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Analysis of the pigments in two modern Egyptian papyri using XRF technique

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ABSTRACT

In this work, two modern Egyptian papyrus belonging to a private collection were analyzed using X-Ray Fluorescence technique (XRF). The papyri are genuine, made from the papyrus plant, and hand-painted. The papyri were bought in the city of Cairo, Egypt, in the '80s and brought to Brazil in the same period. XRF analyses were performed using a portable spectrometer ARTTAX (X-ray tube with Mo anode and a Silicon Drift Detector XFlash®, Bruker AXS Inc.). XRF measurements were carried out under the following experimental conditions: 35 kV, 600 µA, unfiltered x-ray beam, air atmosphere, acquisition time of 600 s. The elements detected in the two papyri were: Si, Al, S, Cl, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, Ba and Pb. Through the XRF analysis it was possible to evaluate the pigments found in the two papyri are different from each other. In the analysis of the blue color, present in the papyrus, it was observed that the composition of this color can be a mixture of two pigments: Egyptian blue ($CaCuSi_4O_{10}$) and Lithopone ($ZnSBaSO_4$). Most of the pigments on the papyri were thus recognized to be modern, their syntheses, or refinement processes not being known to ancient Egyptians.

Keywords: **XRF Technique, Modern papyrus, Pigments.**

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1. INTRODUCTION

Papyrus was the most popular writing material in the world. Before it was replaced by paper, papyrus was a writing material as early as 3,000 BC in ancient Egypt and continued to be used to some extent until around 1100 AD [1]. Nowadays, modern papyrus is used by artists and calligraphers [2]. Papyrus paintings depicting the daily life, mythology, gods, and goddesses of ancient Egypt attract admirers from all corners of the globe of this long and rich history of Egypt, making papyrus art a good reminder of this fascinating place. A relevant subject of study in the sphere of ancient Egyptians is pigment characterization. Many studies can be found in the vast corpus of pigments used in ancient Egyptian [3, 4].

X-ray fluorescence (XRF) is one of the most widely used nondestructive techniques in the analysis of artwork and cultural heritage, providing the elemental composition of the studied artifact. The analytical identification of pigment through the XRF technique involves its color and elemental composition, i.e., the presence of specific key elements [5, 6].

Since the chronology of pigments use is well established in the literature, it is possible to determine in some cases – based on the analysis of XRF spectra – the provenance, historical period, and, consequently, the authenticity of a painting or artifact. Besides that, the information obtained from the XRF analysis can help in the identification of forgeries and the evaluation of conservation and restoration procedures, allowing the cultural heritage of ancient civilizations to live forever [8, 9].

In this work, two modern Egyptian papyrus belonging to a private collection were analyzed using XRF technique. These papyri are genuine, made from the papyrus plant and hand-painted. Both papyri were bought in the city of Cairo, Egypt, in the ‘80s and brought to Brazil in the same period. The purpose of this work was to identify the elemental composition of the pigments that are employed in modern Egyptian hand-painted papyrus artwork and to compare them with the pigments used in the art of ancient Egypt.

2. MATERIALS AND METHODS

2.1. Samples

Two modern papyri belonging to a private collection in Rio de Janeiro were examined using the X-Ray Fluorescence technique (XRF). The papyri in this study were named papyrus 1 and papyrus 2. Papyri were bought to Cairo in the ‘80s and brought to Brazil in the same period. Both papyri are genuine, made from the papyrus plant and hand-painted.

2.1.1 Papyrus 1

Papyrus 1 is a famous scene of king Tutankhamun and his wife Ankhesenamun (Fig. 1). Tutankhamun (18th dynasty, 14th C. BC) became pharaoh was about nine years old after the death of his father Akhenaten. At about the age of eighteen or nineteen, Tutankhamun died suddenly, leaving Ankhesenamun alone. The discovery of his tomb was in 1922 [10]. The painting is a scene of the Tutankhamun receiving an offering from his wife. Papyrus's size 32.8 cm x 41.2 cm.

