EDXRF analysis of Marajoara pubic covers

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Available online 19 April 2007

Abstract

This work evaluated the elemental composition of decorated pottery pubic covers (tangas) from the Marajoara culture of Marajó Island (at the mouth of the Amazon River, Brazil) using EDXRF technique. The XRF system used in this work consists in a Si(Li) detector from ORTEC, with resolution of 180 eV, at 5.9 keV, and a mini X-ray tube with Mo anode. The elements identified in the samples were: S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y, Zr and Pb. Principal components analysis (PCA) was used to evaluated the provenance of the samples.
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1. Introduction

Marajoara ceramics represent one of the most beautiful and sophisticated styles of the pre-Columbian art and its decorative techniques show intricate designs of geometrical forms, representing a mythology based on the local fauna. The period of major growth and expansion of Marajoara Culture occurred between the 5th and 14th centuries and its disappearance occurred during the first decades of the European domination as a result of wars and missionization. However, due to the use of ceramics in funerary rituals, their art has survived until the present day. Decorated pottery tangas were used by Marajoara girls, probably as part of puberty rites, and were anatomically adjustable to the body, containing holes on the corners for string attachment [1].

Provenance studies of ancient ceramics are based on the assumption that pottery produced from a specific clay will show a similar chemical composition that will be distin-guished from that of pottery produced from a different clay. In this way, pottery is assigned to particular production groups, which are then correlated with their respective origin [2,3]. However, in most cases, the natural clay is not directly suitable for ceramic production and must be treated to produce a workable paste, becoming very difficult to assigned ceramics directly to an origin in distinct clay sources by using only one analytical technique [3].

The X-ray fluorescence analysis is a widely used spectroscopic technique in archaeometry to investigate the composition of pigments (in manuscripts, paintings, ceramics and other artifacts) [4], metal alloys, coins and statuary. It is a non-destructive technique that makes possible qualitative and quantitative multielemental analysis with good precision and accuracy.

This work evaluated the elemental composition of Marajoara tangas and fragments belonging to the National Museum collection (Rio de Janeiro, Brazil) using energy dispersive X-ray fluorescence (EDXRF) technique. The results were submitted to principal component analysis (PCA), in order to determine if all samples, including one fragment with different geometric design patterns (sample

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22245), presented the same provenance. Fig. 1 shows the analyzed samples.

2. Experimental

The samples included two Marajoara tangas (9154 and 9158) and four fragments (22236, 22245, 22284 and 22286) from the National Museum collection. EDXRF was performed at the Nuclear Instrumentation Laboratory (COPPE/UFRJ). The system employed a 30 mm² Ortec Si(Li) detector (180 eV resolution at the Mn-K$_\alpha$ line), to detect the fluorescent radiation and a mini X-ray tube with Mo anode. The angle of the incident X-ray beam was 16° and the detector was placed at 90° to the sample surface. The samples were placed in a support and 10 different regions of each one were irradiated with an acquisition time of 1000 s. The XRF spectra were evaluated with the software package QXAS-AXIL, from IAEA. The elemental concentrations were calculated using WinIrrad, software developed by the Nuclear Instrumentation Laboratory. The accuracy and experimental validation were determined by the analysis of a reference clay sample. It was prepared with the same characteristics of the tangas (composition and thickness) containing specific elements (Ni, Mn, Bi and Pb) in known concentrations. An additional X-ray diffraction analysis was performed to confirm the characterization of the samples. The measurements were carried out with the XRD 6000 diffractometer, from Shimadzu, using an X-ray tube with Cu anode, operating at 40 kV and 30 mA, range for diffraction angle: 5–80°, sampling pitch of 0.02° and preset time of 2 s.

