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THE UTILIZATION OF TRACE CHEMICAL COMPOSITION TO CORRELATE CERAMICS WITH CLAY DEPOSITS

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ABSTRACT

In this work, 22 clay samples near Hatahara and Açutuba archaeological sites, and 135 ceramic samples were analyzed by means of Instrumental Neutron Activation Analysis. INAA is the most suitable technique because it does not require mineralization of samples and has high sensitivity, accuracy and precision. The samples were irradiated in IEA-R1 reactor at IPEN-CNEN-SP at thermal neutron flux of $8{,}92 \times 10^{12}$ $cm^{-2}s^{-1}$ during one hour. The elementary concentration results were studied using multivariate statistical methods. The compositions group classification was done through cluster analysis and the similarity/dissimilarity among the samples was studied by means of discriminant analysis.

1. INTRODUCTION

The archaeological sites Hatahara and Açutuba, localized in the merning of Negro and Solimões rivers, Central Amazon, have in all their extension a large quantity of ceramic material. In archaeometry, the classification and identification of these objects by means of physics and chemical techniques, allow understand the origin of the raw material used in the manufacture of these artefacts. The ceramics are formed by sedimentary rocks, whose main component is clay. Clay is a material made of aluminum silicates of indefinite composition. The main components of the clay are AlO_3 and SiO_2, which represent in quantities larger than 10%. Smaller impurities such as Na, Mg oxides are found in concentrations, which vary from 0.1% to 5%. However, trace elements whose presences in clay are accidental are the ones that provide the best information for provenance studies.

Ceramics can be grouped according to similarities and dissimilarities derived from the chemical composition data. By means of determination of chemical composition ceramic and clay, is possible correlate date both of them, to recommending if the ceramic is or not belong of the place where was found. The group differentiation depends on the discriminant element concentration, which will indicate the existence or not of one or more clay deposits. The study realized about these material, can bring important explanation about commercial and cultural exchanges between the pre-colonial occupation, as well as the social organization of the communities that had occupied the region along the time.

The regions formed by Negro and Solimões rivers, are called of the “high terraces”, due to their localization on the margin of rivers. In general, the pottery archaeological sites are found in this high area, describing the standard of living of the pre-colonial occupation. The sites localized near to Solimões river have large resource, fish and nutrients in the soil, while those localized in the margins of the Negro river have limited access to natural resources. However, after 50 km of the mouth, the Negro river still receives influence of the Solimões river. It’s justified by the dimensions of the Açutuba site, with hundreds of meters of size, and also counts with the presence of black lands [1]. In the Figure 1 is showed the localization of the sites.

The Hatahara site is situated on an adjacent terrace to a fertile valley area in the left margin of the Solimões River, in the municipality of Iranduba, State of Amazonas. The area of this site encloses area of the grass, culture of papaya and hoses. The topographical surveys indicate that the site has area of 160.000m^2 [2]. Distinguish four different phases of occupation in the Hatahara site. The Açutuba Phase (300-360 AD), with few ceramics fragments; the Manacapuru Phase (500-900 AD) and Paredão Phase (700-1200 AD), with much ceramics fragments and black land; and the Guarita Phase (90-1600 AD) related to large distribution for all the bed of the Amazon river [3].

