



# International Journal of Architectural Heritage

## Conservation, Analysis, and Restoration

ISSN: (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/uarc20>

## Physicochemical Characterization of Historical Coating Mortars – Case Studies in South Brazil

Fernanda Lamego Guerra , Caroline Giordani , Lucas Volpatto , Jardel Pereira Gonçalves , Mário Mendonça de Oliveira , Angela Borges Masuero & Denise Carpena Coitinho Dal Molin

To cite this article: Fernanda Lamego Guerra , Caroline Giordani , Lucas Volpatto , Jardel Pereira Gonçalves , Mário Mendonça de Oliveira , Angela Borges Masuero & Denise Carpena Coitinho Dal Molin (2020): Physicochemical Characterization of Historical Coating Mortars – Case Studies in South Brazil, International Journal of Architectural Heritage, DOI: [10.1080/15583058.2020.1768320](https://doi.org/10.1080/15583058.2020.1768320)

To link to this article: <https://doi.org/10.1080/15583058.2020.1768320>



Published online: 06 Jun 2020.



Submit your article to this journal [↗](#)



Article views: 47



View related articles [↗](#)



View Crossmark data [↗](#)



## Physicochemical Characterization of Historical Coating Mortars – Case Studies in South Brazil

Fernanda Lamego Guerra<sup>a</sup>, Caroline Giordani<sup>a</sup>, Lucas Volpato<sup>b</sup>, Jardel Pereira Gonçalves<sup>c</sup>,  
Mário Mendonça de Oliveira<sup>d</sup>, Angela Borges Masuero<sup>a</sup>, and Denise Carpena Coitinho Dal Molin<sup>a</sup>

<sup>a</sup>Núcleo Orientado para a Inovação da Edificação (NORIE), Programa de Pós-Graduação em Engenharia Civil: Construção e Infraestrutura (PPGCI), Escola de Engenharia (EE), Universidade Federal do Rio Grande do Sul (UFRGS), Porto Alegre, Brazil; <sup>b</sup>Studio 1 Arquitetura, Architecture Office, Porto Alegre, Brazil; <sup>c</sup>Departamento de Construção e Estruturas, Programa de Pós-Graduação em Engenharia Civil, Escola Politécnica, Universidade Federal da Bahia (UFBA), Salvador, Brazil; <sup>d</sup>Núcleo de Tecnologia da Preservação e da Conservação (NTPR), Programa de Pós-Graduação em Arquitetura e Urbanismo, Universidade Federal da Bahia (UFBA), Salvador, Brazil

### ABSTRACT

The intervention process in historical buildings involves the application of a scientific methodology for the materials characterization. In Porto Alegre — RS, Brazil, several buildings with patrimonial value from the nineteenth and early twentieth centuries were preserved. This study presents the physicochemical analysis of mortar coating samples obtained from two buildings, the commercial and residential building “Frasca House” (1911) and the Metropolitan Curia of Porto Alegre (1888). The visual investigation and aspects of the color and morphology of the samples were determined with a stereoscopic microscope. Chemical analyses provided information on the binder:aggregate proportion and qualitative soluble salts, correlated with deterioration caused by efflorescence. Microstructural analysis allowed to determine the nature of the binders, aggregates and fine particulates. It is expected to contribute, in restoration interventions, to the choice and quantity of materials compatible with the original evaluated here, preserving it and, thus, extending the service life of the building.

### ARTICLE HISTORY

Received 18 November 2019  
Accepted 8 May 2020

### KEYWORDS

Characterization; Frasca house; historical building; Metropolitan Curia; mortar coating

## 1. Introduction

The study of historical buildings, their characterization and registration are recognized as of major relevance, both in terms of the materials composition and original construction techniques description, as a subsidy to intervention practices. These historical materials support important values; hence efficient techniques must be applied to the matter for its conservation and registration. As Brandi (2005) affirms, to reach the practical restoration, it is necessary the scientific knowledge of the matter in its physical constitution. According to Lezzerini et al. (2014), old mortars are part of a complex and often non-homogeneous system. In this way, the study requires an interdisciplinary approach, being able to use different analyses, providing important information about the materials characterization. Based on Apostolopoulou et al. (2017), the process of historical materials characterization, to record and subsidize future interventions, should be considered as the guiding principle for the decisions to be made. The legislation allows a limited number of samples that can be extracted, therefore often results in

statistically scarce data. Thus, since the information comes from the analyses, they are not interpreted as absolute results for the selection of materials, but are still used in the execution of restoration projects.

Considering this context and recognizing the Brazilian assets, Porto Alegre, capital of the *Rio Grande do Sul* state, founded on March, 26<sup>th</sup> 1772 and recognized as a city in 1821, presents several historical remnants with preservation interest.

Among these, two are in the present research. The first corresponds to the so-called “Frasca House”, built in 1911 (30°01'45.36”S, 51°13'01.69”W). The building is included in the Inventory list of EPAHC (2013). In this instance of preservation, the exterior of the building cannot be changed, and all the original characteristics of its façades and roofs must be maintained.

The second edifice is the Metropolitan Curia of Porto Alegre, built in 1888 (30°02'03.96”S; 51°13'47.52”W), next to the Metropolitan Cathedral. The building was listed on March, 31<sup>st</sup> 2009 (Municipal Landmark number 68, registered on page 16 of “*Livro do Tombo*” (EPAHC 1992)), recognized as one of the

main remnants of the historical city center. This edifice is included in the historical site of the Matriz Square, which has National landmark (*Tombamento Federal — Processo 1.468-T-2.000*, inscribed in the *Livro Histórico*, in position 466, volume 2, page 72–75 of 04/24/2003 (IPHAN 2013)).

Many of these buildings, although under protection, present several pathological manifestations that tend to aggravate over time. The alterations that have occurred in external factors, such as weather, vehicle traffic, air pollution, or even the change in the use of these buildings, without planning or adaptation to these new requests, tend to aggravate the problems. Furthermore, interventions and modifications, including the introduction of new materials, without prior analysis regarding the compatibility between them and their behavior related to the different requests, contribute to the acceleration of many degradation processes. From the scientific point of view, there is disagreement in the definition of the parameter that determines the compatibility between the new and the historical ones. However, the aesthetic, chemical, physical, and mechanical parameters are the main aspects to be considered (Apostolopoulou et al. 2017; Papayianni, Pachtá, and Stefanidou 2013; Schueremans et al. 2011; Silva, Ferreira Pinto, and Gomes 2015). To determine the original mortar characteristics, samples were extracted

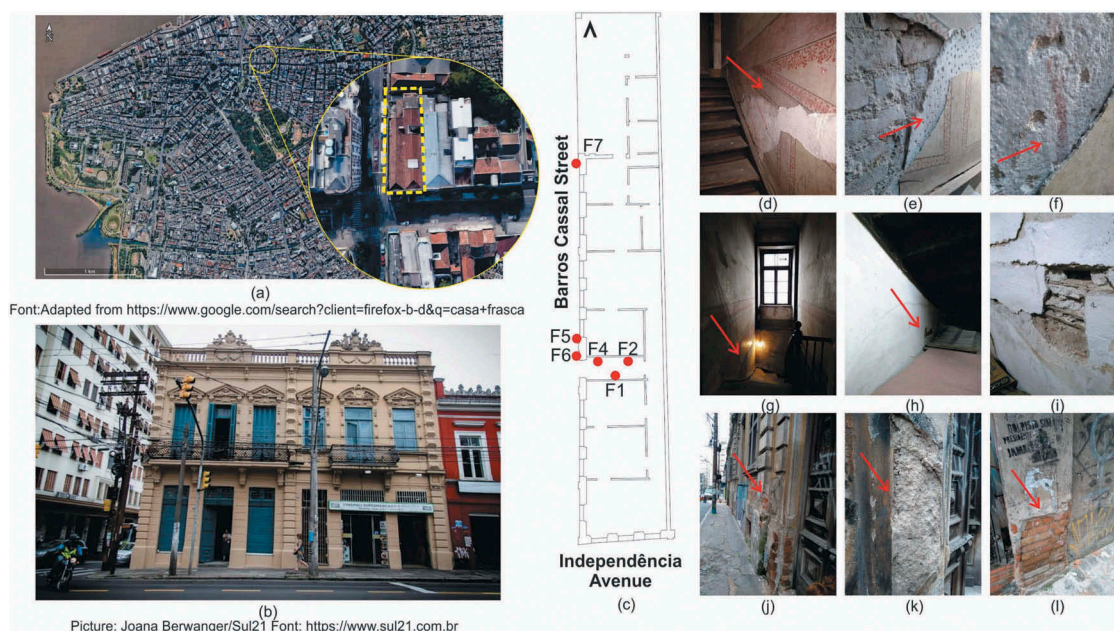
from both historic buildings. Technical analysis, such as visual analysis and stratigraphy of rendering; binder: aggregate proportion, granulometric distribution of aggregates; fines color; and analytical techniques, such as X-Ray diffraction (XRD) and X-Ray fluorescence (XRF), were done to determinate the specific type and properties of the binder used. Besides that, degradation was evaluated through qualitative and semi-quantitative salt soluble characterization.

## 2. Materials and methods

The historical buildings selected, as well as the methodology adopted for the present research, are described below. Mortar coating samples were collected in the two buildings at pre-established points, aiming to characterize the composition of these materials and to identify the presence of soluble salts.

### 2.1. Frasca house

According to a survey carried out by Studio 1 Architecture, established in Porto Alegre, which was responsible for the intervention works in this building, the “Frasca House” (Figure 1a,b) belonged to a family of Italian immigrants who settled in Porto Alegre in the year of 1890. In 1906, they presented in the town



**Figure 1.** Frasca House: (a) localization in Porto Alegre, Brazil; (b) façade of Independência Avenue; (c) floor plan of Frasca House and location of sampling points; (d) internal surface overview; (e) detail of the masonry substrate, mortar undercoat and posterior coating type *stucco lustro*; (f) detail of the mortar undercoat with possible mural painting; (g) sample collection site F1, inside the building, second floor; (h) sample collection site F2, inside the building, first floor; (i) sample collection site F4, inside the building, first floor; (j) sample collection site F5, west façade, first floor; (k) sample collection site F6 west façade, first floor; (l) sample collection site F7, west façade, first floor.

hall the project for the construction of the “Frasca’s Mansion” authored by the builder Germano Pedro Plentz. In 1908, there was already recorded, in the Book of the Municipal Finance Department (*Livro da Secretaria da Fazenda Municipal*), of commercial activities carried out in the mansion. Nevertheless, the date of the building conclusion is 1911. The construction, formed of masonry with massive bricks, mortar coating, and roof with ceramic tile, has an eclectic style, main façades with symmetrical elements and ornaments on the openings and the platband. In 1929, the building undergoes a first intervention, with the extension of the terrace and construction of annexes with bathrooms. From 1934, the building was occupied for several uses: the ground floor for commercial activities and the second floor for residential and cultural occupation. In 2010, the Public Ministry opens an inquiry requesting the restoration of the two buildings façades (Fleck 2018). Restoration projects started in 2012, and the implementation of the intervention at Frasca’s House begins in 2014 and was completed in 2015. The building was recently restored, and the work was concluded in January of 2019.

