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Archaeological and Archaeochemical Analysis of the Painting in the Baths in Julián Besteiro Square, Carmona (Seville, Spain)

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Abstract: This paper addresses the archaeological and archaeochemical study of the fragments of mural painting recovered from the excavation of the baths in Julián Besteiro Square in Carmona. The analysis of the fragments allowed us to associate them with the first phase of the building's decoration, one of the few examples of urban mural painting currently known in Carmona. It was dated between the first half and the middle of the first century AD. The archaeochemical study identified the composition of the mortar and the pigments of the fragments belonging to the middle and upper zones of the wall, confirming the presence of palmitic and stearic fatty acids, as well as traces of oleic and tetradecanoic acids corresponding to the binders used for the execution of the decoration. This discovery provides specific information on the techniques used in Roman architectural decoration, shedding light on the materials and methods used in first-century-AD urban contexts.

Keywords: plinth; column imitation; cornice; XRD; Raman spectroscopy; binders

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1. Introduction

The Roman town of Carmo, today Carmona (Seville), is an important enclave for the analysis of the Roman settlement in Baetica. Since the 19th century, the discovery of the necropolis has focused the interest of a large part of the research efforts [1]. In recent years these have provided interesting advances thanks to various studies of the pictorial decoration and the archaeochemical analysis of the preserved remains of liquids [2–4].

However, the urban zone has also proved an interesting area of research. We have been able to define its evolution from the pre-Roman phase, as well as its buildings; infrastructures; and marble, epigraphic, mosaic, and monetary productions [5]. In this context, the references we have for the study of pictorial production in urban areas are scarce due to the poor preservation of such materials in the town [6]. This has meant that studies to date have been limited almost exclusively to the decoration of funerary spaces [7,8]. Of these, we have an important documentary base from the first half of the 20th century [9] and an archaeochemical study of the Tomb of Servilia [10].

On that basis, the study undertaken here was designed to increase our knowledge of the mural painting of ancient Carmo through the analysis of the few remains preserved in the baths of Julian Besteiro Square, combining their archaeological and archaeochemical studies.

1.1. Archaeological Context

The baths complex from which the analyzed paintings come is located is in the Plaza Julián Besteiro. This square is in the middle of Carmona's historic center, on the slope of a natural hill at the intersection of present-day Hermanas de la Cruz and General Chinchilla Streets. It is part of a plot occupied by the convent of San José built in the late 17th century. It became municipal property after its disentailment in the 19th century, functioning first as a prison and then as a school, until its demolition in the 1970s. It was transformed into a public square in 1986 (Figure 1). Until that date, the only evidence of archaeological research is a survey at its northern end and another in the adjacent square, Plaza San José [11].

Figure 1. Location of the city of Carmo and placement of the thermal complex on the modern urban city. Design by the authors based on Jiménez Hernández, 2012.

It was not until the last decade, as part of a remodeling of the square to build new facilities and an underground car park, that a complete archaeological study of the area was carried out. It was directed by the Municipal Archaeological Service and involved different campaigns between 2012 and 2019 that focused on the study of the central and southern areas of the square. Here, we only refer to the Roman levels documented in the course of the interventions; thus, for the study of the historical sequence of the square, we refer to the publication of those actions [12].

The chronological sequence in the area revealed leveling prior to the first constructions. This has been dated to the Augustan period, a time of major urban expansion with respect to the late Republican core [13,14], probably linked to the granting of the legal status of *municipium* [15]. To this end, stepped terraces were built to overcome the slope of the hillside, a dynamic that has been documented in other areas of the town for the first half of the first century AD [16,17]. In this respect, a height difference of more than 2.5 m was observed between the northern and southern ends of the intervention. This is accentuated with the data extracted from the survey in the northwestern corner of the square in 1986, reaching a height difference of 7.38 m. These data corroborate the existence of an urbanization and monumentalization of the town completed with the configuration of orthogonal patterns adapted to the urban topography and the construction of public buildings that followed the ideal model of the *Vrbs* [18,19], including in this area the construction of the baths complex.

The structures associated with the building could only be partially documented due to the state of conservation in some sectors of the excavation. Those that provided the most information were at the southern end, corresponding to grids A–E and F, and in the northern sector, specifically grid I. However, the data show us the first period of use that would have lasted until the mid-first century AD, when a remodeling of the building led to the abandonment of the rooms located in the northern sector and the transformation of those preserved in the southern sector, which would be provided with new ambiences to complete the baths complex. The reading of the sequences of use from this time becomes complex, given the remodeling and repairs, which would have corresponded to changes during the life of the building from the second half of the first century AD. However, there is a marked uniformity in the construction techniques used. They reveal the execution of walls with a base of mixed masonry and ashlars and a mud wall, similar to the rest of the late Roman buildings in the town. The only difference is the presence of *tegulae*, bricks and marble fragments in the walls of the second phase. For this phase it was possible to clearly document the coeval construction of a system of six manholes or *spiramina* and galleries or *specus* that configured a water source. This would have been the basic infrastructure for supplying the building from the outset, corroborating its function as a thermal bath already in the first phase [12].

The preserved remains allow us to define a clearer architectural morphology for the second phase, which would have been developed from the middle or second half of the first century AD. We found a rectangular 12.65 $\times$ 8.15 m room paved with *signinum*, which resulted from of the expansion of the original space from the first half of the first century AD, now including two cold immersion pools—one individual (P-1) and the other larger (P-2)—and a basin. In addition, the remains of a later *spicatum* pavement and benches with holes for possible lockers at the southern end have led to the interpretation of the space as an *apodyterium/frigidarium* (A–F). The rest of the spaces are structured around this area. Connected to it are rooms E-4, with a rammed earth floor and surface channeling that appears to indicate that it functioned as an open space, perhaps a *palaestra* judging by the remains of an *opus spicatum* floor on the channeling; E5, a service area paved in *opus signinum* and with an auxiliary reservoir designated D-1 lined with hydraulic mortar and with a small access staircase, which served as an overflow for pool P-2, connected by a drain with *fistula plumbea*; and probably H-2, a heated room with a hypocaust interpreted as a *caldarium*, headed by an apse on the west wall and with brick paving. Connected to the latter, another hot room designated as H-1 was documented and interpreted as a possible *tepidarium*, also with a brick floor. It is connected by another opening to room E-1, with an undetermined function and paved with hydraulic mortar on which marble slabs were laid. The rest of the rooms (E-2 and E-3) also bordered the *apodyterium/frigidarium* and also room E-1 in the first case, although no clear function can be defined. From room E-2, an *opus signinum* floor and quarter-round reinforcements were preserved on all the walls, as well as the remains of pictorial and stucco decoration, which we will analyze below. Room E-3 had a pavement and reinforcements in the walls of identical morphology to those of the previous one, with the superimposition of two *signinum* and brick pavements and a hydraulic mortar basin belonging to the previous phase [12] (Figure 2).

The lack of façade or party walls suggests that the remains of the complex extended beyond the excavation area, although we are unable to define its total dimensions.

