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Characterization of Varnish Ageing and its Consequences on Terahertz Imagery: Demonstration on a Painting Presumed of the French Renaissance

Q. Cassar[1] · C. L. Koch-Dandolo[1] · J. P. Guillet[1] · M. Roux[2] · F. Fauquet[1] · J. B. Perraud[1] · P. Mounaix[1]

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Abstract
We report on advance developments of terahertz system data analysis for measuring the thicknesses of multiple films for non-contact control in heritage science. We provide the analysis of time-domain data regarding the measurements conducted on a French Renaissance painting realized on a copper substrate. The piece of art is made of a varnish layer deposited on the different painting layers. We specifically focus on the dielectric characterization of the varnish layer and its ageing consequences on THz images that are also reported here and revealed optically hidden details.

Keywords Terahertz imaging · Heritage science · Inverse electromagnetic problem · Varnish layer

1 Introduction

Thanks to their multiple properties including material characterization, penetration through optically opaque samples, or their non-ionizing nature, terahertz radiations seem to be a first-rate choice to add to the electromagnetic arsenal [1] of curators for the analysis and the restoration of culturally significant paintings [2–4]. While X-rays, ultraviolet, and infrared lights are employed to study underpaints, underdrawings, and varnish surface, respectively, terahertz waves have been mainly used

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✉ P. Mounaix
patrick.mounaix@u-bordeaux.fr

Extended author information available on the last page of the article.

to screen the possible corrosion appearing on metallic substrates, beneath paint layers [5, 6]. The oxidation can be perceived by examining the reflected terahertz time-domain electromagnetic field correlated with paint thicknesses and substrate shallow roughness [7, 8]. Moreover, the dielectric profile of an oxidized metal is—logically—different from its non-altered counterpart, resulting in a contrast between corroded areas and preserved ones. Hence, in such a context, pulsed terahertz inspection is favorable as it provides multivariate information about the analyzed metallic substrate. In addition, time-of-flight measurement linked to pulsed terahertz spectro-imaging may serve to quantify the thickness of the successive paint layers. Although the determination of paint layer thickness is, to date, mainly conducted for car and aeronautic industries due to the dielectric homogeneity of manufactured layers [9, 10], some challenging studies reported cross-section (B-scan) and top-view terahertz images (C-scan) of artworks, providing details that were, until then, non-accessible [11, 12].

In this paper, the analysis of a seventeenth century painting, shown in Fig. 1, realized on a copper substrate is reported. Painting on copper was developed to provide rigid and non-absorbent support for oil techniques [13]. Moreover, sixteenth to seventeenth century painters have favored copper due to its smooth surface allowing fine details, its durability, and its robustness. Copper is more resilient than canvas or wood panel as a support for oil painting as it does not decompose or cannot be plagued by insects. Understanding the way these masterpieces have been made is a challenging

