TEMPERING EFFECT IN CERAMICS CHEMICAL ANALYSIS BY INAA

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ABSTRACT

Archaeological ceramics are manufactured with clay and usually potters added a material named temper that can be a mineral or organic material. Temper modifies the chemical and physical properties of clay and improves its workability. When INAA is used, the analysis reflects total composition, i.e., the elements in the clay as well the ones in the tempering. In this work the concentration of Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, K, La, Lu, Rb, Na, Nd, Sb, Sc, Sm, Ta, Tb, Th, Yb, Zn and U in 161 samples of Marajoara pottery were determined using INAA. The samples were obtained using a tungsten carbide drill and dried in an oven at 105°C for 24 hours. The samples and standards were irradiated in the swimming pool research reactor, IEA-R1 (IPEN-CNEN/SP), at a thermal neutron flux of about 5 x 10^{12} n cm^{-2} s^{-1} for 8 hours. Two measurements series were carried out, after 7 days and 25-30 days. The results were studied by means of modified Mahalanobis filter and multivariate statistical methods to verify the effect of the temper on the determination of trace elements. The results showed that the temper effect in the pottery is negligible.

INTRODUCTION

One of the most important contributions of archaeometry to archaeology is the determination of pottery provenance. These studies provide information on distribution of workshops, diffusion of people, influence of cultures, trading routes and contacts between different sites. The identification of archaeological artifacts according to morphological or stylistic criteria, such as shape, color, style of decoration, kind of temper, etc., sometimes cannot be readily achieved between different production sites based on visual inspection alone.[1] On the other hand, the chemical composition of pottery is strongly related to the source of clay and the recipe of the fabrication. In addition, chemical analysis, together with statistical data treatment, is used extensively to supplement archaeological investigations when provenance studies or socioeconomic aspects are concerned.[2]

Pottery is a multi-component system formed by clay and temper. Adding temper, usually non-plastic material (such as mineral, vegetal and organic material) to clay during paste preparation is a common practice among traditional potters. Non-plastic grains can occur in a clay source itself or it can be added by a potter in the process of assembling a paste. In this sense tempering is a voluntary act made by man and it may cause the ceramic paste chemical composition to differ from the raw clay. Natural non-plastics do not have this effect, being present in both the clay source and in the ceramic paste. There is no mixing (tempering) problem in this case.[3]

The addition of non-plastic material makes it difficult to apply neutron activation analysis or other chemical characterization technique to determine archeological provenance because INAA (or other analytical method) measures elemental concentrations in bulk samples. One problem is that the tempering may blur the compositional distinctiveness of ceramics derived from separate sources. The elemental concentration may be calculated according to[4]

$$S_i = PT (T_i) + PC (C_i) \tag{1}$$

where S_i is the elemental concentrations in the ceramic, T_i is the elemental concentrations in the temper, and C_i is the elemental concentrations in the clay. T_i and C_i are determined analytically. PT and PC are the proportions of temper and clay, respectively, mixed to make the ceramic paste. The sum of PT and PC must be equal one.

In this work, 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 determined in 161 Marajoara ceramic fragments by means of instrumental neutron activation analysis (INAA). Actually, INAA is one of the most successful analysis techniques for composition analysis studies. By this method it is possible to determine simultaneously 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 in the analysis.[5] The data set was studied by means of modified *Mahalanobis* filter to verify the effect of the temper in the concentration data.

EXPERIMENTAL

Sample Preparation and Description of the Method
All 161 ceramic samples were analyzed via INAA. The ceramic powder samples were obtained by cleaning the outer surface and drilling using a tungsten carbide rotary file attached to the end of a flexible shaft, variable speed drill. After that, these materials were dried in an oven 105°C for 24h and stored in a desiccator.

Constituent Elements in Coal Fly Ash (NIST-SRM-1633b) were used as standard and IAEA-Soil-7, Trace Elements in Soil, was used as check samples in all analysis. These materials were dried in an oven at 105°C for 24 h.

About 100 mg of ceramic samples, NIST-SRM-1633b and IAEA-Soil-7 were weighed in polyethylene bags and wrapped in aluminum foil. Groups of 8 samples and one of each reference material were packed in aluminum foil and irradiated in the research reactor swimming pool, IEA-R1, 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 8h.

