ARCHAEOOMETRIC CHARACTERISATION OF RENAISSANCE TIN LEAD GLAZED POTTERY FROM TALAVERA DE LA REINA, PUENTE DEL ARZOBISPO AND SEVILLE (SPAIN)

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1. INTRODUCTION

Majolica ceramics are among the most characteristic tableware from the Medieval and Renaissance times in Europe, achieving a very high technological and artistic flourish in Spain during the Renaissance. As a ceramic artefact, majolica is earthenware characterised by a ceramic creamy buff-light colour body and an opaque white tin lead glaze coating the whole outer surface of the vessel. However, the most characteristic feature of majolica pottery perhaps lies in its decoration. In that sense, decorations, which are made of metallic oxides, usually applied on top of the opaque white glaze coat, have been profusely studied by Art historians. However, too often provenance is just based on the scholar’s expertise, adding a substantial subjective compound to their conclusions. Therefore, just archaeometric techniques can provide an objective tool to the researchers in order to assess provenance of the archaeological artefacts.

Among Spanish production sites, the city of Talavera de la Reina (Toledo) was one of the most important majolica production centres of the Castilian Kingdom during the 16th and 17th centuries, becoming the official majolica supplier for the Spanish Royal Palace. However, a small pottery
village close to Talavera, called Puente del Arzobispo (Toledo), also produced majolica pottery that is believed to usually imitate Talavera decorations. Traditionally, Art researchers have encountered difficulties while discerning among those majolica productions. Therefore, it is important to explore if the application of any analytical technique can discern between both centres. Moreover, Seville is also considered as one of the most important majolica production centres in Spain. Trade with America turned Seville into a cosmopolitan city with a prosperous mercantile economy. This setting allowed Seville’s majolica production to flourish not only in quantity, but also in quality with the introduction of the Renaissance style in the well-known majolica workshops located in the old quarter of Triana. Then, its chemical discrimination from the two previous centres would be very valuable.

It must be pointed out that these production centres are well documented in numerous legal and commercial manuscripts of the period (Sánchez Cortegana 1994; Pleguezuelo & Sánchez Cortegana 1997; Sánchez-Pacheco 1997) and have also been preliminary studied by archaeometric means (Myers et al. 1992; García Iñañez et al. in press).

2. SAMPLING AND METHODOLOGY

Forty-four individual majolica pieces were sampled from these sites in order to characterise archaeometrically each majolica production. All the individuals were analysed by X-Ray Fluorescence (XRF), and 18 out of them were also analysed by means of Neutron Activation Analysis (NAA) (Table 1).

<table>
<thead>
<tr>
<th>Sites</th>
<th>XRF</th>
<th>XRF+NAA</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Talavera</td>
<td>12</td>
<td>6</td>
<td>18</td>
</tr>
<tr>
<td>Puente del Arzobispo</td>
<td>9</td>
<td>7</td>
<td>16</td>
</tr>
<tr>
<td>Sevilla</td>
<td>5</td>
<td>5</td>
<td>10</td>
</tr>
<tr>
<td>Total</td>
<td>26</td>
<td>18</td>
<td>44</td>
</tr>
</tbody>
</table>

Table 1. Individuals analysed by XRF and by XRF and NAA from each production centre.

The statistical procedure followed Aitchison’s approach and Buxeda’s observations on compositional data (Aitchison 1986, 1996; Buxeda 1999; Buxeda & Kilikoglou 2003). Then, the statistical procedure consists in the use of log ratios obtained by dividing all the components, in this case chemical components, by that component which introduces the lower chemical variability to the whole set of individuals taken into consideration, overcoming the compositional data problem called “close to unit sum”, when data necessarily must sum 100%. Moreover, the use of logarithm concentrations allows for quasi-standardisation of data. Furthermore, dividing all components by
the lower one in terms of variability also overcomes relative magnitude problems of a given sub-
composition, because after log-ratio transformation we deal with the same relative magnitudes for
each individual since $s_i/s_j = x_i/x_j$ (Mateu et al. 2003). Finally, log-ratio transformation also provides
a better highlighting of possible perturbations in the chemical data set as a result of contamination
or alteration processes (Buxeda 1999). The resulting data were treated using an array of multivariate
statistical procedures. The aims applying multivariate statistical techniques to chemical data are to
facilitate identification of compositional groups. Therefore, similarity of individuals, and subse-
quently their hypothetic provenance according to the provenience postulate (Weigand et al. 1977),
was firstly tested employing squared Euclidian distance graphically represented by cluster plots
using centroid algorithm in the S-Plus program (MathSoft 1999). Stepwise Discriminant Analysis
(SDA) was performed in order to assess the archaeological classification and the chemical groups
proposed by cluster analysis. Performing SDA was also an option to cluster unknown provenances
of non-classified individuals. In addition, Mahalanobis distance was also used to describe proba-
bilistically the separation between defined groups and some of those individuals that remained
unchlassified (Glascock 1992).

