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Thin layered drawing media probed by THz time-domain spectroscopy†

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Dry and wet drawing materials were investigated by THz time-domain spectroscopy in transmission mode. Carbon-based and iron-gall inks have been studied, some prepared following ancient recipes and others using current synthetic materials; a commercial ink was studied as well. We measured the THz signals on the thin films of liquid inks deposited on polyethylene pellicles, comparing the results with the thick pellets of dried inks blended with polyethylene powder. This study required the implementation of an accurate experimental method and data analysis procedure able to provide a reliable extraction of the material transmission parameters from a structured sample composed of thin layers, down to a thickness of a few tens of micrometers. THz measurements on thin ink layers enabled the determination of both the absorption and the refractive index in an absolute scale in the 0.1–3 THz range, as well as the layer thickness. THz spectroscopic features of a paper sheet dyed by using one of the iron-gall inks were also investigated. Our results showed that THz time-domain spectroscopy enables the discrimination of various inks on different supports, including the application on paper, together with the proper determination of the absorption coefficients and indices of refraction.

I. Introduction

THz pulse imaging and spectroscopy¹⁰ is an emerging non-invasive method for the characterization of cultural heritage artefacts that provides complementary information on traditional analytical tools. With respect to X-rays or UV radiation, THz radiation presents lower risks in terms of molecular stability

due to its non-ionizing property as well as its ability of inducing very low thermal stress. Transmission/reflection geometries and time- or frequency domain set-ups are constantly developed for a variety of applications ranging from pharmaceutical chemical mapping, safe security to atmospheric sensing. The potential to provide non-destructive information in the cultural heritage field has been demonstrated on objects such as paintings,¹⁷ manuscripts,^{1,4,9} mural paintings,¹⁸ metal alloys⁵ and stones.⁸ In particular, Bardoni *et al.*² have reported the investigation of black inks by THz spectroscopy.

T-ray technologies are supported by a series of commercial off-the-shelf systems that enable THz spectroscopic investigations. Designed for few specific applications other than cultural heritage, these systems are not open to full control of signal detection and processing. Therefore, a customized set-up was built for providing a more flexible and powerful application.

In this work, we explored artworks drawing materials with THz-Time Domain Spectroscopy (THz-TDS) extending the investigation to thin layers of inks that was never realized previously. We developed a specific experimental method and data analysis to disentangle multiple reflection signals. Our investigations are based on a well established technique, but the careful building of the THz-TDS experimental set-up and the acquisition procedure enables a very high signal to noise ratio that is not common in this type of experiment. Moreover, the accurate analysis of the data based on the successive iterations in the fitting algorithm enables the calculation of the absolute absorption coefficient and the index of refraction of the materials, as well as the sample thickness down to tens of microns both in single layer and bilayer configurations.

II. Materials and experimental procedures

The inks studied, both iron gall and carbon black inks (Table 1), are commonly used in artworks and can be prepared

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Table 1 Compositions and recipes for the preparation of the studied inks. The rough materials have been purchased from Bizzarri S.A.S. Firenze, Italy

Black	1	Iron gall ink with arabic gum (recipe A): 70 mL water, 10 mL white wine, 10 mL red vinegar, 5 g powdered oak galls, 1.25 g arabic gum, 1.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
	2	Iron gall ink without arabic gum (recipe A): 70 mL water, 10 mL white wine, 10 mL red vinegar, 5 g powdered oak galls, 1.25 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
	3	Iron gall ink with arabic gum (recipe B): 14 mL distilled water, 1.14 g gallic acid, 0.29 g arabic gum, 0.29 g $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
	4	Iron gall ink commercial black ink (Zecchi, Firenze)
	5	Carbon-based ink: 14 mL red wine, 0.57 g carbon black (vegetal), 0.71 g arabic gum

either following ancient recipes (Giovanni Alcherio 1411) or from synthetic materials.¹² They have been sampled from pellets or thin layers; dried inks were blended with polyethylene (PE) powder with a concentration of approximately 33 wt% and pressed to form pellets of 13.2 mm diameter and a thickness of about 1 mm, wet inks were deposited on 10 μm thick PE pellicles to form films with a thickness of the order of tens of micrometers. Moreover, the iron gall ink (recipe B) was also studied when applied to pure cotton paper (Zecchi, Firenze). We investigated the THz spectrum of other inks (*i.e.* red cochineal, red ochre, indigotin-based and white lead) as well as the individual chemical constituents (*i.e.* iron(II) sulfate and gallic acid); these results are not reported here and will be discussed in a future publication.

