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Archaeometric Study of Clay Deposits from the Indigenous Land of the Asurini do Xingu

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Abstract: The Asurini do Xingu occupy a village located along the banks of the Xingu river, in the state of Pará, Brazil. It is based on an indigenous Tupi group, speaking a language stemming from the linguistic Tupi-Guarani family. They are potters, who show a sufficiently diversified artifactual ceramic group and, already, were the object of various studies. This work shows the results of the archaeometric study done with the ceramic and clays derived from two deposits exploited by this indigenous population for the manufacture of it is vessels. The chemical and mineral composition was determined by means of instrumental neutron activation analysis and scanning electron microscopy in order to obtain information on the technology employed by the Asurini in their ceramics production. The results were interpreted by a discriminant analysis procedure that made evident the differentiation between the deposits.

Keywords: Neutron activation analysis, Archaeometry, Asurini, Ceramics, Clay, Discriminant analysis

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INTRODUCTION

The characterization of archaeological ceramic objects is of fundamental interest for the archaeologists whose work has been conducted with the objective of understanding the relative aspects for its conventional, quantitative, and spatial variability in the archaeological record. In recent years, these researches on the life cycles of these artifacts have been perfected with the development of ethnoarchaeological studies and the contributions of the physical and chemical sciences.[1−6] In this work, we intended to show evidence of the importance for this interdisciplinary cooperation, especially in reference to the investigation of the raw materials employed in the manufactures of the ceramic vessels found in the archaeological record.

With the use of various archaeometric studies, we are trying to understand the Asurini criteria in the selection of raw materials or, in other words, what we call Asurini ethnomineralogy. Additionally, we are seeking to verify the similarities and dissimilarities between the clay samples and the manufactured ceramic samples made by this indigenous group. That is, we attempted to verify the correlation, or lack of correlation, among the chemicals used in the manufacture of the vessels.

Given the complexity of the clays—including a variety of products and distinct concentrations of chemical elements in the samples—it is necessary to perform the analyses, considering the concentrations of the trace elements, i.e., elements which are present in ppm (parts per million) concentration levels.

Various analytical techniques may be applied to determine the trace elements, such as various forms of ICP,[7] EDXRF,[8−10] and INAA,[11−13] among others. Within these techniques, INAA, associated with the spectrometric gamma rays of high resolution, have been preferentially used for the determination of the chemical composition in ceramic samples because it has several advantages, such as sensitivity, precision, and accuracy.[14] In this type of study, analytical parameters that have an extreme importance, since there are small differences in the concentrations of elements in the samples, which allows for their differentiation.

It is noteworthy to mention that this study was an opportunity to test the trace elements application viability as an interesting technique in the raw material source determination in the studies of ceramic artifacts. Ethnoarchaeological research allowed the accurate identification of the clay source employed by the Asurini in the manufacture of their vessels, in spite of other existing clay deposits in the area. At the same time, it made it possible to control the information contained in the samples. In other words, we could know, in advance, the origin of the clay samples, as well as which were the fragments that had been produced by each analyzed clay type and, from then on, to verify the coherence between the obtained results from the archaeometric studies and the ethnographic reality.

Three clay deposit samples were analyzed—two related to the deposits exploited by Asurini do Xingu and one that came from the Waura village, in Alto Xingu, and ceramic samples that came from the Asurini village, by means of INAA, to determine 23 chemical elements, and the results of the elemental concentrations, which were interpreted by means discriminant analysis. With the data set we established a link between ceramic compositional groups to raw clay source.

EXPERIMENTAL

Sample Preparation and Standard

In all 33 samples from the two clay deposits we collected at different levels. In deposit A, the depth varied from 10 to 67 cm. In deposit B, the collection was made at a depth which varied from 32 cm to 1 m. The samples were prepared by manually grinding, in an agate mortar and pestle, until a sufficiently fine granulometry was obtained, in order to pass through a 100–200 mesh sieve. The material became more homogenous, considering that it would be predominantly used in a trace analysis. The high contamination, which could have originated from the agate is silicon, which is not a serious problem, since this element was not determined.

The ceramic powder samples were obtained by cleaning the outer surface and drilling to a depth of 2–3 mm, 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 shred as possible without drilling through the walls.[11] Four ceramic samples were analyzed. Finally, these materials were dried in an oven at 105°C for 24 h and stored in a desiccator.

