Chapter 20
Characterisation of Works of Art

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Abstract Terahertz (THz) imaging is an emerging technique for the non-invasive analysis of artworks. Since THz waves can penetrate opaque materials, various imaging systems that make use of THz waves have been developed in order to detect certain chemicals and defects in materials. More recently, THz imaging has been applied to the examination of works of art. The first experiments in the use of THz imaging in the field of art have provided very encouraging results.

20.1 Introduction

The frequency band in the terahertz (THz) region typically refers to the 0.1–30 THz range (from 3 to 300 cm^{-1}). This region of the electromagnetic spectrum lies in the gap between microwaves and the infrared, and has historically been defined as the "terahertz gap", due to its relative lack of convenient and inexpensive sources, detectors and systems for THz waves [1]. In recent decades, this spectroscopic region has been explored mainly by scientists who directly developed the THz systems on their own premises for their own specific research applications. These in-house

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THz systems, which are custom-made, were usually non-friendly devices that were difficult for non-specialised operators to use in general applications. Thanks to the progress of laser technology, various types of stable THz sources have been developed in recent years, with peak power values ranging in scale from microwatts to milliwatts. Stable femto-second fibre lasers that operate at room temperature have encouraged the development of THz spectroscopy and imaging systems for general purposes. Indeed, THz waves can penetrate opaque materials, such as radio waves, and make it possible to obtain spectral features of various materials, such as those for vibrational spectroscopy [2–6]. Since the energy of THz waves emitted from existing systems is extremely low, i.e. of a magnitude similar to that of room temperature, this electromagnetic region is considered to be completely non-invasive for operators, living organisms and objects. Hence, it can be applied to the study of living matters, including human beings. These advantages are effectively used in developing new non-destructive test equipment, especially for security issues. Some international airports have installed THz security cameras to detect concealed weapons of the type which cannot be recognised by metal detectors, and a non-invasive mail inspection system has been developed to detect illegal drugs or poisonous substances inside envelopes and/or packages [7, 8]. The information available from the measurement of THz absorption/reflection is not limited to the level of the absorption or refractive index, which can also be obtained in microwave and millimetre wave regions. Almost all materials show their own particular spectral features in the THz range, thanks to their phonon interactions, molecular rotations, hydrogen bond behaviour and various low-energy excitation modes. Crystal polymorphs, for example, can be recognised easily in THz spectra, rather than in those collected in the mid-infrared region, and the data obtained make it possible to distinguish original/generic medicines [9].

The first THz images were acquired by Hu and Nuss in 1995 by using a terahertz time-domain spectroscopy (THz-TDS) system [10]. In this system, femto-second optical pulses were used to generate broadband THz radiation, also via a second-order nonlinear optical process in which a short optical pulse is used to generate and also detect THz radiation via nonlinear optical interactions between the optical pulse and a medium: typically, a semiconductor [11–16]. The recent history of the field has been one of rapid expansion, with the development of both new imaging techniques and also new technologies for THz sensing [17].

THz imaging can be performed by the transmission or the reflection of THz waves. In particular, THz-TDS reflection imaging uses THz pulses that propagate in specimens: in this technique, pulses reflected from the surface and from the internal boundaries in the reflective index of the specimen are detected. In general, the internal structure of the analysed object is observed in cross-sectional images obtained by using micro-specimens taken from the work that is being analysed. On the other hand, in THz-TDS imaging, a map of the layer of interest can easily be obtained without the need to collect any samples.

Due to the increasing possibilities involved in the commercial use of THz imaging systems at affordable but yet expensive costs, THz imaging is an emerging technique for the non-invasive analysis of artworks. Indeed, the first experiments in the use of THz imaging in the field of art have provided very encouraging results.
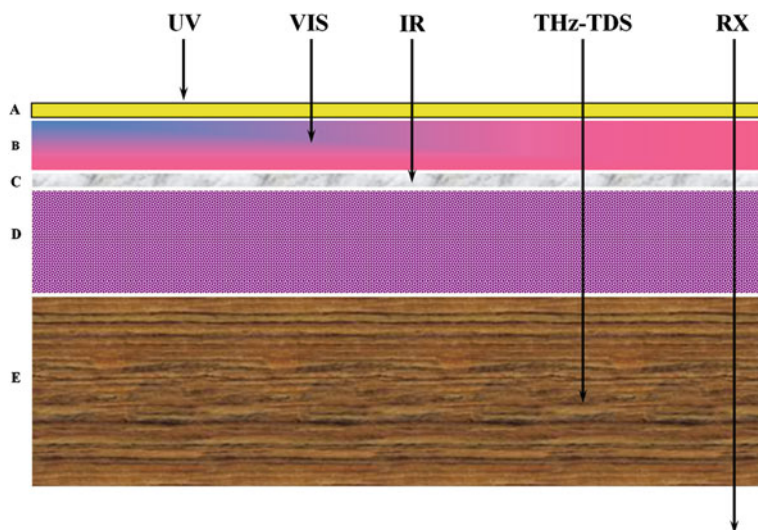
Fig. 20.1 Diagram showing the depth of penetration of the imaging diagnostic techniques, reported in the text, for a panel painting (simplified stratigraphic scheme): (A) varnish layer; (B) paint layers; (C) *imprimitura* layer with drawing; (D) preparation layers; (E) wood support

In studying works of art, and paintings in particular, the most frequently used imaging techniques are trans-illuminance, trans-irradiance and X-ray radiography (XRR) techniques, which work in transmittance, while photographic documentation of the object in diffuse and raking visible light, ultraviolet (UV) fluorescence, infrared (IR) imaging, IR false colour and IR reflectography are usually performed in the reflectance mode (Fig. 20.1). Each of these enables conservators, curators and scientists to obtain specific information on the structure of the painting, the technique and materials used by the artist, as well as about the conservation condition of the object. As far as the first application of a THz imaging system on works of art is concerned, this was performed in 2006 in transmission mode on a nineteenth century canvas painting [18].

