Surface and stratigraphic elemental analysis of an ancient Egyptian cartonnage using Laser-Induced Breakdown Spectroscopy (LIBS)

O. Aied Nassef, Harby E. Ahmed and M. A. Harith

An archeological Egyptian cartonnage dating back to the Greco-Roman period around the third century BC was elementally analyzed via the sample-friendly technique, Laser-Induced Breakdown Spectroscopy (LIBS). The unique characteristics of LIBS as being a simple and fast technique, has been exploited to obtain surface elemental distribution and depth profiles for the investigated sample. An Nd:YAG laser operating at the fundamental wavelength of 1064 nm has been used as the excitation source along with an echelle spectrometer coupled to an ICCD detector for spectral dispersion and detection. Under the experimental conditions, four distinct regions were studied as ten elements were analyzed for spatial distribution along the surface and also for their depth profiles. Rapid and comprehensive visualization of the investigated regions are provided. The most relevant elements i.e. carbon, calcium, silicon, oxygen and iron suggest that the cartonnage was manufactured via the traditional method, mainly dependent on natural pigments such as metal oxides and calcium carbonate (calcite) which is consistent with the previous results of other conventional techniques used in the field of Archaeology. Supporting studies obtained by both scanning electron microscopy with energy dispersive X-ray micro-analysis (SEM-EDX) and X-ray diffraction (XRD) have been presented for comparison purposes.

1. Introduction

The perfection of the archaeological Egyptian arts and pigments is evidently proven by the fact that ancient Egyptian artifacts, manuscripts and crafts made thousands of years ago are miraculously still clear and legible. Thus, studying the chemical composition of ancient materials is often among archaeologists’ main means of shedding light on all possible information that can be gathered about such objects. Investigating the pigments in ancient Egyptian artifacts has been the interest of many researchers. It has been noted, for example, that the black pigment is mainly made up of carbon which was obtained by mixing soot, vegetable gum and beeswax. This was frequently used as a homogeneous paint layer or mixed with other pigments to produce darker tones. To make ink of different colors, they substituted soot with other types of materials such as ochre to make red ink.

The analysis of ancient Egyptian pigments is expected to give information on the past technology and techniques adopted back then and additionally assist in choosing the proper restoration/cleaning methods. Many researchers were stimulated to study the suitable methods of restoration of ancient Egyptian printed textiles while others worked on the conservation of the ancient Egyptian manuscript “Bakai Book of the Dead” that was written in black ink. Moreover, the contribution of conventional spectroscopic techniques such as X-ray fluorescence (XRF) and X-ray diffraction (XRD) methods have been employed to provide the chemical compositions and crystal structures of ancient Egyptian materials, especially for characterization of pigments. Additionally, particle-induced X-ray emission (PIXE) implemented with an external microprobe has shown great ability to infer the elemental composition of ink as well as paper, papyrus and parchment. Thus, the investigated unique samples belonging to specific heritage ages may be quite analyzed without visible damage, however, such conventional techniques used to treat the historic objects may jeopardize them. Consequently, new approaches of more advanced technology are required to provide safer, practical and more reliable analysis/diagnosis/cleaning/conservation techniques.

Laser-Induced Breakdown Spectroscopy (LIBS) has been applied in the past decades 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, metal, glass, and stone artifacts. Its application on the elemental content identification and their spatial distribution for some examined material offers at appropriate spatial resolution a powerful tool in various research areas, where chemical imaging of surfaces and/or depth profile analysis, are required. LIBS has numerous advantages, especially being a sample-friendly analytical technique that implies minimal destruction of the
sample due to the minimum ablated material (~nano gram in a typical LIBS experiment) which promotes its role for heritage exploration. Recently, its capability extended to map the composition of the investigated sample and obtain a spatial distribution of a single chemical specie which eventually produces information in one or two dimensions and/or in higher dimensionality formats such as tomographic analysis. Besides performing elemental quantitative analyses, LIBS is capable of obtaining molecular and structural characteristics of the sample using sophisticated statistical methods, spectral databases and chemometric processing of the LIBS spectra.

