5-2 Terahertz Spectroscopy for Non-Invasive Analysis of Cultural Properties

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The scientific analysis of materials used in art objects can determine the period in which the objects were created, how they were kept for centuries, and how they had been restored. Terahertz spectroscopy (500 to 20 cm^{-1}, or 0.6 to 15 THz), on the other hand, the motions of entire molecules or inter-molecules contribute to the spectra, and can distinguish pigments and binders non-invasively. NICT collected more than 200 spectra of art materials, and most of pigments have specific absorption peaks in terahertz region. Some of the spectra were indicated as THz false colours to show experimental results as a painting with material information.

Keywords
Art conservation, Non-invasive analysis, Spectral database

1 Introduction

Cultural properties, our common human heritage, have often been subject to centuries of restoration. Conservators investigate the materials used in the original work and how it has been restored (or sometimes even altered) before they apply treatments such as cleaning, reinforcing, filling, retouching, and application of protective varnish. For the works of a range of famous artists from the end of medieval times and into the early Renaissance, contracts have been preserved recording the amount of expensive pigments (such as lapis lazuli), gold, and marble that were used, and information on the materials used by these masters can be obtained from available documents — to an extent. When restoring an important work, conservators clarify the history of the work using a number of different techniques of analysis. However, works by unknown artists and those held by individual collectors are studied less extensively, and when they are, such investigation is usually based on infrared photography (as opposed to spectroscopy) or (at best) UV photography; these studies are of necessity based more on the experience of the conservator than on objective analysis.

When the target of the investigation is a cultural property, even a slight amount of sampling is regarded as an act of destruction in most cases. Thus, non-invasive analysis on-site at the location of the cultural property is indispensable. A technique in particularly wide use involves the detection of metal elements in pigments by X-ray fluorescence. It is generally considered possible to identify the pigments employed in most cases, once the elements are known. However, X-ray fluorescence cannot analyze organic materials such as binders.

Terahertz spectroscopy is a non-invasive technique of analysis that can efficiently provide information unique to each material; this method is considered particularly effective in analyzing mixtures[1][2]. Thus, mainly focusing on classic pigments, we have constructed the spectral database that will be required to perform effective terahertz spectroscopy and have investigated the potential applications of terahertz spectroscopy to the analysis of cultural properties.

2 Spectra of mixtures

2.1 Pigment-pigment and pigment-body pigment mixtures

To produce an intended color from a limited number of pigments, the pigments are mixed. For example, there were few vivid green pigments in medieval times, and blue and yellow pigments were mixed in many cases to make green. If the mixed pigments do not react with each other, they can exist in the binder independently. Thus, the spectrum is expected to correspond to the sum of the spectra of the constituent pigments. Figure 1 shows such an example. As shown in Fig. 1 (a), the spectrum is the sum of the spectra for cobalt blue and zinc white, while the color is a mixture of the two, as shown in Fig. 1 (d)[3].

Calcium carbonate, one of the white pigments, becomes almost transparent when mixed in oil and is used as a body pigment added to strengthen or to add bulk to other pigment paints. The spectra indicated as (a) and (b) in Fig. 2 are for pigments both sold as crimson. However, the spectra clearly show that one of them contains calcium carbonate, the spectrum of which is also indicated in Fig. 2 as (c).

Some combinations of pigments fail. For example, a mixture of lead white and sulfur blackens as time passes (over the course of years or decades). This phenomenon is due to the chemical reaction caused by mixing these pigments. We plan to investigate whether this change appears in the spectrum in an accelerated deterioration test by storing the mixture in high-temperature, high-humidity conditions and comparing the results with spectra obtained under control conditions.