Our table top THz-TDS system enables measurements in the 0.1–4 THz range in transmission configuration. The sample and reference THz signals are cyclically acquired; for every sample scan we took a reference scan. Each single scan

is a 300 second long acquisition with a continuous motion of the probe delay line at a velocity of 0.5 mm s^{-1} . Each couple of sample and reference signals is Fourier transformed and their ratio, averaged over all the data, gives the experimental transfer functions defined in the next paragraph. A typical couple of reference and sample signals with their amplitude spectra is shown in Fig. 1 where the Black 3 ink signal from the pellet sample is reported. A detailed description of the experimental set-up and the sample preparation is reported in the ESI.[†]

III. THz transmission and sample parameters

The spectroscopic properties in the THz range of a material can be obtained by measuring the sample and the reference signals. The ratio between the Fourier transforms of the THz field transmitted through the sample, $E_t(\omega)$, and of the inci-

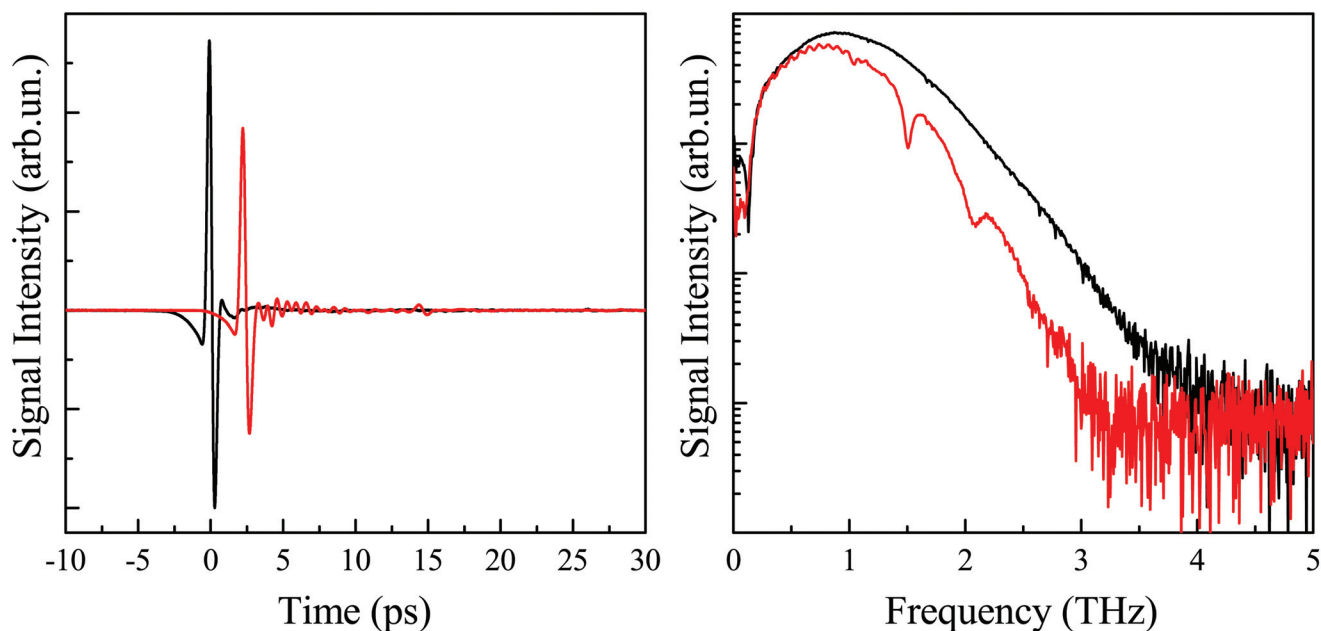


Fig. 1 Left graph: a typical time evolution of the THz electric field of the reference and ink signal from a pellet sample (Black 3 ink), the second pulse at around 15 ps is due to internal reflections of the THz pulse between the pellet surfaces; right graph: amplitude spectra obtained by Fourier transform of the signals on the left. The regular oscillations clearly visible in the lower frequency range of the spectrum are due to the internal reflections. This effect must be carefully considered in order to extract the real spectrum of the sample parameters.



