

# In-situ investigation of mortar fragments from the theatre of the archaeological area of Tindari (Sicily, Italy) through DRIFT and $\mu$ -Raman techniques

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**Abstract** – We report here a multi-technique study by Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and  $\mu$ -Raman spectroscopy aimed at the molecular characterization of three mortar fragments from the theatre of the archaeological area of Tindari (Sicily, Italy). The assessment of the main mineralogical phases allowed us to recognize ancient raw materials and modern compounds, obtaining useful information, other than relative to the manufacturing process, in view of future restorations to be planned.

## I. INTRODUCTION

The theatre of Tindari (Sicily, Italy), built during the Hellenistic age and representing the most suggestive attraction of the archaeological site (See Fig. 1). It underwent several restoration interventions, both in antiquity and in the modern age, in view of its contemporary use.

In spite of several studies are reported regarding its layout and stylistic elements [1, 2], few papers have been published focusing on conservation and degradation phenomena affecting the monument [3]. In addition, previous reconstruction and restoration activities are documented between 1938 and 1965 [4, 5].

In recent years, multi-analytical approaches combining spectroscopic and chemical techniques have been increasingly applied to study ancient mortars in archaeological contexts, providing insights into raw material selection, production technology, and conservation strategies. For instance, Marcaida *et al.* [6] characterized mortars and *tesserae* from Pompeii mosaics using non-invasive techniques, while Gómez-Laserna *et al.* [7] investigated the impact of environmental conditions on building materials in coastal archaeological sites.

Similar integrated studies on Roman structures have been reported by Couvidat *et al.* [8], highlighting the contribution of such analyses to assess the ancient artificial materials formulations in view of the design of compatible, modern mortars. These studies provide a valuable framework for comparing the findings from Tindari with other archaeological sites, contributing to a broader understanding of ancient construction practices and the role of aggregates in mortar formulation.

In this context, mortar fragments belonging to different construction phases were selected based on visual inspections and analysed at molecular scale by Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and  $\mu$ -Raman spectroscopy, with the aim to characterize both ancient and modern restored areas of the theater.

Such analyses were carried out in-situ with the aim of gaining insights not only into the molecular composition of the raw materials, but also in the production technology of the ancient mortars recovered from different areas of the theater. It is worth noting that the molecular recognition of the used materials, as achieved by the employment of the aforementioned spectroscopic techniques, could also shed light on the degradation phenomena occurring on the investigated materials due to stone-environment interactions.



Fig. 1. The theatre of Tindari (Sicily, Italy).

## II. MATERIALS AND METHODS

A total of 25 distinct areas of the monument were selected for in-situ investigations. The areas of interest included both the walls of the scenic building and the *cavea*. Each of them was photographed, with a special focus on the precise point of the monument where the in-situ analyses were conducted, by collecting a single acquisition per area.

In this work, three areas representative of ancient mortars were considered (Fig. 2). In particular, samples TY\_OU\_9 and TY\_OU\_19 - represent the ancient mortars from the podium, whereas TY\_OU\_10, located on the vault of the circular wall in the orchestra, was chosen for comparison.

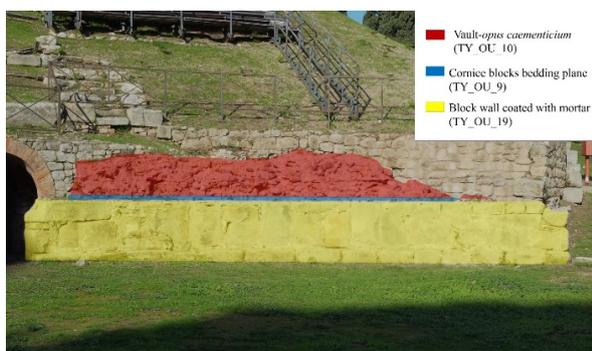


Fig. 2. Different investigated areas representative of ancient mortars. See text for details.

For DRIFTS measurements, a 4300 Topscan hand-held FTIR spectrometer (Agilent), using a diffuse reflectance sampling interface, was employed, operating with a resolution of  $4\text{ cm}^{-1}$  in a spectral range of  $600\text{--}4000\text{ cm}^{-1}$ . Spectra were collected under 32 accumulations, with a spot size of around  $2\text{ mm}$ , using a ZnSe beamsplitter and a DTGS detector. The background was acquired with a diffuse gold reference cap. The spectra treatment was performed using Nicolet Omnic 7.2 software (Madison,

WI, USA). Obtained reflectance spectra were transformed into absorbance spectra using the Agilent MicroLab Software. Band recognition was carried out through comparison with spectra reported in the literature.

