Terahertz spectroscopy and imaging for material analysis in conservation science

Kaori Fukunaga and Iwao Hosako
National Institute of
Information and Communications Technology
Koganei, Tokyo, Japan

Marcello Picollo
Istitute di Fisica Applicata, "Nello Carrara"
Consiglio Nazionale delle Ricerche
50019 Sesto Fiorentino, Italy

Abstract—**Terahertz (THz) waves can penetrate opaque materials and fingerprint spectra appear as those in infrared bands. The technique is expected to be used as a new non-invasive analysis method for various materials. Time domain reflection imaging, in particular, uses THz pulses that propagate in specimens, and in this technique, pulses reflected from the internal boundaries of the specimen indicate the internal structure. We have developed a spectral database of painting materials, and applied THz time domain imaging for analysis of artworks. Experimental results, including first ever non-invasive cross section image of a tempera masterpiece, proved that THz wave can observe layer structure of the artwork from the wood support, gesso preparation layers, and the painting layer. This technique should also be useful to detect internal defect of various types of opaque dielectric materials such as multi layer insulations.**

Keywords-component; terahertz;cultural heritage

I. INTRODUCTION

Terahertz simply refers to a region of frequency of around 0.1~10 THz (wavenumber: 3 to 300 cm^{-1}; wavelength: 30 μm to 3 mm) which exists between radio waves (electronics) and lights waves (optics). Similarly to radio waves, THz waves can pass through opaque materials, and similarly to infrared light, many materials produce fingerprint spectra in the THz region. Unlike infrared region, the spectra in the THz region correspond to weaker intermolecular behaviour. Although there is a rich history in academic research about material analysis in far-infrared (THz) frequency range, such as phonon absorption behaviour of semiconductors using the Fourier Transform THz (FT-THz) system, the frequency range had not been used in practical applications. Thanks to the progress of laser technology, THz spectroscopy and imaging have become emerging techniques in the field of optics research, and they have been used as solutions in security problems; drug detection in envelopes is one such application [1-4]. THz imaging can be performed either by the transmission or by the reflection of THz waves, and the internal physical structure can be non-invasively observed in 3D. Together to the structure of the investigated object THz radiation makes it possible to obtain information on the composition of the materials. THz real-time sensing system has been recently developed by using micro bolometer array detectors and quantum cascade laser THz source [5, 6].

There are attempts to apply THz technology to cultural heritage, including art material analysis and material mapping by using model specimens of fresco, tempera, oil paintings [7-12]. This paper introduces the recent progress of THz technology and example of applications to artwork analysis, including the first ever application to a real masterpiece the *Polittico di Badia* by Giotto of the permanent collection of the Uffizi Gallery [13].

II. TERAHERTZ SPECTROSCOPY

As in the mid-infrared region, fingerprint-like absorption spectra of substances appear in THz frequency region, and the spectral features depend on molecular and intermolecular behaviours, phonon absorptions, as well as weak bonds such as hydrogen bonds. For example, crystal polymorphs which are composed with the same atoms in different shape of molecule can be easily distinguished by THz spectra rather than mid-infrared region. Pharmaceutical industries use THz spectroscopy to justify their originality comparing to various generic products [14]. The interfacial phenomena between fillers and matrix polymers can be investigated to clarify the advantage of nano-size fillers comparing to the micro fillers [15]. However, the meaning and band assignments of these spectra has not been extensively discussed so far, and thus the research of spectral assignment is not active enough yet.

Transmission and reflection spectra of gas, liquid, solid specimens can be obtained by conventional FTIR systems with far-infrared option, and in fact there are data books on spectra of semiconductor devices [16]. Most of commercially available systems cover the frequency range from 0.5 THz to 15 THz. To avoid strong absorption by water vapour in THz region, most systems have sample holders under vacuum or nitrogen purged. A newly developed system with a thin gap (10 mm) to place sample in transmission mode was used (Fig. 1) to allow measurement in normal atmosphere. It uses a ceramic lamp source, a silicon beam splitter [17], and a triglycine sulphate (TGS) detector. Since all optical components are enclosed in vacuum, the influence of water vapour becomes practically negligible, and specimens such as powders and liquids can be measured without special preparation. The spectra of several inorganic pigments in the THz region, including most of the important pigments in historic paintings, such as cinnabar (HgS) and orpiment (As_2S_3) [18], were already observed in

978-1-4244-7944-3/10/$26.00 ©2010 IEEE

1969 by using the very first THz-FT system, and the data obtained in this work are in good agreement.