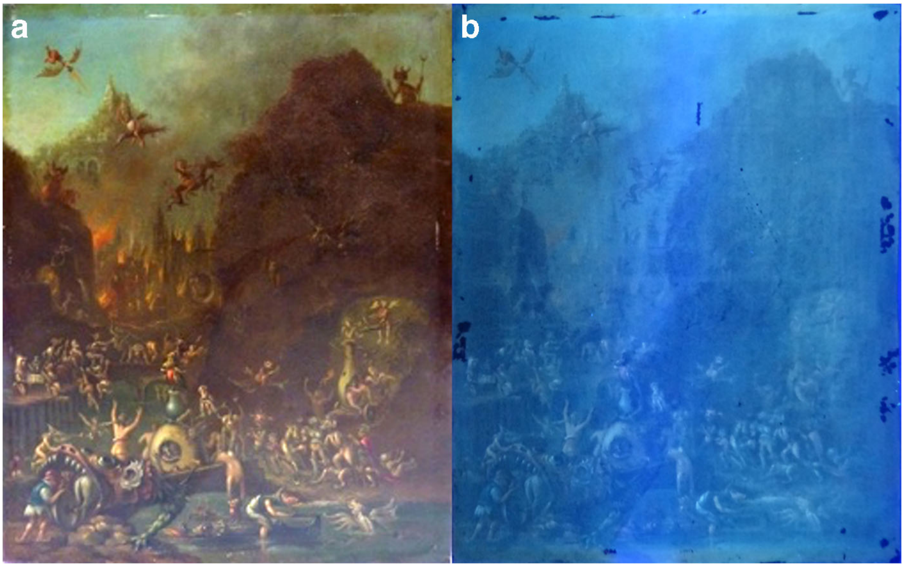

Fig. 1 **a** Photograph of the oil on copper plate painting under inspection (210 × 270) mm^2. **b** Visible/UV superimposition. The lamp is made of glass with mercury vapor, filtered with nickel oxide, and gives a UV light. It highlights the fluorescence and phosphorescence of certain bodies and penetrates the varnish, highlighting the surface repaints. The fluorescence of old varnishes (natural resins) gives a milky, greenish, and slightly cloudy appearance. Dark spots are on their parts, assumed to be latter additions, i.e., overpaintings

task due to the lack of historical reports and documentation. As used material and employed technique identification are preliminary to any restoration acts, the main objective is often to provide from the inspection of the painting information about the different paint layers. Hereafter, the focus is placed on the characterization of the painting varnish layer that degrades over time, and its impact on terahertz imaging. Varnish properties can also be obtained by other imaging devices such as ultraviolet [14] optical coherence tomography (OCT) [15] in a faster and easier way. Nevertheless, Vis fluorescence induced by UV radiation is a photographic technique and not a spectroscopic one. Therefore, it does not provide any information about the varnish thickness and cannot characterize the varnish uniquely. In fact, while varnish fluorescence colors can give an indication to conservators, they are not sufficient to uniquely identify a varnish or the presence of a varnish. Many factors can influence the fluorescence colors and the fluorescence itself, like the aging state of the varnish, the presence of impurities and false positive, the concentration, the type of pigments below the varnish layer, and phenomena such as fluorescence absorption by neighboring pigmented particles. Additionally, the terms that are commonly used to define fluorescence colors, such as *bluish*, *light orange*, or *greenish*, depend on the digital characteristic of the camera (color restitution) and the perception of the operator. Hence, such a method cannot be considered objective and cannot be standardized. On its part, OCT measurements can be tedious due to the presence of metallic supports which may induce signal saturation. Moreover, scanning the painting by means of terahertz time-domain gives simultaneously the view of the painting for larger areas than OCT, plus it penetrates deeper inside the painting, i.e., down to the support [16, 17]. Terahertz may therefore be seen as a tool to overpass the aforementioned limitations and a way to potentially detect overpaintings, painting losses, *pentimenti*, e.g., the change of the final figures as regard to the original artist plan, as well as layer detachment (in B-scans), areas in which the substrate is affected by corrosion and the varnish intrinsic and extrinsic properties.

Varnishes are natural or synthetic resins solubilized in an organic solvent that dry when thinly deposited on a surface. The nature of such varnishes has changed throughout history but tree resins (mastic and dammar), fossil resins (copal), and insect excretions (shellac) stand as the most frequently used materials. Once deposited, the varnish gives to the painting its eventual aspect. Hence, the painting optical properties are directly related to the state of the varnish. The varnish layer degrades over time due to external contamination, inherent ageing, or light pollution. The generic term of degradation denotes concomitantly the cracking, the fading, and the yellowing of the protective layer. Cleaning and restoring the protective layer are therefore essential to preserve any masterpiece.

In the following, the varnish layer properties of the painting under study are extracted by means of inverse electromagnetic problem solving. The compliance of the numerical extraction is evaluated according to other measurement techniques. Ultimately, such a procedure is aimed to provide to curators the thickness and the overall state of the varnish to facilitate its restoration, therefore preserving the pigments underneath [18]. In addition to the extraction of the varnish thickness, the impact of the protective layer onto terahertz imaging was investigated. Both pulsed and continuous regimes were employed respectively from 100 GHz to 2 THz for the pulsed regime and at 2.5 THz and 3.8 THz for the continuous wave one. The varnish layer is reported to have a drastic impact on imaging, fading the overall contrast.

