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New insights into 17th and 18th century glass from Portugal: Study and Preservation

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To my grandfather, who taught me to always seek knowledge;
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RESUMO

O vidro encontrado na Península Ibérica e datado do início do período Moderno tem sido alvo de pouco estudo até à data. O corrente projecto visa o estudo e a caracterização de objectos de vidro que circularam em território português, combinando para isso análises químicas e estilísticas. Este projecto tem como objectivo identificar a origem dos objectos de vidro, visando a identificação de vidro de produção portuguesa.

Foi determinada a composição química de mais de 200 fragmentos de vidro através da técnica analítica de μ-PIXE (determinado até às dezenas de μg/g). Os resultados obtidos permitiram seleccionar alguns objectos para alargar a análise aos elementos traço e terras raras (REE) através da técnica analítica de LA-ICP-MS (determinando até às ng/g). A cor no vidro foi estudada através da espectroscopia de reflectância de UV-Vis e sempre que se justificou, os esmaltes encontrados foram estudados através das técnicas de μ-EDXRF e microscopia de μ-Raman.

De todos os objectos analisados, concluiu-se que na sua grande maioria, o vidro datado até ao século XVII é do tipo silicatado-sodo-cálcico, o que traduz uma tradição vidreira mediterrânica.

De entre as diversas formas estudadas, identificaram-se objectos de estilo veneziano ou *façon-de-Venise* e para alguns deles foi confirmada a proveniência veneziana. Para outras formas identificadas como *façon-de-Venise*, o estudo da sua composição revelou características que levaram ao reconhecimento de novos centros de produção *façon-de-Venise*. Através do estudo do único conjunto de vidros que contém fragmentos datados do período medieval, foi possível atestar a presença de vidro veneziano no território Português desde pelo menos o século XIV.

Foram identificados mais objectos apresentando características particulares na sua composição, como o alto e muito alto teor de alumina, por exemplo, que, tanto quanto se conhece, não encontra paralelo em nenhum dos centros de produção de vidro conhecidos na Europa. Aliando o estudo das características estilísticas com a determinação da composição química do vidro, permitiu levar à identificação de alguns objectos de possível produção portuguesa.

Vários fragmentos de vidro pertencentes a garrafas de vinho foram retirados das escavações arqueológicas realizadas em Lisboa e foram caracterizados quimicamente. A análise química aos fragmentos revelou tratar-se de uma composição rica em cálcio e pobre em teores de óxidos alcalinos (HLLA). Para alguns fragmentos, foi proposta uma proveniência inglesa. Para além da caracterização química, foi proposta a sistematização da forma da garrafa, uma vez que a forma pode ser um factor importante na determinação da sua datação.

Uma pequena percentagem de fragmentos foi identificada como tendo composições químicas alcalinas mistas, composições ricas em potássio, e composições ricas em chumbo. As duas últimas formulações químicas foram encontradas entre os conjuntos arqueológicos de Lisboa e os objectos com estas composições foram datados do século XVIII. Estas são evidências de que Portugal seguia as tendências Europeias em relação ao vidro e a sua composição.

Neste trabalho apresenta-se a primeira caracterização química sistemática do vidro datado do início do período moderno que circulava em Portugal, trazendo novos dados sobre as trocas comerciais entre Portugal e os seus países aliados.

Como parte do estudo, e com o intuito de prolongar a sobrevivência destes conjuntos de vidro, foram desenvolvidos sensores ópticos e de baixo custo para a detecção *in situ* do ácido fórmico. Este poluente orgânico é emitido por materiais normalmente utilizados no armazenamento e exposição do vidro. A detecção atempada da presença deste ácido pode desempenhar um papel importante na preservação deste valioso património, o vidro.

Palavras-chave: Objectos de Vidro, Início do Período Moderno, Arqueometria, Estudos de Proveniência, Estratégias de Conservação Preventiva

ABSTRACT

Early Modern glass from the Iberian Peninsula has - so far - seldom been investigated. The project, combining chemical analysis with a stylistic approach, and focusing on composition and technology, aims to characterise glass objects circulating in the national territory, in an attempt to identify their origins and to eventually bring to light a Portuguese centre of glass production.

The chemical composition of more than 200 glass fragments was determined by means of μ-PIXE down to a level of tens of μg/g. The results obtained allowed one to select some objects to further extend the analysis to the trace and rare earth elements (REE) down to the ng/g level, through the use of LA-ICP-MS. Glass colours and natural hues were studied by means of UV-Vis reflectance spectroscopy and, when necessary, enamels were studied by means of μ-EDXRF and μ- Raman microscopy.

From all the objects analysed, it was possible to conclude that the great majority of the glass dating upto the 17th century, is of a soda-lime-silica type, which indicates a Mediterranean tradition.

Venetian or *façon-de-Venise* shapes were identified, and for some of them a Venetian provenance was confirmed. For other *façon-de-Venise* shapes, the composition presented differences that led to the conclusion that new *façon-de-Venise* production centres could be recognised. From the only assemblage containing glass fragments dated to the medieval period, it was possible to attest the presence of Venetian glass in the Portuguese territory from at least the 14th century.

Additional objects showed particular compositional features, such as high and very high alumina contents for instance, that, as far as it is known, do not match up with any of the known glass production centres in Europe. Allying the stylistic characteristics with the glass chemical composition, allowed one to identify some objects possibly belonging to a Portuguese production.

Several glass fragments belonging to wine bottles were retrieved from archaeological excavations in Lisbon and were chemically characterised. The chemical analysis revealed an HLLA composition for all of them. For some of these fragments it was possible to propose an English provenance. Besides the chemical characterisation, a systematic analysis of the bottle shape was proposed since the shape can be an important factor in determining its chronology.

A small percentage of the fragments were identified chemically as having mixed-alkali compositions, potassium-rich glass, and lead glass compositions. The latter two chemical formulations were found among the assemblages from Lisbon and the objects with these compositions were dated to the 18th century. These constitute evidence that Portugal followed European tendencies in their glass and its compositions.

This is the first systematic chemical characterisation of Early Modern glass circulating in Portugal, providing new insights into trade between Portugal and its trade allies.

As a part of the study, and to prolong the survival of these glass assemblages, simple and low cost optical sensors were developed for the *in situ* detection of the organic pollutant formic acid, which is emitted by materials usually used in storage and in the display of glass. The detection of the presence of this acid can play an important role in the preservation of this valuable heritage; glass.

Keywords: Glass objects, Early modern period, Archaeometry, Provenance studies, Preventive Conservation Strategies

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SYMBOLS AND NOTATIONS

μ-EDXRF – micro - Energy dispersive X-ray fluorescence spectroscopy

μ-PIXE – micro - Particle induced X-ray emission

CPU – courtyard from the Universidade de Coimbra

HLLA – High lime low alkali

LA-ICP-MS – Laser ablation inductively coupled plasma mass spectroscopy

LbL – Layer by Layer

LRA – Rua do Arsenal, Lisbon

LTR – Museu do Teatro Romano, Lisbon

n.d. – non-dated

p.c. – personal communication

PAA – poly(acrylic acid)

PEI – poly(ethylenimine)

PEMs – Polyelectrolyte multilayer

PMF – Praça Miguel Fernandes , Beja

REE – Rare earth elements

SCV – Santa Clara-a-Velha Monastery, Coimbra

SJT – São João de Tarouca Monastery

UV – Ultra Violet

Vis – Visible

VOCs – Volatile organic compounds

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INTRODUCTION

“Vitrum est corpus diaphanum, artificialiter ad naturam quinte essencie redactum, quod argentum populi in libris philosophorum nominatur eo quia similitudinem vasorum auri et argenti in domibus pauperum representat”[1]

Guillaume Sedacer, “La Sedacina ou L’Œuvre au crible”, end of 14th century
(Barthélemy, 2002, p.164, Vol.II)

Guillaume Sedacer, Catalan, and a religious man from the Carmelite Religious Order devoted most of his life to alchemy (Barthélemy, 2002, p.21-22, Vol.I). In his book *Sedacina Tocius Artis Alkimie* (in which several recipes for the making of glass are described) this 14th century alchemist, defined glass as a diaphanous body, an artificial material beyond the four essential elements belonging to the created Universe (referring that is to water, fire, earth and air); it is considered by him to be the fifth element or the *quintessence* (Barthélemy, 2002, p.164, Vol.II; Dedo von Kerssenbrock-Krosigk[2]). For G. Sedacer, glass symbolizes the philosopher’s stone and shares its principles.

G. Sedacer also goes on to describe the experimental methodology that every alchemist should practise in order to achieve his or her purpose. According to Sedacer, the preparation of the

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[1] *“Glass is a transparent body, artificially reduced into the state of the quintessence, called the people’s Money in the books of philosophers, because in the home of the poor, it is the equivalent to gold and silver bowls”.*

[2] Keynote lecture by Dedo von Kerssenbrock-Krosigk entitled “Art and Alchemy – The Mystery of Transformation”, given within the conference GLASSAC – Glass Science in Art and Conservation, held by the University of Durham, from 10th to 12th September 2014.

experiments was key step if the executants' objectives were to be fulfilled. The preparation (which would include the observations) and preparatory research are then seen as essential groundwork in order to obtain the best possible results. According to G. Sedacer, it was necessary to those who practiced this activity, to know exactly how things were composed exteriorly in order to know how they were composed internally and vice-versa (Barthélemy, 2002, p.26-32, Vol.I). For this it was necessary to study, to learn how to prepare things; to learn on the virtue of things, not only by reflecting on them but also through experimentation. He also discusses the importance of having in depth knowledge and comprehension of the properties and composition of the materials involved. When applying these principles in the study of glass either to discuss its provenance or to understand its corrosion processes and contribute to its further preservation, it is fundamental to have a sound knowledge of its constituents – the raw materials employed in its manufacture. Only with this background information can one look at the chemical composition of glass, discuss its possible provenance, and reach a conclusion as to the cause of its degradation. It is known that provenance investigations have been made employing different methodologies, like through the study of historical treatises and glass recipe books. This kind of investigation is fundamental to obtain knowledge on the employed raw materials for instance, and to further cross this information with the glass chemical composition.

Fig.1: Drinking *tazza* from Venice or Low Countries, mid 16th century, Corning Museum of Glass, accession nº 58.3.180 (©2002-The Corning Museum of Glass, available at www.cmog.org, accessed in 24 September 2014).

Throughout history, glass was able to dazzle people, from the poorest villager, to kings, and including the educated clergy. This fascination with glass is related to the metamorphosis it undergoes during the process of its creation; starting with alkaline minerals or ash mixed with sand or with calcined and ground pebbles, these – at the right temperatures - are "transmuted" into an incandescent-red molten material, and it is in the hands of the greatest masters that molten glass is then transformed into the most beautiful and diaphanous objects (*e.g.* see figure 1). Whilst it is known that glass and its production were important in some regions (*e.g.* Murano glass production), over long periods of time, the importance of glass production in Portugal during the early modern period, and how this was related to production in Europe, remains unclear.

Bibliographical research has brought to light some factual elements such as that Portugal has had a glass production since at least the time of the Roman occupation. After that period there is an informational gap until the 15th century, at which point documentary sources start referring again to glass production in the national territory. It is however from the 17th century onwards that more information is brought to us about glass production in Portugal; this relates to the opening of furnaces and factories, the glassmakers operating in those production locations and so on. Allying this information to the increasing number of glass objects found throughout the national territory during archaeological excavations and, dated from the medieval period onwards, it then becomes justifiable and necessary to investigate their provenance.

Research Objectives

Study of Portuguese archaeological glass sets

The glass heritage has been seldom studied in Portugal, resulting in a poor knowledge of the circulating compositions of the glass in the Portuguese territory.

One of the main purposes of this project is the identification and characterisation of glass objects that circulated in Portugal during the 17th and 18th centuries. Attention will be mainly focused on everyday objects, found in monastic and private house contexts. It is expected that similarities and differences among them will be identified, and that this will provide an outline and characterise the evolution of glass production in Portugal. Other important aspects to be elucidated are the trading routes between Portugal and European glass production centres. One of the greatest challenges on studying glass found in Portugal is the knowledge that this territory suffered from very diverse cultural influences, which makes expectable to find a great diversity of glass provenances. Moreover, due to the same reason it is likely that glass produced locally suffered influences from different glassmaking traditions.

The Portuguese situation was perhaps one of a kind in terms of commerce and trading relationships when comparing with other European countries. Being one of the most important harbours of Europe, it is most likely that Lisbon encompassed material from all around, including glass objects from Venice, Antwerp, Central Europe in general (in particular from Bohemia), the British Isles and maybe from other production centres.

This study also aims to clarify singularities and common features in Portuguese glass in order to establish typical patterns associated with it. The ultimate objective is to identify compositional and stylistic features that can be used to distinguish glass objects produced in Portugal from those of a distinct provenance found either in Portugal or other European centres. Lacking archaeological data on furnaces, it is tried to answer these questions by linking together the information obtained from the stylistic approach and from the results of the chemical analyses.

The archaeological finds used in this study were from the following archaeological sites: Santa Clara-a-Velha Monastery in Coimbra (17th century), São João de Tarouca Monastery in Lamego (17th to 18th centuries), the archaeological excavation at Miguel Fernandes Square in Beja (14th to 17th century), the archaeological excavation carried out in the courtyard of the University of Coimbra (17th century), the archaeological excavation carried out in Roman Theatre Museum in Lisbon (17th to 18th centuries) and the archaeological excavation carried out in Arsenal Street in Lisbon (17th to 19th centuries). With the exception of the Roman Theatre Museum (Lisbon) and Rua do Arsenal (Lisbon) contexts, the remaining four assemblages were studied from a stylistic point of view, by the archaeologist Teresa Medici in her Ph.D. dissertation entitled “VIDROS DA TERRA. O vidro tardomedieval e moderno em Portugal (séculos XIV-XVII). O contributo da arqueologia” (Medici, 2014). This was a very important factor when choosing the glass groups to be studied. To clarify the choice of this time-period to study, that is 17th and 18th centuries, this period showed great changes in the raw materials employed, different furnace fuels used and so on, resulting in the appearance of new glass formulations. Glass from this time period is found in Portugal, retrieved in large quantities from archaeological excavations, and it has been seldom studied. Bearing in mind the main purposes of this investigation, it was important to choose well dated contexts. For this reason the archaeological assemblages from Santa Clara-a-Velha Monastery in Coimbra (17th century), São João de Tarouca Monastery in Lamego (17th to 18th centuries), the archaeological excavation at Praça Miguel Fernandes in Beja (14th to 17th centuries) and the archaeological excavation at the courtyard of the University of Coimbra (17th century) were selected. These assemblages are well dated from their archaeological contexts, as it was possible to find ceramic objects or sometimes coins. The great advantage to selecting these four assemblages besides their dated contexts, was the possibility to associate the obtained chemical composition (through chemical analysis) with the insightful study performed by T. Medici (2014) mentioned above. The other two sets of objects from Lisbon contexts served as an opportunity to look at a slightly more recent chronology, in addition to the fact that it was considered very important to compare the results obtained from the other finds with glass circulating in the nerve centre of the country. Moreover, looking to glass assemblages dated to the 18th and the beginning of the 19th century, allowed one to understand that glass circulating in Portugal followed European tendencies in terms of composition.

The geographical locations of the glass assemblages under study are represented in figure 2.

Fig. 2: Map of Portugal with the locations of the glass contexts under study. From North to South, SJT is the São João de Tarouca Monastery, SCV is the Santa Clara-a-Velha Monastery, CPU is the courtyard of the Universidade de Coimbra, LTR is the Museu do Teatro Romano, LRA is the Rua do Arsenal and PMF is the Praça Miguel Fernandes.

As previously mentioned, glass objects found in the Portuguese territory have not been given the attention they deserve in the past few years. The studies that have been performed have mainly been concerned with the stylistic point of view, and only a few have addressed the chemical characterisation of glass. V. Valente (1950) and J. Amado Mendes (2002) are among the first to study the general panorama of the glass production history in the Portuguese territory from the 15th century onwards. In their books, Portuguese glass history is explored on the basis of contemporary historical documentation. J. Custódio (2002) dedicated a book to the Coina Royal Glass Factory, where the history of its foundation is thoroughly described, as well as its years of activity.

Regarding more recent studies, M. Dias da Cruz (2009) wrote his Ph.D. thesis on Portuguese glass from the Roman period, where a multidisciplinary approach allowed discussion of the importance of glass on the day-to-day life of Roman inhabitants from the Iberian Peninsula. With regards to the studies on medieval and post-medieval glass, a selection of glass objects from the Santa Clara-a-Velha

Monastery context was studied by M. Ferreira (2004) in terms of its shapes and decoration features. This study has focused on the *façon-de-Venise* shapes, the filigree glass, the diamond engraving decoration, and so on, outlining the myriad colours, shapes and decorative techniques that one can find within this set of objects. Medici *et al.* (2009) studied a selection of glass bottles and jugs from the same context in terms of shapes and decorative features, and the glass chemical composition was also determined by means of micro-energy dispersive X-ray fluorescence spectrometry (μ-EDXRF). Also within this group, a set of *millefiori* glass objects was studied not only from a stylistic point of view but was also chemically characterised by X-ray electron probe microanalysis (EPMA), Raman microscopy and UV-Visible absorption spectroscopy (Lima *et al.*, 2012). From these approaches it was possible to establish that some of the objects had a clear foreign influence (from Islamic and Venetian glass for instance), but also that there were objects with uncommon shapes and decorative features, as well as chemical compositions that did not relate to any of the coeval published compositions from known European glass production centres.

Some papers were dedicated to the stylistic study of single glass assemblages where the historical context was addressed. The set of glass objects from the Rua da Judiaria in Almada comprises glass objects dating from the 12th to the 19th centuries and was studied by T. Medici (2005a). In this paper, besides the description of the glass finds, the provenance of some objects based on their shapes and decorative features is also discussed. The same author also studied an archaeological glass group dated from Roman time to the 19th century of the present era. This group resulted from the archaeological excavation in the Rua dos Correeiros, Lisbon (Medici, 2011). Once again the provenance of some objects is discussed as well as the trading relations between Portugal and Venice during the medieval and post-medieval period (Medici, 2011, p.313). M. Ferreira (2005a) studied the archaeological glass found in different excavations carried out in the city of Tomar. The glass finds can be dated from the Roman period to the 19th century. In this study the author was able to draw some conclusions about the objects' provenance through the analysis of their shapes (Ferreira, 2005a, p.407).

With the aim of analysing special decorative features, Ferreira & Medici (2010) compared mould blown decoration patterns between assemblages from sites such as S. João de Tarouca Monastery, Santa Clara-a-Velha Monastery, courtyard of the Universidade de Coimbra, and Praça Miguel Fernandes in Beja, among others that are not considered in this present investigation. In this paper the authors concluded the uniqueness of some decorative patterns that have no parallel throughout Europe (Ferreira & Medici, 2010, p.408). Wheel engraved patterns dating to the 18th century were retrieved from an archaeological excavation carried out on the Marquis of Marialva Palace, Lisbon. The analysis of these fragments provided an understanding that in this period, sophisticated glass objects were circulating in Portugal among the court and the wealthy population (Ferreira, 2005b, p.241).

Finally, this brief review of the most up to date studies carried out on glass objects found in the Portuguese territory will conclude with the only excavation and resultant archaeometric study performed on a Portuguese production centre. The preliminary study on the production remains of the Coina Royal glass factory showed that it produced at least four different types of glass compositions (Lopes *et al.*, 2009, p.592).

As it became clear from this brief review of the studies of glass found in Portugal, no systematic approach was carried out on these several glass finds in order to ally the stylistic study to an investigation of the chemical composition. This kind of approach is necessary to highlight differences and similarities among glass groups found in Portugal and among other known European glass production centres, as well as to outline and characterise the evolution of glass production in Portugal. This line of investigation is mandatory because the general idea is that Portuguese glass production was of poor quality and had no expression, a fact that was contradicted by these first preliminary results.

In the study we performed, several analytical methods were selected in order to establish a framework and characterisation methodology for the study of the glass objects. Among the several analytical methods that can be applied for this purpose an attempt was made to mainly use non-destructive ones.

The conservation conditions of the glass objects and their preservation for future generations will also be considered.

Sensor development

Like all existent materials without exception, glass suffers from degradation processes, which in an extreme situation can lead to its full collapse and disappearance. In order to allow this material to be passed on to future generations, preventive conservation measurements must be taken to ensure its continuity through time.

In the context of preservation, attention will be paid to the monitoring of indoor pollutants that can interfere with the integrity of the glass objects. It is known that pollutants such as for instance formic acid and sulphuric acid from acid rain can affect the integrity of glass compromising its stability. The objective is to design an optical sensor for the detection of the organic volatile compound formic acid. In brief, formic acid will enhance and deepen alkali leaching from the glass matrix. This chemical corrosion process will be explained further in *Chapter 1*, *Part II.* Although a new generation of monitoring and analytical devices is currently available to study both indoor and outdoor atmospheric conservation, there are difficulties related to this subject which include limited access to sophisticated measurement equipment, aggravated by the relative high number of places to be monitored and measured (*e.g.* museum halls, interior showcases and storage boxes). Therefore simple and low-cost devices for detecting the pollutants *in situ,* are still required for the preservation of cultural heritage objects.

Some research has been carried out on this subject in which small sensors based on the encapsulation of suitable organic dyes in sol-gel silica films were produced to monitor environmental parameters such as light, humidity, temperature, and environmental pH (see for example Carmona *et al.*, 2008; Dickert *et al.,* 2000; Goicoechea *et al.*, 2008; Han *et al.*, 2007; Janzen *et al.,* 2006; Kowada *et al.,* 2005; among others).

Chemo-responsive dyes will be tested as sensors according to their sensitivity and selectivity towards indoor formic acid vapours. The sensor response should ideally be specific and easily monitored by means of a colour change, in minimum time, offering a suitable alternative to detecting the compound referred to above, without the need for more sophisticated or non-practical instrumentation such as electrodes, solutions, pH meters or batteries.

This thesis is divided into two parts to facilitate its reading. ***Part I*** is dedicated to the archaeometric study of the glass finds under investigation, and ***Part II*** focus on the sensor development. The general Introduction focuses on the other hand, on the research objectives for the study of glass objects found in Portuguese territory and for the sensor development, addressing the conservation issues and the preservation of this heritage. In general, this thesis is structured in such a way so as to present first the historical context and state of the art for the topics covered, followed by the presentation and discussion of the results obtained and respective conclusions.

Part I is divided into four chapters. Chapter 1 is an introduction to archaeometry and archaeometric studies on glass. In Chapter 2, the raw materials employed in glass production over certain periods of time and for different European production centres are addressed. This is followed by a brief review of the most up to date studies on glass in Europe covering the time period between 17th and 18th centuries. Whenever necessary and for the sake of better understanding, a small contextualization of the previous centuries is presented. In Chapter 3 a description of the archaeological context and the historical background of the glass objects follows this for each context being study. This is followed by the methodology used for the selection and sampling objects, the research design and methodology, where the analytical methods and the respective analytical conditions used to perform the glass analysis are described.

Finally, in Chapter 4 the study performed on the glass assemblages is presented. The results of this investigation are presented, where the data obtained is divided into glass chemical type. This division will allow the comparison between the obtained results of the contexts and published data on coeval glass compositions from known European production centres.

In what regards ***Part II***, in Chapter 1, the glass degradation mechanisms, its agents and what has been done so far in terms of identifying and sensing them will be summarily described. Chapter Two comprises the study and development of an optical sensor for the detection of indoor formic acid vapours. In the same line of thought as in the previous chapters, first the methodology and experimental design for the development of the sensor is explained, followed by the description of the analytical techniques employed for the sensors characterisation. Last of all the matrices tested are described, and the final sensor is presented.

Lastly, the final remarks for the previous chapters are presented, highlighting the main conclusions and proposing future work.

Glass as a material has always been a fascination to me. The way an incandescent molten mass is transformed into beautiful objects and colourful stained-glass panels it is something that at a first sight seems wrapped in magic. From the first time I saw glass being blown twenty-four years ago, I developed a passion for this materials and all its potential.

During my master thesis I had the opportunity to work on some glass objects retrieved from Portuguese archaeological excavations and dated from the post-medieval period. It was back then, during my research on this matter, that I understood that glass retrieved from Portuguese archaeological excavations and dated from the medieval period onwards was the subject of interest for only a very limited number of scholars and that no systematic approach was done to study these objects. From this lack of knowledge on medieval to early modern glass circulating in Portugal the need to develop this project was obvious.

A very significant number of glass assemblages, in their majority from Portuguese archaeological contexts, lay forgotten on storage. Archaeologist and other scholars chose most of the times not to study this material due to their lack of knowledge on the subject and because no systematic approach was done so far to demonstrate how the study of glass in Portugal can be important to reveal social and economic aspects of our society. Related to the study of the material itself, other very important aspect that captivated my attention was the conservation of glass objects. In order to keep this material available to present and future generations, it is very important to investigate on further strategies concerning the glass preservation and conservation, in order to minimise the action of the corrosion agents.

I expect that this thesis, together with other fundamental works on this field, namely the PhD thesis from Teresa Medici (2014), will change and improve the knowledge on glass circulating in Portugal, helping also on stimulating the interest of others on this subject.

PART I

NEW INSIGHTS INTO 17TH AND 18TH CENTURY PORTUGUESE GLASS

CHAPTER 1

INTRODUCTION

“Archaeometry is the application of scientific measurement to problems of the study of Man. These “measurements” may be physical analysis, statistical studies, instrument techniques, or even the inferences allowed by evaluation of quantified data.”

Philip C. Hammond, “Archaeometry and Time: A Review”, 1974
(Hammond, 1974, in *Journal of Field Archaeology*, Vol.1(3/4), p.329-335)

The citation above is one of many definitions for the term “archaeometry”, which has been the subject of discussion even since it first appeared in the 1950s. The term is closely related to the scientific journal *Archaeometry* founded in 1958 (Montero Ruiz *et al.*, 2007). In a broader sense, archaeometry can be understood as the set of measurements performed on material of archaeological origin. Its definition has evolved with time, as well as the subjects it covers (Montero Ruiz *et al.*, 2007).

Nowadays archaeometry, always strictly connect with archaeology, has become much more interdisciplinary, the main purpose of which is the application of modern analytical methods to obtain information from historical materials. The information obtained can be of a compositional or structural nature, and can shed light on issues such as materials provenance, raw materials sources, dating, commercial routes, and so on. Currently, the generally accepted areas encompassed by archaeometry are: dating, physical and chemical analysis performed on materials (these include their technology, origin and their applications) paleoenvironmental studies, geophysical survey and satellite remote sensing and finally mathematical and statistical methods that allow one to interpret the data obtained from different fields of investigation (Montero Ruiz *et al.*, 2007).

In terms of the archaeometry of glass, its main focus is the study of the raw materials that compose the glass. Raw materials are the group of basic components that are put together and submitted to a transformation process in order to obtain a final product, in this case glass. According to Navarro (2003, p.129-130), raw materials out of which glass is made can come directly from nature, can be manufactured, or can result from previous recycling actions. In many cases the combination of the three situations are observed when analysing glass compositions from the early modern period.

In order to correctly interpret the resulting data when analysing glass chemical compositions, a solid knowledge of the raw materials is fundamental. It is very important to bear in mind the transformation processes that each raw material can undergo, why it does so, the history of its usage, where it was usually collected and so on. Another important aspect to consider when studying glass compositions is the nature of the impurities that are characteristic for each raw material, since these can sometimes be decisive when the provenance of the object is under discussion.

Along the history of glass making, the most frequently used raw materials to obtain silica – the main component of glass – are quartz pebbles and sand. Apart from the silica, the sand used in the glass batch always contains different type of impurities (Moretti & Hreglich, 2013). The minerals making up these impurities are usually aluminium-rich kaolinite and feldspar, zirconium-rich zircon ($ZrSiO_4$), REE-rich monazite (REE phosphate), titanium-rich rutile (TiO_2) and iron oxides (Moretti & Hreglich, 2013; Wedepohl *et al.,* 2011a). These elements – alumina, iron and titanium oxides- are the main trace elements and trackers for sand, allowing discussion about the provenance of raw materials and, consequently, the provenance of the glass object (Velde, 2013).

The proximity of the raw materials to the production centre is important when studying the economic aspects of early modern glass production (Navarro, 2003, p.130). It would be expected that the glassworkers would use raw materials that could be found in the proximity of the kiln; however, it is possible to find exceptional situations such as that of Venetian glass that will be further discussed in *Chapter 2, Part I.*

Concerning the importance of archaeometry in Portuguese studies of glass dated to between the 17th and 18th centuries, stylistic studies alone are not enough to obtain information on the glass composition and can only be used to form suppositions on probable provenances of the objects. On other hand the written sources with information about raw materials or used recipes are scarce and not yet subject to a systematic and detailed study. Formal and stylistic studies on Portuguese archaeological assemblages have been directed towards the identification of objects with formal characteristics from known European centres, as for instance Venetian objects or those with *façon-de-Venise* attributions (Ferreira, 2004). After this identification, determining the glass chemical composition is mandatory. This will allow for comparisons with chemical compositions from the literature, and confirm or not the supposed provenance. With the spread of glass recipes and knowledge on the employment of raw materials and their treatment throughout Europe from the 16th century onwards, the chemical compositions of most objects from several of the European production centres are very similar, and sometimes impossible to distinguish from one another. Following the example of *façon-de-Venise* glass, several scientific investigations dedicated their work on differentiating *façon-de-Venise* production centres through the analysis of minor and trace elements present in the glass (Cagno *et al.,* 2008; 2010; De Raedt *et al.,* 2001; Šmit *et al.,* 2004; 2005; 2009). It is fundamental to determine the minor and trace elements or Rare Earth Elements (REE) present in glass objects as they are considered to be the glass fingerprints.

With this idea in mind, the objects from Portuguese archaeological excavations to be studied will be analysed in order to determine their chemical composition in major, minor and whenever possible in trace or REE components. To perform these analyses and obtain the glass chemical composition, a few analytical methods can be used. In this current investigation, particle induced X-ray emission (PIXE) was chosen to obtain data on the major and minor glass components, and laser ablation induced coupled plasma mass spectrometry (LA-ICP-MS) was used to obtain information on the trace and rare earth elements. One of the purposes of this investigation is to try and attribute a possible provenance to the largest possible number of fragments. It is important to bear in mind that the process of attributing a final provenance (in this case more specifically local or region production) to a glass object (or objects in general) through its chemical composition it is not a straightforward task. It implies the creation of a database from several productions centres in order to be able to make comparisons between results. These databases should be composed by a minimum of 15 samples in order to establish the variability within a single source (Tykot, 2004, p.417). For this reason, for every glass compositional type and whenever possible, a database was created containing compositional information from known European glass production centres, in order to compare these with the results obtained.

Considering the studies carried out so far on Portuguese archaeological glass objects dated to between the 14th and 15th centuries, it is concluded that the typologies of the objects can be inserted perfectly within those of late-medieval Europe. The majority of the objects are utilitarian, for instance liquid containers and tableware (Medici, 2014). Looking to glass objects dated from the 16th century, shapes such as drinking glasses with feet, and bottles to serve at table were identified. With regard to the drinking glasses, two different feet were identified in majority of cases: a foot with one spherical knop on the stem, and a foot with two spherical knops on the stem. The first case is very common in European glass production centres; on the other hand, the foot with two knops on the stem is rather uncommon (Medici, 2014). Up to the 17th century, the objects found among archaeological excavations are largely related to tableware. From this century onwards, a broader use of glass can be observed, related to medical care, lighting and tableware. The presence of glass imports amongst finds is also more in evidence. On the other hand, among known shapes, uncommon shapes without known parallels are also identified as gourds, globular flasks and a mould blown four-petalled flower embossed motif enclosed within a lozenge pattern decorating some glass objects such as beakers or ink-pots (Medici, 2014). This discrepancy between retrieved objects before and after the 17th century, could be a reflection of a behavioural change between the 16th century man and the 17th century man. One can consider that in the 17th century a pre-consumer man begins to emerge, feeling the need to possess more objects to fill his greater needs.

Finally, to summarise the main questions intended to be answered using archaeometric principles:

- What kind of glass, chemically speaking, was circulating in Portugal during the 17th and 18th centuries?

- Is it possible to identify particular features in terms of composition that can differentiate objects found in the Portuguese territory? (Note that since no furnaces from this time period have so far been excavated in Portugal, and that since no analysed glass coming from this kind of environment has been characterised, one can expect to find specific chemical features that do not have parallels in any of the published compositions from known European production centres. To put it simply, with this information it would then be possible to propose that these objects might be of Portuguese provenance.)

- If the answer to the previous question is positive, what kind of glassmaking tradition was preferred in Portugal, the Mediterranean (soda-rich glass) or Northern Europe (potassium-rich glass)?

- Allying the information gathered from the stylistic study with the chemical analysis, is it possible to find particular typologies with unique compositions?

- Since the end of the 17th and 18th centuries were the time of invention and evolution in terms of glass composition and formulation in Europe, is it possible to find some of those novelties circulating in Portugal?

CHAPTER 2

GLASS: PRODUCTION AND HISTORICAL CONTEXTS

2.1 Glass production in Europe during the 17th and 18th centuries

2.1.1 Chemical formulations of historical glass

It is important to understand how the glass production centres in Europe employed their knowledge of glass compositions and formulated their own empirical glass compositions. Particular cases of various raw materials and their use in different European glass production centres will be analysed.

Beginning with the Venetian glass that has been widely studied by Verità and co-workers (*e.g.* Verità & Toninato, 1990; Verità & Zecchin, 2009a), it is possible to understand, through chemical analysis and research in ancient treatises, that the raw materials employed in Venetian glass production were carefully selected, and came from specific locations in order to produce a high quality glass with particular characteristics, that made it one of the most desired luxury item throughout Europe. The most valued characteristics in glass production were transparency, and an uncoloured and homogeneous matrix. To this end, the selection of raw materials played a major role. During the 14th century, Venetian glassmakers began to use quartz pebbles from the Ticino River as a source for silica, replacing the use of impure sands (Verità & Zecchin, 2009a). Quartz pebbles are characterised by their pure composition, with very low contents of unwanted impurities such as iron, that can give naturally occurring green, blue or yellow hues to glass (see *Appendix I, Part I*). A general description of glass components, and the importance of acquire knowledge about used raw materials is described and explored in *Appendix I, Part I*.

It is important to emphasise that at this time the glassmakers' knowledge was an empirical one.

Venetian glassmaking history is strongly connected to the Islamic tradition. Venetian glassmakers were influenced by the Islamic glassmakers in terms of production methodologies and the decoration processes, as well as in their glassmaking recipes. With this knowledge, and since the 13th century, Venetian glassmakers have employed Levantine ashes (rich in sodium), imported from Syria and Egypt, as a source for the plant alkaline component (Verità & Zecchin, 2009a). During the 15th century, another type of glass appeared in Murano, the famous *cristallo* that was made with the intent of resembling rock crystal. This glass, known for its transparency and a perfectly accomplished decolouration, was obtained as a result of the use of purified Levantine ashes in addition to the employment of the Ticino quartz pebbles. This ashes' purification step was the novelty. The ashes were ground, dissolved in water, and then boiled. The resulting solution was filtered and left to dry. These steps led to the formation of a white salt – *sale da cristallo* – that was mixed with the silica source in the right proportion, and calcined in order to obtain the *cristallo* frit. This purification process resulted in the removal of iron compounds as well as calcium and magnesium, the presence of these last two being essential to the chemical stability of the glass (see *Appendix I, Part I*). During the second half of the 17th century, after the spread of *façon-de-Venise* glass and the development of other glass formulations throughout Europe, the fashion for Venetian glass went into decline. In addition, it was no longer possible to import Levantine ashes, and an attempt to grow halophytic plants in the Venetian lagoon was made without success (Verità, 2013, p.530). Until the decline, during the 18th century, Venetian glassmakers produced the most desired luxury glass throughout Europe.

Aiming to match and surpass Venetian production, other glass production centres appeared in Europe (*e.g.* in the Low Countries and the British Isles) and began making *façon-de-Venise* glass. This glass was generally made by Venetian glassmakers who had escaped from Murano and from its restrictive rules (De Raedt *et al.*, 2002). In terms of raw materials, it was not possible to use the same ones that were employed in Venice. However, it is worth noting that an effort was made to employ the purest raw materials that were available locally. For this reason, the chemical composition of the *façon-de-Venise* glass from the different production centres is similar to that of Venetian made glass. Nevertheless, analysing the minor and trace elements from this *façon-de-Venise* glass allows one, most of the time, to distinguish between production centres.

At the end of the 17th century, this desire to create new types of glass, led to the development of two different compositions: a pure potassium glass matrix in Central Europe, and a pure lead glass matrix in the British Isles.

The Central European potassium crystal glass was made using very pure sources of raw materials, such as quartz pebbles to obtain silica and a selection of the potassium-rich plants from which ashes could be obtained.

Before the creation of the potassium-rich crystal glass, the first step towards the improvement of the Central European glass formulation was taken in southern Bohemia by very talented glass masters (for instance Michael Müller, 1639-1709) through the development of a new recipe in which chalk was added to the batch. This step resulted in a more brilliant glass surface that suited perfectly the wheel-engraving decorative technique (Tait, 2004, p.181). During the first half of the 18th century, Central Europe was producing three types of glass: ordinary glass, white chalk glass and potassium crystal glass. The first one was produced with sand, lime, potash (potassium-rich ashes from a vegetable origin) and pyrolusite (MnO_2), this latter material being the only exception in terms of not being a locally collected raw material[1]. The ordinary glass was the successor to the first forest glass formulation (Kunicki-Goldfinger, *et al.*, 2005). The white chalk glass[2], as it was referred to above, was the result of adding chalk to the batch instead of limestone. For this formulation, a more careful selection of raw materials was made, followed by some purification steps. The potash (from vegetable origin) which had been used formerly was partially replaced by saltpetre, with the addition of some new materials to the batch, such as arsenic and tartar of wine (Kunicki-Goldfinger, *et al.* 2005). Finally, for the crystal glass formulation high quality raw materials were needed. Saltpetre could almost totally replace the use of potash. In terms of chemical analysis, it is not easy to distinguish between chalk glass and crystal glass (Kunicki-Goldfinger *et al.*, 2005).

In the British Isles, a different glass formulation was being developed. This development occurred more or less at the same time as the new potassium-rich glass formulation was being developed in Central Europe. With reference to lead crystal glass, it is again the result of the selection of very pure sources of raw materials, where flint glass[3] was used and to which was added potassium bitartrate ($KC_4H_5O_6$, a by-product of winemaking), sodium borate or borax ($Na_2B_4O_7.10H_2O$) and saltpetre or potassium nitrate (KNO_3, this prevents the formation of metallic lead during the glass melting process, thus avoiding the crucibles breaking) (Lanmon, 2011, p.32-33; Tait, 2004, p.184). For these first attempts by Ravenscroft to make a perfect uncoloured glass, there is no written evidence to indicate the use of lead (PbO) in the

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[1] The author of the paper does not mention from where the pyrolusite was imported.

[2] Personal note: It is mentioned in the paper Kunicki-Goldfinger *et al.* (2005, pp.259) the terminological problem when referring to the diverse glass formulations that emerged on the Central European region during the end of 17th century/ beginning of 18th century. This personal note serves to clarify that white chalk glass refers to an uncoloured transparent glass called white chalk to equate it to the Venetian soda-rich formulation of *vitrum blanchum* (Eng. White glass).

[3] It is important to clarify the meaning of flint glass. Flint is a form of mineral quartz that occurs as nodules or masses in sedimentary rocks such as chalks or limestone, and has very low amounts of impurities. Flint glass is the term employed to designate a very pure form of glass. Ravenscroft's patent referred to the invention of flint glass that was probably a potassium-rich glass formulation employing a very pure form of raw material for silica (flint). When lead began to be introduced into the glass batch, the term "flint glass" was then applied to this lead glass formulation.

batch, however it is commonly accepted that due to the first problems of crizzling, Ravenscroft introduced and increased the PbO content up to 30 wt% (Dungworth & Brain, 2009; Lanmon, 2011, p.32-33; Tait, 2004, p.184; Müller & Stege 2006). The employment and selection of raw materials from specific locations, combined with the purification treatments, resulted in unique set of compositional signatures for the glass. For this reason, when resorting to compositional analysis to determine the chemical composition of a glass, it is nowadays possible to identify and distinguish between production locations, because of these empirical preferences by the glassmakers choosing raw materials to obtain the desired characteristics on their final glass objects.

After this summary of historical formulations of glass, it is important to define a criterion by which to distinguish the various glass compositional types that one can find. Based on their chemical composition it is possible, according to literature, to distinguish five main types of glass in use during the 17th and the first half of the 18th century, as summarised in Table 2.1.

Table 2.1: Criteria used to distinguish among different types of glass (Cílovà & Woitsch, 2012; Dungworth *et al.,* 2006; Mortimer, 1995; Schalm *et al.,* 2007).

Glass type	***Criteria***
Soda-rich glass	$Na_2O > 10$ wt%
Potassium-rich glass	$K_2O > 10$ wt%
HLLA	$CaO > 20$ wt%
Mixed alkali glass	Na_2O and K_2O in similar concentrations
Lead glass	$PbO > 20$ wt%

Soda-rich glass (from plant ash) has high levels of Na_2O and low levels of K_2O. This glass used to be made employing the ashes of halophytic plants as a flux (Velde, 2013, p.71). This glass type developed in the Islamic world, and in Mediterranean Europe (due to the availability of soda-rich coastal plants) and then spread throughout all of Europe during the beginning of the 15th century mainly as *façon-de-Venise* glass (Šmit *et al.,* 2004).

High levels of K_2O and low levels of Na_2O characterise potassium-rich glass. This glass compositional type was usually made using ashes from wood as a flux, which is richer in K_2O. Potassium-rich glass was developed during the medieval period mainly in the Northern and Central Europe, to take advantage of the large forests and to replace the use of natron as a source of alkali; in fact, all the alkalis from plant ashes were used in replacement of the use of natron (Velde, 2013, p.71). Later, purer raw materials were employed as sources of potassium and calcium oxides.

High levels of CaO (>20 wt%) and low levels of alkaline oxides, usually from forest plants or wood ash ($K_2O + Na_2O < 10$ wt%), generally characterise the High Lime Low Alkali (HLLA) glass. This glass composition was widely used for the production of bottles, mainly in the British Isles. It is generally accepted that HLLA glass was taken to the British Isles c. 1567 by immigrant French glassmakers, since this composition was being made in France during the 16th century (Barrera & Velde, 1989; Dungworth & Clark, 2004; Dungworth, 2010).

Mixed alkali glass is usually characterised by having a soda content too low to be a soda-rich glass, a potassium content too low to be considered potassium-rich glass, and a lime content too low to be a HLLA glass. They are therefore considered to be of an intermediate composition between the forest or wood-ash glass and the soda-ash glass made from coastal plant ashes (Dungworth & Mortimer, 2005). This glass compositional type results from a mixture of all these three components having the soda and potassium contents almost in equal parts.

Lead crystal glass was developed and introduced in English glass production around 1674/1676 (Lanmon, 2011, p.24). Lead contents varied between 15 to 40 wt% and this glass was usually produced with very pure raw materials such as white sand or flint (as source of silica), litharge and saltpetre (Dungworth & Brain, 2009).

Throughout *Chapter 4*, five tables corresponding to the chemical composition of Venetian and *façon-de-Venise* glass, high lime low alkali glass (HLLA), potassium-rich glass, mixed-alkali glass and lead glass, are presented. In these tables, the values, presented in average with respective standard deviations, were collected from literature and represent in their majority, glass production locations. The compositions reported in these tables will serve as a base of comparison to help determining the provenance of the glass objects that are the subject of this work.

2.1.2 A short journey through European glass history during the 17th and 18th centuries

In order to give a rough and preliminary idea of what was happening throughout Europe in terms of Early Modern glass production, a short summary of the main production centres is presented below.

Venice

Venetian glass, produced on the famous island of Murano, was one of the most prized and desired luxury items for more than 200 years. The history of Venetian glass is connected and inseparable from glassmaking developments all over Europe. It was the driving force that impelled the other European productions centres to develop new glass formulations, always with the intent of surpassing the virtuosity and refinement of Venetian glass.

This fascination with Venetian glass and its subsequent supremacy was due to the conjunction of several characteristics such as the formulation of the glass and the selection of raw materials, the unique decorative features, and the glassmakers' mastery in creating and developing dazzling shapes (Verità & Toninato, 1990; Whitehouse, 2004, pp.ii).

The evolution and development of glassmaking in Venice is connected and closely related to the history of the Venetian Republic, which in turn had its political and economic growth linked to the Orient, more specifically to the Levant (Verità, 2013, p.515). During the 12th century, Venice became an overseas power and became the link between the East and the Western world (Gaba-Van Dongen, 2004, p.195).

Venetian glass evolved from two different traditions: during the Early Medieval period glass was being produced both with natron (the flux used by Roman glassmakers), and with raw materials from the Levant (Verità, 2013, p.533). Between the 7th and the 13th centuries, natron glass was gradually substituted by a soda-lime-silica glass based on plant ashes. During the Middle Ages, Venetian glass was exclusively produced using soda-rich vegetable ashes imported from the Levant and the glass production was carried out in two steps: soda plant-ash and the silica source were mixed together in almost equal parts and calcined for several hours which resulted in a frit. This frit was then mixed with internal glass cullet[4] and with other compounds (colouring or decolouring agents) to be melted in crucibles (Verità, 2013, p.523).

Until the 15th century, Venice imported not only raw materials from the Levant but most probably also Islamic glass recipes and the ideas for the shapes of the glass objects. From this period onwards, Venice took control of innovation in glassmaking, creating its own shapes, decorative features and most importantly, its own glass recipes with innovations in the composition (Verità, 2013, p.527). Venetian glass can be divided into three groups on the bases of the different compositions: common glass, *vitrum blanchum* and *cristallo*. The first two formulations were exclusive until the second half of the 15th century. Common glass was a colourless transparent glass with natural hues of green, yellow or blue that was mainly used to produce utilitarian items; and *vitrum blanchum* a well-discoloured glass that still presented a slight greyish tint despite the attempt to overcome this problem by the replacement of sand with quartz pebbles from the Ticino River (McCray, 1998; Verità, 2013, p.528). *Cristallo* is mentioned for the first time in 1453 and 1457, in two documents found in Dubrovnik, Croatia and Murano respectively. The word *cristallo* was used to designate a glass that could be compared to natural

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[4] Cullet is the term used to designate the waste of broken glass usually gathered for remelting. The expression "internal glass cullet" is here employed to clarify that Venetian glassmakers used only their own cullet; in other words, they only employed glass waste from their own production in order to control the quality of the glass.

rock crystal due to its acquired properties of homogeneity and decolouration (Verità, 2013, p.528). This new glass composition was achieved by the addition of another step to the procedures already in existence (obtaining of a frit followed by the melting of the frit with the glass cullet), which consisted of the purification of the Levantine soda-plant ashes –*allume catino* –to obtain a flux with fewer impurities like iron (Verità, 2013, p.528). In short, the three main glass types were made from very similar raw materials, with the difference between common glass, *vitrum blanchum* and *cristallo* lying in the selection and purification of the raw materials employed in each case (McCray, 1998). From the 15th century onwards, Muranese glassmakers produced the most astonishing objects with intricate shapes and details, and with fabulous decorative techniques such as gilding, enamelling and filigree (*e.g.* figure 2.1).

Fig. 2.1: Goblet in *cristallo* glass, with enameled and gilded decoration. Dated between 1500 and 1525. The Corning Museum of Glass, accession nº 53.3.38 (©Collection of the Corning Museum of Glass, Corning, New York, available in www.cmog.org, accessed in 7 October 2014).

Renaissance Europe was characterised by a society of consumerism. The increased purchasing power and the demand for luxury items propelled and stimulated glass production and innovation, and in this Venice played the main role with its famous *cristallo* objects (McCray, 1998). In addition to the invention of *cristallo*, other glass formulations were conceived. *Calcedonio* glass (figure 2.2 a) was developed with the intent of imitating the precious chalcedony stone (Whitehouse, 2004, pp.iii). *Lattimo* was a white opaque glass formulated to reproduce expensive white Chinese porcelain (figure 2.2 b) (Tait, 1979, p.95). This white glass was also used to develop one of the most prized decorative Venetian techniques developed at the beginning of the 16th century, the *filigrana* or filigree glass (figure 2.2 c) Filigree rods were produced with *cristallo* glass on the outside and with a core of *lattimo* glass (Verità, 2014, p.59). *Girasole* or *opalino* glass was another Venetian invention dating from the 17th century. This is a dichroic glass, meaning that it changes colour from light blue in reflected light to yellow in transmitted light (Verità, 2014, p.60-61). Finally, the *aventurina* glass appeared in Murano during the second half of the 16th century, composed by metallic copper particles that sparkle on a translucent brown glass matrix. This glass was only worked by the most expert glassmakers, and is thought to have been obtained by chance (Verità, 2014, p.61).

(a) **(b)** **(c)**

Fig. 2.2: Examples of some Venetian creations from the Corning Museum of Glass. (a) Chalcedony ewer, dated between 1500 and 1525. Accession nº 2001.3.56 (©Collection of the Corning Museum of Glass, Corning, New York, gift of Robert and Deborah Truitt); (b) Lattimo glass bowl with enamelled decoration, dated between 1500-1510. Accession nº 76.3.17 (©Collection of the Corning Museum of Glass, Corning, New York, purchased with funds from the Museum Endowment Fund); (c) Goblet with filigree decoration, dated to between 1575 and 1625. Accession nº 77.3.54 (©Collection of the Corning Museum of Glass, Corning, New York gift of Jerome Strauss). All images available in www.cmog.org, accessed in 7 October 2014.

The monopoly of Venetian glass declined during the end of the 17th century, and this decline was the result of several events. In the 16th century, Muranese glassmakers began to emigrate to other countries, taking with them the secret formulations and skills of Venetian glassmaking, which thus removed the exclusivity of the Venetian glass market. Also, the appearance of glass treatises and their subsequent translations, made glass compositions and knowledge of the raw materials employed in the making accessible to glassmakers all over Europe. The development of new crystal glass formulations in the British Isles and in Central Europe brought the monopoly of Venetian glassmaking to a definitive end (Verità, 2013, pp.530).

Low Countries

Venetian glass was one of the most prized and desired items among the middle classes during the first half of the 17th century, regardless of its high prices and the difficulties of obtaining it. The Dutch bourgeoisie, during the 17th century, lived in a period of prosperity, which was a reflection of their commercial prominence. This led to a developed taste for collecting luxury items, in this particular case, Venetian glass (Gaba-Van Dongen, 2004, p.193-196).

During the first half of the 16th century, Antwerp became one of the most important ports in Europe. Several Portuguese families connected to the spice trading were established in Antwerp, making this city one of the most prominent commercial metropolis located north of the Alps (Dupré, 2010). The presence of Portuguese families connected with trading in Antwerp can be found earlier, in 1499 with the establishment of the Portuguese Management post in Antwerp (in Portuguese called *Feitoria Portuguesa de Antuérpia*). Italian glassworkers began to establish glass workshops there due to the rapid growth of this city (Janssens *et al.*, 2013, p.538). During the 1530s, luxury items produced in Antwerp (mainly tapestries, jewellery, paintings and books), were exported abroad, in particular to the Iberian Peninsula (Dupré, 2010).

This, allied to the demand for luxury items that were mainly imported, soon became an encouragement to stimulate the income of foreigner skills to improve the local production (Dupré, 2010). In 1585, because of the Spanish conquest, Antwerp lost its economic domain to Amsterdam. The Scheldt River was blocked by Dutch authorities, leading Antwerp into economic decline, which caused the city to be abandoned by wealthy merchants. For this reason, Amsterdam began to acquire vessels made out of glass from Middleburgh, a small city halfway between Antwerp and Amsterdam (from 1585 to 1597), and in 1597 it was granted permission for the first time for an Italian glassmaker to establish a glass workshop in Amsterdam (Janssens *et al.*, 2013, p.538-539). However, Antwerp never ceased to produce glass and by the year 1609, Antonio Neri, the author of *L'Arte Vetraria* visited Antwerp and saw there *calcedonio* (chalcedony) glass being produced, which is an indication of how quickly the new Venetian recipes were arriving at *façon-de-Venise* production centres, and how developed glass production was in the Low Countries (Liefkes, 2004, p.229).

The establishment of local glass workshops for the production of Venetian shapes resulted in *façon-de-Venise* objects being sold at more reasonable prices (Gaba-Van Dongen, 2004, p.197). Venetian glassmakers producing *façon-de-Venise* glass in these new environments understood that it was not possible to import all the necessary raw materials they were used to working with, and for that reason they had to resort to local raw materials. Barilla ashes from Spain were imported to Antwerp for the same purpose as Levantine ashes were imported by Venetian glassmakers (Dupré, 2010). Another difficulty encountered by Venetian glassmakers was the need to create new glass forms, since their Dutch consumers were fond of new styles that could be add to the already existing Venetian shapes (Gaba-Van Dongen, 2004, p.197). During the 17th century, with regard to drinking glasses, the Dutch preferred taller glasses called *flutes* (figure 2.3) as opposed to the Italians who preferred the famous *tazzas*[5]. However, the depiction of *tazzas* is often encountered in Dutch paintings, but in terms of archaeological finds, flutes are much more commonly recovered than the Italian *tazza*. Another typical object found in the Low Countries is the beer beaker, which was based on Venetian forms. One fine example is the beaker decorated with the waffle pattern that was considered an alternative to the German imported forest glass[6] beakers (figure 2.4). However, the *roemer*[7] was still used to drink white wine imported from Germany (Gaba-Van Dongen, 2004, p.197-202).

Fig. 2.3: Flute with engraved decoration. From the Low Countries, dated about 1640. Accession nº 79.3.252 (©Collection of the Corning Museum of Glass, Corning, New York, bequest of Jerome Strauss). Available at www.cmog.org, accessed in 10 October 2014.

During the 17th century, the local workshops were producing almost exclusively discoloured glass; which led to the decreasing on the consumption of forest glass. In other words, discoloured glass was more available than forest glass. This fact was observed on archaeological excavations carried out in Amsterdam on houses in both poor and wealthy social situations. It was observed that the difference

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[5] Brief definition of <u>tazza</u>: usually used as a drinking cup, display cup, or even used as a vessel to serve food, this object is characterised by a wide and shallow bowl that is usually supported by a stem followed by a foot. The stem can be simple and thin or decorated as the example presented in figure 1 in the *Introduction* section.

[6] <u>Forest glass</u> is the term employed to designate the glass developed in the North of the Alps from the 9th century onwards, where the ashes of forest plants, like wood and ferns, were employed on the glass batch as an alkali source. It gave origin to a potassium-rich glass that is known by its green colouration due to the iron content present as an impurity in the raw materials such as the wood ashes and the source of silica.

[7] Brief definition of <u>*roemer*</u>: drinking cup usually used to drink wine or beer. Characterised in general by an ovoid bowl, with a hollow cylindrical body decorated with prunts, and a conical foot. The glass as a green colour, generally the so called forest glass.

between excavated glass objects recovered in houses from these different social classes differed only in quantity and not in quality, and that uncoloured luxury glass produced locally prevailed over the amount of imported forest glass items (Liefkes, 2004, p.236). The uncoloured glass was becoming the symbol of, and synonymous with luxury and taste. Consumerism in the Low Countries led to a phenomenon of status-enhancement through objects, which resulted in a demand for more glass shapes (Gaba-Van Dongen, 2004, p.205).

As far as the glassmakers working throughout the Low Countries are concerned, they originally came from Murano. In the 17th century, not only were Muranese glassmakers travelling to the Northern Europe, but Altarese glassmakers were also moving to new lands (Liefkes, 2004, p.243). Altarese glassmakers came from Altare, a town in the Italian region of Liguria. This town was a very important glass production centre that had, in the 14th century, at least six active furnaces. In the 15th century, more than twenty furnaces were working in Altare. It is however important to mention that whilst the law in Venice forbade glassmakers to go abroad to work, Altarese glassmakers on the other hand were free to establish glass workshops both in Italy and also in foreign countries (Cagno *et al.,* 2012a). Later, glassmakers from Liége, Belgium became very popular. After 1685 it was possible to find glassmakers from France, Germany and England (Liefkes, 2004, p.243). By this time *façon-de-Venise* glass workshops were appearing throughout all of Europe, creating a tight market within which glassmakers were constantly moving. Local governments and owners of glass workshops, were always in search of the best glass master, which led them to make substantial investments in order to attract the best foreign workers (Liefkes, 2004, p.247-249). This fact is important as it shows that at this time being a glass master was a very honourable profession, free of suspicion, leading on occasion to cases of abuses and frauds.

Fig. 2.4: Waffle beaker with enamel and gilded decoration. From the Low Countries, dated about 1575-1625. Accession nº 56.3.93. (©Collection of the Corning Museum of Glass, Corning, New York). Available at www.cmog.org, accessed in 10 October 2014.

The British Isles

In London, *façon-de-Venise* glass was produced from the second half of the 16th century (De Raedt *et al*., 2002; Mortimer, 1995, p.135; Tait, 2004, p.172; Willmott, 2004, p. 271). However, the glass being produced in the British Isles was not in sufficient quantity to fulfil the market, and glass was still being imported from Venice and from the Low Countries (Lanmon, 2011, p.16-19; Willmott, 2004, p.272-273). Glass production in the British Isles began to improve in quality due to the arrival of French *émigrés* glassmakers at the end of the 16th century (Dungworth, 2003; Crossley, 1998). *Façon-de-Venise* production in the British Isles began on a larger scale with the arrival in London of Jean Carrè in 1567. This glassmaker from Arras (France), who spent the major part of his working career in Antwerp, established a furnace in Crutched Friars to produce *façon-de-Venise* drinking glasses. In 1570, Quiobyn Littery and Jacopo Verzelini, both native Venetian glassmakers working in Antwerp, were brought to work in the Crutched Friars Glasshouse (Willmott, 2004, p. 278). After the death of Jean Carrè in 1572, J. Verzelini controlled the glass workshops and created a monopoly that lasted until 1595 (Willmott, 2004, p. 278).

In 1673, George Ravenscroft, a former merchant of Venetian glass, established a glass workshop in London, at the Savoy, with the intention of developing a new type of glass. This glass was made employing English raw materials and intended to imitate rock crystal (Lanmon, 2011, p.27; Dungworth & Brain, 2009).

Despite all the controversy about who invented lead glass, it is imperative to mention George Ravenscroft. He was responsible for the improvement of glass recipes (with an entrepreneurial role) that culminated with the re-discovery of lead crystal glass (Lanmon, 2011, p.27; Dungworth & Brain, 2009). After the G. Ravenscroft's patent had expired in 1681, the production of lead crystal glass spread throughout the British Isles and also to the rest of Europe, mainly into the Low Countries (Müller & Stege, 2006). Until the first half of the 17th century, the production of drinking glasses in the British Isles suffered a lack of originality, as their design was strongly influenced by the Venetian and Dutch (Wilmott, 2004, p.275-276; Brain & Brain, 2015). H. Wilmott (2004, p.286-288) has identified the goblet with cigar stem as the only type of glass that one can possibly consider to be almost exclusively from the British Isles, in the first half of the 17th century.

During the second half of the 17th century, a desire for innovation led to a demand for more resistant and robust objects, an idea that fitted perfectly with the production of the new thick lead crystal glass goblets that were being produced at that time. The relevant role of the Glass-sellers' Company of London in the development glass design in the British Isles, has recently been emphasised (Brain & Brain, 2015).

The heavy baluster stem goblets (*e.g.* figure 2.5) are considered to be the true expression of Baroque style and taste, being the apogee of English drinking glass design (Lanmon, 2011, p.102). This kind of heavy drinking glass with thick walls was in accordance with the customer demand. It is estimated that they first appeared around 1680 and between 1690 and 1720 different forms and stem combinations were introduced (Lanmon, 2011, p.103).

Fig. 2.5: Heavy baluster stem lead glass goblet from English provenance. Dated between 1700 and 1710. Accession nº C.233-1912 (© Victoria and Albert Museum, London, available in http://collections.vam.ac.uk, accessed in 7 October 2014).

With the beginning of the 18th century, and the spread of Rococo taste, changes in style occurred in the shapes and decorations of the glass goblets, and they became more heavily decorated.

Still relating to the heavy baluster stem goblets, more than forty fragments of colourless glass belonging to this category were recovered during the archaeological excavation of the Casa dos Bicos in Lisbon, Portugal, in 1981 and 1982. Twenty fragments from this assemblage, dated to between the second half of the 1690s and 1755, were studied and analysed by means of micro-energy-dispersive X-ray fluorescence (μ-EDXRF). Based on the chemical composition and typology, it was concluded that the Casa dos Bicos assemblage was probably produced in the British Isles between the late 17th and early 18th centuries (Pulido Valente *et al.*, in press). It is worth noting how remarkably quickly English lead glass, produced in various locations, arrived and was commercialised in Portugal.

Bottle development and evolution

It is not possible to discuss glass production in the British Isles without mentioning the bottle making, and its consequent evolution. This was a progressive advance that began in the middle of the 17th century with the need to develop better and more resistant containers to improve the transport of wine and other beverages. A relevant innovation made by the industry of the British Isles was to produce bottles with thicker walls: the increase of glass thickness made the bottles much more resistant mainly during their transport (Lanmon, 2011, p.19, 287).

The interconnection with the wine trade is believed to also be at the origin of the evolution of the shape of the bottle, which became more cylindrical over time. The cylindrical shape allowed for the transport of more bottles in the same space; a cylindrical bottle could be transported horizontally, which helped to maintain the sealing cork wet, and consequently the wine well sealed and preserved (Jones, 1986, p.17; Lanmon, 2011, p. 309). Wills (1974, p.45) believes that Portuguese Port wine was one of the propelling factors for the evolution of the shape of the bottle. In 1703, the British ambassador in Portugal signed the Methuen treaty, in which it was stated that Portuguese wines would be bought preferentially by the British Isles in place of the French wines. Port wine was the favourite, and it needed to be perfectly sealed in order to maintain its characteristics, this being accomplished with the cylindrical bottle being transported horizontally (Wills, 1974, p.45; Lanmon, 2011, p.54). Undoubtedly, the wine industry had a large influence on the development of the bottle. Portuguese wines were largely exported to the British Isles, and not only Port wine (red and white) but also wine from Madeira and from Lisbon. There are registers dating from the 18th century referring to the large quantities of Port wine that wine merchants kept in stock due to the time required for this beverage to become good and drinkable (Jones, 1986, p.20). Wines like Port or Madeira were stored in bottles for them to mature. These wines could be allowed to mature for as long as ten years (Jones, 1986, p.21). It is possible to interpret this information and relate it with what Wills (1974) has stated about Portuguese Port wine being the propelling factor that allowed the shape of the bottle to evolve into its cylindrical shape. Perhaps one can consider that due to the length of time required for Portuguese wines to mature, it became necessary to re-think the bottle shape and adapt it for long-time storage.

The colour of glass bottles also changed with time from olive green to a very dark green or brown that appears black in the thickest areas of the glass. As far as the author know, no comprehensive study was made so far to understand this black-appearing colour phenomena. In terms of chemical composition, no distinction can be made between the olive green and black-appearing glass bottles.

According to the shapes of the bottles, it is possible to estimate an approximate chronology of production, if one takes into consideration such factors as the shape of the body, the height of the neck, the lips and any applied seal (Jones, 1986, p.29). The evolution in shape of the bottle occurred mainly because of changes in technology (such as the introduction of coal as the furnace fuel, or the introduction of dipping moulds), and also due to a desire to change the aesthetic elements of the bottle shape (Jones, 1986, p.29). According to Wills (1974, p.21), it is in the mid-17th century that bottles began to be made in shapes that bear comparison with today's bottles. In 1662, Henry Holden and John Colnett obtained a patent in which they declared they had obtained a very high level of perfection in the making of glass bottles (Wills, 1974, p.21). The oldest examples of wine bottles date from about 1650, and these examples were dated through their seals. The first bottles were free blown, and in the first decades their shapes were in constant evolution (they were not dependent on moulds). The older bottle shape is known as "shaft and globe" due to its globular body and a high neck (figure 2.6). Until the end of the 17th century, the bottle body tends to become wider and the neck shorted, becoming more resistant to breakage but more difficult to handle. The string applied on the rim was applied closer and closer to the bottle top or finish (Wills, 1974, p.36).

According to Jones (1986, p.29) the development and evolution of the bottle shape in the British Isles was different, and independent of the bottle shape evolution in the rest of Europe. From the mid-17th century until around 1760, the bottle finish did not undergo any significant change in its form, consisting of an applied string to the lip, and the latter could be either fire-polished or not (Jones, 1986, p.33). In contrast, according to Wills (1974, p.36), Dutch glassmakers applied two string-rims to their bottles, where one of them had to be more prominent than the other. In the British Isles, it was only from 1760 onwards that more attention began to be paid to the bottle lip. This part of the bottle was tooled in such a way the glass thickness and consequently the lip shape were altered (Jones, 1986, p.33). During the end of the 18th century, more glass was added to the lip of the bottle to be worked, which lead to an increase in size (both in height and width) of this bottle feature.

Fig. 2.6: English glass bottle, with a "shaft and globe" shape. Dated ca. 1650-1660. Accession nº 71.2.5. (©Collection of the Corning Museum of Glass, Corning, New York), available at www.cmog.org, accessed in 22 December 2014.

To deal now with the shape of the body of the bottle, it is known that the cylindrical form appeared around 1730, and as was stated above, some authors (*e.g.* Wills, 1974) believed that the shape of the bottle evolved from globular and mallet-shaped, to cylindrical because of the necessity for improvement of the wine trade and transport. However, according to Jones (1986, p.73), this evolution is more likely result of the introduction of dipping moulds, since it is possible to form this shape in a dip mould, whilst it was impossible to do this with the earlier shapes. It is also possible that this evolution is due to the combination of both factors; in other words, due both to the necessity of improving transport conditions, and in conjunction with the development of dipping moulds.

As far as the case of square bottles concerned, these are considered to have appeared during the 17th century, and their regularity implies the use of a dip mould (Jones, 1986, p.84). These bottles were very common among the Dutch, and were widely used to export gin. During the 18th century, these square bottles, also known as case bottles, were still being produced and were also used in larger dimensions, of up to two gallons (Wills, 1974, p.40).

To deal now with bottles push-ups, several shapes can be identified, and this feature tends to change over the years. One of the most common is the dome-shaped one. From the late 18th century it is possible to find conically shaped push-ups and in the 19th century, with the introduction of the Rickett's mould, this feature became an integrant part of the mould, and was formed inside it (Jones, 1986, p.86). This mould was composed of three pieces that can be described as follows: a cylindrical one-piece mould formed the bottle body, and two open-and-shut mould parts were responsible for forming the shoulder and sometimes the bottleneck. Sometimes the mould included a fourth part which would form the bottle base. Bottles made with this technique have characteristic lines encircling the body (at the shoulder junction), and two vertical lines along the neck left by the mould (Jones, 1986, p.86).

High lime low alkali (HLLA) glass was usually used for the production of utilitarian glass (including window glass), and by the beginning of the 18th century it was almost exclusively used for bottle production. HLLA glass was widespread in the British Isles during the 17th and 18th centuries, and was also mainly used in bottle production. This type of glass is also characterised by its strong green colouration due to its high iron contents (Dungworth *et al.*, 2006). It is believed that this compositional type of glass was developed in Germany and France during the late medieval period, and that it was probably made using the ashes of trees, particularly employing ashes of oak trees (Dungworth, 2009).

Central Europe

After the Roman occupation with its natron-based glass, it was during the 13th century that the Central European region of Bohemia began to be colonised mainly by German people (to repopulate the territory after the Mongol invasion of Europe in 1241), and that the knowledge of glassmaking techniques was brought to this territory. Glass manufacture in this region was easier because of the presence of large forests that not only supplied furnace fuel, but also potassium-rich ashes (Urešová, 1965 p.3-4). By the middle of the 14th century, the exploitation of the silver mines (considered the richest in Europe) brought prosperity to the Bohemian territory. This success was evident in Central European glass production, and by this time a high quality glass of potassium-lime-silica composition was being produced. It is important to emphasise that in comparison to other potassium-lime-silica formulations produced in other European regions during this period, the Central European composition was remarkably pure, and allowed for the creation of thinly blown objects in an almost uncoloured glass. Central European glassmakers, with their pure glass formulation, were able to create a range of more than twenty different forms of fine tableware. From these creations one can draw attention to one of the finest and most elegant of these: a tall and narrow flute measuring between 40 and 55 cm in height, generally decorated with a dense arrangement of glass droplets much smaller than prunts (Tait, 2004, p.153). These glass creations were exported to neighbouring countries, which propelled the glassmaking development into Central European territory (Urešová, 1965 p.5).

The production of a potassium-rich formulation continued throughout the centuries, and by the end of the 16th century, Central European glassmakers were employing new raw material purification methods, more precisely, they had proceeded to the purification of ashes (Tait, 2004, p.179). The conjunction of these improvements resulted in an almost uncoloured and much harder glass than the soda-lime-silica formulation produced in Mediterranean Europe. This harder matrix allowed for the employment of cutting decoration techniques (Tait, 2004, p.179). When referring to glass wheel-engraving techniques from this region, it is imperative to mention the figure of Caspar Lehmann, who in 1588 arrived in Prague as the “Imperial Gem-engraver”, and in 1608 became the “Imperial gem-engraver and glass-engraver” (Tait, 2004, p.179). C. Lehmann was the initiator and the person responsible for the great development and the supremacy of the Bohemian glass-engraving technique (Urešová, 1965 p.7).

During the first half of the 17th century a new potassium-lime based formulation was created in Bohemia that was distinguished from others by its employment of only very pure raw materials (Kunicki-Goldfinguer *et al.*, 2005). This new glass composition allowed for the making of thick-walled vessels that were very suitable for deep-engraving techniques. Central European crystal glass allowed for the use of decorating techniques such as cutting and engraving, which had been perfected to such a degree by the end of the 17th century, that this became the image of the Bohemian Baroque (Urešová, 1965, p.7-8).

Considering the shapes of objects created with this new Central European crystal glass, some were copied from Murano forms, but the most commonly found were inspired by the goblets and beakers with lids and tall knoped stems from Nuremberg (see figure 2.7 a). In terms of engraving motifs, it is possible to find floral stylised and naturalistic themes, small birds, small human figures, and later these evolved into real engraved portraits, hunting scenes, biblical scenes, and so on (Urešová, 1965, p.7-8). Other object types produced in Central Europe were those using double-walled glass with enclosed etched silver or gold foils that were also engraved (see figure 2.7 b). Some glass objects were also decorated with the painting techniques most commonly used in the decoration of porcelain (Urešová, 1965, p.9).

During the 18th century, Bohemian glass was so fashionable that it was exported all over Europe, and its trade was so well organised that it had established offices in important European and overseas trading centres, especially in Spain and Portugal (Lukàs, 1981). Later, in the beginning of the 19th century, with the Austrian bankruptcy and with the earlier Napoleonic wars, Bohemian glass merchants and glassmakers were forced to turn to Russia and Turkey, adapting their creations to their new consumers (Lukás, 1981).

(a) **(b)**

Fig. 2.7: (a) Goblet and lid with cutting and engraving decoration. From Bohemia, dated ca. 1725. Accession nº 27.185.192a, b (©The Metropolitan Museum of Art, available in http://www.metmuseum.org, accessed in 13 October 2014), and (b) Goblet with respective lid. Double glass with gold-sandwich (engraved gold) with cutting decoration. From Bohemian, dated ca. 1730-45. Accession nº355&A-1876 (©Victoria and Albert Museum, London, available at http://collections.vam.ac.uk, accessed in 13 October 2014).

Germany

As was the case with the entire region north of the Alps, the German territory, with its richly forested areas (that contained all the raw materials required for glass production), developed a potassium-based forest glass. The glass that resulted from these forest workshops was known for its green colouration that was a result of the insufficient cleaning or purification of the raw materials (Drahotová, 1983, p.70-71).

Despite the general belief that rustic shapes characterised the glass produced in these regions, until the 15th century it was possible to observe the creation of fine and delicate objects. During the 15th and 16th centuries, these elegant shapes of tall goblets with thin walls began to disappear, being replaced with thicker glass objects with dark to very dark colourations, in shades of green and brown (Tait, 2004, p.153-154). These glass objects were, in the majority of cases, decorated with large and coarse prunts, and often they were also covered with mould-blown decorations. In the beginning of the 16th century, Germany produced tall drinking glasses with thick walls (*Stangengläser*), decorated with large prunts, and sometimes also with a single handle. Other important and typical German shapes from this time were the bottle with a double conical form, and the *Maigelein* (see figure 2.8), a small cup or short beaker, usually with mould-blown decoration (Tait, 2004, p.154-155).

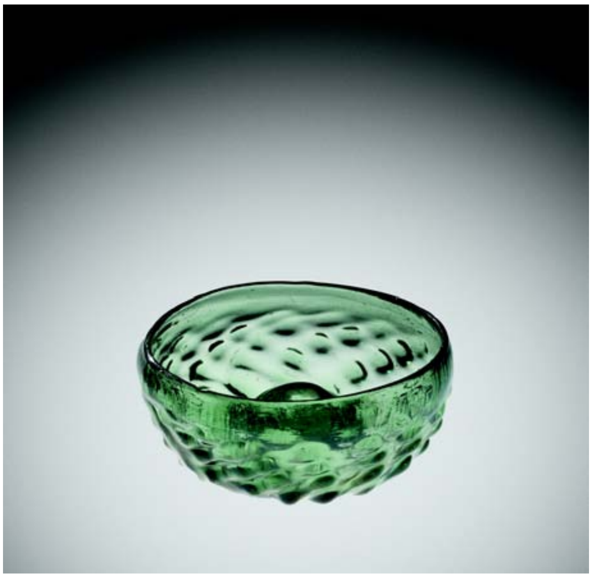

Fig. 2.8: *Maigelein* with mould-blown ribbed decoration. Probably from Germany, dated ca. 1500. Accession nº 69.3.14 (©Collection of the Corning Museum of Glass, Corning, New York), available at www.cmog.org, accessed in 14 October 2014.

By the end of the 16th century, the Venetian arts of gilding and enamelling glass were profoundly admired in Germany and in Bohemia. These techniques were soon learned by local glassmakers that did not simply replicate these decorative glass features but were able to create their own variety of gilded and enamelled objects (figure 2.9). In Germany for instance, it was possible to find the typical shape of the *Humpen* (tall beakers of large dimensions) that were usually profusely decorated with a large palette of colourful enamels, or the *Passglas* with the very fashionable grisaille technique (*schwarzlot*) (Tait, 2004, p.177). It is also important to mention another common shape that was also originated during the medieval period, the *Roemer*. This shape was also widely represented in still-life paintings (Drahotová, 1983, p.72).

Johan Kunckel (1630/38-1703), who in 1689 translated the *L'Arte Vetraria* by Antonio Neri from Italian to German, was a researcher in Potsdam with his own furnace. He has been accredited with the invention of ruby glass, created by means of a precipitated gold. However, according to H. Tait (2004, p.182), it is possible that, instead of being responsible for its invention, J. Kunckel was rather responsible for its production on a large scale.

From this point forward, it is possible to observe the production of goblets with lids and tall knopped stems made of ruby glass, and decorated with cutting and engraving techniques such as those represented in figure 2.9.

(a) **(b)**

Fig. 2.9: (a) Goblet with lid in ruby glass, with cutting decoration. From Germany, dated between 1725 and 1735. Accession nº 79.3.318 (©Collection of the Corning Museum of Glass, Corning, New York, bequest of Jerome Strauss); (b) *Stangengläser* with enamel and gilded decoration. From Germany, dated 1573. Accession nº 62.3.65 (©Collection of the Corning Museum of Glass, Corning, New York, gift of Edwin Beinecke). Both images available at www.cmog.org, accessed in 14 October 2014.

France

French high society developed an exquisite taste for Venetian glass, and in particular for fine Venetian *cristallo*. Period documents refer to the purchase of Venetian glass for the French court from as early as the beginning of the 15th century. This acquisition of Venetian glass by the upper strata of French society continued through the centuries, and, during the 16th and 17th centuries, the emigration of Italian glassmakers to France was encouraged. Under Venetian influence, French glass production from the 16th century onwards, underwent major changes (Rochebrune, 2004, p.143-149).

It is believed that France was the first nation to convince Italian glassmakers (more precisely Muranese ones) to leave their country and to produce glass abroad. Glassmakers from Altare were the most common among Italian masters who left Italy (Altarese authorities allowed glassmakers to leave Altare and work abroad as long as they never revealed glassmaking secrets), and soon they had spread throughout France, working in Nantes, Paris, Bordeaux and in Normandy and Poitou. Some Venetian glassmakers, despite they were legally forbidden, were also working in France. Nevers (in Bourgogne), was the main production centre for *façon-de-Venise* glass between the end of the 16th century and the end of the 17th century (Rochebrune, 2004, p.148-149).

During this period of great Venetian influence, the glass workshops producing forest glass were not indifferent to the changes that were occurring. The wares they produced became refined, and a careful selection of raw materials was introduced to the detriment of the fern glass they had originally been produced (Rochebrune, 2004, p.149).

With regard to the objects produced in France, their shapes and decorative features replicate Venetian ones: the famous *tazzas*, drinking glasses, ewers or goblets made in *cristallo* or coloured glass with gilding and enamelled decoration (Rochebrune, 2004, p.150). It is however possible to observe different features (*e.g.* new recipes) among French glassware, especially during the 17th century. In the mid-sixteenth century, enamel decoration was profusely used in French creations, and by this time Venetian glassmakers working in Murano were no longer enamelling their objects, preferring new decorative techniques such as filigree or diamond-point engraving (Rochebrune, 2004, p.150-152). According to M.-L. de Rochebrune, referring to glass objects produced in France *"It seems, however, that the glassmakers who created these objects took great liberties with their Venetian models, producing large-scale pieces that display a clumsiness of construction and a naïveté in the execution of the decoration that one never encounters in Venice"* (Rochebrune, 2004, p.150). It is possible to conclude from the observation of these objects that the techniques and recipes employed, such as *cristallo* glass, have been absorbed from Muranese traditions, but the shapes show differences (see figure 2.10), perhaps modified according to the customer's preferences (Rochebrune, 2004, p.150-163).

During the last quarter of the 17th century, with the decline of Venetian glass, its popularity among French consumers also declined, giving way to glass from Central Europe and the British Isles which, in combination with French glass, gained popularity and consequently the leading position in the market. Bernard Perrot (1619-1709) was not only a leading figure but was also a technical genius, and further developed several glass types as the *lattimo* white glass, experimental formulas for a translucent ruby glass, agate glass, and so on (Rochebrune, 2004, p.162).

In the beginning of the 18th century, another type of drinking glass was developed by French glassmakers using *verre de fougère* (fern glass). A fashion for "pivette" drinking glasses (see figure 2.11), using a very thinly blown fern glass, was another reason for the decline of *façon-de-Venise* glass. The richest of society preferred the lead crystal glass from the British Isles and the potassium-rich Central European creations, and the more modest of society preferred the locally made *verre pivettes* (Rochebrune, 2004, p.162-163).

Fig. 2.10: Goblet with enamel decoration. French provenance, dated from mid-16th century. Accession nº XXVB96. (© The Wallace Collection, available in http://wallacelive.wallacecollection.org, accessed in 12 October 2014).

Fig. 2.11: Goblet with mould-blown decoration. Probably France, dated between 17th and 18th centuries. Accession nº 58.3.174. (©Collection of the Corning Museum of Glass, Corning, New York). Available at www.cmog.org, accessed in 12 October 2014.

Spain

With the spread of Venetian glassmaking techniques, the Iberian Peninsula also began to produce *façon-de-Venise* objects during the 16th and the 17th centuries. In Spain, the two main regions producing this type of glass objects were Catalonia and Castile (Doménech, 2004, p.85). A theory yet to be confirmed is proposed by field investigators that because of the Islamic occupation that began in the 8th century and lasted until the end of the 15th century, southern Spain inherited their traditions, including the glass shapes, decorative features and techniques (Charleston, 1963, p.7). During the Medieval period, there was some glass production in the Spanish territory, however large quantities of glass objects were arriving from foreign places. Catalonia had a vast fleet of ships that explored not only the Mediterranean Sea but also the Atlantic Ocean before reaching Flemish harbours. From the Mediterranean area (Alexandria, Beirut and Damascus) luxurious and rare glass objects were brought to Catalonia (Frothingham Wilson, 1963, p.19-30). In 1455 the glass circulating in Barcelona were not only the imported items, as it is known that in 1456 a large number of glassworkers organised themselves into a guild and would display their creations in annual fairs. In the Medieval period it is also important to mention Valencia and Tarragona as glass production centres (Doménech, 2004, p.89; Frothingham Wilson, 1963, p.19-30). As far as the rest of the remaining Spanish territory is concerned, few is known and the information about glass production that came to the present day is from documentation. During the 15th century, glass was being produced in Castile and Murcia, and more specifically it is known that Moorish and Jewish glassworkers worked in Burgos (Frothingham Wilson, 1963, p.19-30). Glass from this time was highly influenced by Islamic creations. The enamelled glass objects from 15th to 17th centuries produced in the region of Catalonia were characterised by such beauty and singularity that it became famous and was exported to Castile, France, Italy and the Americas (Doménech, 2004, p.94).

Fig. 2.12: Goblet with *lattimo* threads. Spanish origin, probably Catalonia, 17th century. The Corning Museum of Glass, accession nº 66.3.58 (©Collection of the Corning Museum of Glass, Corning, New York, gift of Jerome Strauss). Available in www.cmog.org, accessed in 7 October 2014.

During the 16th century, Venetian glass was traded with Spain, and the Catalonian glassmakers started to imitate Muranese creations. They were able to produce colourless crystalline glass; frosted or ice-glass like the Venetian glassmakers, and also began to decorate their creations with white threads of *lattimo* glass (filigree) but in a way that was different from that practiced in Venetian glass (*e.g.* see figure 2.12). Spanish glass objects, despite their attempt to imitate Venetian creations, always possessed a different "personality" and its own attributes (Doménech, 2004, p.87; Frothingham Wilson, 1963, p.30-51), perhaps a mixture with the Islamic influences? With regard to the special case of drinking glasses, Spanish creations are slightly influenced by Venetian creations, in terms of decoration (white *lattimo* threads) and mould blown parts (lion heads), however the shapes of these goblets do not relate with the ones created in Venice, as for instance the dragon or serpent stem goblets that were not replicated in Catalonian glass workshops (Frothingham Wilson, 1963, p.30-51). Shapes like *almorratxas* (water sprinklers for perfumed water), *càntirs* (closed jugs with a centred handle and two spouts) and *porrones* (drinking vessel with elongated spouts) were typical and very fashionable items in Catalonian glassware (see figure 2.13) (Doménech, 2004, p.103).

In 1650, Catalonian glass production began to decline. Glassmakers were more preoccupied with enlarging production than in improving its quality. More utilitarian objects were produced in which Venetian features were still present, and Spanish characteristics less in evidence (Frothingham Wilson, 1963, p.30-51).

(a) **(b)** **(c)**

Fig. 2.13: Typical Spanish glass objects. (a) *Almorratxa*, Spanish provenance, Catalonia. Dated from 18th c. Accession nº 53.3.41 (©Collection of the Corning Museum of Glass, Corning, New York); (b) *Porrones*, Spanish provenance, probably Catalonia. Dated between 1650-1750. Accession nºs 79.3.481 and 79.3.910 (©Collection of the Corning Museum of Glass, Corning, New York, bequest of Jerome Strauss); (c) Càntir, Spanish provenance. Dated from 18th c. Accession nº 79.3.361 (©Collection of the Corning Museum of Glass, Corning, New York, gift of The Ruth Bryan Strauss Memorial Foundation). All images available in www.cmog.org, accessed in 7 October 2014.

In southern Spanish (Almeria, Granada and Seville), it is believed that the Islamic *Al-Andalus* influence was present in glass production (Frothingham Wilson, 1963, p.52-59). The objects produced in this area are all very similar in shapes and colours. Glass had bright colouration and colourless glass was not common. Sometimes two coloured glass formulations were combined in one object, for instance, green and amber tonalities. The attempts to decolourise the batch resulted in colourless glass with shades of smoky yellow or amber, as shown in figure 2.12 (Frothingham Wilson, 1963, p.52-59). This amber tonality so typical of Catalonian glass is the result of the method used to remove colour. To the soda-rich vegetable ashes, glassmakers added chalcedony or bloodstone (*pedra sanguina*) as decolourising agents (Doménech, 2004, p.95). The author does not clearly indicate the source of this information, but mentions that the manuscript written by the Jesuit priest Pere Gil entitled *Historia natural de Cataluña*, provides information on various glass recipes (Doménech, 2004, p.88, 95). About the Catalonian glass, it is however mentioned in his manuscript that a glass of superior quality was made with tartar (and not with barilla) to which a small amount of bloodstone from Genoa was added (Doménech, 2004, p.88).

During the 17th century, many glassmakers from Italy and from Flanders moved to settle in Castile. In the centres for glass production, attempts were made to produce colourless crystalline glass with local raw materials; however the glass always appeared a little green or with yellowish/greyish shade. The shapes resembled Flemish works as well as Venetian objects (Frothingham Wilson, 1963, p.60-71). However, once again Spanish personality was imprinted in objects with unconventional proportions and with no enamelling or engraved decoration so typical of Venetian glass (Doménech, 2004, p.104-105).

During the 17th century, the recipes and techniques from *L'Arte Vetraria* written by Antonio Neri were available and circulating among glassmakers all over Europe. In *El tratado de la fábrica de vidrio*[8], by Juan Danís, a Spanish glassmaker, it is written that *façon-de-Venise* glass was being produced at San Martín de Valdeiglesias (Doménech, 2004, p.104-105). The same source also tells us that the strongest barilla[9] was from Cieza near Cartagena, and the barilla from which the best colourless glass was produced came- from the salty marshes around Murcia and Alicante (Frothingham Wilson, 1963, p.60-71). Later, barilla from Alicante was exported to Venice to be employed in glass production there (Verità & Zecchin, 2009a, p.603). In theory, glass produced across Spain had a soda-rich formulation. Glassmakers collected their alkaline raw materials near sea salty shores where species such as *Salsola soda* or *Kali hispanica* and *Salicornia sp.* grow.

