several traces of reagents and conservation treatments applied during its conservation history. The study compared the manuscript materials response obtained with TQR with the response collected using UV-induced visible fluorescence (UVL), UV reflected imaging (UVR), and NIR imaging in the 850–1050 nm and 900–1700 nm bands. Being the TQR technique sensitive to surface materials with MWIR reflectance features, it may especially provide more accurate documentation of the restoration history of the object. TQR imaging discriminated non-homogeneities of products in the surface layer thanks to an enhanced MWIR contrast. The TQR image response on manuscript materials should be further investigated and compared to reflectance spectroscopic data. The results of this study demonstrate the added value of TQR imaging for manuscript diagnostics, for which integration of the TQR technique in the standard protocol is desirable.

1. Introduction and research aim

Book heritage is fascinating and saves our history but is made of very fragile materials such as parchment, papyrus, and paper sensitive to humidity, light, heat and mechanical stresses [1–5]. For this reason, it is most of the time kept in the dark. Scholars can take advantage of digitalisation programs, having this way high-quality images of the manuscript. Nevertheless, common photographic systems do not allow them to overcome stains, ink fading, and degradation issues. In recent years, non-invasive analytical protocols have flanked the current digitalisation practice [6,7]: besides regular photographic instrumentations (cameras or scanners), monochromatic sources in the ultraviolet (UV), visible (Vis), and near-infrared (NIR) up to 1050 nm and high-performance sensors are used to acquire high-resolution images. Thanks to the different penetration levels and interaction of radiation with matter, it is possible to obtain information from the surface to the subsurface of the manuscript. UV-based imaging in reflection (UVR) or induced luminescence (UVL) mode allows pinpointing varnishes, retouchings, and faded ink, or identifying pigments (e.g., cadmium-based), while NIR imaging allows investigating underwriting and underdrawing [8–11]. The use of narrow-band LED sources allows to distinguish smaller spectral features in the response of the materials increasing the diagnostic values of the analysis [12]. Data visualization and elaboration, e.g., the creation of false-colour images or the application of image processing algorithms, can highlight faded text or estimate chemical information about materials [13,14]. These pieces of evidence provide already good information to guide the selection of areas, in which to carry out pointwise spectroscopic analyses to reach the identification of materials employed in the centuries [15], for instance, different inks, pigments, and the solutions used by paleographers for increas-

* Corresponding author.
E-mail address: claudia.daffara@univr.it (C. Daffara).

https://doi.org/10.1016/j.culher.2023.04.009

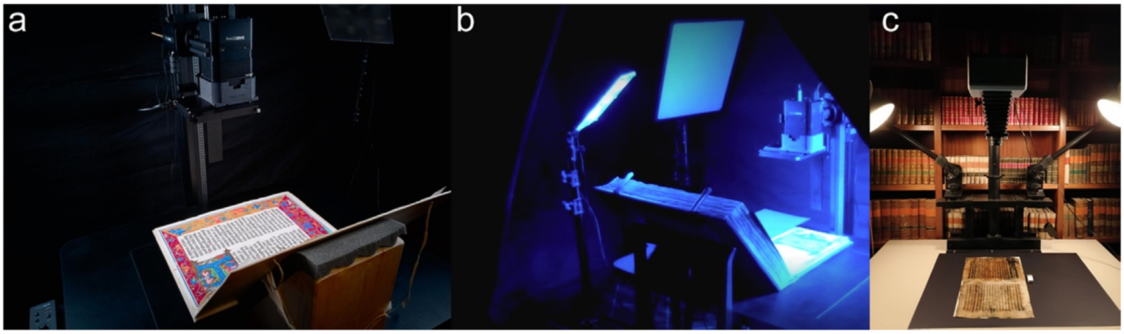

Fig. 1. Setup for the imaging acquisition of manuscripts at the Biblioteca Capitolare of Verona. (a,b) the Phase One RAINBOW system for UV–vis–NIR multimodal imaging in reflectance and luminescence mode. (c) IRR acquisition of the Vergilius Veronensis with the Apollo system.

ing the readability of the scripts or the conservation treatments applied. Nevertheless, some matter features might still be dumb in the mentioned ranges, being detectable with IR reflectography (IRR) at longer wavelengths (up to 2500 nm).

