

Elemental, molecular and mineralogical characterization of polychromes in the Oratory Room of Granada's Madrasah (Spain)

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INTRODUCTION.

The Madrasah palace of Granada (Spain) was built by Yusuf I (of the Nasrid dynasty, 1238-1492) in 1349 in the religious and trading centre of the ancient *Madinat Garnata*. The original *Madrasah Yusufiyya* or *Nasriyya* was the first Islamic University in Granada and the only one still standing, dating back to the epoch of *Al-Andalus*. Soon after the Christian conquest in 1492 the *Madrasah* became the municipal council of the city. Since then the building has undergone numerous reforms including incorporation of new rooms with e.g. Plateresque decoration such as the Knight's Hall (18th century), and restoration interventions such as that currently ongoing by the University of Granada (UGR).

At present, the only original *Nasrid* room is that of the Oratory with polychromed stucco in red, green, blue and gold. However, later interventions also can be observed which date back to the 18th and 19th centuries.



fig 1. View of the Oratory at the Madrasah.

In the framework of the restoration works performed here under the auspice of the UGR, this study focuses on

characterizing the polychromes of the Oratory at elemental, molecular and mineralogical levels. To this end a combination of non-destructive and micro-destructive analytical techniques were applied to Nasrid and Christian paint samples (Fig. 1).

MATERIALS AND METHODS.

Seven samples showing in surface diverse colors, i.e. white, red, blue, green and gold were selected for this work. The objective of the sampling strategy was to obtain representative samples of the original polychromed Nasrid stucco and of possible later interventions. All the samples were prepared as polished thin sections which were studied by Micro-X-Ray diffraction (μ -XRD), Raman microscopy (RM), optical microscopy (OM) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDX) (Fig. 2). They were carbon-

coated to be analyzed by SEM-EDX. Additionally, to identify the type of organic binder used in the paintings, chips of samples were analyzed by gas chromatography-mass spectrometry (GC-MS).

The μ -XRD analysis was used to identify the mineral pigments and extenders. An experimental system equipped with a high-flux Rigaku MSC MicroMax micro-focus X-ray tube, equipped with high flux Rigaku MSC MicroMax micro-focus X-ray tube (with a Kirkpatrick-Baez mirror), and a copper anode was used. Imaging plates were used as bi-dimensional detectors. The use of imaging plates allows reasonably fast data collection (10 min per sample spot) with good angular resolution. The μ -XRD experiments were done in reflection mode with an incidence angle around 10 degrees. A 200 μ m collimator was used for microanalysis.

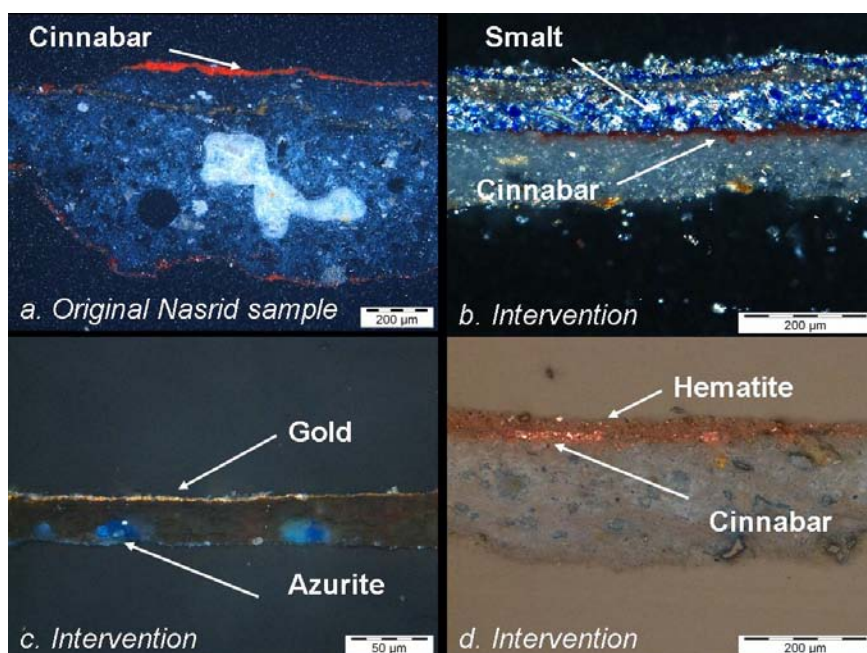


fig 2. OM images of some paintings from the Oratory: a) Original Nasrid polychrome; b, c, d) later interventions using blue smalt, gold and hematite, respectively.

palabras clave: Yesería Nazarí, Pigmentos, μ -DRX, Microscopía Raman.

key words: Nasrid Polychromed Stucco, μ -XRD, Raman Microscopy.

resumen SEM 2010

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For each sample, a set of analyses was performed every 200 μm across a 1 mm line, covering from the inner to the upper superimposed layers in the painting stratigraphies. Due to the thinness of some layers ($< 10 \mu\text{m}$), identified by optical and electronic microscopes, the different measurements did not always correspond exactly to individual layers. However, it is possible to obtain useful information about the evolution of composition along the sample depth profile.

