PRELIMINARY STUDY OF THE EFFECT OF TEMPER IN MARAJOARA CERAMICS

R.G. Tovota[1], C.S. Munita[1], E.G. Neves[2], C.C. Demartini[2]

1) *Instituto de Pesquisas Energéticas e Nucleares - IPEN/CNEN, Av. Prof Lineu Prestes, 2242Cidade Universitária - CEP 05508-000 - São Paulo - SP - Brasil*
2) *Museu de Arqueologia e Etnologia - USP, Av. Prof Almeida Prado, 1466 - Cidade Universitária 05508-900 - São Paulo - SP - Brasil3)*

Chemical characterization of ceramic fragments is of great importance in archeology, due to the fact that relevant aspects of the ancient people can be clarified. Ceramics basically consist of a paste of clay with added temper. The use of temper in ceramic paste has been common practice. To obtain resistant ceramics, the temper should have, among other properties, a thermal expansion coefficient similar to clay, in order to avoid cracks due to material tension. Non-plastic materials can be wood-ash, crushed shell, calcareous stone, lianas, sand and organic materials, among others. Therefore, the presence of the temper can modify the chemical composition of the ceramic fragments, altering their characterization due to temper being a modifier of the natural composition of the clay used. Therefore, it is necessary to study its effect in the concentration of the inorganic elements in the ceramics. In this work, 161 Marajoara ceramic fragments were analyzed by instrumental neutron activation analysis (INAA) to determine the As, Sa, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Na, Nd Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn concentrations, with the purpose of studying the dilution effect provoked by temper. The analytical method is indicated for this kind of study, being a non destructive technique and showing high sensitivity, accuracy and precision in the determination of chemical elements to the level of trace and ultra trace elements, essential characteristics in the study of small concentration variations provoked by temper. The dilution factor was studied using a modified *Mahalanobis* filter. The data were interpreted through discriminant analysis.

Keywords: archaeometry, modified *Mahalanobis* filter, ceramics, temper, discriminant analysis

INTRODUCTION

Because of their high resistance to the environment conditions, ceramics remains are the most commonly found remnants, in archeological excavations. Because of their abundance and durability, ceramics are an extremely important indicator of the socio-cultural and economic interactions of the people who used it.

Archaeometry is a branch of science which studies the physiochemical properties of a diversity of archeological remains. Archaeometry uses several physical and chemical techniques to obtain as much information as possible about materials being studied. Especially, techniques of chemical characterization of ceramics remains have been intensively used, due to the several hypotheses that can be clarified.[1]

Basically, ceramics consist of clay and a temper mix. The use of temper in ceramic pastes is traditional common practice in its manufacture. Temper is the non-plastic materials

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added to clay, thus forming a paste which will be later molded to create the ceramic artifacts. To obtain resistant ceramics, the temper should have a similar-to-clay thermal expansion coefficient, thus resisting to cracks caused by material tension. Non-plastic materials can be ashes, volcanic stone, sand, shell, calcareous stone and organic materials, among others. Shell has been frequently used in pre-colonial ceramics.

An important factor to be considered is the need to distinguish materials added to the clay from the natural presence of non-plastic materials. The temper put in the clay modifies its natural chemical composition, in contrast with what happens when non-plastic materials are naturally present. In the latter situation, the chemical composition of clay is not altered because it follows the whole process of production of the artifact. Therefore, the effect of temper used in ceramic production can alter the chemical composition of the paste, which can to alter its caracterization.[2]

In this study, the As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Na, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn concentrations were defined in a group of 161 Marajoara ceramic fragments, through instrumental neutron activation analysis (INAA). Presently, INAA is one of the most successful analysis techniques for composition analysis studies.[3] By this method it is possible to simultaneously determine more than 30 elements to trace and ultra-trace levels, with high levels of precision and accuracy. Additionally, being an instrumental technique, INAA poses a relative handiness for the preparation of samples, which results in a reduction in experimental errors and in the time spent in analysis.