In practical terms, the THz power applied is usually not strong enough to perform THz transmission imaging of panel paintings, whereas this can be done by means of XRR. However, THz imaging can be used to obtain the internal structure of materials in a non-invasive way by using, for example, THz-TDS tomography, even when it is performed in reflectance. The results obtained with THz-TDS tomography can be compared with those achieved invasively with the study of cross-sections on micro-samples. Traditional cross-section images enable the investigation of the layer composition and depth only on two dimensions, but do not provide analysts with information on the third dimension of the sample (or investigated area). On the other hand, in THz-TDS tomography each pixel of the image contains its own cross-section information (stratigraphic information), so that the area information on the layer of interest is also obtained by extracting the corresponding peaks in signals in

a time domain. A three-dimensional internal structure can be obtained by gathering images.

One drawback of this technique, however, is related to the presence of substances that totally reflect THz radiation. An example of such substances is represented by thick and homogeneous gold leaves that can mask the structure underneath, because they reflect the THz waves.

20.2 State of the Art of Imaging Techniques Applied to the Characterisation of Artworks

Preliminary non-invasive investigations are needed before starting any conservation procedure on valuable artworks, in order to assist conservators in their decision-making process. When one is dealing with artefacts, such as paintings, drawings or other graphics art works that can be considered as flat objects, imaging techniques offer an ideal approach for performing non-invasive, yet in-depth, examinations. Generally speaking, imaging techniques are based on the acquisition of a virtual picture of the surface that can be super-imposed on the visible image. This picture usually provides a 2D map in which features that are not detectable through visual examination can be pointed out. The use of imaging techniques in the art conservation field ranges from well-established methodologies, such as high-resolution digital photography, visible raking light, UV fluorescence, XRR, IR reflectography, etc., to cutting-edge applications, such as multi- and hyper-spectral imaging techniques [19, 20] or THz imaging [21]. In principle, all the above techniques could be used in order to reach the desired level of knowledge on the object under analysis. Nevertheless, in many practical cases, various factors, such as time, costs and the availability of pieces of equipment, may limit one's resorting to a wide set of scientific methodologies, and the investigations needed should be limited to simple and affordable methods [22]. Depending on the needs and importance of the object under analysis, as well as on the resources available, different imaging techniques can be used in order to obtain the information desired. That is, a basic protocol for preliminary diagnostics on paintings can typically include one or more of the following imaging techniques, to which multi-, hyper-spectral and THz imaging methodologies can also be added:

- *High definition digital photography in the visible range (380–750 nm)* for documenting the conditions and characteristics of polychrome surfaces, with the possibility of magnifying details and selected areas.
- *Visible raking light* for highlighting deformations and changes in the flatness of the support due to constraints connected with both the manufacture and use of the support itself, as well as external effects such as climatic variations, earlier conservation treatments, etc.
- *IR imaging (photography or reflectography)* for the examination of underlying drawings, hidden particulars, *pentimenti*, etc., and for obtaining indications for understanding artists' techniques. Obviously, the informative content of IR images

greatly depends on the extension of the spectral interval investigated, and, hence, on the detector used for their acquisition. Devices used for IR imaging are silicon-based CCD cameras (400–1,100 nm), as well as cameras based on solid-state sensors, such as Indium Gallium Arsenite (InGaAs), Platinum Silicide (PtSi), Indium antimonide (InSb) and Mercury Cadmium Telluride (MCT) in the near IR region (approximately 800–2,500 nm) or vidicon-tubes (400–2,200 nm).

- *XRR* for the examination of the nature and structure of the original support due to the high penetration of the X-ray. It enables an in-depth inspection of the artwork, and is especially useful for obtaining information on under layers and the inner structure of the object, the conservation over time of the support and so forth. Although routinely used, this technique requires specific instrumentation, equipped laboratories and trained staff. Thus, its use is limited to selected cases.
- *UV fluorescence imaging* for identifying selected pictorial materials, retouches, non original interventions, etc., on the basis of the fluorescence emitted in the visible and near IR regions by certain materials when illuminated by using UV (e.g. Wood lamps) or blue radiations.
- *Trans-illumination (visible) and trans-irradiation (Near-Infrared)* for inspection of the conservation of supports that are partially transparent to visible light: for example, in the case of unlined canvas [23]. In these Transmitted Imaging techniques, the object is placed between the light source and the camera, with the painted surface generally facing the camera. The radiation transmitted through the investigated surface is then recorded. However, the painting could also be placed in the opposite direction, in order to obtain different and complementary information on the artists' techniques and the conservation conditions of the artwork.

20.3 THz Imaging and Art Conservation: Chronicle

As far as the authors know, to date only a limited number of scientific published papers deal with the application of THz techniques to the analysis of artists' materials, art mock-ups, or laboratory art panel tests, and only a few touch upon actual artworks.