In this scenario, the Thermal Quasi-Reflectography (TQR) technique [16] is expected to provide additional information about the materials employed, working in the 3–5 μm region (Medium Wave IR, MWIR) and collecting thermal images in reflectance mode. The diagnostic potential of TQR, also known as MWIR imaging or mid-IR reflectography, was first demonstrated on paintings [25], also in a dual-mode systematic approach with thermography [17] and was well received by the heritage community since conservators demanded the use of TQR to support the restoration of the *Monocromo* by Leonardo [18]. The application on manuscripts has already been shown [19], underlying the potential for further study. However, the integration of the TQR method in the manuscript imaging protocol and its complementarity with the UV–vis–NIR acquisition techniques have not been evaluated. While NIR photography and IRR provide information related to the layer underneath, the TQR technique acquires in quasi-reflectance approximation the MWIR signal from the artwork surface, also linked with the chemical composition as suggested by preliminary tests [16,25]. After a proper optimization of the imaging protocol and the source-camera setup, the MWIR range ensures a sharp imaging tool with suitable spatial and contrast resolution since this thermal band exhibits low optical diffraction and background radiation [17]. This allows to effectively perform the mosaicking of multiple thermal frames to solve the problem of the low resolution of MWIR sensors: this was shown in [18], where a 500 μm pixel size at object plane was required to effectively investigate the Leonardo fresco.

The present work introduces a multimodal approach which flanks TQR in the MWIR in quasi-reflectance mode to UV–vis–NIR in reflectance and luminescence imaging. Thanks to this multiband protocol the historical book heritage of Verona with its spearheads in the *Biblioteca Capitolare* collection is being investigated in a collaborative project.

2. Materials and methods

2.1. The heritage of the Biblioteca Capitolare *of Verona and the case study of the* Vergilius Veronensis *palimpsest*

The library of the Chapter of Verona, as the heir of an ancient late antique library fund, is believed to be the oldest still-functioning library in the world; it owns a number of precious ancient manuscripts, amongst which the palimpsest Ms. XL (38), containing fragments of classical texts (Vergil, Livy, a Latin translation of Euclid, and a philosophical text), known as *Vergilius Veronensis* for the section with Vergil's fragments. A palimpsest is a manuscript in which the original text was cancelled (*scriptio inferior*) with various methods (scraping or washing the original script) to reuse the parchment to write another text (*scriptio superior*). In this case, the location of both scripts is the subject of discussion: the *scriptio superior* has been dated to the 7th–8th century by a hand trained to write in Luxeuil minuscule, but it is not certain whether the scribe actually copied in Luxeuil or another centre in Gaul or Northern Italy; the *scriptio inferior* contains various fragments of Virgil's works (Eclogues, Georgics and Aeneid), accompanied in the margins by an ancient commentary, and can be dated to the last decades of 5th century, with an uncertain location between Gaul and Northern Italy (Verona or Mantua). The text is written with ink on parchment and nowadays appears with several stains due to two treatments aiming at reading what was cancelled carried out mainly with gallnuts and Gioberti tincture, according to the historical recipe books [20,21].

2.2. Instrumentation

The workflow at the *Biblioteca Capitolare* of Verona follows a standardised imaging protocol to investigate its heritage, based on a multimodal and multiband imaging sequence which took advantage of three cameras working in three different spectral ranges. This approach is based on the CHARISMA European project experience which developed a user manual as output of the research [11].

Data in the UV–vis–NIR range were acquired using the Phase One RAINBOW system equipped with an iXG 100MP Wide Spectrum camera (Si CMOS sensor, 350–1050 nm), a filter wheel and a Schneider Kreuznach RS 72 mm lens mounted on a reprographic column (Fig. 1a, b). A Dedo DLED7 UV 365 nm by Dedo Weigert Film GmbH coupled to a UV pass filter was used for illuminating the palimpsest with UVA light and kept at approximately 1.5 m from the manuscript.