Acknowledging that LIBS examination in the field of archaeology faces a lot of challenges including the value of the archeological object, its size and its surface sensitivity in terms of thickness and coated pigmentation (whether strongly adhering or not), complex spectra resulting from the presence of individual or a mixture of pigments, ..., etc. The specific aims of the present work are (i) to identify all the possible lines representing the cartonnage characterizing the different investigated regions (ii) to check/select sensitive analytical lines of the LIBS emission spectrum which are free of interference and overlapping, (iii) to study the selected emission lines as a function of the number of laser pulses providing a visualization of both surface and in-depth profiles of the cartonnage, and (iv) to provide supporting studies through SEM-EDX and XRD techniques for validation. The whole study is supposed to provide spectroscopic analyses including rapid qualitative assessment and imaging of both surface and depth profiling of the elemental distribution present in this unique archeological Egyptian cartonnage.

2. Samples

In funerary events in ancient Egypt, masks or panels were used to cover all or part of the mummified and wrapped body, the so-called cartonnage. It is used to form an inner coffin for mummies or an envelope around the mummified body of the deceased person before being placed inside a wooden coffin. The main periods in which the cartonnage was used in Egypt were the Middle Kingdom (2025–1700 BC), Third Intermediate Period (1069–664 BC) and Ptolemaic and Early Roman Periods (330 BC–250 AD). Depending on the specific time period of the use of cartonnage, distinct ingredients were used. It is generally composed of plastered layers of fiber or papyrus, flexible enough to follow the irregular surfaces of the body. The plastered surface coated with gesso, gave an even ground for painting motifs with various geometric designs, an assortment of deities and inscriptions, which included verses from the Book of the Dead.

The investigated sample is part of cartonnage pieces that were found in the valley of the golden mummies (Fig. 1a) which is dated back to the Greco-Roman period around the third century BC. It was discovered in 1996 and is considered the largest necropolis in Egypt discovered till the present day. It included about 250 mummies of mostly aristocracy who lived in the Bahariya Oasis during the Greco-Roman period. Based on the visible distinct colored regions appearing on the surface of the cartonnage, we focused on each color to study both the spatial elemental distribution by the application of both LIBS and SEM-EDX and to study the constituent compounds comprising the sample by the application of XRD. Fig. 1 b displays images of some fragments of the Egyptian cartonnage showing an overall sample view, besides the investigated selected face of one sample is shown in Fig. 1c, in which four visually distinct colored regions of interest are presented and listed in Table 1.

Fig. 1 (a) The valley of the golden mummies located in Bawiti Qasr, the capital of Bahariya Oasis and (b) photograph of some fragments of the Egyptian cartonnage under investigation. (c) A close-up photograph showing four distinct investigated regions, assigned for spatial elemental distribution by the application of LIBS, SEM-EDX and XRD.
Analytical Methods

Table 1  The labeling of the ordered distinct regions considered in our study which are subject to the analyses of LIBS, SEM-EDX and XRD

<table>
<thead>
<tr>
<th>Region</th>
<th>Region type</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>Reddish brown pigmentation</td>
</tr>
<tr>
<td>2</td>
<td>Black pigmentation</td>
</tr>
<tr>
<td>3</td>
<td>Yellowish pigmentation</td>
</tr>
<tr>
<td>4</td>
<td>Linen</td>
</tr>
</tbody>
</table>

These four mentioned regions will be subject to the present investigation via LIBS, SEM-EDX and XRD.