Fig. 2(a) shows examples of transmission and reflection spectra of a red inorganic pigment, cinnabar (HgS). The reflection from this pigment is strong enough to be recognised by THz-TDS imaging of which frequency range is from 0.5 to 2 THz. Fig. 2 (b) shows spectra of lead based pigments. A portable X-ray fluorescence, which is a device commonly used to non-invasively analyse art materials, only shows the presence of lead. THz spectroscopy, on the other hand, can distinguish lead based yellow and lead white with organic yellow dye, because almost all organic dye materials have little spectral features in THz region, resulting in the spectra of lead white itself. Spectra of mixtures of a cobalt blue pigment and two binders, and those of binders are shown in Figs. 3(a) and 3(b), respectively. The spectrum of cobalt blue appeared as a superposition in the spectra of all mixtures. Since Venetian turpentine is a natural mixture of oil and resin, the spectra in Fig. 3(b) are realistic. Many synthetic resins have particular features. Beva® was developed for art conservation purposes, which includes polyvinyl acetate (PVAc) and natural resin, the mixed feature appeared also in the spectra.

The recent progress of THz-TDS systems (Fig. 4) allows direct measurement of complex permittivity without K-K transformation [4]. Commercially available systems often use a photoconductive antenna with a femto-second fibre laser as a THz source and photoconductive detector that covers the frequency range from approximately 0.1 THz to 3 THz [19, 20]. The attenuated total reflectance (ATR) systems have been recently developed to investigate liquid specimens, and characteristics of hydrogen state in solutions are successfully investigated [21].

Here it should be noted that there is no commercial spectral library for practical THz spectroscopy. NICT had developed a database of art materials with more than 200 specimens in 2007, and has been expanded with the database from RIKEN which contains more than 200 spectra of pure chemicals measured quantitatively, under controlled temperature. At present, more than 900 spectra, including more than 500 art materials', are available online (http://www.thz.org). Although the number of users of THz spectroscopy is still limited, and no measurement protocol was established, this database can contribute to encourage potential users to join in, by showing various finger-print spectra.

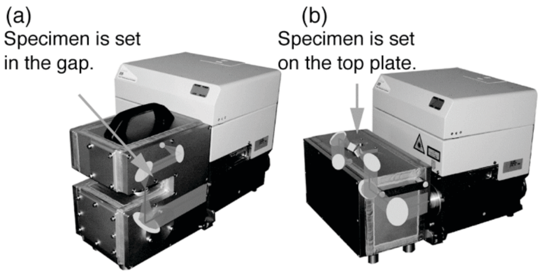

Figure 1. FT-THz System (JASCO, JAPAN)

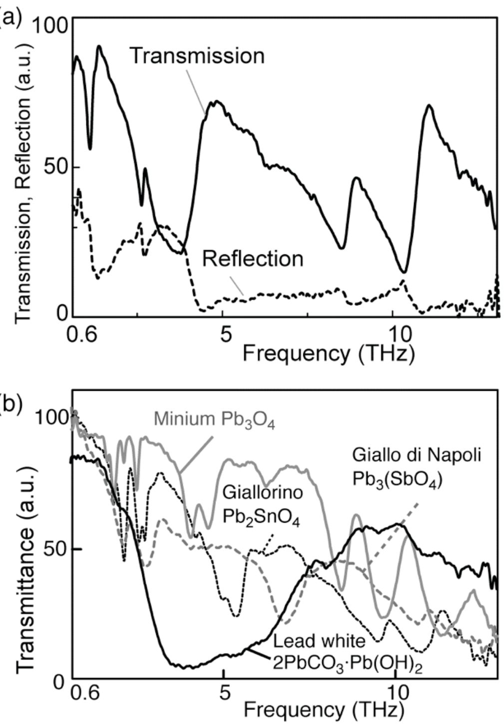

Figure 2. Examples of spectra of pigments, (a) transmission and reflection spectra of cinnabar, (b) transmission spectra of lead base pigments