In the beginning of the 18th century, the Real Fábrica de Cristales de La Granja[10], in La Granja de San Ildefonso (Segovia) was created. This manufactory started in 1727 with only one furnace run by the Catalan glassworker Ventura Sit, and soon (approximately 1737), because of the interest taken by Queen Isabel Farnese in the glass that was produced in that furnace, the manufactory was extended. With the

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[8] Treatise on the glass manufactory

[9] Here it is not clear what the author means by "the strongest barilla".

[10] The Royal Manufactory of Crystals in La Granja.

growth of the manufactory, more glassworkers were hired, not only from Spain but also from abroad, for instance French and Swedish workers (Frothingham Wilson, 1963, p.72-87; Pastor Rey de Viñas, 1994, p.11). In 1775, the manufactory was producing the largest mirrors across Europe. This manufactory produced not only mirrors, but also blown crystal glass[11], and tableware, and the glass objects were then decorated with cutting and engraving techniques (Frothingham Wilson, 1963, p.72-87). In 1809, the manufactory suffered its first interruption in glass production. After this closure, the responsibility for production was taken over by private administration, and the ruling monarch no longer had absolute control over the manufactory. In 1820, the name of the manufactory was changed to Fábrica Nacional de Cristales[12] (Pastor Rey de Viñas, 1994, p.4).

An important comprehensive archaeometric study on Early Modern glass from Spain comes from a recent archaeological excavation performed on the city of Palma, Mallorca (Capellà Galmés & Albero Santacreu, 2015). The furnace is dated from the second-half of the 17th century, and from its excavation several glass production remains were unearthed. The glass retrieved from this excavation presents diverse colourations and hues of green, blue and purple (Capellà Galmés & Albero Santacreu, 2015). Purple glass is considered rare and is usually related with luxury objects. Glass with this colour was produced in Catalonia during the 16th and 17th centuries. A recipe to produce this glass was found in the Balearic Library, in a Majorcan recipe book with recipes dated before 1841 (the document compiles recipes used by several generations and the last one added dates from 1841) (Capellà Galmés & Albero Santacreu, 2015). The recipe that is described refers to a glass made with manganese oxide, where for each ounce of this component, one should add one pound of barilla. It is however worth noting here that purple glass appeared in two archaeological contexts considered for this dissertation. In Santa Clara-a-Velha Monastery this glass is quite abundant and generally appears associated with globular flasks and gourds, two vessel shapes considered by T. Medici (2014) of possible Portuguese production, since no examples in coeval European glass are known. Considering the employed silica sources, it is known that a quartz sandstone was collected in Northern Mallorca (Banyalbufar, Serra de Tramuntana), from 1413 to 19th century. Considering the alkali source, the use of barilla is documented and it was harvested in Mallorca, mainly from the south areas of the island (Capellà Galmés & Albero Santacreu, 2015). Barilla from Alicante was also brought and used in Mallorca.

It is also important to keep in mind glass recycling. In this period it is possible to find registered great amounts of broken glass, probably retrieved by itinerants selling glass that sometimes traded the new

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[11] The author does not clarify if the crystal glass from the La Granja de San Ildefonso manufactory was produced with lead. It is just mentioned that in terms of decoration and shape the glass objects resembled the glass produced in the British Isles.

[12] National manufactory of Crystals.

objects for broken glass. This broken glass was then given to glassmakers to be re-melted (Capellà Galmés & Albero Santacreu, 2015).

Considering its chemical analysis, despite their colouration, the glass retrieved from this production centre in Mallorca is of a soda-lime-silica type and shows a compositional homogeneity, which appears to suggest that this was a primary glass production location, probably employing local raw materials (Capellà Galmés & Albero Santacreu, 2015). Among the findings, some production remains or fragments with a different composition presenting a mixed-alkali matrix were also found. For these examples it is proposed the use of different sources of raw materials or the use of imported cullet (Capellà Galmés & Albero Santacreu, 2015).

2.2 Glass production in Portugal during 17th and 18th centuries

According to documentary evidence, several glass factories were active in Portugal during the 17th and the 18th centuries. These factories were spread throughout Portuguese territory: (see figure 2.14): in the North, Côvo and Gondomar; in the central region, Salvaterra de Magos (near the Tejo River), Tomar, Moita (near the mouth of the Tejo River mouth), Abrantes and Lisbon (central coast line); in the South, Vila Viçosa (Amado Mendes, 2002, p.39; Custódio, 2002, p.24, 43, 45, 51).

Fig. 2.14: Map of Portugal with the locations of the reported glass workshops from the 15th to the 19th century (Amado Mendes, 2002).

According to historical documents, it is also possible to identify the names of individuals connected to the glassmaking. The names of the known glassmakers working in Portugal in several regions and from different origins, between the 15th and the 18th century can be found in Table 2.2**.**

Table 2.2: Glassworkers in Portugal from 15th to 18th centuries (Amado Mendes, 2002; Sequeira, n.d.; Valente, 1950).

Glassworker	***Year***	***Working location***	***Letter of privilege by***
João Rodrigues Vadilho	1439	Palmela (centre, near coast line)	Portuguese king *D. Afonso V*
João Afonso	1443	Lisbon	
Afonso Anes	1449	Lisbon	
Ambrósio	1450	Évora (South, near Spanish frontier)	
Afonso Fernandes	1452	Santarém (centre, near coast line)	
Mafamede (Moorish)	1456	Lisbon	
Vasco Martins	1459	Lisbon	
Diogo Dias (Spanish, Castille)	15th century	Palmela	?
Afonso Pires	15th century	Coina (centre, near coast line)	
Fernando Anes	15th century	Lisbon	
Pero Moreno or Pero Fernandes Moreno	< 1528	Côvo glass manufactory (nowadays Oliveira de Azeméis, North, near coast line)	?
Pero Moreno (Spanish, Castile)	1528	Exclusive privilege from Coruche (Portugal) to Galicia (Spain)	Portuguese king *D. João III*
António Vaz	1541	Santarém	
Manuel Rodrigues	1551	Santarém	
Francisco Corso	16th century	Lisbon	?
Braz Gomes	1563	Alcochete	Portuguese king *D. Sebastião I*
Maria Fernandes	16th century	Lisbon	?
Álvaro Afonso de Almada	1585	Near Alcochete	Portuguese king *D. Filipe I*
Máximo de Pina Marrecos	1595	Asseiceira (margins of *Nabão* river)	
Bento Álvares	1618	Coimbra	Portuguese king *D. Filipe II*
Giacomo Pellizari (Venetian, run away from Spain)	1678	?	?
Francesco Costa (From Altare)	17th century	Lisbon	
Luis Verne (from Antwerp)	1698	Abrantes	
Francisco Jorge	17th century	?	
Pero Paulo (Venetian?)	1647	Vila Viçosa	Portuguese king *D. João IV*
Miguel Kelly	Deceased in 1735	Royal Glass Manufactory, Coina	Portuguese king *D. João V*
João Hedra (German)	1740	Royal Glass Manufactory, Coina	
António Paur (German)	1740	Royal Glass Manufactory, Coina	
Christian Kibolseque (German)	1740	Royal Glass Manufactory, Coina	
Jacob Burnello (Venetian)	Deceased in 1744 or 1745	Royal Glass Manufactory, Coina	

Analysing Table 2.2, it is observed that during the 15th century, one Moorish and two Spanish glassworkers were working in Portugal. It is only at the end of the 17th century that one finds reports of

Italian glassmakers arriving in Portugal. From the 17th century onwards it is possible to find glassmakers from Italy (Venice and Altare) and Antwerp, representing a Mediterranean tradition of glassmaking, and also from and Germany, representing a tradition of glassmaking from the Norh of the Alps, which represents the gathering of two different (if not opposed!) glassmaking traditions in terms of raw materials and working techniques. In Table 2.3 the glass production locations so far known in Portugal are presented.

Table 2.3: Furnaces in Portugal from the 16th to the beginning of 20th century (Custódio, 2002, p.51).

Kilns	*Location*	*Dating*	*Working traditions*	*Fuel*
Côvo farm	Côvo (nowadays called Oliveira de Azeméis)	1528 – 1924 (discontinuously)	Venetian	Wood
Salvaterra manufactory	Salvaterra de Magos	1595 - 1771	Traditional	*idem.*
Máximo de Pina Marecos kiln	Matrena, Tomar	1595 - 1706	Traditional	*idem.*
João Gorron kiln	Moita	1607 - 1744	Spanish (Castille)	*idem.*
Kiln	East Lisbon	? 1620 ?	Traditional	*idem.*
Kiln	Lisbon	?	Traditional	*idem.*
Kiln ?	Coimbra ?	1618	Traditional	*idem.*
Pedro Paulo kiln	Vila Viçosa	1601 / 1607 - 1683	Venetian	*idem.*
Luís Vernes kiln	Abrantes	1680 - 1689	Venetian	*idem.*
Francesco de Costa manufactory	Western Lisbon	1687 - 1806	Venetian	*idem.*
João Pinto Pereira & Brother White and Crystalline Glass manufacture	Melres, Gondomar	1691 - 1694	Venetian	*idem.*
Royal Factory of Crystalline Glass and Mirrors (known as Coina Glass Manufactory)	Coina	1719 - 1747	Venetian, French, Bohemian and English	Coal and wood
John Beare Glass Manufactory	Marinha Grande	1741 - 1767	Venetian, French, Bohemian and English	Wood
Royal Glass Factory (Stephens brothers)	Marinha Grande	1769 - 1826	Venetian, French, Bohemian and English	*idem.*

In Table 2.3, one can see the names, locations, dates, working traditions and the kind of fuel employed on the kilns, manufactories and factories labouring in Portugal between the 16th to 19th centuries. It is now important to refer to a number of important facts to better illustrate national glass production. The sweet flask in figure 2.15 (a) is attributed to the Côvo glass manufactory, the oldest of its kind, and the first large scale production introduced to the North coast of Portugal. This manufactory was first referred to in a document in 1528, but there is no exact date known for its establishment. It is also known that its founder was Pero Moreno or Pero Fernandes Moreno from Castile (Amado Mendes, 2002, p.43).

Fig. 2.15: Example of some objects attributed to Portuguese production. (a) Sweet flask, attributed to Côvo manufactory, dated ca. 1650-1700. Accession nº153 Vid/MNAA; (b) Tray with engraved decoration, attributed to Marinha Grande Glass Factory, dated ca. 18th c. Accession nº 22 Vid CMP/MNSR; (c) Polyhedral flask with engraved decoration, attributed to Marinha Grande Glass Factory, dated ca. 1747-1767 (John Beare administration period). Accession nº 314 Vid CMP/MNSR; (d) Polyhedral flask with enamelled decoration, attributed to Coina Glass manufactory, dated ca. 1719-1747. Accession nº 342 Cer/MNSR; (e) Portuguese jug with wheel-engraved and cutting decoration, attributed to Coina or Marinha Grande Glass manufactories. Accession nº 273 Vid CMP/MNSR. (All images from ©IMC, available in http://www.matriznet.dgpc.pt, accessed in 15 October 2014.

According to Amado Mendes (2002, p.44-45), all the necessary conditions for glass production were gathered together in the location chosen to establish this manufactory. It was close to clay deposits used for the crucibles, it was surrounded by large areas of forest for furnace fuel, the quartz pebbles used as the silica source were collect only a few kilometres away in Vermoim, and finally, it had an abundance of water for the mills to use for the crushing of quartz pebbles (Amado Mendes, 2002, p.44-45). The letter of privilege given to Pero Moreno gave him not only the right to manufacture glass in the Côvo glass manufactory, but also the exclusivity for the selling and producing glass, from village of Coruche up to the frontier with Galicia (Amado Mendes, 2002, p. 45). Information about the type of objects being produced in the manufactory is scarce; however it is reported that during the 17th century its production was dedicated to utilitarian objects (more precisely bottles, vessels with one wing and ewers), and that more delicate glass objects came from abroad (Amado Mendes, 2002, p. 45). During the 18th century, the Côvo glass manufactory produced mainly green glass, but by the end of the same century is was producing glass panes, bottles, drinking glasses and crystal (Amado Mendes, 2002, p. 45). So far no document has been found that might elucidate if this manufactory produced potassium-rich or soda-rich glass, or even if it started producing lead crystal glass during the 18th century. Due to its proximity to the coastline, and consequently to soda-rich plants (*e.g. Salsola Kali*), it would be expected that a soda-rich composition was produced in the Côvo glass manufactory.

In 2009 an archaeological excavation promoted by the Municipality of Oliveira de Azeméis was carried out in the location of the Côvo glass manufactory with the intent of identifying the location of the glass furnaces (Almeida e Silva, 2012, p.2). During this investigation a large number of quartz pebbles were found, already grinded in different grain sizes (Almeida e Silva, 2012, p.22-23; Garcia, 2009, p.47), meaning that some of them were already being prepared to be introduced into the glass batch. Glass fragments of different colours, as well as fragments of glass panes, were also recovered. It was not possible to date these fragments (Garcia, 2009, p.47).

No catalogue has been ever found depicting the objects produced in the Côvo glass manufactory; so that all the museum objects attributed to it are the result of pure speculation. It is also a known fact that the Côvo muleteers distributed glass from this manufacture in the Minho region, Douro region and in Estremadura (Custódio, 2002, p.54). In order to proceed to a proper attribution, one can only rely on chemical analysis performed on the objects in order to compare compositions with production remains of glass to be collected in a future major archaeological excavation in the location of the Côvo glass manufactory.

On the south bank of the Tejo River, the kilns from Salvaterra de Magos and Moita were very important glassmaking points, and their furnaces were precursors of the Coina glass manufactory. In an official document, the Portuguese king D. Sebastião (ruled between 1557 and 1578) recognised the existence of several kilns producing glass in such quantities that the glass imports from foreign countries were forbidden (Custódio, 2002, p.50). In 1625/26 the Côvo lords considered the glass production from Salvaterra de Magos as one of the best in Portugal. In 1768, a contract was made between two German entrepreneurs (João Galo and João Jorge) and this glass manufactory, with the intent of making its production closer to that of the Bohemian tradition (Custódio, 2002, p.52, 54). During the 17th century, the Moita manufactory was producing glass regularly, and its activity continued until the middle of the 18th century.

It is known that the kiln established in Matrena, Tomar was built near the Nabão River during the Philippine dynasty (1581 – 1640) by a local nobleman (Máximo de Pina Marecos). This furnace was prepared to work with hydraulic energy and used sand from Peralva (location near Tomar) as a silica source (Custódio, 2002, p.50, 52).

As far as the kiln that was built in Vila Viçosa (South of Portugal) is concerned, it was directly related to Portuguese royalty, since it was contiguous to the Palace of the Dukes of Bragança. A few references to the glass produced in this kiln were found in private letters, which mention that it was of great quality, and that the person responsible for its production was a Venetian glassmaker called Pero Paulo (Custódio, 2002, p.44). This kiln was prepared to labour day and night, and it is known that it consumed large amounts of wood as furnace fuel. It is also mentioned that in this production centre some of the raw materials employed needed to be ground or crushed like the quartz pebbles that were employed as silica source, and also that magnesium was employed. Historical documents report on the several consignments of glass objects from this manufacture that were sold by muleteers, but no mention is made as to the regions where this occurred (Custódio, 2002, p.45).

As no catalogue is known which refers to the kilns and manufactures reported above, and also lacking any material from archaeological excavations to compare forms and chemical compositions, it can be said that no glass objects are known from this source.

It was only in the 18th century, in a period after these small beginnings, during the reign of D. João V (1698-1750), that the Portuguese glass industry enjoyed a great development. In 1719, this Portuguese king, that had a passion for glass, ordered the installation of a Royal Glass Factory in Coina (located in the centre/south-west of Portugal and only a few kilometres from the coast line) (Amado Mendes, 2002, p.56; Custódio 2002, p.71). This manufactory employed glassmakers from Catalonia, England, Ireland, Flanders, Italy, and Germany, and from 1731 to 1747 it was managed by foreign administrators, such as the Englishmen Joam Butler (1731-1737) and Joam Poutz (1737-1741), and the Irishman John Beare (1741-1747) (Custódio, 2002, p.101). Some of the workers' names linked to the factory were discovered in the parish records of Coina, however their roles inside the factory are unknown. Despite the lack of information on these people's roles, it is important to point out that their different countries of origin such as Spain, England, Ireland, Flanders, Germany, and Italy (Venice) were found in the records, thereby recording the creation of a multicultural community (Custódio, 2002, p.135-137). It is not unreasonable to think that some of these people would be the family members of some of the glassworkers at the factory, thus providing an idea of the origins of the glass masters who worked there. Their origins are linked to different traditions in glass production techniques.

With reference to the region of Coina, it was a very important village from the south bank of Tejo River. It was the county seat, fluvial harbour and the connection point (by land) to the city of Setúbal (Custódio, 2002, p.79). In addition, this region was rich in sand, and in wood that provided the kilns in fuel. Its proximity to the fluvial harbour was also fundamental for transactions and the commercialisation of the glass produced in the factory. Production in the Coina Royal Glass factory included bottles, lead glass and clear glass. The items produced followed the style and technology of the productions dominating the market, and bottles were made in French and English style, and goblets and other vessels in Venetian and Central European style (Custódio, 2002, p.176-181, 215).

According to J. Custódio (2002, p.213), the Coina glass factory produced bottles for both private customers (green and clear glass bottles, with smaller sizes) and more industrially (larger bottles in green or black glass). Between 1719 and 1747 there were essentially two major types of bottle shapes – globular or onion bottles (free blown in terms of the production technique) and cylindrical bottles (free blown or dip moulding techniques). The square bottles, commonly made all over Europe, were also produced in this factory (Custódio, 2002, p.215).

In 1747, when John Beare administrated the manufactory, it was closed because of its large wood consumption, and transferred to Marinha Grande, where more pinewood was available. The manufactory continued its activity there with only a few interruptions until 1992 (see figure 2.16) (Amado Mendes, 2002, p.59, 62; Custódio, 2002, p.229, 232).

Archaeological excavations were carried out both in the area where the Coina glass manufactory had been established (Custódio, 2002, p.13), and in the Marinha Grande location. Some of the glass fragments recovered and believed to belong both to the Coina and Marinha Grande manufactories, spanning from the 18th to the 20th century, were analysed and only preliminary results were published (Lopes *et al.*, 2009; Schalm *et al.*, 2005). Nevertheless, it has been possible to identify some compositions that seem to be strictly related to local productions.

In terms of the shapes attributed to Portuguese provenance that are today spread throughout national museums, they are mainly attributed to the Côvo manufactory, the Coina Royal Glass Factory, and, as a result of comparisons with catalogues, to the Marinha Grande Royal Glass Factory. In figure 2.15, it is possible to see a small selection of some of the objects that are attributed to Portuguese production, and part of two main Portuguese Museums, the National Museum of Ancient Art (MNAA) in Lisbon and the Soares dos Reis National Museum (MNSR) in Oporto. The Coina Glass Factory underwent an archaeological investigation that began in 1984 and ended in 1991 (Custódio, 2002, p.13). It was possible to collect several glass fragments of different typologies and with diverse colourations. In figure 2.15 (d), one can see a polyhedral flask with enamel decoration depicting the Portuguese shield on one side, and on the other side one can read the inscription in Latin "VIVAT/IO/ANNES/V" in enamel. This flask was attributed to the Coina Glass manufactory, most probably because of the inscription dedicated to the Portuguese king D. João V (1689-1750), responsible for the creation of this glass manufactory that was so dear to him. This object is inspired by Central European creations, not only in terms of its shape, but also in terms of its decoration with multicoloured enamels (see for example: Victoria and Albert Museum, accession no C.5:1, 2-1912; Corning Museum of Glass, accession no 59.3.14 and 59.3.15). In 1730, the Friar João Pacheco wrote about the Coina glass manufactory comparing it to the glass manufactories in Murano (Custódio, 2002, p.104). The operational period of the Coina Glass manufactory was considered to be a golden era for Portuguese glass production.

Fig. 2.16: Engraving of the working area of the Marinha Grande Factory published in 1890 in the *Ocidente* Portuguese publication (ed. Saraiva, 1983, p.229).

In 1739, reports were written by Bohemian glass dealers complaining about the ban of Bohemian glass imports to Portugal, which led to the conclusion that the glass produced nationally would be sufficient to fulfil market needs (Vávra, 1954, p.93). This complaining was probably related to the document signed by D. João V on the 10th of May of 1734, in which the Portuguese king forbade the import of foreign glass (Custódio, 2002, p.95). As has been mentioned above, during the 18th century, Portugal and Spain were two of the main Bohemian glass trading centres (Lukàs, 1981, p.60), which implies that these restrictions must have substantially affected Bohemian trade agreements and routes.

It is also known that glass was arriving in Portugal from Venice. The Portuguese king D. Manuel I, who ruled between 1495 and 1521, had the commercial domination and exclusive privilege over Venetian glass, not only in Portugal but also in its colonies. During this period, Venice can be considered one of the main glass suppliers for the Portuguese territory (Medici, 2005b, p.133). However, even after this period, glass was still being sent to Portugal from Venice. In a letter dated ca. 1592, sent to the Grand Duke Ferdinando I de Medici the following is written:

> *"To Lisbon fine glass and several crystals by ducats 10.000.*
> *Boiled[13] crystals, large size, in lire 40 up to 50 hundred, in the shapes of lions, ships, baskets, fountains, each piece lire 1,*
> *1 ½, lire 2, 2 ½ and lire 3 each piece, and mirrors also provided."*[14]

This citation was firstly published by G. Corti (1971, p.653) and then referenced by T. Medici (2005b, p.133) and by Barovier & Tonini (2014, p. 30). As mentioned by T. Medici (2005b, p.133), not only was ordinary glass being brought from Venice to Portugal, but also fine *cristallo* glass objects.

It is important to look at the relations between Portugal and Antwerp. By 1611, there were seventy-two Portuguese commercial-banker families living in Antwerp (Göttler & Moran, n.d.). From these, the Ximenez family, particularly Emmanuel Ximenez, was the most famous. Besides Antwerp, he had commercial offices in Lisbon and Seville (the two most important harbours in Europe during the 17th century), Venice, Cadiz, Florence, Amsterdam, Hamburg, Goa, Bahía, Pernambuco, and many other city harbours (Duprè, 2010; Göttler & Moran, n.d.). Moreover, the Ximenez family was directly connected to the Medici family in Florence and to the Spanish Crown, this last through monetary transactions (Duprè, 2010; Göttler & Moran, n.d.). Another very important and curious aspect is that

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[13] Here the term "boiled crystals" is associated with the process of purifying the plant ashes employed in the glass batch as a source of alkali.

[14] Kindly translated by Teresa Medici from the Italian: *"Per Lisbona vetraria fina e cristalli assai per duc. 10.000. Cristalli bolliti, grandi, di lire 40 fino a 50 cento, foggie di lione, nave, sporte, fontane, tal pezo lire 1, 1 ½, lire 2, 2 ½ e lire 3 il pezo, e spechiere fornite."*

António Neri, the author of the famous recipe book *L'Arte Vetraria* was a close friend to the Ximenez family. Neri stayed in the Ximenez house in Antwerp between 1604 and 1611 (Boer & Engle, 2010). It was during his stay there that he observed the production of *façon-de-Venise* glass in the Gridolphi factory, an experience that partially influenced him to write *L'Arte Vetraria*, published in 1612 (Duprè, 2010). From these facts, one can only wonder how soon the recipe book arrived in Portugal, which could well have happened through the Ximenez family. As far as it is known, the treatise (*L'Arte Vetraria*) was translated into Spanish in the 18th century, by Miguel Jerónimo Suárez Núñez, in an attempt to rekindle the glass industry in Spain (Pérez-Pariente & Martín-Rojo, 2008). This is supposedly the first translation of *L'Arte Vetraria* in the Iberian Peninsula, since, as far as it is known, no translation into Portuguese is known. However, considering that several foreign glassmakers were active in Portugal, the treatise might have reached Portugal in other languages.

Emmanuel Ximenez himself was a collector, and among other things, he collected glass. Along with textile dyes, sugar and spices, paintings, books and precious stones, the Ximenez family traded glassware, which was greatly appreciated especially in West African regions and Asia (Göttler & Moran, n.d.). In the city of Antwerp this family was known for their luxurious life-style and ostentation, demonstrated among others things, through their patronage of glassmakers (Göttler & Moran, n.d.).

2.2.1 Raw materials employed on Portuguese glass production

It is a known fact that the Portuguese coastline was very rich in plants like *salsola kali* and *salicornia*. Nowadays, it is still possible to find these species in abundance along the Portuguese seashore. Knowing that these plants existed in Portugal in large quantities, it is *a priori* expected to find a national glass production that is of the soda-rich type, or in other words, which follows the Mediterranean tradition. Vasco Martins, a 15th century Portuguese glassmaker from Lisbon, complained to the king, in documents dated from 1459, that foreigners were stealing the Portuguese seashore plants, called in that time barilla, from the national coasts (more specifically from the Algarve), and were taking them outside the country, which was prejudicial to national glass production (Sequeira, n.d., pp.I; Valente, 1950, p.26, 107). During the 15th century, the Portuguese king D. Afonso V forbade the Moresque and Andalusian people to harvest and steal the barilla from the Algarve. This activity had become exclusive to the Portuguese glassmakers (Sequeira, n.d., pp.I; Valente, 1950, p.107-108). Is it possible that some of the barilla being consumed by the Venetian during the 17th was also from Portuguese origin.

Table 2.4 shows the origin of some of the raw materials employed in several Portuguese glass production centres. In terms of the source of silica, during the centuries that are being studied here, it is reported that it has always been collected in national territory. The various sands and quartz pebbles were collected nationally, and in regions near the production locations. In the specific case of the Coina glass manufactory, the glassmakers employed not only quartz pebbles but also local sand from the Coina region. The sand from this location was known for its purity and high quality, characterised by a fine grain and a high concentration of silica (Custódio, 2001, p.108).

Table 2.4: Origin and nature of the raw materials employed in the Portuguese glass factories (Custódio, 2002, p.108-112; Valente, 1950, p.30).

Glass factory	***Location***	***Dating ****	***Raw materials***	***Raw materials origin***
Côvo glass manufactory	North coast	1484 – 18th century	Chalk Colouring agents Arsenic	From abroad
			Manganese peroxide	Anadia mines (Portugal)
			Quartz pebbles	Vermoim (Portugal)
			Plastic clays (for crucibles)	Côvo and Bairrada (North Portugal)
Coina Royal glass manufactory	Central coast (south of Lisbon)	1719 -1747	Quartz pebbles	Belas (Portugal)
			Sand	Coina (Portugal)
			Chalk	Leiria (Centre Portugal)
			Soda	?
			Potash	?
			Lead oxide	?
			Saltpetre	
Marinha Grande Royal glass factory	Central coast (North of Lisbon)	1747 – 1994 (with interruptions)	Chalk	Royal pine in Leiria
			Manganese peroxide	From abroad
			Feldspar	Porto de Mós (Portugal)
			Silica	Vale de Maceira (Portugal)
			Quartz pebbles (for crystal production)	Santa Comba Dão (North Portugal)
Vilarinho da Furna Royal glass factory	North, near Cávado river	1807 - 1809	Quartz pebbles Feldspar	Gerês ridge (North Portugal)
Cabo Mondego glass factory	Central coast (North of Lisbon)	1869 - ?	Sodium sulphate	From abroad and national (mixed together)
Rua das Gaivotas glass factory (Lisbon)	Central coast	1811 – 20th century	Manganese peroxide Colouring agents	From abroad
			Sand	Coina (Portugal)

* This dating is referent to the years of activity of the manufactories and factories.

Regarding the source of alkalis, the preferences of Portuguese glassmakers for soda or potassium-rich ashes are never mentioned, with the exception of the Coina glass manufactory that employed both (Table 2.4). Being a Mediterranean country well supplied in Salsola *Kali*, it is expected that the production would be a soda-rich glass, however it is known that, for instance, in Coina glass manufactory, glassmakers working there came from Germany and Bohemian, and it is for this reason that one would expect them to have brought their glassmaking traditions with them, thus also producing potassium-rich glass (Custódio, 2002, p.112; Valente, 1950, p.23).

In Table 2.4, the general origins of the raw materials employed in some of the most important glassmaking centres from the post-medieval period onwards are reported. However, when one speaks about larger manufactories like Coina glass manufactory or Marinha Grande glass factory that went through different periods of administration, it is important to bear in mind that the suppliers of the raw materials would have change from time to time. The dating presented in Table 2.4 refers to the years of activity of the manufactories, and it was not possible to narrow down the use of certain raw materials. However, as it was proposed above, it is highly probable that the origin of the raw materials changed along the years. Moreover, it is important to mention that as these manufactories were more recent, it is easier to find written documents describing the raw materials employed and their origins. With specific reference to the Marinha Grande glass manufactory, between 1793 and 1795, it was importing coarse barilla from Spain and refined barilla from America, saltpetre from India and red lead from the British Isles. A few years later it was reported that the barilla employed on this manufactory was originated from Alicante (Spain) and from Setúbal (Portugal) (Custódio, 2002, p.111). This makes clear that the raw materials employed, with all their specific and unique trace elements according to their specific provenance, were constantly changing, probably as a result of financial considerations.

CHAPTER 3

PORTUGUESE ARCHAEOLOGICAL GLASS ASSEMBLAGES: STUDYING AND COMPARING

3.1 Historical context and description of the archaeological assemblages considered in this work

3.1.1 Glass assemblage from Museu do Teatro Romano, Lisbon

The Roman Theatre was first discovered in 1798 during the reconstruction of the city of Lisbon after the major earthquake in 1755. A major archaeological investigation into this area was initiated in 2001 and ended in 2011 (Fernandes & Fragoso de Almeida, 2012, p.111). This complex site yielded archaeological records dating from the 1st century (date attributed to the edification of the Roman Theatre) and from modern times, from the end of the 15th to the 18th centuries (Fernandes, 2007, p.28, 32-33; Dra. Lídia Fernandes p.c). Some of the elements of the building, such as its stones and its foundations, were re-used in later constructions throughout the following centuries (Fernandes, 2007, p.33). The most relevant structure excavated was the *postscaenium*. This huge wall belonged originally to the Roman Theatre and served as a support to the theatre's scenic façade; in this particular case it served to contain the adjacent hill. Until the 1755 earthquake, this enormous structure was used during the 17th and 18th centuries as the north wall of a house (Fernandes, 2007, p.33).

The glass finds under study here were excavated from the house remains and were almost certainly abandoned and partially destroyed during the earthquake, and thus become part of the disposable wreckage. The glass assemblage was found spread across several stratigraphic layers, all part of this medium/large dimension house (Fernandes, 2007, p.35; Dra. Lídia Fernandes p.c.).

The first archaeological excavation carried out on these ruins dates from 1963 by the archaeologist D. Fernando de Almeida. Since then, several archaeological excavations have been carried out at this location, but it was only in 2001 that the museum was established in order to allow these ruins to be visited, the excavation works to continue, and also to promote the preservation of this historical site (Fernandes, 2007, p.30).

The main archaeological excavations undertaken on the Roman theatre in the past few years were in 2001, 2005, 2006, 2010 and 2011. These excavations were carried out by Serviço de Arqueologia do Museu da Cidade de Lisboa – Divisão de Museus e Palácios (Câmara Municipal de Lisboa, Direcção Municipal de Cultura, Departamento do Património Cultural) and focused on the south area of the monument, and it enabled the discovery of the great structure of the theatre *postcaenium* (Dra. Lídia Fernandes p.c.).

These archaeological campaigns allowed work to be carried out on a house structure (Pombaline style[1]) from the post-earthquake period. Nine meters below this post-earthquake house, another house structure was found dating from the 17th century. This house had 3 stories and it was built using the *postcaenium* structure itself (Fernandes, 2007, p.33-35; Dra. Lídia Fernandes p.c.).

Some objects from the glass assemblage were associated with ash and mortar deposits that were the result of the collapse of the upper walls and supporting beams. The house structure dated from the 17th century was also filled with wreckage resulting from destruction caused by the earthquake. Posterior constructions (in Pombaline style) were characterised by the use of different levels in order to counteract the unevenness of the hill and also because it represented a solution to clear tons of wreckage that covered the entire city. This is the explanation for the presence of wreckage material that filled the pre-earthquake edifications (Dra. Lídia Fernandes p.c.).

Glass objects

Glass objects from the assemblage being studied were found in this archaeological context described above, with the majority of pieces belonging to the 18th century. These objects were almost certainly abandoned and partially destroyed during the earthquake, becoming in this manner part of the disposable wreckage.

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[1] House structure of Pombaline style: this construction style was developed after the major earthquake that devastated Lisbon and its surroundings in 1755. It consisted on a flexible wooden structure, called cadge, that was imbedded on walls, roofs and floors and then covered with the remaining building materials. This system was done using pre-manufactured house pieces that were made outside the city and assembled on site (França, 1983, p. 163-166).

Other finds associated with these glass objects were also recovered including ceramics, tiles (dated from the 18th century as the glass objects) and also some faience dating from the late 17th century to the late 18th centuries (Dra. Lídia Fernandes p.c.).

The glass assemblage studied here comprises ninety-seven glass fragments. These fragments belong for the most part to wine bottles (61 fragments) with different typologies (circular and square shapes) and colours (that vary between olive green and black), and blue coloured glass flasks (8 fragments), which can be considered utilitarian glass. Most of the shapes identified are mould-blown, and the majority have a pontil mark. A group of sixty-three objects was selected to be part of this study.

With regards to the other objects from the set, it was possible to identify 3 fragments from drinking glasses of transparent colourless, and transparent amber coloured glass, one glass cane (colour blue) and 4 fragments (probably belonging to the same square flask) in transparent colourless glass decorated with enamels of the following colours: red, blue, green, yellow, opaque white and black.

Another important find within this glass assemblage, was a seal from a mineral water bottle were it is possible to decipher "Bad Pyrmonter Wasser". This seal belongs to a German Spa located in Lower-Saxony where thermal waters were fashionable since the 17th century[2]. The seal has the depiction of a coat of arms with two rampant lions and two stars.

Another important aspect of this assemblage is that also includes the presence of one major aggregation of molten glass fragments that probably resulted from the high temperatures of the great number of fires that enveloped Lisbon after the earthquake.

The objects analysed are listed in Table II.1 in *Appendix II* with their dating and characteristics described, and the quantification results are presented in Table II.2 in *Appendix II*. Objects catalogue[3] and archaeological drawings are also present in *Appendix II* as Catalogue I.

3.1.2 Glass assemblage from Rua do Arsenal, Lisbon

Early in 2011, an archaeological excavation was begun on a building structure in Rua do Arsenal, Lisbon, near the Tejo River. This excavation was undertaken by the archaeological company Alavanca

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[2] In http://www.badpyrmont.de/ accessed on 14th November 2012.

[3] All the pictures and drawings presented in this thesis where no authorship is indicated were taken/ drawn by the author.

do Tempo, Arqueologia Antropologia Património and carried out in the foundations of the building, in order to evaluate the archaeological potential of this location (Valongo, 2011, p.3).

According to some authors, the location of this building is consistent with the probable location of the Côrte-Real Palace, dating from the 16th century and the second most important palace of Lisbon (França, 1983, p.31). This location is also consistent with the Muralha Fernandina, a construction dating from the 14th century (Valongo, 2011).

During the archaeological excavation, remains of both structures mentioned above were found. The glass assemblage being studied came from the Côrte-Real Palace archaeological context, dating from the 16th century up to the 19th century.

A member of the Côrte-Real family built the Côrte-Real Palace during the 16th century. After the Portuguese Restoration of Independence that took place in 1640, the Palace was transferred to royalty and was given to the Prince D. Pedro by his father, the king D. João IV. After a few years, the Prince D. Pedro became king by the name D. Pedro II and made the above Palace his royal residence (ed. Saraiva, 1983, p.24). The location of this Palace is what made this building so attractive to the royalty. The Palace was located near the Tejo River, where the caravels loaded with foreign and attractive new objects arrived. This was also a beautiful, four stories high, building, with four look-out towers (figure 3.1).

In 1668, peace was re-established in the Portuguese territories, and as a consequence, the properties were given back to their original families. The Côrte-Real Palace was returned to the Castelo Rodrigo Marquis, the former owner before 1640, who then rented the Palace to D. Pedro II, who never left it (ed. Saraiva, 1983, p.24).

In 1751, the Palace was sold to the King D. Pedro III, who used it as a courthouse. According to some authors, this was the year when a huge fire destroyed the Palace, and only the front façade with two balconies over the Tejo River were left standing. This façade collapsed in 1755, during the earthquake (Proença, 1983, p.210-211).

Other authors claim that this building was an active courthouse when the 1755 earthquake destroyed it completely (ed. Saraiva, 1983, p.24).

Fig. 3.1: 18th century engraving depicting Côrte-Real Palace before its destruction. Image taken from Biblioteca Digital Nacional oficial site (http://purl.pt/11578/1/).

Glass objects

The glass assemblage is comprised by 182 objects and fragments, of which 72 fragments belong to olive green and black wine bottles. One dark green globular (or onion) bottle was found whole. The other bottle remains belong mainly to cylindrical bottles with thick walls.

Among a variety of fragments, it is important to highlight one incomplete object (probably a jar or jug) with engraving decoration (floral motifs) in colourless transparent glass, in which one applied handle was identified. From this set, a group of sixty-one fragments was selected for study.

Two colourless transparent glass fragments with enamelled decoration (yellow, red, black and blue enamels) were found. As far as colourless transparent glass is concerned, three drinking glass fragments were found, one of which was mould blown in order to produce a vertical ribbing pattern.

In the same set, a molten glass fragment was found, possibly from a bottle, as it was green in colour. A relatively high number of this kind of molten glass objects can be identified in glass assemblages and archaeological finds from this period because of the fires that ignited throughout Lisbon after the 1755 earthquake (*e.g.* Medici, 2011). The objects analysed are listed in Table III.1 in *Appendix III* with dating and characteristics described, and the quantification results are presented in Table III.2 in *Appendix III*. Objects catalogue and archaeological drawings are also present in *Appendix III* as Catalogue II.

3.1.3 Glass assemblage from Santa Clara-a-Velha Monastery, Coimbra

Between the years 1283 and 1286, D. Mor Dias (1st half 13th century - 1302), a Portuguese noble lady, had the Santa Clara-a-Velha Monastery built in the city of Coimbra. This noble lady chose the location of the monastery on the left bank of the Mondego River, because of its proximity to the already existent Franciscan Monastery, in order to receive ecclesiastic assistance from the latter. This location was also close to the Santa Ana Monastery, where D. Mor Dias' sister, D. Teresa was a prioress (Trindade & Gambini, 2009, p.19, 20). More than anything, this was a strategic location in order to obtain protection and assistance from neighbouring monasteries.

Santa Clara-a-Velha Monastery belonged to the order of the Poor Clarissas. This religious order was created in 1212 by Clara Offreduccio de Favarone inspired by the Franciscan ideals of total renunciation to the possession of goods. This renunciation was seen as a vehicle to individual purification and remission of the sins of society. According to these premises all goods should belong to the community, and the religious sisters should live in absolute poverty (Trindade & Gambini, 2009, p.13, 14).

The Portuguese Queen D. Isabel de Aragão (1270-1336), known for her charitable character, moved to Santa Clara-a-Velha Monastery after the death of her husband the Portuguese king D. Dinis (1261-1325), and was buried there after her death. The presence of D. Isabel in the monastery brought it great prominence and after her death, it became place of pilgrimage. During her life in the monastery, D. Isabel enlarged the number of its buildings and lands, and was the person responsible for the building of the gothic monastery still there today (figure 3.2) (Trindade & Gambini, 2009, p.24-27).

During the following centuries, the great majority of young women joining the order of Poor Clarissas in Santa Clara-a-Velha Monastery were of high social status, probably belonging to noble families. This fact is proven by their family names, and the high quality of the objects retrieved from the archaeological excavation (Trindade & Gambini, 2009, p.26). In order to avoid leisure, the daily religious life was filled with activities such as sewing and cooking, which was distributed among them according to their position inside the monastery. It was also common for foreign people to provide services to the monastery, for instance bricklaying and paving (Trindade & Gambini, 2009, p.44, 45). Bearing this in mind it is reasonable to consider the possibility of services provided by glassmakers working for the monastery and located in its proximities.

The location of the monastery and its proximity to the Mondego River resulted in a constant flooding, which led to the decision to constructing a new monastery (Santa Clara-a-Nova Monastery) on a hill located nearby, further away from the river bank. In 1649 the construction of the new monastery was initiated, and some materials from the old building were employed. In 1672 some of the members of the religious had already abandoned the old building, and finally in 1677 D. Isabel de Aragão's grave was moved from the old monastery to the new one, completing the transition (Trindade & Gambini, 2009, p.65, 66).

Fig. 3.2: Santa Clara-a-Velha Monastery. Picture taken in 2012.

From this date on, the old monastery remained abandoned and partially submersed until 1995, when excavations began.

The archaeological excavation was at first the responsibility of the Instituto de Arqueologia da Faculdade de Letras da Universidade de Coimbra, and then passed to the monastery itself (promoted to a Dependent Service of the Instituto Português do Património Arquitectónico – IPPAR). Archaeological works began in 1995 and lasted until 2000, but it was only in 2009 with the opening of the museum that the monastery rehabilitation program ended (Trindade & Gambini, 2009, p.77-80).

During the archaeological works carried out at the Santa Clara-a-Velha Monastery, several objects and materials were recovered and among them also the graves of several nuns. With regards to the excavated objects, it was possible to identify several metal utensils such as spindles, needles, thimbles and scissors, several jet[4] adornments, a quantity of common and glazed ceramic objects where it was possible to distinguish objects decorated with coats of arms and another set of high quality Chinese

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[4] Jet is a semiprecious stone; black coloured and capable of being carved and polished. It is a variety of lignite.

porcelain. Together with the remains of the nuns, several gold wires used to attach teeth together were found, demonstrating once again the high social status of some of the women. It is also important to mention that the entire monastery building was profusely decorated with Hispano-Moresque ceramic tiles (Coentro *et al.*, 2014) and limestone statues (Trindade & Gambini, 2009, p. 40-47).

Glass objects

With reference to the glass assemblage (Ferreira, 2004; Medici *et al.*, 2009), thousands of objects and fragments were retrieved. Glass objects of all colours were recovered, predominantly various shades of green, blue, yellow, and purple. For this investigation thirty-seven glass objects were selected. The colourless glass is worth noting, as it is possible to identify perfectly discoloured glass, and colourless glass with natural hues (grey, blue, yellow, and green). As far as the glass decoration is concerned, gilded glass, filigree, engraved glass, mould blown pattern decoration (Ferreira & Medici, 2010) and *millefiori* (Lima *et al.*, 2012) were identified. In terms of the typology of the objects, it is worth noting that a variety of vessels such as gourds (so far a unique vessel typology only found in Portugal), bottles, goblets and flasks of several sizes were found. The shapes are characterised by their refinement, and among the objects it is possible to identify Venetian or *façon-de-Venise* forms and decorations. The objects analysed are listed in Table IV.1 in *Appendix IV* with the dating and characteristics described, and the quantification results are presented in Table IV.2 in *Appendix IV*. The objects catalogue is also present in *Appendix IV* as Catalogue III. Archaeological drawings can be consulted in Medici (2015).

3.1.4 Glass assemblage from the courtyard of Universidade de Coimbra

Between 2000 and 2003, archaeological excavations were undertaken in the courtyard of the University of Coimbra (Coimbra, Portugal), as a part of a wider project concerning the architectural and artistic evaluation of the entire complex. This archaeological excavation was promoted by the University Rectory, and directed by Professor Helena Catarino (Catarino & Filipe, 2006).

This investigation enhanced the historical knowledge on this area of the town, which has been inhabited since the Roman *Aeminium* (the Roman name of Coimbra) through to modern time. Of special interest were the remains of the fortification (Alcácer) belonging to the Islamic town of Madinat Qulumbriya. The building has a quadrangular plan, with towers leaning against the wall at regular intervals. The gate, surrounded by two towers, turned to the East is today called *Porta Férrea*. It has always been the main access to the complex despite the alterations that occurred after the Christian Re-conquest of the town in 1064, when the building was first converted into the Royal Palace, and then, in 1537, chosen by king D. João III to host the University.

During the archaeological survey at the North side of the gate, it was possible to partially excavate the content of a small corridor, connecting one of the towers to the wall. The excavation yielded an important archaeological record, including pottery and glass. The pottery assemblage comprises objects belonging to typologies dating from the end of the 16th century to the beginning/first half of the 17th century. Therefore, the end of the use of the corridor, and its subsequent filling, can possibly be correlated to the main renovation of the Porta Férrea, undertaken during the first half of the 17th century by the chancellor D. Álvaro da Costa (1633 - 1637), when the obliteration of the towers was ordered (Pimentel, 2005, p.125).

Glass objects

During the archaeological excavation it was possible to collect several glass fragments (c. 150). From these finds thirty-two fragments were selected for this study. Uncoloured glass with natural green, grey or yellow hues predominate. With regards to the decorative features it is possible to identify mould-blown patterns, and glass with filigree. Among these fragments, a glass flask was retrieved with gilded decoration (inventory no. CPU0032). The objects analysed are listed in Table V.1 in *Appendix V*, dating and characteristics described and the quantification results are presented in Table V.2 in *Appendix V*. Objects catalogue is also present in *Appendix V* as Catalogue IV. Archaeological drawings can be consulted in Medici (2015).

3.1.5 Glass assemblage from Praça Miguel Fernandes, Beja

The glass fragments being studied here are part of an archaeological assemblage discovered in Beja (South of Portugal). The excavations were carried out by the archaeological company Crivarque, Estudos de Impacto e Trabalhos Geo-Arqueológicos, between 2003 and 2004, after the discovery of a set of 137 silos during the construction of an underground car park in Avenida Miguel Fernandes. This avenue is situated outside the walls of the city of *Beja* (Martins *et al.*, 2007).

The silos were structures used during the 14th and 15th centuries as storage containers for food, mainly cereals, usually with rounded forms. Once the silos were no longer used as a place of storage, this meant that they could be used as a disposal site (rubbish pits) for the most diverse materials, including rubble and household debris. The archaeological excavations took place near the city centre to allow the construction of an underground parking lot. The archaeological excavation revealed a highly diverse assemblage, including faunal remains, coins and other metal elements, military objects (daggers), some bone objects, a large number of ceramic pieces in good condition and a number of glass objects. The analysis of archaeological groups, including sherds of pottery and coins, allowed one to situate this set chronologically between the 14th and 17th centuries (Martins *et al.*, 2007).

Glass objects

With regards to the group of glass objects, this comprises mainly utilitarian objects dating from the 14th to the 17th centuries. The presence of more than three hundred objects was estimated, and from this mass twenty-seven glass fragments were selected. From this selection, eleven fragments are dated between 14th and 15th centuries, and the remaining sixteen glass fragments are dated to between 16th and 17th centuries. From both chronologies, the majority of the glass fragments belong to beakers and goblets. Also present in both chronologies are blown decorative motifs, and almost all the selected objects have this kind of decoration.

The objects from the older chronology are characterised by a bright colouration in several shades of green, yellow and blue, whilst in glass dated from 16th to 17th centuries, the colourless glass with natural bluish and greyish hues predominates, which could indicate an attempt to discolour the batch. The objects analysed are listed in Table VI.1 in *Appendix VI*, with dating and characteristics described, and the quantification results are presented in Table VI.2 in *Appendix VI*. The objects catalogue is also present in *Appendix VI* as Catalogue V. Archaeological drawings can be consulted in Medici (2015).

3.1.6 Glass assemblage from São João de Tarouca Monastery

São João de Tarouca Monastery was started to be built in Tarouca (located in the interior in the North of Portugal) between the years of 1152 and 1154. This monastery is believed to be the first belonging to the Cistercian religious order in Portugal. This monastery and the other coeval monastery located in Lafões (also located in the interior in the North of Portugal) are both connected through the figure of the abbot João Cirita, and doubts as to which one was built in first still remains today (Sampaio & Sebastian, 2002a).

In the Cistercian order, the foundation of a new monastery had to be linked or affiliated to an older monastery, as there existed a mother – daughter relationship between abbeys. São João de Tarouca Monastery was linked to the Clairvaux Monastery in France and during the 12th and 13th centuries, the Portuguese monastery had its prime period being responsible for the institution of the monasteries of Santa Maria de Fiães, São Pedro das Águias and Santa Maria de Aguiar. Later, it was surpassed by the Santa Maria de Alcobaça abbey (Sampaio & Sebastian 2002a, p.36).

The Clairvaux Monastery was founded in 1115 (only 40 years before São João de Tarouca Monastery) by the 25-year-old monk Bernardo of Clairvaux. This monastery was responsible for the foundation of 60 other monasteries, with the implied definition of strict rules in order to maintain this spiritual empire, whilst at the same time there was the notion that each monastery needed to have some autonomy.

With regard to the architecture and the principles of construction of the São João de Tarouca Monastery, it is important to note that it translates Cistercian guidelines admirably. The buildings are free of decorations, marked by straight lines with no ostentation. Poverty and simplicity are the most cherished principles, which lead to the absence of mural paintings, stained-glass panels or bell towers. The monastery building was the way to formalize the monk's exclusion and independence from the outside world, and the São João de Tarouca Monastery was the perfect example with its simple aesthetic. It was built in the perfect Cistercian geographical location, near two water-courses, with fertile lands and in total isolation (Sampaio & Sebastian, 2002a).

During the 16th century, the São João de Tarouca Monastery reached its rising period in an economic and social perspective, which lasted until 1834, where all the religious orders were abolished. Over this period, the poverty, simplicity and absence of material goods was no longer manifest in the day-to-day life of the Cistercian monks (Sampaio & Sebastian, 2002a; 2002b). This conclusion is linked to the number and quality of the ceramic and glass archaeological finds retrieved from the monastery. The archaeological excavations were performed by the Instituto Português do Património Arquitectónico (IPPAR) and began in 1998 and lasted until 2001.

Glass objects

A large quantity of glass fragments was recovered during the archaeological excavations. These objects were dated to between the 16th and 19th centuries. For this investigation only the glass objects dated to between the 16th and 17th centuries were considered.

Thirty-four glass fragments were sampled and analysed. Among them it was possible to find glass with filigree decoration, mould-blown decoration patterns, one gilded fragment also with engraved decoration, and two objects with the application of strings.

With regards to the mould-blown decoration objects, some have already been studied by Ferreira & Medici (2010), where fragments of bossed beakers, objects with the lozenge motifs enclosing smaller lozenges, and also enclosing four-petalled flowers, were considered. This last motif that always appears enclosed by the lozenge motif, is considered, as far as it is known, to be unique and only found among glass assemblages retrieved from Portuguese territory. The objects analysed are listed in Table VII.1 in *Appendix VII*, with dating and characteristics described, and the quantification results are presented in Table VII.2 in *Appendix VII*. Objects catalogue is also present in *Appendix VII* under Catalogue VI. Archaeological drawings can be consulted in Medici (2015).

3.2 Research design and methodology

The choice of the assemblages was based on their importance in terms of archaeological context, which, as was stated in the *Introduction*, are all dated, and of which four had been well studied. The geographical localisation and the objects of which the assemblages were constituted, were also considered. With regard to the archaeological context, two of the selected sets originated in a religious environment: two monasteries, one female, a convent (Santa Clara-a-Velha, Coimbra) and one male (São João de Tarouca). These assemblages will highlight the importance of glass in the everyday life of monasteries, as well as the kind of relation that existed between these institutions belonging to different religious orders. It was noted by T. Medici (2015) that there was a great disparity between the quality of the objects from these two monastic sets of objects and the other four assemblages. Luxury objects compose the monastic sets, with *façon-de-Venise* shapes and decoration features (Medici, 2015). Two of the other selected assemblages came from a noble context: one in Lisbon (Rua do Arsenal) and one in Coimbra (University courtyard). Both contexts were royal houses and will allow one to reach some conclusions on the glass used by the nobility. Finally, the last two assemblages came from a civil context, one from a private middle class house in Lisbon (Teatro Romano), and the other from several silos that served as garbage pits in Beja, a town in the South of Portugal (Praça Miguel Fernandes, Beja). These groups will bring some insights on the glass circulating through the different social classes: if it was mainly imported or on the other hand if it was produced locally, and if the different social classes used different objects from different provenances. The great challenge in studying glass objects from this period found in Portugal, is related to the fact that this country was situated at the crossroads of various cultural influences, which might result in a great diversity of provenances for the glass.

Representative glass objects from the archaeological contexts, mainly dated to between the 17th and 18th centuries, were selected. It is important to emphasise the importance of this 17th to 18th century period for European glass production. It was a time of change in terms of glass chemical compositions and also in terms of taste. In Portugal, it is from the 17th century onwards that more records on glass production, glassmakers, the raw materials employed and so on has come to our knowledge. The choice of objects was based on their formal and stylistic characteristics, considering also the available historical and archaeological data. Particular attention was given to special features such as singular decorative motifs or unique object shapes. On the case of the Praça Miguel Fernandes (Beja) assemblage, a smaller group of older objects, dated to between 14th to the 15th century was also selected for this study in order to have an overview of the evolution of glass production and circulation in Portugal. For the same reason, in the instance of the Rua do Arsenal (Lisbon) assemblage, a number of objects from the beginning of the 19th century were chosen for this investigation. According to the number of objects available, an average of thirty to fifty objects were selected from each set.

The research methodology was designed on the basis of an interdisciplinary approach, relating archaeometry, history and conservation science. These different but complementary approaches allowed the characterisation of the chemical composition of the glass (with an emphasis on the application of non-destructive techniques) in terms of major, minor and trace elements, which will thus allow one to better define a possible provenance. This will also allow a discussion of the raw materials employed for the different glass compositional types, and finally a study of the historical materials and techniques used for the production of objects. Hypothesis on commercial routes of the raw materials and objects will also be proposed.

In order to speculate on the provenance of the glass objects, based on their chemical compositions, the analytical results will be compared with the available data from glass production centres active at the time, such as Venice (Verità & Zecchin 2009a, 2009b), the Low Countries (De Raedt *et al.*, 2002; Šmit *et al.*, 2004), the British Isles (Cable, 1987; Dungworth & Brain, 2009; Dungworth *et al.*, 2006; Farrelly *et al.*, 2014; Mortimer, 1995), and Central Europe (Cílovà & Woitsch 2012; Kunicki-Goldfinger *et al.* 2001, 2005; Smrcek, 1999). In terms of the Portuguese territory, it will be possible to compare the results obtained with the preliminary data from analysis performed on glass attributed to the Coina glass manufactory (Lopes *et al.*, 2009) and with some coeval archaeological glass groups (Lima *et al.*, 2012).

Samples

The first phase of the work was to make an inventory of the archaeological assemblages (some sets had already been inventoried, and for those, their institutional inventory number was kept) followed by the selection of samples to be analysed. Fragments were chosen according to its typology, glass colour, and the presence of some decorative features (such as the presence of enamels). Special attention was given to glass bottles.

For the bottles, fragments were selected giving priority to bottoms and necks. The shape (square or cylindrical bodies), the glass colour (black and green glass) and the thickness (some bottles presented thinner walls than others), were the next characteristics considered.

In order to avoid erroneous results by analysing and quantifying corrosion layers rather than the uncorroded bulk of the glass, it was decided to sample the objects selected. Small glass samples of 2-4 mm^2 were dry cut from the selected objects with a diamond wire. These small glass samples were embedded in cross-section in an epoxy resin and polished with SiC sandpapers down to 4000 mesh. This sampling procedure was only performed in broken objects, and on fragments with no connection to other fragments.

3.2.1 Analytical Methods

μ-PIXE

Ion-beam analytical techniques are being more and more employed in the study and characterisation of cultural heritage. One of the great advantages of these techniques, and probably the one that makes them so attractive for use with historical objects, is the almost negligible damage caused by irradiation resulting from the ion beams bombardment (Šmit, 2013, p.155). The Particle Induced X-Ray Emission (μ-PIXE) has been used in historical glass analysis because of its non-destructive nature and its analytical capabilities (Calligaro, 2008).

The bases of ion-beam techniques is the detection of radiation that is induced by a particle beam generated from electrostatic accelerators usually having an energy of around a few MeV (Šmit, 2013, p.155). Looking now at the principles of μ-PIXE, this method is based on the excitation of the characteristic X-rays of each element, which is analogous to XRF or EPMA techniques. The advantage of PIXE over XRF is that the first is much more sensitive to the detection of light elements. To improve the detection of light elements, which are undetectable in air (external beam setup), one can use helium gas flow allowing the detection of elements down to sodium, or even in vacuum, allowing measurements down to carbon (Šmit, 2013, p.157). Relating μ-PIXE with LA-ICP-MS, it is clear that the second is much more sensitive (in orders of magnitude), however the LA-ICP-MS has the disadvantage of leaving holes with ca. 100 µm in the analysed object. When combined with a scanning nuclear microprobe, PIXE has the ability of producing elemental distribution maps with micrometer spatial resolution over sample areas up to ~2.5×2.5 mm^2. This allows the selection of representative areas of analysis, and presents quantitative average values for larger areas (Calligaro, 2008).

This technique has been widely used in analysis of historical glass (Gueit *et al.*, 2010, Šmit *et al.*, 2004) and for the investigation of the corrosion mechanisms of this material (Vilarigues *et al.*, 2011).

Quantitative results were achieved with μ-PIXE ion beam analytical technique using an Oxford Microbeams OM150 type scanning nuclear microprobe setup, either with the in-vacuum or with the external beam configuration. The μ-PIXE equipment is located at the C2TN, Instituto Superior Técnico, Universidade de Lisboa, by Luís Cerqueira Alves. To allow the efficient detection of low energy X-rays such as the ones of Na, all the glass fragments were irradiated in vacuum with a focused 1 MeV proton beam and the X-rays produced collected by a 8 μm thick Be windowed Si(Li) detector. In order to avoid or detect possible local glass heterogeneities, imaging (2D elemental distribution) and X-ray spectra were obtained from an irradiated sample area of 750x750 μm^2. For trace elements quantification (typically elements with atomic number above the one of Fe), a higher proton beam was required, and a 2 MeV one was used. In this case, the external beam setup was chosen in order to prevent sample beam-charging, and consequently X-ray spectra degradation. X-rays were collected with a SDD detector with 145 eV resolution from a sample area of 800x800 μm^2. Whenever possible the entire area of 800x800 μm^2 was analysed and the reported composition is the result of the integration of that area. For that reason, no average or standard deviation is reported. Operation and basic data manipulation, this including elemental distribution mapping, was achieved through the OMDAQ software code (Grime & Dawson, 1995), and quantitative analysis done with GUPIX program (Campbell *et al.*, 2010). The results, expressed in weight percent of oxides, were normalised to 100%.

In order to validate the obtained concentration results, two glass reference standards were also analysed, Corning B and Corning C. The obtained data from all the analysed samples is the result of several days of μ-PIXE analysis, both in in-vacuum and external beam. In each day of analysis, the glass standards were analysed at least one time. The average plus the standard deviation and the relative standard deviation values for Corning B and Corning C are presented in *Appendix VIII*, Table VIII.1.

LA-ICP-MS

The technique of laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) has been widely employed in the study of cultural heritage objects such as glass (Cagno *et al.*, 2010, 2012a; Wedepohl *et al.*, 2011a) and metals (Sarah *et al.*, 2007), and also in the study of the natural glass obsidian (Gratuze, 1999; Chataigner & Gratuze 2014a, 2014b), because of its capability to analyse solid samples.

LA-ICP-MS was developed after two other techniques, that is inductively coupled plasma optical or atomic emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). ICP-MS was then combined with laser ablation during the nineties (Gratuze, 2013, p.201-202). This technique was usually employed in geochemical studies, especially with the intent of determining the rare earth elements (REE) patterns (Gratuze, 2013, p.201-202). The rare earth elements were defined by IUPAC as the elements from the lanthanide series plus scandium and yttrium (eds. Connelly *et al.*, 2005, p.51).

This technique has the great advantage of its very high detection limits that can go to ng/g levels. This is referent to a siliceous material and depends on the measured isotope, on the baseline background level, and on the size of the laser spot (Gratuze, 2013, p.210). The disadvantage of LA-ICP-MS is the hole that the laser ablation leaves behind, and the size of this crater can range between 20 and 200 μm. The ablated material (ca. 80-90% of it) is then deposited around the craters and can be easily removed (Gratuze, 2013, p.204). However, it is important to point out that the advantages of this method, that allows one, in the specific case of glass analysis with the aim of studying provenances, to quantify not only the major, minor but also trace and REE elements, overwhelm the disadvantage of its being a destructive technique, in a micrometer scale.

When analysing the REE in glass, it is necessary to proceed to a normalisation of the obtained values to the elements and REE present in the Continental Earth's Crust. The huge differences in the abundance of neighbouring elements due to even or odd proton numbers, will be annulled by this process of normalisation (Wedepohl *et al.,* 2011a). The reference values used on this process are reported in Wedepohl (1995).

LA-ICP-MS (laser ablation-inductively coupled plasma-mass spectrometry) analysis was carried out on the embedded glass cross-section. The ablation system used here is located at the National Centre of Scientific Research (CNRS) in Orleans, France with Bernard Gratuze. It consists of a Nd:YAG laser working at 266 nm (quadrupled frequency) and a Resonetics M50E excimer laser working at 193 nm coupled with the Thermo Fisher Scientific ELEMENT XR mass spectrometer. The Nd:YAG laser operates at a maximum energy of 2 mJ and at a maximum pulse frequency of 15 Hz. The excimer laser was operated at 3mJ with a repetition rate of 8 to 10 Hz. The beam diameter can be adjusted from 20 µm to 100 µm. A pre-ablation time of 20 s is set in order to eliminate the transient part of the signal which is then acquired for 55 s corresponding to 20 mass scans from lithium to uranium (the signal in count/second is measured in low resolution mode for 58 different isotopes). Calibration for glass was carried out using NIST610 and Corning B, C and D glass reference material (Gratuze, 2013, 2014). The detection limits range from 0.1 to 0.01 % for major elements, and from 20 to 500 ng/g for others. For the gold leaf composition (present in fragment CPU0032), calibration was carried out using a gold reference material SI RAuP7 from MBH containing trace elements in the range of 200 µg/g and a ternary gold/silver/copper alloy containing 90.9 % Au, 6.3% Ag, 2.7 % Cu, 147 µg/g Pd and 2920 µg/g Pt as well as other trace elements. Accuracy ranges from 5 to 15 relative % depending on the elements and their concentration.

The glass body analysis was carried out with the quadrupled Nd:YAG laser at 8 Hz with a beam diameter of 80 µm. The composition is calculated from the average of two ablations carried out in different areas of the sample. The analysis of the gold leaf area on fragment CPU0032 from the CPU assemblage was carried out with the excimer laser with a diameter of approximately 40 µm to avoid saturation of the detector when measuring the gold isotope. The analysis was carried out in 2 different areas. The ablated mass of material contains glass, corroded glass layers (alkali depleted glass) and resin. Only part of the spectrum (the one with the highest gold and silver signals) was used for calculation.

In order to validate the obtained concentration results, glass reference standards Corning A and Nist SRM 612 are regularly analysed as unknown samples throughout all of the analytical sequence. The average values obtained during the analysis are presented in *Appendix VIII*, Table VIII.2.

μ-EDXRF

When inorganic materials are irradiated with X-rays it is commonly accepted that no harm is caused to the matrix. Analytical techniques employing X-rays are recurrently used on cultural heritage, where glass is included, both for structural and compositional analysis (Janssens, 2013, p.79).

With regard to the working principle of XRF analysis, this includes the measurement of the energy and intensity of the characteristic photons emitted from a given sample, glass for instance, when this is irradiated with a beam of primary X-rays. This will result in a spectrum with all the characteristic emission lines stored. This information is necessary for identifying and quantifying the elements present in the sample. All the other interaction processes that occur when the X-ray beam hits the sample (elastic or Rayleigh and inelastic or Compton scattering), will result in the spectrum background (Janssens, 2013, p.88).

In the specific case of this technique, the characteristic fluorescence radiation that is emitted is measured by an energy-dispersive spectrometer. The photons are counted through a solid-state detector that at the same time organises them according to their energy in a multichannel memory resulting in a spectrum of X-ray energy *versus* intensity (Janssens, 2013, p.89).

Results were achieved by energy dispersive X-ray fluorescence (μ-EDXRF) using a portable μ-XRF spectrometer ArtTAX 800, Bruker, located in the Department of Conservation and Restoration (FCT NOVA), and was operated by the author. It operates with a molybdenum (Mo) X-ray source, focusing polycapillary lens and electro-thermally cooled xFlash (Si drift) detector, with 170 eV resolution (Mn Kα). The accurate positioning system and polycapillary optics enabled a small area of primary radiation (70 μm) at the sample. The excitation and detection paths can be purged with helium to allow the detection of low-Z elements down to aluminium. Spectra were acquired under the following conditions: voltage 40 kV, intensity 0.6 mA and live time of 360 s. Helium purging was used to allow the determination of elements down to aluminium. Each glass was analysed in three different areas.

Qualitative analysis was always accompanied by the glass reference standards Corning A (CMoG A), Corning B (CMoG B), Corning C (CMoG C) and Corning D (CMoG D) analysis in order to ascertain the glass type under study. This technique was mainly applied on enamels decorating glass fragments that could not be sampled, and on fragments with gilded decoration to evaluate the decoration technique.

UV-Vis reflectance spectroscopy

Fiber Optics Reflectance Spectroscopy (FORS) technique was firstly applied on the industry since the early seventies. This analytical technique was firstly applied on the field of works of art and conservation at the National Gallery, London, in the late seventies, and successively during restoration in the Brancacci Chapel, Chiesa del Carmine in Florence, and at the Victoria and Albert Museum in London. Currently this technique is beginning to be applied more often in studies of historical and archaeological glass objects, and also on historical stained glass (Arletti *et al.*, 2011).

A MAYA 200 PRO spectrophotometer from Ocean Optics with a single beam dispersive optic fibre was used, together with a 2048 CCD Si detector that allows operating in the 200-1050 nm range. The equipment is located in the Department of Conservation and Restoration (FCT NOVA), and was operated by the author. The light source is a HL-200-HP 20 W halogen from Ocean Optics, with a single optical path between 360-2500 nm.

The spectra were acquired directly on the glass surface, in reflectance (R) mode, with a 45°/45° configuration (illumination angle/acquisition) and ca. 2 mm of diameter of analysed area. Spectra were obtained between 360-1050 nm, with an integration time of 8 ms per scan and 15 scans. A Spectralon® surface was used as a reference. The obtained data were converted and presented as an absorbance $A' = \log_{10}(1/R)$. This technique is very useful for *in situ* analysis, being easily transportable, non-invasive and quick.

UV-Vis reflectance spectroscopy was employed on several glass objects to evaluate and identify the chromophores responsible for the glass colouration and hues. It was also used for the same purpose on opaque enamels present in some of the objects. In Table 3.1, the most common ions responsible for glass colouration are presented as well as their absorption bands and electronic transitions.

Table 3.1: Some metallic ions responsible for glass colouration (Navarro, 2003, p.457; Vilarigues, 2008).

Colour agent	***Oxidation state***	***Colour***	***Absorption bands (nm)***	***Electronic transitions***
Copper	Cu^{2+}	Turquoise blue	790	$^2\Gamma_3$ (F) → $^2\Gamma_5$
Manganese	Mn^{2+}	Yellow	356, 422	
	Mn^{3+}	Purple	499	$^5\Gamma_3$ (D) → $^5\Gamma_5$ (D)
Iron	Fe^{2+}	Blue	440	
			1100	$^5\Gamma_5$ (F) → $^5\Gamma_3$
			2100	
	Fe^{3+}	Yellow	380, 420, 440	
Cobalt	Co^{2+}	Blue (CoO_4)	540	$^4\Gamma_2$ → $^4\Gamma_5$
			590	$^4\Gamma_2$ → $^4\Gamma_4$
			640	$^4\Gamma_2$ → $^4\Gamma_4$ (P)
			1400	
			1600	$^4\Gamma_2$ (F) → $^4\Gamma_4$ (F)
			1800	
		Pink (CoO_6)	510	$^4\Gamma_4$ (F) → $^4\Gamma_4$ (P)
			1180	$^4\Gamma_4$ → $^4\Gamma_5$

µ-Raman microscopy

Raman analysis is a form of vibrational spectroscopy that measures the interaction between photons (or neutrons) and the low energy levels of materials - the vibrational levels. The chemical composition (atomic nature) and structure (the degree of crystallisation for instance) dictate these vibrational levels that correspond to the collective vibrations of atoms and molecules (or atom groups) (Colomban, 2013, p.277).

This analytical technique was used to study the applied enamels on some of the glass fragments whenever it was possible, given that in some cases, the state of conservation of some of the glass objects did not permit them to be handled in such way that allowed this analysis to be carried out.

Raman microscopy was carried out to aid in the identification of the opacifying crystalline compounds. The equipment is located in the Department of Conservation and Restoration (FCT NOVA), and was operated by the Susana Coentro. Analyses were performed with a Labram 300 Jobin Yvon spectrometer, equipped with a He-Ne laser of 17 mW power operating at 632.8 nm and a solid state laser of 500 mW power operating at 532 nm. The laser beam was focused either with a 50x or 100x Olympus objective lens. The laser energy was filtered at 10% using a neutral density filter for all analyses. Analyses were carried out on the surface of the enamels. Spectra were recorded as an extended scan. The attribution of the Raman spectra was made using the RRUFF database project on minerals (RRUFF).

3.2.2 Statistical treatment – Chemometrics approach

When a large quantity of data is generated, extraction of the highest amount of relevant information contained within it is of paramount importance. After completion of the chemical analysis of the glass fragments yielding their compositions, it is recommended to apply a suitable statistical treatment, in this specific case a chemometric treatment, to bring to light the maximum amount of possible hidden information.

Hierarchical clustering can be very useful as a first approach to analyse the relation between data samples (Baxter, 2008, p.14). Here, the method of hierarchical cluster analysis through classification trees (resourcing to the Ward’s method) will be applied first, and the sample grouping will be analysed and discussed. Then, a PCA (Principal Component Analysis) will be applied to specifically analyse variation within defined groups (like for instance the previously identified *façon-de-Venise* objects), in order to better understand the relation between fragments, their typologies and composition.

Statistical analysis has been broadly used in archaeometric studies (Baxter, 2006, p.671). Methods such as PCA and cluster analysis can be found applied to glass chemical compositions in studies where raw materials and provenances are discussed. Cagno *et al.* (2010), Genga *et al.* (2008) and Kunicki-Goldfinger *et al*. (2000) are only a few examples of the application of these multivariate methods. These methods proved to be very useful for identifying groups of samples based on the glass chemical composition.

Cluster analysis designates any statistical method applied to a data set with the objective of identifying groups of samples. When applying a cluster analysis method, samples such as for instance the chemical compositions of glass fragments, are grouped together based on their similarity, which ultimately yields a representation of the difference between them (Baxter, 2008, p.2, 3).

The freeware R-statistica under the terms of Free Software Foundation's GNU General Public License and *Statistica* from StatSoft (Dell software) was used to accomplish these analyses.

With regard to the adopted chemometric methodologies, either classification trees (cluster analysis) or PCA modelling, it was found that some oxides from the glass chemical composition should not be included. In other words, a variable (in this case the oxides) selection is necessary and fundamental before applying these methods since some of them are known to be non-informative (Baxter & Jackson, 2001). Minor oxides that tend to be approximately zero for most of the analysed samples but appear with positive values for some samples, should not be used for the construction of the model (Baxter, 2008, p.14). In addition, all data should be normalized prior to the application of these methods. In this case, auto-scaling was the selected method. This method normalises the oxides (the variables) by removing each oxide average and dividing by its standard deviation (Baxter, 2008). For all chemometric methods, only the major or minor oxides with positive measurements were considered. The minor oxides present only in some samples were discussed aside with their respective influences taken into account. Since the REE were only measured for some samples, this information was not considered for the PCA or the construction of the classification trees.

Because of the relatively limited number of samples (less than 10 samples), no statistical method was applied on the study of mixed-alkali or lead glass.

CHAPTER 4

LOOKING THROUGH GLASS: UNCOVERING RELATIONS

In order to evaluate the relation between glass sets and to identify possible common glass production centres, the results of the chemical composition were divided into five glass compositional types: soda-rich glass, potassium-rich glass, mixed alkali glass, HLLA glass and plumbic or lead glass. For this classification, the criteria described in Table 2.1 (*Chapter Two*, *Part I*) were used. Results will be presented below by order of the compositional type with a larger number of fragments identified.

We will be focusing on specific types of objects and to distinctive decorative features, for instance the gilded objects.

T. Medici in her Ph.D. thesis (2014) classified glass objects according to their typologies, and the nomenclature attributed to each type will be followed and employed in this thesis whenever necessary.

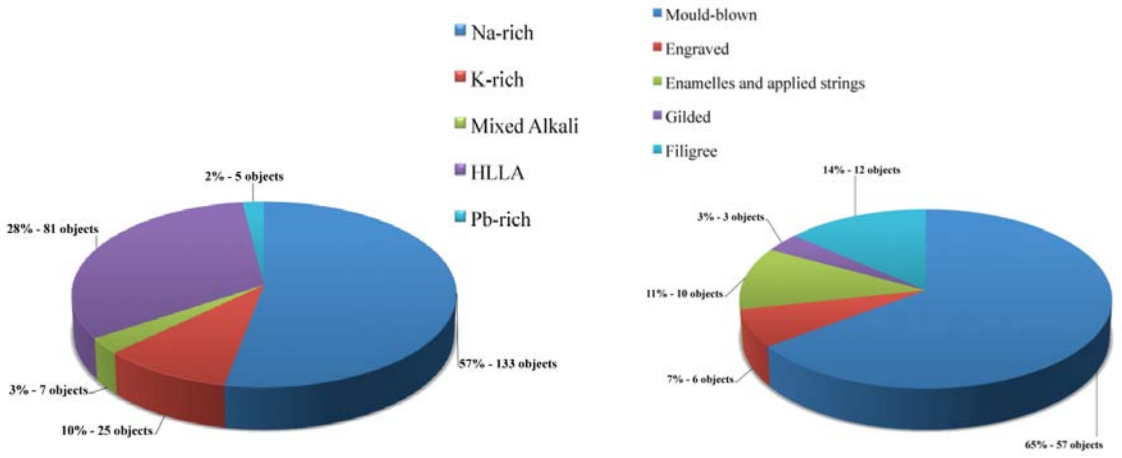
Within each glass compositional type, we tried to establish a possible relation between chemical composition and shape with the aim of attributing a possible provenance, or the tradition that influenced it.

Due to the colourful palette one can find among objects, the glass colourants will be discussed essentially based on the UV-Vis reflectance spectroscopy analysis after considering the relation between fragments and sets based on the chemical composition.

As has been mentioned before, in addition to the comparison between the compositions of the glass objects, whenever possible the results obtained will be compared with published data on coeval glass from other European production centres, and it is for this purpose that a representative survey of compositions from the literature was made.

In figure 4.1 are two pie charts representing the different percentages of glass chemical compositions (figure 4.1 a) and the different types of decorative features (figure 4.1 b) from all the sets of glass objects analysed, and taking into account all the samples analysed. These charts are the summary of the data that will be presented in this chapter.

The first piece of information obtained is that the great majority of the glass objects analysed are of a soda-rich type. After the soda-rich glass, the second largest group is the HLLA glass, mainly composed by wine bottles. Potassium-rich glass composes only ten percent of the totality of analysed fragments, and the mixed-alkali glass taken together with Pb-rich glass represent only five percent. With regard to the decoration, it can be seen that mould blown decorated objects are the most represented decorative feature found among the decorated objects, representing sixty five percent of this category. This is followed by filigree glass, which represents fourteen percent of decorated objects. Eleven percent of the total is made up of the enamelled glass and the objects with applied strings. Only six objects with engraved decoration (representing seven percent of the studied objects with decoration) were found, and only three presented gilded decoration.



(a) **(b)**

Fig. 4.1: Charts representing (a) the percentage of different glass compositional types and (b) the percentage of decorative features found among all the glass assemblages studied.

4.1 Soda-rich glass

Soda rich glass is present in all the assemblages being studied. From a universe of 251 fragments from six assemblages, 133 fragments are of soda-lime silica glass. This includes the following typologies: beakers, bottles, bowls, cupping-glasses, goblets, gourds, flasks, one ink pot, jars and oil lamps. Some shapes are uncommon, as for instance the gourds, that will be discussed below, whilst other shapes are common among other European centres, for instance the oil lamps (representations of these oil lamps can be seen in figures 4.2 and 4.3). In terms of decorative techniques, one can find several mould-blown patterns, gilded decoration, engraved decoration and filigree. As far as the colours of the glass are concerned, examples were found that went from perfectly discoloured glass, to several natural hues of green, blue and yellow and to purposely-coloured glass with colours such as purple or turquoise blue discussed above.

Fig. 4.2: Oil lamps. Stained-glass panel from The Great East Window, York Minster, England. Photograph of *God in Majesty* (15th century), by the York Glaziers Trust (Brown, 2014, p. 78).

Analysing all the soda-rich glass set with regard to the major oxides, the sodium oxide varies between 10.80 and 21.14 wt%, the potassium oxide content varies between 0.31 and 9.74 wt%, the silica content varies between 54.22 and 69.61 wt%, the alumina content varies between 0.41 and 9.23 wt% and finally the calcium oxide content varies between 2.98 and 13.39 wt%.

Due to the large number of analysed samples, to help with the interpretation of the results obtained, a statistical approach –chemometrics- was employed. The first approach was cluster analysis presented as a classification tree (*Appendix IX*, *Appendices Part I*). PCA analysis was used further for the interpretation of other cases. The classification tree was interpreted by splitting the chart through the linkage distance (single linkage) at number two, for a primary approach. This interpretation allowed the definition of five groups of the soda-rich glass that are described in Table 4.1.

Analysing Table 4.1 and with regard to Group 1, this includes objects from all the sets being studied, and the great majority of CPU fragments are contained in this group. This group is characterised by having the lowest averaged in sodium oxide and the highest average in calcium oxide. No direct association can be made between this group and any special shape or decorative feature, but (not being exclusive) the great majority of fragments are made of uncoloured glass with light yellow natural hues.

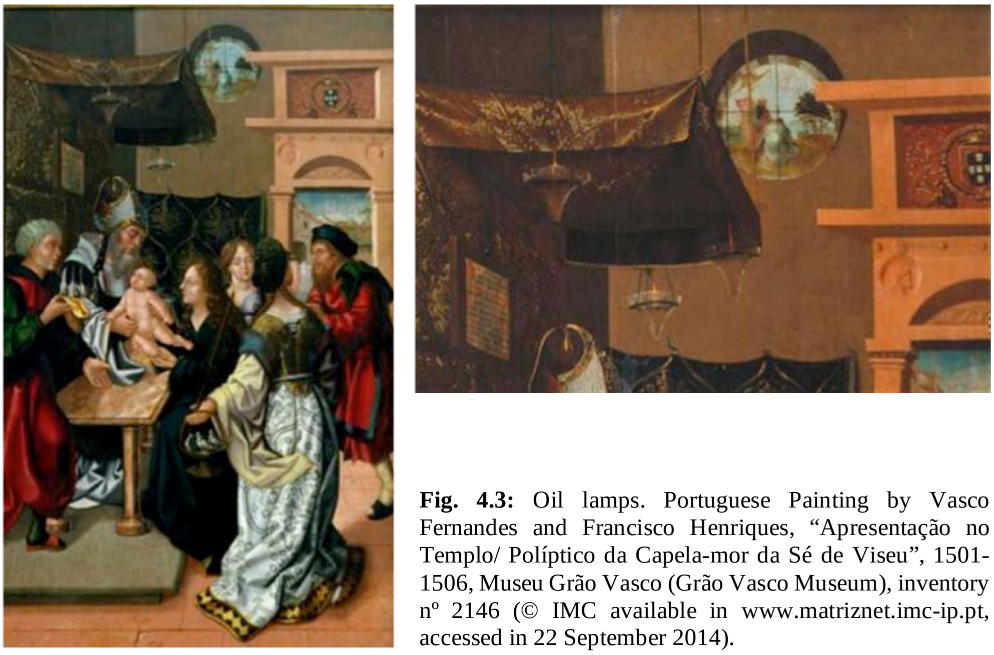


Fig. 4.3: Oil lamps. Portuguese Painting by Vasco Fernandes and Francisco Henriques, "Apresentação no Templo/ Políptico da Capela-mor da Sé de Viseu", 1501-1506, Museu Grão Vasco (Grão Vasco Museum), inventory nº 2146 (© IMC available in www.matriznet.imc-ip.pt, accessed in 22 September 2014).

Giving special attention to Group 2, the alumina content is the highest among all of the groups. Contents of around 6 wt % and higher of alumina, have until now been only rarely found in published coeval compositions for soda-rich glass. It is important to note that the majority of fragments that compose this group came from the SCV set. The chemical composition of these glass objects is quite unique, mainly due to the high alumina contents. As it was mentioned in *Chapter Three*, *Part I*, the SCV archaeological site has a very rich set and one of the largest assets of glass objects found on the national territory. The large number of objects makes one wonder if it was possible, during the 17th century, to import such a huge amount of glass objects. This hypothesis seams unreasonable when compared with the much more plausible possibility of existence of a glass production centre near Coimbra, in other words, a glass furnace (or furnaces) located in the centre of Portugal. This location would allow the provision of several regions with glass, and still take advantage of the proximity of the coastline abounding in soda-rich plants essential to the glassmaking process. It is interesting to note that Group 2, with the higher alumina content, is also the group with the lowest contents of potassium and calcium oxides. Within this group are included six gourds, half of the total number present among all the sets. One of the gourds is from the SJT group and is strongly related with the chemical composition of SCV fragments. The probability of these fragments belonging to the same production centre is high, meaning that these fragments all came probably from the same production centre that not only served Santa Clara-a-Velha Monastery but also São João de Tarouca Monastery.

Table 4.1: Division of objects from the sets under study into groups obtained through the classification tree.

Groups	***Objects belonging to each assemblage***	***Major oxides variation within the groups (wt%)***									
		Na_2O		**Al_2O_3**		**SiO_2**		**K_2O**		**CaO**	
		Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.	Avg.	Std.
Group 1	LRA0013, SJT0132, SCV-V298, CPU0011, CPU0019, CPU0001, CPU0014, SCV-V170, SJT0126, CPU0004, CPU0024, CPU0016, CPU0017, CPU0015, CPU0027, CPU0030, CPU0021, CPU0012, PMF0556, SJT0014, SJT0005, PMF0527, LTR0005, SCV-V408, SJT0135, SJT0112, CPU0028, PMF0387, SCV-V404, LTR0060, LTR0083, SJT0098, LTR0020, LRA0118, PMF0458, LTR0021, SCV-V94	13.8	±1.4	3.3	±1.9	63.8	±3.3	4.72	±1.92	8.93	±1.39
Group 2	SCV-V336, SCV-V352, SCV-V319, SCV-V95, SCV-V79, SJT0128, SCV-V365, SCV-V380, SCV-V182, SCV-V329, SCV-V171, SCV-V154, SCV-V423, SCV-V390, SCV-V342, SCV-V396, SCV-V51	18.3	±1.8	7.3	±1.4	58.2	±3.2	1.70	±0.38	4.20	±1.07
Group 3	CPU0005, SJT0134, SJT0133, PMF1010, CPU0023, V191, LRA0090, LTR0006, LTR0082, PMF0568, PMF0996, PMF0569, PMF1025, SJT0110, PMF0517 (base glass and blue rim), LTR0053, PMF0550, PMF0570, PMF0530, SJT0100, SCV-V82	16.0	±0.6	3.1	±1.0	66.6	±2.4	3.07	±1.37	6.01	±0.85
Group 4	SCV-V247, SCV-V194, SCV-V177, PMF0546, SJT0011, CPU0008, SCV-V335, SCV-V422, SCV-V102, SJT0127, SJT0003, SJT0115, SJT0012, CPU0026, CPU0009, SJT0097, PMF1023, SJT0021, CPU0032, SJT0109, SJT0116, SCV-V355, SJT0006, SCV-V60	17.5	±1.0	4.1	±1.5±	50.5	±2.5	4.42	±1.15	7.19	±1.13
Group 5	SJT0038, SJT0131, SJT0123, SJT0120, SJT0113, SJT0107, SJT0114, CPU0002, CPU0025, CPU0006, SJT0138, SCV-V210, SJT0001, SJT0105, SCV-V195, SCV-V193, SJT0122, CPU0018, SCV-V115, PMF0691, PMF0691, PMF0438 (base glass and blue rim), CPU0010, PMF0540, SJT0007, PMF0510, CPU0022, PMF0617, PMF0605, PMF0444, PMF0610, PMF0600, PMF0401, SCV-V420, SCV-V14	18.7	±1.0	3.1	±1.4	64.1	±2.5	3.11	±0.69	5.10	±0.93

In figure 4.4 it is possible to see the REE and some trace elements signature of the SCV fragments that belong to Group 2. As one can see, the REE and trace elements signatures of these fragments are really close to each other and all share a negative Eu anomaly, which are abundant in granites (Wedepohl *et al.*, 2011b). The North and Centre of the Portuguese territory is abundant in granitic rocks, which can explain the existence of sands from granitic origin in Portugal.

In what regards now Group 3, it is possible to find the majority of fragments from the PMF set dated from the 16th to 17th century that were identified as having *façon-de-Venise* characteristics. The majority of the remaining fragments from the other sets that appear related to this group are all of a glass that has a light bluish/ greenish hue. Once again, with regard to the soda-rich glass, no relation is found between shapes or decoration features, and the chemical composition of the glass fragments. This group has the lowest average alumina content measured for all groups, and the highest silica content. Since alumina is considered an impurity of silica, it is expected that when the alumina decreases, the silica content will increase.