A GoldenThread/DICE Device Level Target (DLT) and an Object-Level Target by Image Science Associates were used for images acquired using Vis light and the Target UV by UV Innovations^{TM} for fluorescence images. The images were elaborated using Capture ONE 20 by PhaseONE and Rainbow MSI software.

IRR was performed with the Apollo scanning camera (InGaAs sensor, 900–1700 nm) commercialised by Opus Instruments and halogen lamps at 150 W (Fig. 1c). The Opus Apollo software was used for controlling the acquisition.

TQR in the MWIR range 3–5 μm was carried out with a FLIR camera, model X6540sc, with a cooled InSb detector with a thermal sensitivity lower than 25 mK. A 25 mm lens with a field of view of 22° × 17° was used. The palimpsest was irradiated using 150 W underpowered halogen lamps kept at 1 m from the object. The ResearchIR software by FLIR was used for assessing the acquisition of the raw thermal images and, in a second step, they were

Fig. 2. Palimpsest Ms. XL (38), folium 324, Vis image.

Fig. 3. Top: folium 324, UVL; bottom: conservation treatment (a) vis, (b) UVL: the product was applied by brush along text lines in a film non-homogeneous in thickness. UVL images were processed to improve contrast.

mosaicked together for producing an image of the manuscript at higher resolution.

The whole parchment sized 41 cm × 26 cm was acquired with the PhaseONE Rainbow setup in a single shot at 640 ppi. With the Apollo camera, an image of 486 ppi was obtained by stitching two scans (each scan is composed of multiple acquisition acquired in the image plane of the camera). A total of 13 acquisitions with the FLIR camera were stitched together to reach an image at 168 ppi.

Data handling and image processing were performed using Python programming language. Using OpenCV library [22] it is