The building would have remained in use until the second half of the second century AD, at which point the partial despoilment of the building materials, mainly the marble cladding, is documented, after which it gradually collapsed. Despite this, the building continued to be taken advantage of for later constructions, with the use of Roman-period elements identifiable in the medieval buildings [12].

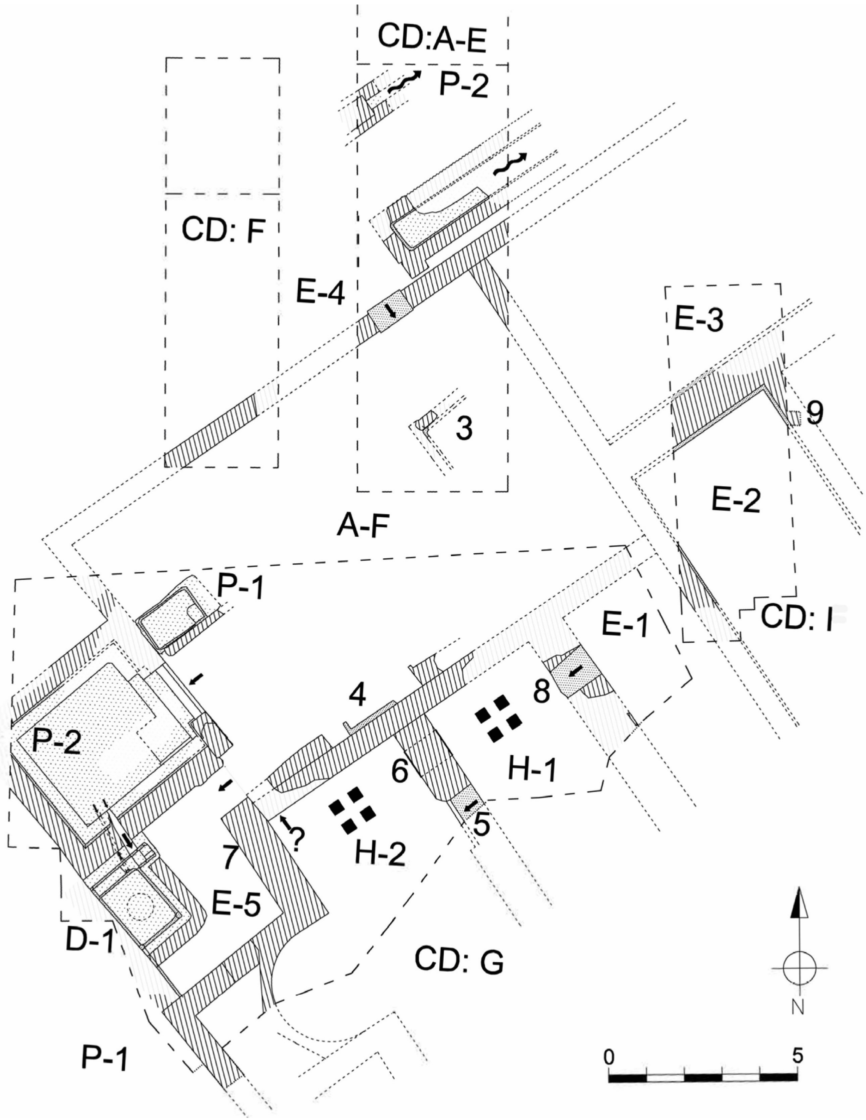

Figure 2. Plan of the thermal complex with identification of the localized rooms. Source: Román Rodríguez, 2019.

1.2. The Pictorial Remains in Room E-2

1.2.1. Descriptive Study

In terms of the pictorial decoration preserved in the baths complex, the remains are sparse and limited to what has been found in room E-2. This appears to be because this room underwent little or no remodeling between the construction of the baths and their abandonment, thus facilitating the preservation of the original decorative phase. However, the fragmentary nature of the remains prevents us from precisely associating some of them with the assemblage that decorated the room, and they may have formed part of the wall coverings of the adjoining rooms.

The best preserved section, which we can clearly associate with the decoration of room E-2, corresponds to the plinth, from which we were able to recover a panel 73 cm high and 76 cm wide, which was found in situ on the east wall. Of the section corresponding to the skirting board, or part of it, only part of a yellow field has been preserved; a height of 7.5 cm remains, although it would probably have been at least 15 cm high. Above this, a white fillet gives way to a black background with two yellow fillets at the top and bottom, framing the figural decoration. The figural decoration consists of a yellow plant stem with green leaves that runs horizontally along the entire length of the plaque, with a bird resting on the stem in the central part of the plaque. The figure is depicted in profile, with its wings folded over its body and an elongated beak; of particular note are the outlines of the neck, the wing, and part of the white plumage marked with red brushstrokes, as well as the legs. In addition, a small, feather-like line emerges from the head. The upper part of the plinth is enclosed by another white fillet, which gives way to a 7 cm wide yellow band; a second white fillet; and, finally, a red field, probably corresponding to the background of a panel located in the middle area (Figure 3A).

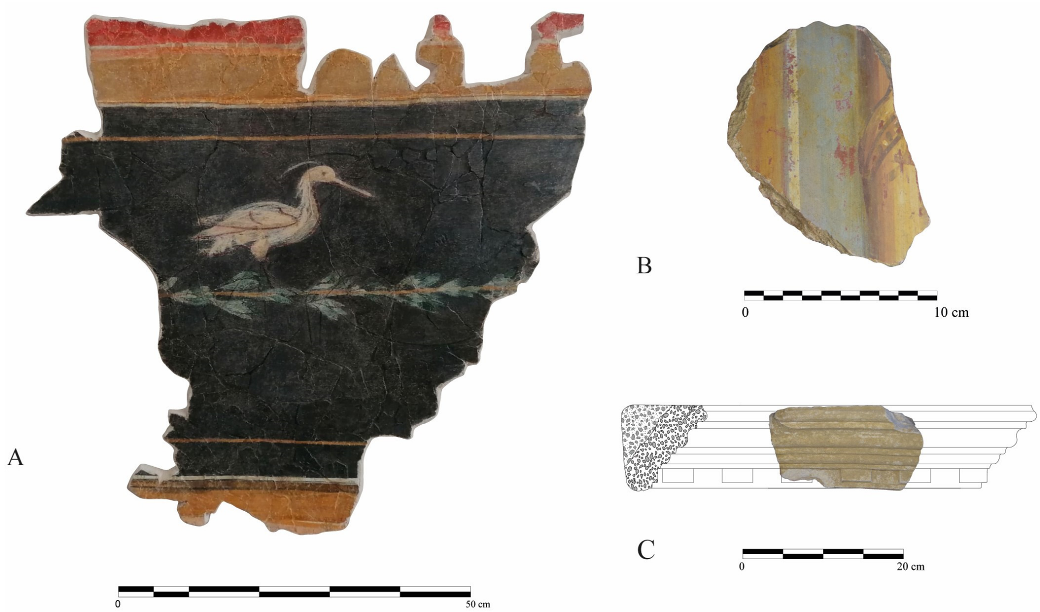

Figure 3. (**A**) Fragment of the plinth decoration. (**B**) Fragment of the middle zone with the remains of an imitation column. (**C**) Fragment of cornice and drawing of the section and profile. Design: G. Castillo.

