

This item is the archived peer-reviewed author-version of:

Characterization of 18th century Portuguese glass from Real Fábrica de Vidros de Coima

Reference:

Lopes Filipa, Lima Augusta, Pires de Matos António, Custódio Jorge, Cagno Simone, Schalm Olivier, Janssens Koen.- Characterization of 18th century Portuguese glass from Real Fábrica de Vidros de Coima
Journal of Archaeological Science: Reports - ISSN 2352-409X - 14(2017), p. 137-145
Full text (Publisher's DOI): <https://doi.org/10.1016/J.JASREP.2017.05.020>
To cite this reference: <https://hdl.handle.net/10067/1435450151162165141>

Characterization of 18th century Portuguese glass from *Real Fábrica de Vidros de Coina*

Filipa Lopes^{a,b*}, Augusta Lima^{a,c}, António Pires de Matos^{a,b}, Jorge Custódio^d, Simone Cagno^e, Olivier Schalm^f and Koen Janssens^e

^a Research Unit VICARTE – Glass and Ceramics for the Arts, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

^b C²TN, Departamento de Engenharia e Ciências Nucleares, Instituto Superior Técnico, Universidade de Lisboa, Campus Tecnológico e Nuclear, Estrada Nacional 10 (km 139,7), 2695-066 Bobadela LRS, Portugal

^c Departamento de Conservação e Restauro, Faculdade de Ciências e Tecnologia, Universidade NOVA de Lisboa, Campus de Caparica, 2829-516 Caparica, Portugal

^d Instituto de História Contemporânea, Faculdade de Ciências Sociais e Humanas, Universidade Nova de Lisboa, Universidade NOVA de Lisboa, Avenida de Berna 26 C, 1069-061 Lisboa, Portugal.

^e University of Antwerp, Department of Chemistry, Groenenborgerlaan 171, 2020 Antwerpen, Belgium

^f University of Antwerp, Conservation Studies, Blindestraat 9, B-2000, Antwerpen, Belgium

Abbreviations ¹

Abstract

A JEOL 6300 Scanning Electron Microscope equipped with an energy dispersive X-ray detector was used

This work reports the first systematic chemical characterization of Portuguese 18th century glassware. 28 selected glass fragments, recovered from an archaeological excavation carried out in the site where King D. João V of Portugal established an important glass manufacture, *Real Fábrica de Vidros de Coina* (Coina Royal Glass Factory), were studied. This factory operated from 1719 until 1747, the year in which the factory was transferred to Marinha Grande. The fragments were analysed by micro-energy dispersive X-ray fluorescence (micro-EDXRF), using a portable spectrometer ArtTAX, and scanning electron microscopy (SEM-EDX). The analytical data showed that a large variety of glass types was manufactured in that factory, namely soda-lime glass, mixed-alkali glass, high lime-low alkali glass, potash glass and lead glass. In

¹ RFVC – Real Fábrica de Vidros de Coina

general, the composition of the glass varies according to the function of the objects. It was demonstrated that micro-EDXRF can be an important tool to characterize museum glass objects when only *in situ* non-invasive analytical methods are allowed.

Keywords: archaeological glass; 18th century; Coina; micro-EDXRF; SEM-EDX.

1. Introduction

The 18th century is the end of the wood and plant ash glass-manufacturing period and can be considered as a pre-industrial period. It is around this era that the *Real Fábrica de Vidros de Coina* (RFVC) was founded in Coina (Portugal). It worked for about 28 years between 1719 and 1747. The Royal Glass Factory had three distinct periods while in Coina. The first period corresponds to the royal administration (1719-1735). In the second period, it was administered by a British company (1735-1741). From 1747 to 1767 (third period) one of the partners, the Irish John Beare, started its transference to Marinha Grande taking with him some glass masters and craftsmen as well as catalogue products and many of the glass manufacturing techniques [Custódio, 2002].

