Mediterranean Archaeology and Archaeometry, Vol. 13, No 2, pp. 103-119

LASER INDUCED BREAKDOWN SPECTROSCOPY AND OTHER ANALYTICAL TECHNIQUES APPLIED ON CONSTRUCTION MATERIALS AT KOM EL-DIKKA, ALEXANDRIA, EGYPT

Sayed Hemeda

Conservation Department, Faculty of Archaeology, Cairo University, Egypt

Received: 12/2/2013
Accepted: 27/2/2013
Corresponding author: e-mail: hemeda@civil.auth.gr

ABSTRACT

In order to retrofit and conserve the archeological site of Kom El-Dikka, Alexandria, Egypt, a systematic study of construction materials was applied. The samples of mortars, brick and limestone samples have been taken from the remains of ancient Auditorium, houses and baths (300 AD). The analytical techniques showed that different qualities of mortars and brick were used for different purposes. Almost impermeable hydraulic mortars were found in contact with draining canals. This was the initiative to start combining advanced analyses of mortars and other construction materials by determining their physical and chemical characteristics in order to find the textural features and the alterations of the structure and understand their resistance to weathering.

Here samples were analyzed and examined by using Laser induced breakdown spectroscopy (LIBS), SEM attached with EDX, Polarizing microscope, Optical microscopy in transmitted polarized light, XRD, DTA-TGA, Grain Size Distribution, Pore Media Characterization, while some limestone and mortars were tested, to determine their uniaxial compressive strength, porosity, water absorption, proportion of constituents of cement mortars, and durability.

The paper focuses on the interrelation of findings from the above-referred examinations. The use of reactive siliceous materials in combination with lime, as well as, the excellent gradation of aggregates used seems to be the ancient protocol of the good performance of the ancient mortars. It is concluded the high skillfulness of ancient masons of the classical period in construction materials.

KEYWORDS: Kom El-Dikka, Oolitic limestone, Ancient mortars, Brick, Durability, Protection, LIBS, analytical.

1. INTRODUCTION

Laser-induced breakdown spectroscopy (LIBS) has emerged in the past ten years as a promising technique for analysis and characterization of the composition of a broad variety of objects of cultural heritage including painted artworks, icons, polychromes, pottery, sculpture, and metal, glass, stone artifacts, building stones and other construction materials (Cremers and Radziemski, 2006). This report describes in brief the basic principles and technological aspects of LIBS, and reviews several test cases that demonstrate the applicability and prospects of LIBS in the field of archaeological science.

LIBS principle relies on the focalization of a laser on the surface of a sample that induces plasma. The spectral emission of the plasma is collected and allows identifying the elemental identification of the material, (Anglos et al, 1997). In the conservation field, it can be used as an in situ, rapid, micro destructive approach for stone and mortars identifications. Different studies demonstrate that it can be performed with a basic observation of the specific emission lines in the spectra to detect characteristic chemical elements, which is a classical spectroscopic approach. The pigments can be identified by taking into account detected and non-detected elements. This method can also be assisted by multivariate treatments (Moropoulou and Polikreti, 2009)

Restoration of historic structures often requires identification of the composition of masonry units and jointing mortars so that a suitable modern masonry unit or a re-pointing mortar can be chosen. Laser Induced Breakdown Spectroscopy (LIBS) and other modern investigation techniques have significant applications in restoration projects in providing detailed information about: (a) the decaying state, composition, and quality of the original masonry unit; (b) the condition, composition, and quality of the original mortar; (c) the type, composition, lithology, size, distribution, soundness, alkali-aggregate reactivity, and durability of sand (quartz or limestone) in the mortar, (d) the type of cemented materials originally used (e.g., lime putty, lime-pozzolans, portland cement, masonry cement); (e) proportions of sand and cemented materials used; (f) effects of atmospheric weathering and alterations on the overall condition of the mortars; (g) composition and sources of efflorescence and staining on masonry walls.

Restoration of historic masonry structures requires a thorough understanding of the composition, behavior, and physical and mechanical properties of these materials, as well as their microstructures, the role of the microstructure in controlling the properties and performance of these materials, and the properties that were particularly responsible for long-term durability and performance.

2. STUDY AREA

Alexandria is located in eastern part of the Mediterranean Basin (Northern Egypt) and it is a place of great historical and religious interest. Numerous Catacombs and cemeteries for Greek-roman were erected in Greek-roman and Christian era has been found. Kom El-Dikka archaeological site refers to the social life of this age (Roman period in Egypt), it seems as complete city, since this area has the roman theater, and the magnificent auditorium of the theatre was adorned with columns of Italian marble at the rear. It was probably originally constructed in the 3rd c. A.D and later modified. Sixth century graffiti carved on the seats reveals connection with the blue and green factions associated with the popular rival teams of charioteers in the hippodrome (Empereur, 1998), (Wilkinson, 2000).

Also, this area has the town houses, the block of houses consist of two ranges of modest units facing each other across a central axis. It shows some affinities with the apartment blocks at Ostia in Italy, but differs in being built of local limestone rather than brick. This site contains also ancient school, this unique building which lies close to the theater and baths consist of three elements, In the center is a main lecture hall, with the lecturer's seat at the center of the short range at the top; the rooms on either side are smaller and may be subsidiary classroom or preparation room-the one on the left is square-ended, the one on the right horseshoe-shaped.

Moreover, this site has the baths, where the large and impressive brick built baths of the third century A.D lay close to the theatre and were supplied by an adjacent complex of water cisterns. On the highest of the three levels is the warm bath and at the base is the steam bath. The excavation reveals the underground columns of the hypocaust (Theodore, 2001).

Over 50 years of excavation have uncovered many Roman remains including this well-preserved theatre with galleries, sections of mosaic-flooring and marble seats for up to 800 spectators. In Ptolemaic times, this area was the Park of Pan and a pleasure garden. The theater at one point may have been roofed over to serve as an Odeon for musical performances. Inscriptions suggest that it was sometimes also used for wrestling contests. The theatre stood with thirteen semi-circular tiers of white marble that was imported from Europe. Its columns are of green marble imported from Asia Minor, and red granite imported from Aswan. The wings on either side of the stage are decorated with geometric mosaic paving. The dusty walls of the trenches, from digging in the northeast side of the Odeon, are layered with extraordinary amounts of potsherds. Going down out of the Kom, you can see the arches and walls, the brick of the Roman baths, and the remains of Roman houses, (Figure 1).

3. METHODOLOGY

The field study includes sampling from the parts presenting sound forms and weathering forms, measuring rates of each weathering form (for example, depth from stone surface, width …etc.) to quantitatively define its damage category. Thirty limestone samples, twenty mortars samples, and seven brick samples were extracted and taken from the foundations

Figure.1. General Overview of Kom El-Dikka archaeological site, the remains of the site is consisted of foundations and of low height brick and stone masonries by which the houses and Baths are circumscribed.