2 Methods for Property Extraction

Sample surface sensing was performed by means of pulsed terahertz spectroscopy. The terahertz pulses were generated by focusing a femtosecond near-infrared laser onto the gap separating the two electrodes of a GaAs photoconductive antenna. The generated charge carriers are then accelerated in the electric force field of the biased antenna. The acceleration of the photogenerated carriers produces a transient current that drives the antenna and that is eventually emitted as terahertz radiation. The emitted terahertz pulses are then focused, using a 50-mm focal length plano-convex tsurupica lens (Microtech Instruments, USA), on the piece of art. Coherent photoconductive detection of the reflected pulses is performed using the reverse effect to the one used for emission. During sensing, the local atmosphere was purged from water vapor molecules that are known for their drastic absorption within the terahertz frequency range. The frequency window, over which the terahertz pulses were generated, ranges from 100 GHz to 2 THz.

The estimation of the intrinsic properties as well as the thickness of the varnish layer was derived from solving inverse electromagnetic problem [19]. Chiefly, it consists of minimizing an objective function that denotes the discrepancy between the measured signal and a signal simulated by different combinations of dielectric constants and thicknesses [20, 21]:

$$\chi = \delta M^2 + \delta \Phi^2, \tag{1}$$

where χ is the objective function to be minimized, δM^2 is the quadratic difference on the modulus, and $\delta \Phi^2$ is the quadratic difference on the phase. Both these differences are related to the transfer function that governs interaction between terahertz pulses and the sample:

$$\begin{aligned} \delta M &= ln(|T^M|/|T^S|), \\ \delta \Phi &= \angle T^M - \angle T^S, \end{aligned} \tag{2}$$

where T^M and T^S are the measured and simulated transfer functions, respectively. The expression of the transfer function can simply be set as the quotient between the detected and emitted electromagnetic fields. The shape of the simulated transfer function was chosen from the one proposed in [10] and based on transfer matrices [22].

3 Results

The dielectric constant and the thickness of the varnish and the paint layer were evaluated in different locations over the painting surface. Here, the main difficulty is that an accurate calibration of individual layers of the painting cannot be achieved. Overall, the varnish layer thickness ranges from 10 to 20 μm while the paint layer is overall around 40 μm thick. The dielectric properties were assumed to be constant over the frequency window due to the lack of specific relaxation mechanisms in those materials within the terahertz range. The interaction between terahertz pulses and the different strata of the painting can, in fact, be seen as a generalized thermal effect.

First, inverse electromagnetic problem was solved on regions where the varnish layer was missing, allowing to extract in different location both the intrinsic properties and the thickness of the paint layer. In Fig. 2, it is represented the signal reconstruction of the paint layer at a specific location for which the combination of the dielectric constant and the thickness minimize the objective function defined in Eq. 1.

Subsequently, an equivalent procedure was applied on regions where the varnish was present. The intrinsic properties as well as the thickness of the paint layer found nearby such regions were fixed. Figure 3 shows a typical reconstruction of the signal reflected by the stratified structure made of varnish and paint layers on the copper substrate.

The quadratic difference between the measured and the reconstructed signals is higher than the one exhibited by the inversion of paint regions deprived from varnish. There are multiple roots for such an observation. First, the properties of the paint layer that were fixed are hardly exactly the same at different locations even though being in close vicinity. Second, the assumption on the non-dispersive behavior of