Buffalo River Sediment (NIST-SRM-2704) and Coal Fly Ash (ICHTJ-CTA-FFA-1) were used as standards, and IAEA-Soil 7 Trace Elements in Soil was used as check samples in all analyses. These materials were dried in an oven at 105°C for 24 h and stored in a desiccator until weighing.[12]

Description of the Method

Generally speaking, the NAA method is based on the properties of nuclei, in which an incident neutron interacts with a nucleus of the target element. During the sample bombardment with neutrons, a small fraction of the nucleus from each of the sample constituent elements will be transformed into unstable radioactive isotopes which decay with a half-life characteristic. During the decay, these isotopes emit gamma rays with energies that are characteristic for each element. The measurement of these gamma rays permits the qualitative and quantitative determination of the sample elements.

About 100 mg of ceramic or clay samples, Buffalo River Sediment, and Coal Fly Ash were weighed into polyethylene bags and covered in

aluminum foil. Groups of 8 samples and one of each reference material were packed in aluminum foil and irradiated in the swimming pool research reactor, IEA-R1m, from the IPEN-CNEN/SP, at a thermal neutron flux of about $5 \times 10^{12} \, \mathrm{n \cdot cm^{-2} \cdot s^{-1}}$ for 8 h.

Two measurement series were carried out using a Ge (hyperpure) detector, Model GX 2020 from Canberra, with a resolution of 1.90 keV at the 1332.49 keV gamma peak of ^{60}Co, and 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 Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Ta, Tb, Th, and Zn after 25–30 days. Gamma ray spectral analysis and concentration determinations were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra.

Additionally, a scanning electron microscope (SEM) from JEOL, Model JSM-5800LV, with low vacuum system and detector Si(Li) for X-ray, was utilized with the program Voyager from NORAN. This procedure permits the observation of the samples without special preparation; therefore, it is without altering the chemical or physical characteristics.

RESULTS AND DISCUSSION

One of the basic premises for the use of a chemical compositional analysis on clay or ceramic samples is that the samples can be differentiated if the analytical technique has a good sensitivity, precision, and accuracy for the analyte of interest. If an element is not measured with good precision, it may obscure real differences in concentration and the discriminating effect of other well-measured elements tends to be reduced. These small differences can be used to form groups of similar composition, because manufactured artifacts with a determined raw material source will be more chemically similar than other ones which were manufactured with a different raw material.[12]

NAA is a highly sensitive technique; it can determine the elements which are found in very low concentrations, such as at ppm (parts per million) or ppb (parts per billion) levels. This characteristic has become recognized as the preferred technique by various researchers who have analyzed samples at trace levels. Due to the fact that it is a highly sensitive technique, it is possible to quantify the small differences that may occur inside a geological formation. Then, the determination of the concentrations of various elements at the trace levels, which differ in their chemical properties, will tend to produce a highly specific "fingerprinter" for a source of clayish raw material.

Another parameter related to the analytical properties of methods, concerns accuracy and precision. Accuracy is related to the real concentration of the sample element, a value that does not depend on the method used. The accuracy of analytical methods are determined by means of reference

materials, where the concentration is determined by various analytical methods. NAA has great accuracy for a variety elements.[11,13,14]

The determination of analytical precision is of great importance and must be quantified. Precision is related to the capacity that the method has to reproduce a given result. Precision limitations can result from the sample being inadequately prepared, either due to contamination with the same element that we want to determine, or due to inhomogeneity problems.

All parameters in the analyses must be measured and quantified to make corrections before applying the method to real samples because small variations may affect the capacity to distinguish between the sample groups.

In this work, to evaluate the analytical process and to establish the chemical elements which can be used in the data interpretation, the elemental concentrations for the reference material IAEA-Soil-7 Trace Elements in Soil were statistically compared with the data found in our laboratory. The results of independent determinations of each element are shown in Table 1. In the present work, the analytes with relative standard deviation, RSD, less than 10% were used.[15] All possible interferences potentially occurring in gamma-ray spectrometry were considered and checked. A possible source of error in the determination of REE elements is the presence of significant amounts of fissionable nuclides (^{235}U and ^{233}U). As is well known, REE nuclides, especially among the light REE elements (La to Sm), are produced both by activation and by fission. In the present work, no interferences were expected in the samples because the very low uranium fission in the determination of La and Ce is negligible when the uranium concentration does not exceed 5 ppm.[11] Although Co has an RSD of 6%, it was not included in the data set because the concentration can be affected by tungsten carbides files.[16] The determination of Zn is not reliable, as a consequence of a strong γ-ray interference by ^{46}Sc and ^{182}Ta. The precision of Cs was better than 10%; however, it was not included because it represented 20% of missing values. Using this criterion, the elements Ce, Cr, Eu, Fe, Hf, La, Lu, Na, Sc, Th, and Yb were used in the subsequent data analysis.