Figure.2. The structural damage of the remains and masonries is obvious.

and walls structures as shown in figure (2).

Laboratory investigations include the following:

1) Mineralogical analyses.

- X-ray fluorescence analysis (for the c rock samples).
- X-ray diffraction technique (for the rock and plaster & painting layers).
- Thermal analyses DTA&TGA (for the rock samples).

2) Thin section analyses.

- Optical microscopy in transmitted polarized light (for the rock samples).
- The fabric of rock material (grain contact (GC)/packing density (PD))
- Scanning electron microscopy (SEM) observations, attached with EDX Microprobe (energy dispersive X-ray) microanalyses.
- Classes of weathering based on linear crack
- Density and classification of the rock types included in this study.
- Stereoscopic observations (for the collected plaster and painting layers).

3) Porous Media Characterization.

- Porosity morphology of porous media
- Pore size measurement and Specific surface area by nitrogen BET-TPV.
- Determination of the specific surface area (SSA).
- Capillary water uptake measurements.
- Saturation coefficient, (S)

4) Laser- induced breakdown spectroscopy (LIBS)

The portable instrumentation was composed of a 1064 nm Nd-YAG laser (Continuum, USAو Minilite II Q-Switched) and the detection system is based on 3 integrated spectrometers (Ocean Optics, USA, HR2000) working from 200 to 940 nm, (Cennini, 2003), (Massart et al, 1988), (Sirven et al, 2007). Samples consisted in air-entrained concrete plates, covered with 2 layers of stones and mortars: render made of coarse sand and lime and a finishing layer made of fine sand and lime tired up and flattened. Samples were diluted in water and applied on wet coating. For the stucco technique a third layer with the medium and samples was applied on the dry plaster.

First, we worked on the reference database of five spectra for each limestone stone and other construction materials in order to define the most efficient method to use for identifications on site analysis, the identification of both It provided 66% of right attribution of construction materials/technique for validation spectra secondly multivariate treatments were used to build identification models with the 25 reference spectra. The SIMCA method was chosen in the first case. Each class corresponded to stone and other construction materials (5 spectra per class, classes in total). This method gave 81% of correct identification for the test set (5 spectra for each technique group). In a second time, on the same set of data a PLS-DA has been carried out for technique identification assigning a class to each technique (5 in total). 99% of right technique identification has been obtained with this method. We report the schema of the methodology used for the identification of stone and building materials and techniques.

The ancient mortars at the site of Kom El-Dikka could be distinguished in three categories:

- Floor bedding (six samples);
- Structural mortars (eight samples);
- Renderings and painting layers (five samples).

It seems that the selection of the raw materials used for each one of them was made according to the functional role they had in the structure.

Mechanical strength in compression was measured in the laboratory (cubic samples of 4x4x4 or 5x5x5 cm). In addition apparent specific gravity and natural absorption of these samples were determined. Based on 94 brick samples for which we have measured compressive strength, apparent specific gravity and absorption, we have tried to find the relationship between these characteristics by using data bank facilities.

5) Visual Examinations and Photographic Documentation

Properties that can be documented from visual examination include color and color variation, surface texture, hardness, softness, integrity, density, porosity, water droplet absorption, variations of these properties between the surface and the interior, visual effects of atmospheric alterations, cracking, spalling, evidence of any other distress or alterations, and any other relevant or even irrelevant features that are worth recording. Prior to any sample preparation, all samples had been adequately photographed to document the pristine condition of the sample.

4. RESULTS AND DISCUSSION

LIBS spectrum analysis revealed the construction materials samples are composed of the following elements in a decreasing order of their abundance as shown below in the following Table 1.

4.1. Mortars

Oolitic Limestone	Mortars	Renders or plaster layers
Ca Al	Si Ca	Si Na
Mg	Al	Ca
Sr	Fe	Cl
Fe Ti	Mg SO_3	Mg Fe

Table 1. LIBS spectrum analysis of oolitic limestone, mortars and renders or plaster on a decreasing order of abundance.

The floor bedding mortars are mainly based on lime and reactive pozzolanic material and they are extremely well compacted. Coarse aggregates with smooth surface, siliceous (sand) in origin are homogeneously distributed in the matrix. Low porosity characterizes the floor mortars. Microscopic analysis reveals the presence of few shrinkage cracks located around the aggregates and inside the floor bedding mortars. but even so, the mortar structure is quite solid see (Figures 8 and 9). The floor bedding mortars.. However, in some structures which were built with

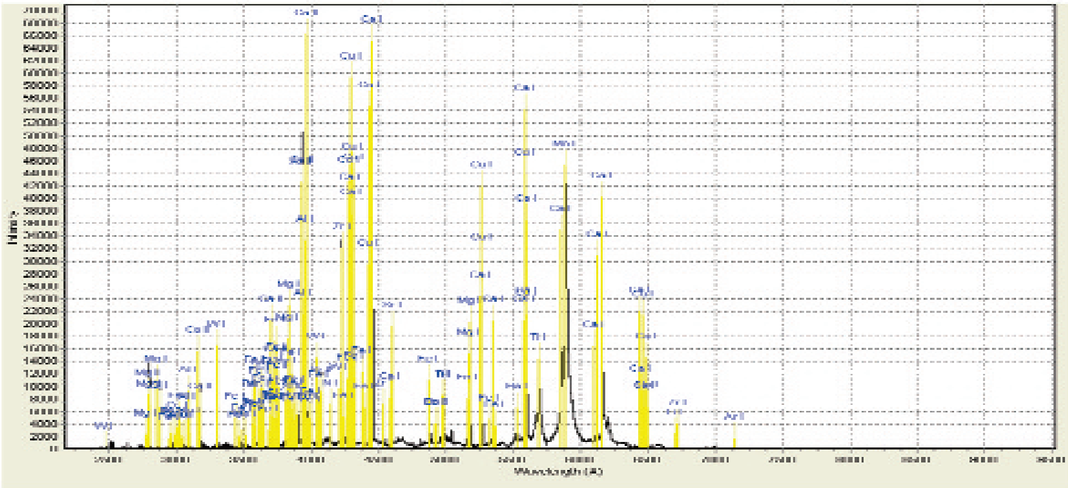


Figure.3. LIBS spectrum for a sample spot on lime based mortars between limestone blocks.

