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A PRELIMINARY STUDY OF ARCHAEOLOGICAL CERAMICS FROM THE SÃO PAULO II ARCHAEOLOGICAL SITE BY INAA

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ABSTRACT

The determination of trace elements plays an important role in the characterization of archaeological ceramics. It is well established that ceramics can be grouped based on similarities/dissimilarities derived from chemical data. Different analytical methods can be applied to determine the sample composition. Instrumental neutron activation analysis (INAA) is the method preferred because present several advantages in relation to the other techniques. In this work, the elements determined were As, K, La, Lu, Na, Nd, Sb, Sm, U, Yb, Ba, Ce, Co, Cr, Cs, I, Fe, Hf, Rb, Sc, Ta , Tb, Th and Zn to carry out a preliminary chemical characterization in 44 ceramic samples from São Paulo II archaeological site by INAA. The site is located in Coari city, 363 km from Manaus, Amazonas state (AM). The elementary concentration results were studied using multivariate statistical methods. The similarity/dissimilarity among the samples was studied by means of discriminant analysis. The compositions group classification was done through cluster analysis, showing the formation of the three distinct groups of the ceramics.

1. INTRODUCTION

The physicochemical study of archaeological ceramics has reached a large number of publications in the field of archaeology in recent years [1]. Those studies fragments can be used provenance characterization study of exchange and manufacturing of ceramics [1, 2]. In this sense, by arquaelogists study of ceramics has allowed more refined studies on the type and degree of social and political relations among the prehistoric peoples [3].

Archaeologists are usually interested in stylistic variation over time, the type of technological process of ceramic production, function and use of artifacts [2, 3]. With these objectives, the classification is based on typological attributes [3]. However, the diversity of philosophies employed in the visual analysis of the fragment does not always produce satisfactory results [3, 4].

Nowadays, many analytical techniques can be used to determine the elemental composition of pottery: X-ray fluorescence (XRF), inductively coupled plasma atomic emission spectrometry (ICP-AES) and instrumental neutron activation analysis (INAA) [5, 6].

The INAA is a non-destructive nuclear analytical technique. In short, it has advantages such as high levels of precision, accuracy and reproducibility [7]. In this context, INAA has been widely used in basic studies of ceramics, coins, marble, iron, bronze and other archeological artifacts [8].

This paper presents the preliminary results of the determination of As, K, La, Lu, Na, Nd, Sb, Sm, U, Yb, Ba, Ce, Co, Cr, Cs, I, Fe, Hf, Rb, Sc, Ta , Tb, Th and Zn in 44 samples of ceramic fragments from the São Paulo II archaeological site. Due to the large number of elements analyzed, the data were treated with two multivariate statistical methods, cluster and discriminant analysis, widely used in archaeometric studies [9].

1.1. Study Area

As can be seen in the Figure 1, the São Paulo II archaeological site is located in the city of Coari, AM [10]. The city is 362 km apart from Manaus, on the left margin of the Solimões river [11]. The site can be arrived by boat or plane.

The archaeological site is characterized by a large quantity of black earth and also by the presence of large amounts of ceramic material. The area has a type of soil rich in organic matter on the surface. The archaeological fragments belongs to the Guarita phase, as classified by the archaeologists [11].

The land located near the site is used for grazing and cultivation of banana, lemon, cassava and papaya [10]. Changes in natural vegetation can be observed, together with lots of pottery fragments and black earth.

Such aspects show that the archaeometric studies are relevant for understanding of the formation process of the site, because it helps in the study of size and chronology of thus occupations [11].