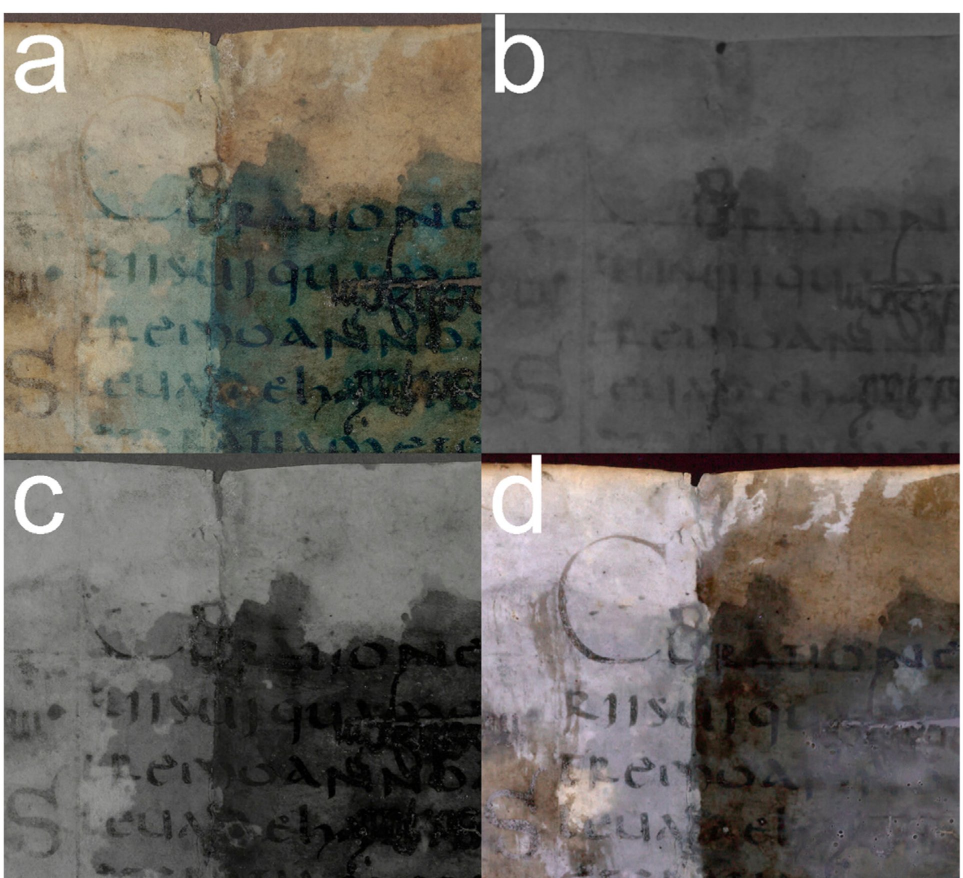

Fig. 4. Folium 324-flipped letter “C”, (a) vis, (b) IRR, (c) NIR at 850 nm, (d) UVL (processed image with improved contrast).

Fig. 5. Folium 324, IRR; highlighted the evidence of material at the surface, not observed in the UVL image.

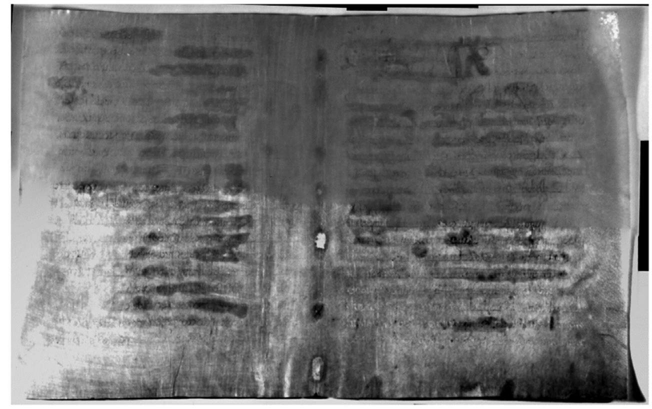

Fig. 6. Folium 267; TQR acquisition.

possible to perform stitching of the images and apply batch processing to them (e.g., background subtraction and histogram adjustment).

3. Results and discussion

The manuscript is in a good conservation state, thanks also to several conservation interventions (filling of holes, lacunae integration, application of a consolidant to prevent further lack of fragments), however, the total overlapping of the scripts and the consequences of the tinctures reaction make the text not fully readable. The *scriptio inferior* is spread in four columns, pinpointing by blue colour as a consequence of the reaction of the Gioberti tincture, whereas the *scriptio superior* is more linear, divided into the two halves of the folium, dark ink writing (Fig. 2).

A diffused corrosion is observable, the consequence of the treatment with the Gioberti tincture. The application of both gallnut and the acidic solution of potassium ferrocyanide creates coloured complexes with the metal iron of the faded ink, but at the same time, it is dangerous for the preservation of the parchment and other inks present, also considering that the chemical reaction might continue longer than the treatment itself. At the same time, residues of these two procedures are visible in large areas of the *folium*, as brownish -due to tannins- and bluish – due to the formation of Prussian blue – stains [21].

In addition to bringing out the inscriptions, the non-invasive protocol allows highlighting different conservation treatments.

UVL imaging (Fig. 3) detects the widespread presence of a product with a weak whitish fluorescence, most probably an organic resin of polymeric origin applied to consolidate corroded areas and fix voids. The resin path follows stripes, suggesting an application by brush along the text lines. Since in the Vis image the aspect of this layer is transparent, whitish areas highlighted in the UVL image can be related to a larger deposition of resin more than a limited miscibility or a phase separation of the product compo-