Figure 1: *Papyrus 1 – King Tutankhamun and his wife.*

2.1.2 Papyrus 2

The other papyrus analyzed (papyrus 2) is a hunting scene of the Tomb of Nakht (Figure 2). Holding the title the "scribe" and the other title "serving priest of Amon" at the Karnak temple, probably during the 18th dynasty. The Tomb of Nakht was discovered by European explorers in 1889. This painting is a double scene, with flocks of rising birds. Nakht is portrayed with his wife and two small sons in a papyrus boat, grasping a hunting stick [11]. Papyrus's size 31,5 cm x 44,8 cm.

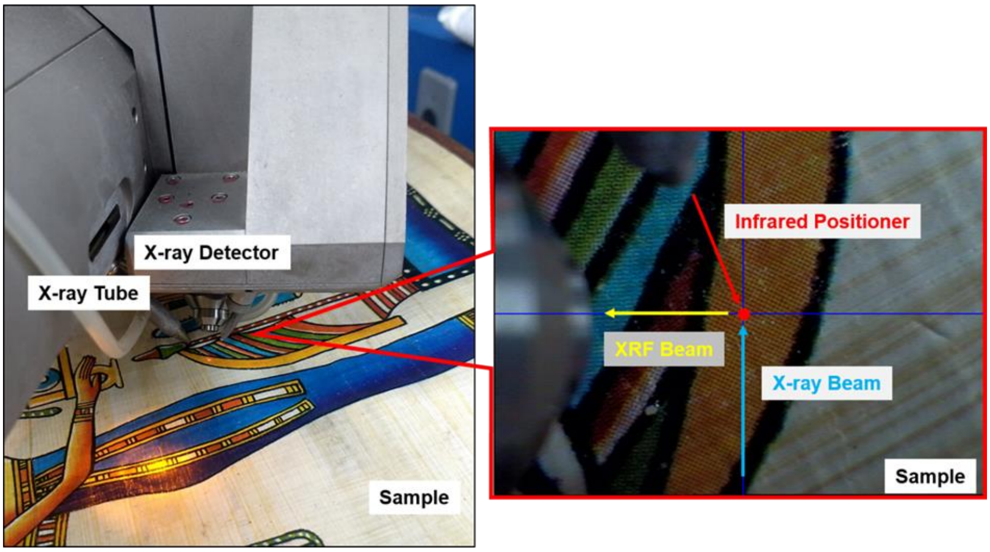
Figure 2: *Papyrus 2 – The hunting scene of the Tomb of Nakht.*

2.2. XRF analysis

The two papyri were analyzed using the ARTAX 200 equipment. ARTAX 200 system (Bruker), consisting in an air-cooled that it has a Mo anode X-ray tube and an X Flash SDD detector (Silicon Drift Detector) with an energy resolution of 145 eV for the Mn-K_{α} energy line. The XRF analyses were performed at three different points in each region, totaling 33 points. The analyses were performed with a voltage and current of 35 kV and 600 μA, respectively, and a measurement time of 600 s. The X-ray beam size on the sample is 600 μm (beam diameter). An integrated CCD camera providing a magnified digital image of the sample region under investigation. In addition, there is a white LED that illuminates the sample to optimize image quality and contrast. On the other hand, a red laser diode is used to control the exact position of the X-ray beam on the sample. So, the laser spot is adjusted to the focus of the mini lens and recorded by the CCD camera, in this way, the operator can always see the exact position of the X-ray beam in the video window of the system software running on a connected notebook.

All the XRF-Spectra were evaluated using the open source PyMCA software package [12]. Figure 3 shows papyrus 1 being positioned for XRF measurements.