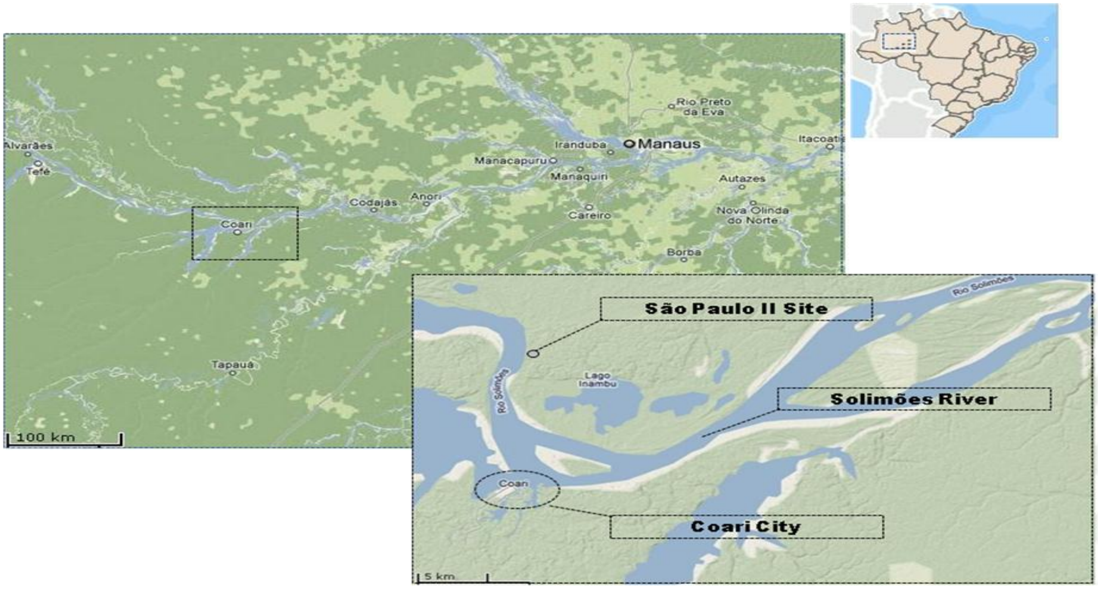

Figure 1. Map of São Paulo II archaeological site. Font: i3Geo Maps.

The region has high lands and river plains formed by plateaus of flat topography [12]. The land is high and so are beyond the reach of river floods [13]. There is a great predominance of the formation of sedimentary rocks, characterized by geological formation Issa [14, 15]. The river plains are flat and low, able to alluvial sedimentation [16, 17].

1.2. Analytical Technique

1.2.1. Neutron activation analysis

NAA comprises a multielement analytical technique able to perform analysis of inorganic chemicals major, minor and trace elements [6, 7]. The neutron activation analysis is based in the measurement of induced radioactivity in sample. [8]. The particle emitted by nuclei of radioactive isotopes can be measured using gamma spectroscopy [9].

For this work, the particles of interest are gamma-rays, emitted for each radioisotope. Thus, it is possible to determine the qualitative and quantitative analysis of elements present in the samples.

2. MATERIAL AND METHODS

2.1. Sample Preparation

The ceramic fragments were, initially, washed with water using a brush of the fine bristles. The fragments surface of ceramics was cleaned with tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. Depending on thickness, 3 or 5 holes were drilled as deep into the core of the fragment as possible without drilling through the walls. Finally, the powdered samples were dried in an oven at 104ºC for 24 hours and stored [8].

The Standard Reference Material, NIST-SRM 1633b, and IAEA Soil 7 were used as standards. These materials were dried in an oven at 105^{o}C for 4 hours and stored until weighing.

2.2. Analytical Procedure

In this work, about 120 mg of ceramic samples, NIST-SRM-1633b and IAEA Soil 7 were weighed into polyethylene bags and wrapped in aluminum foils. The SRM-1633b was used as standard and the IAEA Soil 7 was used as check samples in all the analysis.

Groups of eight samples and the standard were packed in aluminum foils and irradiated in the swimming pool research reactor IEA-R1 at a thermal neutron flux of about 1.37 x 10^{12} n cm^{-2} s^{-1} for 8 hours. Two measurement series were carried out using a Germanium (hyperpure) detector, model GX 1925 from Canberra, resolution of 1.90 keV at the 1332.49 keV of γ-peak of ^{60}Co. Spectra were collected with a Canberra S-100 multi-channel analyzer with 8192 channels.