### 2.1.1. Sample collection from Frasca house

Samples were taken from 7 points in the building, 4 from the interior coating and 3 from the west façade, on Barros Cassal Street (Figure 1c).

Figure 1d-i shows the extracted samples location inside and on the façade of the building. Sample F1, from the interior of the building, and samples F5, F6 and F7, from the façade, were obtained from walls consisting of masonry. Samples F2 and F4, of the interior building, correspond to a partition, built in the technique called rammed earth. This technique corresponds to a wood weft structure filled with clay mortar and faces coated with lime and sand mortar.

The internal samples were collected in the vertical circulation area, next to the lateral access door to Barros Cassal Street (Figure 1d-i). In this environment, it was observed the disintegration of several coating layers, allowing the obtaining of samples where intervention would already be necessary for recovery. Several regions presented superficial alteration due to the presence of dark spotting, with probable biological growth, besides indication of the presence of soluble salts, evidenced in the desegregation and detachment of coating parts. From the history of the building and the characteristics verified in the place, it was possible to be inferred that the materials present in this environment were from the building construction time or of some intervention carried out in a later period, however, probably still

in the early twentieth century. One of the points of the surface selected for extraction corresponded to sample F1 (Figure 1g), on the second floor. At this point, it was identified that, prior to the final finishing layer, there was a wall paint in different shades (evidenced in the Figure 1e), probably the original layer. At some point in the history of the house, this coating was hammered and plaster of fine thickness (~5 mm) was applied to it with a *stucco lustro* finish, a technique that imitates stone surfaces such as marble (Figure 1f). It is possible to suppose that this finish was accomplished in order to, beyond the aesthetic effect, minimize a possible problem related to humidity in the ground floor and the previous layer (original), quite porous, would allow the percolation of the moisture to the surface.

Table 1 shows the description of the extracted samples. According to the total mass obtained, the main tests were selected for physicochemical characterization of the coatings, as well as the presence or absence of soluble salts.

The nomenclature adopted for the coating layers studied was carried out based on Sandin (1995): undercoat corresponds to the layer that promotes the surface leveling, serving as regularization for the final finish layer; the final coat is the final finish layer; and *stucco lustro*, according, Guirdzhiiska, Zlateva, and Glavcheva (2017) it is a technique of creating a polished wall painted surfaces in combination with organic coatings.

**Table 1.** Description of coating samples obtained from Frasca House (F).

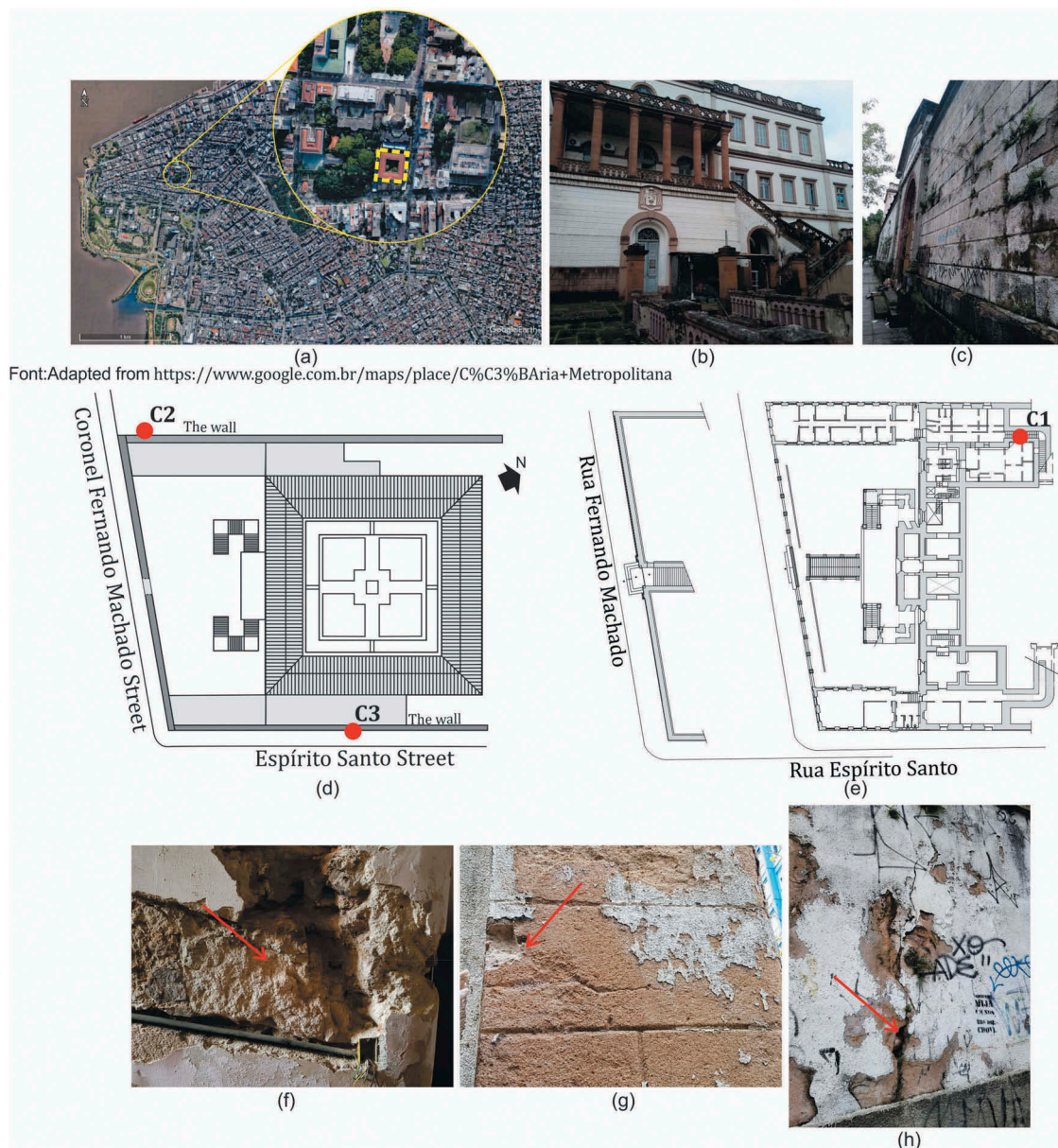
Sample	Description	Wet mass (g)		Tests
F1.1	Undercoat	80		BAP; GRAN; SALTS; XRD; XRF
F1.2	Final coat ( <i>stucco lustro</i> )	42		SALTS (sulphates verification); XRD; XRF
F1.3	Undercoat (2x)	35.94	25.04	ABS
F1.4	Undercoat/final coat/paint interface	-		POL
F2.1	Undercoat	62		BAP; GRAN; SALTS
F2.2	Final coat	53.72		BAP; GRAN; SALTS
F2.3	Undercoat (2x)	66.60	67.79	ABS
F4.1	Undercoat	63.79		BAP; GRAN; SALTS
F4.2	Undercoat (2x)	126.18	37.50	ABS
F4.3	Undercoat/final coat/paint interface	-		POL
F5	Undercoat/final coat	46.95		BAP; GRAN; SALTS
F6.1	Undercoat/final coat	53.2		BAP; GRAN; SALTS; XRD; XRF
F6.2	Undercoat/final coat (2x)	46.52	28.56	ABS
F7.1	Undercoat/final coat	47.05		BAP; GRAN; SALTS
F7.2	Undercoat/final coat (2x)	31.75	8.72	ABS

\*BAP: Binder:aggregate proportion; GRAN: Granulometry of aggregates; ABS: Total absorption; SALTS: Analysis of soluble salts; POL: Polished section; XRD: X-ray diffraction; XRF: X-ray fluorescence

## 2.2. Metropolitan Curia

The place where today is the building of the Metropolitan Curia (Figure 2a-c) was, until the year 1850, occupied by a cemetery of the city. Between 1865 and 1867, the French architect Jules Vilain started the ground preparation for the seminar construction. In 1867, the German architect Johann Grünewald assumed the construction and complete the roof of the edifice in 1869. Although still incomplete, the building was inaugurated in 1879. The edification was finally completed in 1888. In 1970, the building went through

several renovations, including exterior painting and replacement of the ceramic roof with a metallic zinc roof. In 2009, a restoration project is recommended. In 2010, restoration works begin, and the ceramic tiles were replaced again in the roof, rescuing the original appearance of the building. In 2012, a work of archeology is realized, with the recollection from the old cemetery vestiges. In the same year, the restoration works were interrupted. A new restoration project is requested in 2016, aiming at the installation of a museum of sacred arts and cultural center, being



**Figure 2.** Metropolitan Curia of Porto Alegre: (a) localization in Porto Alegre, Brazil; (b) main façade (south); (c) exterior wall (south); (d) schematic cover plan for location of sampling points C2 and C3; (e) basement plan for location of sample C1; (f) sample collection site C1, inside the building; (g) west façade of the wall, where sample C2 was collected; (h) east façade of the wall, sample collection site C3.

maintained the archiepiscopal residence and transferred the administrative activities to the fourth district of the capital.

The surroundings of the Metropolitan Curia also changed over time. To the east and south occurred the verticalization of the buildings, mainly of residential character, but with some commercial areas. To the north and west, the surroundings edifices remained, whereas they are also of patrimonial interest, such as the Metropolitan Cathedral of Porto Alegre, the Piratini Palace (state government headquarters) and the historical buildings of Paula Soares School.

The Curia edifice is characterized as a neoclassical style, typical of the nineteenth century. It has a modulated composition of the façades, with symmetrical elements bilaterally and a triangular fronton arrangement on the south façade. The main access is through a staircase. The stair guard is composed with a rich ornate balustrade sculpted in sandstone, the same material of the columns. The sandstone, abundant sedimentary rock in the Rio Grande do Sul, has frequent application in civil construction. Although in the past its use was limited, mainly to the construction of foundations and masonry bricks, its application in the Metropolitan Curia of Porto Alegre stands out as a beautiful ornamental work, sculpted by a master of the period (Di Benedetti 2006).

The building has a basement, ground floor, and a second floor, which is interconnected with the Parish House through a passage. A wall surrounds it externally, with a central access gate, where, through a staircase, it is possible to access the ground floor, considering the unevenness in the ground.

### 2.2.1. Sample collection from the metropolitan Curia

From the Metropolitan Curia edifice, three main places were selected to obtain the samples (Figure 2d,e). Inside the building, it was possible to extract the coating mortar in a single environment, on the surface of a brick and stone mixed masonry, Sample C1

(Figure 2f). In this surface, an earlier intervention was made to pass through an electric duct, making possible the collection of material for analysis. This location corresponds to a connecting place between the internal courtyard at ground level and the basement. The second sampling site corresponded to the external wall, one of the points on the west face, Sample C2 (Figure 2g) and the other, in the east orientation, Sample C3 (Figure 2h). This wall works as a restraint element, considering that the Curia edifice is built on an unevenness. It is believed that it has not changed over time, in this way, it is seeking out the characterization of the composition of the materials, which are considered original.

