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THz time-domain spectroscopy: investigation of thin layers of inks.

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***Abstract* – 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. The method based on the THz – Time Domain Spectroscopy is applied to recover material parameters on drawing inks deposited on polyethylene pellicles with thicknesses down to tens of micrometers. In particular, we investigated three commercial inks: a red ink (based on cochineal carmine), a blue ink (indigo) and a black ink (iron-gall). The implemented experimental procedure and numerical method enable us to extract the absorption coefficient and refractive index spectra in an absolute scale, opening the possibility to investigate the material parameters in the THz range with a complete quantitative study.**

I. INTRODUCTION

The THz spectroscopy has proven to be a non-destructive tool able to provide valuable information in the cultural heritage field. Its application to the investigation of painting and drawing media has been recently demonstrated in a few studies [1-3]. In particular, the THz-Time Domain Spectroscopy (THz-TDS) is a powerful THz spectroscopic technique that can measure different parameters of a media using the transmission or reflection of pulsed THz radiation [4-7].

In the transmission THz-TDS experiments the THz pulse passes through the sample; the induced time/amplitude variations enables the characterization of the material. The extraction of the transmission parameters (i.e. absorption coefficients and indices of refraction) from the THz pulse features is not a trivial task [8], this becomes even more complex when the sample is a thin film [9].

We have recently implemented an innovative experimental and analytical method enabling a reliable extraction of the THz parameter from a TDS experiment on multi-layered thin sample [7]. We report here the investigation of commercial inks by means of this innovative THz-TDS approach. The experimental apparatus yields data characterized by a very high signal to noise ratio; the accurate analysis we implemented enables us to disentangle the multiple reflection signals allowing for the calculation of the absolute absorption coefficient, refractive index of the materials, as well as the sample thickness down to tens of microns.

II. EXPERIMENTAL APPARATUS

The THz-TDS system uses the conversion of femtosecond optical laser pulses, at 780 nm with a pulse duration of less than 120 fs and repetition rate of 100 MHz (T-light fiber laser, MenloSystems), in a low-temperature GaAs photoconductive antenna, PCA. The generated THz electromagnetic radiation is characterized by a broad spectrum, 0.1 - 4 THz.

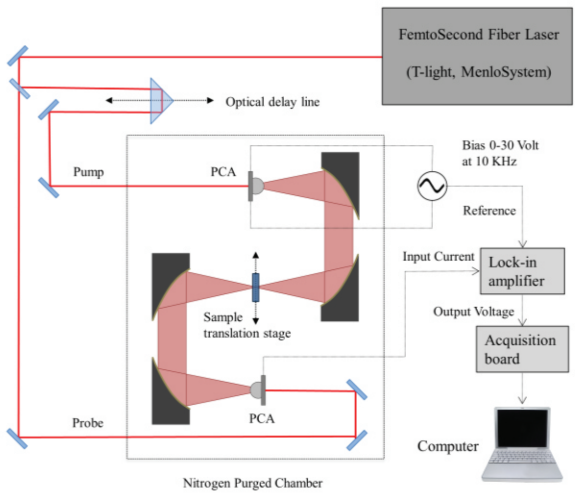

Fig. 1. *Experimental system for THz Time-Domain Spectroscopy.*

The emitted THz field is extracted and collected by a hemispherical silicon lens to obtain a divergent beam, which is then collimated and subsequently focused on the sample by a couple of parabolic off-axis mirrors. The signal, transmitted through the sample, is collimated and focused on the detector PCA by a second couple of parabolic mirrors and hemispherical silicon lens.

III. THZ DATA ANALYSIS

In the Figure 2 we report a typical signal measured by this THz-TDS apparatus. The sample is a thick pellet made by dried ink and powder of polyethylene microspheres. The sample thickness is about 1 mm. The THz electric field of the signal (top panel of figure 2) shows a series of modifications induced by the transmission through the sample; in the frequency window (bottom panel), these appear as variations in the THz pulse spectrum. In particular, the signal shows a second pulse at around 15 picoseconds of delay time. This is due to the internal reflections of the THz pulse between the sample surfaces and it produces the fast oscillations in the low frequency side of the signal spectrum.

In thick-layered samples, the reflections are clearly distinguishable and the data analysis is relatively simple. Contrarily, in thin-layered sample the reflection signals are close in time and partially superimposed, so a correct extraction of the material parameters requires a complex data analysis where the multi-reflection processes are properly taken into account [8]. Otherwise, the refractive index and absorption coefficient spectra are distorted by fake oscillations.

In a TDS transmission experiment, the transfer function is given by the ratio between the complex Fourier transforms of the sample and reference signal, see eq. (1) in ref [7]. The main objective is the extraction of the refractive index, $n(\omega)$, absorption coefficient, $\alpha(\omega)$, and sample thickness from the measured transfer function.