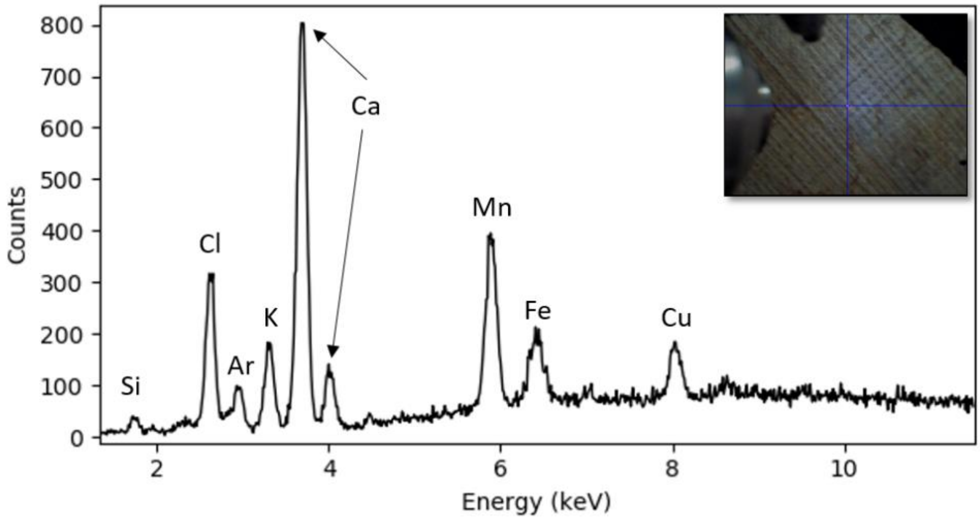
Figure 3: *ARTAX with zoom of geometric set-up of the X-ray beam on the sample*



3. RESULTS AND DISCUSSION

The characterization of the pigments used in papyrus paintings can be identified by the presence of key elements in the spectra associated with the color of the analyzed region. It should be noted that not all the elements found in the analyzed point are characteristic of the pigment. This is due to the contribution of the XRF lines of the ground layers and also because the colors are often laid one over the other [5, 6]. The first analyses were on the papyrus sheet, a region without pigment, in order to know its elemental composition, our control. Figure 4 shows an XRF spectrum of a region of papyrus without pigments. Both papyri have the same elemental composition.

Figure 4: *XRF spectrum of papyrus sheet - region without pigment (control)*



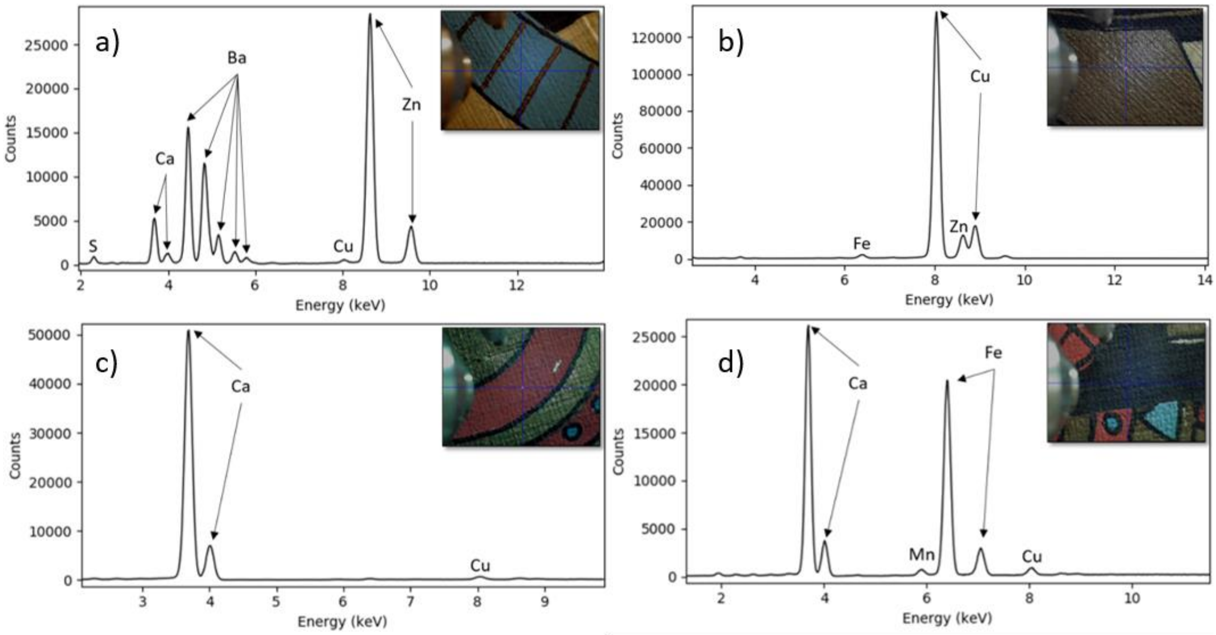
Seven elements were detected in the papyrus sheet: Si, Cl, K, Ca, Mn, Fe and Cu. The XRF analyses were not performed in vacuum and the presence of the Ar in the XRF spectrum is the contribution of the air (dry air contains about 1.0 % of Argon by volume, 1.0 atm, 20°C).