Table 2 shows the concentration results for the clay samples of two deposits, A and B, and for the clay from Alto Xingu, as well as, the ceramic samples manufactured by Asurini with the clay from one of the deposits. None of the elements considered presented missing values. In all, 38 samples were analyzed (deposit A 15, deposit B 18, clay from Alto Xingu 1 and 4 samples of ceramic).

Initially, the results were transformed to $\log_{10}$ to compensate for the large differences of the magnitudes between the measured elements at the trace level and the larger ones.[17] The $\log_{10}$ transformation of data before a multivariate statistical method is common. One reason for this is a belief that, within the raw materials of manufacture, elements have a natural lognormal distribution, and that normalization of the data is desirable. Another

Table 1. Results for IAEA Soil 7 in $\mu g\,g^{-1}$ unless otherwise indicated

Element	Found*	SD	RSD	Recommended value	95% Confidence interval
As	14.1	4.0	0.28	13.4	12.5–14.2
Ce	55.2	2.2	0.04	61	50–63
Co	8.4	0.5	0.06	8.9	8.4–10.1
Cr	65.0	2.6	0.04	60	49–74
Cs	5.8	0.4	0.07	5.4	4.9–6.4
Eu	0.98	0.05	0.05	1.0	0.9–1.3
Fe, %	2.54	0.07	0.03	(2.57)	(2.52–2.63)
Hf	4.9	0.4	0.08	5.1	4.8–5.5
K, %	1.16	0.1	0.09	(1.21)	(1.13–1.27)
La	28.6	1.1	0.04	28	27–29
Lu	0.3			(0.3)	(0.1–0.4)
Na, %	0.22	0.01	0.05	(0.24)	(0.23–0.25)
Nd	28.9	8.1	0.28	30	22–34
Rb	41.8	5.7	0.14	51	47–56
Sb	1.5	0.2	0.13	1.7	1.4–1.8
Sc	8.6	0.2	0.02	8.3	6.9–9
Sm	6.8	6.0	0.88	5.1	4.8–5.5
Ta	0.8	0.2	0.25	0.8	0.6–1.0
Tb	0.7	0.2	0.21	0.6	0.5–0.9
Th	8.1	0.3	0.04	8.2	6.5–8.7
U	2.6	0.3	0.12	2.6	2.2–3.3
Yb	2.3	0.1	0.05	2.4	1.9–2.6
Zn	104.6	3.5	0.03	104	101–113

*$n = 8$.

reason is that a logarithmic transformation tends to stabilize the variance of the variables and would, thus, give them approximately equal weight in an unstandardized multivariate statistical analysis. All individual determinations in each data set were tested for discordant results. The Mahalanobis distance, D_i, is suggested by many authors as a method for detecting outliers in multivariate data.[18] For each of the n observations (samples) in a p variable data set, a distance value D_i was calculated. Let $\bar{x}$ be the sample mean vector and let S be the sample covariance matrix,

$$S = \sum_{i=1}^{n}(x_i - \bar{x})(x_i - \bar{x})^T/(n-1)\ \text{and}$$

$$D_i = \sqrt{\{(x_i - \bar{x})^T S^{-1}(x_i - \bar{x})\}}$$

Table 2. Results for clay sample from deposits A and B and ceramic samples in $\mu g\,g^{-1}$, unless otherwise indicated, and Mahalanobis distance

