INTERNATIONAL JOURNAL OF CONSERVATION SCIENCE

ISSN: 2067-533X Volume 14, Issue 1, January-March 2023: 3-18 www.ijcs.ro

DOI: 10.36868/IJCS.2023.01.01

# FTIR AND THERMOGRAVIMETRIC ANALYSIS OF ANCIENT MORTAR FROM AL-AMUWAQQAR EARLY ISLAMIC BATHHOUSE IN JORDAN FOR CONSERVATION USE

Ruba SEISEH[1], Abdulraouf MAYYAS[2], Hussein AL-SABABHA[3], Wassef AL SEKHENEH[3,*], Jürgen POPP[4]

[1]Department of Cultural Resources Management and Conservation, School of Archaeology and Tourism, The University of Jordan, Amman, Jordan
[2]Department of Conservation Science, Queen Rania Faculty of Tourism and Heritage, The Hashemite University, P.O. Box. 330127, Zarqa 13133, Jordan
[3]Department of Conservation and Management of Cultural Resources, Faculty of Archaeology and Anthropology, Yarmouk University, Irbid, Jordan
[4]Leibniz Institute of Photonic Technology (IPHT), Chair of Physical Chemistry at Friedrich Schiller University, Jena, Germany.

***Abstract***

*This paper aims to analyze and evaluate the function of two types of ancient mortars in the bathhouse at al-Muwaqqar archaeological site in Jordan to promote the awareness level of cultural heritage conservation of ancient buildings and mortars in Jordan. The conservation of archaeological structures requires a thorough characterization and identification of the mortar components before carrying out the restoration, after the preserved results, and during the restoration process to decide how it responds. This work creates an experimental contribution through FTIR to study the influence of organic components on the mechanical performance of the mortar. The application of new techniques in terms of sustainability and compatibility is nowadays more and more important to preserve historical monuments, especially in the context of the increasing damage to the mortar joints in the al-Muwaqqar site. The paper presents new results concerning the identification of the binding materials of mortars, especially the organic parts as egg white or other organic components used in the bathhouse to connect the mosaics, and the collection of further information for compatibility challenges. The results will provide a new pioneering approach application in Jordan in the field of ancient restoration using mortar. The study concludes that it is easy to identify all the organic components of the mortar using Fourier Transform Infrared spectroscopy (FTIR) in the different bands of the organic material supported by thermogravimetric analysis TGA/SEM-EDX. The investigations of both methods have provided accurate information about the technology of mortar production and have indicated a proteinaceous additive in the mortar.*

***Keywords**: FTIR, Mortar; Conservation; Al-Muwaqqar; Organic material; TGA; SEM-EDX*

## Introduction

Cultural heritage sites and monuments are the tangible assets of every country which indicate their stereotype, identity, and illustrious past. Jordan is known for its significant monuments and heritage sites, which testify to the architectural tastes of the population. Due to the rich diversity of ancient cultures, Jordan has preserved numerous temples, mosques, bathhouses, churches, and theaters that manifest the form and approach of the people to

* Corresponding author: Sekhaneh@yu.edu.jo

promote their interests. This study aims to increase awareness of the importance of conserving ancient buildings and mortars to promote them as part of Jordan's cultural heritage and tourism. The work concentrates on sustainability goals and heritage management to contribute to the improvement of the interventions in ancient monuments and structures to avoid the tragic destruction of external and internal mortar that is used in the historic facades and buildings in Jordan [1]. Fundamental elements of the building have to be examined; besides their protective function, they often have an important enhancing function, therefore, these coatings and mortars need to be preserved because of their technical, historical, and aesthetic importance. Therefore, the objective of this paper is to use the compatible materials and techniques used by plastering or coating materials. Emphasis is given to the butted material, the hand-rammed mud, the making of crushed bricks, and the mortars for covering and laying the walls of the buildings under study.

Installing restoration and conservation of cultural heritage sites in any country is necessary to sustain the culture and heritage of societies. However, these processes can be challenging as they require a lot of attention. One of the challenges facing conservators is the inability to find suitable materials used in the past to effectively restore the site closer to its original form. On the other hand, using available cementitious binders during the restoration process may damage the old materials. For this reason, it is necessary to study these ancient materials and develop similar materials with similar properties. The surrogate material should have similar mineral composition and physical properties to prevent damage during and after restoration.

The first use of a pyrotechnically produced inorganic binder dates back to the Epipalaeolithic period (ca. 12,000 BC) in the Levant, as a lime-based cement for assembling a flint microlith tool at the Kebaran geometric site Lagama North [2, 3]. The first phase of the cycle involves heating calcareous rock or calcium carbonate ($CaCO_3$) between 800° and 1000° C, during the heating process, about 44% of carbon dioxide is released (Fig. 1). This reaction results calcium oxide which is called quicklime:

$$CaCO_3 \rightarrow CaO + CO_2 \qquad (1)$$


**Fig. 1.** Lime cycle

Figure 1 shows the lime cycle where carbon dioxide ($CO_2$) is released during the combustion process and quicklime (CaO) is produced. Then the quicklime is slaked with water, it forms $Ca(OH)_2$, then through carbonization or absorption of carbon dioxide ($CO_2$) back to limestone, after returning to nature, the lime absorbs $CO_2$ from the air, what returns to $CaCO_3$. Quicklime cannot be directly used in construction; it is necessary to apply the slaking process which involves adding water to quicklime in a controlled environment to produce slaked lime:

$$CaO + H_2O \rightarrow Ca(OH)_2 \quad (2)$$

The quenching reaction is highly exothermic. Therefore, the consequent increase in the temperature then part of the water evaporates and another part absorbs by the lime which disintegrates, strongly increasing its volume. The lime cycle ends with the carbonation phase in which there is the transformation of calcium hydroxide into calcium carbonate according to the following reaction:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \quad (3)$$

