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Microscopic Studies on Wooden Holder of Decorative Glass Remaining from Middle Elamite Era (1280 B.C)

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Abstract: Wood is made of organic components including cellulose, hemicellulose, and lignin with traces of inorganics. Thus, it is possible to investigate a wooden material status using both molecular spectroscopies and elemental analysis. Degradable intrinsic of wood causes having it rarely found through archaeological excavations of ancient sites. Therefore, archeologists will be delighted with finding an intact wooden tool because it enables them to configure virtually the structure of the other ancient stuff found at the same place and conclude meaningfully about their application taking into account the location of excavation. In this article, identification of a piece of wooden rod discovered in Chogha Zanbil (Al-Untash-Napirisha) was performed using an optical microscope and SEM, EDS and, FTIR. Optical microscope helped to find the genus of the wood which was further confirmed by SEM images. Elemental analysis results of the rod using EDS were in accordance with the previous findings in the literature. FTIR worked out all the bonds between building up atoms prooving the wooden structure. These characterizations have revealed that the wood belongs to date palm tree. In fact, this piece of wood was being used to hold the cone-shaped glass on the door surface of the temple in the middle Elamite era (1280 B.C).

Keywords: Middle Elamite, Wooden Holder, Date Palm, Microscopic Studies, FTIR, SEM-EDS

1. Introduction

Chemical defined, wood is a combination of biopolymers composed of a bonding network of cellulose, hemicellulose, and lignin plus traces of inorganics. The chemical components in dry wood are carbohydrates 65-75% and lignin 18-35%. Altogether, the elemental composition of dry wood is about 50% carbon, 6% hydrogen, 44% Oxygen, and a trace amount of inorganic materials [1]. Thus, regarding the chemical composition of wood, it is not common to find the remaining wooden stuff in ancient sites. The wood texture that remains intact is unique but wood charcoal is one of the most abundant materials in ancient sites. Post-depositional processes of charcoal or wood in archaeological contexts are diverse [2].

To study prehistoric wood stuffs one of the most common techniques is scanning electron microscopy (SEM). SEM analysis of some wooden tools dated back 171,000 y B.P. excavated from Poggetti Vecchi (Italy) displayed the increment of porosity in charred woods [3]. Deterioration of a wood sample from the Hanson Logboat in Derby Museum and Art Gallery was assessed using SEM images [4]. Decay process of waterlogged woods due to bacterial activities was investigated with the help of SEM micrographs [5].

Another usual technique for wood analysis is Fourier transform infrared (FTIR) spectroscopy. Chemical composition of prehistoric bark samples collected from Hallstatt, Upper Austria was studied by ATR-RTIR [6]. FTNIR was also applied to explore the changes of chemical materials as a result of fungi presence in an old spruce wood [7]. Infrared spectroscopy presented the effect of environmental condition on degradation of pine wood in Biskupin (Poland) dating to the 8th century BC [8].

To explore the elemental constituent of wooden materials Energy-dispersive X-ray Spectroscopy (EDX) is a routine technique. The technique was used to determine the elements present in the rock-painting pigment samples obtained from Egypt (Gilf Kébir area) [9]. The analysis of element composition in the wooden ceiling of the House of the Telephus Relief in Herculaneum (Italy) with EDX discovered the secret of that unique ceiling [10].

In this article, the study of the organic components, morphology, and elemental content of a wooden rod used as a glass holder discovered from the Chogha Zanbil temple was implemented. This is an extraordinary opportunity to achieve such an old wooden piece from unearthing. Analysis of the sample by different techniques including optical microscope and SEM, EDS and, FTIR ensured us to conclude the wood is a type of palm tree.

1.1. Palm Wood in Historical Sources

Wilcox mentions that the birth of the Mesopotamian city-states coincided with the maximum forest cover in the region, and timber resources were available more than in any other period [11]. Early historical evidence shows the importance of growing trees and using their wood in Mesopotamia. The gardens of Babylon palace have been considered since the early reign of Adad-suma-usur (c. 1200-1180 B.C.) [12, 13]. Date palms were especially grown in the orchards of southern Mesopotamia during the Old Babylonian era [14, 15]. For example, Balumama archives of Larsa state mention that growing fruit trees including date palms was common in orchards [16]. The date palm could be used as a column for the prototype of Mesopotamian columnar architecture [17]. This wood has also been sawn to make doors and window frames.