Among the other fragments, only one would have been part of the middle area of the set, although its partial nature prevents us from clearly associating it with the described plinth. It could belong to another of the adjoining rooms, although the chronological similarity intuited from the decorative elements leads us to believe that it belonged to the same assemblage. At one end of the fragment, part of a yellow field is preserved, perhaps corresponding to a band, which gives way to a white fillet and a second band, this one blue and 3.2 cm wide. Next to it are the remains of a column shaft, whose total width we cannot determine. It is a brown/yellowish color and presents a gradation of a dark tone at its limit toward a lighter one in the central part, generating a chiaroscuro effect. On the shaft there is a series of dark brown/black fillets arranged obliquely, forming part of a helical decoration in the form of a possible textile or vegetal element that would have developed along the length of the shaft. Between the fillets we can distinguish, in one case, an alternation of dark brown/black and white drops, while in another case we find a beige/yellowish background. It is interesting to note a red undercoat that can be seen at various points on the fragment, especially under the white fillet, the blue band and the shaft, as well as below the yellow field. It indicates the possible presence of a larger red field and confirms a secco execution of the elements described. Apart from the finishing layer, the mortar has only two preparatory layers, the first 1.1 cm thick and the second

2.1 cm thick, both with abundant lime nodules and imprints of plant material, with no traces of any fastening system (Figure 3B).

Of the rest of the wall, only a cornice fragment has survived, which could have formed part of the upper finish of the room paneling. On the lower part there is a listel that could mark the start of the cornice after the pictorial decoration and gives way to a band of dentils. Above this, there is a succession of a listel, a quarter-rib, and a second listel, leaving a straight cyma above it, which gives way to a listel and a possible torus or a second straight cyma, partially lost, which would have closed the development of the cornice. The mortar shows two layers of preparation, the first between 1.4 and 3 cm thick and the second between 1.7 and 4 cm thick, in both cases with hardly any aggregate and a very light whitish color (Figure 3C).

1.2.2. Compositional Analysis

As for the decoration of the lower part of the wall, the simplicity of the compositional scheme only allows for an analysis of the central part of the plinth. The sole plant stem running horizontally across it is reminiscent of compositions with a garden background. However, the model we find here differs from the majority of schemes of this type as in most examples, there are isolated plant clumps, or they alternate with animals [20,21], while the representations that use a fillet as a surface for the arrangement of the figures are more similar [21].

With regard to the decoration of the lower part of the wall, there is a similar example, although with a more richly ornamented undulating stem and without animals and structured in slabs, from the Maison des Bacchantes in Sainte-Colombe (Rhône), belonging to the third Pompeian style [22]. In our case, the partial nature of the remains does not allow us to define whether it is a continuous or compartmentalized plinth. Despite the above, the models of plaques or fields with vegetal decoration in the form of a garland, which we find especially in plinths and upper areas from the fourth Pompeian styleonward [23], among which animals are also depicted on the stems [24], are closer in morphological terms. If we analyze the bird in detail, the shape of the body with its elongated legs and particularly prominent bill, allows us to identify it as a spoonbill (*Platalea leucorodia*), a wading bird, generally white in color, that inhabits wetland areas. It should be noted that the plume of feathers hanging from the nape of the neck indicates that it is a male specimen in the breeding season. The largest population of this bird in Spain is in the wetlands of the Atlantic coast of Andalusia and the La Janda area of Cadiz [25]. This would indicate direct observation of the local fauna by the *pictor*. On the other hand, the depiction of birds during the breeding season is no exception as they have also been found in, for example, tomb paintings in *Tarraco*.

Despite its size, the fragment in the middle section is interesting from an interpretative point of view in terms of the compositional scheme of the middle section of the wall. The presence of an imitation column shaft suggests, due to its small size, compositions typical of thethird and fourth Pompeian style, and it may be part of a building structure. The existence of a separating band next to a field that could have been part of a panel reinforces the presence of an aedicule that would have been located in a central position on the wall, following a scheme similar, perhaps, to ensembles such as the one we see in the Casa di Giuseppe II VIII 2, 39 in Pompeii [26]. Nevertheless, the decoration and morphology of the column are reminiscent of forms we can also see in compositions with architecture of the fourth Pompeian style. Although the preserved remains are too sparse to be able to associate them with a specific model, the decoration arranged in a helical pattern around the shaft suggests a model similar to Eristov's type 2 or 3 [27]. Examples of these can, among others, be found in *Cubiculum* 23 of the Casa delle Vestali VI 1, 7, also in Pompeii [26].

Finally, as far as the cornice is concerned, the mere presence of a denticulated frieze does not allow for an in-depth analysis, since it is a very common motif in Roman-era stuccoed production, and we can find examples from the Late Republic [28] to the Lower Empire [29]. Therefore, it does not serve as a chronological marker or provide us with any specific stylistic evidence.

2. Materials and Methods

To complete the archaeological study of the fragments, a chemical study of the mortars and pigments was undertaken. It was applied only to the fragment from the middle zone and the cornice, given the impossibility of analyzing the plinth, which had been restored. The fragments were initially observed by optical microscopy, which made it possible to identify the different layers, analyze their microscopic properties, and select the appropriate areas for study. Next, the combination of X-ray diffraction and X-ray fluorescence (XRD and XRF) provided information on the composition of the mortar layers present in the fragments. Subsequently, micro-Raman spectroscopy (μ-Raman) analysis made it possible to precisely identify the chemical nature of the pigments used. Finally, through gas chromatography coupled to mass spectroscopy, use of the al secco painting technique was determined, and the binder used in the process was identified. Table 1 shows the analyzed fragment of column shaft and cornice, together with the composition of the pigments and the specific areas examined, as well as the composition of the mortars.

Table 1. Analyzed fragments and composition of pigments and mortars.

<table>
<tr><th>Photograph</th><th>Information</th></tr>
<tr><td rowspan="4">
</td><td>Fragment 1 (F1)</td></tr>
<tr><td>Macroscopic color:
Yellow, red, white, blue</td></tr>
<tr><td>Compound found:
Goethite (α-FeOOH),
Hematite (α-Fe_2O_3);
Calcite ($CaCO_3$);
Egyptian blue ($CaCuSi_4O_{10}$)</td></tr>
<tr><td>Mortar components:
Calcite (C); quartz (Q)</td></tr>
<tr><td rowspan="4">
</td><td>Fragment 2 (F2)</td></tr>
<tr><td>Macroscopic color:
White</td></tr>
<tr><td>Compound found:
Calcite ($CaCO_3$)</td></tr>
<tr><td>Mortar components:
Calcite (C); quartz (Q);</td></tr>
</table>

2.1. Optical Microscopy

The target samples were visually examined at 100× magnification under a LEICA DCM8 Confocal-Interferometric Microscope for Materials, whose 3D material surface metrology system allowed for the study of rough surfaces through confocal microscopy.

