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Elemental mapping of Moroccan enameled terracotta tile works (*Zellij*) based on X-ray micro-analyses

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HIGHLIGHTS

- Tiles from 13th to XXth century have been studied out in this work.
- This study on pottery, gives the elemental mapping in original Moroccan tiles (*Zellij*) collected in Marrakech.
- Non-destructive X-Ray Fluorescence spectrometry has been used.
- Comparison on elemental composition for modern and old ceramics has been obtained for the glaze and the colors.

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ABSTRACT

The purpose of this work is the elemental mapping of enameled terracotta samples (*Zellij*), produced between the 13th and 20th centuries in Morocco, collected from five different monuments from Marrakech. These pieces were analyzed by two non-destructive micro X-Ray Fluorescence (XRF) spectrometers, aiming to obtain elemental distribution and elemental composition.

From the obtained spectra we have identified the main elements present in the tin-opacified lead glaze. The identification of the decoration colors is based on the different ratios between the fluorescence lines of the main component of the glaze (Pb-Lα line) and the fluorescence lines of the main components of the pigment (Co-Kα, Mn-Kα, Ni-Kα,… lines). The semi-quantitative calculations based on these ratios revealed significant differences between modern and ancient samples.

1. Introduction

Ceramics can be grouped in categories that rely on their chemical composition, firing temperature or superficial treatment. The major division is made between glazed or not glazed bodies.

The ceramic pastes have in its constitution several groups of materials, which confer the desired properties: plastic components (clay minerals – compounds based on silicon and aluminum), temper (crystalline or grinded silica) and fusing agents (mainly feldspars). During the firing process, clays decompose and react with the rest of minerals in the paste giving as a result a new mineral assemblage which constitute the ceramic body.

As any kind of glass, the glaze contains: (i) network formers (mainly SiO_2 and Al_2O_3, which built the structure); (ii) network modifiers (fusing agents), which are oxides to introduce holes in the network and lower the melting point of silica like K_2O, PbO, CaO and MgO; (iii) network stabilizers or intermediates (Al_2O_3, PbO, ZnO, ZrO_2 and CdO), which are oxides that replace silica in order to increase the glaze viscosity (lost by the network modifiers), giving strength to the glaze during the firing process, also preventing crack and keeping the compounds unchanged with time; (iv) opaque elements for small nucleation within the crystallographic network, such as Ti, Sn, Fe, and others, (Guilherme et al., 2013, 2011; Zarghili et al., 2008; Casas et al., 2008; Rice, 1987; Blair and Bloom, 1995).

The glazes can be applied on the ceramic body in its raw state or in the form of frits. The former means that the raw materials to form the glaze are mixed, and later, just put together and applied directly to the ceramic surface. The latter means that there has to be a pre-melted procedure of the raw materials composing the glaze. Then they are cooled down and grinded until a powder is obtained, in order to have a low-melting point material which can

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Table 1
Identification of the analyzed samples.

Sample	Origin	Age
MC1B	Mausoleum of Sidi Abd El Aziz	16th century
MC2A	Massine mosque	13th century
MC2B	Massine mosque	13th century
MC3A	Massine mosque	13th century
MC4	Ancient riad	19th century (end)
MC5	El Badi palace	16th century
MC7	Bahia palace	19th century (beginning)
MC8	Modern residential quartier	20th century

be fired at temperature up to some hundreds of degrees below the firing temperature of the ceramic body. Concerning the type of the studied Moroccan ceramics almost no compositional study has been carried out until present. Guilherme et al. (2013) presented a comparison of Portuguese and Moroccan ceramics. Zarghili et al. (2008) describes a method that allows Arabo-Moresque décor image retrieval especially for the case of *Zellij*'s decors. The other study found was the one from Casas et al. (2008), in which the authors present archaeometric dating techniques giving a new contribution to the databases from samples from a region of Morocco on 16th century.

In the present work, measurements through micro-XRF were carried out in order to provide compositional information about these typical Moroccan ceramics. A better description of the samples can be found in Table 1.

2. Sample origin and description

The type of samples here described is *Zellij*, a kind of art which is typically Moroccan. They are characterized by a terracotta body with an enameled surface. This sort of objects was prepared manually. The craftsman unified the paste with his arms and feet, making it less stiff, then the pieces were split into blocks and hardened again under sun light and flattened with a bat. Then, parts of 10×10 cm were obtained and placed under sun light for as long as it took to fully dry, which corresponded to the first burnt stage.