Concerning 18th century Portuguese glassware, until recently, only a few stylistic studies have been made. Manuela Ferreira [1997, 2005] has studied Portuguese glasses from this period, either recovered from archaeological excavations or belonging to National museums or private collections. From a stylistic point of view, Coina and Marinha Grande productions cannot be distinguished. Since the raw materials used in the two factories were almost certainly different [Custódio, 2002; Medici, 2014], the distinction of manufactures can probably be made by means of chemical analysis. Therefore 28 samples were selected from the excavated artefacts from the RFVC archaeological site and analysed by means of scanning electron microscopy – energy dispersive detector (SEM-EDX) and by means of micro-energy dispersive X-ray fluorescence spectrometry (micro-EDXRF) Their analytical characterization is expected to bring a new light to the history of glass technology from 18th century in Portugal: understand the technology and raw materials used in the RFVC. The study of the relation between typology and chemical composition was also made. The compositions were compared with a larger dataset of glass compositions including ordinary Northwestern European vessel glass and 16th-17th centuries luxury glass fabricated in Venice and in Northwestern Europe [De Raedt et al., 2001; Janssens et al., 1998;]. Finally, a non-invasive analytical technique was validated so that chemical analysis of valuable glass objects can be done.

1.1 Historical context

The 18th century RFVC was an important royal glass manufacture established near Lisbon, in Coina (Barreiro), by King D. João V of Portugal. Several foreign glass masters came from Italy, Catalonia, England, Flanders, Ireland, France, Germany and Bohemia to start developing there a great mass production of glass tableware, bottles, mirrors, window glasses and utilitarian and decorative objects [Barros, 1969; Custódio, 2002]. This manufacture was established in the vicinity of important raw materials needed for glassmaking: white sand and coastal plants, the latter used to prepare *barrilha*, i.e. soda ash [Custódio, 1989, 2002]. Fuel for the furnaces was also available, from the wood of the surrounding forest.

It is important to mention that before the establishment of the glass manufacture (16th and 17th centuries) the surrounding wood was mainly used for Lisbon internal consumption at low prices [Custódio, 1989; Valente, 1950]. During the operation of the RFVC, its furnaces began to consume much more wood. There were complaints with the Municipal Council of Lisbon on 13 October 1746, given the wood shortage for use by people on the left bank of the Tagus river. In the time of the English Company (1735-1741) and up to about 1744, RFVC imported coal from Britain [Custódio, 2002].

During the 18th century, several types of glass were manufactured all over Europe [Janssens, 2013]. It is possible to classify glass in the following categories according to its chemical composition, as shown in Figure 1:

High lime-low alkali (HLLA) glass: Glass containing more than 2 times CaO than K₂O and low/no soda. This glass is obtained by mixing white sand with the ashes of hardwood such as beech or oak (i.e., a source of K and Ca). During the 18th century ashes were sometimes purified by using only the water-soluble part of the ashes in order to obtain a colourless glass. In that case, lime (i.e., a source of Ca) must be added to the batch. Such technology can be identified by the lowered amounts of P₂O₅.

Mixed-alkali glass: Glass containing both Na₂O and K₂O in similar amounts. In some recipes glassmakers used ashes rich both in sodium and potassium, probably obtained from seaweed [Dungworth et al., 2009] or a mixture of different raw materials rich in alkalis [Tite et al., 2006], or even adding cullet, originating a glass designated by mixed-alkali glass [Dungworth, 2003].

Potash glass: Glass where the K₂O:CaO ratio is higher than 0.5 wt.% and low/no Na₂O. This glass type is made from K-rich ashes from wood or fern ashes. Besides Ca, such ashes contain large amounts of K [Barrera and Velde, 1989]. Rather pure K-rich compounds, such as tartrate and later saltpetre, could be used as well [Kunicki-Goldfinger et al., 2001].

Soda glass: In the same period, Na-rich ashes were used as well. This was obtained from coastal plants such as *Salsola soda* or plants growing in salty deserts [Tite et al., 2006]. Such plants grow in a large extent in Iberian Peninsula and were available to the RFVC.

Lead glass: A recent paper reappraises the quest for fine crystal glass in London and Dublin in the decade from 1672 [Brain and Brain, 2016]. In this period, the lead glass used to make tableware had a PbO concentration of about 30 wt.%. The development of a good lead glass crystal was very fast and the main components are silica, lead and potassium. Glass with a PbO content below 15% is not considered as a lead glass.