Physiological and geographical conditions of Mesopotamia extend to the Khuzestan region in Iran. Arboricultural events in Southwestern Iran like Mesopotamia during the middle Elamite period could have resulted in urban civilization [18].

1.2. Geographical Distribution of Wooden Holder of Glass

Al-Untash-Napirisha (The Site known as Chogha Zanbil Ziggurat) is an ancient complex in Khuzestan province in Iran. In the excavation carried out at this site by Roland De Mecquenem and Michalon between 1935-1939 AD and 1946 AD, many tubular glass rods were discovered [19]. They are colored with dark blue and white or amber color with a length of 20 to 28 cm. Also, After World War II, Roman Ghirshman excavated the site from 1951 A.D to 1962 A.D and discovered pieces of wooden doors. Roman Ghirshman's wife, Tania mistakenly reconstructed this door so that the glass tubes were placed diagonally on the door, and the authors reconstructed a new model of doors (Figures 3-4) [20].

This piece was part of a practical tool and was used to hold the cone-shaped glass on the door of Chogha Zanbil (Al-Untash-Napirisha) in the middle Elamite period (1280 B. C).

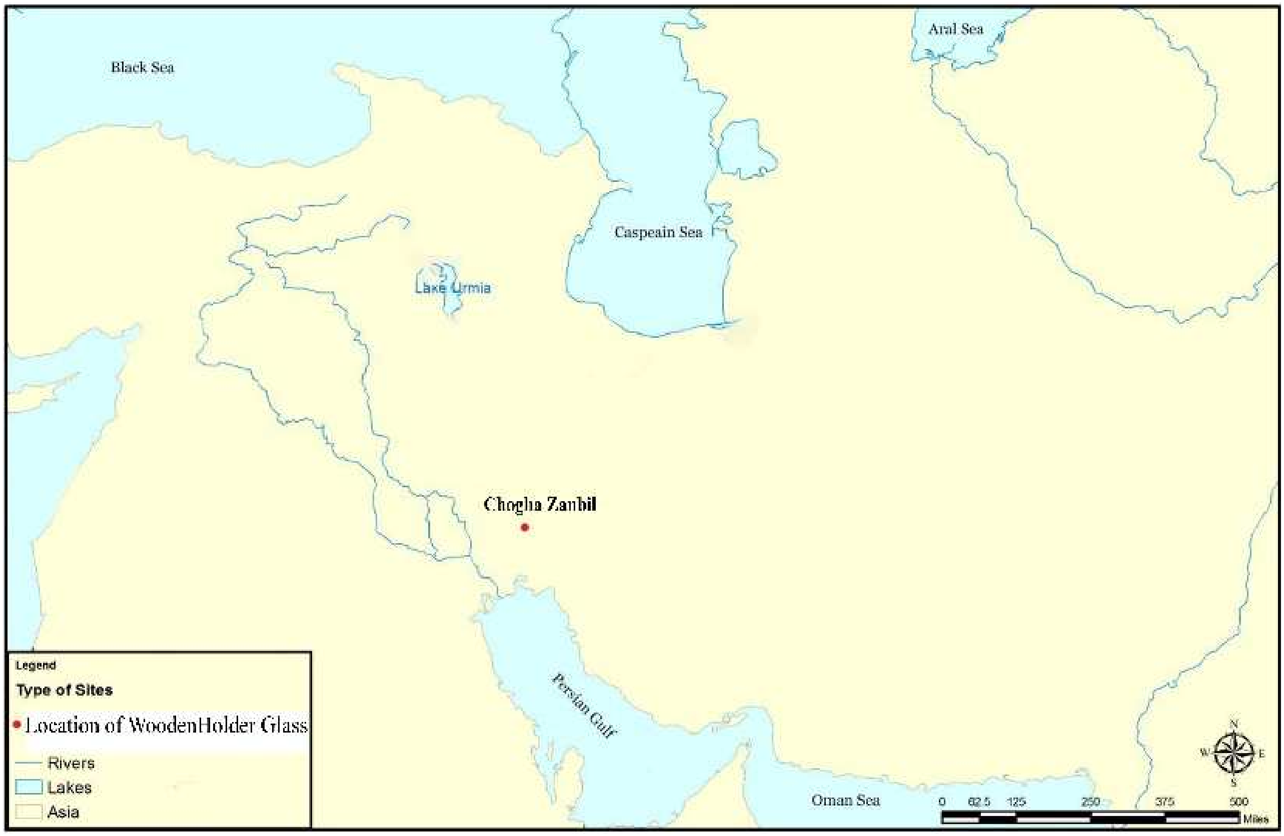

Figure 1. *Location of Chogha Zanbil.*

Figure 2. *Reconstruction of a door of Chogha Zanbil by Tania in the National Museum of Iran [20].*

