

## MING PORCELAIN FROM THE SANTA CLARA-A-VELHA MONASTERY IN COIMBRA, PORTUGAL. FIRST RESULTS USING A PORTABLE $\mu$ -EDXRF SPECTROMETER

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**ABSTRACT.**  $\mu$ -EDRFX was applied for a non destructive analysis of 12 sherds of Chinese porcelain from the archaeological site of the Monastery of Santa Clara- a-velha, Coimbra.(Portugal).Ten of them are typically Chinese, but two are slightly different from the rest of the sherds, possibly of a different origin. The glazes, pigments and pastes were analysed. The analysis was done by comparison of the ratios Mn/K, Fe/K and Co/K. The results might indicate the use of different cobalt pigments, one rich in iron and other rich in Mn. The light and dark blue areas also did not show the same proportion in the studied ratios, which might indicate different compositions in the pigments. Concerning the two slightly different sherds the obtained results were not conclusive.

### Introduction

The Monastery of Santa Clara-a-Velha, located on the left bank of the Mondego river, was built in 1314 at the site of an earlier church of Clarisse Nuns (founded in 1283), under the patronage of the Saint Queen Isabel of Aragão. The gothic style monument was repeatedly flooded by the rise of Mondego waters which demanded some architectonic transformations such as the inclusion of an intermediate floor, with the consequent abandonment of the flooded lower floor. During the XVII c. the religious community was transferred to the new monastery of Santa Clara-a-Nova on higher grounds (Santos, 2003). Recently a vast archaeological campaign was launched which included the lowering of the water table by permanent pumping, to allow excavations and clearing of the cloister and church to the ground level. During the excavation process several important finds allowed acquiring better knowledge of everyday life of this monastic community, such as adornments, tools, utensils, textile, glass and ceramics (Santos, 2003).

The present work is concerned with porcelain finds in the archaeological site of Santa Clara-a-Velha. Over 7000 sherds of Chinese porcelain were unearthed and until now more than 360 pieces have been partially reconstructed.

### Materials

The materials for the present study were provided by the Archaeologic Nucleous of the Santa Clara-a-Velha Monastery and include 12 selected sherds with different characteristics and manufacture periods (Fig. 1) mainly belonging to the Ming dynasty. The use of blue under-glaze was introduced during the Yuan dynasty and also during the Ming period that was proved to be highly successful and popular (Wen et al., 2007).

Although recently it has been considered to be more correct to classify the Chinese Porcelain according to the date of the best studied sherds, the classification was made according to the reign. It was done in the most common way recurring to previous classified object. The most ancient pieces probably date from the Zhengde reigns (1506-1521). The other sherds are from the Jiajing (1522-1566) and Wanli (1575-1619) reigns (Table 1).

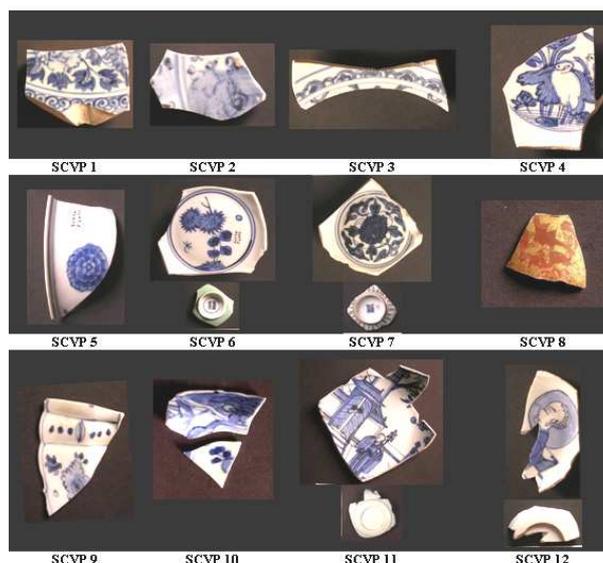


Fig. 1. Photographs of the samples SCVP1 to 12 (the photographs are not in the same scale)

However, three of the sherds are of unknown date or origin. Pictorial and manufacture characteristics of SCVP11 and 12 are slightly different and that gave grounds to suggest a

possible Japanese origin. Towards the end of the Ming period the quality of porcelain declined and the monopoly of the trade was lost (Bartle et al., 2007; Wen et al., 2007). During this time Japanese porcelain had a major role in the ceramic trade with Europe, the Imari porcelain as one the best known (Bartle et al., 2007).