2. Materials and methods

2.1 Archaeological finds

A set of 28 glass fragments was selected from an archaeological excavation carried out at the RFVC site by Jorge Custódio between 1984 and 1990 (Fig. 2). The production of these artefacts is mainly attributed to the second and third periods (1735-1747) of the factory [Custódio, 2002]. Based on the drawings depicted in a design catalogue with drawings of glass objects [Barros, 1969], attributed to the Coína production [Correia,

1999; Custódio, 1989, 2002], the glass fragments analysed were of drinking glasses and vessels, jugs, double cruet, flasks, a large variety of bottles with cylindrical, globular or squared body and also window glass. Most of the glasses are moderately weathered showing slight iridescence, crusts and some pitting (observed in some bottle fragments). A brief description of the studied glass fragments is given in Table 1.

2.3 Chemical analysis of the samples

Major and minor element composition was determined by SEM-EDX. Small fragments of glass were embedded, perpendicular to the original surface, into acrylic resin. The resin blocks were then ground with silicon carbide paper and polished with diamond paste up to 1 μm in order to obtain a smooth cross-section on which bulk measurements can be done without interference of the corroded surface layers of the glass fragments. Finally, these resin blocks were coated with a thin carbon layer to prevent charging of the surface during SEM-EDX measurements. These were performed with a JEOL 6300 scanning electron microscope, equipped with an energy dispersive X-ray detector. For every sample 4 different areas of approximately 0.5 x 0.5 mm were analysed. For each sample, zones have been selected that appeared to be homogeneous. Compositional fluctuations on a larger scale are considered by reporting the average composition of the 4 analyses. Spectra were acquired for 100 s with a beam current of 1 mA and at a voltage of 20 kV. The net elemental X-ray intensities were calculated with the program AXIL (Analysis of X-ray spectra by Iterative Least squares) and a standardless ZAF correction procedure was used to calculate the glass samples elemental contents [Schalm, 2000; Schalm and Janssens, 2003]. The accuracy was tested by analysing the Corning Museum of Glass (CMoG) reference glasses B (soda-lime), C (lead) and D (potash) silicate glasses [Brill, 1999] (Table 2).

Major and minor elements were also determined by micro-EDXRF on the same cut and polished sections of the SEM-EDX samples. An ArtTAX spectrometer was used which consisted of an air-cooled low-power X-ray tube with a molybdenum target, a silicon drift detector that is electro-thermally cooled, and a measurement head fixed on a tripod with a motor-driven x,y,z 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 focused by means of a polycapillary X-ray down to a diameter of ca. 70 μm , and the excitation and detection paths can be purged with helium to allow the detection of low-Z elements. This spectrometer detects elements between aluminium and uranium. Each sample was analysed in three different spots. The measuring conditions were 40 kV of tube voltage, 0.6 mA of current intensity and 300 s of live time, helium atmosphere. WinAxil analytical software was used for quantification of major and minor elements. Calibration was made using the Corning Museum of Glass (CMoG) reference glasses B, C and D [Brill, 1999] (Table 2).

2.4. Statistical processing of the analysis

Divide data into groups. Clustering can be used to partition the dataset of glass compositions into groups so that the degree of association is high among glass samples of the same group and low among samples of different groups. Hierarchical clustering was performed on the data matrix obtained from SEM-EDX by means of the software package SPSS. During the hierarchical clustering (Ward's method, squared Euclidian distance, concentration values standardized to a range of 0-1) the most variable oxides

present in glass in concentrations higher than 1 wt.% (Na_2O , MgO , SiO_2 , K_2O and CaO) were employed in order to subdivide the analysed set into four clusters. Clustering algorithms are limited to the number of clusters specified by a human user. To find a reasonable number of clusters, hierarchical clustering must be run repeatedly with different parameters. The number of clusters is systematically increased until the newly formed clusters have no meaning when related to glass recipes or raw materials. The scheme shown in Figure 1 was used as a guideline for cluster formation.

