Investigation of natural and synthetic pigments: terahertz continuous-waves spectroscopy (THz-CW) as a reliable high-resolution approach applied to the Cultural Heritage field.

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Abstract – **In this work, the optical properties of historically produced synthetic and natural pigments were obtained by exploiting a coherent terahertz continuous wave (THz-CW) spectroscopic system in transmission mode. In particular, these pigments were investigated for the first time with THz-CW in the spectral region within (0.1-3) THz and in a non-invasive way by a high resolution portable experimental set-up. The materials investigated in this study showed different absorption features that allowed to identify their spectral fingerprints. The results demonstrated the possibility to discriminate between molecular structures belonging to the same chemical and mineralogical class, and to distinguish synthetic pigments from natural ones thus proving that THz-CW spectroscopy can represent an innovative approach for the Cultural Heritage field.**

I. INTRODUCTION

Recently, techniques based on terahertz (THz) radiation have attracted increasing interest in a variety of technological fields and research disciplines (i.e., biomedicine, environmental monitoring, agricultural and food inspection, etc.) [1–10]. Furthermore, THz radiation has given rise to promising perspectives in the field of Cultural Heritage science and in particular for the characterization of synthetic e natural pigments [11–20].

In fact, THz-based methods show valuable properties such as high penetration in dielectric materials, coherence, and non-ionizing properties due to the low photon energies involved (4.2 meV at 1 THz).

In addition, the technological advancements in the THz field led to the development of portable, high-resolution, and compact devices. The aforementioned properties are particularly intriguing for the Cultural Heritage field. In fact, it is important to be able to characterize the materials of interest with a non-invasive approach since the intrinsic nature of the objects and/or the fragility of the substrates make sampling often forbidden or at least not recommended. Moreover, some materials used in the Cultural Heritage field can be considered transparent in the THz range (including parchment, paper, some varnishes, binders, etc.), guaranteeing few influences in the resulting spectra.

In this work, we present, experimental spectra of natural and synthetic pigments obtained by terahertz continuous wave (THz-CW) spectroscopy.

The results of this work together with the portability of the system employed, and its high-frequency resolution (down to 10 MHz) prove that THZ-CW spectroscopy can represent an innovative methodology for pigment identification on Cultural Heritage related materials in a compact and non-invasive way and it opens the possibility to exploit THz-based methods to identify single pigments in mixtures.

II. MATERIALS AND METHODS

A. *Terahertz continuous wave spectroscopy (THz-CW)*

Terahertz measurements were performed by exploiting a commercial terahertz continuous wave spectroscopic system (THz-CW), TeraScan 100 1550 (TOPTICA Photonics AG, Germany), schematically represented in Fig. 1. The radiation is generated by heterodyning two distributed feedback lasers (DFB, #LD-1550-0040-DFB at 1533, 1538, and 1550 nm) combined by a system of optical fibers into a laser combiner (Fib-MIX) which generates a beat signal divided into two beams that have the same average power (around 35 mW). One of them pumps the photoconductive antenna (PCA) made by a low temperature grown InGaAs that acts as transmitter (TX) while the other drives the PCA that acts as receiver (RX). The emitted THz radiation is collimated and focused by four off-axis parabolic mirrors (PMs). The detected THz signal drives the photo-carriers pumped by the other laser beat to form a photocurrent amplified by a lock-in amplifier.

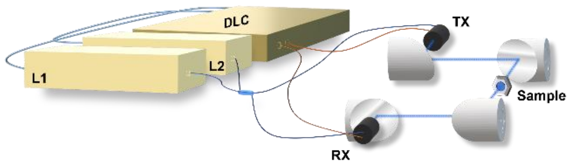

Fig. 1. Schematic representation for THz-CW experimental set-up in transmission configuration.

The transmitter is biased by an AC modulation frequency of ~ 39.67 kHz and a voltage of 0.9 V. The samples were analysed in transmission configuration placing them between two off-axes PMs at the focal point of the THz radiation. All the experiments were performed at room temperature (293 K) and the presence of the water vapour absorption was reduced by closing the experimental set-up in the presence of a dehumidification/ventilation system. THz spectra were collected in the spectral range between 100 and 2800 GHz with a frequency resolution of 100 MHz and an integration time of 30 ms. Raw data were processed and analysed with an algorithm based on the Hilbert transform method in MATLAB (ver. 2019a, MathWorks Inc., USA) [20]. The transmittance through the sample was obtained:

$$T(\nu) = \left(I_{sample}(\nu)\right)^2 / \left(I_{reference}(\nu)\right)^2 \qquad (1)$$

Where I_{sample} and $I_{reference}$ are the amplitudes of the photocurrents of the sample and of the reference. The reference measurements were performed by collecting the spectra without the sample placed at the focal point of the THz beam path and they were conducted each time before the analysis of the samples of interest. The experimental absorbance was then calculated as:

$$Absorbance(\nu) = -log\left(T(\nu)\right) \qquad (2)$$

Afterwards, the absorption coefficient was calculated as:

$$\alpha(\nu) = -\frac{1}{d} log\left(T(\nu)\right) \qquad (3)$$

Where d is the thickness of the sample and $T(\nu)$ is the transmittance.