As, K, La, Lu, Na, Nd, Sm and Yb were measured after 7 days cooling time and Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, Zn and U after 25 days [18]. Gamma ray spectra analysis was carried out using the software Genie 2000 NAA Procedure from Canberra.

3. RESULTS AND DISCUSSION

One of the basic premises underlying the use of chemistry in ceramic analysis is that clay sources can be differentiated if an adequately precision analytical technique is used. If an element is not measured with good precision it can obscure real differences in concentration and the discriminating effect of other well-measured elements tends to be reduced. These differences can be used to form ceramic compositional groups because vessels manufactured from a given clay source will be more similar to each other than to other type of vessels which were manufactured from a different source.

In this work the precision was studied using the IAEA Soil 7. For that, were made 20 independent determinations and the results found were compared with the certified values. The relative standard deviation (RSD), was calculated and the elements with RSD less than 10% were considered. This precision is considered appropriate by several authors for the choice of the chemical elements for studies of archeological objects using multivariate statistical methods [19].

Although Co had RSD around 3%, was not included in the data set because the concentration can be affected by tungsten carbides files [20]. The precision of K and Rb was better than 10%; however, they were not included because they presented 15% of missing values. The determination of Zn is not reliable due to the strong gamma ray interferences of ^{46}Sc and Ta. Although As, Nd, Ba, Sb and Rb present a good precision, previous studies showed that they are not reliable elements to be inserted in the data base because they show a significant dispersion in ceramics concentrations. The interference of ^{235}U fission in the determination La, Ce, and Nd was negligible because U concentration did not exceed 5 ppm and the rare earth elements were not extraordinarily low [21].

Based on these screening criteria, 13 elements: Na, La, Yb, Lu, U, Sc, Cr, Fe, Cs, Ce, Eu, Hf and Th were used in subsequent data analyses. None of these elements considered contained missing values. The concentration data of ceramic chemical elements is presented in Table 1.

Initially, the data of elementary concentrations of the ceramic samples was made a transformation to compensate for the difference in magnitude among elements given in percentages and at trace level. The transformation of the concentrations before applying multivariate statistical methods is a usual procedure in archaeometric studies. One of the reasons for this is that it tends to stabilize the variance of the variables, which would have an approximately equal weight in a multivariate statistical analysis.

Table 1: Results for ceramic samples from São Paulo II archaeological site, in µg/g, unless otherwise indicated, (n=44).