$\mu$ -Raman measurements were performed by means of a “BTR111MiniRam™” (BW&TEK Inc) spectrometer. The instrument operates with a  $785\text{ nm}$  excitation wavelength and a thermoelectric cooled charge-coupled device (CCD) detector. The instrument was equipped with a BAC151B Raman microscope. The laser spot was focused through a  $80\times$  objective, which guaranteed a working distance of  $1.24\text{ mm}$  and a laser beam spot size of  $25\text{ }\mu\text{m}$ . Spectra were collected between  $60$  and  $3150\text{ cm}^{-1}$ , with an acquisition time of  $40\text{ s}$  and a resolution of  $8\text{ cm}^{-1}$ , by accumulating 32 scans in order to improve the signal-to-noise ratio. The identification of the peaks was obtained by comparing the experimental spectra with those reported in various databases and in the literature [9,10].

## III. RESULTS AND DISCUSSION

Fig. 3 shows representative DRIFTS spectral behavior as well as significant peaks for the examined mortar samples, in the wavenumber range between  $600\text{ cm}^{-1}$  and  $4000\text{ cm}^{-1}$ .

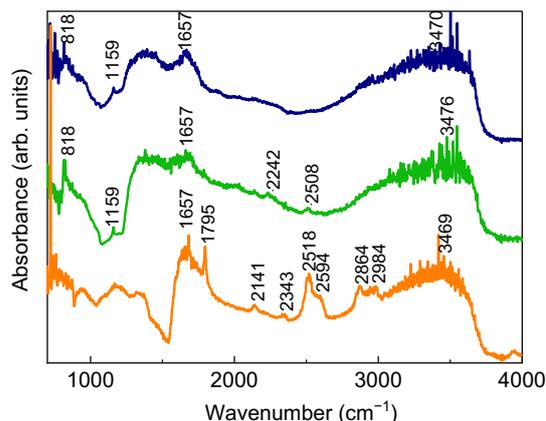


Fig. 3. DRIFTS absorption spectra collected on the TY\_OU\_9 (green line), TY\_OU\_10 (orange line) and TY\_OU\_19 (blue line) areas in the wavenumber range between  $600\text{ cm}^{-1}$  and  $4000\text{ cm}^{-1}$ . Spectra were vertically offset for clarity.

A first comparison of the obtained spectral profiles revealed significant similarities in the DRIFTS spectra associated to sample TY\_OU\_9 and TY\_OU\_19. Both exhibited strong absorption features indicative of a molecular composition mainly based on quartz ( $\sim 818\text{ cm}^{-1}$  and  $\sim 1159\text{ cm}^{-1}$ ), kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) ( $\sim 1657\text{ cm}^{-1}$ ), and water molecules within the mineral lattices ( $\sim 3470\text{ cm}^{-1}$ ). This suggests a similar recipe used for both areas, indicating a common manufacturing technique characteristic of a specific construction phase.

Interestingly, only in the case of TY\_OU\_9, minor trace

of organic compounds and calcite were detected, evidenced by low-intensity contributions centered at, respectively,  $\sim 2242\text{ cm}^{-1}$  and  $\sim 2508\text{ cm}^{-1}$ . In contrast to these findings, DRIFTS spectrum of TY\_OU\_10 exhibited a molecular signature mainly characterized by the presence of calcite with characteristic bands at  $\sim 1795\text{ cm}^{-1}$ ,  $\sim 2141\text{ cm}^{-1}$ ,  $\sim 2343\text{ cm}^{-1}$ ,  $\sim 2518\text{ cm}^{-1}$ ,  $\sim 2594\text{ cm}^{-1}$ ,  $\sim 2864\text{ cm}^{-1}$  and  $\sim 2984\text{ cm}^{-1}$  [6-8]. Worth of note, no spectral features associated to quartz can be observed. However, kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) ( $\sim 1655\text{ cm}^{-1}$ ) and water molecules within the crystal lattices ( $\sim 3469\text{ cm}^{-1}$ ) were identified. These DRIFTS results revealed that the molecular composition of TY\_OU\_10 was predominantly calcite-based, suggesting the use of lime as a binder, and possibly a carbonatic aggregate. Furthermore, the absence of detectable quartz, despite the relatively large measurement area (2 mm in diameter), may indicate the use of minimal sand or other siliceous aggregates. This could suggest a variation in mortar composition depending on its function within the monument, such as structural versus coating applications.