In regions where dolomite is the prevalent carbonate rock, the most used lime is magnesian lime. The dolomites are heavier and harder than carbonate rocks and contain primarily the mineral dolomite. Dolomite limestones ($MgCa(CO_3)_2$) are calcined at the same temperature as pure carbonates, but there is evidence that if dolomite is calcined at a temperature between 750° and 820°C the resulting reaction is a mixture of calcite and periclase (MgO) that can cause hydraulic setting as expressed in the following reaction:

$$MgCa(CO_3)_2 \rightarrow CaO + MgO + 2CO_2 \quad (4)$$

During the quenching process, calcined dolomite reacts more slowly than pure lime. When it is quenched in a pit for many months, all the magnesium oxide has time to hydrate; calcium hydroxide and magnesium hydroxide will form two different layers because $Mg(OH)_2$, which is denser, will sediment in the bottom of the pit. The quenching reaction is:

$$CaO + MgO + 3H_2O \rightarrow Mg(OH)_2 + Ca(OH)_2 + H_2O \quad (5)$$

For the magnesium component, the cycle also closes with a quenching reaction:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O \quad (6)$$

Depending on the amount of water added to the slaked lime, the result is

- the slaked lime, a thick and unctuous white paste that dried in the air with large cracks;
- the milk of lime or an excess of water, a much less consistent than the slaked lime (20-30% of water and the rest of lime) used for painting. Fat lime was recommended for this use.

Lime is a very old binder used as a building material; it was used in plaster in the Neolithic period, and firstly comes across the Mycenaean and Minoan civilizations (1700 BC) at the palace of Knossos [4]. It was used much later (300 BC) in Egypt. In Roman times, lime was a binder widely used in manufacturing hydraulic mortar by mixing it with artificial or natural pozzolanas well as in ordinary mortar manufacture [5, 6].

## The Site

Al-Muwaqqar district (liwa'in Arabic) which became affiliated with the Amman Municipality is located approximately 30 km southeast of Amman on the eastern edge of the cultivated land at the transition to the semi-arid steppe east (Fig. 2). The liwa' of Al-Muwaqqar consists of a population of 47,753 people and an area of 608.5 km2 (Information regarding the population and area was taken from the electronic site of the Ministry of Interior on March 11$^{th}$, 2022). It is surrounded by three other districts, al-Jizah from the South, Na'ur from the west, Sahab from the North, and the governorate of al-Zarqa from the east .

The region enjoys a distinguished geographical location as it overlooks desert lands to the east and agricultural lands to the west. It also controls the crossroads roads to Qasr Al-Kharranah and Qasr Al-Mashash in the east, and Al Qastal in the south. It is characterized by a mild climate in summer and cold and rainy winters.

The area of al-Muwaqqar holds various antiquities from different periods, the oldest dating to the paleolithic period (c. 1,500,000 to 19,000 BCE), Neolithic period (c. 8500 to 4600 BCE), Roman period (64 BCE to 323 CE), Umayyad period (661 to 750 CE), and Abbasid period (750 CE to 1258 [7]. The bathhouse complex which is related to the palace is located about 700m southeast of it (Fig. 3) [8-10].

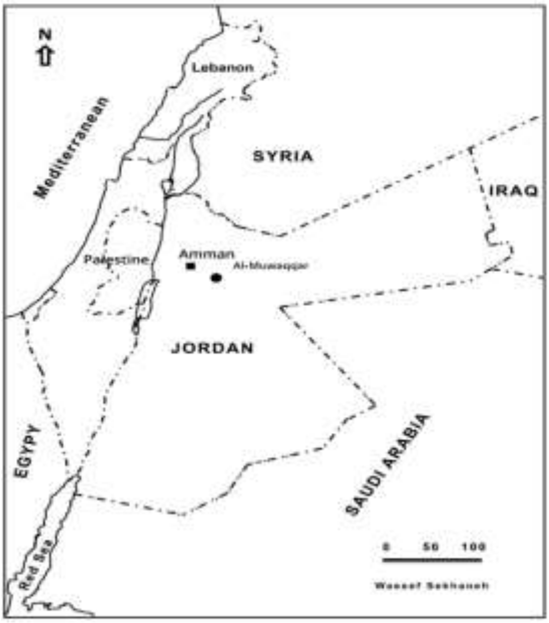


**Fig. 2.** Location of al-Muwaqqar Site

**Fig. 3.** Al-Muwaqqar Palace and Bathhouse Complex (Oliver Pilz)

The first time that the archaeological excavations were carried out in the study area, which is the area of the bathhouse complex, was in 2007 by Mr. Ibrahim Al-Zeben from the Department of Antiquities of Jordan (DoA) where the mosaic floors were first revealed in 1949, which was the reason for an accidental archaeological excavation at the site in 2007. In June 2021 in collaboration with the Madaba Institute Mosaic Art and Restoration (MIMAR) carried out a thorough cleaning of the bathhouse complex as well as some preparatory conservation of the mosaic floors, where the outer edges of the mosaic floors were reinforced with a layer of mortar. Also, documentation and conservation works were carried out in some different places in the early Islamic bathhouse complex and for the mosaic floors in the 22 August to 1 October 2021 season, which was funded by the Embassy of the Federal Republic of Germany in Jordan, through the Cultural Heritage Preservation Program of the German Ministry of Foreign Affairs, and was implemented by Professor Dr. Oliver Pilz the visiting Professor from the University of

Mainz and DAAD delegate at the School of Archeology and Tourism in the University of Jordan.

The bathhouse complex in Al-Muwaqar's site was subjected to illegal tampering and destruction several times, which led to the detection of several archaeological areas, which exposed them to natural and human factors of damage. Given the importance of the site archaeologically and historically, it deserves more attention and protection by the government authorities, especially the DoA, to protect it from theft by and vandalism and modern urban sprawl towards the archaeological site which may cause the loss of many monuments. Hence the importance of this study, which focuses on the reuse of old mortars in preserving and restoring archaeological monuments to keep them alive for as long as possible.

## Material and Methods

Three samples of Umayyad mortar (Sample 1, Sample 3) were collected from the north-west corner of the reservoir, the second sample is collected from under the mosaic floor from room 2, and the third sample from the paved room 7, (Figs, 4, 5 and 6).