Samples	Na,%	La	Yb	Lu	U	Sc	Cr	Fe,%	Cs	Ce	Eu	Hf	Th
1	0.04	38.83	3.28	0.45	3.12	17.22	72.99	3.80	7.43	65.72	0.97	7.04	13.50
2	0.07	35.32	3.09	0.33	3.87	19.03	73.47	3.39	9.56	72.35	1.17	4.58	14.97
3	0.34	36.17	3.56	0.41	4.73	18.12	63.55	4.01	8.57	79.40	1.27	4.64	14.60
4	0.13	30.65	2.27	0.39	4.89	16.16	66.67	4.15	10.55	56.24	0.83	4.35	14.28
5	0.21	43.91	2.61	0.36	2.85	18.44	69.57	4.07	9.88	75.95	1.18	4.04	16.01
6	0.05	34.74	3.01	0.35	3.23	14.05	57.34	3.55	6.57	63.16	1.04	6.46	12.98
7	0.10	39.73	2.66	0.43	3.90	13.54	56.45	2.44	6.05	79.57	1.32	5.50	11.06
8	0.11	36.19	2.95	0.38	3.27	13.85	64.26	2.50	4.17	75.40	1.22	5.83	11.70
9	0.14	34.57	2.54	0.38	2.29	11.93	64.30	2.18	2.95	58.01	0.99	7.78	10.72
10	0.14	42.39	3.56	0.49	5.12	14.75	70.17	3.03	3.77	85.40	1.89	8.53	13.03
11	0.35	28.71	2.42	0.39	3.65	14.96	57.70	4.11	10.24	55.52	1.11	7.40	13.03
12	0.20	28.88	2.84	0.48	5.15	14.29	59.07	2.61	5.02	66.68	1.07	9.75	13.63
13	0.11	29.28	3.08	0.41	6.40	15.12	75.65	2.50	6.43	62.02	0.92	12.22	14.26
14	0.34	42.55	2.47	0.33	3.38	19.01	81.76	5.00	6.75	86.92	1.57	6.03	16.72
15	0.52	48.92	3.19	0.49	3.90	19.96	93.37	4.64	4.73	99.45	1.65	7.85	17.24
16	0,,14	33.50	2.58	0.46	3.98	12.44	71.44	2.51	5.60	63.96	0.74	5.91	11.85
17	0.48	51.54	3.86	0.60	4.73	20.19	89.24	4.34	8.57	101.10	1.79	5.06	17.43
18	0.33	46.39	3.17	0.52	5.25	17.17	70.32	3.61	7.58	81.23	1.49	3.56	14.45
19	0.45	47.60	2.44	0.50	4.58	20.41	79.62	4.24	11.39	95.29	1.59	7.26	18.24
20	0.40	58.70	3.49	0.63	3.59	19.51	84.22	4.82	7.66	97.18	1.65	4.34	17.66
21	0.20	29.12	2.93	0.55	4.35	14.35	66.47	2.82	5.04	55.17	1.04	5.29	12.38
22	0.12	39.23	3.36	0.55	2.72	16.61	76.46	2.17	4.21	64.01	0.87	9.10	13.72
23	0.21	38.36	3.56	0.46	4.03	18.15	78.62	1.99	6.71	61.77	0.86	6.05	15.45
24	0.12	33.68	2.76	0.46	2.72	15.30	74.70	2.75	7.99	66.89	0.89	4.18	13.54
25	0.17	41.86	3.29	0.51	3.30	16.94	73.42	4.02	9.31	86.15	1.20	5.81	14.07
26	0.15	44.47	3.00	0.56	3.15	16.17	71.65	2.68	11.00	75.53	1.07	3.82	13.16
27	0.17	48.97	3.91	0.65	2.36	16.44	74.59	2.85	5.42	82.78	1.20	4.50	13.12
28	0.06	58.52	3.40	0.62	4.10	15.45	70.53	2.21	8.79	99.36	1.56	5.50	13.93
29	0.22	45.80	2.95	0.66	4.16	17.86	83.97	3.21	8.52	70.80	1.13	5.20	14.70
30	0.05	37.88	3.15	0.52	4.38	18.32	80.53	4.29	10.51	66.22	0.99	11.69	15.44
31	0.12	42.77	3.68	0.63	4.26	17.62	81.43	3.47	8.18	88.51	1.47	9.31	15.16
32	0.16	38.44	3.09	0.54	6.42	20.01	82.22	4.63	14.87	79.07	0.94	6.84	16.86
33	0.09	30.17	2.24	0.38	5.01	14.59	60.02	2.21	4.93	66.74	0.75	9.01	11.76
34	0.24	34.15	2.71	0.45	2.57	14.97	56.87	2.91	7.46	67.04	1.13	7.14	11.59
35	0.28	37.47	2.65	0.45	4.69	17.53	64.94	4.25	10.71	75.39	0.99	6.03	14.61
36	0.12	50.66	3.83	0.60	4.53	18.26	70.53	4.65	7.14	88.84	1.28	10.32	15.06
37	0.08	52.84	3.99	0.62	3.84	16.95	76.94	3.10	6.76	109.25	1.35	8.21	15.71
38	0.54	49.52	3.96	0.51	3.72	18.92	76.01	3.99	7.76	97.46	1.59	7.11	15.11
39	0.27	43.10	3.09	0.41	3.47	18.61	72.29	3.60	11.45	83.48	1.04	5.91	14.98
40	0.08	36.46	2.31	0.44	4.25	19.08	75.55	3.35	9.88	77.86	0.91	4.64	14.97
41	0.09	52.55	3.41	0.52	3.92	16.60	67.91	3.89	10.80	103.57	1.13	5.80	15.84
42	0.40	52.01	3.15	0.53	3.84	17.00	65.04	3.37	8.18	88.69	1.47	4.15	14.49
43	0.47	48.70	3.67	0.64	3.75	18.40	75.34	3.52	12.15	88.86	1.68	4.82	15.53
44	0.40	46.78	3.16	0.51	2.41	17.59	60.20	3.52	11.25	99.13	1.63	5.30	15.11