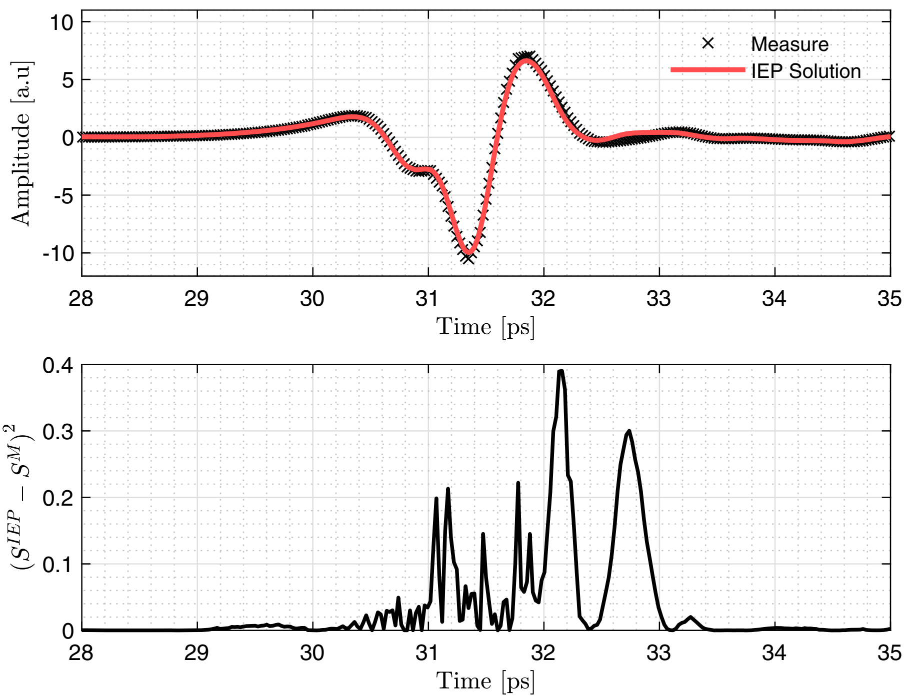

Fig. 2 Inverse electromagnetic problem solved on a region derived from varnish. Top: signal reconstruction for $n = 1.94 - 0.064i$ and a thickness of 40 μm. Bottom: quadratic difference between the inverse electromagnetic solution S^{IEP} and the measurement S^M

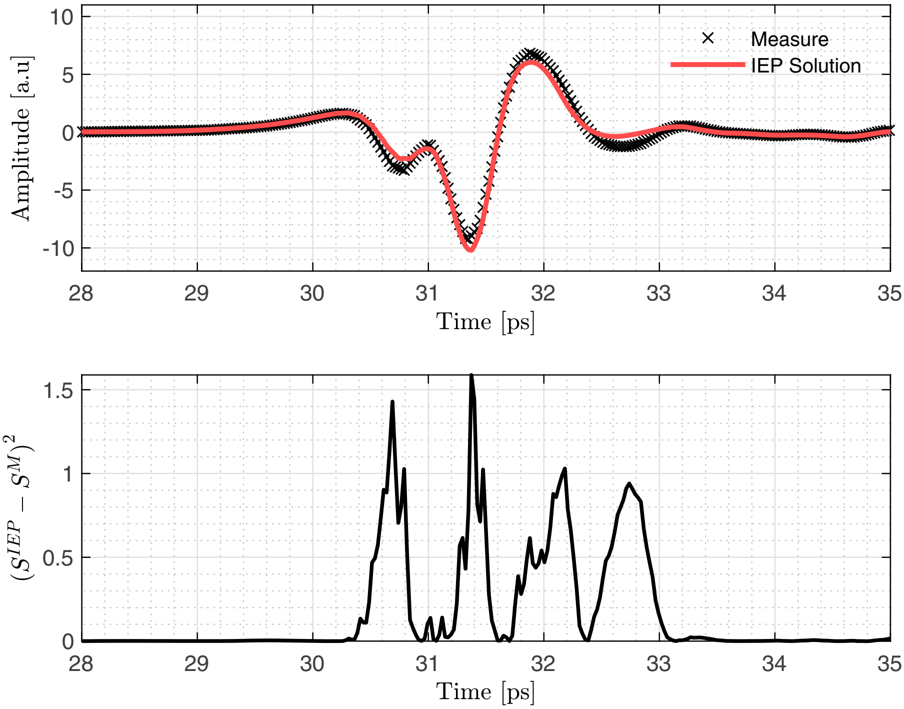

Fig. 3 Inverse electromagnetic problem solved on a region successively made of varnish, paint, and copper substrate. Top: signal reconstruction for a varnish index of $n = 1.48 - 0.070i$ and a varnish thickness of 12 μm. Bottom: quadratic difference between the inverse electromagnetic solution S^{IEP} and the measurement S^{M}

each of the layer may induce a generalized error that progressively increases with both the number of layer and the stack global thickness.

