Non-Destructive Investigation of Paintings with THz-Radiation

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Abstract. Nowadays the investigation of paintings is mainly done by means of X-ray radiography or ultra violet and infrared reflectometry. The latter is a non-invasive technique since damage to the paint by breaking molecular bonds, as it is known to be caused by UV-radiation, doesn't occur with the very low photon energies of the infrared radiation.

Another advantage of infrared reflectometry appears when it is extended to picosecond pulses in the THz-frequency band: X-ray radiography provides only an additive signal from absorption by all paint layers, which may be sufficient for revealing older painting hidden below the surface but does not provide information on the sequence of paint layers. However, THz-time domain spectroscopy has the potential for providing depth information from the paint layers. In addition to this, the substances which the paint consists of can be identified by their absorption bands in the spectrum of the reflected ps-THz-pulses.

Particularly evident is the potential of the THz-technique for the investigation of wall paintings where X-ray radiography cannot be applied. Conventional infrared reflectometry is unsuitable for detecting hidden paintings when the cover layer is thick as it often is the case with wall paintings. THz-radiation is able to penetrate thicker layers and become partly reflected from them, thereby retrieving useful information from the depth.

The present contribution provides first results of transmission measurements on paintings in the frequency band up to 4 THz. It becomes evident that the different paints show a significantly different THz-transmission. First THz-transmission images of paintings give rise to the hope that hidden wall pictures can be made visible with a reflection technique.

Introduction

Paintings and murals are valuable genuine pieces of evidence of the cultural heritage of mankind. Often they consist of several layers subsequently applied in the course of time. Every one is to be considered as an artwork in itself which should be conserved [1, 2]. Up to now, revealing the images hidden below without damage to the likewise valuable top layers has been successfully done in exceptional cases only [3, 4]. Infrared light and X-rays are usually applied for this purpose [5, 6]. The success of those techniques is restricted by inherent limits to penetration and depth resolution. It would be useful to have a non-invasive technique capable of high-resolution 3D-imaging of paintings and murals. Such technique should offer transmission and reflection options and possibly provide information concerning the paint components. These requirements could be met with a technique based on the THz-band of the electromagnetic spectrum. The present investigations of a painting fragment concern this application range. They are to demonstrate the suitability of the THz-technique for the investigation of paintings, murals, and similar artworks.

Experiments

2.1. Sample

The tests described below were done on a piece of painting on canvas, 10 x 10 cm^2. The size was restricted by the clamps in the various testing sets. The painting itself, a female portrait from the flea market was of no value but suitable for the present purpose as its material consisting of canvas, whiting, paint layers, and varnish, typical for 19th century paintings.

2.2. Preexamination

2.2.1 Technique

For orientation and the comparison with different imaging techniques like THz-imaging the painting was photographed with a digital camera (Fig. 1a)).

First physical investigations were made using x-ray fluorescence analysis (XRA). The exciting X-ray beam is generated by a 45 kV tube for the device “Spectro Midex M” of the company Spectro Analytical Instruments GmbH that was employed for the investigation. The beam was formed by a 200 x 200 µm² aperture. The painting sample of the dimensions 100 x 100 mm^2 was scanned by moving underneath the probe beam and analyser using a motorized table. In this way a pattern of 128 x 128 analysed points was generated to get images of the element distribution. The measuring time of each point was 25 s. The element distributions were calculated automatically from the recorded spectra by the device software.

2.2.2 Results

Fig. 1 shows a photograph and the element distributions of iron, lead and copper. These elements are constituents of the different color pigments of the paint. The X-ray spectrum of a point measurement at the center of the woman’s left eye is shown in Fig. 2.