Most representative  $\mu$ -Raman spectra of samples TY\_OU\_9, TY\_OU\_10 and TY\_OU\_19 are reported in Fig. 4, in the wavenumber range between  $100\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$ .

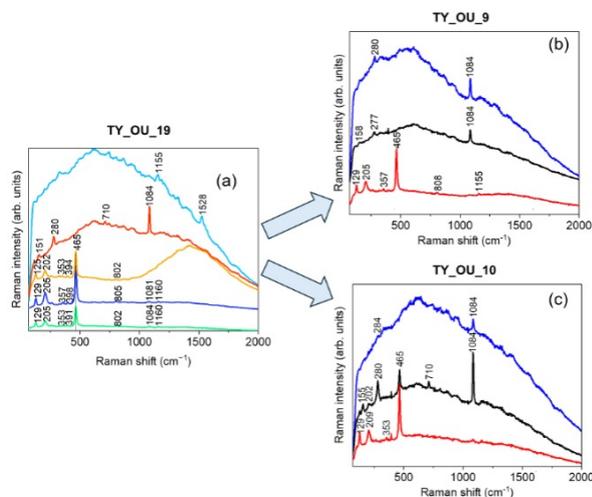


Fig. 4. Comparison of the most representative  $\mu$ -Raman spectra collected for TY\_OU\_19 (a), TY\_OU\_9 (b) and TY\_OU\_10 (c), in the wavenumber range between  $100\text{ cm}^{-1}$  and  $2000\text{ cm}^{-1}$ . Spectra were vertically offset for clarity.

From a first comparison of  $\mu$ -Raman spectra collected from different spots of each surface, the presence of calcite ( $\text{CaCO}_3$ ) can be recognized, by the prominent peak around  $\sim 1084\text{ cm}^{-1}$ , along with minor contributions falling at  $\sim 155\text{ cm}^{-1}$ ,  $\sim 280\text{ cm}^{-1}$  and  $\sim 710\text{ cm}^{-1}$ . This appears to contradict the DRIFTS results, which indicated significant

calcite only in TY\_OU\_10. However, the  $\mu$ -Raman detection of  $\text{CaCO}_3$  may be explained by the microscope's high spatial resolution. The focused laser beam (with a spot size of  $\sim 25\text{ }\mu\text{m}$ ) may have isolated a single grain predominantly composed of this mineral. Beside the molecular signature of calcite, prominent peaks corresponding to quartz were also observed in all fragments, with varying relative intensity reflecting differences in the molecular concentration of these components. Although preliminary, the Raman and DRIFTS spectra of TY\_OU\_9, TY\_OU\_10, and TY\_OU\_19, provide interesting insights and raise new questions for future investigations. In all three cases, the mortars can be attributed to the second Roman construction phase and are linked to a specific part of the building, namely the annular corridor. This corridor was constructed by demolishing the lower steps of the *cavea* when the Theatre began to host spectacles featuring wild animals. The corridor encircles the orchestra at the base of the *cavea*; it is characterized by a barrel vault made of *opus caementicium*, whose original external facing has not been preserved.

#### IV. CONCLUSIONS

A preliminary molecular characterization of ancient mortars from the Theatre of the archaeological area of Tindari (Sicily, Italy) is here reported, combining Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) and  $\mu$ -Raman spectroscopy.

Although only partial data are available for this group of samples, it is possible to draw some useful considerations that shed light not so much on the construction phases of the monument, but rather on peculiar technological strategies adopted during the second Roman phase of the Theatre. The most significant insight pertains to the potential differentiation of mortars based on their specific function within the structure.

The integrated approach applied in this study proves promising for understand ancient construction technologies and guiding future strategies in monumental archaeology.

Future investigation are planned, aimed at integrating the obtained data with those achieved, always in-situ, at elemental level through X-ray fluorescence (XRF) spectroscopy and laser induced breakdown spectroscopy (LIBS). Finally, chemometric approaches will be also applied to get deeper insights in discriminating between different materials or phases.

#### V. ACKNOWLEDGEMENTS

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