2.2. X-Ray Diffraction

X-ray diffraction data were collected with a Bruker D8 Advance diffractometer featuring a goniometer and an automated DACO-MP recording system. The samples were irradiated using copper Kα radiation (λ = 1.54 Å). The device was equipped with a nickel filter and a graphite monochromator, functioning at a goniometer scan rate of 2 degrees per minute. The analysis was performed by taking samples from different points of the mortar layer under study to obtain a representative sample of each layer. The identification and determination of the different layers within the samples were carried out by archaeologists, who carefully distinguished the various layers. This approach ensured a sufficiently representative area to accurately determine the composition of each layer. The acquired sample was then pulverized and analyzed.

2.3. X-Ray Fluorescence

X-ray fluorescence (XRF) spectroscopy was used to identify and quantify the chemical elements present in the paint layers. The XRF analysis was carried out on a small portion of the sample from the different layers, which was pulverized, then pressed and transformed into a pellet. The measurements were performed using a Rigaku ZSX Primus IV wavelength-dispersive X-ray spectrometer, equipped with a 3 kW Rh-target X-ray tube, ten analyzer crystals, a sealed proportional counter for detecting light elements, and a scintillation counter for heavy elements. Spectral data were collected at multiple locations on the surface of each sample and subsequently averaged.

2.4. Micro-Raman Spectroscopy

Raman spectroscopy was used to identify the pigments used to paint fragment 1. Raman spectra were recorded with an InVia Raman Renishaw spectrometer equipped with a Leica microscope featuring various lenses, monochromators, filters, and a charge-coupled device (CCD). Spectra were acquired over the wavenumber range of 140–1700 cm^{-1} using green laser light (532 nm), adjusting the different experimental variables for each sample to optimize the signal-to-noise ratio.

2.5. Gas Chromatography-Mass Spectrometry

Gas chromatography-mass spectrometry (GC/MS) analysis was performed using a Bruker Mod Scion Triple Quadrupole mass spectrometer. Compound separation was achieved with a capillary column featuring a 5%-phenyl silicone stationary phase (30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness). The chromatographic conditions were as follows: the injector temperature was set to 250 °C; the oven program was an initial temperature of 55 °C (held for 1 min), ramped at 5 °C/min to 235 °C, followed by 8 °C/min to 310 °C (held for 5 min). Mass spectrometer settings included electron ionization (EI), a source temperature of 250 °C, and mass scanning in the range of 40–450 u at 0.6 s per scan. Compound identification was performed by comparing EI spectra with both the NIST library and an internal reference library.

2.6. Binding Media Extraction Process

The search for organic binders in fragment 1 was conducted using gas chromatography coupled with mass spectrometry (GC-MS). This required hydrolysis and derivatization processes for the detection of proteinaceous materials, as well as derivatization for the identification of fats.

To achieve protein hydrolysis, if present, we followed a procedure described by Casoli et al. [30], which allowed for the identification of amino acids found in egg proteins, animal glue, casein, and others. For this purpose, 10 mg of the mural painting sample was dissolved in 2 mL of 6M HCl and heated at 100 °C for 5 h in a polyethylene glycol bath under a nitrogen atmosphere. Norleucine was added as an internal standard (100 µL of a 1 g/L solution). During hydrolysis, all amino acids from the proteins were released. For derivatization, the hydrolyzed sample was evaporated to dryness and dissolved in 3 mL of a 2 M HCl solution in isopropanol in a screw-cap vial, maintaining a temperature of 90 °C for 1 h. The solvent was then evaporated again, and the residue was dissolved in 2 mL of dichloromethane and treated with 0.2 mL of trifluoroacetic anhydride, heated to 60 °C for 1 h. Finally, the mixture was evaporated to dryness, and the residue was re-dissolved in 0.2 mL of dichloromethane, which was used for chromatographic analysis (0.2 mL).

To evaluate the presence of fatty materials in the paint sample, a transesterification process was carried out prior to GC-MS analysis. All samples were pretreated by hydrolysis, and fatty acids were derivatized for conversion into methyl esters (FAMEs), increasing their volatility as a result. This was achieved using the method described by Manzano et al. [31]. Specifically, 15 mg of the wall painting sample was placed in a microvial and treated with 15 mL of a methanol solution of m-(trifluoromethyl) phenyltrimethylammonium hydroxide (TFTMAH) and 200 µL of toluene to transesterify triglycerides. The mixture was sonicated for 30 min and then centrifuged at 3000 rpm for an additional 5 min, with the resulting supernatant being analyzed by GC–MS.

3. Results

3.1. Mortar

The study of Roman mortar is of great interest as it provides valuable information about the construction techniques used in the buildings of the time. As Vitruvius indicated, mortar was applied in multiple layers, up to a maximum of seven, allowing for the creation of smooth surfaces suitable for the homogeneous application of paint [32]. This makes the analysis of the mortar composition particularly relevant in decorative architectural elements, such as columns, which featured high levels of polychromy and required uniform surfaces for the proper application of color.

In this study, the analyzed fragments came from a polychrome column painted as part of the wall decoration (fragment F1) and a cornice (fragment F2), both with two well-differentiated layers of mortar. These mortars were subjected to X-ray fluorescence (XRF) and X-ray diffraction (XRD) analysis. The XRF results, presented in Table 2, show the oxide percentages in the layers of the fragments: entries 1 and 2 correspond to the polychrome fragment, and entries 3 and 4 correspond to the cornice.

In the case of the polychrome fragment, the main components were calcium oxide and silicon oxide in similar proportions. The other components appeared in smaller concentrations, indicating that this mortar did not have hydraulic properties [33]. In contrast, the cornice fragment was primarily composed of calcium oxide, which was consistent with the use of stucco, employed to mold specific shapes in cornices. However, XRF identified the calcium content, but it could not distinguish between CaO (calcium oxide) and $CaCO_3$ (calcium carbonate), which required XRD or Raman analysis for clarification.

Table 2. Chemical composition of the fragments as determined by X-ray fluorescence (XRF) spectroscopy.

Fragment	Layer	Composition (%)						
		MgO	Al_2O_3	SiO_2	K_2O	CaO	Fe_2O_3	Others
F1	Layer closest to the paint layer	0.35	2.58	42.9	0.57	47.8	3.57	2.23
	Layer farthest from the paint layer	0.30	2.57	43.9	0.57	49.6	1.76	1.3
F2	Decorative cornice mortar	1.14	1.15	6.43	0.28	87.9	0.98	2.12
	Cornice base mortar	0.5	1.18	4.91	0.26	90.1	1.06	1.99

The XRD analyses (Figure 4) confirmed these findings. For the polychrome fragment, both layers exhibited similar XRD patterns, characterized by a high presence of calcite ($CaCO_3$, JCPDS No. 05-0586) and quartz (α-SiO_2, JCPDS No. 46-1045). In contrast, the layers of the cornice showed only calcite ($CaCO_3$) bands, confirming the results obtained from the XRF analysis and highlighting the predominance of stucco in this type of decorative structure.