If the sample is thick, the pulse reflections are distinguishable in the THz signals and they can be cut off in the data analysis. If the sample thickness is known a priori, the material parameters can be obtained from the experimental transfer function using a relatively simple procedure, see eq.s (5) and (6) in ref.[7].

In order to extend the THz-TDS data analysis to thin samples and/or preserve all the experimental information, we must retain the pulse reflections and include those in the data analysis. Therefore, the transfer function becomes more complex and the material parameters, $n(\omega)$ and $\alpha(\omega)$, can be extracted only using an articulated data analysis based on iterative fitting procedures [7-9].

Recently, we implemented an innovative experimental procedure and numerical method to analyze the transmission THz-TDS signal of sample composed by multiple thin layers [7]. This data analysis enables a reliable and robust extraction of the frequency dependence of optical parameters, opening the possibility to measure even weak and broad peaks present in the $\eta(\omega)$ and $\alpha(\omega)$ functions. Moreover, it allows measuring the sample layer dimensions, even when they are so thin that not generate visible reflections in the time-domain data.

In this experimental investigation, we applied this method on the THz-TDS data from sample made by two thin layers: an ink film deposited on polyethylene (PE) pellicles.

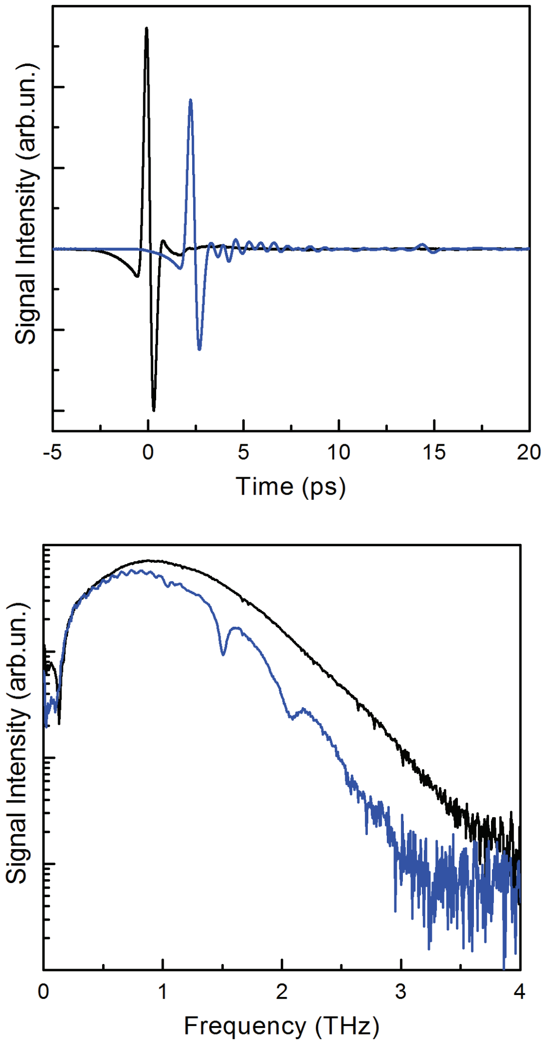

Fig 2. *Typical THz signals obtained by the experimental TDS apparatus. Top panel: typical time evolution of the THz electric field of the reference and ink signal from an ink-polyethylene pellet sample, thickness of around 1 mm; Bottom panel: spectra of the signals obtained by their Fourier transforms.*

IV. RESULTS

We studied three type of inks; - Red ink based on cochineal carmine pigments, - Blue ink based on indigo pigment and - Black ink of the iron-gall type. All inks are commercial and were purchased from Zecchi (Firenze, Italy). THz-TDS studies of a series of black inks in thin layered and pellet forms were previously reported in ref. [7] and [6], respectively.

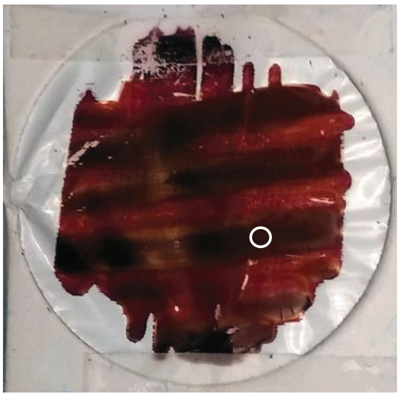

Fig. 3 Here we show a sample of Red Ink, investigated by THz-TDS spectroscopy. The ink is deposited on the PE pellicle by a small brush; the stripes correspond to a single or double deposition of the ink. The investigated zones are on the darker stripes, corresponding to a double deposition, and have dimensions similar to that restricted by the white circle in the figure, about 1 mm of diameter.