The study of chemical trace elements in the raw materials used in the preparation of the ceramics fragments can show unique chemical compositions, which can indicate the source of the raw materials used in the artifacts.[4] Generally, to evaluate the link of a particular sample to a certain group, the use of the Mahalanobis filter is indicated.[5] This method tests the hypothesis (which can be accepted or rejected within a reliability level) of a sample belonging to a certain group. The quadratic Mahalanobis distance is given by:

$$d_M^2(\vec{x}, \vec{y}) = {}^t(\vec{x} - \vec{y}) S_Y^{-1}(\vec{x} - \vec{y}) \qquad (1)$$

where t denotes the transposed matrix; $\vec{x}$ is the vector of the sample in the m-dimensional space which contains the concentrations of m elements (vector of the average of the samples), $\vec{y}$ is the vector of the average of the whole group and S_Y is the co-variance matrix of the group which contains the square of diagonal dispersion. Equation 1 is the quadratic distance of the $\vec{x}$ sample to the medium point of the group $\vec{y}$ in group-dispersion units along the line that joins $\vec{x}$ and $\vec{y}$. For a given S_Y, expression 1 displays a χ^2_m distribution for group members. The index m gives the number of freedom degrees.

During the ceramic production with the addition of tempers in the clay, the values of elementary concentrations in the ceramics can be diluted, generating distortions in the statistical analyses of the data when, for instance, cluster analysis, principal components analysis and discriminant analysis, are used. In this case, it is necessary to apply the modified *Mahalanobis* filter,[5] which includes the measurement uncertainties such as measurements of the dissimilarity of the samples,[6] which can be used to verify if a sample belongs to a given group. A simplified version without considering the correlation is given by the expression:

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$$d^2_{M+U,n.c,dil,red}(\vec{x},\vec{y}) = \frac{1}{m-1}\sum_{k=1}^{m}\frac{(f_0 x_k - y_k)^2}{f_0^2\sigma_{Xk}^2 + \sigma_{Yk}^2} \quad (2)$$

where x_k and y_k are the concentrations values of the k element in the samples or groups x and y; σ_{Xk} and σ_{Yk} are the corresponding uncertainties. Factor f is the best relative adjustment, also called dilution factor that is applied to each data group of each sample. The dilution effect can hold several causes, among them: the dilution effect by temper during manufacturing process, errors in the analysis, alteration of the concentration due to leaching, errors during weighing, etc.

The f among two samples x and y can be calculated by the expression:

$$\frac{\partial}{\partial f}\left[{}^t(f\vec{x}-\vec{y})(f^2 S_x + S_y)^{-1}(f\vec{x}-\vec{y})\right] = 0 \quad (3)$$

including the basic co-variance matrix. Details of the mathematical methods can be found in Beier and Mommsen. [6]

EXPERIMENTAL

Equipment and sample preparation

The measurements of induced gama activity were executed using a Canberra Ge hiperpure detector, resolution of 1.90 keV at the 1332 keV of the ^{60}Co peak, a Canberra S-100 MCA plate with 8192 channels and associated electronics. The spectra of gama rays were obtained and analyzed through the Genie-2000 NAA Processing Procedure program, developed by Canberra.

The ceramics fragments were initially washed with Milli Q water, removing the external surface with a fine bristled brush. Then, the external surface of the fragments was eliminated with rotating tungsten carbide file, adapted to a multi-speed drill, in order to eliminate contamination. About 500 mg of sample powder were obtained by means drilling 3 to 5 holes in the internal part of the fragments, keeping the drill from perforating through their walls. This powder was then collected, dried in an oven at 105ºC for 24 hours and stored in a desiccators. [7]

Analytical procedure

For the analysis, about 100 mg of each sample were weighed in polyethylene envelopes and sealed with a solder iron. The envelopes were wrapped in aluminum foil. A set of eight samples together with about 100 mg of reference material. Standard Reference Material - NIST-SRM 1633b Constituent Elements in Coal Fly Ash, was used as pattern. The samples were submitted to an 8 hour irradiation at the IEA Reactor - R1m at IPEN - CNEN / SP, at a thermal neutron flux of about 10^{12}n cm^{-2}s^{-1}.