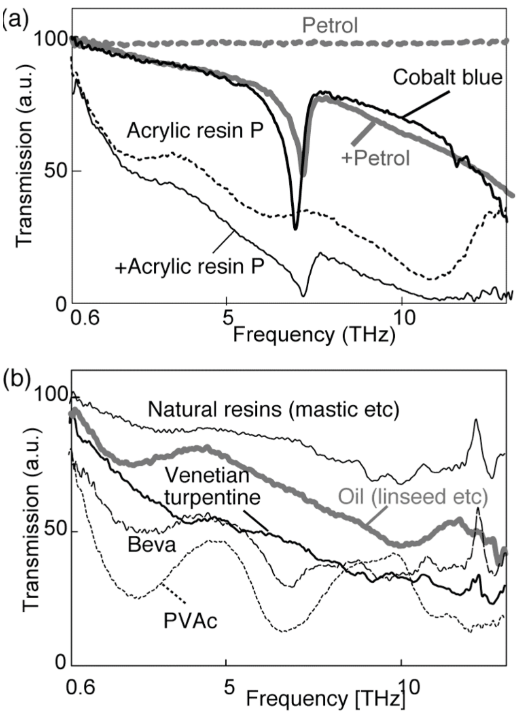

Figure 3. Example of spectra of mixtures, (a) cobalt blue and binders, (b) binders.

III. TERAHERTZ IMAGING

THz imaging is used to map the spatial distribution of materials and/or to observe the inner structure of a non-metal object. Although the map of materials could have been fully based on the spectra described in the previous section, existing imaging systems have rather limited frequency band approximately up to 3 THz. Thus, the applications of this technique are limited to detect specific materials, such as plastic explosives whose spectra have already been recorded. The high sensitivity of THz radiation to the water [22] can be used to monitor the water content in various dielectric materials.

The biggest advantage of THz imaging is that THz can observe the internal structure of a non-metal object noninvasively from its surface by using THz pulses. This is similar to the time domain reflectometry (TDR) technique, which has been used to detect breakdown point along cables. Fig. 5 shows a typical structure of a painting and a comparison of different imaging diagnostic methods using diverse electromagnetic wavelengths ranges. Ultraviolet is useful for examining the most superficial layers of a painting, such as the varnish layers, whereas infrared can reveal the under-drawings. X-rays radiography pass through most of the non-metal materials. THz can be used to analyse the materials slightly below the paint layers, such as the preparation layers. According to conservators, information in the preparation layers is important to better understand the artists' technique of works of art.

Having observed various types of model paintings, it was analysed an actual panel painting, one of the masterpieces at the Galleria degli Uffizi. The *Polittico di Badia* is a tempera panels (painted on wood), by Giotto di Bondone [23]. A transportable THz system (Picometrix, T-Ray 4000) was used to investigate the painting by placing the scanner in front of the *Polittico* at the distance of about 15-20 mm. Fig. 6 shows an example of THz reflection images compared with visible photographs. As shown in Fig. 6 (a), existence of gold foil under paints was clearly observed at the outline of the head and wings of Angel. The non-invasive cross-section image of a crack was also clearly seen in Fig. 6 (b). The preparation of the painting was made with two gesso layers and a canvas between them. The cross-section image revealed that there is no preparation layer in the area of the crack, and only the surface was restored.

Here, in the case of medieval and early renaissance panel paintings, a gypsum layer was made directly on a base wood to flatten the carved wood base. A cloth was placed on the gypsum layer; subsequently, another gypsum layer was made as a preparation layer for painting. The THz imaging results non-invasively proved that Giotto used the medieval technique structure. By extracting peaks from output signals in time domain, a map of the layer of interest was obtained [13]. The information obtained here using THz imaging would never be obtained by conventional methods. If necessary, it is possible to construct a full three-dimensional model of the internal structure.