Figure 1. Dendrogram resulting from the cluster analysis using the squared Euclidean distance and the
centroid agglomerative algorithm on the sub-composition $\text{Fe}_2\text{O}_3, \text{Al}_2\text{O}_3, \text{MnO}, \text{MgO}, \text{Na}_2\text{O}, \text{K}_2\text{O}, \text{SiO}_2, \text{Ba},
\text{Nb}, \text{Zr}, \text{Ce}, \text{V}, \text{Zn} \text{and Ni, using TiO}_2 \text{as divisor in the logratio transformation.}
3. CHEMICAL RESULTS

The study of the XRF data dendrogram reveals a clear structure in two main groups, Seville and Talavera-Puente (Fig. 1). However, the different productions of Talavera and Puente remain unclear, because of their chemical similarities revealed by the fusions in the dendrogram, performed with the S-Plus program (MathSoft 1999), of the individuals from these sites. Likewise, NAA data exhibits the same behaviour as the XRF ones, so a clear separation between Seville and Talavera-Puente exists by Principal Component Analysis (PCA), performed with the S-Plus program, whereas an inhomogeneous group includes all the individuals from these latter sites (Fig. 2).

Figure 2. Plot resulting from the NAA data using the two first Principal Components resulting on the covariance matrix of the subcomposition As, La, Lu, Nd, Sm, U, Yb, Ce, Cr, Fe, Hf, Rb, Sb, Sc, Sr, Ta, Tb, Th, Zn, Zr, Al, Ba, Ca, Dy, K, Mn, Na, Ti and V, using Eu as divisor in the logratio transformation.
Nevertheless, using the samples recovered at the Talavera site and those recovered at Puente as the respective reference groups for both sites, stepwise discriminant analysis on the NAA data, performed using the BMDP program (Dixon 1983), clearly discriminates between both production centres (Fig. 3, upper). Regarding XRF data, stepwise discriminant analysis did not provide such a clear-cut separation (Fig. 3, lower). To test forward these results, Mahalanobis Distances (MD) was calculated to the centroids of these two groups, using for each technique the most discriminant log-ratio transformed components. Then, probabilities were assigned to the calculated MD (Davis 1986). In the first case, MD calculated on NAA log-ratio transformed data (Fig. 4, upper) seem to exhibit a clear group separation, although the assigned membership probabilities do not allow to separate both groups. This result must be forced by the low number of individuals considered. On the other hand, MD calculated on XRF log-ratio transformed data (Fig. 4, lower) separate both groups on probability grounds. This is especially

**Figure 3.** Stepwise discriminant analysis on Talavera (T) and Puente (P) groups. Upper: NAA logratio transformed data using Eu as divisor. The most discriminant variables are the transformed Sm, Zr, Al, Ca and Ti values. The first canonical variable (VC1) explains 100% of the total dispersion. Lower: XRF logratio transformed data using Nb as divisor. The most discriminant variables are the transformed Fe$_2$O$_3$, Ba, V and Zn values. The first canonical variable (VC1) explain 100% of the total dispersion.
true when compared to the Puente group, because it is more chemically homogeneous than the Talavera group. Therefore, it seems acceptable that Puente and Talavera would be discriminated, especially by increasing the number of individuals analysed.

4. Conclusions

Majolica production from the three studied producing towns can be, most probably, chemically differentiated. Although Seville production can be easily discriminated from Talavera and Puente, this discrimination cannot be easily achieved between the latter ones due to their chemical similarities, which might be related to their geographical proximity and subsequent geological similarity. However, present results are encouraging and a much better discrimination is expected if sampling is increased in both sites.

Figure 4. Histograms of Mahalanobis Distances (MD) calculated on the NAA logratio transformed data using Eu as divisor. Upper left: calculations to the Talavera centroid. Upper right: calculations to the Puente centroid. Histograms of MD calculated on the XRF logratio transformed data using Nb as divisor. Lower left: calculations to the Talavera centroid. Lower right: calculations to the Puente centroid. In Histograms squares P = individual from Puente; T = individual from Talavera. Out of histograms P = membership probability.
Thus, NAA and XRF are revealed as powerful tools, together with multivariate statistical procedures, to help with the discrimination between Talavera and Puente productions, historically joined until now.

ACKNOWLEDGEMENTS

The work presented here forms part of the project “Identification, Recovery and Improvement of ancient Mediterranean ceramic manufacturing technologies for the reproduction of ceramic artefacts of archaeological value (CERAMED)”, from the Research Directorate General, European Commission, European Community (ICA-3-CT-2002-10018). Javier García Iñañez is also indebted to the support of Departament d’Universitats, Recerca i Societat de la Informació de la Generalitat de Catalunya i Fons Social Europeu. Besides, Javier García Iñañez is also indebted to the Comissió de Recerca de l’Agrupació en Humanitats de la Universitat de Barcelona for providing the allowances to assist to the 34th ISA conference. Authors are also indebted to the Museu de la Ceràmica de Barcelona and to Mr. Sánchez Cabezudo for his collaboration by providing the samples.
REFERENCES


