Non-destructive analysis of material detachments from polychromatically glazed terracotta artwork by THz time-of-flight spectroscopy

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Abstract
The damage caused by the environment to exposed glazed terracotta objects is usually not externally visible. For instance the detachment of the glaze owing to subsurface crack formation or whole cavities in the area of the terracotta cannot be located visually. In this article we demonstrate that terahertz time-of-flight spectroscopy is suitable to locate and measure the air gaps under the glaze detachments which could only be done by X-ray axial tomography before. This tool will be very useful to guide the restoration process, particularly for pieces that are still attached to buildings or other structures that can not be transported to a tomography facility.

Keywords: **terahertz, non-destructive test, cultural heritage, terracotta, engobe, glaze**

1. Introduction

In recent years the field of conservation science has incorporated many scientific techniques capable to provide information about the objects under study that could not be accessed in the past.[1] Terahertz time-domain spectroscopy (THzTDS) is a technique that has given scientists an unprecedented power to access the elusive band of the electromagnetic spectrum between ~30 GHz and 10 THz (30 μm and 10 mm) which was relatively unexplored until three decades ago.[2,3] Roughly over the last ten years a small but active group of terahertz scientists have established fruitful collaborations with researchers from the conservation community demonstrating the enormous potential that terahertz radiation has for the investigation of the manufacture techniques, materials and state of conservation of a variety of culturally valuable objects.[4] In particular paintings,[5–7] sculptures,[8,9] and other forms of artwork have been studied with this technique.[10,11] In this article we present the study of one polychromatically glazed terracotta medallion from the 16th century which show detachment of the glazing layer caused by various environmental conditions such as frost and salinity.

Monochrome glazed terracotta artwork were produced in North Germany since the Middle Ages and had a common use as architectural elements in Hanseatic towns. The utilized manufacturing technique for polychrome objects, as the object examined by us were first used for stove tiles, and can be dated back to the the mid-16th century. So far there is no clear evidence of how the art of polychrome glazes has spread and which are the reasons for the use of polychromatic glazed ceramics medallions in Lüneburg. The polychromatic medaillon we examined was part of an originally fourteen-part ensemble of the façade ornamentation of a townhouse in Lünerstrasse 3, Lüneburg, Lower Saxony (53°15'05.9"N, 10°24'36.5"E), shown in Fig. 1(a) from the middle of 16th century built between 1543 to 1548. The portrait of a man, shown in Fig. 1(b) can not be clearly assigned to a person historically. At the moment the objects are not present at the building. Due to the persistent problem of saline and resultant loss of material the objects of the townhouse are under investigation at the Lower Saxony office for the protection of monuments and sites. This polychrome glazed terracotta medallion is part of an ensemble that show portraits of various kinds as well as in the lower frieze three medallions with scenes of Samson legend.

The three medallions have a diameter of about 38 cm, while all the others are smaller with a diameter of about 28 cm. These historical glazes usually are lead based. The medallions were produced in a three-layered construction. Under the polychrome glaze (green/white/blue/brown/yellow) a fine-grained bright engobe is located, with underlying red shard. In order to shape the clay, a model was used. Due to the delicate modeling, like the collar of the portrait shows, a painstaking rework on the details can be assumed. It is assumed that the molded clay model was burned in one or two steps at around 900°C to 950°C. Some glazes exhibit a play of colors, resulting from changing glaze thicknesses and inhomogeneities of the composition. Thin-areas in particular fine, sublime form details in transparent green and yellow glazes, and partly also in brown glazes show a lighter shade than in the deepening. This results from running glazes during the glaze firing by its reductions in viscosity. The presence of thicker and thinner areas of glaze can also be seen in the examined object. (Fig.2)