4 Imaging

Additionally, to these extractions, terahertz images have been performed over different painting locations to evaluate the impact of the varnish layer onto the imaging process. The varnish layer was removed from specific parts to evaluate a possible blurring effect. Figure 4 depicts the terahertz image acquired by raster scanning over two different areas. The images given hereafter correspond to the integration of the modulus between 200 GHz and 2 THz.

No significant influence of the varnish on the resulting image has been noticed. We can recognize on the top left the shape and head of the monster. The resolution is not sufficient to distinguish the small details of the figure.

Due to the lack of spatial resolution at frequencies ranging from 200 GHz to 2 THz and the low signal-to-noise ratio in the upper frequency band, additional imaging at 2.5 THz and 3.8 THz has been performed using CW compact quantum cascade lasers

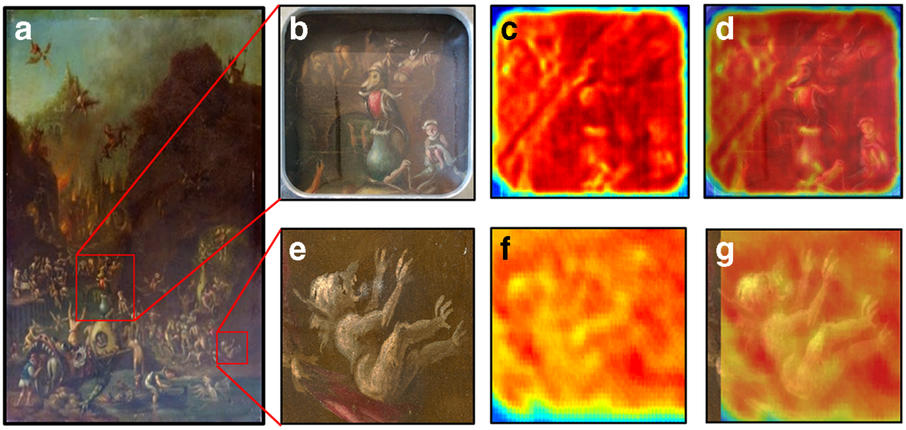

Fig. 4 Photograph and terahertz images of the artwork. **a** Global optical view of the painting; **b** optical view at a specific location; **c** corresponding terahertz image (module integration between 200 GHz and 2 THz); **d** overlay of the optical and the terahertz images; **e** optical view at a specific location; **f** corresponding terahertz image (module integration between 200 GHz and 2 THz); **g** overlay of the optical and the terahertz images

(QCL) as lighting sources. Both are commercial lasers provided by the company Lytid, the TeraCascade 1000 (TC 1000) at 2.5 THz and the TC 100 at 3.8 THz with a maximum power of 3 mW and 0.1 mW respectively. The close circuit cooling at 44 K of the TC 1000 is carried out using a cryogenic Stirling pump previously put under a primary vacuum. The source at 3.8 THz is cooled at 77 K with liquid nitrogen (77 K). Both lasers are powered by a high frequency (10 kHz) modulated voltage to limit their heating and with a variable duty cycle to control the output power. An over-modulation of the voltage by a function generator can be used to synchronize the detection. The 3.8-THz images were acquired using a raster scanning system with a numerical aperture NA = 0.5 and an amplified pyroelectric sensor. Concerning the acquisition at 2.5 THz, an uncooled terahertz camera combined with a $\frac{1}{4}$ magnification objective was used allowing video rate imaging on a 64×48 mm^2 area with an average signal-to-noise ratio of more than 30 dB on each pixel. We estimated the depth of field of the objective about 6 mm (Rayleigh distance = 3 mm).

Different parts of the painting were imaged. Figure 5 depicts the terahertz images acquired at 2.5 THz and 3.8 THz over the artwork. The varnish layer has a significant impact at 3.8 THz while such an impact seems less evident at 2.5 THz.