In the interior of the building, near the place where it was possible to extract the sample, in the basement access environment, there was a white powdery on the coating, corresponding to saline deposits. In general, salt degradation is due to the pressures generated by precipitation of these salts in the pores of mortars (Sousa et al. 2011). The type of degradation caused by soluble salts depends on where the solubilization and crystallization reaction occurs; when it occurs on the surface (efflorescence) results in a change in an aesthetic level, mainly. When it occurs inside the pores of the material, it is characterized as cryptofflorescence (Groot et al. 2004; Sousa et al. 2011). This phenomenon could be evidenced by the superficial disintegration of the mortar coating analyzed in this work (Figure 3). In addition to the presence of soluble salts, there was intense biological proliferation, not characterized in this paper.

The Table 2 shows the description of the samples obtained in the Metropolitan Curia, as well as the applicable tests.

### 2.3. Materials characterization

From the material collected in the two buildings, the transport was made to the laboratory, where the

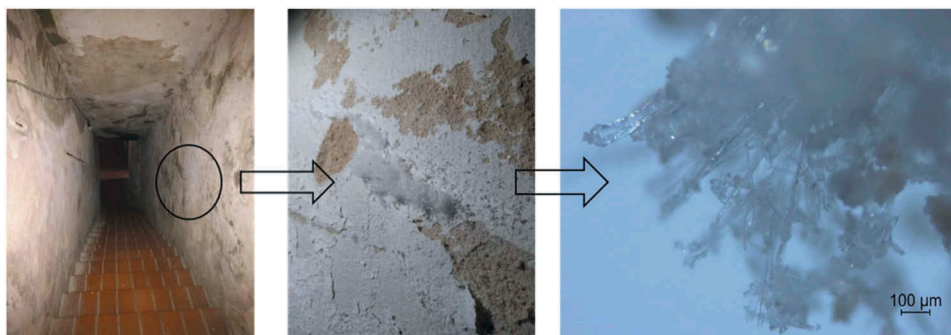


Figure 3. Efflorescence, cryptofflorescence, and image of saline crystals in stereoscopic microscope.

**Table 2.** Description of the mortar samples obtained from the Metropolitan Curia edifice (C).

Sample	Description	Wet mass (g)		Tests
C1.1	Undercoat/final coat	53.6		BAP; GRAN; SALTS; XRD; XRF
C1.2	Undercoat/final coat	46.79	109.70	ABS
C2.1	Undercoat/final coat	45.7		BAP; GRAN; SALTS; XRD; XRF
C2.2	Undercoat/final coat	34.35	60.01	ABS
C3.1	Undercoat	39.74		BAP; GRAN; SALTS
C3.2	Final coat	40.68		BAP; GRAN; SALTS
C3.3	Undercoat (2x)	46.08	50.10	ABS

\*BAP: Binder:aggregate proportion; GRAN: Granulometry of aggregates; ABS: Total absorption; SALTS: Analysis of soluble salts; XRD: X-ray diffraction; XRF: X-ray fluorescence

samples were prepared to carry out the analyses described below. First, the intact samples were photographed and evaluated visually with the use of a stereoscope. The tests were carried out using the analysis methodology used at NTPR/UFBA, modified from Teutonico (1988), developed and adopted in ICCROM.

### 2.3.1. Visual analysis and stratigraphy of rendering

In macroscopic scale, samples were photographed as they were taken from the buildings, for general visual analysis.

Extending this evaluation, the low power observation with stereomicroscope (magnifications 5x to 100x) is indicated by Weber, Köberle, and Pintér (2013) for the initial identification of the mortar microstructural features, as binder and aggregate, for 3D or plane samples. With this equipment it is possible to visually analyze the existing phases (binder, aggregates, pores), binders characteristics (colors and probable origin), aggregate grains (colors, shapes, sizes, minerals) and general aspects (thickness, adhesion and voids between materials, and contaminants), as verified in a similar way by Dalto, Ribeiro, and de Moura (2018) e Lezzerini et al. (2014). For stratigraphy of rendering, fragments of samples composed of different coatings were obtained from Frasca House. In these, a cross-section was made in order to exhibit the coating layers (undercoat, final coat, plaster and painting). Three specimens were individually arranged in silicone molds, covered by polyester resin, sanded until the mortar was exposed and, subsequently, polished for a good visualization of the surface in the stereoscopic microscope Zeiss Stemi 508 doc.

### 2.3.2. Binder:aggregate proportion and fines colorimetry

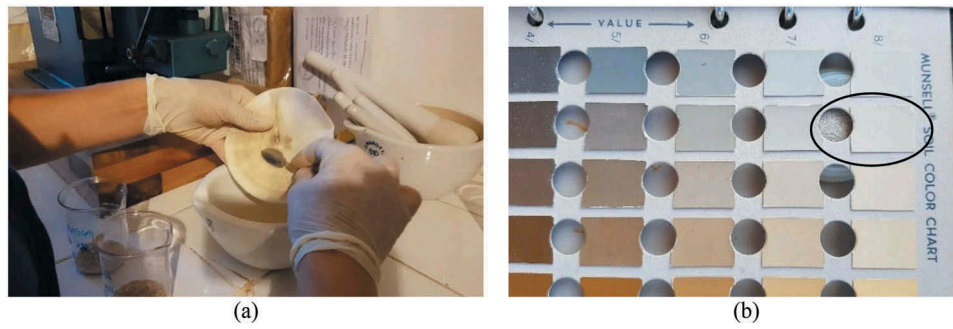
The objective of the test was to determine the proportion of the mortar components analyzed: the

binder (probably  $\text{Ca}(\text{OH})_2$  and/or  $\text{Mg}(\text{OH})_2$ , transformed into carbonates in the hardened state), fines (clay and/or silt) and the aggregate (sand). A total of 11 samples were analyzed between the two buildings. This method of analysis involves the dissolution of the binder in an acidic solution, as described in several types of research (Hauková, Frankeová, and Slízková 2018; Kurugöl and Güleç 2012; Middendorf et al. 2005; Schueremans et al. 2011).

Samples selected to determine the binder:aggregate ratio granulometric distribution of the sand and soluble salts analysis were previously disaggregated with the aid of a ceramic mortar and pestle. In the samples, previously dried and measured mass, P. A. hydrochloric acid solution (HCl 37%) in deionized water (1:4 ratio) was added. After a filtering process, the beakers with the aggregate, and filter papers with the fines were dried and subsequent weighed, allowing to know the proportioning between binder, aggregates, and fines of each sample. For the final determination of the mass rate, the mass of fines was added to the mass of the binders, recognizing that these also present this property in the composition of the mortar.

After drying the fines retained in the filters, it was possible to determine its coloration, technique that assists in the selection of materials of similar aesthetic characteristics in an intervention process. The material was removed from the filters (Figure 4a) disintegrated in a ceramic mortar, compacted in a cylindrical container (diameter of 1 cm) and compared the surface to a soil color catalog (Figure 4b).

The atlas used in this study consisted of the Munsell Soil Color Charts (1994). This catalog subsists of a North American system, which allows the specific identification of soil color, thus being ideal for identifying colors of lime-based mortars, such as those analyzed in this paper. The atlas has nine cards with the organization of 322 different standard colors. The colors arranged in each card have a constant hue, identified by a symbol to the right at the top of each page. In the vertical direction, the darkest colors are located at the bottom of the page, going to the lightest at the top, thus determining their luminosity. In the horizontal direction, from left to right, saturation within each hue is determined (Bezerra 2010). The color is identified through visually comparing the sample with the approximate coloration verified in the catalog (Figure 4b). According to the notification of this atlas, the code 10 YR6/3, for example, indicates the section “10” of the catalog, hue between yellow and red (YR), luminosity index “6” and saturation “3”, a color identified for this code is “Pale Brown”.



**Figure 4.** Identification of the fines color: (a) removal of fines from filter paper for disintegration; (b) identification of the color code comparing the fines with the catalog of the Munsell Chart.

### 2.3.3. Granulometric distribution of the aggregate

The remaining aggregates from the proportioning analysis were completely dried, and the duplicates of each sample were united in a single one. It was performed the granulometric distribution, to determine the grain size distribution, the fineness modulus and the nominal maximum aggregate size. The methodology was adapted from *Associação Brasileira de Normas Técnicas* NBR NM 248 (ABNT, 2003) using the sieves with opening 1.18 mm, 0.5 mm, 0.25 mm, 0.15 mm and 0.075 mm. The fineness module was made considering the sum of the accumulated retained percentages of all sieves, except 0.075 mm. The nominal maximum aggregate size corresponded to the sieve in which the accumulated retained percentage was less than 5%.

### 2.3.4. Total water absorption

The test allowed to identify the percentage of open porosity of the samples, through the total absorption of water, from integers samples fragments. Similar methodology was described in Teutonico (1988). Five duplicate samples of Frasca House and three duplicate samples of the Metropolitan Curia were analyzed. The samples were dried at 75°C for 24 hours, cooled in a desiccator for 20 minutes, weighed and subsequently immersed in a water-filled vessel with a vacuum closure. The vessel was connected to a high vacuum pump for 60 min, which allowed the withdrawal of the air from inside the samples and filling the pores with water. The samples remained submerged in the container until 24 h. After this time, the samples were removed, lightly wiped and weighed on a precision scale. By Equation 1, the percentage of absorption was determined.

$$\text{absorption}(\%) = \frac{\text{wet mass} - \text{dry mass}}{\text{dry mass}} \times 100 \quad (1)$$

### 2.3.5. X-ray diffraction and X-ray fluorescence

According to Yildizlar, Sayin, and Akcay (2019), for the characterization of historical materials, taking into

account the principles of compatibility in restoration interventions, it is necessary, in addition to identifying the nature of the binder and aggregates, the determination of the mortar's formulation. To perform the mineralogic analysis by X-Ray Diffraction (XRD) and X-Ray Fluorescence (XRF), the mortars samples were carefully disaggregated with mortar and pestle, allowing to segregate the aggregates from the paste, but avoiding the grinding of sand grains. The isolated paste was sieved through 53  $\mu\text{m}$  mesh, collected in eppendorfs and sent for analysis at LACER/UFRGS. In this way, it would be possible to characterize the binder present in the mortar.

The XRF analyses were performed in a Shimadzu XRF1800 spectrometer, standardless. This equipment directly quantifies the percentage of oxides present in the sample, which facilitate the search for the compounds in XRD analysis.

The XRD analyses were performed on a Phillips X'Pert MDP diffractometer (Cu  $K\alpha$  radiation) with standard interval angle  $2\theta$  5–75°, step size of 0.02° in 2s,  $\frac{1}{2}^\circ$  slits, and 20-mm window. In this test, the intensities of the X-Ray beams diffracted in different directions (angles) are obtained, resulting in a graph with several peaks, which are compared with the compounds patterns in the Powder Diffraction File (PDF) database, through the software X'Pert Highscore Plus (PANalytical 2012). When the greatest intensity peaks of some compounds in the database match the diffractogram of the analyzed sample, this material is considered to be present in the binder. Guerra et al. (2019) and Giordani and Masuero (2019) carried out similar test with the same equipment. Guerra et al. (2019) research also evaluated similar materials, historic buildings mortars, from the same region of this study.