**Fig. 4**. The reservoir (source: Oliver Pilz)

It is important to note that conservation and restoration methods vary depending on the type of deterioration and the materials required for conservation. Therefore, any restoration work requires a careful prior study of the state of preservation of the coating, which must be carried out by an expert, so that the methods and materials used can be properly determined. Therefore, the use of modern technologies to conduct this work is required.

Most of man's architectural heritage was constructed using lime mortar, one of the most important building materials used throughout history. Its applications and purposes are and have been very diverse, ranging from structural to purely decorative functions. The study uses modern analytical techniques to determine raw materials and manufacturing technology. Petrography (thin section), X-Ray Diffraction (XRD), electron microscopy, infrared spectroscopy, and thermogravimetry all were utilized to investigate the mortar. On the other hand, there are some properties such as specific gravity, bulk density, void content, and porosity that should be taken into consideration. The role of this study is to work, protect and preserve local cultural heritage through the characterization of ancient mortar. Therefore, knowledge of traditional materials and techniques is bridging cultural diversity for competitive advantage, for future generations to preserve and protect local cultural heritage.

**Fig. 5.** Room 2 the mosaic floor (source: Oliver Pilz)

**Fig. 6.** Room 7 a paved room, one of the bathhouse complex rooms (source: Oliver Pilz)

## Results and Discussion

The chemical composition of the mortar was determined under an electron microscope using Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray analysis (EDX). Mainly it consists of quartz, calcite, alumina, and a little quantity of Ferrous oxide. The characterization of mortars is usually carried out by a combination of macroscopic observations, and mineral and microchemical techniques. First, a preliminary naked-eye test of specimens is conducted followed by studies on thin sections, which allow basic information about the main characteristics and properties of these man-made materials to be obtained. The data collected via (EDX), X-Ray diffraction (XRD), scanning electron microscopy with dispersive X-ray spectroscopy (SEM-EDX), and thermogravimetric analysis (TGA) greatly enhance the information acquired by the preliminary studies and allow a complete characterization of the binder and aggregate fractions. It is necessary to understand the chemical and mineralogical composition, texture, microstructure, and grain size distribution to generate a final product of effective conservation. The study of mortar antiquity provides essential information about the construction technologies used in the past, characteristics of the construction materials, phases of construction, questions of provenance, evaluation of the relation between binder/ aggregate ratio, as well as composition for restoration purposes.

***FTIR Spectroscopy***

The most compatible replacement mortars are those that have chemical, mineralogical, physical, and mechanical characteristics which are similar to the original. To ensure compatibility, it is essential to first determine the characteristics of the existing materials. Therefore, a well-founded knowledge matrix can be developed to support future conservation and renovation interventions.

For properties of significant historical value, the first option for conservation of the ancient mortar or plaster must be through suitable techniques for its preservation according to the international charters. If this is not feasible, a consolidation operation is selected as the humblest level of intervention. If the level of degradation of the place is already advanced, one should choose a partial replacement of the coating. Infrared spectroscopy is the method by which the absorption or emission of radiant energy caused by the interaction between electromagnetic radiation and the material under study is analyzed. Infrared spectroscopy is based on the fact that molecules can rotate and vibrate at different frequencies (normal vibrational modes). In other words, a molecule can absorb photon energy in the infrared range. The molecule which has a dipole moment will rotate or vibrate. The molecules vibrate when the frequency associated with the radiation resonates with the vibrational movement, allowing to identify of functional groups of organic molecules. The interpretation will use reference tables and software. The bands will be analyzed by considering the position in wavenumber, intensity, and shape of the peak, to identify the compounds that are present in the samples.

Fourier Transform Infrared spectroscopy (FTIR) measurements analysis was performed on the samples to 32 scans, in the wavenumber range from 4000 $cm^{-1}$ to 400 $cm^{-1}$, with a resolution of 2 $cm^{-1}$, the equipment brand Bruker, model Tensor 27, from the laboratory of the Faculty of Archaeology and Anthropology at Yarmouk. The samples in powder form were applied in their natural state directly to the sample holder of the instrument.

The spectra of the FTIR absorption signals (Fig. 7) belong to the inorganic and the organic part as additive materials to the mortar samples. All are recognizable from the absorption peaks of the binder components, mainly calcite $CaCO_3$. This is evident from the sharp peaks of in-plane C-O bending ($\upsilon 4$) at 710 $cm^{-1}$ and out-of-plane C-O bending ($\upsilon 2$) at 870 $cm^{-1}$ [11-13]. The sharp peak at 870 $cm^{-1}$ demonstrates the detection of carbonates in the spectra of the old mortar samples of al-Muwaqqar. In addition, the broad peak of the C-O multiband for organic material centered at the asymmetric stretching ($\upsilon 3$) at 1433 $cm^{-1}$ [14]. There are peaks at 1805 $cm^{-1}$, and 2515 $cm^{-1}$, and all are assigned to $CaCO_3$ [15, 16]. Pozzolan can be seen in the spectra; it is present in a small amount in the studied mortar and is characterized by the vibrational mode of the symmetric vibrational mode of the strong band Si-O of silica at 1140 $cm^{-1}$ [17, 18]. Saravanapavan and Hench found in their study that the strength of the main maximum of the Si-O-Si stretching vibrations increased and shifted with a decrease in the calcium content in the calcium silicate structure [19, 20]. This means that there is more silicate material in the mortar of the mosaic floor in the bathhouse sample (Sample 2) [18, 20, 21]. The absorption band around 870 $cm^{-1}$ is attributed to the Si-O mode of quartz in the samples [22, 23]. Since sand is a major component of the old mortar, absorption peaks for the mineral quartz should be present in the measured spectrum. These were identified in both spectra and are based on the Si-O stretching peak at about 487 $cm^{-1}$ [24]. There is a group that has significant amounts of iron in the mortar sample, which was completed by the presence of the Fe-O bending peak for the mineral Ferrous oxide at 610 $cm^{-1}$ [25].