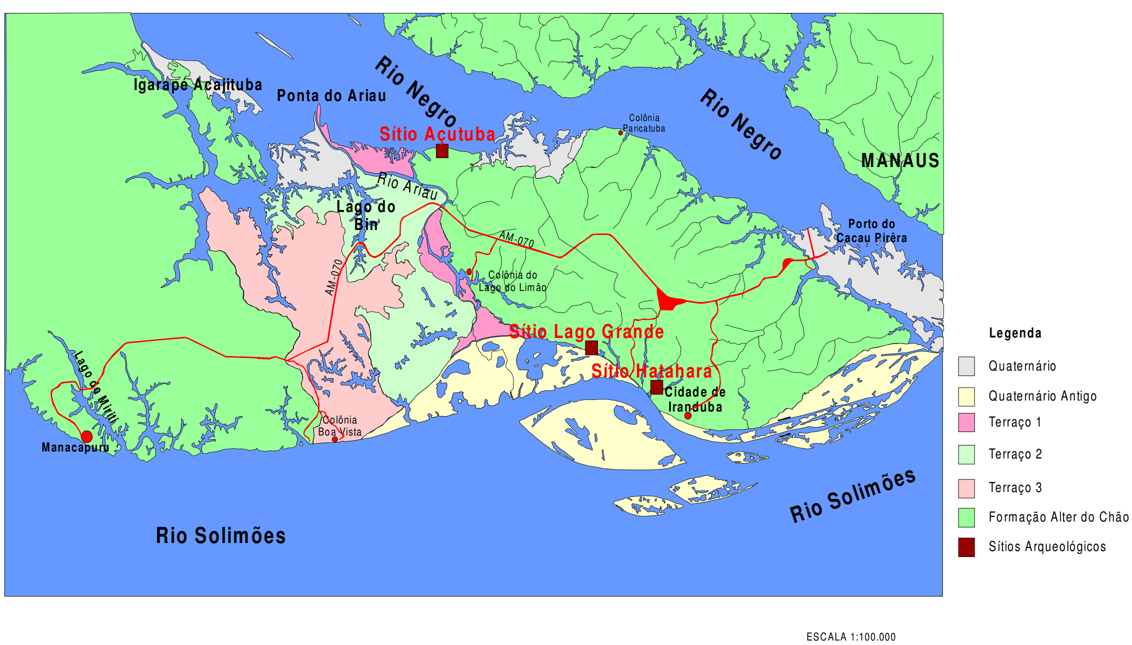

Figure 1. Localization of the archaeological sites: Hatahara and Açutuba.

1.1 Neutron activation analysis

The neutron activation analysis is distinguished between the instrumental non-destructive methods, for presenting some advantages, such as for being a multielemental analytical technique, for having good sensitivity, precision, and accuracy and to use small amount of sample. The identification and quantification of the elementary concentrations had been realized by means of gamma spectroscopy, which uses the energy of the gamma rays and the taxes of decay of the radioisotopes governed for the mid-life ($T_{1/2}$).

2. EXPERIMENTAL

2.1 Sample preparation

The ceramic fragments had been, initially, washed with water using a brush of the fine bristles. Soon later, they had been placed in a 104ºC stove for 24 hours. Following this procedure, the surface of ceramics was cleaned with tungsten carbide drill bits, with the purpose to prevent any contamination. About 500mg of sample, in the powder form, 3-5 orifices in the internal part of the fragment had been gotten. This powder was collected, and later dried in 104ºC stove for 24 hours.

The clay samples were ground in agate mortar and put through a 100 to 200 mesh sieve in order to obtain a fine enough powder for the trace and ultra trace element analysis [4,5].

2.2 Analytical procedure

In this work, 135 samples of ceramic fragments and 22 samples of clay had been analyzed. About 100mg of each sample together with the Standard Reference Material NIST-SRM 1633b, used as standard, were weighed in polyethylene involucres and stamped with iron for weld. These involucres had been mingled with sheets of aluminum paper. The samples and the standard had been irradiated by one hour at Reactor IEA-R1 of the IPEN/CNEN/SP under a flow of termical neutrons of the $8{,}92x10^{12}$ $cm^{-2}s^{-1}$.

Two counting were realized, being determined after seven days of decay, As, K, La, Lu, Na, Nd, Sb, Sm, U and Yb. And, after 25-30 days of decay, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Tb, Th and Zn [6].

2.3 Statistical Studies

The interpretation of the results was realized by means of two statistical methods. The cluster analysis and discriminant analysis. The cluster analysis is a multivariate statistical technique that has a main objective to group the similar samples in accordance with their characteristics. For formation of the groups is necessary consider the proximity between the points, since points that are next represent regions whose samples are similar. In the final phases of aplication of the cluster analysis the groupings can be represented graphically by means of dendrogram. The dendrogram present the elements and the respective points of fusing or division of the groups formed in each period of training. The visual inspection of the dendrogram, allow the identification of the groups.

The discriminant analysis is a multivaried statistic technique that has the objective to discriminate population and/or classify objects in populations definite prior [7]. Thus, the main objectives of these techniques are finding functions of the original variables (discriminant functions) that explain the differences between the populations and allow insert new objects (sample) in the populations involved in the analysis. For the application of the discriminant analysis, the population must be well defined.

3. RESULTS AND DISCUSSION

Initially, were determined the concentrations of As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb e Zn in 8 samples of the Reference Material IAEA-Soil 7 Trace elements in soil, with the aim to study the precision and accuracy for each one of the elements. Some statistical studies were applied to the data, such as mean and standard deviation determination, mean confidence interval, precision and accuracy. The results showed that the most elements show the precision $\leq$ 10%. This precision is considered, for the several authors [8], appropriate for the choice of the chemical elements for studies of chemical characterization of archaeological objects, using multivariate statistical analysis.

Co and Ta, although show precision less that 10%, were eliminated, by contamination by means of tungsten carbide during the sample preparation [9]. The Zn also was eliminated because to suffer interference in the gamma ray spectra of the ^{46}Sc. Although As, Nd, Ba, Sb e Rb show well precision, previous studies showed that not are reliable elements for are insert in the database off showed great disperse in the ceramic concentrations. Therefore, the elements that were used are Na, K, La, Yb, Lu, U, Sc, Cr, Fe, Cs, Ce, Eu, Tb Hf e Th.