3. Experiment and methodology

In applying the LIBS technique, a Q-switched Nd:YAG pulsed laser (BRIO, Quantel, France), 5 ns FWHM, operating at the fundamental wavelength of 1064 nm was used as the excitation source. A plano-convex fused silica lens with a 10 cm focal length is used to focus the laser beam onto the surface of the sample to a spot of ∼86 μm and produce the induced plasma. For the present experiment, the pulse energy was set to 75 mJ and a repetition rate to 1 Hz which provide a laser fluence of ∼1300 J cm⁻². The samples were mounted on an X-Y translational stage for controlling the irradiated position. The emitted light from the laser-induced plasma is transferred to a 1.5 m optical fiber (600 μm diameter) which is coupled to an echelle spectrometer (Mechelle 7500, Multichannel instruments, Sweden) provided with an ICCD camera, DiCAM-PRO (PCO computer optics, Germany) for the detection of the produced plasma emission. The echelle spectrometer provides a constant spectral resolution of 7500 corresponding to 4 pixels FWHM, over a wavelength range 200–1000 nm, displayable in a single spectrum. The overall linear dispersion of the Mechelle spectrometer-camera system ranges from 0.0078 (at 200 nm) to 0.032 nm per pixel (at 700 nm) with a high-resolution sensor of 1280 × 1024 pixels (9 × 9 μm²). The obtained atomic emission spectra are displayed on a PC where data analysis and processing are carried out using the commercial 2D- and 3D-Gram/32 software programs (National Instruments, USA). Additionally, peak identification is performed using LIBS++ software the main task of which is to compare the measured center wavelengths and intensities to those of each element as listed in a large emission spectra database based on the National Institute of Standards and Technology (NIST).²⁵

The parameters affecting the diameter of the formed crater have been carefully considered, thus, a proper choice of the applied laser wavelength, beam divergence and focal length of the optical system was considered in order to minimize the spot diameter of the focused laser beam. Additionally, the availability of a laser source working in well-defined temporal and spatial modes (TEM₀₀) enabled us to focus the laser to its diffraction limit with high precision to obtain the best lateral resolution. The lateral resolution was set to ∼100 μm as the calculated waist of the crater was found to be ∼50 μm. Spectral acquisitions resulting in visually overlapped craters were ignored and repeated for accurate results.

Due to the rigorous nature of LIBS shot-to-shot signal variation, the laser pulse energy was monitored and recorded, before running the experiment, using a joule meter (SCIEN-TECH, model AC5001, USA energy meter). High stability of successive laser pulses was ensured at a fixed flash lamp voltage of 620 V. Additionally, the control of the detection system was performed using special multichannel software and the CCD intensifier high voltage was triggered optically at a typical optimized delay time of 1500 ns and a gate width of 2000 ns to avoid electronic interference and jitters. Moreover, to improve the S/N ratio of the spectral intensity, line emission was analyzed either as it was measured under the specified experimental conditions (laser pulse energy, focusing geometry and gate parameters) minus the background intensity or normalized with respect to their total intensity which allows estimation of the relative abundance of the elements of interest.

Taking advantage of the inherent feature of laser-induced plasma, its spatial localization,²⁴ the LIBS capability to determine compositional variations among different sample regions was exploited. This was performed by analyzing the output spectral data of line scans of sampling points covering enough surface and also digging deeper by successive laser pulses for investigating the depth profiles. During each scan for each investigated region of the cartonage, we considered that the mean signal represents the average concentration of a particular element in the sample, while variations of the signal reflect elemental distribution within the sample. Moreover, monitoring the intensities of some elements at consecutive laser shots on the same sample position provides the depth profile at this specific position. In our approach, two sets of data were collected for each region; one set represents spectra acquired as the focused laser beam irradiates fresh spots while the other set is obtained as the focused laser pulses successively hit the same spot. In other words, the application of a single laser pulse on a fresh spot, then three laser pulses on another fresh spot then five, seven, ten, and twenty laser pulses on fresh spots resulted in the intensity change that corresponds to the first set of data (regime 1). The second dataset is the application of a single laser pulse on some position then three laser pulses on the same position, five, seven, ten, and twenty laser pulses on the same position which leads to the sixty-one pulses accumulated in the same spot leading to a visibly deep crater (regime 2). In brief, the same series of laser pulses were applied either on fresh spots (regime 1) or on the same spot (regime 2). In both cases, the spectral analyses were based on the acquired spectral data resulting from one laser pulse, three laser pulses, five, seven, ten, fifteen, and twenty laser pulses which definitely form different laser-produced craters as systematically increased laser pulses dig deeper into the sample for both mentioned regimes. As an example, the spectral data analyzed when seven consecutive laser pulses hit either a fresh spot (regime 1) or a previously produced crater (regime 2) constitute the acquisition resulting from only such seven consecutive laser pulses. The spatial distribution and depth characterization of the sample were performed by simultaneously monitoring eight elements for each of the four distinct regions shown in Fig. 1(c).
The investigated cartonnage was examined, imaged, and analyzed via a scanning electron microscope (SEM) and an energy dispersive X-ray (EDX) microanalysis unit (Model Philips Quanta FEG 250, Holland) along with an electron probe microanalyzer with an accelerating voltage of 20 kV. The samples were mounted on a holder and were investigated directly without any surface coating. The special design of the vacuum system allows a working pressure up to approximately 60 Pa. SEM-EDX analyses were applied to the samples to examine the surface morphology, the samples’ composition, and elements’ concentration.