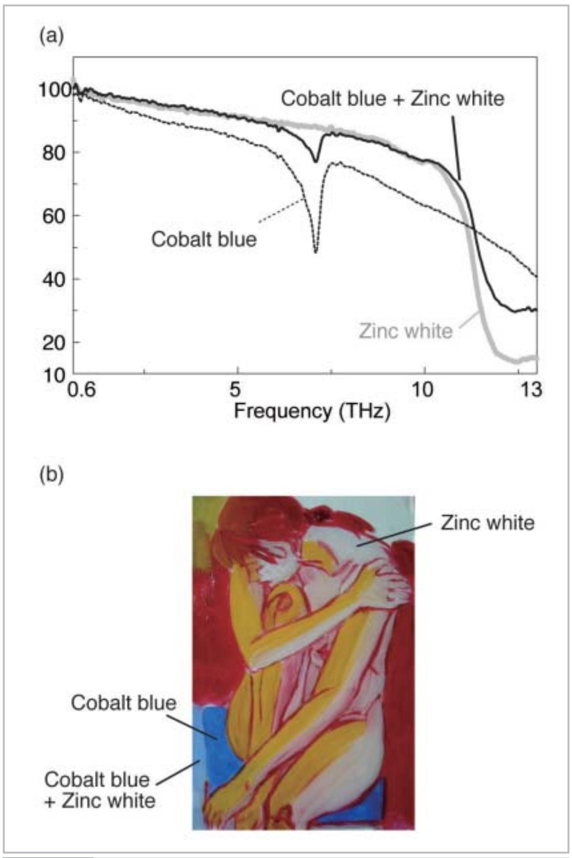

Fig.1 *Example of mixing cobalt blue and zinc white*

(a) Spectrum, (b) color of mixture

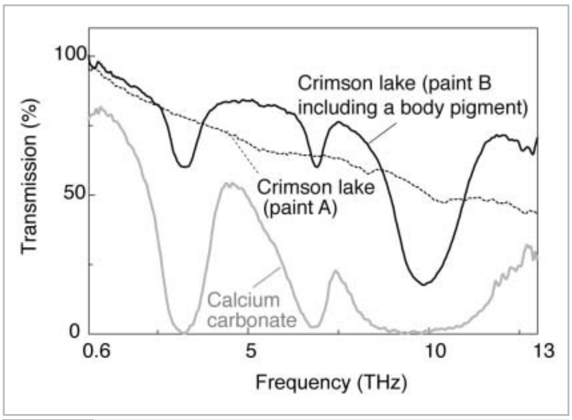

Fig.2 *Example of presence of body pigment (crimson lake)*

2.2 Pigment-binder and adhesive mixture

What we call "paints" are mixtures of pigments or dyes and binders. The binder of the Japanese traditional painting is animal glue, the binder of ordinary watercolor pigment is arabic gum, and the binder of oil paint pigment is oil, which often contains resin. The spectrum of a pigment fixed in a binder is extremely complex in the mid-infrared range and therefore difficult to analyze. In addition, infrared can only analyze the outermost surface. Terahertz waves penetrate substances more deeply than infrared waves, enabling

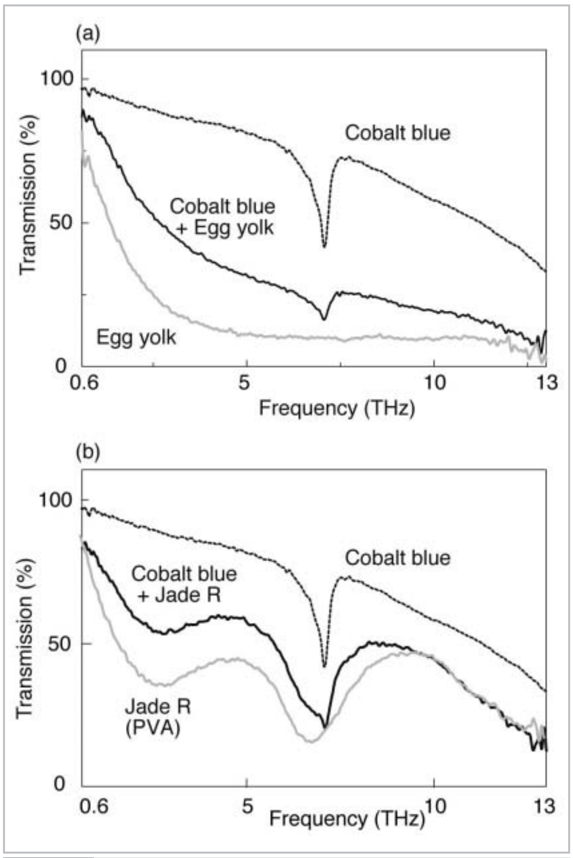

Fig.3 *Spectra of paints:*
(a) Cobalt blue and egg yolk (egg tempera),
(b) Cobalt blue and PVA

