In situ measurements of Tiwanaku ceramics by portable EDXRF

Jorge Lisme Ticona¹, Fabio Lopes¹, Carlos R. Appoloni¹ Jose Luis Paz Soria² and Irene Dalaveris²

¹ Applied Nuclear Physics Laboratory, State University of Londrina. Londrina, Brazil.
² Laboratory of Lithic, Universidad Mayor de San Andrés. La Paz, Bolivia.

E-mail: lismeticona@yahoo.com

Abstract

In this work Tiwanaku ceramics were analyzed qualitatively. Three fragments and six pottery vases came from the archaeological site of Achocalla and five pottery fragments from the Tiwanaku Museum in La Paz - Bolivia. The surfaces of the pottery vases had red color engobe, whereas the surfaces of the fragments were red and black colored. For in situ data acquisition a portable EDXRF spectrometer was used. It has a Si-Drift X-ray detector, a mini X-ray tube with silver anode and 0.7 mm spot size, a FTC 200 power supply (40kV and 100mA) and a notebook for data recording. A silver collimator with 2 mm diameter was placed at the entrance of the detector to prevent scattered radiation. The study focused on the elemental characterization of the pottery samples, comparison of the fluorescence spectra and analysis of possible groupings. The chemical elements K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr and Zr were identified in the composition of clays used to manufacture pottery. It was observed that the chemical element potassium (K) is not present in the pottery fragments from Tiwanaku. Two-dimensional graphs of the X-ray intensities Zr Vs. Rb, Mn Vs. Fe, Ca Vs. Mn and Mn Vs. Zn, with data from all samples, showed a tendency to form three different groups while the graphs of intensity Mn Vs. Zn and Ca Vs. Mn showed a tendency to form two different groups. Also two-dimensional graphs of intensity ratios Rb/Zr Vs. Fe/Zn, Rb/Zr Vs. Mn/Zn and Sr/Rb Vs. Fe/Mn, Sr/Rb Vs. Mn/Zn, Sr/Zr Vs. Mn/Z showed a tendency to form three and two different groups, respectively. The analysis of these Tiwanaku ceramics showed interesting differences among the samples composition, indicating the discrimination of at least two groups of clays.

Keywords. Tiwanaku, ceramics, clays, PXRF.

1 INTRODUCTION

The analyses of archaeological materials from pre-colonial times are of great importance to the study and characterization of ancient cultures [1,2,3,4]. In particular, the artifacts and pottery fragments found in archaeological sites and stored in museums are material evidences of the past and also sources of information and technology [5,6,7].

The study of archaeological ceramics using non-destructive spectroscopic techniques, such as energy dispersive X-ray fluorescence (EDXRF) [7,8,9], provides information about the elemental composition, identification of their provenance, traces of paintings, type of the used production technology, among others. Therefore, the characterization of ceramic samples allows the archaeologists to better understand the various exchange routes, as well as to know if other cultures employed these same materials.

The EDXRF is a non-destructive analytical technique that has been used to study pre-colonial ceramics. In addition, the development of portable EDXRF allows performing in situ measurements [10,11] of artifacts and works of art that are unique and of great historical and cultural value.

One of the pre-Hispanics civilizations that inhabited in the region of "Los Andes" of South America was the Tiwanaku Empire (400 B.C. - 1100 A.C.). This culture reached levels of social and technological development higher or similar to other ancient cultures in the world that was later was interrupted by Spanish
colonization. Intact ceramic artifacts, thousands of fragments and other remaining materials are among the archaeological materials of that civilization [12,13,14,15].

Ceramic samples of Tiwanaku stored at museums in Bolivia have never been analyzed from a scientific point of view, e.g. applying modern non-destructive and non-invasive methods such as the energy dispersive X-ray fluorescence (EDXRF).

The objectives of this work in its first phase were: identify the elemental composition of ceramics samples of Tiwanaku and Achocalla, possible cluster analysis and to show fluorescence spectra comparisons. The global analysis of the ceramic samples of Tiwanaku is a research that is in progress at the Laboratory of Applied Nuclear Physics, State University of Londrina, Brazil [16,17,18,19,20,21].

2 MATERIALS AND METHODS

Three fragments and six pottery vases that came from the archaeological site of Achocalla and five pottery fragments stored in the Tiwanaku Museum in La Paz - Bolivia were analyzed. The Figure 1 shows the archeological site of the Tiwanaku Empire.

The Tiwanaku culture that flourished in the period 400 B.C. - 1100 A.C. [14,15] was declared Cultural Patrimony of Humanity in 2000 by UNESCO; there are decorated artifacts with pigments and rustic materials among their archaeological materials. The decorated ceramics exhibit typical shapes and symbols, antiplastics of fine sand, red colored engobe and black painting. However, the ceramics from the archaeological site of Achocalla - interpreted by archaeologists as a former colony of Tiwanaku- were characterized as artifacts utilities (rustic) by the fact that they do not have the attributes of Tiwanaku ceramics and because it is believed that they were manufactured at the same location.

The X-ray fluorescence spectra of the ceramics were acquired at the Museum of Tiwanaku and at the Lithic Laboratory of the Universidad Mayor de San Andrés in La Paz - Bolivia. For in situ data acquisition a portable EDXRF spectrometer was used.