A complementary analytical technique, X-ray diffraction (XRD) which is well known for the analysis of pigments and minerals is applied for the analysis of the most probable existing compounds in the sample. In applying this technique, we were faced by a substantial difficulty that the sample needs to be ground to form a powder. XRD analysis was carried out using an Empyrean-PANalytical X-ray diffractometer equipped with a variety of different sample holders including a rotating one. The X-ray source is comprised of a Cu radiation tube of wavelength 1.54 Å at 45 kV, 40 mA, 0.004° sec⁻¹ with a beta filter nickel. Measurements were performed on both bulk and minute amounts of the powdered sample using a PIXcel 3D detector, in the range 0° < 2θ < 100° with a step of 0.013°.

4. Results and discussion

4.1 LIBS analysis

In laser-induced plasma, the spectral emission lines of an element are ideally proportional to its concentration. However, this depends on the optical thickness of the plasma which is commonly related to a complex interaction mechanism between the laser, the ablated species and the emitted radiation, which could suffer immediate re-absorption by the cold absorbing atoms in the periphery of the plasma. Thus, the laser-induced plasma can be optically thick for some particular wavelengths, especially the most intense lines (resonance lines) of elements present at concentrations greater than approximately 0.1%. It can also become thick for less intense lines at higher elemental concentrations. This leads to lower intensities of the self-absorbed lines and hence incorrectly indicates a lower concentration of the element. Consequently, the spectral emission lines were carefully chosen to be representative of the actual sample constituents. As an example, two calcium emission resonance lines Ca II 393.366 nm and Ca II 396.847 nm that suffer self-absorption were avoided when analysis was performed. Fig. 2 shows an example of LIBS spectra for Region (2) (black pigmentation), when single and five laser pulses hit two fresh spots, respectively. The characteristic spectral emission lines are identified and listed in Table 2. For the four investigated regions, twelve spectral emission lines were chosen to represent the first eight elements, shown in Table 2. Such spatially distributed elements whether on the surface or deep into the layers of the sample are examined and analyzed to construct the elemental profiles for the investigated Egyptian cartonnage.

Under constant experimental conditions, the laser irradiance plays the main role that will affect both the averaged ablation rate and depth resolution. The experiment was carried out at fixed parameters, namely the laser wavelength (1064 nm), laser pulse width (5 ns), and the experiment geometry. The synchronization of the laser pulses with the spectra acquisition was set automatically while the lateral sample positioning was performed manually considering that the distance travelled