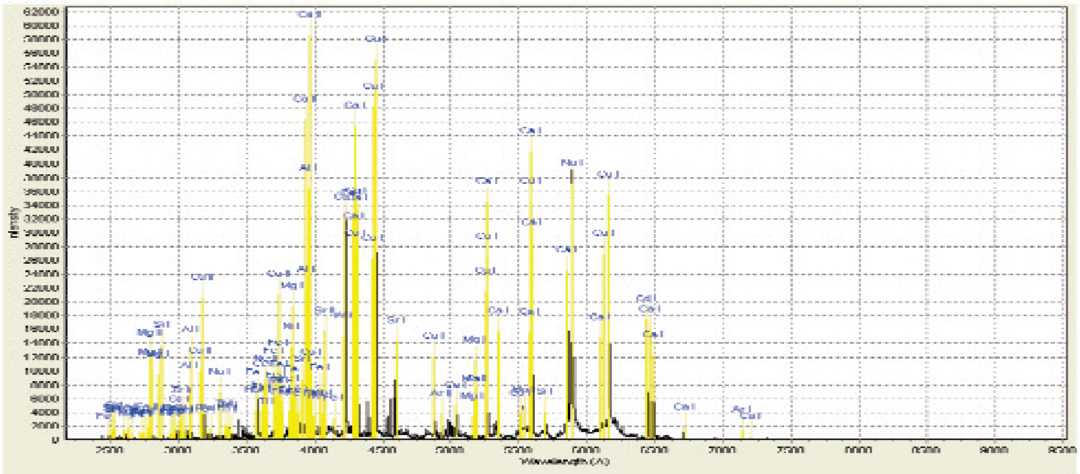


Figure.4. LIBS spectrum for a sample spot on plaster or renders layers (black crusts)

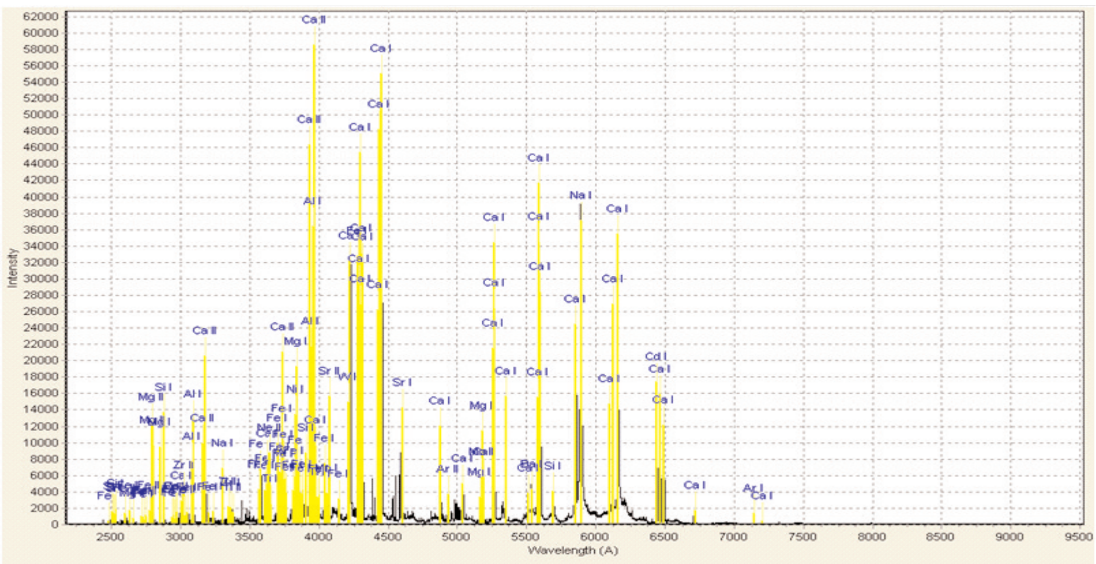
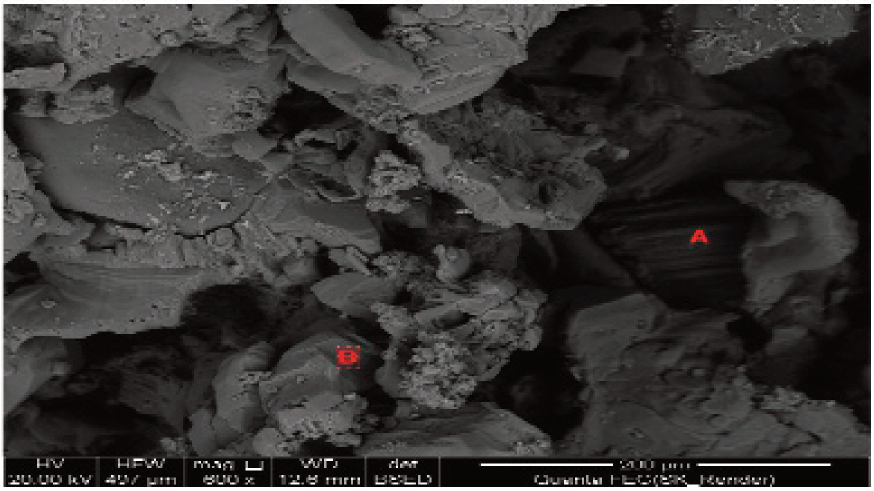
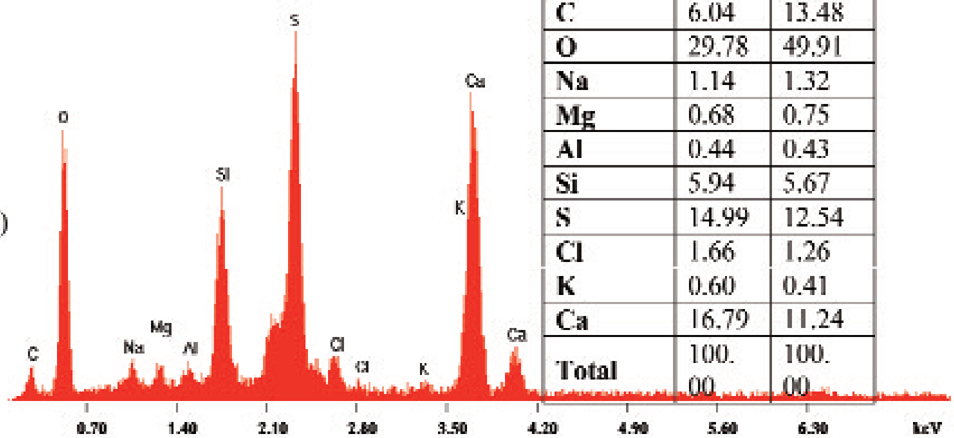


Figure.5. LIBS spectrum for a sample spot on plaster and renders layers.