dent field, $E_t(\omega)$, referred to as the transfer function of the material, $H(\omega)$, expresses how a plane wave of frequency ω is modified by the absorption and refraction from the medium it encounters. For a homogeneous dielectric slab of thickness d and complex refractive index \hat{n}_s , surrounded by nitrogen, and for normal incidence, the theoretical expression of the transfer function can be written as:²⁰

$$H(\omega) = \frac{E_t(\omega)}{E_i(\omega)} = \tau\tau' \exp\left\{-i[\hat{n}_s(\omega) - n_0] \frac{\omega d}{c}\right\} \cdot \text{FP}(\omega) \quad (1)$$

$$\text{FP}(\omega) = \sum_{m=0}^{\infty} \left\{ \rho'^2 \exp\left[-2i\hat{n}_s(\omega) \frac{\omega d}{c}\right] \right\}^m \quad (2)$$

where

$$\tau = 2n_0/(n_0 + \hat{n}_s) \quad (3)$$

is the nitrogen-sample complex transmission coefficient and

$$\tau' = 2\hat{n}_s/(n_0 + \hat{n}_s), \quad \rho' = (n_0 - \hat{n}_s)/(n_0 + \hat{n}_s) \quad (4)$$

are the sample-nitrogen complex transmission and reflection coefficients for normal incidence, with $\hat{n}_s = n_s(\omega) - ik_s(\omega)$, where $n_s(\omega)$ is the refractive index, $k_s(\omega)$ is the extinction coefficient, and n_0 is the real refractive index of nitrogen. Yet in eqn (1) and (2), c is the vacuum speed of light and $\text{FP}(\omega)$ represents the Fabry-Pérot effect due to the multiple reflections inside the sample.

In a TDS transmission experiment the material can be characterized by measuring the experimental transfer function, $H_{\text{exp}}(\omega)$, given by the ratio between the complex Fourier transform of the sample signal and the reference signal, from which using eqn (1) and (2) the refractive index, $n_s(\omega)$, the absorption coefficient, $\alpha_s(\omega) = 2\omega k_s(\omega)/c$ and the thickness could be in principle extracted.

However, a complete analytical solution of eqn (1) and (2) is not available, so the extraction of the sample parameters must be pursued following alternative methods. These are strongly dependent on the nature of the THz signal measured.

If the FP pulse reflections are distinguishable and separable from other contributions in the sample temporal signal, the transfer function can be obtained from the THz signals cutting off the pulse reflections. This simple method enables an immediate extraction of material parameters, but the sample thickness must be known *a priori* and the detection time-window is limited by the cut (*i.e.* the $n_s(\omega)$ and $k_s(\omega)$ spectra are characterized by a lower resolution).

If the FP pulse reflections are close in time and partially superimposed with the main pulse, due to a short optical path, the cutting process can't be applied. Also in the case where the reflection peaks are well separated but the sample signal shows a long time evolution after the main peak, because of a structured absorption of the medium, see Fig. 1, the simple method can give wrong evaluations of the material parameters. In these cases, the solution methods are based on an iterative process of calculation.^{7,13–16,19}

We implemented a new method of data analysis, described in detail in the ESI,[†] which is an iterative fitting process based on a polynomial fit of the transmission parameters that enables the extraction of the real physical material parameters (*i.e.* the index of refraction, absorption coefficient and layer thickness). This method applies to both the free standing single slab or layer (*i.e.* our pellet samples) and a bilayer system, (*i.e.* the layered inks on PE pellicles).^{6,11}

