REAL FÁBRICA DE VIDROS DE COINA - CHEMICAL ANALYSIS OF ARCHAEOLOGICAL GLASS FRAGMENTS

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The study of glasses in Portugal has been mainly oriented to the historical, economic and social aspects of the glass industry, exception given to the studies of glass production developed by Vasco Valente (Valente 1950) and Carlos Barros (Barros 1998) about 50 years ago. More recently, Ferreira (Ferreira 1997) and Custódio (Custódio 2002) have been developing an important work, concerning the study, identification and characterisation of the glass production in 18th century Portugal.

Due to the lack of written sources about the chemical characterisation of objects manufactured in Portugal, their manufacturing centres and the production dates, the Portuguese glass is today unknown. Many high quality glasses from collections of national and city museums, national palaces, private owners, etc., continue to be identified as being manufactured in well-known European glass centres. Many historians believe that the Portuguese production was of bad quality and without any expression. These facts contrast with cases where the studies made by Portuguese historians on some objects, obtained from archaeological sites, indicate that they were produced in Portugal, and not in Bohemia, Italy, or another European manufacturing centre.

As in the ceramics field, Portugal has known, during about half a millennium of glass manufacture, several production centres which made objects of high quality, either in their glass composition, or in their design (Côvo, 15th century, later Coina and Marinha Grande in the 18th century, and since then several glass houses).

Ferreira (Ferreira 1989) has studied glasses from excavations, as well as glass objects from national collections, probably produced in Portugal, but their provenance can only be unequivocally determined after analytical characterisation. So, in the absence of sources that can prove and certify the research which has been made based on archaeological and historical considerations, analytical characterisation can sometimes indicate the provenance of the studied glasses.

The archaeometry studies will focus first on the archaeological glasses from the sites where the glass factories existed before.

Glass fragments from the first excavation in Marinha Grande have been analyzed in Antwerp by Schalm and Janssens (Schalm *et al.* 2005), but according to their results they were produced in the 19th - early-20th century. A new excavation will be made in Marinha Grande in the location where the first glass furnaces are supposed to have worked and we hope to find glass of earlier productions.

A large and important collection of glass fragments were obtained as a result of excavations made in the locality where the Coina factory was established. In this work we report preliminary analyses of a series of selected glass fragments from Coina by means of micro energy-dispersive X-ray fluorescence (μ-EDXRF) with a portable spectrometer ArtTAX.

COINA FACTORY

The Coina factory was an important manufacture established near Lisbon by King D. João V of Portugal, which was operational from 1719 to 1747. Then it was transferred to Marinha Grande under the administration of John Beare. Some years later it was named *Real Fábrica de Vidros da Marinha Grande* (Royal Glass Factory of Marinha Grande) under the administration of William Stephens.

Marinha Grande continued to produce the same type of glass objects made in Coina as indicated by a catalogue from Coina used in Marinha Grande. So, objects from the Marinha

Grande factory are very similar in shape and decoration to those that were produced in Coina. Today it is still very difficult for museums to distinguish the two productions based just on style and aesthetic criteria.

A detailed historical study of the Coina glass factory was published by Custódio (Custódio 2002), who was also responsible for the archaeological excavations on its grounds. A large set of samples was selected as representative of the typological categories identified by archaeologists during these excavations. Based on archaeological findings and some drawings from the catalogue II (Barros 1998) mentioned above, the type of objects produced includes drinking glasses (beakers, cups and goblets), jugs (Fig. 1), and decorated dishes. A large variety of bottles (Fig. 2) were produced, with round, globular or squared body, and some types had a stopper; other typologies such as olive oil and vinegar containers – double cruet –, vessels for flowers, and beakers, bottles and flasks with special shapes, engraved and enamelled decorations, and also window glass and mirrors were manufactured.

