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THE ARCHAEOMETRIC CHARACTERIZATION OF MAJOLICA CERAMICS FROM TALAVERA DE LA REINA AND EL PUENTE DEL ARZOBISPO (TOLEDO, SPAIN)*

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In this study, an archaeometric characterization of 32 ceramic fragments from Talavera de la Reina and El Puente del Arzobispo, dated between the 16th and 18th centuries, has been carried out. Together with three fragments of biscuit, they have been analysed through X-ray diffraction (XRD), X-ray fluorescence (XRF), differential scanning calorimetry and thermogravimetric analysis (DSC–TGA). From these chemical results, a statistical study using exclusively majolica ceramics has been carried out. This work has allowed us to find certain differences between the manufactures of the two production centres on the basis of their chemical composition. The mineralogical study has allowed us to determine the estimated firing temperatures of each sample, using the estimated firing temperature (EFT) as an argument for their classification into three fabrics.

KEYWORDS: MAJOLICA, CERAMICS, STATISTICAL TREATMENT, VARIATION MATRIX, TALAVERA DE LA REINA, EL PUENTE DEL ARZOBISPO, CHEMICAL ANALYSIS, MINERALOGICAL ANALYSIS

INTRODUCTION

The ceramic produced in Talavera de la Reina and El Puente del Arzobispo, located in the centre of the Iberian Peninsula (Toledo), is known as majolica. It is a fine earthenware, the main characteristic of which is its coat of white glaze, which is decorated with a variety of different metallic oxides of a very specific range of colours (Iñañez *et al*. 2006). In the case of the Talavera and Puente majolicas, the colours are as follows: cobalt blue, emerald green, antimony orange yellow, iron dark orange, manganese purple and black tonalities.

The decoration was conditioned by the influences that these production centres received over the centuries. In the 15th century, Italian potters inspired by Chinese porcelain became the main influence amongst European potters. Talavera de la Reina was one of the first centres to imitate the Italian models, due to two determinant factors: the arrival of Renaissance authors such as Niculoso Pisano and Ian Floris in Spain and, in the second half of the 16th century, the start of the trade route of the Manila Galleon, a fleet of Spanish trading ships that sailed across the Pacific Ocean between Manila and Mexico, and which involved the arrival of Chinese ceramics (Iñañez 2005; Coll Conesa 2008).

The Renaissance influence involved the introduction of new decorative motifs, such as the use of liners, ironwork, busts or entire human figures, and new decorative types, such as the

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ferronerie (ironwork) or tricolour (Pleguezuelo 1992; González 2004) series. Once in the 17th century, the Baroque abruptly reached the Talaveran pottery workshops and imposed the new style that was prevailing across Europe. From an artistic point of view, the evolution was continuous, and it was to be conditioned by external influences and political and economic changes (González 2002).

In the 16th century, Talavera de la Reina would become one of the main majolica ceramic production centres in the Iberian Peninsula (Portela 1999). Due to its fineness and high quality, the monarchy and the aristocracy would become the most important customers (Ballesteros 1983). Amongst the most devoted clients, there was also the Order of the Jeromes (Orden de los Jerónimos), who ruled the Monastery of El Escorial. This order acquired a great collection of tiles and vessels throughout the years, which allows us to accurately date the majority of Talavera's artistic series (Martínez Caviró 1984). However, the monarchy's interest in Talavera ceramics decayed when the Bourbons came to the throne at the beginning of the 18th century. The new French dynasty had other artistic preferences and so the Talaveran potters had to adapt to the trends. This new monarchy supported the Royal Factory of Alcora (founded in 1727 by the Count of Aranda in Alcora, Valencia), dedicated to replicating French-style pottery, together with the Silk Factory in Talavera (1749) and the Buen Retiro Factory (1759). All these facts and the initial refusal to adopt the new trend meant, for Talavera and Puente, a process of decline that would not end until the beginning of the 20th century (González 2002).

The township of El Puente del Arzobispo was founded in the 14th century by the archbishop of Toledo. The greater part of its population came from the neighbouring town of Talavera de la Reina, amongst whom were a group of potters who brought the traditions and their Talaveran ways with them (Pleguezuelo 2001). From the artistic point of view, the pottery produced in Puente has been considered to be of an inferior quality, since it consisted of copies of the ceramics first made in Talavera (Vaca González and Ruiz de Luna 1943; Martínez Caviró 1984). However, on many occasions, only an expert can really distinguish between the two productions—a good indication of the high quality of these copies. On the other hand, there were also artistic series from the 19th century that were exclusive to Puente (Vaca González and Ruiz de Luna 1943).

The raw materials used to make the Talavera de la Reina and El Puente del Arzobispo productions from the 16th to the 18th century came from a quarry called 'La Calera', in the district of Calera y Chozas, 15 km from Talavera and 20 km from Puente (Vaca González and Ruiz de Luna 1943; Hurley 1989; Alvigini 2006). They are calcareous pastes, with a calcium oxide level of 19–21%, and very similar in the two production centres. In the case of Talavera and Puente, these high levels of calcium helped to yield whiter biscuit bodies from the first firing, which in turn favoured the opacity of the glaze.

After the depletion of the La Calera quarries at the end of the 18th century, the potters started to use clay from El Puente del Arzobispo.

At that time, it was customary that craftsmen's guilds would supply all of the raw materials for production (clays, additives, pigments etc.) to all the craftsmen within the same guild, so that they would all receive the same materials. However, this is a practice that has not been verified for Talavera.

Every ceramic piece made in those production centres had to go through several manufacturing processes before decorating the tables and walls of the aristocratic Spanish houses. The first step to produce the pottery was the extraction and preparation of the clays from the ponds where they were kneaded, decanted and left to rot, so that they would obtain purified clays, free from any organic matter. This refined clay was used to elaborate greenwares, which were worked on the morisco potter's wheel to obtain the desired shapes (Alvigini 2006). The dry pieces (leather-hard) were placed in the morisco kiln, a convection kiln, where they were fired in a not completely oxidizing atmosphere (Picon 1973). After the firing, they were left to cool down for about 40 h: these pieces go by the name of ‘biscuit’. The technique used in Talavera and Puente in the decorative process is known as *sobrecubierta* (on-glaze). This technique refers to the pictorial decoration on the ceramic surface, which has previously been glazed. Both the glazing and the decoration are made on the biscuit, taking advantage of its optimum porosity.

The Talavera glaze is based on tin, which provides waterproofing and a white cover. The piece was immersed in a frit, which is a preparation that has been melted, cooled and dissolved in water, and whose main elements, in the case of Talavera, are tin oxide, lead oxide, sand and other fluxes. The piece was then decorated with the specified oxides and was fired for a second time. The vitrification process began at a temperature of 850°C (Lambert 1998). In the case of Talavera, most written sources believe that the normal firing temperatures would have been around 880–920°C (Hurley 1989). However, the first firing was usually at around 900–1100°C for the biscuits, and the second would depend on the glaze and pottery types (Henderson 2000).

Traditionally, the glaze has been used to identify and differentiate between the Talavera and Puente tableware. The Talavera glaze is considered the purest and the most intense white, whereas the one from Puente is more yellowish. This could be due to the reduced use of tin in Puente, in consideration of its high price (Alvigini 2006). However, each craftsman had his own secret formula, so that the ingredients and proportions could vary, commonly due to the shortage or lack of raw materials.