3.1. Papyrus 1 (King Tut and His Wife Scene)

In the papyrus 1, were analyzed four different colors: Blue, gold, red, and black. The XRF analysis detected seven elements: S, Ca, Mn, Fe, Cu, Zn e Ba. Figure 5 shows the XRF spectra of each pigment analyzed. Based on the elements that exhibited the highest intensities, the possible pigments were established. Table 1 shows the elemental intensities of each color of Papyrus 1.

In the blue pigment, the elements that presented the highest intensities were Ca, Cu, Zn and Ba. The presence of Ca and Cu suggest the possibility of Egyptian blue ($CaCuSi_4O_{10}$), the oldest synthetic pigment, produced in Egypt from the 4th Dynasty (2600 BC) [3, 4]. The presence of Zn and Ba indicate a possible mixture of the Egyptian blue pigment with White Pigment Lithopone ($ZnS + BaSO_4$). White pigments are commonly used as a bleaching agent [8]. However, this white pigment was first synthesized in 1878 [5].

Figure 5: *XRF spectra of pigments found on the papyrus 1: (a) Blue, (b) Golden, (c) Red and (d) Black.*



In the gold pigment analysis, Cu and Zn presented the highest intensities. The copper-zinc alloy is known as bronze. The gold bronze pigment is obtained by melting respectively copper and zinc raw material. [6, 13].

In the red pigment, the highest intensities were exhibited in Ca and Cu. In this case, probably the contribution of Cu is due to the nearby golden pigment. At some points on papyrus 1, the red pigment is above the golden pigment. Besides, according to Calza et al. [5], the minerals hematite (or red ochre) and goethite, used to obtain ochre pigments, can be found associated with cuprite (Cu_2O) and other minerals. Thus, only Ca would be the characteristic element of red. One hypothesis is that perhaps this red pigment is Lithol Bordeaux 2r ($C_{21}H_{12}CaN_2O_6S$), an organic pigment powder of Chinese origin [14]. The red pigments found in the literature that were used in ancient Egypt are Orpiment (As_2S_3); Realgar (As_4S_4) and Hematite (α-Fe_2O_3) [3, 5]. Anyway, only with Ca is it not possible to obtain sufficient information about the possible red pigment used in this painting. The XRF technique is able to determine only the elemental composition and not the molecular composition of the analyzed samples. However, the presence of calcium in the XRF spectrum obtained in the red pigment may be indicative of an organic pigment.

The organic pigment refers to colored material made of an organic compound with pigment properties. Common types include azo pigments, lake pigments (such as aluminum lakes (Al), calcium lakes (Ca) and Barium (Ba)), phthalocyanine pigments and quinacridone pigments [15,16]. Since the organic pigments are derived from minerals, this red pigment found on papyrus 1 may be from mineral source.

In the black pigment, Ca and Fe exhibited the highest intensities. There are many possibilities for this pigment. One of them is the magnetite (Fe_3O_4) and the other possibility is the Asphalt pigment. Asphalt is a complex mixture of organic (bitumen) and inorganic components cannot be characterized by a single chemical formula. The mineral components of Asphalt pigment also vary according to the location where the mineral was found and contain in most cases aluminum silicates and carbonates as well as silicon, aluminum, iron, and calcium oxides [17]. Table 1 shows the elemental intensities of each color of Papyrus 1.

