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APPLICATION OF INAA TO PROVENANCE STUDY OF CERAMICS FROM BAIXO SÃO FRANCISCO RIVER, SERGIPE, BRAZIL

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ABSTRACT

The study of the physical and chemical characteristics of crafts, in association with historical and archaeological research, has allowed for the reconstruction of ancient community habits. Archaeological studies include several techniques to reconstruct ancient cultures. Since ceramics represent a sophisticated merging of previously separate domains of human knowledge and experience, these objects are studied by means of archaeometric methods. In recent years an interdisciplinary research program was started between Museu Arqueológico de Xingó (MAX) and Instituto de Pesquisas Energéticas e Nucleares (IPEN/CNEN – SP) to study the ancient ceramist cultures from Xingó region, located in Sergipe, Brazilian Northeast. Recent studies conducted in the area have showed the existence of an independent ceramist group without relation to the ceramist group well established in the Brazilian Northeast, Tupiguarani and Aratu. Instrumental neutron activation analysis, INAA, is a suitable technique for provenance studies. In this work the chemical composition of 103 samples: 30 clays and 73 ceramics from Barracão archaeological site, from Baixo São Francisco, were analyzed. This analysis allowed for the definition of compositional groups of ceramics according to the chemical similarities of ceramic paste, which reveals the raw material composition used in the manufacturing process by prehistoric man. The outliers were identified by means robust Mahalanobis distance. The results were interpreted by means of cluster analysis, principal components analysis and discriminant analysis. The results obtained in this work, in association with archaeological information, allowed for the identification of the ceramic groups in relation to the ceramist occupations of the Xingó area. This work contributes for the reconstruction of the Baixo São Francisco region communities and for the reconstitution of the Brazilian Northeast ceramist population.

1. INTRODUCTION

Archaeology may be defined as the Science which yields information and develops theories about past human activity by means of a study of ancient material remains. Nowadays the

Archeology has used a variety of methods and tools to reconstruct the ancient cultures, such as environmental analysis, sociology, scientific and historical dating methods, historic and iconographic source, material analysis of found artifacts, among others [1]. The use of adopted method from natural sciences is currently subsumed under the term Archaeometry. Archaeometry is an interdisciplinary research field that covers aspects of analytical chemistry and spectroscopy, organic chemistry, electrochemistry, physics, electrochemistry, anthropology, archaeology, among other fields. Usually, research in this area attempts investigate the degradation, provenance or relationship between several artifacts.

Since pottery represents a sophisticated merging of previously separate domains of human knowledge and experience these objects are intensely studied by means of archaeometric methods. Broken pottery fragments are among the most common artifacts found at archaeological sites around the world [2]; as a result, it is one of the most common studied materials by archaeologists. Besides its abundance and durability, pottery has several macroscopic and microscopic attributes of interest to archaeologists [3]. Visual properties such as shape and surface decoration are frequently used as cultural and chronological indicators. Additionally, microscopic properties such as the texture of the paste (i.e., the clay and temper combination) can be used to study preparation techniques. Especially, the compositional study of the clay, sand and other natural material from which the pottery were fashioned can indicate the local source from which they were take, once a chemical composition these materials can be unique [4,5].

The main components of clays (i.e., Al_2O_3 and SiO_2) are generally present in amounts well above 10 percent and minor impurities such as the oxides of Na, Mg, K, Ca, Ti, and Fe are typically found in amounts between 1000 ppm and 5 percent. However, it is the trace constituents – elements present at concentrations below 1000 ppm – whose presence in clays is effectively accidental that usually provide the best information for provenance studies [6].

In recent years a multidisciplinary research program was started between the Federal University of Sergipe (UFS) and Research Institute of Nuclear and Energy (IPEN/CNEN-SP) to study the ancient ceramist cultures from Xingó region, situated in Canindé do São Francisco, Sergipe State, in the Northeast Brazilian (Figure 1). Recent studies conducted in the area has showed the existence of an independent ceramist group without relation to the ceramist group well established in the Brazilian Northeast, called Tupiguarani and Aratu [7]. Dating obtained by means of carbon-14 from skeletons has indicated that there is evidence of human occupation 9,000 years before present in "Xingó" region. So this work aims to contribute to the understanding of the Low São Francisco River occupation dynamics by mean an archaeometric approach.