![Fig. 2 LIBS spectra when single laser pulse (low intensity) and five laser pulses (high intensity) are focused on region 2 (black pigmentation). Some spectral emission lines of the most common elements are identified.](Image)
between successive craters is set to avoid overlapping between adjacent craters. Additionally, for depth profiling, the experiment was run at a low laser fluence to obtain information about the lowest number of atomic layers. However, this affected the appearance of some emission lines in the spectra which could be attributed to lowering the rate of ablation, vaporization, atomization and ionization processes. Thus, we performed the experiment at a higher laser pulse energy of \( \sim 75 \text{ mJ} \) that was focused on the sample surface creating a laser fluence of \( \sim 1300 \text{ J cm}^{-2} \). The relative intensity of some elements was plotted as a function of the number of pulses for two cases, when the laser beam successively hits fresh spots and when it is consecutively accumulated on the same spot (Fig. 3). It is observed that the behavior of the line intensity increases with increasing number of laser pulses as the laser pulses hit consecutive fresh spots on the surface (Fig. 3a) while it shows an intensity increase followed by a decrease as the laser digs deeper as shown in Fig. 3b. This might be attributed to the formation of a laser-induced crater that changes the geometry of the collection parameters by increasing the laser pulses that hit the same position.

The normalized intensity of twelve selected emission lines (Table 2), associated with the common elements (C, Mg, Si, Al, Cu, Fe, Ca, and Na) relevant to our sample, was plotted as a function of the number of laser pulses for two cases, for fresh irradiated spots (Fig. 4) and for laser hitting in the same position, as shown in Fig. 5. The use of two spectral emission lines for Mg, Fe, Ca and Na, as listed in Table 2, showed almost the same behavior as the number of laser pulses increase. As previously mentioned, the LIBS spectra were normalized to the total emission intensity, thus the plots allow evaluation of the variations in the relative concentration of each of the ten elements. Following this methodology, we obtain a semi-quantitative multi-elemental chemical profile of the different regions. Also, the plots have been stacked for comparison purposes. For each of the individual chemical profiles, values to the right represent higher element concentration. Two different vertical zones can be identified in all eight profiles (Fig. 4 and 5) depending on the number of laser pulses hitting the sample. Zone 1 presents high variability for several elements upon the application of one pulse, for the four investigated regions as observed in both Fig. 4 and 5. This is consistent with the presence of surface alteration of the pigmentation coatings that correspond to the four investigated regions labeled in Fig. 1(c). Digging deeper by increasing the number of laser pulses, a high concentration of Si and Fe near the surface sooner depletes as a function of depth (Zone 2). This could be interpreted as a Fe-Si-rich coating possibly due to Fe-oxides + silica or Si-enriched Fe-oxides. On the other hand, some elements, such as Ca and Mg, are found to increase in concentration with depth (Zone 2). The graphs cannot precisely define the transition between zones which is consistent with previous findings for LIBS analyses of rock coatings.26 This could be attributed to the natural variability and geometric irregularities of the different layers. Furthermore, the interaction of matter with nanosecond laser pulses induces melting of the sample that causes modification and mixing of different layers and therefore deteriorates depth resolution.27 The results support the previously reported scenario of cartonnage manufacture that moist layers of soaked linen and gesso either in the form of a calcium carbonate- or

### Table 2

<table>
<thead>
<tr>
<th>Element</th>
<th>Spectral emission line(s)</th>
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<tbody>
<tr>
<td>1 Carbon</td>
<td>C I 247.842 nm</td>
</tr>
<tr>
<td>2 Magnesium</td>
<td>Mg II 279.55 nm, Mg II 280.20 nm</td>
</tr>
<tr>
<td>3 Silicon</td>
<td>Si I 288.15 nm</td>
</tr>
<tr>
<td>4 Aluminum</td>
<td>Al I 308.21 nm</td>
</tr>
<tr>
<td>5 Copper</td>
<td>Cu I 324.75 nm</td>
</tr>
<tr>
<td>6 Iron</td>
<td>Fe I 344.09 nm, Fe I 404.58 nm</td>
</tr>
<tr>
<td>7 Calcium</td>
<td>Ca II 370.60 nm, Ca II 373.93 nm</td>
</tr>
<tr>
<td>8 Sodium</td>
<td>Na I 285.28 nm, Na I 588.99 nm</td>
</tr>
<tr>
<td>9 Oxygen</td>
<td>O II 429.04, O II 430.17 nm</td>
</tr>
</tbody>
</table>