B. Samples

The materials investigated in this work were purchased from Kremer Pigments Inc. (Munich, Germany). Due to its availability, natural azurite (*Azzurro della Magna "M"*) was purchased by Zecchi (Florence, Italy). In Tab. 1 the information on the samples used and the raw pigment formulas, as stated in the data safety sheet provided by the manufacturer of the pigments, are reported.
The samples were pressed in a containment bolt in their pure powder form without following any procedure of powder grinding or purification nor with the addition of further materials (i.e., high-density polyethylene or microfine polytetrafluoroethylene). For each sample replica, the thickness measurements were performed through the use of a digital calliper with a resolution of ±0.01 mm. The thickness measurements were different for each sample. However, the average range of thickness was included between 230 µm and 430 µm.

Table 1. Samples' information according to the manufacturer.

Pigment	Code	Chemical Characterization
Egyptian Blue	#10060	$CaCuSi_4O_{10}$
Han Blue	#10071	$BaCuSi_4O_{10}$
Han Purple	#10074	$BaCuSi_2O_6$
Azurite	0107-M/10	$Cu_3(CO_3)_2(OH)_2$
Bice Blue	#10184	$Cu_3(CO_3)_2(OH)_2$
Blue Verditer	#10180	$2CuCO{\cdot}Cu(OH)_2$
Atacamite	#103900	$Cu_2Cl(OH)_3$
Antlerite	#103700	$Cu_3(SO_4)(OH)_4$

III. RESULTS

A. Egyptian Blue, Han Blue, and Han Purple

Egyptian Blue (EB) is the first man-made pigment synthesized at least starting from the late pre-dynastic period in Egypt [22].
Its structure ($CaCuSi_4O_{10}$) corresponds to cuprorivaite, a mineral belonging to the gillespite group.
The spectral response of EB was investigated in the spectral range 100-2500 GHz. The synthetic copper

silicate presents an increasing absorption with a peak centered at 2.072 THz with a bandwidth of approximately 80 GHz (Fig. 2).

Han Blue (HB) is a synthetic barium copper silicate pigment ($BaCuSi_4O_{10}$) produced and used in many Chinese artefacts until the Han dynasty. Its mineral form was first identified and named by FitzHugh and Zycherman [23]. At room temperature, the crystal structure belongs to the gillespite group and corresponds to the rare mineral effenbergite, whose presence was first detected in the Kalahari manganese field in South Africa. HB is isostructural with EB, containing barium instead of calcium and the Cu − O distances are almost identical in the two compounds [24]. The pigment investigated by means of THz radiation presents a broad absorption band centered around 1.798 THz with a full width half maximum (FWHM) of approximately 140 GHz as determined by the Gaussian peak shape analysis (Fig. 2).

Han Purple (HP) is a synthetic copper silicate ($BaCuSi_2O_6$) produced with a complex process where barium was used in preparation with lead compounds and quartz [25]. The presence of a Cu–Cu bond is a very uncommon feature and has been associated with the possible low chemical stability that this pigment can present [26]. Its natural analogue has been found in the Wessels mine, Kalahari Manganese Field (South Africa) as the mineral colinowensite. The THz-CW spectral response of HP (Fig. 2) was characterized by a broad absorption band centered around 1.526 THz with a FWHM of around 332 GHz.

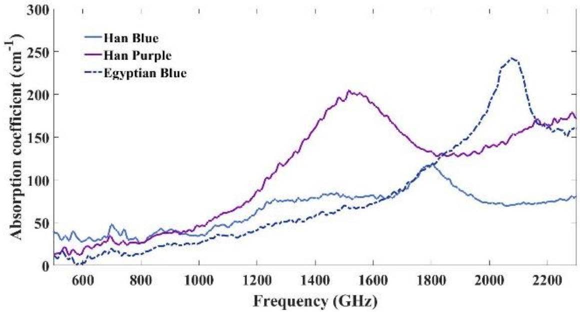

Fig. 2. Egyptian Blue, Han Blue, and Han Purple's THz-CW spectra in the range 500-2300 GHz.