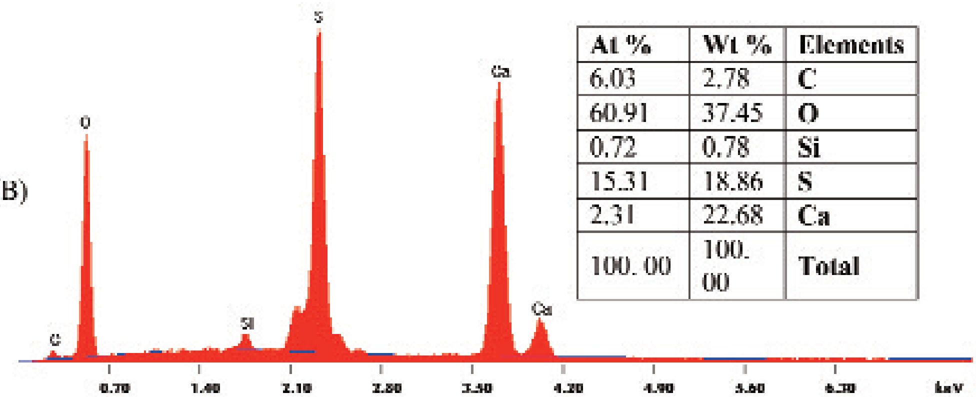


(A)



Elements	Wt %	At %
C	6.04	13.48
O	29.78	49.91
Na	1.14	1.32
Mg	0.68	0.75
Al	0.44	0.43
Si	5.94	5.67
S	14.99	12.54
Cl	1.66	1.26
K	0.60	0.41
Ca	16.79	11.24
Total	100. 00	100. 00

(B)



At %	Wt %	Elements
6.03	2.78	C
60.91	37.45	O
0.72	0.78	Si
15.31	18.86	S
2.31	22.68	Ca
100. 00	100. 00	Total

Figure.6. SEM micro structure image with EDX micro analysis spectra for renders and plaster layers.

special care (such as more spacious rooms for men, well decorated internal courtyard), lime was used as the main binding material in combination with reactive mud (Table 2). Most of the structural mortars have a color resembling that of the soil in the area.

Sieve analysis showed that in floor mortars the coarser aggregates predominate

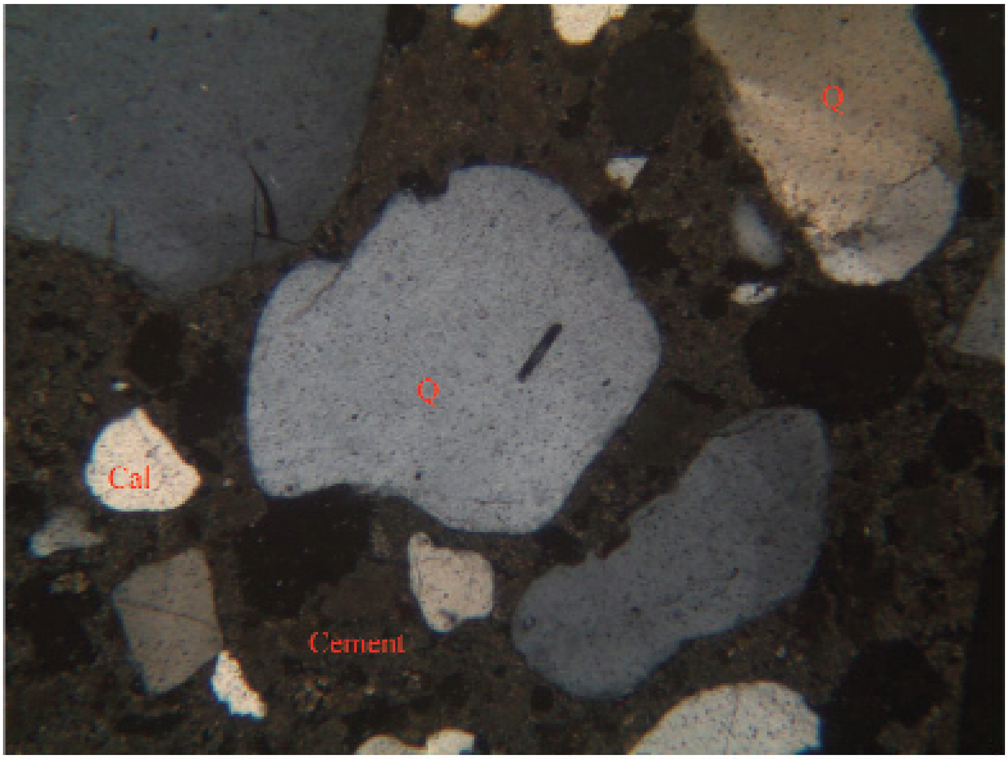


Figure. 7. Well-compacted floor bedding with shrinkage cracks. X8.

Figure. 8. Well-compacted structural mortar with shrinkage cracks.

while in structural mortars and in renderings the finer aggregates prevail (Table 2). The renderings are rich in lime and they had been applied in many thick

Table. 2. Chemical analysis and gradation of different mortars.

MORTAR CATEGORY	Constituents %	Granulometry
FLOOR	Insoluble residue 45-55 CaO 20-30 MgO 0.5-1.0	Fines (0-4 mm) 35-45% Coarse (>4 mm) 65-55%
	Insoluble residue 70-80 CaO 5-10 MgO 0.5- 0.9	
STRUCTURAL		Fines (0-4 mm) 82-88% Coarse 12-18%
	Insoluble residue 40-50 CaO 25-45% MgO 0.5-0.9	
LIME BASED	Insoluble residue 10-12 CaO 40-45 MgO 2-3	
RENDERINGS		Fines (0-4 mm) 75-85% Coarse
EXTERNAL	Insoluble residue 35-65 CaO 15-30 MgO 0.3-0.7	(>4 mm) 25e15%

layers (Figures 7, 8). The thickness of renderings ranges from 6 to 7 cm. In the mortar layers of the external coverings of the corpus of the stone and brick masonry that were in contact with draining channels, a reactive soil acting as pozzolanic material seems to have been used. The analysis shows that the insoluble residue of their composition as well as the content in SiO_2, Al_2O_3 and Fe_2O_3 are relatively high. These mortars with pozzolanic material are dense in structure and it seems that they were purposely manufactured to resist moisture.

Therefore, it could be concluded that ancient masons of the classical period were familiar with making mortars of hydraulic character.

The internal layer which is in contact with the stone masonry is usually the thickest (about 5- 6 cm). Rounded aggregates mainly of siliceous origin are used. The minerals which prevail are:

Quartz, feldspars, pyroxene and limestone fragments are also present. The binder is based on lime while in some cases a weak pozzolanic material has been detected (Table 2). This layer is compact with strong paste-aggregate interfaces. The binder/aggregate ratio ranges from 1:2.5 to 1:3. Re-crystallization phases are often observed and secondarily formed calcite fills small cracks and pores, contributing to the strengthening of the structure.