![Fig. 3](image) The relative intensity of some chosen elements as a function of the number of laser pulses when hitting fresh spots (a) and when hitting the same position (b). These output intensity data belong to Region (2) (black pigmentation).
calcium sulphate-base were moulded into the mummy’s body and after drying, the gessoed surface was smoothed (the wash layer) before application of paint or gold leaf. A further layer of gesso was often applied with a brush to the underside of the casing to give it further strength and rigidity.28–31

4.2 Scanning electron microscope SEM-EDX

The Scanning Electron Microscope (SEM) images provide a characteristic surface morphology and are useful for judging the surface structure of the investigated sample.32–34 A combination of SEM (Model Philips Quanta FEG 250, Holland) and an electron probe micro-analyzer with an accelerating voltage of 20 kV, along with an EDX microanalysis unit, was used to reveal both morphological diagnostic features for each of the cartonnage investigated regions and the corresponding qualitative and quantitative elemental analysis. Fig. 6 displays SEM images of the Egyptian cartonnage where reflected e-beam micrographs of the different assigned regions previously mentioned provide both a front view, shown in (a) and a cross-sectional view of the sample layers, shown in (b). SEM images showed that the surface is extremely roughened, damaged, and cracked with small holes and slits. The cartonnage is clearly made of several layers; the first layer of very thin pigmentation of less than 3 μm (which includes the different colored regions under investigation) followed by a yellowish layer of thickness ~0.8 to 1 mm. The thickness of the textile part ranges from 1.5 mm to 2 mm. The textile structure includes two types of weaving; one is a plain 1/1 weave which is the simplest of all weaves and it has one-over one-under interlacing yarns. The other type is yarns twisted in circular turns.

Scanning electron micrographs of the areas, listed in Table 1, subject to EDX mapping, are represented in Fig. 7(a, c and e), while their corresponding EDX spectra representing the elemental composition of each region is shown in (b, d and f). The concentration results are taken as the average of three
different concentrations of three different spots on the sample. A close-up view of all regions demonstrated a high concentration of carbon (C) that exists as a major element while the elements Si, Al, Cl and Ca have also been found throughout the sample which might be the constituent of regular formation of the wash layer. Evidence of Fe and K were obtained in both

Fig. 5 The normalized intensity of some elements as a function of depth for the four investigated regions: (a) Region (1), (b) Region (2), (c) Region (3) and (d) Region (4) under the application of laser pulses on the same position.

Fig. 6 SEM images of the Egyptian cartonnage. (a) Reflected e-beam micrograph of the cartonnage showing a front view of the different assigned regions previously mentioned. (b) A side-view showing a cross-section of the sample layers which agrees with the conventional method of constructing a cartonnage belonging to this specified period.
Fig. 7  (a) Reflected e-beam micrographs (1000×) of the four investigated regions of the cartonnage (listed in Table 1) are displayed in (a, c, e and g). Their corresponding EDX spectra representing the main elemental peaks superimposed on the background for each of the investigated regions are displayed in (b, d, f and h).
Regions 1 (reddish brown) and 3 (yellow) as minor elements. The presence of oxygen suggests that most elements are present as oxides. Alumina was known to be added as a stiffening agent and to prevent pigmentation from running off the surface. The elemental EDX output is listed in Table 3 referring to elements’ concentration of each element detected in surface analysis of the four investigated regions.