A Renishaw Invia Raman microscope system fitted with a Peltier-cooled CCD detector and with a Leica DMLM microscope was used for Raman microanalysis. Samples were excited with a 785 nm laser. Spectra were collected within the wavenumber range of 3000 cm^{-1} to 200 cm^{-1} , with an average spectral resolution of around 1 cm^{-1} . To improve signal/noise ratios, a set of spectra ($n = 3-10$; exposure time = 20 s) were collected in each layer of the samples.

RESULTS AND DISCUSSION.

The different colored layers observed in the surface of the studied samples were applied on top of a white layer (Fig. 2) (preparation) composed mostly of gypsum as identified by RM and $\mu\text{-XRD}$ (Fig. 3b-5 and 3c-black diagram).

The Raman analysis of the blue sample revealed the presence of blue smalt (462 cm^{-1}), i.e. a potassium cobalt glass which was not detected by $\mu\text{-XRD}$ due to its amorphous character. The second blue layer was also composed of gypsum (497 cm^{-1} and 1005 cm^{-1}) and some barite content in the third blue layer (465 cm^{-1} and 991 cm^{-1}) (Fig. 3b, 1-3). These blue layers appear over the original Nasrid red layer of cinnabar (HgS) (Fig. 3b-4) (at 251 cm^{-1} and 343 cm^{-1}) which also was identified by $\mu\text{-XRD}$ as shown in Fig. 3c (red and blue diagrams with characteristic peaks at 26.5 and 31.2 2θ degrees). The presence of barite and gypsum were better detected by $\mu\text{-XRD}$ (Fig. 3c, green and blue diagrams/upper diagrams).

The existence of hematite was better identified by RM (Fig. 2d). This pigment was used as substitute for cinnabar in a later intervention (18th century). The characterization of iron oxides and iron oxyhydroxides using $\mu\text{-XRD}$ was difficult due to the large size spot of the XR beam, the small amount of pigment

Another difficulty is the strong X-ray fluorescence of the Fe-bearing minerals when analyzed using Copper radiation. On the contrary, the presence of calcite was detected clearly by RM and $\mu\text{-XRD}$.

In summary, the combined application of RM and $\mu\text{-XRD}$ together with OM, SEM-EDX and GC-MS has allowed the full characterization of the studied polychromes and their historical correlation. In this sense, the blue smalt and hematite correspond to interventions applied over original Nasrid paintings showing red color at the surface made of cinnabar and gilded with gold. In addition, the study of the organic binder by GC-MS and RM identified protein binders in Nasrid paint samples and drying oil in samples corresponding to later interventions.

ACKNOWLEDGEMENTS.

Financial support for this work was provided by Andalusian Research Group RNM-179, Project RNM-4169 and the contract MEC/FECYT 2007. We thank A. Yebra-Rodríguez for helping with Raman microscopy using equipment from the University of Jaén, C2RMF staff and J. Ramos from "Restauración del Patrimonio S.L." for collaborating with sampling campaign.

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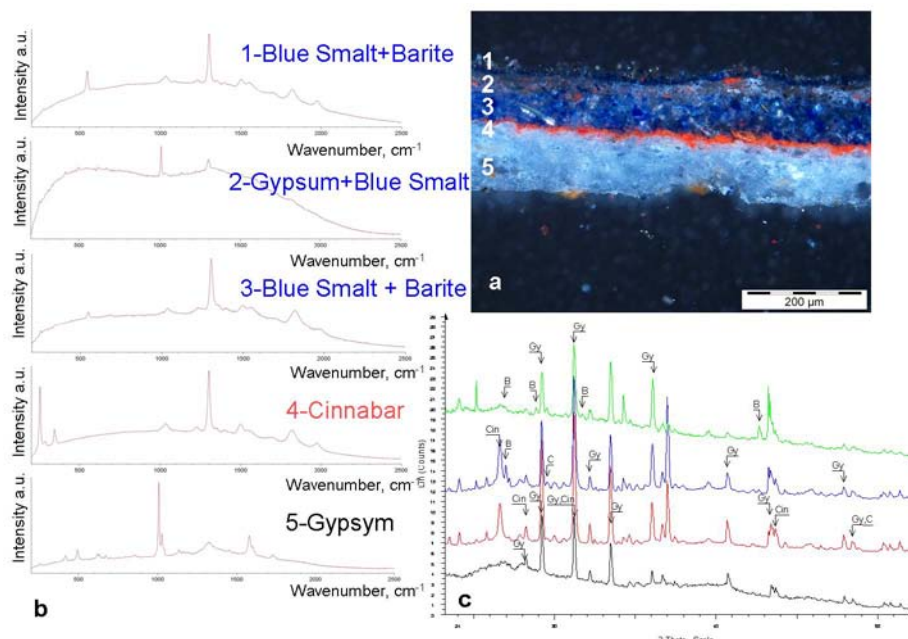


fig 3. Analysis of blue sample from the Oratory Room: a) Image of OM. Note the fourth original Nasrid layer of cinnabar; b) Raman spectra of every layers; c) Diffractograms at 0, 35, 70 and 130 μm from surface. *(Gy=Gypsum, B=Barite, Cin=Cinnabar and C=Calcite).