The studied sherds, as the majority of the pieces found in the archaeological site, are decorated with blue under-glaze (BU) except a red Kinrande piece (SCVP8). Three fragments are polychrome (P) two are Kinrande pieces (one apple green, SCVP6, and one red, SCVP8) and one decorated with red, green, yellow and black/brown enamels, SCVP7.

Table 1  
Short characterization of the samples SCVP 1 to 12. Glaze (G), Blue (B), Dark Blue (DB) and Enamel (E)

Sample	Century	Descrip	Part analysed			
			G	B	DB	E
SCVP1	Early 16 <sup>th</sup> cent.	BU	G	B	DB	E
SCVP2	Early 16 <sup>th</sup> cent.	BU	X	X	X	
SCVP3	Unknown Wanli?	BU	X	X	X	
SCVP4	Jiajing	BU	X	X	X	
SCVP5	Jiajing	BU	X	X	X	
SCVP6	Jiajing	BU/P	X	X	X	X
SCVP7	Jiajing	BU/P	X	X	X	X
SCVP8	Jiajing	P	X	X	X	X
SCVP9	Wanli	BU	X	X	X	
SCVP10	Wanli	BU	X	X	X	
SCVP11	Unknown	BU	X	X	X	
SCVP12	Unknown	BU	X	X	X	

## Experiment

An optical microscope (OM) Zeiss, Axioplan 2 Imaging, equipped with a digital camera (Nikon DXM1200F) was used for observation of micro samples of the sherds mounted in resin.

Non-destructive chemical characterization of the porcelain glazes and colorants was made by micro energy dispersive X-ray fluorescence spectrometry ( $\mu$ -EDXRF) at the Department of Conservation and Restoration of the Faculty of Sciences and Technology (New University of Lisbon) using a portable spectrometer ArtTAX. Excitation is provided by a Mo target x-ray tube that uses electro-thermally cooled silicon drift detector and the measurement head is fixed on a tripod with motor-driven XYZ stage for sample positioning. The system is combined with a colour CCD camera that provides a magnified digital image of the probed area. The primary X-ray beam is focused by means of polycapillary X-ray minilens and the excitation and detection paths can be purged with helium to allow the detection of low-Z elements.

The irradiated area was approximately of 70  $\mu$ m and the measuring conditions were: voltage 17 kV, intensity 0.6 mA and live time 300 s. Helium purging was used to allow the determination of elements down to aluminum.

The glaze, paste and pigment of each sherd were analysed in three different spots. The blue under-glaze was analysed in light blue areas and dark blue areas. Before the analysis the

sherds were cleaned with distilled water and non-ionic detergent Triton XL-SON to remove possible contaminants. The measurements were carried out directly on the surface of the objects, without any previous preparation.

Non-destructive X-ray microfluorescence analyses performed at the samples allowed peak assignment of elements present, based on the usual  $K\alpha$  diagnostic lines in the X-ray spectrum of elements with medium atomic number. The data handling and processing software was ArtTAX (Bronk et al. 2001) for spectra deconvolution and analysis. Quantification of peak areas of major and minor elements was made using the WinAxil analytical software (Vekemans et al., 1994).

## Results and discussion

The observation under the optical microscope shows that the layer constitution of the samples is similar. The porcelain paste has an over-layer of pigment covered with glaze (Fig. 2). Differences in the intensity of the blue tonality and the thicknesses of glaze and pigment could be observed. The transparent glaze exhibits many bubbles typically formed during firing.

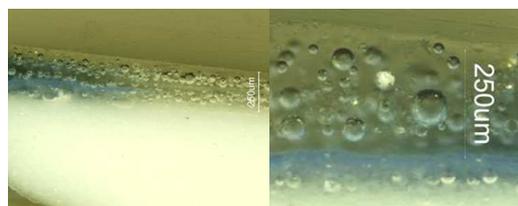


Fig. 2. Example of the pictures obtained under the OM (detail on the right). Three layers are visible: paste (white), pigment (blue) and transparent glaze; type-case for sample SCVC10

X-ray fluorescence spectra were collected from the different porcelain fragments on several different layers, namely the glaze, the light blue and dark blue areas, in order to assess the chemical composition of the used pigment. The results showed a similar trend between areas of the same typology, as exemplified by the type-case of fragment SCVC4 (Fig. 3).