### 2.3.6. Semi-quantitative analysis of soluble salts

After finishing the characterization of coating mortars, a semi-quantitative analysis method was applied to identify the soluble salts present in 12 samples of the two buildings, visibly altered by the occurrence of

efflorescence, or even apparently intact but possibly contaminated by salts. This methodology was applied according to Teutonico (1988) and similarly in Guerra et al. (2016). The test consisted of extract soluble salts from the samples with deionized water and, into this filtrate, apply the reagents: 1% diphenylamine in  $\text{H}_2\text{SO}_4$  to identify nitrate by blue color;  $\text{HNO}_3$  and  $\text{AgNO}_3$  to verify chlorides, if occurred turbidity;  $\text{HCl}$  and 5%  $\text{BaCl}$  in deionized water to identify sulfate, also by the turbidity.

In addition to the observation of the presence or absence of salts, a comparative semi-quantitative analysis was also carried out between the samples, indicating the intensity of the coloring or turbidity observed if there was the presence of the soluble salt analysed.

### 3. Results and discussion

It was possible to characterize the coating samples with the proposed tests. These are considered indicated and applied for description and registration of historical materials, to subsidy the restoration interventions.

#### 3.1. Visual analysis and stratigraphy of rendering

The image of the samples, as they have been collected in the Frasca House and Curia is presented in Figure 5.

The internal samples of Frasca House (Figure 5a-e) present distinct paintings and treatments among the collected sites. The external samples (Figure 5f-h) show high disaggregation and have darkened surface coloration, probably due to the staining present on the façade.

For Curia, it is observed light coloring in the internal sample C1 (Figure 5i), the similarity between the C2 and C3 undercoat samples (Figure 5j,k), and the smaller thickness of the C3 final coat (Figure 5l).

Stratigraphy images by stereoscope of three samples were made. F1.4 was divided into two samples: the most external, F1.4.1, with undercoat, final coat *stucco lustro* and painting (Figure 6a,b); and the one below this, more internal, F1.4.2, with undercoat, plaster layer and painting (Figure 6c). The last sample, F4.3, had undercoat, plaster layer and painting (Figure 6d-f).

Figure 6a,c,d indicate the painting layer, pigmented with white, grey and orange, respectively. The final coat *stucco lustro* (Figure 6a,b), which had a predominantly white binder, reveals a material of low porosity and with the presence of few fine quartz aggregates, in comparison to the other layers. The plaster layer of

samples F1.4.2 and F4.3 (Figure 6c,f) also have similar features to *stucco lustro*, but a thinner layer, and, although both binders are white, it is not possible to affirm their origin only by visual analysis.

The images show a good extent of adherence between undercoat and *stucco lustro* (Figure 6b), and between undercoat and plaster layer (Figure 6c,e,f). The undercoat aggregates are fully involved by the final layer.

The color and morphology of the undercoats are very similar (Figure 6c,f). They present white binders, indicating lime origin; aggregates of several sizes and colors, angular when larger but mostly rounded, probable of quartz origin with some impurities; and some pores between the phases.

#### 3.2. Binder:aggregate and colorimetric results

The results found for the binder:aggregate proportion of Frasca House and Metropolitan Curia are shown in Table 3. The samples F1, F2, and F4 correspond to the coating inside the Frasca building, and F5, F6 e F7, to the external. The Curia sample C1 corresponds to the interior coating, and the samples C2 and C3, to the wall.

The proportion obtained for the analyzed samples of Frasca House was between 1:1.96 and 1:5.89, by mass, with a higher frequency between 1:3.0 and 1:4.0. One of the exceptions, the proportion 1:1.96 from sample F6.1, may indicate that the detail on the façade was made with a richer mortar. In another case, the sample F7.1 presented a lower binder content (1:5.35), compared to the other samples of this house, which may be justified by its extraction in the soil near the floor and outside the building, where there was superficial disintegration, and there may have been loss of binder.

Samples from Curia varied from 1:3.43 and 1:6.48, by mass. Sample C1.1 (Curia) also presented a proportion with lower binder content (1:6.48). Like sample F7.1 (Frasca), there was a possible change in the material, resulting from deterioration; in the case of Curia, possibly by the presence of soluble salts, observed in loco.

The values verified are consistent with those indicated in the literature. The former authors and constructors indicated proportions 1:1 and 1:2 (Couto,<sup>1</sup> 1631–1641, apud Souza 2013), 1:2 and 1:3 (Vitruvius 1997; Palladio<sup>2</sup> 1570, apud; Souza 2013), 1:3 and 1:4 (Plínio,<sup>3</sup> 77–79 d.C., apud Souza 2013), similar to what was identified in both buildings. Kurugöl and Güleç (2012) found that the binder/aggregate ratios

<sup>1</sup>Couto, M. *Tractado de architectura*. 1631–1641, L. II, cap. IX, p. 37.

<sup>2</sup>Palladio, A. I. *Quattro libri dell'Architettura*. Venezia, Dominico de'Franceschi, 1570, L. I, Cap. V, p. 8.

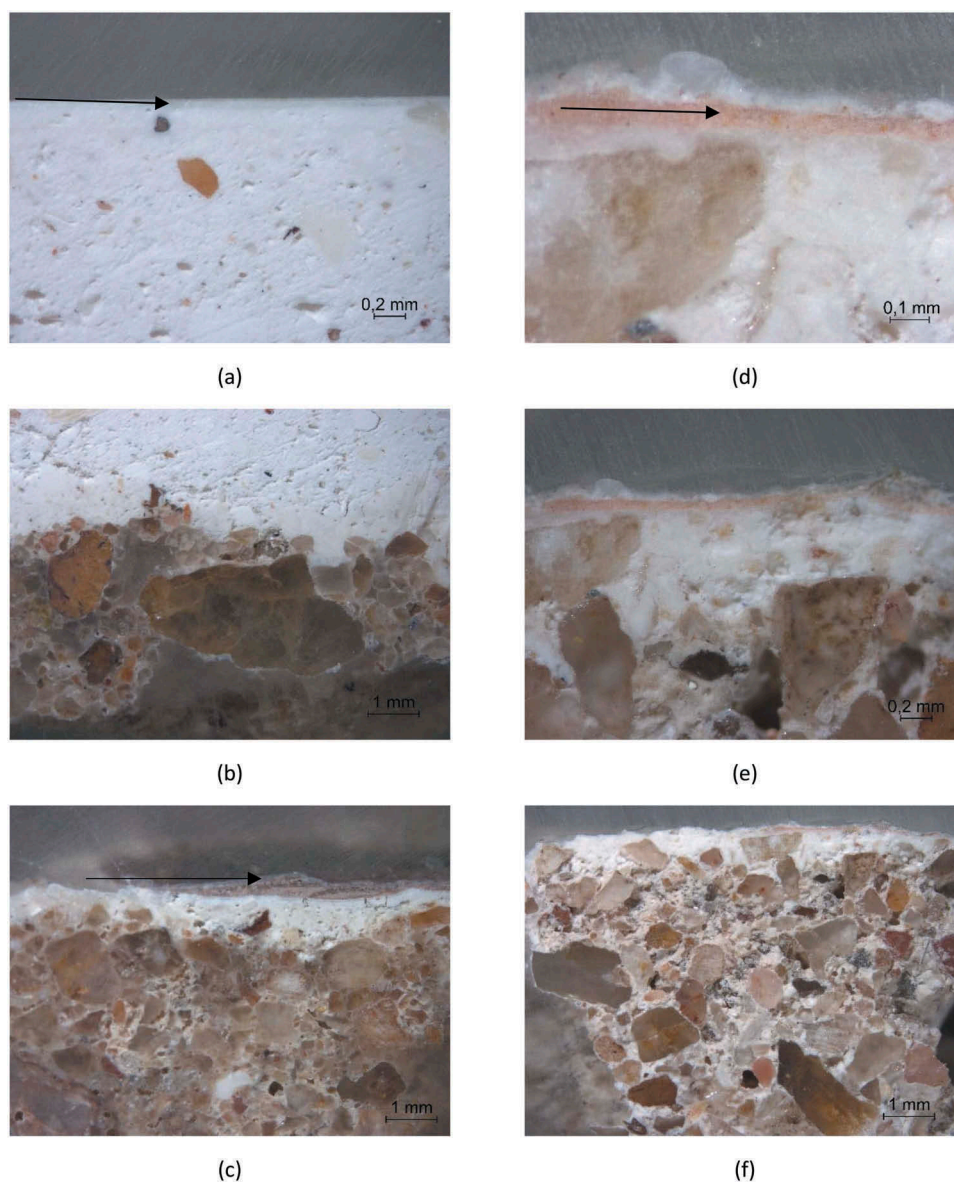
<sup>3</sup>Plínio. *Naturalis Historia*. 77–79 d.C.



**Figure 5.** Images of the samples of: Frasca House (F), internal: (a) F1 — undercoat; (b) F1 — final coat (*stucco lustro*); (c) F2 — final coat; (d) F2 — undercoat; (e) F4; Frasca House (F), external: (f) F5; (g) F6; (h) F7; Metropolitan Curia (C), internal: (i) C1; Metropolitan Curia (C), external: (j) C2; (k) C3 — undercoat; (l) C3 — final coat.

of all mortars analyzed in Yoros Castle (Turkey) varied between 1:2 and 1:3 by weight. In the analysis of interior and exterior coatings of two churches (14th and 18th century), Bochen and Labus (2013)

identified lime and sand composition with a mass ratio ranging from 1:2.0 to 1:4.3, using a similar methodology, with the dissolution of the samples in hydrochloric acid.



**Figure 6.** Cross-sectional images of the coating layers, obtained in stereoscope, from Frasca House: (a) F1.4.1 — final coat *stucco lustro* and painting detail; (b) F1.4.1 — interface between undercoat and final coat *stucco lustro*; (c) F1.4.2 — undercoat, plaster layer and painting; (d) F4.3 — plaster layer and painting detail; (e) F4.3 — interface between undercoat, plaster layer and painting detail; (f) F4.3 — undercoat, plaster layer and painting.

Moropoulou, Bakolas, and Anagnostopoulou (2005) affirm that it is generally seen that the binder/aggregate ratios in mortars of historic buildings vary between 1:1 and 1:4. Roden et al. (2009) analyzed samples obtained at the “Igreja das Dores” in Porto Alegre-BR, a building that began its construction in 1807, and identified binder:aggregate proportions that varied in 1:2, 1:3, 1:4, 1:6 and 1:7, out of a total of 17 samples, being predominant the 1:6 ratio. Guerra et al. (2019) analyzed samples of historical mortar in the same city and of similar composition to that found in the present work, observing values between 1:2 and 1:5.4.