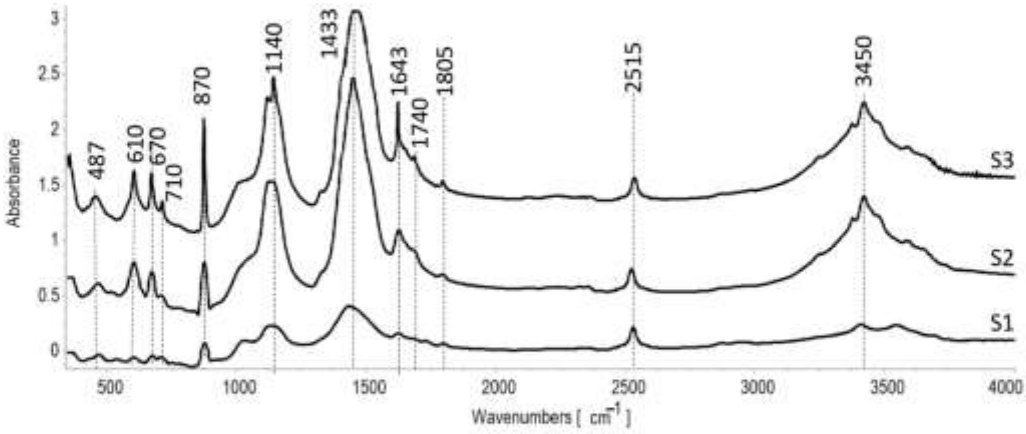


**Fig. 7.** FTIR absorption bands of the inorganic and the organic part as additive materials to the mortar samples

There are several examples of conservation or restoration interventions that have accelerated the damage to the authentic historic structure because incompatible materials and treatments were applied. Therefore, the development and the use of evaluation techniques for appropriate conservation are crucial. To know the approximate composition of historic mortars, and the proportions of lime and sand (binder and aggregate). The resulting spectra (Fig. 7) were smoothed by Fast Fourier Transformation (FFT) and then the frequency range from 1750 to 1650 $cm^{-1}$ (amide I) is shown for further analysis of egg white as new innovated results in mortar studying in Jordan. This band is largely due to the C=O stretching vibrations of the peptide linkages and is very sensitive to the secondary structural components. The quantification of the secondary structure of proteins of egg is based on the assumption that proteins can be viewed as the linear sum of the certain basic secondary structural elements: α-helix, β-sheet, β-turn and random (or disordered) structure. After baseline correction, the amide I band decomposed into components of Gaussian curves (Figure 7).

***SEM-EDX Spectroscopy***

The mortars in their entirety showed calcium as the element in greater quantity in the EDX analysis supported with SEM images which are shown in figure 8, followed by silica and iron. The high content of calcium and silica indicates the presence of sand as a siliceous aggregate which was verified by the disaggregation of the material. The mortars Sample 1, Sample 2, and Sample 3 showed the highest percentage of calcium in their EDX results, followed by silica and iron. These samples also showed magnesium, aluminum, potassium, zirconium, strontium, manganese, titanium (except for sample Sample2), and zinc (except for sample Sample1), which probably indicates the presence of clay in these mortars as will be confirmed in the X-ray diffraction results (see figure 8). In addition to the elements mentioned, sulfur in the mortar samples1 mortar. The internal Sample2 was the mortar that had the greatest divergence regarding the chemical composition of the others, as it did not present magnesium and aluminum in its EDX result and after lime, the next element in greater quantity is iron oxide. This expressive percentage of iron indicates the presence of the Ferrous oxide compound, as will be shown in the X-ray diffraction results, and explains the particularity spectra of the samples when compared to the others.

The mineralogical compositions identified in all mortars are consistent and additional to the results of the EDX analysis of the samples presented in table 1. The diffractogram of the mortars (Samples 1, 2, and 3) showed similar results, corroborating their EDX. The predominant peaks detected correspond to quartz (Q), calcite (C), and, to a lesser extent, anorthite (A) and kaolinite (K), except for Sample 3. Kaolinite can be confirmed by the use of unwashed sand in the mortar composition, which indicates the presence of clay in the mortar. The existence of anorthite can be explained by the presence of calcium and magnesium. Anorthite is a product resulting from the calcination of bentonite clays, used as raw materials in the presence of calcite. In the result of Sample 2 mortar diffractogram, the appearance of Ferrous oxide (F) is identified in addition to the predominant peaks corresponding to quartz (Q) and calcite (C). The appearance of this ferrous oxide compound confirms the existence of the intense amount of iron in this sample and its peculiar color, as already mentioned in its XRF result, making it different from the other samples of mortar from the plant.

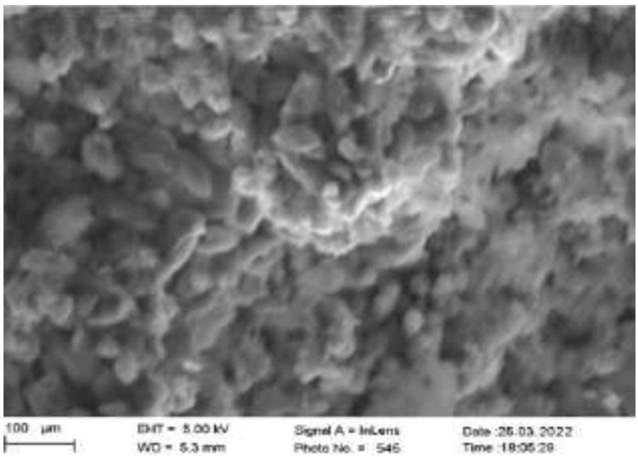


**Fig. 8.** SEM images of sample mortar

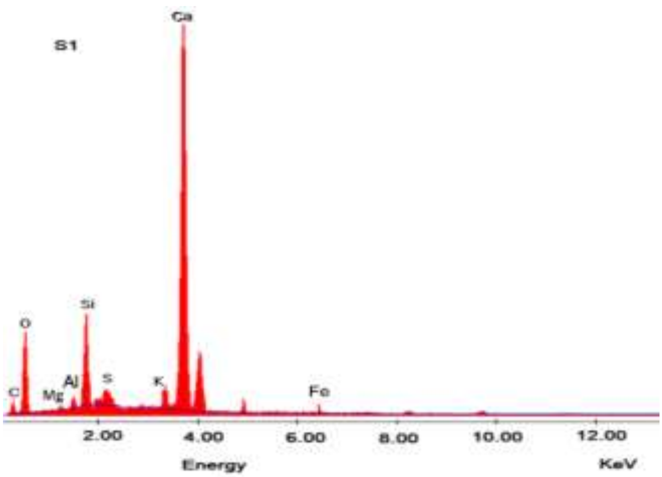


**Fig. 9.** Energy Dispersive X-Ray Analysis (EDX). Mainly it consists of Si as quartz, Ca as calcite, Al as alumina, and a little quantity of Fe as Ferrous oxide.