In geochemistry, concentration data are often assumed to follow a lognormal distribution after being $\log_{10}$ – transformed, as suggested by Ahrens [22]; however, in geochemistry, this assumption rarely holds true. For the majority of the variables, a log base 10 transformation does not result in a normal distribution [23]. This may have serious consequences for the further statistical treatment of data sets because the vast majority of advanced statistical methods require not only that each variable shows a normal distribution, but also that the variables show a multivariate normal distribution.

In addition, although the data set does not present the total composition of the samples (i.e., the variables measured are < 100%) this type of data frequently displays a curvature and linear techniques, such as principal component analysis cannot be used.

The present study used the transformation proposed by Aitchison, [24] which transforms each sample x_{ij} ($i = 1,\ldots.n$ and $j = 1,\ldots.,p$) in y_{ij} by taking the natural log transformation and subtracting the mean of the transformed variables (1), i.e.,

$$y_{ij} = \ln x_{ij}, \qquad \bar{y}_i = \frac{1}{p}\sum_{j=1}^{p} y_{ij} \qquad z_{ij} = y_{ij} - \bar{y}_i \tag{1}$$

In addition, the data were standardized to compensate for the large difference in magnitude between the measured elements at the trace level and the larger elements [25]. The method used was the z-transformation (2), in which the median is subtracted from the raw data and then divided by the median absolute deviation (MAD) as follows [25].

$$\text{z-transformation} = \frac{z_{ij} - median\left(z_i\right)}{MAD\left(z_i\right)} \tag{2}$$

After being transformed, the data set was submitted to two multivariate statistical analysis: cluster and discriminant analysis. The multivariate statistical analysis techniques are designed to determine the existence of groups in the data set according to similar or distinct chemical groups [26].

Cluster analysis is a multivariate statistical technique that has a main objective to group the similar samples in accordance with their characteristics [26]. For formation of the groups is necessary to consider the distance between the samples, since the samples that are next represent regions whose samples are similar. The results of cluster analysis are commonly presented in the form of dendrograms which show the order and levels of specimen clustering [27].

How cluster analysis is based on a dissimilarity matrix in which the distances between all pairs of samples are calculated using one of several possible distances measures, in this work the distance used was the squared-mean Euclidean distance and the Ward method.

The dendrogram is showed in Figure 2, and as can be seen in the figure the preliminary classification showed the existence of three groups very well defined.