As regards imaging methodologies, the first application of a THz imaging system in the art conservation field was performed in transmission mode to a $10 \times 10\,cm^2$ portion of a nineteenth century canvas painting (a female portrait found at a flea market), and the data obtained were then compared with those acquired using the X-ray fluorescence (XRF) technique [18]. Laboratory tests on different areas (measuring about 3 mm in diameter) of the painting, using a THz-TDS spectroscopic device in transmission, showed that the output signal depended on the materials investigated. However, even if XRF data were registered on the same areas of the painting where the THz-TDS spectroscopic information was acquired, identification of the actual composition of the paint layers was not made by the authors. Hence, the comparison between the THz-TDS transmission spectra and the chemical composition of the paint layer was incomplete. The authors acquired their THz images by means of a photoconductive antenna detection system, with 0.1–1 THz width frequency

windows, which was extensively reported in the article by Rutz and co-authors in the same book of proceedings [24]. In it, THz-images were taken by moving the painting in a 2D grid pattern with a resolution of 0.5 mm/pixel through the focus of the THz-beam, and the corresponding waveform was measured at each step-position. Each waveform was transformed with the FFT algorithm in order to obtain its frequency content, which held information on several parameters suitable for plotting THz-images: for instance, differences in the refractive indexes or in the thickness of the paint layers could be seen by plotting an image with the temporal position of the main peak. In the case of thicker layers or materials with more highly refractive indexes, the delay in the pulse was greater. In addition, it was possible to report the information obtained about the absorption features of the paint materials in other images by considering the peak-to-peak values. By playing with THz-TDS images, each pixel could combine information regarding absorption, scattering, and reflection losses of the investigated material. Consequently, a THz-imaging measurement made it possible to produce multiple false colour pictures, which provided different information on the properties of the paint layers.

At the same time, experiments were performed at the National Institute of Information and Communications Technology (NICT) in Tokyo on painting mock-ups that were focused on acquiring THz spectra of various artists' materials, such as pigments and binders (www.thzdb.org), as well as the application of THz imaging to the analysis of artworks [25, 26]. This study was the first actual application of false-colour THz imaging methodology, obtained by developing THz false colour algorithms, to the investigation and discrimination of artists' materials in paintings and stained glass (Fig. 20.2). Although several types of THz systems have become commercially available in recent years, a very promising development in THz devices has been seen, by the authors, namely in a THz camera system based on micro bolometer array technology. With this system, real-time THz false colour maps of paintings and stained glass have been created by dividing the 0.5–15 THz frequency range into three bands, which were represented in RGB colours, respectively. The THz false colour of each spectrum was obtained by replacing the average transmittance rate in each band with a 0–255 gray-scale level (Fig. 20.3). As far as the authors are concerned, the camera control software could be upgraded by means of this procedure, or using similar algorithms, in order to directly show on the camera display. In addition, the authors noted that NICT and the Riken (Rikagaku Kenkyūsho, a natural sciences research institute in Japan) have been the first institutions to make a spectral database on artists' materials, which included more than 200 spectra of products related with art materials, available online. With the use of these spectral data, THz spectroscopy can be utilised to determine materials found in artworks, such as pigments with similar composition and the same colour, e.g. natural and artificial blue ultramarine.

Subsequently, a fresco-painting model was studied by researchers of the University of Michigan, of the École Nationale Supérieure de Techniques Avancées in Paris, and of the Louvre Museum, who found that THz reflection imaging makes it possible to distinguish pigments [27, 28]. In their research, the time delays and intensity signatures of THz pulses reflected from multilayer systems of plaster, painted sur-
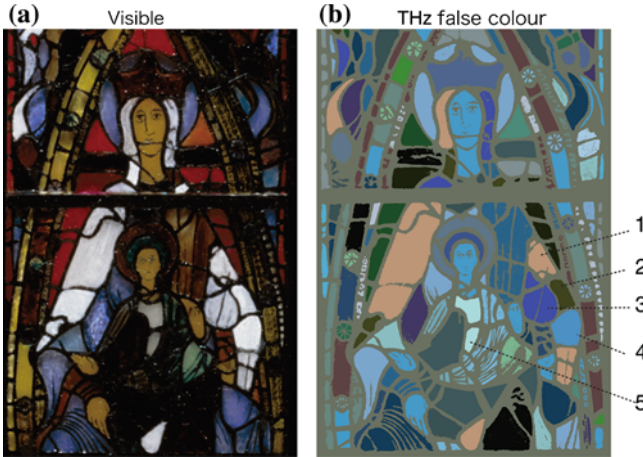
Fig. 20.2 a Detail of the Virgin of Vendome, twelfth century stained glass from the Holy Trinity Abbey in Vendome (France), and **b** its THz false colour image. In the THz false colour image **b** five different white materials, used to produce white glass, are differentiated by their diverse THz spectra: (*1*) *lead white*; (*2*) lithopone; (*3*) *zinc white*; (*4*) *titanium white*; (*5*) *lime white*. Figure modified from Fukunaga et al. [25]
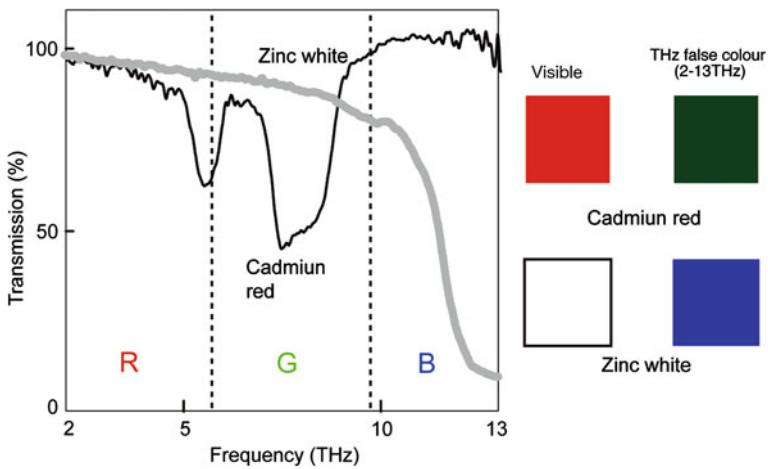