Afterwards, these pieces were submersed into a coloring, containing a mixture of lead, sand and other oxides that promote the desired color. This mixture was applied together with water, which helped the process of dying. The pieces were submitted to a firing process in an oven and they were placed in it according to an order: the ones with white surfaces on the bottom (exposed directly to heat) and on the top the green ones (which are more sensitive to the firing process). An important step of the whole manufacturing process is, afterwards, when the artisan draws onto the pieces using drawn and cut molds of paper. In the end, all pieces are rearranged according to their shape and color (Blair and Bloom, 1995).

Some of the analyzed samples were from Bahia Palace in Marrakech, which has been commissioned between 1859 and 1873. The older part of the palace has two ornately decorated rooms roofed with ceramic tiles surround this lush garden, which contain inscriptions dating the construction of this part of the palace to 1867. One of the finest elements of the Bahia Palace is the grand marble-paved courtyard, constructed between 1896 and 1897. It is divided into quadrants by paths of multicolored *zellij*, in a simple checkered pattern (Deverdun, 1912; Hillenbrand, 1999; Grube et al., 1978; Métalsi et al., 2000; Catling et al., 1963).

Other samples belonged to El Badi palace, by the *Saadian* Sultan *Ahmed el-Mansour* in the 16th century and destroyed when this dynasty fell. It was one of the most beautiful and impressive buildings of the Muslim world. The palace became known as "The Incomparable", although what remains today is crude. It is a good illustration of the quality of its original magnificent decoration. It was laid out with 360 rooms, with a huge inner courtyard of 135×110 m with four sunken gardens and a fountain decorated with *zellij* tile work.

The mausoleum Sidi Abd El Aziz dating from the beginning of 16th century, is one of the tombs of the Seven Men of Marrakesh, established as a pilgrimage circuit in the 17th century.

Massine Mosque was built by the Saadian Sultan Ghalib Al–Bi Allah during the 12th century and represents the art of Almohades. It is one of the most ancient monuments in Marrakech. Some samples from an ancient Riad from the end of 19th century have also been collected, as well as samples from a modern residential building. All samples present only one color except the sample from both riads and one of the samples of the mosque.

3. Experimental setup

3.1. Micro X ray spectrometer

A benchtop energy dispersive X-ray spectrometer (XDV-SD model, Helmut Fischer GmbH, Sindelfingen, Germany), designed for coating-thickness measurement and materials testing was used for elemental mapping of the samples. It consists of a microfocus tungsten anode X-ray tube, able to operate at fixed voltage of 10, 30 and 50 kV and within a range of 0.1 to 1 mA of tube current (max power of 50 W), and a Si–Pin semiconductor detector (Peltier cooling at -50 °C; energy resolution 170 eV at Mn-Kα line, count rate up to 100 kcps).

A color video microscope allows selection and viewing of the irradiated area with up to 45x magnification. The spectrometer is equipped with five primary filters of nickel (10 μm), aluminum (500 and 1000 μm), titanium (300 μm) and molybdenum (70 μm). Four collimators with different diameters (0.1, 0.3, 1 and 3 mm) are also available in the spectrometer to irradiate selected areas, which can be used to reduce spectral background and eliminate the tungsten tube signal.

The impinging X-ray beam reaches the sample surface at 90° and the detection system to collect emerging secondary X-rays from the sample is placed at 45°. The instrument is controlled by the WinFTM software, which is also used both for the spectra acquisition and for the spectral data treatment. This software is based on the physical principles detailed in the Roessiger and Nensel work and allows designing different layered structure models (single, double, multilayers, etc.) taking in consideration the main features of the layers and the substrates. It also can do evaluation by using quantitative standard based models or by standard free fundamental parameters method.

The analyses were performed with a 1 mm diameter collimator and an Al filter on the incident radiation path to reduced the background noise in the spectra.

The voltage applied to the tube was 50 kV and the current is normally automatically adjusted by the system in order to reduce the dead time in the detector. In our case it was 128 μA.

In Fig. 7 we see one of collected spectra for the mapping of elemental content obtaining an areal density in μg/cm^2. In this sample (MRRC-4) the mapping was performed in a 20×15 points $= 300$ spectra, each measured during 50 s.

3.2. Energy dispersive X-ray fluorescence (EDXRF)

For semiquantitative elemental analysis of the ceramic body and colored parts, EDXRF analysis was carried out with a 45° tube-detector geometry setup enclosed in a chamber submitted to a 10 mbar