3. Results and discussion

3.1 Glass compositions

Table 2 gives an overview of the compositions obtained by both analytical techniques. By considering the amounts of Na_2O , SiO_2 , K_2O , CaO and PbO it is clear that soda-lime, mixed-alkali, high lime-low alkali, potash and lead glass has been made in the same factory. The scatter plot of CaO versus K_2O highlights the five groups identified (Fig. 3). The results shown in Table 2 demonstrate that the factory used several compositions to fabricate their glass. This means that a single production site mastered the technology to fabricate glasses with different compositions simultaneously. This is in accordance with the existent historical documents about manufacture and trade of the glass produced by this factory [Custódio, 2002, 94-104 and Document V, 274-280]. The average concentrations of the five types of glass identified from SEM-EDX analysis are shown in Table 3 and it will be discussed below.

3.2 Soda-lime glass (samples 42, 49, 73, 83, 89, 111, 136 and 148)

In this group (comprising glass fragments of various types of clear glass vessels, bottles, one flask and one window glass), two different soda sources - used as fluxing agents - seem to be distinguished among the glass samples. The analysis of the fragments 42, 49, 83 and 111 (Table 3: soda-lime I) may indicate that a Na-rich plant ash (probably *barrilha*) may have been used, as high average values of MgO (4 wt.%), Cl (1 wt.%), K_2O (4 wt.%) and CaO (12 wt.%) were found (Tite et al., 2006). The average content of Na_2O is 11 wt.%. This particular composition has also been proposed to stem from a different glassmaking tradition than the Venetian/Levantine one, including different types of plants for the production of the flux [Cagno et al., 2012]. The other soda-lime fragments, 73, 89, 136 and 148 (Table 3: soda-lime II), with 15 wt.% Na_2O and lower percentages of K_2O (1 wt.%) and CaO (9 wt.%), and very low contents of MgO (0.1 wt.%) and Cl (0.1 wt.%), indicate that a very purified soda ash could have been used. It is interesting to mention that in the same period in Belgium, soda glass is seldom found among luxury glass and had a Venetian-like composition, with low amounts of K_2O (< 3.5 wt.%). The presence of low amounts of PbO in two samples might indicate recycling practices.

3.3 Mixed-alkali glass (samples 139, 141 and 163)

The three mixed-alkali fragments, 139, 141 and 163, which belong to squared and cylindrical green bottles, were probably produced with a mixture of coastal plant ash and forest plant ash rich in K_2O suggested by the average values of 7 wt.% for Na_2O and 5 wt.% for K_2O [Tite et al., 2006]. The use of non-purified soda ash from coastal plants or seaweed is suggested by the presence of MgO and Cl .

The concentrations of MgO, Al₂O₃, TiO₂ and Fe₂O₃ are also relevant in these glasses, and are only comparable to the contents found in high lime-low alkali glasses, which suggest that they may have been introduced in the glass not only through the use of impure sands but also by the source of CaO. In the plots shown in Fig. 4 it is evident the correlation CaO/MgO, CaO/Al₂O₃ and CaO/Fe₂O₃. The use of badly sorted cullet might be the explanation for the presence of PbO found in small quantities [Kunicki-Goldfinger et al., 2000].

The purchase of the glass cullet in the market, as raw material for the manufacture of glass in the Real Fábrica de Vidros de Coima, is not documented in the Portuguese historical archives. The documentation is scarce due to its material loss on the occasion of the Lisbon Earthquake of 1755. However, the explanation for the coexistence of different compositions of the glass in the manufacture of Coima glass might be due to another reason. In their workshops they worked, in different periods, glass masters of several manufacturing centres of Europe (Venice, England, France, the Netherlands and Ireland). These glassmakers brought with them their own technologies and manufacturing revenues that they had developed in those centres. These diversified experiences were eventually reflected in the compositions of Coima glass, resulting in their sedimentation in the archaeological strata.