Sample	Na, %	Lu	Yb	La	Th	Cr	Sc	Fe, %	Eu	Ce	Hf	D^{2a}
A₁ 1	0.17	0.39	2.40	71.50	19.80	30.40	7.60	2.52	1.10	131.80	53.20	9.2
A₁ 2	0.17	0.40	2.20	93.00	31.60	32.50	8.10	2.55	1.01	169.90	58.70	4.6
A₁ 3	0.16	0.24	0.95	104.00	40.40	52.10	10.70	4.32	0.96	178.60	29.70	10.1
A₁ 4	0.17	0.22	1.20	72.70	30.40	50.00	10.90	4.30	0.90	121.00	28.30	9.3
A₁ 5	0.27	0.34	0.95	84.50	34.10	81.40	17.60	5.15	0.88	153.70	39.10	11.6
A₁ 6	0.27	0.23	1.30	74.50	30.00	90.30	18.10	5.30	0.80	130.00	32.70	11.6
A₁ 7	0.31	0.51	3.00	238.10	76.80	29.30	7.70	2.25	1.60	447.60	88.40	9.5
A₁ 8	0.33	0.60	3.00	177.90	63.40	29.60	8.40	2.50	1.50	333.00	83.20	7.9
A₁ 9	0.62	0.51	4.80	324.80	33.10	117.40	18.90	4.78	7.50	633.10	27.30	7.9
A₁ 10	0.58	0.50	4.00	265.40	22.90	111.00	18.00	4.70	6.50	510.00	20.40	9.9
A₁ 11	0.40	0.23	1.40	86.40	22.00	117.30	21.50	6.29	1.60	161.40	22.10	9.5
A₁ 12	0.41	0.22	1.30	91.20	27.50	125.00	22.50	6.60	1.50	171.00	17.10	10.7
A₁ 13	0.35	0.84	6.70	178.10	14.90	95.20	31.20	9.66	5.90	376.70	10.40	7.4
A₁ 14	0.34	0.80	6.20	161.00	14.00	92.00	31.30	9.70	5.70	355.00	8.90	7.7
A₁ 15	0.20	0.24	1.60	60.40	21.40	35.70	16.30	4.70	0.60	99.40	22.10	12.9
B₂ 1	0.08	0.20	1.10	130.90	52.50	22.90	4.90	1.52	0.50	244.70	25.30	8.2
B₂ 2	0.08	0.17	1.10	111.00	46.00	20.70	4.50	1.40	0.50	207.00	26.40	9.4
B₂ 3	0.13	0.28	1.50	104.60	46.10	36.20	10.10	2.90	0.70	195.10	31.10	10.7
B₂ 4	0.09	0.17	1.03	89.30	38.40	28.40	7.40	2.10	0.50	167.00	20.50	8.1

(continued)

Table 2.   Continued

Sample	Na, %	Lu	Yb	La	Th	Cr	Sc	Fe, %	Eu	Ce	Hf	D^{2a}
$B_{2\,5}$	0.21	0.28	1.50	128.70	56.90	52.30	12.70	4.30	1.10	237.50	21.20	8.6
$B_{2\,6}$	0.18	0.20	1.10	114.60	51.80	38.70	9.00	3.10	0.80	215.00	18.40	9.4
$B_{2\,7}$	0.21	0.28	1.60	161.40	61.80	56.90	17.20	4.90	1.20	298.20	33.60	8.7
$B_{2\,8}$	0.15	0.21	1.20	70.30	30.60	43.00	12.70	3.60	0.80	128.00	23.00	7.4
$B_{2\,9}$	0.16	0.23	1.60	114.30	47.10	31.40	8.90	2.80	0.80	214.60	35.90	9.1
$B_{2\,10}$	0.12	0.22	1.30	94.50	37.00	28.00	7.10	2.20	0.60	179.00	24.20	6.7
$B_{2\,11}$	0.14	0.33	2.10	158.50	59.70	30.10	9.20	3.00	0.90	302.00	26.80	10.3
$B_{2\,12}$	0.11	0.30	1.50	101.50	42.00	26.00	7.30	2.40	0.60	190.00	17.20	11.6
$B_{2\,13}$	0.14	0.25	1.50	137.50	47.40	32.10	9.40	2.80	0.80	254.10	30.70	10.8
$B_{2\,14}$	0.15	0.21	1.30	118.00	47.40	32.10	9.70	2.80	0.80	226.00	25.30	12.8
$B_{2\,15}$	0.17	0.24	1.50	168.00	74.90	55.70	13.80	4.40	0.98	312.90	25.00	10.4
$B_{2\,16}$	0.14	0.20	1.10	113.00	48.60	49.60	11.60	3.70	0.80	210.00	15.40	7.6
$B_{2\,17}$	0.17	0.28	1.70	95.10	42.20	75.90	28.50	7.70	1.50	160.60	16.10	10.9
$B_{2\,18}$	0.14	0.25	1.40	82.20	34.00	70.60	23.40	6.10	1.20	140.00	14.30	9.5
Ceramic 11	0.42	0.21	1.60	115.20	31.40	110.00	20.80	7.25	2.20	229.80	12.10	
Ceramic 12	0.42	0.30	1.40	97.80	26.90	113.00	21.80	7.60	2.10	200.00	12.20	
Ceramic 15	0.39	0.93	7.90	219.60	11.20	103.10	28.50	9.41	7.60	403.90	8.00	
Ceramic 16	0.37	0.97	7.80	200.90	10.40	94.20	29.00	9.50	7.00	368.00	7.10	
Alto Xingu B	0.01	0.40	2.50	36.40	9.80	72.30	11.20	1.90	1.50	71.80	5.50	