To date, certain criteria based on the typology, enamel and artistic decoration of the pieces have been used to establish the differences between the Talavera and Puente production (see, e.g., Vaca González and Ruiz de Luna 1943; Martínez Caviró 1984; Pleguezuelo 2001; Alvigini 2006). However, the similarities between the two productions are such that it is very hard to distinguish them, especially when they have no any identifying hallmark.

The aim of this paper is to mineralogically and chemically characterize 32 majolica ceramic fragments and three fragments of biscuit from Talavera de la Reina and El Puente del Arzobispo, in order to provide new criteria by means of which to be able to distinguish the ceramic productions from the two centres.

MATERIAL AND METHODS

In this work, 35 sherds have been analysed (Table 1), 21 of which came from different excavations in Talavera, so we have gathered information from various parts of the township. Of the Puente fragments, 14 came exclusively from the Puente *testar*, a deposit where the craftsmen threw the disused and broken ceramics. The findings cannot be linked to any workshop. All the analysed samples in this work have been archaeologically and artistically dated and have been classified according to their origin. Sherds T-11 and T-12 have not been analysed because they did not have enough weight. Samples T-5 and T-7 have been removed from the chemical study because they did not have enough weight, but a mineralogical study was made.

The study also includes the analysis of a Talaveran biscuit (B-3) that comes from the excavations beneath the Ruiz de Luna Museum (Talavera de la Reina) and two biscuits that come from the Puente *testar* (B-1 and B-2).

For the sample preparation, the following process has been carried out: mechanical removal of the glaze using an IsoMet® 1000 Buehler cutting saw, ultrasonic cleaning, drying in ovens at 100°C, grinding and homogenizing in agate mills. Glaze removal was confirmed using an Olympus SZX7 stereo microscope.

Table 1 *The Puente and Talavera fragments classified according to the place and the artistic and chronological criteria**

Talavera de la Reina	Esponjillada *series, 16th century*	*Fern series, 17th century*	*Tricolour series, 17th century*	Polychrome *series, 17th century*	*White series, 18th century*	*Alcoreñas series, 18th century*
Adalid Meneses Street	T-17	T-18, T-19			T-21, T-22	T-20
Lechuga Street					T-5, T-6, T-7	
Pescaderías Street		T-15	T-14			T-16, P-2
Lagar de Postiguillos					T-8, T-9, T-10, T-13	
Castillejos Street						T-1, T-2, T-3, T-4
Testar from El Puente del Arzobispo		P-1, P-9	P-10, P-12	P-8, P-11	P-3, P-4, P-5, P-6	P-7

*P, Puente; T, Talavera; number of individuals, 35.

Each of the studied fragments has been analysed using the following analytical technologies:

- Mineralogical analysis has been performed using X-ray diffraction, working with the powdered sample and using approximately 1 g for each sample. The samples have been ground to less than 50 µm. The equipment used was a Philips PW-1710 diffractometer with an automatic divergence slit and graphite monochromator, applying the copper Ka radiation wavelength ($\lambda = 1.5405$). The mineralogical results permit us to learn the estimated firing temperature (EFT) of the samples.
- The chemical analysis of the ceramic paste has been obtained through X-ray fluorescence (XRF). The equipment utilized was a MagiX Super Q Version 3.0 X-ray fluorescence spectrometer, (Philips, The Netherlands). The analyses were performed on pressed pellets using up to 8 g, which was required in order to obtain the trace elements. The major and minor elements were determinated by means of glassy pills, using 0.5 g of powdered sample fused with 5 g of lithium tetraborate. The studied chemical elements are presented in Tables 2 and 3. The loss on ignition was determinated by calcination of the samples at 1100°C for 5 h.

Table 2 *The average of the chemical elements obtained by XRF, and the standard deviation of the glazed ceramic fragments**

Elements	*Talavera de la Reina*		*El Puente del Arzobispo*	
	Average	*Standard deviation*	*Average*	*Standard deviation*
Na_2O (%)	0.83	0.33	0.55	0.22
MgO (%)	5.82	0.97	5.76	0.45
Al_2O_3 (%)	14.95	1.55	14.99	0.73
SiO_2 (%)	43.06	2.70	44	1.69
P_2O_5 (%)	0.35	0.12	0.23	0.10
K_2O (%)	2.34	0.50	2.60	0.53
CaO (%)	19.95	1.56	20.24	1.56
TiO_2 (%)	0.66	0.05	0.68	0.02
MnO (%)	0.08	0.01	0.08	0.01
Fe_2O_3 (%)	5.22	0.57	5.52	0.32
PbO (%)	**0.96**	**0.41**	**1.46**	**1.42**
Sc (ppm)	13	1.03	12.97	0.87
V (ppm)	55	6.38	61.06	5.73
Cr (ppm)	50	7.30	53.59	4.31
Co (ppm)	12	1.94	13.58	2.00
Ni (ppm)	25	3.89	29.16	2.89
Zn (ppm)	78	10.66	82.76	6.98
Rb (ppm)	108	20.17	105.95	12.76
Sr (ppm)	288	46.46	344.58	62.43
Zr (ppm)	227	30.79	209.59	21.76
Nb (ppm)	17	1.28	17.54	0.84
Cs (ppm)	5	1.77	6.13	1.40
Ba (ppm)	317	28.22	317.17	24.46
La (ppm)	27	3.34	27.35	3.39
Th (ppm)	16	1.81	15.18	1.29
Ga (ppm)	**39**	**10.35**	**42.93**	**8.31**
Y (ppm)	**40**	**6.66**	**40.66**	**4.75**
Sn (ppm)	**22**	**15.12**	**27.15**	**32.09**

*Major and minor elements in wt%; trace elements in ppm (parts per million); number of individuals, 30.

Table 3 *The chemical results of the three biscuits analysed by XRF—the Pb, Sn, Ga and Y levels are highlighted in bold**

Elements	*B-1*	*B-2*	*B-3*
Na_2O (%)	0.52	0.49	0.28
MgO (%)	5.58	4.67	6.45
Al_2O_3 (%)	14.91	15.27	15.39
SiO_2 (%)	42.93	42.37	38.99
P_2O_5 (%)	0.20	0.25	0.30
K_2O (%)	0.06	0.13	0.32
CaO (%)	3.18	3.74	2.75
TiO_2 (%)	0.65	0.74	0.63
MnO (%)	0.06	0.09	0.07
Fe_2O_3 (%)	5.46	5.78	5.56
PbO (%)	**0.121**	**0.179**	**0.007**
Sc (ppm)	13	13	14
V (ppm)	53	57	66
Cr (ppm)	47	42	49
Co (ppm)	12	11	12
Ni (ppm)	26	21	25
Zn (ppm)	28	23	84
Rb (ppm)	87	73	107
Sr (ppm)	405	288	315
Zr (ppm)	203	181	133
Nb (ppm)	17	16	16
Cs (ppm)	3	2	4
Ba (ppm)	329	303	341
La (ppm)	30	25	30
Th (ppm)	14	14	13
Sn (ppm)	**16**	**6**	**6**
Ga (ppm)	**22**	**20**	**19**
Y (ppm)	**31**	**28**	**26**

*Major and minor elements in wt%; trace elements in ppm (parts per million); number of individuals, three.

- Differential scanning calorimetry and thermogravimetric analysis (DSC–TGA) has also been conducted, which corroborates the mineralogical phases and compares the results with the chemical and mineralogical analysis (Boch and Lejeune 1984; Tsetlin and Volkova 2011). For the test, a temperature of 1100°C has been reached at a heating rate of 10°C min^{-1}, in an air atmosphere and a platinum crucible. The equipment used was a SDT Q600 TA instrument.