The external layer of the renderings is thin; the thickness varies between 1.5 and 2 mm. It constitutes the face of the rendering. The layer between the two layers is 10 mm thick. The composition of the external layer is different in comparison to the internal one. Crushed carbonate aggregates of various sizes (maximum 700-800 mm) are the only aggregates found in the paste. The binder is also based on lime with the addition of soil as pozzolanic material.

The longevity of the renderings up to these days gives an idea of the knowledge the technicians had in manufacturing and applying mortars, studies (Papayianni et al, 1994), (Papayianni, 1995), (Papayianni and Stefanidou, 1995).

The application of a multi-layer rendering and the way the layers were succeeded seems to have followed some rules. From internal to external, the layers are more compact, reducing the porosity and blocking the moisture to enter in the masonry. The compact transition zones between the layers confirm the stability of the structure.

4.2. Roman brick

Here we present the results of the study of brick samples taken from the Roman Baths at the Kom El-Dikka archaeological site. In comparison with modern bricks the old ones differ in many features:

Morphology: the bricks of the roman are plates of 20x20 or 25x25 or 20x30 cm. Their thickness varies from 3.5 up to 5.0 cm. The surface texture is rough, with hollows and chips far removed from the smoothness of modern bricks.

An indicative value measured from a block taken from the Roman baths is 3.5 to 5 kg/cm^2. For comparison reasons it is said that according to experimental tests made at the laboratory of construction materials, civil engineering department. Cairo University and Aristotle University of Thessaloniki, Greece, the bond developed between modern brick and lime based mortars does not reach over 1.5 kg/cm^2. Different Roman marking symbols, grooves at the upper surface were found or trademarks especially in bricks of modern historical buildings provide useful information to restorers.

Many enclosed materials such as: shells, chips of unburnt wood, thin roots, animal hairs, granules of carbon and lime can be used as data to make conclusions about the origin of clays and temperature of burning. The phenomenon of different colored zones is very common. The darker colored zone in the centre of the section indicates a lack of uniformity in burning methods (may be in clamps). Parts from sand, fine aggregates are often find (4mm). In some cases coarse aggregates up to 10mm or ever 16mm are enclosed. This seems to be significant for the strength of the brick. In some cases pieces of crushed bricks are embodied in the brickmass. Hand compaction is not always sufficient, resulting in great voids like nests inside the brickmass.

When cracks are present in the mass of the brick the absorption is over 20%. For the sound forms brick samples absorption ranges from 12 to 17%. For 50% of the samples absorption is below 20%. For the 65% of the samples the density ranges from 1.5 to 1.7gr/cm^3.

Furthermore, it seems that coarse aggregates, greater than 4mm grain size, do not contribute to brick strength. As is shown, there are cracks around aggregate grains, while sand and calcite grains present good adhesion with burnt clay mass. The grade of compaction is particularly important for strength. Well treated clays without voids exhibit high strength. The thickness of brick does not influence the strength of the material itself whereas, as is known, it does not contribute to brick masonry strength.

In the following Table 3 the characteristics of Roman brick at the site under investigation are given.

The type of damage recognized: Flakes or scaling at the surface, Loss of mass, Changes in shape (worn rectangular angles), Efflorescence, Changing in colour (smoked brick), Presence of fungus, and Pulverization.

4.3. Oolitic Limestone

The remains of the original building stone were quarried from the Alexandria

Table 3. Main features of sound forms brick of Roman period at Kom El-Dikka archaeological site.

No Sample	Thickness of brick (cm)	Absorption	Cracking	Compressive strength (kg/cm^2)	Materials
A	6.7	14-15%	no	171	Clay mineral, coarse aggregates, chips of wood
B	6	28%	No consid.	79.9	Clay mineral, coarse aggregates, lime
C	4.5	16.3%	no	145	Clay mineral, fine aggregates, chips of wood
D	6.4	23%	No consid.	66	Clay mineral, fine aggregates
E	4.5	18.21%	no	110	Clay mineral, coarse aggregates, chips of wood

Coastal ridge (Pleistocene) and composed mainly of oolitic calcarenite and aeolianite rocks. The stone of these constructions subjected to different weathering processes. Rainfall, Irrigation and surface water, sea water splash, are the most effective weathering agencies, in addition to human activities e.g. scratching and removing stones to be used in other purposes.

Calcarenite is a biogenic sedimentary soft rock resulting from marine sedimentation, which took place during the transgression and regression of the region in the Plio-Pleistocene. The calcarenite is composed by nearly pure calcium carbonate and lays directly on the calcareous sub rock of the cretaceous.

Calcarenite size 58% of the allochems are medium size, subrounded, micritic, and internally structure less ooides. 10 % oval shape micritic peloids. 30% large to small size angular to subrounded, wavy extinction, monocrystalline quartz grains. 2% plajioclase and microcline crystals. Porosity reached to 20% of the thin section field area. Pores are filled with neomorphic microspare. Allochems are surrounded with isopachous microspare (Figures 11, 12).

The EDX micro analysis indicated that, the elemental arrangement for the oolitic limestone samples can be put in a decreasing order according to their concentration as follow:

Ca (33.50%), O (29.80%), S (16.94%), K (9.01%), C (6.53%), Fe (1.76%), Si (1.48%), Al (0.55%), Mg (0.44%). Total 100.00% (Wt%) (Figure 11).

For the calcarenitic stone sample which collected from the weathered layers, we notice that: the pore diameter distribution of this stone is: 10-20A (Angstrom) (0.07%), 20-30A (0.0236%), 30-50A (1.06%), 50-100A (2.03%), 100-200A (17.18%), 200-2330A (79.76%), and nm (micro porosity) = 2.95707E-05, BET(m^2/gr) = 3.69748, TPV (ml/gr) = 1.73453, and micro porosity % is 75.32496 (see Figure 13a).

But for the collected rock samples from sound or non-weathered layers collected from the same site: we noticed that the pore diameter distribution of these stone samples is: <10 A (Angistrom) (2.674%), 10-20A (5.294%), 20-50A (16.06%), 50-100A (10.66%), 100-200A (9.956%), 200-1996A (55.34%), and nm = 2.19145E-05, and BET(m2/gr) = 1.95777, and TPV (ml/gr) =0.0149, and micro porosity % is 4.23966. see (Figure, 13b). It was shown that the NaCl content is not directly proportional to the susceptibility of the stone type to sea-salt decay. This susceptibility is mainly determined by the pore network characteristics. In addition, the results with regard to these representative examples provide a model, which explains the causes and processes of alveolar weathering at the sites under investigation (Pratt, 1988).

The microscopic observations correlated well the results of the pore size distribution measurements (gas sorption experiment).