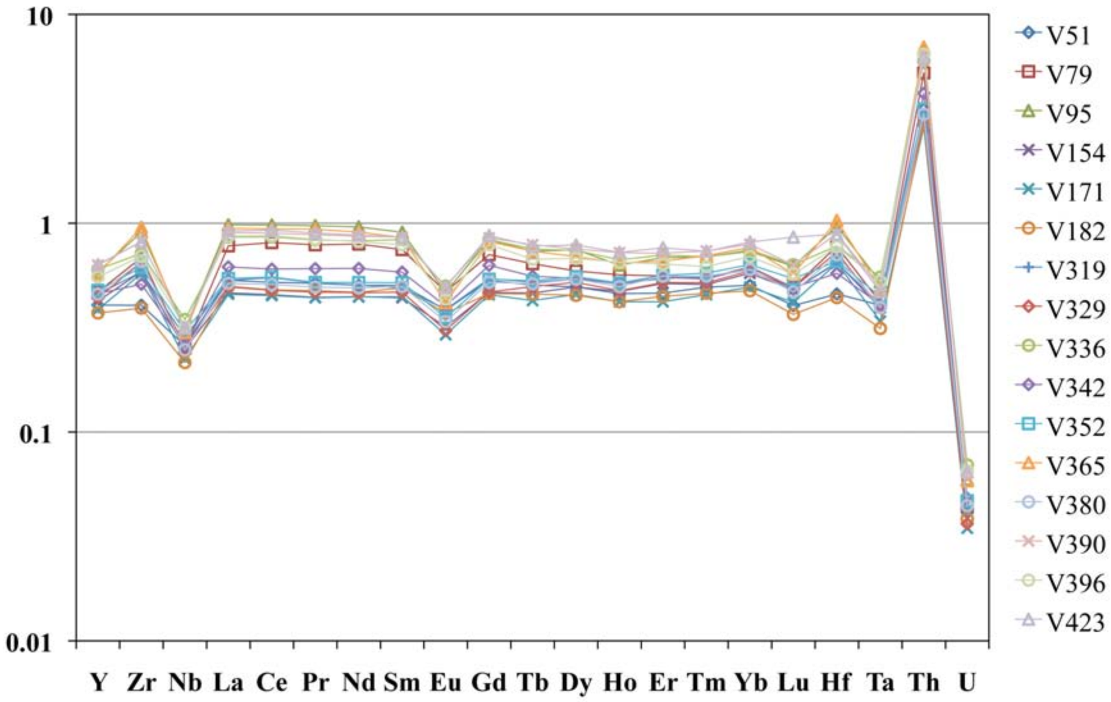


Fig. 4.4: Contents of some Rare Earth elements and trace elements normalised to the upper Earth crust (Wedepohl, 1995) for the SCV fragments belonging to Group 2, in logarithmic scale.

Fragments from Group 4 have the lowest average silica content and the second higher value of alumina contents. SJT glass together with some CPU and SCV fragments are the main constituents of this group. It is possible once again to find a relation between these fragments through colour. The great majority of fragments from the several sets that appear related in this group have an intense glass colouration.

Finally, Group 5 comprehends all the fragments from the PMF set dated from the 14th to the 15th century (with the exception of fragment PMF0517 that appears in Group 3), meaning that these fragments are definitely different in composition when compared with the other fragments from the PMF set, dated to between the 16th and 17th centuries. Besides these fragments, Group 5 also relates fragments from SCV, SJT and CPU sets. The majority of fragments with filigree decoration were grouped together in Group 5. In this group it is possible to find fragment SCV-V210 that corresponds to a blue gourd with a chemical composition different from all the other analysed gourds. This fragment is characterised by a low alumina content and with the presence of lead oxide (~1.90 wt%) and tin oxide (~2 wt%). The colour of this fragment plus fragment SCV-V14 is discussed in the Glass Colouration section.

Looking to the alumina content in all the identified groups, it can be deduced that in general the average contents for this oxide are slightly higher compared with that found in coeval glass from other European production sites (Cagno *et al.,* 2010; De Raedt *et al.,* 2002; Herremans *et al.,* 2012; Šmit *et al.,* 2004; Van der Linden *et al.,* 2005 and Verità, 2013, among others). However, in the Portuguese territories, these alumina contents in glass objects dated between the 17th and 18th centuries have already been recorded. In the literature, the higher alumina values found for soda-rich glass, belong to two samples dated between the 15th and 16th centuries from Savona, Italy, and with values around 5 wt% (Cagno *et al.,* 2012a). It is also possible to find high values of this oxide (around 4 wt%) in glass objects dated from the 16th century and found in two Tuscan sites Gambassi and S. Giovanni Valdarno (Cagno *et al.,* 2010). During the study of a set of glass objects with *millefiori* decoration, dated from the 17th century and found in the archaeological context of Santa Clara-a-Velha Monastery in Coimbra (the archaeological context described in *Chapter Three, Part I*) it was possible to quantify alumina values from 1 wt% up to about 8 wt%. It is for this reason that the author created a classification by alumina content, as described in Table 4.2 (Lima *et al.,* 2012).

Table 4.2: Group division by alumina content (Lima *et al.,* 2012).

Alumina Concentration / wt%	***Classification of composition***
$Al_2O_3 < 2$	Low alumina
$2 < Al_2O_3 < 3$	Medium alumina
$3 < Al_2O_3 < 6$	High alumina
$Al_2O_3 > 6$	Very high alumina

The classification by the alumina content above, taken from this paper will be employed on the further analysis of the chemical compositions of the glass objects.

4.1.1 A small set from the medieval period [1]

A group of eleven medieval glass fragments from the archaeological excavation in Avenida Miguel Fernandes, Beja (PMF), was studied. These objects were at first investigated apart from the others, because of their chronology. This small set provides the only information obtained for the medieval period, and their study will allow to have an idea on the type (or types) of glass circulating in Portugal and if a continuity is observed to the following centuries. Due to the small number of fragments, no statistical treatment was applied to this data.

The glass finds from Beja dated between the 14th and the 15th centuries, can be considered a typical group of glass objects from medieval tradition, with parallels in all European territory. Portuguese finds can be compared with coeval objects from France, Spain, Italy, Germany and the British Isles, not only in terms of the shapes of the objects, but also in the glass colour (greenish, yellowish and more scarcely, colourless glass), and in decorative elements as the applied strings. It is yet interesting to point out that the use of goblets in Portugal finds a parallelism with findings from French Mediterranean regions (Coutinho *et. al.*, 2016).

During the middle ages, glass was subjected to long-distance trading. As an example, during the 14th and the 15th centuries, several archaeological evidences attest the glass importation from Germany, Italy and France to the region of Flanders (Caluwé, 2005, p. 219-220). Numerous furnaces of small dimensions were producing forest glass in Germany with the intent of distributing and exporting the resultant objects through Frankfurt (Caluwé, 2006). Glass imports from Venice and Damascus arriving in France and Cataluña are well documented (Doménech, 2004, p. 86; Frothingham Wilson, 1963, p. 22; Rochebrune, 2004). The most relevant and abundant information on glass production and trading comes from Venice.

Since no medieval furnaces were so far discovered in Portugal, in order to provide comparable production material, the employed methodology must combine both a stylistic and archaeometric approach to discuss the provenance problem.

Considering the glass group from Beja under study here, some objects can be considered imported due to their typological and decorative characteristics. The most evident example is the prunt fragment, belonging to a beaker, the *Krautskrunk*, generally considered of a Central European tradition (Medici, 2014). The discoloured glass beakers decorated with applied coloured glass strings (spiralled) also

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[1] The content of this sub-chapter is published in the *Journal of Medieval Iberian Studies* under the title "First archaeometric study on medieval glass found in Beja (Southern Portugal)" (Coutinho *et al.*, 2016).

suggest a Central European tradition, as well as the discoloured beakers decorated with a blue rim (Medici, 2014).

The remaining glass fragments from Beja, in terms of their stylistic features, seem to have come from the same production centre. Simple shapes made in glass with green hues characterise this production. The beaker with a string applied near the rim stands out, since no parallels were found outside Portuguese contexts (Medici, 2014).

The composition of the analysed glass fragments was obtained by means of μ-PIXE and it is presented in Table VI.2 in *Appendix VI, Part I*. All the analysed objects are composed by a soda-lime-silica glass (Table VI.2 in *Appendix VI, Part I*). The contents of MgO (2.2-4.4 wt%), K_2O (2.3-3.9 wt%), P_2O_5 (0.15-1.1 wt%) and the presence of chlorine (circa 1 wt%) are consistent with the use of coastal plant ashes, thus showing a connection with the Mediterranean tradition.

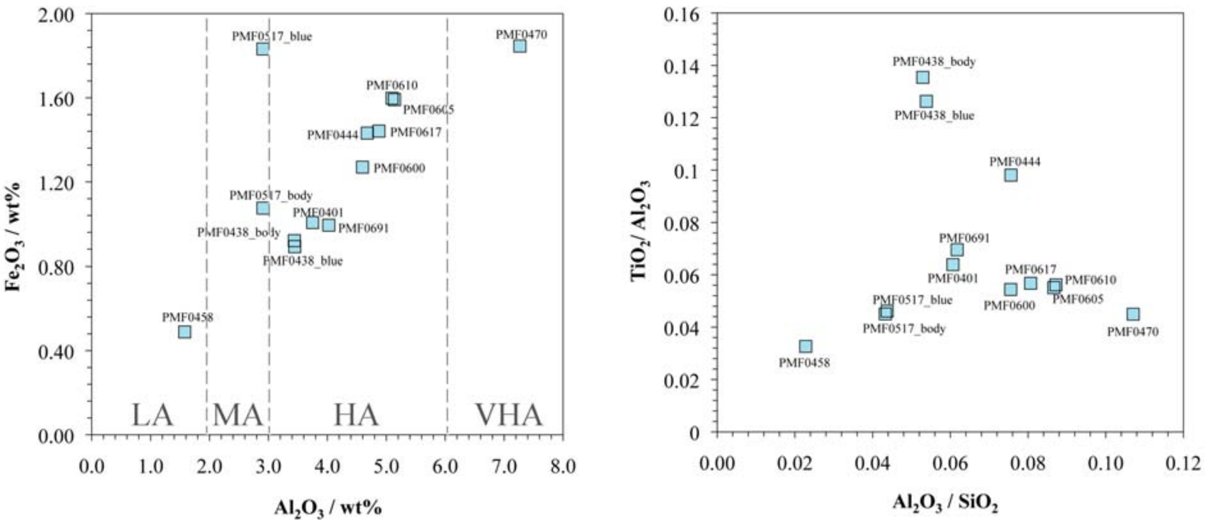
The studied glasses do not differ significantly in terms of chemical composition, except in the cases where the colour of the glass was changed intentionally (*e.g.* between colourless and blue glass). The main compound of the glass, silica (SiO_2), is present in a quantity that varies between 58 and 68 wt%.

The production of soda glass was predominant in the southern countries of medieval Europe, particularly in Mediterranean countries, due to the abundance of marine plants (for instance salsola kali and barilla), whose ashes contain high percentages of sodium and low percentages of potassium (Casellato *et al.*, 2003; Velde, 2013, p.71). The presence of chlorine in all the examined glasses is also indicative of the use of these ashes as fluxes.

Silica

In addition to the silica, the sand used in the glass batch always contains different types of impurities (Moretti & Hreglich, 2013). The minerals which make up these impurities are usually the aluminium-rich kaolinite and feldspar, the zirconium-rich zircon ($ZrSiO_4$), the REE-rich monazite (REE phosphate), the titanium-rich rutile (TiO_2) and iron oxides (Moretti & Hreglich, 2013; Wedepohl *et al.*, 2011a). These elements are the main trace elements and trackers for sand, allowing discussion about the provenance of raw materials and, consequently, about the provenance of the glass (Velde, 2013). Further information relating to the raw materials employed in the glassmaking process is presented in *Appendix I, Part I*.

Following what was explained above, an overall look to the silica trace elements was performed and is presented in figure 4.5. Starting with figure 4.5 a), through the division of the samples by their alumina contents, one can identify a major group in the high alumina area, with contents between 3 and 6 wt%. Studies on the chemical composition of 14th-15th century European glass have identified alumina contents up to 4 wt % (see for instance Cagno *et al.*, 2010; Duckworth *et al.*, 2014; Verità & Zecchin, 2009). Considering these fragments with high alumina glass and analysing figure 4.5 b), that allows to look at important silica tracers, one can relate fragments PMF0401 with PMF0691 very close to each other (fragment PMF0517 is not far), and fragments PMF0660, PMF0617, PMF610 and PMF0605 as another group. One can regard these two groups has having very close sources of silica with similar characteristics in terms of trace elements. PMF0444 and PMF0438 appear completely apart from the others and from each other, which probably implies different silica sources richer in TiO_2.



(a) **(b)**

Fig. 4.5: (a) Binary plot of alumina *vs.* iron oxide with the defined areas for low, medium, high and very high alumina contents according to Lima *et al.*, 2012, and (b) plot of the weight ratios of Al_2O_3/SiO_2 *versus* the weight ratio of TiO_2/Al_2O_3.

Analysing figure 4.5 a), the two obvious outliers are the fragments PMF0458 and PMF0470. Fragment PMF0458 has a low amount of alumina (< 2wt %), suggesting the use of a very pure source of silica such as siliceous pebbles, comparing with the other fragments under study. Fragment PMF0470 has a very high alumina content (> 6wt%), which indicates the employment of a source of silica richer in impurities, probably from sands richer in feldspar. Connecting this information with figure 4.5 b), these fragments remain outliers, which suggests once again the employment of different sources of silica.

In what regards the case of fragment PMF0517, the analytical results for the blue rim of this fragment also presents a very high content of iron oxide comparing with the remaining fragments. This is because of the ore used to obtain the blue colouration. For this reason, this fragment is not considered an outlier (see figure 4.5 b), and for the discussion of its provenance, only the discoloured body glass will be considered.

In general, the fragments presenting an high alumina composition are characterised for having natural hues in green and yellow. In terms of sources of silica, this naturally "coloured" glass can be compared with compositions of Venetian glass with a greenish-brownish hue and dated to between the 11th and

14th centuries (Verità *et al.*, 2002; Veritá, 2013). Since the fragments under study here belong to utilitarian glass, this does not necessarily mean that they were imported from Venice, but more likely that similar recipes were being used around Mediterranean Europe. Furthermore, it is possible to find glass from production sites in Tuscany with similar characteristics in terms of sources of silica glass dated to between 13th and 14th centuries (Cagno *et al.*, 2010).

It is from the 14th/15th century onwards, that a major care in terms of selecting raw materials to produce glass is noticed, and starts to reflect on the glass chemical compositions. For this reason, it is possible to find similarities among Mediterranean glass analysed from this time period.

As it was explained above, stylistically, the two beaker fragments with blue rims were very popular in Venice and all around Europe. Fragments PMF0438 and PMF0517 are for this reason discussed in more detail here, since are eligible to have been imported. The chemical composition of the fragments PMF0438 and PMF0517 was first compared to published compositions of coeval Venetian glass (Verità & Zecchin, 2009a; Verità, 2013). From this comparison, it was not possible to attribute these samples to imports from Venice. From this period, the discoloured glasses had low contents of alumina (around 1 wt %), and lime contents around 8 wt% (Verità, 2013). Analysing the published compositions for glass found in France from the considered period, soda-rich glass was so far only identified on the south of the country, and it belongs to different typologies (found in flasks for instance). This French glass is also characterised for having very low contents of alumina, suggesting the use of a pure silica source (Barrera & Velde, 1989). Looking now to Spanish glass compositions, as far as the author knows, no published glass compositions from this chronology are available. The closest compositions in terms of chronology date to the 9th to the 12th century, and were obtained from glasses collected in the al-Andalus region (Duckworth *et al.*, 2014). It was decided to compare this data with the results obtained for the PMF glasses, in order to evaluate a possible connection with the Islamic tradition. In terms of sources of silica, the group defined by Duckworth *et al.* (2014) as low-lead can be compared with the two PMF0438 and PMF0517 samples in terms of alumina, titanium and iron oxides. However, no lead was found on the samples from PMF, Beja.

Fragment PMF0458 is also eligible to be a foreigner import, since this kind of prunted beakers (*Krautstrunk*) were very fashioned in Central Europe. In Germany, this kind of beakers were characterised for a potassium-rich composition (typical of Central European tradition), and dated to the 14th century. Similar prunted beakers of a potassium-rich composition were also found in Belgium (Caluwé, 2005, p. 219, colour plate 58, d). These examples found in Belgium were considered an import from Germany. As it was mentioned above, a Venetian origin for these beakers cannot be discarded. Analysing the source of silica of the fragment PMF0458, one can conclude that it is consistent with Venetian glass produced at this time. This fragment will be further discussed in more detail considering its fluxing agents.

Flux agents

Considering the flux components, the levels of MgO are all above 2 wt%, which indicates the employment of ashes from halophytic plants into the glass batch (Šmit *et al.*, 2009). The distinct fractions of Na_2O and K_2O employed in the flux are represented in figure 4.6. This relation between oxides serves to try to distinguish among the different employed fluxes (Cagno *et al.*, 2012b, Šmit *et al.*, 2009). Fractions of both oxides were normalized to the content of all alkaline and alkaline-earth oxides. The two marked dashed lines on the chart represent the use of unpurified ashes (correlation line of $Na_2O^* + K_2O^* = 0.6$) and purified ashes ($Na_2O^* + K_2O^* = 0.75$) (Cagno *et al.*, 2012b). Lower K_2O^* values implies higher contents of soda, which is compatible with the identification of Levantine ashes used in the production of genuine Venetian glass (Cagno *et al.*, 2012b).

Analysing the distribution of the samples from PMF, Beja on the chart represented in figure 4.6, it is verified that the majority of the analysed glasses are coherent with the use of purified ashes. Comparing with glass found in the al-Andalus region and according to Duckworth *et al.* (2014), the low lead Islamic glasses (dated between 9 and 12th c.) are coherent with the use of unpurified ashes. This was also verified for plant ash glass from al-Raqqa and dated to between the 8th and 9th centuries (Henderson, 2002). This shows marked differences between the glasses under study here, and the 12th c. Islamic glasses from Cordoba. It is worth noting that the chronological difference of at least two centuries may be an explanation for the evolution in the glass production and in the treatment applied to the raw materials. Moreover, between the 9th and 12th centuries it was a transition period in terms of glass compositions.

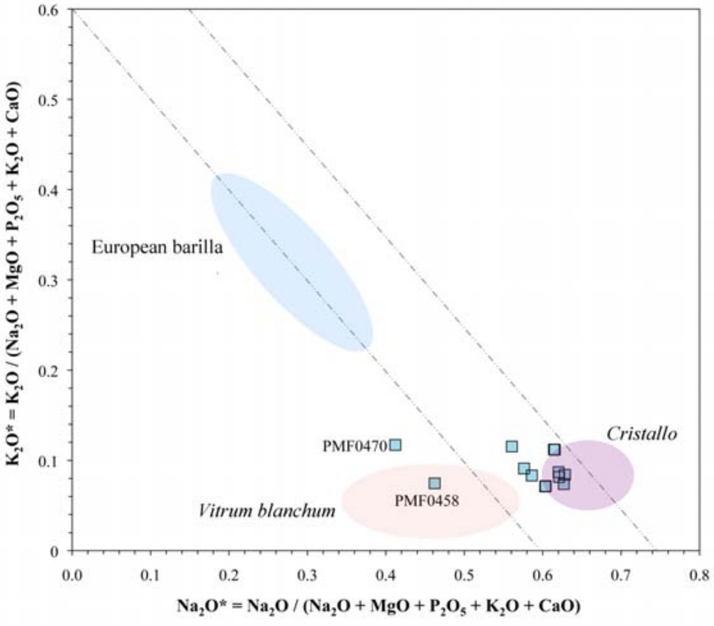


Fig. 4.6: Binary plot of Na_2O^* *vs.* K_2O^*. Na_2O^* and K_2O^* values are obtained through the division of the respective oxide by every components introduced by the ash (Na_2O, MgO, P_2O_5, K_2O and CaO). The two correlation lines represent the purified ash ($Na_2O^* + K_2O^* = 0.75$) and the unpurified ash (($Na_2O^* + K_2O^* = 0.6$). It is also possible to observe the Venetian *cristallo* boundaries, as well as the two *vitrum blanchum* known areas and the European Barilla area (Cagno *et al.*, 2012b; Šmit *et al.*, 2009).

A group of glass fragments from PMF assemblage is perfectly compatible with the *cristallo* boundaries (PMF0401, both PMF0438, PMF0444, PMF0600, PMF0610, PMF0617 and PMF0691), meaning that a special care was taken on the choice and on the treatment of these ashes, making them close to the characteristics of the Levantine ashes. More or less in between the two correlations lines, one can find both PMF0517 and PMF0605 fragments. This can be the result of using less quantity of pure plant ashes. Due to high levels of P_2O_5 in these samples a purification of the ashes is less probable, and the use of pure sources for the plan ashes, like Syria for instance is proposed.

The fragments PMF0458 and PMF0470 are the two outliers identified in this relation of the flux components, and they are both consistent with the use of less pure plant ashes. The fragment PMF0458 has a very close composition to Venetian glass dated to between 11th and 14th centuries, and according to figure 4.6, it is consistent with *vitrum blanchum* glass (Verità, 1986; Verità & Zecchin, 2009a, p. 239). In Bohemian examples of prunted beakers with a soda-rich composition, were identified and attributed to Venetian imports dated from the end of the 14th century and to the 15th century (Sedláčková, 2007, p. 202). A different type of prunted beakers was also found in the archaeological excavation of Rocca di Asolo (Northern Italy), and was considered as a possible Venetian import (Gallo & Silvestri, 2012). Comparing the reported composition from Rocca di Asolo fragments with the one of fragment PMF0458, it is possible to attest their similarity (Gallo & Silvestri, 2012).

Fragment PMF0470 was clearly made using unpure ashes. Relating this information with the one obtained from analysis to the sources of silica, it is highly suggested that this fragment was made employing raw materials (both the silica and the flux) from a different origin. Since the flux from fragment PMF0470 was not treated, this also suggests that this object was made in a different production centre comparing to the other fragments, and probably using a different recipe.

4.1.2 Venetian and *Façon-de-Venise* glass [2]

Among all sets, some shapes were identified as Venetian or *façon-de-Venise* objects, not only because of their shapes, but also due to their decorative features (examples in figure 4.7) (Medici, 2014).

From the 16th century onwards, *façon-de-Venise* glass was the manifestation of Venetian taste, spreading in Europe throughout several production centres, mainly as a consequence of the emigration of Venetian glassmakers. A number of papers devoted to the analysis of Venetian and *façon-de Venise* glass objects discussed not only the raw materials employed in the manufacture of these items, but also their probable production locations (De Raedt *et al.*, 2001; 2002, Šmit *et al.*, 2004; 2009; Verità & Zecchin, 2009a; Moretti & Hreglich, 2013). Chemical analysis and research on ancient treatises (Verità & Zecchin, 2009a) led to the understanding that the raw materials employed in Venetian and *façon-de Venise*

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[2] The content of this sub-chapter is published in the *Journal of Archeological Science: Reports* under the title "Provenance studies on *façon-de-Venise* glass excavated in Portugal" (Coutinho *et al.*, 2016b).

production were carefully selected, in order to achieve the high quality glass that made it one of the most desired luxury items throughout Europe. For example, during the 14th century, Venetian glassmakers began to use quartz pebbles from the Ticino River as a source of silica, replacing the use of impure sands.

Fig. 4.7: Some examples of *façon-de-Venise* fragments present in the sets being studied.

For glass production in Portugal, documentary sources report that glassmakers from Italy (Venice and Altare) and from Antwerp had settled in Portuguese territory from the 17th century onwards (Frothingham Wilson, 1941; Valente, 1950; Custódio, 2002; Amado Mendes, 2002). A glass furnace directly related to the Royal House of Bragança was built in the village of Vila Viçosa (Southeast of Portugal) and run by the Venetian Pero Paulo. Private letters mention the glass produced in this kiln, referring to its great quality. Details referring to raw materials include references to the use of both ground and crushed quartz pebbles as the source of silica (Custódio, 2002). Unfortunately, there is no archaeological data available for this furnace so far, and the objects resulting from this production are currently unknown. However, considering this documentary information, the possibility is raised that there was production of *façon-de-Venise* glass in Portugal.

All the analysed *façon-de-Venise* objects are composed of soda-lime-silica glass (Tables IV.2, V.2, VI.2 and VII.2 in *Appendices IV, V, VI and VII*, *Appendices Part I*, respectively). The contents of MgO (2.5-4.1 wt%), K_2O (2.4-6.5 wt%), P_2O_5 (0.1-0.6 wt%) and the presence of chlorine are consistent with the use of coastal plant ashes, the usual alkali used in the production of Venetian and *façon-de-Venise* glass (Šmit *et al.*, 2004; Verità & Zecchin, 2009).

In order to assist the interpretation of the data, a chemometric method (Principal Component Analysis – PCA) was applied. The PCA model created allowed one to observe relations between *façon-de-Venise* objects from all of the sets studied (figure 4.8). The first two components explain circa 62% of the total variance. Looking at figure 4.8, it is possible to identify a close relationship between SCV – SCV-V193, SCV-V195 and SCV-V191, which form Group I_{fdV}. It is also possible to infer that these objects do not relate with any other objects from the same set or from the other contexts. Group II_{fdV} includes the majority (ca. 70%) of PMF fragments (dated from the 16th to the 17th century) and ca. 55% of SJT objects, in particular relating fragments PMF0568, PMF0569, PMF0570, PMF0996, PMF1010 and PMF1025, and fragments SJT0011, SJT0038, SJT0105, SJT0122 and SJT0123. This result opens up the possibility for fragments of both collections (PMF and SJT) either having a common production centre, or having employed the same raw material sources and recipes, even if in different production centres. See Table XIII.1 with the composition of the fragments organised by groups in *Appendix XIII, Appendices Part I.*

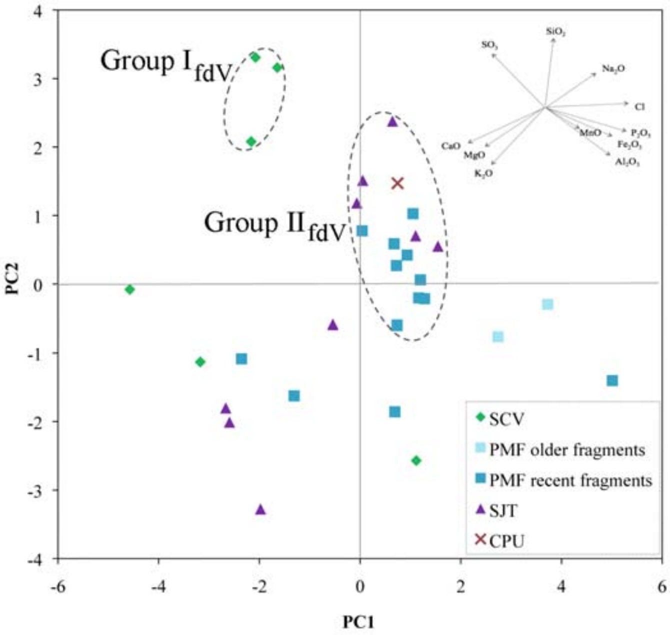

Fig.4.8: Scores and loadings on the 1st and 2nd principal components, explaining circa 62% of the total variance, for the *façon-de-Venise* objects.

On the basis of what was stated above regarding the importance of the raw materials employed in the discussion of glass provenance, the raw materials used in the objects being study will now be analysed. This analysis will start with the examination of the major component of glass, silica, and the fluxes and minor components will be discussed further below.

The remaining fragments do not show a clear relation with the identified groups or between them.

Silica

Taking into account the elements referred to above, the contents of alumina and iron oxide of the fragments under study were plotted. The chart presented in figure 4.9 a) appears divided according to alumina contents, using the division reported in Lima *et al.* (2012). The values for the body glass from the *millefiori* fragments from Santa Clara-a-Velha monastery reported by Lima *et al.* (2012) and presented in Table X.1 in *Appendix X, Appendices Part I* were also plotted. When analysing this chart (figure 4.9 a), it is possible to see that some fragments present very high alumina contents of around 6 wt%, while most fragments are in the regions of 1.6-4.6 wt% alumina. Alumina contents this high are not usually found among *façon-de-Venise* glass from known European centres like Antwerp, Amsterdam, London, and Spain, with alumina values reported equal to or less than 2.0 wt% (see *Table X.1 in Appendix X, Appendices Part I*) (De Raedt *et al*., 2001; 2002; Ulitzka, 1994). In *façon-de-Venise* glass from Tuscany, Italy (Gambassi and San Giovanni Valdarno) alumina contents reach values around 4.0 wt% (Cagno *et al.,* 2010), and in Lezha, Albania (Šmit *et al*., 2009), a few samples reached values higher than 3.0 wt%. Venetian glass alumina content is below 2.0 wt%, even in common glass (Verità & Zecchin, 2009a).

Looking to the chart represented in figure 4.9 a) it is possible to observe that all but one of the SCV fragments have low alumina content (below 2.0 wt%). Notice that these five SCV samples (SCV-V191, SCV-V193, SCV-V195, SCV-V408 and SCV-V404) have alumina and iron oxide contents that are both similar to the ones of the SCV *millefiori* glass reported by Lima *et al.* (2012) as being of Venetian origin and consistent with the values reported for Venetian glass (Verità & Zecchin, 2009a). Fragment SCV-V194[3], with alumina content of 6.1 wt% belongs to a *tazza* with gilded decoration and a lion head on the stem.

According to values in the literature, Venetian glass (both *cristallo* and *vitrum blanchum*) is characterised by low contents of TiO_2 (up to 0.07 wt%) when compared with coeval *façon-de-Venise* glass (Verità, 2013). Looking further into the chemical compositions of these fragments, the comparison with coeval and genuine Venetian and *façon-de-Venise* production confirms that SCV-V191, SCV-V193, SCV-V195 and SCV-V408, are probably genuine Venetian objects (*cf.* Figure 4.9 b), with alumina contents below 2.0 wt% and a titanium oxide contents below 0.07 wt% (Verità & Zecchin, 2009a). The fragments from the remaining sets do not fall within the Venetian boundaries and, for this reason, are considered to be from a different *façon-de-Venise* production centre.

Figure 4.9 c) plots the concentrations of the iron and titanium oxides against each other, in order to evaluate the relation between these two impurities of silica. A positive linear correlation exists, allowing one to conclude that they probably entered the glass composition through iron–titanium minerals, such as ilmenite (Cagno *et al.,* 2012a; Šmit *et al.,* 2009). In this plot, it is possible to recognise and separate two regions: the line that appears in the plot provides a visual division between two groups. The first

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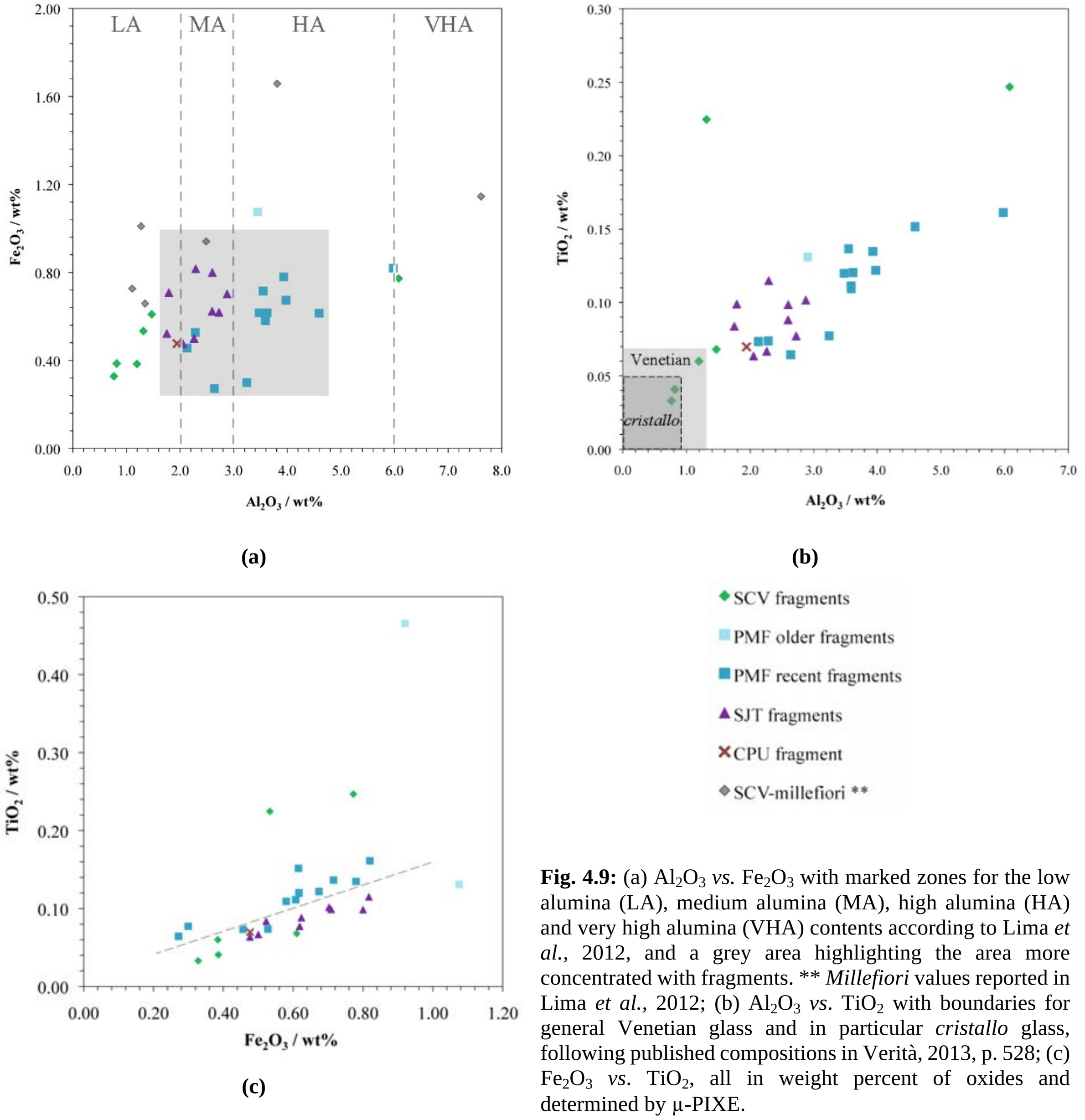
[3] It is important to mention that this object is broken into several fragments and the bowl is apart from the foot. The analysed sample was cut from a fragment of the bowl. Due to the type of decoration and colour of the glass from both the bowl and foot we believe that they belong to the same goblet.

one comprises the SCV, SJT and CPU sets, plus two PMF fragments with the lower alumina values. The other group includes the majority of PMF fragments plus the SCV fragment with high alumina value. A closer look at the compositions in figure 4.9 further confirms that the line in the plot of figure 4.9 c) separates compositions lower in alumina content from compositions richer in alumina: the upper group in the plot being assigned to less pure silica sources, the lower group probably uses silica of higher purity. As no clear correlation was found between the Al_2O_3 and Fe_2O_3 contents as silica impurities, this results would seem to indicate that the contents of Al_2O_3 impurity is a better fingerprint for silica sources.



(a) **(b)** **(c)**

Fig. 4.9: (a) Al_2O_3 *vs.* Fe_2O_3 with marked zones for the low alumina (LA), medium alumina (MA), high alumina (HA) and very high alumina (VHA) contents according to Lima *et al.*, 2012, and a grey area highlighting the area more concentrated with fragments. ** *Millefiori* values reported in Lima *et al.*, 2012; (b) Al_2O_3 *vs.* TiO_2 with boundaries for general Venetian glass and in particular *cristallo* glass, following published compositions in Verità, 2013, p. 528; (c) Fe_2O_3 *vs.* TiO_2, all in weight percent of oxides and determined by µ-PIXE.

The PMF set is richer in impurities like alumina, and seems to have a different silica source from the other sets (SCV, SJT and CPU). Observing the charts represented on figure 4.9 and comparing these with reported values summarised in Table X.1 in *Appendix X, Appendices Part I*, it becomes clear that, due to the elevated alumina contents for both represented chronologies, a Venetian provenance has to be discarded, as already stated. The fragments PMF0527, PMF0556 and PMF1010, with an alumina content below 3 wt%, can be compared with published results on *façon-de-Venise* production centres. The remaining *façon-de-Venise* fragments from this set are related to each other not only in terms of shapes and decorations (stem glass with mould blown ribs) and the hue of the glass (light blue), but also in terms of major and minor elements and most of these PMF fragments were clustered together in the PCA analysis (see figure 4.8). For this reason the existence of a *façon-de-Venise* production centre not recognised yet is highly probable. Due to the absence of excavated glass furnaces of this period in Portugal, and on the rest of the Iberian Peninsula as well, one can only speculate about the origin of these objects.

The SJT fragments appear to have been made with the same or related silica sources. Due to the alumina values (between 2 and 3 wt%), the fragments from this assemblage cannot be related with any of the known *façon-de-Venise* production centres (see Table X.1 in *Appendix X, Appendices Part I*).

A more detailed analysis was performed on the SCV glass fragments attributed to Venetian origin by means of LA-ICP-MS (Table VI.3 and VI.4 in *Appendix VI, Appendices Part I*). From this analysis it was possible to quantify trace and REE contents in the glass.

According to De Raedt *et al.* (2001), it is possible to distinguish between Venetian and Antwerp *façon-de-Venise* glass through the contents of Zr and Hf measured in the glass. Zirconium comes from the zircon mineral, and Hf is an accessory element present in this mineral (Cagno *et al.*, 2012a) The Zr contents of Venetian glass is low, ranging between 20 and 40 µg/g; and the Hf content is less than 1 µg/g. Looking at the charts represented in figure 4.10, one can see that SCV-V191, SCV-V193, SCV-V195, and SCV-V408 have Zr values of between 20 and 40 µg/g as well as an Hf content below 1 µg/g. Relating this information to that obtained through major oxides analysis and with REE contents, it is possible once again to confirm that these glass objects are of Venetian provenance.

Looking deeper at the glass composition, and considering trace elements and REE of SCV glasses (Table VI.3 and VI.4 in *Appendix VI, Appendices Part I*) in a trace element Earth crust normalised plot (see figure 4.11), it is possible to confirm that the fragments SCV-V191, SCV-V193, SCV-V195 and SCV-V408 have a very similar trace element pattern, which in the case of SCV-V193 and SCV-V195 seems to be identical. These four glasses have enrichment in Sr and depletion of the remaining crustal elements, confirming the use of a pure silica source (Cagno *et al*., 2012a). Their resemblance in terms of trace and REE elements concentration can be explained by the use of the same raw materials. In this case, the fragment SCV-V408 could have been produced in a different Venetian production centre since its chemical composition in major elements differs from SCV-V191, SCV-V193 and SCV-V195 fragments (*cf.* Table IV.2 in *Appendix IV, Appendices Part I*). A different ratio of the employed raw materials can also explain the compositional disparity between SCV-V408 and the other three SCV Venetian fragments.

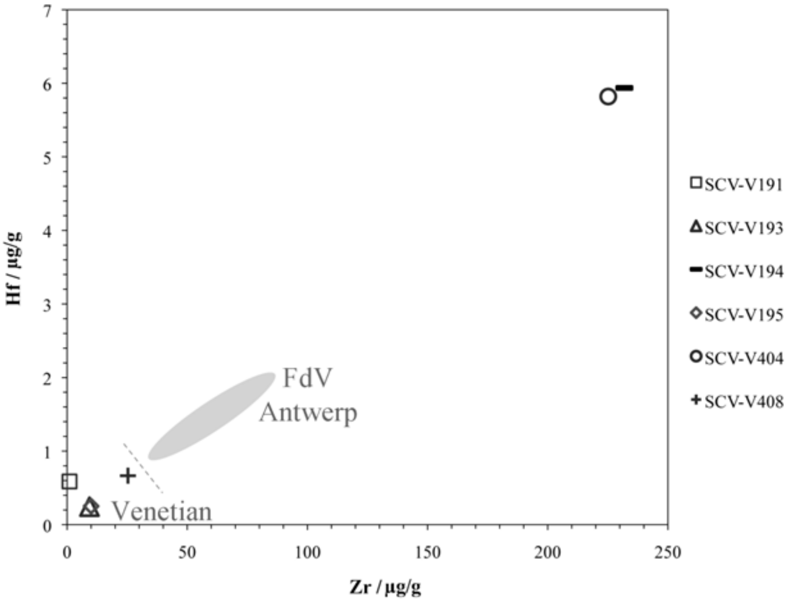


Fig. 4.10: Binary plot of Zr *vs*. Hf concentrations in µg/g, determined by means of LA-ICP-MS for the SCV *façon-de-Venise* objects. The grey area represents the general Antwerp *façon-de-Venise* region, and the dashed-line represents the area for the general Venetian region taken from the literature (De Raedt *et al.*, 2001).

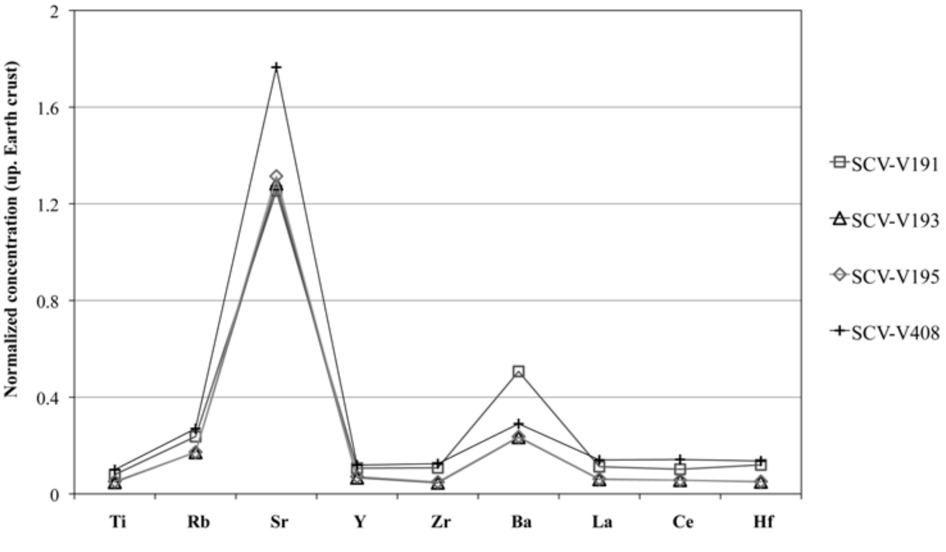


Fig.4.11: Contents of some trace and Rare Earth elements normalised to the upper Earth crust (Wedepohl, 1995) for the Venetian or *façon-de-Venise* glass objects from the SCV set.

Flux agents

Analysing Tables IV.2, V.2, VI.2 and VII.2 in *Appendices IV, V, VI and VII*, respectively, in *Appendices Part I*, with quantification of the major and minor elements, it is possible to verify that MgO levels are all above 2 wt%, which indicates that ashes from halophytic plants were employed in the glass batch (Šmit *et al.*, 2009).

In order to observe the distinct fractions of Na_2O and K_2O employed in the flux, and thus to distinguish among the different possible fluxes employed (Cagno *et al.*, 2012b; Šmit *et al.*, 2009), the fractions of both oxides normalised to the content of all alkaline and alkaline-earth oxides were plotted in figure 4.12. The two dashed lines marked on the chart represent the use of un-purified ashes (correlation line of $Na_2O^* + K_2O^* = 0.6$) and purified ashes ($Na_2O^* + K_2O^* = 0.75$) (Cagno *et al.*, 2012b).

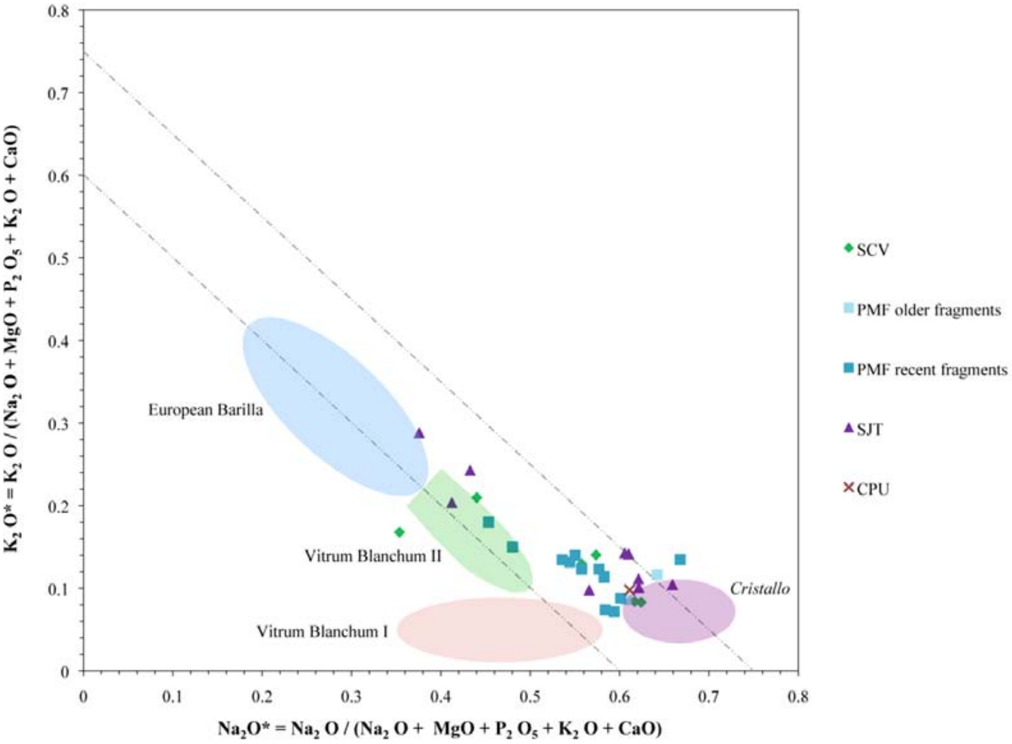


Fig. 4.12: Binary plot of Na_2O^* *vs.* K_2O^*. Na_2O^* and K_2O^* values are obtained through the division of the respective oxide by every component introduced by the ash (Na_2O, MgO, P_2O_5, K_2O and CaO). The two correlation lines represent the purified ash ($Na_2O^* + K_2O^* = 0.75$) and the un-purified ash (($Na_2O^* + K_2O^* = 0.6$). It is also possible to observe the Venetian *cristallo* boundaries, as well as the two *vitrum blanchum* known areas and the European Barilla area (Cagno *et al.*, 2012b, Šmit *et al.*, 2009).

A large group of fragments arrange themselves along the inverse correlation line of glass made using purified ashes and are close to the *cristallo* boundaries. It is proposed that objects from this group were manufactured using pure ashes like the ones brought to Venice from the Levantine region. The lower K_2O^* values imply higher contents of soda, which is compatible with the identification of Levantine ashes used in genuine Venetian glass production (Cagno *et al.*, 2012b). The three SCV objects (SCV-V191, SCV-V193 and SCV-V195) identified as Venetian imports are within this region (the points overlap) and for this reason the employment of Levantine ashes in their batch is proposed. These fragments are considered a genuine import of Venetian *cristallo* glass. Fragment SCV-V408, the other one identified as a genuine Venetian import, appears in the *vitrum blanchum II* area, apart from the other fragments from SCV set.

The remaining objects to which a provenance could not be attributed and which belonged to this cluster were made from carefully chosen plants capable of producing pure glass. The majority of PMF fragments are arranged between the purified and un-purified ashes trend lines. Recalling the alumina content of these objects and the discussion over their silica trace elements, this fact reinforces the idea that these objects were made in a different - yet to be discovered - *façon-de-Venise* production centre. The raw materials of the flux employed in their manufacture were chosen in order to be able to imitate *cristallo* glass.

Some SJT and CPU fragments are also within the *cristallo* boundaries. It is interesting to note that the CPU fragment always appears related with SJT and some PMF fragments, not only in terms of flux but also in terms of silica sources, a fact already highlighted by the PCA analysis. This might indicate that these objects were produced in the same production centre, or in different production centres using the same or highly related sources of raw materials.

One group, which includes fragments from SCV, SJT and PMF set, was clearly made using un-purified ashes and is within or close to *vitrum blanchum* II boundaries (Šmit *et al.,* 2009).

One SJT sample (SJT0135_body glass) falls close to the border of the European Barilla area. This object presents a decoration of white strings freely applied around the rim. The available fragments seem to be consistent with the shape of a *tazza* but no foot or stem is available, which would allow one to draw more conclusions.

The presence of strontium in the glass composition can be explained by plant ash flux or limestone. In figure 4.13, CaO and SrO were plotted and it is observed that the majority of samples have SrO contents below 400 µg/g. SrO contents above 400 µg/g are characteristic of limestone of shell derivation (Šmit *et al.,* 2009). When the SrO contents are lower, as is the case in the majority of the analysed glass fragments, it can be due to the employment in the batch of limestone of terrestrial origin, like calcite, or of a flux made from purified plant ash (Šmit *et al.,* 2009). From these results it is then possible to propose that all the raw materials employed as the flux of all the samples with SrO below 400 µg/g, because of the low SrO contents, were well purified through an identical method of purification (Šmit *et al.,* 2009).

As far as the remaining samples are concerned, it is possible to conclude that the older PMF samples were made employing a different flux than the more recent ones. However, in figure 4.12, these fragments also appear within the *cristallo* boundaries indicating that they also were manufactured using purified ashes, having SrO content between 100 and 150 µg/g.

De-colouration and glass natural hues in *façon-de-Venise* objects will be discussed further ahead (section 4.6 Glass colourants and opacifiers).

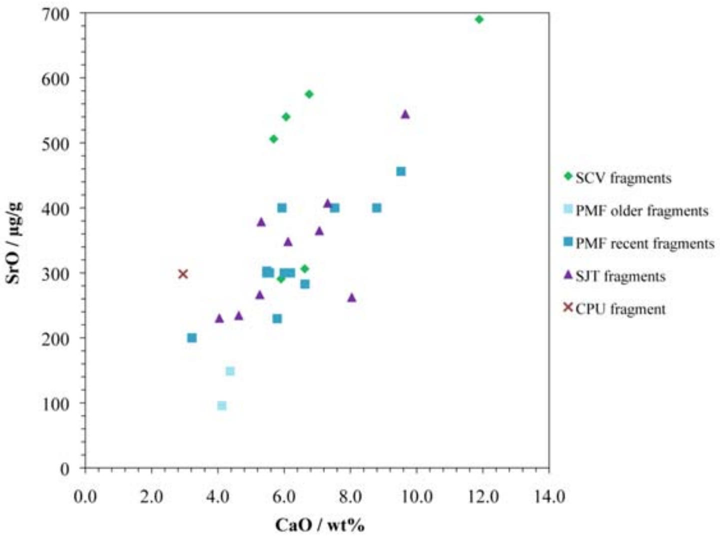
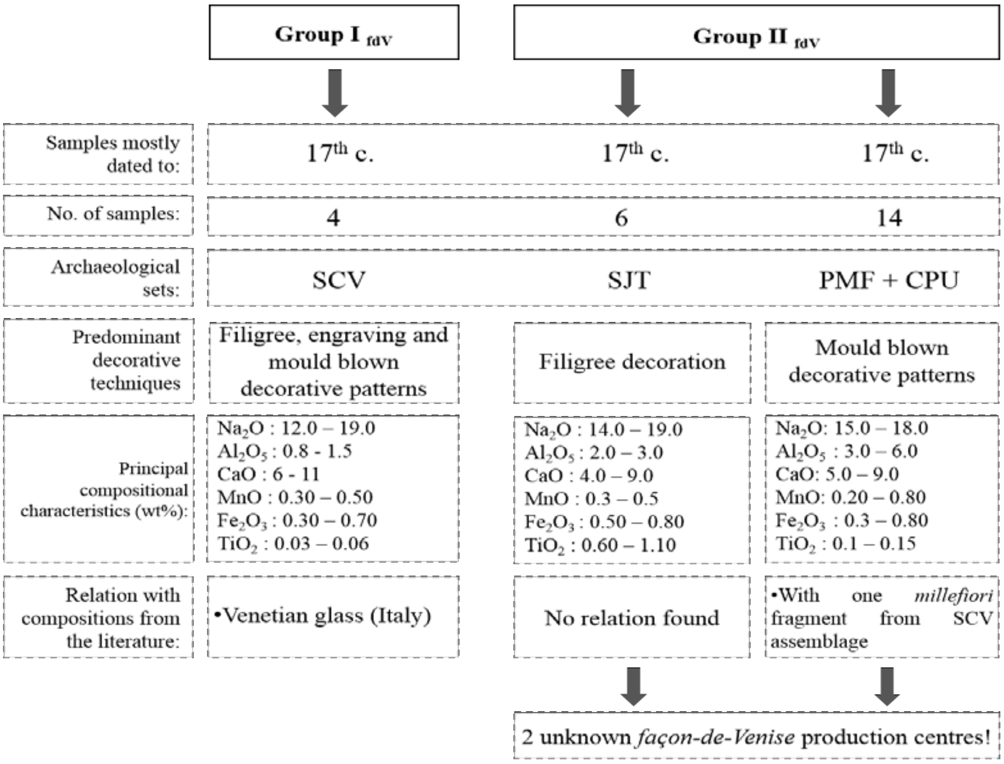


Fig. 4.13: Binary plot of CaO in weight percent of oxides *vs.* SrO in µg/g determined by means of µ-PIXE.

In order to summarise the results obtained from the study of the *façon-de-Venise* and Venetian objects, a scheme was made and it is presented as figure 4.14.



	Group I $_{fdV}$	Group II $_{fdV}$	
Samples mostly dated to:	17th c.	17th c.	17th c.
No. of samples:	4	6	14
Archaeological sets:	SCV	SJT	PMF + CPU
Predominant decorative techniques	Filigree, engraving and mould blown decorative patterns	Filigree decoration	Mould blown decorative patterns
Principal compositional characteristics (wt%):	Na_2O : 12.0 – 19.0 Al_2O_5 : 0.8 - 1.5 CaO : 6 - 11 MnO : 0.30 – 0.50 Fe_2O_3 : 0.30 – 0.70 TiO_2 : 0.03 – 0.06	Na_2O : 14.0 – 19.0 Al_2O_5 : 2.0 – 3.0 CaO : 4.0 – 9.0 MnO : 0.3 – 0.5 Fe_2O_3 : 0.50 – 0.80 TiO_2 : 0.60 – 1.10	Na_2O: 15.0 – 18.0 Al_2O_5 : 3.0 – 6.0 CaO: 5.0 – 9.0 MnO: 0.20 – 0.80 Fe_2O_3 : 0.3 – 0.80 TiO_2 : 0.1 – 0.15
Relation with compositions from the literature:	•Venetian glass (Italy)	No relation found	•With one *millefiori* fragment from SCV assemblage

2 unknown *façon-de-Venise* production centres!

Fig. 4.14: Scheme summarising the main characteristics (stylistic and compositional) of the two groups of Venetian and *façon-de-Venise* objects.

4.1.3 The Gourds: a shape of Portuguese production?

In several Portuguese archaeological excavations, a recurrent shape was retrieved that until now has only been found with such a wide diffusion in national territory: the gourd shaped bottle (figure 4.15). This shape has already been described (Medici, 2014; Medici *et al.*, 2009), and the conclusion was reached that these gourd-shaped vessels were a common glass container in Portugal during the 17th and

18th centuries. These vessels were still produced in the Marinha Grande Royal Glass Factory, as they are present in the factory's catalogue (Medici, 2014, p. 240). According to J. Custódio (2002, p.57), this shape shows an influence that dates back to the Arab legacy.

Fig. 4.15: Examples of some necks of gourds from SCV and SJT sets. Gourds are organised by resemblance between shapes.

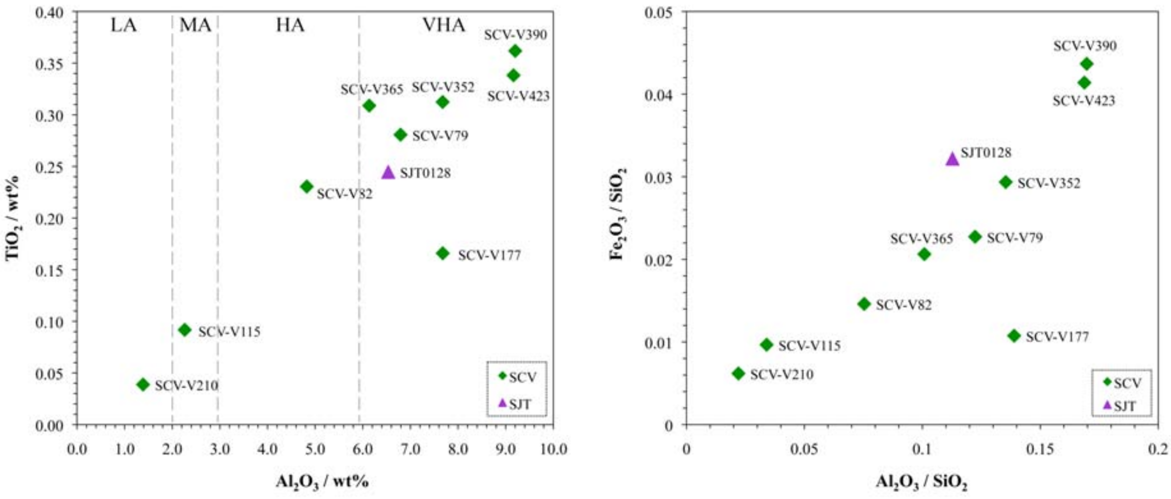
This uncommon shape is present in two of the analysed sets, SCV (nine gourds) and SJT (one gourd). Besides these sets, several gourds were found in archaeological assemblages from Rua da Judiaria in Almada (Medici, 2005a), located on the South bank of Tejo River, and from the Municipal Museum of Moura, located in the South of Portugal (Medici, 2014).

As far as the chemical analysis are concerned, their sodium oxide content varies between 15 and 20 wt%, the silica content varies between 54 and 66 wt%, and the potassium oxide varies between 1.40 and 4.30 wt%. As is the case with all the analysed soda-rich glass, these fragments are consistent with the use of plant ashes as an alkali source, due to the relatively high contents of K_2O (between 1.8 and 4.3 wt%), P_2O_5 (P_2O_5 varies between < 0.05 and 0.70 wt%), and the presence of chlorine.

Because of the small amount of selected objects with this typology (ten gourds within the six studied sets), no statistical method was applied to their study. See Table XIII.2 with the composition of the gourd shaped bottles in *Appendix XIII, Appendices Part I.*

Silica

Taking into consideration the elements mentioned, described in *Appendix I*, *Appendixes Part I,* the contents of alumina and titanium oxide of the gourds under investigation were plotted (figure 4.16 a). This chart appears divided according to the alumina content, using once again, the division reported in Lima *et al.* (2012). According to this division, at least three different silica sources can be identified. The two gourds situated on the left corner of the chart (SCV-V115 and SCV-V210) are the ones presenting the lower amounts of alumina, which implies the employment of a purer source or sources of silica. The remaining gourds, which have an alumina content higher that 5 wt%, were produced using silica sources much richer in impurities. Analysing reported compositions from coeval glass objects from known production centres, these alumina contents are not commonly found (see Table X.1 *in Appendix X*, *Appendices Part I*). The gourd from the SJT (SJT0128) set is very close to the SCV gourds, sharing most probably the same source of silica.



(a) **(b)**

Fig. 4.16: Binary plots of (a) alumina *vs.* titanium oxide, in weight percent of oxides, divided by alumina contents following the division proposed by Lima *et al.* (2012), and b) alumina *vs.* iron oxide, both normalised to the silica content. Results measured by μ-PIXE.

Analysing figure 4.16 b), alumina and iron oxides were normalised to the silica content and plotted against each other. Once again, the two gourds with lower amounts of alumina appear close to each other. With a ratio of 0.1 to 0.15 of alumina to silica it is possible to identify five gourds from the SCV set (SCV-V79, SCV-V82, SCV-V177, SCV-V352 and SCV-V365) and the SJT gourd. Four of the SCV samples appear highly related (SCV-V79, SCV-V82, SCV-V352 and SCV-V365), presenting a positive correlation between the alumina and iron oxides normalised to the silica contents. The SJT gourd once again appears very close to these SCV gourds, inferring that the same source of silica was employed to produce this glass. The SCV-V177 gourd appears outside this positive correlation, which may indicate that this gourd was made using a different source of silica. Finally, two SCV gourds (SCV-V390 and SCV-V423) can be identified on the upper right corner of the chart, being the two objects with the highest alumina content. These two gourds were probably made from the same silica source, very reach in impurities.

To better understand the relation between these objects, the gourds from SCV were also analysed by means of LA-ICP-MS what allows one to look to the REE and other trace elements pattern of the glass. In figure 4.17, the REE and trace elements signature for the SCV gourds is represented. Analysing the trace elements and REE pattern for these objects, it is possible to identify some objects that are more related, for instance the fragments SCV-V390 and SCV-V423 have a perfectly coincident signature.

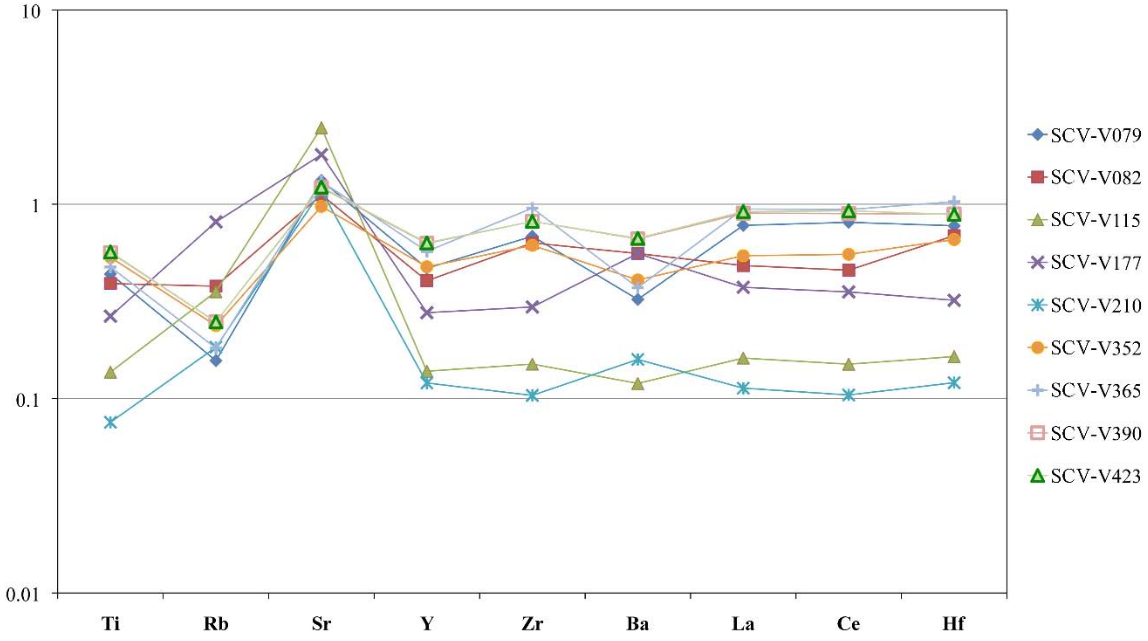


Fig. 4.17: Contents of some trace and Rare Earth elements normalised to the upper Earth crust for the glass gourds from the SCV set, in logarithmic scale.

In figure 4.16 a) and b) these fragments (SCV-V390 and SCV-V423) also appear together on both of the represent charts, and on the quantification Table IV.2 in *Appendix IV* (*Appendices Part I*), the resemblance between these two samples is confirmed in all the quantified oxides. The coincident REE and trace elements signature, plus the resemblance between all the major oxides, indicates that the SCV-V390 and SCV-V423 gourds were made from the same silica source and probably in the same production centre. Objects SCV-V079 and SCV-V365 have also a very similar REE and trace elements signature. These two samples are also very close to each other in figures 4.16 a) and 4.16 b). Gourds SCV-V082 and SCV-V352 have a similar REE and trace elements signature for the majority of elements, differing mainly on the Rb and Ba contents. These two fragments are related in some way with fragments SCV-V079, SCV-V365, SCV-V390 and SCV-V423, not only in trace elements and REE terms, but also in the charts represented in figures 4.16 a) and 4.16 b). Once again, it is possible to infer that this group of gourds with a high and very high alumina content were made from the same silica source, or from highly related silica sources in geographical terms.

With regard now to sample SCV-V115, it is the one with the higher Sr value and a depletion in the remaining reported crust elements, which can be related to the use of a purer silica source containing Sr-bearing aragonite from seashells (Cagno *et al.*, 2012b). Sample SCV-V210 has a trace elements and REE signature very close to SCV-V115, with depletion in most of the determined trace elements and REE, which also indicates the use of a purer silica source, however it does not present such an elevated Sr value. Both these gourds appear very close in the charts represented in figures 4.16 a) and 4.16 b) and they present the lower alumina values. As it was mentioned above, fragment SCV-V210 has a unique composition with the presence of lead and tin oxides. The composition can possibly be attributed to recycled cullet, without any concern shown for the separating of the coloured from the uncoloured glass. The object SCV-V177 has a REE and trace pattern that can be compared in terms of shape to the REE pattern of SCV-V115 and SCV-V210 objects. Fragment SCV-V177 differs from these last two gourds because of a higher Rb and Ba contents. In fact, fragment SCV-V177 presents the higher Rb content of all the analysed gourds. The Sr content of this fragment is the second higher, almost comparable with the Sr content of SCV-V115 object. This can indicate that silica from a different location was used in the production of SCV-V177 gourd. This object is the one that in both figures 4.16 a) and 4.16 b) is always apart from the rest of the samples, which might indicate that this object has a different provenance than the rest of the analysed gourds.

Flux agents and other glass components

Verifying the MgO levels, for most of the gourds the values are above 2 wt%, which once again indicates that ashes from halophytic plants were employed in the glass batch (Šmit *et al.*, 2009).

Analysing the relation between potassium and calcium oxides (figure 4.18), it is observed that, with the exception of SCV-V177, the remaining objects are closely related, which might suggest that even the glass with lower alumina contents can be related to the other objects. These two oxides come from the plant ashes rich in alkalis employed on the batch. In the specific case of these analysed gourds, it seems that the plant ashes used in their batches were collected from the same region, justifying the similarity in CaO and K_2O contents (figure 4.18).

The SJT gourd appears related with the SCV gourds with high and very high alumina content, suggesting once again that these gourds share the same raw materials and possibly the same provenance.

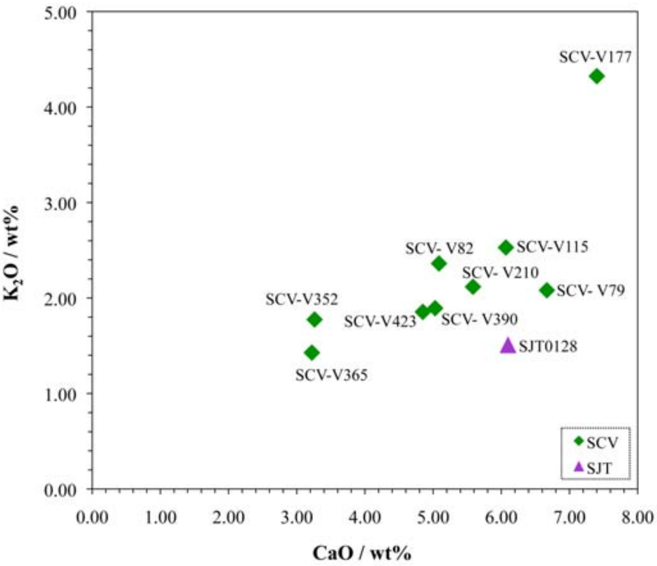


Fig. 4.18: Binary plot of CaO *vs.* K_2O in weight percent of oxides, measured by μ-PIXE.

In conclusion, because of the uniqueness of this shape (see figure 3.15), and because of its diffusion in Portuguese territory as well as because of its composition (high and very high alumina contents with the exception of two gourds), the hypothesis that these objects were produced in national territory has to be considered.

4.1.4 Mould blown objects

Mould blown decorated objects represent 65 % of the totality of all the objects, and 72 % of the soda-rich glass objects. These objects were selected to be treated as an independent category because their mould blown decorations encompass some peculiarity related to their production. For this reason, the decoration can be used as an indication of the locality of the production of the objects.

Among the analysed objects it was possible to identify a specific mould blown decoration pattern that so far is considered unique and exclusive for objects found in Portuguese territory. The pattern is a four-petalled flower that appears embossed inside lozenges. This four-petalled flower pattern was found in objects from the SCV (SCV-V14 and SCV-V335) and PMF (PMF510) sets. This design had already been identified by Ferreira & Medici (2010) and so far no published parallels involving its use on glass objects are known. Apart from glass, this four-petalled flower pattern was employed in textiles, musical instruments and tiles. In the case of textiles, this pattern was found for example in France and in Italy (the Italian examples were found in some paintings and illuminations) and in the case of musical instruments it was found in Germany (Ferreira & Medici, 2010). Figure 4.19 shows a detail of a Portuguese painting depicting a musical instrument decorated with this four-petalled flower. This pattern was also identified in Portuguese tiles dated from the second half of the 18th century (Ferreira & Medici, 2010).

Fig. 4.19: Four-petalled flower motif. Detail of a Portuguese painting by Gregório Lopes, “A Virgem, o menino e os anjos”, 1536-1539. Museu Nacional de Arte Antiga (National Museum of Ancient Art), inventory nº 30 Pint (© IMC available in www.matriznet.imc-ip.pt, accessed in 21 September 2014).

The lozenge motif is also present in other fragments as a decorative pattern always enclosing other decorative embossed motifs. Besides the four-petalled flower, smaller lozenges enclosed by bigger ones were also identified in objects SJT007 from the SJT set and SCV-V336 from the SCV set. This decorative typology had been already identified by Ferreira & Medici (2010), and besides the SJT set, it was also found in the glass assemblage from S. Francisco Convent in Lisbon and dated to the 17th century.

Apart from this decorative motif, other mould blown patterns were identified that are very common in glass objects from known European glass production centres. It is possible to find objects decorated with “bossed” patterns, as the commonly called bossed beakers. These beakers have their origins in the Low Countries and Belgium and were produced between the second half of the 16th century and end of the 17th century, and spread throughout all of Europe (Medici, 2014). The beakers identified with these characteristics belong to the PMF (PMF0387) and to the CPU (CPU0008 and CPU0009) sets.

There are also objects with prominent ribs present in different combinations. There are vertical ribs (SCV-V60 and SCV-V386), oblique ribs (PMF438 and PMF517) and S-shaped ribs (PMF570 and PMF617).

As to the chemical composition of the three fragments with the four-petalled flower, in the PCA analysis (figure 4.20) the fragments (SCV-V14 and PMF0510) appear related with fragments from a group defined as Group II_{MB} that will be discussed further ahead. Fragment SCV-V335 is not related to any of the other four-petalled flower fragments. Since objects with this kind of mould-blown decoration appear throughout the Portuguese territories, it is not expected that all of the fragments will have the same chemical composition, or that all fragments came from the same production centre. Given that fragments SCV-V14 and PMF0510 have a very close and related composition (figure 4.20 and figure 4.21) the hypothesis that these fragments came from the same production centre can be put forward. On the other hand, fragment SCV-V335 must have been produced in a different production centre that employed different raw materials in the glass batch.

Analysing now the chemical composition of these objects, more specifically the alumina and iron oxide contents to study the silica origins (figure 4.21), one can observe a wide diversity among objects. There are only four objects, all from different sets, identified as having less than 2 wt% of alumina. The differences in the chemical compositions of these fragments, invalidates the possibility of them sharing the same production centre, or even having the same silica source. With between 2 and 3 wt% contents of alumina, one can observe mainly fragments from the SJT set, two fragments from the PMF set, and two fragments from the SCV set. The great majority of fragments are distributed between high and very high alumina contents. It is important to mention that the fragments with very high alumina contents are all from the SCV set, and that these fragments show a positive correlation between alumina and iron oxide. Resorting to PCA, it is observed in figure 4.20 that these fragments form a very cohesive cluster, meaning that they have the same origin, or in other words, were made using the same silica source. See Table XIII.3 with the composition of the fragments organised by groups in *Appendix XIII*, *Appendices Part I*. These fragments – SCV-V51, SCV-V79, SCV-V95, SCV-V154, SCV-V182, SCV-V336, SCV-V380 and SCV-V396 – form Group I_{MB}.

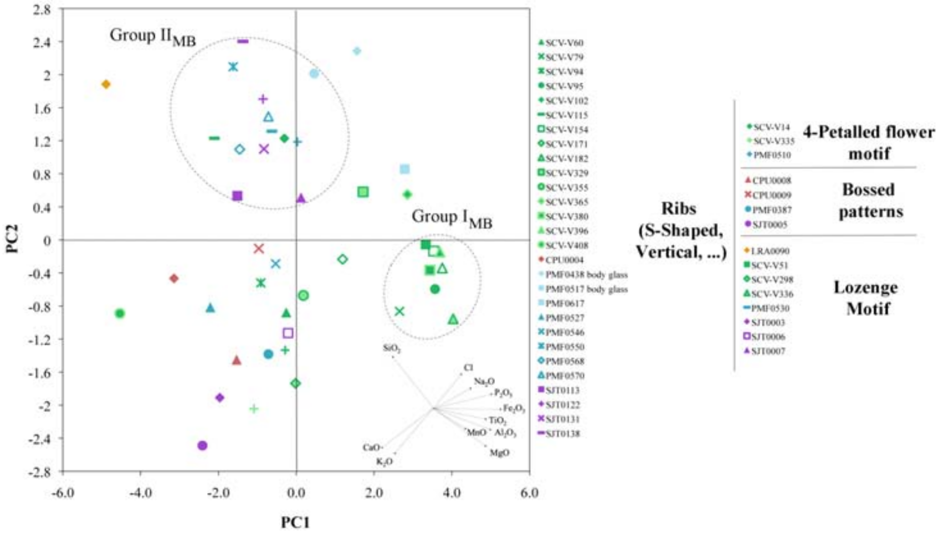


Fig. 4.20: Scores and loadings on the 1st and 2nd principal components, explaining circa 61% of the total variance, for the mould blown decorated objects.

When analysing the contents of K_2O and CaO in figure 4.22, it is observed that the majority of fragments from Group I_{MB} are still in a very close cluster, showing and confirming the relation between these fragments. It is interesting to note that fragment PMF0617, dated to the 14th to the 15th century, appears to be related to certain fragments from the SCV set (SCV-V171 and SCV-V336) not only in the PCA analysis, but also on the binary chart relating the alumina content with the iron oxide (figure 4.21), with an alumina content of almost 5 wt%. On the binary chart of K_2O *versus* CaO (figure 4.22), this fragment from the PMF set appears related to the other PMF fragments dated between the 14th and the 15th centuries, but also to fragments SCV-V171 and SCV-V336. From this, one can infer that these fragments came from the same production centre that used the same source of raw materials and recipes over the centuries, or that these fragments came from different production centres that used the same source of raw materials and recipes over the centuries. The first hypothesis however seems the more plausible.

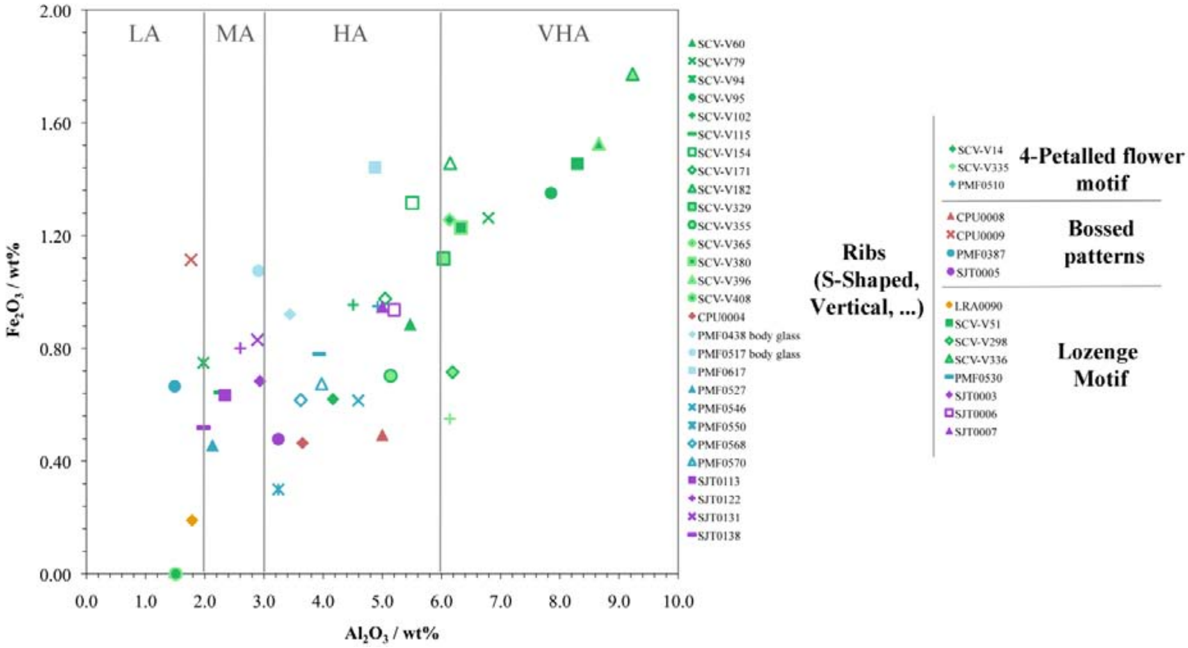


Fig. 4.21: Binary plot of Al_2O_3 *vs*. Fe_2O_3, in weight percent of oxides and determined by means of μ-PIXE for the mould blown decorated objects.

In the chart represented in figure 4.22, a good correlation between K_2O and CaO is observed, what means that both oxides where introduced into the batch with the alkali source. On the PCA analysis, both oxides appear in the same chart quadrant confirming they are positively correlated.

If one looks now to the bossed beakers, it is possible to see in the PCA analysis that fragment PMF0387 appears related to fragments SCV-V60, SCV-V102, SCV-V298, SCV-V355, CPU0008 and SJT0006. Analysing the chart of alumina against iron oxide, one can see that the two fragments from the CPU set, CPU0008 and CPU0009, are in the high alumina group and low alumina group, respectively. Fragment PMF0387 is in the low alumina group, however it has a lower iron content (0.67 wt%) comparing with CPU0009 with an iron content of 1.11 wt%, thus invalidating the possibility that these three fragments are related in terms of the raw materials employed. In the PCA analysis, however, fragment PMF0387 appears related to fragment CPU0008. Fragment CPU0009 appears related to fragments SCV-V94 and PMF0546. The fragment from the PMF set, as well as CPU0009, due its alumina content, can be further considered for comparison with other European production centres. Fragment CPU0008, due to its high alumina content cannot be related with any coeval European production centre. In figure 4.22, where K_2O and CaO are related, the fragments from CPU set appear positively correlated; on the other hand, fragment PMF0387 has one of the highest potassium oxide contents of the mould blown decorated vessels. Comparing the composition of fragment PMF0387 with the chemical composition of Antwerp glass defined as mixed alkali (Table 4.4), it is possible to say that the oxide content in general are very alike with the exception of MgO and MnO that present a higher value on the PMF fragment. CPU0009 is not compatible with the mixed alkali composition from Antwerp because it as a lower K_2O content and a higher Na_2O content, therefore is not possible to designate this glass as a mixed alkali, such as the one designated for Antwerp glass.

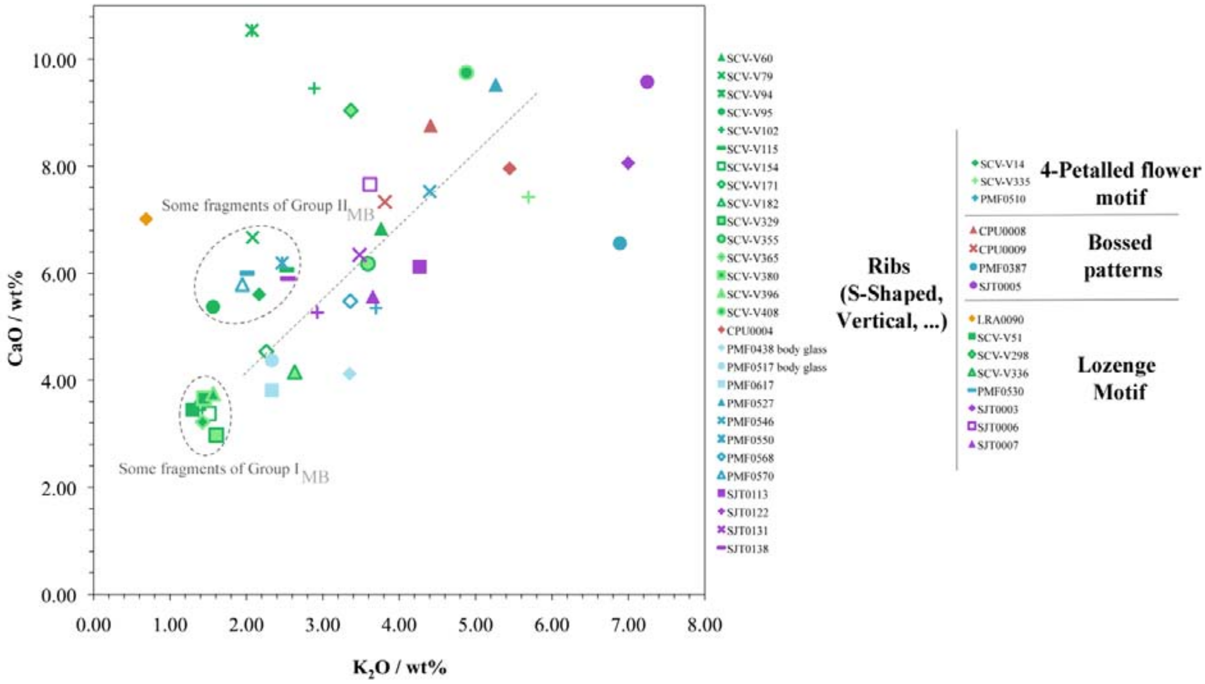


Fig. 4.22: Binary plot of K_2O *vs*. CaO, in weight percent of oxides and determined by means of μ-PIXE for the mould blown decorated objects.

Analysing the PCA chart (figure 4.20), another close cluster is identified – Group II_{MB} – that relates fragments PMF0510, PMF0530, PMF0550, PMF0568, PMF0570, SCV-V14, SCV-V115, SJT0007, SJT0122, SJT0131 and SJT0138. The fragments from the PMF assemblage were already identified as a cluster when the *façon-de-Venise* fragments were analysed. Regarding the chart of alumina *versus* iron oxide, the fragments from this group are spread across the medium and high alumina chart zones. The fragments SJT0122, SJT0131 and SJT0138 from SJT set, plus fragment SCV-V115 from the SCV set are in the medium alumina zone and the fragments from PMF set plus SCV-V14 and SJT0007 are in the high alumina zone. Looking at chart of K_2O *versus* CaO, certain fragments of Group II_{MB} are very close together (SCV-V14, SCV-V115, SJT0138, PMF0530, PMF0550 and PMF0570) and the remaining fragments (SJT0007, SJT0113, SJT0122, SJT0131, PMF0510 and PMF0568) are part of the positive correlated trend line between these two oxides. However all the fragments referred to from Group II_{MB}

are very close to each other. It is important to point out again that the PMF fragments mentioned in this section have already been dealt with, and their composition discussed in the *façon-de-Venise* section. It was concluded back then, that these fragments could be of local provenance and from a new *façon-de-Venise* production centre. The fact that other fragments with mould blown decorations from several assemblages relate in terms of composition with these *façon-de-Venise* fragments, emphasises the hypothesis of a new *façon-de-Venise* production centre, and raises the possibility that this centre did not only produce *façon-de-Venise* objects, but also other varieties of glass objects such as mould blown ones, differently coloured.

Analysing fragments PMF0438 and PMF0517 (both dated between 14th and 15th centuries), the PCA chart shows them to be related. The chemical composition of these fragments was discussed in the *façon de Venise* section; as it was stated in this chapter, due to the different dating of these fragments, is was expected that their chemical composition would be different. However, in the case of fragment PMF0617, also dated to between the 14th and 15th centuries, it does not relate to the other coeval fragments in the PCA analysis, showing a closer relation with fragments SCV-V365 and SCV-V329 from the SCV set. Looking at the chemical composition of these three fragments, it is observed that all the oxides, major and minor, have very close values, which means that these objects were made from geographically related raw materials.

Continuing the analysis of the PCA chart, another small group is identified, in which the fragments CPU0009, SCV-V94 and PMF0546 are related. Observing their chemical composition, in terms of alumina and iron oxide contents (figure 4.21), only two fragments can be related, CPU0009 and SCV-V94. Fragment PMF0546 is in the high alumina content zone. From this information one can conclude that these fragments cannot be related in terms of their silica source, however, when the MgO, K_2O, CaO, P_2O_5 and chlorine contents are compared, it becomes clear that these fragments are closely related in terms of the alkaline source employed to produce the glass. In other words, the plant ashes employed in the batch of these three glass fragments are closely related in geographical terms.

Regarding fragment SCV-V408, this is another example that does not relate with any of the other fragments. The chemical composition of this fragment has already been discussed in the *façon-de-Venise* section.