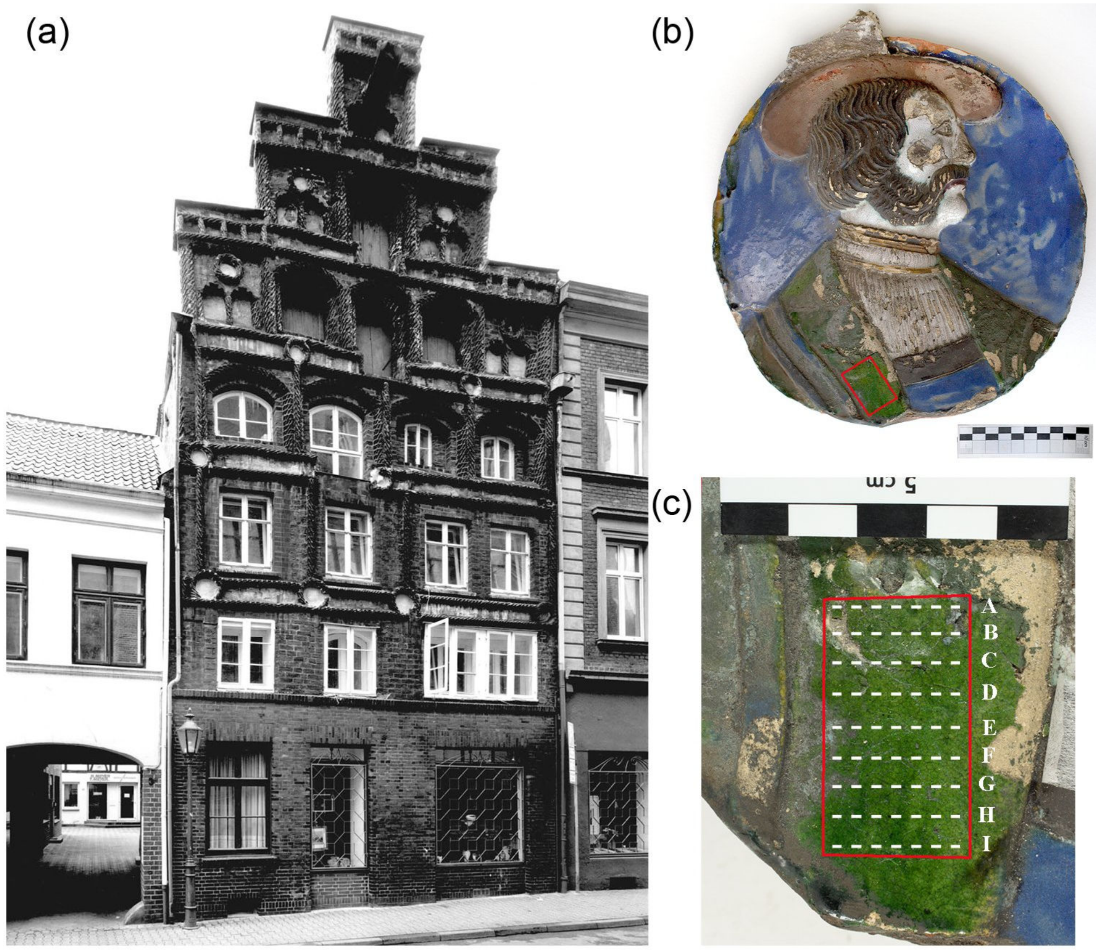

Fig.1 (a) Façade of the townhouse in Lünerstrasse 3, Lüneburg, Lower Saxony where the medallion (shown in b) was removed from for analysis and restoration [photo by Gerhard D´ham]. (b) Polychrome glazed Terracotta medallion-portrait of a man- from the 16th. The red line indicate the examined area. (c) Close-up of the region studied, the dashed white lines correspond to the approximate positions of the cross sections presented in Fig. 5.