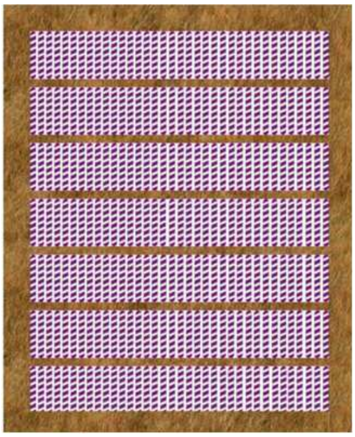

Figure 3. *New design of a door in Chogha Zanbil [20].*

2. Materials and Methods

2.1. Materials

The wood sample provided by National Museum of Iran is a rod with a length of 5 cm. One end of that wooden rod is partially burnt but most of part it is intact. An image of the wood is presented in figure 4.

Figure 4. *The wooden rod next to a scaled plate to indicate its dimensions.*

A distilled water prepared by an in-house system was used throughout the process. Sodium hypochlorite 50% (Merck), methylene blue, Herzberg reagent, ethanol 70% (Merck), xylene and, glycerine (ACS, ISO, Reag. PhEur, Merck) were used for the treatment of the wood sample to be investigated by optical microscope. Potassium bromide was mixed with milled wood powder to prepare a transparent pellet for FTIR analysis.

2.2. Methods

2.2.1. Optical Microscope

James Swift's polarizing microscope with 4x and 10x magnifications was used in the laboratory of the Cultural Heritage Research Institute to examine the anatomical structure. A small piece of the wooden rod was boiled in some distilled water in Erlenmeyer for 20 min to be softened. The soft wood sample was then placed in 15 ml of sodium hypochlorite, distilled water, methylene blue, ethanol, xylene and, glycerine, respectively, to obtain a microscopically detectable texture when exploring by optical microscope.

2.2.2. Fourier Transform Infrared (FTIR) Spectroscopy

FTIR analyses were performed in the laboratory of the Cultural Heritage Research Institute using the Nicolet 510P in the wavenumber range of 450-4000 cm^{-1}. The background and the measurements spectra were recorded at 32 scans and 4 cm^{-1} resolution. The wood sample was milled and then ground together with potassium bromide to provide a transparent pellet for FTIR analysis.

2.2.3. Scanning Electron Microscopy (SEM)

SEM analyses with VEGA\TESCAN-LMU microscope characterized the wood microstructure at Razi Metallurgical Research Center**.** A slice of the wooden rod was mounted on an SEM sample stub with carbon conductive adhesive and coated with gold using a gold sputter coater with the EMITEC (UK) spattering machine.

2.2.4. Energy-dispersive X-ray Spectroscopy (EDS)

The elemental composition of the wooden rod was studied by EDS. Three points of the rod including the intact, burnt, and intact-burnt interface were analyzed.

3. Results and Discussion

3.1. Optical Microscope

The anatomical structure of the wooden rod was investigated using an optical microscope as shown in figure 5. The magnification obtained by the microscope enabled us to distinguish this wood from other botanical species. Comparing this structure with the images in literature reveals that the wood belongs to a date palm tree. Dark brown fiber cells with at least two Metaxylems have made a vascular bundle surrounded by parenchymatous ground tissue. Metaxylems are visible in white color in the image [21].

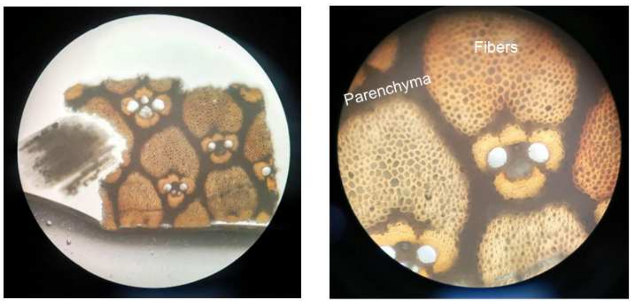

Figure 5. *Magnification image of the wooden rod cross-section by optical microscope; left: 4x magnification, right: 10x magnification.*

