5 Terahertz Spectral Database

5-1 Construction of Open Terahertz Spectral Database

FUKUNAGA Kaori

The terahertz spectroscopy is expected to become a new non-invasive analyser in various applications since the terahertz wave can penetrate into opaque materials and can analyse multi-layered specimens with a time domain spectroscopy described in the previous section. Terahertz spectra correspond to molecular or inter-molecular behaviour unlike mid-infrared spectra which give intra-molecular information. Any kind of spectroscopy requires spectra databases for practical applications. Limited number of spectra is sufficient when the target materials are specific, such as explosives and illegal drugs. Although there are some terahertz spectral data book which contain spectra for atmospheric transmission studies etc., construction of common database with various substances is essential to enlarge the application fields of terahertz spectroscopy.

Keywords
Terahertz spectroscopy, Common spectral database communication, Industrial applications

1 Introduction

The development of stable terahertz sources that operate at room temperature has led to astounding progress in terahertz spectroscopy and imaging technologies. These technologies are now attracting a great deal of attention as new methods of non-invasive testing and analysis[1][2]. As terahertz waves penetrate through opaque substances in a manner similar to radio waves, terahertz imaging is being applied around the world in the field of security, including detection of hidden hazardous objects or concealed illegal drugs[3]-[5]. While the mid-infrared absorption spectra of substances, already established in generic analysis techniques, depend on intra-molecular bonding between atoms, terahertz absorption spectra depend on the motion of molecules themselves, or on the bonding between molecules. As a result, terahertz spectroscopy is considered an efficient means of obtaining information unique to a given substance. Further, it is also possible to analyze each layer of multi-layered materials using the terahertz-based time-domain spectroscopy described in Section **4**.

Any type of spectroscopy requires spectral databases to identify unknown substances, regardless of the frequency used. When the target materials are specific — such as substances of interest in the field of security — a special database containing a limited number of spectra is sufficient. To make terahertz spectroscopy a general non-invasive test method, a database similar to the spectral data library for the mid-infrared range is required. Existing spectral databases are limited to gases and high-purity crystals and are mainly used by researchers in specific research fields.

Currently no existing database enables identification of a material, semi-automatically or otherwise, using data obtained by a spectrometer in the terahertz range. Given this background, NICT began constructing an open spectral database of various materials in the terahertz range, as the first such initiative worldwide. This article describes the construction of the database, including the situation both within and outside of Japan, and discusses potential challenges in terms of long-tem operation.

2 Terahertz databases

Atmospheric spectra are discussed in Section **6** in detail. Here, we focus on the solid and liquid databases (spectral libraries) required when the terahertz spectrometer is used as a general analyzer.

2.1 Existing databases

The databases listed below provide terahertz spectral data to the public via the Internet as of the end of 2007.

(1) THz BRIDGE Spectral Database

http://www.frascati.enea.it/THz-BRIDGE/database/spectra/searchdb.htm

This database provides terahertz spectral data for biology-related materials, including membranes and biomaterials collected through the "Tera-Hertz Radiation in Biological Research, Investigation on Diagnostics and Study of Potential Genotoxic Effects" project conducted as part of the Quality of Life Programme of the European Union from February 2001 to January 2004. The database includes values measured using several different types of analyzers, including free electron lasers, the THz-TDS, and the THz-FTIR. A portion of the database provides numerical data.

(2) NIST THz Spectral Database

http://webbook.nist.gov/chemistry/thz-ir/

This database provides 36 spectra measured by the THz-FTIR with respect to foodstuffs (such as baking powder) and drugs (such as aspirin) in the form of polyethylene diluted pellets. The database includes numerical data, graphs, and additional data showing the effects of grain size on spectrum, as in the cases of sugar and salt.

(3) RIKEN database

http://www.riken.jp/THzdatabase/

RIKEN provides spectra of medicines and high-purity agents, along with corresponding numerical data.

As the frequency range of the data depends on the spectroscopic system, we cannot directly compare the data in these databases, and simply browsing them cannot help users to select a particular type of terahertz spectroscopic system. Comparative tests will be necessary to evaluate various terahertz spectroscopic systems with a standard specimen for the establishment of measurement protocols.