3. Results and discussion

The elements found in the samples were: S, Cl, K, Ca, Ti, Mn, Fe, Cu, Zn, Ga, Rb, Sr, Y, Zr and Pb. Table 1
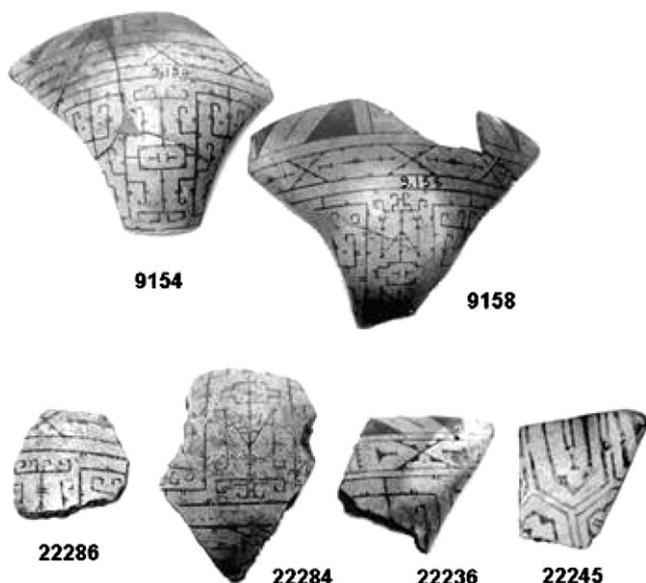

Fig. 1. Marajoara tangas and fragments analyzed in this work.

shows the mean concentrations (in $\mu g\ g^{-1}$) and standard deviations. The elements that exhibited the highest concentrations were: K, Ca, Fe and Ti. It was expected to find high concentrations of Al and Si because clay is an aluminosilicate, but these elements are of low atomic number, below the system detection limits. However, in the additional XRD analysis Quartz (SiO$_2$) and Kaolinite (Al$_4$Si$_4$O$_{10}$(OH)$_8$) were found. The presence of S and Cl could be associated to environmental pollution [5] or to some treatment used to clean the pieces. The superficial presence of sulphur compounds is due to the combustion of coke, petroleum and gasoline and is an index of pollution. It is often present, in various chemical forms, mainly as CaSO$_4$ on the surface of frescoes and monuments, producing black colouring [6].

The sample 22245 (Fig. 2), a fragment of tanga with distinct design patterns, seemed to present a different provenance. Nevertheless, the result of the EDXRF analysis showed the same elements and similar concentrations for this fragment in regarding to the other samples, as seen in Table 1. In Fig. 2 EDXRF spectra of samples 22245 and 9154 are shown, in order to demonstrate its similarity. Correlation tests applied to the mean concentrations revealed strong correlation among the samples, including the fragment 22245. In despite of these results that reinforced the hypothesis of same provenance to all samples, it was applied a multivariate statistical method (PCA, principal component analysis) to the results.

PCA is a very powerful visualization tool, which allows the representation of multivariate datasets in a new reference system characterized by a lower number of orthogonal variables than in the original set, called principal components (PCs). This characteristic is especially important when spectra are studied, because it helps to visualize and to extract important hidden information. PCA carries out a graphical representation that allows the identification of groups of samples that show similar behaviours or different characteristics. The information from the original data is summarized in the graphics of scores and loadings. By looking at the corresponding loading plot, it is possible to identify the variables, which are responsible for the analogies or the differences detected, while the score plot provides information about the samples [7–9].

In this work, PCA was performed using the mean of the counts for each group of replicates obtained to the samples. Looking at the results shown in Fig. 3, it is possible to conclude that the samples are separated in three distinct groups. In the first group: samples 22236, 9154 and 9158, in the second: 22284 and 22286, and, so far from the others in the third group, the sample with different design patterns, 22245. These results are in accordance with the XRD patterns obtained for the samples, which represent three different groups, as shown in Fig. 4. As the first principal component (PC1) incorporates 81% of the data variance (PC2 incorporates 14%) it may be used to represent the set of the studied variables. The principal variables that contribute to this variability are the Cu concentration

Table 1

Mean concentrations ($\mu g\ g^{-1}$) found to the Marajoara tangas (concentration ± S.D.)