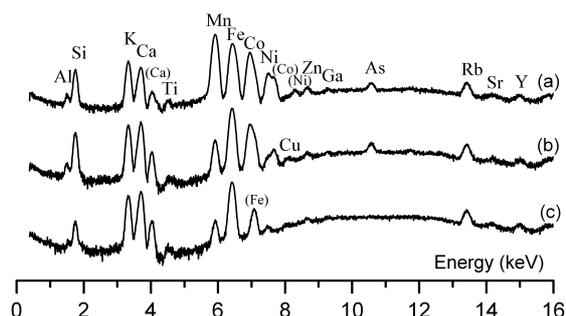


Fig. 3.  $\mu$ -EDXRF spectra collected at 17 keV from Ming porcelain fragment SCVC4: (a) dark blue; (b) light blue; (c) glaze (intensity in arbitrary units, semi-log scale). Diagnosis  $K\alpha$  lines for the identified elements are assigned, as well as  $K\beta$  lines (in brackets) for elements present in high concentration, when justified

Elements present in the samples identified by X-ray fluorescence (XRF) as major and minor components were Al, Si, K, Ca, Ti, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr and Y, being in accordance with the chemical composition of glassy and ceramic materials (Yaocheng et al., 1994; Yu, Miao, 1996; 1999; Cheng et al., 2005; Wen et al., 2007).

Spectra analysis shows that the blue pigment is cobalt based, with the presence of arsenide phase in clear relation to the mineral ore used. Cobalt sources can be sulphides, arsenides or oxides, having as major intergrowth metals Fe, Ni, Cu, Mn (Yaocheng et al., 1994), Pb, In, Sr and Zn (Gratuze et al., 1992; Gratuze et al., 1995), and its chemical characterization could permit the distinction of different production sites, kilns or dates (Gratuze et al., 1992; Yaocheng et al., 1994). Present in low concentration As is better detected in the analysed dark blue areas, occurring in all samples except SCVP 1 and SCVP 5 (Table 2).

Table 2  
Qualitative content of arsenide on analysed samples inferred from EDXRF spectra (n.d. – not detected)

Sample	Glaze	Light blue	Dark blue
SCVP1	n.d.	n.d.	n.d.
SCVP2	n.d.	n.d.	+
SCVP3	n.d.	+	+
SCVP4	n.d.	+	+
SCVP5	n.d.	n.d.	n.d.
SCVP6	n.d.	+	+
SCVP7	n.d.	++	+++
SCVP8	n.d.	+	++
SCVP9	n.d.	n.d.	+
SCVP10	n.d.	+	+++
SCVP11	n.d.	n.d.	+

Aluminum, silica, calcium and potassium are typical components of the glassy layer. However, other elements such as iron and manganese and possibly nickel and arsenic (Yaocheng et al., 1994) are also related to the pigment source and can be used to study the relation between the samples.

Since a quantitative study of these archaeological porcelains would presume a destructive analysis, a semi-quantitative approach was followed based on peak area ratios of selected elements. This methodology has legitimacy for museological pieces and is valid for comparison effects of its chemical constitution. The use of element ratios will also counterbalance the contribution to the XRF spectra from the glaze layer since the variability of results is mainly due to the pigment (Yu, Miao, 1999; Wen et al., 2007).

Elemental normalization was achieved with potassium due to its absence from the pigment and presence in similar proportions in all porcelain fragments. For blue areas the Mn vs. Co and Mn vs. Fe plottings seem to indicate different trends in the amount of these components in the pigment, indicating the possible use of raw materials of various origins (Fig. 4), most notably in Fig. 4b where two trends in composition are observed. Fragments SCVC5, 7, 9 and 10 are manganiferous in respect to cobalt content when compared with Fig. 4a while the remaining fragments seem to follow a tendency of an iron rich pigment. It has been determined that cobalt blue pigment employed for the under-glaze decoration in Ming porcelain is low in manganese and rich in iron before 1425 AD while afterwards cobalt (asbolite) that contains significant amount of manganese was used (Yaocheng et al., 1994; Yu, Miao, 1997; Yu, Miao, 1999; Cheng et al., 2005; Wen et al., 2007).

