Statistical and Analytical Procedure for the Estimation of the Provenance of Archaeological Ceramics

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Abstract

The chemical compositions of several archaeological, ethnographic and clay samples have been determined. That allowed, by means of an appropriate statistical procedure, to estimate the probability that archaeological ceramic samples from Casa do Infante (Porto) and those found inside one boat from the XVth century, sunk at Ria de Aveiro, be from certain pottery production centres. The probability that the main red ceramics group found at the excavations of Casa do Infante (Porto), be from Aveiro, is high.

Introduction

The estimation of the provenance of archaeological ceramic fragments is frequently a matter of interest for researchers who intend to understand commercialisation circuits, technical aspects of production and other features concerned with ceramic uses in former times.

The chemical compositions of ceramics are closely related to the chemical compositions of the raw materials employed to their fabrication. Taking into account that, in older times, commerce of clay type raw materials at long distances should be rare, because of the spread availability of clays in nature, it is

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acceptable to consider that the chemical composition of ceramic fragments is a good indicator of their provenance. For that, it is essential to know the chemical composition pattern of clays and ethnographic ceramic production, from well and surely known provenance.

The comparison of the chemical composition of one fragment with the typical chemical composition of a certain production centre allows to determine, by appropriate statistical calculations, the probability for the case where the fragment is from that provenance.

Some examples of this type of calculations are presented in this paper, for ceramics of Casa do Infante, Porto, and for ceramics found inside one bottle sunk at Ria de Aveiro in the XVth Century.

Chemical analysis of ceramic fragments and clays

The chemical characterisation of ceramic fragments – archaeological or ethnographic – and clays, is done by X-ray fluorescence spectrometry. To employ this analytical method it is necessary to prepare samples to be analysed, to uniformise conditions of analysis and to avoid contaminations by elements present in glass coatings.

Sample preparation is done by the following procedure:
a) For clays

Samples are dried at 110°C during 24 hours, to eliminate moisture. Then they are milled to obtain a fine powder that is pressed to form one disk with 30 mm diameter. This disk is ready to be put into the spectrometer chamber, for analysis.

b) For archaeological or ethnographic ceramics

When the sample is glazed, the glass coating is removed by mechanical means, to minimise the presence of lead, tin and other constituents of glass, in the sample. Surface of samples is cleaned with ultrasonics in ethlic alcohol, to remove grass materials. Then the procedure is the same as for clays.

Chemical analysis is done using different types of detecting crystals: LiF 220, Pe, Ge and TLAP, allowing the measurement of the contents of chemical elements with atomic number greater than 11 – sodium. Quantification of the chemical elements is done by previous calibration of the equipment with clay type certified reference materials (C.R.M.) and with internal standards produced by the addition of certain pure substances to the C.R.M.s.

Statistical data handling

Chemical composition data, obtained by the procedure described above, is treated in the following ways (CASTRO1997):
a) **Previous calculations**

To avoid the influence that, eventually present, contaminant elements may have in the overall chemical composition, those elements are not considered for the calculations. For instance, elements like sodium and chloride (possible contamination due to culinary uses), phosphor and sulphur (possible contamination due to the conditions of preservation of archaeological samples) and lead and tin (present in glazes), are excluded from the analysis.

A transformation of the chemical composition to a new weight 100 % basis is then done. This eliminates differences on loss on ignition values (l.o.i), due to different types of clay materials, different cooking conditions, different residual moisture contents and different organic material contents. This calculation procedure allows also to eliminate the eventual effect that different degrees of contamination of the samples would have on the results to be treated.

b) **Cluster analysis**

When a lot of chemical composition data coming from one sure provenance (clays or ethnographic samples), or coming from a same excavation, is available, the first thing to do is to try to identify groups of similar chemical compositions within the data. For that purpose, cluster analysis is the statistical tool employed.

In order to eliminate the different effects related with the variations in chemical contents for the several elements, due to their different relative content in the sample, all the composition values are transformed in reduced variables:

\[ Z_i = \frac{\%i - \bar{\%i}}{\sigma_i} \]
where $\%i$ is the content of the element $i$ in the sample, $\bar{\%i}$ is the average of the contents of that element in all the samples considered and $\sigma_i$ is the corresponding standard deviation. This transformation of variables makes that all the elements will be equally important for the statistical analysis. Otherwise, variations in the major constituents, like silica or alumina, would be much more strongly considered than variations in minor elements like manganese, strontium, titanium, zirconium, etc.