Table 1: The relationship between the detected elements and the pigments present on papyrus 1 (n = 3)

Elements	**Color of the analyzed region**			
	Blue	**Golden**	**Black**	**Red**
S	7258 ± 671[a]	ND[b]	ND	ND
Cl	ND	4951 ± 1895	1417 ± 88	1318 ± 43
K	ND	ND	1331 ± 81	ND
Ca	**50309 ± 7079**[c]	6063 ± 3345	**263667 ± 28688**	**517372 ± 64656**
Cr	ND	615 ± 152	ND	ND
Mn	ND	3031 ± 696	5547 ± 1912	ND
Fe	1496 ± 37	17813 ± 6773	**240006 ± 23414**	ND
Ni	ND	ND	ND	2678 ± 229
Cu	4439 ± 629	**1783578 ± 216721**	2352± 781	6754 ± 1324
Zn	**404765 ± 279**	**164768 ± 24435**	ND	2748 ± 431

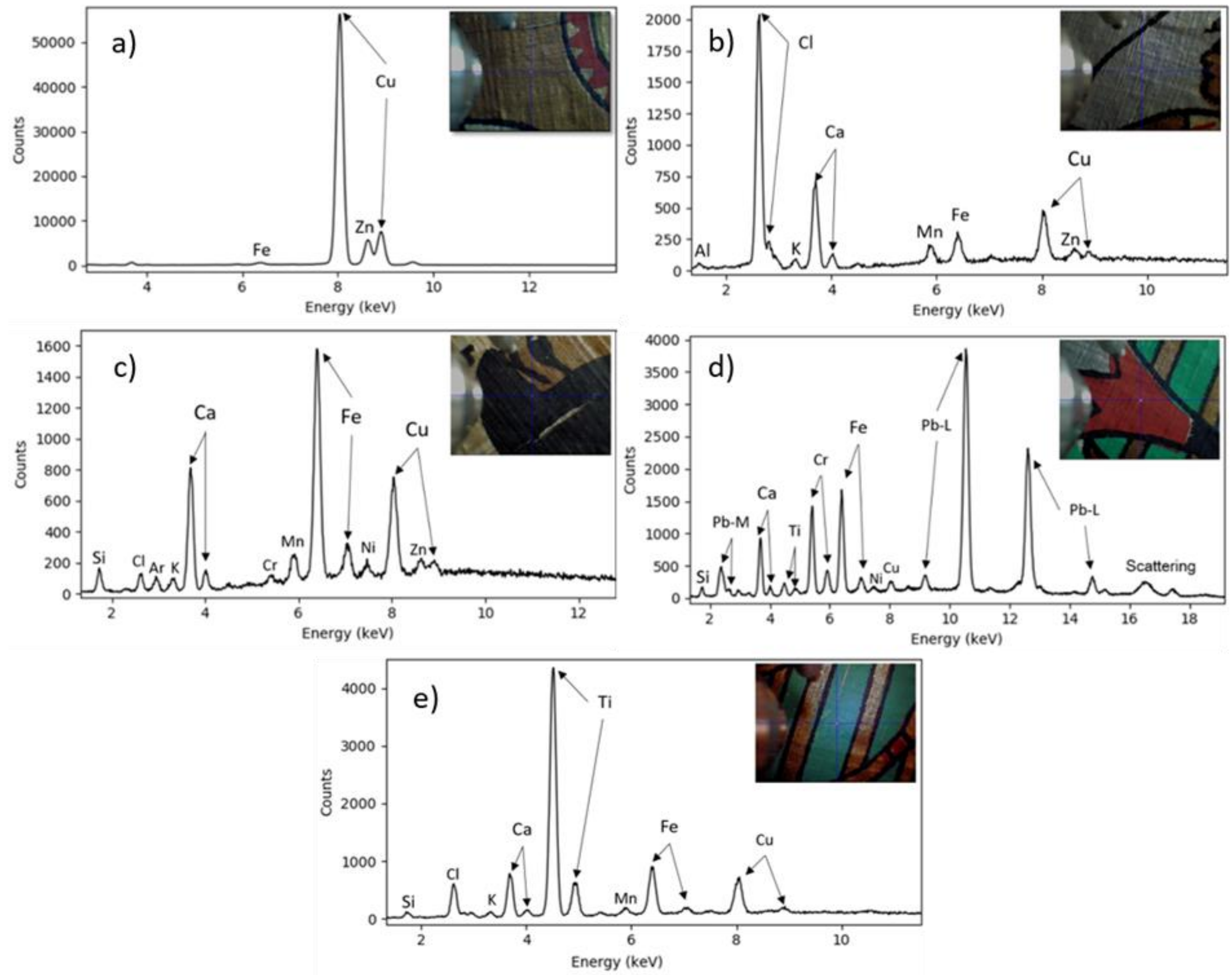
Sr	ND	ND	ND	1151 ± 127
Ba	**221425 ± 8934**	ND	ND	ND