3.2. Fourier Transform Infrared Spectroscopy

As mentioned, wood is composed of cellulose, hemicellulose, and lignin in terms of organic materials. Lignin, as an organic polymer, is made of several phenolic rings with methoxy and hydroxyl groups. Cellulose, the unbranched polymer, is build up of glucose rings with hydroxyl groups. While hemicellulose is a branched polymer of glucose. Thus, the bands recorded in the spectrum are esulting from these ingredients. The FTIR spectrum of the wooden rod (glass holder) in figure 6 shows broadband at 3428 cm^{-1}, attributed to the hydroxyl (OH) groups in phenolic and aliphatic structures, and C-H asymmetric stretching of methylene (CH_2) groups at 2928 cm^{-1} originate from aliphatic parts of lignin and cellulose. The sharp band at 2363 cm^{-1} is due to carbon dioxide (CO_2) that is present everywhere. The shoulder at 1730 cm^{-1} is assigned to carbonyl (C=O) groups stretched in hemicellulose and lignin. The band at 1645 cm^{-1} may be a result of conjugated OH and C=O groups. The weak band at 1514 cm^{-1} can be caused by vibrations of the aromatic skeleton. The band at 1460 cm^{-1} is assigned to C-H deformation in methyl (CH_3) and methylene (CH_2) groups. The absorption at 1383 cm^{-1} represents C-H bending in lignin or cellulose. The bands resulting from the aromatic C-O stretching are observed at 1252 cm^{-1}. The shoulder at 1159 cm^{-1} is due to C-O-C stretching. The symmetric C-O-C stretching results in the broad band at 1051 cm^{-1}. The weak band at 897 cm^{-1} is due to the C-H deformation in cellulose. C=C bending is assigned at 665 cm^{-1}, and, the peak at 605 cm^{-1} is due to sulfate SO_4^{2-} which can be the result of oxidation of sulfur in the wood [22-25].