This work has been done via some of the commonly used techniques for archaeometric characterization studies. The theoretical bases of the techniques and their applications follow the guidelines set out in Picon (1981a), Bishop *et al*. (1982), Buxeda *et al*. (1994), Hein *et al*. (2002) and Pollard *et al*. (2007).

A statistical analysis of each individual ceramic (I_c) has been performed on the basis of the chemical elements using the MATLAB program.

RESULTS

Chemical analysis

The chemical study of the ceramic fragments offers us very similar results for the totality of the samples (Tables 2 and 3).

The chemical results show a clear proximity between the Talavera and Puente productions. These tables comprise all of the elements used for this study, including PbO, Ga and Y, which are items that are not subsequently used in the statistical treatment, since they are treated as alterations or contaminations of the sample (Buxeda 1999). The Pb and Sn are elements that appear in the body chemical analysis, but they are part of the glaze and penetrate into the ceramic matrix during firing. This is a normal process in lead-glazed majolica ceramics (Iñañez 2005; Iñañez *et al*. 2005). The Ga and Y are elements that have been removed given that they have a direct connection with Pb; that is to say, the larger the amount of Pb, the higher are the Ga and Y contents.

Statistical analysis

In this section, the chemical results analysed by means of XRF have been statistically treated. In the subsection 'Compositional relative variation', the variation of the chemical components is introduced by means of the covariance matrix of the components. The subsection 'Bivariate correlation graphics' describes the correlation between the relative variation of the components by means of bivariate diagrams. Finally, a cluster analysis by means of a dendrogram is presented. The statistical treatments in these subsections are analysed on 30 ceramic fragments (I_c) from Talavera de la Reina (18 I_c) and El Puente del Arzobispo (12 I_c).

The chemical variability of the different groups, $\tau_{i,j}$, was analysed by means of the relative variation matrix between the different chemical components. This is defined by logratio transformation in Buxeda (1999) and Aitchison (1986) as follows:

$$\tau_{i,j} = \mathrm{var}\left(\ln\left(x_i/x_j\right)\right), \qquad \text{with } i, j = 1, 2, \ldots, D,$$

where $\tau_{i,j}$ is the logratio covariance matrix, which is a symmetric $D \times D$ matrix such that any element of the main diagonal, $\tau_{s,s}$, is zero, and D is the number of chemical components. The components are denoted by $z_{i,j} = \ln(\mathbf{x_i}/\mathbf{x_j})$ with fixed ij, where x_i indicates the chemical component by group. Each I_c has D chemical components, denoted by x_i, and the component $z_{i,j}$ is any combination of the chemical components x_i by the logratio transformation $\ln(x_i/x_j)$. The variance of $z_{i,j}$, var($z_{i,j}$), is the sample variance formula $S^2{}_{i,j}$, which is described as follows:

$$\mathrm{var}\left(z_{i,j}\right) = S^2{}_{i,j} = (N-1)^{-1} \sum\nolimits_k \left(z^k{}_{i,j} - Z_{i,j}\right)^2, \qquad \text{with } k = 1, 2, \ldots, N.$$

$Z_{i,j}$ is the arithmetic mean of the I_c's sample ($z^1{}_{i,j}, z^2{}_{i,j}, \ldots, z^N{}_{i,j}$) and N is the number of individuals.

Another important statistical concept is the total variation, *vt*, of all the components of the logratio covariation matrix, defined in Picon (1981b), Aitchison (1986) and Buxeda (1999).

Through variation, the *vt* percentage is defined in the logratio covariation matrix by means of the components x_j as divisor, vt/$\tau_{:,j}$, where $\tau_{:,j} = \sum_i \tau_{i,j}$, with $i = 1, 2, \ldots, D$.

Compositional relative variation The variations after a logratio transformation using the chemical components x_i are shown in the columns in Table 4 (Talavera de la Reina and El Puente del Arzobispo). The number of chemical components considered is $D = 24$.

The statistical formulas treated to analyse the compositional relative variations are described as follows:

$$\tau_{:,j} = \sum_{i} \tau_{i,j}, \qquad \text{with } i = 1, 2, \ldots, D,$$

where $\tau_{:,j}$ represents the variation total sum shown in the column of the elements j; $vt/\tau_{:,j}$ is the percentage of the variation in the logratio covariance matrix; r is the correlation between the values $\tau_{:,j}$, with $i \neq j$, and the corresponding values $\tau_{i,j}$ for any of the components of the column; and, finally, vt is the total variation.

The above statistical formulas are applied to the chemical components from Talavera de la Reina and El Puente del Arzobispo:

- In Talavera de la Reina, the element SiO_2 imposes less variability, $\tau_{:,SiO2} = 0.66806$, and its respective percentage is higher, $vt/\tau_{:,j} = vt/\tau_{:,SiO2} = 0.95357$. But Na_2O is the component that imposes a variability $\tau_{:,Na2O} = 3.4583$ that is higher and therefore its percentage is below 50%: $vt/\tau_{:,j} = vt/\tau_{:,Na2O} = 0.18421$.
- With regard to El Puente del Arzobispo, the component Nb imposes less variability, $\tau_{:,Nb} = 0.42474$, and a higher percentage, $vt/\tau_{:,j} = vt/\tau_{:,Nb} = 0.96588$. And Na_2O is the component that imposes a greater variability, $\tau_{:,Na2O} = 2.5006$, and its percentage is less than those of the other components: $vt/\tau_{:,j} = vt/\tau_{:,Na2O} = 0.16406$.
- Finally, in Table 4, the compositional relative variation from Talavera de la Reina and El Puente del Arzobispo indicates that Nb is the component with the least variability, $\tau_{:,Nb} = 0.67243$, and the highest percentage: $vt/\tau_{:,j} = vt/\tau_{:,Nb} = 0.95775$. The component with the greatest variability is Na_2O, $\tau_{:,Na2O} = 4.0918$, and it has a percentage below 50%: $vt/\tau_{:,j} = vt/\tau_{:,Na2O} = 0.15739$.

Table 4 *The compositional relative variation from Talavera de la Reina and El Puente del Arzobispo*

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	K_2O	CaO	TiO_2
$\tau_{:,j}$	4.0918	1.2936	0.7155	0.6837	3.9007	1.9474	0.9808	0.7154
$vt/\tau_{:,j}$	0.1573	0.4978	0.8999	0.9418	0.1651	0.3307	0.6566	0.9001
r	0.2524	0.9725	0.9961	0.9974	0.2100	0.9687	0.9777	0.9962
	MnO	Fe_2O_3	*Sc*	*V*	*Cr*	*Co*	*Ni*	*Zn*
$\tau_{:,j}$	0.9602	0.7477	0.7206	0.8511	0.8865	1.1234	1.0391	0.8211
$vt/\tau_{:,j}$	0.6706	0.8613	0.8937	0.7566	0.7264	0.5733	0.6198	0.7843
r	0.9924	0.9922	0.9963	0.9845	0.9796	0.9881	0.9669	0.9882
	Rb	*Sr*	*Zr*	*Nb*	*Cs*	*Ba*	*La*	*Th*
$\tau_{:,j}$	1.1916	1.4767	1.2376	0.6724	2.3031	0.7953	0.8954	0.8618
$vt/\tau_{:,j}$	0.5404	0.4361	0.5203	0.9577	0.2796	0.8097	0.7192	0.7472
r	0.9685	0.9564	0.9104	0.9976	0.9240	0.9833	0.9912	0.9637
vt	0.6440							

Bivariate correlation graphics The correlation between the relative variation of all the components $\tau_{i,j}$ with $i \neq j$, in front of the relative variations of each element with all the others, $\tau_{:,j}$, is represented in Figure 1 for Talavera de la Reina and El Puente del Arzobispo. The relative variations in regard to the components with the least variability are shown on the left-hand side, and the relative variations regarding the components with higher variability are shown on the right-hand side.

