On-site XRF characterization of archaeological materials in CERA center of Rissani (Morocco)

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Abstract. Different glazed ceramics and glass artifacts, coming from the excavations of the Sijilmassa site and exhibited in CERA (center for Alaouite studies and research) in Rissani (Morocco), were analysed by portable X-ray fluorescence spectrometry. All glazed ceramics are lead glaze and their ceramic bodies are calcareous clay. Glass objects are different nature: lead-glass, lead-lime-alkaline and potassium-lime glass. Classical elements were used to colour glaze and glass: tin for white, cobalt ore for blue, copper for green, manganese and iron for black and iron for yellow.

Keyword. Glazed ceramic; Glass bead; oil lamp, Sijilmassa site; Portable X-ray Fluorescence.

1. Introduction
On-site characterization of archaeological and cultural heritage materials by portable instrumentation is growing in a remarkable way. This non-invasive approach, avoiding sampling and risk of loss or damage during transportation of artefacts outside sites or museums, contributes also to a great collaboration of curators and managers of cultural heritage. X-ray fluorescence spectrometry (XRF) is among the main used techniques in these investigations, allowing multi-elemental identification and quantitation of the chemical constituents of samples [1]. It is suitable for ceramics, glasses, gems, pigments, frescos, coins, etc [2-9].

The purpose of the present work is the characterization of a set of archaeological ceramics, belonging to the CERA center, by mean of XRF analysis; the goal is the establishment of a scientific documentation enriching historic data on these artefacts.

2. Materials and instrumentation

2.1. Materials
The CERA center, created in 1990 by the Moroccan Ministry of Culture, harbours various and rich archaeological sets of materials: glazed ceramic, potteries, painted plasters, glasses, coins, metal objects and other materials coming from excavation of the Sijilmassa site.

The investigated materials consist of sets of: i) architectural glazed ceramics (Zellige attributed to the 18th -19th centuries period, ii) oil lamps (9th - 11th century), iii) fragments of glazed ceramics bowl with polychrome floral decoration (Fatimid period, 10th century) and iv) glass pearls along with a blue glass fragment. All artefacts are shown on Fig.1 and described on Table 1.
2.2. Instrumentation
The spectrometer consists of a X-ray tube with Mo anode emitting at lines K\(\alpha\) and K\(\beta\) of energy 17.44 and 19.60 KeV respectively. The emitted ray characteristics of each chemical element were detected by means of a Si (Li) detector, with a 30 mm\(^2\) active area and 8 \(\mu\)m beryllium window. The energy resolution is 138 eV at 5.9 KeV and a Nucleus PCA card acquisition system is used. The X-ray generator was operated at 50 KV and 200 \(\mu\)A and the acquisition time for each spectrum was 200s. The nominal beam diameter is <150 \(\mu\)m at position of the sample. All measurements were performed in air. After each measurement, the spectra were deconvoluted by MCA software in order to determine the chemical elements. Besides lines (K\(\alpha\), K\(\beta\), L\(\alpha\), L\(\beta\), M\(\alpha\), etc.) characteristics of chemical elements present in the sample, the spectra include Compton and Rayleigh scattering lines of Mo, generator of excitatory X-ray.

![Image of archaeological materials](image)

**Figure 1.** Archaeological materials analysed.

3. Results and Discussion

3.1. Glazes and supports (Zelliges)

*White glaze:* The XRF spectrum of white glaze is shown in Figure 2.a. In addition to K\(\alpha\) and K\(\beta\) lines of Molybdenum excitation source, L\(\alpha\), L\(\beta\), M\(\alpha\), LI, L\(\eta\) and L\(\gamma\) lines of lead (Pb) along with L\(\alpha\) and LI lines of tin (Sn) were identified. Consequently, Lead is used as melting agent (flux) and tin is likely used to produce opaque and white glazes. Indeed, using tin as cassiterite (SnO\(_2\)) to opacify glazes in medieval and Islamic glazed ceramics has been reported by several authors [10,11]. Iron, calcium; and potassium were also highlighted. Their presence in the glaze can be due to their diffusion from terracotta or as impurities in the sand used as raw material to make the glaze. In addition, glazes can fix the calcium provided by infiltration of water during burial in marl soil. Copper and titanium were also identified in low amounts in the glaze by their lines with very low intensities; they may be present as impurities in the raw materials.
Table 1. The list of examined objects.

