Terahertz imaging for analysis of historic paintings and manuscripts

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***Abstract*— Through the application of terahertz spectroscopy and imaging to the analysis of art, we have developed a spectral database of art materials containing more than 200 spectra of various pigments and binders. With this database, a red ink used in a thirteenth-century manuscript was identified; the results were verified by X-ray fluorescence elements mapping. Terahertz transmission spectral component analysis successfully distinguished stains on the red ink. Reflection imaging also can be used to distinguish materials. Similar techniques can be applied to construct images of specific materials on objects not only in art conservation science but also in various other industries.**

I. Introduction and Background

TERAHERTZ (THz) spectroscopy and imaging techniques are one of the fastest-progressing topics in research on applied optics, and various practical applications have been developed so far, especially in the security and pharmaceutical fields [1] [2]. It is a non-invasive analysing technique of organic and inorganic materials, multi-layer specimens, and even hidden object in an envelop or under clothes.

Almost all great works in art have the history of restoration. For the modern restoration, it is essential to investigate materials and techniques used in original works as well as previous restorations. We believe that THz spectroscopy has great advantages in the field of art conservation science, and have developed a spectral database by using a conventional Fourier transform infrared (FTIR) spectroscopy system, containing more than 200 spectra of various pigments and binders (http://www.thz-spectra.com/). Since ultraviolet to mid-infrared spectroscopy and imaging techniques have been used in the field of scientific analysis of art, specimens for the spectra were chosen by following the previous works with these frequency ranges [3] [4]. The availability of the fingerprint spectra suggests that THz spectroscopy can be used for the non-invasive analysis of art objects [5].

We applied THz-Time Domain Spectroscopy (TDS) system for transmission imaging with the component analysis technique. THz transmission imaging is applicable to thin specimens such as those made of parchment, and reflection imaging should be used for most murals. A THz imaging system with a free electron laser, developed by Ente per le Nuove Tecnologie, l'Energia e l'Ambiente (ENEA), Frascati, was applied to perform reflection imaging of art objects.

In this paper we introduce examples of character recognition from a medieval manuscript by transmission imaging, and analysis of tempera paintings by reflection imaging.

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II. Results

A. Identification of a medieval ink

The specimen used in transmission imaging was a parchment manuscript dated to the thirteenth century. The spectrum of the red ink used in the manuscript was compared with the entries in the database. As shown in Figure 1, the spectrum of the unknown ink had peaks around 1.1 and 3.8 THz. This spectral feature revealed that the red pigment was a type of natural cinnabar, though not a natural pigment called 'cinnabar Monte Amiata'.

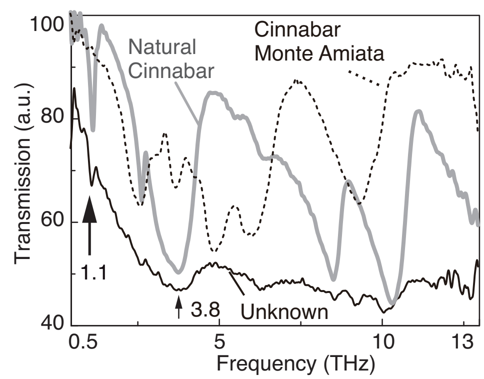

Fig. 1. Spectra of red ink and two cinnabar pigments

Here, there was some doubt as to whether natural cinnabar Monte Amiata actually contains HgS. This was because, in the Riken database, reagnet-grade (pure) HgS has exactly the same profile as that of the natural mineral cinnabar [6] (Figrue 2), which does not match the profile of this pigment, and indeed, pigments can be named by their manufacturers without strict regulation.

In a previous study using X-ray diffraction and mid-infrared spectroscopy [7], this product, cinnabar Monte Amiata, which was actually stored in the same container, was thought to be composed of litopon (a $BaSO_4$-based white pigment) and cadmium red (CdS-CdSe composite). We compared the spectra of all three pigments. As shown in Figure 3, the results revealed that sharp peaks exhibited by cinnabar Monte Amiata originate from litopon and the relatively broad peaks from cadmium red. This proves that THz spectroscopy can non-destructively identify the components of mixed pigments.