Table 4 shows the results of the colorimetric analysis from the fines of the coating mortar samples of the

Frasca House and Metropolitan Curia and Figure 7 presents the four different colorations observed.

The interior samples of Frasca House presented, in their composition, fines with light brown or grey color, except the sample F2.1 (undercoat), which was light grey, as the three façade samples of this building. The fines obtained from Curia samples exhibit predominantly white coloration, possible indicating pure binder use. The difference in the color of samples allows hypotheses related to the origin of the carbonate rock, presence or absence of impurities, as well as the calcination time to originate the binder used in the mortars of the two buildings. The Metropolitan Curia is older

**Table 3.** Proportion (binder:aggregate) of Frasca House (F) and Metropolitan Curia (C) mortar coating samples.

Sample Repetition	Total dry mass (g)		Binder (%)		Fines (%)		Aggregates (%)		Probable proportion (binder:aggregate)	
	1	2	1	2	1	2	1	2	1	2
F1.1	10.11	10.59	22.00	20.38	2.54	2.29	75.46	77.33	1:4.01	1:3.41
F2.1	10.38	9.77	23.02	22.90	4.00	3.74	72.97	73.35	1:3.47	1:3.55
F2.2	10.25	10.17	23.29	22.87	4.00	3.63	72.71	73.50	1:3.42	1:3.58
F4.1	10.37	10.13	20.73	20.40	2.91	3.24	76.36	76.36	1:4.18	1:4.16
F5	10.10	10.13	19.37	20.45	1.73	2.06	78.89	77.49	1:4.91	1:4.51
F6.1	10.21	10.18	36.15	31.57	3.90	3.60	59.95	64.83	1:1.96	1:2.40
F7.1	10.15	10.18	16.24	17.55	1.87	2.05	81.88	80.40	1:5.89	1:5.35
C1.1	10.36	10.59	17.47	15.91	1.20	1.04	81.33	83.05	1:5.76	1:6.48
C2.1	10.63	10.05	20.09	19.98	2.37	2.11	77.54	77.92	1:4.50	1:4.61
C3.1	10.29	10.20	18.85	18.61	2.08	2.12	79.07	79.27	1:4.93	1:4.99
C3.2	10.24	10.17	23.29	24.20	3.17	3.24	73.55	72.56	1:3.61	1:3.43

**Table 4.** Fines colorimetry from mortar samples of Frasca House (F) and Metropolitan Curia (C).

Sample	HUE	Value/Chroma	Munsell color
F1.1	10 YR	6/3	Pale Brown
F2.1	10 YR	7/2	Light Grey
F2.2	10 YR	6/3	Pale Brown
F4.1	10 YR	6/1	Grey
F5	10 YR	7/1	Light Grey
F6.1	10 YR	7/1	Light Grey
F7.1	10 YR	7/1	Light Grey
C1.1	5 YR	8/1	White
C2.1	10 YR	8/1	White
C3.1	10YR	8/1	White
C3.2	5 YR	8/1	White

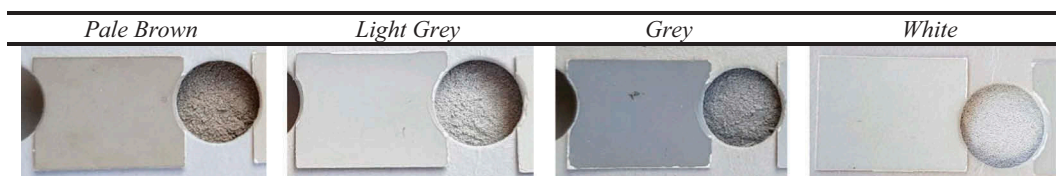
concerning Frasca House, in addition to being considered a more important building because it represents a religious institution when compared to Frasca House, which was a private building. Thus, it is possible to suppose that in the composition of the mortar from Metropolitan Curia, possibly the lime used had a purer origin, with a lower percentage of impurities, which can be correlated to its lighter color. On the other hand, Frasca House's grayish-colored mortar allows us to assume the presence of amount levels of impurity. Moropoulou, Bakolas, and Aggelakopoulou (2001) evaluated the effects of limestone characteristics (microstructure and texture) and calcination temperature on the reactivity of the produced quicklime of two types of mortar, one of light-colored gray limestone with hardly distinguished crystals, and other was a dark gray limestone comprised of indiscriminate, tiny crystals. The limestone with light-colored gray was characterized as high-calcium limestone with low content of impurities.

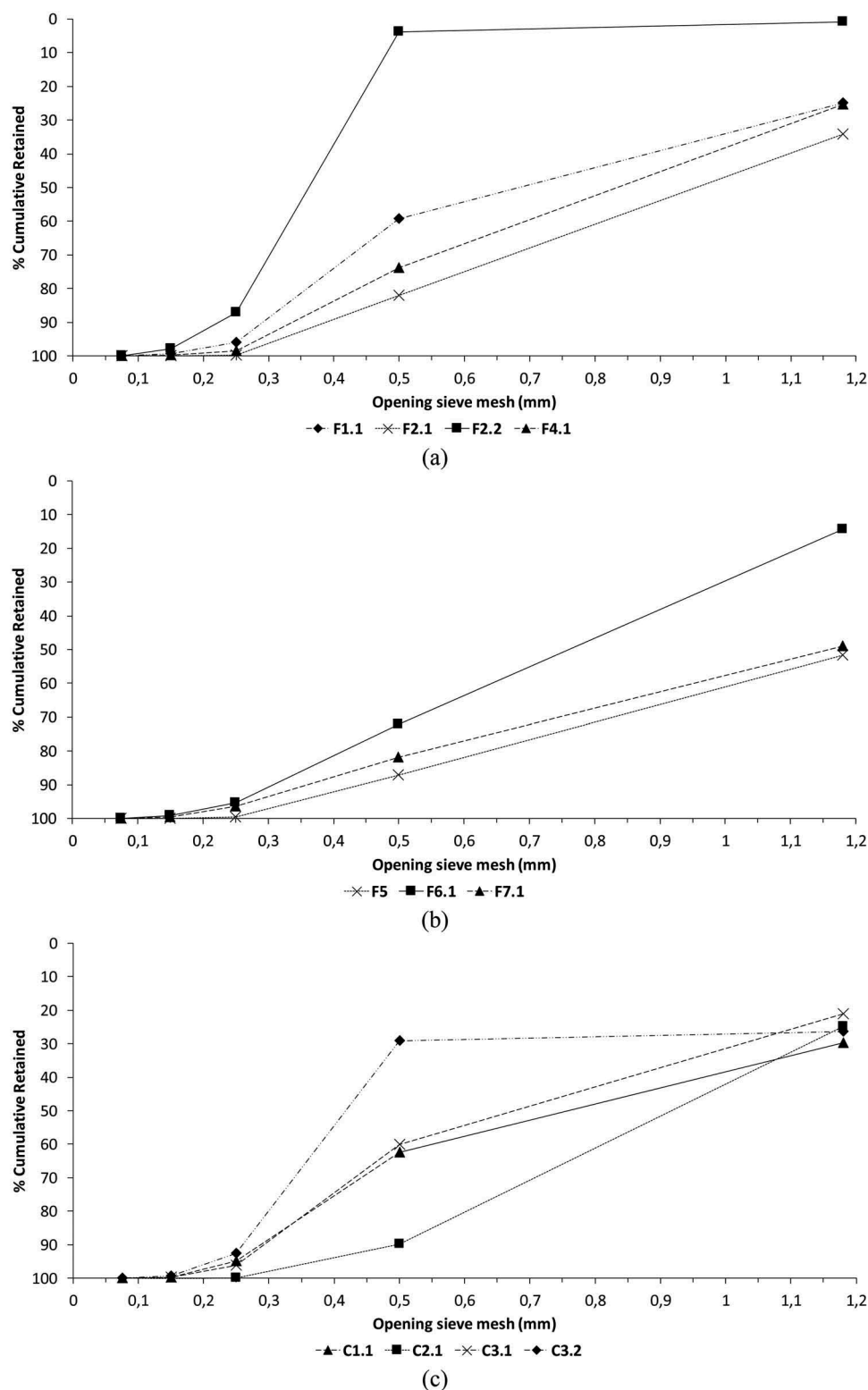
Darker colors, such as pale brown and grey, may also indicate the possible use of ceramics fines or ashes as an addition in the mortar.

### 3.3. Granulometric distribution of the aggregates

The dry aggregates were yellowish and rounded, like to river quartz, which is commonly found and used in the region. Figure 8a,b shows the granulometric distribution of the aggregates from the interior and façade samples of Frasca House, respectively. It is identified that the layer F2.2 exhibited higher fines content, as expected for a final coat, while the undercoat (F1.1, F2.1 and F4.1) presented similar granulometry of the aggregate. Regarding the façade mortars (Figure 8b), the granulometric curves were similar in shape, except for F6.1, which has a higher content of fines than the others, possibly because it's a façade detail. In general, the granulometric distributions of undercoat mortars, both internal and from façade, were similar, assuming their probably execution in the same period, without interventions at the points where the samples were extracted.

Table 5 shows the fineness modulus and nominal maximum size of Casa Frasca samples' aggregates. The lowest value of the fineness modulus (1.90) and nominal maximum dimension (0.50) verified correspond to the final coat F2.2, demonstrating consistency in the values. The other samples, internal and from façade, varied the fineness modulus between 2.79 and 3.38, in a relatively small range, and

**Figure 7.** Fines color obtained from the samples.



**Figure 8.** Granulometric distribution of the aggregate from: (a) internal mortars of Frasca House; (b) façade mortars of Frasca House; (c) Metropolitan Curia.

maintained the maximum dimension of 2.38, considering the sieves used in this work.

According to Recena (2011), conventional rendering systems have the undercoat with coarser aggregates

with thickness ranging between 10 mm and 25 mm, and finishing layer with fine aggregate and thickness not greater than 5 mm. This arrangement allows for greater carbonation of the undercoat, improving the

strength of the material. Groot et al. (2012) explain that, due to its greater thickness, the undercoat should have greater porosity, and the final layer, minor thickness due to its lower porosity.

Figure 8c shows the aggregates granulometric distribution and Table 5 presents the fineness modulus and nominal maximum aggregate dimensions of internal and wall samples from the Metropolitan Curia. It should be noted that samples C1.1 and C2.1 were extracted and analyzed in a single layer, while in sample C3 it was possible to distinguish two layers: undercoat (C3.1) and final coat (C3.2). According to Figure 8c, it can be seen that samples C1.1 (mortar inside the building) and C3.1 (undercoat of the wall) showed very similar granulometric distribution, which allows to suppose that both were executed possibly in the same period. The final coat of sample 3 (C3.2) presented finer grain size, evidenced by both the grain size curve and the fineness modulus (2.48); and high binder percentual (1:3.61/1:3.43), which may protect the C3.1 layer (undercoat). According to Kanan (2008), final mortars for protection have fine aggregate granulometry and high lime content in their composition. Sample C2.1 has similar proportioning binder:aggregate as sample C3.1 (1:4.50/1:4.61 and 1:4.93/1:4.99, respectively), but is more exposed to weathering, since it does not have a final coat. Thus, the particle size distribution showed larger particles of aggregates than C3.1, possibly due to its exposed to worse weather conditions, which may have leached the finer surface particles.