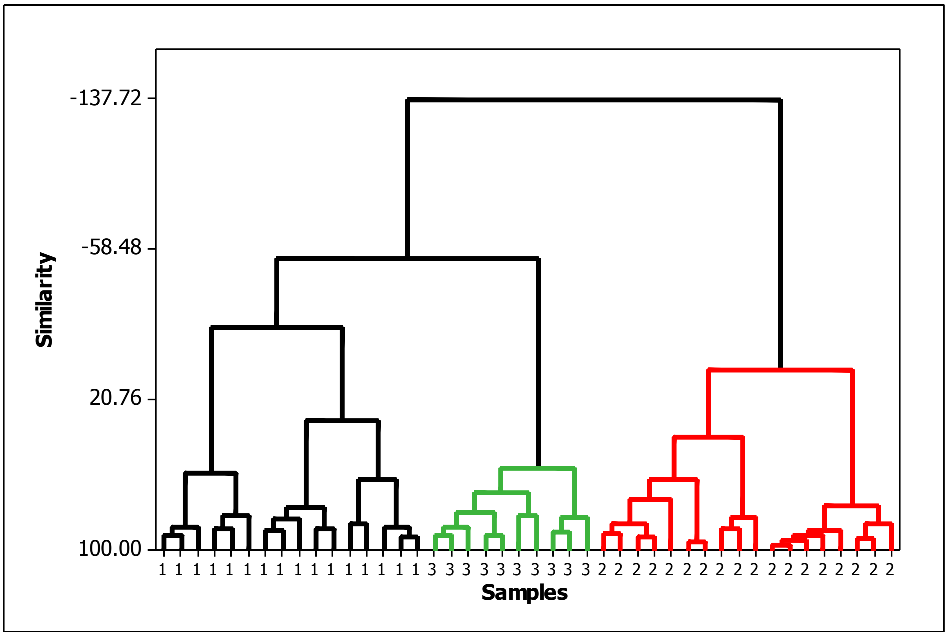

Figure 2: Dendrogram of the ceramic samples using squared Euclidean distance and Ward's method, (n=44).

In order to confirm the latter assumption the data were submitted to discriminant analysis. The basis for all multivariate analyses is that all the elements included are independent variables. This is not necessary true, but it can be tested using the pooled within-groups correlation matrix provided by discriminant analysis. After identifying the cluster within samples, discriminant analysis was used to isolate those variables which can most effectively reveal the differences between clusters and establish a discriminant function for this purpose.

The plot obtained by the linear discriminant function 1 versus the linear discriminant function 2 is presented in Figure 3.

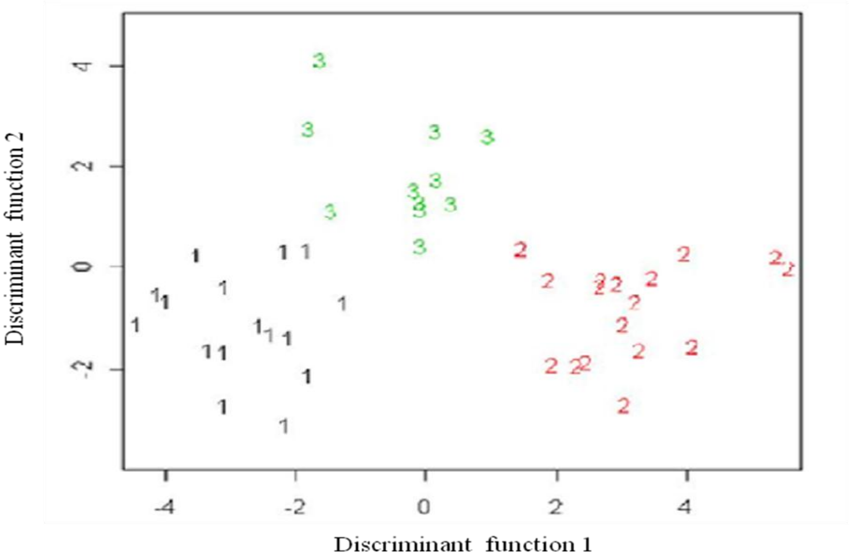

Figure 3: Plot of the linear discriminant function 1 vs linear discriminant function 2.

As shown in the Figures 2 and 3, the plot reveals three chemical groups that are well separated from one another, showing that the samples are clearly different in their chemical composition. As can be seen in the figures, three different row material in the ceramics production in the São Paulo II archaeological site was used.

4. CONCLUSIONS

The preliminary study made in the São Paulo II archaeological site showed the ability of the trace elements special variability in the site. Although, differences exist in the elements concentrations, simple inspection of the data cannot be used to differentiate the chemical groups. Our preliminary results provide evidence that the São Paulo II ceramic were manufactured from a least three different clay sources. Whether are local or not will become clear by systematic clay analysis.

Finally, INAA of ceramics from São Paulo II archaeological site was successful in identifying different compositional groups.

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