Two measurement series were carried out using Ge (hyperpure) detector, model GX 1925 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. K, La, Lu, Na, Nd, U, and Yb were measured after 7 days cooling time and Ba, Ce, Co, Cr, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Sm, Ta, Tb, Th, and Zn after 25-30 days. Gamma ray spectra analysis and the concentrations were carried out using the Genie-2000 Neutron Activation Analysis Processing Procedure from Canberra. A detailed description of the standard sample preparation and the procedure were published elsewhere.[6]

Modified *Mahalanobis* Filter
The study of chemical trace elements in the raw material used in the preparation of the ceramic fragments can show unique chemical compositions, which can indicate the source of the raw materials used in the artifacts.[7] Generally, to evaluate the link of a particular sample to a certain group, the use of the *Mahalanobis* distance[8] and the dilution factor fit are most useful.[9] 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:

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

where ^{t} denotes the transposed matrix; $\vec{x}$ is the sample vector in the m-dimensional space which contains the m chemical element concentrations (sample average vector); $\vec{y}$ is the whole group average vector and S_Y is the group co-variance matrix which contains the diagonal dispersion square. Equation (1) is the $\vec{x}$ sample quadratic distance to group $\vec{y}$ medium point in group-dispersion units along the line that joins $\vec{x}$ and $\vec{y}$. For a given S_Y, expression (1) follows the χ^2_m distribution for group members.[9] The m index gives the freedom degree number . For samples $\vec{x}$ in question, the well-known χ^2 test can decide from the value of (1) whether or not they are probable members of the group.[9]

During ceramics production with the addition of tempers to the clay, the values of elementary concentrations in the ceramics can be diluted, generating distortions in the data statistical analyses 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,[9] which includes measured uncertainties such as sample dissimilarity measurements, 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:

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

where x_k and y_k are the *k* element concentration values 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 triggered by temper during the manufacturing process, errors in the analysis, alteration of the concentration due to leaching, errors during weighing, etc.

The f among two samples $\vec{x}$ and $\vec{y}$ as close as possible can be calculated by the expression:

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

including the basic co-variance matrix. Details of the mathematical methods can be found in Beier and Mommsen.[9]

RESULTS AND DISCUSSION
Neutron activation analysis is a sensitive enough analytical technique that can determine elements found in very low concentrations, such as ppm (parts per million) or ppb (parts per billion). This characteristic has contributed to the recognition of NAA as the preferred technique by several researchers when analyzing samples for trace levels. Due to the fact that NAA is a sensitive technique, it is possible to quantify the small differences that may occur

inside a geologic formation. These small differences can be used to form groups of similar chemical composition. Pottery manufactured with a determined raw material source will be more chemically similar than other ones which were manufactured with different raw material. So the concentration determination of various elements for trace level, which differ in their chemical properties, will tend to produce a highly specific "fingerprinter" raw material source.

Another parameter highly related to this kind of study is the analytical precision. Precision is related to the ability that the method has to reproduce the same result. The precision limitations can result from sample inadequate preparation, either due to contamination with the same element that is being determined or due to lack of homogeneity problems. The determination of all parameters in the analyses must be measured and quantified to make corrections before applying the method in real samples because these small variations may affect the power capacity to distinguish between sample groups.

In this work elemental concentrations for the reference material IAEA - Soil 7 were statistically compared with the data found in our laboratory in order to evaluate the analytical process and to establish the chemical elements which can be used in data interpretation. Analytes with relative standard deviation, RSD, less than 10% were used.[10] All possible interference potentially occurring in gamma-ray spectrometry were considered and checked. A possible source of error in the determination of rare earth elements is the presence of significant amounts of fissile nuclides (^{235}U and ^{233}U). As it is well known rare earth elements nuclides mainly among the light rare earth elements (La to Sm) are produced both by activation and by fission. In the present work no interferences were expected in the samples due to the very low uranium fission in La and Ce determination. This interference is negligible when the uranium concentration does not exceed 5 ppm.[6] Although Co and Ta had RSD less than 10%, it was not included in the data set because the concentration can be affected by tungsten carbides files.[11] The Zn determination is not reliable as consequence of a strong γ-ray interference by ^{46}Sc. Using this criteria the elements Na, K, Lu, U, Yb, La, Th, Cr, Cs, Sc, Fe, Eu, Hf and Tb were used in subsequent data analysis.