Specific details that were not revealed from optics have been highlighted by means of terahertz imaging and are depicted for two specific locations on Fig. 6. Figure 6a. depicts a half-naked lady with hands up, located on the low middle left part of the painting. Different observations revealed by terahertz imaging are underlined by red circles and arrows on Fig. 6b. First, part of the shawl is clearly visible on the lady's body but not under her left arm. This contrast change may be due to different painting materials or different reflection coefficients of the underpainting layers. The arrow on the left arm indicates a black line appearing that likely denotes the signature of a previous restoration. The hairs are also very different on comparing the visual image

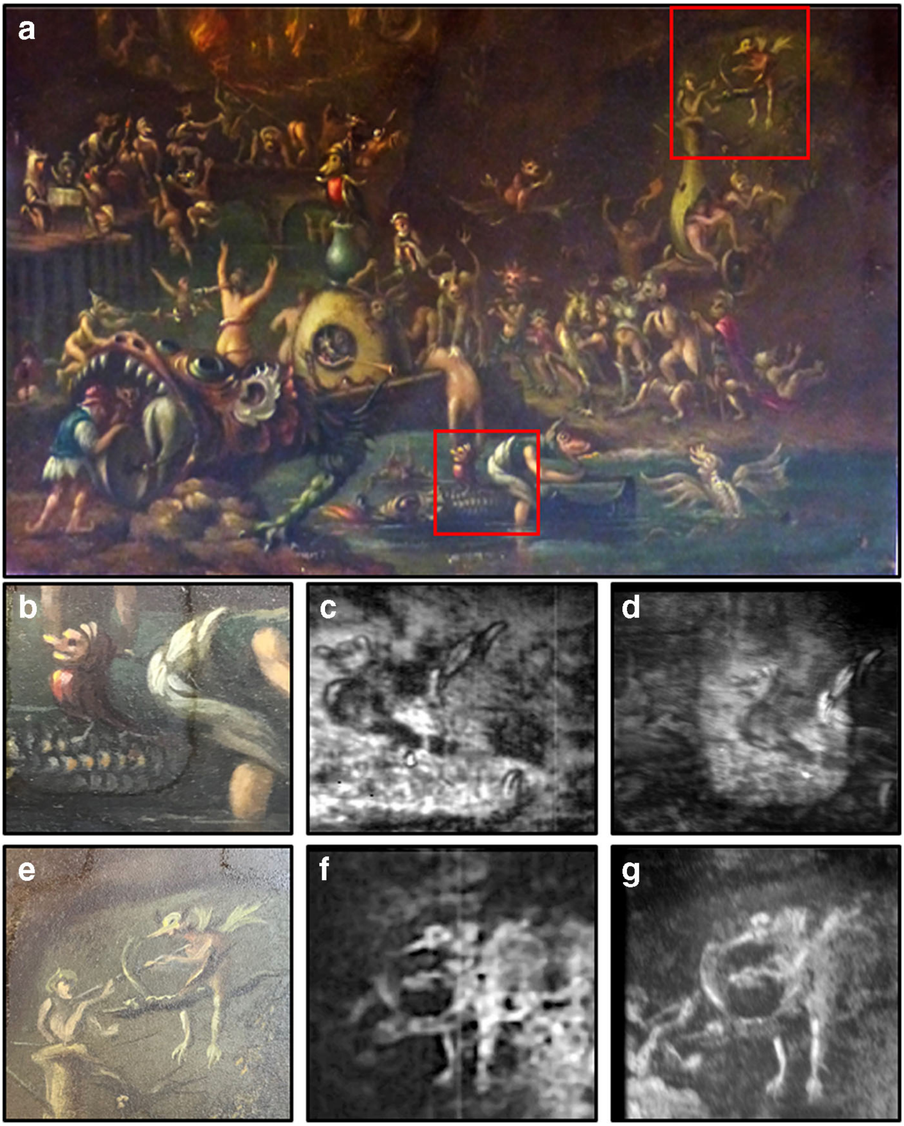

Fig. 5 Photograph and 2.5–3.8-THz images of the artwork. **a** Section of the photograph of the painting. Red squares denote the specific region imaged; **b** optical view at a specific location; **c** corresponding terahertz image at 2.5 THz; **d** corresponding terahertz image at 3.8 THz; **e** optical view at a specific location; **f** corresponding terahertz image at 2.5 THz; **g** corresponding terahertz image at 3.8 THz

with the terahertz one. The contour suggests that the artist modified them with regard to a previous version. At least, some features are present on the top left part of the drawing but nothing is visible on the painting. Figure 6d is a detail of Fig. 6c. The head of the monster, localized by a red circle, is quite different from the visual cliché.