The object shows a variety of damage types common in terracotta pieces from this building which are listed below:

- loss of glaze
- iridescent of the glaze surface
- flaking of the engobe
- larger and smaller areas with glaze flaking
- fine hairline cracks in the glaze
- salt content with partiell salt deposits

Former research projects with a focus on conservation methods for glazed brick and terracotta on nationally important cultural monuments in northern Germany shown that salt and gypsum crystallization are among others, the main reasons for glaze damage. The increased salinity represents one of the damage symptoms with a long-term effect of loss of original substance of the terracotta caused by calcium and sulfate ions (Ca [SO_4] • $2H_2O$).[12] The presence of these salt corroders is to be found primarily in the area of the glaze. Among other influences like weather changes and air pollutants, salt crystallization is the cause for a partial detachment manly at the engobe, which is the link between terracotta and glaze. In these areas of the object a good knowledge about the adhesion/detachment between materials must be given to be able to decide about a restoration method such as the back filling to prevent the glaze from loss. This article shall show the detection and measurement of these cavities behind glaze detachment using the comparative examinations of THz reflection measurements and X-Ray computerized tomography (CT) at a medallion from Lüneburg. Given that this particular piece was already detached from the original building, the THz measurements presented here were performed in a laboratory, yet a THz imaging system could potentially be taken to the field in order to measure pieces "on-site" unlike the X-ray CT system.

2. Experimental techniques

Terahertz spectroscopy

A standard fiber coupled terahertz time-domain spectrometer was used.[13] This spectrometer uses an ultrafast laser in order to produce pulses of light at 1550 nm (central wavelength) with a duration of ~90 fs. The pulses are divided into two separate beams. The first one is directed using an optical fiber onto a photoconductive emitter that converts the optical pulses into terahertz pulses. The other part of the beam is sent to a computer controlled mechanical delay line that produces a controllable time delay on it. The beam is subsequently guided to a photoconductive detector, also using an optical fiber. The system could be configured in transmission or reflection geometries shown in Fig. 2 (a) and (b) respectively. The waveforms were acquired on a domain of 80 ps with a temporal resolution of 33 fs. This resulted in a spectral resolution of 12.5 GHz and a longitudinal space resolution of 0.01 mm.

For transmission a polyethylene lens collects and collimates the THz radiation produced in the emitter, a second lens focuses it onto the sample, a third lens collects and collimates the radiation transmitted through the samples and a fourth lens focuses it onto the detector. In the reflection geometry the THz pulses produced in the emitter are collimated by a polyethylene (PE) lens and transmitted through a silicon beam splitter, these are then focused by a second PE lens onto the sample. This pulse is then partly reflected by each material-air or material-material interface that it finds on its path, with each subsequent reflection having an increasing temporal delay (see Fig. 2(c)). The reflections are then re-collimated by the second lens and reflected by the beam splitter. A third PE lens focuses the terahertz radiation onto the receiver, which records the reflected waveform as function of time. Therefore THzTDS provides us a measurement similar to that of an ultrasound or a radar system based on the echoes of the interfaces found in the optical path, with the difference that it is non-contact and therefore requires no coupling substances such as the gels used for ultrasound.[2,14] By taking multiple measurements across a grid of positions over the object we can generate a full 3D reconstructions of the external surface and the internal structure of the object under study.

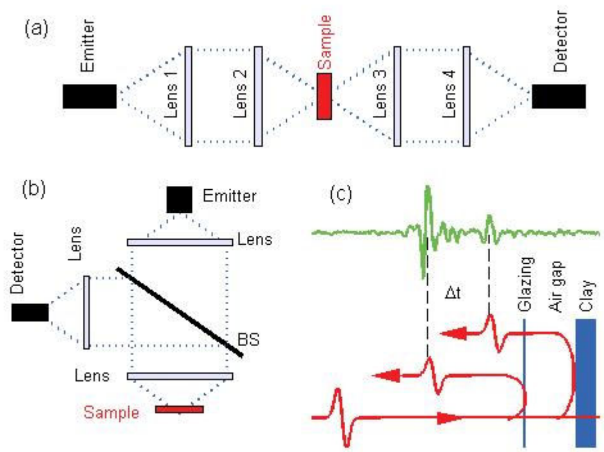

Fig. 2. (a) Schematic of the transmission setup used for characterization of the dielectric properties of materials. (b) Schematic of the reflection setup used for time-of-flight imaging. (c) Schematic representation of the formation of the echoes observed in the time-of-flight waveform and how they correspond to the different layers found in the glazing-gap-clay system.