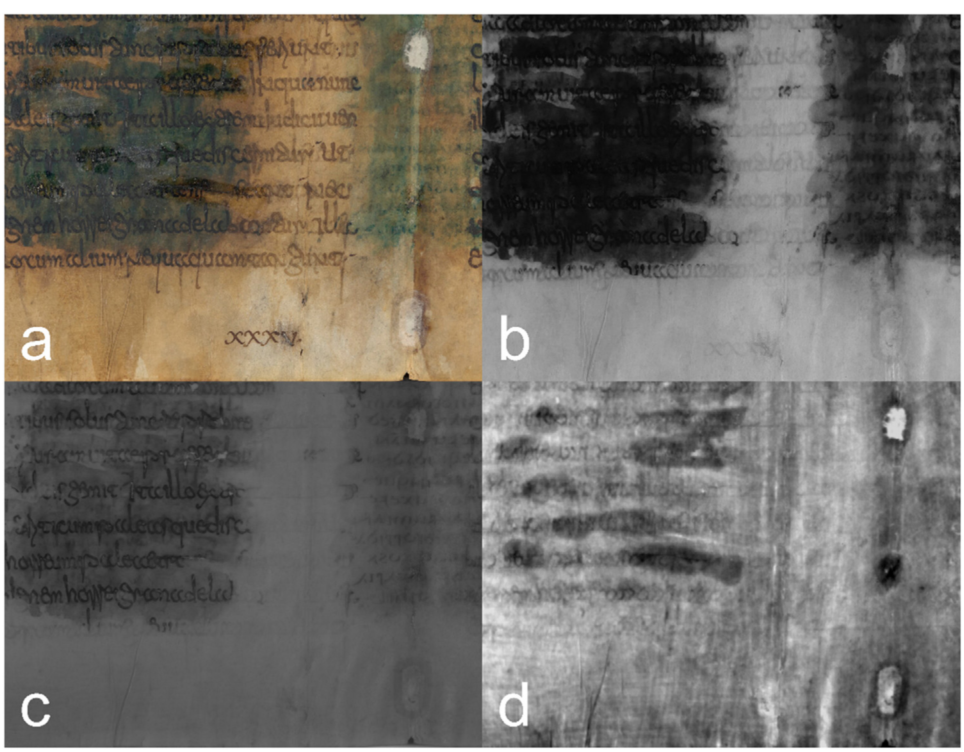

Fig. 7. Folium 267; detail of the bottom part with the integrations along the central line: (a) vis, (b) NIR, (c) IRR, (d) TQR.

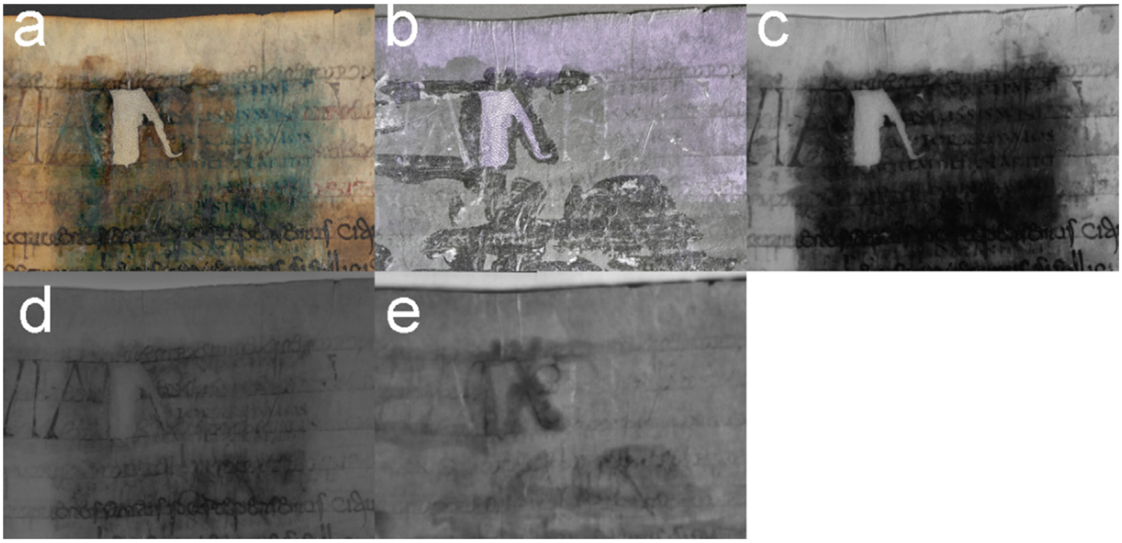

Fig. 8. Folium 267; detail of the upper part with the parchment integration: the adhesive can be observed on the surface of the original parchment in the UVR, while on the modern material is documented only by TQR. (a) Vis, (b) UVR, (c) NIR, (d) IRR, (e) TQR.

nents (in case of a multicomponent formulation) [23,24] and the formation of bubbles occurred during the polymerisation, with the evaporation of the solvent (Fig. 3a, b).