It has a Si-Drift X-ray detector, a X-ray mini-tube with silver anode and 0.7 mm spot size, a FTC 200 power supply (40kV and 100mA) and a notebook for data recording. A silver collimator with 2 mm diameter was placed at the entrance of the detector to prevent scattered radiation Figure 2. The measurement conditions were 28 [kV], 5 [μA] in the X-ray mini-tube and acquisition time of the spectra was 500s.

Figure 1. The Tiwanaku Empire. (a) Shows the expansion of Tiwanaku in the pre-Hispanic period. (b) Shows the current location of the archaeological site[22].
Figure 2. Portable system of EDXRF used to acquire the spectra. (a) The equipment acquiring a X-ray spectra from pottery vase that had red colored engobe. (b) The same vase, but now the black painting can be observed.

The X-ray fluorescence spectra were acquired in three or two different points on each of the ceramic sample. The chosen points were the surfaces where the red colored engobe was observed, the ceramic paste and the black painting. The analyses of the spectra were performed by using the AXIL software distributed by the International Atomic Energy Agency (IAEA).

3 RESULTS AND DISCUSSION

The EDXRF spectra for all ceramics showed similarities in the composition of the main chemical elements. The Figure 3 and 4 show two overlapped spectra corresponding to the surfaces with red colored engobe and black painting (Figure 2)

Figure 3. The EDXRF spectra of the surfaces with red colored engobe (red line) and with black painting (black line).

Figure 4. Spectrum of the Figure 3 enlarged, in which the peak of the element manganese (Mn) in black painting (black line) is observed.

From the spectral intensity, ten chemical elements (K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr e Zr) were identified in the composition of clays used in the pottery manufacturing. All samples showed high concentrations of iron element (Fe), followed by the chemical elements Sr, Rb, Sr, K and Ti, whereas small amounts of the chemical elements Ca, Cu and Zn were detected in all spectra. The surfaces with black painting showed relatively high concentrations of the element manganese (Mn). In addition, it was observed that the chemical element potassium (K) is not present in the pottery fragments from Tiwanaku.

With the intensities of the chemical elements two-dimensional graphics (element versus element) were
plotted for all possible combinations of the elements. Thus, two-dimensional graphs of the X-ray intensities of Zr vs. Rb, Mn vs. Fe, Ca vs. Mn and Mn vs. Zn, with data from all samples, showed a tendency to form three different groups while the graphs of intensity Mn vs. Zn and Ca vs. Mn showed a tendency to form two different groups. The Figure 5 shows these clustering tendencies and suggests that the elements Rb, Zr, Ca and Mn characterize the clays used in the manufacture of ceramic samples.

On the other hand, to determine the combinations of chemical elements that tend to cluster ceramic samples according to their chemical similarities, two-dimensional graphs of the X-ray intensity ratios (element$_i$ / element$_j$ versus element$_x$ / element$_y$) were plotted. From all the possible combinations, the two-dimensional graphics of intensity ratios Rb/Zr vs. Fe/Zn, Rb/Zr vs. Mn/Zn and Sr/Rb vs. Fe/Mn, Sr/Rb vs. Mn/Zn, Sr/Zr vs. Mn/Zn tend to form three and two different groups respectively, as showed in the Figure 6.

In the Figure 6, the tendency to form three and two different groups may be visualized. This would suggest the existence of at least two sources of different clays used to manufacture the ceramic samples of Tiwanaku. However, to verify the clustering tendencies, it will be necessary to carry out an analysis with more samples, as well as exploring other characteristics of Tiwanaku ceramics.

**Figure 5.** Two dimensional graphs of the X-ray intensities of Rb versus Zr (a) and Ca versus Mn (b), for fourteen ceramic samples analyzed.

**Figure 6.** Two-dimensional graphs of the X-ray intensity ratios Rb/Zr versus Fe/Zn (c) and Sr/Rb versus Mn/Zn (d), for fourteen ceramic samples analyzed.

**4 CONCLUSIONS**

The portable EDXRF system was used to perform *in situ* measurements in the nine and five ceramic samples that came from the archaeological sites of Achocalla and Tiwanaku, respectively. The comparisons of fluorescence spectra showed
similarities in the intensities of the main chemical elements.

The chemical elements that have been identified in the clay composition are: K, Ca, Ti, Mn, Fe, Cu, Zn, Rb, Sr and Zr. It was observed that the chemical element potassium (K) is not present in the pottery fragments from Tiwanaku. Two-dimensional graphs of the X-ray intensities Zr Vs. Rb, Mn Vs. Fe, Ca Vs. Mn and Mn Vs. Zn, with data from all samples, showed a tendency to form three different groups while the graphs of intensity Mn Vs. Zn and Ca Vs. Mn showed a tendency to form two different groups. Also two-dimensional graphs of intensity ratios Rb/Zr Vs. Fe/Zn, Rb/Zr Vs. Mn/Zn and Sr/Rb Vs. Fe/Mn, Sr/Rb Vs. Mn/Zn, Sr/Zr Vs. Mn/Z tend to form three and two different groups, respectively.

The analyses of these Tiwanaku ceramics showed interesting differences among the samples composition, indicating the discrimination of at least two groups of clays. In the second phase of this study these results might be confirmed by the analysis of more samples that came from the mentioned archaeological sites.

5 REFERENCIAS