### 3.4. Absorption test results

From the total absorption test, were obtained the percentages indicated in Table 6. For Frasca House, the values obtained ranged from 10.32% to 17.88%.

**Table 5.** Frasca House (F) and Metropolitan Curia (C) aggregates fineness module and nominal maximum size of mortar coating samples.

Frasca House		
Sample	Fineness Modulus	Nominal Maximum Size
F1.1	2.79	2.38
F2.1	3.16	2.38
F2.2	1.90	0.50
F4.1	2.97	2.38
F5	3.38	2.38
F6.1	2.81	2.38
F7.1	3.27	2.38
Metropolitan Curia		
Sample	Fineness Modulus	Nominal Maximum Size
C1.1	2.87	2.38
C2.1	3.15	2.38
C3.1	2.77	2.38
C3.2	2.48	2.38

Analysis from Metropolitan Curia samples showed values between 10.91% and 14.79%. The water absorption can be correlated to the open porosity of the materials, since in the case of sample saturation, the open and intercommunicating pores are filled with water, according to Bertolini (2010).

The samples obtained from the exterior of the Frasca House and Curia had a lower absorption and consequently less open porosity, this aspect may be related to the fact that they were dosed to allow less degradation because they are exposed to weathering and environmental factors. The interior coating of the buildings, in general, may present greater porosity compared to the outer ones, thus allowing the release of moisture that may have infiltrated the masonry, in addition to the fact that they are less susceptible to degrading agents.

### 3.5. XRF and XRD

XRF analysis of the binder of mortar samples is shown in Table 7. The mortars (F1.1 and F6.1 from Frasca House; C1.1 and C2.1 from Curia) presents high CaO content, greater than 50%, and also MgO, from 17.21% to 29.38%. The relation CaO/MgO indicates that it possibly refers to a binder with dolomitic limestone origin. This was expected, once dolomitic limestone is common in the region under study (Rohde et al. 2012). This relationship was found to be higher in external cases (3.15 in Frasca F6.1 and 3.17 in Curia C2.1) than in internal cases (1.79 in Frasca F1.1 and 1.99 in Curia F1.1), that is, the MgO content is lower externally.

SiO<sub>2</sub> levels (6.51% to 12.67%) are probably derived from the residual mortar aggregate. Kurugöl and Güleç (2012) characterized the lime mortars in historic Yoros Castle (Turkey) and observed a chemical binder composition with a high level of CaO (25% to 30%) and SiO<sub>2</sub> (28% to 35%), possibly indicating the pozzolanic content. According to Maravelaki-Kalaitzaki, Bakolas, and Moropoulou (2003), it is documented that pozzolanic mortars have high content ratios for SiO<sub>2</sub> and low content ratios for MgO, what seems not to be the case of the analyzed mortars.

Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> present similar contents between the samples and maybe originated from impurities in the sand and lime, as well as from possible clay additions to the mixture. For all mortars, even small amounts of sodium (Na<sub>2</sub>O) were identified.

Analyzing the sample F1.2, originated from the *stucco lustro* final coating, it is verified the high CaO and SO<sub>3</sub> content, as expected, contributing to the confirmation of the CaSO<sub>4</sub>·2H<sub>2</sub>O (calcium sulfate) plaster. However, the

**Table 6.** Absorption of Frasca House (F) and Metropolitan Curia (C) mortar coating samples.

Frasca House					
Sample	Dry mass (g)	Wet mass (g)	Absorption (%)	Mean absorption (%)	Standard deviation
F1.3.1	30.84	35.94	16.54	16.3	0.4
F1.3.2	21.59	25.04	15.98		
F2.3.1	56.69	66.6	17.48		
F2.3.2	58.25	67.79	16.38	16.9	0.8
F4.2.1	107.04	126.18	17.88		
F4.2.2	32.39	37.5	15.78		
F6.2.1	41.48	46.52	12.15	12.5	0.4
F6.2.2	25.33	28.56	12.75		
F7.2.1	28.78	31.75	10.32		
F7.2.2	7.68	8.72	13.54	11.9	2.3
Metropolitan Curia					
Sample	Dry mass (g)	Wet mass (g)	Absorption (%)	Mean absorption (%)	Standard deviation
C1.2.1	41.67	46.79	12.29	13.0	1.1
C1.2.2	96.39	109.7	13.81		
C2.2.1	30.8	34.25	11.20		
C2.2.2	52.28	60.01	14.79	13.0	2.5
C3.3.1	41.42	46.08	11.25		
C3.3.2	45.17	50.1	10.91		

**Table 7.** XRF analysis of Frasca House (F) and Metropolitan Curia (C) coating samples.

Compounds (%)	Frasca			Curia	
	F1.1	F1.2 stucco lustro	F6.1	C1.1	C2.1
CaO	52.73	43.21	57.32	50.68	54.52
MgO	29.38	20.34	18.14	25.49	17.21
SiO <sub>2</sub>	8.11	0.37	6.51	8.24	12.67
Fe <sub>2</sub> O <sub>3</sub>	4.43	0.44	4.63	4.80	7.04
Al <sub>2</sub> O <sub>3</sub>	2.12	0.15	1.99	2.88	3.79
TiO <sub>2</sub>	1.32	-	1.23	0.53	0.87
K <sub>2</sub> O	0.65	0.11	0.45	1.67	0.81
SO <sub>3</sub>	0.59	35.26	6.95	1.23	1.43
Na <sub>2</sub> O	0.18	-	0.53	2.51	0.90
CaO/MgO	1.79	-	3.15	1.99	3.17

expressive presence of MgO may also indicate that this is a coating with a mixture of gypsum and lime binders. Boan and Alfaro (2008) mention as common practice the implementation of the stucco technique from different formulations, described from ancient treaties to the early twentieth century, one of the formulations related indicates the use of lime, plaster and marble fines.

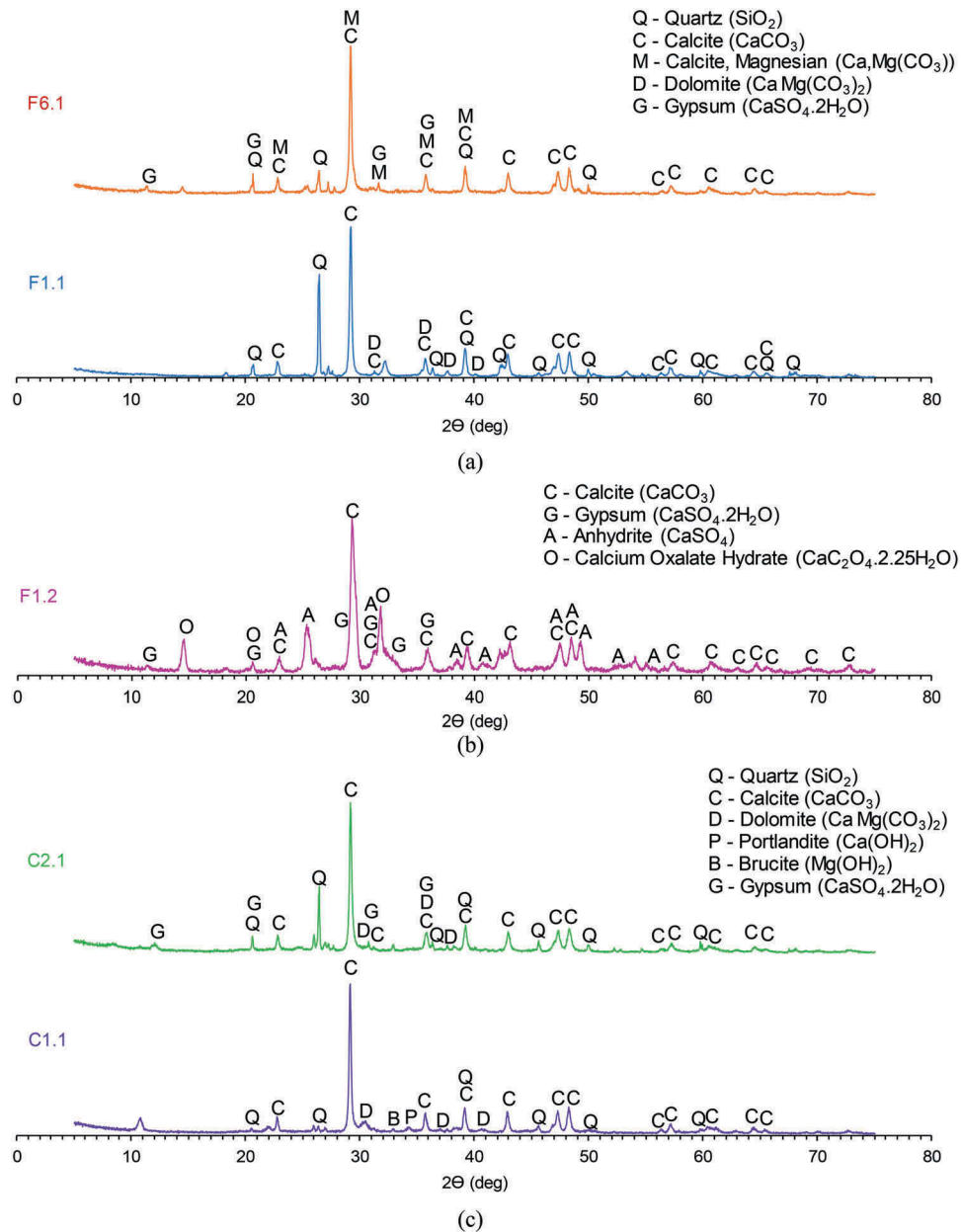
Considering XRD analysis, the binder of mortar samples from Frasca House (Figure 9a) present mainly calcium and magnesium carbonates (CaCO<sub>3</sub>; Ca,Mg(CO<sub>3</sub>); CaMg(CO<sub>3</sub>)<sub>2</sub>), and traces of quartz (SiO<sub>2</sub>), probably originated from the aggregate of this material.

The XRD analysis of the binder from Curia mortar samples (Figure 9c) is very similar to Frasca House. The calcium carbonate (CaCO<sub>3</sub>) is predominant, dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>) also appears, and traces of quartz (SiO<sub>2</sub>) remains. The difference between the specimen is the probable presence of Portlandite (Ca(OH)<sub>2</sub>) and Brucite (Mg(OH)<sub>2</sub>) from C1.1, corresponding to internal sample.

The F6 sample from exterior of Frasca House indicates the presence of Calcium Sulfate Hydrate. It is

possible to infer that the origin of this sulfate is the reaction of sulfites present in the atmosphere (verified with intensity in the XRF analysis) with the carbonate matrix of the analyzed sample. Although with moderate traffic, the Metropolitan Curia is located in the central region of the city, therefore, even with less intensity, it is also exposed to air pollutants. Thus, in the XRD results of sample C2, peaks were also identified regarding the presence of sulfates in the sample extracted from an exterior place.