Two measurements were made to determine, As, K, La, Lu, Na, Nd, Sb, Sm, U and Yb after seven days of decay time, and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sc, Ta, Tb, Th and Zn after 25-30 days of decay time. [8]

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Analytical quality control

The precision, accuracy and the sensibility of the method were studied by means of the analysis of As, Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, In the, Nd, Rb, Sb, Sc, Sm, Ta, Tb, Th, U, Yb and Zn in the IAEA Soil 7 reference material, Trace Elements in Soil.

RESULTS AND DISCUSSION

With the purpose of studying the quality control of the analytical method, 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 and Zn were determined in 18 samples of the IAEA Soil 7 reference material. From these data some statistical parameters were calculated, such as the average, standard deviation, level of average reliability of the, homogeneity of results, and precision and accuracy. The results showed that most of the elements presented a ≤ 10% precision. This precision is considered appropriate by several authors as for the choice of the chemical elements for chemical characterization studies of archeological objects using multivariate statistical methods.[1]

Elements such as Co and Ta were eliminated, although they presented a precision lower than 10%, because there is evidence of contamination by the tungsten drill during the preparation of the sample.[9] Zn was also eliminated because it undergoes an interference in the spectrum of gama rays at the Sc peak.[10] 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. Therefore, the elements used were K, La, Yb, Lu, U, Sc, Cr, Fe, Cs, Ce, Eu, Tb, Hf, and Th.

Initially, the data of elementary concentrations of the samples of Marajoara ceramics fragments (161) were transformed in log_{10} to compensate for the difference in magnitude among elements given in percentages and at trace level. The transformation of the concentrations into log_{10} before applying multivariate statistical methods is a usual procedure in archaeometric studies. One of the reasons for this is that the normal distribution of the elements in the soil is logarithmic. Another reason for the logarithmic transformation it tends to stabilize the variance of the variables, which would have an approximately equal weight in a multivariate statistical analysis.

The study of the outliers values was made by means of the Mahalanobis distance, while using the lambda Wilks criterion as critical value.[11] For the sample that showed Mahalanobis distance values higher than the critical value were eliminated. After the elimination of the outliers, the Mahalanobis distance was calculated again in the new group of data. This process was repeated until all of the samples showed Mahalanobis distance values lower than the critical value. In all, 12 outliers were found.

Next, a preliminary classification was accomplished through cluster analysis by Ward and Euclidian distance methods.

The dendogram showed the existence of two very defined groups. With the purpose of confirming the existence of these two groups, the data were studied by means of discriminant analysis. Figure 1 shows the discriminant function 1 versus the discriminant function 2. It can be seen clearly that the elementary concentrations of the Marajoara ceramics fragments are divided into two very well-defined groups.
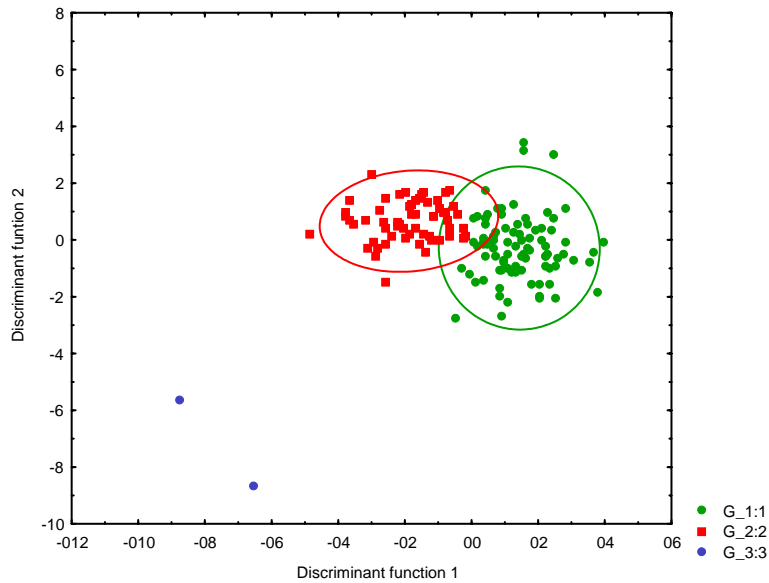
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Figure 1. Discriminant function 1 versus discriminant function 2, the ellipses represent a confidence level of 95%.