These graphics show that the component with lower variability (Nb) has the highest correlation compared with the relative variations of each component with all of the others. The component with the highest variability Na_2O as divisor produces a distortion with respect to the relative variations of each component with all the other $\tau_{:,j}$.

Cluster analysis

The cluster analysis from Talavera de la Reina and El Puente del Arzobispo has been developed through a dendrogram (Fig. 2), using the mean-squared Euclidean distance on $D = 24$ components with Nb as divisor component in the logratio transformation for the individuals.

Results The variation matrix provides a very high total variation of 0.64402, which implies that the chemical composition has a very high variability, somehow very far from what can be considered as a homogeneous group. This is perhaps due to the fact that the individuals from the two production centres were analysed together, and also because they came from diverse excavation localities. This study also includes the separate individual analyses for Puente and Talavera, the variation matrices of which present total variations that are very different from each other. Talavera has a total variation of 0.63705, and Puente has a total variation 0.41025. These

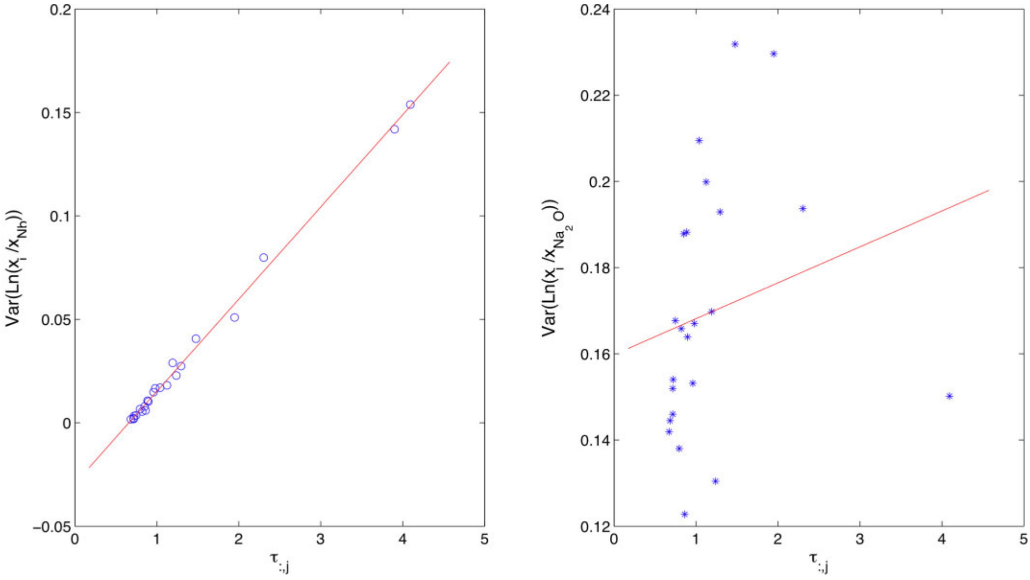

Figure 1 *Talavera de la Reina and El Puente del Arzobispo: bivariate graphics with $\tau_{:,j}$ values on the x-axis. Left-hand side, $\tau_{:,Nb}$ on the y-axis; right-hand side, $\tau_{:,Na2O}$ on the y-axis.*

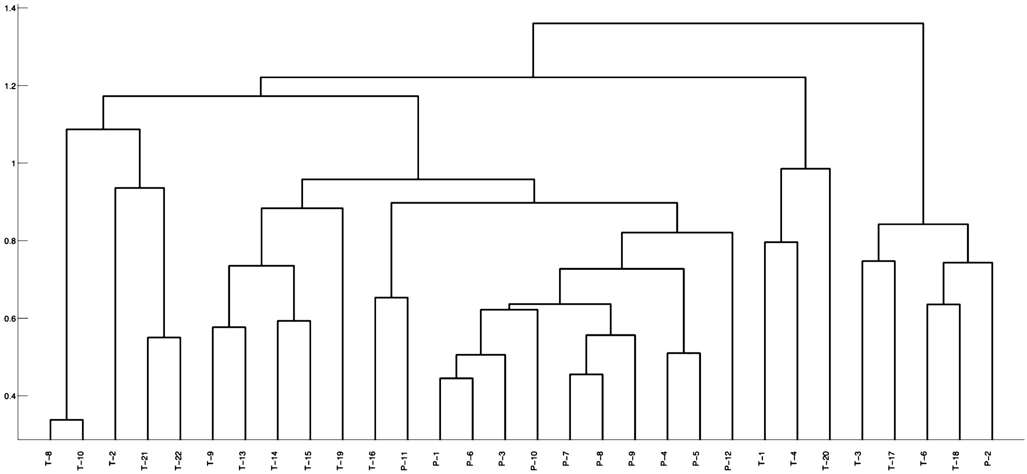

Figure 2 *A dendrogram from Talavera de la Reina and El Puente del Arzobispo, using Nb as divisor in the logratio transformation on the subcomposition of* Na_2O, MgO, Al_2O_3, SiO_2, P_2O_5, K_2O, CaO, TiO_2, MnO, Fe_2O_2, *Sc, V, Cr, Co, Ni, Zn, Rb, Sr, Zr, Nb, Cs, Ba, La and Th. The dendrogram plot has been obtained using the routine of the MATLAB dendrogram.*

results show that there is homogeneity in the Puente production, something that is not present in that of Talavera.

The chemical elements that provide the main differences between the two productions (see Table 2) are mainly P_2O_5 and Na_2O, and Sr and Zr to a lesser extent. The average P_2O_5 level in Talavera is double that of Puente, and the Talavera average Na_2O level is 45% higher than that of Puente. These two elements should be used cautiously because they are conditioned by external factors. In fact, P_2O_5 and Na_2O, along with Cs and K_2O, are elements that provide a greater variability, and the $vt/\tau_{.j}$ of which is less than 0.4 (Table 4). Na_2O and K_2O are two elements the levels of which are influenced by alteration and contamination processes during burial. The process is related to the formation of analcime during the burial period and it involves the leaching of Rb and K_2O and Na_2O fixation on the pieces, so that the individual items with analcime have below average K_2O and Rb levels and higher Na_2O levels (Buxeda 1999). This variability can be seen in Figure 3, which shows the results of the variation matrix graphically. P_2O_5 is the element that brings about greater variability due to alteration that originates during the burial process and not, in any case, during the ceramic production process (Lemoine and Picon 1982).

The dendrogram study allows the identification of up to six different possible groups. Amongst them, there is a prominent group in the central part of the graph that represents the majority of the fragments corresponding to production from El Puente del Arzobispo. Within this group, there are two exceptions in two fragments, one of which, I_c T-16, is found within this group, while the other one, I_c P-2, is outside the Puente group.