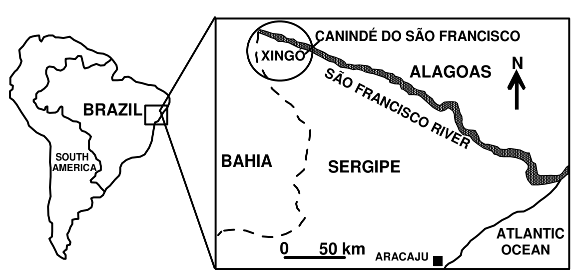

Figure 1. Localization map of the study area

Once archaeometric studies on possible clay sources contribute to determine a "fingerprint" of raw materials used to manufacture of potteries, in this work Instrumental Neutron Activation Analysis (INAA) was utilized to determine the elemental composition of pottery fragments and clays from Barracão archaeological site, situated in Canindé do São Francisco, to establish a categorization these potteries and the raw material sources. In addition, it was verified the hypotheses of the clays samples analyzed to be raw material to obtain the ceramic paste of potteries from Barracão archaeological site.

2. EXPERIMENTAL

2.1 Material

In this work, 103 samples, 73 ceramic fragments and 30 clay samples, from Barracão archaeological site were analyzed by means of INAA. The clays samples were collected near to Barracão site from three places, called Clay A, B and C. Although several chemical methods have been employed to analyze pottery and clays, the analytical technique that has dominated pottery provenance research from the late 1960s up to the present time has been INAA [8-11]. According archaeological studies, the ceramist occupation at Xingó area is one of the most ancient of the Brazilian Northeast [12].

2.2. Sample preparation and standard

Ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 1-2 cm using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on the thickness, 3 or 5 holes were drilled as deep into the core of the fragment as possible without drilling through the walls. Clay samples were ground (< 100 mesh) and homogenized in pestle constituted of agate. Finally, the powered samples were dried in an oven at $105^{o}C$ for 24 h and stored in desiccators.

Constituent Elements in Coal Fly Ash - NIST-SRM-1633b, were used as standard in all analysis. The standard reference material Brinck Clay - NIST-SRM-679 was used to check the analytical quality of the results. The standard and the samples were dried in an oven at $105^{o}C$, the standards for 4 h and samples for 24 h and stored in a desiccator until weighing.

2.3 Irradiation and radioactivity measurements

About 100 mg of ceramics samples, and NIST-SRM-1633b were weighed in polyethylene bags and involved in aluminum foil. Groups of 8 ceramic samples and two reference materials were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1m (IPEN/CNEN – SP) at a thermal neutron flux of about 5×10^{12} $n \cdot cm^{-2} \cdot s^{-1}$ for 8h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 2020 from Canberra, resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, with S-100 MCA of Canberra with 8192 channels. As, K, La, Lu, Na, Nd, Sm, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25-30 days. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

2.4. Statistical methods

To study outliers several robust estimators to arithmetic mean and sample covariance matrix, in Mahalanobis distance, have been proposed in the literature, such as estimators that include the minimum covariance determinant (MCD) [13-16].

In this work, to identify outlier cases, the robust Mahalanobis distance (RD) based on MCD estimator, was utilized. It was possible construct the ellipse corresponding to the squared Mahalanobis distance equal to $\chi^2_{2;0.98}$ (often called a tolerance ellipse) for each group. The observation found outside of the tolerance ellipse, in the space established for the first two principal components, was considered outlier [17].

Cluster analysis is a general term that applies to a variety of specific techniques but the essential components are (a) a measure of the similarity-dissimilarity between specimens is defined and (b) a clustering algorithm [18,19]. In general, cluster analysis is used to identify initial groups after which other techniques for group refinement and classification are subsequently applied. To identify initial groups of pottery from Justino site, it was performed a cluster analysis using Ward's Method and squared Euclidian distance [20].

Discriminant analysis is a widely used multivariate statistical technique in archaeometry to identify elements which are most useful in discriminating between groups and graphically displaying the chemical distinction between these groups [21]. In this work discriminant analysis was used to identify the groups of samples.