**Table 1**. Percentages by weight of elements and oxides obtained in EDX analyses taken from different parts of the mortar sample.

| | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|
| **Ca** | 19.13 | 12.47 | 33.52 |
| **Mg** | 3.42 | 4.17 | 0.72 |
| **Si** | 11.12 | 17.63 | 7.32 |
| **Al** | 4.28 | 7.17 | 2.93 |
| **Fe** | 4.39 | 4.05 | 1.68 |
| **K** | 1.91 | 2.87 | 1.16 |
| **Na** | 0.43 | 0.83 | 0.39 |
| **Cl** | 0.28 | 0.39 | 0.21 |
| **Ti** | 0.20 | 0.28 | 0.11 |
| **O** | 54.84 | 50.14 | 51.96 |
| **CaO** | 35.15 | 25.03 | 60.55 |
| **MgO** | 7.10 | 6.49 | 2.72 |
| **$SiO_2$** | 36.55 | 41.21 | 20.77 |
| **$Al_2O_3$** | 11.26 | 14.77 | 9.52 |
| **FeO** | 6.78 | 7.63 | 3.11 |
| **$K_2O$** | 2.49 | 4.11 | 3.01 |
| **$TiO_2$** | 0.67 | 0.76 | 0.32 |

### Petrography

The examination of thin sections under the polarizing light microscope is considered as a prime tool for identifying the mineralogical constituents and the fabric [4]. The mortars were pre-consolidated by impregnation in a resin under vacuum. Thin sections were then cut and polished to the standard thickness of 30μm, covered with a glass slip, and examined using Leica refracted polarized light microscope. Petrographic inspection of the thin sections allowed specifying the raw materials. Petrographic analysis proved that the studied mortars influenced a homogeneous interrelated binder exhibiting a durable binder aggregate bonding. The lime binders are fine-grained hardly showing fractures (Fig. 10).

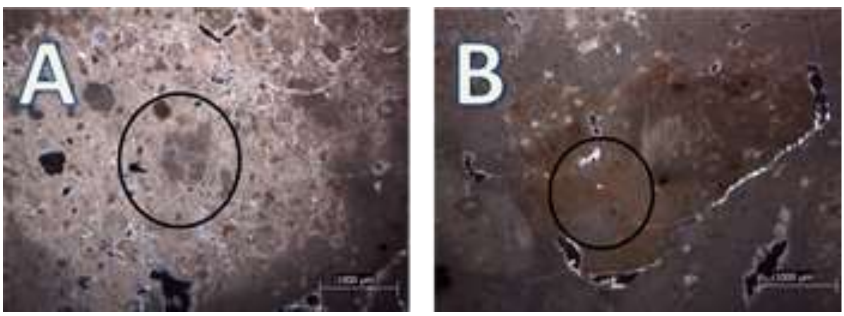


**Fig. 10.** Thin sections under the polarizing light microscope: **A**. compact durable binder aggregate; **B**. iron stains

The petrographic analysis demonstrated that about two-thirds of the studied mortars are in good condition (durable) and still functioning as they were meant to be (Fig. 10).

Samples showed lime's high specific surface and low shrinkage which suggests the raw limestone was soft burned. According to Boynton and Gutschick [26], the lower temperatures and the shorter burning duration produce the desirable soft-burned, highly reactive limes with low shrinkage and high porosity. On the contrary, high burning temperatures and long calcining periods produce hard-burned quicklime that has high shrinkage, low porosity, and low chemical reactivity. The petrographic analysis is poor in delivering data concerning lime slaking nevertheless, the observation of the fine-grained retro fabrics of the binders and the absence of over-burned and under-burned lime lumps shows good plasticity and workability of the lime. Whereas the absence of fractures corresponds to a high-water retention capacity. As well as the absence of unslaked lime lumps corresponds to a long, and slow slaking [26].

According to petrographic analysis, mortars were made with non-hydraulic lime which shows a highly developed technology of lime mortar production using a pure carbonate rock for lime making.

***X-Ray Diffraction***

Mortar samples were subjected to X-Ray diffraction (XRD) analysis. X-ray diffraction tests were performed using a Shimadzu LabX, XRD-6000 X-ray Diffractometer, in the Archaeology Laboratory at Yarmouk University. The test consists of the incidence of an X-ray beam that interacts with the crystalline planes of the sample, changing the direction of its propagation, generating a spectrum with the characteristics of the crystallinity of the mortar sample. During the characterization of the samples, the equipment operated with the Copper $KL_{2,3}$ ($\alpha_{1,2}$) Radiation ($\lambda$ = 1.5418Å) was used for the analysis and, at a voltage of 40kV and a current of 30mA, in sampling pitch of 0.02º, preset time is 0.60 seconds, drive axis is Theta-2Theta in the scanning range from 3º to 60º and a scan speed of 2º/min. For sample preparation, a small amount of mortar powder has been taken, then shuffled and distributed throughout dissolved in ethanol and spread on a microscope slide. After evaporating ethanol, the slide was placed in the XRD instrument for analysis, the material was pressed against the sample holder to distribute it evenly. It was verified that the sample was ready when the sample holder was turned vertically, and the samples did not fall. The assignment of minerals was based on the database of the Joint Committee Powder Diffraction Standards International Center for Diffraction Data (JCPDS-ICDD).