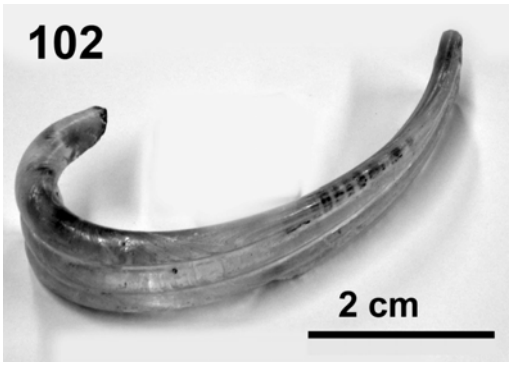

Fig. 1. Fragment of jar from Coina excavation.

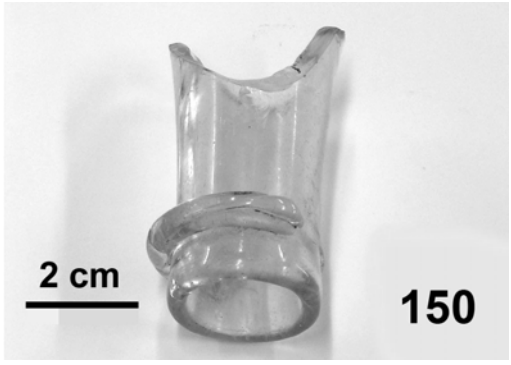

Fig. 2. Fragment of bottle from Coina excavation.

Most of the findings studied in this work are free-blown and mould-blown glass made of transparent glass lightly coloured in various hues from yellow to green and blue-green. Only a few fragments of opaque white glass, intense purple, and just one of cobalt blue were found, but they were not selected for this study. In general, the bottles are dark green and brownish and some of them are heavily corroded.

GLASS ANALYSIS

Preliminary chemical characterisation of glass fragments from the objects described above was made using non-destructive analysis by micro energy-dispersive X-ray fluorescence spectrometry (μ-EDXRF). This analysis was carried out at the Department of Conservation and Restoration of the Universidade Nova de Lisboa using a portable spectrometer ArtTAX, which consists of an air-cooled low-power X-ray tube with a molybdenum target, an electrothermally cooled silicon drift detector, and a measurement head fixed on a tripod with a motor-driven XYZ stage for sample positioning. This system is combined with a colour CCD camera that provides a magnified digital image of the area under investigation. The primary X-ray beam is focussed by means of a polycapillary X-ray mini-lens. The excitation and detection paths can be purged with helium to allow detection of low-Z elements. This instrument is being used for non-destructive multi-element analysis of art and archaeological objects and determination of elements between aluminium and uranium.

Measurements were carried out directly on the surface of fragments without any previous preparation. Three different points on the surface of each fragment were measured, and for each point just a single measurement was made. The measuring conditions were the following: X-ray tube voltage 40 kV; intensity 0.6 mA; live time 300 s; helium atmosphere.

WinAxil analytical software was used for quantification of major and minor element oxides. The fundamental parameter method (FPM) combined with calibration using glass standards from The Corning Museum of Glass (CMOG-B, -C and -D) and from the Society of Glass Technology (SGT-8) were used.

Sodium oxide was determined by difference after analysing all the other oxides.

To evaluate the error obtained by this analytical procedure two reference glasses, SGT-5 and -7, were analyzed using the same standard. The results obtained differ from the certified values by less than 15 % for the major element oxides and 25 % for the minor elements oxides (*Note*: element oxides with abundances less than 5 % were considered minor components).

RESULTS AND DISCUSSION

The 29 glass fragments analyzed were divided into groups accordingly to their chemical composition (Figs. 3-5). Different types of glass composition can be roughly distinguished in the binary plot of potassium oxide content versus calcium oxide of Fig. 3: potash glass, soda-lime glass, high-lime low-alkali glass, and lead glass.