For sample F1.2 from Frasca House, corresponding to the *stucco lustro* finish, the XRD (Figure 9b) presents sulfate compounds as gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) and anhydrite (CaSO<sub>4</sub>), as expected. The calcite also appears, possibly indicating the use of lime in this plaster. The predominant peak identified in 14.5° 2θ in this sample indicates the presence of hydrated calcium oxalate. As verified in loco, the sample extraction site had a dark-colored biofilm. Although no analysis was performed for biological characterization, the morphological characteristics verified corresponded to the growth of the microorganisms, probably with a fungi predominance. According to Gadd et al. (2014), calcium oxalate is the oxalate most abundantly found in living organisms and in the environment, the main forms are monohydrate (whewellite) and dihydrate (weddellite). Oxalate production is involved in the biodeterioration of rocky and mineral substrates, lignocellulosic materials and alteration and deterioration of cultural heritage (Gadd et al. 2014; Pinzari et al. 2013, 2010). Biosynthesis of oxalic acid and the formation of oxalates, especially those of calcium, is a property found in a wide variety of free-living and symbiotic fungi (Gadd et al. 2014).



**Figure 9.** XRD analysis of: (a) Frasca House mortars samples F1.1 and F6.1; (b) Frasca House *stucco lustrato* F1.2; (c) Metropolitan Curia mortars samples C1.1 and C1.2.

A: Anhydrite —  $\text{CaSO}_4$  (PDF 00-037-1496); B: Brucite —  $\text{Mg}(\text{OH})_2$  (PDF 00-044-1482); C: Calcite —  $\text{CaCO}_3$  (PDF 00-005-0586); D: Dolomite —  $\text{Ca Mg}(\text{CO}_3)_2$  (PDF 00-036-0426); G: Gypsum —  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  (PDF 00-021-0816); M: Calcite, Magnesian  $\text{Ca,Mg}(\text{CO}_3)$  (PDF 00-043-0697); O: Calcium Oxalate Hydrate —  $\text{CaC}_2\text{O}_4 \cdot 2.25\text{H}_2\text{O}$  (PDF 00-020-0233); P: Portlandite —  $\text{Ca}(\text{OH})_2$  (PDF 00-044-1481); Q: Quartz —  $\text{SiO}_2$  (PDF 00-046-1045). PDF: Powder Diffraction Files.

### 3.6. Salt analyses

Table 8 shows the results obtained for the presence of soluble salts, as well as the semi-quantitative verification of the color intensity or turbidity, observed in the analyzed samples of the two buildings.

Figure 10 shows images obtained during the soluble salts test execution to verify its occurrence in Frasca House samples. For the nitrate analysis, the blue color

is indicative of this saline contamination (Figure 10a). The turbidity of the samples is indicative of chlorides and sulfates presence in Figure 10b,c, respectively.

Internally, in the Frasca House, the nitrate and chloride presence were more evident in sample F4, which is located on the ground floor of the building, near the entrance door, place subject to the passage of animals, at the time the house was inhabited. The

**Table 8.** Qualitative/semi-quantitative test of soluble salts of Frasca House (F) and Metropolitan Curia (C) coating samples.

Frasca House			
Sample	Semi-quantity salt soluble		
	Nitrate	Chloride	Sulfate
F1.1	+	+	-
F1.2	+	++	+++ *
F2.1	+	+++	++
F2.2	++	+++	+
F4.1	+++	+++ *	++
F5	+++	+++	+++
F6.1	+++	+++	+++
F7.1	++	+++	+++
Metropolitan Curia			
Sample	Semi-quantity salt soluble		
	Nitrate	Chloride	Sulfate
C1.1	+++	+++	+++
C2.1	+++	++	++
C3.1	+++	+++	+
C3.2	+++	++	+

(-) Absence; (+) low content; (++) medium content

sample F1.2, *stucco lustro*, presented high turbidity due to the sulfate, confirming to be composed of gypsum (calcium sulfate). Externally, in this same building, all the salts were identified in expressive quantities.

The Metropolitan Curia edifice showed high amounts of nitrate in all samples, which were collected near the ground, a fact that may be related to possible contamination due to the cemetery that existed before construction, besides possible contamination by human or animal urine or even other type of waste disposed near the wall. Like nitrates, chlorides also appeared in all samples. Concerning sulfate, this was more evident in sample C1.1, internal to the construction, possibly due to contamination of other building materials (ceramic brick, aggregates, repair mortar cement).

Kurugöl and Güleç (2012) also verified the presence of Chlorine salt ( $\text{Cl}^-$ ), probably from soil or material composition, nitrate salt ( $\text{NO}_3^-$ ), originated from

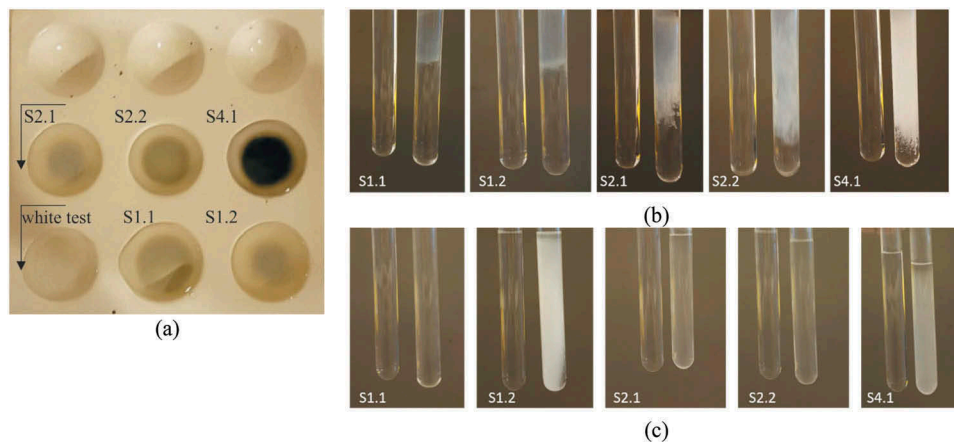
residues of organisms such as insects and birds near material in the samples obtained from Yoros Castle (Turkey).

According to Torrielli et al. (2016), the high capillarity and water circulation rate in the masonry are the main causes of mobilization and crystallization of salts in the materials. Its mobility and precipitation reflect cyclical wetting and evaporation, so the behavior regarding crystallization and consequent damage to materials will depend on the specific characteristics of the materials and conditions of environmental exposure.

#### 4. Conclusions

Although built twenty years apart, some of the characteristics of the Frasca House and the Metropolitan Curia's coating resemble, mainly concerning the constituent materials. The proportioning (binder:aggregate) was found to be most frequently between 1:3.0 to 1:4.0; the aggregates were siliceous and had similar particle size distribution, since they were probably extracted from rivers near the two buildings; and the binders presented high CaO content, but also expressive MgO values, as expected, since the closest reserves in the region are dolomitic limestone, also corroborated with the XRD study. These aspects are normally seen in historic buildings from this period in South Brazil, whose main construction system corresponded to the structural masonry of solid bricks with mortar coating.

Regarding the other factors, the results obtained varied between the two buildings and also between the location of the samples. The fines color was light brown or light gray in Frasca House, while in Curia it was predominantly white, probably indicating a greater

**Figure 10.** Presence of soluble salts verification of Frasca House coating: (a) nitrates analysis; (b) chlorides analysis; (c) sulfates analysis.

purity of the mortar from Metropolitan Curia. Water absorption from internal mortars was higher than from external, evidenced mainly in the case of Frasca House. It was also observed that all analyzed mortar samples indicated the presence of salts, a very important factor to be considered in the restoration intervention solutions. At Frasca House, external samples generally showed higher concentrations than internally, while at Curia there was no such distinction.

This study also approached the characterization of a plastering mortar, which presented a finer particle size distribution of the aggregate compared to the others. Furthermore, it was also evaluated a sample of the *stucco lustro* coating, which was found to be composed of  $\text{SO}_3$ ,  $\text{CaO}$ ,  $\text{MgO}$ , probably a mixture originated of calcium sulfate with dolomitic lime of the region, as shown in the XRD.

The characterization of the building coating is important both for compiling data from a history relating to the original composition of the materials and as a subsidy for future interventions, which may use compatible materials with the properties obtained in this paper.

## Acknowledgments

This study was partially supported by the research teams Núcleo de Tecnologia da Preservação e Conservação (NTPR/UFBA), Laboratório de Materiais e Tecnologia do Ambiente Construído (LAMTAC/NORIE/UFRGS) and Laboratório de Materiais Cerâmicos (LACER/UFRGS).

## Funding

This work was supported by the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPQ) and Programa de Cooperação Acadêmica em Defesa Nacional/Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (PROCAD/CAPES).