a. Mean ± Standard deviation; b. ND = Element not detected; c. Counts in bold = Major elements of each color.

3.2. Papyrus 2 (The Hunting Scene of the Tomb of Nakht)

In papyrus 2, five different colors were identified: gold, silver, black, red, and green. The XRF analysis showed the presence of twelve elements: Si, Cl, Ar, K, Ca, Mn, Fe, Ni, Cu, Zn and Pb. Figure 6 shows the XRF spectra obtained from the pigments. Table 2 shows the elemental intensities of each color of Papyrus 2.

Figure 6: *XRF spectra of pigments found on the papyrus 2: (a) Golden, (b) Silver, (c) Black, (d) Red and (e) Green.*



In the gold pigments, the predominant elements detected were: Cu and Zn (cf. the situation for papyrus 1). It is probably the same pigment used in papyrus 1, obtained by melting raw materials of copper and zinc. [6, 13].

In the silver pigment, XRF analysis showed the presence of Al, Cl, K, Ca, Mn, Fe, Cu and Zn. In this pigment, Cl and Ca exhibited the highest intensities. Therefore, this may be indicative of the mixing of mineral pigment and a metallic pigment due to the presence of Fe, Cu and Zn.

In the black pigment, Ca, Fe and Cu exhibited the highest intensities. The difference between the black pigments in the two papyri is the Cu intensity. The black color regions analyzed in papyrus 2 are very close to the golden regions; therefore, it should be the contribution of the golden color and not necessarily of the black pigment. As in papyrus 1, for the black pigment, there are several possibilities, such as the mixing of different black pigments or the use of the pigment Asphalt [17].

Table 2: Intensities of the major elements on papyrus 2 (n = 3)

Elements	Color of the analyzed region				
	Golden	Silver	Black	Green	Red
Al	ND [a]	294 ± 19[b]	ND	ND	ND
Si	ND	ND	1484 ± 230	950 ± 89	950 ± 89
Cl	10416 ± 449	**19409 ± 2468**[c]	498 ± 87	7065 ± 1075	1275 ± 213
K	829 ± 139	858 ± 213	745 ± 111	741 ± 104	865 ± 84
Ca	6761 ± 969	**9795 ± 2066**	**7699 ± 735**	7633 ± 364	245 ± 135
Ti	ND	402 ± 102	ND	**66081 ± 14767**	7746 ± 1719
Cr	ND	ND	823 ± 242	ND	**1947 ± 45**
Mn	1672 ± 263	2524 ± 725	1666 ± 195	1571 ± 394	18886 ± 2571
Fe	7757 ± 2491	4000 ± 1938	**20524 ± 2530**	**12702 ± 2357**	1541 ± 847
Ni	ND	ND	989 ± 195	520 ± 149	22154 ± 2289
Cu	**708908 ± 72990**	ND	**7841 ± 1607**	10612 ± 2333	1052 ± 181
Zn	**72382 ± 7492**	4083 ± 827	437 ± 81	575 ± 231	2637 ± 1494
Pb	ND	ND	ND	1078 ± 393	**97906 ± 15568**

a. Mean ± Standard deviation; b. ND = Element not detected; c. Counts in bold = Major elements of each color.