3.4 High lime-low alkali glass (samples 144, 149, 152, 154 and 156)

High lime-low alkali glass group (fragments 144, 149, 152, 154 and 156) includes only fragments of green bottles, most of them being heavily corroded. They have a composition similar to the mixed-alkali glasses, in terms of impurities from the sand, lime and soda ash, but with higher content of CaO (>21 wt.%). The use of high-calcium glasses, with CaO varying from 18 to 29 wt.%, is reported from 16th-18th glasshouses in Europe [Dungworth, 2003; Stevenson et al., 2007].

3.5 Potash glass (samples 37, 58, 70, 81, 94, 104 and 138)

The potash glass fragments (37, 58, 70, 81, 94, 104 and 138) correspond to a large variety of objects which have 13-20 wt.% of K₂O. It seems that an ash from forest plant rich in potassium have been used as a fluxing agent, because the contents of MgO and Cl are very low (<0.5 wt.% and <0.3 wt.%) [Uboldi and Verità, 2003]. PbO and As₂O₅ are present in all fragments. Samples 70, 81, 94, 104, 138 have higher concentrations of PbO (2-5 wt.%) comparing to the samples 37 and 58, which have lower amounts of PbO (0.2-0.3 wt.%). The relatively low amounts of PbO present in the glass might be explained by the addition of cullet with lead glass into the potash batch. Purified sand might have been used due to the very low concentrations of contaminants found, such as iron. This composition shows a resemblance to a large group of Belgian luxury glass of the same period excavated in the Clairefontaine nunnery (Group 1.1 in Hellemans et al., 2014). However, more RFVC glass fragments should be analysed to support a real link between the two glass groups.

3.6 Lead glass (samples 72, 74, 88, 91 and 131)

Lead glass group can be divided into two quite different subgroups. The first subgroup comprises an ink-pot fragment (91) and a window glass fragment (131) (Table 3: lead I) with PbO contents from 16 to 18 wt.% and relevant amounts of Na₂O and MgO, which might indicate that the glass has been produced with coastal plant ash. Generally,

window glass was made of soda-lime glass at this period, so probably the thick glass fragment 131, which was classified as a window glass, should correspond to a wall of a squared flask or similar tableware element. The second subgroup that includes colourless tableware (fragments 72, 74, 88) (Table 3: lead II) is instead, characterized by higher PbO contents (39-42 wt.%) and a pure source of potash, as no sodium and almost no magnesium were detected.

3.7 Evaluation of micro-EDXRF results

The accuracy of the measurements calculated with the CMOG reference glasses B, C and D is presented in the Table 4. For SEM-EDX the relative error was found to be better than 13% for major oxides (>1%) and 18% for minor oxides (<1%), except for the CMOG D analysis with low PbO content that showed a larger error. For micro-EDXRF the relative error was found to be better than 12%.

In order to evaluate the reliability of micro-EDXRF results, the correlation of the two data sets from SEM-EDX vs micro-EDXRF for all oxides analysed by both techniques is shown in Fig. 5. It shows a good correlation for major oxides (SiO₂, CaO, K₂O, PbO) and for some of the minor oxides, namely TiO₂, MnO and Fe₂O₃. Some deviations observed for Al₂O₃, Cl are mostly related with concentrations near the detection limits and for As₂O₃ with peak overlapping (particularly As-K α and Pb-L α).

In spite of micro-EDXRF being unable to detect Na and Mg in glasses, it was possible using this analytical technique to distinguish the four major compositional groups (soda-lime, HLLA, potash and lead) identified through SEM-EDX, based on the content of SiO₂, K₂O, CaO and PbO. In this scenario, the identification of mixed-alkali glasses is rather difficult based only on the scheme of the Fig. 1, because the K₂O content, despite to be present is not a preponderant factor by itself for their classification.

4. Conclusions

From the elemental characterization of the glass fragments found in the archaeological excavation of the RFVC five types of glass were identified as follows: soda-lime glass, mixed-alkali glass, high lime-low alkali glass, potash glass and lead glass. The glass compositions and the decorations used in this glass factory, which was operating in the 18th century, reflect the technology and aesthetics of the North of Europe glassware. In general, the composition of the glass varies according to the function of the objects. The low contents of Al₂O₃ and Fe₂O₃ in the potash and lead glasses, which includes some of the most refined objects, suggest that they were produced with purified raw materials - washed sand and purified ashes or alkali mineral sources - following the lead crystal and the Bohemian crystal (potash glass) traditions: made of lead and potash glass. The ordinary glass of drinking bottles was probably made with local and not purified raw materials to produce high lime-low alkali and mixed-alkali base compositions. Their use was probably intentional to obtain common, inexpensive green bottles.

