ARCHAEOMETRIC ANALYSIS OF ASTURIAN POTTERY IN XVI-XVII CENTURIES

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Resumen

Ofrecemos en este trabajo los resultados de los primeros análisis arqueométricos realizados sobre producciones cerámicas elaboradas en Asturias (España) entre principios del siglo XVI y mediados del siglo XVII. Se han seleccionado 10 muestras pertenecientes a las tipologías más representativas de la cerámica asturiana de esta época. Las muestras han sido estudiadas utilizando diversas técnicas de análisis: Fluorescencia de Rayos X (XRF), para la cuantificación elemental de los componentes de cada muestra y Glow Discharge Time of Flight Mass Spectrometry (GD-ToFMS) para conocer los elementos minoritarios presentes. Los datos aportados nos permitirán caracterizar y conocer desde un punto de vista físico-químico las producciones que se elaboraban en Asturias a finales de la Edad Media.

1. Introduction

At the beginning of the modern age, most of the pottery produced and widely used in Asturias (Spain) came from Faro (Oviedo) and Miranda (Avilés). The place of Faro was active from the XI-XII centuries (Fanjul et al., 2013, pp. 2-3) while Miranda, although we do not have reliable data, it is thought that the potters worked as long ago as Late Middle Ages (Feito, 1985, p. 145).

The pottery found at these production sites are the most abundant in any urban archaeological excavation that has taken place in Asturias. Furthermore, these productions sites are the precedent of the *cerámica negra*. Therefore, when the pottery from Faro and Miranda were studied, a key production sites used to understand the Middle and Modern ages in Asturias were investigated. Due to this historical relevance, the archaeometric characterization is used to learn about the production methods in these areas and to define reference for compositional analysis.

2. Material and Methods

In order to characterize the production sites of Faro and Miranda, we have chosen a population of 10 individual pieces of pottery as representative samples (Figure 1). These samples belong to the archaeological excavation of *Casa Carbajal Solís*, dated from the XVI-XVII centuries and they have been samples of different functional, formal and typological studies (Busto Zapico, Gutiérrez González and Estrada García, 2015, p. 466). Based on this previous research, we are able to establish the provenience of our 10 samples and relate them to their production site through macroscopic analysis of the different techno-typological groups (Busto Zapico, 2015, pp. 36-37). Therefore, we will not work with the fragments recovered in the pottery centre and it will be not possible to define Reference Groups, just Paste Compositional Reference Units (Buxeda i Garrigós, Cau Ontiveros, Gurt i Esparraguera and Tuset i Bertran, 1995, 1995).

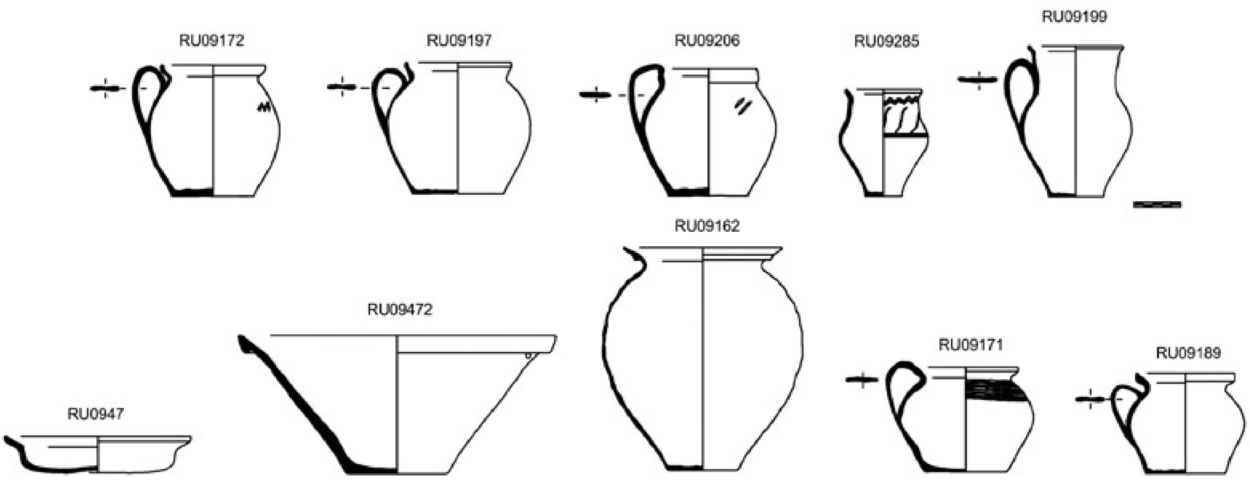

Fig. 1 Pottery cases analyzed.