***Thermal Analysis***

This method is very important for the study of phenomena subject to pyrolyzes, such as many metals and inorganic substances, as well as for the pyrolysis of organic materials. It has therefore been used to investigate whether an old mud sample contains organic materials as well as minerals that have lost mass due to high temperature. It is a quantitative method that allows an indirect evaluation of the aqueous or carbonate phases that have formed in the mortar over time. It can be divided into two parts or ranges: (a) mild loss of 3% between room temperature and 170°C, agreeing to the outflow of moisture and adsorbed water; (b) a marked loss of 23% between 410°C and 600°C, with a peak of mass outflow at 800°C with 60% loss (Figures. 11 and 12).

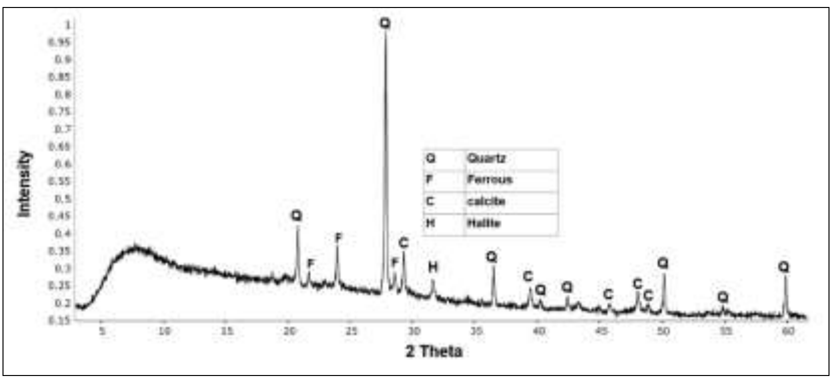


**Fig. 11.** XRD spectrum of sample S1. C: calcite ($Ca(CO_3)$), Q: quartz ($SiO_2$), F: ferrous oxide (FeO), H: halite (NaCl).

The loss of the material referes to the decomposition of calcite ($CaCO_3$), with the emission of $CO_2$ (pyrolysis). In this case, this loss occurred in a lower temperature range than that of natural calcite, from limestones and marbles, which shows this peak at a higher temperature. This is indication that the calcite present in the sample is not natural, but generated by the carbonation of hydrated lime, which was present in the fresh mortar. The thermogravimetry data are consistent with the loss of ignition and moisture content determined in the quantitative chemical analysis. The XRD results indicate that calcite as a binder is the main constituent of all samples of historic mortar from the site and that quartz is present in the aggregates, a mineralogical composition already found in other samples of the mortar composition as shown in figure 11.

***DSC of the mortar samples***

The DSC curve of the mortar is shown in Illustrations (Figs. 12 and 13). The analysis indicates a pure lime mortar in which most of the binder is usually composed of calcite ($CaCO_3$) without the presence of hydraulic components. The hygroscopic property of hydraulic components has no significant endothermic peak, it is observed in the range of 100–450°C. This analysis allows hydraulic mortars to be distinguished from lime mortars since the latter contain a lower amount of absorbed water [26]. TG-DTA (Thermo-Gravimetric/Differential Thermal Analyzer) analyses were performed by the thermal analysis to determine the weight loss of mortar samples with temperature increases that were conducted by a TGA-DTA instrument with a heating rate of 5°C/min and a maximum temperature of 1000 °C. As can be seen from the TGA-DTA curves, there is mobility in the TGA and DTA curves as the samples lose their moisture content between 100-200°C temperature values. The transformation to MgO begins at about 450 ºC and concludes at about 780ºC. The mass losses in the mortars at certain temperature ranges in TGA analysis are given in table 1. When these results are evaluated together with the DTA analysis, the decrease in the mortars between 25-120ºC temperatures is the physical water content absorbed by the pores in the mortar.

The decrease between temperatures of 120 ÷ 200ºC due to the removal of water in the structure of hydrated salts in the samples, the decrease between temperatures of 200 ÷ 600ºC due to the removal of rigid bound water (chemical water) in hydraulic phases such as C-S-H and C-A-H in the structure, at the temperatures between 600 ÷ 1000ºC is due to the removal of carbon dioxide ($CO_2$) in the structure of $CaCO_3$.

In figures 12 and 13, the mass losses in the mortars at certain temperature ranges in TG analysis. The study indicates the thermal properties of mortars found the amount of $CO_2$ in non-hydraulic mortars and it was above 30%, and the amount of water is below 3%.

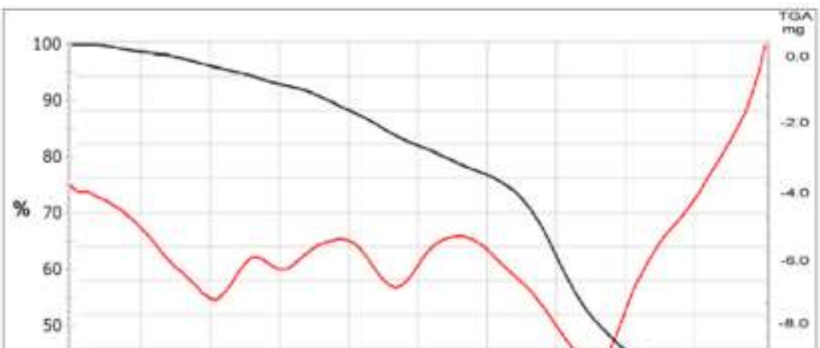


**Fig. 12.** Hydraulic properties of sample 2 were determined by TG/DTA analysis, which observed the mass losses against temperature changes, 23-850˚C.