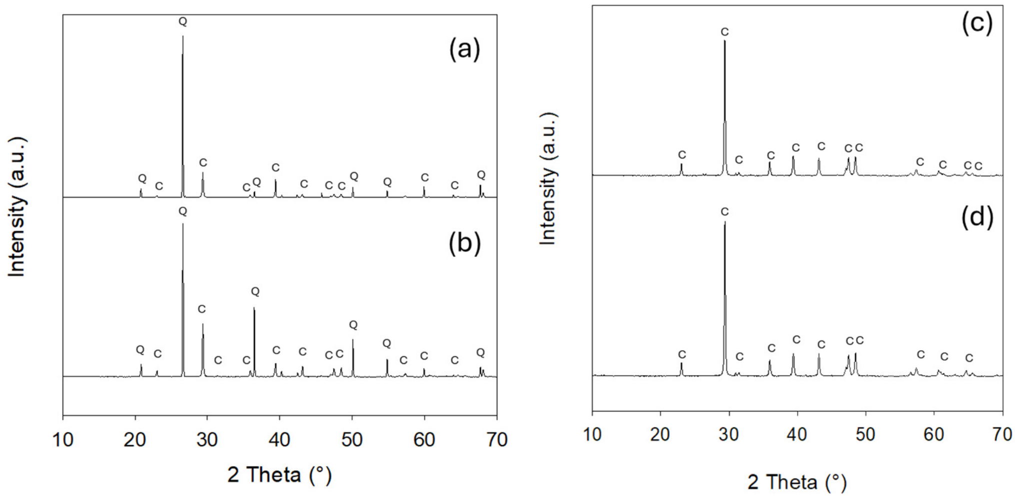

Figure 4. XRD patterns for the mortar: layers closest to (**a**) and farthest from (**b**) the paint layer of F and the decorative cornice (**c**) and the cornice base (**d**) mortar of F2. Legend: C Calcite; Q Quartz.

3.2. Surface Morphology

Figure 5 shows an image of the polychrome fragment observed through confocal-interferometric microscopy for materials. This analysis revealed the presence of several layers of paint applied at different stages. First, a base layer of red paint was applied across the entire surface of the column, which was visible in the degraded areas of the fragment. Blue and yellow paint layers were then added in specific areas, suggesting that broad color stripes were painted [34–36]. Additionally, small blue particles could be distinguished in the blue area of the sample; this technique, widely documented by authors such as Vitruvius, was used to enhance the brightness and hue of the color. Finally, decorative details were incorporated, such as black floral motifs at the top and a white line in the middle section of the fragment.

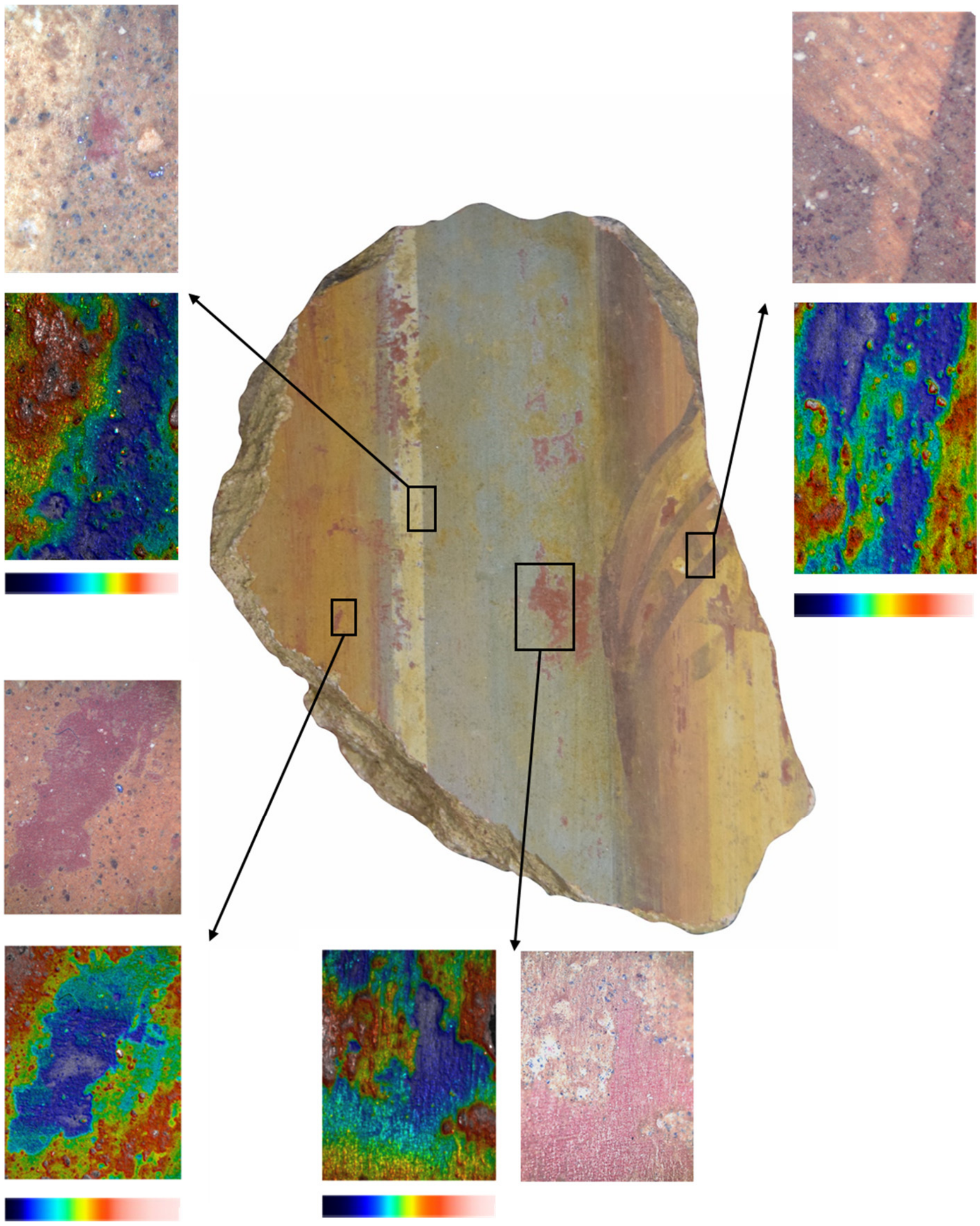

Figure 5. Representative image of F1 observed through a confocal interferometric microscope (the blue and red shades represent the deeper and outer areas of the sample, respectively).