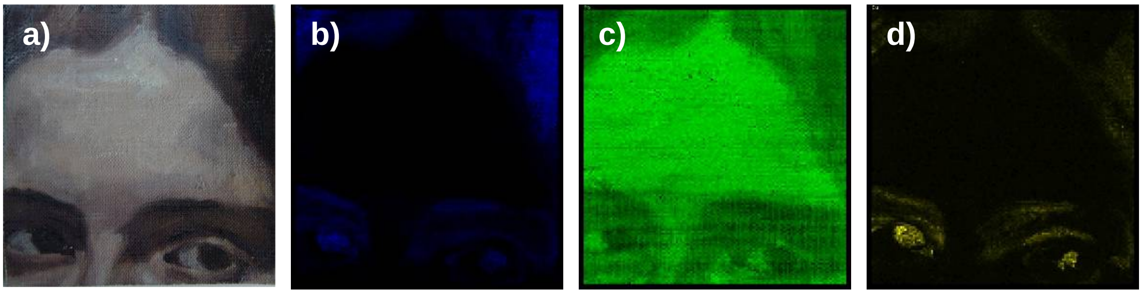

Figure 1 Preexamination of the painting sample by XRA
a) photograph, b) iron distribution, c) lead distribution, d) copper distribution

Imaging of the element distribution is possible by a reflective technique, for example to identify paintings that were repainted. In this way the XRA is often used to analyse paintings utilising the mobile device “ARTAX” of the company RÖNTEC Berlin [7], for example. Unfortunately the XRA is inappropriate for imaging of hidden wall paintings since strongly absorbing top layers often avoid the penetration of X-rays.

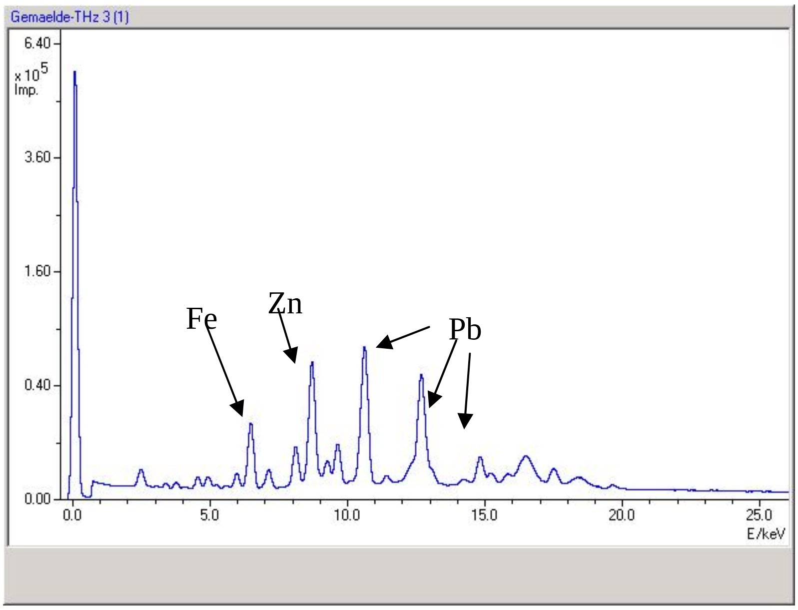

Figure 2 X-ray spectrum of a single point measurement at the center of the woman’s left eye on the painting sample

2.3. THz-Spectroscopy

2.3.1. Technique

THz-spectroscopy has been applied to a wide variety of materials including biomolecules [8], semiconducting polymers [9] and pharmaceuticals [10]. In terahertz time-domain spectroscopy (THz-TDS), single cycle or few cycle THz-pulses are used. Such pulses, which are generated by applying femtosecond laser pulses to either nonlinear crystals [11] or photoconductive antennas [12], cover a broad spectral range. The THz-radiation pulses can be detected coherently either by using electro-optical crystals [13] or photoconductive antennas. The detected signals are proportional to the THz electric field rather than the intensity which is measured by conventional incoherent detectors. Thus amplitude and phase of the THz-wave are measured allowing the determination of both the real and imaginary part of the refractive index of the material without the use of Kramers-Kronig relationships. For the analysis of systems composed of layers with different refractive index, short THz-pulses are of special interest. With durations of the order of 1 ps, these pulses are suitable to produce clearly separated echoes from multilayer samples in reflection mode. The depth resolution depends on the refractive index and is typically in the range of 0.1 – 1 mm. In transmission mode, signals from multiple reflections are expected.

In a THz-TDS setup the transmission through different areas of the painting was measured. A GaAs photoconductive emitter with an interdigitated electrode structure serves as a source for intense single cycle THz pulses [14]. It is excited with a titanium sapphire laser (800 nm central wavelength, 65 fs full width at half maximum (FWHM) pulse duration, 78 MHz repetition rate, maximum 800 mW average power). The THz radiation is created at a spot of 300 µm diameter on the emitter and then collected and refocused by two off-axis parabolic mirrors. The refocused THz-pulse is detected electro-optically with a 25 µm thick ZnTe (110) crystal. The setup was purged with dry nitrogen in order to reduce the absorption by water vapour. Details of the THz-TDS setup can be found in Ref. 14.