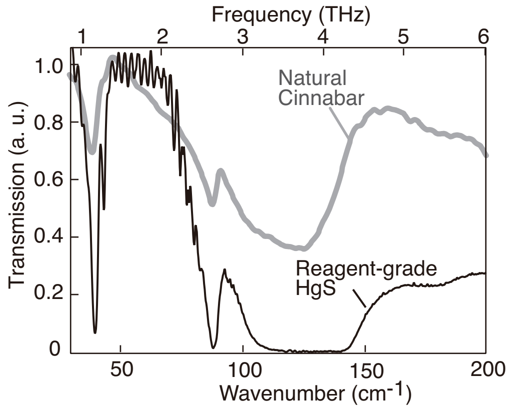

Fig. 2. Spectra of natural mineral cinnabar and pure HgS

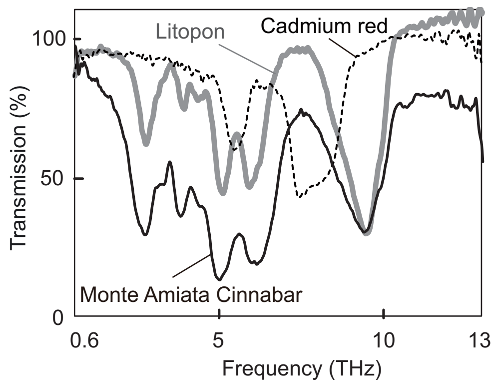

Fig. 3. Possible compositions of cinnabar 'Monte Amiata'

B. THz transmission imaging: Extraction of a particular pigment

Based on the spectrum in Figure 1 (a), the text in red ink was extracted from the manuscript by component analysis [8] [9]. As shown in Figures 4 (a) and 4 (b), the red text was clearly distinguished from the base parchment and two stain spots recognised on the top of the visible image were successfully removed.

To compare the present results with those of existing analysis methods, X-ray fluorescence (XRF) element mapping was used. XRF is currently a common tool in art conservation, although it has ionising effects. The constituent elements of cinnabar, i.e. HgS. Both Hg and S were detected in the same region, while Pb, found in another possible red ink (minium) used in medieval manuscripts, was not detected (Figure 4 (c)).

C. THz reflection imaging

We have reported that THz imaging can identify the gold parts in a tempera painting covered by white plaster by detecting the reflection at the metalized areas [10]. Some pigments have large reflections in the THz region, and can therefore be detected and identified through layers of plaster. Figure 5 (a) shows the transmission and reflection spectra of natural cinnabar. It is clear that the decrease in transmission level of pigments is due to reflection, in addition to possible absorption. Figure 5 (b) shows the spectra of lead white.

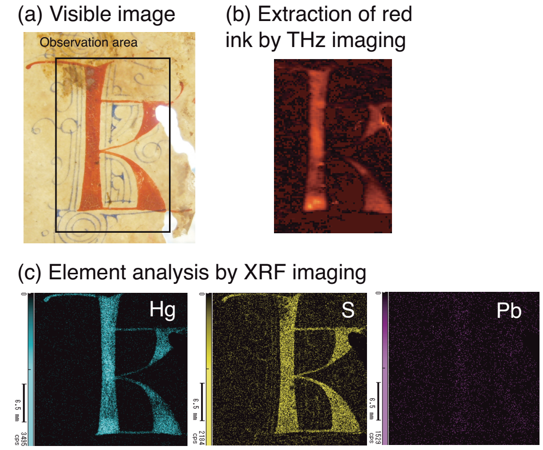

Fig. 4. THz and XRF imaging results.

Since lead white was widely used as both a paint and an underpaint, it would disrupt measurement, or on the contrary, could improve measurement by affording the transmission spectra of the paints on the lead white base.