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

The study of the outliers was made through the *Mahalanobis* distance, while using the lambda Wilks criterion as critical value.[12] For the sample set the critical value was calculated, and the samples that showed *Mahalanobis* distance values higher than the critical value were eliminated. After the elimination of the outlier samples, the *Mahalanobis* distance was calculated again in the new data group . This process was repeated until all of the samples showed *Mahalanobis* distance values lower than the critical value. In total, 12 outliers samples were found. Next, a preliminary classification was accomplished through cluster analysis by Ward and Euclidian distance methods.

The dendrogram showed the existence of two very defined groups. With the purpose of confirming the existence of these two groups the data were studied through discriminant analysis. In Figure 1, discriminant function 1 plot versus discriminant function 2 is shown. It can be seen that the elementary concentrations of Marajoara ceramic fragments are divided into two very well-defined groups.
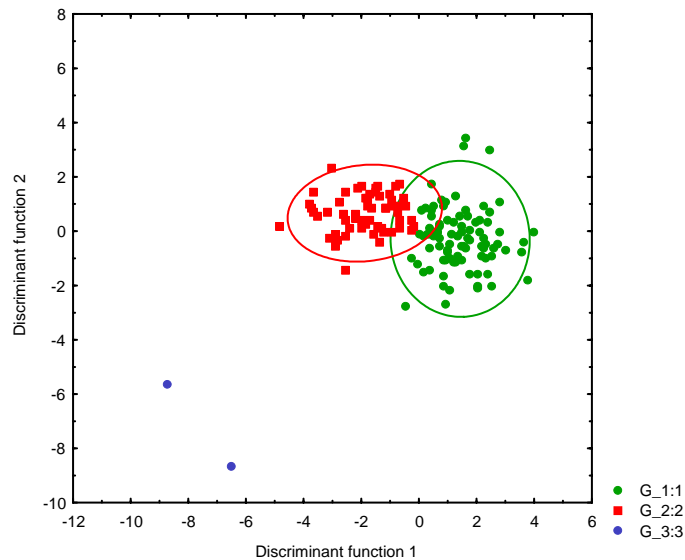

Figure 1. Discriminant function 1 versus discriminant function 2, the ellipses represent a 95% confidence level.

To study the effect of the added temper to the ceramics the data group was submitted to modified *Mahalanobis* filter, thus obtaining a new set of elementary concentrations, including the dilution factor in the concentration data. The corrected concentrations were studied by means of discriminant analysis. In Figure 2 the discriminant function 1 versus discriminant function 2 is presented. As it can be seen in both plots (Figures 1 and 2) the analysis result showed the existence of two groups with a very similar spatial distribution. Furthermore, the results showed that the temper effect in the studied Marajoara pottery is negligible.
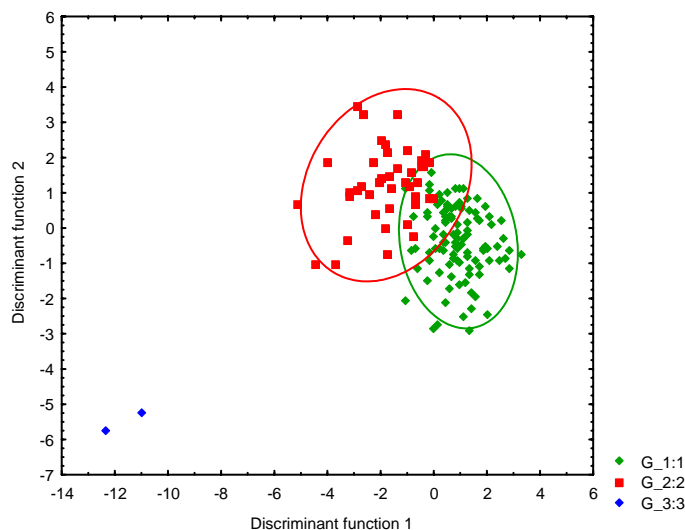

Figure 2. Discriminant function 1 versus discriminant function 2 using the concentration data obtained by modified Mahalanobis filter. The ellipses represent a confidence level of 95%.

By comparing the two graphs, it can be verified that there is no temper influence in the analyzed samples because the graphs show two groups with very similar distributions and groupings.

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

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