2.3.2. Measurements

The painting was placed in the THz-beam at a distance of 2 cm behind the emitter. At this distance, the diameter of the THz-beam is approximately 3 mm. The THz-waves transmitted through different positions of the painting were recorded. The position of the terahertz beam on the painting could be located easily by removing the THz-emitter and using the 800 nm radiation as a guiding beam. In Fig. 3a) the THz-time-domain waveforms for the beam transmitted through different parts of the painting are shown. The waveforms without a sample and after transmission through a reference canvas are shown for comparison. The reference canvas is similar to the canvas of the painting. The intensity spectrum of the THz wave without a sample is displayed in Fig. 3b). Transmission spectra for the THz-intensity obtained from these data via Fourier transformation are shown in Fig. 3c).

2.3.3. Results

All measured THz-waveforms could be measured with a very high signal/noise ratio within short time since the maximum THz-field was only reduced by one order of magnitude by introducing the painting. All THz-waveforms after transmission through the painting are broadened compared to the initial waveform. The THz-waveforms for different areas on the painting clearly differ from each other and from the waveform corresponding to the reference canvas. The different painting layers retard the THz-waves by different amounts of time. Also the shape of the waveform differs for the different positions on the painting. By comparing the waveforms corresponding to the “hair” and the “eye” it can be seen that these areas, which have a very similar optical appearance for the viewer, differ strongly in their THz-transmission properties. The fact that the peak THz-field for the transmission through the “hair” in the painting is stronger than the peak THz-field for the transmission through the reference canvas can indicate that the colour of the “hair” serves as a THz-anti-reflection dielectric layer for some THz-frequencies. Possibly it reduces the scattering from the rough canvas surface. The bandwidth of the THz emitter and detection system allows to extract spectroscopic information in the frequency band from 50 GHz to 4 THz as can be seen from the recorded intensity spectrum displayed in Fig. 3b). The frequency resolution of this spectrum and the transmission spectra shown in Fig. 3c) is 70 GHz. It is determined by the length of the THz waveform which is Fourier transformed. All transmission spectra exhibit a broad absorption region between 1 and 4 THz. Hence, this broad absorption can be attributed to the canvas. The spectra for different positions on the painting differ significantly for frequencies below 1 THz and in the range of 2.5 – 3 THz, however, further studies are necessary to distinguish between absorption, scattering and Fabry-Perot type effects.