I_c T-16 was archaeologically categorized as coming from Puente because of its decoration, but was then renamed and included in the Talavera group, among other reasons because it was found in the centre of Talavera (in Pescaderias Street). It is not unusual to find fragments from one production centre in the other one. However, considering that Talavera pieces were represented in Puente (Sánchez Pacheco 1997), it is more probable that Talavera fragments will be found in

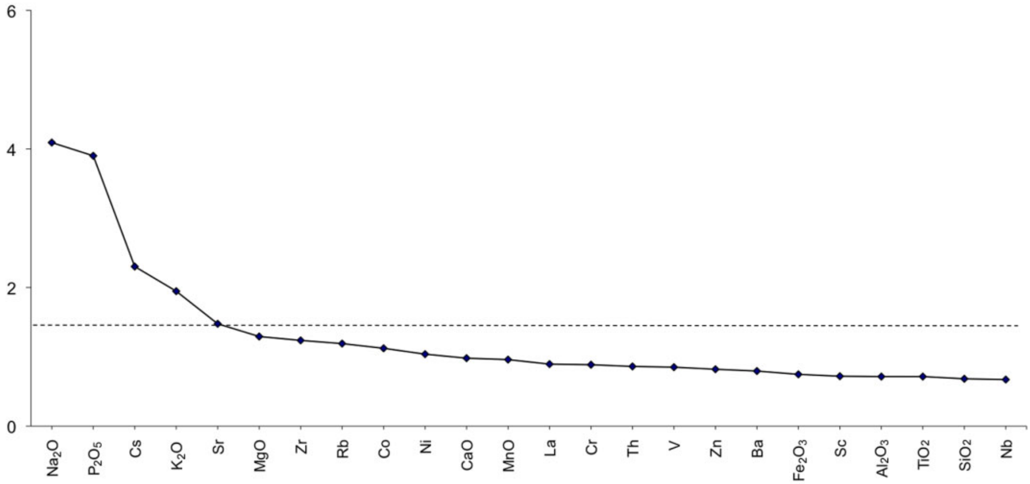

Figure 3 *A uniform chart: the y-axis corresponds to* $\tau_{:j}$ *and the x-axis to the 24 studied elements.*

Puente than the other way round. I_c P-2 was archaeologically classified from Puente even though it was found in the centre of Talavera (also in Pescaderias Street). This fragment was not renamed. From the dendrogram, we can observe that I_c T-16 could be included within the named Puente group. If we take into consideration the initial archaeological classification, this fragment should be included in the Puente group due to its closer chemical composition to this group. However, I_c P-2, which appears to be distant from the rest of the Puente fragments, could be reclassified as coming from Talavera, given that it has a chemical composition that is closer to the fragments from the last but one group classified as such.

The other five possible groups, considered to be from Talavera, are made up from only a few fragments. In contrast, the first group, consisting of fragments T-8 and T-10, stands out because they are the ones that have more in common. They have a very similar chemical composition, but also they were both found in the same physical space (Lagar de Postiguillos) in the 18th century. However, most groups that appear in the dendrogram do not present similarities or differences based on their provenance, chronological or decorative origin.

These fragments come from very different excavations and periods, and they do not present a nexus as far as a chemical composition study is concerned. As an exception, we must point out the fragments from Lagar de Postiguillos, the aforementioned T-8 and T-10, and also fragments T-9 and T-13, which were also found in the same place and are shown together in the dendrogram.

Another point to be considered is the formation of secondary minerals such as analcime or calcite (discussed in the mineralogical and thermal analysis sections) that could provide an explanation for the different groups presented in Figure 2.

In summary, the statistical analysis of the samples reflected in the dendrogram seems to show homogeneity for the production from El Puente del Arzobispo, which is not found in Talavera de la Reina, as also observed by Iñañez *et al.* (2006). It is difficult to determine the causes of the differences between the two productions. We propose several options separately, although the phenomenon might be multi-causal:

- The homogeneity in the Puente production could be due to the common physical origin of the samples. It should be noted that all of them could have some kind of characteristic alteration of burial place. However, the Talaveran samples were recovered from five different excavations.

- Another explanation to illustrate the homogeneity in El Puente del Arzobispo could focus on its pottery tradition. Potters from Puente used to imitate Talaveran models, their decorative motifs and their ceramic typology; however, they might not have had the same determination or resources as the Talaveran potters, who tried to innovate in their technological processes. These modifications, conditioned by the different trends that influenced the Iberian Peninsula, could involve changes in the formulation of raw wares and glazes.
- Also, it is possible that the quarry had separate areas for each of the two production centres.

Mineralogical analysis

The mineralogical study of the analysed ceramic fragments indicates estimated firing temperatures higher than those previously mentioned in the introduction to this work, and that range between 880°C and 920°C. Diffractogram analyses allow us to place these analysed individuals into different groups, according to their mineralogical similarities and differences. The presence or absence of some specific minerals allows us to learn the estimated firing temperature of each sample (EFT). On the basis of these criteria, and using the chemical study, a division has been made into different factories. Also, we have followed Iñañez's criteria (Iñañez 2005; Iñañez *et al.* 2005), who in his turn took his lead from Whitbread (1989): 'understanding by factory (F), the distribution, frequency, shape, size and composition of the ceramic components'.

Every ceramic fragment analysed in this study has a common mineral composition based on quartz crystalline phases, feldspars (plagioclase) such as anorthite, and pyroxenes. In some diffractograms, crystalline phases have been detected associated with micas (muscovites), pyroxenes (augite or diopside), gehlenite and hematites, the formation of which can occur in the presence of iron (Velde and Druc 1999).

In individuals T-5, T-6, T-7 T-17, T-18, T-21 and all those from Puente, except for P-11, a reflection appears at 3.04 Å, assigned to calcite. This is a mineral that may have been formed during burial (Fig. 4, central diffractogram). This point will be discussed in greater detail in the section on the scanning calorimetry study.

Individuals marked with an asterisk in Table 5 have a peak at 3.43 Å, which has been assigned to analcime, the formation of which has taken place during the burial process due to the leaching of potassium and rubidium, in which the sodium from the circulating waters has been fixed on such individuals (Fig. 4, central diffractogram) (Tsantini *et al.* 2004).

From this mineralogical study, we have considered the existence of three factories, each one with a different EFT. In Table 5, the individuals have been classified according to their locations in these three factories:

- *Fabric 1*. The first group has the presence of gehlenite as a common denominator, and also traces of mica (muscovite). Gehlenite forms at 800–850°C and starts decomposing at 1050°C.

Table 5 *Individuals according to their EFT and place of origin: an asterisk indicates the presence of analcime on the marked individuals; number of individuals, 32*

Individuals	*Fabric 1 (850–950°C)*	*Fabric 2 (950–1050°C)*	*Fabric 3 (1050°C)*
Talavera	T-1, T-2, T-5,* T-8, T-10, T-15, T-16, T-21	T-3, T-4, T-6,* T-9, T-17,* T-18,* T-19,* T-20, T-22	T-13, T-5, T-14
Puente	P-11	P-1, P-2,* P-3, P-8, P-9	P-4,* P-5,* P-6, P-7,* P-10, P-12*

The presence of micas indicates that the firing temperature has not exceeded 950°C; otherwise decomposition would have taken place. Therefore, an estimated firing temperature of around 850–950°C corresponds to this group.