SEM observations on the collected limestone samples show increase of the porosity of various sizes has been greatly reduced as noted due to filling with drusy sparite, different percentages and sizes of quartz grains. At some places, we can find cracks at minerals contacts or even inside of minerals. Microscopic examinations show a very inhomogeneous distribution of the salt along the sample cross-section, and The observations indicate the occurrence of geometrical shapes not related to the

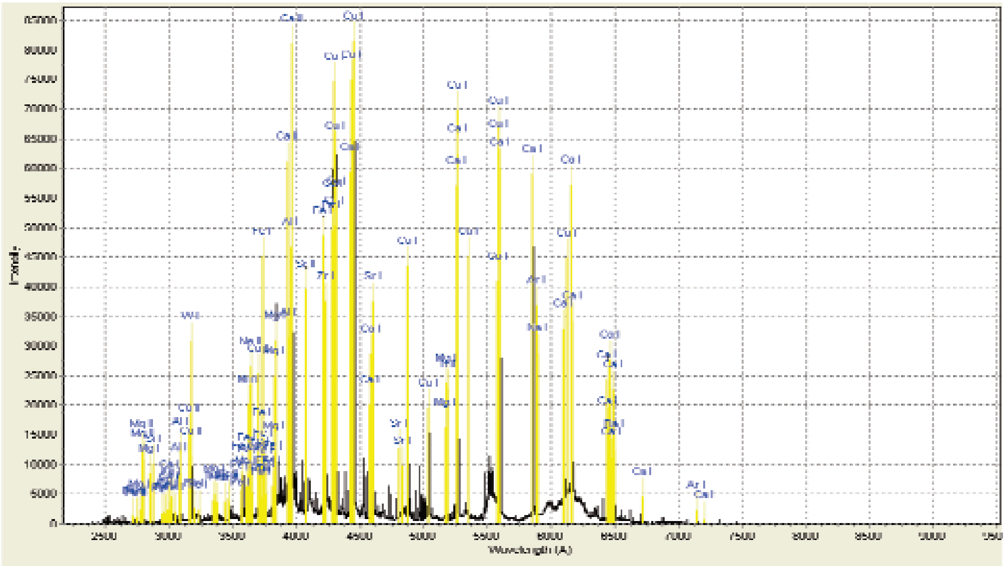


Figure.9 . LIBS spectrum (black and yellow lines) for a sample spot on oolitic limestone (black hard crust).

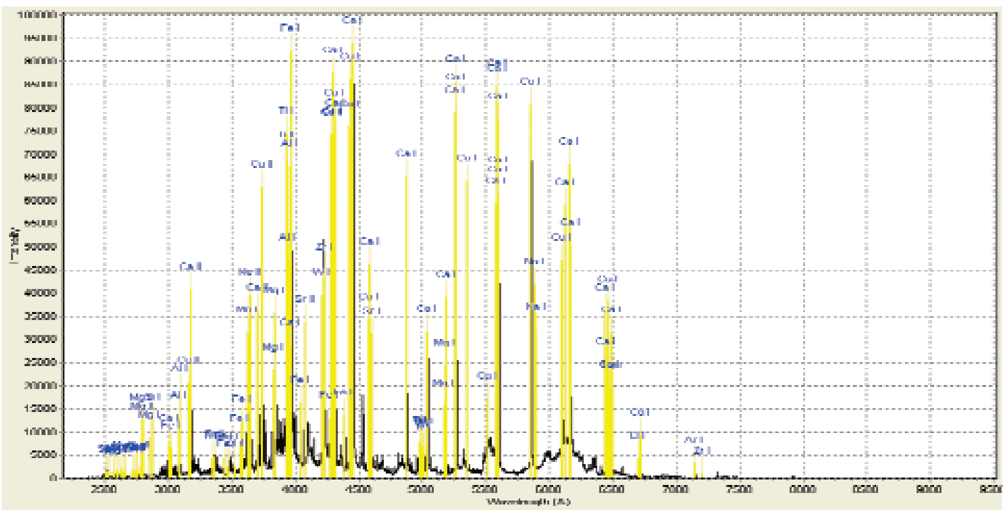
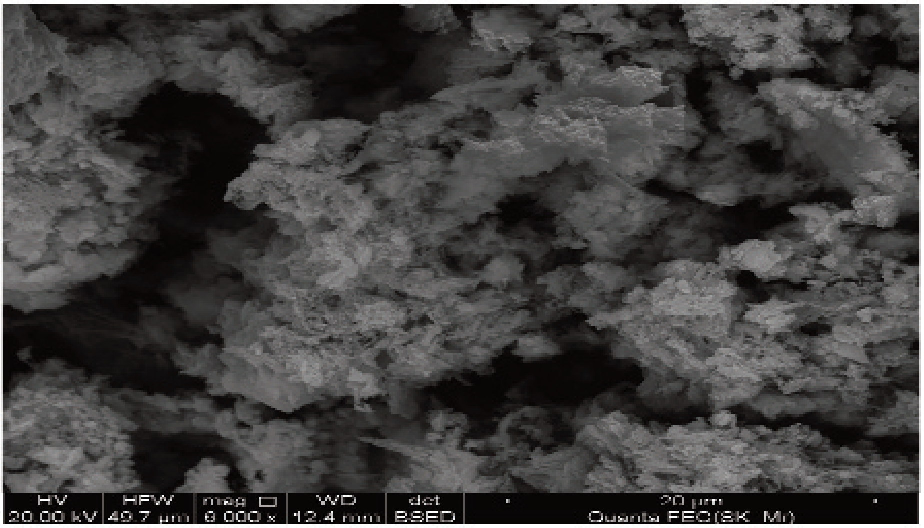


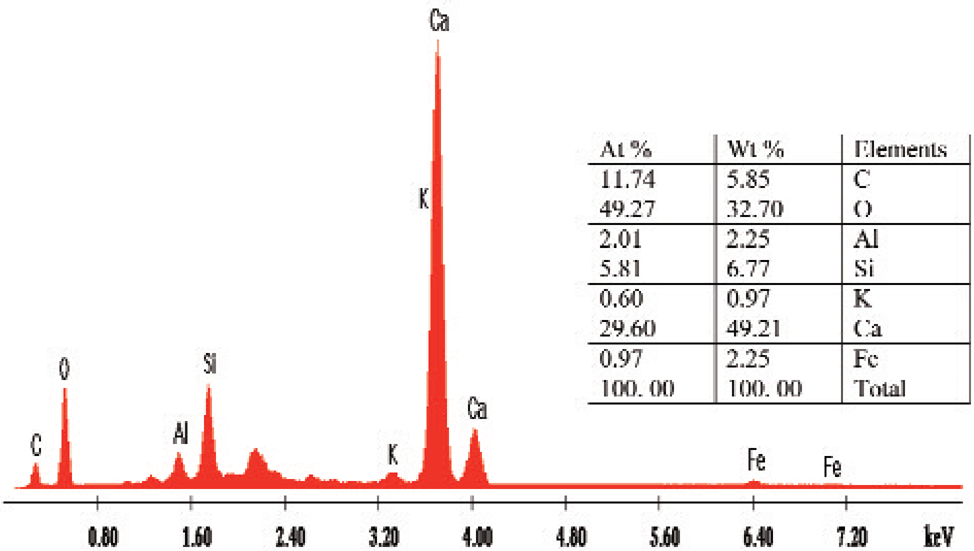
Figure.10 . LIBS spectrum for a sample spot on oolitic limestone.