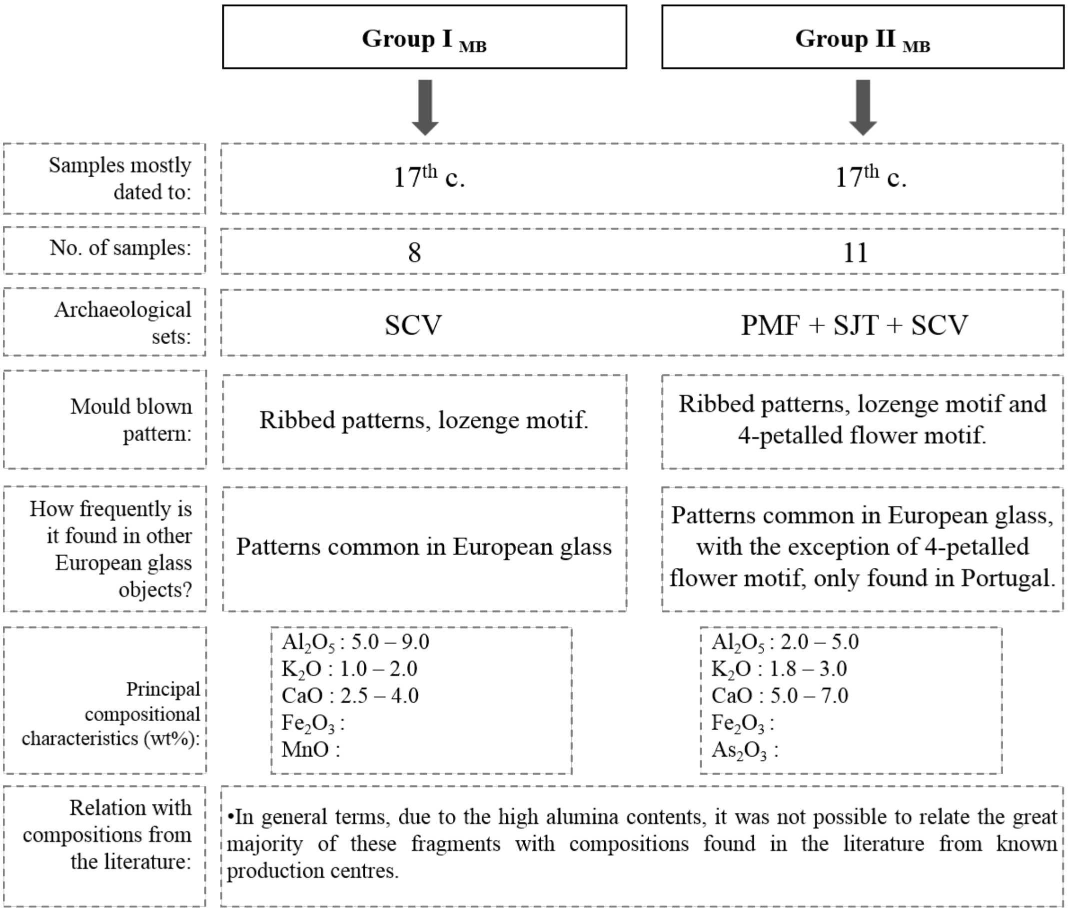
Dealing now with fragment LRA0090, it does not relate to any of the other fragments from any of the assemblages. This fragment dated from the 17th century, has a very low contents of manganese and potassium oxides, which makes it difficult to relate them to the use of plant ashes as an alkali source. Because of its dating, one cannot consider the possibility that this fragment was made using the Leblanc process, which was only created at the end of the 18th century by Nicholas Leblanc. This process consisted in the production of industrial soda using marine salt (Navarro, 2003, p.43). For this reason, the hypothesis is raised that this fragment was made using highly purified plant ashes, resulting in the reduced amounts of manganese and potassium oxides. The other hypothesis that one has to consider is that due to the complex archaeological stratigraphy of the site where this fragment was recovered, an erroneous dating of the fragment was made, and in that case the Leblanc process can be proposed. In terms of shape, due to the small size of the fragment it is not possible to draw other conclusions; however, the lip of the neck of the flak suggests the kind used in wine bottles from the end of the 18th century/ beginning of the 19th century. This lip seems a continuation of the neck but thicker, with no string applied (see picture in Catalogue II, *Appendix III, Appendices Part I*).

The last group of fragments suggested in the PCA analysis, relates fragments from four of the assemblages referred to above in the section of the mould blown decorated objects. In this group the following fragments are associated: SCV-V60, SCV-V102, SCV-V298, SCV-V335 and SCV-V355 from the SCV set, SJT0003, SJT0005 and SJT0006 from the SJT set, PMF0387 from the PMF set and CPU0008 from the CPU set. When analysing the binary charts, it does not seem that these fragments are closely related among themselves. In terms of alumina *versus* iron oxide, if one excludes fragments PMF0387 and CPU0008, both belonging to beakers with bossed decoration that have low alumina content, the remaining fragments referred to above have high and very high alumina contents. These bossed decorated beakers can be distinguished in the Al_2O_3 against Fe_2O_3 chart by their iron oxide contents, since the fragment PMF0387 has a content of about 0.60 wt% of this oxide, and fragment CPU0008 has a content of about 1.10 wt% of the same oxide. Observing the relation of these fragments in the binary chart of K_2O *versus* CaO, the two bossed beakers are not related, in that they have a different ratio between these two oxides. PMF0387 has almost the same content of both oxides (around 6.50 wt%) and fragment CPU0008 has half the content of K_2O (around 4 wt%) relative to the CaO (around 8 wt%). The other fragments, in relation to the K_2O *versus* CaO chart, show some positive correlation. In the case of fragments SCV-V60, SCV-V335, SCV-V355, SJT0006 and CPU0008, these are closer to the trend line marked in figure 4.21. In relation to the other fragments, one can say that these are also part of the trend line with the apparent exception of fragments SJT0003, SJT0005 and PMF0387 that are completely apart from this positive correlation. Finally, it was decided not to consider these fragments a cohesive group since no consistent relation was found between their compositions.

In conclusion, in reference to the mould blown decorated objects, once again the glass objects with high and very high alumina levels are the ones that can be considered to be locally made. In other words, the glass objects that because of the composition of their raw materials do not find parallels in any other production centre found in the literature could therefore considered to be of possible Portuguese production. In terms of the types of motifs decorating the objects, it is possible to find some relations between the objects with ribs. It was also evident that among all the objects with mould blown decorations, the patterns with ribs (vertical ribs, S-shaped ribs, and so on) are by far the most common.

Considering the objects with four-petalled flowers enclosed in lozenges, no obvious relation was found between them, and these objects appear mixed among the other decorative patterns along the charts. The same situation was verified for the objects decorated with bossed patterns and lozenge motif. This seems to indicate that there was no glass production centre that applied only one type of decoration in the objects. The chemical relation between these objects show exactly otherwise, meaning that the production centre that made for instance, the objects from Group I_{MB}, used different decorative moulds in their objects.

In order to facilitate the understanding of the results obtained for the mould blown decorated objects, a scheme was made and it is presented in figure 4.23.



	Group I_{MB}	**Group II_{MB}**
Samples mostly dated to:	17^{th} c.	17^{th} c.
No. of samples:	8	11
Archaeological sets:	SCV	PMF + SJT + SCV
Mould blown pattern:	Ribbed patterns, lozenge motif.	Ribbed patterns, lozenge motif and 4-petalled flower motif.
How frequently is it found in other European glass objects?	Patterns common in European glass	Patterns common in European glass, with the exception of 4-petalled flower motif, only found in Portugal.
Principal compositional characteristics (wt%):	Al_2O_5 : 5.0 – 9.0 K_2O : 1.0 – 2.0 CaO : 2.5 – 4.0 Fe_2O_3 : MnO :	Al_2O_5 : 2.0 – 5.0 K_2O : 1.8 – 3.0 CaO : 5.0 – 7.0 Fe_2O_3 : As_2O_3 :
Relation with compositions from the literature:	•In general terms, due to the high alumina contents, it was not possible to relate the great majority of these fragments with compositions found in the literature from known production centres.	

Fig. 4.23: Scheme summarising the main characteristics (stylistic and compositional) of the two groups of mould blown decorated objects.

4.1.5 Gilded objects

Only three objects were analysed with gilded decoration. Because of the small number of samples with this decorative feature, no statistical method was applied to their study.

One belongs to the SCV set (SCV-V194) and is a goblet in dark grey glass with a mould-blown lion head on the stem. It has a typical attachment of the gold leaf, where the leaf is picked up from the marver by a glass blob, which is then followed by the blowing of the glass, creating the effect seen in fragment SCV-V194 with the gold leaf broken and spread onto the glass surface. The chemical composition of the glass of this fragment has already been discussed in the Venetian and *Façon-de-Venise* glass sub-chapter (sub-chapter 4.1.2), where it was determined that mainly because of the too high alumina content, it was not possible to attribute a provenance (from a known *façon-de-Venise* production centre) to this fragment.

The other fragment with gilded decoration belongs to the SJT (SJT0105) set. In this case, only a small remnant of gold decoration attached to the glass is seen (maybe gold-leaf or gold paint applied cold?). For this reason no design or pattern can be identified in the applied gold. The glass from this fragment was previously discussed in the Venetian and *Façon-de-Venise* glass sub-chapter, and it was identified as belonging to a larger group of *façon-de-Venise* fragments that related objects from the PMF set with objects from the SJT set. Once again, no provenance was attributed to this fragment that belongs to Group $\mathrm{II}_{\mathrm{fdV}}$ identified in figure 4.8, which relates *façon-de-Venise* objects from the two sets.

The last object that presents gilded decoration belongs to the CPU assemblage, and it is a globular flask (CPU0032) [4]. The flask is decorated with a gilded plant motif, with foliate branches beginning at the base of the flask and rising vertically up the body, following the direction of the ribbing. At the top of the vase, the same plant pattern runs horizontally around the base of the neck. Some fragments of the sides of the flask show the foliate branches crossing the ribbing in an almost perpendicular way, suggesting that at some moment the plant decoration should begin spiralling around the body of the flask. Among the leaves, three birds complete the scene. Despite the moderate weathering of the glass, it was established that there was strong adhesion of the gold to the glass surface (Coutinho *et al.,* 2016).

The gilded decoration and its production technique were studied and investigated by means of optical microscopy (MO), by energy-dispersive micro X-ray fluorescence spectroscopy (μ-EDXRF) to perform *in situ* qualitative analysis of the glass (surface and bulk) and gilded decoration, by Scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS) and by LA-ICP-MS in order to determine the composition of the gold layer. The analytical conditions are described elsewhere (Coutinho *et al.,* 2016).

The glass of the gilded flask, with ca. 4 wt% of Al_2O_3, can be classified as a high alumina glass (3 - 6 wt%). Such high alumina content excludes a Venetian origin for the glass, the latter usually characterised by alumina content below 2 wt%. As we saw above, among *façon-de-Venise* glass produced in different

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[4] A more exhaustive study of this object is accepted for publication in the *Journal of Archaeological Science* under the title: “Gilding on glass: new evidence from a 17th century flask found in Portugal” (Coutinho *et al.,* 2016c).

European centres high alumina compositions are rare, the exception being a group of glass from Tuscany, Italy, analysed by Cagno *et al.* (2010). However, the content of Na_2O, SiO_2, K_2O and CaO of the Tuscan glass is not comparable to that of the Portuguese flask. The glass composition, due to a high alumina content (ca. 4 wt%), is comparable to other contemporaneous glass objects also found in Coimbra and distinct from the typical Venetian and *façon-de-Venise* compositions. In addition, the flask shape is quite common among archaeological 17th century glass found in Portugal. It was possible to quantify small amounts of barium, lead, cobalt, arsenic and tin oxides that were probably introduced into the batch due to the recycling of the glass cullet.

In terms of the gilded decoration, the analyses showed that lead is present in a higher proportion in the gilded regions in comparison to the undecorated surface or bulk glass. In fact, in the twelve fragments analysed by μ-EDXRF, an intense lead peak was always observed in the spectra from the gilded areas (figure 4.24), whereas in the undecorated surface (both internal and external sides) lead was barely detected. This fact suggested the use of a base mordant prior to the application of the gold.

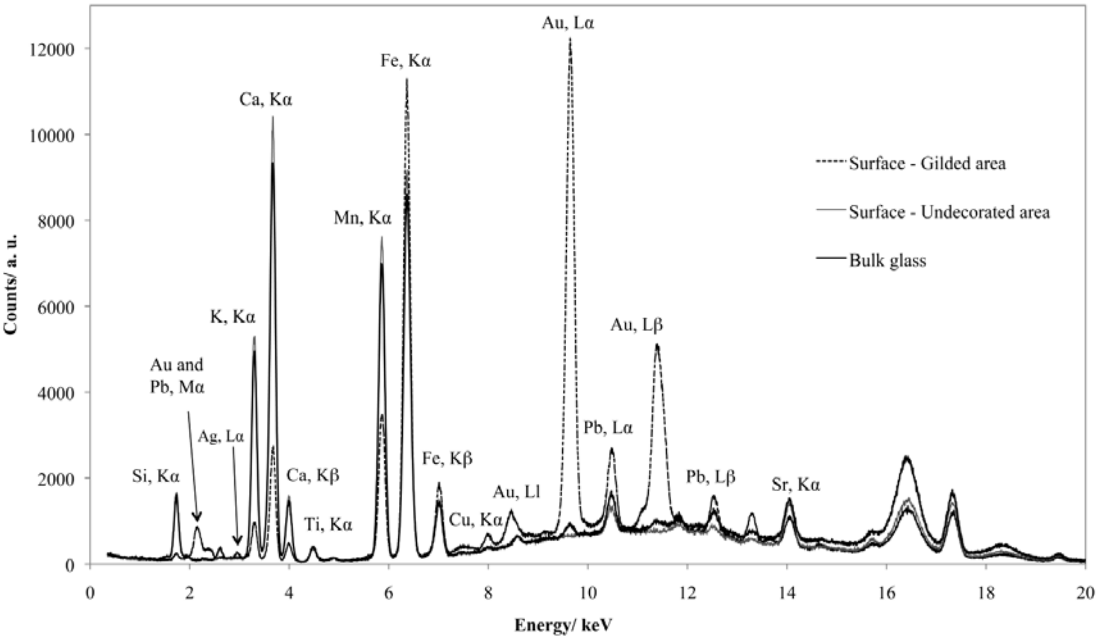


Fig. 4.24: μ-EDXRF spectra from a gilded area in comparison with one from undecorated surface and other from bulk glass.

As one can observe in figure 4.25, under a very thin layer of gold appears another layer with an orange coloration and that probably is due to the presence of a lead-base mordant. Electron microscope images suggest that gold was applied as gold leaf, as folds and wrinkles are visible in some of the images (figure 4.26). In the elemental mapping (figure 4.26 b), lead appears clearly related to the gilding surface, suggesting once again the use of a mordant to promote better adhesion of the gold to the glass surface of the flask.

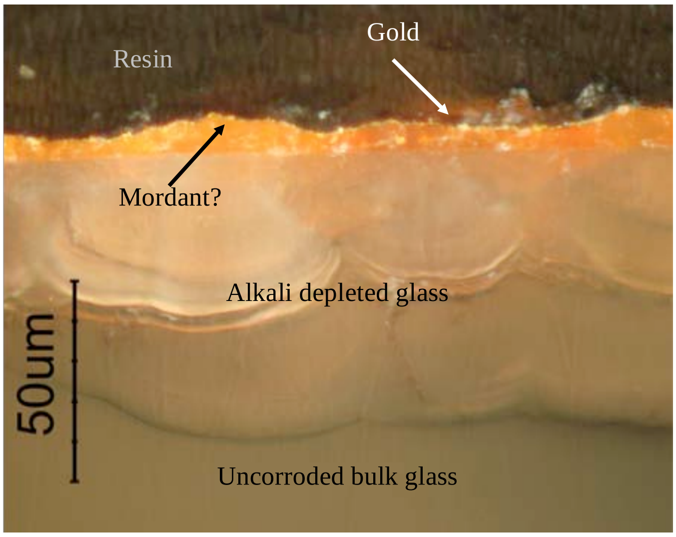
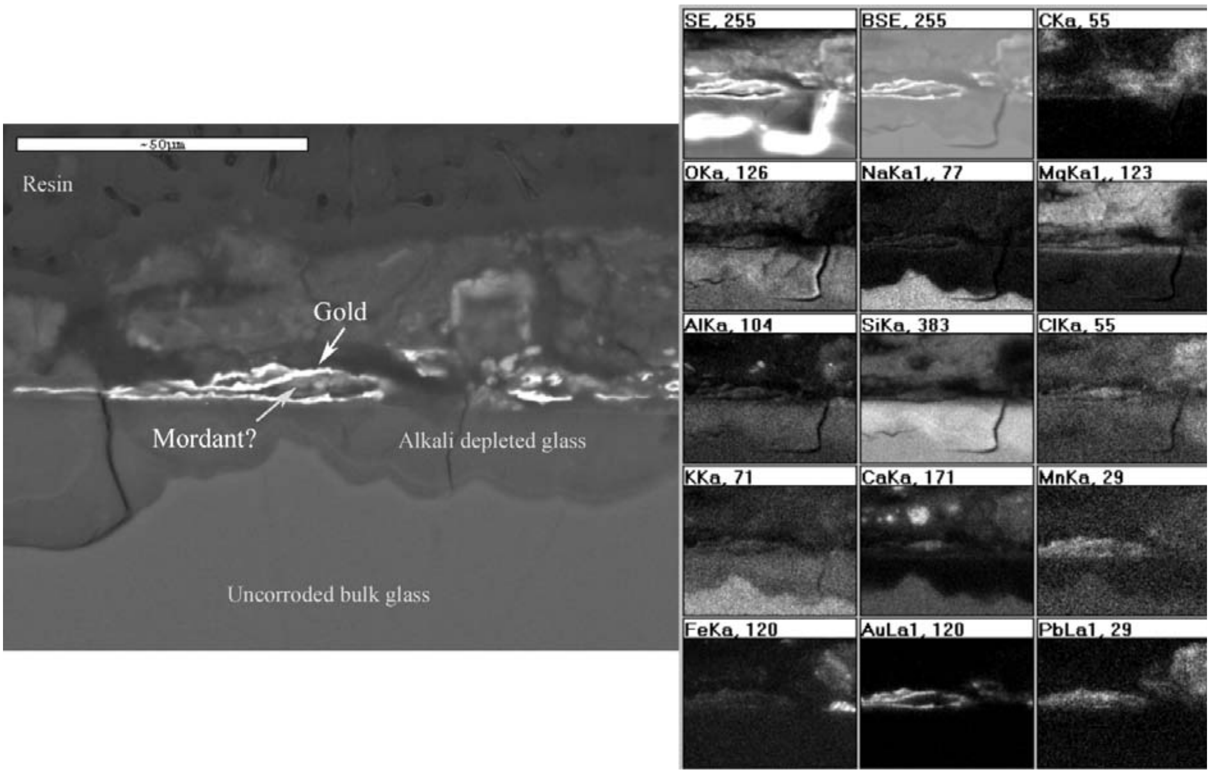


Fig. 4.25: Optical microscope observation of a gilded glass sample from the flask CPU0032 in cross-section. The image magnified 50x, was observed under polarized light in order to see the gold leaf/ glass interface.



(a) **(b)**

Fig. 4.26: SEM (BSE) image of a cross-section of **(a)** a gilded area showing folds and wrinkles in the gold rich region and **(b)** its respective elemental mapping.

The results showed that a lead-based mordant was used to attach the gold leaf to the glass, and the later re-heating, required to permanently fix the gold to glass, was probably carried out in a muffle, and not in the furnace, as no second pontil mark is visible on the flask. With the use of a lead mordant, the object is re-heated at a lower temperature, below the glass softening point. The lead will act as a flux favouring a local softening of the glass surface and therefore no distortion occurs.

This gilding technique is referred to in ancient recipes mentioning lead compounds in the formulation of the mordant but as far as we know it has never been observed in historical glass objects. Moreover, a gilding technique using a lead-based mordant is currently used in Murano, where the tradition of enamelling and gilding on glass vessels flourished from the middle of the 15th century onward.

The composition of the gold leaf was measured by LA-ICP-MS analysis (cross section sample), which showed that the gold used in the decorative patterns was obtained from a triple Au-Ag-Cu alloy. The content of Au in the alloy (between 92.44% and 95.33%) allowed one to classify it as having between 22 and 23 carat, and being ca. 1μm in thickness. According to Darque-Ceretti *et al.* (2011) and Gialanella *et al.* (2013), the higher the gold percentage in an alloy, the thinner the gold leaf obtained. The real copper concentration in the gold leaf may be lower than the measured content, as it may have come from the lead mordant, also present in the sampled area.

The absence of lead in the undecorated surface may indicate that this lead mordant was applied as a paint and used to define the desired motifs. Gold leaf was then applied, becoming attached only to the glass surface areas with the mordant. The excess gold was removed and details, such as the birds' eyes, were carried out using a *sgraffito* technique. This technique was widely used in the Iberian Peninsula (and out of fashion on Northern Europe) during the 17th and 18th centuries to define shapes into the gold leaf (Serck-Dewaide *et al.*, 2004). Finally, the flask was re-heated in a muffle at a low temperature in order to soften the glass surface and, thus, achieving a strong adhesion of the gold leaf to the glass.

The *Ars Vitraria Experimentalis* treatise (Kunckel, 1679) for example, mentions cerussite ($PbCO_3$), lead glass, and minium (Pb_3O_4). Also in this treatise, re-heating of the gilded glass in a muffle is mentioned (Kunckel, 1679, chapters XI - XXVI). An accurate observation under stereoscopic microscope excluded the existence of a second pontil mark on the flask, which suggests that it was not reheated in the furnace, but instead placed in a muffle to soften the glass beneath the gold leaf, and, in this manner, promoting the adhesion of the gold to the glass. The use of a lead-based mordant allows one the reheating at a lower temperature than the glass substrate softening point, because lead will act as a flux at the glass surface. An eventual distortion of the object during the reheating process in the furnace is thus avoided. Moreover, the gilded decoration, although weathered during the burial processes, does not seem to show the typical fissures caused by the stretching of the glass when it is reheated in the furnace (Gudenrath, 2006).

Gold alloys, having the same combination of elements and purity, have been identified among several contemporaneous gilded objects from all over the Portuguese territory such as Alcobaça, Azores, Coimbra, Aveiro and Tibães (Serck-Dewaide *et al.*, 2004*;* Moura *et al.*, 2004). In Spain also, it was possible to identify this triple alloy with approximately the same contents that were used in Portugal (Serck-Dewaide *et al.*, 2004).

Both the chemical composition and the thickness proved to be in accordance with gold leaf used in the Iberian Peninsula during the 17th and 18th centuries. According to this evidence a local provenance cannot be excluded.

4.2 HLLA glass

The High Lime Low Alkali glass is present in this study in the form of the two archaeological sets from Lisbon. The objects that have this kind of chemical composition are the commonly called wine bottles (see figure 4.27). Eighty-one objects with this chemical composition were analysed, thirty-nine bottles came from the LTR set and forty bottles came from LRA set. From the eighty-one objects, only two did not belong to bottles, and they will be discussed later.

Fig. 4.27: Some examples of bottles found among the LTR and LRA sets. Fragments are chronologically organised.

Prior to discussing the chemical composition of the bottles, it is important to differentiate them by their shapes. In both assemblages it is possible to find square or case bottles (sometimes also called prismatic bottles), globular or onion bottles, and the cylindrical bottles in black glass. The square shaped bottles always occur in green glass with an olive tonality, as opposed to globular and cylindrical bottles, that occur mostly in black glass. The bottles were divided in three categories according to their shapes (see Table 4.3): type A, which corresponds to square bottles (see for example figure 4.27, LTR0040), type B which corresponds to globular or onion bottles (see for example figure 4.27, LRA0012), and type C corresponding to cylindrical bottles (see for example figure 4.27, LRA0059). The bottle anatomy and the nomenclature employed are based on the scheme developed by Jones (1986, p.34) and present in

Appendix XI, (*Appendices Part I*). The bottle evolution according to specific body shapes and features is discussed in *Chapter Two, Part I.* The great majority of bottles from the LRA archaeological remains are type C, whilst bottles from the LTR set is balanced between types A and C. It was also possible to observe that the LRA set is richer in black glass bottles. If one takes both sets into consideration, the majority of the bottles are type C.

Table 4.3: Summary of the types of bottles, their typology, the glass colour and the number of samples per archaeological set.

Types of bottles	***Typology***	***Glass colour***	***Nr. of samples***		***Compositional groups***	
			LTR	***LRA***	***LTR***	***LRA***
Type A	Square or case bottles	Olive green	7	3	Group II_{HLLA}	Group III_{HLLA}
Type B	Globular or onion shape bottles	Olive green or black	2	1	Group II_{HLLA}	Group I_{HLLA}
Type C	Cylindrical bottles	Black	5	20	Group I_{HLLA}	Group I_{HLLA} and IV_{HLLA}
Type B or C	Globular or cylindrical bottles	Olive green or black	13	5	Majority in Group II_{HLLA}	Group I_{HLLA}
Type unknown		Olive green or black	13	10	Majority in Group I_{HLLA}	Group I_{HLLA}

Chemical composition of the analysed bottles [5]

Current knowledge on the chemical composition of bottles, originates mostly from a number of archaeological excavation reports and papers, dealing with bottles from British Isles contexts (Blakelock, 2007; Dungworth, 2005; 2006; 2007; 2010; Dungworth & Mortimer, 2005; Dungworth *et al.* 2006; Farrelly *et al.* 2014; Gartner, 2009 among others). More recently, some insights into the composition of French and Belgium bottles were published (Gratuze & Serra, 2010; Herremans *et al.*, 2012). The results from these analytical investigations are summarised in Table X.2 in *Appendix X, Appendices Part I.*

The main purpose is to try to understand the production localities of the wine bottles circulating in Lisbon. Results obtained for the two Lisbon archaeological bottle sets will be compared with the results presented in Table X.2 in *Appendix X, Appendices Part I.* This will allow one not only to discuss some of the provenances, but also to understand if the raw materials employed and the recipes were similar between production sites. Finally, the trace elements and REE signatures of the Lisbon bottles analysed will be discussed as a way to better verify the relation between bottle fragments.

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[5] The content of this sub-chapter is accepted for publication in the journal *Archaeometry* under the title: “Wine bottles from Lisbon: archaeometric studies of two archaeological sites dated from the 17th to the 19th centuries” (Coutinho *et al.*, n.d., in press).

All the seventy-nine bottles analysed from both sets being studied, were revealed to be of a HLLA glass type (Tables II.2 and III.2 in *Appendices II* and *III*, *Appendices Part I*). Analysing the composition of the bottle fragments, their CaO contents varies between 19 and 28 wt%, their SiO_2 content varies between 55.5 and 70 wt%, the iron oxide between 0.8 and 4 wt%, MgO between 0.3 to 5 wt%, P_2O_5 between 0.2 and 3wt% and MnO varies between 0.1 and 1.8 wt%.

In general, high lime low alkali (HLLA) glass was used to produce utilitarian glass (including window glass) and by the beginning of the 18th century it was almost exclusively used for bottle production. Wine bottles of this type are characterised by their strong green coloration due to the high iron content (Dungworth *et al.*, 2006). This compositional type of glass was developed in Germany and France during the late medieval period and it is believed that it was probably made using the ashes of trees, in particular oak (Dungworth, 2009). HLLA glass was the typical composition used for bottles in the British Isles and continental Europe since its introduction in the 16th century until the 19th century (Dungworth *et al.*, 2006). As far as Portugal is concerned, HLLA glass was identified by Lopes *et. al.* in the analytical study of the glass fragments from the archaeological excavation of the Real Fábrica de Vidros de Coina (Royal Glass Manufactory of Coina) (Lopes *et al.*, 2009).

In the case of bottles, it is generally accepted that no particular care was taken in the choice of raw materials to be employed in their production, and normally the cheapest ones were preferred (Dungworth, 2012). In what regards the choice of alkalis for the HLLA glass during the 17th century, ashes from wood or from forest plants are the raw materials that are assumed to have been employed, mainly because of the contents of sodium, potassium and calcium oxides. From the 18th century onwards, plant ashes were still used in the glassmaking process, however in lower proportions. The leached ashes, rich in calcium, were employed in the batch in higher proportions (Dungworth, 2012). Moreover, components coming from other industrial processes (waste material) were also used in glassmaking, such as slags from iron furnaces (Dungworth, 2012). Kelp was another source of cheap alkali employed in the glass batch of the wine bottles, which presence can be identified through an increased of the strontium content in the glass (Dungworth, 2012). The majority of calcium oxide in these bottles was most probably introduced into the batch through the plant ashes employed and also from the leached ashes (Dungworth, 2012). Plant and wood ashes employed on bottle manufacture started to be washed in order to obtain the *charrées* (the remains after wood ashes had been washed – insoluble residues which are rich in calcium – mentioned in French glass recipe books from the 19th century, mentioning specifically the bottle production[6]) (Gratuze & Serra, 2010).

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[6] See for instance: Jéhan, L.-F. 1851. Encyclopédie Théologique, ou séries de dictionnaires sur toutes les parties de la science religieuse. Tome 46 - Dictionnaire de chimie et de mineralogie. Paris, M. L'Abbé Migne, pp.1547-1548.

In order to assist the interpretation of the data, a chemometric method (Principal Component Analysis – PCA) was applied to the obtained data using the freeware R-statistic under the terms of Free Software Foundation's GNU General Public License. This PCA analysis accounts for circa 55 % of the data analysed (figure 4.28). See Table XIII.4 with the composition of the fragments organised by groups in *Appendix XIII*, *Appendices Part I*.

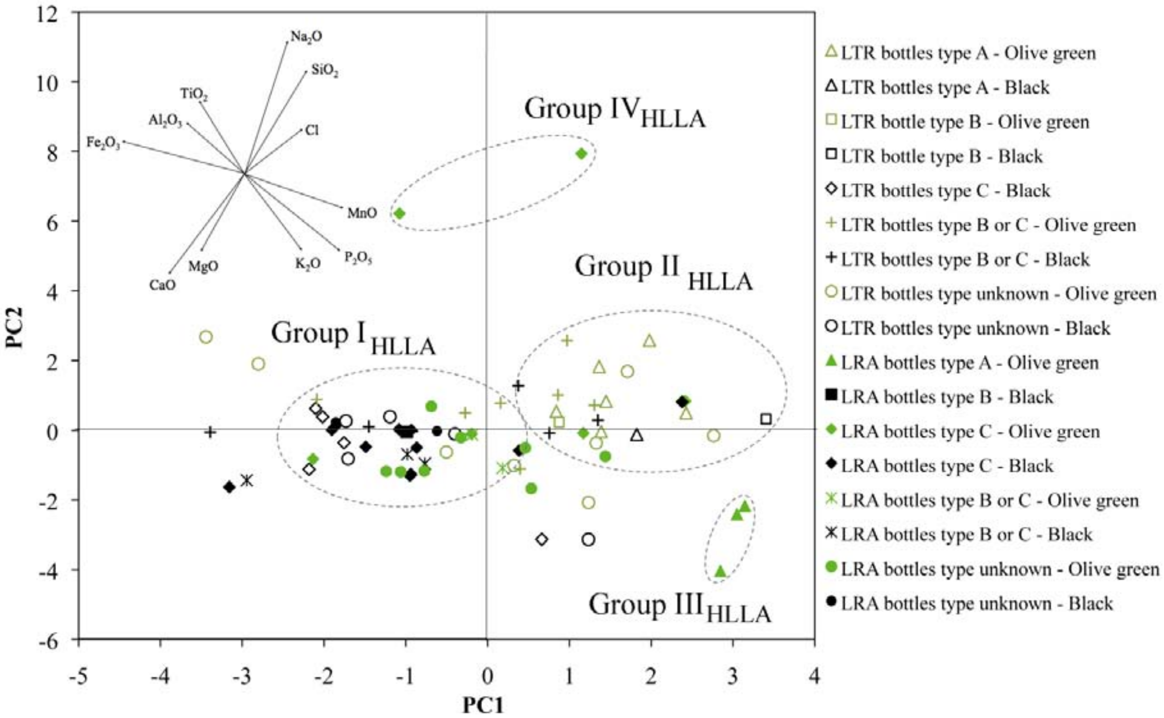
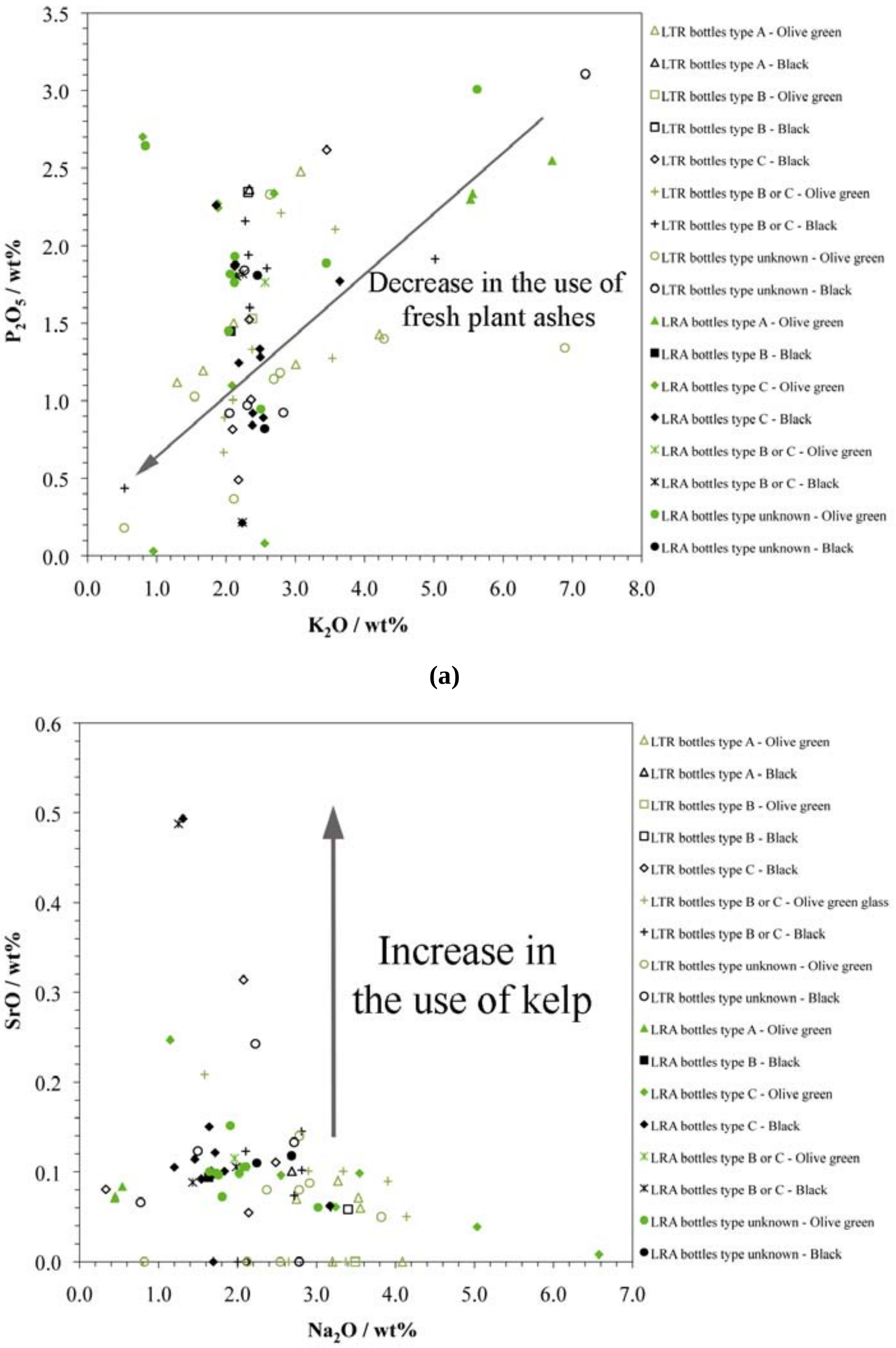


Fig. 4.28: Scores on the 1st and 2nd principal component for both sets explaining ca. 55% of analysed data.

Considering that a numerous range of materials were employed in the production of bottles as sources for the alkali material, it is not possible to disclose all the employed fluxes. For this reason two plots are presented in figure 3 that can shed some light on the type of fluxes employed in the bottles being studied here. The binary plot from figure 4.29 a) relates two important oxides – K_2O against P_2O_5 – both entering the glass through the employed flux. From the analysis to this plot, one can conclude that the bottles following the tendency arrow marked in the chart show a decrease in the employment of fresh plant ashes (Dungworth 2012). In figure 4.29 b, the relation between Na_2O and SrO is shown. Through the sodium contents it is possible to identify the groups defined in the PCA analysis. Analysing the binary plot (figure 4.29 b), with Na_2O contents between 1.0 and 3.0 wt% it is possible to find a close relation between bottles identified as belonging to Group I_{HLLA} (some bottles type C in black-appearing glass and bottles of unknown type in olive green glass both from LRA set and majority of LRA bottles type C in black-appearing glass). Bottles that form Group II_{HLLA} (LTR bottles type A both in olive green and black-appearing glass) are located in the chart area with soda content between 3.0 and 4.0 wt% and strontium oxide content below 0.10 wt%. With the lowest amounts of sodium oxide in their compositions and strontium oxide content below 0.10 wt%, appears Group III_{HLLA} (LRA bottles type A in olive green glass, plus two LTR bottles, one bottle type C in black-appearing glass and other bottle of unknown type in olive green glass). It is worth noting the two LRA bottles type C in olive green glass with Na_2O content higher than 5 wt% that are dated from the 19th century and form Group IV_{HLLA}. According to Dungworth (2012), the increase of sodium content in the glass employed in bottle production in the British Isles is directly connected with the use of synthetic sodium. Nicholas Leblanc developed the process of producing synthetic sodium in the end of the 18th century, where sodium chloride was transformed into sodium carbonate through a series of chemical processes (Navarro, 2003). In Portugal, synthetic sodium was known to be employed in the Marinha Grande Glass Factory (labouring since 1769) during the 19th century (Barros, 1998, p.94), and was possibly employed in other glass factories in the Portuguese territory. The use of this new material can justify the increased Na_2O content found in the two more recent bottles. As far as the strontium oxide is concerned, the increasing of its content shows the use of kelp in the batch, where it is possible to suggest that the two LRA fragments with SrO content around 0.5 wt% were made using only kelp as a flux.

After this brief visualization of the relation between bottle fragments of each set, a more detailed analysis concerning the major, minor and trace elements will be done. Some samples were related in groups and these groups will now be discussed separately.

Analysing the chemical composition of both groups LTR and LRA together and with the use of this PCA approach, the conclusion was reached that the LRA set presents a closer relation between bottle fragments compared with the LTR set. It has then been possible to define the existence of three major clusters, which will be further explained, together with a 4th Group comprising only two LRA bottle type C in olive green glass. The composition of these two last glasses appear separated from all the other fragments and are the ones identified as belonging to a 19th century context. Group I_{HLLA} includes a majority of type C bottles of black-appearing glass from both archaeological sets, and a majority of bottles from an unknown type in black-appearing glass from the LTR set, and in olive green glass from the LRA set. Type A bottles in olive green glass from the LTR set defines the majority of Group II_{HLLA} (plus some bottle samples of different types and two samples from the LRA set), and Group III_{HLLA} includes only three bottles of type A in olive green glass from the LRA set. It is important to mention that these groups present some compositional similarities, with the exception of Group IV_{HLLA} that shows clear differences in terms of chemical composition.



(a)

(b)

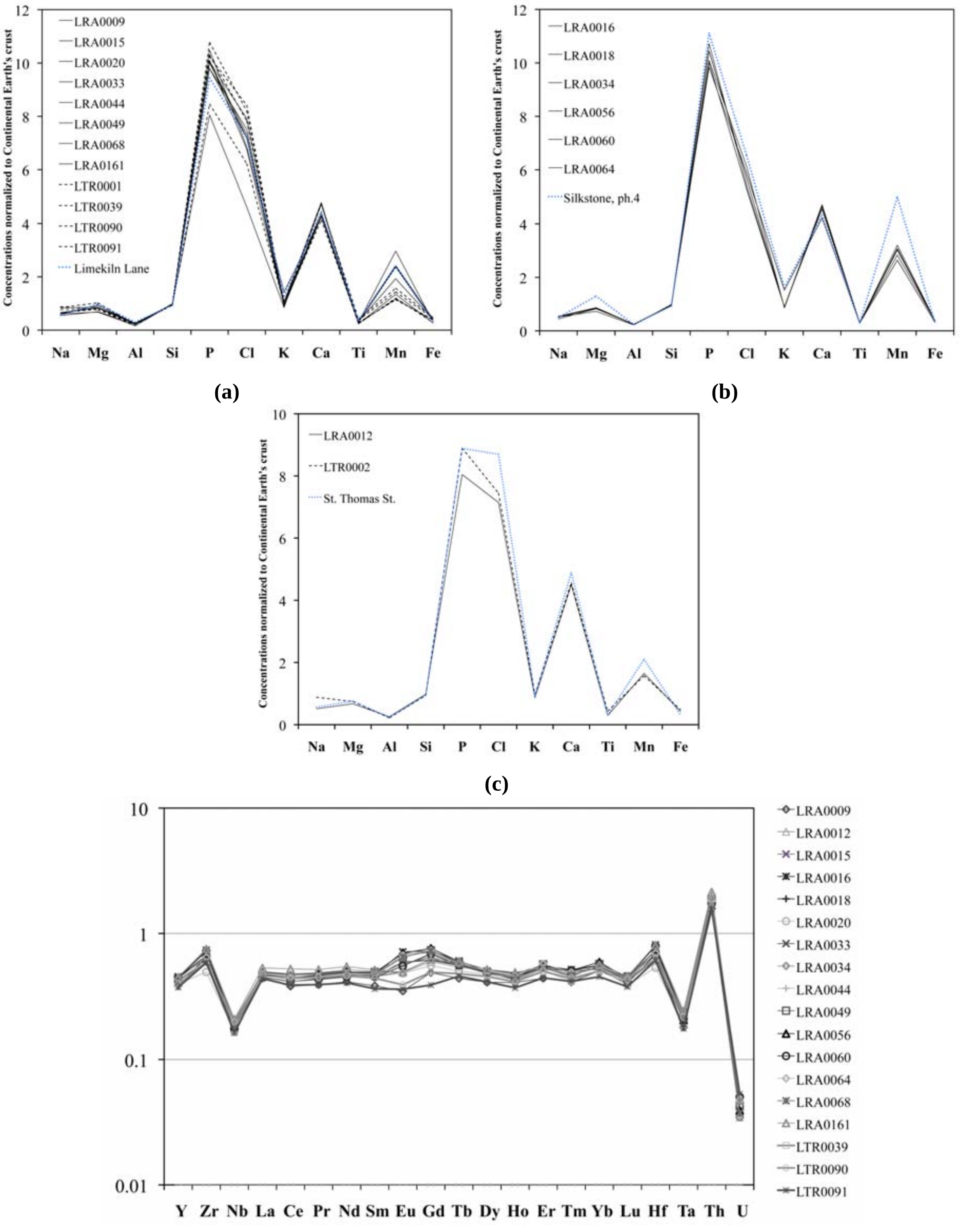
Fig.4.29: Binary plots of a) K_2O *vs.* P_2O_5, with a trend line representing the decrease in the use of fresh plant ashes in the glass batch, and b) Na_2O *vs.* SrO with a trend line representing the increase in the use of kelp in the glass batch. Both plots have the concentrations in weight percent of oxides.

Following the analysis of the differences in the glass chemical composition in association with the types of bottles and glass colouration, it was decided to carry out a survey of the composition of the bottle samples without dividing them into types of bottle, but instead through the PCA groups division. This was done to evaluate more precisely how the samples from both archaeological excavations related between each other. For this reason the major oxides will be considered all together instead of analysing only two oxides at a time like it was done with the binary plots. The results obtained for the bottle fragments will also be compared with data found in the literature that are summarised in Table X.2 in *Appendix X, Appendices Part I*. Concerning the comparison with literature results, only the compositions that are similar to the ones obtained for the bottles under study are presented.

Group I_{HLLA}

In figure 4.30 three different charts with the majority of Group I_{HLLA} samples is represented. These charts have the contents of major elements that constitute the glass normalised to the concentration of the continental earth's crust (Wedepohl, 1995). In this way, the relation between eleven different elements is compared, instead of comparing only two when analysing a binary chart. All the samples defined as belonging to Group I_{HLLA} have a very similar pattern, however three different sub-groups can be seen. For each sub-group it was possible to find a relation with the literature that showed a close similarity in terms of composition. In figure 4.30 a) the represented samples are similar to the glass produced in Limekiln Lane (Bristol) in England. In figure b) the samples from Group I_{HLLA} have a similar composition to HLLA glass produced in the Silkstone glass factory (phase 4) in England. It is important to note that the manganese content in the English factory is considerably higher than that in the samples analysed from Lisbon. This is important because according to Farrelly *et al.* (2014) it is possible to distinguish between HLLA production sites when relating the MnO and P_2O_5 contents from the glass samples. The authors state that Irish HLLA glass dated to the late 16th and early 17th century was poorer in MnO than the one produced in England. At this time, similar raw materials, glass recipes and furnace conditions were being used both in Ireland and England, which resulted in similar glass compositions. However, both the MnO and P_2O_5 contents are higher in English glass.

Plant ashes employed in glass manufacture were gathered locally and it is believed that these compositional differences are due to the region's geology where the plants have grown (Farrelly *et al.*, 2014). It is important to bear in mind that the production from Silkstone phase 4 is dated to the end of the 17th century and 1700; and if one compares the contents of MnO and P_2O_5 with the ones obtained for bottles produced in the British Isles during the 18th century (closer to the chronology of the bottles being analysed here), the values for both these oxides are similar. One can also consider the hypothesis that the bottles from both LTR and LRA archaeological sets that are comparable with Silkstone phase 4 were produced earlier and for this reason match the Silkstone composition from the end of the 17th century.



(a) **(b)**

(c)

(d)

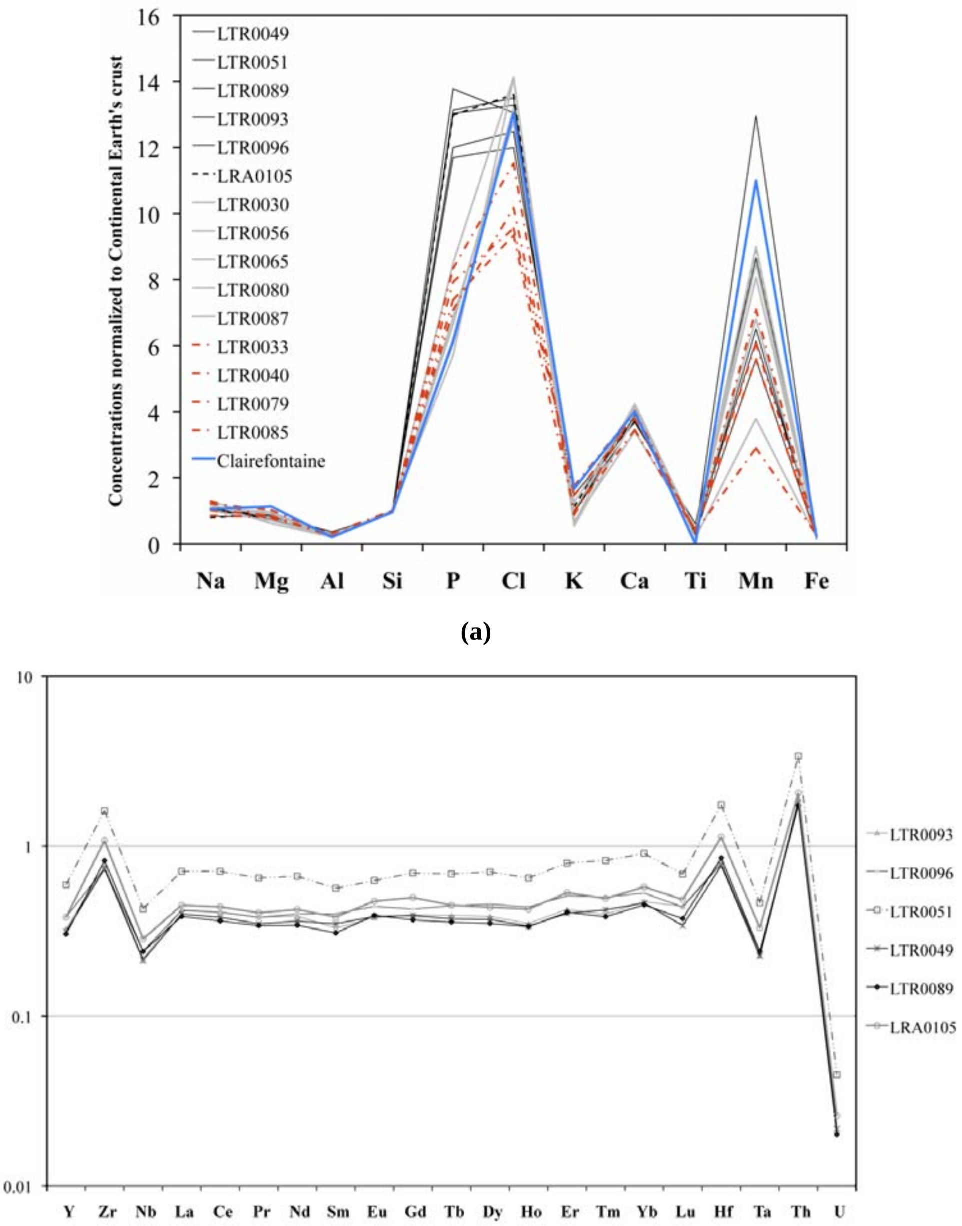
Fig. 4.30: Representation of samples from Group I_{HLLA} divided by identified sub-groups. Charts represented in a), b) and c) are the major elements pattern from Group I_{HLLA} normalised to the concentration of the continental earth's crust (Wedepohl, 1995), plus composition from the literature presented in Table X.2 in *Appendix X, Appendices Part I*. The composition from literature in a) is from Limekiln Lane in England, in b) from Silkstone, phase 4, England, and c) St. Thomas t., Bristol, England. The chart represented in d) is the trace elements and REE pattern of samples from Group I_{HLLA} analysed by LA-ICP-MS and represented in logarithmic scale.

Analysing figure 4.30 b), it is perceptible that the phosphorous content is very similar between the Lisbon samples and the HLLA glass produced in the Silkstone glass factory, however the disparity in manganese content leaves some doubts in terms of attributing these bottles to the production of this English factory.

Finally, in figure 4.30 c), the two samples represented from Group I_{HLLA}, appear closely related to glass produced in St. Thomas Street (Bristol) in England. In figure 4.30 d), the trace elements and REE signature of all samples belonging to Group I_{HLLA} was represented. This chart confirms the close relation between these bottles and the origin of the raw materials employed in their production. It is proposed that this can represent the employment of raw materials from different origins, but still geographically close to one another. This hypothesis is proposed with the idea that for bottle production, the cheapest and most accessible raw materials were the ones to be used, so in the same production centre, glassmakers might use different sources for the same raw material (*e.g.* sand), depending on its availability and price.

Group II_{HLLA}

Bottles from Group II_{HLLA} are represented in figure 4.31. As was determined in the PCA analysis, Group II_{HLLA} is formed mostly by type A bottles in olive green glass from the LTR set together with some bottle samples from different types. Looking at figure 4.31 a), three sub-groups are visible and these were represented with different grey shades. The main differences between the identified sub-groups are the contents of phosphorous oxide and chlorine. The MnO contents vary randomly, not following the trend of the sub-groups. Despite the differences observed, bottles from Group II_{HLLA} are still very similar to each other, being mainly composed by LTR samples, and only one LRA sample can be related to this group. Comparing the composition of Group II_{HLLA} (in particular samples LTR0030, LTR0056, LTR0065, LTR0080 and LTR0087) to compositions discussed in the literature, it was possible to relate this group with a group of bottles found in the Cistercian nunnery in Clairefontaine, Belgium. Before analysing the trace elements and REE signature for some of these bottles, it is important to mention that bottle LTR0051 has a seal from Bad Pyrmonter Wassers. It is assumed that this bottle was imported. This type of seal was found among archaeological remains of the Gawber glasshouse near Barsnley, Yorkshire (Ashurst, 1970, pp.125 fig.38-1). Despite the German origin of this SPA waters, the bottles might have been made elsewhere. Its composition in major oxides fits well with the other fragments from Group II_{HLLA}. In the trace elements and REE chart (4.31 figure b), the similarity between samples is evident. Again, sample LTR0051 has a REE line shape comparable to the other samples, but in different concentrations. This can indicate that very similar raw materials (containing more minerals bearing REE) were employed in the batch but in different proportions.



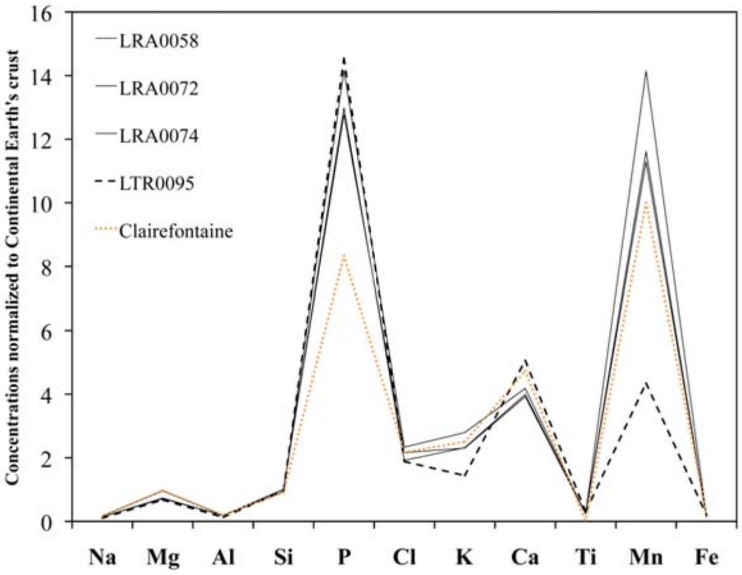
(a)

(b)

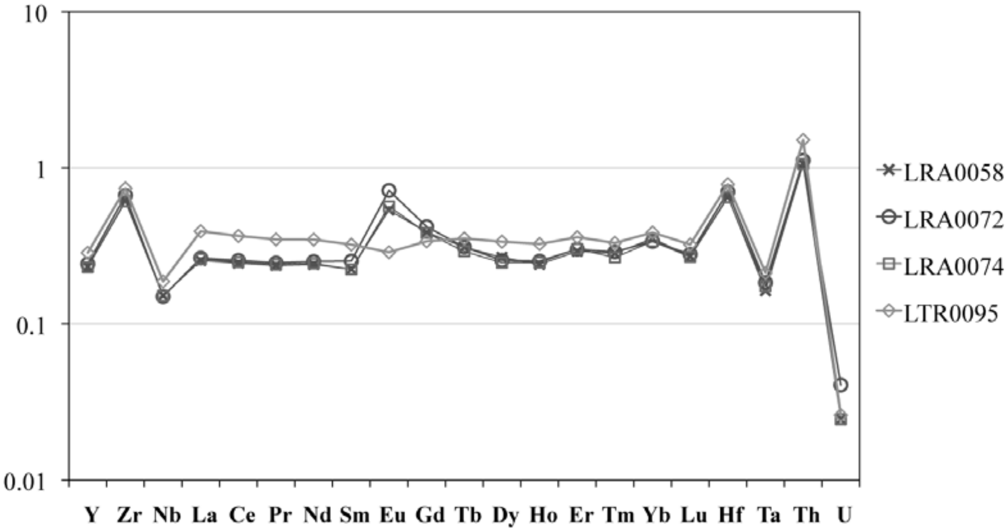
Fig. 4.31: Chart represented in a) is the major elements pattern from Group II$_{HLLA}$ normalised to concentration of the continental earth's crust, with represented compositions from the literature presented in Table X.2 in *Appendix X, Appendices Part I* (Clairefontaine – Cistercian nunnery, Belgium); and (b) trace elements and REE pattern for samples from Group II$_{HLLA}$ analysed by LA-ICP-MS and represented in logarithmic scale.

Group III$_{HLLA}$

In figure 4.32 the composition of the fragments belonging to Group III$_{HLLA}$ is represented. The similarity between LRA fragments is remarkable, since their trace elements and REE pattern is practically coincident. Only in the case of fragments LRA0058 and LRA0074 one can propose that they belong to the same bottle. These bottles were made employing the same raw materials and probably from the same batch.



(a)



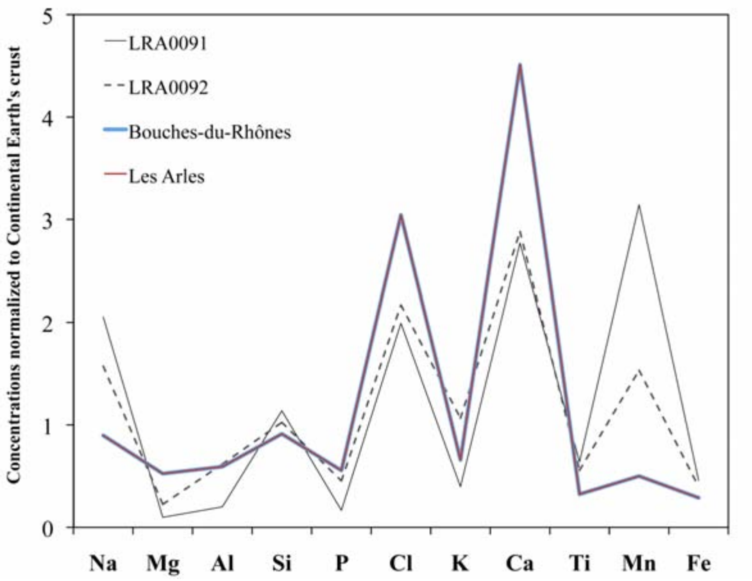
(b)

Fig. 4.32: Chart represented in a) is the major elements pattern from Group III$_{HLLA}$ normalised to concentrations of the continental earth's crust with represented compositions from the literature presented in Table X.2 in *Appendix X, Appendices Part I* (Clairefontaine – Cistercian nunnery, Belgium); and (b) trace elements and REE pattern for samples from Group III$_{HLLA}$ analysed by LA-ICP-MS and represented in logarithmic scale.

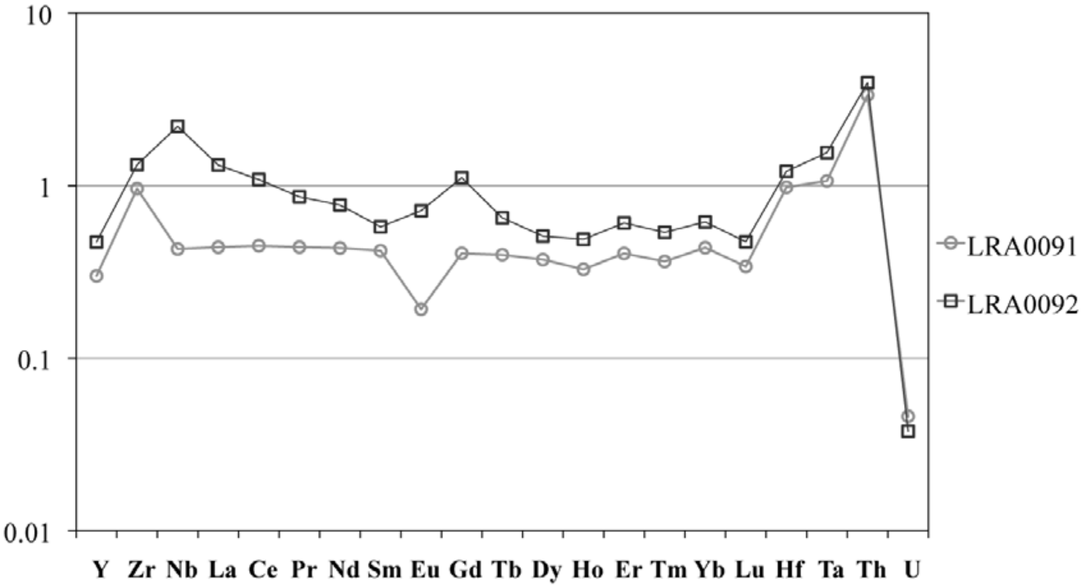
Fragment LTR0095 from LTR set is similar to the other represented fragments; however, once again a huge disparity between manganese contents is observed. This could be an indication that similar recipes and raw materials were employed in the batch, but a different combination of plant ashes was used, causing this disparity on the manganese content. Fragments from this group are comparable with finds from the Belgium Cistercian nunnery in Clairefontaine. Fragment LTR0095 presents a different REE signature mainly due to Nb, Eu and Gd contents. From this one can conclude that fragments LRA0058, LRA0072 and LRA0074, all belonging to square shaped bottles, were made from the same raw materials, and probably from the same batch. Fragment LTR0095 that belongs to a cylindrical bottle, was made with similar raw materials, however it shows some differences that prevents us from attributing this fragment to the same moment of production of the other three fragments. LTR0095 was probably made in a different time than the other three fragments.

Group IV$_{HLLA}$

Finally, in figure 4.33, the composition of Group IV$_{HLLA}$ is represented (only two 19th-century samples from the LRA set).



(a)

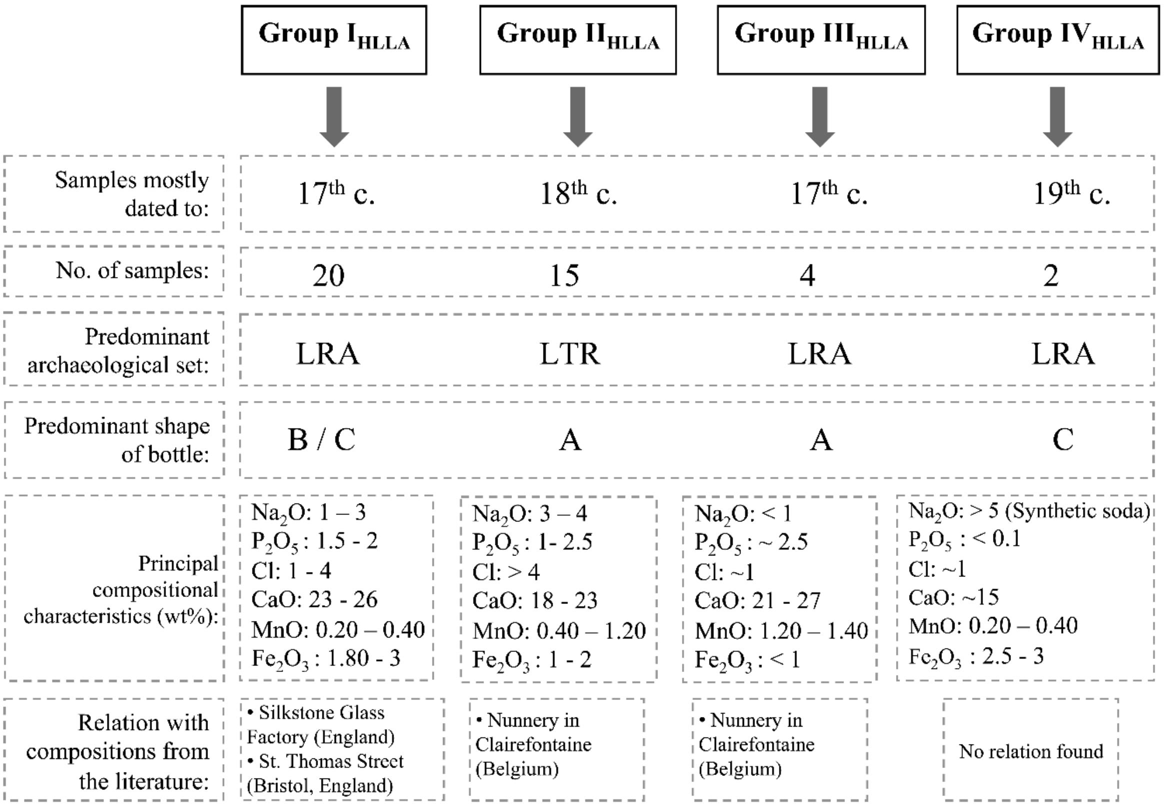


(b)

Fig. 4.33: Chart represented in a) is the major elements pattern from Group IV$_{HLLA}$ normalised to concentration of the continental earth's crust with represented compositions from the literature presented in Table X.2 in *Appendix X, Appendices Part I* (Les Arles and Bouches-du-Rhône, both in France); and (b) REE pattern for samples from Group IV$_{HLLA}$ analysed by LA-ICP-MS and represented in logarithmic scale.

In terms of the major elements, these bottles differ significantly in their MnO contents. It is possible to perceive some similitude between them maybe due to the use of similar recipes. Similar raw materials might have been employed, but probably in different proportions. Their composition was only compared with bottles found in France (both Bouches-du-Rhône and Arles, which coincide perfectly), because it was the only data found in literature for 19th century glass bottles. This comparison was done in order to test if glass from the 19th century was similar regardless its origin. As one can observe, Lisbon bottles have a composition that is close to the French bottles in terms of proportions of measured oxides. This probably reflects the change in the raw materials employed from the 17th /18th centuries to the 19th century. Concerning their trace elements and REE signature, the samples differ from each other (figure 4.33 b). All the gathered information indicates that these bottles were made using raw materials from different provenances, and probably in different production locations.

To summarise the results, a scheme is presented in figure 4.34. The PCA analysis proved to be very helpful when it was necessary to analyse large amounts of data, which made possible the division into groups for the further comparison with data from the literature.



	Group I_{HLLA}	Group II_{HLLA}	Group III_{HLLA}	Group IV_{HLLA}
Samples mostly dated to:	17th c.	18th c.	17th c.	19th c.
No. of samples:	20	15	4	2
Predominant archaeological set:	LRA	LTR	LRA	LRA
Predominant shape of bottle:	B / C	A	A	C
Principal compositional characteristics (wt%):	Na_2O: 1 – 3 P_2O_5 : 1.5 - 2 Cl: 1 - 4 CaO: 23 - 26 MnO: 0.20 – 0.40 Fe_2O_3 : 1.80 - 3	Na_2O: 3 – 4 P_2O_5 : 1- 2.5 Cl: > 4 CaO: 18 - 23 MnO: 0.40 – 1.20 Fe_2O_3 : 1 - 2	Na_2O: < 1 P_2O_5 : ~ 2.5 Cl: ~1 CaO: 21 - 27 MnO: 1.20 – 1.40 Fe_2O_3 : < 1	Na_2O: > 5 (Synthetic soda) P_2O_5 : < 0.1 Cl: ~1 CaO: ~15 MnO: 0.20 – 0.40 Fe_2O_3 : 2.5 - 3
Relation with compositions from the literature:	• Silkstone Glass Factory (England) • St. Thomas Street (Bristol, England)	• Nunnery in Clairefontaine (Belgium)	• Nunnery in Clairefontaine (Belgium)	No relation found

Fig. 4.34: Scheme summarising the main characteristics (stylistic and compositional) of the four groups of bottles.

As it was mentioned in the beginning of this section, two fragments with an HLLA chemical composition where identified as fragments from a different typology than the wine bottles previously discussed. One of the fragments belongs to the CPU assemblage (CPU0033) and was identified as a window glass fragment. The other fragment belongs to the LTR assemblage (LTR0047) and is a fragment of a light green flask.

As it was discussed in this section, HLLA glass composition is strongly connected with the bottle production and its development is attributed to glassmakers from the British Isles. However, the HLLA glass formulation was not exclusively used in the bottle manufacture, and it is possible to find also window glass with this compositional type of glass. In the British Isles, HLLA window glass was produced between 1570 and 1700 and it is related with the arrival of French glassmakers to that territory (Dungworth, 2011, p.33). Ashes of several plants and wood were employed, which justifies the high levels of lime in the glass composition (Dungworth, 2011, p.33). In what regards the Portuguese glass production, window glass was also manufactured in glass production centres like Côvo, Coina and later in Marinha Grande. In written sources, some information about window glass being produced in Lisbon and Abrantes can also be found (Custódio, 2002, p.53, 57). Considering that the majority of these centres also produced glass bottles in HLLA glass, it is not surprising to find window glass with this chemical composition. In what concerns the small flask from the LTR assemblage, it was the only object among all assemblages being studied that was identified with this chemical composition. It is for this reason concluded that HLLA glass was not commonly employed in glass objects besides bottles, at least not in Portuguese territory. It is also necessary to consider the hypothesis that this glass object could be an imported product, and even considering this possibility, one can say that it was also not common the income of objects with an HLLA glass composition. For instance, in France it is known that HLLA glass was used during a considerable period of time to produce quite a few different typologies. If in the beginning, this compositional type was only found in eastern France, from the 16th century onwards some objects were also found in northern areas of France (Barrera & Velde, 1989, p.99).

4.3 Potassium rich glass

Potassium-rich objects were found only in the two sets from Lisbon, LTR and LRA (examples on figure 4.35). This group represents 10% of all analysed fragments, which corresponds to a total of 25 potassium-rich objects of the total of 251 objects studied in this investigation. All fragments from this category and from both sets are made with colourless glass. These glasses are characterised by a K_2O content that varies from 12 to 19 wt%, a CaO content from 5 to 11.5 wt%, and a silica content ranging between 64 and 78 wt%. The presence of arsenic oxide was detected in all the analysed samples. All fragments have an alumina content below 2 wt% with the exception of LTR0019 that presents a very high alumina content of 8 wt%. The presence of P_2O_5 was confirmed for the majority of analysed fragments from this compositional type, always below 0.1 wt%. Dealing now with particular cases, fragment LTR0019 exhibits some engraved decoration with plant motifs (archaeological drawing in *Appendix II, Catalogue I: Archaeological drawings*); it has a potassium rich composition and the highest alumina content of all fragments analysed from this group, which is not common for potassium rich glass from this period. This composition could be the result of the attempt to imitate a glass composition typical of Central Europe. Moreover, the engraved decoration is reminiscent of the contemporary engraved Central European glass (more specifically from Bohemia), in fashion during the 18th century, a fact that was also noticed among other archaeological glass assemblages from Portuguese territory (Ferreira, 2005b). No published parallels were found for the LTR0019 chemical composition, mainly because of the very high alumina content. It is also important to mention the fragment LRA0122 (picture of this fragment in *Appendix III, Catalogue II*) that has a phosphorous oxide content of more than 5 wt%. Comparing this with the potash-rich compositions collected from literature, it is not possible to find such a high phosphorous oxide content, the highest reported value being of 2.2 wt%, which belongs to glass objects from Potsdam, Germany (Smrcek, 1998; see Table X.3 in *Appendix X, Appendices Part I*.

Fig. 4.35: Some potassium rich objects found among the assemblages studied. It is possible to observe mould blown, enamel and engraved decoration.

Bearing in mind the dating of these fragments, it is more or less expected that these objects are of Central European origin or an attempt to imitate the glass made in that region during the 17th and 18th centuries. The presence of Central European glass in Portuguese sets is not surprising, since, as it has been stated before, the crystal glass produced namely in Bohemia was exported to Portugal (Lukás, 1981). However, according to J. Custódio, glass *à la façon de Bohème* was being produced in the *Coina* Glass Factory (Custódio, 2002, p.113). A fragment worth noting is the clear glass object LTR0014 (picture of this fragments in *Appendix II*, *Catalogue I*), which belongs to an octagonal flask decorated with polychrome enamels that was identified as being a typical feature of Central European glass from the 17th to 18th century (see for example: Metropolitan Museum of Art, Accession Number 13.179.70a). Flasks with the same shape and similar decorations were identified among the objects excavated from the *Coina* Glass Factory. One of the flasks with this shape and exactly the same motif design as fragment LTR0014, is present in the Soares dos Reis Museum, attributed to the Marinha Grande Glass Factory, and is shown in figure 2.15 c), *Chapter Two, Part 1*. The difference between the two objects is that the design on fragment LTR0014 is enamelled, and on the object from the Soares dos Reis Museum, the motif was engraved (Custódio, 2002, p.244, 246).

Analysing the PCA charts (figure 4.36), a large cluster is observed – Group I_K – composed of objects from both sets, including fragments LTR0007, LTR0014, LTR0042, LTR0043, LTR0044, LRA0001, LRA0002, LRA0003, LRA0005, LRA0006, LRA0007, LRA0076 and LRA0126. Within this large cluster, it is noticeable that some fragments relate more with each other than others, and these relations will be explored later. Fragment LTR0013 appears in the same quadrant as this cluster, but further away, not being included in this group. One can also group fragments LTR0017, LTR0063 and LTR0064. Finally, fragment LRA0112 appears related to LRA0122 and fragment LRA0123 relates with LRA0134. Fragment LTR0019 was considered and identified as an outlier. The PCA model does not explain its oxides relations. See Table XIII.5 with the composition of the fragments organised by groups in *Appendix XIII, Appendices Part I.*

With regard to the fragments from Group I_K, the objects from the LTR set belong to drinking glasses (LTR0007) or flasks and jars (LTR0014, LTR0042, LTR0043 and LTR0044), whereas it was mentioned previously, LTR0014 has a polychrome enamelled decoration. From the LRA set, all fragments are made of colourless glass, some with enamelled decoration (LRA0001 and LRA0005), some with engraved decoration (LRA0002, LRA0007, LRA0076), some have ribs of mould blown decoration (LRA0126), and some are plain fragments of vessels (LRA0003 and LRA0006).

Object LRA0002 is worth noting. It is probably a jug with one handle, composed by five fragments, all of them presenting floral and geometric engraved motifs. This type of engraving with motifs (floral and geometric) very similar to the ones observed in fragment LRA0002, were also found in objects from an archaeological excavation in Lisbon, and are very well described by Ferreira (2005b). It is concluded by this author that several fragments with this type of decoration were found in at least in five archaeological excavations in Portugal, and since Central European craftsmen were working here, a national provenance could not be discarded (Ferreira, 2005b).

Concerning fragments LTR0017, LTR0063 and LTR0064, the first is an undecorated colourless vessel fragment, and the other two fragments belong to ribbed mould blown beakers. Lopes *et. al.* (unpublished data) identified at least one beaker fragment with the same characteristics, which suggests that these fragments may be of Portuguese production, more specifically produced in the Coina Glass Manufactory (Lopes *et al.* 2009). Furthermore, the shapes of the goblets LTR0063 and LTR0064 are described by J. Custódio as a Coina Glass factory design and production, mostly inspired by the Muranese tradition (Custódio, 2002, p.164).

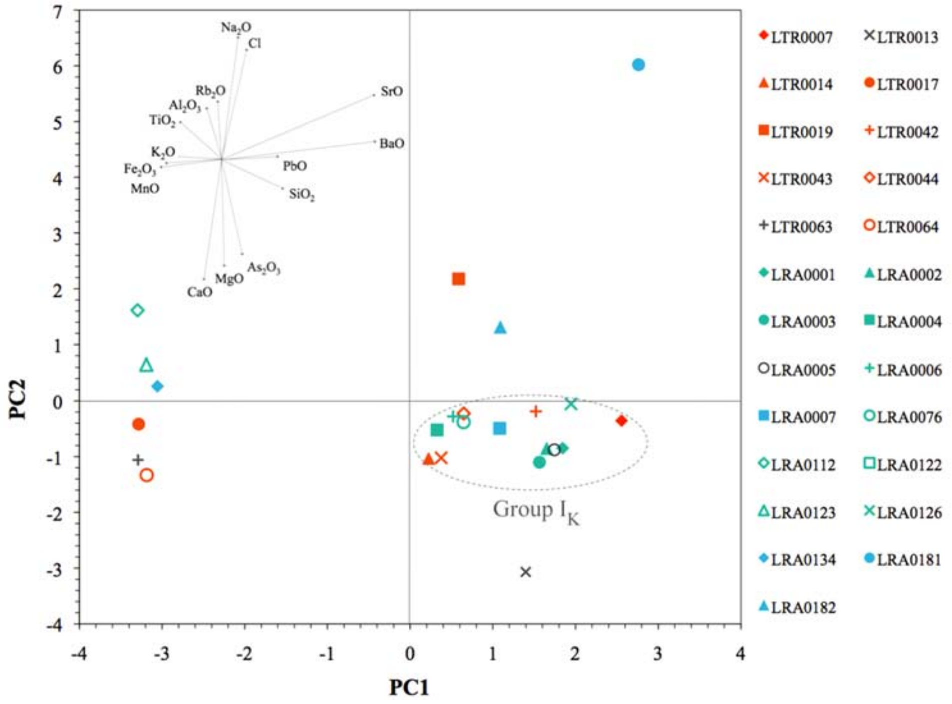


Fig. 4.36: Scores and loadings of the 1^{st} and 2^{nd} principal components, accounting for 50% of the total variance, for the potassium rich glass objects.

With regard to the fragment LRA0112, it is a rim fragment from a vessel with ribbed decoration. Fragment LRA0122 is a handle made of colourless glass, presenting a bluish opalescence that could be a corrosion phenomenon. Fragment LRA0123 also presents engraved decoration and belongs to the rim of a vessel, and finally LRA0134 is a colourless rim fragment from a vessel.

With regard now to the chemical composition of this set, the sources of silica will be discussed. Analysing the chart represented in figure 4.37, the relation between two silica impurities is observed. In this chart, with alumina plotted against iron oxide, the fragments from Group I_K appear all close together with an alumina content below or around 0.40 wt%, and an iron oxide content below 0.15 wt%. In general, all fragments have a low alumina content, which means that a pure silica source, such as quartz pebbles, was employed to make these glass objects. Fragments from Group I_K have particular low contents of these two oxides. This is the basis for the hypothesis that these fragments to have the same source of silica.

As it was explained in *Chapter Two, Part I*, it is known that three distinct types of potassium rich glass were being produced in Central Europe during the 18th century: ordinary glass, white or chalk glass, and crystal glass. These three formulations bear chemical differences on their formulations due to the raw materials employed in their batch. For instance, according to Kunicki-Goldifinger *et al.* (2001), the employment of arsenic in the white and crystal glasses formulas was certain. It is sometimes usual to find lower Ca/K and As/K ratios for crystal glass, mainly as a result of the purification steps and special raw materials that were added to the batch (Kunicki-Goldifinger *et al.*, 2001).

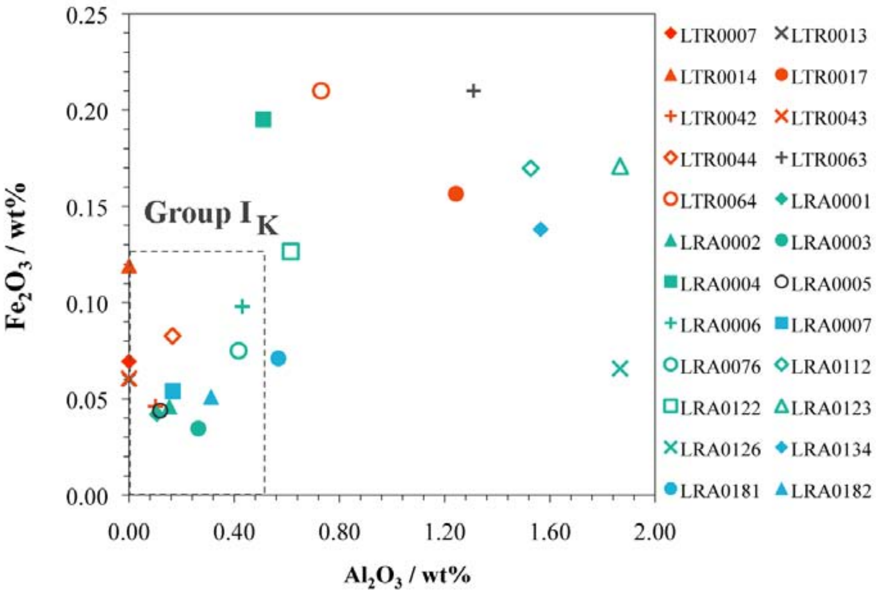


Fig. 4.37: Binary plot of Al_2O_3 *vs.* Fe_2O_3, in weight percent of oxides and determined by means of μ-PIXE and LA-ICP-MS for the potassium rich objects.

Analysing figure 4.38, the weight ratio of CaO/K_2O *versus* the weight ratio of As_2O_3/K_2O are represented. Fragments that constitute Group I_K appear divided between two distinct zones in this binary chart. The importance of looking at the weight ratios of CaO relative to K_2O is associated with the recipes that were used throughout time, and the raw materials employed in the batch. As one can observe in the chart, the ratios of CaO relative to K_2O vary mainly between 0.5 and 0.8. This variation is associated to the uneven composition of the raw materials employed, such as the plant ashes. This division of Group I_K into two distinct zones suggest that two different recipes were used to manufacture these objects, or that they were manufactured in two different periods using different raw materials, which could be translated into different oxide ratios. In other words, the fact that fragments from Group I_K are split to two different zones does not necessarily means that they are not part of the same production. The remaining samples appear related with samples from Group I_K.

To understand if lime was introduced into the batch, it is necessary to look at the relation between CaO and SrO, since a positive correlation is observed when lime is present (Kunicki-Goldifinger *et al.*, 2001). In figure 4.39, one can observe that a trend line is represented and some fragments present a positive correlation between the two oxides referred to above. On the other hand, the majority of LTR fragments and fragment LRA0182 from the LRA set do not present this positive correlation between CaO and SrO. For this reason, the hypothesis of lime being introduced into the batch of the fragments that respect this positive correlation is to be considered seriously. For the other fragments the most probable situation is that the calcium oxide comes from the plant ashes employed.

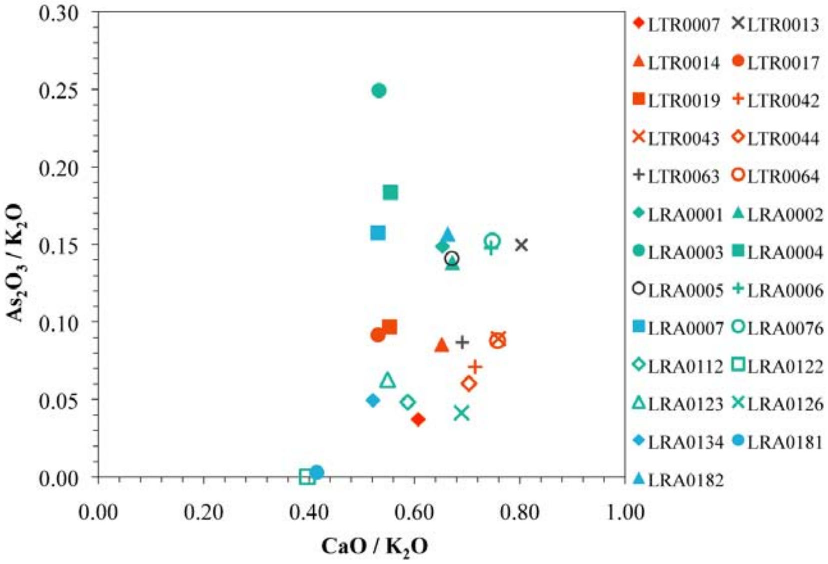


Fig. 4.38: Binary plot of As_2O_3/K_2O *vs*. CaO/K_2O for the potassium rich objects.

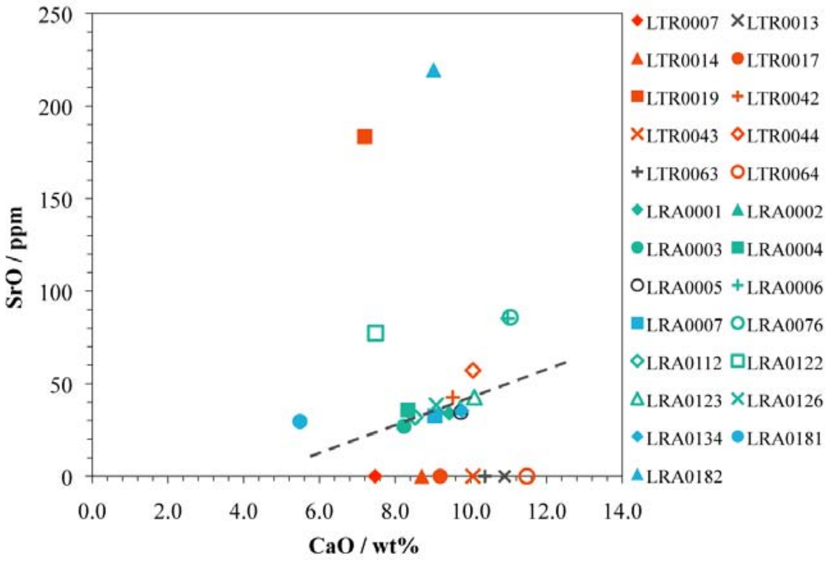


Fig. 4.39: Binary plot of CaO *vs*. SrO, in weight percent of oxides and µg/g and determined by means of µ-PIXE and LA-ICP-MS for the potassium rich objects.

It is now important to try to understand if the glass from these fragments is ordinary glass, white or chalk glass, or crystal glass. The hypothesis of being ordinary glass can only be considered for the fragments that do not have arsenic introduced into the batch, or the fragments that have it in very low concentrations. If the concentration of As_2O_3 is very low, one can conclude that its introduction into the batch was unintentionally made through cullet (Kunicki-Goldifinger *et al.*, 2005). Looking to the CaO *versus* As_2O_3 chart (figure 4.40), it is observed that some fragments have a very low (sometimes almost non-existent) As_2O_3 content, meaning that it was accidently introduced into the batch probably through cullet. Most fragments from the LRA set are located in the chart region with more than 1 wt% of arsenic oxide, and for that reason were considered to have high arsenic content. For these fragments – LRA0001, LRA0002, LRA0003, LRA0004, LRA0005, LRA0006, LRA0007, LRA0076, LRA0182, and LTR0013 – the hypothesis that they are white or crystal glass is the one favoured.

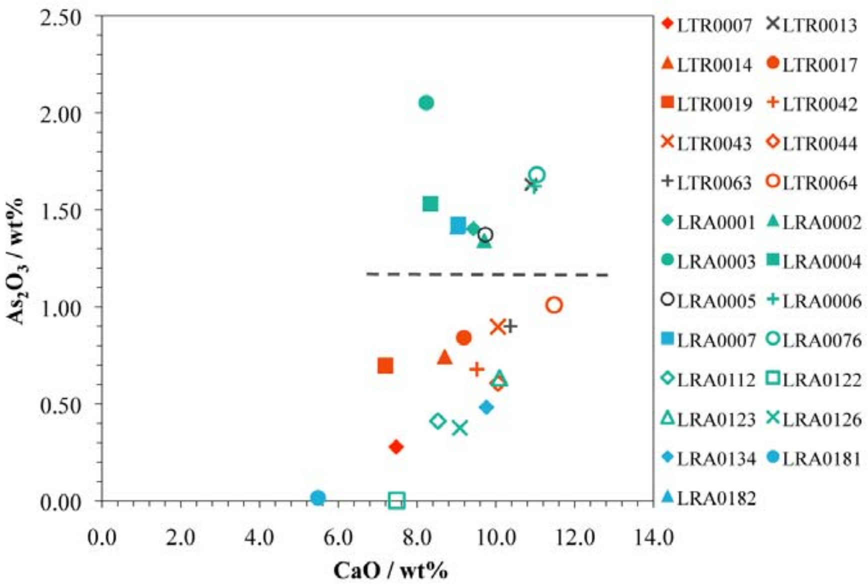


Fig. 4.40: Binary plot of CaO *vs.* As_2O_3, in weight percent of oxides and determined by means of µ-PIXE and LA-ICP-MS for the potassium rich objects.

The chart represented in figure 4.41 allows one to evaluate the concentration of alkaline and alkaline earth oxides in the glass composition (Kunicki-Goldfinger *et al.* 2005). From the analysis to this chart, it is deduced that the potassium rich fragments under study belong mainly to the white glass category. For their position in this chart, fragments LRA0122 and LRA0181 could be considered crystal glass, however, due to their As_2O_3 content (the lowest contents of all the potassium rich samples analysed), this hypothesis has to be discarded. These glasses are definitely attempts to develop potassium rich glass following Central European traditions.