Fig. 20.3 THz transmittance spectra of cadmium *red* and *zinc white* pigments with three different false RGB zones. The THz false colour obtained for the two pigments are shown in the *right*

faces and graphite sketches were investigated in order to demonstrate the feasibility of using THz techniques for inspecting and resolving fresco artworks embedded in subsurface layers within a wall or ceiling. The authors acquired THz data on two different fresco samples, using two different THz-TDS devices. The first sample was a $60 \times 35 \times 4.35$ mm thick plaster-of-Paris (calcium carbonate/calcium sulphate

semihydrate/silica) slab. It was prepared following the *buon fresco* traditional paint-
ing technique using dielectric pigments, such as titanium dioxide (white), limonite
iron oxide-based clay (burnt Sienna) and mixed carbon-iron oxide (black). The back
surface of the plaster sample was painted with a conductive paint layer consisting
of two separate strips prepared with silver epoxy, which contained 50–70 % silver
flake and 30–50 % of phenol novolac epoxy resin (a reaction product of epichloro-
hydrin and phenol–formaldehyde novolac), and titanium dioxide bound with water,
respectively. The second sample consisted of a 2D graphite sketch of a butterfly
covered by 4 mm of plaster-of-Paris that terminated with an opaque paint layer (pig-
ment with water as a binder) split into four colour quadrants: black, white, yellow
ochre (limonite iron oxide-hydroxide clay) and burnt Sienna. The first THz-TDS
system, which was intended to establish the feasibility of time-domain ranging for
layered media in the first sample, employed a free-space THz-TD reflectometer con-
sisting of an interdigitated metal finger, semi-insulating-photoconductive-GaAs THz
emitter, and a low temperature-grown-GaAs (LT-GaAs) Hertzian-dipole receiver. In
the second experiment, the integrated optical-fibre coupled transceiver head of a
Picometrix T-Ray™ terahertz-imaging system was scanned over the second fresco
sample, providing a normal THz-beam incident angle, a spatial resolution down to
2 mm, a selectable focal plane and rapid data acquisition (<5 min for a 7 × 7 cm
plaster sample with 0.5 mm step size).

From the data reported by the authors, the high contrast in reflectivity in the THz
region of the white, the burnt Sienna and the black painted layers on the front sur-
face made it possible to easily distinguish these materials one from the other. As
expected, the silver paint stripe on the back surface generated a greater reflection
than the white paint stripe did. The second test showed that the pulsed-THz beams
were able to penetrate the 4-mm depth of the plaster substrate, and made it possible to
image the graphite lines of the depicted butterfly from the far side of the plaster when
the THz-transceiver focal plane was adjusted to the back of the plaster substrate. The
experimentation conducted on this laboratory sample, together with THz spectro-
scopic measurements on the pure pigment powders, which provided the complex
refractive index values for those materials, revealed that in the 0.14–0.48 THz range
it was possible to have the optimum contrast between the different pigments based
on their reflectivities (Fig. 20.4). In particular, the titanium dioxide white pigment
showed the greatest reflectivity, whereas the yellow ochre paint appeared to be the
darkest. The other two pigments presented similar reflectivity to the THz radiation
applied. Furthermore, in the region above 0.6 THz, both white and yellow ochre pig-
ments became opaque, while the butterfly drawing was still visible through the burnt
Sienna and the carbon-iron oxide black pigments.

A recent work confirmed that THz imaging can successfully be applied to inves-
tigations of oil paintings on canvas [29]. In this paper, the authors showed that it
was possible to image the substructure of paintings on canvas by monitoring the
time delay between reflections off different layers (THz-TDS). THz-TDS enabled
them to measure the optical thickness of the different layers which constituted the
structure of the painting, thus providing information on the depth of the painting
structure. As a case study, THz-TDS images acquired on a linseed-oil laboratory test