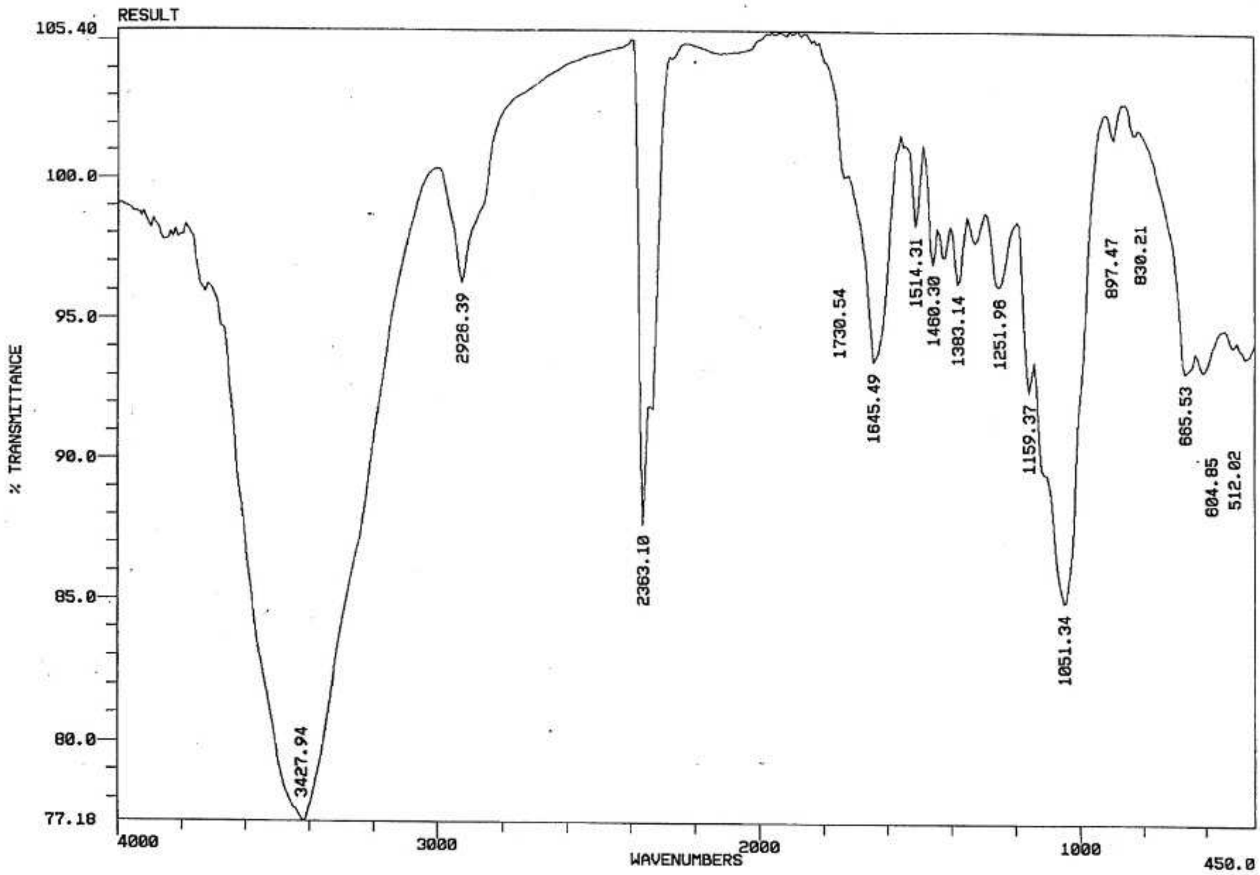

Figure 6. *FTIR spectrum of the wooden rod.*

3.3. Scanning Electron Microscopy

SEM was used to study the morphology of the wooden glass holder. As can be seen in Figure 7, some parts of the wooden rod appear to be partially burnt. The SEM micrograph reveals the difference between this part and the intact part of the rod. Because wood is a natural composite material, composed of cellulose fibers cemented together by lignin (a natural aromatic polymer), the differences between the two parts can be explained. The picture of the intact part of the wood represents cylindrical fibers oriented in a parallel pattern with some residues appear on the surface [26, 27]. Whereas in the burnt part, the parallel structure has been covered by some material, which can be attributed to the wood components with a lower glass transition temperature (T_g). The latter is assumed to have transformed or expelled from the hard texture by exposure to heat. Considering the polymeric structure of cellulose, hemicellulose, and lignin, it can be concluded that the residues on the surface of the cylindrical fibers have resulted from hemicellulose or lignin. The glass transition temperature of hemicellulose, lignin, and cellulose are respectively 40°C, 50-100°C, and above 100°C [28].

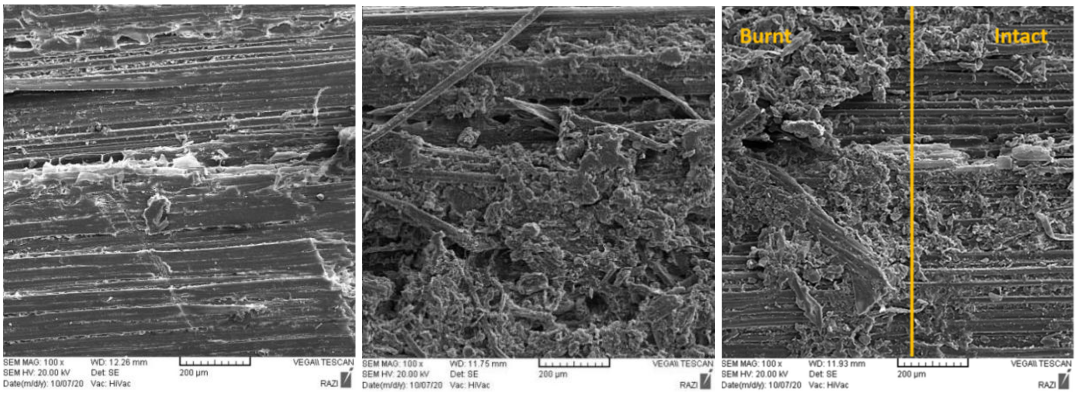

Figure 7. *SEM images wooden rod. Top left: Intact part, top right: burnt part and, down: the interface of an intact and burnt part.*

3.4. Energy-dispersive X-ray Spectroscopy

EDS was used for elemental analysis of the wooden rod. Table 1 reports the chemical elements present in the intact, burned part, and the intact-burnt interface. The spectra of this analysis are shown in figure 8 for the intact and burnt part. These elements include carbon, oxygen, silicon, sulfur, chlorine, potassium, calcium, and iron. The percentage of these elements is in accordance with findings in the literature [29]. The absence of Sulfur and Chlorine in the burnt part of the wooden holder is because of the release of these elements in gaseous form during burning in the past [30].