In Figure 3 we report the image of one of the investigated samples. The inks are deposited by a small brush on the PE pellicles. These are PE sample cards for infrared spectroscopy.

In Figure 4 we report the absorption coefficient and the index of refraction of the investigated inks measured as thin films deposited on PE pellicles by THz-TDS. The THz transmission parameters of the bare PE pellicle were characterized performing preliminary THz-TDS measurements. We utilized the experimental procedure and data analysis summarized in the previous section.

While the studied red and blue inks show a featureless absorption spectra in the frequency range investigated, the black ink spectrum suggests a presence of a couple of weak absorption peaks at about 1.5 and 1.9 THz; these are likely the signatures of the presence of iron(II) sulfate, as reported in previous investigations [6, 7]. The THz-TDS enable us to measure the thickness, d, down to about 10 µm. For these samples we found: d ≤ 10 µm for Red Ink; d ≅ 15 µm for Blue Ink and d ≤ 10 µm for Black Ink.

We can observe how the absolute scales of absorption and refraction are clearly different for the series of inks and not limited by the presence of noise in the spectra.

So, an identification of the inks can be pursued on the base of the absolute values of the transmission parameters.

In the THz studies of drawing materials, the identification of inks is typically made based on the assignment of spectral features, because the transmission or reflection parameters are measured in an arbitrary scale of intensities [1, 4, 6]. If the spectral features are smooth or absent a correct identification can be precluded.

These THz-TDS data show that the complete quantitative investigation of transmission parameters of ink media is possible even for samples of very small thickness.

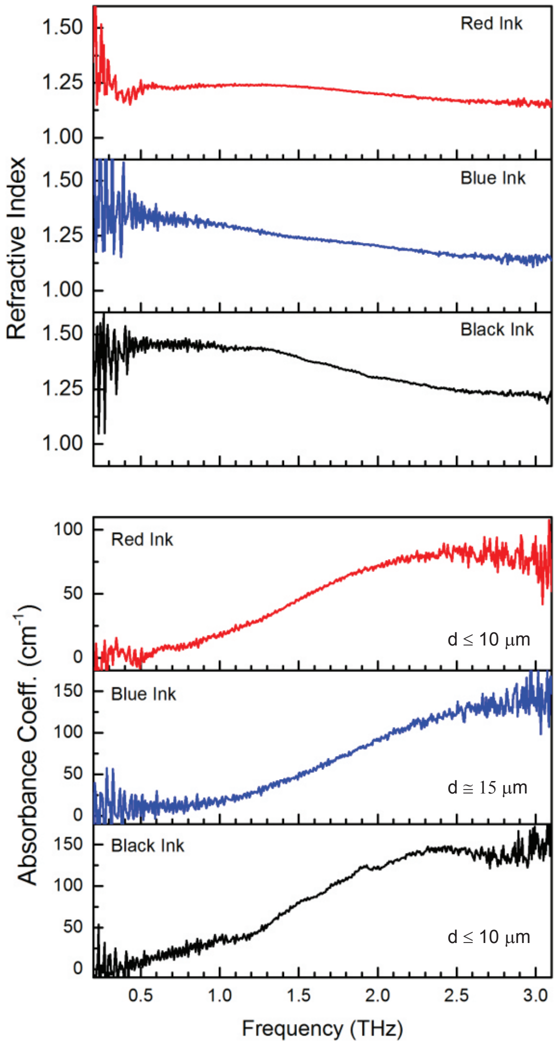

Fig 4. The refractive index (top panel) and absorption coefficient (bottom panel) as a function of frequency for the series of inks on PE pellicles. The present THz-TDS investigations enable the determination of the absolute values of both THz transmission parameters and the drawing media thickness. For each sample, the measured thickness, d, is reported.

CONCLUSION

The ink parameters are normally studied by the investigation of pellet samples [6]. This type of samples provide good THz data of the drawing media, but they have some drawbacks. In a pellet, the drawing materials are not in a form immediately relevant for the cultural heritage studies (e.g. inscriptions, brushstrokes, etc.). The molar concentration of inks in pellets are normally unknown, so no absolute measurements of the absorbance coefficient and refractive index may be obtained. The presence of inhomogeneities in the sample produces scattering processes that can lead to spectra distortions.

The study of drawing media in the form of thin layers overcomes the previous problems. Moreover, the direct investigation on artworks requires the knowledge of THz properties of these media in the form of layers. Here we shown that the THz-TDS enables the direct investigation of ink media as thin layer. Furthermore, employing the implemented numerical method, the absorbance coefficient and the refractive index can be measured in an absolute scale introducing the possibility to make a complete confrontation of different inks even in the absence of distinct spectral features.

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