In general, the chemical compositions of the fragments analysed in this section are very pure, in other words, have very low contents of impurities from the raw materials employed. Also the contents of MgO and Na_2O appear in general to be below 1 wt%, with the exception of fragment LRA0181 with a Na_2O content close to 8 wt%, where a larger amount of plant ashes was probably added to the batch. Looking at the amounts of P_2O_5, chlorine, MnO and Fe_2O_3, they appear in very low concentrations in comparison with soda rich glass, for instance. This low concentration in contaminants and in some alkaline oxides is the translation of the employment of purer raw materials like saltpetre, lime and so on. For some fragments, the presence of PbO in their composition was identified. PbO could have been introduced through cullet or intentionally, as in the case of LRA0112 that has a PbO content of 5.5 wt%.

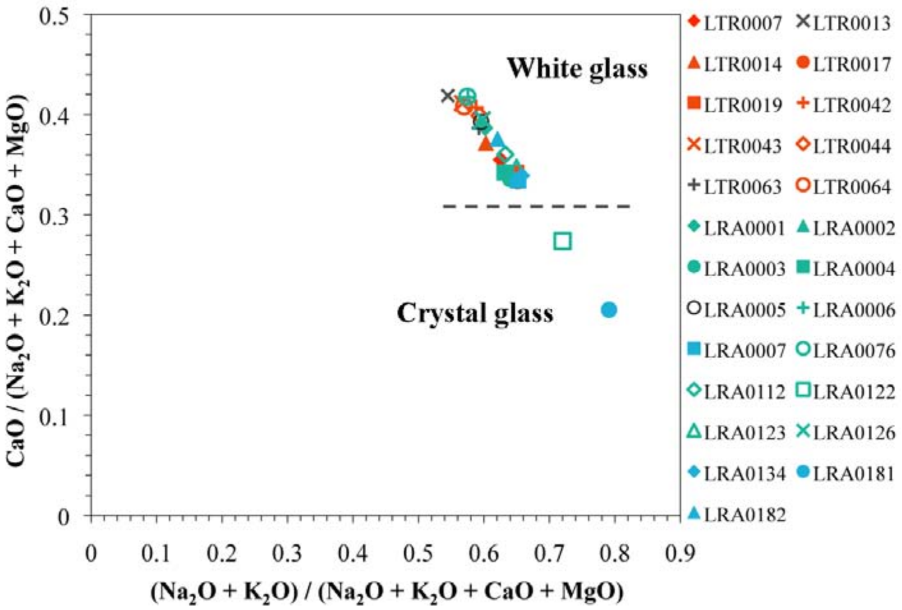


Fig. 4.41: Binary plot of variables calculated from the alkaline and alkaline earth oxides concentration for the potassium rich fragments (Kunicki-Goldfinger *et al.*, 2005).

The chart in figure 4.42 has the representation of literature values for K_2O *versus* CaO contents taken from Table X.3 in *Appendix X, Appendices Part I*. This comparison with literature is based on limited number of data and for that reason the conclusions withdrawn are no definitive, only tentative. The reported values for Bohemian glass have very high contents of CaO with the exception of one reported group (Group F). The great majority of fragments analysed from the LTR and LRA sets are cohesive with the Portuguese production from the Coina Glass Manufactory. Fragments LRA0003, LRA0004 and LRA0112 are cohesive with values reported for Antwerp potassium rich glass, however, when comparing the alumina values, the first two LRA fragments have alumina contents around 0.5 wt%, which is less than half of that found in the Antwerp reported value. LRA0112 has an alumina value comparable with Antwerp glass.

To deal now with the trace elements and REE analysis, in figure 4.43 it is possible to identify a group of fragments with a very low content of two typical silica trace elements, zirconium and yttrium oxides. This low concentration in ZrO_2 and Y_2O_3 is probably the result of employing a very pure silica source such as quartz pebbles.

In figure 4.44, analysing now the trace elements and REE signature of the glass fragments identified as having a high arsenic oxide content, it is observed that not all the glass samples are alike, but it is possible to group fragments LRA0001, LRA0002 and LRA0005 and fragment LRA0006 with LRA0076. As far as fragments LRA0003, LRA0004, LRA0007 and LRA0182 are concerned, it was not possible to relate them with each other or with any other glass fragment. For the fragments that can be related with each other, the hypothesis is raised that they share the same source of raw materials, and recalling figure 4.43, also the same production centre. The fragments that do not relate with each other were made from different raw materials that resulted in different trace elements and REE signatures; however, this does not mean that the fragments came from a different production locality. According to figure 4.42, and considering the CaO/K_2O ratios, these fragments are very similar to the Coina Glass Manufactory production, and the different trace elements and REE signature could be the result of the same production centre employing raw materials from different sources.

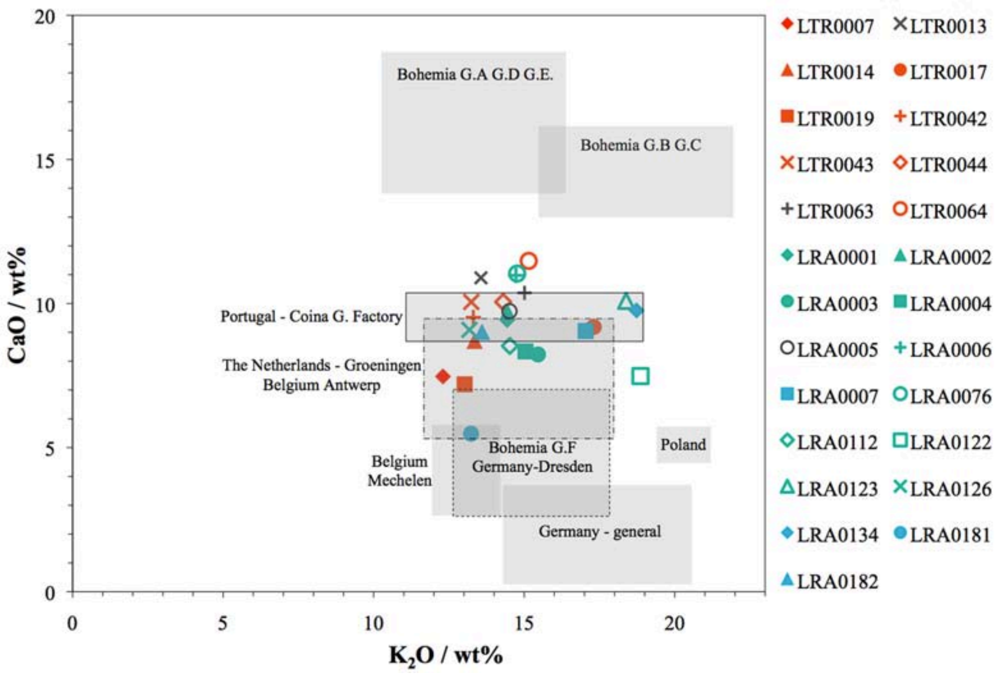


Fig. 4.42: Binary plot of K_2O *vs.* CaO concentrations, in weight percent of oxides and determined by means of μ-PIXE and LA-ICP-MS for the potassium rich glass. It is possible to observe mean values (considering the standard deviation) collected from literature and present in Table X.3 (*Appendix X, Appendices Part I*) for potassium rich glass.

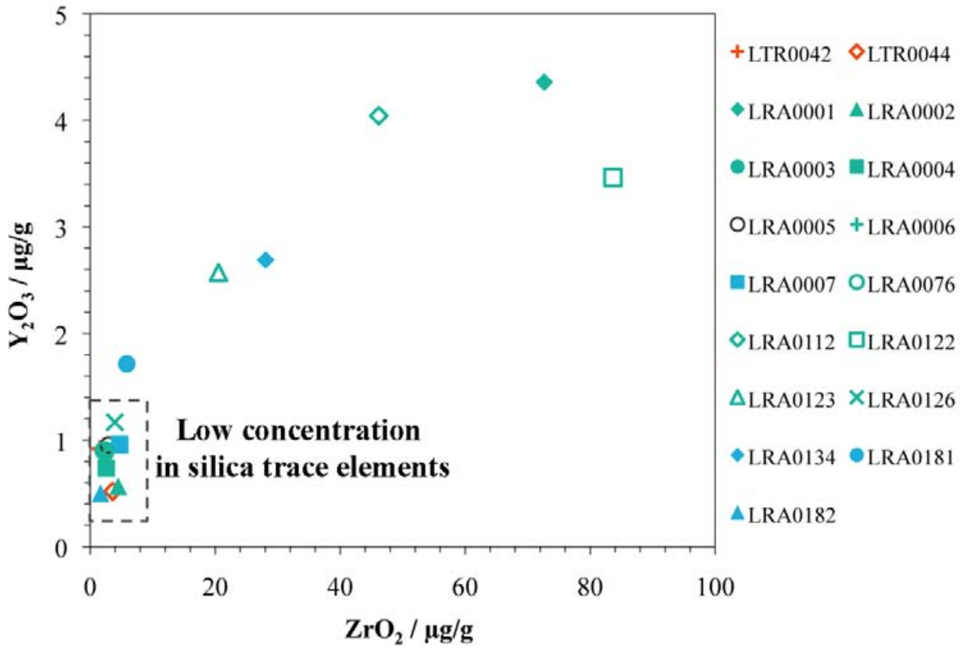


Fig. 4.43: Binary plot of ZrO_2 *vs.* Y_2O_3 concentrations, in µg/g and determined by means of LA-ICP-MS for some fragments of the potassium rich glass.

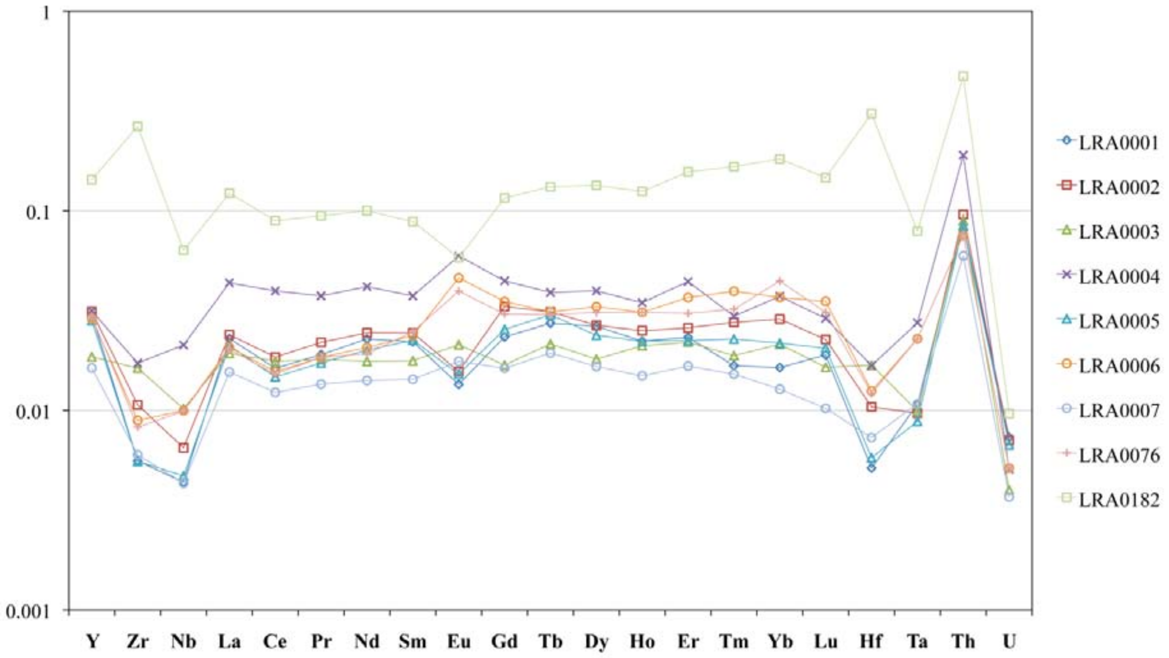
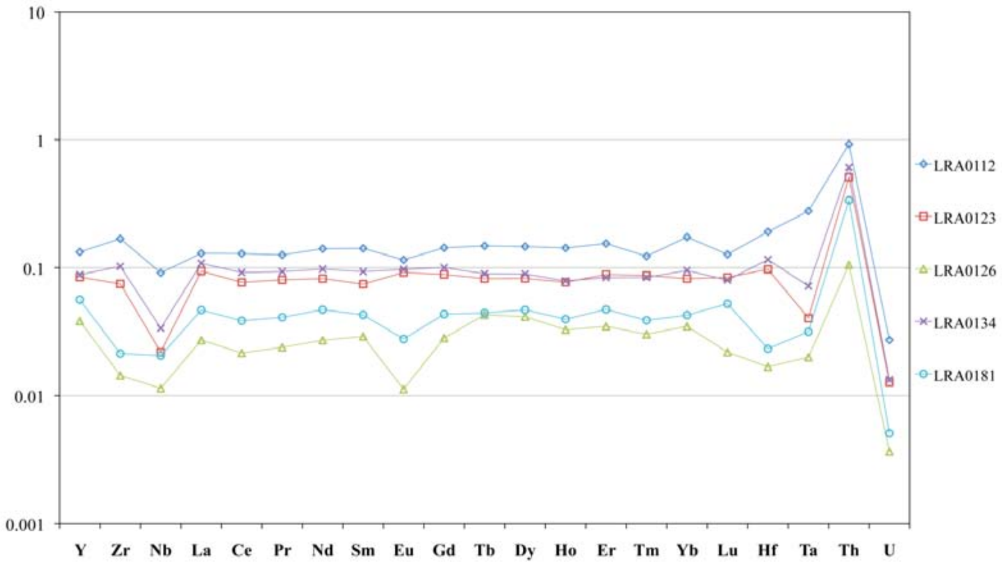


Fig. 4.44: Contents of some trace elements and Rare Earth elements normalised to the upper Earth crust (Wedepohl, 1995), for the fragments with high arsenic oxide content from the potassium rich glass, in logarithmic scale.

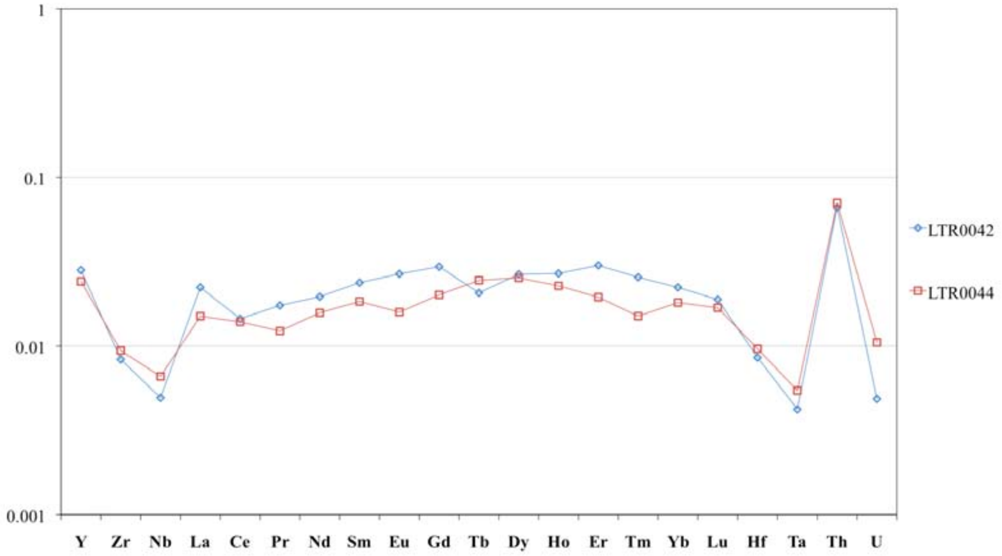
Fragments LRA0112, LRA0123 and LRA0134, which present a higher PbO contents, these were plotted together to evaluate their trace elements and REE signature (figure 4.45 a). Fragments LRA0123 and LRA0134 are closer to each other in terms of trace elements and REE signature, however not exactly equal. Regarding fragment LRA0112, it has a different trace elements and REE signature. With regard to the fragments that are more closely related to one another, this can indicate that the raw materials employed were not the same, but were closely related in geographical terms. Fragments LRA0126 and LRA0181 have a similar trace elements and REE signature; which, once again, can be an indication of geographically related raw materials.

Finally, turning to fragments from the LTR set, LTR0042 and LTR0044, these are similar to each other, as there seems to be some relation between their trace elements and REE signatures. Looking at figure 4.45 b), one can see the resemblance between these fragments that belong to small vessels.

The two fragments from the LTR set are not related at a trace elements and REE level with fragments from the LRA set. However, the CaO/K_2O are still similar to the other LRA fragments and cohesive with the Coina Glass Manufactory fragments. These fragments could be from the same production centre, or from production centres using similar recipes and related raw materials.



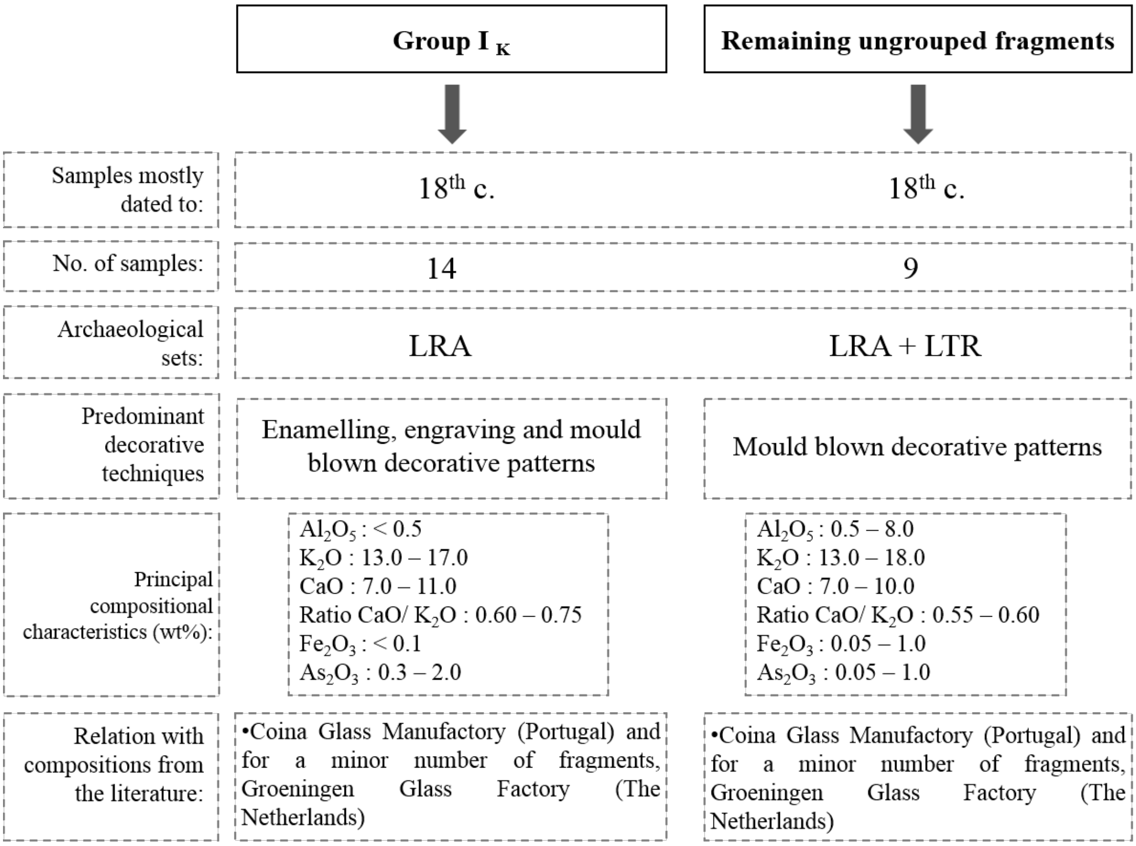
(a)



(b)

Fig. 4.45: Contents of some trace elements and Rare Earth elements normalised to the upper Earth crust for some fragments from the potassium rich glass a) with higher PbO content, and (b) two small vessel fragments, both in logarithmic scale.

In order to summarise the results obtained during the study of the potassium rich glass objects, a scheme was made and it is presented in figure 4.46.



	Group I $_K$	**Remaining ungrouped fragments**
Samples mostly dated to:	18th c.	18th c.
No. of samples:	14	9
Archaeological sets:	LRA	LRA + LTR
Predominant decorative techniques	Enamelling, engraving and mould blown decorative patterns	Mould blown decorative patterns
Principal compositional characteristics (wt%):	Al_2O_5 : < 0.5 K_2O : 13.0 – 17.0 CaO : 7.0 – 11.0 Ratio CaO/ K_2O : 0.60 – 0.75 Fe_2O_3 : < 0.1 As_2O_3 : 0.3 – 2.0	Al_2O_5 : 0.5 – 8.0 K_2O : 13.0 – 18.0 CaO : 7.0 – 10.0 Ratio CaO/ K_2O : 0.55 – 0.60 Fe_2O_3 : 0.05 – 1.0 As_2O_3 : 0.05 – 1.0
Relation with compositions from the literature:	•Coina Glass Manufactory (Portugal) and for a minor number of fragments, Groeningen Glass Factory (The Netherlands)	•Coina Glass Manufactory (Portugal) and for a minor number of fragments, Groeningen Glass Factory (The Netherlands)

Fig. 4.46: Scheme summarising the main characteristics (stylistic and compositional) of the group of potassium rich objects and also with the main characteristics of the ungrouped potassium rich objects.

4.4 Mixed alkali glass

Among all the archaeological assemblages studied, seven glass fragments with a mixed-alkali chemical composition were identified. Due to the small number of objects with this chemical composition no statistical method was applied to their study.

Two fragments are from the CPU set (CPU0003, which belongs to a light green vessel fragment, probably a beaker or an oil lamp, and CPU0013, which belongs to a colourless vessel fragment with a folded rim), one fragment belongs to the PMF set (PMF0470, which belongs to a green goblet stem and part of the base), one fragment belongs to the LRA set (LRA0158, which belongs to a light blue window glass), and the final three fragments belong to the LTR set (LTR0011, which belongs to a dark brown vessel, LTR0059, which is a turquoise blue flask of small dimensions and finally, LTR0070, which belongs to a colourless flask of small dimensions with mould blown decorations).

As was mentioned in *Chapter Two, Part I*, during the 16th century several Italian glassmakers established glass workshops in northern Europe, with the aim of producing soda-rich glass objects similar to Venetian ones (Tait, 2004, p.172). The glass that resulted from these productions was intended to imitate *cristallo* and when compared with it, was usually characterised by a lower content of Na_2O and a higher content of K_2O. This was probably due to the use of lower quality plants from which the ashes were obtained, or because of the applied purification treatments. When the composition of these glasses has soda/potash ratios close to one, they are called mixed alkali (Dungworth *et al.,* 2006).

The fragments found among the assemblages being studied are characterised by having a Na_2O content of between 7 and 15 wt%, the K_2O content ranges between 3 to 12 wt%, and the CaO content varies between 5 and 12 wt%. The relatively high contents of MgO, P_2O_5, K_2O and the presence of chlorine suggest the use of coastal plant ashes. Some fragments present a P_2O_5 content of around 1 wt%, which might also indicate also the use of wood ash in the batch. This was to be expected since the mixed-alkali glasses are believed to be made using the mixture of ashes, that can be from marine plants (such as kelp), coastal plants or with wood-ash, resulting in a chemical composition characterised by being a combination of alkaline oxides from several origins.

It is known that this type of glass was used in the British Isles among other places during the 17th and 18th centuries to manufacture ordinary objects such as utilitarian tableware (Dungworth & Mortimer, 2005). If one looks at the objects identified belonging to this category, this exact situation is observed.

Analysing now the chemical composition determined for these fragments, a suggestion of a negative correlation between potassium and magnesium oxides is perceived (figure 4.47). Can this be an indication that these two oxides came from different types of raw material?

Discussing the hypothesis of the introduction of kelp into the batch, it has to be discarded when one considers that the SrO values are all below 0.05 wt%. As it was discussed above in the HLLA glass section, when kelp is introduced into the batch, even in small proportions, it generates SrO values above 0.15 wt%.

Analysing the relation between alumina and iron oxide (figure 4.48), the different silica sources employed in the glass objects are evaluated. Using the same division criterion by alumina contents that has been employed previously, one can conclude that at least three different silica sources might have been used. This does not necessarily indicate that these glass objects were made in different production locations. Since it is believed that mixed-alkali compositions weren’t subject to a great selection of raw materials, the same production centre could employ silica from different locations.

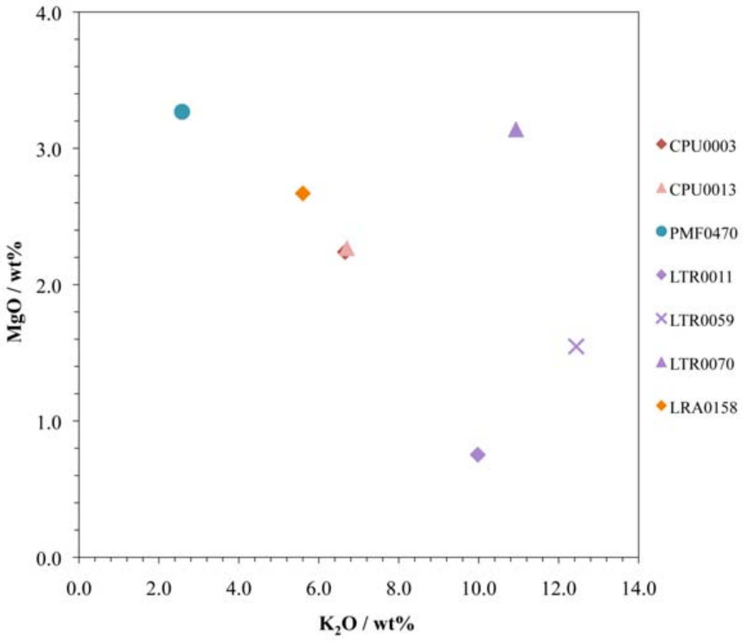


Fig. 4.47: Binary plot of K_2O *vs.* MgO, in weight percent of oxides, determined by means of μ-PIXE and LA-ICP-MS for the mixed alkali glass.

Regarding MnO and Fe_2O_3 contents of these samples, the manganese oxide contents is always below 1 wt%, which indicates that no attempt was made to make these glasses colourless. Once again this fact is related to the utilitarian nature of this glass type.

Analysing the chemical composition of these fragments, a close relation between CPU fragments is observed for all the quantified oxides (Table V.2 in *Appendix V, Appendices Part I*), strongly suggesting that these fragments came from the same production centre, and most probably from the same batch. The other fragments do not seem so closely related to each other, mainly the case with the PMF fragment dated from the 14th to the 15th century. The PMF fragment was considered here despite its chronology, in order to observe the differences between the same types of chemical composition over the centuries. Again with regard to this fragment, and relating it to the other fragments, it is possible to conclude that it has the highest alumina and iron oxide contents (a silica source of lower quality) and the lower lime content in comparison with the other samples.

Comparing now the samples being studied with the values in the literature gathered in Table X.4 (*Appendix X*, *Appendices Part I*), for sodium and potassium oxides (figure 4.49), it is observed that fragment LRA0158 is compatible with glass produced in Silkstone Glass Factory, phase 1, England. Fragments from the LTR set cannot be related with any of the reported compositions, having a higher K_2O content. The LTR fragments are not apparently related to each other, and it is only possible to say that fragments LTR0011 and LTR0070 probably share the same silica source, since these two fragments have a medium alumina content. The iron oxide content of these two samples however, are not related. The two fragments from the CPU set are still closely related to each other, and not being particularly related to any of the values from the literature, are closer to values from the Silkstone Glass Factory, phase 1 and from both phases from Vauxhall (London), England. Fragment PMF0470 is also not related to any of the reported compositions from the literature, however - as it was stated before - this was already expected because of the chronological differences.

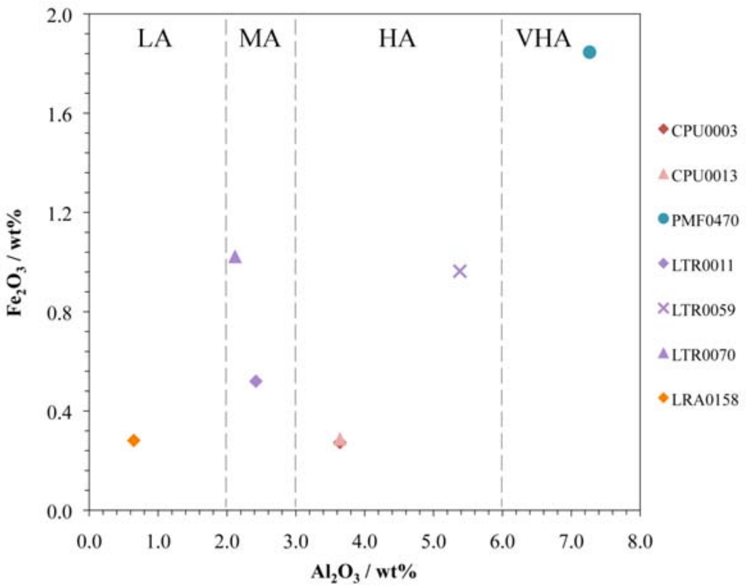


Fig. 4.48: Binary plot of Al_2O_3 *vs*. Fe_2O_3, in weight percent of oxides, determined by means of μ-PIXE and LA-ICP-MS for the mixed-alkali glass.

The mixed alkali composition is probably one of the most difficult to discuss, and to determine a provenance without resorting to the trace elements and REE analysis and further comparison. This is due to the hypothesis that if it was used to manufacture utilitarian glass, no special control or care was taken in the choice of raw materials employed, being that lack of control consequently also reflected in the heterogeneity of the chemical composition. This can indicate that the same production could use different sources of silica and of alkali, combining them into the bulk in different ratios, resulting probably in glasses apparently similar (in terms of colour and workability) but completely different in terms of chemical composition.

In conclusion, it is possible to say with a high degree of confidence that fragments from the CPU set came from the same production centre. The fragment from the LRA set is closely related in terms of Na_2O and K_2O to the production from Silkstone, England (phase 1), however, when comparing the contents with other oxides such as MgO, alumina, MnO, Fe_2O_3 or PbO, these are quite different, which in the light of what has been said above does not invalidate the possibility that this fragment was produced in Silkstone, but this does not allow one to reach a more definitive conclusion on the provenance of this fragment. Even within the Silkstone production, the compositional differences between phases is quite evident, which was not so obvious in other glass compositional types reported here (for instance the HLLA composition, in which the different Silkstone phases are related). On the other hand, different production locations have closely related compositions such as Bolsterstone, Cheese lane, Gawber and St. Thomas Street, all in the British Isles. Regarding the LTR fragments, the relation between them is poor even in terms of colour. It is likely that these fragments came from different production locations.

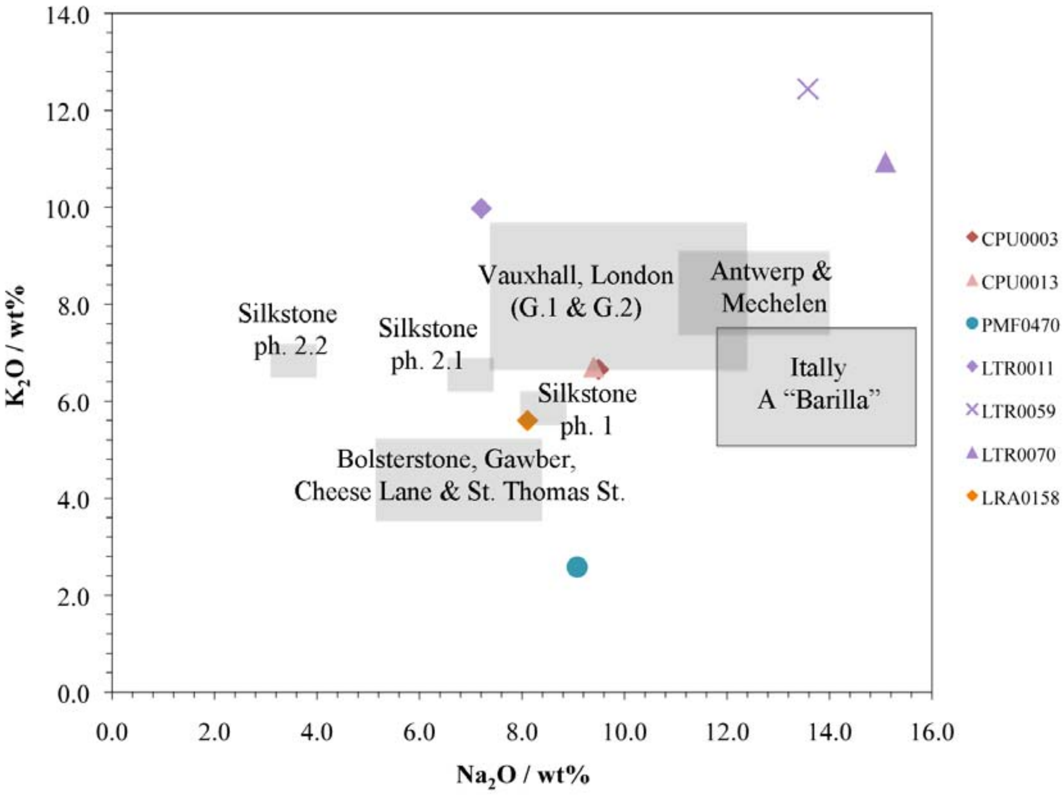


Fig. 4.49: Binary plot of Na_2O *vs.* K_2O concentrations, in weight percent of oxides and determined by means of µ-PIXE and LA-ICP-MS for the mixed alkali glass. It is possible to observe mean values (considering the standard deviation) collected from the literature and presented in Table X.4 (*Appendix X, Appendices Part I*) for mixed alkali glass.

4.5 Lead glass

Among all of the sets analysed, only five lead glass fragments were found, representing only 2% of the totality of objects analysed. Because of the small number of objects with this chemical composition, no statistical method was applied to their study.

From these five fragments only one was not from Lisbon, belonging to the PMF set. The Lisbon sets are slightly more recent in terms of chronology than the other sets being study, which explains the existence of lead glass among the other fragments. The limited number of samples[7] with this glass composition it is possibly a consequence of the fact that during the considered period, lead glass was still a novelty in Portugal, and its production was still at its beginning in national territory.

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[7] At this point it is important to explain that only for two assemblages (LTR and LRA) was possible to analyse all of its colourless fragments. In the case of SCV, CPU, PMF and SJT assemblages, a selection of fragments was made, so it is not possible to know if among the unselected fragments exists samples in lead glass.

The five fragments from this section are characterised by a PbO content between 26 and 37 wt%, a K_2O content between 8 and 11 wt% and finally, a SiO_2 content between 51 and 55 wt%. In general, the five fragments are very poor in terms of raw materials impurities such as alumina, iron and calcium oxides for instance. All the fragments analysed are potassium-oxide-lead-oxide-silica glass, where silica, potassium oxide, and lead oxide represent more than 90% of the glass matrix. Since the sum of the averages of the silica, lead, and potassium oxides is more than 90 wt%, and considering the quantities of trace elements measured, it is possible to conclude that the raw materials employed were very pure. As an example, and according to the literature, the raw materials employed for lead glass were pure sands, flint, saltpetre, and potassium tartrate (Dungworth & Brain, 2009; Lanmon, 2011).

Two of the fragments analysed present contents of alumina, lime and iron oxide higher than the others, and higher comparing to the published compositions of lead glass present in Table X5 in *Appendix X, Appendices Part I.* Fragment PMF0863 belongs probably to a colourless goblet stem and LTR069 is a colourless vessel fragment. These fragments also have a similar K_2O/CaO weight ratio between 4 and 5.

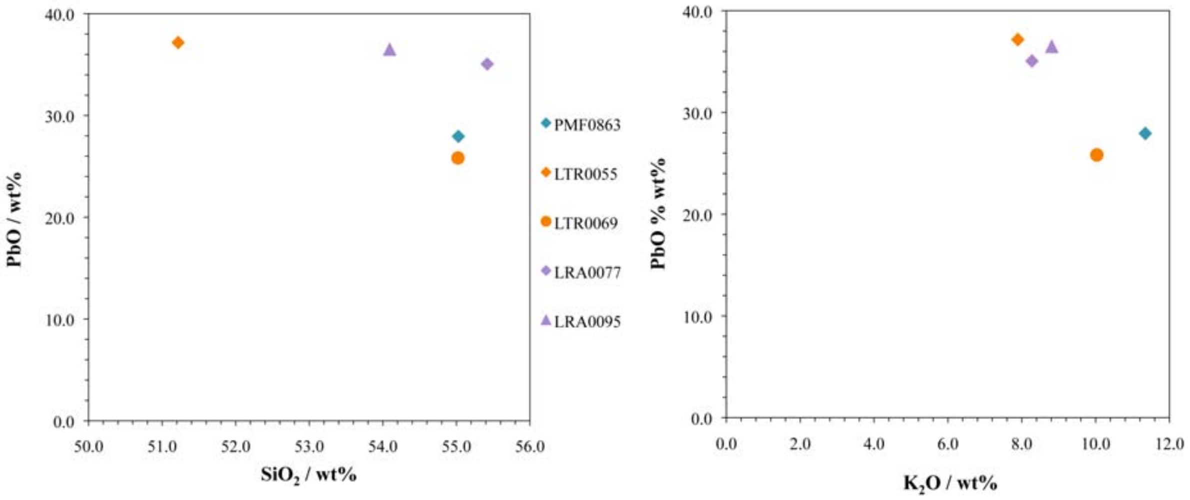
Despite the small number of fragments, it seems in figure 4.50 (a) that a negative correlation between silica and lead oxides is present, which - according to Dungworth & Brain (2013, p. 579) - is a casual result of the fact that these two oxides represent circa 90% of the glass composition.

Looking at the chart represented in figure 4.50 (b), in which the relation between potassium and lead oxides is observed, fragments PMF0863 and LTR069 are close together as well as in the chart represented in figure 4.50 (a). Because of their higher contents in impurities and the related content of their major oxides, it is possible that these two fragments came from the same production centre.

Recalling that lead oxide was intentionally introduced into the glass composition, and its content increased, in order to solve a severe crizzling problem (caused by the lack of stabilizers in the glass network), it is worth noting that these fragments do not present any signs of this phenomena, apparently as a consequence of the fact that the lead oxide content was sufficiently high to stabilise the glass network.

This glass production technology, with high levels of lead oxide in the glass composition (29.4 +/- 2.2 wt%) was also known in the Netherlands, in the Groningen Glass House, that operated between 1687-1698 (Müller & Stege, 2006, Group 4). However, the glass produced there presented higher values of calcium oxide, around 1.8 ± 1.0 wt%, and can only be compared with fragments PMF0863 and LTR0069. The K_2O/CaO weight ratio of lead glass from this house is around 7.3 as reported in Table X.5, approximately twice the value of that for the two glass objects from Portuguese sets; and the alumina value for the Portuguese glass objects is slightly lower when compared with the glass from

Groningen house. However, looking at the alumina content of these two samples, the closest values in the literature are the ones from the Groningen house. The differences in glass composition of the objects found in Groningen allow one to conclude that the probability of the Portuguese set being studied having a Dutch origin must be considered.



(a) **(b)**

Fig. 4.50: Binary plots of (a) SiO_2 vs. PbO concentrations and (b) K_2O vs. PbO concentrations, both in weight percent of oxides and determined by means of μ-PIXE and LA-ICP-MS for the lead glass objects.

Looking to weight ratios of K_2O/CaO in the fragments and comparing these with the weight ratios of K_2O/CaO from the reported production locations presented in Table X.5 (*Appendix X, Appendices Part I*), one can observe that, as has been explained above, fragments PMF0863 and LTR0069 are more comparable with the objects produced at the Coina Glass Manufactory. Looking to the other oxides, there is no parallel for the content of iron oxide (around 3 wt%) of fragment LTR0069. The fragment is perfectly colourless; no arsenic oxide was measured in the glass (probably it was below the μ-PIXE detection limit), and the manganese oxide content is too low to be able to annul the colouring effect of such an amount of iron oxide.

Fragments LTR0055, LRA0077 and LRA0095 have higher K_2O/CaO weight ratios that are comparable to the ratios from Silkstone, Group I. However, these fragments present PbO levels above 35 wt%, and the fragments from Silkstone Group I, have PbO contents around 20 wt%, which invalidates the possibility that these fragments come from this group. Considering the other groups from Silkstone, one can observe that their K_2O/CaO weight ratios changed significantly with time as well as the PbO content, all of which increased over time. This means that these fragments could have been produced at the Coina Glass Manufactory or in a different production locality at different periods of time, employing different raw materials or different proportions of raw materials.

Analysing figure 4.51, in which the potassium oxide values were plotted against the lime values reported in the literature presented in Table X.5 (*Appendix X, Appendices Part I*), and from the fragments being studied here, it is observed that fragments PMF0863 and LTR0069 are close to the composition of lead glass retrieved from the Groningen Glasshouse in The Netherlands. Nevertheless, as has been stated before, the alumina content is lower for these fragments than that found in Groningen glass. The compositional resemblance between Groningen glass and these two fragments cannot be ignored. These fragments where retrieved from two different archaeological sites with different geographical locations. Two hypotheses can be raised: these fragments were brought to Portugal from The Netherlands, or glassworkers from The Netherlands were working in certain Portuguese furnaces, producing lead glass with their recipes. It is known that from the 15th/16th centuries onwards, several glassworkers of different nationalities began working in Portugal, and brought with them the glass recipes that they traditionally used in their home countries, which makes this premise plausible. Looking to more recent production, the Coina Glass Manufactory employed English glassmakers, and was under the English and Irish administration (Custódio, 2002, p. 101).

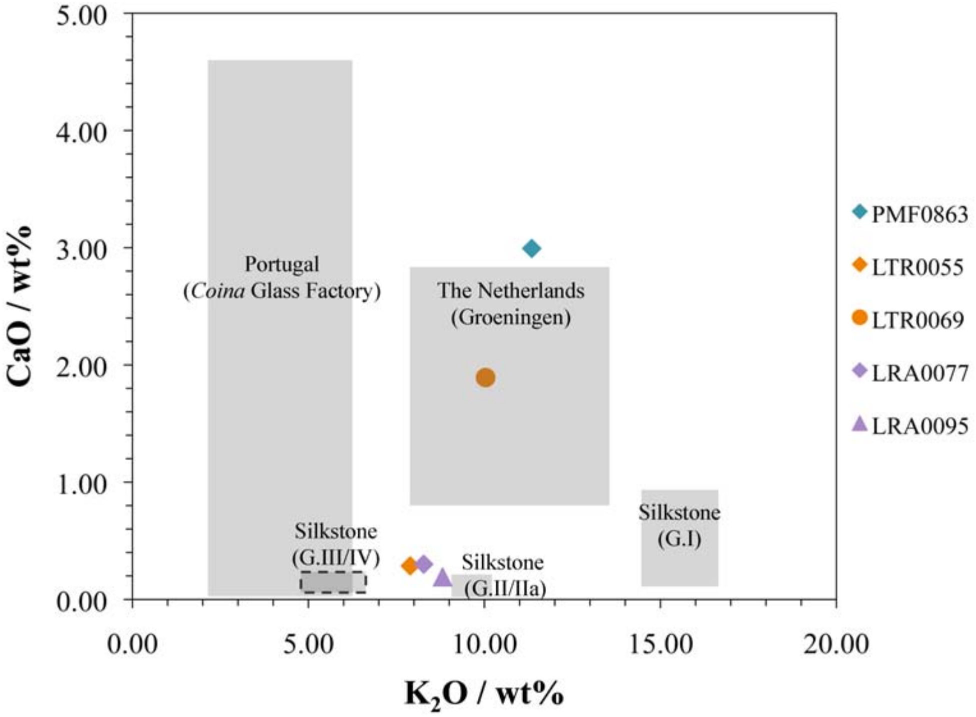


Fig. 4.51: Binary plot of K_2O *vs.* CaO concentrations, in weight percent of oxides and determined by means of μ-PIXE and LA-ICP-MS for the lead glass. Mean values (considering the standard deviation) collected from the literature and presented in Table X.5 (*Appendix X, Appendices Part I*) for lead glass are represented.

The remaining fragments LTR0055, LRA0077 and LRA0095 can only be related with glass from Silkstone group II and IIa. These three fragments, however, present a higher lead oxide content than the glass from these Silkstone groups. The same hypotheses considered for the previous situation has to be considered here too.

Looking at figure 4.52, one can conclude that fragments LRA0077 and LRA0095 have exactly the same trace elements and REE signature, strongly suggesting that both fragments had the same source of raw materials, and probably came from the same production centre. In terms of style, is not possible to compare these fragments, since fragment LRA0077 belongs to a small vessel, for which no shape is discernible, and fragment LRA0095 belongs to a chunk of colourless glass that probably melted during a fire. Since it was not possible to attribute a date to this fragment, and fragment LRA0077, which presents a closely related chemical composition, is dated from the 17th century, the hypothesis can be considered that these fragments melted during the fires that ran through Lisbon during the weeks after the great earthquake of 1755.

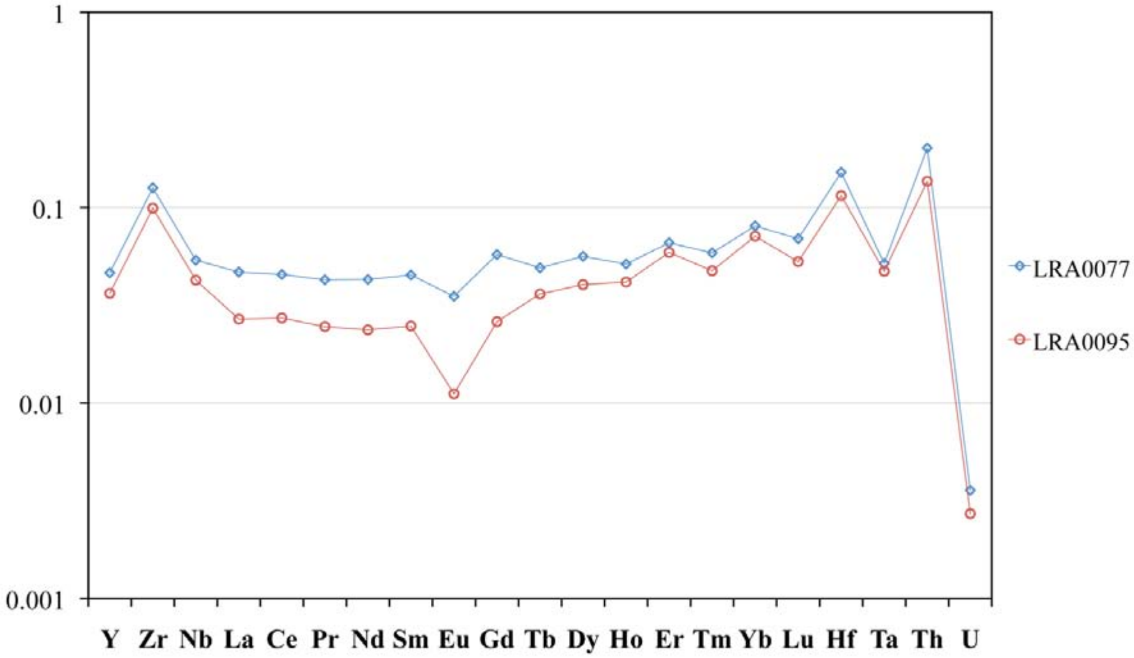


Fig. 4.52: Contents of some trace elements and Rare Earth elements normalised to the upper Earth crust (Wedepohl, 1995) for the two analysed lead glass fragments from the LRA assemblage, measured by LA-ICP-MS, in logarithmic scale.

4.6 Glass colourants and opacifiers

For the most part of the glass considered in this work, glass colouration can be attributed to the presence of contaminants that have been involuntary introduced into the batch with the major raw materials. This is the case with iron oxide, for instance, the presence of which is commonly attributed to silica. There are some cases where the colouration is considered intentional and this is the case for cobalt blue, where the presence of cobalt in the glass matrix is considered to be deliberate.

The colour of the glass will be discussed in this section, as well as the glass opacifiers found in the enamels that decorate some of the objects. The chromophores will be identified, as well as the intentionality on the colour will be discussed. The nature of the glass matrix will always be specified, however, it is important to point out that in the case of potassium-rich glass and lead glass all the fragments are made of colourless glass, and for this reason are not discussed in this section.

4.6.1 Colourants in transparent glass

Natural hues - Green, Yellow, Grey and Brown glass

The fragments of the soda-rich glass present the most colourful palette of all the glass types studied. The mixed alkali glasses studied have some coloured glass, and the HLLA glass all have the dark green and black glass typical of wine bottles.

Façon-de-Venise objects

Considering first the *façon-de-Venise* objects, in order to evaluate if the glass was intentionally discoloured the relation between iron and manganese oxides was inspected (figure 4.53). It is generally accepted and established that contents above 1 wt% of MnO imply intentional introduction in the glass batch in order to counteract the colouring effect of the iron oxide impurity, while MnO contents below 1 wt% result from unintentional introduction into the batch through raw materials such as sand (Cagno *et al.*, 2012b). From figure 4.50, it is possible to conclude that all samples analysed have MnO contents below 1 wt%. Looking at the chart, three linear correlation lines can be observed. This indicates that both iron and manganese oxides reached the glass batch through the source of silica. In addition, the iron oxide is present in low amounts, exceeding the content of 1 wt% only in one sample (PMF0517). This reinforces the hypothesis advanced in sub-chapter 4.1.2 Venetian and *façon-de-Venise* glass that the silica sources employed in these glasses were of high purity and chosen carefully in order to produce *façon-de-Venise* objects and not just ordinary glass.

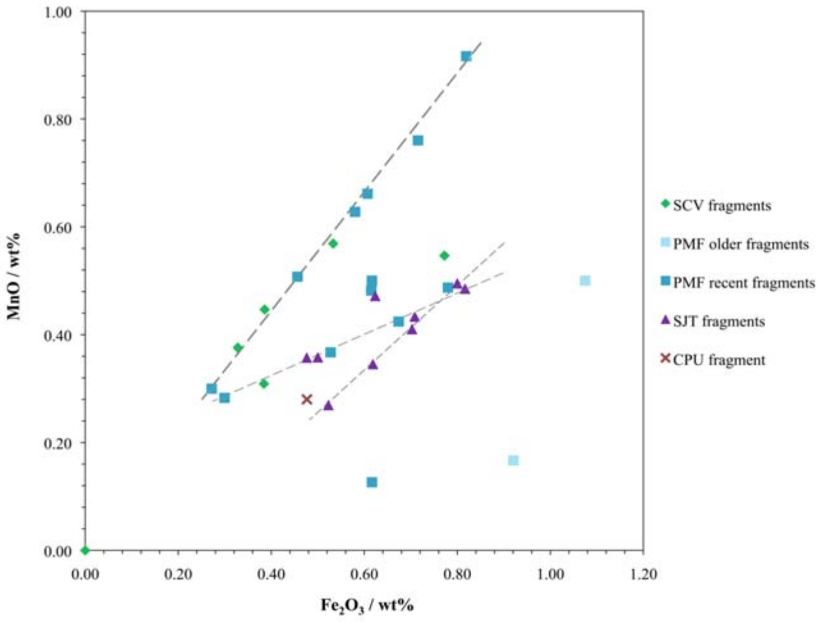


Fig. 4.53: Binary plot of iron vs. manganese oxides. Three visual trend lines are marked in the chart.

Looking first at the bluish/ greyish hue, as one can see in figure 4.54 (representative spectrum of fragment PMF0570 from the PMF set; remaining spectra in *Appendix XII*, *Appendices Part I*), *façon-de-Venise* fragments from three of the assemblages studied (PMF, SJT and one object from SCV) present this natural hue. Analysing the chemical composition of these fragments, no obvious reason was found as a justification for the existence of this tonality, and for this reason the glass colouration was investigated by means of UV-Vis reflectance spectroscopy.

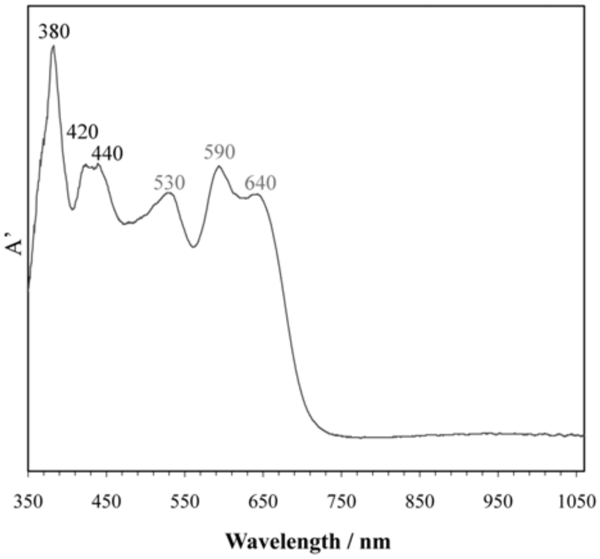


Fig. 4.54: UV-Vis spectrum of fragment PMF0570 from PMF set, identified as a *façon-de-Venise* object, and presenting a natural bluish/ greyish hue.

From the UV-Vis spectra (*cf.* figure 4.54), the presence of iron and cobalt cations was detected. The presence of Fe(III) is confirmed by its typical absorption bands at 380, 420 and 440 nm, corresponding to tetrahedral coordination. It is also clear the presence of cobalt Co(II) visible by its characteristic triple bands with absorptions at 530, 590 and 640 nm (Navarro, 2003). Due to the pure nature of the silica sources employed in these glass objects, determined and confirmed above, one can conclude that this grey/blue hue is caused by the simultaneous presence of iron and cobalt oxides. As far as is know, the presence of cobalt in colourless *façon-de-Venise* glass has rarely been reported in the literature (Coutinho *et al.*, 2016b; Jackson, 2006). The simultaneous presence of Co and As can also indicate that these entered in the glass through recycled cullet.

Green glass

With regard now to the green glass, UV-Vis reflectance spectroscopy (figure 4.55) allowed one to identify the presence of octahedral Fe(II) with a broad band centred around 1100 nm, and tetrahedral Fe(III) by its typical absorption bands at 380 and 420 nm in the great majority of the green and yellow glass fragments analysed. This impurity is typically attributed to the silica source. Looking to the green tonalities on the SCV set, the intentionality of this colouration is debatable. The hypothesis is raised that the glassmakers probably knew that using certain sources of silica they could or would obtain bright green tonalities, since no attempt seems to have been made to annul the effect of the iron oxide. Another situation was identified in some green glass fragments from the SJT set – SJT0007 and SJT0131 – from the SCV set – SCV-V60 – and from the CPU set – CPU0010, CPU0022 and CPU0033 – in which, besides the presence of iron Fe(II) and Fe (III), the presence of Co(II) was also identified, as one can see in figure 4.51 (remaining spectra in *Appendix XII, Appendices Part I*).

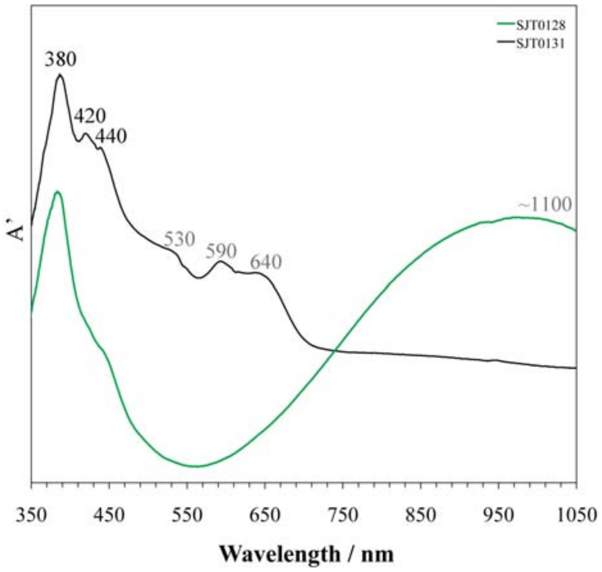


Fig. 4.55: UV-Vis spectra of fragments SJT0128 and SJT0131 from the SJT set, presenting a green colouration.

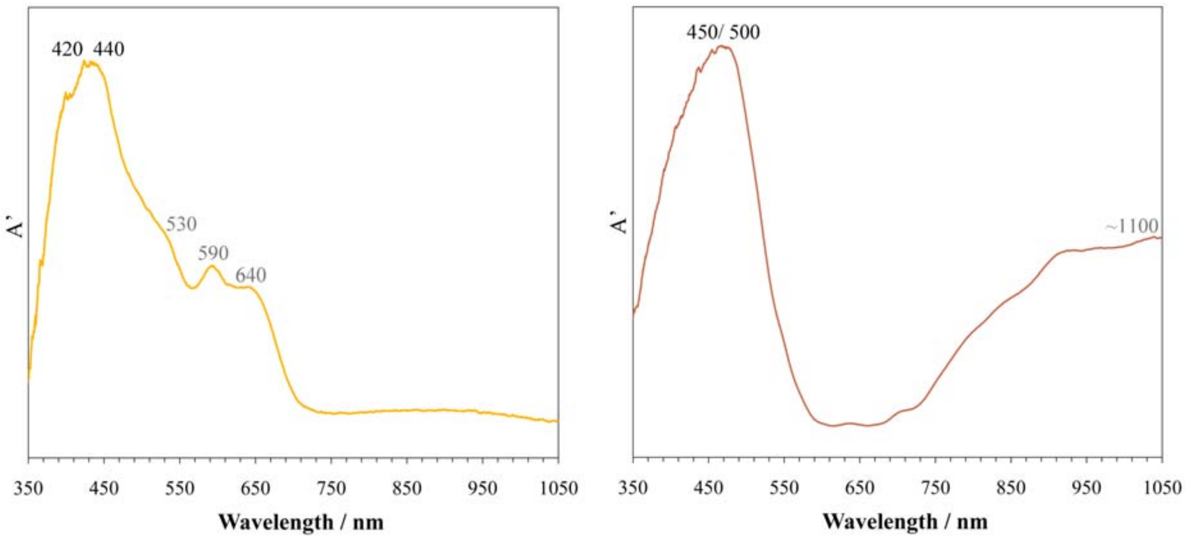
The simultaneous presence of iron and cobalt oxides can be found in greyish, green and yellow glass fragments both in utilitarian (beakers, oil lamps, window glass and so on) and in *façon-de-Venise* glass. Could the cobalt oxide come from the silica source? Or is it the result of using indiscriminate cullet?

Another hypothesis is that the presence of cobalt can be related with manganese. Depending on the used ore to obtain manganese, it can bring barium and cobalt into the glass batch (Baba *et al.*, 2014). In the great majority of SJT fragments it is possible to observe a greyish tonality due to the presence of iron and cobalt oxides.

Yellow and Brown glass

In the case of yellow glass, the presence of the same chromophores was identified as in green glass samples. Concerning the iron oxide, the atmosphere of the furnaces will determine the final colour of the glass, that can range between yellow given by the ferric ion (Fe^{3+}), blue given by the ferrous ion (Fe^{2+}) or green, where this last colour is given when both Fe(II) and Fe(III) ions are present in the glass in certain proportions (Navarro, 2003). Again, yellow glass fragments (*e.g.* SCV-V177 from SCV set, spectrum in *Appendix XII*, *Appendices Part I*) that owe their colouration to the presence of Fe(III) were identified, as well as yellow fragments such as the bossed beaker CPU0009 in which the presence of iron and cobalt oxides was identified (figure 4.56 a).

As far as the brown or dark amber glass is concerned, this colour was only identified in one fragment from the LTR set. In this fragment (LTR0011), the presence of Mn(III) and Fe(II) was observed, as one can see in figure 4.56 (b). The presence of Fe(III) is probably masked by the broad band of Mn(III) that appears between 450 and 500 nm (Arletti *et al.*, 2011).



(a) **(b)**

Fig. 4.56: UV-Vis spectra of (a) fragment CPU0009 from CPU set presenting a yellow hue, and (b) fragment LTR0011 from the LTR set presenting a dark amber colouration.

Purple glass

Purple glass was only identified in one of the studied sets. Among the SCV set one can find five fragments (SCV-V82, SCV-V154, SCV-V170, SCV-V171 and SCV-V182) with a dark purple colour that seems almost black in the thicker areas of the glass. The presence of this colour is considered intentional, as deliberate adding of manganese to the batch was necessary to achieve this colour.

In these purple glass fragments, the presence of Mn(III) was identified by UV-Vis reflectance spectroscopy (figure 4.57) as the main chromophore, which is characterised by an absorption band between 450 and 500 nm (Arletti *et al.* 2011). This broad band masks the presence of Fe(III) as has been stated above, but the presence of iron can be identified through the chemical analysis (by μ-PIXE or LA-ICP-MS).

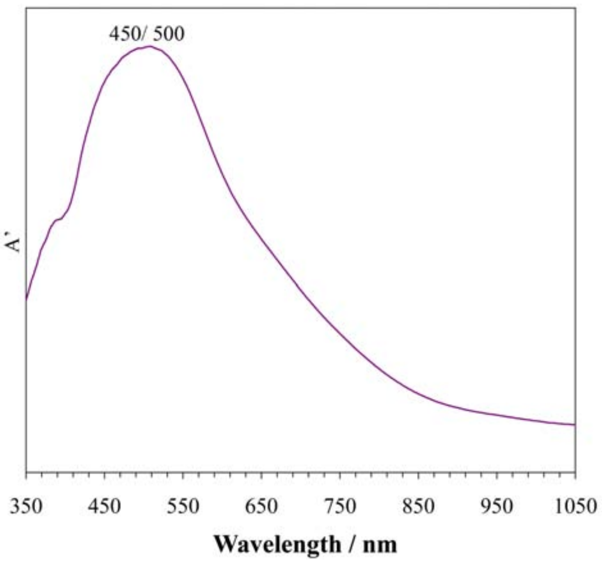


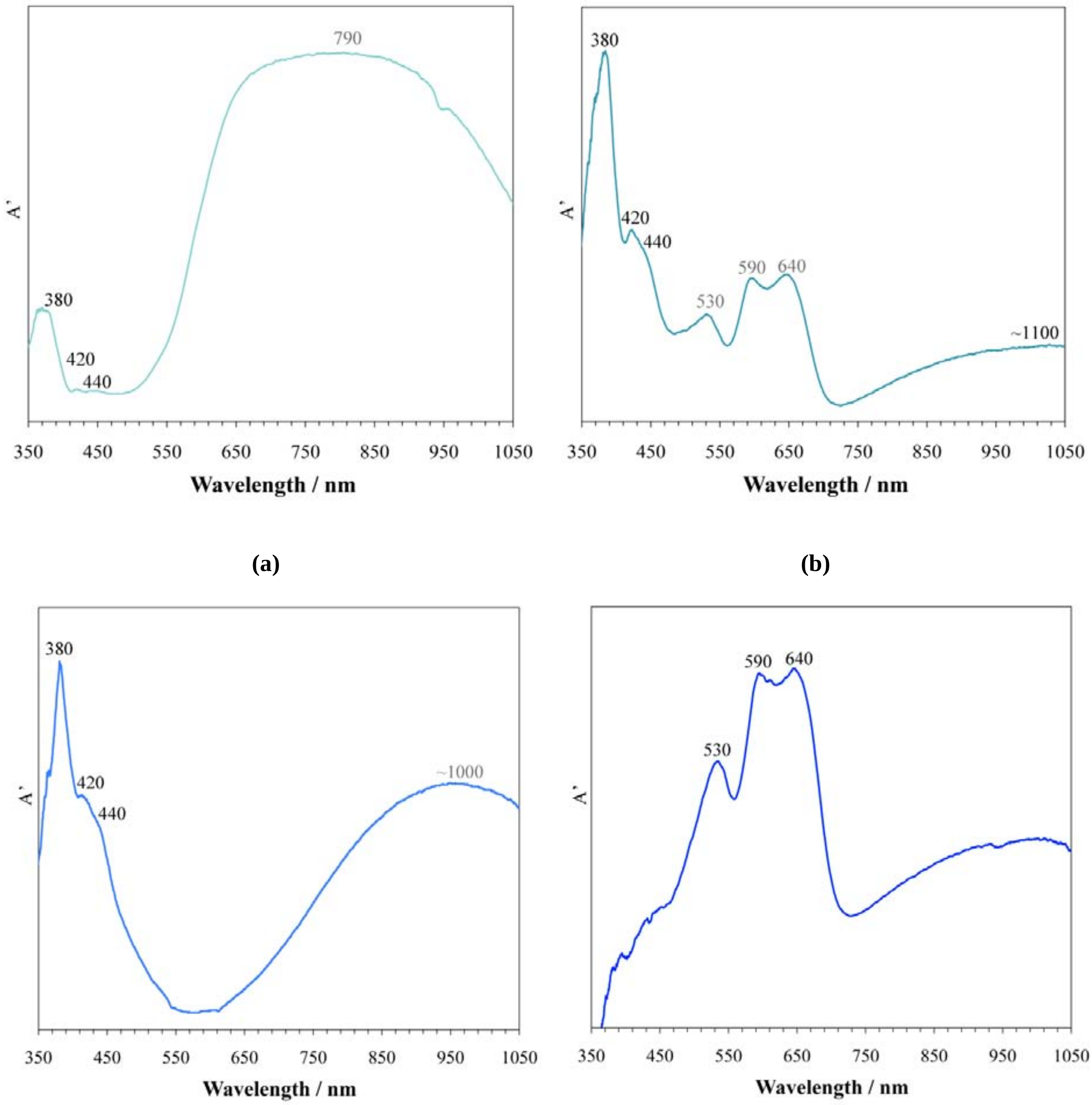
Fig. 4.57: UV-Vis spectrum of fragment SCV-V170 from the SCV set presenting a purple colouration.

Blue glass

Among the blue glass objects it is possible to distinguish between turquoise and blue colours.

The turquoise tonality is present in several fragments, however, two different ways of obtaining this tonality were observed: through the simultaneous presence of iron and copper oxides (figure 4.58 a) and through the simultaneous presence of iron and cobalt oxides (figure 4.58 b). For instance, in fragment SCV-V210 the presence of copper and Fe(III) was identified. On fragment SCV-V335, on the other hand, Fe(III) and Co(II) were identified, and the glass tonality is also turquoise.

The colour blue is present in a darker hue that can be the result of the presence of two different chromophores: iron and cobalt oxides. In the case of fragment SCV-V115, as one can see in figure 4.58 (c), the blue colour is only due to the presence of Fe(II) and some Fe(III). This is also the case with fragment LRA0013 for instance (UV-Vis reflectance spectrum in *Appendix XII, Appendices Part I*). The presence of Co(II) with its intense broad band is visible in figure 4.58 (d) and was identified in fragment SCV-V14 for instance. The blue colour of this fragment is due to the presence of Co(II) in a tetrahedral coordination with its typical d-d absorption band around 600nm that appears split into three sub-bands due to the Jahn-Teller effect (Arletti *et al.*, 2001). The three sub-bands have their absorption at 530, 590 and 640 nm respectively, that correspond to the transitions presented in Table 3.1 (Navarro, 2003, p.457).



(a) **(b)**

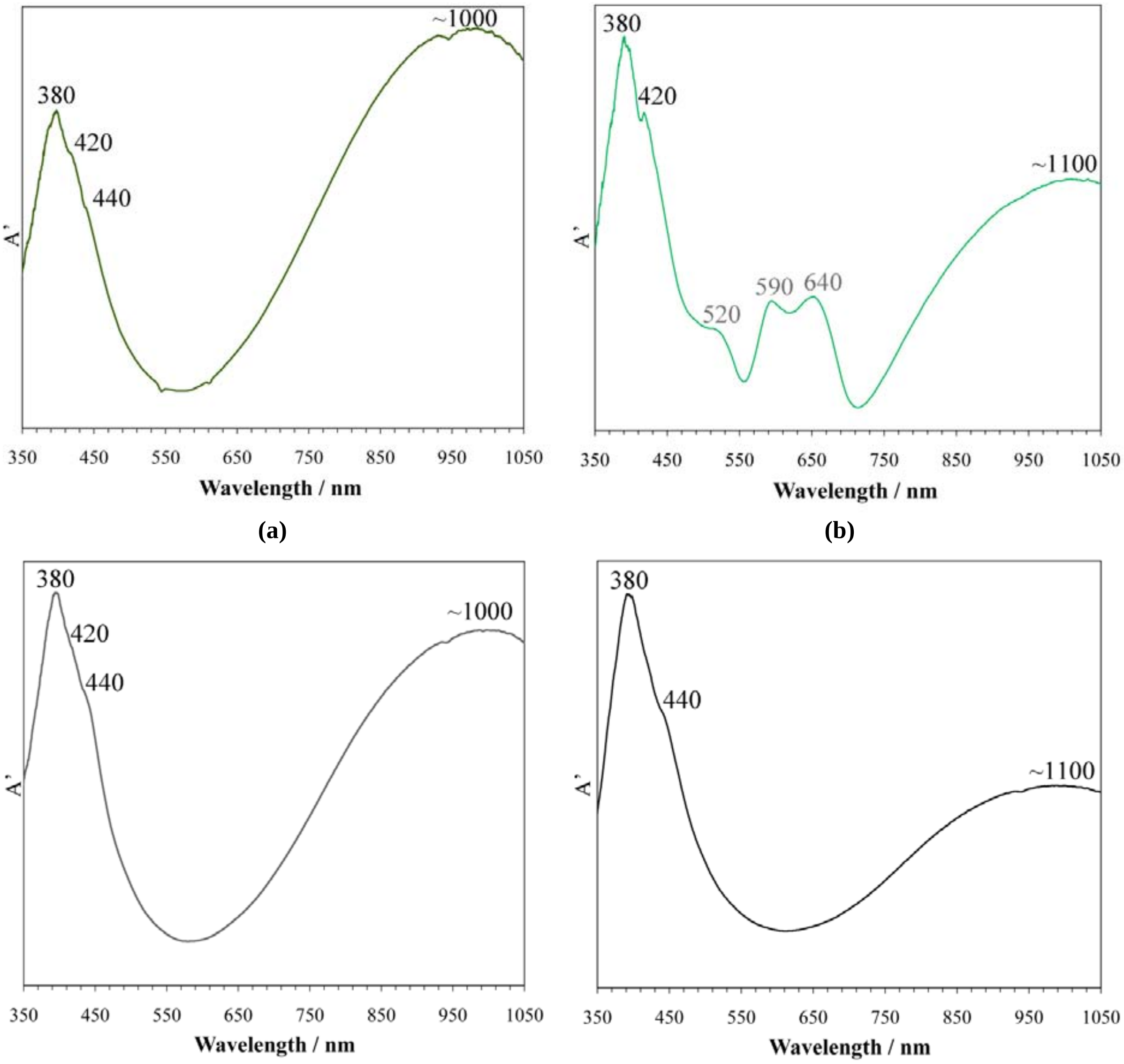
(c) **(d)**

Fig. 4.58: UV-Vis spectra of (a) fragment SCV-V210 from the SCV set, (b) fragment SCV-V335 from the SCV set both presenting a turquoise colouration, (c) fragment SCV-V115 from the SCV set, and (d) fragment SCV-V14 from the SCV set, both presenting a blue colouration.

The presence or absence of bismuth and arsenic are very important indicators that disclose different sources of cobalt available during the medieval and post-medieval periods. In the specific case of fragment SCV-V14, no bismuth was detected but the presence of arsenic, zinc and nickel was observed. This is consistent with the employment of a cobalt ore imported from Schneeberg - Erzgebirge, a mining district in Germany that exported this ore to Europe during the 16th century (Coentro *et al.*, 2012; Gratuze *et al.*, 1996). The trade of *zaffre* (in English, and *zaffera* in Italian; which means calcined cobalt ore) between Germany and Portugal is documented and dates from the beginning of the 16th century (Coentro *et al.*, 2012).

Dark green and black glass

In the assemblages being studied, the dark olive green and black-appearing glass colourations are exclusive to the wine bottles with an HLLA composition (figure 4.59). As was said in *Chapter Two, Part I,* this very dark colouration is attributed to natural causes and results from the use of coal instead of wood as furnace fuel, together with the fact that the crucibles were left open resulting in the increase of the phosphorous and sulphur oxides contents in the glass (Mortimer, 1995). However it is the author belief that this phenomenon is not fully understood.



(a) **(b)**

(c) **(d)**

Fig. 4.59: UV-Vis reflectance spectra of (a) fragment LTR0024 from the LTR set and (b) fragment LRA0072 from the LRA set, both presenting an olive green colouration. UV-Vis reflectance spectra of (c) fragment LRA0091 from the LRA set and (d) fragment LRA0094 from the LRA set, both presenting a black-appearing colouration.

However, this explanation seems unlikely. If one looks to the composition of the wine bottles analysed in this work and compare the contents of P_2O_5 and SO_3 in the glass between the olive green and the black-appearing bottles, it is possible to observe that these values vary a little randomly. It is the opinion of the author that this darkening of the glass is not yet fully understood.

When comparing the UV-Vis reflectance spectra for both olive green and black-appearing glass, it is concluded that both situations owe their tonalities to the presence of Fe(II) and Fe(III) as is observed in figure 4.59 (a), (c) and (d). Among the several bottle fragments studied, only one proved to be different. In the olive green fragment LRA0072 that belongs to a prismatic or case bottle and is dated from the 17th century, one was able to identify not only the presence of Fe(II) and Fe(III), but also of Co(II), as seen in figure 4.59 (b).

It is interesting to note that in the specific case of 19th century black-appearing fragments (LRA0091 and LRA0094), it is possible to observe in figure 4.59 (c) and (d) that the first, presenting a more greenish tonality, has a higher fraction of Fe(II) than LRA0094 which has a more brownish tonality, and has a higher fraction of Fe(III). Since Fe(II) is responsible for the blue hues and Fe(III) is responsible for the yellow tones, this result was expected but it is still very interesting to observe this in practice.

4.6.2 Colourants and opacifiers in enamels

Fig. 4.60: Fragment LTR0014 from the LTR set, decorated with polychrome enamels.

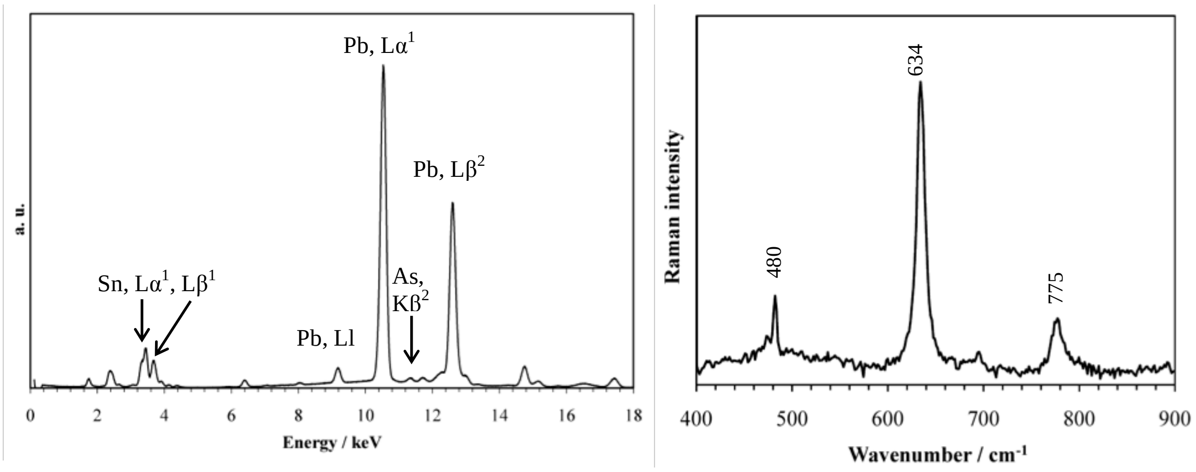
Opacifiers were found to be employed on purpose in enamels used to decorate some glass objects.

Concerning the fragments with enamel decoration, only fragment LTR0014 (figure 4.60) was analysed by means of μ-EDXRF and μ-Raman microscopy. The remaining fragments that had an enamel decoration were not in sufficiently good condition to allow the necessary manipulation for them to be analysed; those fragments were LRA0001, LRA0005 and LRA0182. The analysis performed on fragment LTR0014 was a qualitative evaluation in order to understand the nature of the enamels, and to try and understand the ions responsible for the colours of the enamels. μ-Raman microscopy was used with the intent of complementing the elementary information obtained by the previous analytical technique.

The μ-EDXRF spectra obtained from all the enamels that decorate fragment LTR0014 were compared with the spectrum from the certified glass standard CMOG C (composed by ca. 37 wt% of PbO). From this comparison, the first conclusion one can draw is that these enamels are rich in lead oxide and they all seem to share the same glass matrix, to which chromophores were added depending on the colour desired. The presence of tin was also identified in all the enamels analysed, suggesting that tin oxide was the opacifier employed.

White enamel

Looking to the µ-EDXRF spectrum in figure 4.61 a), the presence of lead and tin is identified. µ-Raman microscopy allowed one to observe the presence of cassiterite (SnO_2) in figure 4.61 b), through its signature bands at 633-775 cm^{-1}, and a less intense peak is at ca. 474 cm^{-1} on the white opaque enamel (Lima *et al.*, 2012; Prinsloo & Colomban, 2008).



(a) **(b)**

Fig. 4.61: Fragment LTR0014 white enamel (a) µ-EDXRF spectrum and (b) µ-Raman spectrum, corresponding to cassiterite, a precipitate of tin dioxide.

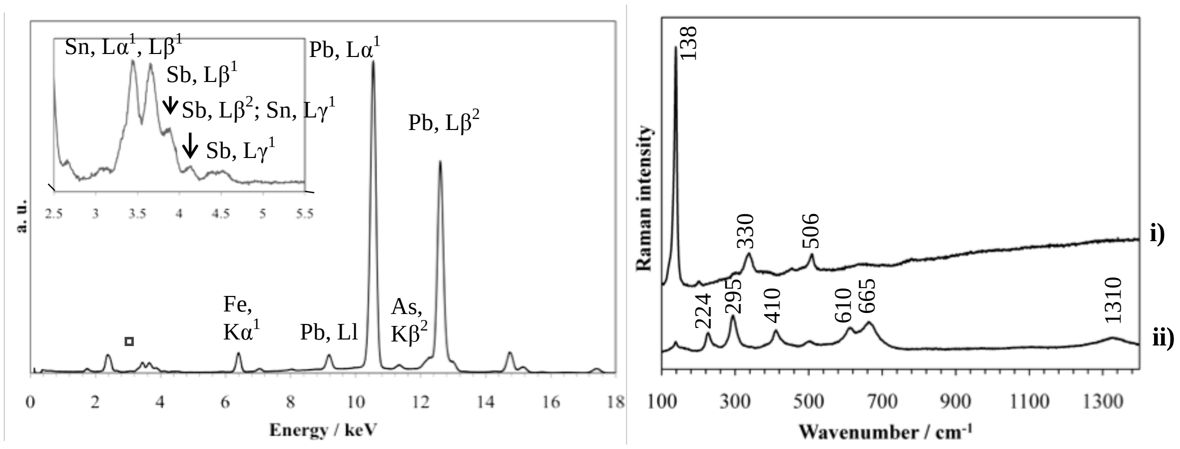
Cassiterite was the typical opacifier used by Venetian glassmakers to create the famous opaque white glass known as *lattimo*. The recipe for this opacifier is mentioned in treatises that go back at least to the 14th century. This opacifier is obtained through the precipitation of tin dioxide – cassiterite – into the glass matrix (Moretti & Hreglich, 2013, p.31). In this way, the cassiterite crystals became dispersed in the glass (Verità, 2013, p.531). Tin calx or lead/tin calx was used to introduce tin into the glass batch. These were obtained by burning tin or a metallic mixture of tin and lead (Moretti & Hreglich, 2013, p.31). Recipe to manufacture this lead/tin calx are described in treatises like L'Arte Vetraria by Antonio Neri (1612), the treatise written by Giovanni Darduin (1644), and the in the recipe book by Gasparo Brunoro (1645) (Moretti, 2012a; 2012b).

Yellow enamel

Looking to the µ-EDXRF analysis of the yellow enamel (figure 4.62 a), it was identified the presence of lead, antimony, and tin, which basically implies that Naples Yellow ($Pb_2Sb_2O_7$ – bindheimite mineral) was the employed pigment. Through this analysis, the presence of iron and arsenic was also detected.

Due to the overlapping of Sn and Sb peaks, the presence of Sb was not clear, and for that reason the μ-Raman analysis was fundamental to clarify the pigment used (figure 4.62 b). Naples Yellow was commonly used throughout Europe to obtain this bright yellow tonality, and the recipes on how to obtain it appear in three important sources: Piccolpasso's treatise, Valerio Mariani's treatise on miniature painting from the 17th century, and in the Darduin manuscript, a recipe book on glass from the 15th century (Coentro *et al.*, 2012). Naples Yellow was identified through the Pb-O lattice vibration at ca. 120-139 cm^{-1}, and the symmetric elongation of SbO_6 octahedra at ca. 510 cm -1 (figure 3.62 b) i) spectrum). The wavenumbers and respective assignments of the compounds found in the analysed enamels by μ-Raman are presented in *Appendix XIV, Appendices Part I.* Several studies on this pigment and its various recipes have already been made, therefore these compositional variations will not be discussed and considered here. In the yellow enamel the presence of haematite mixed with magnetite was also identified (figure 4.62 b) ii) spectrum).

The presence of Naples Yellow with several compositional variants had already been identified in coeval glazed tiles found in Portugal (Coentro *et al.*, 2012).



(a) **(b)**

Fig. 4.62: Fragment LTR0014 yellow enamel (a) μ-EDXRF spectrum and (b) μ-Raman spectra where were identified i) bindheimite (Naples Yellow) and ii) a mixture of haematite and magnetite.

Blue enamel

In the μ-EDXRF analysis (figure 4.63), the presence of lead and tin was identified and attributed to the enamel matrix. Concerning the colourants, the presence of iron and cobalt was identified. The presence of nickel, bismuth and arsenic were also identified which are elements that coexist with cobalt in the mineral added to the glass matrix in order to obtain colour, as has been explained above. The presence of bismuth and arsenic once again point to the employment of a cobalt ore from Schneeberg – Erzgebirge in Germany. In the μ-Raman analysis, the presence of cassiterite used to opacify the enamel was observed, and no Co containing mineral was identified. On the other hand, in the UV-Vis spectrum, it was possible to clearly identify the typical triple band of cobalt (figure 4.64 a).

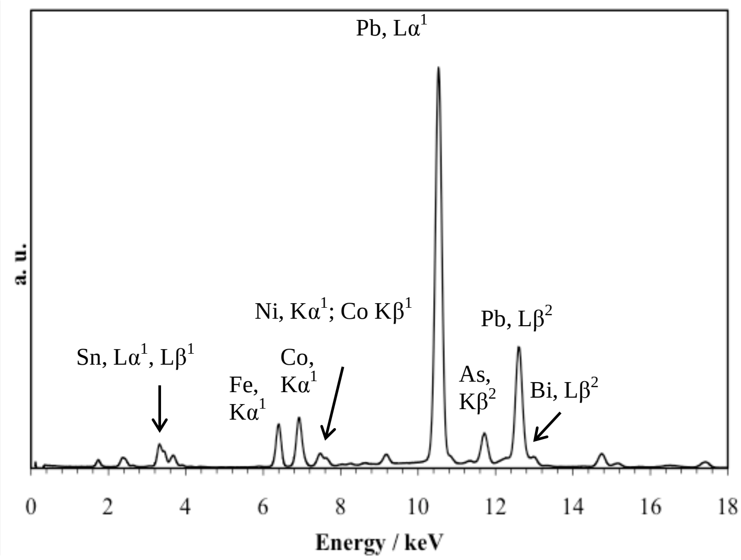
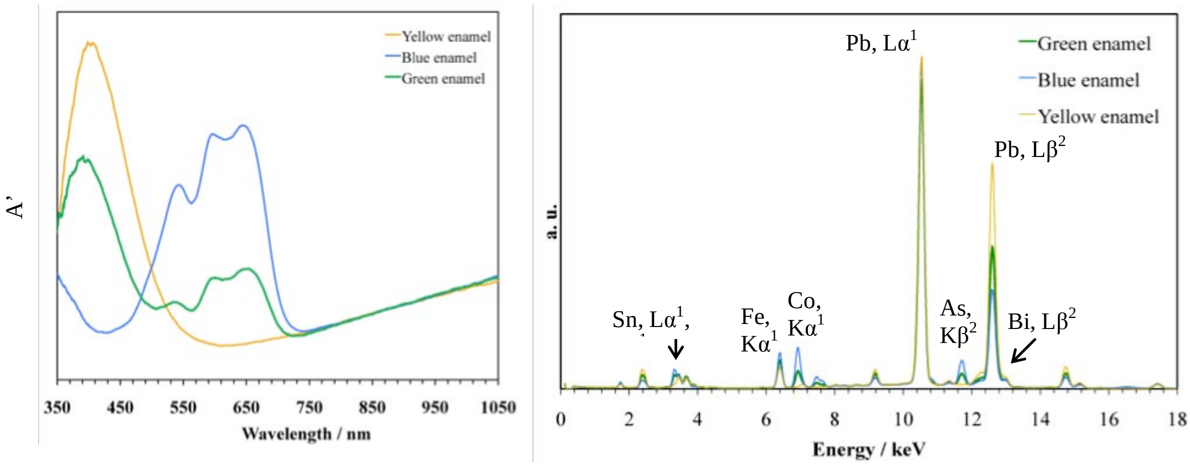


Fig. 4.63: Fragment LTR0014 blue enamel spectrum by μ-EDXRF.

Green enamel

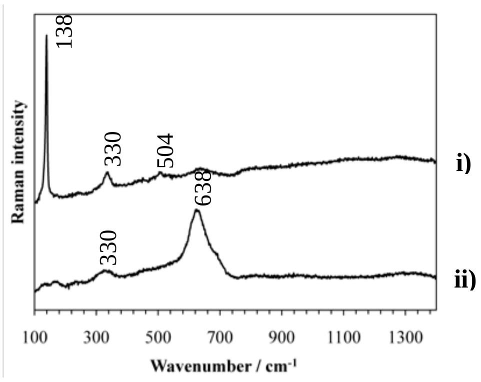
In the UV-Vis spectra of blue, yellow and green enamels (figure 4.64 a), one can see that the green enamel is the exact combination of the blue and yellow enamels. In the yellow enamel, the presence of Fe(III) is observed, and on the blue enamel one can identify the presence of Co(II). Mixing these two enamels together, as can be seen in figure 4.64 a), probably made green enamel. This was also evident on the μ-EDXRF analysis (figure 4.64 b), in which the presence of antimony from the yellow enamel and cobalt and arsenic from the blue enamel were observed.