Fig. 20.4 THz-TDS image
in reflection mode of a 2D
graphite sketch of a butterfly
covered by 4 mm of plaster-
of-Paris with an opaque paint
layer on top. The graphite
figure of a butterfly is clearly
recognisable in the THz-TDS
image formed integrating the
spectral information in the
0.14–0.48 THz range. Figure
modified from Jackson et al.
[27]
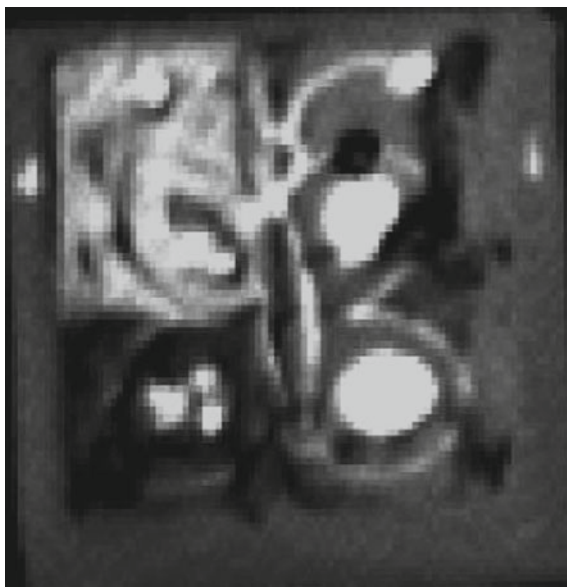
panel on canvas, which consisted of several rectangular patches of raw umber, an iron
and manganese oxide-based brown earth pigment, with different thicknesses covered
with lead white, were examined. Here, the reflection measurements were performed
on the verso of the painting, from the canvas side. This is because it is relatively flat
compared with the recto; therefore, the reflection/refraction problems caused by the
curvature of the front surface of the painting were partially overcome. The THz-TDS
results were also compared with those obtained by using the infrared reflectography
and XRR techniques on the same object. By means of the data reported, the authors
showed that it was possible to use the THz-TDS imaging technique for analysing the
substructure of a painting, since it provides information on the thickness of the paint
layers.

The experimental set-up was provided with a photoconductive switch to generate
broadband THz pulses, which were focussed onto the back of the test panel. The
THz beam was directed perpendicular to the canvas.

The most important part of this work was related to the authors' prediction of the
smallest absolute thickness measurable using their THz-TDS methodology. Indeed,
by assuming a refractive index of 1.9 for the raw umber and the ground of the canvas,
they estimated that two peaks separated by about 0.65 ps could still be identified as
two separable signals, which meant that paints with a thickness of 50 μm could still
be measured using their experimental set-up. In addition, they estimated that, for
materials with a refractive index of 1.9, it was still possible to measure thicknesses
of about 12 μm by means of the changes in the time separation of 0.15 ps. However,
in order to reach these values, the deconvolution of the contributions of the closely
spaced layers would require a more elaborate signal processing.

In the paper by Abraham and co-authors [30], a broadband THz-TDS was used to reveal hidden sketches and underdrawings on laboratory canvas panels. The authors also demonstrated that it was possible to obtain information from their THz data about the different thicknesses of the paint layers. They acquired THz images in both transmission and reflection geometry, while they simultaneously provided the 0.1–1.5 THz range transmittance spectra of the pigments used in their study. The authors concluded from these spectroscopic data that, in their case study, it was not possible to distinguish specific fingerprint absorption of the THz radiation of the selected pigments. Indeed, only a global attenuation of THz amplitude after the transmission through the specimens was observed, although the different intensities in the transmission of some of the investigated pigments could be used for their identification. In general, however, a spectroscopic distinction of these materials in the 0.1–1.5 THz range was not very obvious.

The broadband THz spectrometer used in this work was based on a standard transmission THz-TDS setup: a 50 fs Ti–Sapphire laser with a 76 MHz repetition rate. THz imaging was obtained by raster scanning the sample with a XY linear motor stage. The lateral resolution of the system was previously measured and evaluated at 220 μm at 2 THz, which corresponds to the Rayleigh diffraction limit. However, in order to reduce the acquisition time, a 0.5-mm scan step in both X and Y directions was generally applied.

The authors computed the THz images acquired by using the temporal and/or spectral amplitude of the signal, as well as directly using the arrival time of the THz pulse, such as the temporal phase shift. In this way, the 3D maps obtained made it possible to extract information on the refractive indexes and about the thickness of the investigated samples. The accuracy of the measurement of the thickness was related to the registration of the arrival time of the THz pulse and the acquisition step of the delay line.

The smallest variation in thickness measured in transmittance by the authors was determined by the ability to precisely determine the temporal position of the THz main peak. In their paper, a minimum variation of 30 μm in the paint thickness was calculated for the blue ultramarine pigment, with an estimated refractive index of 1.93. As expected, when working in reflection, the evaluation of the system was different, because a more complex THz waveform was obtained. Nevertheless, the results obtained were compatible with those obtained in transmission geometry, and the slight discrepancies were tentatively explained by the authors as being due to the reflection geometry, which did not require any previous reference measurement (canvas without painting), unlike what was done for the transmission measurements. The possibility of evaluating the thickness of a layer, once the refractive index of its compounds is known, was also an advantage offered by the reflection geometry, which provided a direct measurement of the painting thickness by taking into account the time of flight of the THz pulse, over the transmission geometry. In their paper the authors also estimated the smallest variation in thickness that can be measured with their system. They found that, with a rough precision of 100 fs for the time delay between the two peaks, the corresponding smallest change in the paint thickness (using a refractive index of 1.93) was about 8 μm. This result was also in agreement

with the work by Adam et al. [29]. However, as reported in Abraham et al. [30], the images acquired in reflectance mode usually had a lower signal-to-noise ratio than the ones registered in transmittance mode, due to the complexity of the THz signal after being reflected by the investigated object.