The analysed Coina archaeological glass fragments belong to a period of transition between the traditional production and the industrial processes. This is reflected in the technological experimentation and composition of the glass finds: some of the soda-lime glasses were probably manufactured using plant ash. In these glasses the high contents of Al₂O₃ and Fe₂O₃ found indicate that impure sand was used. New production techniques seemed to be used in other soda-lime glass objects in which a pure supply of

soda from washed ashes must have been provided as a fluxing agent as the concentration of Cl, Fe₂O₃ and MgO are very low. Potash glasses are also characterized by a pure source of potash and the presence of arsenic. Small quantities of PbO were frequently found in some fragments of soda-lime and potash glass.

In this study, it was also demonstrated that micro-EDXRF could be an important tool to characterize glass objects when only *in situ* non-destructive analytical methods can be used. This was demonstrated comparing the results obtained from the analysis of Coina glass by micro-EDXRF and SEM-EDX. Although, in some cases it is hard to distinguish mixed-alkali compositional group from soda-lime by micro-EDXRF.

Future work can be envisaged to distinguish Coina production from Marinha Grande glass: from the History and the History of Art point of view, it will be a very important step, as well as characterize both manufactures continuity and change. Unfortunately, as no more furnaces were found in the remains of the 18th century Marinha Grande factory, the future step is to analyse well dated museum glass objects.

Acknowledgments

This study was supported by FCT (Fundação para a Ciência e a Tecnologia) under the project POCI/HAR/55882/2004 and UID/EAT/00729/2013. The PhD grant SFRH/BD/85329/2012 by FCT to Filipa Lopes is also acknowledged. The authors are grateful to Rosário Gil and Câmara Municipal do Barreiro for their help in accessing the archaeological glass collection. We would like to thank in particular Manuela Almeida Ferreira for her valuable support in this project.

References

- Barrera, J., Velde, B., 1989. A study of French medieval glass composition. *Archéologie Médiévale* 19, 81-130.
- Barros, C., 1998. Real Fábrica de Vidros da Marinha Grande, II Centenário 1769 – 1969. Edições Magno, Leiria.
- Brain, C., Brain, S., 2016. The development of lead crystal glass in London and Dublin 1672-1682: a reappraisal. *Glass Technology: Eur. Journal Sci. Technology A*, 57 (1), 37-52.
- Brill, R. *Chemical Analysis of Early Glasses. The Tables*. Corning, NY: The Corning Museum of Glass, 1999, p. 540.
- Cagno, S., Badano, M.B., Mathis, F., Strivay, D., Janssens, K., 2012. Study of medieval glass fragments from Savona (Italy) and their relation with glass produced in Altare, J. *Archaeol. Sci.*, vol. 39, 2191-2197. doi: 10.1016/j.jas.2012.03.013
- Correia, J., 1999. A Fábrica de João Beare na Marinha Grande. Câmara Municipal da Marinha Grande, Marinha Grande.
- Custódio, J., 1989. A Real Fábrica de Vidros de Coina e as origens da indústria vidreira na Marinha Grande (1719-1826), *Actas do I Encontro Nacional sobre Património Industrial*. Coimbra Editora, Coimbra.