| Elements	Samples					
	#22236	#22245	#22284	#22286	#9154	#9158
K	$7.7 \times 10^3 \pm 4.4 \times 10^2$	$9.7 \times 10^3 \pm 1.4 \times 10^3$	$5.5 \times 10^3 \pm 5.6 \times 10^2$	$6.5 \times 10^3 \pm 2.1 \times 10^2$	$7.2 \times 10^3 \pm 7.7 \times 10^2$	$9.5 \times 10^3 \pm 1.8 \times 10^3$
Ca	$1.5 \times 10^3 \pm 2.2 \times 10^2$	$2.2 \times 10^3 \pm 4.5 \times 10^2$	$1.5 \times 10^3 \pm 1.5 \times 10^2$	$1.3 \times 10^3 \pm 1.8 \times 10^2$	$1.2 \times 10^3 \pm 1.6 \times 10^2$	$1.5 \times 10^3 \pm 3.8 \times 10^2$
Ti	$1.4 \times 10^3 \pm 9.6 \times 10^1$	$1.4 \times 10^3 \pm 6.7 \times 10^1$	$9.8 \times 10^2 \pm 3.6 \times 10^1$	$1.2 \times 10^3 \pm 6.2 \times 10^1$	$1.6 \times 10^3 \pm 8.4 \times 10^1$	$1.6 \times 10^3 \pm 1.0 \times 10^2$
Mn	$3.8 \times 10^1 \pm 0.4 \times 10^1$	$4.8 \times 10^1 \pm 1.0 \times 10^1$	$2.5 \times 10^1 \pm 0.3 \times 10^1$	$2.7 \times 10^1 \pm 0.4 \times 10^1$	$2.7 \times 10^1 \pm 0.5 \times 10^1$	$6.0 \times 10^1 \pm 1.1 \times 10^1$
Fe	$2.9 \times 10^3 \pm 4.8 \times 10^2$	$2.9 \times 10^3 \pm 2.6 \times 10^2$	$1.4 \times 10^3 \pm 2.1 \times 10^2$	$1.9 \times 10^3 \pm 1.4 \times 10^2$	$3.2 \times 10^3 \pm 3.6 \times 10^2$	$3.5 \times 10^3 \pm 2.9 \times 10^2$
Cu	$0.9 \times 10^1 \pm 0.2 \times 10^1$	$1.0 \times 10^1 \pm 0.1 \times 10^1$	$0.7 \times 10^1 \pm 0.1 \times 10^1$	$0.8 \times 10^1 \pm 0.1 \times 10^1$	$1.0 \times 10^1 \pm 0.1 \times 10^1$	$1.1 \times 10^1 \pm 0.2 \times 10^1$
Zn	$2.6 \times 10^1 \pm 0.4 \times 10^1$	$2.0 \times 10^1 \pm 0.2 \times 10^1$	$1.3 \times 10^1 \pm 0.2 \times 10^1$	$2.0 \times 10^1 \pm 0.2 \times 10^1$	$1.8 \times 10^1 \pm 0.2 \times 10^1$	$2.9 \times 10^1 \pm 0.8 \times 10^1$