The samples are classified as follows: 6 pieces came from the pottery center of Faro (Busto Zapico, 2015, pp. 39-52). Specifically, the types that are present as follow: *Puchero II* (RU09172, RU90197), *Puchero III* (RU09206), *Jarrita II* (RU09285), *Jarrita IV* (RU09199) and *Plato II* (RU0947). From Miranda there are only two typologies (Busto, 2015, pp. 52-55): *Vedrio I* (RU09472) and *Cántaro I* (RU09162). Finally, two samples do not reveal clear parallels to any others. They could seem to be related to ancient productions sites or a different pottery center not readily known (Busto Zapico, 2015, pp. 55-59). They are *Puchero I* (RU09171) and *Puchero IV* (RU09189). In this study, the objective was to study the most represented Asturian pottery typologies from the XVI-XVII centuries, taking into account the products destined for food processing, as well as their presentation and social consumption.

Using the 10 samples, we have conducted different chemical analyses using X-ray fluorescence (XRF) and Glow-discharge time-of-flight mass spectrometry (GD-ToFMS) at the Scientific-Technical Services at the University of Oviedo. From each individual sample, 1g was taken, pulverized, and homogenized by mill RS4494364 (Retsch Mühle, Germany). The preparation of the was pearls done following the standard procedure (alkaline fusion in $LiBO_4$ matrix). The sample analysis by XRF was performed using a spectrometer PHILIPS PW2404 (Philips, Germany) equipped with an automatic loader PW2540, and a 4Kw power Rh excitation source. The GD-ToFMS used is an instrument equipped with a pulsed radiofrequency source and a time-of-flight mass analyzer (Nelis et al., 2015, pp. 389, 763-767). The used prototype is composed by a glow discharge (Horiba Jobin Yvon, Longjumeau, France) coupled to a time of flight mass spectrometer with orthogonal geometry (Tofwerk, Switzerland).

3. Results

The results obtained by XRF have been used to perform the quantification of the mayor constituents in the samples. Results provided by XRF has been also used to validate the date obtained from GD-ToFMS analysis as it will be discussed later on. Thus, it can be observed how all the analyzed pottery pieces are mainly composed by SiO_2, Al_2O_3, Fe_2O_3, and to a lesser extent, K_2O. There is no appreciably great variability among the analyzed samples with regard to major components (Figure 2). It is worth noting the low content of calcium oxide, even in the RU0947 sample, as it is discriminant, because the sample is a glazed piece and as such, a high calcareous content is expected.

Furthermore, the results obtained by XRF have been used to corroborate the use of the GD-ToFMS technique for the qualitative analysis of the minor elements. As it can be seen in Figure 3, the signals obtained by the GD-ToFMS technique show a linear correlation when they are represented facing the concentrations obtained by the XRF (reference technique for this type of analysis). This allows us to use the GD-ToFMS signals for minor elements as new factors for the discrimination and characterization of units of compositional reference.

After GD-ToFMS results validation, the different mass spectra (Figure 4) obtained for minor elements shows how the signal, and therefore the