3.3. Pigment Analysis

Raman microspectroscopy was used for the characterization and identification of the pigments used in fragment 1 (F1). Two distinct yellow areas (1 and 7) were clearly visible, and their Raman spectra (Figure 6) were similar. Both spectra showed a strong signal around 395 cm^{-1}, indicative of the presence of goethite, α-FeOOH. The signals at 300, 480, and 550 cm^{-1} confirmed the use of this pigment to obtain the yellow color [37]. In both cases, in addition to the goethite signals, a significant signal at 1086 cm^{-1} was observed, typical of calcium carbonate in its calcite phase [38]. The presence of this compound could be associated with the use of a fresco technique as this yellow layer was applied over a red underlying layer, as seen in the photograph in Figure 5. This suggested that the calcite signals in the Raman spectrum could not be attributed to the preparatory layer (intonaco).

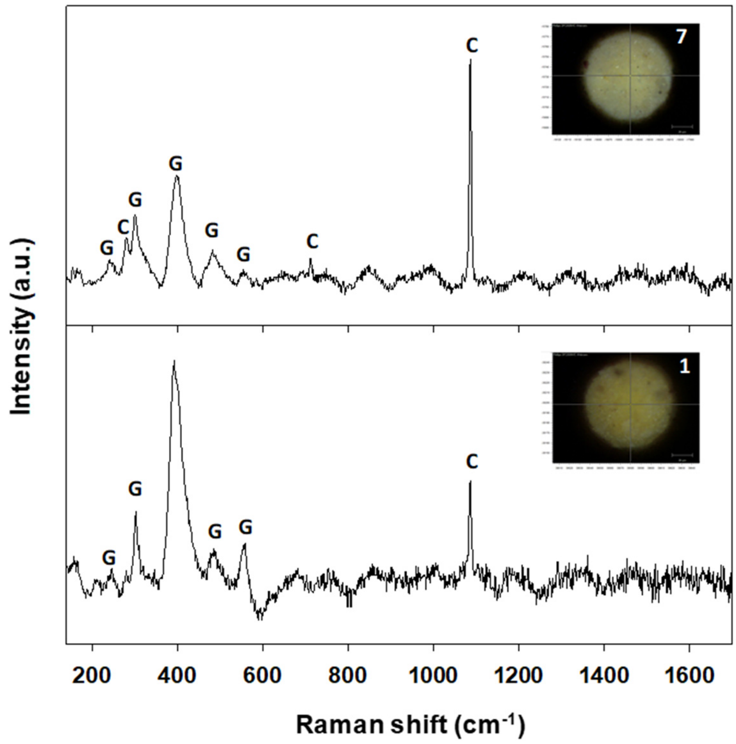

Figure 6. Raman spectra of the yellow-colored areas (1 and 7) of the fragment are shown. The microphotographs of the areas where the spectra were acquired are shown in the inset. Legend: C, calcite; G, goethite.

On the other hand, the insets in the spectra of Figure 6 are microphotographs of the areas where the spectra were recorded, clearly showing that the yellow color in area 1 was darker than that in area 7, a difference that was also visible macroscopically in the fragment. This tonal variation was related to the amount of lime, which later transformed into calcite due to the action of atmospheric carbon dioxide. The amount of lime was higher in area 7 than in area 1, which explained why the intensity of the signal at 1086 cm^{-1} was greater in the former than in the latter.

The study of the underlying red layer revealed a spectrum with bands (225, 246, 291, 408, 499, and 612 cm^{-1}) that matched those described for hematite, α-Fe_2O_3 (Figure 7) [39]. The spectrum also showed another broad signal at 1315 cm^{-1}, which could be attributed to two-magnon scattering derived from the multi-ferromagnetic behavior of hematite [40]. The intensity of this signal could vary significantly from one hematite sample to another, depending on the intensity of the red color, which was related to the degree of distortion in the Fe^{3+} centers [41]. Finally, a band at 660 cm^{-1} was observed, the assignment of which is subject to controversy in the literature. It has been attributed to magnetite (Fe_3O_4) in some cases and to maghemite (γ-Fe_2O_3) in others, which often occur naturally as impurities in hematite [42]. In our case, this signal was assigned to a Raman-forbidden but infrared-allowed vibration mode, which may have been triggered and thus observed in Raman spectroscopy by an effect of disorder in the hematite crystal lattice, as we have confirmed in previous studies [43,44]. In addition to these bands, those corresponding to calcite (1086, 712, and 278 cm^{-1}) were also observed, which, as shown in the microphotograph shown in the inset in the spectrum of Figure 7 (white particles), was mixed with hematite (red particles).

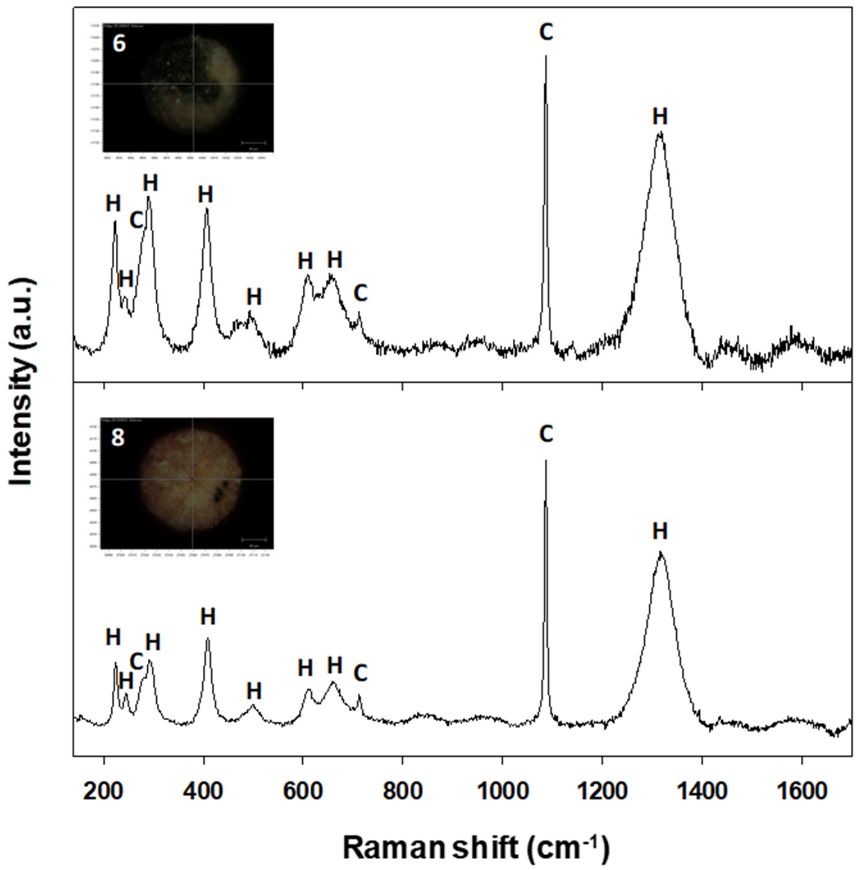

Figure 7. Raman spectrum of zones 8 and 6 of the fragment. The microphotographs of the areas where the spectra were acquired are shown in the inset. Legend: C, calcite; H, hematite.

Area 6, which appeared darker to the naked eye, when studied by Raman spectroscopy produced a spectrum similar to the one described earlier, again showing all the bands of hematite and calcite (Figure 7).