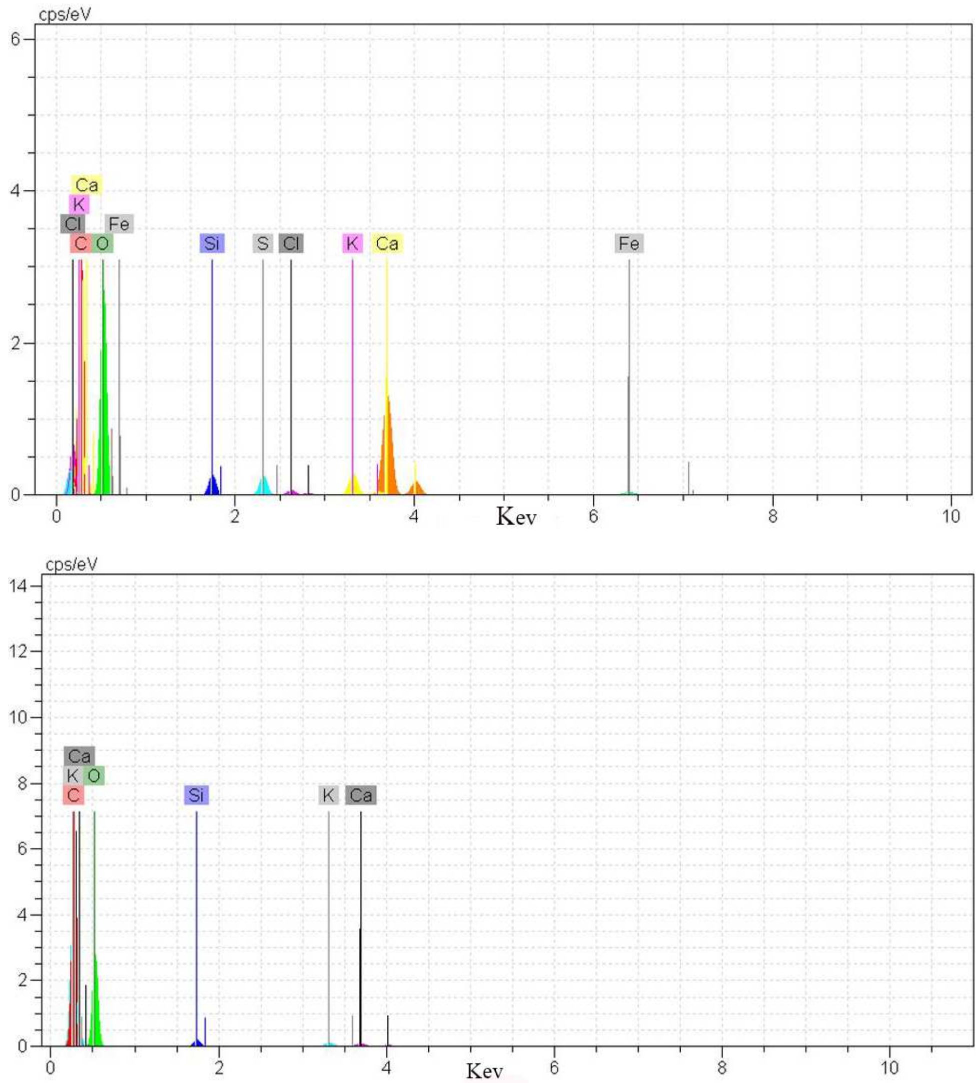

Figure 8. *EDS spectra of the wooden rod. Top: intact part and, down: burnt part.*

Table 1. *Chemical composition of the wooden rod in both intact and burnt part.*

Element	Intact		Burnt	
	%Weight	%Atomic	%Weight	%Atomic
Carbon	32.94	41.10	45.42	52.83
Oxygen	59.94	56.15	53.52	46.74
Silicon	0.33	0.17	0.36	0.18
Sulfur	0.43	0.20	-	-
Chlorine	0.18	0.07	-	-
potassium	0.95	0.37	0.34	0.12
Calcium	5.01	1.87	0.36	0.13
Iron	0.21	0.06	-	-

4. Conclusion

Different analytical techniques were used to investigate the status and the structure of a wooden rod discovered in the ancient region named Chogha Zanbil (Al-Untash-Napirisha). Optical microscope helped to distinguish the type of wood which is date palm tree. FTIR analysis of the wooden rod confirmed it has been applied on the door without any treatment. The spectrum represents all the bands resulting from vibration of wood ingredients including cellulose, hemicellulose and lignin with bands related to some inorganic elements can be found naturally. Images of SEM revealed the morphology of the rod which is in accordance with the previous findings for date palm wood. Furthermore, the difference between intact part and the burnt part of the rod was clear in the images. The results of EDS analysis was complementary to these images where the amount of some elements has changed due to partial burning in the past.

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