- *Fabric 2*. This group is associated with an EFT between 950°C and 1050°C. This is because micas have decomposed completely (from 900–950°C) and also because gehlenite still remains, usually decomposing around 1050°C. We have subdivided this fabric for those individuals with analcime, as identified in Table 5.
- *Fabric 3*. This group is formed of samples with quartz crystalline phases, the intensity ratio of which is lower than that of pyroxene. For the rest of the group, the relative intensity of quartz is always superior to the other minerals that form the diffractogram. In this case, the relative intensity of augite is considerably higher than that of quartz, meaning that higher temperatures have been reached. We have to take into consideration the presence of a peak at 3.27 Å, assigned to leucite. The presence of this feldspathoid and gehlenite allows an EFT of around 1050°C. There is also a subdivision in this group corresponding to those individuals with analcime.

The mineralogical analysis of biscuits B-1 and B-2, both of which come from Puente, indicates the presence of crystalline phases of quartz, gehlenite, pyroxene and feldspar. Only B-2 presents muscovite levels, which are fairly characteristic of pieces that have not reached high temperatures and need to be glazed afterwards. A biscuit must have a certain level of porosity to allow this glazing process. Sample B-2 presents calcite and analcime levels, which have probably been formed during the burial process. Nevertheless, sample B-1 does not fit in with the definition of a biscuit, because its diffraction pattern indicates a pyroxenes relative intensity that is almost identical to that of quartz and an absence of micas. This means that we are able to estimate a firing temperature above 950°C, which would make the glazing very difficult.

Talaveran biscuit B-3 has a similar mineralogy to the rest of the biscuits. It presents mica (muscovite), which indicates a firing temperature range around 850–950°C.

At a technological level, the results from the mineralogical study show that the majolica ceramics from Talavera and Puente are calcareous. The existing differences among the 32 glazed ceramic fragments analysed here correspond to the technological differences that the actual manufacturing process entails, and correspond especially to the differing EFTs. However, Table 5 shows a different tendency in that respect. Most of the Talavera samples are situated within the first two factories, the EFTs of which correspond to the lower temperature levels. On the other hand, half of the Puente samples belong to the last factory, with an assigned average temperature of 1050°C. In the Talaveran case, only 15% of the samples belong to this factory. On the basis of the results shown in Table 5, we could say that there is a considerable difference between the two production centres, since the Puente potters have fired at higher temperatures than those from Talavera.

In the introduction to this paper, we cited the criteria used by the experts to differentiate between the glazes from Talavera de la Reina and El Puente del Arzobispo. The premise is that the Puente production is of a lower quality than that from Talavera. According to most authors, this difference in terms of quality and tonality is due to the differences in the chemical composition of the glaze—especially in the use of tin in these formulations. With regard to firing temperatures, a minor use of tin, which is in fact a flux, would imply having to fire at higher temperatures. In fact, several authors assert that there is a tendency to use a lower amount of tin—which is also one of the most expensive ingredients—in El Puente del Arzobispo (Vaca González and Ruiz de Luna 1943; Martínez Caviró 1984). Vaca González and Ruiz de Luna (1943) even quantify the amount of tin for each producing centre, with 25% for Talavera and only

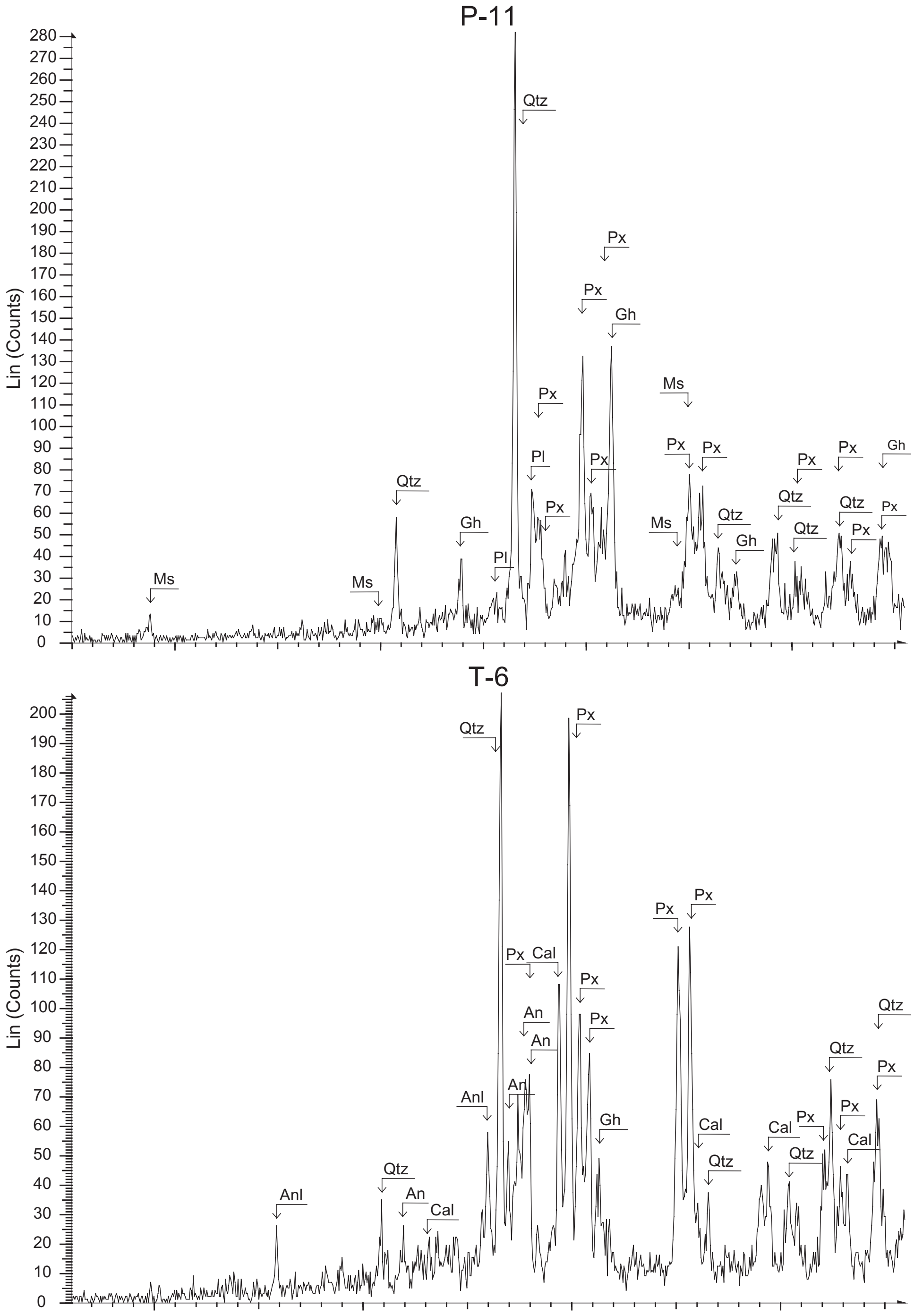

Figure 4 *Upper diffractogram, P-11, representing Fabric 1; central diffractogram, T-6, representative Fabric 2; bottom diffractogram, P-5, representing Fabric 3. Abbreviations after Kretz (1983). Ms, muscovite; An, anorthite; Qtz, quartz; Lct, leucite; Anl, analcime; Cal, calcite; Px, pyroxene; Gh, gehlenite; Pl, plagioclase.*