In the red pigment, the elements that presented the highest intensities were Pb, Fe and Cr. The presence of Pb and Cr suggests the possibility of Chrome Red ($PbCrO_4.Pb\ (OH)\ _2$), a modern pigment, first synthesized in the early nineteenth century [5, 8].

In the green pigment, the elements with the highest intensities were Ti, Ca, Fe and Cu. The presence of Fe and K suggests the possibilities of Terra Verde (K [(Al^{III}, Fe^{III}) (Fe^{II}, Mg^{II})], ($AlSi_3$,Si4)$O_{10}(OH)_2$), a pigment of mineral origin used since ancient times [3, 4]. Besides, the presence of Cu may also indicate Verdigris (Cu $(C_2H_3O_2)_2$ 2Cu$(OH)_2$), mineral and synthetic pigment (BC), or Malachite ($CuCO_3Cu(OH)_2$), mineral pigment [5]. The presence of Ti in pigment is usually associated with modern pigments. However, the presence of Ti could indicate the use of the white pigment, Anatase (TiO_2), first synthesized in 1923 or Rutile (TiO_2) started in 1947 [8]. For the green pigment present in papyrus 2, as well as for the black pigment present in the two papyrus, there are several possibilities, because the XRF technique is able to determine only the elemental composition and not the chemical forms of the samples analyzed.

A summary of the major elements identified on each papyrus is given in Table 3.

Table 3. Major elements detected on the two papyrus

	Color	Major elements	Possible pigment
Papyrus leaf	No color	Si, S, **Cl**[a], K, **Ca**, **Mn**, Fe, Cu	NI[b]
Papyrus 1	Blue	S, K, Ca, Fe, Cu, **Zn**, **Ba**	Egyptian Blue + Lithopone
	Golden	Cl, Ca, Mn, Fe, **Cu**, **Zn**	Copper-zinc
	Black	S, Cl, **Ca**, Mn, **Fe**, Cu, Zn	NI
	Red	S, Cl, K, **Ca**, Ti, Mn, Fe, **Cu**, Zn	Mineral
Papyrus 2	Golden	Cl, K, Ca, Mn, Fe, **Cu**, **Zn**	Copper-zinc
	Silver	Al, **Cl**, K, **Ca**, Ti, Mn, Fe, **Cu**, Zn	NI
	Black	Si, Cl, K, **Ca**, Cr, Mn, **Fe**, Ni, **Cu**, Zn	NI
	Green	Si, Cl, K, Ca, **Ti**, Mn, Fe, Ni, Cu, Zn, Pb	NI
	Red	Si, K, Ca, Ti, **Cr**, Mn, **Fe**, Ni, Cu, Zn, **Pb**	Chrome red

a) The elements in bold correspond to the major elements;
b) NI = the detected elements have not provided enough information to link them to any possible pigment

4. CONCLUSION

The present work characterized the elemental composition of the pigments used in two modern papyrus paintings belonging to a private collection using XRF. Four pigments were analyzed in papyrus 1 (blue, golden, red, and black) and five pigments in papyrus 2 (golden, silver, black, red, and green). The analysis of the papyrus sheet showed the same elemental composition in both papyri.

Golden, red, and black colors are common in both papyri. The XRF spectra of the golden pigments suggest the possibility that both are the same pigment, formed by the copper-zinc alloy. The XRF spectra of the black and red pigments were discrepant from each other. Despite having the same color, possibly the pigments were synthesized with different raw materials.

The possible blue pigment found in the Papyrus 1 (Egyptian blue) is in accordance with the used by Egyptian craftsmen from 2600 BC, however, the XRF spectrum also showed the presence of the Ba and Zn, elements associated a modern white pigment, Lithopone. This may be indicative of possible mixing with Egyptian blue and Lithopone. Thus, the possible pigments found in the samples do not follow those used in ancient Egypt. Through the XRF technique, it was possible to verify that the pigments used in both papyri were recognized as modern and are not part of the pigments used in ancient Egypt.

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