X-ray Computed Tomography

This technique allows the 3-dimensional reconstruction of many materials as long as they have enough contrast at X-ray wavelengths. In particular, given that the glazing contains lead, the glazing should appear in bright white in the CT images, while other materials will appear in darker gray tones depending on their particular composition. Given that X-ray CT is a standard imaging technique, well established both in medical and cultural heritage applications, we do not consider that an extensive technical description is required. Yet, the equipment used was a Philips multidetector spiral CT type Brilliance 64 with 64 detector rows each having an average thickness of 0.625 mm.

Optical microscopy

This technique was used to determine the thickness of the glazing layers. Once again optical microscopy is a standard technique in cultural heritage so it does not require extensive description. The system used was a *VHX keyence digital microscope* with a 200-fold enlargement.

3. Results

Firstly, samples of glazing were prepared in the laboratory following the recipes known for the time of the Lümberg medallion. The glaze was prepared by mixing 1.00 PbO.1.00 SiO_2, quartz flour**,** K_2O . Al_2O_3 $6SiO_2$, Na_2O . Al_2O_3 $6SiO_2$, chalk, aluminium oxide, iron[III]-oxide, zinc oxide, copper oxide, cobalt oxide and water which matches the historical composition analysis. The sample was baked with an increase of temperature at a rate of 125°C / h until reaching 1050°C which were maintained for 15min. The samples were cooled at a rate of -500°C / h. Subsequently the glaze was detached from the underlying clay and its thickness was determined by microscopic measurement (see Fig. 3(b)). The thickness was found to be 169µm in the particular spot measured but was relatively uniform at around 170µm. The complex refractive index of the glazing was determined by terahertz time-domain spectroscopy in transmission geometry of the free-standing glazing film. Subsequently the data was processed according to.[15] The real and imaginary parts of the refractive index for the three different colours of glazing (green, blue and white) are presented in Fig. 3(b). The real refractive indices for the white and green glazing are relatively constant with a value in the vicinity of 2, the blue sample shows significantly more dispersion with values between 1.7 and 2.5 as seen in the plot. The imaginary part for all three samples remained relatively small, below 0.5, showing an increase with frequency, which is typical of amorphous materials such as this one.

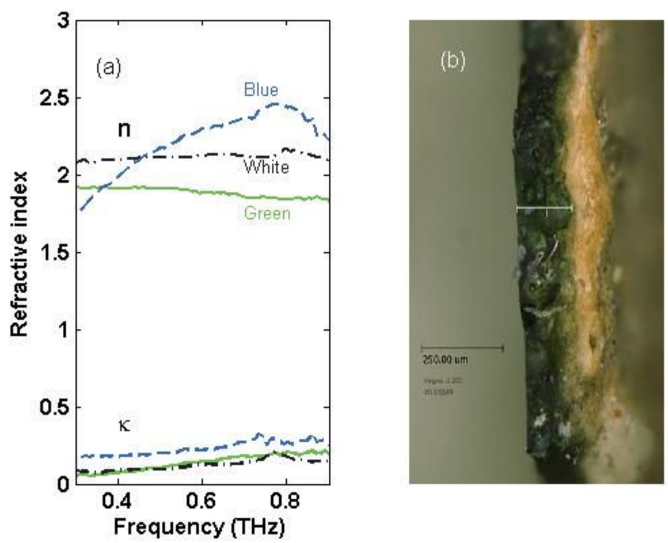

Fig. 3 (a) Shows the real (n) and imaginary (k) parts of the refractive index measured for glazing coatings with green, white and blue pigmentation. (b) Shows a micrograph of the edge of a free-standing glazing coating. A 250um bar is given as a reference.