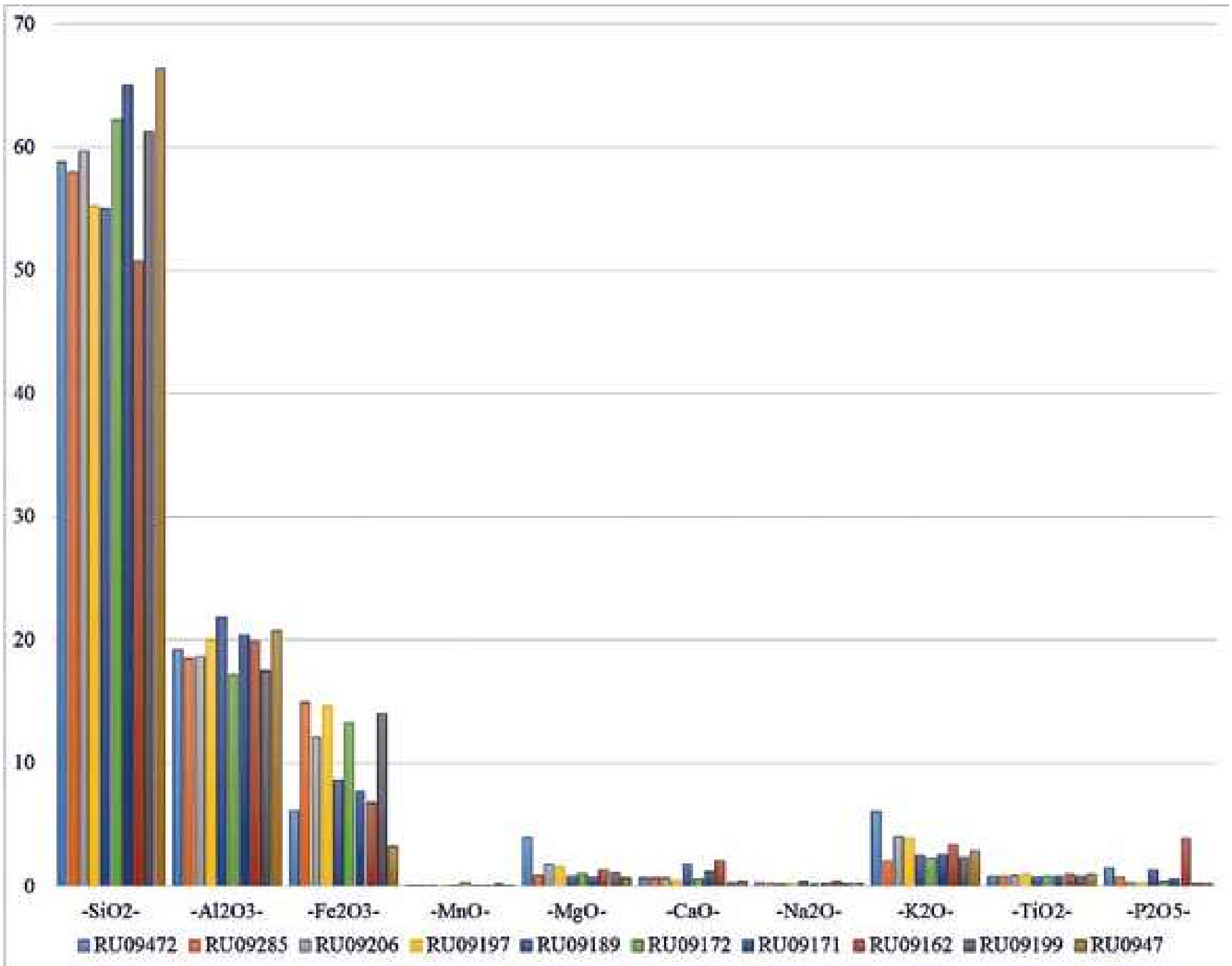

Fig. 2 XRF quantitative results of the different samples analyzed.

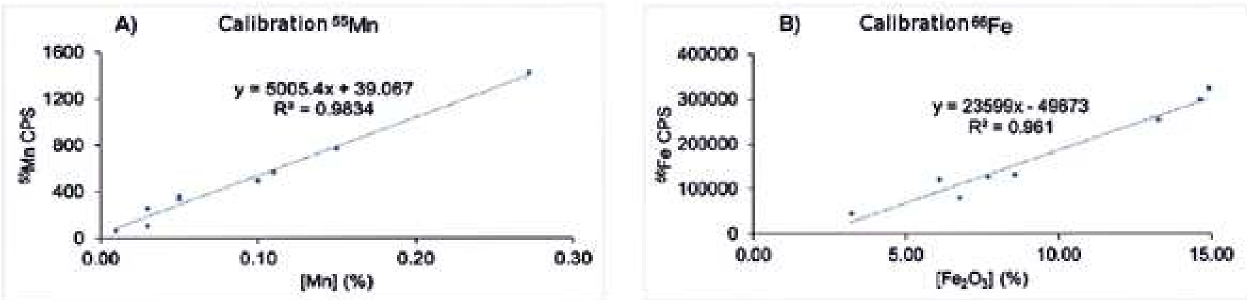

Fig. 3 A) Calibration curve of the signals obtained through GD-ToFMS for ^{55}Mn, where "y" is the intensity of the signal per second, and "x" is the concentration obtained by XRF for the Mn. B) Calibration curve of the signals found through GD-ToFMS for ^{56}Fe, where "y" is the intensity of the signal per second, and "x" is the concentration obtained by XRF for the Fe. In both cases, "R^2" is the determination coefficient of the analysis by linear regression of the calibration curve.

concentration of the minor elements (e.g. Pt, Au, and Hg), vary significantly between the analyzed samples. It can be observed that all the samples include Au and Pt, but not in the same amount. At the same time, in all cases small signals of Hg are obtained. On the other hand, only five samples contain Bi and Pb (RU0947, RU09189, RU09206, RU09285, and RU09472). Hence, the qualitative results obtained for minor elements will be used to carry out a statistical analysis including these elements as discriminant factor, looking for a better differentiation between the samples.