$^{a}D^2_{\text{crit, A}} = 13.0.$
$^{*}D^2_{\text{crit, B}} = 15.4.$

for $i = 1,\ldots, n$, where $(x_i - \bar{x})$ is the difference vector between of measured values in one group and the mean values of the other group. Wilks[19] suggested the use of

$$p(n-1)^2 F_{p,n-p-1}/n(n - p - 1 + pF_{p,n-p-1})$$

to calculate the critical values for D_i when searching for a single outlier. Wilks used so-called scatter ratios to search for outliers in multivariate normal data. To search for a single outlier, the author calculates a scatter ratio, R_i,

$$R_i = |A_i|/|A| \text{ where } A = \sum_{i=1}^{n}(x_i - \bar{x})(x_i - \bar{x})^T$$

and $|A|$ = determinant (A), A_i is calculated as for A with observation i eliminated from the sample. The most outlying observation is that which has the smallest scatter ratio R_i, where $R_1 = \min\{R_i\}$, i.e., the observation whose removal leads to the greatest reduction in $|A|$. This procedure, at a confidence level of 95%, was applied to a data set. As can be seen in Table 2, the D values were calculated for samples from both deposits and, as is shown in the last column (Table 2), the D critical values were higher than the calculated D (the critical values were 13.3 and 15.4 for deposits A and B, respectively). Then, none of the samples is an outlier.

The application of statistical methods to experimental results aims to classify and order the objects related to each other in function, exclusively, from their chemical compositions. Various multivariate statistical techniques have been developed. However, discriminant analysis maximizes the difference between two or more groups; it is based on the fact that the principal variance-covariance matrix is an accurate representation of the total variance and covariance.

With the purpose of studying the similarities and the dissimilarities between the clay and ceramic samples, the results were submitted to discriminant analysis. What we intend accomplish is to group similar samples according to their characteristics (variables). The purpose, therefore, is to consider many simultaneously related variables, all having equal importance in the beginning of the analysis. Another consideration is that the data must follow a normal distribution. Generally speaking, if each studied variable follows a normal distribution, the resulting distribution of the group of all the variables will also be normal.

Figure 1 shows the discriminant function 2 versus discriminant function 1 for all the studied clay samples and, in Figure 2, the discriminant functions, including the ceramic samples. The results show that the separation, in both cases, is 100%. In other words, there is a clear difference in the chemical composition between the clay deposits A, B, and from Alto Xingu. However, with the purpose of establishing a raw material source of ceramics, ceramic samples were included in the database and the discriminant analysis was applied. As can be seen in Figure 2, the ceramic samples fall together in a
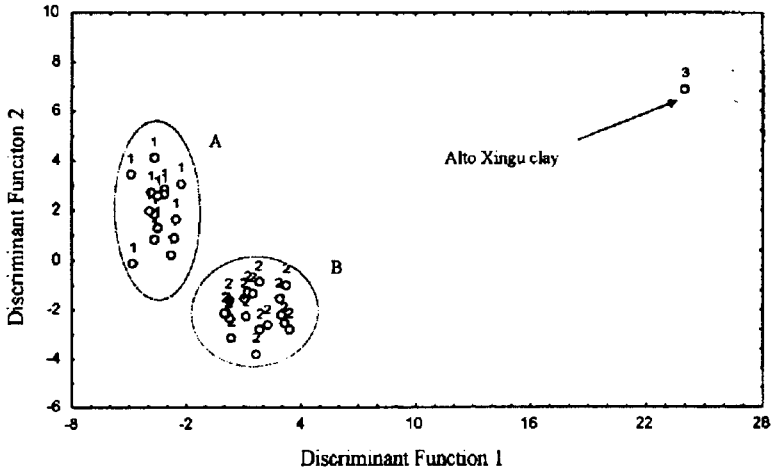
Figure 1. Discriminat functions for clay deposits A, B, and Alto Xingu. Ellipses represents a confidence level of 95%.

sample group of deposit A, which indicates that the raw material source used in the manufacturing of ceramics is from deposit A.