One of the most important applications of THz imaging in the art conservation field has been the case study performed at the end of 2008 on the panel painting *Polittico di Badia* (*circa* 1300) by Giotto di Bondone, on display at the Uffizi Gallery in Florence, Italy [21]. This work could be considered to represent the first applications of the pulsed THz-TDS reflection imaging technique on an actual tempera panel painting belonging to one of the most important museums in the world. It was investigated using a portable TDS-THz imaging system T-Ray™ 4000 by Picometrix, which worked approximately in the 0.5–1.2 THz range that required a scanning time of about 10 min in order to investigate an area of 150 mm^2, with the detection unit placed in front of the painting at a distance of approximately 20 mm. The THz imaging methodology involved focused mainly on: (a) an understanding of the conservation and appearance of the gold leaves of both the background and the decorations; (b) the possibility of identifying pigments and the conservation over time of the paint layers; (c) an analysis of the internal physical structure of the painting (stratigraphy of the different layers).

The results of this analysis revealed that the artist, in following a medieval procedure for making panel paintings, had spread a gesso layer directly over the wooden support in order to flatten the carved wood base. A canvas was then placed on the gesso layer, and, subsequently, another gesso layer was used as a preparatory layer for the painting itself. In the paint layer, gold foils covered by paint could be clearly observed, and the consumption or ageing of the gold could be estimated by noting the amount of reflection. This application stressed the fact that THz-TDS imaging using THz pulse had made it possible to fill in the information gap about panel paintings that had hitherto existed between two other diagnostic imaging techniques, namely IR reflectography and XRR, because it provided useful data on the internal physical structural information on non-metal objects, similar to the THz tomography technique (Fig. 20.5). THz tomography technique made it possible to acquire non-invasive cross-section images of works of art, thus obtaining results that could be compared with those obtained by taking micro-samples from the investigated object.

In addition to the above-mentioned studies, a THz reflective imaging system with a free electron laser has been developed by the *Ente per le Nuove Technologie, l'Energia e l'Ambiente* (ENEA, Frascati, Italy) [31]. This system has been used to perform non-invasive diagnostics in various fields of research, including the cultural heritage. Although the proposed system is not transportable, high-power source systems can be profitably applied in order to observe artworks that are masked by a thick layer of plaster or hidden items in archaeological and historic objects (Fig. 20.6). The same research group at ENEA, in collaboration with the colleagues of the NICT, have initiated a mutual project in the area of Technologies as applied to the Cultural Heritage within the framework of the Agreement between the Governments of Italy and Japan for cooperation in Science and Technology, entitled THz-ARTE "Terahertz
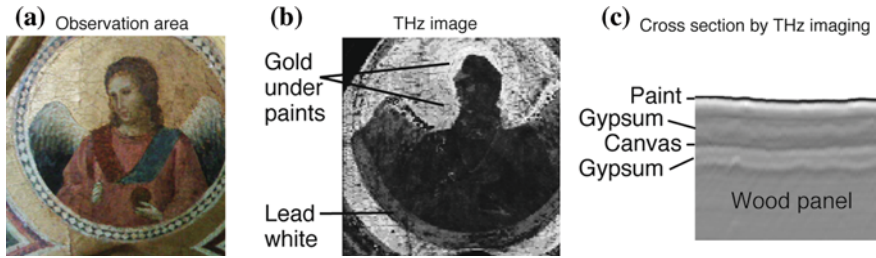
Fig. 20.5 RGB image (**a**) and THz-TDS reflectance image (**b**) of a detail of the Polittico di Badia polyptych by Giotto. The pulsed THz-TDS image revealed high reflection values of the gold leaf. In addition, the presence of gold leaves beneath the paint layers can clearly be observed around the outline of the head and wings of the Angel. The non-invasive cross-section image, whose structure can be observed in all the examined parts in the work, is shown in image (**c**). Here, the layered structure of the painting is clearly noticeable based on the reflection waveform in the time domain. Figure modified from Fukunaga and Picollo [21]

Fig. 20.6 Image in the visible range of the painting mock-up, partially cover with a thick layer of gesso (*left*). The other image, in the THz region (*right*), is a detail (rectangular frame) where the pattern of the painting covered by gesso is clearly evident. The THz image was acquired with the free electron laser THz system developed by ENEA
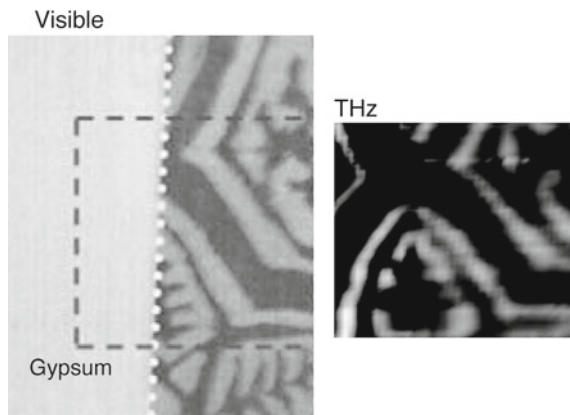
Advanced Research TEchniques for non-invasive analysis in art conservation" [32].

Other considerations relative to the use of the THz imaging technique in the art conservation field have dealt with the feasibility of extending this technique to the investigation of ancient papyruses, mummies and archaeological bones, as well as to the study of art and/or archaeological wood found in the cultural heritage, where it has been used for dendrochronological purposes [33–36].