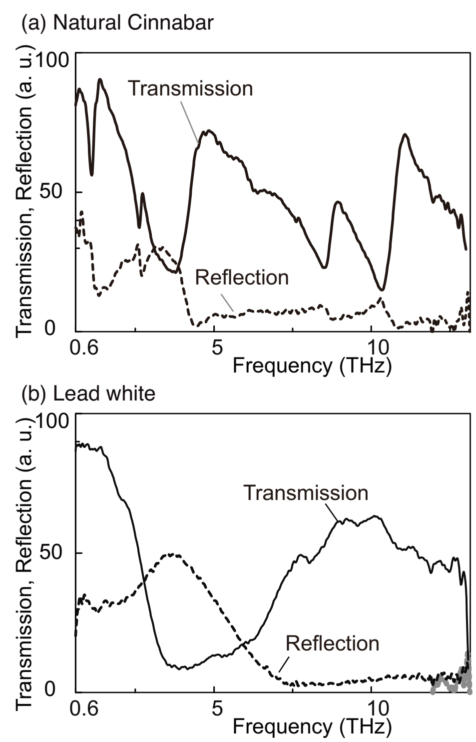

Fig. 5. Transmission and reflection spectra.

Figures 6 and 7 show an examples of reflection images obtained by the imaging system at 150 GHz with the compact Free Electron Laser, developed by ENEA-Frascati [11]. Specimens were prepared by traditional tempera painting technique with preparation of gesso ($CaSO_4$) on wood plates, and were painted with pigments grinded into less than several tens microns. As shown in Figure 6, the reflection of cinnabar and malachite was high, and that of natural ultramarine (lapis) and giallorino (lead-tin yellow) was low. The nonuniformity would be due to the difference in the thickness of paint layer. This

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result proves that the reflection measurement at 150 GHz can distinguish materials. Details of the measurement using the phase information of the reflection waves can be found in the reference [10].

One of the most important advantages of THz spectroscopy is the ability of detecting hidden object. Figure 7 proves that the THz reflection imaging can detect the metallized part with gold covered with gesso, and moreover, pigments under gesso can be distinguished when the difference in their responses is relatively large.

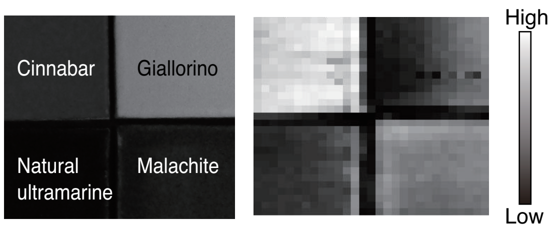
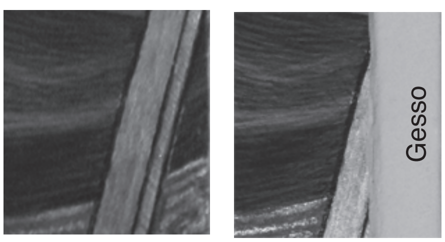


Fig. 6. THz reflection imaging of various paints.

(a) Specimen before and after covering with gesso.



(b) THz imaging of the specimen covered with gesso.

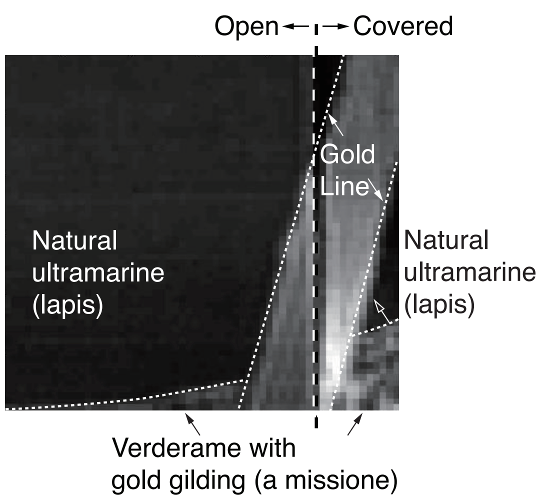


Fig. 7. THz reflection imaging of tempera painting covered with gesso, (a) specimen and (b) THz reflection image.

III. Conclusions

We applied THz spectroscopy and imaging techniques to the scientific analysis of objects of art. The experimental results revealed that both transmission and reflection spectra can be used to analyse art, and materials, including pigments and binders, can be identified using a database of the spectra of various original and aged materials. As future work, we will attempt to fully elucidate the advantages and disadvantages of THz spectroscopy in the field of art conservatio science.

Many mineral pigments containing transition metal elements have sharp characteristics peaks in their spectra which can be assigned theoretically. This technique should contribute to various other research fields such as earth science and non-destructive testing.

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