IV. Results and discussion

A. Ink-PE pellets

Fig. 2 shows the absorbance spectra and frequency evolution of the refractive indexes for all five black inks, see Table 1, measured on pellets. The inks prepared following the old recipe of mixing mainly iron(II) sulfate and oak gall powder (*i.e.* recipe A used for Black 1 and 2) show a featureless response in the THz range. The comparison between these two spectra suggests that the arabic gum weakly contributes to the spectral response with a smooth increase of the absorption in the higher frequency range. On the other hand, ink containing synthetic gallic acid (*i.e.* Black 3 prepared according to recipe B) and commercial ink (*i.e.* Black 4) show structured spectra with several peaks. Carbon black ink, Black 5, does not exhibit any spectral features. Moreover, the investigation of the Black 1 and 5 inks in the higher frequency range is somehow limited by the saturation phenomena.

Our results are in agreement with other THz spectroscopic investigations on similar drawing media.² The inks prepared following recipe A, Black 1 and 2, do not show any features related either to gallic acid or to iron(II) sulfate. Actually, it is known that under hydrolysis gallic acid is extracted from the oak galls and the related spectroscopic features should appear in the THz spectra. The absence of spectroscopic signatures of gallic acid and iron sulfate is probably due to the chemical processes taking place in the ink preparation. More likely, the iron-gallic complexes oxidized supporting the formation of iron-tannic complexes that are expected not to show any spectroscopic features in the 0.15–3 THz range.² In the spectra of Black 3, prepared according to recipe B that uses ferrous sulfate and synthesized gallic acid instead of oak-gall powder, we can clearly see the spectroscopic signature of the gallic acid (peaks at about 1.04, 1.50, 2.06, and 2.57 THz) while no ferrous sulfate contribution is present in the spectra. This is likely due to the low molar ratio between the two chemical compounds, about 0.1, which prevents the observation of iron sulfate features.² In contrast, the commercially available iron gall ink, Black 4, shows a couple of features typical of the iron sulfate (peaks at about 1.52, 1.92 THz) and lacks those of gallic acid.

B. Ink layers on PE

The pellet samples provide very good spectra of the drawing media, as shown in the previous paragraph, nevertheless they have several drawbacks. First of all, these spectra are not