B. Azurite, Bice Blue, and Blue Verditer

Natural azurite ($Cu_3(CO_3)_2(OH)_2$) is produced by grinding to powder the corresponding mineral which is founded in the upper oxidized portions of copper ore deposits.
Synthetic forms of azurite have been produced since the seventeenth century according to different recipes.
Among them, two artificial basic copper carbonates are Blue Verditer and Bice Blue. The discrimination of artificial copper pigments from natural ones is still complex in a non-invasive way since the main difference is in but the habitus of their crystal particles [27].

Natural azurite presents two absorption peaks centered around 1.835 and 2.235 THz [13]. These fingerprints have been assigned through vibrational simulations to simultaneous translational motions of the Cu^{2+} ion layers along the b- and a-axes and the rotational mode of the CO_3^{2-} ions about the b- and a-axes of the azurite crystal [13]. The presence of the two absorption bands of the natural basic copper carbonate, investigated by a coherent THz-CW system, is reported (Fig. 3). The linewidth of the peak located approximately at 2.23 THz is approximately 37 GHz, while the peak centered at the lowest frequency has a FWHM of 23 GHz.

Bice blue presents a shift to lower frequencies of the main peaks. In fact, the first peak is shifted of about 13 GHz with respect to natural azurite while the one at higher frequencies is shifted by approximately 14 GHz (Fig. 3), please note that the measurement are performed with a resolution of 100 MHz.
THz-CW spectrum of Blue Verditer (Fig. 3) is characterized by the presence of two broad peaks centered approximately at 1.827 and 2.215 THz.
The two synthetic compounds exhibit broader features with FWHM almost doubled with respect to natural azurite.
These differences open the possibility to discriminate mineral and synthetic compounds by means of THz-CW spectroscopy.

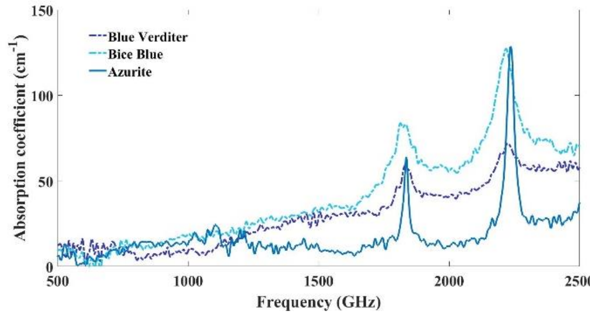

Fig. 3. Azurite, Bice Blue, and Blue Verditer THz-CW spectra in the range 500-2500 GHz.

C. Atacamite and Antlerite

Atacamite ($Cu_2Cl(OH)_3$) was discovered in the Atacama Desert in northern Chile, where secondary copper ore deposits were found to contain it. This mineral is the most common trihydroxychloride involved in copper-based metal corrosion and it was used as a pigment in wall paintings, icons, sculptures, manuscripts, sarcophagi, and maps [27-29].

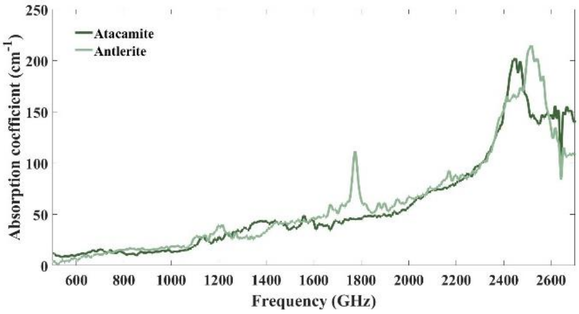

Fig. 4. Atacamite and Antlerite THz-CW spectra in the range 500-2700 GHz.

Its THz-CW absorption spectrum (Fig. 4) is characterized by the presence of an increasing absorption with a distinctive peak centred at 2.451 THz, with a FWHM of approximately 77 GHz as evidenced by a Lorentzian fitting procedure.
Antlerite ($Cu_3(OH)_4SO_4$) is a copper sulfate-hydroxide salt a frequent component of patinas in bronze alloys, and copper artefacts but it has also been found used as a pigment in illuminated manuscripts and mural paintings [29-32].

Antlerite spectral response showed the presence of two absorption peaks. The low frequency resonance is centred at 1.771 THz while the second absorption feature is centered approximately around 2.521 THz (Fig. 4). The lowest-frequency peak has a FWHM of 27 GHz whereas the other absorption peak is characterized by broad band of approximately 60 GHz.

IV. CONCLUSIONS

The possibility of a non-invasive identification with a portable experimental set-up makes THz-CW spectroscopy a highly interesting technique for the Cultural Heritage field. In this work, we characterised the spectral fingerprint of different materials with molecular structures that belong to the same chemical and mineralogical class as well as synthetic and mineral compounds. Due to the high spectral resolution (100 MHz), this methodology can be capable of recognising and discriminating different pigments in a non-interacting mixture. THz-CW technology therefore can be considered of great importance in the field of Cultural Heritage.

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