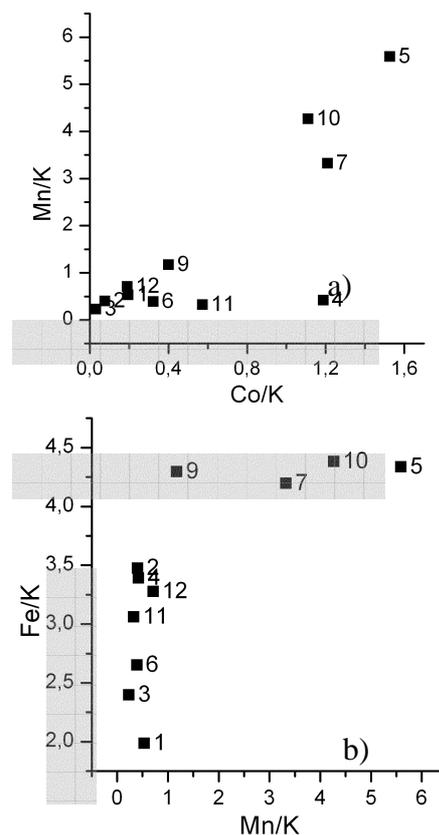


Fig. 4. Plot of calculated peak areas for light blue regions: a) Mn/k against Co/K ratios; b) Fe/K against Mn/K ratios

Since cobalt ores occurring in China normally contain a high proportion of manganese, whereas those occurring in Iran are manganese free, it was suggested that around 1425 AD there was a switch from the use of cobalt imported from Iran to a local ore (Yaocheng et al., 1994; Yu, Miao 1997; 1999; Kerr, Wood, 2004; Cheng et al., 2005; Wen et al., 2007; Feng et al., 2008).

During the late Ming period corresponding approximately from Zhengde to Wanli periods, there is a greater variation in concentration values of iron and manganese (Yu, Miao, 1996; Wen et al., 2007), which very well may indicate the use of two different cobalt resources, as observed in several studies (Kerr, Wood, 2004; Yaocheng et al., 1994; Yu. Miao 1997; 1999; Cheng et al., 2005; Wen et al., 2007; Feng et al., 2008).

On the other hand, when comparing the results obtained for the dark blue areas, elemental ratio results show a different tendency (Fig. 5). There seems to be a separation in two groups as shown in Fig. 5b, with samples of unknown origin SCVP 3, 11 and 12 standing out as having the highest concentrations in Mn and Fe, distinction not observed in the light blue area. The results obtained from light and dark blue areas may suggest the use of different pigments for blue colouring on different parts of the drawing (Feng et al., 2008) and a mixture of pigments in darker regions. Also a higher concentration of pigment in darker areas could lead to chemical processes during firing (Wen et al., 2007), being possible as a superficial crystallization although a micro X-ray diffraction analysis didn't show any indication of this fact.

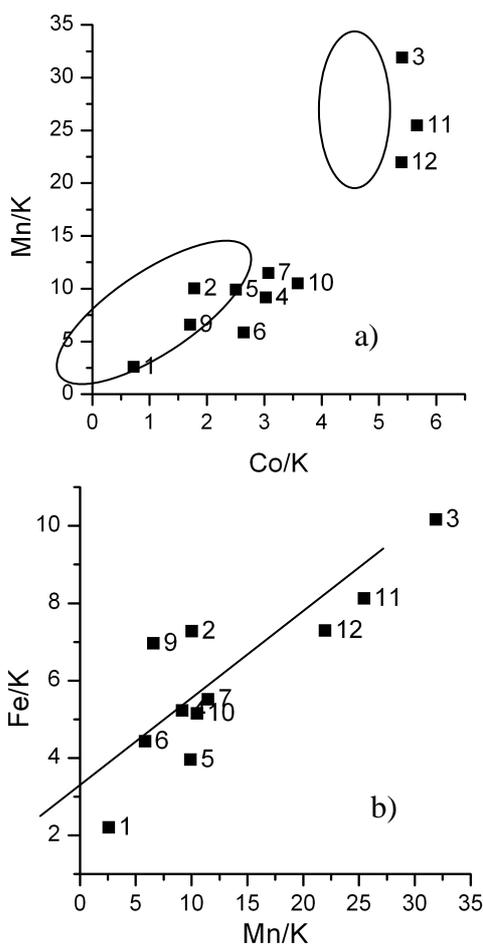


Fig. 5. Plot of calculated peak areas for dark blue regions: a) Mn/k against Co/K ratios; b) Fe/K against Mn/K ratios