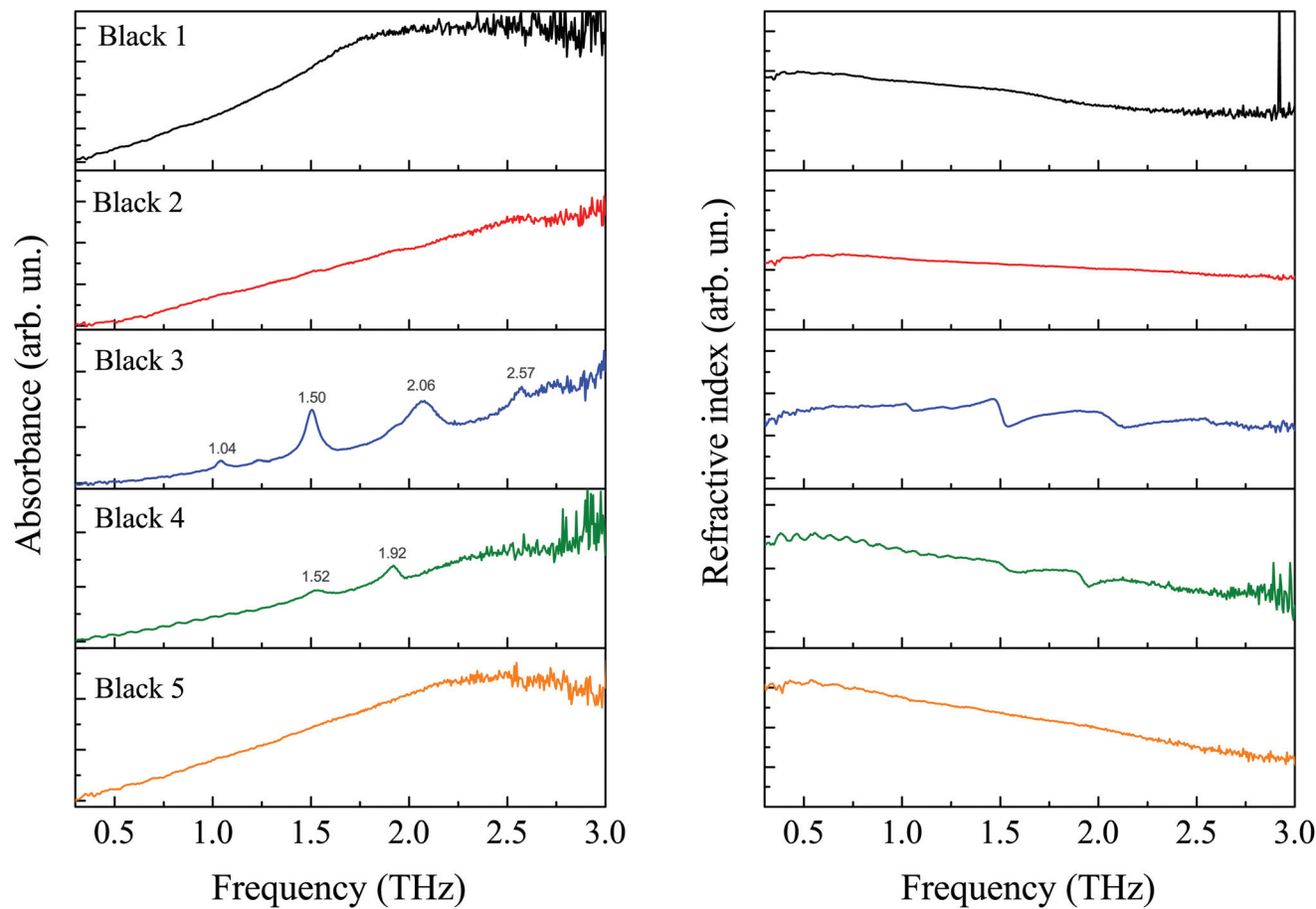


Fig. 2 THz spectra for the iron-gall inks measured on pellets. The left panel shows the absorption coefficients; the pigments prepared following the ancient recipe (recipe A) containing oak galls (Black 1 and Black 2) and the carbon-based one (Black 5) do not show any particular spectral feature in contrast to what is observed in the inks containing synthesized gallic acid (Black 3 and Black 4) which instead exhibit well distinguished peaks. The right panel reports the frequency behaviour of the refractive indices measured on the same series of black ink pellets. The dispersive features of the refractive index for Black 3 and Black 4 inks confirm what is measured in the respective absorbance spectra.

acquired on drawing materials in the form of inscriptions, brushstrokes, *etc.*

Moreover, due to difficulties in calculating the molar concentration of inks in pellets, no absolute measurements of the molar absorption coefficient and refractive index may be obtained. Furthermore, scattering processes due to inhomogeneities in the sample must be taken into account as, for example, the band distortions in the absorption spectra, named the Christiansen effect, due to the phenomena of Mie scattering.³ The direct investigation of ink layers by THz-TDS overcomes the previous problems and enables the study of drawing media in their common forms. Nevertheless, this turns out to be a quite difficult task especially if the absolute measurement of the THz transmission parameters is searched for.

In Fig. 3 we show the optical parameters[‡] in the THz range of thin bi-layer samples made by deposition of thin ink films on PE pellicles, as obtained from the data analysis of the TDS investigation. The analysed inks are from the same series reported in Table 1. Our experimental apparatus and data ana-

lysis procedure give spectra of a very good signal-to-noise ratio even for thin film samples. We highlight that the determined optical parameters and the layer thickness are in an absolute scale.

Ink layer data confirm the spectral features shown by the pellet samples; the layered inks prepared with oak gall powder (Black 1 and 2) again do not manifest spectral features; the ink prepared by recipe B (Black 3) reveals the presence of gallic acid by peaks in absorbance at 1.50 and 2.06 THz; the commercial iron-gall ink (Black 4) shows the 1.92 THz feature of ferrous sulfate. Therefore the THz-TDS technique proves to be able to distinguish among the various black inks even when they are in the form of a thin film.