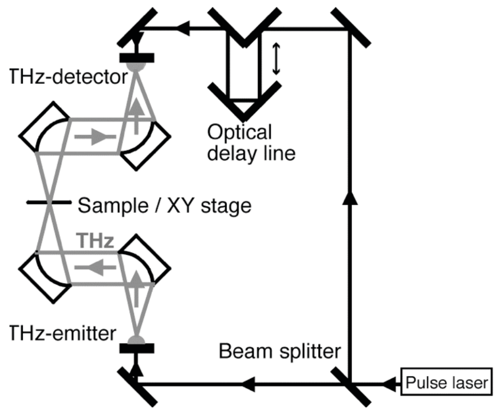

Figure 4. Diagram of THz-TDS system.

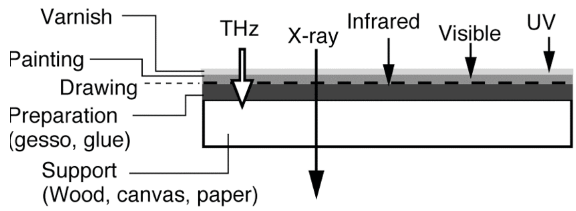

Figure 5. Typical structure of painting and analysing electromagnetic waves.

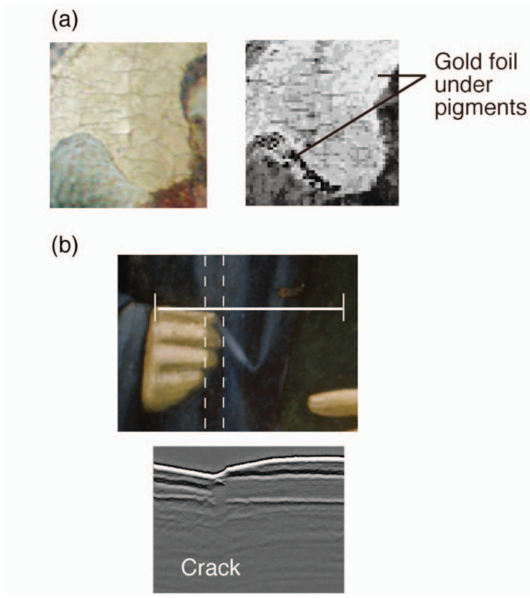

Figure 6. THz imaging of a tempera masterpiece by Giotto, (a) Near surface observation, (b) non-invasive cross section image.

IV. CONCLUSIONS

THz spectroscopy and imaging technique are introduced as new analytical methods for the study of cultural heritage objects. Judging from the obtained experimental results, such as non-invasive cross-section images of a panel painting, THz spectroscopy and imaging should be considered as a complementary non-invasive analytical and diagnostic methodology in the cultural heritage science research field. In particular, this new imaging technique provides non-invasively information on the internal physical structures of non-metal objects.

ACKNOWLEDGMENT

The authors would like to thank Cristina Acidini (soprintendente per il Polo Museale Fiorentino), Antonio Natali, and Angelo Tartuferi (director and curator of the Uffizi Gallery, respectively), who kindly gave the authors the permission to investigate the painting. The authors greatly appreciate the collaboration with Stefano Scarpelli and Susanna Bracci.

REFERENCES

[1] Ed. G. Gruner, Millimeter and Submillimeter Wave Spectroscopy of Solids, Springer, Berlin (1998)

[2] D. M. Mittleman, M. Gupta, R. Neelamani, R. G. Baraniuk, J. V. Rudd, M. Koch, "Recent Advances in Terahertz Imaging", Applied Physics B, 68, (1999), pp. 1085-1094.

[3] D. M. Mittleman, Sensing with terahertz radiation, Springer, Berlin (2003).

[4] M. Tonouchi, "Cutting edge terahertz technology", Nature Photonics, 1, (2007), pp. 97-105.

[5] N. Oda, H. Yoneyama, T. Sasaki, M. Sano, S. Kurashina, I. Hosako, N. Sekine, T. Sudoh, T. Irie, "Detection of terahertz radiation from quantum cascade laser, using vanadium oxide microbolometer focal plane arrays", Proc. SPIE, 6940 (69402Y), (2008).