2.2 Spectral database of art materials

To demonstrate the effectiveness of the database, NICT collected spectra of a number of materials used in art, including classic pigments and materials used in restoration. Art materials vary diversely when viewed as samples, as they may include any combination of organic, inorganic, synthesized, and natural substances. The raw materials are rocks, the traditional research objects of geology. Many art materials also contain pollutants such as lead and cadmium, and many others are used in food and general industrial products. We decided to construct a database that could also be expanded into a general database, based on the cross-disciplinary applications referred to above. Mid-infrared spectroscopic databases of pigments and dyes are already commercially available, and the online database for restoration materials referred to below was constructed with the collaboration of art galleries and museums around the world.

http://www.irug.org/

Of the samples, we obtained pigments from a shop specializing in classic pigments. We chose this provider because many "classic" pigments commercially available are classic in name only; many are actually synthesized. We considered it particularly indispens-

Table 1 *Art materials included in database*

Mineral pigments	Lime white, Leadwhite, Almina white, Zinc white, Litopne, Titanium white, Cadmium yellow, Litharge, Orpiment Yellow Ochre (various types), Lead Tin Yelow, Aureolin, Naples Yellow, Raw umber, Burnt umber, Cassel earth, Raw sienna, Cadmiun orange, Smalt, Turchoise blue, Zinc yellow, Amatist, Arzica yellow, Vescica green, Burnt sienna, Green earth (various types), Veronese greem, Criscolla, Verdigris, Malachite, Cobalt Green, Azrite, Cobalt blue (various types) , Cerulean blue (various types), Prusian blue, Cadmium red (various types), Coral rose, Red orche, Minium, Realgar, Cinnabar, Cobalto violet (various types), Vine black, Lamp black, Ivory black, Lapis lazuli, Artificial ultramarine, Emerald green, Verdaccio green, Cadmium green, Cobalt green, Ultramarin green, Mangaese violet
Organic dyes	Indigo, Indian yellow, Stil de Grain, Alizalin carmine, Rose madder, Saffran, Dragon's blood, Alizalin crimson, Cochineal, Asphalt, Bistro, Seppia, Phtalocyanine green, Phtalocyanine blue, Tannin ink, Purple lake
Natural binders	Maise glue, Copal resin, Mastic resin, Dammar resin, Sandrac, Colofony, Shellac, Venetian Turpentine, Arabic gum, Elemi, Walnut oil, Linseed oil (various types), Petrol, Poppy oil, Black oil, Olifa, Casein, animal glue (various types), Bees' wax
Synthetic binders	Beva 371, Laropal K80, Jade R, Mowilith, Klucel G, Metil cellulose (various types), Paralod B67, Paraloid B72, Regalrez, Plexisol P550. Plextol
Mixtures	Commercial cobalt blue oil paint (various types), Cobalt blue with binders (various types), Copper resinate

Fig.1 *External appearance of samples for spectroscopy*

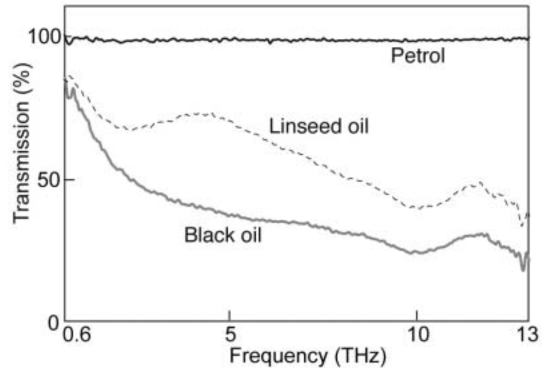


Fig.2 *Spectra of oils for painting*

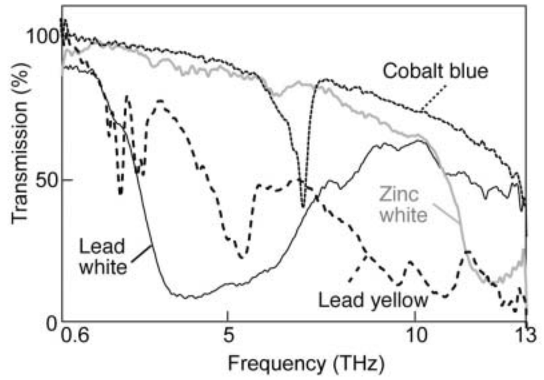


Fig.3 *Examples of spectra of inorganic pigments*

able to analyze pigments with previously available spectral data in frequency ranges other than the terahertz range[6]. We obtained synthesized pigments and synthesized resins from manufacturers of restoration materials. Table 1 shows a number of representative materials among the 207 materials for which we have obtained spectra as of December 2007.