C. Ink on paper

We applied the investigation by THz-TDS experiments on a sample prepared by depositing a few drops of Black 3 ink on a piece of drawing paper. This sample is quite different from the previous ones; in fact the ink penetrates into the paper forming a complex structure where ink particles and paper



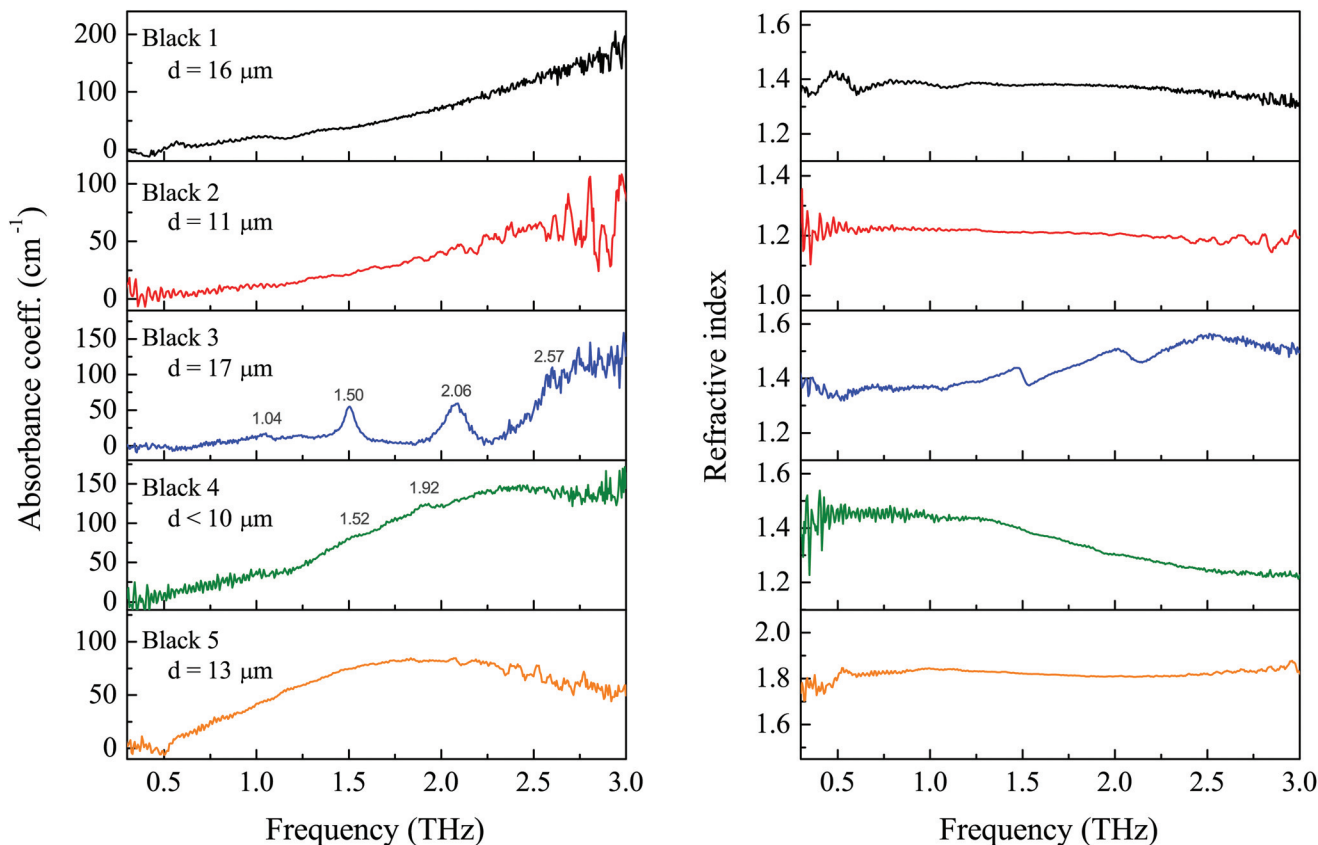


Fig. 3 Absorption coefficient (left panel) and refractive index (right panel) as a function of frequency for the series of black inks on PE pellicles. Thickness, d , measured from each sample, is also reported. The present THz-TDS investigations enable us to obtain absolute values of both THz transmission parameters and of the drawing media thickness.

fibres are interpenetrated. We treated the sample as a homogeneous system. In Fig. 4 we report the results of data analysis. The paper sheet shows a relatively smooth THz spectrum

characterized by some very weak absorption bands, after ink deposition, the spectrum shows clearly the signature of Black 3 ink with a calculated sample thickness of about $40 \mu\text{m}$.

