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More than meets the eye: depth-resolved THz chemical mapping of multilayered samples

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Abstract: A novel depth-resolved THz multispectral mapping method for uncovering hidden layers in artworks is presented. Exploiting spectral fingerprints related to chemical specificity of each pigment we successfully deciphered concealed text in multilayered mock-ups, resulting in better resolution compared to conventional temporal domain analysis.

Non-invasive imaging through thin stratified layers represents a significant analytical challenge in Cultural Heritage conservation as well as in many fields of material sciences. Well-established methodologies for this purpose, such as NIR, SORS or XRF analysis, usually face important limitations regarding this matter. They are typically hindered by scarce elemental contrast between different layers, fluorescence hindrance, or overlapping spectral signatures. At the same time, it is renowned that the terahertz spectral region offers a unique frontier for overcoming these hurdles: instrumentation operating in this range is considered almost unrivalled when it comes to depth-resolved non-invasive analysis of multilayered structures, thanks to its ability to penetrate non-conductive materials. Terahertz Time-Domain Spectroscopy (THz-TDS), in particular, has been conventionally exploited for stratigraphic reconstruction using time-of-flight analysis of the reflected echoes [1]. However, standard time-domain imaging often lacks chemical specificity, especially when refractive index contrasts are low. Our work, leveraging the interesting capability of THz radiation, presents a novel methodology based on THz reflection spectroscopy and evaluates data in the frequency domain. This is achieved thanks to a specifically designed algorithm that deciphers concealed images and separates pigment layers within stratified pictorial materials based on their specific vibrational modes.

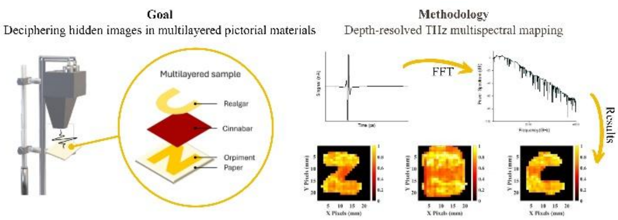

Fig.1 | Graphical representation of the study's objective (right) and schematic workflow of the presented approach (left)

Concerning experimental details, in this study we utilized a fiber-based femtosecond laser system operating in the 0.1–6 THz range. Measurements were conducted in reflection geometry, equipping the instrument with a supplementary reflection module (incident beam angle of approximately 8°) and using a mechanical X-Y raster scanner with a spatial

step of 1 mm, consistent with the beam spot size measured at the focal plane ($\sigma \approx 500\ \mu m$). The subjects of this study were pictorial mock-ups prepared using historical red and yellow pigments such as cinnabar (HgS), orpiment (As_2S_3), and realgar (As_4S_4), bound with gum Arabic on paper to paint variously arranged letters. Lastly, one mock-up featured a peculiar multilayered structure designed to test depth-resolved imaging, where a hidden letter ("Z" in orpiment) was obscured by a cinnabar layer beneath a visible letter ("C" in realgar). Prior characterization of pure pigment pellets in transmission (0.5–3 THz) established a reference database, retrieving refractive indices and absorption spectra, including previously experimentally unreported peaks for realgar. The crucial objective was to move beyond standard time-domain echo detection to reach chemical specificity. Therefore, we developed a custom frequency-domain reconstruction algorithm that integrates spectral intensity (L_{signal}) within a narrow bandwidth ($v_0 \pm 0.02$ THz) around unique resonances. This strategy allowed for the selective identification of materials even when optically hidden: our frequency-domain analysis successfully revealed the concealed text "Z", a feature that was essentially indistinguishable using standard time-domain maximum/minimum amplitude mapping. The resulting high-contrast chemical maps demonstrated a pixel recognition discrepancy of approximately 13%. This deviation is primarily observed near structural boundaries (i.e., borders between the letter and the background), where the finite beam waist size limits spatial resolution. These artifacts, however, were refined through visual inspection of the spectral data.
Finally, sparse deconvolution resolved temporally overlapping echoes. Combining this with measured refractive indices granted for a precise thickness quantification (down to ~50 µm), validated against cross-sectional optical microscopy: minor discrepancies can be attributed to the inherent variability of handmade specimens.
From what is exposed above, this work sets THz multispectral imaging as a crucial tool for unravelling hidden layers in Cultural Heritage artefacts. By shifting the focus from time-domain to frequency-domain spectral fingerprints, we demonstrate the ability to chemically differentiate and spatially reconstruct hidden layers with high specificity, bridging the gap between fundamental spectroscopy and diagnostic applications [2].

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