μ-Raman microscopy allowed one to identify the presence of the typical peaks for bindheimite (figure 4.64 c) i) spectrum) and magnetite (figure 4.64 c) ii) spectrum), that came from the yellow enamel, but from the blue enamel, again no compound was identified.



(a)

(b)

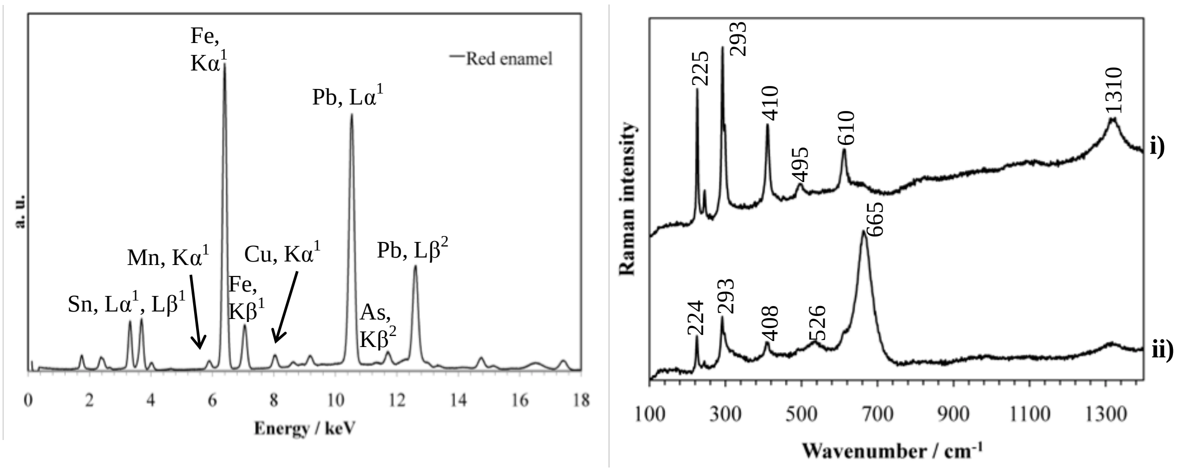


(c)

Fig. 4.64: LTR0014 green enamel (a) UV-Vis spectra of green, blue and yellow enamels; (b) µ-EDXRF spectra of green, blue and yellow enamels and (c) µ-Raman spectra where it was identified i) bindheimite (Naples Yellow) and ii) magnetite.

Red enamel

In the red enamel, the presence of iron and manganese oxides was identified by µ-EDXRF analysis (figure 4.65 a). Comparing these with the other enamels, the intensity of iron and manganese in the red enamel is much greater. A mixture of haematite (α-Fe_2O_3) and magnetite (Fe_3O_4) proved to be responsible for the red colouration in this enamel. In µ-Raman analysis, the typical peaks of these two pigments were identified. In figure 4.65 b) i) spectrum, a clear haematite spectrum with its signature peaks at 220, 295, 410, 495, 610 and 1310 cm^{-1} was observed (Colomban, 2013, p.294). As mentioned above, the wavenumbers and respective assignments of the compounds found in the analysed enamels by µ-Raman are presented in *Appendix XIV, Appendices Part I.*



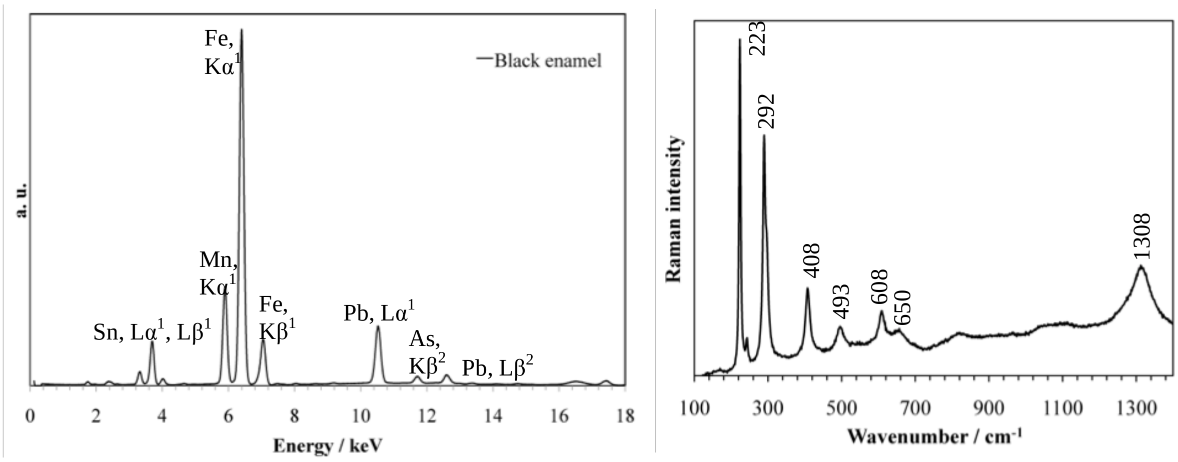
(a) **(b)**

Fig. 4.65: LTR0014 red enamel (a) μ-EDXRF spectrum and (b) μ-Raman spectra where were identified i) haematite and ii) magnetite mixed with haematite.

Black enamel

In the black enamel, by μ-EDXRF analysis, the presence of iron and manganese with intense peaks (figure 4.66 a) was identified. It was not possible to proceed to the analysis of the black and red enamels by UV-Vis reflectance spectroscopy, because of the high levels of noise. The presence of iron and manganese is not so evident in the green, yellow and white enamels, which were probably present in the matrix as contaminants.

Through μ-Raman microscopy, the presence of very dark particles was observed, as well as small red particles. These red particles were identified as haematite (figure 4.66 b), but no manganese mineral was identified.



(a) **(b)**

Fig. 4.66: LTR0014 black enamel (a) μ-EDXRF spectrum and (b) μ-Raman spectrum where the presence of haematite (α-Fe_2O_3) was identified.

4.7 Conclusions

Among the 251 fragments analysed it was concluded that the great majority of fragments (133) dated to the 17th century, were of the soda-rich type, which indicates that the glass circulating in Portugal mainly followed the Mediterranean tradition.

The first set presented in this dissertation concerns the objects dated to the medieval period. Objects belonging to this chronology were only found in the PMF assemblage. It was determined that the glass compositions circulating in national territory follow a Mediterranean tradition, in which ashes from coastal plants (soda-rich ashes) were employed in the glass batch (Coutinho *et al.*, 2016). In general, the chemical composition of the glass is similar among the group, except for the identified outliers (fragments PMF0458 and PMF0470). The main group of glasses is characterised by high contents of alumina and it is generally rich in impurities. From the study of the sources of silica, two major groups were perceptible. These two groups are highly related to one another, and were probably made with silica sources from close geographical locations. Besides the two mentioned outliers, two other outliers were discovered (fragments PMF0438 and PMF0444), where the source of silica employed was significantly richer in titanium oxide. Fragment PMF0458, which belongs to a prunt from a *Kaunstrunk* beaker, has the lowest amount in alumina and titanium oxide, suggesting the employment of a much purer silica source, comparing with the other studied fragments. On the other hand, fragment PMF0470 presents the higher amount in alumina, suggesting the use of a silica source rich in impurities, and probably from feldspatic origin (Coutinho *et al.*, 2016). In the flux study, it was revealed that the great majority of analysed samples is consistent with the careful choice of plant ashes or the treatment of the ash, in order to remove part of its impurities. Two fragments were consistent with the use of ashes richer in impurities. Relating this information with the one obtained from the study of the silica sources, the prunt fragment from a *Kaunstrunk* (PMF0458), was identified as a probable Venetian import with a composition closely related to *vitrum blanchum* (Coutinho *et al.*, 2016). The Venetian production of the *Kaunstrunk*, a typical Central European shape, had been previously proposed. The two fragments of colourless body glass decorated with blue rims and considered of typical Venetian production (PMF0438 and PMF0517) could not be compared with any of the known European glass production centres (Coutinho *et al.*, 2016). With the exception of fragment PMF0458, it is proposed for the remaining fragments to be part of an unknown production centre. Fragments PMF0438, PMF0444 and PMF0470, were the fragments identified as being different in composition, and could have been made in different glass production centres, or could share the same production centre, where different recipes and sources of raw materials were used. It could also represent a chronological difference among fragments.

In the studied sets, genuine Venetian glass objects dated to the 17th century were so far identified only among the Santa Clara-a-Velha Monastery finds (SCV-V191, SCV-V193, SCV-V195 and SCV-V408)

(Coutinho *et al.*, 2016b). As far as the remaining *façon-de-Venise* glass are concerned, the existence of two groups of *façon-de-Venise* glass (mostly the Miguel Fernandes Square, Beja, samples and another group with mostly the samples from the São João de Tarouca Monastery) the composition of which demonstrate an attempt to employ pure raw materials, but present unique features (such as medium and high alumina levels), allowing one to propose the existence of two yet unknown *façon-de-Venise* production centres. These unique characteristics also invalidate the possibility that these objects have been produced in some known *façon-de-Venise* production centre. Could these objects have been produced in Portugal? It is a known fact that Italian glassmakers emigrated to Portugal from the 16th century, which makes this a plausible possibility.

As far as the other soda-rich glass objects are concerned, namely the mould blown decorated ones, it was possible to identify one unique decorative pattern (four-petalled flower enclosed by a lozenge motif) that as far as is known has only been found in glass objects excavated in Portuguese territory. As far as the composition of the fragments with the four-petalled flower motif is concerned, they all present high and very high alumina contents, which makes the possibility of a Portuguese provenance plausible. In terms of the chemical composition, it was also possible to find fragments that, mainly as a result of their very high alumina contents (above 6 wt%), cannot be compared with known production centres. For instance, a set of fragments from the SCV set presents a very similar chemical composition with high alumina content, and for these fragments a national production is proposed, not only because of their chemical composition but also to their uncommon shapes. This leads to the conclusions reached in the section devoted to gourds, where this shape was discussed. The gourd can be considered an inherited influence from the Arabic invasion. This shape can be found in archaeological excavations from northern to southern territories, and again putting together its uncommon shape together with the chemical composition a national production for these objects is proposed.

During the study of the soda-rich glass objects, some fragments with gilded decoration were also identified. During the study and characterisation of these objects, one object caught one’s attention (CPU0032), and was studied more exhaustively (Coutinho *et al.*, 2016c). The results showed that a lead based mordant was used to attach the gold leaf to the glass, and that afterwards the re-heating required to permanently fix the gold the to glass was probably carried out in a muffle, and not in the furnace, as no second pontil mark is visible on the flask. With the use of a lead mordant the object is re-heated at a lower temperature, below the glass softening point. The lead will act as a flux favouring a local softening of the glass surface and therefore no distortion occurs. Although this gilding technique is mentioned in historical treatises, as far as it is known it has never been found before in historical glass objects. As far as the chemical composition of the gold leaf is concerned, a possible Au-Ag alloy estimated between 22 and 23 carats with ca. 1μm in thickness was determined. Also the chemical composition of the gold (in major elements) proved to be in accordance with gold leaf used in Portugal during the 17th and 18th century, in the regions of Coimbra and Aveiro. The gold trace elements allowed to determine that it might have came from both West and Eastern African coasts, both exploited by the Portuguese until mid-17th century (Coutinho *et al.*, 2016c).

The second larger group identified, belongs to the HLLA glass, and this glass type appears for the most part in the assemblages excavated in Lisbon. This glass type appears related only to one object: the wine bottle. Between the two assemblages (LTR and LRA), different bottle shapes were identified and were related to different chronologies. The bottles shapes were divided into three categories according to their shapes: type A for square bottles, type B for globular or onion bottles and type C for cylindrical bottles. It was concluded that among the eighty glass bottles the majority are of type C. This composition was usually employed for bottle production and is in accordance with the data found in the literature. In the bottles dated from 19th century, the composition analysed suggests the employment of synthetic soda in their batch. PCA analysis allowed one to divide the data into four compositional groups (Coutinho *et al.*, n.d., in press). These groups presented cohesive characteristics throughout their compositional analysis. The various compositional groups were compared with HLLA compositions drawn from the literature. Despite the similarity found between the composition of the bottles from the literature and the bottles excavated in Lisbon, the comparison between the major oxides is not enough to attest their provenance. This comparison allows one to suggest provenances or similarities in the raw materials employed, recipes, and also furnace conditions. It was possible to prove the relation between some samples from both archaeological assemblages. No similarity was found with the few examples analysed of bottles from the Coina Glass Manufactory. However other production centres were active in Portugal during the chronological period studied, meaning that some of the studied bottles might come from there (Coutinho *et al.*, n.d., in press).

With regard to the potassium rich objects, this glass type was only found in the two glass assemblages from the Lisbon excavations. These two assemblages are the ones that have a more recent chronology, where the LRA set dates to the 18th century until the beginning of the 19th century. All the potassium-rich samples are made of colourless glass, and most of them are engraved, enamelled or have mould blown decorations. It was possible to verify that the majority of samples analysed can be classified as white glass, and due to their decorative features it is possible to propose that these glass objects are attempts to imitate the glass developed and produced in Bohemia. Comparing the results with published data from known production centres in Central Europe, it was concluded that the majority of samples can be related to the production of potassium rich glass from the Coina Glass Manufactory, and that no genuine Central European glass could be identified.

The compositional type considered next is the mixed alkali that represents only a very small percentage of the samples analysed. Considering the chemical composition of the seven fragments identified with this compositional type, it is possible to conclude that there is not an obvious relation between fragments with the exception of both objects from the CPU set that have a closely related chemical composition. Due to the very low number of samples from this category, the hypothesis is raised that these glass objects were not produced with this composition on purpose.

Finally, considering the lead glass objects, these represent the smallest compositional group with only five fragments. From these fragments only one was not retrieved from Lisbon and belongs to the PMF set. From the point of view of chemical composition, it was possible to conclude that the raw materials employed were very pure. By means of trace elements and REE analysis, it was possible to conclude that both fragments from the LRA set have the same provenance or were manufactured employing the same silica source. From the comparison with data from known production centres, it was possible to conclude that three fragments were related with the production from the Silkstone Factory (England), and the remaining two with the composition from the Groningen Glass House (The Netherlands). No fragment presented any relation with the samples analysed from the Coina Glass Manufactory.

PART II

SIGHT SENSING

CHAPTER 1

INTRODUCTION

Alongside with the study of the glass collections, it is important to assure the preservation of their constituting objects into the future generations. The study and characterisation of such glass assemblages would become obsolete if their preservation was not a concern. In order to preserve and elongate the objects existence it is important to guarantee that glass collections present in museums, whether they are in display or in storage, are conditioned in the best environment and are kept safe from pollutants that can compromise their better preservation.

First studies developed on this matter only paid attention to the effect of strong inorganic acids on glass, like sulphuric and nitric acids. These experiments intended to reproduce and understand the role of the external environment and its pollutants on glass corrosion (Cummings *et al.*, 1998; Romich, 1999). Recent studies concluded that the combination of VOCs with relative humidity fluctuations and unstable glass compositions is critical for the stability of museum glass objects (Fearn *et al.*, 2004; 2006; Robinet *et al.*, 2006; 2009). In recent studies on glass degradation mechanisms due to the presence of VOCs, formic acid was considered the one which has more impact on the kinetic of these mechanisms, being responsible for accelerating and deepening the alkali leaching from glass matrix (Robinet *et al.*, 2006; 2009).

Glass corrosion mechanisms

Processes of glass degradation due to the presence of water or high humidity values are well known as well as the visual alteration and physical damage suffered by this material. In 1770 Lavoisier established that water was the primary degradation agent of glass and in 1931, Laubengager discovered that the glass surface deterioration develops faster in descent way than to its sides (Davinson, 2003, p.174-175). Every time that glass reacts with water or with an aqueous solution, chemical alterations will occur on the glass surface migrating then to its bulk (Clark *et al.*, 1979, p.1).

According to literature there are two main responsible factors that can be determinant to glass alteration: water and glass composition. Glass composition will determine its stability when in contact with water, since the presence of different modifier cations in the silica matrix will result in a different behaviour of this material (Robinet *et al.*, 2009; Romich, 1999). Alkali ions are the most easily leached from the glass silica matrix, since they are the least strongly coordinated to this matrix. The bigger the alkaline ion is, the least strong will be its coordination inside the glass silica matrix. For this reason, a soda-rich glass will be slightly more resistant to corrosion than a potash-rich glass (Robinet *et al.,* 2009; Romich, 1999).

The introduction of alkaline-earth ions in the glass silica matrix will contribute to the resistance of this material to corrosion, since these double charged ions will coordinate with non-bridging oxygens blocking the alkali migration (Robinet *et al.,* 2009).

In presence of high humidity levels, a water film will be formed on the glass surface. Glass will start to absorb this water and the number of glass layers absorbing water will increase with atmospheric relative humidity. The highly modified glass compositions like *cristallo* are characterised by its high contents on alkali and low contents on lime, this combination resulting on a glass with a very good capability of absorbing water contents from the atmosphere (Fearn *et al.*, 2004; 2006). It is also important to notice that when glass absorbs water from atmosphere it also absorbs organic molecules that might be present in it (Robinet *et al.,* 2009).

After a water film is formed on the glass surface, the presence of this water will lead to two different corrosion processes that will be controlled by the solution pH. When the solution pH is lower than 9, the dominant corrosion process is selective leaching, changing to the silica matrix dissolution when the solution pH increases above 9 (Clark *et al.,* 1979, p.2-3; Robinet *et al.* 2009).

The first degradation phase developed at pH below 9, the leaching process, is itself complex and composed by 3 different reactions that occur simultaneously and every reaction has direct influence on all the others, being the final result the glass hydration (Robinet *et al.,* 2009).

Chemical reactions occurring during the degradation process and its detailed description is presented in Appendix I, *Part II*.

Glass corrosion in presence of VOCs

The kinetics from these degradation mechanisms is influenced by volatile organic compounds (VOCs) present in the atmosphere. First studies developed on this matter only paid attention to the effect of strong inorganic acids on glass, like sulphuric and nitric acids (Cummings *et al.,* 1998, pp.858). More recent and developed studies concluded that VOCs combined with relative humidity fluctuations and unstable glass compositions are the ones responsible for glass degradation (Robinet *et al.*, 2006).

The origin of these VOCs has been discussed. It is generally accepted and well known that VOCs present in indoor museum environments are mainly emitted by wood from storage or display cabinets (Robinet *et al.,* 2004).

Wood or wooden composites are known for their characteristic of unleashing VOCs such as formaldehyde, formic acid and acetic acid (Gibson *et al.,* 1997a; Gibson & Watt 2010; Hyttinen *et al.,* 2010; Manninen *et al.,* 2002; Ryhl-svendsen & Glastrup, 2002).

A study developed by Ohta *et al.* allowed to conclude that formic acid can be spontaneous generated on natural silicate rocks (like granite, quartzdiorite or gneiss) in presence of CO_2, light and water (Ohta *et al.,* 2000). With this in mind, Fearn and co-workers extrapolated this conclusion to glass, explaining that the presence of formic acid could be attributed to its spontaneous generation when in contact to CO_2, light and water being catalysed by metallic ions like iron present in glass composition (Fearn *et al.,* 2006).

It is also known that formaldehyde can oxidise originating formic acid. This is a very low process however; it could be accelerated in presence of metals or oxidising agents like ozone or peroxides (Robinet *et al.,* 2004).

Despite the origin of VOCs, it is well known that they can have an armful effect when in contact to glass. Initially, formaldehyde was thought to be the one responsible for glass degradation (Robinet *et al.,* 2004). More recent investigation concluded that organic pollutants present in ambient air including formaldehyde could have beneficial effects on glass preservation by stopping leaching, since they neutralize the hydroxide solution responsible for dissolution of the glass silica matrix (Robinet *et al.,* 2009).

After a review of literature on glass degradation mechanisms due to the presence of VOCs, it was possible to conclude that formic acid was the one responsible for accelerating and deepening the alkali leaching from glass matrix leading to the formation of crystalline sodium formats ($NaHCO_2$) on the glass surface (Robinet *et al.*, 2009).

Glass degradation mechanism in presence of formic acid will, once again, start with formation of a water film on the glass surface. This thin water film will become saturated in the acid with the higher dissociation constant (K_a), or the acid than can dissolve faster. Comparing the K_a values of formic acid with acetic acid, formic acid is the one presenting a higher K_a value, meaning that this acid will dissolve faster than the others and will saturate water. This explains why formic acid is the one affecting glass instead of acetic acid or formaldehyde. The acid will be a H^+ source, accelerating and deepening this way the corrosion mechanisms (Robinet *et al.*, 2009).

Comparing the K_a values of formic (K_a=1.77*10^{-4}) and acetic acid (K_a=1.74*10^{-5}), formic acid presents a higher K_a value, meaning that this acid will dissolve faster than the acetic acid and will saturate the water film.

This degradation mechanism is independent of formic acid concentrations present in indoor environments since the lowest quantity of water will become saturated in this acid no matter how low this quantity is. Robinet *et al.* proposes that there is no minimum value of formic acid bellow which glass corrosion will not occur (Robinet *et al.*, 2009).

In presence of formic acid, the corrosion product formed will be sodium or potassium formats (Robinet *et al.*, 2004; 2006). Potassium format is a highly hygroscopic compound being this way always at liquid form at room temperature. The existence and formation of these deposits on the glass surface implies a reaction from this material with the surrounding environment and consequently changes in its structure (Robinet *et al.*, 2004).

It is possible to identify two different types of sodium formats on the glass surface: sodium format *phase I* and anhydrous sodium formate *phase II*. Robinet *et al.* (2009) concluded that sodium format *phase I* is formed in presence of formaldehyde. This compound results from the reaction between formaldehyde and NaOH present on the glass surface, neutralizing it and stopping glass corrosion. It is recommended not to remove these crystals from the glass surface once they are acting like protective agents (Robinet *et al.*, 2009).

The presence of formic acid leads to the formation of sodium format *phase II*, being this, the main identified phase from this compound among corrosion deposits (Robinet *et al.*, 2004). These formats are formed during the reaction between formic acid and glass itself, leading to an extremely accelerated leaching of alkali ions (in average, leaching reactions are 10 times faster in presence of VOCs in comparison with leaching reactions occurring in an unpolluted environment) (Robinet *et al.*, 2009).

This sodium formate *phase II* will create a deliquescent film on the glass surface, which will maintain the environmental pH bellow 9 (Robinet *et al.*, 2009). In presence of formic acid the second degradation step of the silica matrix dissolution wont take place, being the selective alkali leaching the only degradation process occurring (Robinet *et al.*, 2009).

In conclusion, alkali ions leaching will lead to the disappearance of a non-polymerized structure (non-bridging oxygen) coordinated with metallic ions. With this silica network polymerization, glass will be transformed from a homogeneous diffusion barrier into a silica colloidal aggregate characterised by its heterogeneity and porosity (Robinet *et al.*, 2006). Formic acid, being a source of H^+ ions, will accelerate and enhance this ionic exchange, becoming the second factor (after water) to have in attention when dealing with glass conservation (Robinet *et al.*, 2007; 2009).

The circulating amount of formic acid in museum environments was measured for some museums. Results are summarised in Table 1.1.

Regarding for instance, the values collected for the National Museum of Scotland Islamic cabinets (Gibson *et al.*, 1997a), it becomes obvious the necessity of identifying this VOC and remove any objects susceptible to its action from these cabinets. It is also really important to refer the human factor, since this pollutant can severely affect the human health. The OSHA standard for human exposure is of 10000 µg m^{-3} and it is possible to find in literature values of 500 µg m^{-3} and >1000 µg m^{-3} measured in museum cabinets. Despite the fact that the measured values are below the maximum value recommended for human exposure, this still represents a risk for the conservator's health.

In what concerns the amounts measured for specific types of wood, it was determined that red pine unleashes the lowest amount of formic acid (18 µg/m^{-3}), comparing for instance with yew (187 µg/m^{-3}) and mahogany (171 µg/m^{-3}). These values were obtained after placing these types of wood inside desiccators and measuring the atmosphere after 7 days (Gibson *et al.*, 2010). For this reason, it is also important to evaluate the type of wood when analysing a wooden storage or display cabinet to contain historical glass objects.

Table 1.1: Formic acid vapours concentration measurements performed in museum environments.

Measurement location	*Formic acid measured concentrations/ $\mu g\ m^{-3}$*	*Measuring technique*
Coin collection drawer (Ryhl-Svendsen & Glastrup, 2002)	507.2	Gas chromatography
Pine wood shelf (Ryhl-Svendsen & Glastrup, 2002)	107.3	Gas chromatography
Oak wood plank (Ryhl-Svendsen & Glastrup, 2002)	61.6	Gas chromatography
Royal Museum of Scotland cases (Robinet *et al.*, 2004)	520	Ion chromatography
Leith Costum House cases (Robinet *et al.*, 2004)	366	Ion chromatography
National Museum of Scotland cupboard (Robinet *et al.*, 2009)	416	-
National Museum of Scotland Islamic cabinets (Gibson *et al.*, 1997a)	>1000	Ion chromatography

Sensors development for the presence of VOCs - State of the art

The most common methods to identify the presence of formic acid are usually passive ones, like chromatography, which implies a passive sampling step followed by analysis with expensive equipment. The most employed chromatography methods are the gas chromatography (Ryhl-Svendsen & Glastrup, 2002) and the ion chromatography (Gibson *et al.*, 1997a; Robinet *et al.*, 2004). These types of methodologies are extremely accurate not only identifying present VOCs but also quantifying them (Gibson *et al.*, 1997a; Ryhl-Svendsen & Glastrup, 2002). The sensors developed specifically for formic acid identification have different applications but in all the situations they remain linked to less practical instrumentation in order to determine or identify formic acid (Edwards *et al.*, 2007; Gibson *et al.*, 1997a*;* Sandström *et al.*, 2000; Yan *et al.*, 2012). The development of a low-cost sensor capable of direct identifying in a simple way (without any instrumentation) the presence of formic acid in the atmosphere would be of major importance.

In a general approach, sensors can be divided in two categories: passive and direct identification of the analytes. As referred above, the passive identification is related with a first step of collecting the analyte for further identification through (most commonly) expensive analytical systems as chromatography. Furthermore, since the samples usually have to be sent to a laboratory to be analysed, the time-consuming factor cannot be discarded as a disadvantage. Considering the employed methods for detecting the presence of formic acid under the form of vapour, Edwards *et al.* (1997) describes how ion-exchange chromatography was used to identify and quantify the presence of formic and acetic acids in corrosion products present in lead roofs of historical buildings. Formate and acetate ions are present in lead corrosion products due to the wooden building materials such as the roof supports. These products were separated from the other corrosion products using a borax solution that was further analysed by ion-exchange chromatography (Edwards *et al.*, 2007). An amperometric biosensor for the passive detection of formic acid present in the air was developed by Sandström *et al.*, (2000). In this paper the problematic of continuous exposition of the human being to formic acid is approached. With the intent of developing a specific personal passive “real-time” air sampler to detect formic acid, the enzymatic reaction between this acid and formate dehydrogenase with nicotinamide adenine dinucleotide as a co-factor and Meldola’s blue as mediator, is explored. The biggest limitation of this passive air sampler is the fact that, since it depends on enzymatic reactions, the storage stability proved to decrease by 50% after 1-day in storage (Sandström *et al.*, 2000). A polyaniline-modified quartz crystal microbalance sensor to detect vapours of formic acid was presented by Yan *et al.* (2012). A quartz crystal microbalance (QMC) evaluates the mass variation (per unit area) by measuring the change in frequency of a quartz crystal resonator. This QCM sensor responded effectively to the increasing concentration of formic acid. It was possible to observe a frequency shift since it increased gradually as the concentration of the formic acid gas increased (Yan *et al.*, 2012). Finally, Gibson *et al.* (1997a; 1997b) developed a passive tube sampler (Palmes tubes) to collect formic and acetic acids from the environment for further chromatographic analysis. These tubes use a solution of KOH and glycerol to form complexes with the acids, giving origin to potassium formats or acetates depending on the present acid. The obtained solution is then analysed by means of ion chromatography (Gibson *et al.*, 1997a). It was yet possible to find the report on a specific microbial sensor to detect formic acid in solution. Matsunaga *et al.* (1980) describe the production of a specific sensor consisting on the immobilization of *Clostridium butyricure*, two gas permeable Teflon membranes and fuel cell type electrode, which proved to be suitable for the determination of formic acid in solution through the change in the measured current.

The second type involves the direct detection and identification of the analyte. A discriminating approach for the direct detection of gases has been commonly referred to as “electronic nose” and is proposed in several studies (see for instance Janzen *et al.*, 2006; Suslick *et al.*, 2004; Feng *et al.*, 2010). These devices were developed to imitate the mammal olfaction system and are capable of distinguish amongst VOCs mixtures (Wilson & Baietto, 2009). They have been widely investigated and their fields of application are under continuous development. These electronic aroma detection devices have been used in the fields such as the manufacturing, industrials production and processing. The electronic noses can find applicability for such purposes as quality control and grading, product uniformity, gas leak detection, environmental protection, biomedical diagnoses, food degradation sensing purposes, personnel safety, among several others (Wilson & Baietto, 2009). Their function is based on the response of an array of organic dyes, which implies that the response to a specific analyte is given by a combination of determined dyes. Among the used dyes the acid-base indicators and solvatochromic dyes present a better response to the presence of formic acid (Janzen *et al.*, 2006). Whereas on the first type of dye changes in the absorption/emission spectra are due to a change on the electronic configuration trough coordination to the H+ from formic acid, on the second type differences are due to changes on the polarity of the system.

It is also possible to find some *in situ* devices to analyse and semi-quantify the presence of VOCs, without discriminating the acidic species (as for instance the Draeger tubes®, available information in http://www.draeger.co.uk/, last consulted on May 13th 2013). This is the only direct identification device available, as far as it is known, and has the limitation of not being specific for the detection of formic acid if the measured atmosphere has the presence of other acids, situation that happens in most cases, especially in museum wooden cabinets.

With these principles in mind it is proposed the development of an optical sensor capable of directly identifying the presence of vapours of formic acid in presence of other VOCs.

CHAPTER 2

SENSOR DEVELOPMENT

2.1 Methodology

The methodology used to develop a simple and low-cost sensor for the detection of formic acid vapour was based on the immobilization of chemo-responsive dyes (such as acid-base indicators, solvatochromic dyes, among others) in a thin film matrix and consisted mainly in two steps. In a first step, an adequate responsive dye, capable of selectively reacting when in presence of formic acid under the form of vapour, was chosen. After the dye was chosen, the second step consisted in testing its efficiency in the thin film matrixes. These dyes were then trapped in the matrixes and submitted to several tests in order to choose the most viable dye/matrix combination.

It is important to mention that sometimes these steps did not occur independently. In other words, the choice of matrix and acid-base dye are interconnected and one influences the other. With this in mind, one can say that the obtained sensor will be a combination between the matrix and the dye characteristics.

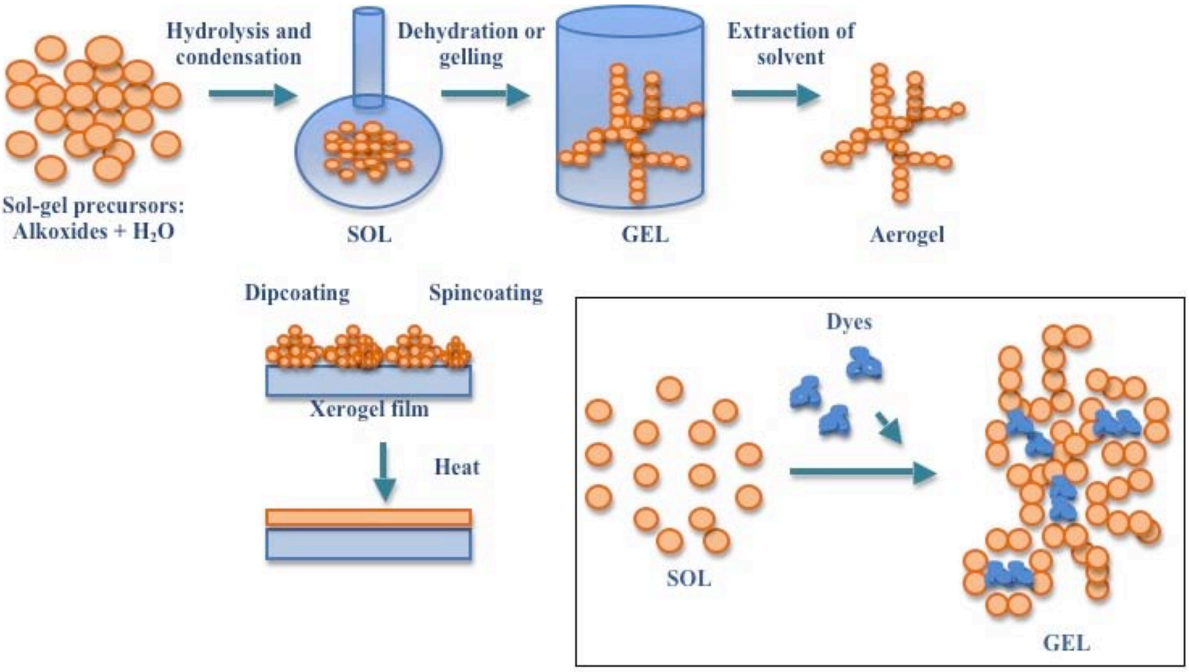
2.1.1 Thin Films

The manufacture and application of thin films is an ancestral technique. If one thinks in the physical manufacture of gold leafs that were beaten until achieve 1 µm of thickness, its thinking in ancestral thin films. Nowadays it is also possible to observe the development of chemical methods to produce thin films (Ohring 2002, pp.xix), which can be deposited in various substrates such as silica glass, metals, plastic and so on, having for this reason numerous applications in several fields (Walters & Parkin, 2009).

Considering the different thin films deposition techniques, some of the most common are the dip coating, spin coating, aerosol assisted chemical vapour deposition, sol-gel, multitarget magnetron sputtering, layer-by-layer (LbL), chemical vapour deposition, among others (Walters & Parkin, 2009). For the development of the proposed sensor two main deposition techniques were used: the sol-gel, using both dip coating and spin coating for deposition in the substrate; and LbL using dip coating for deposition in the substrate. Both sol-gel and LbL techniques will be looked upon in more detail.

2.1.1.1 Sol-Gel thin films

The sol-gel process can be defined by the manufacture of organic-inorganic matrixes through the formation of a colloidal suspension (sol phase) that after dehydration or gelling forms a wet gel (which is a linked solid matrix). After drying this wet gel, a dry gel – monolith of thin film – is obtained (scheme in figure 2.1) (Lev *et al.* 1995).



(a) **(b)**

Fig. 2.1: (a) Simplified scheme of the sol-gel preparation, deposition and heat treatment, followed by (b) the dye encapsulation by the sol-gel matrix.

As presented in figure 2.1, the sol phase is a colloidal suspension of solid particles into a liquid. A colloid is a suspension where the dispersed phase is quite small (between 1 and 1000 nm) and the interactions are dominated by van der Waals attraction, surface charges and other short-range forces (Brinker & Scherer, 1990, p.2). The precursors or starting compounds used to prepare the colloid, consist of a metal or metalloid element surrounded by ligands, such as the alkoxydes, the most used class of precursors in the sol-gel process (Brinker & Scherer, 1990, p.2). The preference for alkoxydes is explained by the fact that they react very fast with water giving place to the hydrolysis step (Brinker

& Scherer, 1990, p.3). When two molecules are hydrolyzed they can link together in a condensation reaction that by definition, is a reaction where a small molecule (of water or alcohol) is released. This condensation reaction will continue, giving origin to larger molecules in a process called polymerization (Brinker & Scherer, 1990, p.4). The gel point occurs in a degree of the reaction where the last bond is formed and the macromolecule is formed (Brinker & Scherer, 1990, p.8). The reactions referred to here are assisted by a catalyst.

The sol-gel process can also be defined as a process that employs highly purified liquid raw materials to obtain glass at room temperature. The highly pure raw materials will generate a pure matrix whose homogeneity can be achieved by the constant agitation of the liquid mixture. In the end of the process, a monolith or a thin film is obtained (Shelby, 2005, pp.269). This process is then an approach to achieve inert inorganic or hybrid organic–inorganic matrices at room temperature that are stable at thermally, chemically and photochemical levels. The sol-gel matrices can be transparent to the UV–Vis radiation, allowing optical measurements, being this parameter sometimes fundamental to the sensor development. These obtained matrixes can trap different organic or inorganic dopants (chromophores) that become enclosed into their microporous structures. This can be done in such a way that the optical properties of chromophores are preserved once trapped into the solid-state gel matrix (Carmona *et al.,* 2008).

Nowadays the sol-gel method can be considered one of the most popular methods to prepare thin films with pH indicators (see for instance Kowada & Ozeki, 2005).

Experimental procedure used for sol gel films

Tetramethoxysilane (TMOS), methyltrimethoxysilane (MTMS) and Trimethoxy(propyl)silane (PTMS) were used as raw materials and sol-gel initiators. The sol-gel initiators were mixed in a 1:2:5 ratio with water and ethanol, and then the selected dyes were added in a proportion of 0.1 mol% to the previous mixture.

The three sol-gel initiators were used by mixing TMOS with the other two in a ratio of x TMOS + (1 - x) MTMS or PTMS were $x = 0$ to 1. Once the solutions were ready and the dyes incorporated, it was left for mixing for two hours at room temperature.

The chosen formulation is based on the work reported by Kowada *et al.* (2006) where no catalysts such as the HCl so common in other sol-gel formulations, were used. Since acid-base dyes are being incorporated in the formulation, the use of an acidic catalyst could interfere with the dyes' pK_a and it would also cause their leaching from the sol-gel matrix (Kowada *et al.,* 2006).

After the mixing step was completed, the thin films were prepared and applied on glass sheets by the spin-coating method. The films were applied at 1000 rpm for 5 seconds. The films were left to dry at room temperature during 24 hrs and then at 50ºC during 1 hrs. The heat treatment was concluded by submitting the films to a temperature of 150ºC for 5 minutes.

2.1.1.2 PEMs thin films assembled trough the LbL method

The layer-by-layer (LbL) self-assembly technique was developed in the 1960s, and its applications suffered a great expasion for the last few years (Ariga *et al.*, 2007, Decher *et al.* 1998). It is considered one of the most simple and adaptable techniques for the formation of thin films, which can be applied in several substrates independently of its nature, size and topology. This technique, based on electrostatic interactions between opposite charges, can be assembled in a substrate by the alternate dipping into solutions (figure 2.2) of different materials such as polyelectrolytes, dyes, proteins, metals and nanoparticles, among others (Ariga *et al.*,2007, Decher *et al.*, 1998, Egawa *et al.*, 2006, Goicoechea *et al.*, 2008, Liu & Cui 2007, Villar *et al.*, 2006). The adsorption of dyes into thin films, due to its inexpensiveness and simplicity, is widely used in the creation of sensors with extensive applications (Ariga *et al.*, 2007).

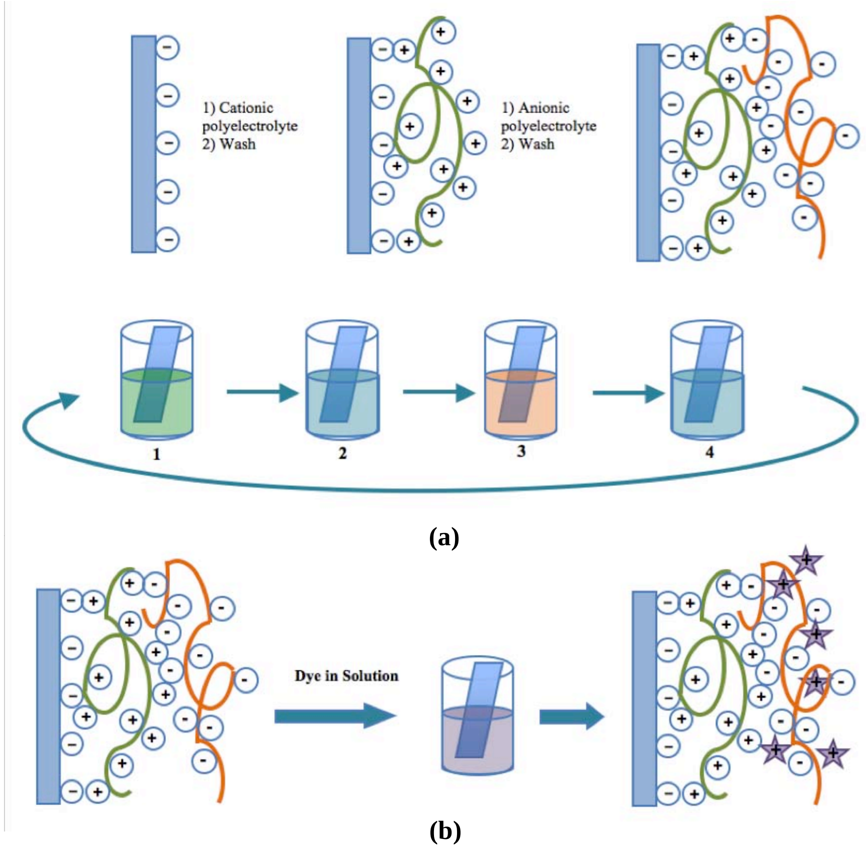


Fig. 2.2: (a) Simplified scheme of the polyelectrolytes alternate deposition, followed by (b) the dye molecules attraction by the polyelectrolytes in the LbL matrix.

The incorporation of several acid-base dyes in LbL systems has been pursued for several applications, such as pH sensing using brilliant yellow with poly(allylamine hydrochloride) (PAH) (Raoufi *et al.*, 2012), and hazardous gases optical sensing with oppositely charged polysaccharides doped with Congo red and bromothymol blue (Yu *et al.*, 2013). Congo red was also used in other LbL matrixes such as PAH, poly(p- phenylenevinylene) (PPV) and poly(sodium-4-styrene sulfonate) (PSS) for different purposes (Cardoso *et al.*, 2012; Dalkiranis *et al.*, 2013; Laureto *et al.*, 2011; Sansiviero *et al.*, 2011).

Also the incorporation of acid-base dyes has been used to study their rate of loading and release from the LbL matrix. Dyes as methylene blue and methyl orange were used in LbL systems as PAH/PAA and PAH, poly(vinyl sulphate) (PVS) or PSS respectively, for further development of drug delivery systems (Chung & Rubner, 2002; Sato *et al.*, 2009).

Considering the film construction on the LbL method, it is important to have in mind that each new layer of polyelectrolyte is highly influenced by the previous layer, more specifically its charge density and morphology. The PEMs characteristics can be easily controlled through changing the degree of ionization of the polyelectrolytes. Weak polyelectrolytes are rather used on the LbL assembly, once through manipulating the pH of their solutions; it is possible to control the interactions between the polyions and the functional groups on the surface (Clark & Hammond, 2000). When both polyelectrolytes are at a neutral pH value, they are highly charged becoming adsorbed on the surface in the form of thin layers. However, when changing the pH values to acidic or basic values, the ionization of one of the polyelectrolytes will increase while the other will decrease, which will originate thick films of the least ionized component (Clark & Hammond, 2000). The substract can also have influence in the multilayer film thickness for (at least) the first 10 to 15 bilayers (Clark & Hammond, 2000), and hence, interactions between its charge and the one from the polyelectrolytes may not be disregarded.

Experimental procedure used for LbL films

Branched poly(ethylenimine) (PEI, MW~25,000), poly(acrylic acid) (PAA, MW~1,250,000), polystyrene sulfonate (PSS, MW~75,000) and poly(4-vinylpyridine) (PPV, MW~60,000) were purchased from Sigma-Aldrich and their chemical structure is given in figure 2.3. Sulphuric acid (H_2SO_4 96% PA-ISO) and hydrogen peroxide (H_2O_2 30% w/v (100 vol.) PA) were purchased from Panreac. The pH of the solutions was adjusted using a 0.1 M and 1M HCl or NaOH solutions.

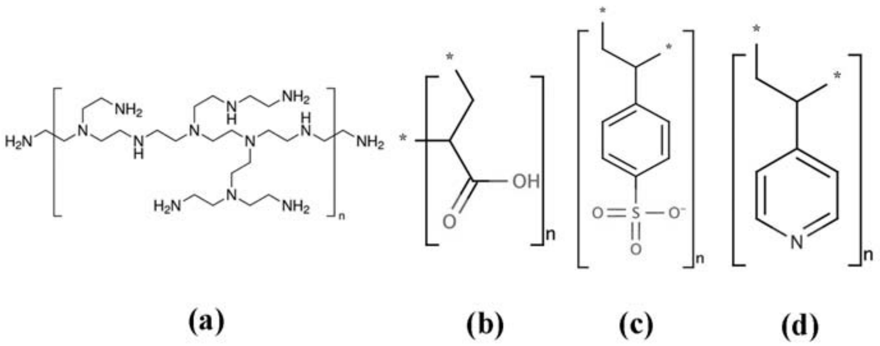


Fig.2.3: Molecular structures of a) poly(ethylenimine), b) poly(acrylic acid), c) polystyrene sulfonate, and d) poly(4-vinylpyridine).

The polyelectrolytes were prepared in aqueous solution with a concentration of 1mg/ml. PEI solution pH was adjusted to 7.5 and PAA solution pH was adjusted to 3.5. The PEI/PAA system was also tested using both solutions with a pH value of 3.5. Two other systems were tested, the PEI/PSS system whose pH values of solutions were corrected to 3.5 and 7.5 respectively and, the PPV/PAA system with solutions at pH values of 7.5 and 3.5 respectively. PEMs films were deposited on float glass sheets. The glass sheets were cleaned through immersion in piranha solution 1:1(v/v) of H_2SO_4 and H_2O_2 during 30 min at 90^oC and then rinsed with distilled water and dried with compressed air.

The PEMs films were assembled by dip-coating (Thermo Scientific Varistain 24-4) through consecutive immersion of samples into the two oppositely charged polyelectrolites during 20 min, until the desired number of bi-layers was formed. Each application layer was followed by three water-rinsing steps (2 min, 1 min, 1min). The number of bi-layers chosen for the present work was 16. The polyelectrolites system used in this work has the number of bilayers indicated, and whenever necessary the pH of the solutions will also be displayed, as an example: $(PEI/PAA)_{16}$.

The films were then immersed in the aqueous solution containing the dissolved dyes for a period of 35 min., which were prepared in a concentration of 2 mg/ml without pH adjustment. No rinsing was done after the dyes adsorption on PEMs films. All films showed good stability and homogeneity.

2.1.2 Chemo responsive dyes

Chemo responsive dyes can be defined as dyes that change colour due to modifications in their chemical environment. These colour changes can occur in both reflected and absorbed light. The dyes that fit in these characteristics are within the classes of Lewis acid/base dyes, Brønsted acidic or basic dyes (e.g., pH indicators), and dyes with large permanent dipoles (e.g., zwitterionic solvatochromic dyes) (Janzen *et al.,* 2006).

The principle of detection is strongly connected with the interaction between molecules and atoms, both from the chemo responsive dye and the analyte. The reactions occurring between the chemical compound one is trying to identify and the chemo responsive dyes can be enumerated as bond formation and coordination, acid-base interactions, hydrogen-bonding, charge-transfer and π-π molecular complexation, dipolar and multipolar interactions, and van der Waals interaction and physical adsorption (Janzen *et al.,* 2006).

When choosing a chemo responsive dye for the identification of a certain analyte it is important to have in consideration certain requirements. First of all it is mandatory that the chosen dye (or dyes) has a centre capable of strongly interact with the analyte (this interaction implies strong chemical relations rather than a simple physical adsorption); secondly this interaction centre must be associated to an intense chromophore (Janzen *et al.*, 2006).

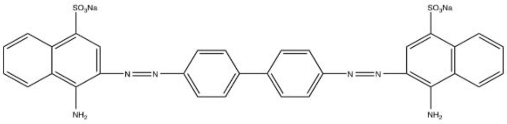
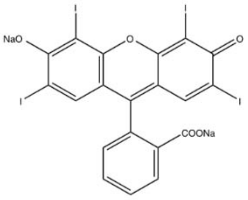
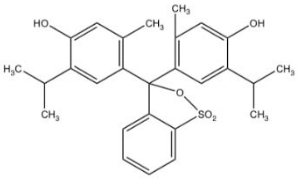
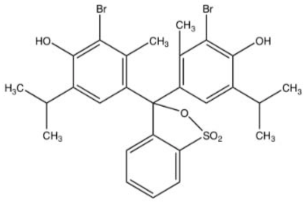
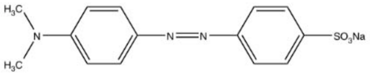
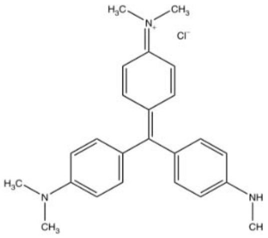
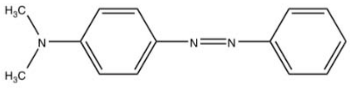
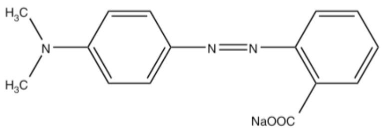
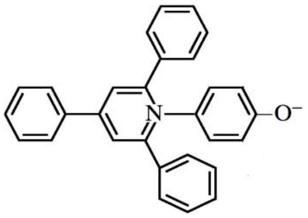
Acid-base indicators and solvatochromic dyes

For the sensor development several acid-base indicators plus one solvatochromic dye were used. The choice of these dyes was connected to the fact that these are very well studied compounds and their characteristics (chemical and physical properties) are well known. In their majority these dyes are also non-toxic to the user. The chosen dyes were Congo red, Erythrosine B, Thymol Blue, Methyl Orange, Methyl violet, Methyl yellow, Methyl red sodium salt and Reichardt’s dye. The chemical structure, λ máx. of absorption, and literature pK_a for each dye is reported in Table 2.1.

The Reichardt’s dye, 2,6-Diphenyl-4-(2,4,6-triphenyl-1-pyridinio)phenolate, or in a simplified way, $C_{41}H_{29}NO$, was used as the solvatochromic dye.

All acid-base indicators plus the Reichardt’s dye were purchased from Sigma-Aldrich.

Table 2.1: Chemical formula and structure of the dyes used for this investigation (Sabnis, 2008).

Chromophore	*Chemical structure*	*λ max. (nm)*	pK_a **in aqueous solution**
Congo red		497, 488, 595	4.1
Erythrosine B		525	4.1
Thymol blue		594, 376, 544, 430	1.65, 8.90
Bromothymol blue		420, 435, 620	7.0, 7.1
Methyl orange		507, 522, 464	3.76, 3.40
Methyl violet		584	0.8 – 1.2
Methyl yellow		408, 256, 508	3.3, 3.4
Methyl red sodium salt		437, 410, 493	2.3, 5.0
Reichardt's dyes		306, 551	

2.1.2.1 Dye pK_a determination in the thin film

The first important step of this investigation was to determine the pK_a value of the chosen acid-base dyes (MV, CR, MR, EB and BTB) when inserted into this new medium – the thin film, in order to understand if they were still reacting in the same pH range. This determination is fundamental since it serves to verify if the acid-base indicator will still be able to detect the presence of the formic acid.

The determination of the pK_a values of the chosen acid-base indicators in the polymeric matrix, was made by dipping the samples with each dye into a range of buffer solutions from pH 0.3 until pH 13, followed by the absorbance measurement. The used solutions were universal buffer solutions of Theorell and Stenhagen (Kunster & Thiel, 1982). The immersion time was ~1.5 min and the optical response was recorded. To obtain the pK_a value the resulting data was treated and analysed through least-squares fittings of the experimental data, using Solver from MS Excel.

The pK_a values of the chosen dyes in aqueous solution were also determined and compared with the respective literature values.

2.1.3 Sensor characterisation

It is very important to characterise the sensor under development in order to understand its potential and its limitations. The sensor evaluated parameters were its specificity to identify formic acid, its photosensibility, its response time in function of the amount of formic acid present in the atmosphere and its reversibility. The reversibility is one of most important capabilities that it is necessary to assure in its functioning. This is not only due to the need of reducing costs that museums are constantly experiencing but also in environmental terms. Recycling and reutilizing are very important characteristics on current materials and despite the interest here to produce a reutilizing product, it is also important to assure that the materials (at least some of them) employed on the sensor are recyclable. This is the case of the used substrate for both tested matrixes: glass.

The concentrations of formic acid measured in museum cabinets are in the order of a few hundred $\mu g/m^3$ so it is important for the developed sensor to be able to detect low atmospheric concentrations of this acid.

The selectivity of the produced sensors was tested with organic compounds unleashed by wood, with common solvents and dairy products used for cleaning purposes and with some inorganic acids. The former group comprised acetic acid, benzoic acid, propionic acid; and the latter hydrochloric acid, nitric acid, sulphuric acid. The common solvents tested were methanol, ethanol, acetone and toluene and the tested cleaning dairy products were commercial lye and commercial glass cleaner liquid. Each glass supporting LbL sensor was submitted to pure vapours of these substances for 1.5 min (in the case of methyl red, a period of one hour was also tested) and, the optical responses recorded by measuring its absorbance.

Further tests involved the determination of selectivity for the remaining three systems (with EB, CR and MR dyes). This was done using formic acid and other organic acids, which are also unleashed from wood such as acetic acid, benzoic acid and propionic acid (Robinet *et al.,* 2006; 2009). The spectral response of the produced systems to the referred acids plus hydrochloric acid, nitric acid and sulphuric acid were recorded after 1.5 min of exposure.

Sensors were exposed to window and room light for a period of 150 days in order to study their photosensitivity. Control samples were kept in the dark. Optical response of the sensors was measured at different periods of time.

The systems containing CR, EB and MR were tested to observe their stability to light. In order to study the behaviour of these systems when exposed to indoor daylight, one system containing each dye was displayed inside laboratory installations, another set was placed in a window and a final set was kept in the dark to serve as reference samples. The sensors spectral response was recorded at every two days for a week and after 5 months exposure.

The reversibility test was performed exposing sensors alternately to the saturated atmosphere of a strong base (ammonia) and a strong acid (hydrochloric acid) for eight cycles using different exposure times. To perform this test, the sensor was placed inside a closed Petri dish with 450 μl of acid and base, alternately and its absorbance was measured.

In order to establish the range of formic acid concentrations in the atmosphere that can be detected by the developed sensor, as well as the required exposure times, a simulation of different atmospheres was performed, in accordance with Gibson *et al.* (2010). Atmospheres of approximately 10, 30, and 100 mg/ m^3 were initially simulated, but a simulation of a fourth atmosphere with a higher formic acid concentration (> 100 mg/ m^3) was further necessary. The $(PEI/PAA/MR)_{16}$ sensors were placed inside each of five 640 cm^3 desiccators. Inside each desiccator five different solutions were placed with the intent of creating the different atmospheres of formic acid. Their composition is presented in Table 2.2. The proposed methodology was to collect a set of two sensors from each desiccator as soon as the first created atmosphere triggered the colour change in a sensor. Each set of two sensors collected from the five desiccators were then analysed though UV-Vis absorbance spectroscopy, in order to evaluate the colour change that has occurred.

The proposed methodology was to collect a set of two sensors from each desiccator as soon as the first created atmosphere triggered the colour change in a sensor. Each set of two sensors collected from the

five desiccators were then analysed though UV-Vis absorbance spectroscopy in order to evaluate the colour change that has occurred.

Table 2.2: Solutions and respective created atmospheres inside 5 desiccators to test the sensors' response.

Solution	*Composition*	*Created atmosphere*
Desiccator 1	50 ml distilled water + 62g Magnesium nitrate (To maintain the environment inside the desiccator with 55% of relative humidity)	No formic acid
Desiccator 2	50 ml distilled water + 62g Magnesium nitrate + 50 µl formic acid	10 mg m^{-3}
Desiccator 3	50 ml distilled water + 62g Magnesium nitrate + 250 µl formic acid	30 mg m^{-3}
Desiccator 4	50 ml distilled water + 62g Magnesium nitrate + 1000 µl formic acid	100 mg m^{-3}
Desiccator 5	50 ml distilled water + 62g Magnesium nitrate + 4000 µl formic acid	> 100 mg m^{-3}

2.1.4 Analytical methods

UV-Vis absorbance spectroscopy

The suitability of the chosen dyes for sensing purposes was determined after their incorporation on the polyelectrolyte multilayer (PEMs) films. Variables such as the pH range of identification (pK_a determination), the selectivity and the photosensitivity were studied.

The sensors properties were determined through the optical response, which was measured by absorption spectroscopy. The UV–Vis absorption spectra were recorded in a Varian-Cary 100 Bio spectrophotometer.

SEM

SEM analysis were preformed in the CENIMAT installations in the FCT NOVA. Cross-section Scanning Electron Microscopy (SEM) observations were carried out using a Carl Zeiss AURIGA CrossBeam (FIB-SEM) workstation.

Scanning electron microscopy (SEM) observations were carried out using a Carl Zeiss AURIGA CrossBeam (FIB-SEM) workstation coupled with energy dispersive X-ray spectroscopy (EDS). The materials have been previously coated with an Ir conductive film for avoiding charge effects.

2.2 Results and Discussion

2.2.1 Matrix selection

Sol-Gel

In figure 2.4 the best results in terms of colour presence and homogeneity are presented. The films obtained with erythrosine B and Thymol blue presented very homogeneous films and fair intense colourations. The remaining dyes (methyl violet, methyl yellow and Congo red) originated heterogeneous films) Methyl violet was the formulation with the most intense coloration, despite the film heterogeneity. The other tested compositions of the film did not allow the dye to incorporate, probably because of inadequate pore size.

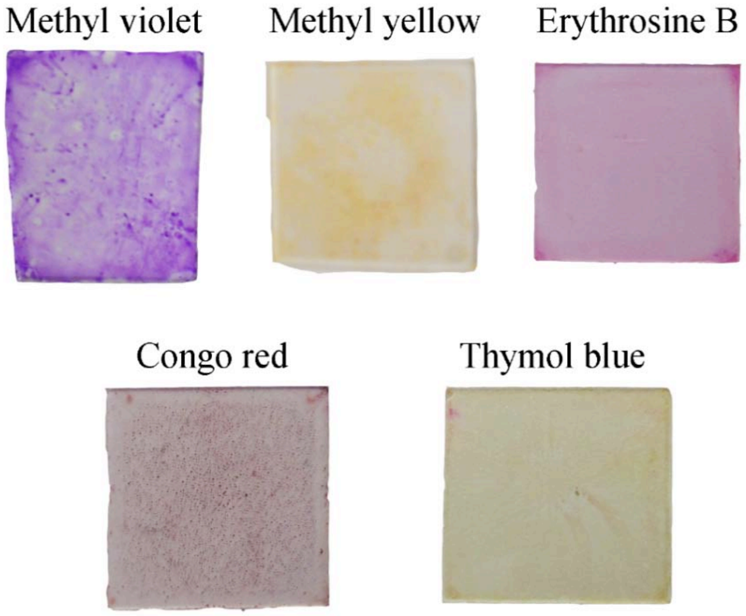


Fig. 2.4: Obtained sol-gel thin films for the tested dyes. Methyl violet, Methyl yellow and Erythrosine B were in a matrix of 0.5 MTMS + 0.5 TMOS. Congo red was in a matrix of 0.8 TMOS + 0.2 MTMS and Thymol blue was in a matrix of 0.8 + 0.2 PTMS. All dyes were in a concentration of 1%.

However when the sol-gel obtained sensors were submitted to the presence of pure formic acid vapours independently of the trapped dye and of the sol-gel composition, the reaction time took several minutes. This might be due to the matrix structure, mainly the pore size. The pores size and shape can foreclose the formic acid vapours to reach the dye molecules; or, the shape and the size of the pores may disable the alterations in the dye molecule that would allow its colour shifting. For this reason, another matrix was tested. In a similar study, 2.5 wt% of erythrosin B was entrapped in a tetraethoxylane (TEOS) film matrix and the authors have considered that its response time (in the range of minutes) was inappropriate and with further need of improvement (Montero *et al.*, 2008).

Layer-by-Layer

The values of the chosen dyes in aqueous solution and in the LbL $(PEI/PAA)_{16}$ matrix were determined and are presented in Table 2.3. It is possible to observe a pK_a shift to lower values of the acid-base indicators when these are incorporated in polymeric matrix comparing with the respective pK_a value in aqueous solution. This phenomenon could be explained by the interaction between the polymeric matrix and the dyes; the observed decrease in the pK_a value is justified by the stabilization of the basic form of the dye. The charge that is associated to each dye will interact with the polymeric matrix. The exception on this behaviour was the BTB dye which kept a similar pK_a value when inserted in the PEMs film making it not suitable for identifying the presence of acidic species. This fact might be due to a poor interaction established between polyelectrolytes in the matrix and the molecule dye under our conditions. With pK_a values in the acidic range the remaining acid-base indicators were considered suitable to detect acidic species when inserted in the polymeric matrix. The pK_a shift was already expected and it is important to emphasize that the pK_a value of a PEMs film is only valid for that film on those exact conditions and if for instance the number of bilayers or the dye concentration is changed so will shift the pK_a system value (Raoufi *et al.*, 2012).

Table 2.3: Measured (in acid-neutral range) and literature pK_a values of the chosen dyes in aqueous solution and in LbL $(PEI/PAA)_{16}$ matrix.

	MV	*CR*	*MR*	*EB*	*BTB*
$(pK_a)_{\text{literature in aq. sol. (Sabnis, 2008)}}$	0.8 – 1.2	4.1	5.0	4.1	7.1
$(pK_a)_{\text{aq. sol.}}$	0.61	4.05	5.53	4.04	7.27
$(pK_a)_{\text{LbL}}$	< 1	1.95	0.90	2.50	7.14

The sensor containing MV was the second to be excluded based on the fact that when incorporated in the polymeric matrix it cannot hold the colour change whenever submitted to an acidic vapour. This fact prevents carrying out the measurements at the rate at which the colours switches.

During the performance of this experiment it was possible to observe that for some pH values a dye release from the PEMs films occurred. The leaching of dyes from the PEMs films when immersed in buffer solutions is related to the fact that weak polyelectrolytes such as PEI and PAA when submitted to different pH environments tend to change easily the degree of ionization (Chung & Rubner, 2002).

In order to evaluate the response of MR when incorporated in other polymeric matrices, three more systems were tested. $(PEI/PAA)_{16}$ system with solutions adjusted to pH 3.5 each, a $(PPV/PAA)_{16}$ system and finally a $(PEI/PSS)_{16}$ system.

In case of the $(PEI/PAA)_{16}$ system using both solutions with a pH value of 3.5, the system assembly with the MR dye was apparently and to the naked eye very similar to the one with different pH values (7.5 and 3.5 respectively) but when this sensor was immersed in a buffer solution and despite the solution pH value, leaching was observed. This fact can be justified by the weak coordination between the MR dye and the PEMs system. At these pH values the $(PEI/PAA)_{16}$ system probably has less available functional groups to coordinate with the dye once whenever the polyelectrolytes solutions pH is altered the system properties such as the multilayers thickness, the degree of layers interpenetration and the number of available functional groups will be affected (Chung & Rubner, 2002).

The $(PPV/PAA)_{16}$ system was tested using the solutions at a pH value of 7.5 and 3.5 respectively. In this case the adsorption of the dye into the PEMs film was not done on an effective way and, in consequence the colour of the system was almost imperceptible. This sensor was not used for further testing.

The $(PEI/PSS)_{16}$ system was tested using solutions with correct pH values to 3.5 and 7.5 respectively. Observing the final obtained system with the naked eye the colour is vivid but not so bright compared with $(PEI/PAA)_{16}$ system. In the spectra presented in (figure 2.5) it is possible to observe that despite the difference on absorbance intensity there is no band shift when the sensor is submitted to a basic, neutral or acidic solution what makes it not proper to sensing purposes. From what was described above, none of these systems showed a better performance than the system $(PEI/PAA)_{16}$ with the solutions pH corrected to 7.5 and 3.5 respectively.

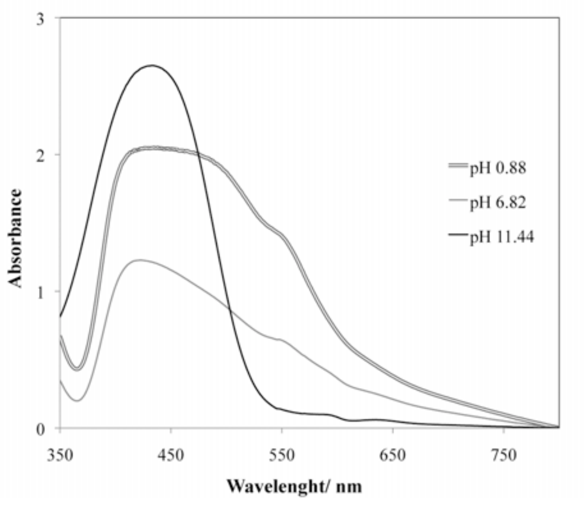
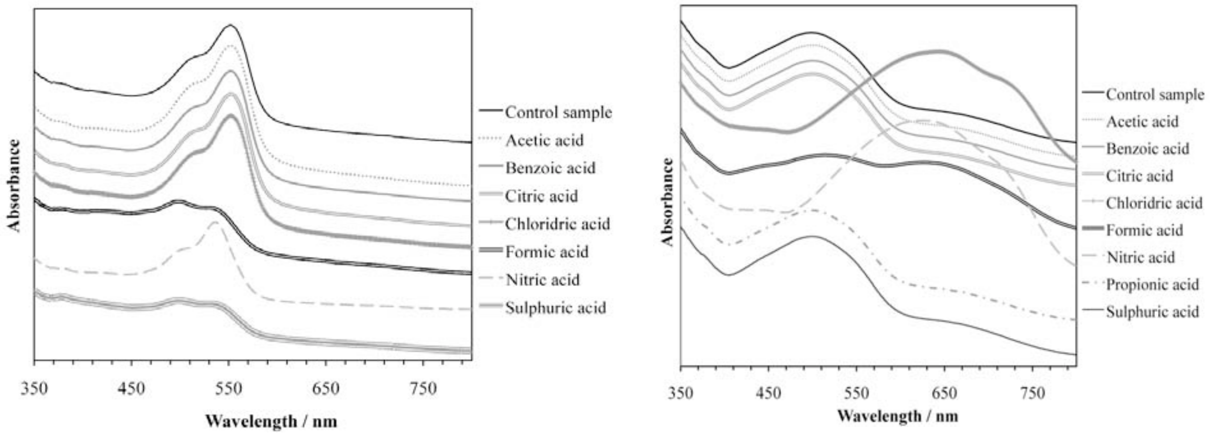


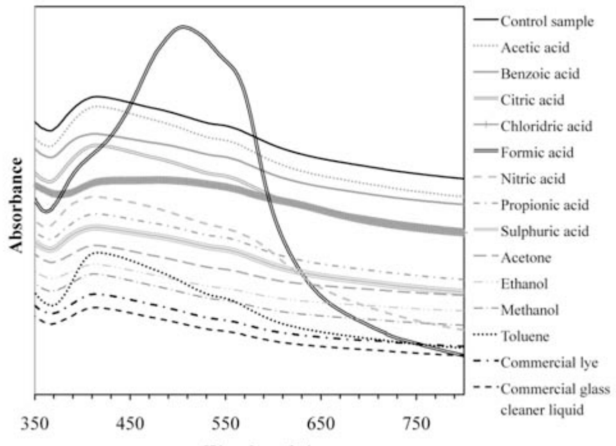
Fig. 2.5: Spectral evolution of MR in $(PEI/PSS)_{16}$ system when submitted to buffer solution with different pH values.

Sensibility to VOCs

The sensors built with EB and CR acid-base indicators both react to the presence of hydrochloric, nitric and formic acids showing no response to the presence of acetic, benzoic, citric, sulphuric or propionic acids (figure 2.6 (a) and (b). The third dye, the MR acid-base indicator in the polymeric matrix reacted only to hydrochloric and formic acids (figure 2.6 (c) on the 1.5 min exposure and further testing showed that only after 1 hour it reacted to nitric acid (pure vapour). When these systems were submitted to formic acid vapours, the one produced with EB showed no change on the shape or shift of the absorbance bands, but a significant decrease was observed in their intensity. The system with CR suffered a change in colour on the presence of formic acid; however, the absorbance bands observed are completely different from the typical bands of the CR acidic form, which appeared in presence of nitric or hydrochloric acids (figure 2.6 (b). According to these results, MR incorporated in the PEMs film was considered the most promising system to selectively detect formic acid and for further sensing purposes. This system was also tested in presence of acetone, ethanol, methanol, toluene, commercial lye and commercial glass cleaner liquid (figure 2.6 (c). The PEI/PAA/MR system did not react to any of these substances.



(a) (b)



(c)

Fig. 2.6: Absorbance spectra of a) PEI/PAA/EB, b) PEI/PAA/CR when submitted to 1.5 min of exposition to saturated vapours of acetic acid, benzoic acid, citric acid, chloridric acid, formic acid, nitric acid, propionic acid and sulphuric acid and (c) PEI/PAA/MR when submitted to 1.5 min of exposition to saturated vapours of acetic acid, benzoic acid,citric acid, chloridric acid, formic acid, nitric acid, propionic acid, sulphuric acid, acetone, ethanol, commercial lye, methanol, toluene and commercial glass cleaner liquid.

Photosensitivity tests

In figure 2.7 are presented the absorbance spectra obtained for each dye before and after two, four, seven days and finally five months of exposure. Observing the UV-Vis absorbance spectra for all the tested systems one can conclude that they all suffer photodegradation, which was already expected when dealing with organic dyes. The system with MR seems the most affected by light exposure, since when comparing the absorbance intensity of the control sample with the sample exposed for a period of 5 months; it is the one with the greater loss of intensity. However, considering that this sensor is the one presenting the most intense colouration *a priori*, and even after 5 months exposure this sensor is the one visually presenting a more intense colouration. EB after the five months exposure presents a tenuous colouration, being almost discoloured to the naked eye. The CR system doesn't appear to change in the first seven days of light exposure, however, after five months it presents a reduced loss of intensity. Since this CR system presented a faded colour a priori, this loss of intensity, regardless of how small, made the film almost totally discoloured.

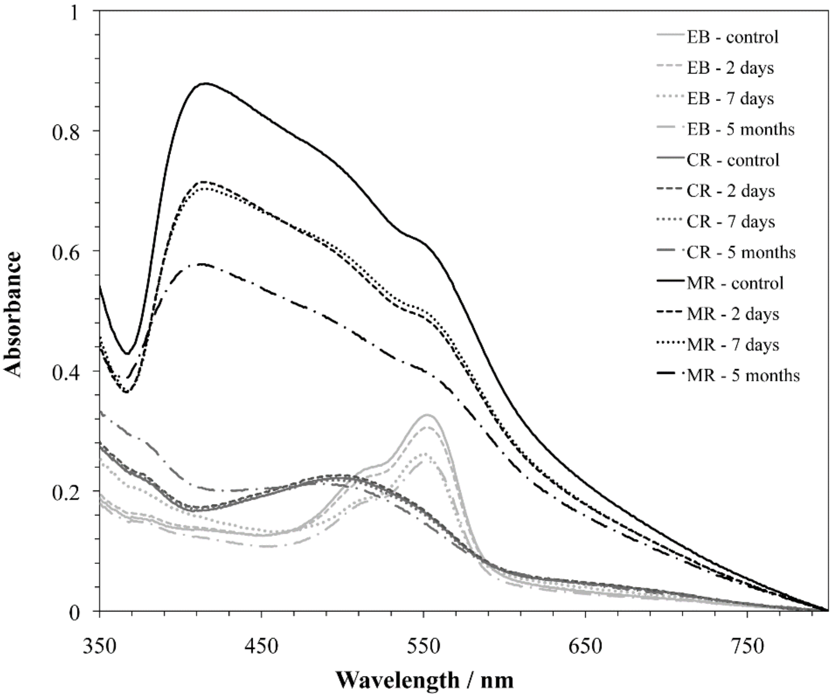


Fig. 2.7: Absorbance spectra of PEI/PAA/EB, PEI/PAA/CR and PEI/PAA/MR before and after 2, 4, 7 days and 5 months of indoor light exposure.

2.2.2 Characterisation of PEI/PAA/MR system

Methyl red is a commonly used indicator on acid-basic titrations whose acidic form presents a strong red colour and the basic form presents a yellow colour (figure 2.8).

The basic form of MR in aqueous solution is present at around 427 nm and it is possible to observe the disappearance of this basic species and the appearance of the acidic form with two peaks at around 505 nm and 544 nm, allowing to determine a *pKa* of 5.0, in accordance with published data (Sabnis, 2008).

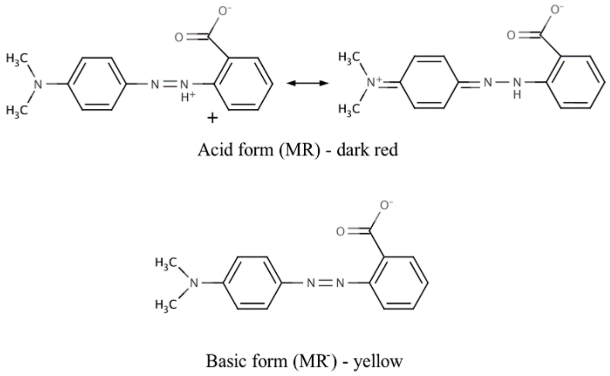


Fig. 2.8: Acid and basic form of MR dye.

In order to optimise the number of used bilayers, a spectroscopic study accompanied with a SEM visualisation of a crescent number of bilayers (from 2 to 20) was performed. In figure 2.9 it is possible to observe the absorbance on film with the increasing number of bi-layers. SEM observation confirmed this, as it is possible to see in figure 2.10, together with the image of each produced sensor.

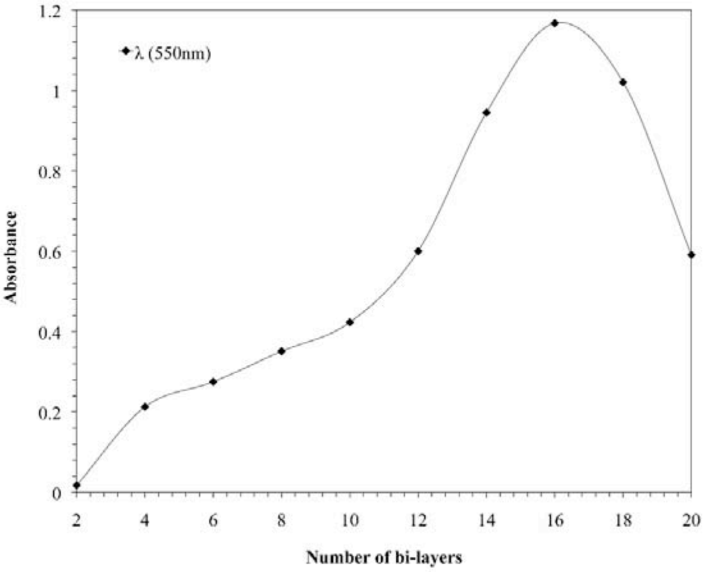


Fig. 2.9: Absorbance value of PEI/PAA/MR at 550 nm when the number of layers is increased from 2 to 20.

In figure 2.9, a direct relation between the number of layers and the film thickness up to the 16th bilayer is observed. After the 16th bilayer, a noteworthy decreasing of colour is perceptible, which is associated with film degradation. Film degradation that occurs after the 16th bilayer can be explained both by a charge density effect in the film that causes a destabilisation in the film construction, more specifically in the following bilayers, and by the absence of charge effect of the substrate. Reminding what was described in 2.1.1 (PEMs thin films assembled through the LbL method), each new layer of polyelectrolyte is highly influenced by the previous layer (Clark & Hammond, 2000), and the destabilisation effect will probably result in a weaker polyelectrolytes aggregation, which by its turn, can lead to a film expansion and consequent film thickening observed at the 16th bilayer. From this point onwards, the film construction (18 and 20 bilayers) suffers disintegration and a resultant diminishing of the measured film intensity (figure 2.9). In order to keep a good homogeneity and intensity in sensor colouration, it was decided to use the maximum number of bilayers (16) just before film disintegration on the film assembly.

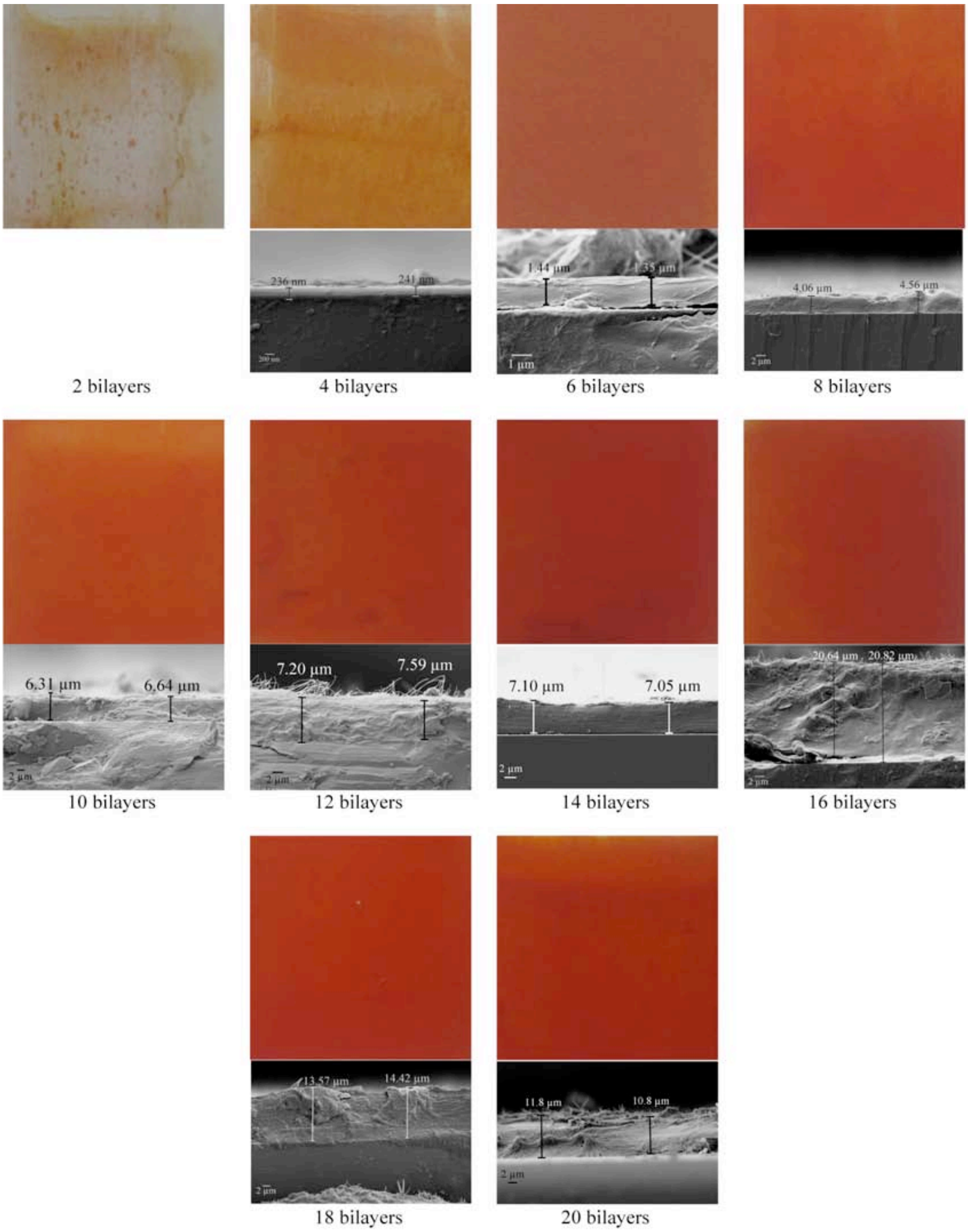

2 bilayers
4 bilayers
6 bilayers
8 bilayers
10 bilayers
12 bilayers
14 bilayers
16 bilayers
18 bilayers
20 bilayers

Fig. 2.10: Picture of the PEI/PAA/MR system with the respective cross-section SEM image from 2 to 20 layers.

When incorporated on the PEMs film the dye assumes an orange colour (see figure 2.11), which might be an indication that the deprotonated (basic) form can be present simultaneously with the acid form influencing in this way the final colouration of the sensor.

The spectrum of MR when incorporated into the polymeric matrix by comparison with spectra of acid and basic forms in aqueous solution is presented in figure 2.11. In fact, two components on the MR spectrum in the polymeric matrix are observed which can be assigned to the basic and acid forms of the indicator with the greater component belonging to the basic form. The wavelength at maximum absorbance for the $(PEI/PAA)_{16}$ with adsorbed MR system appears at 425nm for the basic form and at 555nm for the acid form.

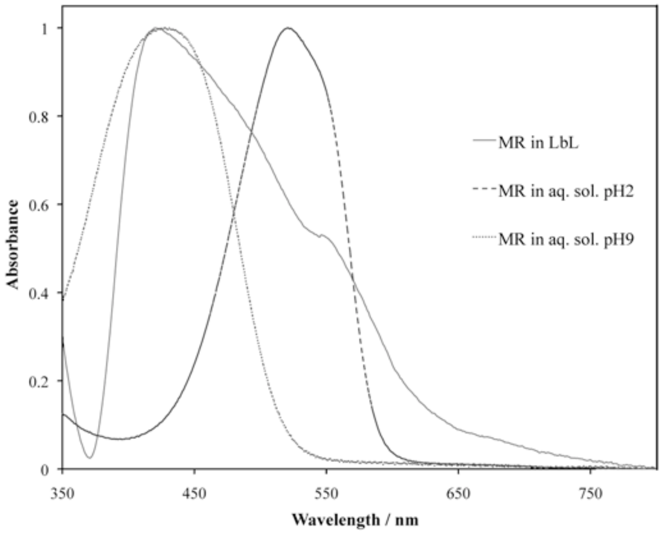


Fig. 2.11: Absorbance spectra of the MR sensor (dye in PEMs $(PEI/PAA)_{16}$ with MR system) compared with the MR dye in aqueous solution when submitted to pH2 and pH9 buffer solutions (normalised spectrum).

The determination of the pK_a value for the MR indicator incorporated in the film can also give an indication about the behavior of the MR indicator when incorporated in the polymeric matrix and hence, on the sensor performance. The response of the system to several buffer solutions with different pH values is presented in figure 2.12.

Above pH 8 a dye releasing from the system is observed. MR is an anionic dye and is connected to the $(PEI/PAA)_{16}$ system mainly by electrostatic forces. Dye releasing from PEMs films is accelerated in environments with higher ionic strength due to the shield effect, where the ionic interactions between the MR dye and the PEMs films are shielded (Sato *et al.*, 2009).

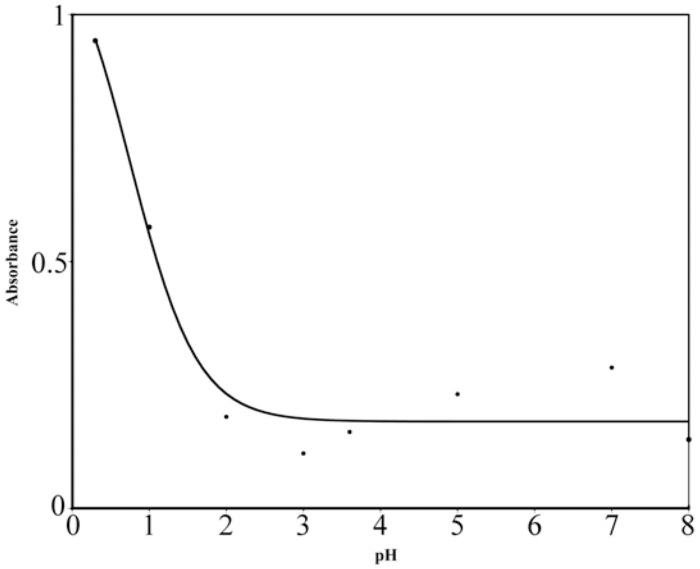


Fig. 2.12: Spectral evolution of MR sensor when submitted to buffer solutions with different pH values. Absorbance measured at 520nm.

The fitting curve suggests a *pK_a* value around 1. By comparison with *pK_a* in aqueous solution (see Table 2.2) there is a shift to lower values, which can be associated, as explained before, to a stabilisation of the basic form of the dye when inserted in the polymeric matrix, fact that is in agreement with the previous results. The stabilisation of the basic form is probably due to the interaction of the carboxilate groups in deprotonated MR with the amine functional groups of PEI polyelectrolyte in the PEMs film. On the other hand, with two charges, the acidic form might offer greater difficulty on its stabilization inside the polyelectrolyte charge network. With such low value of *pK_a* the sensor will in principle be able to detect acids with lower *pK_a* when compared with that of formic acid. The faster response obtained for the formic acid, when compared with other compounds, can be related with factors such as the vapour pressure, the dimension of the molecules or the molecular interactions with the polymers in the matrix, allowing a more efficient penetration into the layers. Both HCl and HNO_3 have higher vapour pressures than the one for formic acid at the same temperature (40, 57 and 212 mmHg at 25 ^{o}C, for formic, nitric and hydrochloric acids, respectively) (Lide, 1991/92). The higher efficiency observed on the detection of formic acid can be attributed to the size of the molecule and the capacity to establish hydrogen bonds with the functional groups of the polyelectrolytes. In this way the penetration into the film and impregnation of it with formic acid would be more efficient.

Some authors (Goicoechea *et al.*, 2008) reported that the absorbance of the dye incorporated into the PEMs film could be affected by the swelling effect, which is caused by pH fluctuations. These variations in thickness and roughness happen in some cases due to changes in the ionization degree of the weakest polyelectrolyte since its charge densities are pH-dependent. When the solution pH is altered, the degree of ionization of the weakest polyelectrolyte suffers some changes resulting on a swelling/ deswelling effect that can be translated in practice on a refractive index alteration (Choi & Rubner, 2005; Goicoechea *et al.,* 2008). One of the reported problems was the sensor's response becoming masked by the polymeric matrix swelling effect. For that reason the spectral response of the sensor's polymeric matrix under development (PEI/PAA)$_{16}$ to different pH values (pH 2-8) was observed by absorption spectroscopy.