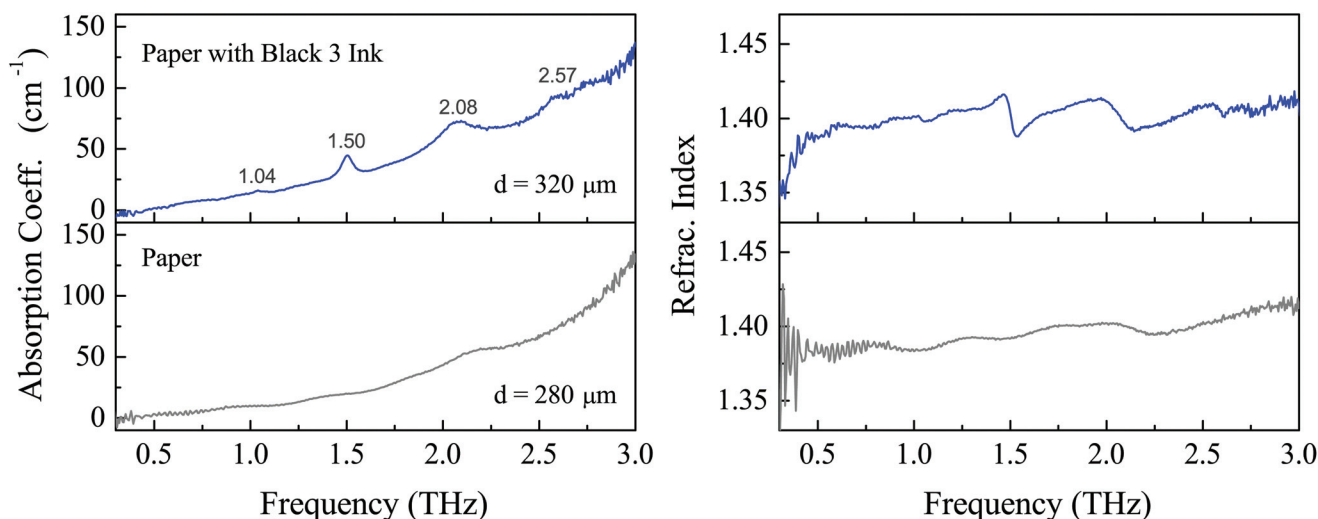


Fig. 4 Absorption spectra and refraction index of a paper sheet dyed with Black 3 ink. The typical THz spectroscopic signature of Black 3 ink is still clearly visible even when it impregnates its original support.



V. Conclusions

We develop an original experimental procedure and a comprehensive method of data analysis to measure the optical parameters of drawing media in the THz spectral range. THz time-domain spectroscopy was applied to investigate black inks, as iron-gall and carbon based inks commonly used in artworks. We determined the absorption coefficient and refractive index spectra of pellet and layered ink samples. The THz spectroscopic measurements on thin films of ink enable the determination of the optical parameters in an absolute scale, making the present research unique and pushing the investigation to a complete quantitative analysis of the real-practice problems and suggesting potential applications of THz spectroscopy in the heritage field. We found that the THz-TDS techniques are able to discriminate between iron-gall black inks prepared either with an old recipe or with modern/commercial preparations both in the pellet sample and in the layered film. Measurements on inked paper, the most commonly utilized support for inks, confirm that it is possible to discern the spectroscopic features of ink also when it penetrates a paper sheet. The reported results point out some common challenges present in THz spectroscopy and imaging of artworks and suggest the possible methods to overcome them.

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Notes and references

‡To conform us with the previous literature, the transmission characteristics of the material are referred to as "optical parameters" even if they concern the THz spectral region that is outside the commonly defined optical region.

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