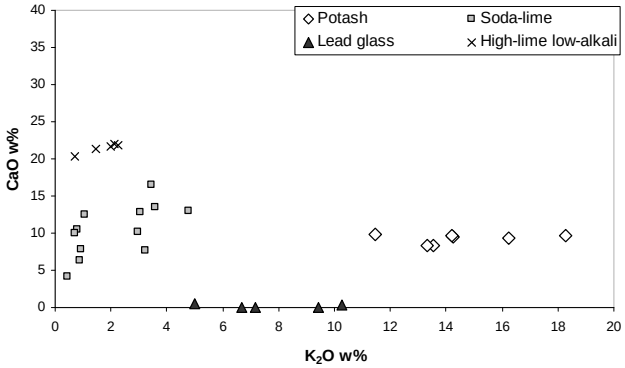

Fig. 3. Plot of potassium and calcium oxides contents for the Coina fragments.

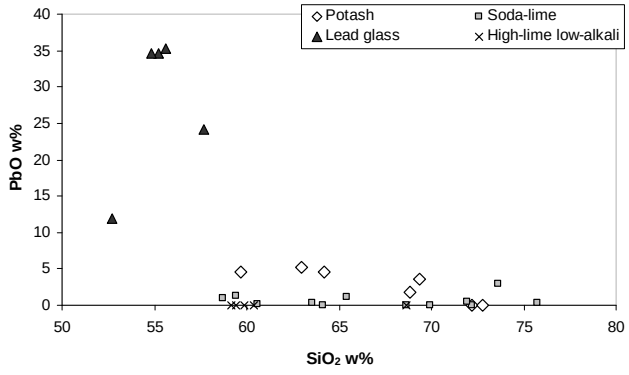

Fig. 4. Plot of silica and lead oxide contents for the Coina fragments.

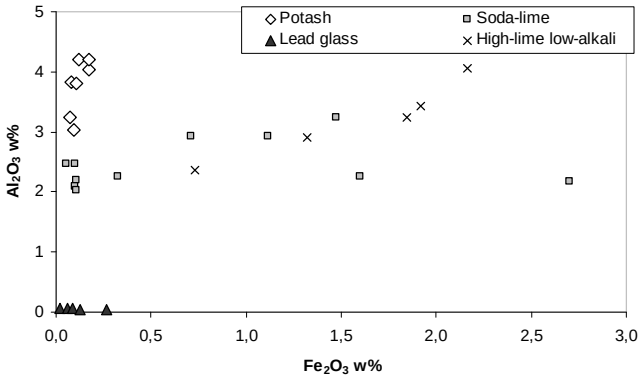

Fig. 5. Plot of iron and aluminium oxide contents for the Coina fragments.

The potash group with a wide range of potassium oxide content has moderate levels of calcium oxide (8 - 10 wt% CaO) (Fig. 3) and lower concentration of lead oxide (0 - 5 wt% PbO) (Fig. 4). Fig. 5 shows that the potash group has aluminium oxide values around 3 to 4 wt%, the group that presented the highest value of this oxide.

In the soda-lime group, the largest one, there are 5 fragments with a quite high content of calcium oxide (CaO > 20 wt%) and so this cluster was isolated, and these glasses classified as HLLA. These 5 glasses are from dark green bottles.

The last group presents 5 fragments: 3 with high levels of lead oxide (~ 35 wt% PbO) and 2 with lower concentration (12 and 24 wt% PbO) (Fig. 4). Their concentration of potassium oxide varies between 5 and 10 wt%.

FINAL REMARKS

The chemical analysis of Coina glass fragments has shown that this factory produced at least four types of glass using different raw materials for each group. The fragments of the potash group include some drinking vessels, the soda-lime group includes bottles and window glass, the HLLA group includes just green bottles, and the lead glass uncoloured tableware.

This work is just the first contribution for the project Provenance Studies of Portuguese Glass supported by our National Science Foundation FCT.

We expect that based on the data obtained from the Coina glass fragments and with the results

of future analysis from the next Marinha Grande excavation we may be able to distinguish both productions. Moreover in the Marinha Grande manufacture we may distinguish productions that used raw materials before and after the use of soda ash obtained by the Leblanc process. Study of the archives of Marinha Grande may help us to confirm the use of different raw materials.

ACKNOWLEDGMENTS

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