At the bottom of the *folium*, just behind the central line, UVL well detects the initial “C” letter, not fully treated with the tincture (Fig. 4a, d). This detail is not detected in the NIR (Fig. 4b,c), probably because written with an ink free of carbon particles, transparent in this region. This chemical information in the areas where Gioberti tincture reacted was lost. The employment of NIR radiation in a narrow range (850 nm, Fig. 4c) results in difficult readability because of the high absorbance of Prussian blue at this wavelength, which hides the script. Further features are highlighted at longer wavelengths (900–1700 nm), where both Prussian blue and gallnut inks are more transparent and the image contrast amongst the different texts is higher (Fig. 4d), increasing their detectability. From IRR images (Fig. 5), it is also possible to follow the guidelines drawn by the scribe and obtain more evidence of the consolidation treatment. Furthermore, on the left, the presence of a shade due to an applied transparent film not detected by UVL imaging led to the hypothesis of the employment of another conservation resin. However, additional analyses are needed for investigating the material on this region of interest.

Fig. 6 reports the acquisition of the manuscript with the added TQR technique. TQR imaging provides information about non-homogeneity of the resin film thanks to a high image contrast in the MWIR range. The different response could be due to thickness variations. This feature is unclear in the UVL image, due to the weak fluorescence signal. Interestingly, TQR detects a different thermal behaviour of the integrations in the *folium*, made by Japanese paper (lighter spots), parchment, and resin (darker spots), thus highlighting the different application methods. Indeed, the integrations made with paper slightly overlapped the original substrate and the joint was spread with the adhesive (Fig. 7). In the case of the parchment integration, the edges of the recent material are linked by glue to the original one (Fig. 8). It is worth to notice how TQR detects the presence of the adhesive also on the modern parchment (Fig. 8e). This result is unclear in the UVR images (Fig. 8b). It is possible to suppose that the same organic polymeric resin was used as consolidant and adhesive, just in different dilution.

4. Conclusion

The practice of investigating book heritage through non-invasive optical imaging is common and advantages derived by the employment of UV-based photography are well known since the surface can be well described in terms of the distinction of materials employed and applied. The imaging campaign carried out on the palimpsest Ms. XL (38) of the *Biblioteca Capitolare* of Verona, was the opportunity to extend the standard UV–vis–NIR imaging protocol to the IR range up to 5000 nm thanks to the application of IRR and TQR techniques. The case-study manuscript is in a good conservation state, but corrosive treatment to recover cancelled writings compromised the readability of the text, damaging the parchment as well. Data acquired revealed a widespread presence of conservation treatments, in particular a consolidation action to fill *lacunae* of the original substrate. UVR and UVL imaging detected the areas treated suggesting inhomogeneities, while the TQR imaging was shown to better discriminate the thicknesses of the product layer thanks to an enhanced MWIR contrast amongst materials at the surface level due to their chemical differences. For the same reason, in addition, TQR discriminated the Japanese paper from the modern parchment employed for the integration of the *lacunae*. TQR provided results complementary to UV-based and IR-based imaging using CMOS (850–1050 nm) and InGaAs (900–1700 nm) cameras.

The results of this work, although preliminary, have demonstrated the added value of TQR imaging for manuscript diagnostics, for which integration of the TQR technique in the standard protocol is desirable. Considering that off-the-shelf TQR platform are not available, so far, and that the integration of TQR acquisition in the routine imaging of manuscripts requires efforts, it should be preferably applied to a selection of objects, for instance, with a particular conservation history. The UV–vis–NIR image stack, the IRR and TQR reflectance maps, spatially registered and jointly used, were shown able to highlight several matter features. Being the TQR technique sensitive to surface materials with MWIR reflectance features, it may especially provide more accurate documentation of the restoration history of the object. TQR results should be further investigated and compared to spectroscopic data, in particular external reflection infrared spectroscopy in the MWIR region, to evaluate correlations between imaging response and present materials in order to extract information on the chemical families on the art matter at the surface. Thus, the described protocol can be helpful for a first materials discrimination, other than in the selection of areas to be further investigated through spectroscopic pointwise analyses, with the introduction of TQR making this supervision more accurate. On this regard, the proof-of-concept given on the *Vergilius Veronensis* of the *Biblioteca Capitolare* of Verona underlines the potential for further investigations. Future work is planned involving chemical investigations on a testbed with material mockups.