The PEMs films produced in this experiment containing no indicator were submitted to different pH buffer solutions and its absorbance was measured as a blank control. It was possible to observe the described effect on the (PEI/PAA)$_{16}$ matrix (figure 2.13).

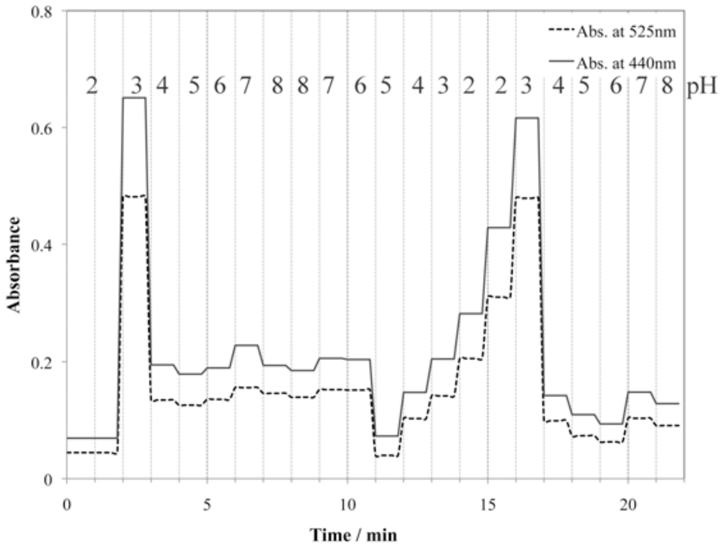


Fig. 2.13: Spectral response of (PEI/PAA)$_{16}$ system when submited to 3 cycles of immersion in buffer solutions with different pH values. Absorbance mesured at 525nm and 440nm.

A substantial increment on the absorbance value obtained for the PEMs film is observed at pH 3. However, the observed swelling effect does not interfere with MR system function and reading. This conclusion is based on the fact that this matrix did not have a masking effect of the MR dye. In other words, the characteristic absorbance bands of MR in the polymeric matrix are still present and very well defined when incorporated in this polymeric matrix as one can see when comparing figure 2.11 with figure 2.14. Since MR at pH 3 (basic form) will coordinate preferentially with PEI, this will probably result in polymeric matrix stabilization. The dye will probably diminish the polymeric chains free movements reducing this way the swelling effect of the system (Goicoechea *et al.*, 2008).

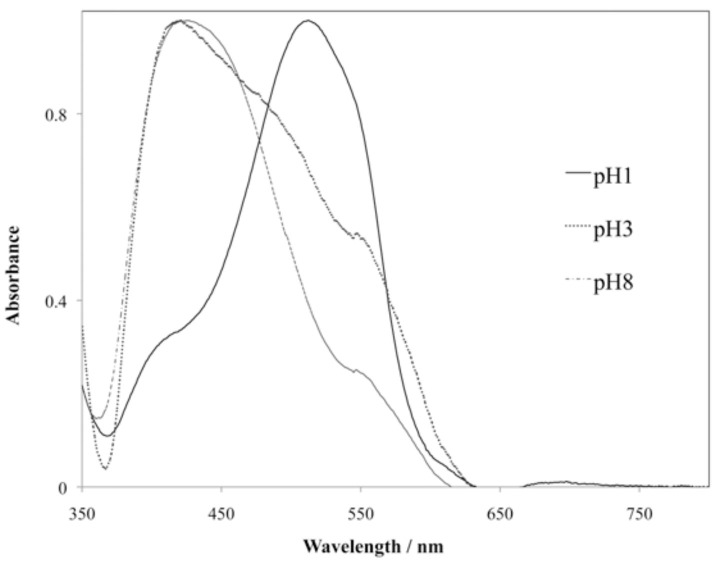


Fig. 2.14: Absorbance spectra of the MR sensor (dye in PEMs PEI/PAA/MR system) when submitted to basic and acid buffer solutions.

Reversibility tests

The performance of the sensor was also evaluated through its reversibility. The sensor was alternatively submitted to saturated atmospheres of pure ammonia and pure HCl for different periods of time. Regarding the obtained chart (figure 2.15) it is possible to conclude that the $(PEI/PAA)_{16}$ with adsorbed MR system is stable, reversible and reusable for at least eight cycles maintaining the same colour intensity until the last performed cycle. It is also possible to observe that a complete sensor's reversibility is time dependent. During cycle six the sensor was exposed for only a few seconds to the saturated atmosphere of the strong base, which resulted on a non-complete change of the dye from its acid form to its basic form. On the other cycles the sensor was exposed to saturated atmospheres for time periods of at least one minute, being the maximum exposure time of 4.5 minutes.

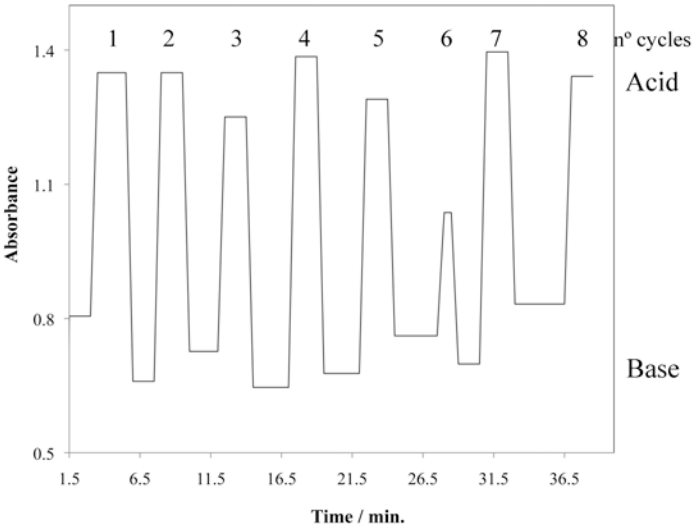


Fig. 2.15: Reversible behaviour of MR sensor when submitted to a strong acid and a strong base alternatively. Absorbance measured at 427nm.

Detection and Response time

Visible changes in the colour of the sensors were observed for the higher formic acid concentration after 43 days of exposure. After this exposure time, the sensors placed inside the desiccator with the higher formic acid concentration, changed significantly their colour but no visible changes were obtained for the remaining formic acid concentrations, 10, 30 and 100 mg m^{-3}. In figure 2.16, the pictures taken before and after the exposure to four different acid formic atmospheres during 43 days is presented. It is possible to observe the same bright orange colouration in all sensors, except in the sensors taken from the desiccator 5 after 43 days, which reacted to the presence of this VOC and changed its colour to a dark reddish colour. Figure 2.17 a) has the representation of the absorbance spectra for the sensors before the exposure, and figure 2.17 b) has the representation of the absorbance spectra for the sensors after the 43 days exposure. Once again, it is possible to confirm the reaction of this PEMs film to the atmosphere created in desiccator 5.

In the context in which this sensor was developed, 40 days of needed exposure time to trigger the sensor to respond can be considered acceptable on the overall scale of time. The glass corrosion mechanisms take several years to develop and even in the presence of formic acid, despite being faster that only with water, the glass will take several years to be in a severe degradation situation. Nevertheless, the only value detected by the sensor during this exposure period is considerably above those values of formic acid determined for certain museums that are in the order of μg m^{-3} (see table 1.1 in *Chapter 1, Part II*), and this may constitute a limiting factor in the sensor performance for the proposed goal. In the present circumstances, the sensor will be able to detect concentrations in the range of mg m^{-3} whereas detection values in the order of μg m^{-3} are needed and would be more appropriated. Further work will be needed in order to determine if the detection of lower values of formic acid in atmosphere in association with non compromising exposure times, considering the scale of time of the processes involved on glass degradation, is possible.

The developed sensor is being tested in situ, in the glass storage cabinets in the Museo Nacional de Arte Antiga, Lisbon. The storage cabinets are made of wood, and for this reason they were considered ideal to test the sensors. After 1 month of exposure to the wooden storage cabinets, the sensors did not show any signs of changing its colour. The cabinets of this museum are made of pine wood that unleashes very low amounts of formic acid (Gibson *et al.*, 2010). It is also important to mention the fact that the doors of the wooden cabinets are kept open in order to allow a good air circulation. With the air circulating, the accumulation of formic acid inside the cabinets is less probable and thus the concentration of formic acid can be very low. However, the presence of the sensor inside the cabinets will allow one to monitor any change occurring in the cabinet’s environment, giving the chance to the conservator of being aware of any critical situation and consequently to practice informed preventive conservation.

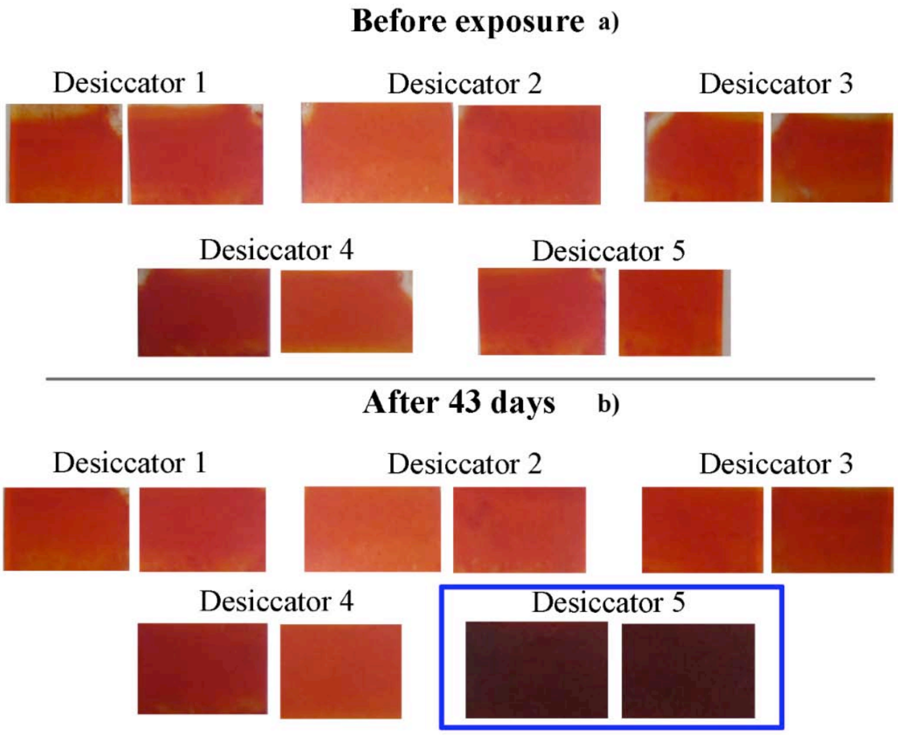
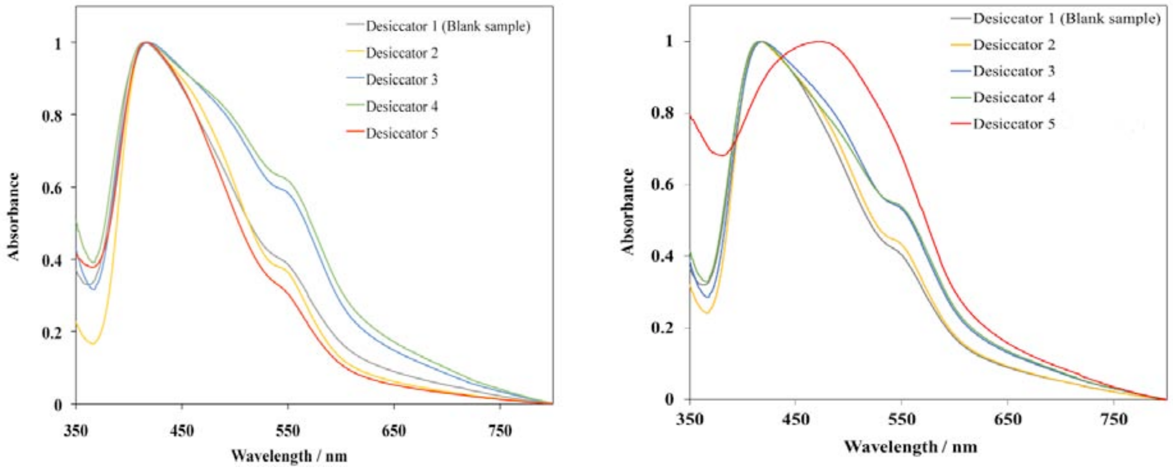


Fig. 2.16: Visual information (photographies) of the several sensors placed inside the desiccators before their exposure (a) and after its 43 days exposure (b). In a blue rectangle appear the sensors that changed its colours after 43 days exposure to the atmosphere created in desiccator 5.



(a) **(b)**

Fig. 2.17: Absorbance spectra of a) sensors before the exposure to the desiccators' atmospheres and b) sensors after the exposure to the desiccators' atmospheres, where the sensors exposed to the atmosphere in desiccator 5 show a clear change of colour. Each spectrum is the average of measurements in three different sensors, and all spectra were normalised.

2.3 Conclusions

Five acid-base indicators, BTB, MV, EB, CR and MR were successfully adsorbed in an LbL matrix of PEI/PAA at pH values of 7.5 and 3.5 respectively. $(PEI/PAA)_{16}$(pH 7.5/3.5) matrix showed good film homogeneity with all the tested dyes and after 30min adsorption via dye diffusion process all the systems had enough dye to be perceptible and vivid to the naked eye.

With the purpose of further develop an optical sensor for the detection of indoor formic acid vapours all the dyes adsorbed in $(PEI/PAA)_{16}$(pH 7.5/ 3.5) matrix were characterised and the first approach was the determination of the pK_a values for each dye in the LbL matrix. It was possible to conclude that pK_a value for all the dyes tended to drop with the exception of BTB that remains almost the same when compared with its pK_a in aqueous solution, being for this reason excluded from the following tests. Also MV dye was excluded because once its adsorbed in $(PEI/PAA)_{16}$ it cannot hold the colour change whenever submitted to an acidic vapour, preventing the carrying out of measurements at the rate at which the colours switches.

Following tests evaluated the sensibility of the remaining dyes (MR, EB, CR) adsorbed in $(PEI/PAA)_{16}$ to several acids (pure vapours), where it was possible to determine that $(PEI/PAA)_{16}$ with MR was the one reacting to less substances in the same exposure time (hydrochloric and formic acids) and to nitric acid after 1 hour exposure.

The light stability of MR, CR and EB in $(PEI/PAA)_{16}$ was evaluated being the MR dye the less susceptible to photodegradation.

Being MR the most promissory dye it was tested in other LbL matrices ($(PEI/PSS)_{16}$ assembled at pH 3.5/7.5, $(PPV/PAA)_{16}$ assembled at pH 7.3/3.5, and $(PEI/PAA)_{16}$ assembled at pH 3.5/3.5), however, the best tested matrix was $(PEI/PAA)_{16}$ assembled at pH 7.5/3.5.

Swelling effect of $(PEI/PAA)_{16}$(pH 7.3/3.5) was evaluated in order to determine if it would mask the MR reaction to acidic species which was not verified. The reversibility of this system with MR was also verified for at least eight cycles.

$(PEI/PAA)_{16}$ (pH 7.3/3.5) with adsorbed MR showed good and promising results for further application as optical sensor for gaseous formic acid.

The developed sensor is able to detect formic acid concentration present in the atmosphere in the range of mg m^{-3} during an exposure time that can be considered acceptable on the scale of time of the processes involved on glass degradation. The simulated atmospheres are however considerably above the ones typically present in museums, which have presented issues on glass preservation.

Future work will be needed to assess exposure times required to detect lower concentrations and thus determine whether the sensor is suitable for use in the preventive conservation of glassware exposed in museums.

Final remarks and future work

The results presented in this thesis are the outcome of a multidisciplinary investigation that began with the study of historical data about glass production from the 17th and 18th centuries. This study had in mind the aesthetic taste and the influences it suffered through times, the importing and exporting tendencies from certain production locations, and the raw materials employed in its manufacture. If in some regions the production of glass is thoroughly studied (*e.g.* Murano glass production), the knowledge on glass production in Portugal during the early modern period and how was it related with the glass production in Europe, remains vague. The study on historical background allowed one to conclude that the production of glass in Portugal existed, and during certain periods of time it was considered of good quality and comparable (in terms of quality) to glass produced in other European production centres. With this in mind, several representative glass objects were selected from available archaeological assemblages excavated in the Portuguese territory, in order to be studied from the formal and chemical points of view. The main purpose of this investigation was the study of the raw materials employed in the glass manufacture, and finally, the attribution of a probable provenance to the objects being studied. Since no furnaces were so far excavated in the Portuguese territory in order to provide production remains to be analysed, to accomplish these goals, it was fundamental to characterise the types of glass, chemically speaking, circulating in Portuguese territory. This information allowed one to speculate about the most probable glass types being produced in Portugal, and also to discuss on the most probable employed raw materials. This information allowed also one to propose certain European regions from where Portugal imported glass. Another important aspect proposed in this work, was the identification of unique compositional and stylistic features capable of characterising the glass objects produced in Portugal, and distinguish it from glass objects produced in other European centres.

In this archaeometric investigation, the chemical composition of more than 200 archaeological glass fragments was obtained through analytical techniques such as μ-PIXE and LA-ICP-MS. The obtained results were treated employing statistical methods, which helped on the extraction of the maximum information contained in these data. The archaeometric approach was applied with the final intent of identifying the raw materials used in the glass production, and attributing a provenance to as many objects as possible. As a consequence of this study, it was possible to propose some trading relations between Portugal and other European regions. The aspect of the trading relations is considered of high importance, in order to understand the society's economical aspects and its social and political operating systems (Tykot 2004, pp.407).

The research in the literature allowed one to take notice of several documents attesting the quantity and quality of the glass production in Portugal, in such a way that led kings to forbid the income of foreigner glass. On the other hand, it was also possible to become aware of other documents (mainly from foreigner people visiting Portugal) that say otherwise. In these documents it is said that the glass production in Portugal was almost inexistent and of poor quality. It is important to notice that the countries of origin of these foreigners had commercial or trading interests with Portugal, making one wonder if these statements were to be trusted or were mere played policies.

As far as the glass assemblages being studied are concerned, the first conclusion is that a considerably high number of glass objects circulated in the Portuguese territory between the 17th and the 18th centuries. A soda-rich glass type composes the great majority of these assemblages.

The glass assemblages being studied here came from different social origins (monasteries, palaces and middle class houses), which allowed one to observe if the glass used among these ambiences was related or if the social and financial status were translated in the objects owned by them.

Looking to the assemblages selected to be part of this study, the Santa Clara-a-Velha monastery set was identified as the one being composed with the most prized objects. Within this assemblage, several *façon-de-Venise* objects were identified, as well as several decorative techniques including the gilding decoration. This assemblage is followed in richness by the São João de Tarouca monastery set, the other assemblage belonging to a clergy environment. In this set, one can also find *façon-de-Venise* objects, however more utilitarian glass is identified. The two monastic assemblages show how luxury items surrounded the clergy, thereby contradicting all their ideals of renunciation to mundane goods. It also shows that this social class was the one with a broader access to the goods entering in Portuguese territory. These two monasteries, one female (Santa Clara-a-Velha monastery) and one male (São João de Tarouca monastery), belong to two different religious orders; it was possible to find some glass objects from both these assemblages which are related in chemical composition, meaning that these two monasteries probably had a common glass production location from where objects were bought.

From Praça Miguel Fernandes assemblage, some *façon-de-Venise* objects were also identified, however it is possible to understand that the objects have a more utilitarian nature. This glass set provided the unique opportunity of analysing glass objects from the medieval period, since this excavation involved contexts dated from the 14th to the 17th centuries.

In what regards the assemblage from the Coimbra University courtyard, it is mainly composed by utilitarian objects such as oil-lamps and small flasks; however a remarkable object was identified: a globular flask with gilded decoration that was submitted to a broader investigation and discussed in this thesis.

Finally, from the two excavations situated in Lisbon (Museu do Teatro Romano and Rua do Arsenal), the unearthed material was mainly composed by wine bottles, which can be more recently dated. These two glass assemblages are richer in utilitarian objects present in diverse compositional types.

As far as the chemical composition of the six sets being studied is concerned, one of the main conclusions achieved in this investigation was that the glass type circulating in Portuguese territory (either produced here or imported) and dated to between the 14th and 17th centuries, was of a soda-rich composition, with Venetian forms present in the repertoire of shapes. Until the end of the 17th century, Portugal followed a Mediterranean tradition concerning the production of glass. In the case of the glass being imported, this means that the commercial trading in glass with the North and Central European areas was low or inexistent. According to the literature, also Spain followed a Mediterranean tradition concerning the glass production, this meaning that soda-rich compositions were generalised through the Iberian Peninsula. Soda-rich glass was strongly present (so far exclusive!) in the four older assemblages dated until the 17th century: Santa Clara-a-Velha monastery, São João de Tarouca monastery, Praça Miguel Fernandes in Beja and the courtyard in Coimbra University.

The other compositional types here identified were: HLLA glass, potassium rich glass and lead glass. These compositional types are present in majority (with the exception of only two fragments) in the glass assemblages from Lisbon. This can be analysed from different angles: these two assemblages from Lisbon have a more recent chronology, which can go up to the end of the 18th/ beginning of the 19th centuries what might justify the presence of these compositions that were more common from the 18th century onwards; and the other important factor is that Lisbon was the economical and trading centre of the country, where ships loaded with goods from all around Europe arrived with new products to be traded. This last statement means that all the novelties in terms of glass chemical composition that were happening in production centres as Central Europe or the British Isles, were arriving in Lisbon to be traded. These are the hypothesis assuming that the objects were imported. Considering a Portuguese production, these objects were probably made in a production centre employing foreigner glassmakers like Coina glass manufactory or the Salvaterra de Magos manufactory (that had a contract with German entrepreneurs to produced glass in Bohemian style), and would be probably sold and distributed first in the capital. Considering both possibilities, of importing or of national production, this shows that Portugal was updated in relation to what was being developed in other parts of Europe. This fact had already been put to evidence in other published works (Pulido Valente *et al.*, 2016, in press; Coutinho *et al.*, n.d., in press).

The first results presented concerned the older glass set dated to between the 14th and 15th centuries that came from the excavation in Praça Miguel Fernandes, Beja. Eleven fragments from this chronology were studied, and one fragment with Venetian origin was identified. In terms of shape, this fragment can be related with the Central European production, since it's a prunt from a prunted beaker (known as *Krautstrunk*). However, beakers of this kind had already been identified elsewhere as a Venetian production due to its chemical composition. Instead of being a Central European forest glass composition (rich in potassium), this prunt from Praça Miguel Fernandes assemblage has a soda-rich composition compatible with a Venetian production, both in terms of major and minor elements. The study of this assemblage, allowed one to prove the existence of a commercial relationship between Portugal and Venice, and to attest the presence of genuine Venetian glass in the Portuguese territory from as early as the 14th century, fact already proposed during the study of an enamelled beaker (of the Aldrevandin type) found in an archaeological excavation in Lisbon and dated to the 14th century (Medici, 2008). From this assemblage, other fragments were stylistically identified as possible Venetian productions, but their composition cannot be related with Venetian glass. The other analysed fragments are, in terms of composition, related with the Mediterranean tradition, but cannot be compared with any of the known coeval production centres. Also due to the utilitarian character of the glass objects, a local provenance has to be considered.

In what regards the Venetian and *façon-de-Venise* glass amongst the studied sets, genuine Venetian glass objects dated to the 17th century were so far identified only in the Santa Clara-a-Velha monastery assemblage (SCV-V191, SCV-V193, SCV-V195 and SCV-V408). The *façon-de-Venise* fragments from Praça Miguel Fernandes (Beja) were made either from the same silica source or from highly related or geographically close silica sources. This assemblage seems to have a different silica source in comparison with the *façon-de-Venise* fragments from the other sets, which is richer in impurities such as alumina, and it is proposed that these fragments were produced in a *façon-de-Venise* production centre yet to be discovered. Two *façon-de-Venise* fragments with more than 6 wt% of alumina, were identified: one from the Santa Clara-a-Velha Monastery set (SCV-V194) and the other from Praça Miguel Fernandes (Beja) set (PMF0540). The titanium oxide content in these two fragments is very close, which remits for silica from the same source. These two fragments were probably made in the same production centre. When inspecting some flux characteristics, it became clear that the fragments subdivided between two different groups, distinguished by the purity of the ashes employed in their manufacture. The majority of Praça Miguel Fernandes (Beja) *façon-de-Venise* fragments were made with purified ashes and are very close to the *cristallo* boundaries. Highly related to the Praça Miguel Fernandes samples is also a previously analysed *millefiori* fragment from SCV (Lima *et al.*, 2012), indicating that these glasses might have been made using raw materials from the same sources or have the same provenance.

Concerning the São João de Tarouca monastery group, all the analysed *façon-de-Venise* samples are very similar in terms of composition, and were also made using purified ashes, however it was not possible to relate them with any of the known *façon-de-Venise* production centres in Europe, mainly because of the medium alumina contents, close to 3 wt%. Again, it is proposed that these samples were also made in a *façon-de-Venise* production centre yet to be discovered. A general feature of all the analysed *façon-de-Venise* glass, is that the MnO contents is below 1 wt%, which implies that no attempt was made to discolour the batch. Iron and manganese oxides entered the glass composition through the silica source. Their concentration and correlation supports the idea that the silica sources used in these glasses were of high purity and chosen carefully to produce *façon-de-Venise* objects and not just ordinary glass. Another important aspect was the identification of cobalt in *façon-de-Venise* objects, which, as far as we know, has rarely been mentioned. Finally, the existence of two groups of *façon-de-Venise* glass (most Praça Miguel Fernandes (Beja) samples and other group with most São João de Tarouca monastery samples), whose composition demonstrates the attempt in employing pure raw materials, but present unique features (as the medium and high alumina levels), allows one to propose the identification of two new *façon-de-Venise* production centres.

Looking to unique shapes, the vessels in gourd shape were spread in the Portuguese territory, as far as it is known this shape was not found in other European contexts. Their chemical composition has a generalised presence of high alumina contents, which reinforces the hypothesis of these objects being produced in national territory. The gourds in study here are from the Santa Clara-a-Velha monastery and São João de Tarouca monastery assemblages. These vessels show a close relation in terms of composition between fragments from both sets. The majority of the gourds share a type of chemical composition highly related, mainly in terms of silica source. This typology is considered an heritage from the Arab occupation and for the reasons described above and the lack of its presence in other coeval European glass production centres known so far, the gourd is considered of probable Portuguese production. In this case it was possible to relate a certain chemical composition to a specific typology.

Looking to the mould blown decorated objects, this decorative feature was the one present in a higher number of objects. Among the objects from this category, glass with very high alumina levels was identified, being these mainly from the Santa Clara-a-Velha monastery assemblage. A local production is proposed for those objects. A specific mould blown decoration pattern that is so far unique and exclusive for the objects found in Portuguese territory, was identified. The pattern is a four-petalled flower that appears embossed inside a lozenge motif. Since no parallel outside Portugal was so far identified for this kind of decoration, for the fragments presenting it, a national production was proposed. To conclude about the mould blown decorated objects, once again the glass presenting high and very high alumina levels are the ones considered as locally made. For the other mould-blown glass objects, a national or local production is not however discarded. Common patterns like the bossed beakers or the lozenge motif were identified in some vessels. For these objects it was not possible to find parallels for its composition in published literature from coeval European production sites. Being the majority of these objects utilitarian, a local production has to be considered.

Among the gilded decorated objects, one particular object and its gilding decorative technique was subject of a more in depth study. Both the chemical composition and the thickness of the applied gold foil were proved to be in accordance with the gold leaf used in the Iberian Peninsula during the 17th and 18th centuries. The gilding technique was based in the use of a lead-based mordant that allowed one to reheat the objects at a lower temperature than the softening point of the glass underneath, acting as a flux on the glass surface, and attaching the gold leaf. This gilding technique is mentioned in ancient recipes, which revealed lead compounds in the mordant's formulation, but as far as it is known, it has never been found in historical glass objects. However, this technique is currently in use in Murano, where the tradition of enamelling and gilding on glass flourished from the middle of the 15th century onwards. Although in presence of a gilding technique of apparent Venetian tradition, the glass composition, mainly because of its high alumina content (ca. 4 wt%), prevents us from placing the origin of the flask in Venice or in any other of the known *façon-de-Venise* production centres. The comparison with other contemporaneous glass objects also found in Coimbra pointed out a strong similarity with items considered of possible Portuguese origin, not only in terms of chemical composition but also concerning the object's shape, quite common among archaeological glass dated to the 17th century and found in Portugal. Concerning the chemical composition of the gold leaf, it was possible to estimate an Au-Ag alloy with a composition between 22 and 23 carats, and with ca. 1µm in thickness. Also the chemical composition of the gold (in major elements) proved to be in accordance with the gold leaf used in Portugal (in the regions of Coimbra and Aveiro) during the 17th and 18th centuries. The trace elements of the gold allowed one to propose that it might have come from both the West and Eastern African coasts, which were exploited by the Portuguese until mid-17th century. Even though the origin of the gilded flask cannot be indubitably attributed, according to these evidences a local provenance cannot be excluded.

HLLA glass was the second larger type to be identified, which appears in the assemblages excavated in Lisbon. This glass type appears related only to one object: the wine bottle. Between the two sets (Teatro Romano museum and Rua do Arsenal, both in Lisbon), different bottle shapes were identified, and these shapes were related to different chronologies. In terms of chemical composition, the Teatro Romano museum assemblage presents a very heterogeneous one, which probably implies that the bottles from this set were produced in different production localities that used raw materials from different origins. On the other hand, a large number of bottles from the Rua do Arsenal assemblage appear related, suggesting that these bottles were manufacture in the same production centre or in different centres using geographically related raw materials. Comparing with values from the literature, Teatro Romano museum and Rua do Arsenal assemblages have no match with the bottles analysed from the Coina glass manufactory; instead their chemical composition can be compared with some English production sites. It is however important to mention that only a very small amount of fragments from the Coina glass manufactory were studied and analysed, which is definitely not enough to characterise an entire production; and also the bottle production in Portugal was for sure not exclusively made in the Coina glass manufactory. This item was being produced in other national glass production centres as the Côvo glass manufacture for instance.

Potassium-rich glass objects were only found in the two assemblages excavated in Lisbon. These two sets are the ones that have a more recent chronology, where Rua do Arsenal assemblage has objects dated up to the beginning of the 19th century. All the potassium-rich glass samples are made of discoloured glass, and most of them present engraved, enamelled or mould blown decorations. It was verified that the majority of analysed samples can be classified as white glass, and due to their decoration features it is proposed that these glass objects were attempts on imitating the glass developed and produced in the Central European regions. Comparing the obtained results with published data from known production centres such as Bohemia, Germany and so on, it was concluded that the majority of samples can be related with the production of potassium-rich glass from the Coina glass manufactory, and no genuine Central European glass could be identified. For the majority of these objects, a national production is considered; being also important to mention again that Central European glassmakers worked in the Coina glass manufactory, as well as in the Salvaterra de Magos furnace. These Portuguese production locations were probably using Central European recipes for making glass.

Mixed alkali glass objects represent only a very small percentage of all the analysed samples. Only seven fragments were identified with this composition, and no obvious relation between fragments was found, with the exception of both objects belonging to the courtyard in Coimbra University assemblage that have a highly related chemical composition. For the fragments from the courtyard in Coimbra University, is it proposed that they share the same provenance, since their chemical composition have an almost perfect match. Due to the very low amount of samples from this category it is raised the hypothesis that these glass objects were not produced on purpose with this composition, but were instead the result of employing different proportions of raw materials or using different source of raw materials.

On the topic of the lead glass fragments, only five examples were identified and only one does not belong to the Lisbon assemblages. Three of these fragments can be related with each other and their composition is similar to the composition used in Silkstone, England. For both fragments from Rua do Arsenal assemblage, their trace elements and REE analysis showed that their signature is identical and for this reason is highly suggested that both fragments had the same source of raw materials and probably came from the same production centre. No fragment could be compared with the fragments analysed from the Coina glass manufactory, however it is important to remind that only a few fragments were analysed from this production centre, and more analysis are required in order to characterise the production in Coina.

With an overall look to the glass assemblages and their chemical compositions, it is possible to conclude that utilitarian fragments from Santa Clara-a-Velha monastery set are very chemically alike, which allows one to propose a national provenance for these fragments, even perhaps a local production. On the other assemblages it is possible to observe some diversity among compositions for the utilitarian objects, which does not necessarily imply a different provenance. It can be the translation of the lack of choice in the employed raw materials or in other words, the raw materials were not carefully selected to the production of utilitarian glass. The same production centre could be employing raw materials from more than one location over time and this could happen because of financial reasons or the availability of raw materials. This would result in different chemical compositions over time. In the Praça Miguel Fernandes assemblage analysis, fragments dated from the 14th to the 15th century were also analysed and it was possible to observe that in the statistical tree clustering these older fragments were separated from the recent ones, however it is possible to observe some similarities in the silica impurities. Again, the alumina and iron oxide contents of these older glass objects can be related to some of the more recent ones and it is possible to propose that perhaps these fragments are part of a local continuous production. The changing in recipes and sources of some raw materials would justify the differences in some oxides from the composition, and the usage of the same silica source (or different silica sources related geographically), would justify the similarities found between different dated fragments.

Finally, it is important to reinforce that the novelties in terms of glass compositions were arriving in Portugal in short periods after they were first formulated; genuine Venetian glass was found in the Portuguese territory as soon as the 14th century (fig.1), potassium-rich glass formulated in Central European regions in the end of the 17th/ beginning of the 18th centuries was found in assemblages dated to the beginning of the 18th century, and finally, lead crystal glass formulated in the British Isles in the first half of the 18th century was found in assemblages dated from the same period.

Gourds, four-petalled flowers in mould blown patterns and chemical compositions with high alumina contents are considered the features that, so far, can be proposed for a national provenance, however no systematic comparison can be made with Portuguese production centres because of the absence of archaeological excavations on glass furnaces. To conclude, this investigation allowed one to propose that the glass production in Portugal might be of better quality and have occurred in higher number than what was usually assumed. It is now legitimate to propose that not only utilitarian glass (some examples of good quality glass worked by skilled glassmakers can be found among utilitarian objects) was produced in national territory but also glass with *façon-de-Venise* and Central European styles among others, with several decoration features, showing a modern attitude and a willing to be updated in terms of glass production techniques and raw materials with what was fashionable in the most important European glass production centres. The Mediterranean tradition, more specifically the soda rich glass prevailed until the end of the 17th century. From this period onwards, Portugal, as the rest of Europe, responded quite rapidly to the change in taste and quest for new glass products. The glass assemblages dated to the beginning of the 18th century are richer in potassium-rich glass and lead glass objects, showing modern attitude towards glass.

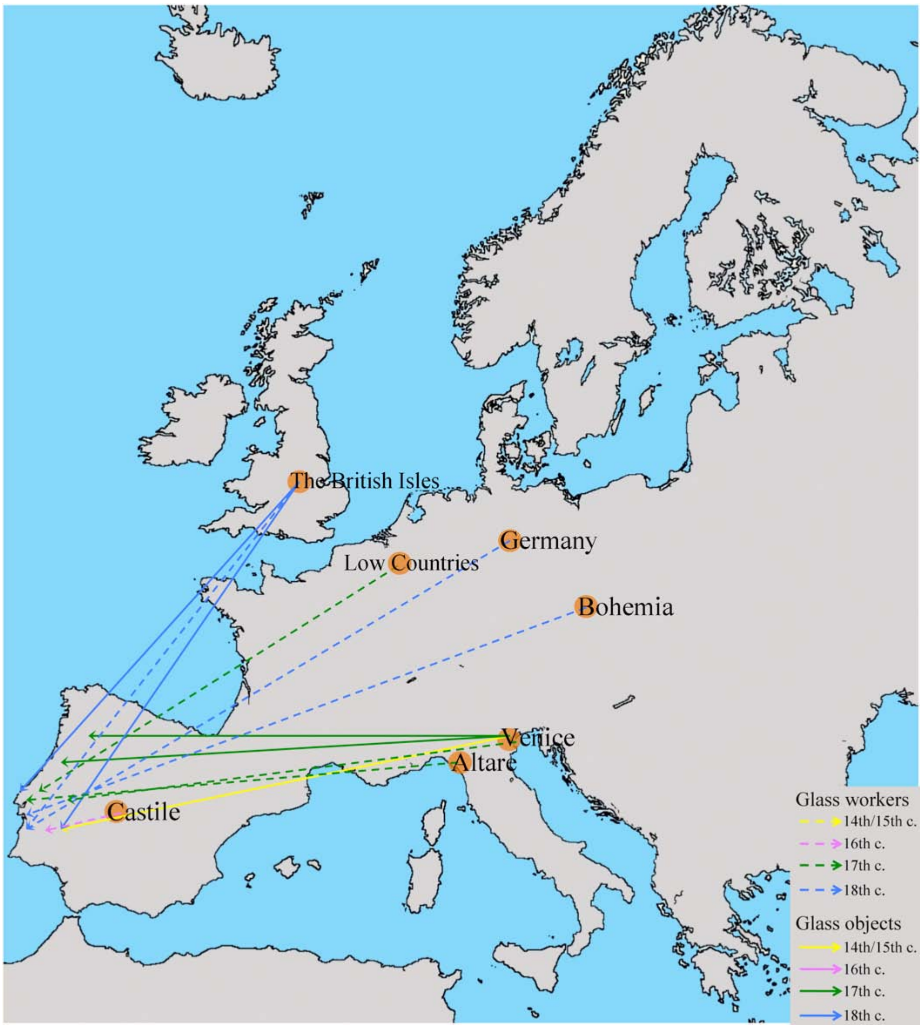


Fig. 1: Map of Europe showing the presence, in Portuguese territory, of glass objects (full lines) and glass workers (dashed lines). Based in the literature (Amado Mendes, 2002; Custódio, 2002; Medici, 2014; Valente, 1950) and in new insights from the current investigation.

For the preservation of a legacy as important as glass, the preventive conservation of the glass assemblages was also part of this project. It was proposed the design of an optical sensor for the detection of the organic volatile compound formic acid.

In what concerns the sensor development, two different matrixes (sol-gel and polyelectrolytes by LbL deposition) and several dyes (acid-base indicators and solvatochromic dyes), were tested in order to define the better matrix / dye combination to be specific for the formic acid vapours identification.

The matrix showing a best performance was the one using the polyelectrolytes through the layer-by-layer deposition method. Among the acid-base indicators and solvatochromic dye tested, Methyl red (MR) exhibited the best performance after its incorporation in the polymeric matrix constituted by both polyethylenimine and poly(acrylic acid).

The sensor produced in this way has demonstrated good selectivity detecting only HCl and HNO_3 in addition to the formic acid. The detection of these two acids was not considered problematic because they are not expected to exist in the indoor environment of museums.

In general, the most prized characteristics in a sensor are its ability to identify only the desired analyte (or analytes) in the least time possible and with the lowest limit of detection possible. However, in the case of the sensor developed during this work, its purpose is to detect the presence of formic acids in indoor museum environments. For this reason, it is not problematic that it reacts to the presence of nitric and hydrochloric acids. The presence of these two mentioned acids are not expected in a museum environment. Another important aspect is the response time. Again, considering the purpose for which this sensor was developed, taking a few weeks to change his colour is not a problem. Considering that the time that the sensor takes to change its colour is related with the amount of formic acid: if the amounts of formic acid in a certain atmosphere are very high, the sensor will take less time to change its colour. In this situation, it will be necessary to remove the glass exposed to this acid in a very short time. The sensor has a cumulative effect, meaning that even if the amount of formic acid present in the atmosphere is low, with time it will trigger the sensor to change its colour. Another important aspect is that if anything changes in the environment where the sensor is exposed, and for some reason a higher quantity of volatile formic acid becomes available in the atmosphere, the sensor will also change his colour.

Future Work suggestions

In terms of future work it is essential to emphasise the needing of archaeological excavations in locations known to have been places of glass production. It is crucial to find the remaining of glass production from production locations such as the glass manufacture in Côvo. The remains from furnaces located in the Portuguese territory need to be analysed and chemically characterised, in order to define compositions and probable used raw materials. This is the most assertive way for the creating of database concerning the glass production in national territory, for the later comparison with analysis of objects found all over the territory from non-production locations, such as the case of the assemblages studied in this thesis and all the objects laying in national museums with probable and not certain attributed production locations.

It would also be very important as complementary work and for the cases where an archaeological excavation is not possible, to collect glassmaking raw materials, in this case sand and other silica sources, because it is the material that suffered less compositional alterations in the last centuries (in comparison for instance with plants used as an alkali source, and that have their composition depending for instance from the season in they are harvested). The main idea would be to analyse these silica sources (already transformed into glass) and compare them, mainly in terms of their contents in alumina, iron and titanium oxides (plus REE), with the ones found in the analysed glass. If the contents are similar and the signatures in trace and REE were similar and comparable, it would be possible to discuss the glass provenances with a higher degree of certainty.

As a proposal of future work it would definitely be very important to study and characterise more glass assemblages found in the Portuguese territory, starting for instance with the other glass assemblages studied by T. Medici in her PhD thesis. This way the investigation would be based on a very complete characterisation done previously. Another suggestion concerning assemblages to be further analysed it would be very important also to make a deeper investigation and acquire more data on the glass objects from the Santa Clara-a-Velha monastery. This is so far the assemblage with a larger number of objects dated from the 17th century unearthed in the Portuguese territory; moreover it is composed by utilitarian objects and luxury items, giving us the possibility to have a broader view on the objects possibly produced in the national territory and the objects of probable importation.

Another important subject to consider for future work is the study of historical treatises. It would be very important to try to identify the presence of recipes from historical treatises circulating in Europe (as the Antonio Neri’s *L’Arte Vetraria*), reproduced in the glass through the study of its chemical composition. Treatises such as *Schedula diversarum atrium* (Theophilus), *L’Arte Vetraria* (Antonio Neri), or the *La Sedacina ou l’Œuvre au crible* (Guillaume Sedacer), would be very interesting to study and to try reproducing the recipes they contain, in order to compare with the glass analysis from historical objects.

In what regards the validation of the sensors, the next important step would be to test them in several museum environments. This would allow one to observe and evaluate the sensor and its characteristics *in situ*. At the same time, it is important to use other techniques to measure the formic acid concentrations, validating this way the sensor. Moreover, it would be very interesting to observe the sensor’s reaction to different museum environments, with different temperatures and relative humidity values and study the effect of these in the performance of the sensor.

Another important aspect would be the determination of the exact concentration that triggers the sensor. From the performed tests it was possible to established that it is necessary an amount superior to 100 mg m^{-3} of formic acid to set off the produced sensor, to be in accordance to the concentrations measured in several wooden cabinets present in museums. Considering all the tests performed to the sensor, it shows promising results to be an inexpensive and direct alternative to identify the presence of formic acid. Moreover, during this investigation it was very difficult to currently find a company available to perform measurements of formic acid in the form of vapours, which comes to emphasize the necessity of developing in situ sensors without the need of a passive sampling.

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Appendices Part I

Appendix I: Tracers to track glass: raw materials employed in glass production

Silica

Fig. I.1: Quartz pebbles from the Ticino River, Italy.

The glass structural component or vitrifying agent is silica, which can be obtained from sand or crushed quartz pebbles (see figure I.1). Concerning the use of sand, despite its purity, in addition to silica several other components considered impurities would be introduced into the glass batch (Moretti & Hreglich, 2013, p.29). Calcium carbonate, magnesium oxide and alumina are the sand impurities known for giving glass chemical stability and iron oxide is responsible for the natural (and sometimes unwanted) green, blue or yellow hues. The minerals that are considered sand contaminants are usually the aluminium-rich kaolinite and feldspar, the zirconium-rich zircon ($ZrSiO_4$), the REE-rich monazite (REE phosphate), the titanium-rich rutile (TiO_2) and the iron oxides (Moretti & Hreglich, 2013, p.29; Wedepohl *et al.*, 2011a). These elements present in the sand structure like Titanium, Zirconium, REE and so on, are the main trace elements and trackers for sand, giving us the possibility to discuss the raw materials provenance and consequently to consider, in a more informed way, the glass provenance through its main component (Velde, 2013, p.68).

Fluxing agents

(a) **(b)** **(c)**

Fig. I.2: Flux raw materials. a) *Salicornia europaea*, as a source for soda-rich ashes, available in http://en.wikipedia.org (GNU Free Documentation License, accessed in 25 September 2014), b) detail of a branch from *Salicornia europaea*, available in http://ztopics.com (© Jenny Seawright, accessed in 25 September 2014) and c) Fern plants (*nephrolepis* family), as a source of potassium-rich ashes.

Regarding now the other glass components, fluxing agents are responsible for lowering the glass fusion temperature. This will reflect on the glass workable time and consequently on the time that melted glass takes to solidify. These oxides can be denominated as network modifiers, since their introduction will alter the glass network in such a way that, depending on its concentration modifiers, can compromise the network stability (Moretti & Hreglich, 2013, p.29; Navarro, 2003, p.137).

The most common fluxing agents used in the past were natron, and soda-rich and potassium-rich ash, being the last ones of vegetal origin. Natron was widely used as a flux in glass production since the first millennium B.C. until the 9th century from the present era, when it was replaced by plant ash (Velde, 2013, p.71; Shortland *et al*., 2006). This flux came from lakes located between Alexandria and Cairo, and are mainly constituted by hydrated sodium carbonate (tronite or trona Na2CO3•2H2O). Unlike plant ashes, it is very pure, not having in its composition the impurities that help in the glass stabilization (Moretti & Hreglich, 2013, p.29). Due to its scarcity, from the 9th century onwards, natron was no longer the main flux agent employed in glass production, being replaced by plant ash (Shortland *et al*., 2006). In the Mediterranean area, the use of natron was replaced for ashes obtained from plants located near coastlines like the *Chenopodiaceae* family (comprehending many genera like Suaeda, Salsola and Salicornia, figure I.2), which were rich in soda (Tite *et al.*, 2006; Velde, 2013, p.71). On the North of the Alps region, natron was replaced with ashes from forest plants (for instance fern, figure I.2) and wood that were richer in potassium oxide (potash-rich ashes) with the contents of calcium and magnesium oxides also higher in comparison with soda-rich ashes (Velde, 2013, p.71). The glass that was produced using potassium-rich ashes had a natural green hue and was commonly called *forest glass*. This glass owes its colouration to the iron contents present in the plant-ashes usually obtained from wood or ferns. During the 16th century this regional division started to blur due to the emigration of Italian glassmakers to the North of the Alps bringing to this region the soda-rich glass tradition (Velde, 2013, p.75). The 16th and 17th centuries were marked by a coexistence of both soda-rich and wood-ash glasses, and progressively the wood-ash formulations ceased to be used (Velde, 2013, p.75). The exception to this situation was the bottle production that continuing to be produced using wood ashes in order to obtain the HLLA dark green or black glass (Velde, 2013, p.75). Regarding this soda/wood-ash transition period, could it be the reason for the existence of a mixed alkali glass composition? The mixture of soda-rich plants with potash-rich ones could be an explanation for some mixed-alkali glass compositions, however another explanation has to be considered. According to Tite *et al.* (2006), it is possible to obtain a mixed-alkali glass composition from a *Salsola kali* plant if the ash obtained from this plant is first purified by dissolution followed by evaporation (or suffers any other treatment) with the objective of reducing its lime-plus-magnesia content. The ash employed in the batch would give origin to a mixed alkali glass (Tite *et al.,* 2006).

As it was mentioned above, Northern Europe ceased the production of wood-ash glass, however their glass formulations were still rich in potassium oxide rather than in soda. At the end of the 17th century/ beginning of the 18th century, raw materials like saltpetre (potassium nitrate), chalk and limestone were being introduced into the batch as sources of potassium and calcium (Kunicki-Goldfinger *et al.*, 2001). About the same time in England, lead was being introduced into the batch to lower the glass melting temperature. In both situations the main purpose was to achieve a perfectly discoloured glass formulation even when the glass walls had a higher thickness.

Stabilizers

In order for the glass to be stable and water resistant, its composition needs to contain stabilizers. Alkaline-earth oxides and alumina are natural glass stabilizers that were introduced into the batch together with silica and flux (e.g. sand and plant ashes) raw materials as their impurities (Moretti & Hreglich, 2013, p.30). In the case of alumina, it was introduced into the batch through less pure sand (rich in feldspars) and also, even though in less quantities, through non-purified vegetable ashes. The ashes are also responsible for the introduction of calcium and magnesium oxides, once again through its impurities (Moretti & Hreglich, 2013, p.30). At this point it is important to point out that it is generally accepted that until the 19th century, stabilizers were added to the batch without the glassmakers knowing their role on the glass matrix stability (Moretti & Hreglich, 2013, p.34). It is however discussed by Brems *et al.* (2012) including several opinions on this matter where it is referred to that skilled glassmakers might have realized that adding some lime to the batch in the form of shells for instance (a fact mentioned by Pliny), improved the glass resistance when in contact with water.

Concerning lead oxide, it was primarily used as a glass stabilizer and it was commonly introduced into the batch as litharge or minium, however it was later used as a flux agent. Depending on its concentration, lead oxide can be a glass stabilizer, fluxing or vitrifying agent (Navarro, 2003, p.143; Moretti & Hreglich 2013, p.30).

Fining agents

A fining agent is used to reduce or eliminate bubbles from the glass matrix. The first intentionally used fining agents were arsenic and antimony oxides. These components were first mentioned in the 17th century treaty *De Arte Vetraria* written by Antonio Neri (Navarro, 2003, p.191-192, 200). Magnesium oxide was employed with the purpose of decolourizing glass, however it also acts as a fining agent (Moretti & Hreglich, 2013, p.31).

Opacifiers and colouring agents

Regarding the opacifiers used in the past, calcium antimonate was the first to be employed, dating from the 15th century B.C (Moretti & Hreglich, 2013, p.31). Later in Venice, tin dioxide or cassiterite was the preferred opacifier for the glass production. Adding lead to the tin dioxide, Venetian glassmakers were able to produce a white opaque glass called *lattimo*. The opacification using lead arsenate was used for the production of another new Venetian formulation called *girasole*. This designation was due to its milky appearance and optical properties, since this glass colour in reflected light is of a pale blue tone and in transmitted light presents a reddish to orange-yellow colouration just like the sunflower (Moretti & Hreglich, 2013, p. 31; Verità, 2013, p. 523).

Concerning now the colouring agents elements like manganese, iron, copper, cobalt and silver are mentioned from the 14th century. Manganese oxide in quantities between 0.3 and 0.8 in weight percentage of oxides, was used as a decolourizing agent, and when employed in a larger quantity is used for the production of a purple coloured glass (Moretti & Hreglich, 2013, p.32). Iron oxide, depending on its oxidation state can be responsible for a blue colouration (ferrous ion - Fe^{2+}, obtained in a reducing kiln atmosphere), for a yellow colouration (ferric ion - Fe^{3+} obtained in an oxidizing kiln atmosphere) or for a green colouration when the mixture of both oxidation states is present (Navarro, 2003, p.449-450). Copper and its turquoise blue colouration in glass is the most ancient glass tonality known and was widely used in the Egyptian period (Navarro, 2003, p.452). A red ruby colour can also be obtained by the presence of copper nanoparticles (Kunicki-Goldfinger *et al.*, 2014). Glass with cobalt has an intense blue colouration, due to the high colouring capability of the Co^{2+} ion even when present in low concentrations. Finally silver was employed in the preparation the chalcedony glass, giving a brown to yellow colouration (Moretti & Hreglich, 2013, p.32).

Regarding now ruby glass, this colouration is attained by the presence of nanoparticles or gold colloids inside the glass matrix. As was referred to before, copper nanoparticles can give origin to this glass colour. It is also important to mention that gold nanoparticles can also give origin to ruby glass. Both copper and gold were used since ancient times to obtain ruby glass and knew a great splendour during the end of the Middle Ages in Venice. The use of gold to produce ruby glass only reappeared on the 16th century by the hands of Kunckel in Potsdam, and until the end of the 19th century, its mechanism was involved in mystery. The ruby colouration is a result of the colloid’s light absorption and simultaneously of the light dispersion caused by the small colloidal gold particles (Navarro, 2003, p.462-463).

Appendix II: ***Museu do Teatro Romano*** **(Lisbon) set (LTR)** – Objects information, chemical composition, objects catalogue and archaeological drawings catalogue.

Table II.1: Description of analysed samples from Museu do Teatro Romano in Lisbon (LTR) with inventory number, object type, glass colouration, part of the object preserved and dating.

Fragment	***Type***	***Colour***	***Part Preserved***	***Dating (century AD)***
LTR0001	Bottle (cylindrical) – C	Black	Base and part of wall	18th
LTR0002	Bottle – B or C	Black	Fragment of wall	18th
LTR0004	Bottle (cylindrical) – C	Black	Fragment of base and part of wall	18th
LTR0005	Flask (cylindrical)	Blue	Base and part of wall	18th
LTR0006	Vessel	Dark blue	Fragment of wall	18th
LTR0007	Drinking glass	Colourless	Stem (cut glass)	18th
LTR0008	Bottle – B or C	Olive green	Fragment of wall	18th
LTR0011	Vessel	Brown	Base and part of wall	18th
LTR0013	Vessel	Colourless	Fragment of wall	17th/18th (1st half)
LTR0014	Flask (hexagonal)	Colourless with enamel decoration	Fragment of walls and base	17th/18th (1st half)
LTR0017	Vessel (deformed by fire)	Colourless	Fragment of rim wall	17th/18th (1st half)
LTR0019	Vessel (with engraved decoration)	Colourless	Fragment of rim wall	18th
LTR0020	Flask (cylindrical) – C	Blue	Base and part of wall	18th (2nd half)
LTR0021	Bottle	Light green	Fragment of bottleneck	18th (2nd half)
LTR0024	Bottle	Olive green	Fragment of bottleneck	17th/ 18th (1st half)
LTR0027	Bottle	Olive green	Fragment of bottleneck	18th (2nd half)
LTR0028	Bottle	Olive green	Fragment of wall (very thin glass)	18th (2nd half)
LTR0030	Square Bottle – A	Olive green	Fragment of wall	18th
LTR0031	Bottle (with production marks)	Olive green	Fragment of bottleneck	18th
LTR0032	Bottle – C	Black	Base	18th
LTR0033	Bottle –B or C	Olive green	Fragment of wall (very thin glass)	18th

LTR0034	Bottle (probably cylindrical body) – C	Black	Base	18th
LTR0035	Bottle	Olive green	Fragment of neck	18th
LTR0036	Bottle	Black	Fragment of lip	18th
LTR0037	Bottle – B or C	Olive green	Fragment of neck and body	18th
LTR0039	Bottle – B or C	Black with turquoise zones	Part of base push-up	(?)
LTR0040	Square Bottle (with inscription mark on bottom: IM) – A	Olive green	Base	17th/ 18th (1st half)
LTR0042	Vessel (probably a flask of small dimensions)	Colourless	Rim	17th/ 18th (1st half)
LTR0043	Vessel	Colourless	Fragment of wall	18th
LTR0044	Vessel (probably a jar of small dimensions)	Colourless	Rim and fragment of wall	17th/ 18th (1st half)
LTR0047	Vessel	Turquoise	Part of wall and rim	18th
LTR0049	Prismatic bottle – A	Olive green	Part of base and wall	18th
LTR0050	Bottle	Black	Part of neck	18th
LTR0051	Bottle with seal from “Bad Pyrmonter Waters) – B or C	Olive green	Part of wall with seal	18th
LTR0052	Bottle	Black	Part of neck and lip	18th
LTR0055	Vessel (mould blown, faceted)	Colourless	Fragment of base and wall	18th (2nd half)
LTR0056	Square bottle – A	Olive green	Base	18th (2nd half)
LTR0057	Bottle – B or C	Black	Fragment of base	17th/ 18th (1st half)
LTR0059	Flask	Blue	Base	17th/ 18th (1st half)
LTR0060	Flask	Blue	Base	17th/ 18th (1st half)
LTR0061	Bottle – B or C	Olive green	Fragment of wall	17th/ 18th (1st half)
LTR0063	Drinking glass (mould blown, faceted)	Colourless	Whole shape	18th
LTR0064	Drinking glass (mould blown, faceted)	Colourless	Base and fragment of wall	18th
LTR0065	Bottle (globular or onion shape) – B	Olive green	Fragment of bottleneck and wall	18th
LTR0066	Bottle	Olive green	Fragment of bottleneck	18th
LTR0069	Vessel	Colourless	Fragment of wall	18th
LTR0070	Lid handle (cut glass)	Colourless	Fragment of lid handle	18th
LTR0071	Bottle (with production marks)	Black	Fragment of bottleneck	18th
LTR0073	Bottle – B or C	Olive green	Fragment of wall	18th
LTR0077	Bottle (with production marks)	Olive green	Fragment of bottleneck	18th

LTR0079	Square bottle – A	Olive green	Base	18th
LTR0080	Vessel (deformed by fire)	Olive green	Fragment of rim walls	18th
LTR0082	Vessel (deformed by fire)	Blue	Fragment of wall	18th
LTR0083	Vessel	Blue	Fragment of wall	18th
LTR0085	Vessel – B or C	Olive green	Fragment of wall	17th/ 18th (1st half)
LTR0087	Square bottle – A	Olive green	Fragment of wall	17th/ 18th (1st half)
LTR0088	Bottle – B or C	Black (?)	Part of base push-up	18th
LTR0089	Bottle (probably mallet shaped) – B	Black	Part of body, neck and lip	18th
LTR0090	Bottle	Black (?)	Part of body	18th
LTR0091	Bottle – B or C	Black (?)	Part of base push-up	18th
LTR0093	Prismatic bottle – A	Black	Part of body	17th/ 18th (1st half)
LTR0095	Bottle, probably cylindrical shape with conical push-up –C	Black	Part of wall, base and push-up	17th/ 18th (1st half)
LTR0096	Bottle with very small push-up – B or C	Black	Part of base	17th/ 18th (1st half)

Table II. 2: Composition of samples from Museu do Teatro Romano in Lisbon (LTR) determined by µ-PIXE and LA-ICP-MS in weight percent of oxides.

Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SrO	BaO	PbO
LTR0001	2.5	2.8	3.4	57.4	1.52	0.10	0.29	2.34	25.97	0.29	0.16	2.98	< 10 µg/g	0.03	0.01	0.05	< 80 µg/g	0.11	0.10	0.02
LTR0002	2.8	2.8	3.3	57.8	1.60	0.09	0.34	2.34	25.12	0.30	0.16	3.04	< 20 µg/g	0.03	0.01	0.05	< 130 µg/g	0.10	0.16	< 500 µg/g
LTR0004	2.1	1.7	6.3	56.9	0.82	0.09	0.35	2.10	26.92	0.32	0.20	2.09	< 40 µg/g	0.03	0.01	0.02	< 90 µg/g	0.05	0.06	< 100 µg/g
LTR0005	15.1	1.8	1.8	62.6	0.77	0.05	1.34	4.12	10.22	0.21	0.54	0.90	< 10 µg/g	0.01	0.01	0.02	< 110 µg/g	0.03	0.59	< 100 µg/g
LTR0006	16.9	0.2	2.39	69.2	< 5µg/g	0.07	0.97	0.63	7.48	0.07	0.47	1.19	0.09	0.01	0.11	0.01	< 100 µg/g	0.04	0.03	< 100 µg/g
LTR0007	0.9	0.4	< 5µg/g	78.4	< 5µg/g	0.09	0.14	12.30	7.47	0.01	0.01	0.07	< 30 µg/g	< 0.01	< 60 µg/g	< 70 µg/g	0.28	< 300 µg/g	< 35 µg/g	< 500 µg/g
LTR0008	2.9	3.5	3.1	57.7	2.21	0.24	0.32	2.80	24.84	0.25	0.41	1.54	< 40 µg/g	0.02	0.01	0.04	0.02	0.10	0.09	< 200 µg/g
LTR0011	7.2	0.8	2.4	65.8	1.07	0.06	0.50	9.98	10.98	0.26	0.36	0.52	< 20 µg/g	< 40 µg/g	< 50 µg/g	0.01	< 200 µg/g	0.02	0.05	< 300 µg/g
LTR0013	0.6	0.9	< 5µg/g	72.0	< 5µg/g	0.13	0.11	13.56	10.89	0.01	0.08	0.06	< 20 µg/g	< 40 µg/g	< 50 µg/g	< 70 µg/g	1.63	< 300 µg/g	< 35 µg/g	< 100 µg/g
LTR0014	0.8	0.6	< 5µg/g	75.2	0.08	0.12	0.11	13.35	8.70	0.03	0.16	0.12	< 10 µg/g	< 25 µg/g	0.01	0.01	0.75	< 130 µg/g	0.02	< 380 µg/g
LTR0017	0.6	0.4	1.2	66.2	< 2µg/g	< 9µg/g	0.09	17.31	9.19	0.03	0.25	0.16	< 20 µg/g	< 40 µg/g	< 40 µg/g	0.01	0.84	< 260 µg/g	0.03	3.57
LTR0019	0.7	0.2	8.1	69.8	0.06	0.10	0.12	13.02	7.20	0.01	0.03	0.05	< 20 µg/g	< 30 µg/g	< 30µg/g	< 55 µg/g	0.70	0.02	0.03	< 160 µg/g
LTR0020	14.7	0.4	1.6	66.3	< 2µg/g	0.36	0.69	1.37	12.63	0.17	0.38	0.35	0.03	0.02	< 50 µg/g	0.03	0.15	< 160 µg/g	0.03	0.62
LTR0021	12.0	5.6	0.4	69.6	0.90	0.13	0.11	0.31	9.86	0.07	0.10	0.46	< 20 µg/g	0.01	< 25 µg/g	0.01	1.27	< 150 µg/g	0.05	< 100 µg/g
LTR0024	2.8	3.0	2.3	60.6	1.14	0.15	0.22	2.69	24.01	0.24	1.04	1.34	< 20 µg/g	0.01	< 30 µg/g	0.03	< 160 µg/g	0.08	0.29	< 200 µg/g
LTR0027	2.8	2.9	4.2	58.6	0.18	0.12	0.78	0.53	24.98	0.49	0.12	4.07	< 10 µg/g	< 30 µg/g	< 30 µg/g	0.03	< 100 µg/g	0.14	0.11	< 100 µg/g
LTR0028	2.5	3.1	4.8	57.6	0.37	0.15	0.22	2.11	22.36	0.56	0.25	2.78	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 50 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	3.06
LTR0030	3.2	2.6	3.6	61.5	1.12	0.13	0.60	1.29	21.08	0.27	0.68	1.40	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 50 µg/g	2.67	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0031	0.8	3.9	4.9	57.1	1.34	0.07	0.05	6.89	20.48	0.39	1.79	1.54	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 50 µg/g	< 100 µg/g	< 150 µg/g	0.73	< 100 µg/g
LTR0032	2.1	4.0	4.3	59.9	0.49	0.15	0.18	2.18	23.82	0.32	0.17	2.33	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 50 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0033	4.1	2.9	4.9	62.4	1.33	0.08	0.43	2.38	19.02	0.25	0.29	1.72	< 10 µg/g	0.01	< 30 µg/g	0.04	< 100 µg/g	0.05	0.08	0.02
LTR0034*	2.1	4.6	3.9	57.1	1.01	n.m.	0.24	2.36	25.41	0.28	0.15	2.37	< 10 µg/g	30 µg/g	30 µg/g	0.01	50 µg/g	0.31	0.06	30 µg/g
LTR0035*	2.9	2.9	3.5	60.1	2.33	n.m.	0.52	2.63	21.73	0.22	1.36	1.34	< 10 µg/g	30 µg/g	0.01	0.03	20 µg/g	0.09	0.19	0.02
LTR0036*	2.2	3.8	5.1	59.9	0.92	n.m.	0.24	2.83	22.14	0.25	0.09	2.05	< 10 µg/g	30 µg/g	20 µg/g	0.01	30 µg/g	0.24	0.07	0.01
LTR0037*	1.6	3.3	3.8	62.1	0.67	n.m.	0.45	1.97	22.97	0.19	0.16	1.76	< 10 µg/g	20 µg/g	30 µg/g	0.02	10 µg/g	0.21	0.70	0.01
LTR0039*	2.1	2.9	3.9	59.0	1.86	n.m.	0.36	2.59	23.61	0.25	0.14	2.81	< 10 µg/g	30 µg/g	0.01	0.04	20 µg/g	0.12	0.07	0.01
LTR0040	3.3	3.2	3.6	61.0	1.50	0.05	0.53	2.11	22.14	0.24	0.71	1.37	< 10 µg/g	0.02	< 30 µg/g	0.02	< 100 µg/g	0.09	0.20	< 100 µg/g
LTR0042*	0.4	0.1	0.1	75.3	0.05	n.m.	0.20	13.31	9.52	0.01	0.15	0.05	< 10 µg/g	< 10 µg/g	30 µg/g	10 µg/g	0.68	40 µg/g	0.01	< 10 µg/g
LTR0043	0.6	0.5	< 3µg/g	73.9	0.07	0.16	0.23	13.24	10.05	0.01	0.16	0.06	< 20 µg/g	< 20 µg/g	< 20 µg/g	< 30 µg/g	0.90	< 300 µg/g	0.04	< 200 µg/g
LTR0044*	0.6	0.2	0.2	73.4	0.07	n.m.	0.21	14.30	10.06	0.01	0.21	0.08	< 10 µg/g	10 µg/g	40 µg/g	10 µg/g	0.61	0.01	0.01	< 10 µg/g
LTR0047*	3.2	3.4	3.8	59.4	2.15	n.m.	0.56	3.70	21.18	0.20	0.79	1.18	< 10 µg/g	30 µg/g	0.01	0.02	< 10 µg/g	0.10	0.23	0.02
LTR0049*	3.5	3.0	3.8	60.4	2.48	n.m.	0.60	3.08	20.80	0.20	0.56	1.20	< 10 µg/g	30 µg/g	50 µg/g	0.02	< 10 µg/g	0.07	0.18	0.01
LTR0050*	0.8	3.4	4.1	55.5	3.11	n.m.	0.16	7.19	22.02	0.34	1.03	1.90	10 µg/g	0.01	0.01	0.07	20 µg/g	0.07	0.15	0.02
LTR0051*	3.3	3.2	5.5	57.8	2.10	n.m.	0.55	3.58	20.25	0.41	0.87	1.83	< 10 µg/g	40 µg/g	0.01	0.02	10 µg/g	0.10	0.27	50 µg/g
LTR0052*	1.5	4.4	4.6	58.8	0.97	n.m.	0.24	2.31	24.16	0.23	0.18	2.14	< 10 µg/g	20 µg/g	50 µg/g	0.03	20 µg/g	0.12	0.20	0.01
LTR0053	16.7	3.5	2.3	65.5	0.07	0.07	1.00	1.57	7.01	0.32	0.89	1.13	< 10 µg/g	< 30µg/g	< 25 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0055	0.5	0.3	0.3	51.2	0.37	0.15	0.23	7.89	0.29	0.57	0.02	0.03	< 10 µg/g	< 30µg/g	0.01	< 30 µg/g	0.96	< 150 µg/g	< 35 µg/g	37.17
LTR0056	4.1	2.9	4.3	61.9	1.19	0.04	0.61	1.67	18.68	0.27	0.85	1.38	< 10 µg/g	< 30µg/g	< 25 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	2.14	< 100 µg/g
LTR0057	2.0	4.7	4.4	58.2	0.43	0.12	0.21	0.54	25.37	0.29	0.17	3.05	< 10 µg/g	< 30µg/g	< 25 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	0.54	< 100 µg/g
LTR0059	13.6	1.6	5.4	56.6	0.94	0.10	0.77	12.44	6.98	0.42	0.15	0.96	< 10 µg/g	< 30µg/g	< 25 µg/g	0.02	< 100 µg/g	0.03	0.05	0.02

LTR0060	10.8	2.1	2.6	62.4	0.37	0.08	0.62	5.16	13.39	0.14	0.91	1.19	< 10 µg/g	0.01	0.01	0.01	0.03	0.05	0.08	0.09
LTR0061	2.7	2.6	2.6	62.1	1.01	0.18	0.28	2.10	23.73	0.24	0.24	1.83	< 10 µg/g	< 30µg/g	< 25 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	0.45	< 100 µg/g
LTR0063	0.9	0.6	1.3	65.7	< 5µg/g	0.13	0.16	15.01	10.37	0.03	0.29	0.21	< 10 µg/g	0.01	0.01	< 30 µg/g	0.90	< 150 µg/g	0.02	4.38
LTR0064	0.9	0.6	0.7	66.8	0.71	0.13	0.13	15.15	11.48	0.04	0.32	0.21	< 10 µg/g	< 30µg/g	0.01	< 30 µg/g	1.01	< 150 µg/g	0.02	2.47
LTR0065	3.5	3.6	4.1	57.8	1.53	0.09	0.65	2.38	23.31	0.29	0.90	1.57	< 10 µg/g	< 30µg/g	< 30 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	0.33	< 100 µg/g
LTR0066	2.1	2.5	2.6	59.1	1.18	0.20	0.25	2.78	26.10	0.27	0.47	2.30	< 10 µg/g	< 30µg/g	< 30 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	0.45	< 100 µg/g
LTR0069	0.8	0.3	1.6	55.0	0.88	0.14	0.29	10.03	1.89	0.25	0.24	2.79	< 10 µg/g	< 30µg/g	< 30 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	25.83
LTR0070	15.1	3.1	2.1	59.2	0.06	0.06	0.90	10.93	6.34	0.29	0.81	1.02	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0071	2.8	3.2	3.7	58.5	0.92	0.15	0.30	2.05	24.93	0.26	0.25	2.92	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 30 µg/g	< 70 µg/g	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0073	3.4	3.2	3.7	57.6	0.89	0.15	0.28	1.98	23.77	0.33	0.26	3.27	< 10 µg/g	< 30 µg/g	< 30 µg/g	< 30 µg/g	< 100 µg/g	< 150 µg/g	< 35 µg/g	< 100 µg/g
LTR0077	2.4	2.7	2.5	58.9	1.40	0.17	0.28	4.28	24.78	0.21	0.31	1.83	< 10 µg/g	0.02	0.01	0.02	< 100 µg/g	0.08	0.06	0.02
LTR0079	2.8	3.0	3.5	60.0	1.43	0.08	0.44	4.21	22.07	0.24	0.56	1.32	< 10 µg/g	0.02	0.01	0.04	< 10 µg/g	0.07	0.18	< 50 µg/g
LTR0080	3.8	2.3	3.2	62.7	1.03	0.03	0.65	1.55	22.77	0.13	0.38	1.29	< 20 µg/g	0.01	0.01	0.03	< 60 µg/g	0.05	0.16	< 100 µg/g
LTR0082	15.0	2.3	4.4	64.6	0.30	< 3µg/g	0.88	3.76	6.95	0.26	0.21	1.32	< 40 µg/g	< 50 µg/g	0.01	0.01	< 120 µg/g	0.04	0.08	< 200 µg/g
LTR0083	11.1	3.0	0.6	68.8	< 3µg/g	0.08	0.65	5.39	9.38	0.13	0.02	0.60	< 30 µg/g	< 30µg/g	< 20 µg/g	< 40 µg/g	< 70 µg/g	0.08	0.03	0.08
LTR0085	3.9	3.8	3.6	59.8	1.27	< 3µg/g	0.47	3.54	20.86	0.28	0.61	1.30	< 20 µg/g	0.02	0.01	0.03	< 160 µg/g	0.09	0.44	< 200 µg/g
LTR0087	3.6	3.3	3.4	58.8	1.23	0.10	0.59	3.01	22.68	0.29	0.81	1.87	< 50 µg/g	0.02	0.01	0.04	< 100 µg/g	0.06	0.22	< 100 µg/g
LTR0088*	2.7	3.1	4.4	59.5	1.91	n.m.	0.48	5.02	19.80	0.27	0.52	1.83	< 10 µg/g	30 µg/g	0.01	0.02	< 10 µg/g	0.07	0.20	0.02
LTR0089*	3.4	2.8	3.3	61.0	2.35	n.m.	0.61	2.32	21.40	0.20	1.30	0.96	< 10 µg/g	0.002	30 µg/g	0.02	< 10 µg/g	0.06	0.20	0.01
LTR0090*	2.7	3.8	3.3	59.8	1.84	n.m.	0.39	2.27	22.72	0.19	0.11	2.56	< 10 µg/g	30 µg/g	0.01	0.02	20 µg/g	0.13	0.03	0.03
LTR0091*	2.8	2.9	2.5	61.0	1.94	n.m.	0.38	2.32	23.65	0.16	0.12	1.81	< 10 µg/g	30 µg/g	0.01	0.02	20 µg/g	0.14	0.04	0.02
LTR0093*	2.7	3.0	3.6	59.9	2.36	n.m.	0.62	2.34	22.87	0.21	0.65	1.30	< 10 µg/g	30 µg/g	40 µg/g	0.02	< 10 µg/g	0.10	0.16	50 µg/g
LTR0095*	0.3	2.5	2.0	59.9	2.62	n.m.	0.09	3.45	27.84	0.20	0.43	1.26	80 µg/g	40 µg/g	0.01	0.03	0.02	0.08	0.06	0.01
LTR0096*	3.2	3.1	4.7	59.6	2.16	n.m.	0.57	2.28	20.51	0.31	0.61	2.66	10 µg/g	30 µg/g	40 µg/g	0.03	< 10 µg/g	0.06	0.14	0.01

n.m. stands for “not measured”

* these samples were analyzed by LA-ICP-MS

Table II.3: REE and trace elements concentration in µg/g for the LTR samples, measured by LA-ICP-MS.

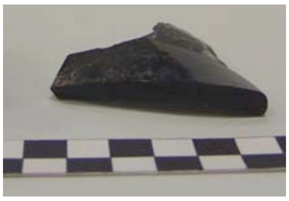
Samples	B	Ti	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	La
LTR0034	310	1692	31.8	22.2	7.3	25.2	23.2	61.7	34.0	12.6	2655	7.8	161	4.7	1.4	2.4	0.6	577	11.1
LTR0035	192	1320	23.8	13.4	6.2	21.0	45.7	203	12.9	37.2	742	8.5	169	4.5	1.5	18.2	4.7	1665	13.1
LTR0036	213	1528	34.3	21.3	6.2	20.7	15.0	53.5	24.6	26.6	2053	9.8	119	4.5	1.2	2.1	1.0	650	14.0
LTR0037	118	1121	24.9	12.9	2.9	10.9	23.3	135	9.8	18.5	1762	17.1	93.6	2.7	1.5	10.6	0.8	6279	19.1
LTR0039	192	1519	33.6	29.8	7.1	21.5	62.8	324	17.7	27.4	1038	12.0	282	4.6	3.1	32.8	1.6	640	20.1
LTR0042	55.9	36.1	3.9		1.6	6.2	20.6	8.9	5129	121	36.1	0.7	1.7	0.1	1.1	0.2	0.6	77.0	0.7
LTR0044	76.7	43.6	8.1		2.3	11.0	28.1	9.2	4593	116	48.3	0.6	1.9	0.1	1.3	0.3	0.5	62.9	0.5
LTR0047	221	1189	16.7	8.8	5.2	22.3	54.2	195	2.2	80.5	819	7.3	151	3.9	0.6	18.7	0.6	2071	11.7
LTR0049	186	1206	17.2	8.7	4.1	21.0	36.3	194	2.4	48.3	603	7.5	149	4.0	1.3	9.5	0.4	1617	11.9
LTR0050	247	2063	26.7	32.7	10.5	43.1	101	553	12.2	91.6	559	13.7	281	6.5	1.6	15.1	16.3	1303	20.8
LTR0051	196	2466	27.2	27.0	6.0	32.0	44.3	178	11.6	53.4	850	14.2	328	8.1	0.7	5.2	0.7	2393	21.3
LTR0052	164	1361	29.7	15.1	3.7	11.4	38.0	238	14.6	32.6	1041	16.0	122	3.4	2.5	17.8	1.0	1761	18.8
LTR0088	197	1645	24.2	9.5	6.6	25.0	61.7	160	2.2	92.9	622	9.7	201	5.0	0.6	19.0	0.6	1768	14.7
LTR0089	181	1209	14.3	7.7	3.8	19.1	22.3	186	1.5	33.8	492	7.3	166	4.6	0.5	2.1	0.2	1770	11.6
LTR0090	255	1154	34.8	17.3	6.9	21.2	85.0	193	18.4	19.4	1124	9.5	118	3.8	1.7	54.1	1.5	234	14.4
LTR0091	250	966	29.9	9.4	7.1	19.7	45.6	156	17.5	17.1	1225	8.9	118	3.1	1.7	21.2	1.8	400	13.1
LTR0093	182	1272	17.1	7.7	4.6	23.0	27.6	146	1.4	29.1	851	7.8	153	4.1	0.5	11.8	0.2	1439	12.6
LTR0095	190	1223	20.9	24.9	61.2	33.5	80.5	264	154	49.2	680	6.7	150	3.6	1.1	37.9	0.7	517	11.8

Table II.3 (cont.): REE and trace elements concentration in µg/g for the LTR samples, measured by LA-ICP-MS.