| Material      | Reference    | Period                        | Analysed zone       |
|---------------|--------------|-------------------------------|---------------------|
| Oil lamp      | CERA93-215   | (9th – 11th) century          | Green Glaze         |
|               |              |                               | Terra cotta         |
|               |              | Medraride period (9th – 11th) | Green glaze         |
|               |              |                               | Terra cotta         |
| Oil lamp      | CERA88-722   | (9th – 11th) century          | Black glaze         |
|               |              | (9th – 11th) century          | Terra cotta         |
| Oil lamp      | CERA02-771   | (9th – 11th) century          | White glaze         |
| Zelliges      | CERA09-610   | (18th – 19th) century        | Black glaze         |
|               |              |                               | Terra cotta         |
|               |              |                               | Blue glaze          |
|               |              |                               | Green glaze         |
| Bowl          | CERA92-186   | 10th century                  | Yellow glaze        |
|               |              | Fatimid period                | Black glaze         |
|               |              |                               | Blue glaze          |
|               |              |                               | Green glaze         |
| Fragments of glazes | CERA06-910 | 11th -14th centuries               | Blue               |
| Beads         | CERA09-106   | 11th -14th centuries               | Black               |
|               |              |                               | 11th -14th centuries | Blue               |
| Bead of necklace | CERA10-906  | 11th -14th centuries               | Blue               |

Black glaze: Figure 2.b shows that lead was used as flux while manganese and iron were used to produce a black colour of glaze. Manganese and iron produce colour of glaze ranging from brown to black depending on the ratio of their concentrations and the nature of firing atmosphere, oxidizing or reducing [12]. Silicon, calcium, potassium, titanium and copper are also identified.

Terracotta: Calcium and iron are present in high amounts in terracotta of zelliges as it’s shown in Fig.2.c. Therefore, a ferruginous calcareous clay is used to produce the terracotta of the zelliges. The use of calcareous clays in the manufacture of glazed ceramics, faience and majolica was a common practice in the medieval Islamic world [10,13,14].

Besides their compatibility with the white colour of the glaze, these clays permit to reduce the amount of tin used for glaze opacifying. Also, their viscosity helps to prevent glaze cracking due to thermal expansion coefficient between glaze and terracotta during firing [14]. Potassium, manganese, sulphur, zinc titanium, chlorine, rubidium and strontium are present but in low concentrations. Strontium is in relatively high content because it can substitute to calcium [15]. Lead is found in terracotta, it originates probably from the dissolution of the glaze over time 'leaching phenomenon'; this is an indicator of ageing [4].

3.2. Fragment of glazed ceramic bowl

The polychrome part of a glazed ceramic bowl with blue, green, yellow and black floral decoration (Fatimid period - 10th century) has been analysed. The XRF spectra recorded on the different coloured areas of the glaze are presented in Figure 3; the presence of lead in high amount reveals its use as flux.

Yellow glaze: High intensity Ka and Kβ lines characteristic of iron are observed (Fig. 3.a). Iron gives colours ranging from brown to yellow, depending on amount, nature of the firing atmosphere (oxidizing or reducing) and associated chemical elements in the glass matrix. Calcium, potassium, titanium, copper and manganese were also identified in low quantities compared to lead and iron. The non-appearance of Tin as cassiterite, commonly used as opaquening agent in glazed ceramics, may likely due to the overlapping of its La and LI lines by Ka and Kβ lines of potassium.
**Black décor:** Manganese and iron have been identified in the XRF spectrum of black glaze (Fig. 3.b). Association of these two transition elements in lead glazes produces black colour [16]. Calcium, potassium, titanium and copper were also identified but in low content.

**Blue décor:** Cobalt, nickel, arsenic, manganese, copper, iron, calcium, titanium, potassium and tin are the principal chemical elements of the blue glaze (Fig. 3.c). Cobalt ore rich in arsenic and nickel is used to produce the blue colour, while tin is likely used to opacify the glaze; cobalt correlated with arsenic has been identified in glazed ceramics of fourteenth century [16,17].

![XRF spectra](image)

**Figure 2.** XRF spectra recorded on (a) Zellige's white glaze, (b) Zellige's black glaze and (c) terracotta supports

**Green pattern:** The spectrum of green decor (Fig 3.d) shows that lead, copper, iron, manganese, nickel, calcium and potassium are the principal chemical elements. Copper and lead, showing high contents, are used respectively for the green colour and as flux of glaze. The green colour can be attributed to the dissolution of copper in the glass matrix [11,18]. In general, the green colour of glazes is often linked to the presence of copper as Cu$^{2+}$. The presence of iron, manganese, calcium and potassium in the glaze may originate probably from impurities in the raw materials or contamination of terracotta.
3.3. Oil lamps

**Green glazes:** X-ray fluorescence spectra (Fig. 4.a) of green glazes of two oil lamps referenced SM93T2/AD15 and L-3-88/722 show that lead (Pb) is used as melting agent to produce the glaze. The identified tin (Sn) was probably used as opacifier. Cu is identified in all green glazes studied. Dark green areas of the lamp SM93T2/AD15 present Mn which is likely used to darken the green colour. Zinc, tin, iron, calcium, titanium and potassium were also identified in the glazes. The presence of iron makes the green colour darker, while the presence of calcium improves its mechanical properties and particularly hardness [19]. The zinc gives flexibility to glazed ceramics and prevents cracking due to differences in thermal expansion coefficients of glazes and their supports [20]. This suggests the presence of zinc as an impurity in the raw materials or advanced technological knowledge of craftsmen of the period [21].