The analysis of the microstructures of the Asurini pottery shred studied by means of SEM indicates that the technology employed was, more or less, the
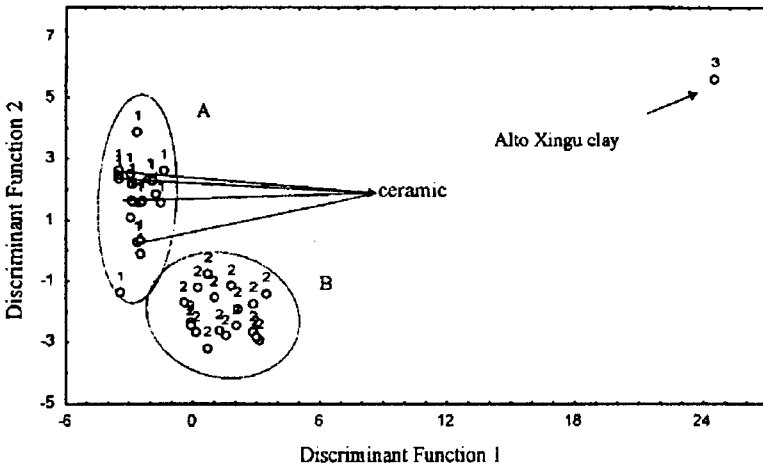

Figure 2. Discriminant functions for clay deposits (A, B, and Alto Xingu) and ceramic. Ellipses represents confidence level of 95%.

same for all the ceramics. However, the clay samples studied by means of SEM showed that the microstructure of clays from deposit A do not have Ca and Mg and, for deposit B, the concentration of Ca is greater than the concentration of Mg. On the other hand, the granulometry is similar in both deposits.

CONCLUSION

The analyses that were performed showed very interesting results to be reflected on, concerning the Asurini ethnomineralogy. According to what we saw, the deposits are distinct between themselves in terms of chemical composition and, in this sense, the clays behave in a distinct way in their performance characteristics. By associating the chemical, mineralogical, and granulometric analyses of the deposits, we can say that deposit A has a composition of minerals that implies a good plasticity, showing low contraction during drying, thus making possible good performance during the burning process. Deposit B, on the other hand, shows a mineral composition which absorbs and retains larger amounts of water and, because of this, has greater plasticity, leading to a greater probability of breakage during the vessel heating process. Both, however, have a high granulometry that eliminates the need to add other ingredients to the paste.

Asurini potters are knowledgeable of these distinct properties in their own practical experience. Their preference is for deposit A, which they understand to have a plasticity and granulometry that is more suited to their ceramic technology. What seems to be interesting, also, is to verify that, despite the deposits being different in terms of trace elements, they are not constituted to be radically distinct clays, in terms of performance and, without a doubt, it seems that the most important element of their composition is the granulometric similarity, which is noticeable to the Asurini potters, through their senses (by touch of hand and tongue).[20]

This ethnographic study allows us, therefore, to note that the choices of the raw material employed during the manufacturing of the archaeological ceramic material must have been made beginning with various selection mechanisms, taking into consideration their performance characteristics. For this reason, it is very important to perform archaeometric studies of ceramic paste, aiming at the quality of information that we can obtain for our reflections on the production processes of these artifacts. In conclusion, our research consisted of an effort to test and create an efficient analytical methodology for the treatment of the archaeological material whose control does not have the precision of an ethnographic method. Finally, discriminant analysis, together with INAA, provided a consistent, objective perspective on provenance; that perspective helps the petrologist and archaeologist

arrive at a consensus regarding a shred composition and clay provenance in the archaeological record.

ABBREVIATIONS

INAA   Instrumental neutron activation analysis
SEM   Scanning electron microscope
AAS   Atomic absorption spectrometry
ICP   Inductively coupled plasma
IAEA   International Atomic Energy Agency
RSD   Relative standard deviation

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