structure, there are about 50 μm in size and appear as ghost structures of cubic minerals, this samples show also a few white cubic patches, with a same size range as the ghost structures. Ghost structures could originate from salt crystal removal. The very loose particle arrangement of the Calcarenite is apparent from the SEM, such structure is made possible by the particles angularity and interparticles cement, (Dipayan, 2005), (Kamh, 1994).

5. REPOINTING AND TUCK POINTING MASONRY STRUCTURES

Repointing is the process of removing deteriorated mortar from the joints of a masonry wall and replacing it with new mortar. Tuck pointing describes a primarily decorative application of a raised mortar joint or lime putty joint on top of flush mortar joints. In a restoration project, both





At %	Wt %	Elements
11.74	5.85	C
49.27	32.70	O
2.01	2.25	Al
5.81	6.77	Si
0.60	0.97	K
29.60	49.21	Ca
0.97	2.25	Fe
100. 00	100. 00	Total

Figure 11. (a) SEM image, (b) EDX micro analysis spectra for oolitic limestone

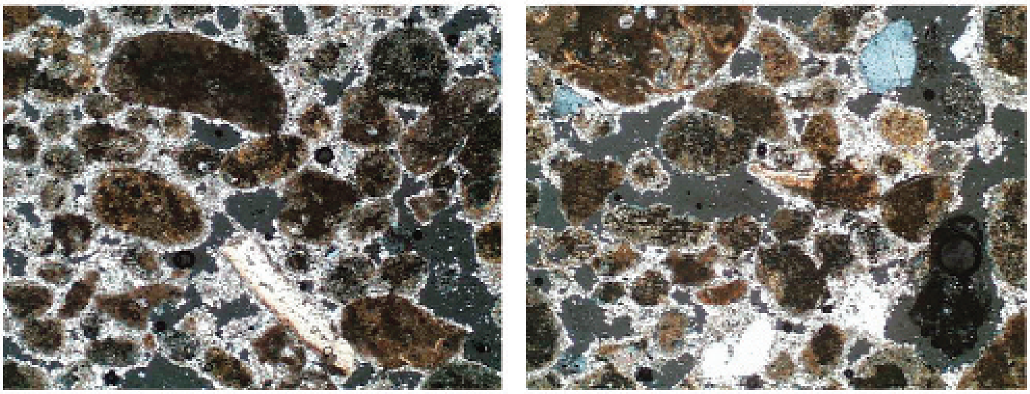


Figure.12. Photomicrograph of oolitic limestone under crossed polarizers, showing wackestone texture with drusy sparite, Kom El-Dikka archaeological site. (Weathered sample, heterogeneous pore system). X8.

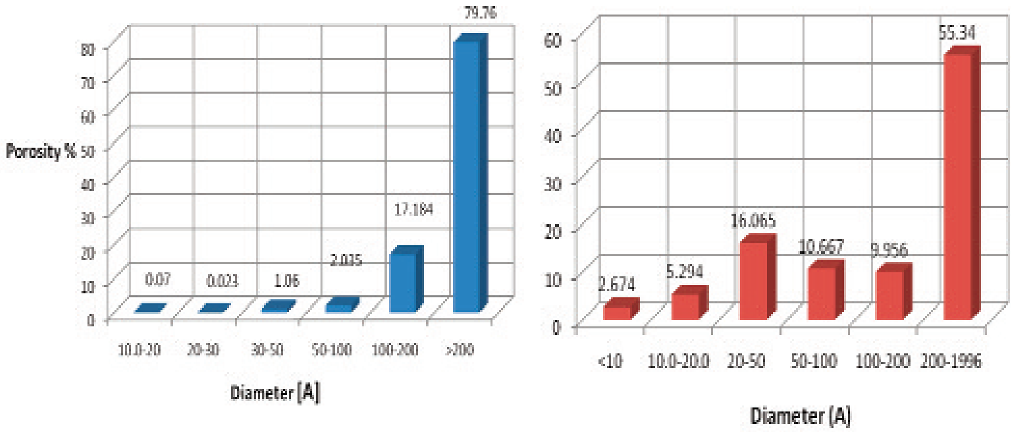


Figure 13. Pore size (diameter A) distribution for collected (a) weathered and (b) sound stone sample from Kom El-Dikka archaeological site.

terms, however, are used synonymously to indicate installation of a new mortar in an existing masonry wall. Cracking and disintegration of mortar, loose bricks or stone, damp walls, or damaged plaster indicate the need for repointing. Repointing, if properly done (after proper determination of the cause of the problem), can restore the original visual and physical integrity of the building. Improper repointing can detracts the appearance of the building and even cause physical damage to the wall. An appropriate match in composition, strength, and moisture permeability between the new and historic mortar is essential. The new mortar should match the historic mortar in color, texture and tooling, and in the properties of sand; the new mortar should have greater moisture permeability and be softer (in strength) than the masonry units; and the new mortar should be as moisture permeable and as soft as or softer than the historic mortar. A similar approach should be followed for masonry units if they are in the need of replacement, (Henriques, 2004).

If the original mortar were a lime-sand mortar, a close match for re-pointing purposes would be a hydraulic lime mortar, or an ASTM C 270 Type N portland cement-lime mortar or a masonry cement mortar. Other alternatives as suggested by ASTM C

270 are: (a) for interior applications Type O (alternatives K or N); (b) for exterior above grade application unlikely to be frozen when saturated and not exposed to high wind or other lateral load Type O (alternatives N or K); and (c) for exterior application other than the above type N (alternative O). The volumetric proportions of portland cement-to-hydrated lime-to-sand in these portland cement-lime mortars are: Type N 1: (½ to 1¼): (4½ to 6¾); Type O 1: (1¼ to 2½): (6¾ to 10½); Type K 1: (2½ to 4): (10½ to 15). Due to good workability, water retention and freeze-thaw durability, a Type N masonry mortar (which is air entrained) can also be used.