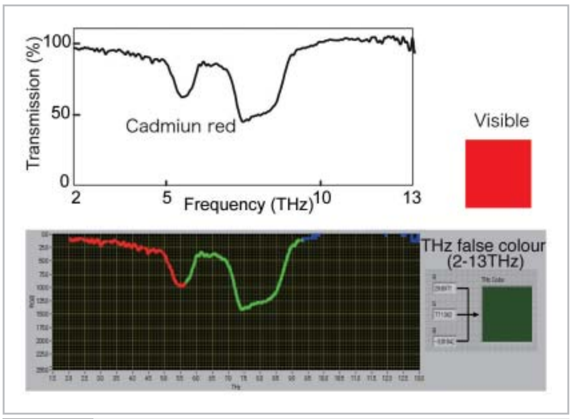

Fig.4 *Terahertz spectra false-colors for cadmium red*

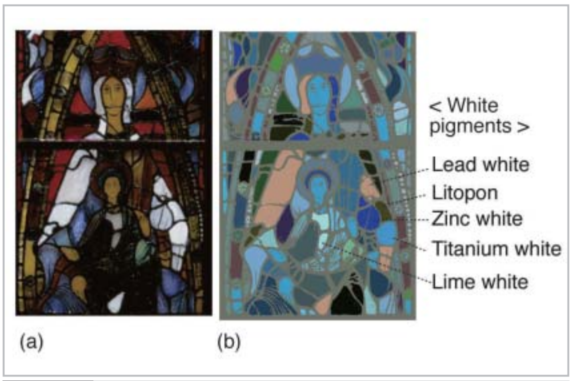

Fig.5 *Painting analysis by terahertz false-color representation*
(a) Visible image, (b) THz false color

analysis of pigments under protective varnish. In general, pigments have sharp absorption peaks while binders have broad spectra. The measured spectrum can be recognized as the sum of the two spectra. Figure 3 (a) shows the example of cobalt blue pigment mixed with an egg binder, in tempera. The spectrum for the paint is the sum of those for the pigment and the binder. Figure 3 (b) shows an example of cobalt blue pigment mixed with PVA (Polyvinyl acetate) adhesive used for restoration. The figures show the resultant characteristics when the two materials are combined.

3 False-color representation of terahertz spectra

To express a paint directly in terms of the spectra of its materials, we developed a method for creating false-color images by dividing the spectral data for each color into three regions within a certain frequency range and attributing the average of the intensity in each region to each of the RGB values. Figure 4 shows an example of the false-color representation of a cadmium red spectrum created by dividing the frequency range from 2 THz to 13 THz into three equal parts. In the future, combining this method of presentation with imaging systems such as terahertz cameras will enable displaying the image in a visual manner that also conveys information on the composite material.

3.1 Stained glass-like sample

Here we show an example of analysis of different materials in the same color based on false-color representation using a stained glass-like sample. Figure 5 (a) shows a photograph taken using visible light. Figure 5 (b) shows the terahertz false-color representation. The sample uses five types of material to form white, blue, red, yellow, green, black, and brown. For example, white sections that appear almost the same to the naked eye using lead white and titanium white appear completely different in the terahertz false-color representation. While lead white has been used since ancient times, titanium white has been in use only since 1920. If a work of art originally created in medieval times contains titanium white, it has clearly been touched up in later years.

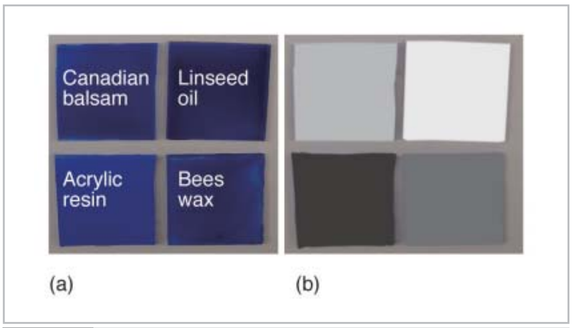

Fig.6 *Visualization of binders*
(a) Visible image, (b) THz false color

3.2 Visualization of binders

Among the various art materials, pigments can be identified to an extent by X-ray fluorescence elemental analysis. However, to date no practical non-invasive analysis methods have been developed to identify the type of binder. Different binders show a wide range of transmittance in the terahertz range (See Fig. 5 of Article **5-1**). Given the differences in the terahertz spectra, different binders can be expressed as different gray tones, as shown in Fig. 6, even if the paints themselves show the same blue to the naked eye. For example, if a part of a medieval painting contains synthetic resin, this visualization technique can show that this portion has previously been touched up and filled by a subsequent conservation.

4 Development of on-site system of scientific analysis

The construction of an art material database and the results of experiments with various samples have demonstrated that terahertz spectroscopy is a promising method of non-invasive chemical analysis for cultural properties. However, the measurements achieved in this study all used the THz-FTIR; unfortunately, this is not a portable analyzer. Since cultural properties are most preferably studied on-site, we must work toward miniaturization of a terahertz spectroscopy system. A portable terahertz spectroscopic imaging system would prove effective not only in investigating cultural properties but also in a range of other applications, such as non-invasive inspection of industrial products in factories. Reducing the size of the system will thus be indispensable in expanding the range of industrial applications of terahertz waves.

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