For the investigation of the medallion, a field of green glaze has been selected. The green glaze shows the most pronounced type of damage by salt (Fig. 1(c)). Areas with visible detachments of glaze are to be seen in the top of the picture. Other areas show an uneven surface that may indicate detachment, but can also have production-related reasons. In order to determine if there is an air-gap under the glazing and to measure its width the area marked in Fig. 1(c) was scanned with a terahertz setup in reflection configuration (shown in Fig. 2(b)). In the reflection configuration each one of the interfaces that the terahertz pulse finds in its path generates a reflected echo, the temporal separation between echoes Δt is related to the spatial separation d between the interfaces in the object by $d = c\,\Delta t / 2$ if the separation is filled with air, else, the refractive index of the material in the gap has to be taken into account. This process is schematically represented in Fig. 2 (c), where an actual waveform collected from the medallion is shown, containing two clearly distinguishable echoes.

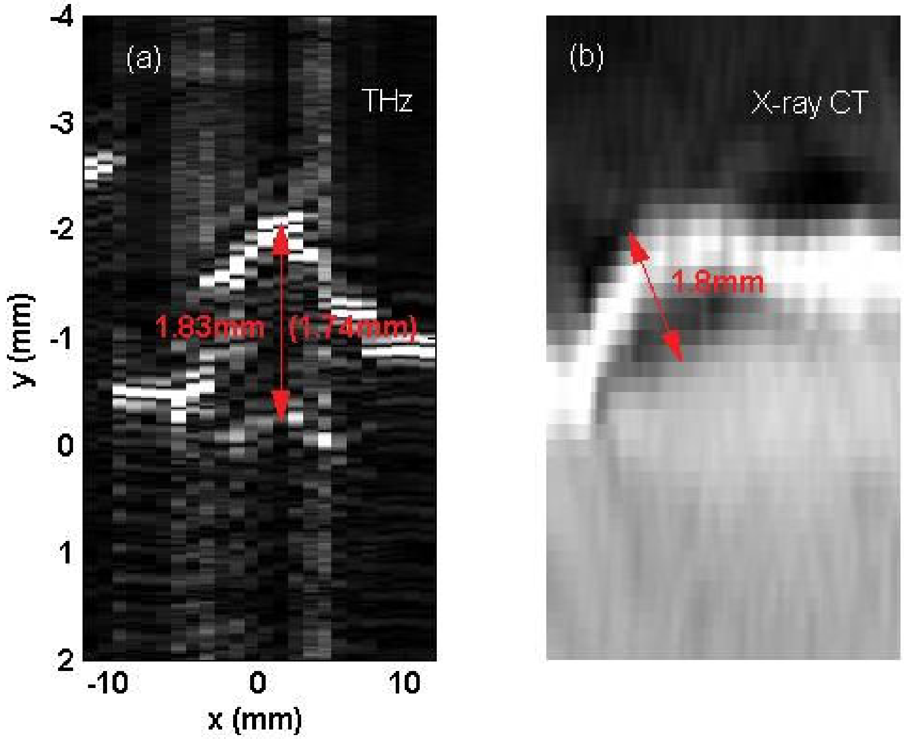

Fig. 4 (a) A tomographic cut of the air gap obtained from the terahertz time-of-flight measurements. (b) An X-ray computed tomography cut of the same air gap. The two measurements allow determining the air-gap width, yet, THz is a portable technology that does not require the use of ionizing radiation.

A cross section of the area under investigation obtained from the THz waveforms is shown in Fig. 4(a) obtained from the absolute value of the waveforms. By assuming that optical path added by the glazing is negligible we determined that the the distance between the top glazing surface and the surface of the underlying clay is 1.83mm. Of course the transit of the terahertz pulse through the glazing gives an additional delay to the terahertz pulse which is relatively small, considering this we can correct the measurement of the air gap to 1.74mm. The object was also taken to the X-ray tomographer and the same area was found in the X-ray CT. In this case the CT measurement resulted in a distance between surfaces of 1.8mm.