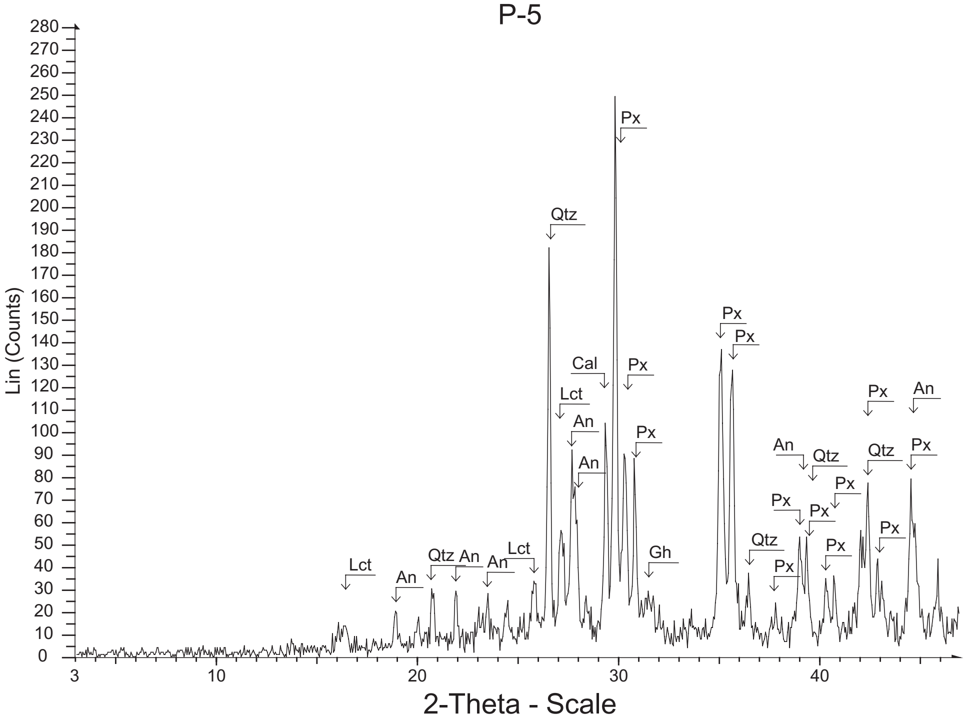

Figure 4—*continued.*

5% for Puente. In accordance with the cited references, a reduced use of tin in Puente could mean an increase in the average of the firing temperatures.

Differential scanning calorimetry and thermogravimetrical analysis (DSC–TGA)

The mineralogical characterization has shown the presence of calcite in the majority of the studied diffractograms (Fig. 4, central diffractogram). A more accurate study of this mineral appears to indicate its origin. There seem to be crystalline phases of secondary calcite, which means that they have been formed after the manufacturing process, and not during firing. There are various studies (Buxeda and Cau 1995; Papachristodoulou *et al*. 2006) that try to offer a number of explanations of the secondary calcite problem and propose different solutions in order to determine its origin. In spite of divergent opinions among the experts, it is commonly accepted that in most cases, calcite has been formed because of an allochthonous contribution, such as circulating water.

The thermogram of individual T-21 (Fig. 5) is used as a representative example of those individuals with calcite in the diffractograms. The DSC curve indicates an endothermic peak at 705°C, which corresponds with a loss on ignition of 6.5%, reflected in the TGA. The total loss on ignition is 8.7%. This sample comes from a ceramic fired at around 850°C, and its loss is associated with neoformation calcite, which originates during the burial process, thus confirming what the mineralogical analysis has indicated.

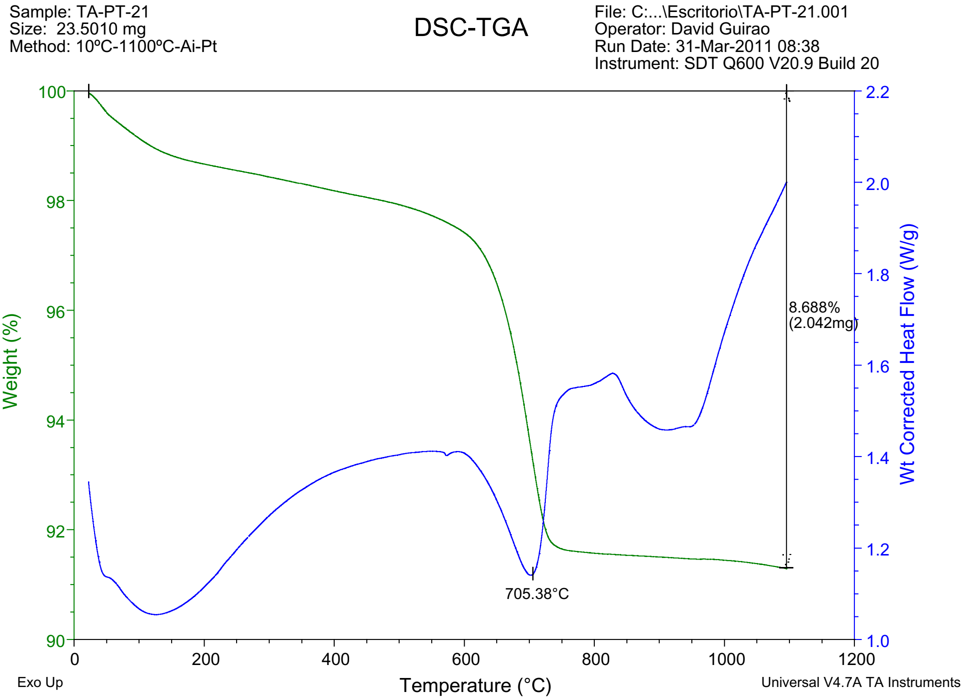

Figure 5 *The thermogram of* I_c *T-21.*

CONCLUSIONS AND FUTURE STUDIES

This archaeometric study of 35 individuals has allowed us to define the chemical and mineralogical composition of the ceramic production from Talavera de la Reina and El Puente del Arzobispo.

The chemical analysis confirms common origin of the the raw materials, which the bibliographical sources corroborate. The chemical composition study of the two producing centres seems to show certain differences, which could be used to differentiate between the productions from Talavera and Puente. The statistical analysis realized on 30 glazed fragments provides a graphical and global view of how individuals interrelate and how they are chemically grouped together. This is a very useful tool for our study, because it offers a new panorama in which the Puente production seems to present a greater homogeneity compared to that of Talavera. This may be because the Puente production comes from a single place, the Puente *testar*, or simply because its working method followed a more rigorous standard than in Talavera. In order to to corroborate the hypotheses presented in this study, it would be necessary to prepare a larger sample.

The mineralogical study of the individuals from Talavera and Puente, obtained by XRD, shows that there are certain differences concerning the technological process related to the firing temperatures of the ceramics. These differences can be explained by the glazing manufacturing process, since each craftsman had his own formula and also mixed in different proportions. Therefore, the mineralogical study shows that the estimated firing temperatures of these ceramics considerably exceeds the temperature range that has been traditionally accepted (880–920°C). In fact, only the first factory would fall into the aforementioned range.

The DSC–TGA analysis, which complements the mineralogical study, has allowed us to detect certain alterations (calcite and analcime) that occur during burial.

In future studies, it would be interesting to work with a larger number of samples for each artistic series, so that we can obtain more criteria with which to characterize the production of each population. Talavera de la Reina supplied numerous points of the peninsula and colonies overseas. This kind of study can engender deeper knowledge of the trade relationships between the different geographical areas (the colony and the production centre) and also other aspects of the artistic influences, and the economic and social characteristics.