3. RESULTS AND DISCUSSION

To evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for reference material Brick Clay - NIST-SRM-679 were statistically compared with the data found in our laboratory. The precision of several elements (La, Th, Sc, Fe, Eu, Ce, Zn, Hf, and Co) was better than 5% and matched with the precision obtained by other authors. Some elements presented RSD (Relative Standard Deviation) less than 10% (Nd, Rb, Sm, Ba, Sb, Ta, and Tb) and are similar to those from the literature [22]. The interference ^{235}U of fission in the determination of La, Ce and Nd was negligible because U concentrations did not exceed 5 ppm and the rare earth concentrations were not very low.

One of the basic requirements underlying the composicional characterization of the archeological pottery is that analytical technique presents appropriate precision. Elements that have low precision can reduce the discriminating effects of other well measured elements. In this work all the elements with precision above 10% were considered for interpretation of the results (Na, Lu, Yb, La, Th, Cr, Cs, Sc, Ce, Fe, Eu, Zn, Co, Ta, U and Hf) [23]. The Zn presented RSD better than 10% but was excluded from the data set because its determination suffers strong gamma ray interferences of ^{46}Sc and ^{182}Ta. The elements Co and Ta were eliminated because their concentrations can be affected by tungsten carbides drills [24], even though their precision was smaller than 10%. The K and Sb were better than 10%, however they were excluded because they presented 15% of missing values. Based on these screening criteria 13 elements: Na, Lu, Yb, La, Th, Cr, Cs, Ce, Sc, Fe, Eu, U and Hf were used for the interpretation of the results.

The results were transformed to $\log_{10}$ to compensate for the large magnitude difference between the measured elements at the trace level and the larger ones. The $\log_{10}$ transformation data before a multivariate statistical method is common. One reason for this is the belief that, within manufacture raw materials, elements have a natural lognormal distribution, and that data normalization is desirable. Another reason is that a logarithmic transformation tends to stabilize the variance of the variable and would, thus, give them approximately equal weight in unstandardized multivariate statistical analysis [25]. After logarithmic transformation the data set was submitted to outliers test by means of robust Mahalanobis distance using minimum covariance determinant, where critical values were obtained $\chi^2_{2;0.98}$. The samples out of the tolerance ellipse $\chi^2_{2;0.98}$ were considered outliers. Only one sample was considered outlier.

To grouping process of potteries, hierarchic cluster analysis, HCA, was used to study the clusters of the pottery and clay samples. Figure 2 shows the cluster using as similarity measured the square Euclidean distance and the Ward's method among of 13 chemical elements to pottery samples. The Figure shows the separation of the pottery in four groups . The groups are labeled as A, B, C and D potteries.