To study the effect of the added temper in the ceramics, the data were submitted to the modified *Mahalanobis* filter, thus obtaining a new set of elementary concentrations. The corrected concentrations were studied by means of a discriminant analysis. Again, the cluster analysis showed the existence of two groups. Figure 2 shows the discriminant function 1 versus discriminant function 2 calculated from the modified *Mahalanobis* filter.
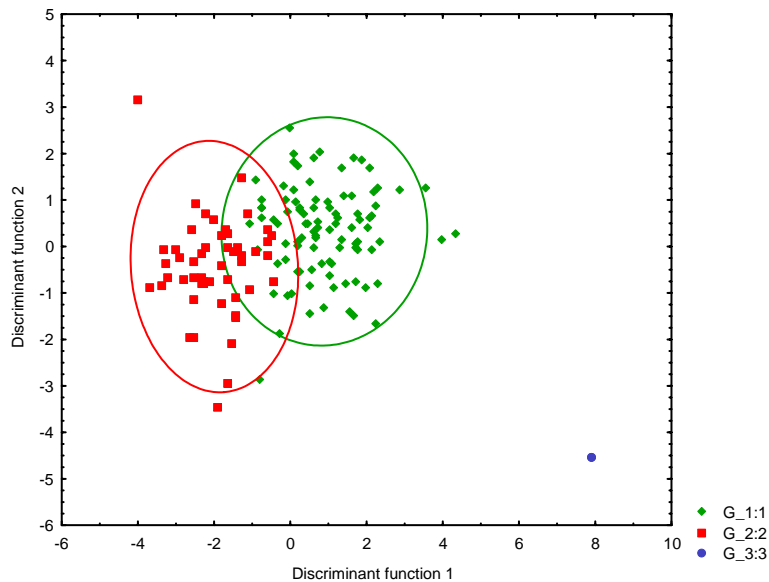

Figure 2. Discriminant function 1 versus discriminant function 2 calculated from the modified *Mahalanobis* filter. The ellipses represent a confidence level of 95%.

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By comparing the two Figures, it can be verified that there is no influence of the temper in the analyzed samples, since the Figures 1 and 2 show the cluster of two groups with very structure.

CONCLUSIONS

In this work, it was verified that the precision of the analytical method for the studied elements was good. The discriminant analysis showed the existence of two groups, indicating that different raw-material were used in the production of the artifacts. The effect of the temper, as well as the error in the analysis, studied through the modified *Mahalanobis* filter, clearly showed that is not significant.

In the future, complementary studies through other analytical techniques will be made with the samples having in view complementing the studies accomplished in this work.

REFERENCES

1. Munita CS, Paiva RP, Alves MA, Oliveira PMS, Momose EF. *J. Trace Microprobe Tech.* 2000; **18(3)**: 381-387.

2. Neff H, Bishop RL, Sayre ED. *J. Archaeol. Sci.* 1988; **15**: 159-172.

3. Munita Cs, Nascimento A, Schreiber SB, Luna S, Oliveira PMS. *J. Radioanal. Nucl. Chem.* 2004; **259(2)**: 305-309.

4. Schwedt A, Mommsen H. *J. Archaeol. Sci.* 2004; **31**: 1251-1258.

5. Harbottle G. Activation analysis in archaeology. In *Radiochemistry 3*, G.W.A. Newton (ed). Chem. Soc.: London, 1976; 33-72.

6. Beier T, Mommsen H. *Archaeometry.* 1994; **36(2)**: 287-306.

7. Munita CS, Paiva RP, Alves MA, Oliveira PMS, Momose EF. *J. Trace Microprobe Tech.* 2003; **21(4)**: 697-695.

8. Munita CS. *Caninde.* 2005; **6**: 159-181.

9. Attas M, Fossey JM, Yaffe L. *Archaeometry.* 1984; **26(1)**: 104-107.

10. Perlman I, Asaro F. (eds.). *Science and Archaeology.* RH Brill: London, 1971.

11. Penny KI. *Appl. Statist.* 1987; **35:** 153-162**.**