The white line of the fragment, marked with the number 5, showed a Raman spectrum (Figure 8) matching that described for calcite [38], indicating that this pigment was prepared from lime, which subsequently formed calcium carbonate through a reaction with atmospheric carbon dioxide.

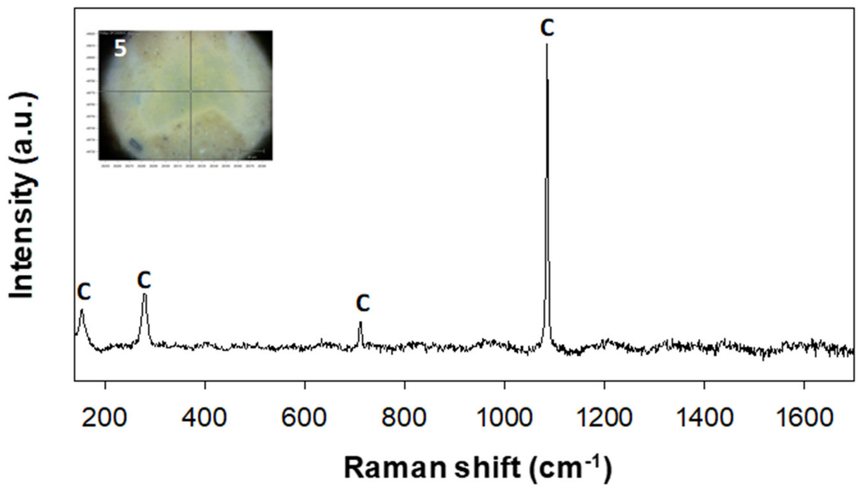

Figure 8. Raman spectrum of zone 4 corresponding to the white band of the fragment. The microphotograph of the area where the spectrum was acquired is shown in the inset. Legend: C, calcite.

If we closely examine the microphotograph shown in the inset in Figure 8, we can see that the white line was placed over a bluish background, which likely corresponded to the bluish area of the fragment marked with the number 2. This suggested that this line was painted over area 2, the Raman spectrum (Figure 9) of which was dominated by two intense signals at 430 and 1085 cm^{-1}, indicative of Egyptian blue pigment [45]. In the area marked with the number 3, Raman spectroscopy was also performed, and once again, the spectrum indicated that Egyptian blue pigment was used. Egyptian blue is a calcium copper tetrasilicate with the chemical formula $CaCuSi_4O_{10}$, which has been used as a pigment for centuries. However, in the mid-20th century, a natural mineral with the same composition as Egyptian blue was discovered in the lava of Mount Vesuvius, and it was named "cuprorivaite".

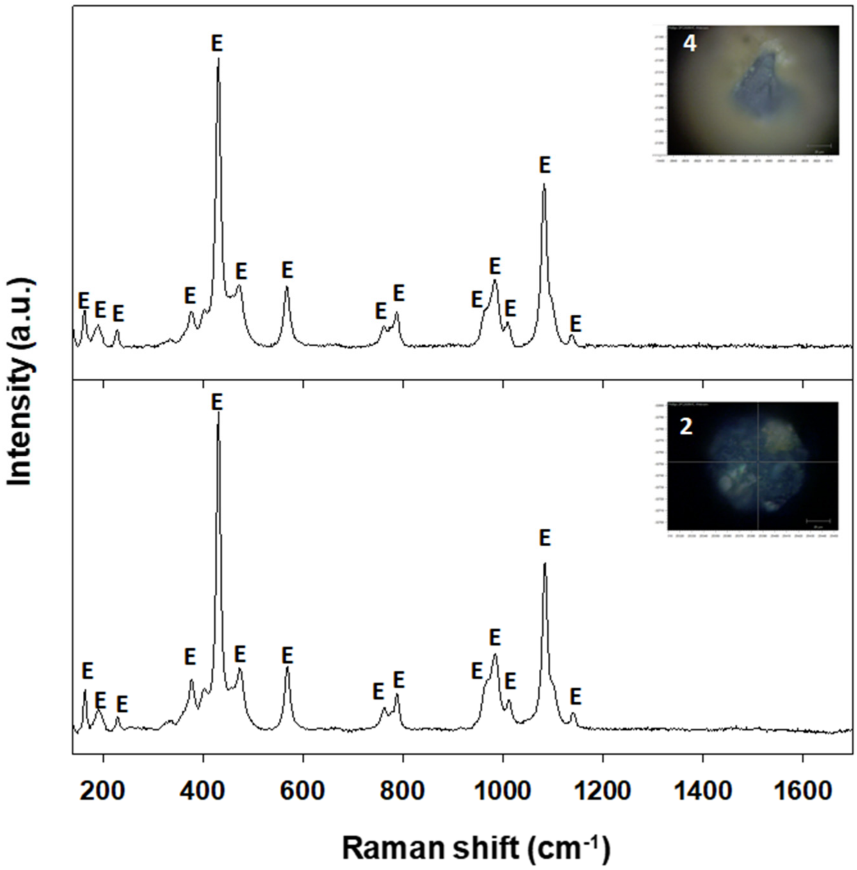

Figure 9. Raman spectrum of zones 4 and 2 of the fragment. The microphotographs of the areas where the spectra were acquired are shown as insets. Legend: E, Egyptian blue.

The Raman study was completed by recording the spectrum at a point on the line marked with the number 4 (Figure 9), which corresponded to the layer beneath the white line. As seen in the microphotograph shown in the inset in Figure 8, the spectrum was similar to that previously described for Egyptian blue.

3.4. Binding Media Extraction Results

In ancient Rome, pigments were applied using either the fresco or the secco technique. Although not all mural paintings were created using the fresco method, they were commonly referred to by that name. The fresco technique involved applying pigments onto lime mortar while it was still wet. The secco technique relied on an organic binder, such as egg, fat, or gum, to ensure pigment adhesion [46–48]. This often allowed pigments to be applied directly onto a surface without the need for a prior coating of calcium carbonate or gypsum. Additionally, there was another technique known as "encaustic painting", which involved mixing pigments with wax to enhance adhesion [49,50].

The study of organic compounds presents a complex analytical challenge due to the difficulty of preserving organic residues in archaeological samples. Specifically, identifying the organic binder within a mural painting sample involves a tedious process because in most cases the amount of organic material that has survived over time is minimal or non-existent due to degradation processes. The scarcity of archaeochemical studies focused on organic binders highlights the significant difficulty of analyzing such samples. However, in recent years, some studies using archaeochemical techniques have confirmed the use of various organic binders, such as beeswax, fats, and/or proteins [46,49].

The study of the extraction and determination of the used binder was carried out on the decorative areas of the polychrome fragment. The chromatographic analysis showed only the presence of methyl esters in the hydrolysis and derivatization tests performed, as shown in the chromatogram in Figure 10, where methyl esters of palmitic and stearic fatty acids were identified and, in smaller amounts, oleic and tetradecanoic acids. These results made the use of a secco technique plausible, using a fat as the binder, although it was not possible to determine its exact nature.