The latter application, in particular, compared THz and X-ray tree-ring imaging techniques by adapting tree-ring analysis methods that are used in dendrochronology (the science of dating wooden objects by comparing the tree-ring patterns). As reported by the authors [35, 36], some of the tree-ring measurement techniques are invasive and time-consuming. Hence, art-conservators usually prefer to use a few mechanically non-destructive techniques, which can provide satisfactory measurement of tree rings in wooden objects. A few years ago, excellent results were obtained

by resolving tree rings as narrow as 0.15 mm, using soft XRR [37]. Moreover, the same authors were able to resolve rings in three-dimensional painted-wood folk art by using micro-focus X-ray computed tomography (XRCT). Despite the fact that THz imaging is performed in either transmission or reflection mode, the authors explored and implemented two methods of reflection-mode, time-domain THz pulse imaging for resolving tree-ring information, in order to facilitate the tree-ring dating of artefacts. In this work, tree-rings in the tangential (parallel to ring growth) and cross-sectional (parallel to grain fibres or to the end-grain surface) planes, THz ranging, and *en face* tomographic methodologies, respectively, were sampled and investigated. The data acquired were compared with those obtained with routine photographic techniques, to determine the statistical accuracy of the THz images. In addition, the THz-TDS imaging methodology focused on analysing primed and paint wood, so as to check the applicability of this technique in extracting information from the wood surface hint by opaque materials, such as paint layers in the case of panel paintings. Indeed, it would be very profitable to be able to determine the ring patterns that exist under the paint layers within these framed substrates without removing the frame or otherwise disturbing the integrity of the painting. Furthermore, for validation purposes the results reported by the authors were compared with similar measurements of wood that had been made using X-ray imaging methodologies.

For their research, the reflection measurements were carried out using a Picometrix QA-1,000 terahertz time-domain imaging system, consisting of a femtosecond laser fibre coupled to an XYZ-translatable, photoconductive and co-linear THz transceiver.

As stressed by the authors in their conclusions, the THz-TDR measurements of wood reported were very preliminary. THz ranging tangential measurements were found to be not very penetrative; however, the tree-rings measured showed a good correlation to their photographic references. The tree rings imaged along the longitudinal and end-grain surfaces were spatially resolvable using *en face* tomography, and the statistical accuracy of the ring series for the wood samples was good as compared to their reference chronologies. However, the ring series for the varnished specimen were unsatisfactorily matched. As regards the THz measurements on the primed and painted wood specimens, their tree-rings were not uniformly resolved, but enough information was obtained from these measurements for their ring series to be satisfactorily compared to the reference chronology (Fig. 20.7). In the authors' opinion, however, the THz imaging technique could have further applications in this field, apart from dating application, that deal with the study of stress and fatigue in wood by monitoring the water content, or with the conservation of artworks over time.

The study by Öhrström and co-authors, instead, focused on the feasibility and the morphodiagnostic impact of THz imaging of historic remains, such as Egyptian mummified tissues and macerated bone [33]. These delicate materials need to be analysed using minimal-impact methodologies at a macroscopic and/or microscopic scale for studying tissues and/or cell structures/DNA, respectively. In their paper, these authors examined artificially embalmed ancient Egyptian mummy tissues, a fish, a human hand and a macerated human lumbar vertebra, using THz-pulse imaging system.
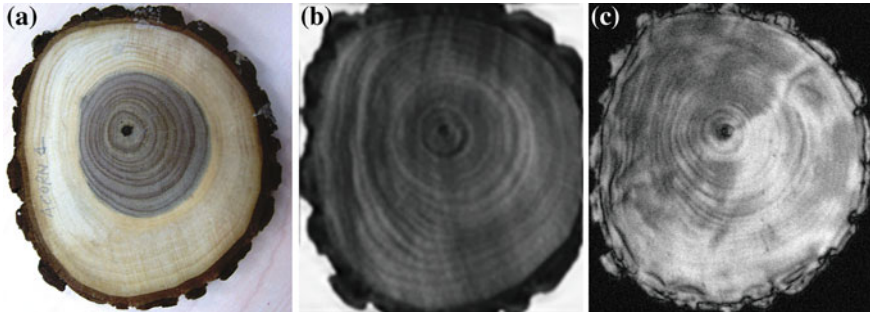
Fig. 20.7 RGB image (**a**) and THz-TDS reflectance image of the uncoated walnut sample (**b**) as well as THz.TDS image of the walnut specimen beneath the primer (**c**). Figure modified from Jackson et al. [35]

The THz images in transmission mode were recorded by spatially raster-scanning the samples through the focus of a standard THz time-domain spectroscopic system [10, 38]. From the data reported, it was evident that the spatial resolution information provided by THz imaging system used was not as good as the information provided by conventional X-ray imaging techniques. Broadband THz time-domain imaging on mummified tissues provided the authors with frequency-dependent information on the THz transmission and optical density distribution in the sample. However, in the case of thick and optically dense materials being used in order to obtain better quality images, the authors suggested utilising a different instrumental approach, with the use of a stronger continuous wave as reported by Karpowicz et al. and Appleby and Wallace [39, 40]. In any case, the THz imaging technique can be applied to the non-invasive investigation and detection of concealed items in archaeological and historic objects, such as funerary amulets or metallic objects/tools hidden in shrouded mummies. In addition, it is probable that the THz spectroscopic technique can also be used successfully to identify organic materials, e.g. balsamic essences used for embalming processes. Finally, as the authors suggested, THz techniques could be more extensively experimented in the field of paleopathology.