The samples for spectroscopy were prepared by painting each art material on a reference cycloolefin polymer (Zeonex, provided by Zeon Corporation)(Fig. 1), which exhibits very little absorption in the terahertz range. Binders such as animal glue, gum Arabic, and resins were painted as they were. Pigments and dyes were painted using petrol, which has little absorption in the terahertz range (Fig. 2).

(1) Examples of spectra for inorganic pigments

Many inorganic pigments contain transition metals, and thus can be estimated by X-ray fluorescence elemental analysis. The advantage of terahertz spectroscopy is that compounds including the same elements can be identified, such as lead white and lead yellow.

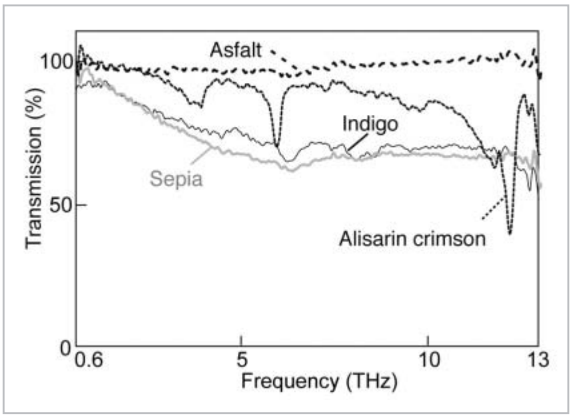


Fig.4 Example spectra of organic pigments and dyes

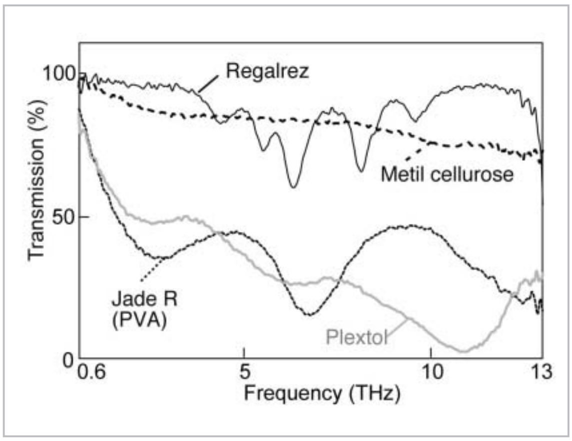


Fig.6 Example spectra of synthetic resins

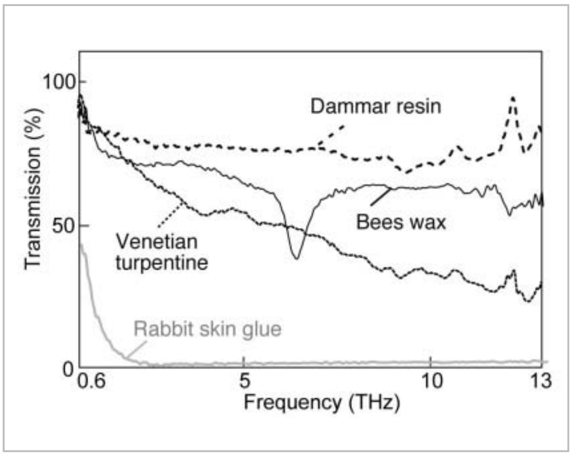


Fig.5 Examples of spectra of natural binders

(2) Examples of spectra of organic pigments and dyes

Organic pigments and dyes tend to lack unique spectral structures. Many dyes are sold in the form of lakes insoluble in water by combining dyes with inorganic substances that do not change the color of the dye. Thus, sharp absorption peaks may be due to these inorganic substances or the mixture of the dyes and these inorganic substances.