Ga	$0.3 \times 10^1 \pm 0.1 \times 10^1$	$0.4 \times 10^1 \pm 0.1 \times 10^1$	$0.2 \times 10^1 \pm 4.0 \times 10^1$	$0.2 \times 10^1 \pm 0.1 \times 10^1$	$0.4 \times 10^1 \pm 0.1 \times 10^1$	$0.4 \times 10^1 \pm 0.1 \times 10^1$
Rb	$1.8 \times 10^1 \pm 0.2 \times 10^1$	$1.6 \times 10^1 \pm 0.1 \times 10^1$	$1.1 \times 10^1 \pm 0.2 \times 10^1$	$1.4 \times 10^1 \pm 0.1 \times 10^1$	$1.8 \times 10^1 \pm 0.2 \times 10^1$	$2.1 \times 10^1 \pm 0.2 \times 10^1$
Sr	$2.0 \times 10^1 \pm 0.3 \times 10^1$	$2.4 \times 10^1 \pm 0.3 \times 10^1$	$1.6 \times 10^1 \pm 0.3 \times 10^1$	$1.7 \times 10^1 \pm 0.1 \times 10^1$	$2.2 \times 10^1 \pm 0.3 \times 10^1$	$2.5 \times 10^1 \pm 0.3 \times 10^1$
Y	$1.7 \times 10^1 \pm 0.3 \times 10^1$	$1.5 \times 10^1 \pm 0.3 \times 10^1$	$1.2 \times 10^1 \pm 0.2 \times 10^1$	$1.2 \times 10^1 \pm 0.1 \times 10^1$	$1.2 \times 10^1 \pm 0.1 \times 10^1$	$1.5 \times 10^1 \pm 1.2 \times 10^1$
Zr	$8.9 \times 10^1 \pm 0.8 \times 10^1$	$1.0 \times 10^2 \pm 1.5 \times 10^1$	$6.1 \times 10^1 \pm 0.9 \times 10^1$	$6.1 \times 10^1 \pm 0.6 \times 10^1$	$7.4 \times 10^1 \pm 1.1 \times 10^1$	$7.8 \times 10^1 \pm 1.2 \times 10^1$
Pb	$8.0 \times 10^1 \pm 0.6 \times 10^1$	$4.7 \times 10^1 \pm 0.9 \times 10^1$	$4.8 \times 10^1 \pm 1.2 \times 10^1$	$3.2 \times 10^1 \pm 0.2 \times 10^1$	$8.3 \times 10^1 \pm 2.3 \times 10^1$	$6.6 \times 10^1 \pm 2.0 \times 10^1$
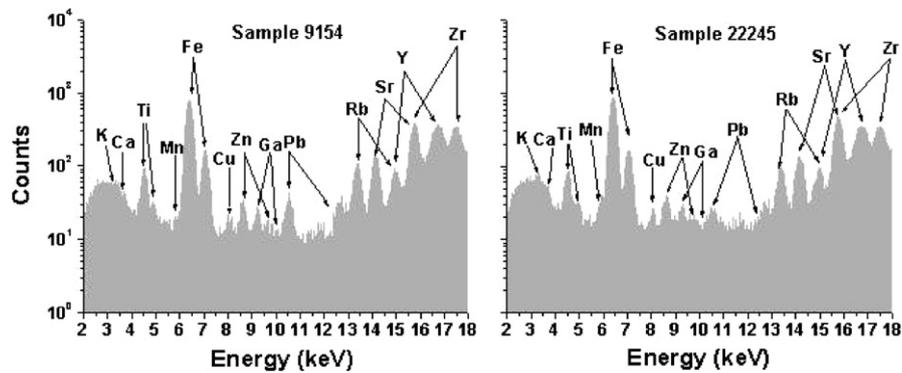
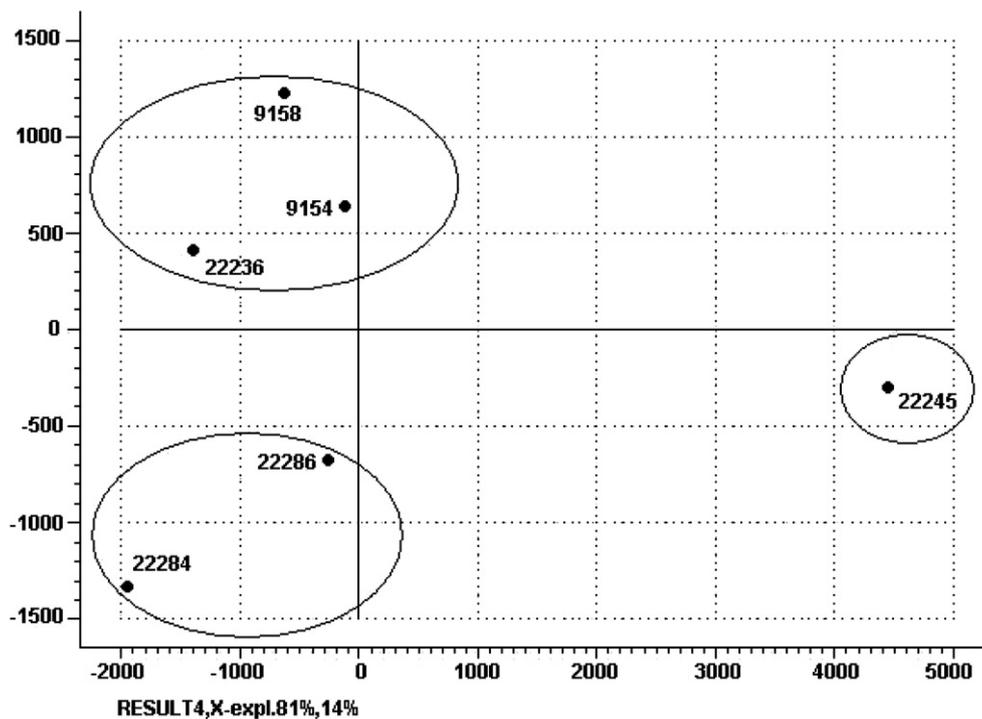Fig. 2. EDXRF spectra from the samples 9154 and 22245.