CRediT authorship contribution statement

Dafne Cimino: Writing – original draft, Writing – review & editing, Data curation. **Giacomo Marchioro:** Conceptualization, Validation, Visualization, Writing – review & editing. **Paolo De Paolis:** Writing – review & editing. **Claudia Daffara:** Conceptualization, Resources, Writing – review & editing, Supervision. All authors have read and agreed to the published version of the manuscript.

Acknowledgements

The authors thank the project manager, Dr. Timoty Leonardi, and the president, Mons. Bruno Fasani, of the Foundation of the Biblioteca Capitolare of Verona. They also would like to thank Prof. Paolo Pellegrini, coordinator of the LaMeDan laboratory of the University of Verona.

Funding

The research was partially funded by the Italian National Research Programme MUR-DM 737/2021 of PNR.

References

[1] A. Boukir, L. Hajji, B. Zghari, Effect of moist and dry heat weathering conditions on cellulose degradation of historical manuscripts exposed to accelerated ageing: 13C NMR and FTIR spectroscopy as a non-invasive monitoring approach, J. Mater. Environ. Sci. 9 (2018) 641–654, doi:10.26872/jmes.2018.9.2.71.

[2] C. Chahine, Changes in hydrothermal stability of leather and parchment with deterioration: a DSC study, Thermochim. Acta 365 (1–2) (2000) 101–110, doi:10.1016/S0040-6031(00)00617-1.

[3] E. Badea, G. Della Gatta, T. Usacheva, Effects of temperature and relative humidity on fibrillar collagen in parchment: a micro differential scanning calorimetry (micro DSC) study, Polym. Degrad. Stab. 97 (3) (2012) 346–353, doi:10.1016/j.polymdegradstab.2011.12.013.

[4] P. Budrugeac, E. Badea, G. Della Gatta, L. Miu, A. Comănescu, A DSC study of deterioration caused by environmental chemical pollutants to parchment, a collagen-based material, Thermochim. Acta 500 (1–2) (2010) 51–62, doi:10.1016/j.tca.2009.12.010.

[5] Z. Sebestyén, Z. Czégény, E. Badea, C. Carsote, C. Şendrea, E. Barta-Rajnai, J. Bozi, E. Jakab, Thermal characterization of new, artificially aged and historical leather and parchment, J. Anal. Appl. Pyrolysis 115 (2015) 419–427, doi:10.1016/j.jaap.2015.08.022.

[6] W.L. Filho, P. Yang, J.H.P.P. Eustachio, A.M. Azul, J.C. Gellers, A. Gielczyk, M.A. Pimenta Dinis, V. Kozlova, Deploying digitalisation and artificial intelligence in sustainable development research, Environ., Dev. Sustain. (2022), doi:10.1007/s10668-022-02252-3.

[7] I. Beavan, M. Amott, C. Mclaren, Text and illustration: the digitisation of a medieval manuscript, Comput. Hum. 31 (1997) 61–71, doi:10.1023/A:1000494006349.

[8] A. Pelagotti, L. Pezzati, N. Bevilacqua, V. Vascotto, V. Reillon, C. Daffara, A study of UV fluorescence emission of painting materials, Proceedings of ART'05 8th International Conference on Non Destructive Investigations and Microanalysis for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Lecce, Italy, 2005, pp. 1–14.

[9] E.R. De La Rie, Fluorescence of paint and varnish layers (part 1), Stud. Conserv. 27 (1) (1982) 1–7.