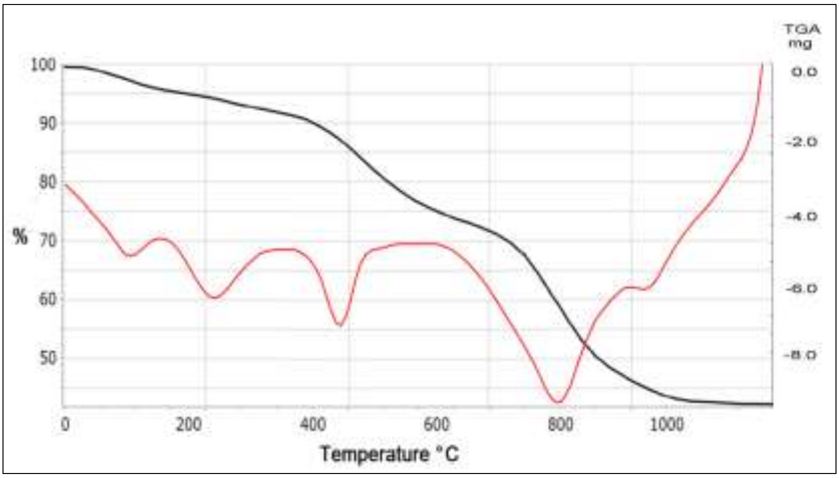


**Fig. 13.** Hydraulic properties of sample 3 were determined by TG/DTA analysis, which observed the mass losses against temperature changes, 23-850˚C.

Linseed oil comes from flax. It contains acids called omega-3 (alpha-linolenic acid) and omega-6 fatty acids (linoleic acid) also contain phytoestrogens. Flaxseed oil serves as a sealing and hydrophobic additive in mortar. Lard-pork, but also poultry fat, has been involved in human nutrition for many centuries among important energy sources [27-29].

## Conclusions

The principal objective of this study was to characterize the mortar binders used in the bathhouse to obtain new evidence about this important site in al-Muwaqqar, which can be deemed suitable for the restoration of the archaeological buildings on the site. This study is focused on the use of FTIR spectroscopy to analyze ancient binders in archaeological samples. The study concludes that the FTIR method is effective in identifying the top components of carbonate and silicate materials in the samples. The results also indicate that the sample contains a significant amount of amorphous calcium carbonate, along with crystalline calcite and other constituents. Additionally, the study found that the silicate bands in the mosaic floor mortar were stronger than in the wall and column structures, which may suggest a higher proportion of silicate phases in the floor mortar. These findings demonstrate the usefulness of the FTIR method for investigating ancient binders and comparing them to contemporary restoration materials.

This study has investigated the use of FTIR and TGA/DTA to analyze the composition of egg white mix and mortars in archaeological samples. The results showed that the samples were mainly composed of various forms of pozzolanic and other organic materials, as well as protein-based materials. The study also concluded that gypsum was present in different amounts in both samples. The thermal analysis results showed that heating the mortars and adhesive pastes led to significant color changes, which were mainly attributed to the physicochemical transformations within the main components of the mortar and aggregates. The mineralogical composition of the old mortar was also found to play an important role in the color change slight color change with aggregates containing organic components undergoing a significant color change when heated above 250°C light gray color. The study observed the oxidation of iron components, such as limonite, Ferrous oxide, and goethite, through the observation of the FTIR bands. Further sampling of mortars along with the 2021 excavations and associated buildings is recommended to further expand the understanding of the composition of these materials.

**Acknowledgements**

The researchers are grateful to Professor Oliver Pilz for providing us with the archaeological samples, and for valuable discussions. Also, the researchers are grateful to Yarmouk University laboratories of the Faculty of Archaeology and Anthropology and Faculty of Pharmacy. Gratefully acknowledge Prof. Aya Akawi for proofreading this work. The researchers are also grateful to great Prof. Jürgen Popp group the Director of the Leibniz Institute of Photonic Technology (IPHT) in Jena and the Chair of Physical chemistry at Friedrich-Schiller-University in Jena.

**References**

[1] A. Powter, S. Ross, *Integrating Environmental and Cultural Sustainability for Heritage Properties*, **APT Bulletin**, **36**, 2005, pp. 5-11.
[2] O. Bar-Yosef, J.L. Phillips, P. Goldberg, *Prehistoric Investigations in Gebel Maghara, Northern Sinai*, Qedem, **7**, 1977.
[3] M. Secco, L. Valentini, A. Addis, *Ancient and modern binders: naturally nanostructured materials*, (Chapter) **Nanotechnologies and Nanomaterials for Diagnostic, Conservation and Restoration of Cultural Heritage**, **Advanced Nanomaterials series**, edited by: Giuseppe Lazzara and Rawil Fakhrullin, Elsevier, 2018, pp. 205-237.
[4] M.A.S. Cameron, **A General Study of Minoan Frescoes with Particular Reference to Unpublished Wall Painting from Knossos**, volume III, Catalogue to the plates and restorations of a thesis submitted for the degree of Ph.D. from the University of Newcastle upon Tyne, 1975, https://scholar.google.com/scholar?hl=ro&as_sdt=0%2C5&q=A+general+study+of+Minoan+frescoes+with+particular+reference+to+unpublished+wall+painting+from+Knossos&btnG=
[5] G. Artioli, M. Secco, A. Addis, *The Vitruvian legacy: Mortars and binders before and after the Roman world*, **EMU Notes Mineral**, 20, 2019, pp. 151-202.
[6] G.A. Smith, *The Traveler's Guide to Greek Archaeology: Getting the Most from your Mediterranean Trip*, **Friesen Press**, Canada, 2014.
[7] M. Waheeb, *The Second of Excavations at al-Muwaqqar*, **Annual of the Department of Antiquities of Jordan / Hashemite Kingdom of Jordan: ADAJ**, **37**, 1993, pp. 5-22.
[8] M. Waheeb, *Archaeological Rescue Survey of the Tafileh-Ghor Feifeh Road Alignment, Sections I+II*, **Annual of the Department of Antiquities of Jordan / Hashemite Kingdom of Jordan: ADAJ**, **37**, 1993, pp. 135-146.
[9] J.L. Bacharach, *Marwanid Umayyad Building Activities: Speculations on Patronage*, **Muqarnas**, **13**, 1996, pp. 27-44.
[10] A. Walmsley, *Production, Exchange and Regional Trade in the Islamic East Mediterranean: Old Structures, New Systems?*, chapter in **The Long Eighth Century. Production, Distribution and Demand**, Series: **Transformation of the Roman World**, volume 11, editors: Inge Lyse Hansen and Chris Wickham, Brill Publisher, Leiden, Boston, Köln, 2000, pp. 265-343, https://doi.org/10.1163/9789004473454_013
[11] F. Puertas, M. Palacios, T. Vázquez, *Carbonation process of alkali-activated slag mortars*, **Journal of Materials Science**, **41**, 2006, pp.3071-3082.
[12] F. Puertas, M. Palacios, *Changes in C-S-H of Alkali-Activated Slag and Cement Pastes After Accelerated Carbonation*, **12th International Congress on the Chemistry of Cement - ICCC,** Montreal, Canada, July, 2007.