## References

- Apostolopoulou, M., E. Aggelakopoulou, L. Siouta, A. Bakolas, M. Douvika, P. G. Asteris, and A. Moropoulou. 2017. A methodological approach for the selection of compatible and performable restoration mortars in seismic hazard areas. *Construction and Building Materials* 155:1–14. doi:10.1016/j.conbuildmat.2017.07.210.
- Associação Brasileira de Normas Técnicas. 2003. *NBR NM 248: Agregados - Determinação da composição granulométrica*. ABNT.
- Bertolini, L. 2010. *Materiais de Construção*. São Paulo: Oficina de Textos.
- Bezerra, A. L. F. 2010. As cores das fachadas de edificações históricas pintadas a cal. Master diss., Programa de Pós-Graduação em Arquitetura e Urbanismo. Centro Tecnológico da Universidade Federal de Santa Catarina, Florianópolis. <https://repositorio.ufsc.br/xmlui/bitstream/handle/123456789/93795/290636.pdf?sequence=1&isAllowed=y>
- Boan, F. A., and A. A. Alfaro. 2008. *Principios y técnicas de conservación: Patrimonio arquitectónico Argentino 1850-1950*. Buenos Aires: Editorial Habitat.
- Bochen, J., and M. Labus. 2013. Study on physical and chemical properties of external lime – Sand plasters of some historical buildings. *Construction and Building Materials* 45:11–19. doi:10.1016/j.conbuildmat.2013.03.086.
- Brandi, C. A. 2005. *Teoria da Restauração*. Segunda edição, Tradução de Beatriz M. Kühl. São Paulo/Brasil: Ateliê Editorial. ISBN 85-7480-225-5.
- Dalto, D. P. D. S., R. C. D. C. Ribeiro, and L. C. R. de Moura. 2018. Characterization of the lime mortars of the Rui Barbosa House Museum in Rio De Janeiro, Brazil. *Minerals* 8 (2):50. doi:10.3390/min8020050.
- Di Benedetti, V. 2006. Estudo das alterações ocorridas nas rochas ornamentais utilizadas em monumentos arquitetônicos: Museu Júlio de Castilhos e Cúpula da Catedral de Porto Alegre. Master diss., Programa de pós-graduação em Geociências, Universidade Federal do Rio Grande do Sul, Porto Alegre.
- EPAHC. 1992. Secretaria Municipal de Cultura, Prefeitura Municipal de Porto Alegre, *Livro do Tombo*, Bens tombados pelo município – Listagem completa. Last Modified 1992. Accessed November 11, 2019. [http://www2.portoalegre.rs.gov.br/smc/default.php?reg=8&p\\_secao=87](http://www2.portoalegre.rs.gov.br/smc/default.php?reg=8&p_secao=87).
- EPAHC. 2013. Secretaria Municipal de Cultura, Prefeitura Municipal de Porto Alegre, *O Inventário de Porto Alegre*, Bens Tombados e Inventariados em Porto Alegre. Last Modified October, 2013. Accessed November 11, 2019. [http://www2.portoalegre.rs.gov.br/smc/default.php?reg=9&p\\_secao=87](http://www2.portoalegre.rs.gov.br/smc/default.php?reg=9&p_secao=87).
- Fleck, G. 2018. Porto Alegre precisa conhecer sua própria história: Com quase 130 anos, Casa Frasca é restaurada. *Sul 21*. Last Modified Dec. 22, 2018. Accessed November 11, 2019. <https://www.sul21.com.br/cidades/2018/12/porto-alegre-precisa-conhecer-sua-propria-historia-com-quase-130-anos-casa-frasca-e-restaurada/>.
- Gadd, G. M., J. Bahri-Esfahani, Q. Li, Y. J. Rhee, Z. Wei, M. Fomina, and X. Liang. 2014. Oxalate production by fungi: Significance in geomycology, biodeterioration and bioremediation. *Fungal Biology Reviews* 28 (2–3):36–55. doi:10.1016/j.fbr.2014.05.001.
- Giordani, C., and A. B. Masuero. 2019. Blended mortars: Influence of the constituents and proportioning in the fresh state. *Construction and Building Materials* 210:574–87. 0950-0618. doi:10.1016/j.conbuildmat.2019.02.077.
- Groot, C., J. J. Hughes, K. Van Balen, B. Bicer-Simsir, L. Binda, J. Elsen, R. Hees, T. Von Konow, J. E. Lindqvist, P. Maurenbrecher, et al. 2012. RILEM TC 203-RHM: Repair mortars for historic masonry: Performance requirements for renders and plasters. *Materials and Structures* 45:1277–85. doi:10.1617/s11527-012-9916-0.
- Groot, C., R. Van Hees, B. Lubelli, T. Wijffels, M. de Rooij, and J. Petkovic. 2004. Aspects of salt and moisture transport in restoration plasters and renders/Zum Salz- und Feuchtigkeitstransport in Mörteln und Putzen des

- Bauinstandsetzens. *Restoration of Buildings and Monuments* 10 (6):593–608. doi:10.1515/rbm-2004-5900.
- Guerra, F., W. Lopes, J. Cazarolli, M. Lobato, A. Masuero, D. Dal Molin, F. Bento, A. Schank, and M. Vainstein. 2019. Biodeterioration of mortar coating in historical buildings: Microclimatic characterization, material, and fungal community. *Building and Environment* 155:195–209. doi:10.1016/j.buildenv.2019.03.017.
- Guerra, F., R. Socoloski, B. Mondini, D. Dal Molin, and A. Masuero. 2016. Reabilitação de edificação histórica do século XX em Porto Alegre-RS: Identificação de sais e caracterização de materiais para compatibilidade na intervenção. Paper presented at *Rehabend*, Burgos, Spain, May 24–27.
- Guirdzhiiska, D., B. Zlateva, and Z. Glavcheva. 2017. Polished decorative fields in Thracian Fresco Tombs from the Hellenistic period - Archaeometrical research. *STAR: Science & Technology of Archaeological Research* 3 (2):428–36. doi:10.1080/20548923.2017.1396723.
- Hauková, P., D. Frankeová, and Z. Slízková. 2018. Characterization of historic mortars for conservation diagnosis. In *Historic Mortars: Advances in research and practical conservation*, ed. J. Huges, J. Válek, and C. J. W. P. Groot. pp. 109–118, Prague: Springer.
- IPHAN. 2013. Instituto do Patrimônio Histórico e Artístico Nacional (IPHAN), *Lista dos bens culturais inscritos nos Livros do Tombo (1938-2012)*. Last Modified 1992. Accessed November 11, 2019. [http://portal.iphan.gov.br/uploads/ckfinder/arquivos/bens\\_culturais\\_livros\\_do\\_tombo.pdf](http://portal.iphan.gov.br/uploads/ckfinder/arquivos/bens_culturais_livros_do_tombo.pdf).
- Kanan, M. I. 2008. *Manual de conservação e intervenção em argamassas e revestimentos à base de cal*, 172p. Brasília, DF: IPHAN/Programa Monumenta.
- Kurugöl, S., and A. Güleç. 2012. Physico-chemical, petrographic, and mechanical characteristics of lime mortars in historic Yoros castle (Turkey). *International Journal of Architectural Heritage* 6 (3):322–41. doi:10.1080/15583058.2010.540072.
- Lezzerini, M., S. Legnaioli, G. Lorenzetti, V. Palleschi, and M. Tamponi. 2014. Characterization of historical mortars from the bell tower of St. Nicholas church (Pisa, Italy). *Construction and Building Materials* 69:203–12. doi:10.1016/j.conbuildmat.2014.07.051.
- Maravelaki-Kalaitzaki, P., A. Bakolas, and A. Moropoulou. 2003. Physico-chemical study of Cretan ancient mortars. *Cement and Concrete Research* 33 (5):651–61. doi:10.1016/S0008-8846(02)01030-x.
- Middendorf, B., J. J. Hughes, K. Callebaut, G. Baronio, and I. Papayianni. 2005. Investigative methods for the characterization of historic mortars - Part 2: Chemical characterization. *Materials and Structures* 38:771–80. doi:10.1007/BF02479290.
- Moropoulou, A., A. Bakolas, and E. Aggelakopoulou. 2001. The effects of limestone characteristics and calcination temperature to the reactivity of the quicklime. *Cement and Concrete Research* 31 (4):633–39. doi:10.1016/S0008-8846(00)00490-7.
- Moropoulou, A., A. Bakolas, and S. Anagnostopoulou. 2005. Composite materials in ancient structures. *Cement & Concrete Composites* 27 (2):295–300. doi:10.1016/j.cemconcomp.2004.02.018.
- Munsell Soil Color Charts. 1994. *Munsell® color*. New Windsor, NY: Macbeth Division of Kollmorgen Instruments Corporation.
- PANalytical, B. V. 2012. *Highscore Plus*, v. 3.0.5. Netherlands: PANalytical.
- Papayianni, I., V. Pacht, and M. Stefanidou. 2013. Analysis of ancient mortars and design of compatible repair mortars: The case study of Odeion of the archaeological site of Dion. *Construction and Building Materials* 40:84–92. doi:10.1016/j.conbuildmat.2012.09.086.
- Pinzari, F., J. Tate, M. Bicchieri, Y. J. Rhee, and G. M. Gadd. 2013. Biodegradation of ivory (natural apatite): Possible involvement of fungal activity in biodeterioration of the Lewis Chessmen. *Environmental Microbiology* 15 (4):1050–62. doi:10.1111/1462-2920.12027.
- Pinzari, F., M. Zotti, A. De Mico, and P. Calvini. 2010. Biodegradation of inorganic components in paper documents: Formation of calcium oxalate crystals as a consequence of *Aspergillus terreus* Thom growth. *International Biodeterioration & Biodegradation* 64 (6):499–505. doi:10.1016/j.ibiod.2010.06.001.
- Recena, F. A. P. 2011. *Conhecendo Argamassa*, 2 ed., 188p. Porto Alegre: EDIPUCRS.
- Roden, A., B. Mota, D. Viana, D. Fonseca, E. Polesello, M. Pinto, and S. Muñoz. 2009. Contribuição ao estudo da evolução construtiva e da manutenção e conservação do monumento Igreja Nossa Senhora das Dores. *Trabalho acadêmico da disciplina: Patologia das Edificações - PPGEC-NORIE-UFRGS*. Porto Alegre.
- Rohde, G. M., L. C. Bonin, J. E. Mallmann, and O. Zwonok. 2012. Cal Pozolânica no Estado do Rio Grande do Sul: Abordagem Técnica para Produtos Inovadores. In *Série Técnica Especial* 3. pp. 54. Fundação de Ciência e Tecnologia (CIENTEC), Porto Alegre, Brazil.
- Sandin, K. 1995. Mortars for masonry and rendering choice and application. *Building Issues* 7 (3):1–16.
- Schueremans, L., Ö. Cizer, E. Janssens, G. Serré, and K. Van Balen. 2011. Characterization of repair mortars for the assessment of their compatibility in restoration projects: Research and practice. *Construction and Building Materials* 25 (12):4338–50. doi:10.1016/j.conbuildmat.2011.01.008.
- Silva, B. A., A. P. Ferreira Pinto, and A. Gomes. 2015. Natural hydraulic lime versus cement for blended lime mortars for restoration works. *Construction and Building Materials* 94:346–60. doi:10.1016/j.conbuildmat.2015.06.058.
- Sousa, V., N. Almeida, I. Meireles, and J. Brito. 2011. Anomalies in wall renders: Overview of the main causes of degradation. *International Journal of Architectural Heritage* 5 (2):198–218. doi:10.1080/15583050903487633.
- Souza, J. S. C. 2013. *Estudo de argamassa à base de cal e metacaulim para intervenções em revestimento das edificações históricas*. Master diss., Programa de Pós-Graduação em Engenharia Civil, Universidade Federal de Pernambuco, Recife.
- Teutonico, J. M. 1988. A laboratory manual for architectural conservators. In *International centre for the study of the preservation and restoration of cultural property*. pp. 168. Rome: ICCROM.
- Torrielli, G., L. Gaggero, V. Caratto, and M. Ferretti. 2016. Innovative method and apparatus for deep cleaning of soluble salts from mortars and lithic materials. 2016. *Energy Procedia* 97:523–30. doi:10.1016/j.egypro.2016.10.066.

- Vitruvio, P. M. 1997. *De Architectura*. Tradução de José Luis Oliver Domingo. Madrid: Alianza Editorial, S. A Spain. ISBN: 84-206-7133-9.
- Weber, J., T. Köberle, and F. Pintér 2013. Methods of microscopy to identify and characterise hydraulic binders in historic mortars—A methodological approach. 3rd Historic Mortars Conference, Glasgow, Scotland, september 11-14, 2013. doi:[10.1007/978-3-319-91606-4\\_2](https://doi.org/10.1007/978-3-319-91606-4_2).
- Yildizlar, B., B. Sayin, and C. Akcay. 2019. A case study on the restoration of a historical masonry building based on field studies and laboratory analyses. *International Journal of Architectural Heritage* 1–19. doi:[10.1080/15583058.2019.1607625](https://doi.org/10.1080/15583058.2019.1607625).