After that transformation of variables, the clustering method employed is the nearest neighbour method applied to the Euclidean distances between samples. This is done with the aid of statistical softwares, generating a certain number of clusters which is previously indicated by us. In order to verify if the formed clusters are significantly different, a multivariate test is done that compares two clusters, taking into account the average value for each element (variable) and the standard variation of the values. The employed test is the Hotelling $t^2$ test. This allows to estimate the probability that two clusters be dissimilar and, hence, this is the criterion of acceptance – or not – of the formed clusters. If the probability of being different is greater than 95%, then the clusters are accepted. If not, they are merged in only one group. When merging of further clusters have less than 5% of probability for being due to hazard, formed clusters are accepted.

With the formed clusters, discriminant analysis may be done. This allows to evidence the principal components responsible for the differentiation between
the clusters. This technique will not be considered in the examples presented bellow.

**Characterisation of ceramics of the region of Ovar/Aveiro**

The region of Ovar/Aveiro is located at the central and coastal part of Portugal, about at midway from Porto to Coimbra. This is a traditional ceramic production region, with high variety and availability of clay reserves, that makes this region the main portuguese production centre of ceramic products like bricks, tiles, sanitary articles and porcelain.

The production groups considered from this region were:

- **Aveiro** – “archaeological” samples taken from house walls at the Bairro das Olarias, inside the town;
- **Ovar** – “archaeological” samples taken from house walls at the Bairro das Olarias, inside the town (15 Km northeast of Aveiro);
- **Ovar** – ethnographic samples, made surely with clays from Ovar;
- **Aguada de Cima** – clay samples, from this important clay extraction site (20 Km east from Aveiro). From these samples, two different groups have been considered: strong clay and weak clay, according to the physical properties of the clays;
- **Bustos** – clay samples, from another important clay extraction site (15 Km east from Aveiro)
Vagos – clay and brick samples, from this ceramic production site (10 Km south from Aveiro)

Two archaeological collections of ceramic fragments have been considered, for the seek of illustration:

*Casa do Infante (group I)* – Samples from this important excavation, located at the city of Porto. Only one group of red ceramics has been considered. This group is typologically very similar to the ceramics produced at Ovar, from older times until this century (REAL1992).

*Boat sunk at Ria de Aveiro* – Samples from the ceramic charge found inside a bottle that sunk at Ria de Aveiro, in the XVth century (ALVES1997 and ALVES1998).

Table I presents the average chemical composition for the production centres from the region of Ovar/Aveiro. For the purpose of estimation of provenance, only 12 elements have been considered. Certain elements are not considered because of possible contamination effects (see above). Sodium and chlorine are not considered here, also because of the probable contamination due to saline water conditioning in samples taken from the boat of Ria de Aveiro. Other elements, despite they have been quantified, were not considered because of the low levels of concentration, leading to high relative scattering in chemical contents. The inclusion of these elements in the statistical treatment would cause
difficulties in the estimation of provenance. This was the case of elements like zinc, copper, nickel, barium, cerium, lanthanum, cobalt and arsenic.

The statistical treatment applied to the groups data enable to a first conclusion that the groups from "archaeological" and ethnographic samples from Ovar are very similar and, hence, should be considered as a unique group.

From these data, it has been possible to estimate the probability that the archaeological ceramics from Casa do Infante-I and Boat-Aveiro comes from the region of Aveiro. This allowed to the results presented in Table 2.
Table 2 - Probability that the archaeological groups "C.Infante I" and "Boat-Aveiro" be the same as "Ovar-arch+ethn" and "Aveiro-arch"

For all the other ceramic groups, "Ovar-tiles", "Aguada-weak", "Aguada-strong", "Bustos" and "Vagos", the calculated probability was lower than 1%.

From these results we can conclude that the red ceramics found at the excavations of Casa do Infante present a chemical composition very similar to that of the samples taken from house walls at the Bairro das Olarias, inside the town of Aveiro (93%). The probability of being from Ovar is much lower (45%).

For the ceramics found inside the boat at Ria de Aveiro, the probability of being from Ovar is negligible (< 1%), but the probability of being from Aveiro is appreciable (77%). However, this value obliges us to admit that, even if those ceramics may be from Aveiro, they should be produced with slightly different clays (or procedures) than the ceramics taken from the house walls at Bairro das Olarias - Aveiro. Further work is necessary, to better characterise the whole production of the region of Aveiro and to help in determining more precisely the provenance of those archaeological ceramics.
Bibliographic references