[6] I. Hosako, N. Sekine, M. Patrashin, S. Saito, K. Fukunaga, Y. Kasai, P. Baron, T. Seta, J. Mendrok, S. Ochiai, H. Yasuda, "At the Dawn of a New Era in Terahertz Technology", Proceedings of IEEE, 95, (2007), pp. 1611-1623.

[7] W. Köhler, M. Panzer, U. Klotzach, S. Winner, M. Helm, F. Rutz, C. Jördens, M. Koch, H. Leitner, "Non-destructive investigation of paintings with THz-radiation", Proceedings of European Conference of Non-Descructive Testing, No. P181 (2006).

[8] K. Fukunaga, Y. Ogawa, S. Hayashi, and I. Hosako, "Terahertz Spectroscopy for Art Conservation", IEICE Electronics Express, 4(8), (2007), pp. 258-263.

[9] J. -M. Manceau, A. Nevin, C. Fotakis, S. Tzortzakis, "Terahertz time domain spectroscopy for the analysis of cultural heritage related materials". Applied Physics B, 90, (2008), pp. 365-368.

[10] J.B. Jackson, M. Mourou, J.F. Whitaker, I.N. Duling III, S.L. Williamson, M. Menu, and G.A. Mourou, "Terahertz imaging for non-destructive evaluation of mural paintings," Optics Communications, 281, (2008), pp. 527-532.

[11] N. Sunaguchi, Y. Sasaki, M. Kawai, T. Yuasa, C. Otani, "THz-wave tomographic imaging: An approach via CT reconstruction from limited projections", Proc. IRMMW-THz 2008, No. R5D14 (2008).

[12] A. J. L. Adam, P. C. M. Planken, S. Meloni, J. Dik, "Terahertz imaging of hidden paint layers on canvas", Optics Express, 17, (2009), pp. 3407-3416.

[13] K. Fukunaga, I. Hosako, I. N. Duling III, M. Picollo, "Terahertz imaging systems: a non-invasive technique for the analysis of paintings" Proc. SPIE, (2009) No. 7391D, 2009.

[14] C. J. Strachan, P. F. Taday, D. A. Newnham, K. C. Gordon, J. A. Zeitler, M. Pepper, T. Rades, "Using terahertz pulsed spectroscopy to quantify pharmaceutical polymorphism and crystallinity", Journal of Pharmaceutical Sciences, 94, (2005), pp. 837-846.

[15] Yoshimichi Ohki, Masahide Okada, Norikazu Fuse, Kentaro Iwai, Maya Mizuno, Kaori Fukunaga, "Terahertz Time-domain Spectroscopic Analysis of Molecular Behavior in Polyamide Nanocomposites", Applied Physics Express, 1(122401), (2008).

[16] E. D. Palik, Handbook of Optical Constants of Solids, Academic Press, New York, (1997)

[17] K. Abe, S. Hayashi, N. Doki, C. Otani, K. Kawase, T. Miyazawa and Y. Ogawa, "Measurement of Hydrated Water in D-Glucose Powder Using THz-Wave Spectroscopy," Bunseki Kagaku, 56, (2007), pp. 851-856, in Japanese with English abstract.

[18] C. Karr Jr. and J. J.Kovach, "Far-Infrared Spectroscopy of Minerals and Inorganics", Applied Spectroscopy, 23, (1969), pp. 219-223.

[19] Y. Shen, P. F. Taday, "Development and application of terahertz pulsed imaging for non destructive inspection of pharmaceutical tablet", IEEE Journal of Selected Topics in Quantum electronics, 14, (2008), pp. 407-417.

[20] D. Zimdars, J. S. White, G. Stuk , A. Chernovsky, G. Fichter, and S. Williamson, "Security and Non Destructive Evaluation Application of High Speed Time Domain Terahertz Imaging", Proc. Lasers and Electro-Optics and 2006 Quantum Electronics and Laser Science Conference, No. CMLL1, (2006).

[21] D. A. Newnham, and P F Taday, "Pulsed terahertz attenuated total reflection spectroscopy", Applied Spectroscopy, 62, (2008), pp. 96-112.

[22] B. B. Hu and M. C. Nuss, " Imaging with terahertz waves", Optics Letters, 20(16), (1995), pp. 1716-1718.