One of the most recent applications of THz-TDS spectroscopic imaging methodology focuses on the measurements of papyrus texts, including images of hidden papyri [34]. This technique, which is already used in the non-invasive imaging of several materials, such as postal envelopes [41] and, for the artistic field, in multilayer mural paintings [27], parchment manuscripts [42] and pigment identification [25], was proposed here by the authors as a non-ionising and non-invasive technique for building layer-by-layer images of archaeological and ancient texts, e.g. papyri. Using a T-Ray 4000 commercial system by Picometrix, Inc., which covers the 0.1–1.5 THz frequency range, samples of new papyrus were investigated. These specimens were prepared, following traditional preparation techniques for materials and ancient papyri, using contemporary papyrus sheets (approximately 120-µm thick) and inks prepared from carbon black and red ochre pigments bound with Arabic gum. In order to perform reflection and transmission measurements at
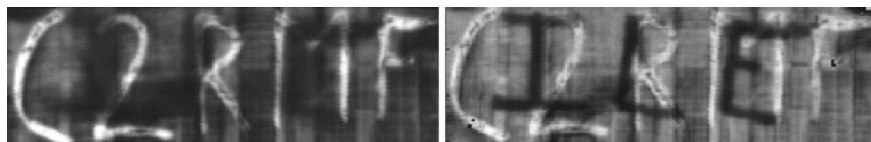
Fig. 20.8 THz images of multiple layers of papyrus samples layers from which exposed and hidden papyrus texts are readable in the THz domain. *Left* THz image of second layer of papyrus with a distance of 13 mm between the two layers. *Right* THz image of second layer of papyrus with a distance of 5 mm, in white the ink and in dark the shadow of the top layer. Figure modified from Labaune et al. [34]

normal incidence on the papyri, with minimal set-up reconfiguration of the system, the
T-Ray 4000 instrumentation utilised an INCONEL®-coated pellicle beam splitter, with 30 % reflection, 30 % transmission and 40 % absorption. The reflection measurement scheme presented a major advantage compared to the transmittance mode, which deals with the possibility of obtaining information on the internal structure directly from the reflections produced by dielectrically heterogeneous interfaces inside the sample.

The authors demonstrated that the THz transmission and reflection analysis of different inks make it possible to differentiate between the inks that were used to produce papyrus texts. Furthermore, scans of multiple layers of samples demonstrated that it is possible to read exposed and hidden papyrus texts in the THz domain (Fig. 20.8). For the moment, the instrumental set-up described by the authors was capable of correctly viewing the texts on different papyrus sheets when the distance between two papyri was of a few millimetres. However, in their opinion, it should be possible to increase the resolution to <1 mm.

The above-mentioned experiments/applications were carried out by using mainly THz-TDS systems. In addition, as already mentioned above, a THz camera with micro-bolometer arrays sensor that has been developed at NICT and NEC can be used as a portable THz imaging system [43].

In addition, there are various types of THz imaging systems under development in research institutes around the world; for example, computed tomography (CT) THz with a continuous wave [44]. This means that, in a few more years' time, different THz systems will be ready for use in several different fields, including art conservation.

20.4 Conclusions

In practical terms, the THz power applied is usually strong enough to perform THz transmission imaging of paper or canvas paintings; however, unlike XRR, it is not penetrating enough for panel paintings. All the same, THz imaging can be used to establish the internal structure of materials in a non-invasive way by using, for

example, THz-TDS tomography, even when it is performed in reflectance. The results obtained with THz-TDS imaging can be compared with those achieved invasively with the study of cross-sections on micro-samples. Traditional cross-section images make it possible to investigate the layer composition and depth only in two dimensions, but do not provide analysts with information on the third dimension of the sample (or investigated area). On the other hand, in THz-TDS imaging each pixel of the image contains its own cross-section of information (stratigraphic information). Thus, area information on the layer of interest is also obtained by extracting the corresponding peaks in signals in the time domain. A 3D internal structure can be established by gathering images. However, one drawback of this technique involves the presence of substances that totally reflect the THz radiation. Thick and homogeneous gold leaves that can mask the structure underneath because they reflect the THz waves are an example of these substances.

THz-TDS imaging can be used to acquire spectra of the compounds constituting the paint layers (pigments, dyes, binders), even when these are covered by layers of varnish, because most of the natural and synthetic resins used as varnish show little and weak spectral features. However, since the available frequency range of existing THz imaging systems is still limited to less than 3 THz, the spectral information in the frequency domain would not be enough to unequivocally determine unknown materials. Certain artists' materials, such as lead white and cinnabar, for instance, show high reflection, compared to other white and red pigments. The area painted only by these pigments can be easily seen; but in order to better determine the analysed materials, other analytical methodologies, such as NIR or XRF, are usually required.

As far as THz imaging techniques applied to the investigation of ancient papyrus, mummies and archaeological bones, as well as to the study of art and/or archaeological wood found in cultural heritage for dendrochronological purposes, are concerned, the very promising first results reported in a few papers need to be extended to a more extensive set of case studies, in order to better refine the experimental methodologies.

The experiments with THz imaging systems introduced above have suggested that this technique could have a useful application in the cultural heritage field. The THz imaging technique, however, is a new technique and consequently, as already mentioned, THz data on artists' materials and on actual artworks will need to be collected extensively, thoroughly studied, and verified by means of careful comparisons of the results with those obtained by using other well-established diagnostic and analytical methodologies.

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