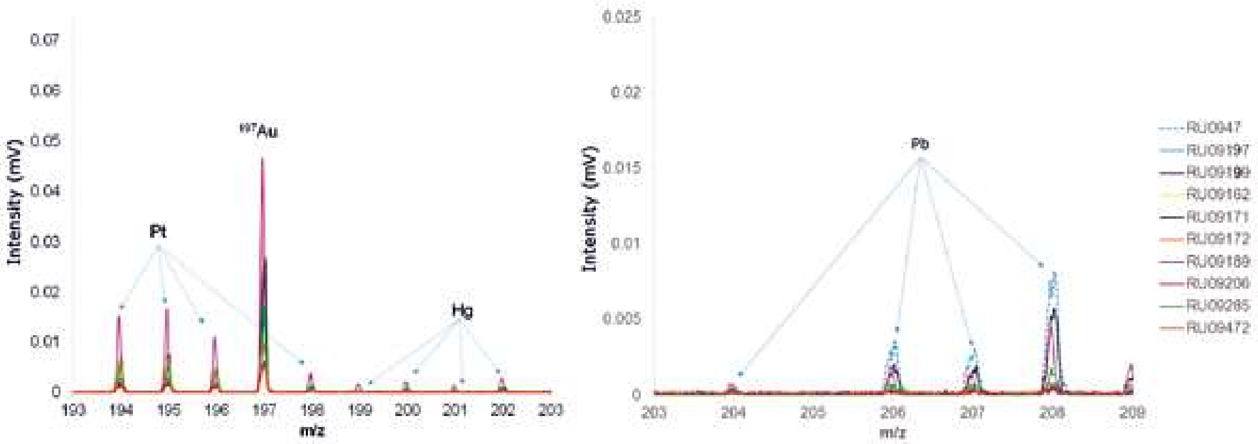

Fig. 4 A) GD-ToFMS Mass spectra for minor elements (Pt, Au, Hg, and Pb) in the analyzed samples.

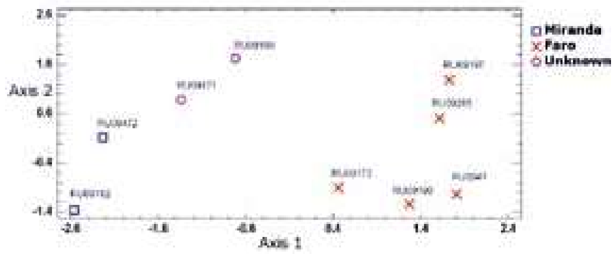

Fig. 5 Result of the discriminant analysis using Fe, Al, Au and Pb as variables.

Joining the results of both analytical techniques (XRF and GD-ToFMS), a discriminant analysis has been performed. The result of the analysis, using the variables (Fe, Al, Au and Pb), due to the better differentiation obtained between the different samples, can be observed in Figure 5. It can be seen that the samples congregate around three different groups or Paste Compositional Reference Units.

4. Discussion

Since the samples analyzed were just 10, the conclusions are a preliminary statement. Even though; this research opens the door to other archaeometric studies in the future. The capabilities of GD-ToFMS technique for the identification of major and minor elements constituting the different samples has been proved. It has been checked the potential capabilities to develop qualitatice analysis of the minor elements from the different samples, as the results were validated for the mayor elements based on the concentration results obtained by XRF.

In this context, it is possible to analyze different elements that usually are not studied in this type of samples due to their low concentration. The minor components could be used as discriminant factor during the classification study upon the different pottery pieces origin. As it has been observed, the discriminant analysis offers better results when these variables are used during the classifying study.

Faro and Miranda production sites are specific Paste Compositional Reference Units. It is worth to notice that it does not seem to exist any chemical difference among the production sites of Faro regarding the common pottery and the glaze one that we have analyzed (RU0947). Therefore, it is probable that the clay was the same, and the differences are due to the production process.

In the same way, a third group seems to be identified. In this group, we found pieces with an older chronology, probably from Late Middle Ages (Busto Zapico, 2015, pp. 49-58). We cannot made a conclusion about this third group of classification but, yo lo quitaría, we can presume different possibilities. In one hand, it could be a different pottery workshop or different productions made around Faro. In the other hand if they are productions from Faro, their chemical differences could indicate that different points of clay caption change between the Middle Ages and the Modern Ages. Other possibility is that the pottery made at the production site of Faro change during that time too. If they are producing in a different manner the composition could be also altered and form this third group.

As previously said the conclusions here presented are preliminary. It is necessary to expand the number of samples, using fragments directly recovered in the pottery centre, and analyze autochthonous clays supposedly used for the production of potteries. Thus, the study could be completed in a reliable manner and chemical reference groups for the Asturian pottery could be established from the sixteenth and seventeenth centuries.

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