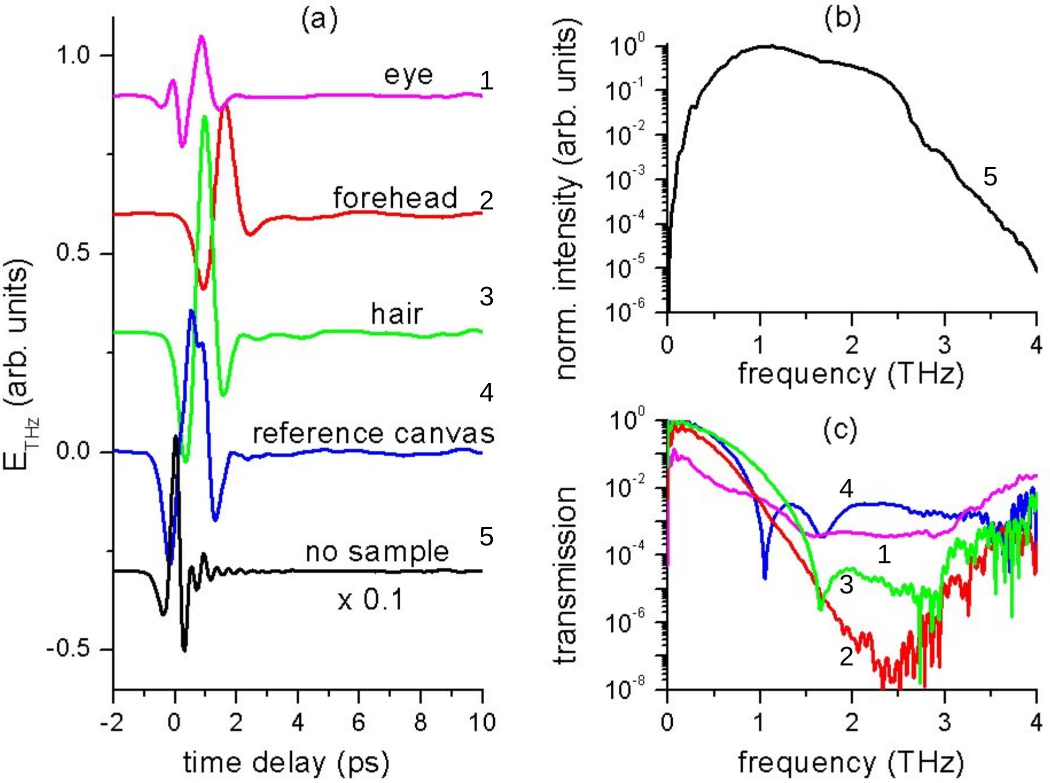

Figure 3 a) THz time-domain waveforms after transmission through different positions on the painting and the waveform without a sample and after transmission through the reference canvas. The curves are shifted vertically for clarity; the vertical scale for the waveform without sample is adjusted by a factor of 0.1.
b) Normalized intensity of the THz radiation without a sample.
c) Transmission spectra for the THz intensity corresponding to the curves in part a). Similar colours belong to similar measurements.

2.4. THz-scan

2.4.1. Technique

The imaging experiments were performed with a system that uses a photoconductive antenna for detection. For details see the article by RUTZ et al in this proceedings.

THz-images are taken by moving the sample in a two-dimensional grid pattern through the focus of the THz-beam. A waveform is measured at every position. To obtain the frequency content of the waveforms every one is Fourier transformed with the FFT-algorithm. Every waveform measurement carries information on many parameters suitable for plotting THz-images. An image with the temporal position of the main peak reveals differences in the refractive index or the thickness of the material, for example. With thicker material or higher refractive index, the pulse is more delayed. The peak-to-peak value provides information on absorption which gives another image. The absorption is seen even more clearly as a spectral damping in the frequency domain. Here, the intensity within a certain frequency interval is integrated. The frequency windows have a width of 0.1 to 1 THz. Each pixel gets a certain colour according to its intensity. These intensity pictures combine information about absorption, as well as scattering and reflection losses. With this technique, multiple false colour pictures with different information about the sample properties are obtained with only one THz-imaging measurement.

2.4.2. Measurements

The painting sample was subjected to a THz-imaging measurement [15]. It was scanned in x- and y-direction with a resolution of 0.5 mm/pixel. A photograph of the imaged region and some of the obtained THz-images are shown in Fig. 4. Fig. 4~~(~~b) displays the pulse delay image, where the grey value of each pixel represents the temporal position of the transmitted THz-pulse maximum [16]. In contrast, the pixel values of Fig. 4~~(~~c) and ~~(~~d) are determined by the relative power transmission integrated over the frequency intervals 0.3 – 0.4 THz and 0.1 – 0.2 THz, respectively. The grey scale was chosen in a way that resembles the painting best.