(3) Examples of natural binders

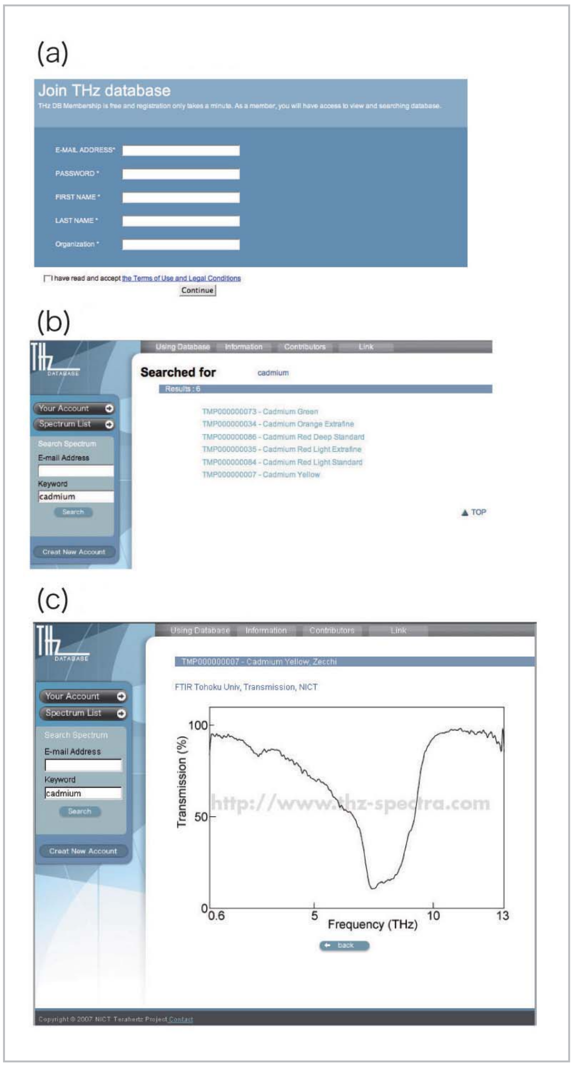
Figure 5 shows the example of linseed oil, but poppy oil and walnut oil reveal nearly the same spectra as that shown here. All of these oils feature relatively high transmittance. Natural resins also transmit terahertz waves well. However, natural resins show characteristic absorption in the high-frequency range near 8 THz. The spectrum of Venetian turpentine, which is a natural mixture of oil and resin, is the sum of the spectra of the oil and the resin. Beeswax is used in drugs and for giving luster to food, and features a large absorption band near 6 THz. Rabbit-skin glue is used in Japanese-style painting. Regardless of the type of animal source, from fish to deer, animal glues display large absorption values.

(4) Example of spectra of synthetic resins

The synthetic resins shown here include those used as binders and also those used as adhesives and filling materials. We measured five types of methylcellulose and found that they may be classified into two categories. All types of methylcellulose feature high transmittance. As synthetic resins tend to have specific absorption peaks, some parts treated with a synthetic resins in a historic painting can be detected by terahertz imaging.

2.3 Construction of open database

In terahertz spectroscopy, there is no standard method of acquiring a spectrum, including the preparation of the sample. The spectra acquired in this study corresponded to samples painted with a certain amount of pigments sufficient to reveal their standard colors and to allow for their use as practical analysis targets. The aim of the open database is to indicate the frequency of absorption peaks in the terahertz range and to show whether or not a given material can be analyzed by terahertz spectroscopy. For this reason, we would limit the use of numerical data to users who understand



Join THz database

THz DB Membership is free and registration only takes a minute. As a member, you will have access to view and searching database.