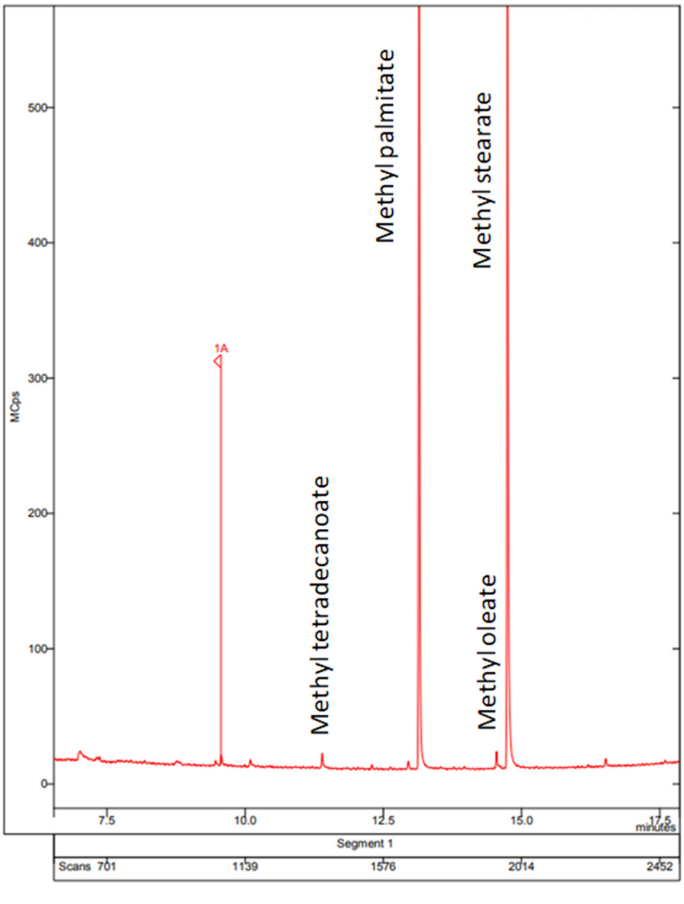

Figure 10. Chromatogram of the derivatization product with TFTMAH of the mural paint sample from fragment 1.

4. Discussion

From the archaeological point of view, the fragments confirmed the existence of a rich ornamental program that, based on its characteristics and given the scarcity of fragments, must have been part of an assemblage datable to around the middle of the first century AD and whose characteristics we observed in productions of the last phase of the third and in the fourth Pompeian style. Thus, it could have been part of the decorative program developed following the reform of the building dated to the middle of the aforementioned century, a time when different pictorial assemblages from the tombs of Carmona can also be placed. The plinth decoration did not constitute a scheme we could associate with spaces that had a specific function. However, plant themes, especially garden imitations, are a recurring theme in Italic baths [51], although uncommon in Hispanic baths [52]. It is worth noting the depiction of a native bird in the breeding period, which suggests the direct observation by artisans who must, therefore, have been responsible for different decorative assemblages in Carmona and the surrounding territory, given that the bird's habitat is concentrated in the Bay of Cadiz and the Doñana marshes.

More interesting from the interpretative point of view was the fragment from the middle zone. This was because the presence of the column and the different bands allowed us to hypothesize the existence of an aedicule or even a figurative scene, which would make the room more important than a simple storage space or auxiliary area. Therefore, we must consider that it could have functioned as another main space in the complex, perhaps within the cold cycle. In this respect, we should remember that most of the pictorial decorations with figures found in Hispanic baths are documented in *frigidaria* [52], probably because they were better preserved in those spaces.

Although its restoration meant it was not possible to apply the archaeochemical analyses to the plinth decoration, they did provide interesting technical data regarding the decoration of the middle zone and the cornice. The composition of the mortars did not differ from the general data obtained to date in other studies of Hispanic painting [52,53], apart from the absence of gypsum, which is more clearly detected in the Ebro Valley [54]. The XRD and XRF results showed similar compositions with a calcite base, with the presence of quartz only in the fragment with the column motif. This was in line with the data obtained from the visual analysis, which showed a much more refined mortar for the cornice and hardly any aggregates. Regarding the interpretation of the room's function, although the materials that made up the mortar did not show hydraulic properties that indicated a relationship with a room with water, the percentage of elements that showed these hydraulics was very low, so it could not be ruled out that they did.

The Raman spectroscopy study of the pigments confirmed the hypotheses put forward on the basis of macroscopic observation, confirming the use of hematite for the red, goethite for the yellow, Egyptian blue for the blue, and calcite for the white, all widely attested in other studies. However, the analysis was complemented by the reading of the pictorial layer of the fragment with the column, which confirmed the use of fresco and secco already documented in the visual analysis. Thus, only the red background seemed to have been executed al fresco, given the superimposition of the rest of the pigments that made up the motifs. In this respect, although the presence of calcite was documented in the red and yellow samples, in the first case it must have been due to the calcite present in the preparatory layer, while in the case of the goethite it was feasible to believe that it was combined for its application by means of a fresco–secco technique. Only in the case of the column was it possible to clearly establish the presence of an organic binder, which clearly corroborated the mixed technique already mentioned in the written sources. Despite this, the identification of this type of component in Roman pictorial production is uncommon due to its disintegration over time. Examples of the use of wax and plant components have been found in the painting of the House of the Bracciale d'Oro in Pompeii and the Villa dei Papiri in Herculaneum, although it is not possible to determine the specific type or whether their presence is due to an ancient restoration [48]. Similar results are provided by the analyses carried out on the paintings of a *domus* in Santa Maria Capua Vetere, in which several fatty acids derived from methyl esters were identified, in particular palmitic and steric acids associated with animal and vegetable matrices, which make it impossible to determine their exact provenance. However, the presence of abietic acid, considered a marker identifying the use of pine resin, was also documented [47,55]. Recently, the presence of beeswax has been identified in the *triclinium* of the House of the Satyr in Córdoba, dated to the second century AD and associated with the architectural decoration of the upper area [49].

5. Conclusions

The results obtained therefore confirmed a rich pictorial program dating from around the middle of the first century AD. It included the use of compositions that suggested a possible association of the space with the cold areas of the baths complex, specifically one that did not have a pool because it lacked a half-round pavement. This was supported by the technical quality used in its execution and confirmed by archaeochemical analysis for the middle zone, revealing the use of fresco and fresco–secco, based on the identification of a vegetal binder.

The study of the pictorial remains found in the baths in Julián Besteiro Square in Carmona constitutes an interesting testimony to the town's ornamental programs. The analyses carried out allow a clearer approach to our knowledge of wall painting in Roman Carmo, which until now has been practically non-existent, apart from the funerary painting. They have also provided information on the execution practices and techniques of pictorial artisanship.

This series of fragments allows us to broaden our vision of the pictorial production of the city beyond the known repertoires of the funerary sphere, being one of the few examples of public thermal spaces with painting before the second century AD.

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