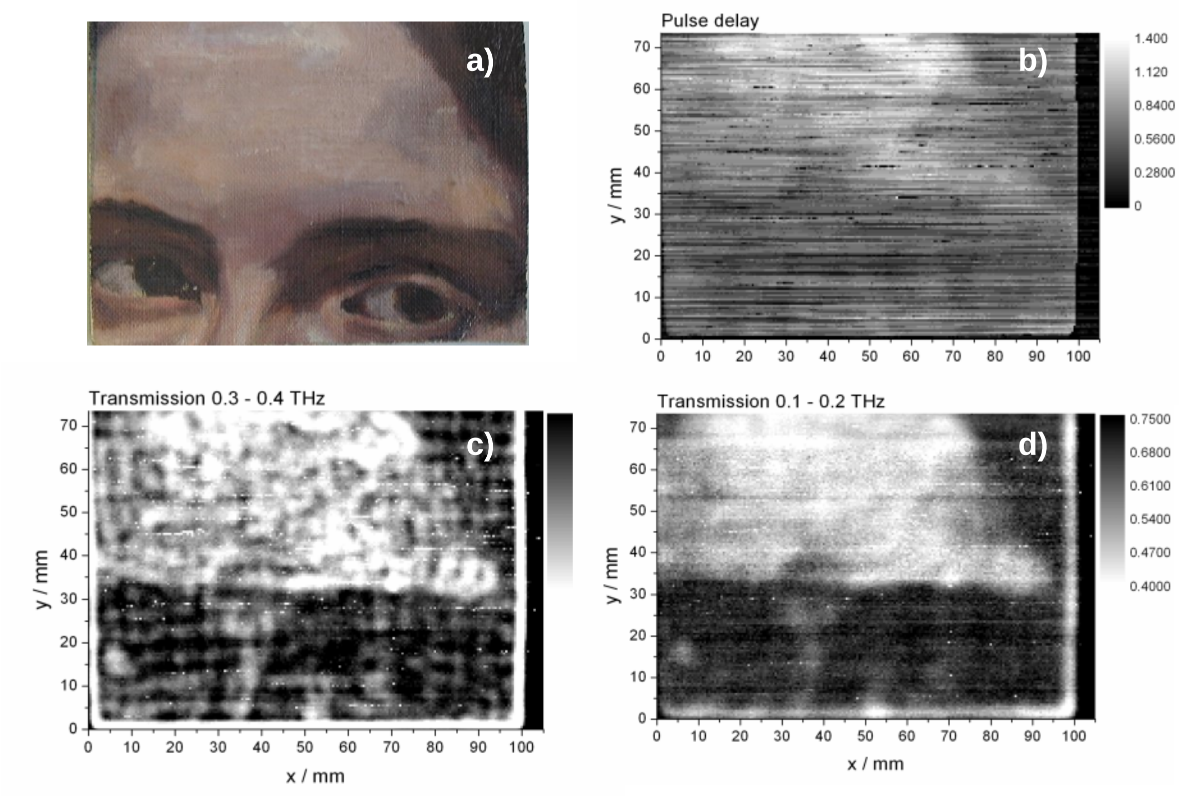

Figure 4 a) Photograph of the painting sample. Corresponding THz-images:
b) Delay of the transmitted THz-pulse maximum.
Power transmission integrated over the frequency interval
c) 0.3 – 0.4 THz and d). 0.1 – 0.2 THz

2.4.3. Results

The delay of the transmitted THz-pulse is determined by the optical thickness *nd* of the sample, with *n* the refractive index and *d* the geometrical thickness. Hence, the light areas in Fig. 4b), especially on the forehead, indicate optically thick regions [17, 18]. With a precise knowledge of either the geometrical thickness or the refractive index of the applied paint, one can detect hidden layers of different paint or other features.

On the other hand, the power transmission is dominated by the absorbance of the sample. Thus, different absorption coefficients of different paints are revealed by light and dark areas in Fig. 4d). Note the good recognition of the original painting Fig. 4a) within the THz-image. Once calibrated with a series of dedicated paint samples, a non-destructive way to determine multiple layers of different paints is possible.

With the frequency interval of 0.1 – 0.2 THz examined in Fig. 4d) the corresponding wavelength of 1.5 – 3 mm is much bigger than the structural dimensions of the canvas. Yet, considering higher frequencies, like 0.3 – 0.4 THz in Fig. 4c), the wavelength of 0.75 – 1 mm approaches the dimensions of the canvas texture. Additional patterns appear in higher frequency THz-images which can be used to study the canvas properties of paintings.

Summary

The investigations show that the whole painting consisting of canvas and paint layer structure transmits THz-radiation with relatively low losses by absorption or scattering. More research is necessary to explain the structure of the different transmission spectra. Absorption, scattering and Fabry-Perot type effects of the canvas and paint substances have to be considered.

An image of the painting sample showing the picture by visualisation of time delay or attenuation of the THz-pulses could be generated by THz-transmission measurements in a scanning mode.

The results of these investigations give rise to expectations that hidden wall paintings, too, could possibly be imaged by THz-radiation in reflection mode. Moreover, the THz-time domain spectroscopy should have the potential to detect paint substances by investigation of spectra and to determine the layer structure of the paints and coating layers by tomography.

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