☐ I have read and accept the Terms of Use and Legal Conditions

Searched for cadmium

Results : 6

TMP000000073 - Cadmium Green
TMP000000034 - Cadmium Orange Extrafine
TMP000000086 - Cadmium Red Deep Standard
TMP000000035 - Cadmium Red Light Extrafine
TMP000000084 - Cadmium Red Light Standard
TMP000000007 - Cadmium Yellow

Keyword: cadmium

TMP000000007 - Cadmium Yellow, Zecchi

FTIR Tohoku Univ, Transmission, NICT

Keyword: cadmium

Copyright © 2007 NICT Terahertz Project Contact

Fig.7 (a) Screenshot of database user information input window, (b) Screenshot of atabase earch window, (c) Example of database spectral data

the measurement conditions, such as our partners in joint research projects, and show only the “image” of the spectrum on the Internet. The contents displayed consist of the spectral data, sample name, acquired location, system used, and measurement organization.

Figure 7 (a) shows a screenshot of the user information input window, Fig. 7 (b) shows a screenshot of the search window, and Fig. 7 (c) shows an example of spectral data. The Spectra List displays a list of all samples in alphabetical order by general sample name.

http://www.thz-spectra.com/

2.4 Problems in constructing generic database

For the present database, which aims to indicate whether a given material features absorption peaks in the terahertz range, we intend to continue to add spectral data from materials closely resembling practical analysis targets, including potential target mixtures. We are also considering adding reflection spectra as well as transmission spectra incorporating additional information, including data on surface conditions.

The mid-infrared spectral databases commercially available are generally constructed using pure agents. We will also require a similar database for the terahertz range. However, it is likely that such a database can be constructed as a global project as the demand for terahertz spectroscopy increases. NICT will supplement the present database by acquiring spectra for major components of pigments, such as the HgS found in Cinnabar, using high-purity agents.

Theoretical understanding of the absorption spectrum in the terahertz range — in other words, the spectral assignment (determination of the molecular or intermolecular behavior that causes the absorption peaks) — is so complicated that the calculations involved require a supercomputer, even if the sample structure is as simple as that of trehalose[7]. Thus, until now it had been extremely difficult to obtain theoretical explanations of terahertz spectra. We hope progress will be made in the numerical analysis of molecules. The quantitative aspect of spectral data needs to be reconsidered beginning with the preparation of the samples. Large differences may also arise between diverse measurement systems, even when the same sample is used. Thus, we plan to study how far we ought to pursue quantitative performance, as well as the standardization of measurement methods, based on close communications with all relevant parties both within and outside of Japan.

The most important aspect of a database is the amount of data it holds. We intend to invite domestic and international researchers currently studying terahertz waves to join the project, with the aims of increasing the amount of available data and improving the search functions of the database.

References

1 D. Mittleman, “Sensing with Terahertz Radiation”, Springer, Berlin, 2005.

2 M. Tonouchi, “Cutting-edge terahertz technology”, Nature Photonics, Vol.1, pp.97-105, 2007.

3 K. Kawase, Y. Ogawa, Y. Watanabe, and H. Inoue, “Non-destructive terahertz imaging of illicit drugs using spectral fingerprints”, Opt. Express, Vol.11, pp.2549-2554, 2003.

4 Y. C. Shen, T. Lo, P. F. Tady, B. E. Cole, W. R. Tribe, and M. Kemp, “Detection and identification of explosives using terahertz pulsed spectroscopic imaging”, Appl. Phys. Lett., Vol.86, No.241116, 2005.

5 J. F. Federici, B. Schulkin, F. Huang, D. Gary, R. Barat, F. Oliveira, and D. Zimdars, “THz imaging and sensing for security applications, explosives, weapons and drugs”, Semicond. Sci. Technol., Vol.20, pp.5266-5280, 2005.

6 A. Aldrovandi, M. L. Altamura, M. T. Cianfanelli, and P. Riitano, “Pictorial materials: the creation of a sample charge for the characterization of materials by means of multispectral analysis”, OPD Restauro, Vol.8, pp.191-210, 1996.

7 M. Takahashi, Y. Kawazoe, Y. Ishikawa, and H. Ito, “Low-Frequency Vibrations of Crystalline a a-Trehalose Dihydrate”, Chem. Phys. Lett., Vol.429, pp.371-377, 2006.

***FUKUNAGA Kaori**, Dr. Eng.*

Senior Researcher, Electromagnetic Compatibility Group, Applied Electromagnetic Research Center

Dielectrics and Electrical Insulations