The concentrations of the samples ceramics and clay were transformed in $\log_{10}$ for make up the difference magnitude between elements that it was found in percentage and trace level. The transformation of the concentration in $\log_{10}$ before of apply multivariate statistic techniques, is a usual procedure in the archaeometry studies. One of the reasons for its, is explained by the fact the have a normal logarithmical distribution of the elements.

After, the detection of the discrepancy results or *outliers* was done by means of *Mahalanobis* distance, D_i^2, a method utilized when are determined various variables [10]. For each sample in the set variables, D_i^2 is calculed. Was developed by *Wilks* a statistic method to determine values discrepancy in the multivariate results, when the distribution is normal, to research discrepancy values sequentially. The bigger discrepancy value is that has the smaller reason of the dispersion R_i, where $R_i = min(R_i)$, that is the removed result [11]. In this work, were identified ten samples *outliers* and were removed.

The data for the logged elemental concentrations from Hatahara and Açutuba ceramic samples were submitted to cluster analysis using Ward´s method and Square Euclidean distances. Examination of dendrogram indicated that the ceramic analyzed samples from Hatahara and Açutuba separate into two and three groups, respectively. Such dendrograms, however, are subject to considerable distortion, and since we were interested on overall patterns of variation rather than the formation of discrete groups, was explored those relationships among the data of ceramic samples that reflect patterns of interelemental covariance, as well magnitude of elemental abundance. Accordingly, the data were submitted to principal components analysis. Three components with eigenvalues greater than 1.0 were extracted from a variance–covariance matrix of the log-transformed elemental concentration values.

After that, the data were submitted to discriminant analysis. Figure 2 shows the discriminant function 1 vs discriminant function 2 for the ceramic and the clays, the plots show the group very clearly. As can be seen the results show that the samples of each site form a very tight chemically homogeneous group, showing a high degree of chemical similarity. Examination of the plot it is possible to see that the Hatahara ceramic samples form two compositional groups and Açutuba samples form three chemical groups with similar composition. Similar conclusions were obtained using the plots of cluster analysis and principal component analysis.

Since differences in chemical composition are typically interpreted as evidence for distinct source of raw material, our main purpose was to identify and distinguish the similarities among the ceramic samples and the clay samples collected close of Hatahara and Açutuba archaeological sites. Figure 1 reveals that the chemical composition of the three clays samples are included in the chemical composition of the Açutuba ceramic samples. Then, the chemical compositions of the clays are similar to chemical composition to Açutuba ceramic. The clay samples analyzed in this paper were collected no more than 6 km from the sites.

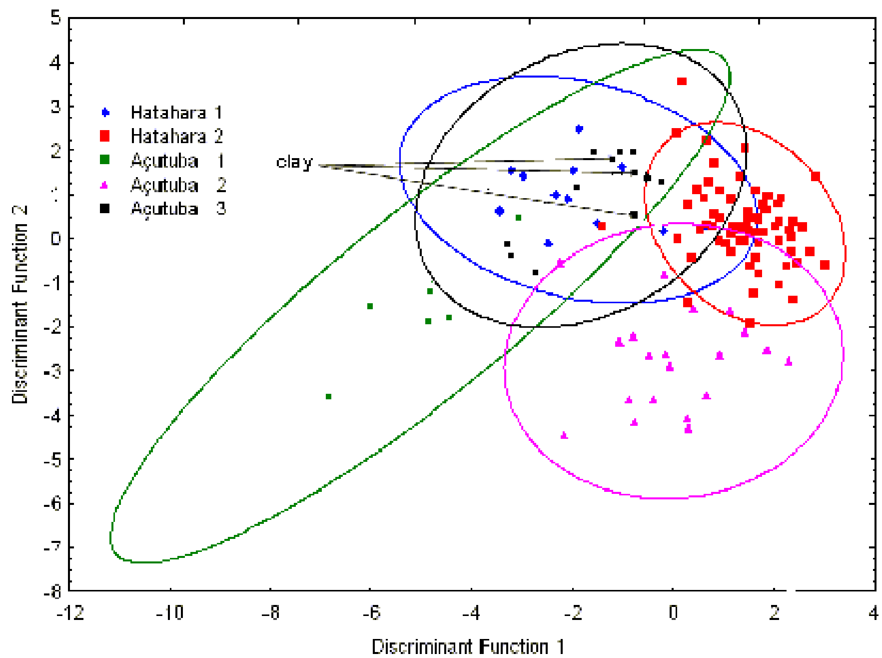

Figure 2. Discriminant function 1 versus discriminant function 2. The ellipses represent 95% confidence level.

4. CONCLUSIONS

The clay samples collected near Hatahara archaeological site and analyzed in this paper were not used for the manufacturing of the vessels. Whereas, were found three clays samples used in manufacturing of vessels from Açutuba. INAA contributed for the studies realized in the ceramic samples.

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