We finally present a series of tomographic cuts Figs. 5(a-i) at 2mm distance from each other that show how the air gap changes in shape and thickness as the cutting plane moves from top to bottom in the area highlighted in Fig. 1 (c). The curves shown in Figs. 5(A-I) are the reconstructed width profile of the air gap as measured from the tomographic cuts (continuous lines). The widths corrected for the glazing optical path are also shown (dashed lines). Given that the glazing is very thin in our case, the correction observed in Figs. 5(A-I) are marginal, however, this must be taken into account for thicker coatings. The correction was calculated by subtracting the optical delay introduced by the glazing layer to the total delay between interfaces.

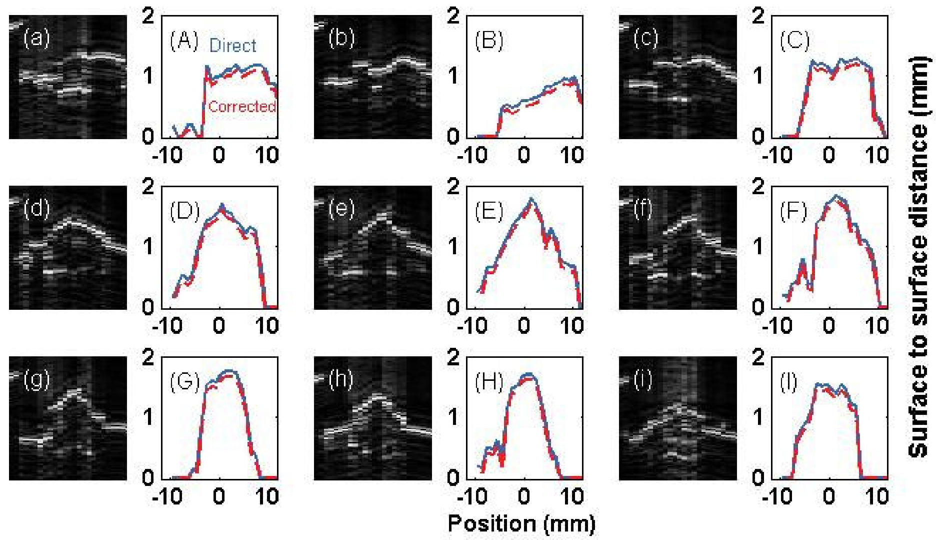

Fig. 5 (a to i) Tomographic cuts of the air gap obtained from the terahertz time-of-flight measurements each one at 2mm from each other. (A to I) Calculated surface to surface distance obtained directly from the images (a-i) (continuous lines) and the distance considering the correction for the optical path introduced by the glazing refractive index (dashed lines).

4. Conclusions

In this article we presented the use of THz time-of-flight for the conservation assessment of a glazed terracotta medallion dating from the 16th century from the Lower Saxony region in Germany. This technique allowed us to obtain a full tomographic reconstruction of a region where the glazing was detached owing to weather induced damage. We included measurements of the dielectric properties of glazing layers prepared with the same methods used then. The blue glazing showed significant dispersion which might need to be taken into account when analyzing pieces containing that material, especially if the glazing is significantly thicker than in the art piece examined here. Terahertz time of flight gave results comparable to those obtained from X-ray computed tomography which is commonly used in art conservation. Of course terahertz has two very important advantages over X-ray CT. Firstly it does not require the use of ionizing radiation, therefore removing personal exposure hazards. Secondly, THz spectrometers can now be taken to the field in order to do these kind of measurements which for many architectural or sculptural artwork pieces is essential given that they have fixed locations, and therefore on-site assessment of their conservation state is desirable and in some case indispensable. This is therefore a new form of artwork successfully characterized with terahertz technology which is becoming an extremely useful tool in the area of cultural heritage study conservation.

Dedication

This article is dedicated to the work and life of Prof. Jan Schubert (1954 -2012) who inspired the collaboration of researchers in the field of conservation and other disciplines so that the knowledge about artwork and its conservation could develop for the preservation of art and cultural heritage.

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