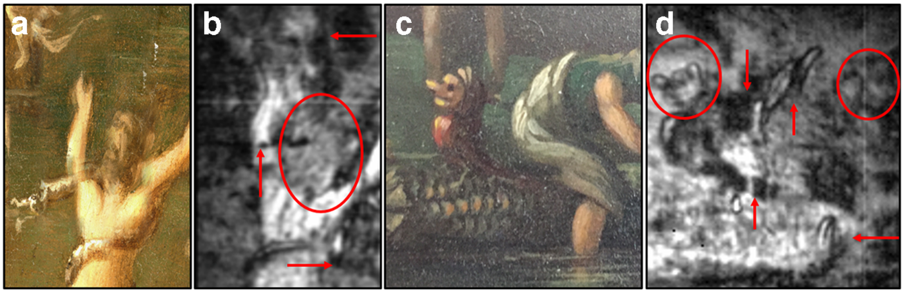

Fig. 6 Hidden details revealed by terahertz imaging. **a** Optical view at a specific location; **b** corresponding terahertz image at 2.5 THz; **c** optical view at a specific location; **d** corresponding terahertz image at 2.5 THz. Red circles and arrows depict the presence of specific details that are not compliant with the optical view

The noise is bigger and other parts of the portrait differ significantly. The red part of the crop is also detected with a clear black line. Secondly, the feathers of the back monster seem longer than the visible one (marked with a red arrow). Identically, the green painting layer between the two person reacts differently: one part is absorbed (dark) and the green looks bright at the other location. The white trouser of the second monster is also very disturbed. Terahertz imaging reveals a different shape of the contour. Only the top white part of the trouser is visible, but the part on the thigh, the white lead pigment is clearly retrieved. The green layer also presents a different contrast than the neighborhood. At least, a scale is clearly distinguished near the calf and a second head monster.

5 Conclusion

Due to the presence of a metallic support, a wide majority of conventionally employed techniques to characterize and to analyze paintings for restoration purposes are not suitable. Here, to inspect a painting made on a copper support, terahertz waves have been used, as no saturation from the background is expected to appear on acquired images. Moreover, the sensitivity of terahertz waves to dielectric changes within a stratified structure like a painting allows determining the intrinsic properties and the thickness of each individual layer. The concomitant use of such a property and algorithms dedicated to solve inverse electromagnetic problems allowed characterizing both the paint layer and the varnish one that acts as a protective layer. The determination of the varnish layer is of paramount importance since it permits the curator to restore such a layer without altering the paint layer underneath.

The impact of the varnish layer on terahertz imaging was also investigated. Although no significant impact has been observed for frequencies under 2.5 THz, the imaging at 3.8 THz revealed important demarcations between coated and uncoated regions, resulting in a blurring effect. This observation legitimately leads to think that varnish absorption increases with the frequency axis, therefore limiting the use of terahertz radiations for heritage science in the upper band of the submillimeter window.

Compliance with Ethical Standards

Conflict of interest The authors declare that they have no conflict of interest.

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Affiliations

Q. Cassar[1] · C. L. Koch-Dandolo[1] · J. P. Guillet[1] · M. Roux[2] · F. Fauquet[1] · J. B. Perraud[1] · P. Mounaix[1]

Q. Cassar
quentin.cassar@u-bordeaux.fr

C. L. Koch-Dandolo
corinnakd@gmail.com

J. P. Guillet
jean-paul.guillet@u-bordeaux.fr

M. Roux
atelierdesrenaissances@gmail.com

F. Fauquet
frederic.fauquet@u-bordeaux.fr

J. B. Perraud
jean-baptiste.perraud@u-bordeaux.fr

[1] IMS Laboratory, University of Bordeaux, UMR CNRS 5218,351 cours de la Libération 33405 Talence, France

[2] L'Atelier des Renaissances, 1 allée de Gieu, 33650 Saucats, France