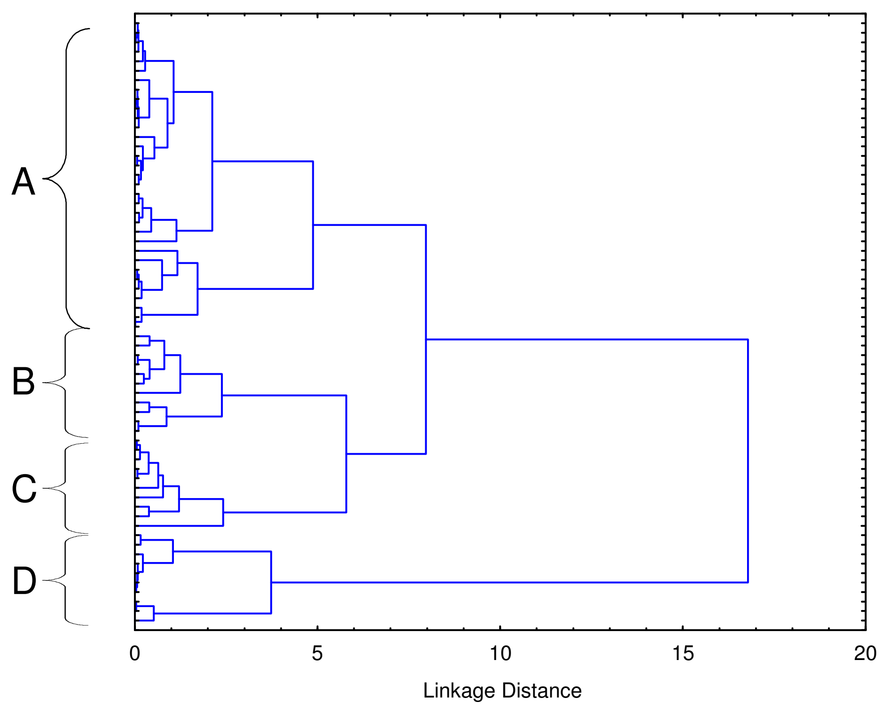

Figure 2. Dendrogram for pottery samples from square Euclidean distance and cluster analysis.

As shown elsewhere [6], cluster analysis alone is not the most reliable technique for grouping samples in provenance studies. In order to confirm the latter assumption, the data were submitted to discriminant analysis (DA). The clay samples were classified by means of cluster analysis '*a priori'* as belonging to one of the three investigated areas and according results from DA. According with results from HCA *'a priori'* to pottery samples was defined. Figure 3 presents a bivariate plot of discriminant function 1 versus discriminant function 2 showing seven main groups, three groups of clay samples (Clay A(19), clay B (10) and clay (10))and four groups of potteries (Pottery A(10), Pottery B (12), Pottery C(9) and Pottery D(32)). The Forward Discriminant analysis procedure indicated that the elements Lu and U are not relevant to discriminant the groups. In addition, the results from DA indicated that raw materials used to manufacture of potteries analyzed are distinct and the clay samples investigated were not used to obtain ceramic paste of Barracão sites. Once clay samples investigated was available nearly the Barracão archeological site, it can be inferred that potters who lived at Barracão area searched their raw materials far from this site. Therefore, the search for clay of appropriate properties to manufacture of the potteries, perhaps, it has induced craftsman to seek raw materials far from place where lived.

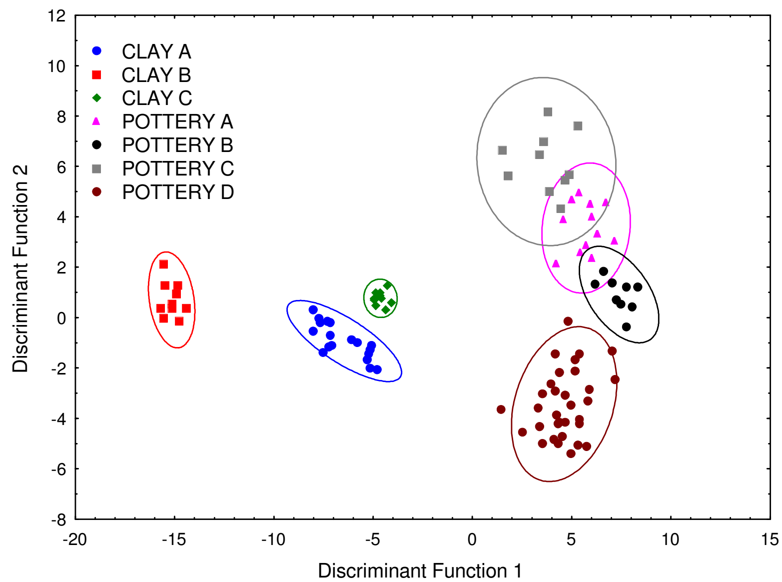

Figure 3. Linear discriminant analysis of the archaeological pottery and clays samples from Barracão archaeological site. Ellipses represent 95% confidence.

3. CONCLUSIONS

The INAA of potteries from Barracão site was successful in identifying distinct compositional groups from elemental chemical composition of pottery. It was identified four groups of the potteries and three clay sample groups. Results from DA indicated that clay samples analyzed in this work were not used to prepare ceramic pastes of potteries from Barracão archaeological site. Thereby, it can be inferred that raw materials to manufacture of potteries at Barracão site was not local. The results provided information about occupation dynamic of ceramist groups who lived in Xingó area on prehistorical period.

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