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REFERENCES

Aitchison, J., 1986, *The statistical analysis of compositional data*, Chapman and Hall, London.

Alvigini, A., 2006, *El hombre y el barro: historia de la cerámica de Talavera*, Excmo. Ayuntamiento de Talavera de la Reina, Talavera de la Reina.

Ballesteros, G. A., 1983, *Cerámica de Talavera: tres tiempos para una historia*, Diputación Provincial de Toledo, Toledo.

Bishop, L. R., Rands, R. L., and Holley, R. G., 1982, Ceramic compositional analysis in archaeological perspective, in *Advances in archaeological method and theory*, vol 5 (ed. M. B. Schiffer), 275–330, Academic Press, New York.

Boch, Ph., and Lejeune, M., 1984, Le feu et l'argile: physico-chimie des cerámiques, *PACT*, **10**, 223–36.

Buxeda i Garrigós, J., 1999, Alteration and contamination of archaeological ceramics: the perturbation problem, *Journal of Archeological Science*, **26**, 295–313.

Buxeda i Garrigós, J., and Cau Ontiveros, M. A., 1995, Identificación y significado de la calcita secundaria en cerámicas arqueológicas, *Complutum*, **6**, 293–309.

Buxeda i Garrigós, J., Cau i Ontiveros, M. A., Gurt i Esparraguera, J. M., and Tuset, F., 1994, Análisis tradicional y análisis arqueométrico en el estudio de las cerámicas comunes de la época romana, *Monografies Ampuritanes*, **VIII**, 38–63.

Coll Conesa, J., 2008, La Loza decorada en España, *Ars Longa*, **17**, 151–68, Universitat de Valencia.

González Moreno, F., 2002, *Decadencia y revival en la azulejería talaverana: retablos, altares y paneles del 'Renacimiento Ruiz de Luna'*, Excmo. Ayuntamiento de Talavera de la Reina, Talavera de la Reina.

González Zamora, C., 2004, *Talaveras*, Antiquaria, Madrid.

Hein, A., Tsolakidou, A., Iliopoulos, I., Mommsen, H., Buxeda i Garrigós, J., Montana, G., and Kilikoglou, V., 2002, Standardisation of elemental analytical techniques applied to provenance studies of archaeological ceramics: an inter laboratory calibration study, *The Analyst*, **127**, 542–53.

Henderson, J., 2000, *The science and archaeology of materials: an investigation of inorganic materials*, Routledge, London.

Hurley Molina, M. I., 1989, *Talavera y los Ruiz de Luna*, Instituto Provincial de Investigaciones y Estudios Toledanos, Toledo.

Iñañez G. J., 2005, *Caracterització arqueométrica de la cerámica vidriada decorada de la Baixa Edat Mitjana al Renaixement als centres productors de la Península Ibèrica*, Doctoral thesis, Universitat de Barcelona, Barcelona.

Iñañez, G. J., Buxeda i Garrigós, J., Speakman, R. J., and Glascock, M. D., 2006, Archaeometric characterization of Renaissance tin lead glazed pottery from Talavera de la Reina, Puente del Arzobispo and Seville (Spain), in *ISA 2006: proceedings/acts—36th International Symposium on Archaeometry/36^e Symposium International d'Archéometrie, Quebec (Canada)* (eds. J.-F. Moreau, R. Auger, J. Chabot and A. Herzog), 279–87, Cahiers d'archéologie du CELAT 25, Université Laval.

Iñañez, G. J., Schwedt, A., Madrid i Fernández, M., Buxeda i Garrigós, J., and Gurt i Esparraguera, J. M., 2005, Caracterización arqueométrica de los principales centros catalanes de cerámica mayólica de los siglos XVI y XVII, in *Avances en arqueometría 2005*, *VI Congreso Ibérico de Arqueometría de Girona (Spain)*, 97–108.

Kretz, R., 1983, Symbols of rock-forming minerals, *American Mineralogist*, **68**, 277–79.

Lambert, J. B., 1998, *Traces of the past: unraveling the secrets of archaeology through chemistry*, ch. 3, 48–70, Perseus Publishing, Cambridge, UK.

Lemoine, C., and Picon, M., 1982, La fixation du phospore par les ceramiques lors de leur enfouissement et ses incidences analytiques, *Revue d'Archaeometrie*, **6**, 101–12.

Martínez Caviró, B., 1984, *Cerámica de Talavera*, Consejo Superior de Investigaciones Científicas, Madrid.

Papachristodoulou, C., Oikonomou, A., Ioannides, K., and Gravani, K., 2006, A study of ancient pottery by means of X-ray fluorescence spectroscopy, multivariate statistics and mineralogical analysis, *Analytica Chimica Acta*, **573–4**, 347–53.

Picon, M., 1973, *Introduction à l'étude technique des céramiques sigillées de Lezoux*, Centre de Recherches sur les techniques gréco-romaines, vol. 2, Université de Dijon.

Picon, M., 1981a, Problèmes de detérmination de l'origine des cerámiques, *PACT*, **10**, 423–33.

Picon, M., 1981b, Le traitement des donnés d'analyse, *PACT*, **10**, 379–99.

Pleguezuelo, A., 1992, Sevilla y Talavera: entre la competencia y la colaboración, *Laboratorio de Arte*, **5**, 275–93, Sevilla.

Pleguezuelo, A., 2001, *Lozas contrahechas: ecos de Talavera en la cerámica española, Talavera de la Reina y Puente del Arzobispo*, 37–53, Colección Bertrán y Musitu, Museo de Cerámica de Barcelona.

Pollard, M., Batt, C., Stern, B., and Young, M. S., 2007, *Analytical chemistry in archaeology*, Cambridge University Press, New York.

Portela Hernando, D., 1999, Apreciaciones sobre la evolución de 'Las Talaveras': siglos XVI–XVIII, *Boletín de la Sociedad Española de Cerámica y Vidrio*, **38**, 329–34.

Sánchez Pacheco, T., 1997, *Cerámica de Talavera de la Reina y Puente del Arzobispo: cerámica española*, 305–42, T. Sanchez Pacheco, Summa Artis, Espasa Calpe, 42. S.A., Madrid.

Tsantini, E., Buxeda i Garrigós, J., Cau i Ontiveros, M. A., and Orfila Pons, M., 2004, Caracterización arqueométrica de la cerámica común producida en la villa romana de Sa Mesquida (Mallorca), *Pyreanae*, **35**(1), 157–86, Barcelona.

Tsetlin, Yu. B., and Volkova, E. V., 2011, The role of science-based methods in the study of ancient pottery as a source of historical information, *Archaeology Ethnology & Anthropology of Eurasia*, **38**(4), 52–9, SB RAS Press, Novosibirsk.

Vaca González, D., and Ruiz de Luna, J., 1943, *Historia de la cerámica de Talavera de la Reina y algunos datos sobre la de Puente del Arzobispo*, Editora Madrid Nacional.

Velde, B., and Druc, I. C., 1999, *Archaeological ceramic materials: origin and utilization*, Springer-Verlag, Berlin.

Whitbread, I. K., 1989, A proposal for the systematic description of thin sections towards the study of ancient ceramic technology, in *Archaeometry: proceedings of the 25th International Symposium, Athens* (ed. Y. Maniatis), 127–38, Elsevier, Amsterdam.