[10] A. Pelagotti, L. Pezzati, A. Piva, A. Del Mastio, Multispectral UV fluorescence analysis of painted surfaces, in: 14th European Signal Processing Conference, 2006, Florence, Italy, 2006, pp. 1–5.

[11] Dyer, J., Verri, G., Cupitt, J., Dyer, J., Verri, G., & Cupitt, J. (2013). Multispectral imaging in reflectance and photo-induced luminescence modes: a user manual, version 1.0

[12] R.L. Easton, W.A. Christens-Barry, K.T. Knox, Spectral image processing and analysis of the Archimedes Palimpsest, in: 2011 19th European Signal Processing Conference, Barcelona, Spain, 2011, pp. 1440–1444.

[13] A. Tonazzini, E. Salerno, Z.A. Abdel-Salam, M.A. Harith, L. Marras, A. Botto, B. Campanella, S. Legnaioli, S. Pagnotta, F. Poggialini, V. Palleschi, Analytical and mathematical methods for revealing hidden details in ancient manuscripts and paintings: a review, J. Adv. Res. 17 (2019) 31–42, doi:10.1016/j.jare.2019.01.003.

[14] F. Pottier, A. Michelin, L. Robinet, Recovering illegible writings in fire-damaged medieval manuscripts through data treatment of UV-fluorescence photography, J. Cult. Herit. 36 (2019) 183–190, doi:10.1016/j.culher.2018.08.012.

[15] P. Ricciardi, A. Mazzinghi, S. Legnaioli, C. Ruberto, L. Castelli, The choir books of San Giorgio Maggiore in Venice: results of in depth non-invasive analyses, Heritage 2 (2) (2019) 1684–1701, doi:10.3390/heritage2020103.

[16] C. Daffara, D. Ambrosini, L. Pezzati, D. Paoletti, Thermal quasi-reflectography: a new imaging tool in art conservation, Opt. Express 20 (13) (2012) 14746–14753, doi:10.1364/OE.20.014746.

[17] C. Daffara, S. Parisotto, D. Ambrosini, Multipurpose, dual-mode imaging in the 3–5 μm range (MWIR) for artwork diagnostics: a systematic approach, Opt. Lasers Eng. 104 (2018) 266–273.

[18] C. Daffara, S. Parisotto, P.I. Mariotti, D. Ambrosini, Dual mode imaging in mid infrared with thermal signal reconstruction for innovative diagnostics of the "Monocromo" by Leonardo da Vinci, Sci. Rep. 11 (1) (2021) 22482, doi:10.1016/j.optlaseng.2017.10.006.

[19] N. Orazi, Mid-wave infrared reflectography and thermography for the study of ancient books: a review, Stud. Conserv. 65 (8) (2020) 437–449, doi:10.1080/00393630.2020.1734383.

[20] F. Briguglio, Il Codice Veronese in Trasparenza. Genesi e Formazione Del Testo Delle Istitutzioni di Gaio, BUP Bonomia University Press, 2012.

[21] Albrecht F., in Driscoll M.J. (ed.) Care and Conservation of Manuscripts, Museum Tusculanum Press, Between boon and bane: the use of chemical reagents in palimpsest research in the nineteenth century, 2012, 13

[22] G. Bradski, Dr. Dobb's Journal: software tools for the professional programmer, OpenCV Lib. 25 (11) (2000) 120–123.

[23] R. Ploeger, Differential scanning calorimetry for art conservation graduate students: a practical laboratory exercise using polymer blends, J. Chem. Educ. 95 (7) (2018) 1192–1197, doi:10.1021/acs.jchemed.7b00976.

[24] C. Invernizzi, G.V. Fichera, M. Licchelli, M. Malagodi, A non-invasive stratigraphic study by reflection FT-IR spectroscopy and UV-induced fluorescence technique: the case of historical violins, Microchem. J. 138 (2018) 273–281, doi:10.1016/j.microc.2018.01.021.

[25] C. Daffara, D. Ambrosini, L. Pezzati, P.I. Mariotti, Mid-infrared reflectography for the analysis of pictorial surface layers in artworks, AIP Conf. Proc. 1537 (1) (2003) 68–75.