The plotting of Mn vs. Co ratios shows less dispersal in concentrations for the dark blue areas with an indication of increase of iron with cobalt (Fig. 6). The variation of the results is dependent on the amount of samples available for analysis. Manufacture date and quality is also variable as the production of porcelain for export was not made exclusively in Jingdzheng but also in other known production sites (Yu, Miao, 1997; 1998). Furthermore the production recipes may vary between each other and from the official Jingdzheng kiln (Wen et al., 2007, Feng et al., 2008).

## Conclusion

The results show that there is a difference in the chemical composition of the blue pigment of the analysed sherds in the different colour tonalities. The small and diverse universe of the studied pieces only allows advancing hypothesis to explain this difference such as the use of two different pigments in the same period and that a mixture between those pigments could be used for a stronger tonality. Assessment of a Japanese origin for samples SCVC10 and 11 was not possible, although some differences were noticed in elemental concentrations, it is possible that these pieces come from a different production site in China.

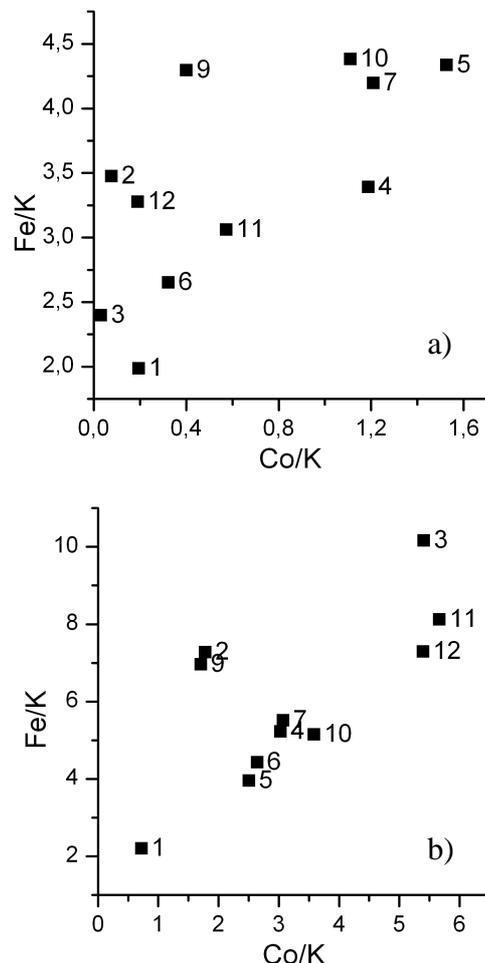


Fig. 6. Plot of calculated peak areas Fe/K against Co/K ratios: a) light blue; b) dark blue

The analysis of the paste was not discussed in this work, since the characterization was only made for the major and minor elements and provenance studies of the paste are usually conducted by recurring to trace elements or other analytical techniques (Cheng et al., 2005; Bartle et al., 2007). This study is the beginning of our understanding of the provenance of the exported pieces from China during the Ming dynasty to Portugal. The large amount of pieces found in the Santa Clara-a-Velha Monastery is representative of the exported pieces during the late Ming dynasty and its further characterization could lead to a better understanding of their production as well as of the commercial links with Portugal at that period. Along with the chemical characterization with XRF, other techniques such as micro X-ray diffraction ( $\mu$ -XRD), Scanning Electron Microscopy (SEM) and tentatively  $\mu$ -Raman, will certainly prove helpful.

*Acknowledgments.* The authors wish to acknowledge Dr. Artur C  rte-Real, coordinator of the project of recuperation and valorisation of the Santa Clara-a-Velha Monastery and surrounding grounds, IPPAR, for the availability of the porcelain sherds for analysis; Dr. Maria Ant  nia Pinto de Matos from The National Museum of Ancient Art (MNAA – Museu Nacional de Arte Antiga); Conservation and Restoration Department of the New University of Lisbon for technical help with ArtTax equipment.

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