**Black glaze:** Fig. 4.b shows the X-ray fluorescence spectrum measured on the black glaze of the oil lamp referenced BH/K2/771. Characteristic lines of lead show high intensities implying thus that lead was used as flux to produce the glaze. In addition to copper, iron and manganese are present and are likely responsible for the black colour. Copper produce green glaze, while iron associated to manganese produce black colour. The mixture of the two colours gives a more or less deep colour according to Cu/Mn ratio [22]. Calcium, potassium and titanium are also identified; they may originate from clay, during firing process, or they may exist as impurities in the raw materials used to make glaze (sand, pigments, flux...).

**Terracotta:** X-ray fluorescence spectra of terracotta of oil lamps presented in Fig. 4.c show high amounts of calcium and iron. Bodies are thus made of ferruginous calcareous clay. This type of clay was commonly used to manufacture glazed ceramics with colour of terracotta often cream pink to
white, depending on the content of iron [14,23]; the colour of terracotta has a significant effect on the colour of glazes. The spectrum shows the presence of Lead in high content; this occurrence is likely due to phenomena of glaze leaching. Potassium, titanium, manganese and copper are identified in low amounts along with traces of rubidium and strontium.

3.4. Glass fragments and Beads

Blue glass fragment: The XRF spectrum reveals that Si, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn and Pb are the principal chemical elements (Fig. 5.a.). High contents of calcium and iron are also observed while potassium shows a low content. Sodium is not detected because of its low cross section. The melting agent (flux) used to make glass is probably alkaline since the amount of lead is very low. The blue colour of glass can be attributed to copper; this element is reported as responsible of the blue colour of glazes and glasses [24,25]. Zinc contributes to increasing the chemical resistance and hardness, reducing the thermal expansion coefficient and increasing the refractive index [12,19,20]; it gives shine to glass [26]. Chlorine is present and it’s probably due to the alteration of glass after its burial in the soil for long periods.

Blue glass bead: The X-ray fluorescence spectroscopy analysis of the blue glass bead shows that it consists mainly of calcium, potassium and iron (Fig. 5.b). Characteristic lines of titanium and sulphur have been also identified in the spectrum; sulphur may be due to gypsum which is an indicator of alteration of the glass during burial time in the soil. Lead is also present; it may exist as impurity in the raw materials or may originate from contamination during the manufacture of glass.

Figure 4. XRF spectra recorded on oil lamps: (a) green glaze, (b) black glaze and (c) terracotta supports.
Blue pearl necklace: Calcium, iron, lead, silicon and potassium are the main constituents of necklace as revealed by the XRF spectrum (Fig. 5.c). The material seems likely a lead-alkaline-lime glass. Cobalt, manganese, arsenic, nickel and titanium have been also identified. The blue colour of necklace is attributable to cobalt ore associated with arsenic and nickel [24,25].

Black glass bead: The corresponding spectrum is shown in Fig.5.d. The characteristic peaks of lead (Pb) are the most intense; this suggests that lead is used as melting agent in this glass. Silicon, potassium, calcium, manganese, iron, copper and zinc are also identified in the bead. The black colour of the glass bead is likely due to the association of transitional elements mainly manganese and iron.

![XRF spectra of glasses](image)

**Figure 5.** XRF spectra of glasses: bleu fragment (a), blue bead (b), blue bead necklace (c) and black bead (d).

**4. Conclusion**

On-site XRF measurements were carried out on a large set of archaeological artefacts exhibited at the CERA centre: architectural glazed ceramics tiles, utilitarian glazed ceramics, oil lamps, glasses and glass beads. These multi-elemental analyses allowed the identification of the chemical constitutions of all materials. The glazed ceramics are lead glaze with bodies consisting of calcareous clays. Different flux, lead, lead-lime-alkaline and lime-potassium are used to produce glasses and glass beads. All elements used to colour glazes and glasses are classic; they are those commonly used in Mediterranean recipes. Further investigations using supplementary analytical techniques for a good characterization and dating of these materials are envisaged.

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