[13] N. Li, N. Farzadnia, C. Shi, *Microstructural changes in alkali-activated slag mortars induced by accelerated carbonation*, **Cement and Concrete Research,** 100, 2017, pp. 214-226.

[14] M.M. Ilmi, N. Nurdini, E. Maryanti, C. Saiyasombat, P. Setiawan, G.T.M. Kadja, Ismunandar, *Multi-Analytical Characterizations of Prehistoric Rock Art Pigments from Karim Cave, Sangkulirang–Mangkalihat Site, East Kalimantan, Indonesia*, **Microchemical Journal**, **155**, 2020, article number: 104738.

[15] T. Bühler, R. Zurbriggen, U. Pieles, L. Huwiler, R.A. Raso, *Dynamics of Early Skin Formation of Tiling Mortars Investigated by Microscopy and Diffuse Reflectance Infrared Fourier Transformed Spectroscopy*, **Cement and Concrete Composites, 37**, 2013, pp. 161-170.

[16] J.D. Rodriguez-Blanco, S. Shaw, L.G. Benning, *The kinetics and mechanisms of amorphous calcium carbonate (ACC) crystallization to calcite, via vaterite*, **Nanoscale**, **3**, 2010, pp. 265-271.

[17] A.M. Yusof, N.A. Nizam, N.A.A. Rashid, *Hydrothermal Conversion Of Rice Husk Ash to Faujasite-Types and NaA-Type of Zeolites*, **Journal of Porous Materials, 17**, 2010, pp. 39-47.

[18] M. Catauro, S. Pacifico, *Synthesis of Bioactive Chlorogenic Acid-Silica Hybrid Materials Via the Sol–Gel Route and Evaluation of Their Biocompatibility*, **Materials**, **10**, 2017, article number 840.

[19] M. Arinat, A. Shiyyab, W. Al Sekhaneh, *Analytical Characterization of Ancient Mosaic Floor Preparatory Layers and Tesserae from the Hippolytus Hall in Madaba, Jordan: Case Study*, **Mediterranean Archaeology and Archaeometry**, **20**(3), 2020, pp. 149-158.

[20] P. Saravanapavan, L.L. Hench, *Mesoporous Calcium Silicate Glasses. II. Textural Characterisation*, **Journal of Non-Crystalline Solids**, **318**(1-2), 2003, pp. 14-26.

[21] W. Al Sekhaneh, A. Shiyyab, M. Arinat, N. Gharaibeh, *Use of FTIR and Thermogravimetric Analysis of Ancient Mortar from the Church of the Cross in Gerasa (Jordan) for Conservation Purposes*, **Mediterranean Archaeology and Archaeometry**, **20**(3), 2020, pp. 159-174.

[22] D. Neuville, L. Cormier, *Structure of $Na_2O$-$CaO$-$Al_2O_3$-$SiO_2$ glasses using Raman spectroscopy*, Proc. Glass Odyssey, no. 6, Montpellier, France, 02-06. June, 2002.

[23] M. Hino, S. Toshio, *Infrared Absorption Spectra of Silica Gel-$H_2{}^{16}O$, $D_2{}^{16}O$, and $H_2{}^{18}O$ systems*, **Bulletin of the Chemical Society of Japan**, **44**(11), 1971, pp. 33-37.

[24] N. Maxim, A. Overweg, P.J. Kooyman, A. Nagy, R.A. van Santen, H.C.L. Abbenhuis, *Synthesis and Characterisation of Microporous Bimetallic Fe–Cr–Si–O Materials Derived from Silsesquioxane Precursors*, **Journal of Materials Chemistry**, **12**(12), 2002, pp. 3792-3798.

[25] D. Bikiaris, S.X. Daniilia, S. Sotiropoulou, O. Katsimbiri, E. Pavlidou, A.P. Moutsatsou, Y. Chryssoulakis, *Ochre-differentiation through micro-Raman and micro-FTIR Spectroscopies: Application on Wall paintings at Meteora and Mount Athos, Greece*, **Spectrochimica Acta Part A - Molecular and Biomolecular Spectroscopy**, **56**(1), 2000, pp. 3-18.

[26] R.S. Boynton, K.A. Gutschick, *Strength considerations in mortar and masonry*, **Masonry Mortar Technical Notes**, **2**, 1964, pp. 1-8, https://www.lime.org/documents/publications/free_downloads/sc-mortar-masonry1989.pdf

[27] E. Dickinson, *Protein Adsorption at Liquid Interfaces and the Relationship to Foam Stability*, in Foams: Physics, Chemistry and Structure, Editor: A. Wilson, Springer-Verlag Berlin Heidelberg, London, 1989, pp. 39-53.

[28] E.C.Y. Li-Chan, W.D. Powrie, S. Nakai, *The Chemistry of Eggs and Egg Products* (Chapter) **Egg Science and Technology**, 4th edition, editors: W.J. Stadelman & O.J. Cotterill, CRC Press, 2017, pp. 105-175.
[29] T. Strixner, U. Kulozik, *Egg proteins*, (Chapter 7) **Handbook of Food Proteins**, Editor: G.O. Phillips & P.A. Williams, Woodhead Publishing Series in **Food Science, Technology and Nutrition**, Cambridge UK, 2011, pp. 150-209.

*Received: July 26, 2022*
*Accepted: February 28, 2023*