The repointing mortar should be prepared properly, such as according to the following ASTM C 270 instructions: (a) Dry mix all dry, solid (sand and cementitious) materials; (b) Add sufficient water to produce a damp mix that will retain its shape when pressed into a ball by hand; (c) Mix for at least 3 and not more than 7 minutes, preferably with a mechanical mixer; (d) Let mixed mortar stand for not less than 1 hour nor more than 11/2 hours for prehydration; (e) Add sufficient water to bring the mortar to the proper consistency for tuck pointing, somewhat drier than mortar used for laying masonry units; (f) Mix by hand for 3 to 5 minutes; (g) Use the repointing mortar within 21/2 hours of its initial mixing; permit tempering of the mortar within this time interval.

Aggregates in the repointing mortar can be natural or manufactured sand, which can be siliceous, calcareous, or a mixture of the two. The lithologic type, size, color, texture, and gradation of the sand in the repointing mortar must match with that used in the original mix. Petrographic examinations provide this information. Sand may conform to the specification of ASTM C 144 "Specification for Aggregate for Masonry Mortar". The color of the particles should be as close as possible to the color of the original sand.

For removal of the original mortar, common industry recommendations for solid masonry units are to remove jointing mortar to a minimum 5/8-in. deep until solid and sound mortar is reached (up to a maximum depth of half the masonry unit depth or a minimum depth of 2 to 2½ times the width of the joint). Mortar should be removed cleanly from the head or bed joints without damaging the units. Repointing mortar should be placed in successive lifts, preferably without delay between the lifts.

6. CONCLUSION

This article describes various techniques and applications of petrographic examinations in masonry and archaeological structures that can be used during restoration of historic buildings. This relatively “new” science shows great potential in both materials evaluation of future masonry and failure investigation and restoration of ancient masonry structures.

The remains of the original building limestone were quarried from the Alexandria Coastal ridge (Pleistocene) and composed mainly of oolitic calcarenite and aeolianite rocks. The stone of these constructions were subjected to different weathering processes.

SEM observations on the collected limestone samples show increase of the porosity of various sizes has been greatly reduced as noted due to filling with drusy sparite, different percentages and sizes of quartz grains. At some places, we can find cracks at minerals contacts or even inside of minerals. Microscopic examinations show a very inhomogeneous distribution of the salt along the sample cross-section, and The observations indicate the occurrence of geometrical shapes not related to the structure, there are about 50 μm in size and appear as ghost structures of cubic minerals, this samples show also a few white cubic patches, with a same size range as the ghost structures. Ghost structures could originate from salt crystal removal. The very loose particle arrangement of the Calcarenite is apparent from the SEM, such structure is made possible by the particles angularity and interparticles cement

The ancient mortars at the site of Kom El-Dikka could be distinguished in three categories:

- Floor bedding
- Structural mortars
- Renderings and painting layers

The analysis shows that the insoluble residue of their composition as well as the content in SiO_2, Al_2O_3 and Fe_2O_3 are relatively high. These mortars with pozzolanic material are dense in structure and it seems that they were purposely manufactured to resist moisture.

It could be concluded that ancient masons of the classical period were familiar with making mortars of hydraulic character.

The bricks of the Roman at Kom El-Dikka are plates of 20x20 or 25x25 or 20x30 cm. Their thickness varies from 3.5 up to 5.0 cm. The surface texture is rough, with hollows and chips far removed from the smoothness of modern bricks.

An indicative value measured from a block taken from the Roman baths is 3.5 to 5 kg/cm2. For comparison reasons it is said that according to experimental tests made at the laboratory of construction materials, civil engineering department. Cairo University and Aristotle University of Thessaloniki, Greece, the bond developed between modern brick and lime based mortars does not reach over 1.5 kg/cm^2. Different Roman marking symbols, grooves at the upper surface were found or trademarks especially in bricks of modern historical buildings provide useful information to restorers.

REFERENCES

Anglos. D., and Couris. S., Fotakis. C, (1997) Laser diagnostics of painted artworks: Laser-induced breakdown spectroscopy in pigment identification., *Appl. Spectrosc.* 51, 1025–1030

Cennini. C, (2003) *Il libro dell'arte,* Neri Pozza.

Cremers. D.A., and Radziemski. L.J, (2006) *Handbook of Laser-Induced Breakdown Spectroscopy,* John Wiley & Sons Ltd, West Sussex, England.

Dipayan. J, (2005) *Applications of petrography in restoration of historic masonry structures,* 10th Euroseminar on Microscopy Applied to Building Materials, Scotland.

Empereur. J, (1998) *Alexandria Rediscovered*, British Museum Press, London.

Henriques. F.M.A, (2004) *Replacement mortars in conservation: an overview,* 10th International Congress on Deterioration and Conservation of Stone (Editors D. Kwiatkowski, R. Lofvendahl), Stockholm, June 27-July 2, pp. 973-984.

Kamh. G. M, (1994) *The impact of geological conditions on the Islamic archaeological sites at El-Gammalia area,* Cairo City, Egypt, MSc Thesis, Geology Dept., Fac. of Science, Menoufiya University, Egypt

Massart. D.L, Vandeginste. B.G.M, Deming. S. N, Michotte. Y, Kaufman. L , (1988) *Chemometrics,: A Textbook.* Elsevier Science Publishers B.V.

Moropoulou. A., and Polikreti. K., (2009) *Principal component analysis in monument conservation: three application examples,* Journal of Cultural Heritage 10, 73-81.

Papayianni. I, Karaveriroglou. M, Athanasiou. F, Georgisoudi. K, Revithiadou. K, *(1995) Mortars Used for Intervention in Archeological Site of Ancient Olynthos,* STREMAH 95 Conference, Crete, Greece, pp. 245-251.

Papayianni. I, (1994) *Durability Lessons from the Study of Old Mortars and Concretes,* Symposium on Durability of Concrete (Editor P.K. Mehta), Nice, France, May, pp. 23-35.

Papayianni. I, and Stefanidou. M, *(1995) Characteristics of bricks of old masonries.* Workshop on "Materials for consolidation and restoration of monuments and historical buildings: reading, interpreting and recovering the knowledge of traditional materials", Museum of Byzantine Culture. Thessaloniki, Greece, pp.36-37.

Pratt. P. L, (1988) Physical methods for the identification of microstructures, *Materials and Structures* 21, pp.106-117.

Sirven. J.B, Sallé. B, Mauchien. B, Lacour. J.L, Maurice. S, Manhès. G, (2007) *Feasibility study of rock identification at the surface of Mars by remote laser-induced breakdown spectroscopy and three chemometric methods,* Journal of Analytical Atomic Spectrometry, 22, pp. 1471-1480.

Theodore. V, (2001) *Alexandria, City of the Western Mind,* Free Press, New York

Wilkinson. R, (2000) *The Complete Temples of Ancient Egypt,* Thames and Hudson, Ltd,