### Table 3 The output results of the energy dispersive X-ray (EDX) analytical technique for the elements’ concentration for each of the investigated regions of the Egyptian cartonnage

<table>
<thead>
<tr>
<th>Elements</th>
<th>Region 1 (reddish-brown)</th>
<th>Region 2 (black)</th>
<th>Region 3 (yellow)</th>
<th>Region 4 (linen)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Weight%</td>
<td>Atomic%</td>
<td>Weight%</td>
<td>Atomic%</td>
</tr>
<tr>
<td>C</td>
<td>28.12</td>
<td>38.23</td>
<td>58.28</td>
<td>66.06</td>
</tr>
<tr>
<td>O</td>
<td>50.36</td>
<td>51.39</td>
<td>38.15</td>
<td>32.46</td>
</tr>
<tr>
<td>Na</td>
<td>1.08</td>
<td>0.77</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mg</td>
<td>0.63</td>
<td>0.42</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Al</td>
<td>1.49</td>
<td>0.9</td>
<td>0.58</td>
<td>0.29</td>
</tr>
<tr>
<td>Si</td>
<td>2.41</td>
<td>1.4</td>
<td>0.74</td>
<td>0.36</td>
</tr>
<tr>
<td>S</td>
<td>5.13</td>
<td>2.61</td>
<td>0.5</td>
<td>0.21</td>
</tr>
<tr>
<td>Cl</td>
<td>0.35</td>
<td>0.16</td>
<td>0.3</td>
<td>0.11</td>
</tr>
<tr>
<td>K</td>
<td>0.26</td>
<td>0.11</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Ca</td>
<td>8.99</td>
<td>3.66</td>
<td>1.44</td>
<td>0.49</td>
</tr>
<tr>
<td>Fe</td>
<td>1.7</td>
<td>0.54</td>
<td>—</td>
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**4.3 X-ray diffraction (XRD) analysis**

A supporting high-tech qualitative analytical technique, X-ray diffraction (XRD) is applied in the present work that may provide a clearer picture of the investigated sample’s compounds. The identification of thin paint layers or layers with very low pigment content by XRD can be simply obtained since the technique relies on the dual wave/particle nature of X-rays that can conclude information about the structure of crystalline materials. XRD is basically based on the scattering process of the incident X-rays with sample particles which results in the formation of a diffraction pattern. A noteworthy drawback of such a technique in terms of archeological purposes is that the sample should be processed and prepared in the form of powder before being exposed to XRD. However, due to the rarity of the investigated sample and the dire need for its conservation, the XRD examination was performed following two regimes; the analysis of only minute powdered fragments and the analysis of the surface of the bulk sample. The available resulting spectra using the aforementioned experimental conditions are presented in Fig. 8 where the peaks are assigned and identified using PANanalytical XRD analysis software with a typical reference database. Qualitative identification of powdered minute fragments of the sample indicates the existence of calcite (Fig. 8a) while the detected components corresponding to the surface of the bulk sample show that Cu–Fe–S represents the major surface compound (Fig. 8b).

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**5. Conclusions**

In the present study, Egyptian cartonnage fragments, from the Valley of the Golden Mummies excavation in the Bahariya Oasis, dating back to the Greek Roman period have been characterized by LIBS. The capability of the technique of spatially resolved analysis from discrete points with instantaneous detection of the plasma emission offered immediate...
information about the distribution of the surface chemical elements and depth profiling of the investigated samples. Under the adopted experimental conditions, the application of successive laser pulses on fresh spots gradually drills (micro-scale depth profiling) through the different layers of the sample, enabling us to analyze the locally produced spectra and thus provided both the surface and in-depth elemental distribution of eight elements for the four investigated regions. The results provided a visualization of the four distinct investigated regions of the archeological Egyptian cartonnage in terms of surface and in-depth analysis. This agreed with previous reports on Egyptian cartonnage manufacture. Supporting techniques SEM-EDX and XRD LIBS provided elemental analyses which validate LIBS results.

This work offered a fast, semi-quantitative elemental image of the investigated archaeological sample and gave an idea of the technology of cartonnage making: sticky linen surrounded with layers of gesso which is composed of either calcium sulfate or calcium carbonate as a base covered with a top wash layer for the surface painting coating. This may suggest that the availability of a portable or transportable LIBS unit would effectively satisfy the need for archeological tactical operations for simple and rapid analyses that could be conducted in situ at the museum, an excavation site, or certainly at the cleaning and/or restoration laboratory.

References