Fig. 3. Score plot of the first two principal components showing the samples separated in three groups.
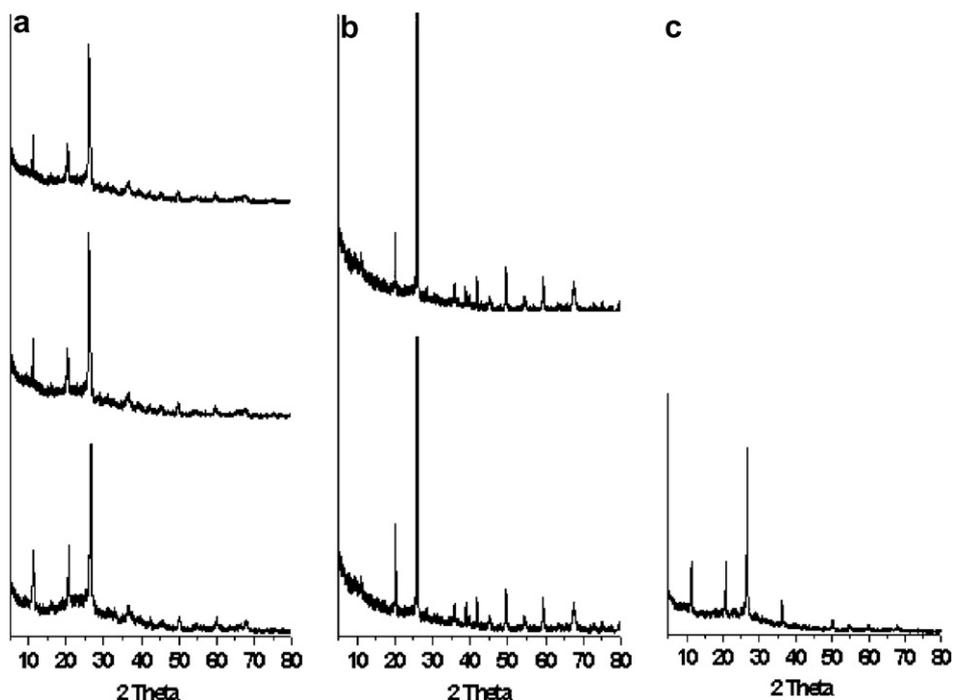
Fig. 4. XRD results for the samples. (a) Group I: samples 22236, 9154 and 9158. (b) Group II: samples 22284 and 22286. (c) Group III: sample 22245.

(8.04 keV) and the Mo scattering from the X-ray tube anode. Although in XRF measurements the scattering effect is considered an inconvenience, recent applications that employ Compton, Rayleigh and Raman scattering as measurement signals, after treatment with chemometric methods like PCA and HCA, have been reported [8,9].

4. Conclusions

The elemental composition of the Marajoara tangas was characterized by means of EDXRF technique. Although qualitative and quantitative XRF analysis of the tangas have indicated, at first, the same provenance to all samples, the multivariate statistical analysis by PCA proved that the samples were separated in three distinct groups, with different provenances.

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