- Custódio, J., 2002. *A Real Fábrica de Vidros de Coima (1719-1747) e o vidro em Portugal nos séculos XVII e XVIII*. Instituto Português do Património Arquitectónico, Lisboa.
- De Raedt, I., Janssens, K., Veeckman, J., Vincze, L., Vekemans, B., Jeffries, T.E. 2001. Trace analysis for distinguishing between Venetian and façon-de-Venise glass vessels of the 16th and 17th century, *J. Anal. At. Spectrom.* 16(9), 1012-1017. doi: 10.1039/B102597J
- Dungworth D., Degryse P., Schneider J., 2009. Kelp In *Historic Glass: The application of strontium isotope analysis*, in Degryse, P, Henderson, J and Hodgins, G (eds) *Isotopes in Vitreous Materials*. Leuven: Leuven University Press, 113-130.
- Dungworth, D., 2003. *Scientific examination of glass and glassworking materials from silkstone, Yorkshire*, Centre of Archaeology Report 90/2003, English Heritage, London.
- Dungworth, D., Brain, C., 2005. *Investigation of late 17th century crystal glass*. Centre of Archaeology Report 21/2005, English Heritage, London.
- Ferreira, M., 1997. *Seventeenth and eighteenth century glass drinking vessels and bottles from Lisbon - Portugal*. *Conimbriga* 36, 183-190.
- Ferreira, M., 2005. *Eighteenth century wheel-engraved glassware from Lisbon*. *Post-Medieval Archaeology* 39, 2, 233-242.
- Hellemans, K., Vincke, A., Cagno, S., Herremans, D., De Clercq, W., Janssens, K., 2014. *Composition and state of alteration of 18th-century glass finds found at the Cistercian nunnery of Clairefontaine, Belgium*. *J. Archaeol. Sci.* 47, 1, 121–133.
- Janssens, K. H., Deraedt, I., Schalm, O., Veeckman, J., 1998. *Composition of 15-17th century archaeological glass vessels excavated in Antwerp, Belgium*. *Microchimica Acta Supplementary*, 15, 253-267.
- Janssens, K., 2013. *Modern Methods for Analysing Archaeological and Historical Glass*. Wiley, 74-76.
- Kunicki-Goldfinger, J., Kierzek, J., Kasprzak, A., Malozewska-Bucko, B., 2000. *A study of eighteenth century glass vessels from Europe by X-ray fluorescence analysis*. *X-Ray Spectrom.* 29, 310-316.
- Kunicki-Goldfinger, J., Kierzek, J., Kasprzak, A., Malozewska-Bucko, B., 2001. *Analyses of 18th-century Central European colourless glass vessels*. *Annales of the 15th Congress AIHV*, 224-229.
- Medici, T., 2014. *Vidros da Terra. O vidro tardomedieval e moderno em Portugal (séculos XIV-XVII). O contributo da arqueologia*. 2 vols. Tese de Doutoramento. Universidade de Coimbra. Coimbra
- Schalm O., 2000. *Characterisation of paint layers in stained-glass windows: main causes of the degradation of nineteenth century grisaille paint layers*, PhD, University of Antwerp, Antwerp.

- Schalm, O., Janssens, K., 2003. A flexible and accurate quantification algorithm for electron probe X-ray microanalysis based on thin-film element yields, *Spectrochim. Acta Part B*, 58, 669-680. doi: 10.1016/S0584-8547(02)00290-2
- Schalm, O., Janssens, K., Wouters, H., Caluwé, D., 2007. Composition of 12th–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings, *Spectrochim. Acta Part B* 62, 663-668.
- Stevenson, C., Wheeler, D., Novak, S., Speakman, R., Glascock, M. D., 2007. A new dating method for high-calcium archaeological glasses based upon surface-water diffusion: preliminary calibrations and procedures. *Archaeometry* 49, 1, 153-177.
- Tite, M., Shortland, A., Maniatis, Y., Kavoussanaki, D., Harris, S., 2006. The composition of the soda-rich and mixed alkali plant ashes used in the production of glass. *J. Archaeol. Sci.* 33, 9, 1284-1292.
- Uboldi, M., Verità, M. 2003. Scientific Analyses of Glasses from Late Antique and Early Medieval Archaeological Sites in Northern Italy. *J. Glass Stud.* 45, 115–137.
- Valente, V., 1950. *O Vidro em Portugal*. Portucalense Editora, Porto.
- Verità, M., 1985. L'invenzione del cristallo muranese: una verifica analitica delle fonti storiche. *Rivista della Staz. Sper. Vetro* 1, 17-29.