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Ancient covering plaster mortars from several convents and Islamic and Gothic palaces in Palma de Mallorca (Spain). Analytical characterisation

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Abstract

Analysis of historic mortars including Islamic, Gothic and later ones taken from palaces, convents and mansions in Palma de Mallorca has been carried out. Scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectrometer (EDX), Fourier transform infrared spectroscopy (FTIR), and X-ray diffraction (XRD) techniques were used to characterise the morphology and analytical composition of the samples analysed. Generally, covering plaster mortars presented a low percentage of small size aggregate. The reported results show that mixed and lime mortars have been used, thus, the establishment of a relationship between the type of mortar employed and its age is not feasible. In the painted mortars, polychromy has also been studied. The most common pigments to be found are natural earths.

Keywords: Covering plaster mortars; SEM; XRD; FTIR; Polychromed walls; Restoration of historical buildings

1. Research aims

The importance of characterising the ancient covering plaster mortars has been highlighted [1–4]. In this way, several institutions in Spain, such as "Instituto Eduardo Torroja" (CSIC) [5,6] and "Instituto Andaluz de Patrimonio Histórico" [7], have developed important investigations.

Different methodological approaches for these investigations have been proposed [8–11]. The meetings organised by the ICCROM and the RILEM organisations must be pointed out. These are directed to establish a methodology for the characterisation of ancient mortars and those used in restoration. Moreover, la Carta del Restauro de 1987, annex B, recommended the use of the same original material for restoration purposes of buildings of historical interest.

Up to the present, the knowledge of ancient building techniques traditionally used in Mallorca is only based on the visual observations and properties. In this way, the compositional parameters of mortars from covering plasters are very important from a historical and a scientific point of view.

The main objective of the present experimental work is to reduce this lacuna and to produce a background knowledge of ancient mortars. Its content is focused on two aspects:

(a) An attempt towards the characterisation of the materials and techniques that have been handed down to us by different cultures. As stated earlier, their characterisation is useful for restoration projects of historical buildings.
(b) The knowledge of the ancient techniques and their evolution in order to establish chronological correlations with the cultural evolution of the place.

2. Experimental section

2.1. Instrumentation and operating conditions

Scanning electron microscopy (SEM) observations were accomplished with a HITACHI S-530 microscope equipped with an energy dispersive X-ray spectrometer (EDX). Transmission IR spectra were recorded using a Brucker IFS 66 FTIR spectrophotometer. KBr pellets of powered samples were examined between 4000 and 400 cm^{-1} at a resolution of 4 cm^{-1}.

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Table 1
Provenance, data, and colour of the mortar samples

Sample	Source (Provenance)	Century	Width (cm)	Polychromy
ALM 2149	La Almudaina's Palace	X–XI	4	Surface painted in red, white and black
ALM2035	La Almudaina's Palace	X–XI	1.5	Red layer
ALM2036	La Almudaina's Palace	X–XI	0.5	–
SCL	Santa Clara's Convent	XII	–	–
DES-RE	Can Desbrull's Palace	XII	1.4	–
DES-RI-1				
DES-RI-2				
CAT 6-1	Santa Catalina de Siena's Church	XII	1.3	Surface with red drawings
CAT 6-2			1.1	
CAT 8-1			1.7	
EG1	Gothic House	XIV	1.8	Surface with ochre, red and black drawings
EG2	Gothic House	XIV	2	Surface painted in black and red
CT2024rf	Constitució	XIV	2	Red layer
CT2024rfd	Constitució	XIV	1.2	Surface with red drawings
CT2006[a]	Constitució	XIV	(r1) 0.5	Surface with black drawings
			(r2) 0.4	
CSB(v)	Saint Bonaventura's Cloister	XVII	0.5	Green layer
CSB(g)	Saint Bonaventura's Cloister	XVII	1.0	Grey layer
CSB(n)	Saint Bonaventura's Cloister	XVII	0.4	Black layer

[a] This sample presents two different covering plasters which have been named as CT2006r1 and CT2006r2.

For thermogravimetric analysis (TG-DTG), the samples were dried at room temperature (in desiccator with silica gel blue) for at least 48 h. The TG-DTG curves were obtained using a thermobalance from TA instruments (SDT 2960) with temperature and weight precision of 0.1 °C and 0.1 μg, respectively. The sample was varied between 5 and 10 mg and weighted on ceramic pans. TG-DTG experiments were performed in flowing dry nitrogen atmosphere (100 ml min^{-1}) at a heating rate of 10 °C min^{-1} within the temperature range 25–1000 °C.

X-ray diffraction (XRD) was performed on a Siemens D5000 powder diffractometer equipped with a primary beam monochromator and CuKα radiation.

Conductivity measurements were carried out with a Crison GLP32 conductometer.

Nitrates were determined using a Cary 300 Bio UV–visible spectrophotometer.

2.2. Sampling and analytical methodology

Fragments from mortars and plasters of churches and buildings of historical interest (X–XIV centuries) from Palma de Mallorca (Balearic Islands, Spain) were analysed. Samples belonging to the Royal Palace of La Almudaina, Santa Catalina de Siena's Church, the Palace of Ca'n Desbrull, the Convents of Santa Clara and San Bonaventura and several Gothic style mansions were studied. From 19 selected samples, nine presented polychromed wall decoration. Table 1 gives source, data and colour of the samples and several studied fragments can be seen in Fig. 1.

The basic methodology included the following steps:

(a) the first corresponds to the visual observation of the samples with the aid of a stereoscopic microscope followed by the analysis by means of scanning electron microscope, equipped with an EDS X-ray spectrometer (SEM–EDS).
(b) Chemical characterisation of the main molecular components by means of Fourier transform infrared spectroscopy (FTIR).
(c) XRD spectra in order to identify the crystalline structure of the mortar components.
(d) Thermogravimetric (TG-DTA) analysis for the quantitative determination of calcium carbonate and dihydrate calcium sulphate.

Furthermore, treatment with 2 M hydrochloric acid was carried out in order to determine the insoluble residue. Thus, 100 ml of hydrochloric acid were added to 1 g of sample and the mixture was stirred mechanically for 30 min. If the mortar happened to be rich in gypsum, the methodology employed was slightly different: hydrochloric acid added to the sample had been heated previously and the mixture was stirred every 5 min for 30 min.

On the other hand, soluble salts were extracted and conductivity measured according to the 13/83 NORMAL. The determination of nitrate in the aqueous extract was carried out by means of ultraviolet spectroscopy [12] should any presence of nitrates be suspected following FTIR or XRD analysis or finding high conductivity values.

3. Experimental results and discussion

Naked eye or magnifying glass macroscopic examination of the tested samples generally revealed high aggregate/matrix cohesion. The widths of the plaster coverings were measured and the results are shown in Table 1.

The morphology and particle size were examined on secondary electron images by SEM. Results of mortar samples