Samples	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th	U
LTR0034	24.0	2.4	9.6	1.8	0.5	1.4	0.2	1.4	0.3	0.9	0.1	0.9	0.1	4.0	30.4	2.7	4.3
LTR0035	25.7	2.7	11.0	2.0	0.5	1.6	0.3	1.6	0.3	1.0	0.1	1.0	0.2	4.4	231	3.3	1.5
LTR0036	26.0	2.9	11.8	2.1	0.6	1.7	0.3	1.8	0.4	1.0	0.1	1.1	0.2	3.0	66.6	3.0	3.2
LTR0037	34.8	4.0	17.5	3.4	1.3	3.1	0.5	2.8	0.5	1.5	0.2	1.4	0.2	2.4	53.8	3.7	6.1
LTR0039	41.3	4.5	19.2	3.6	0.7	2.6	0.4	2.2	0.4	1.3	0.2	1.3	0.2	7.0	133	4.4	2.2
LTR0042	0.9	0.1	0.5	0.1		0.1		0.1							8.7	0.1	0.2
LTR0044	0.8	0.1	0.4	0.1		0.1		0.1							5.3	0.1	0.4
LTR0047	22.4	2.4	9.1	1.6	0.5	1.5	0.2	1.4	0.3	0.8	0.1	0.9	0.1	4.0	158	3.1	0.9
LTR0049	22.9	2.3	9.8	1.9	0.5	1.6	0.2	1.4	0.3	0.8	0.1	0.9	0.1	3.8	90.8	3.1	0.9
LTR0050	39.5	4.3	17.3	3.2	0.7	2.7	0.4	2.5	0.5	1.6	0.2	1.6	0.2	7.3	151	4.9	1.6
LTR0051	42.6	4.4	17.9	3.0	0.8	2.8	0.5	2.7	0.5	1.7	0.3	1.8	0.2	8.6	45	5.8	1.9
LTR0052	36.8	4.2	17.7	3.6	0.9	2.9	0.5	2.7	0.5	1.6	0.2	1.6	0.2	3.2	98.9	4.2	5.6
LTR0088	28.9	3.0	12.1	2.2	0.6	1.8	0.3	1.8	0.3	1.0	0.1	1.1	0.2	5.1	200	3.8	1.1
LTR0089	21.7	2.3	9.2	1.6	0.5	1.5	0.2	1.3	0.3	0.9	0.1	0.9	0.1	4.2	62.0	2.9	0.8
LTR0090	26.9	3.0	12.4	2.3	0.5	2.0	0.3	1.7	0.3	1.1	0.1	1.0	0.2	3.1	255	3.2	2.0
LTR0091	23.	2.6	10.9	1.9	0.5	1.6	0.3	1.6	0.3	0.9	0.1	0.9	0.1	3.0	178	2.7	2.2
LTR0093	24.6	2.6	10.5	1.8	0.5	1.6	0.3	1.5	0.3	0.9	0.1	0.9	0.2	4.0	45.6	3.2	0.9
LTR0095	22.0	2.3	9.4	1.7	0.4	1.4	0.2	1.3	0.3	0.8	0.1	0.8	0.1	3.9	88.5	2.6	1.1
LTR0096	24.5	2.6	10.8	2.1	0.6	1.7	0.3	1.7	0.4	1.1	0.2	1.1	0.2	3.8	100	3.1	0.9

Catalogue I

LTR0001



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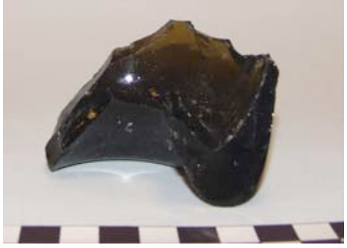

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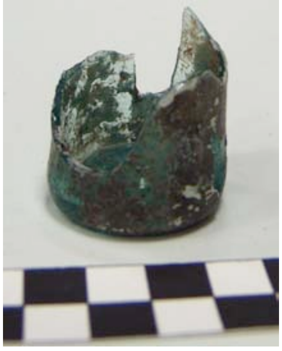

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LTR0006

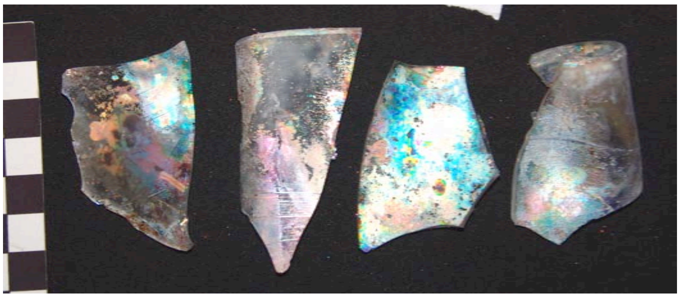
LTR0007

LTR0008

LTR0011

LTR0013

LTR0014



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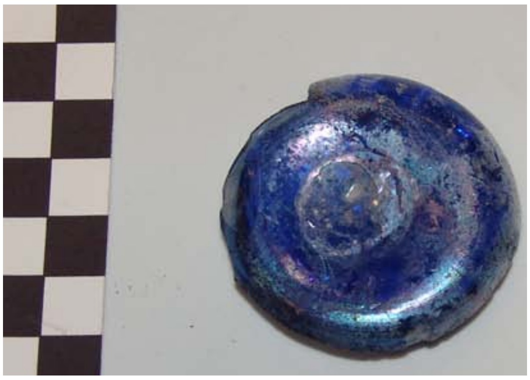

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LTR0021

LTR0024

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LTR0031

LTR0032

LTR0033

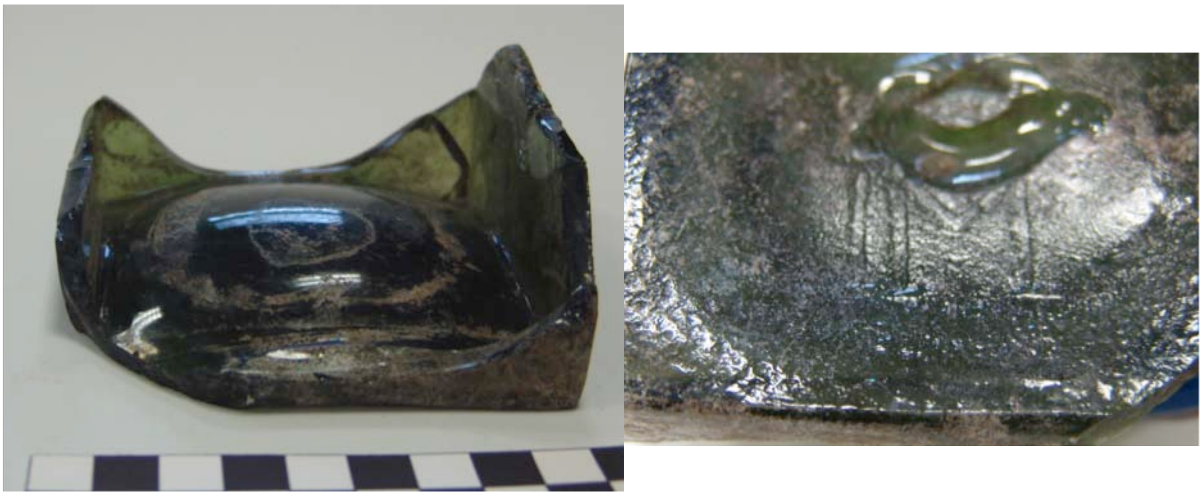
LTR0034

LTR0035

LTR0036

LTR0037

LTR0039



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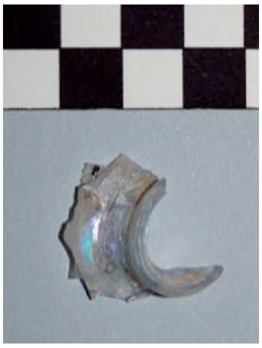

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LTR0044

LTR0047

LTR0049

LTR0050

LTR0051

LTR0052

LTR0055

LTR0056

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LTR0058

LTR0059

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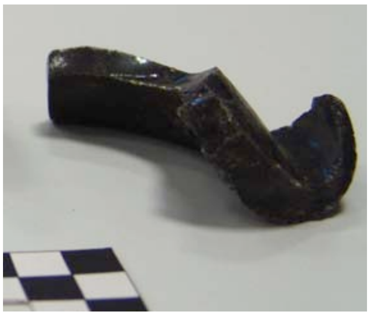
LTR0071

LTR0073

LTR0077



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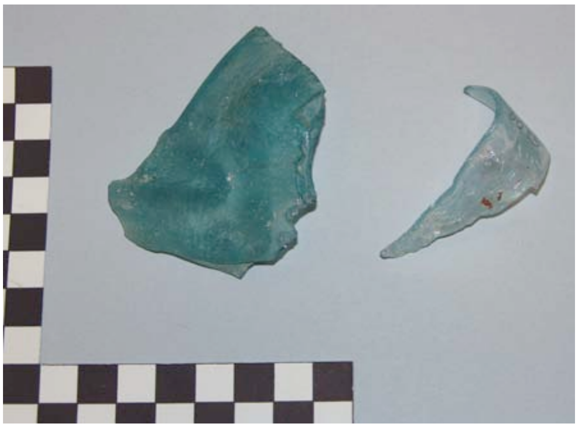

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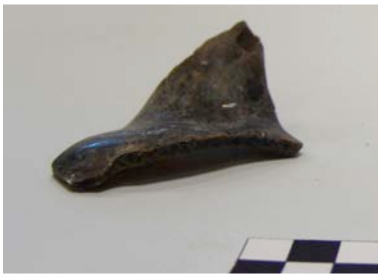
LTR0085

LTR0088

LTR0089



LTR0090

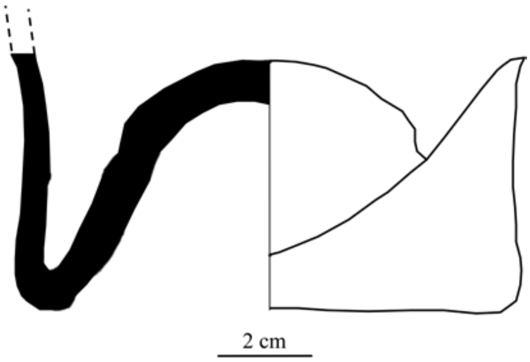
LTR0091

LTR0093

LTR0095

LTR0096

Catalogue I: Archaeological drawings



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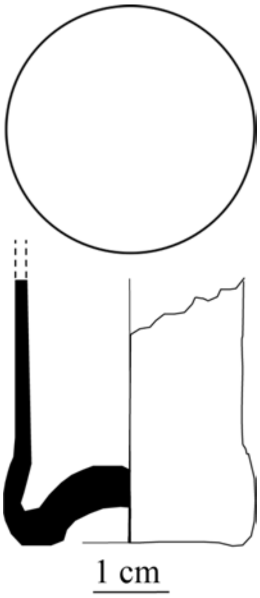

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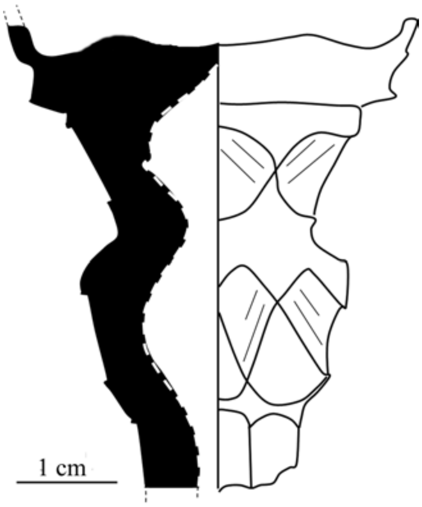

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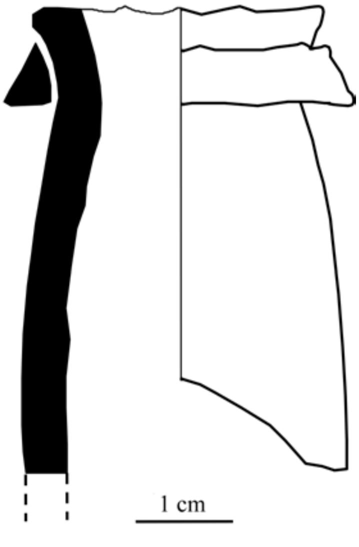

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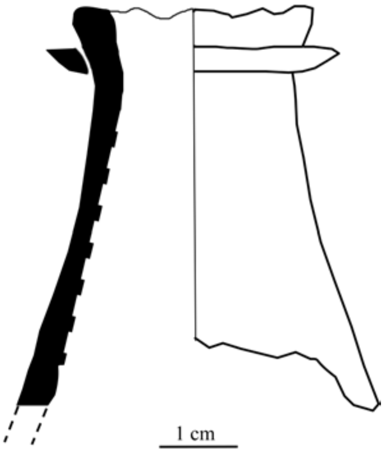

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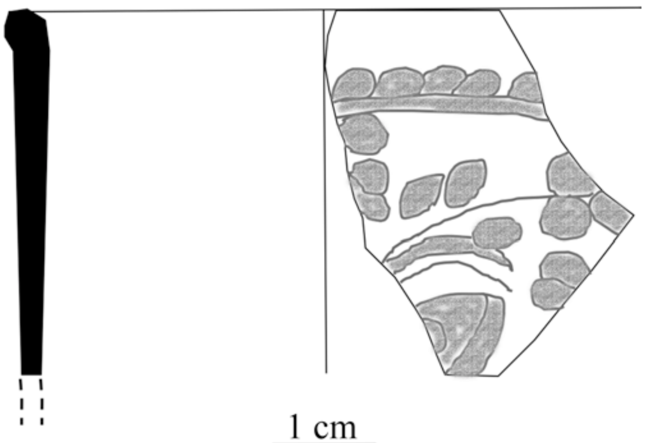

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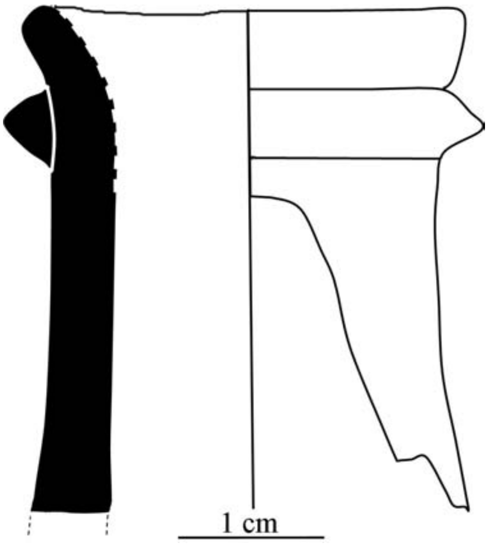

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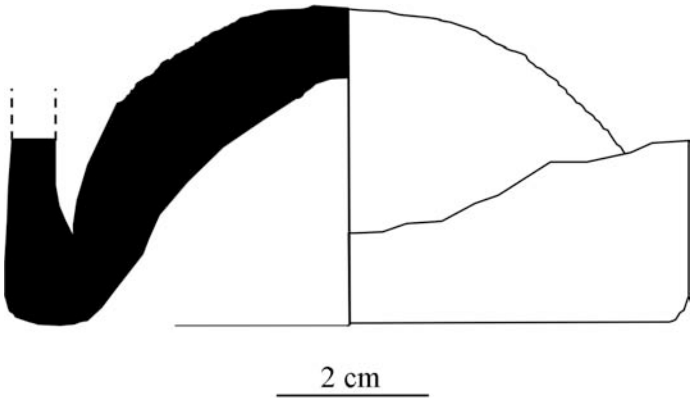

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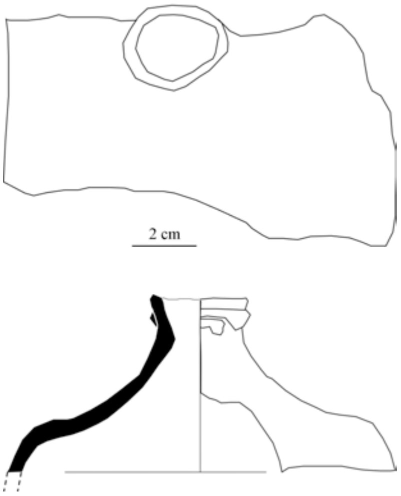

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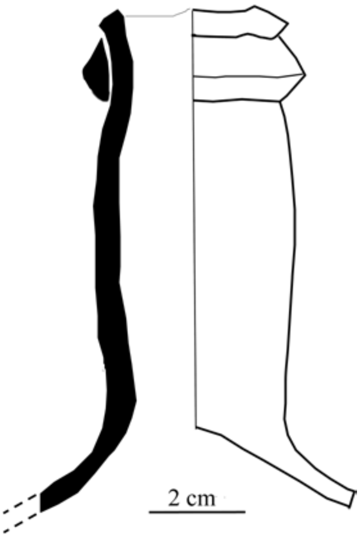

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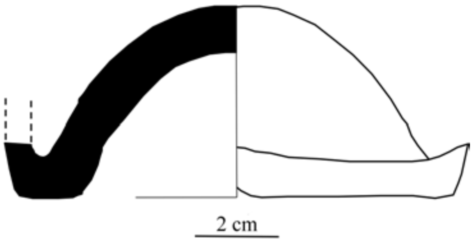

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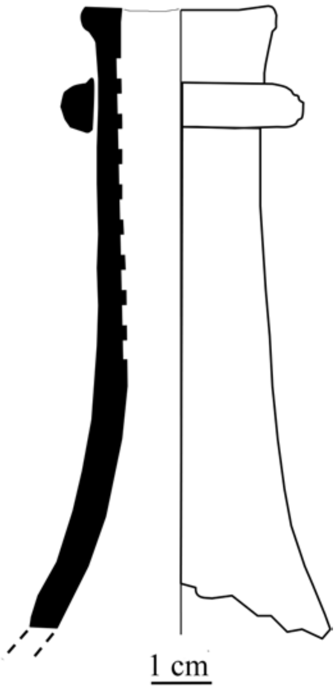

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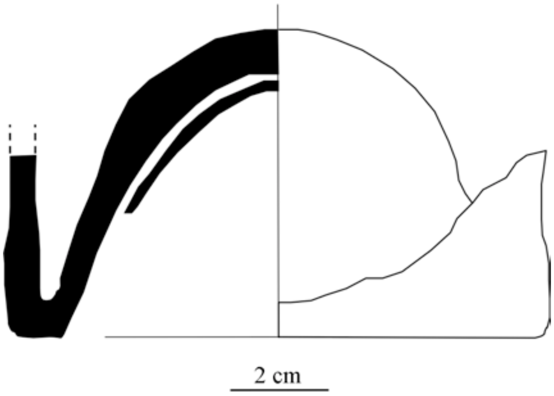

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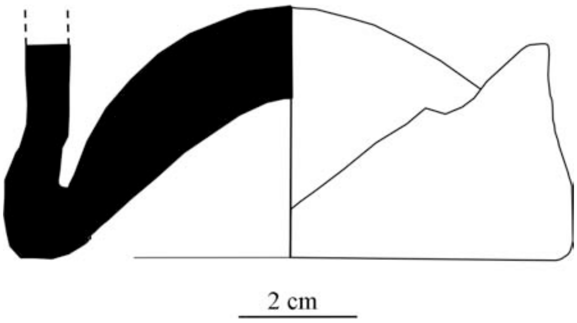

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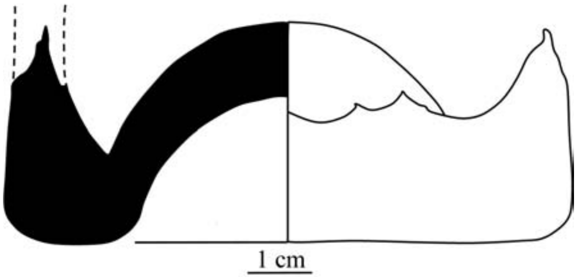

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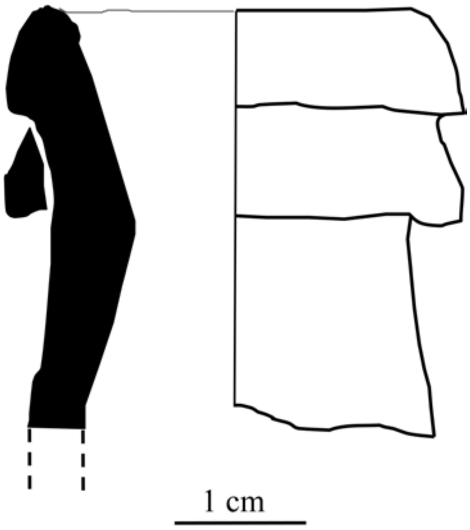

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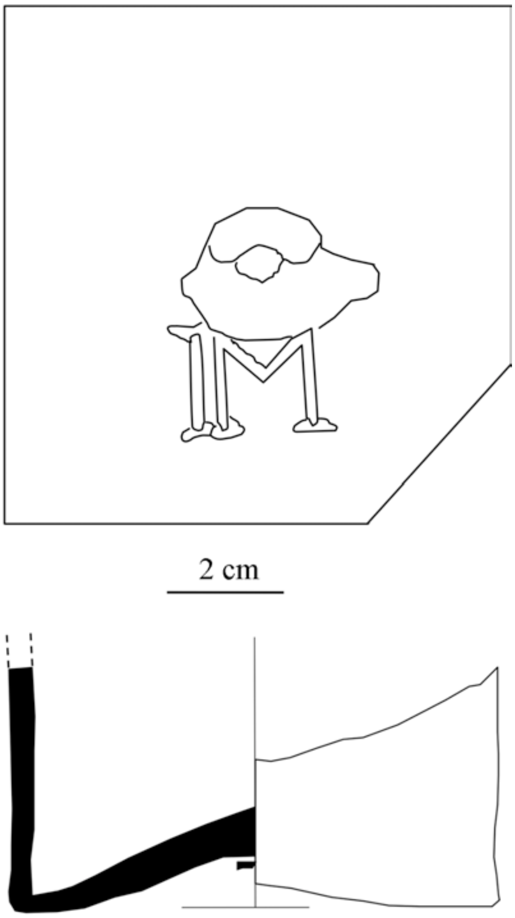

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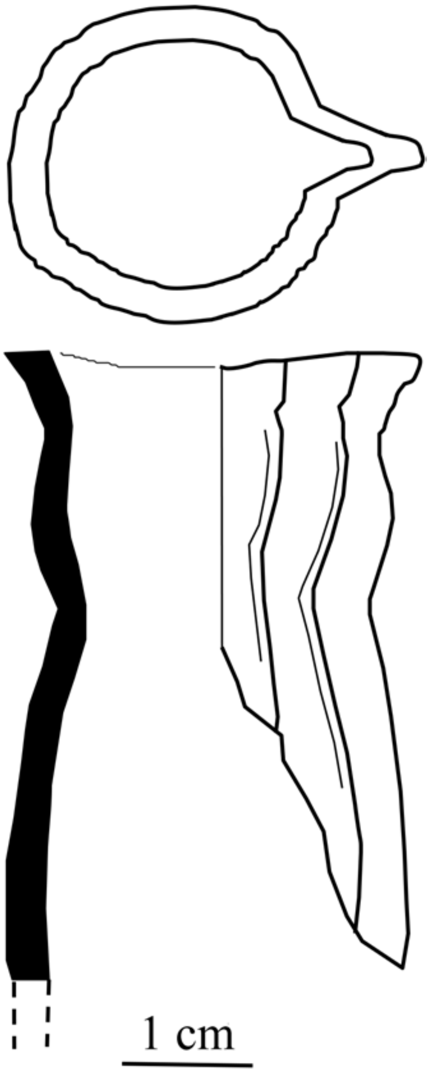

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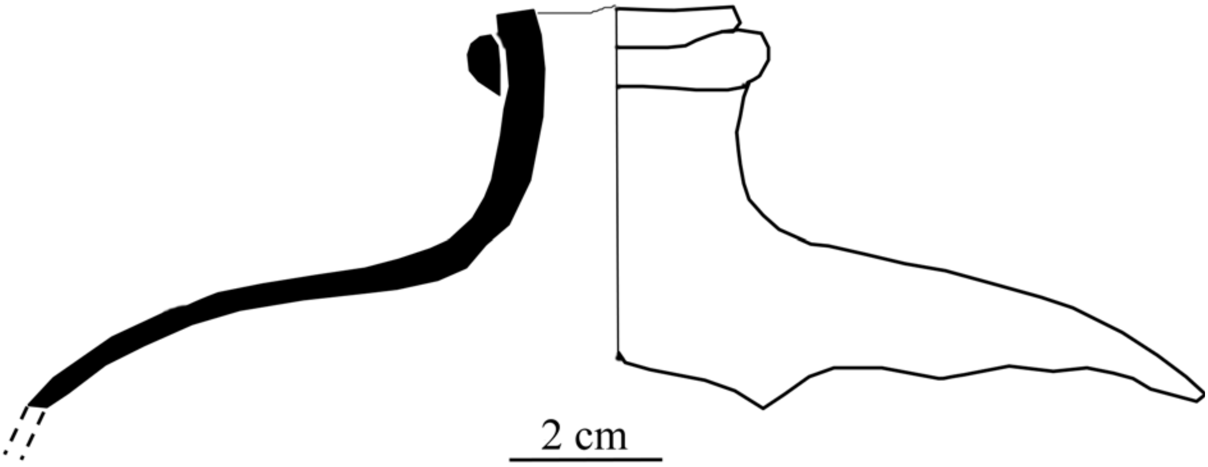

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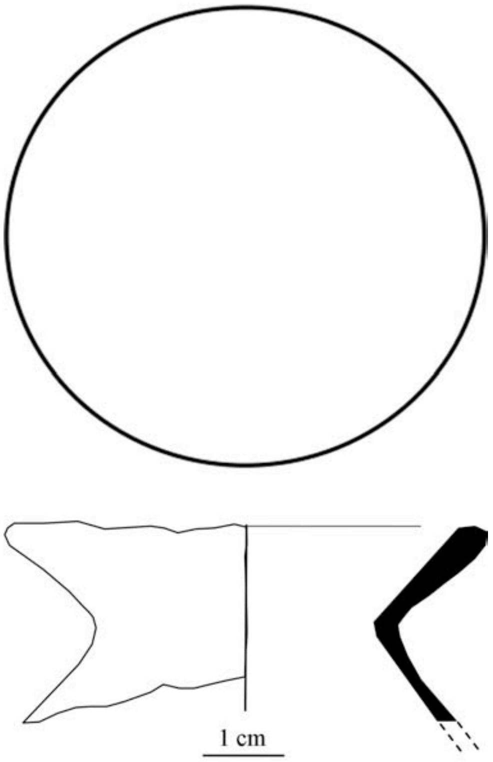

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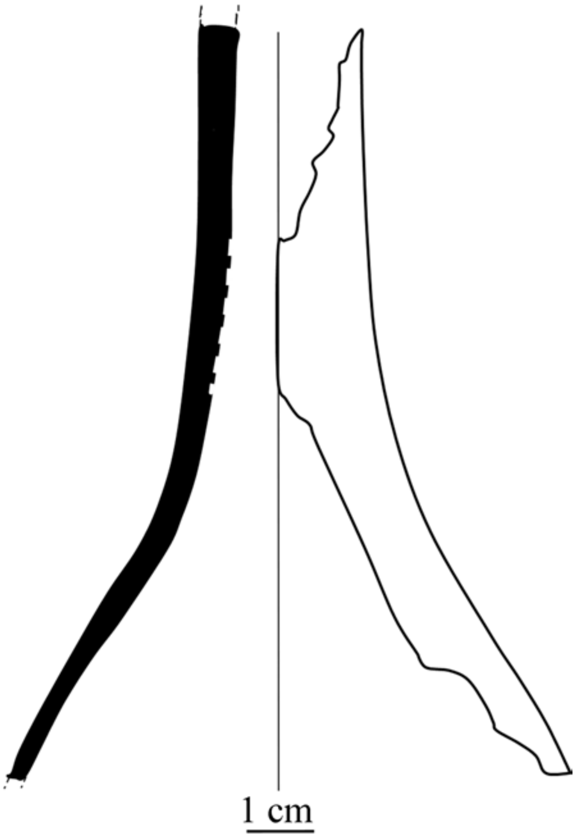

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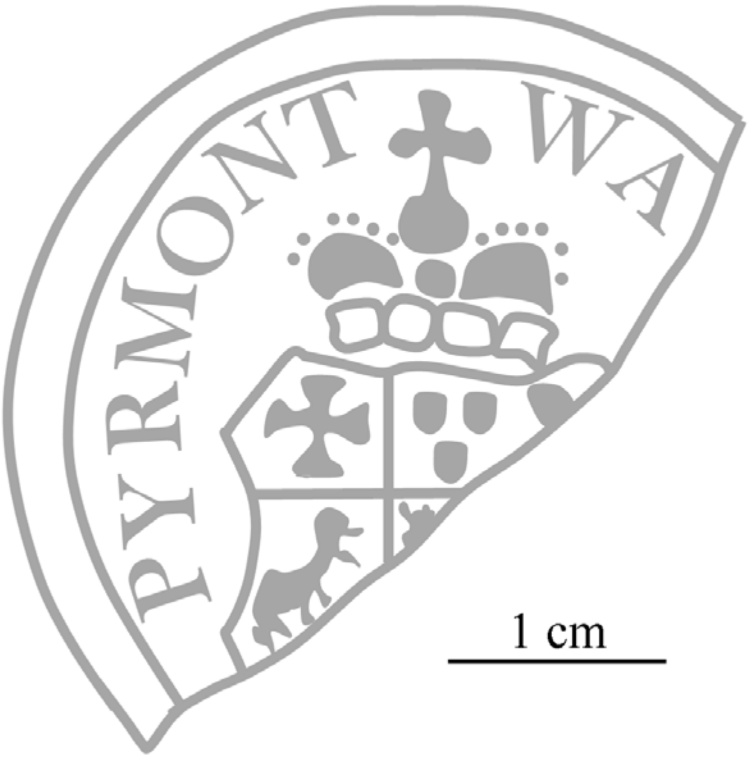

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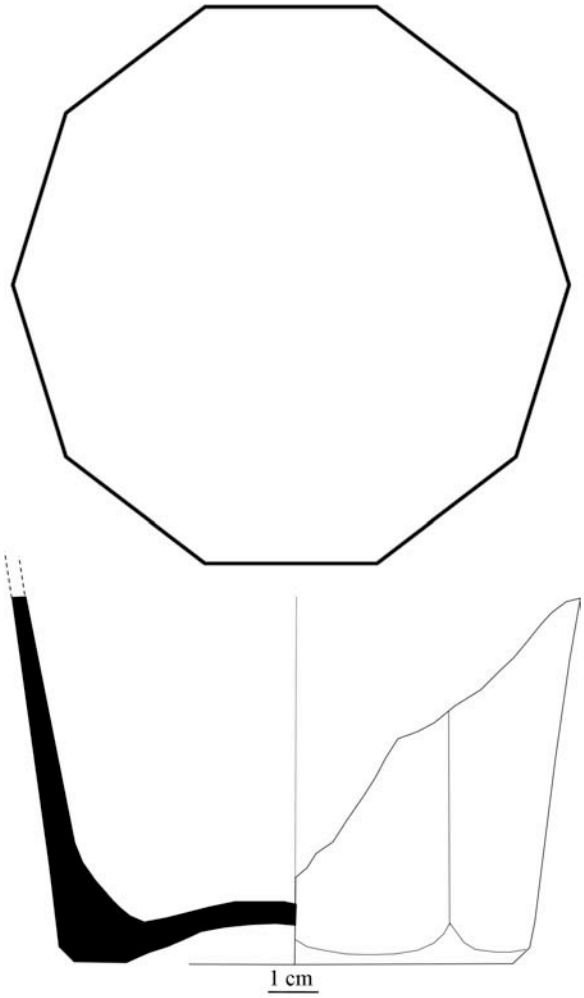

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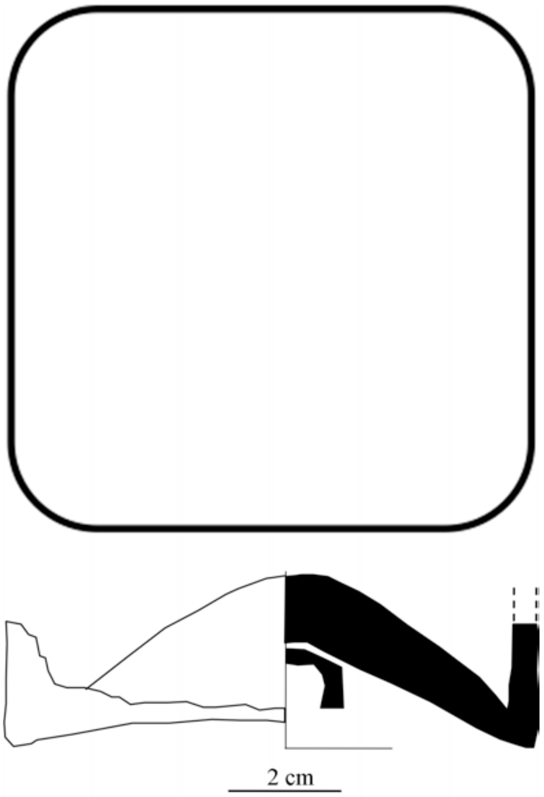

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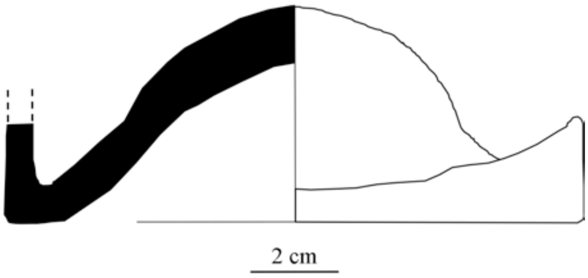

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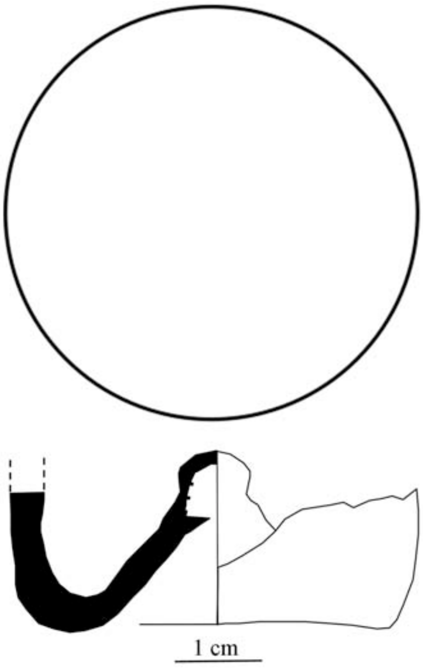

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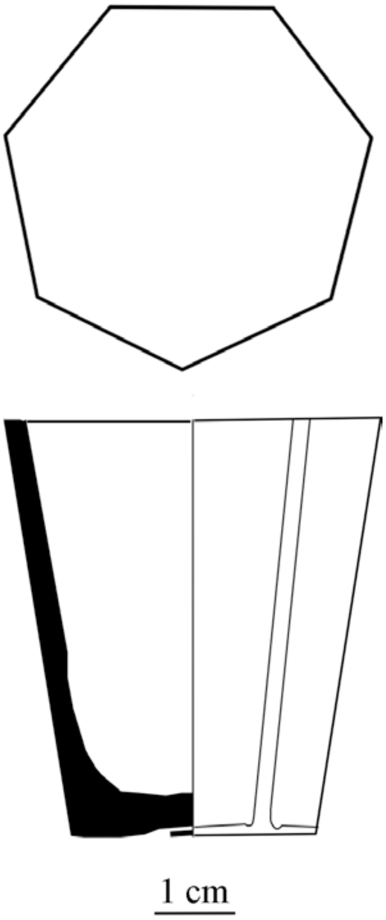

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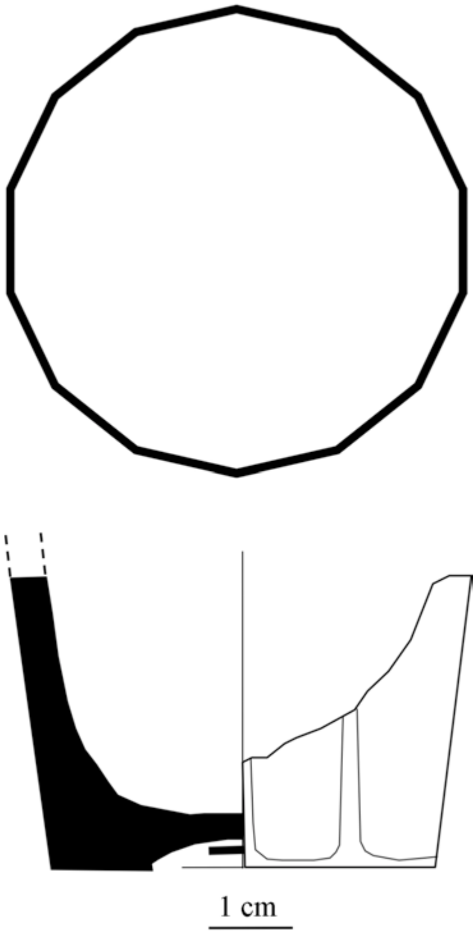

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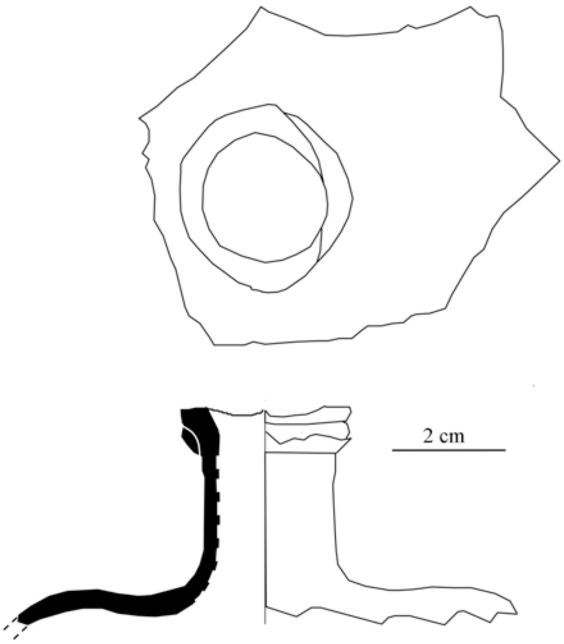

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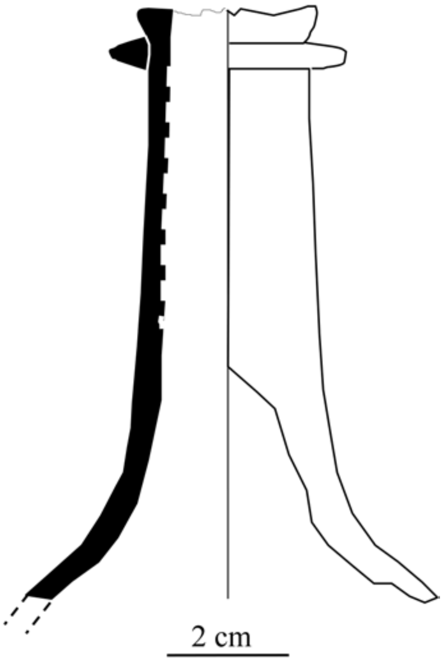

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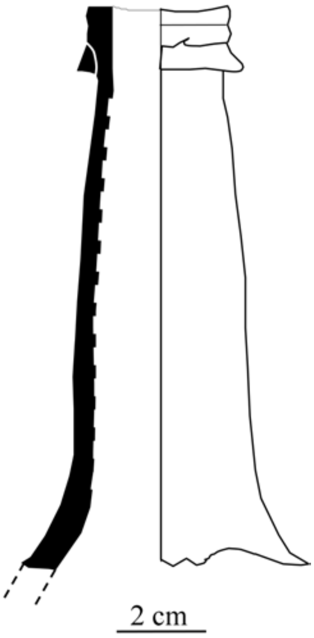

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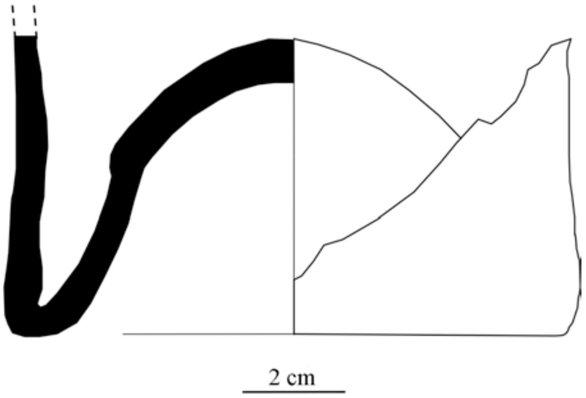

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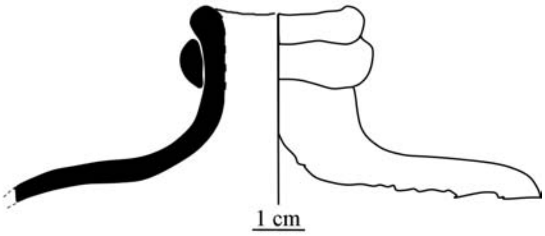

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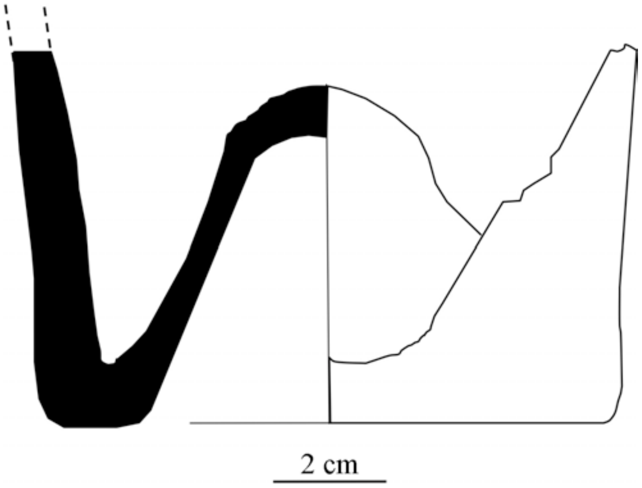


LTR0095

Appendix III: Rua do Arsenal (Lisbon) set (LRA) - Objects information, chemical composition, objects catalogue and archaeological drawings catalogue (Catalogue II).

Table III.1: Description of analyzed samples from Rua do Arsenal in Lisbon (LRA) with inventory number, object type, glass colouration, part of the object preserved and dating.

Fragments	*Type*	*Colour*	*Part preserved*	*Age (century A.D.)*
LRA0001	Vessel with enameled decoration	Uncoloured base glass with yellow enamels with black outline	Rim	17th
LRA0002	Vessel with one wing and engraved decoration (vegetable motifs)	Uncoloured glass	Base, wing and part of the body	17th
LRA0003	Beaker	Uncoloured glass	Base and part of wall	17th
LRA0004	Beaker	Uncoloured glass	Base and part of wall	17th
LRA0005	Vessel with enamel decoration	Uncoloured base glass with blue enamel	Base and a small part of the body	17th
LRA0006	Vessel	Uncoloured glass	Rim	17th
LRA0007	Vessel with engraved decoration	Uncoloured glass	Rim	17th
LRA0009	Bottle – B or C	Olive green	Base	17th
LRA0011	Bottle – B or C	Black	Base	17th
LRA0012	Bottle, onion shape – B	Black, interior base is turquoise blue.	Complete	17th
LRA0013	Vessel (probably a flask)	Uncoloured with light turquoise hue	Neck	17th
LRA0015	Bottle	Olive green	Neck	17th

LRA0016	Bottle	Olive green	Neck	17th
LRA0017	Bottle	Black	Neck	17th
LRA0018	Bottle	Olive green	Neck	17th
LRA0020	Bottle	Olive green	Neck	17th
LRA0022	Bottle – C	Black	Base (circular)	17th
LRA0024	Bottle – C	Olive green	Base (circular)	17th
LRA0025	Bottle – C	Black	Base (circular)	17th
LRA0029	Bottle	Olive green	Neck	17th
LRA0033	Bottle – B or C	Olive green	Part of body	17th
LRA0034	Bottle – C	Turquoise blue	Base (circular)	17th
LRA0036	Bottle – C	Black	Base (circular)	17th
LRA0038	Bottle – C	Black	Base (circular)	17th
LRA0044	Bottle – C	Olive green	Base (circular)	17th
LRA0045	Bottle – C	Olive green	Base (circular)	17th
LRA0047	Bottle – C	Green / turquoise blue	Base (circular)	17th
LRA0049	Bottle – B or C	Black	Part of body	17th
LRA0056	Bottle – B or C	Turquoise blue	Small base fragment	17th
LRA0058	Bottle (square or prismatic shape) – A	Olive green	Base	17th

LRA0059	Bottle – C	Black	Base (circular)	18th
LRA0060	Bottle – C	Black	Base (circular)	18th
LRA0064	Bottle – C	Green / turquoise blue	Base (circular)	18th
LRA0068	Bottle	Olive green	Neck	18th
LRA0069	Bottle – C	Black	Base (circular)	18th
LRA0072	Bottle (square or prismatic shape) – A	Olive green	Lip, neck and part of body	17th
LRA0074	Bottle (square or prismatic shape) – A	Olive green	Part of body	17th
LRA0076	Vessel with engraving decoration	Uncoloured glass	Part of wall	17th
LRA0077	Vessel	Uncoloured glass	Part of wall	17th
LRA0090	Flask with rectangular shape	Uncoloured glass with light green hue	Neck and part of body	17th
LRA0091	Bottle with mark on the bottom (no push-up) – Letters “FCN” with the infinity symbol open in one of the sides, with a snake head. – C	Olive green	Base and part of body (cylindrical)	19th c.
LRA0092	Bottle (cylindrical) – C	Olive green with brownish hue	Part of body	19th c.
LRA0095	Melted fragment	Uncoloured		?
LRA0097	Bottle	Olive green	Neck	?
LRA0105	Bottle – C	Emerald green	Base (circular)	19th
LRA0112	Vessel (probably a beaker) with mould-blown ribbed decoration	Uncoloured glass	Rim and part of wall	19th
LRA0114	Bottle	Olive green	Neck	18th
LRA0118	Vessel	Uncoloured glass	Wall	19th

LRA0122	Vessel with wing	Seems opalescent (corrosion?)	Wing	18th
LRA0123	Vessel with engraved decoration	Uncoloured glass	Rim	18th / 19th
LRA0126	Beaker with mould-blown ribbed decoration	Uncoloured glass	Base and part of body	18th / 19th
LRA0134	Vessel	Uncoloured glass	Rim	16th / 17th
LRA0141	Bottle – C	Black	Base (circular)	19th
LRA0146	Vessel	Green glass	Rim	19th
LRA0158	Window glass	Uncoloured with light blue hue	Part of window glass	18th
LRA0160	Bottle – C	Black	Base (circular)	17th
LRA0161	Bottle	Black	Neck	17th
LRA0170	Bottle – C	Olive green	Base (circular)	18th
LRA0181	Window glass	Uncoloured glass	Part of window glass	18th
LRA0182	Vessel with enameled decoration	Uncoloured with enameled decoration (red enameled dots)	Fragment of wall	18th

Table III.2: Composition of fragments from Rua do Arsenal in Lisbon (LRA) determined by LA-ICP-MS in weight percent of oxides.

Samples	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**As_2O_3**	**SrO**	**BaO**	**PbO**
LRA0001	0.2	0.3	0.1	73.7	0.08	0.20	14.43	9.43	0.01	0.06	0.04	< 10 µg/g	< 10 µg/g	< 10 µg/g	< 10 µg/g	1.40	30 µg/g	10 µg/g	< 10 µg/g
LRA0002	0.3	0.3	0.2	73.4	0.08	0.20	14.45	9.71	0.01	0.07	0.05	< 10 µg/g	< 10 µg/g	< 10 µg/g	< 10 µg/g	1.34	40 µg/g	20 µg/g	< 10 µg/g
LRA0003	0.3	0.6	0.3	72.8	0.05	0.17	15.46	8.23	0.01	0.04	0.03	< 10 µg/g	< 10 µg/g	< 10 µg/g	< 10 µg/g	2.05	30 µg/g	0.01	< 10 µg/g
LRA0004	0.3	0.6	0.5	72.9	0.08	0.27	15.04	8.34	0.02	0.08	0.20	< 10 µg/g	< 10 µg/g	10 µg/g	20 µg/g	1.53	40 µg/g	0.01	< 10 µg/g
LRA0005	0.3	0.3	0.1	73.3	0.08	0.21	14.51	9.73	0.01	0.06	0.04	< 10 µg/g	< 10 µg/g	< 10 µg/g	< 10 µg/g	1.37	30 µg/g	10 µg/g	< 10 µg/g
LRA0006	0.4	0.2	0.4	71.1	0.05	0.22	14.72	10.98	0.01	0.09	0.10	< 10 µg/g	< 10 µg/g	< 10 µg/g	10 µg/g	1.62	0.01	0.01	< 10 µg/g
LRA0007	0.6	0.4	0.2	70.9	0.06	0.22	17.04	9.05	0.01	0.04	0.05	< 10 µg/g	< 10 µg/g	10 µg/g	< 10 µg/g	1.42	30 µg/g	50 µg/g	< 10 µg/g
LRA0009	2.0	2.5	2.5	59.7	1.76	0.33	2.56	26.35	0.16	0.13	1.69	< 10 µg/g	30 µg/g	0.01	0.02	0.01	0.12	0.05	0.03
LRA0011	1.3	4.7	4.9	56.6	0.22	0.24	2.24	26.42	0.24	0.20	2.19	< 10 µg/g	10 µg/g	10 µg/g	0.01	0.01	0.49	0.10	20 µg/g
LRA0012	1.6	2.5	3.8	60.1	1.45	0.33	2.07	24.75	0.20	0.17	2.67	< 10 µg/g	30 µg/g	0.01	0.03	30 µg/g	0.09	0.08	0.01
LRA0013	14.2	1.5	8.0	58.4	0.64	0.95	4.62	10.27	0.28	0.04	0.90	< 10 µg/g	10 µg/g	20 µg/g	0.01	< 10 µg/g	0.04	0.03	0.01
LRA0015	1.8	2.6	3.3	60.4	1.89	0.32	3.45	23.42	0.21	0.30	2.02	10 µg/g	30 µg/g	0.01	0.03	20 µg/g	0.10	0.11	0.08
LRA0016	1.7	3.2	3.8	57.9	1.82	0.28	2.06	25.94	0.21	0.28	2.34	< 10 µg/g	30 µg/g	0.01	0.05	40 µg/g	0.10	0.22	0.02
LRA0017	2.2	3.8	5.3	58.3	0.82	0.34	2.56	23.07	0.25	0.24	2.70	< 10 µg/g	20 µg/g	0.01	0.05	20 µg/g	0.11	0.10	0.01
LRA0018	1.6	3.1	3.6	58.5	1.93	0.25	2.13	25.52	0.20	0.30	2.31	< 10 µg/g	30 µg/g	0.01	0.05	20 µg/g	0.10	0.20	0.02
LRA0020	1.9	3.5	3.2	58.7	1.45	0.21	2.04	26.00	0.17	0.12	2.32	< 10 µg/g	20 µg/g	0.01	0.04	30 µg/g	0.15	0.11	0.02
LRA0022	3.2	2.7	3.8	61.2	2.26	0.77	1.86	22.11	0.18	0.55	1.08	< 10 µg/g	20 µg/g	50 µg/g	0.03	< 10 µg/g	0.06	0.13	0.01
LRA0024	3.2	2.7	3.9	61.1	2.24	0.79	1.89	22.05	0.18	0.56	1.09	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.06	0.13	0.01
LRA0025	1.2	3.1	4.8	60.7	0.92	0.26	2.39	23.58	0.22	0.23	2.13	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.11	0.14	0.01
LRA0029	3.0	4.4	3.0	59.0	2.64	0.84	0.84	24.17	0.15	0.38	1.26	< 10 µg/g	20 µg/g	50 µg/g	0.03	50 µg/g	0.06	0.05	0.01
LRA0033	2.1	3.1	3.5	60.4	1.81	0.34	2.14	23.46	0.20	0.24	2.29	< 10 µg/g	30 µg/g	0.01	0.05	30 µg/g	0.11	0.14	0.01
LRA0034	1.7	3.2	3.7	58.0	1.88	0.26	2.12	25.83	0.20	0.31	2.34	< 10 µg/g	30 µg/g	0.01	0.05	20 µg/g	0.10	0.20	0.02
LRA0036	1.5	3.9	5.5	59.3	0.84	0.31	2.38	22.83	0.25	0.24	2.57	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.09	0.10	0.01
LRA0038	1.8	3.8	5.5	58.3	0.89	0.35	2.54	23.37	0.24	0.22	2.64	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.10	0.09	0.01
LRA0044	2.1	3.1	3.6	60.5	1.80	0.33	2.14	23.38	0.20	0.24	2.30	< 10 µg/g	30 µg/g	0.01	0.05	30 µg/g	0.11	0.14	0.01
LRA0045	3.2	2.7	3.8	61.3	2.27	0.77	1.88	22.01	0.18	0.55	1.07	< 10 µg/g	20 µg/g	50 µg/g	0.03	< 10 µg/g	0.06	0.13	0.01
LRA0047	1.1	4.0	4.7	58.6	1.10	0.21	2.09	24.52	0.23	0.17	2.58	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.25	0.15	0.01
LRA0049	2.0	3.4	3.9	58.6	1.82	0.31	2.24	24.27	0.21	0.24	2.61	10 µg/g	30 µg/g	0.01	0.05	30 µg/g	0.11	0.16	0.01
LRA0056	1.4	3.0	3.7	59.2	1.80	0.24	2.15	25.02	0.20	0.32	2.36	< 10 µg/g	30 µg/g	0.01	0.05	20 µg/g	0.09	0.18	0.02
LRA0058	0.4	2.6	2.8	62.1	2.30	0.10	5.53	21.57	0.16	1.13	0.80	90 µg/g	50 µg/g	0.01	0.02	0.03	0.07	0.24	10 µg/g
LRA0059	1.6	3.4	4.0	59.2	1.24	0.40	2.18	24.17	0.18	0.20	2.26	< 10 µg/g	20 µg/g	0.01	0.03	20 µg/g	0.15	0.88	0.01
LRA0060	1.7	2.7	3.3	60.6	1.77	0.27	3.64	23.20	0.20	0.26	1.96	< 10 µg/g	30 µg/g	0.01	0.02	20 µg/g	0.10	0.11	0.08
LRA0064	1.7	3.2	3.7	57.9	1.88	0.26	2.14	25.84	0.20	0.31	2.35	< 10 µg/g	30 µg/g	0.01	0.05	20 µg/g	0.10	0.20	0.02
LRA0068	2.1	3.1	3.6	60.0	1.76	0.35	2.12	23.74	0.20	0.24	2.30	< 10 µg/g	30 µg/g	0.01	0.05	30 µg/g	0.11	0.14	0.01
LRA0069	1.3	4.9	5.2	55.9	0.21	0.25	2.23	26.60	0.23	0.21	2.25	< 10 µg/g	10 µg/g	10 µg/g	0.01	20 µg/g	0.49	0.10	20 µg/g
LRA0072	0.5	3.5	2.8	57.7	2.55	0.11	6.71	23.00	0.16	1.41	0.87	0.02	0.01	0.01	0.03	0.06	0.08	0.34	0.01
LRA0074	0.5	2.7	2.8	61.5	2.34	0.09	5.56	21.96	0.16	1.16	0.82	0.01	50 µg/g	0.01	0.02	0.02	0.07	0.25	10 µg/g
LRA0076	0.4	0.2	0.4	70.9	0.04	0.20	14.77	11.04	0.01	0.09	0.07	< 10 µg/g	< 10 µg/g	< 10 µg/g	10 µg/g	1.68	0.01	0.01	< 10 µg/g
LRA0077	0.1	0.0	0.3	55.4	0.01	0.10	8.28	0.30	0.04	0.07	0.12	< 10 µg/g	10 µg/g	0.01	20 µg/g	0.16	< 10 µg/g	50 µg/g	35.06
LRA0090	15.5	0.1	1.8	74.4	0.01	0.11	0.69	7.01	0.05	0.02	0.19	< 10 µg/g	< 10 µg/g	20 µg/g	30 µg/g	0.01	50 µg/g	0.01	0.02
LRA0091	6.6	0.4	3.0	70.0	0.03	0.09	0.95	15.23	0.44	0.31	2.88	< 10 µg/g	<10 µg/g	<10 µg/g	50 µg/g	< 10 µg/g	0.01	0.01	30 µg/g
LRA0092	5.0	0.8	9.3	63.0	0.08	0.10	2.56	15.85	0.38	0.15	2.49	< 10 µg/g	10 µg/g	<10 µg/g	0.01	10 µg/g	0.04	0.06	30 µg/g

LRA0095	0.0	0.0	0.1	54.1	0.02	0.09	8.81	0.19	0.03	n.d.	0.04	< 10 µg/g	< 10 µg/g	0.01	< 10 µg/g	10 µg/g	< 10 µg/g	20 µg/g	36.51
LRA0097	1.8	2.9	4.1	56.4	3.01	0.30	5.62	22.79	0.33	0.36	2.00	< 10 µg/g	40 µg/g	0.01	0.04	20 µg/g	0.07	0.05	40 µg/g
LRA0105	2.6	3.4	4.2	58.8	2.34	0.63	2.69	22.58	0.27	0.89	1.30	< 10 µg/g	30 µg/g	40 µg/g	0.02	< 10 µg/g	0.10	0.19	30 µg/g
LRA0112	0.5	0.2	1.5	67.9	0.05	0.26	14.52	8.53	0.07	0.27	0.17	< 10 µg/g	< 10 µg/g	20 µg/g	30 µg/g	0.41	30 µg/g	0.01	5.57
LRA0114	2.0	2.1	3.9	61.1	0.95	0.29	2.50	24.26	0.22	0.11	2.27	< 10 µg/g	20 µg/g	40 µg/g	0.01	30 µg/g	0.10	0.07	0.01
LRA0118	13.2	1.0	1.5	73.4	0.02	0.15	0.64	9.84	0.04	n.d.	0.06	< 10 µg/g	< 10 µg/g	< 10 µg/g	< 10 µg/g	0.02	30 µg/g	20 µg/g	< 10 µg/g
LRA0122	0.8	0.2	0.6	65.7	5.48	0.18	18.86	7.48	0.04	0.39	0.13	< 10 µg/g	10 µg/g	40 µg/g	0.01	20 µg/g	0.01	0.03	0.01
LRA0123	0.5	0.1	1.9	64.9	0.08	0.15	18.38	10.09	0.02	0.27	0.17	< 10 µg/g	< 10 µg/g	30 µg/g	40 µg/g	0.63	40 µg/g	0.02	2.69
LRA0126	0.6	0.2	0.3	76.0	0.08	0.17	13.18	9.09	0.01	0.01	0.07	< 10 µg/g	20 µg/g	30 µg/g	10 µg/g	0.38	40 µg/g	40 µg/g	< 10 µg/g
LRA0134	0.2	0.1	1.6	65.1	0.05	0.08	18.73	9.76	0.03	0.18	0.14	< 10 µg/g	< 10 µg/g	20 µg/g	20 µg/g	0.48	40 µg/g	0.01	3.46
LRA0141	1.7	4.5	4.7	58.8	1.33	0.33	2.49	22.56	0.23	0.27	2.69	< 10 µg/g	20 µg/g	0.01	0.05	20 µg/g	0.12	0.09	0.01
LRA0146	5.1	4.1	2.5	61.5	2.36	0.92	3.72	17.51	0.25	0.51	0.99	< 10 µg/g	30 µg/g	20 µg/g	0.02	40 µg/g	0.19	0.05	0.01
LRA0158	8.1	2.7	0.6	68.9	0.73	0.68	5.60	11.76	0.07	0.15	0.28	< 10 µg/g	< 10 µg/g	30 µg/g	0.01	20 µg/g	0.09	0.03	0.21
LRA0160	1.5	3.3	4.4	60.3	1.28	0.37	2.50	23.25	0.22	0.16	2.40	< 10 µg/g	20 µg/g	0.01	0.05	20 µg/g	0.11	0.07	0.01
LRA0161	2.7	3.2	4.0	58.8	1.81	0.36	2.45	23.40	0.22	0.19	2.53	10 µg/g	30 µg/g	0.01	0.06	40 µg/g	0.12	0.09	0.02
LRA0170	3.5	3.0	3.4	58.1	2.70	0.76	0.80	25.33	0.21	0.39	1.42	< 10 µg/g	10 µg/g	30 µg/g	0.04	< 10 µg/g	0.10	0.13	0.01
LRA0181	7.9	0.1	0.6	71.7	0.08	0.63	13.23	5.48	0.01	0.01	0.07	< 10 µg/g	< 10 µg/g	10 µg/g	10 µg/g	0.02	30 µg/g	40 µg/g	< 10 µg/g
LRA0182	1.3	0.1	0.3	73.8	0.08	0.16	13.60	9.02	0.06	0.06	0.05	< 10 µg/g	< 10 µg/g	10 µg/g	20 µg/g	1.41	0.02	0.01	10 µg/g

Table III. 3: REE and trace elements concentration in µg/g for the LRA samples, measured by LA-ICP-MS.

Samples	B	Ti	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	La
LRA0001	44.5	34.4	1.60		0.5	3.0	5.9	4.49	10623	204	28.7	0.7	1.1	0.1	0.3	0.1	4.7	10.5	0.6
LRA0002	45.3	44.8	1.66		0.7	3.4	6.1	5.2	10173	210	31.4	0.8	2.1	0.1	0.3	0.1	5.0	19.8	0.7
LRA0003	85.7	80.4	4.41		0.7	2.0	6.3	6.7	15542	401	22. 8	0.5	3.3	0.2	0.2	0.1	5.6	62.1	0.5
LRA0004	63.5	138.5	5.81		0.8	3.3	8.4	15.7	11585	296	30.3	0.8	3.5	0.4	0.2	0.5	2.5	64.0	1.3
LRA0005	46.2	35. 8	1.64		0.7	3.4	6.2	4.9	10391	208	29.2	0.7	1.1	0.1	0.4	0.1	5.2	10.6	0.6
LRA0006	80.4	49.9	4.56		2.2	3.1	4.7	11.4	12279	537	72.1	0.7	1.8	0.2	0.2	0.1	5.5	131	0.6
LRA0007	87.7	36.4	5.37		1.0	3.9	11.5	6.3	10776	236	27.7	0.4	1.2	0.1	0.6	0.1	2.8	40.9	0.4
LRA0009	201	953	25.98	13.2	6.2	24.2	66.4	159	50.7	21.1	973	9.2	131	3.1	1.9	35.8	1.3	432	13.1
LRA0011	105	1437	27.22	15.4	2.4	8.3	8.8	46.0	45.7	30.5	4123	21.6	179	3.3	1.5	1.8	0.6	9250	25.0
LRA0012	163	1193	27.86	17.8	6.8	20.8	54.3	220	19.0	25.6	795	10.2	122	3.6	2.0	29.0	1.2	698	14.8
LRA0013	135	1699	29.23	48.5	1.9	8.9	12.7	45.6	5.3	42.9	314	8.3	127	5.4	0.5	3.6	3.3	240	14.5
LRA0015	177	1237	31.22	20.6	7.5	22.9	69.4	209	14.5	37.8	818	10.5	149	3.7	2.6	48.3	4.0	1000	14.3
LRA0016	195.	1230	26.38	21.4	6.9	22.6	71.5	418	26.9	24.7	833	10.9	1301	3.5	1.4	31.7	1.5	1984	13.8
LRA0017	183	1481	36.40	17.5	5.8	13.9	55.9	377	18.4	30.7	931	19.2	140	3.7	1.5	25.5	1.0	921	22.9
LRA0018	189	1225	26.40	20.2	6.7	22.3	71.6	422	17.2	24.7	846	10.7	135	3.6	1.4	31.4	1.4	1799	14.8
LRA0020	219	1025	28.58	14.7	6.6	17.3	59.7	324	25.1	21.5	1281	9.5	100	3.1	1.9	28.3	1.3	949	13.7
LRA0022	159	1094	14.66	7.2	3.9	15.4	39.2	260	2.0	29.8	526	6.4	138	4.1	1.7	10.8	0.5	1174	10.3
LRA0024	166	1084	14.74	8.5	4.0	15.8	40.2	255	17.9	30.9	514	6.2	134	3.9	1.7	10.6	0.7	1159	9.7
LRA0025	150	1321	32.57	16.6	4.7	13.0	44.9	254	18.4	35.8	889	17.4	119	3.4	2.2	19.2	1.1	1259	20.2
LRA0029	219	921	19.32	9.5	5.0	18.1	38.6	257	34.9	11.1	511	6.9	72.0	3.2	0.4	37.6	2.0	476	10.8
LRA0033	239	1175	27.10	19.7	7.1	21.6	58.7	374	22.2	21.9	888	10.3	122	3.4	1.8	29.6	1.5	1291	13.8
LRA0034	198.	1217	26.28	22.2	7.0	23.1	72.9	417	16.9	25.0	831	10.5	131	3.5	1.4	31.9	1.7	1828	14.0
LRA0036	147	1522	35.02	17.6	5.4	14.6	41.9	217	13.2	34.6	778	19.5	145	3.6	1.6	21.8	0.9	885	21.9
LRA0038	152	1445	34.60	15.7	5.8	15.0	40.1	214	15.3	33.1	850	19.2	126	3.4	1.9	19.3	0.9	807	20.9
LRA0044	237	1183	27.15	19.9	7.0	21.4	58.2	376	21.6	21.8	894	10.3	122	3.5	1.7	29.6	1.4	1290	14.0
LRA0045	163	1092	14.85	6.7	3.9	15.3	39.7	253	1.6	30.4	524	6.3	138	3.9	1.7	10.7	0.4	1174	10.2
LRA0047	163	1353	29.10	15.3	6.4	16.8	59.0	274	17.6	32.3	2088	16.3	147	3.2	2.8	30.2	1.2	1354	18.8
LRA0049	222	1242	29.79	21.4	8.1	22.8	69.4	363	25.4	25.8	891	10.5	129	3.5	1.9	28.7	1.2	1426	13.9
LRA0056	190	1204	25.95	22.2	7.0	23.6	76.3	423	17.5	28.1	748	10.7	127	3.5	1.3	35.6	1.8	1636	14.0
LRA0058	174	949	9.98	4.8	70.5	41.1	50.9	184	201	94.3	599	5.6	125	2.8	2.1	1.4	0.3	2185	7.6
LRA0059	165	1108	28.04	17.5	5.3	18.8	43.3	273	13.3	22.6	1271	14.2	92	2.8	1.6	19.1	1.5	7900	15.3
LRA0060	190	1193	30.32	20.4	6.9	22.3	67.8	192	12.8	41.1	855	10.6	146	3.5	2.3	39.7	3.7	942	13.4
LRA0064	199.55	1211	26.52	22.4	7.0	23.3	73.5	416	15.9	25.3	825	10.5	130	3.5	1.4	32.3	1.7	1807	13.7
LRA0068	243	1171	27.06	22.1	7.2	21.7	59.6	371	22.6	22.1	895	10.0	119	3.3	1.6	29.7	1.5	1293	13.3
LRA0069	112	1399	27.04	18.1	2.75	9.7	9.1	45.6	13.0	31.6	4173	20.8	1694	3.1	1.3	1.81	0.9	927	22.4
LRA0072	204	948	10.84	7.8	148	73.2	64.9	231	448	152	708	5.8	135	2.8	2.6	23.1	1.0	3001	7.9
LRA0074	176	964	10.45	4.9	61.9	39.0	51.5	187	186	93.8	615	5.5	123	2.8	2.0	1.5	0.5	2257	7.8
LRA0076	79.1	46.7	4.51		2.1	2.61	4.3	10.9	12730	539	72.6	0.7	1.6	0.1	0.2	0.1	4.6	131	0.6
LRA0077	5.3	252	2.10		1.1	8.31	80.5	18.7	1192	6.2	6.7	1.1	25.6	1.0	0.1	67.2	667	40.5	1.4
LRA0090	66.7	287	2.23		0.9	1.8	19.5	26.6	72.9	24.8	40.3	2.0	33.1	0.9	0.0	2.3	18.2	106	3.1
LRA0091	82.8	2607	13.52	8.5	3.8	5.7	7.3	37.9	6.8	36.1	67.0	7.2	194	8.1	0.8	18.3	0.9	122	13.2
LRA0092	12.2	2269	44.7	13.8	4.6	9.4	7.3	73.0	10.1	66.8	327	11.3	268	41.9	0.7	1.1	0.6	577	39.4
LRA0095	35.3	197	2.6		0.2	6.0	49.4	4.0	10.1	88.9	2.0	0.9	20.1	0.8	0.4	0.2	434	14.2	0.8
LRA0097	252	2004	28.6	30.1	7.1	28.0	73.4		16.7	79.1	612	15.5	271	6.0	1.7	13.5	0.8	449	20.3
LRA0105	211	1600	19.1	13.7	4.9	24.2	31.5		2.31	43.1	813	9.2	218	5.4	1.1	10.8	0.1	1743	13.4
LRA0112	184	426	4.3		3.2	3.8	14.0	25.2	3116	286	26.9	3.2	34.1	1.7	0.9	3.8	2.7	125	3.8
LRA0114	151	1333	29.9	20.5	4.4	14.5	33.2	119	26.1	28.0	831	13.6	204.	4.0	1.9	17.6	1.4	613	19.6
LRA0118	28.6	229	3.4		0.8	2.2	1.3	4.2	134	45.3	26.0	3.0	116.8	0.9	9.7	1.8		17.4	3.6
LRA0122	147.	221	7.2		4.5	8.0	33.1	45.0	12.8	373	65.4	2.7	61.9	0.6	1.1	7.8	2.9	304	3.4
LRA0123	173	124	4.4		3.6	3.5	20.4	33.8	4802	402	36.1	2.0	15.2	0.4	7.6	1.3	3.6	146	2.8
LRA0126	55.9	67.9	4.4		1.7	13.2	20.9	8.1	2848	87.5	32.5	0.9	2.9	0.2	0.7	0.2		31.5	0.8
LRA0134	103	188	10.0		2.2	4.2	17.3	15.1	3655	209	30.0	2.1	20.7	0.6	1.4	1.8	2.5	132	3.2
LRA0141	184	1405	29.4	19.4	5.0	15.5	50.4	378	13.8	32.8	1025	16.1	139	3.6	1.2	25.8	1.2	835	19.5
LRA0146	371	1503	17.9	16.1	7. 2	26.0	12.6	185	28.5	22.9	1595	11.1	233	4.7	0.3	22.2	1.2	444	15.7
LRA0158	105	442	6.8		2.0	6.5	24.1	78.6	12.5	45.2	753	2.7	50.6	1.6	1.8	5.1	62.0	271	3.7
LRA0160	164	1304	29.3	19.5	5.9	16.8	53.4	413	15.3	35.1	966	13.4	144	3.7	1.8	32.3	1.4	600	17.8
LRA0161	202	1311	29.4	22.8	7.8	21.7	70.5	444	32.7	23.2	998	10.7	153	3.9	2.3	40.8	1.6	803	15.9
LRA0170	227	1265	16.3	12.7	3.8	11.3	25.1	360	0.5	13.2	831	7.2	200	3.9	0.6	15.2	0.7	1167	10.6
LRA0181	102	88.2	5.7		0.4	2.3	7.7	8.0	119	420	25.1	1.3	4.3	0.3	0.1	0.2	1025	38.7	1.4
LRA0182	79.0	369	5.8		0.9	2.7	8.6	13.0	10707	340	185	3.4	53.7	1.2	0.4	3.6	6.8	60.1	3.6

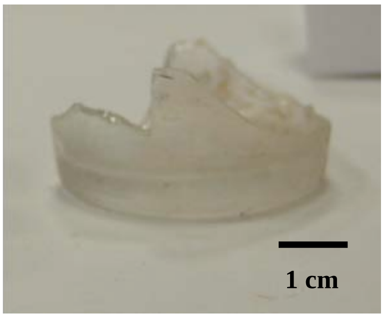
Table III.3 (cont.): REE and trace elements concentration in µg/g for the LRA samples, measured by LA-ICP-MS.

Samples	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th	U
LRA0001	0.9	0.1	0.6	0.1		0.1		0.1		0.1					0.5	0.1	0.3
LRA0002	1.1	0.1	0.6	0.1		0.1		0.1		0.1		0.1		0.1	1.4	0.1	0.2
LRA0003	1.0	0.1	0.4	0.0		0.1		0.07		0.1				0.1	0.7	0.1	0.1
LRA0004	2.3	0.2	1.1	0.2	0.08	0.1		0.1		0.1		0.1		0.1	4.9	0.3	0.2
LRA0005	0.8	0.1	0.5	0.1		0.1		0.1		0.1					1.2	0.1	0.2
LRA0006	0.9	0.1	0.5	0.1	0.06	0.1		0.1		0.1		0.1		0.1	2.4	0.1	0.2
LRA0007	0.7	0.1	0.3	0.1		0.1		0.1							0.2	0.1	0.1
LRA0009	22.8	2.6	11.1	2.0	0.4	1.9	0.2	1.5	0.3	0.9	0.1	1.0	0.1	3.3	254	2.6	1.4
LRA0011	45.0	5.3	22.9	4.4	1.0	4.0	0.6	3.5	0.6	2.1	0.2	1.9	0.2	4.7	15.3	5.0	7.8
LRA0012	28.6	3.2	13.8	2.6	0.6	2.3	0.3	1.9	0.3	1.1	0.1	1.1	0.1	3.0	120	3.3	1.4
LRA0013	28.7	3.0	12.0	2.3	0.4	2.0	0.3	1.6	0.3	1.0	0.1	1.0	0.1	3.4	83.2	6.0	1.5
LRA0015	26.6	3.0	12.7	2.4	0.6	2.4	0.3	1.9	0.3	1.1	0.1	1.1	0.1	3.9	788	3.1	1.9
LRA0016	26.0	3.0	13.1	2.4	0.9	2.9	0.3	1.8	0.3	1.1	0.1	1.1	0.1	3.3	169	3.0	1.5
LRA0017	43.3	4.8	20.6	4.0	0.9	3.6	0.5	3.1	0.6	1.8	0.2	1.7	0.2	3.7	95.1	4.6	7.9
LRA0018	28.0	3.2	13.5	2.4	0.7	2.4	0.3	1.8	0.3	1.1	0.1	1.0	0.1	3.5	175	3.4	1.6
LRA0020	26.5	2.9	12.3	2.4	0.6	2.2	0.3	1.8	0.3	1.0	0.1	1.0	0.1	2.6	143	3.0	1.9
LRA0022	19.8	2.1	8.3	1.5	0.5	1.7	0.2	1.2	0.2	0.7	0.1	0.8	0.1	3.5	87.7	2.7	0.7
LRA0024	18.9	2.0	8.0	1.4	0.5	1.6	0.2	1.2	0.2	0.7	0.1	0.8	0.1	3.4	88.6	2.5	0.7
LRA0025	39.2	4.3	18.8	3.7	0.9	3.4	0.5	2.9	0.5	1.7	0.2	1.6	0.2	3.1	86.5	4.2	6.2
LRA0029	20.3	2.2	9.5	1.8	0.4	2.0	0.2	1.3	0.2	0.7	0.1	0.7	0.1	1.9	128	2.9	1.1
LRA0033	25.9	3.0	12.8	2.4	0.7	2.5	0.3	1.8	0.3	1.1	0.1	1.0	0.1	3.0	132	3.1	1.6
LRA0034	26.4	3.0	12.9	2.6	0.9	2.8	0.3	1.9	0.3	1.2	0.1	1.1	0.1	3.4	172	3.2	1.5
LRA0036	42.4	4.8	21.0	4.2	1.0	4.2	0.6	3.3	0.6	1.9	0.2	1.8	0.2	3.8	92.1	4.4	8.5
LRA0038	40.4	4.6	20.2	3.7	0.9	4.1	0.5	3.1	0.6	1.9	0.2	1.7	0.2	3.4	90.7	4.4	8.1
LRA0044	26.0	3.0	13.0	2.5	0.7	2.6	0.3	1.8	0.3	1.1	0.1	1.0	0.1	3.1	129	3.1	1.6
LRA0045	19.9	2.0	8.4	1.4	0.5	1.6	0.2	1.2	0.2	0.8	0.1	0.8	0.1	3.7	87.8	2.7	0.7
LRA0047	36.8	4.1	18.5	3.5	1.0	3.6	0.5	2.8	0.5	1.7	0.2	1.6	0.2	3.7	127	4.0	5.7
LRA0049	26.5	3.0	13.2	2.6	0.8	2.9	0.3	1.8	0.3	1.1	0.1	1.1	0.1	3.3	137	3.2	1.7
LRA0056	26.7	3.1	13.2	2.5	0.9	3.0	0.3	1.9	0.3	1.1	0.1	1.1	0.1	3.3	189	3.1	1.6
LRA0058	14.7	1.5	6.5	1.1	0.7	1.5	0.2	1.0	0.1	0.6	0.1	0.7	0.1	3.2	10.9	1.8	1.0
LRA0059	27.9	3.3	15.0	2.9	2.6	4.0	0.4	2.3	0.4	1.3	0.1	1.3	0.1	2.4	1195	3.1	3.5
LRA0060	24.8	2.8	12.1	2.3	0.7	2.7	0.3	1.8	0.3	1.1	0.1	1.1	0.1	3.9	751	2.9	2.0
LRA0064	26.2	3.0	12.8	2.4	0.8	2.9	0.3	1.9	0.3	1.2	0.1	1.1	0.1	3.4	171	3.0	1.4
LRA0068	24.7	2.9	12.6	2.4	0.8	2.9	0.3	1.9	0.3	1.1	0.1	1.0	0.1	3.0	130	3.0	1.5
LRA0069	40.5	4.9	21.8	4.2	1.1	4.8	0.6	3.5	0.7	2.1	0.2	2.0	0.2	4.4	15.6	4.5	7.2
LRA0072	15.3	1.6	6.7	1.3	0.9	1.6	0.2	0.9	0.2	0.6	0.1	0.6	0.1	3.4	50.0	1.9	1.6
LRA0074	14.9	1.6	6.5	1.1	0.7	1.5	0.1	0.9	0.2	0.6	0.1	0.6	0.1	3.1	10.8	1.8	1.0
LRA0076	0.9	0.1	0.5	0.1	0.1	0.1		0.1		0.1		0.1		0.1	3.7	0.1	0.2
LRA0077	2.7	0.2	1.1	0.2	0.1	0.2		0.2		0.1		0.1		0.7	325463	0.3	0.1
LRA0090	5.3	0.6	2.5	0.5	0.1	0.5	0.1	0.3	0.1	0.2		0.2		0.9	139	1.1	0.5
LRA0091	26.9	2.9	11.7	2.2	0.2	1.6	0.2	1.4	0.2	0.8	0.1	0.8	0.1	4.7	25.0	5.6	1.9
LRA0092	65.0	5.7	20.8	3.0	0.9	4.4	0.4	1.9	0.3	1.2	0.1	1.2	0.1	5.9	28.0	6.7	1.5
LRA0095	1.6	0.1	0.6	0.1		0.1		0.1		0.1		0.1		0.5	338908	0.2	0.1
LRA0097	37.9	4.2	17.8	3.4	0.7	3.8	0.5	2.7	0.5	1.8	0.2	1.8	0.2	7.1	40.8	4.7	1.5
LRA0105	26.3	2.7	11.4	2.0	0.6	1.9	0.2	1.6	0.3	1.1	0.1	1.1	0.1	5.5	26.4	3.4	1.0
LRA0112	7.7	0.8	3.8	0.7	0.1	0.5	0.1	0.5	0.1	0.3		0.3		0.9	51683	1.5	1.1
LRA0114	35.6	4.2	17.9	3.4	0.7	3.0	0.4	2.6	0.4	1.5	0.1	1.4	0.19	5.4	76.3	4.6	2.2
LRA0118	6.1	0.7	3.1	0.5	0.1	0.5	0.1	0.4	0.1	0.2		0.3		2.9	7.5	1.3	0.9
LRA0122	6.6	0.7	3.1	0.6	0.1	0.4	0.1	0.4	0.1	0.2		0.3		1.5	60.9	1.6	0.8
LRA0123	4.6	0.5	2.2	0.3	0.1	0.3	0.1	0.3	0.1	0.1		0.1		0.4	24944	0.8	0.5
LRA0126	1.2	0.1	0.7	0.1		0.1		0.1		0.07		0.1		0.0	1.2	0.1	0.1
LRA0134	5.5	0.6	2.6	0.4	0.1	0.4	0.1	0.3	0.1	0.1		0.1		0.5	32144	1.0	0.5
LRA0141	37.7	4.1	17.7	3.4	0.8	3.0	0.5	2.7	0.5	1.6	0.2	1.5	0.2	3.6	92.4	4.3	5.4
LRA0146	28.2	3.0	12.4	2.2	0.4	2.0	0.3	1.9	0.3	1.2	0.1	1.2	0.1	6.0	80.2	3.6	2.2
LRA0158	6.7	0.7	2.9	0.6	0.1	0.4	0.1	0.4	0.1	0.3		0.3	0.1	1.3	1988	0.9	0.5
LRA0160	35.5	3.8	16.3	3.2	0.7	2.6	0.4	2.4	0.4	1.3	0.1	1.4	0.1	3.7	112	4.0	4.0
LRA0161	31.3	3.4	14.7	2.7	0.6	2.4	0.3	1.9	0.3	1.1	0.1	1.1	0.1	3.9	160	3.6	1.9
LRA0170	21.0	2.2	9.0	1.6	0.4	1.4	0.2	1.3	0.2	0.8	0.1	0.9	0.1	5.0	134	2.9	0.8
LRA0181	2.3	0.2	1.2	0.2		0.1		0.1		0.1		0.1		0.1	4.0	0.5	0.2
LRA0182	5.3	0.6	2.7	0.4	0.1	0.4	0.1	0.5	0.1	0.3	0.1	0.3	0.1	1.5	9.7	0.8	0.4

Catalogue II

LRA0001

LRA0002



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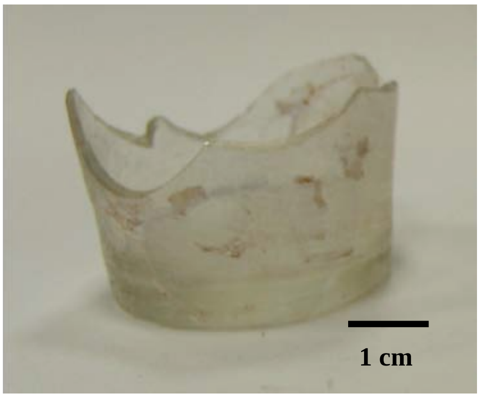

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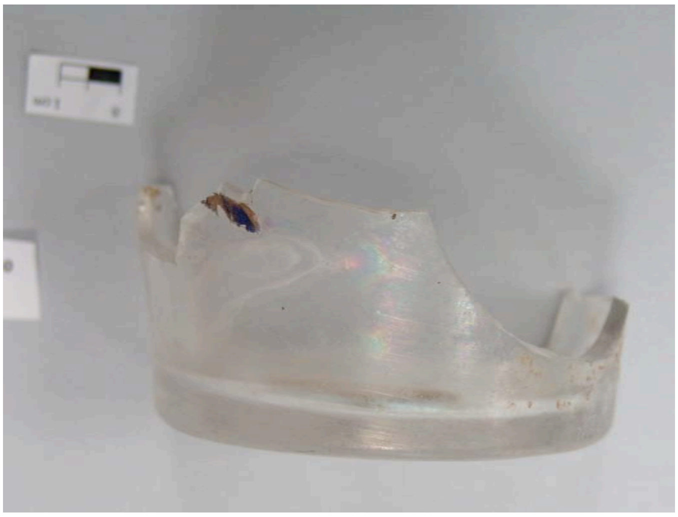

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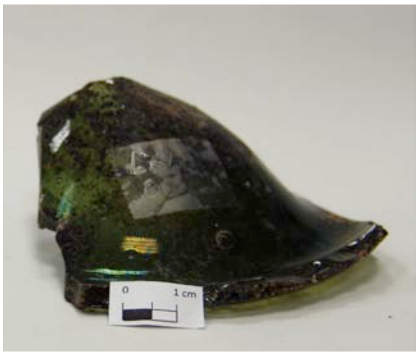

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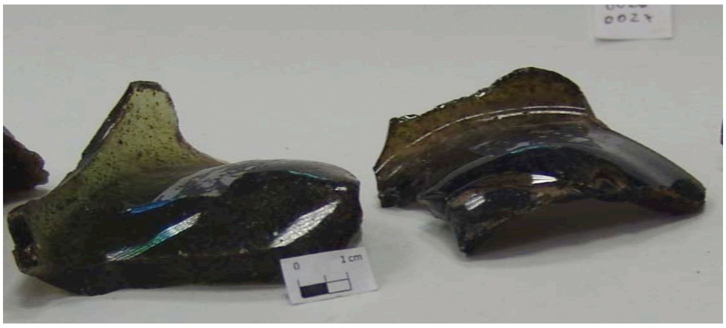

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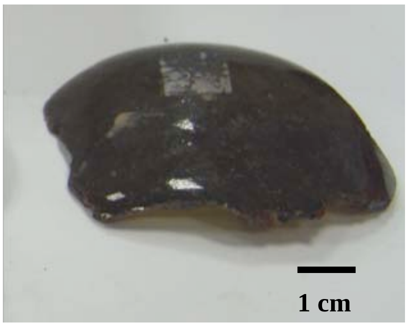

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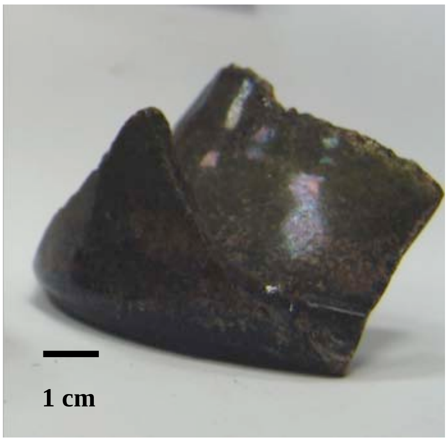

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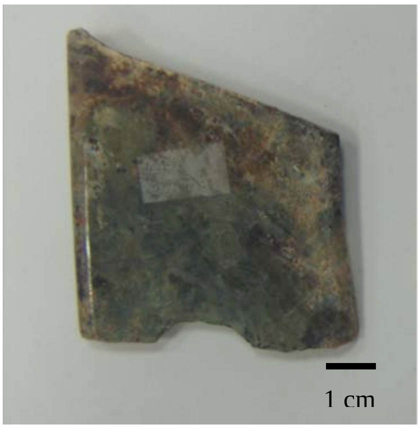

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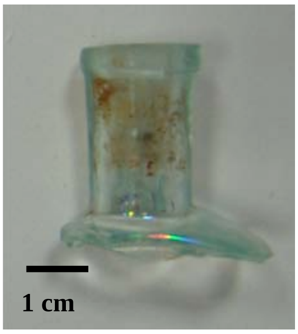

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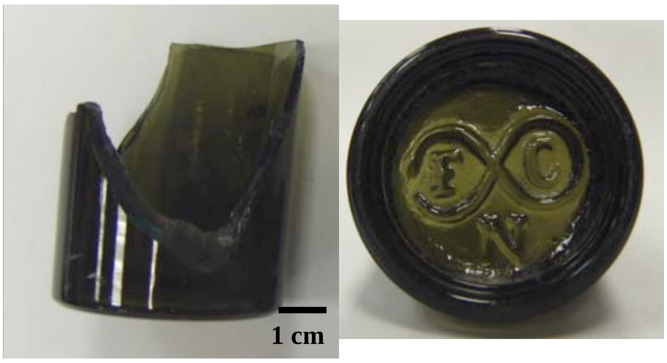

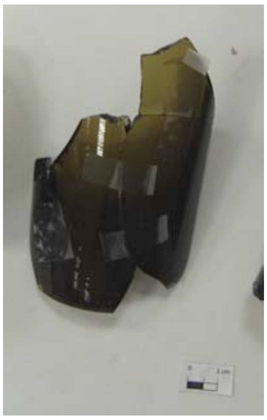

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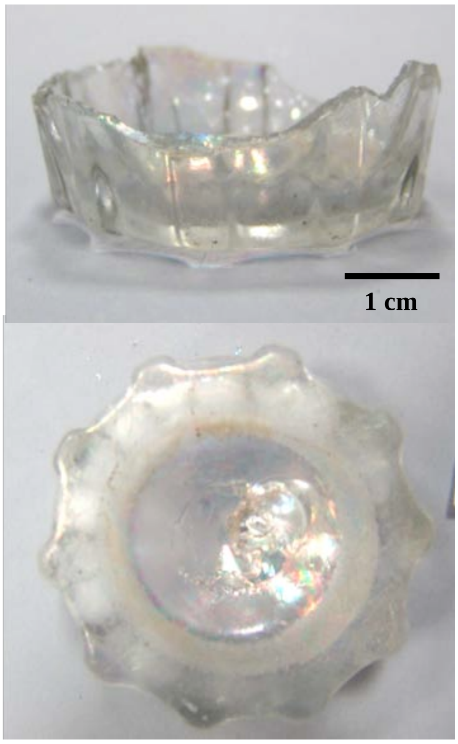

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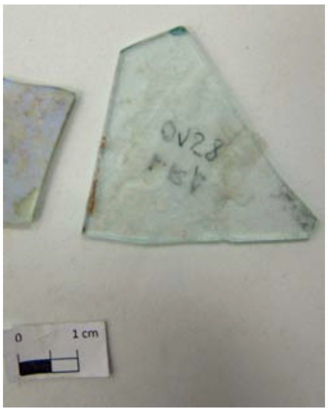

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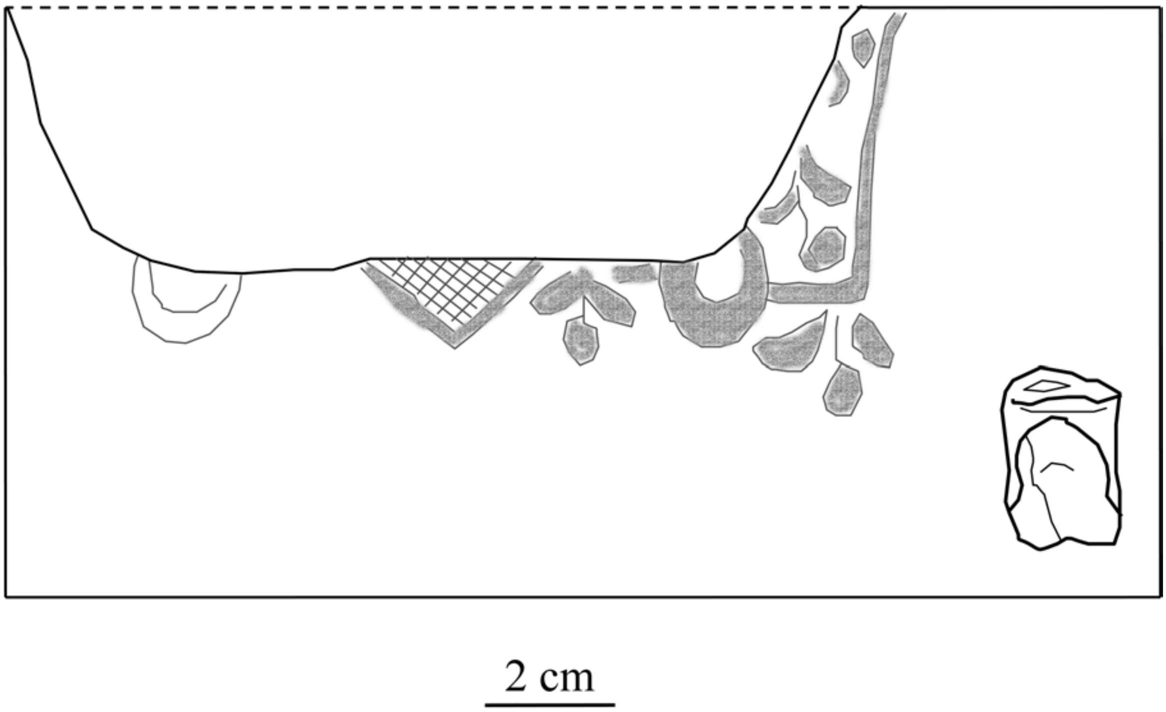
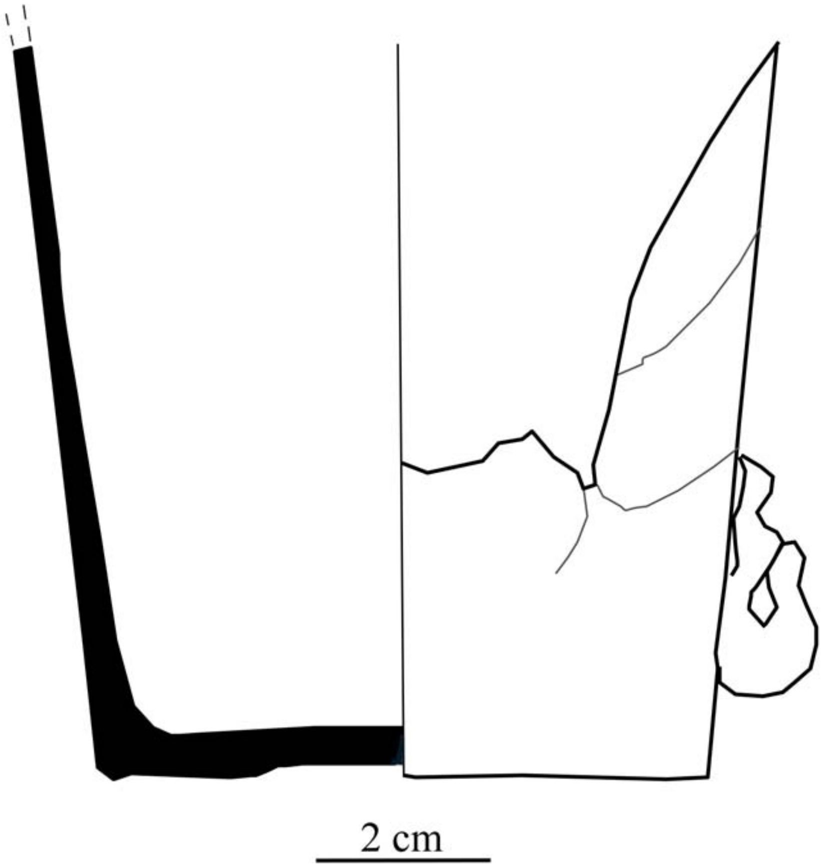
Catalogue II: Archaeological drawings





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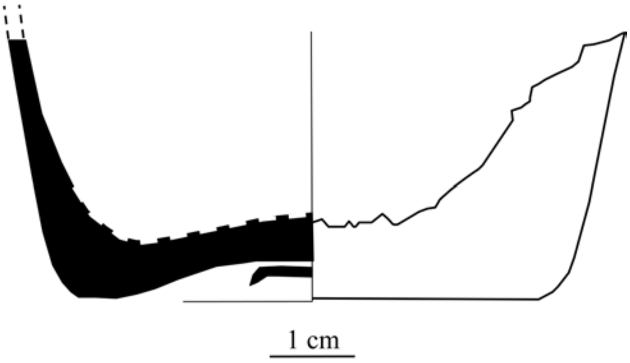

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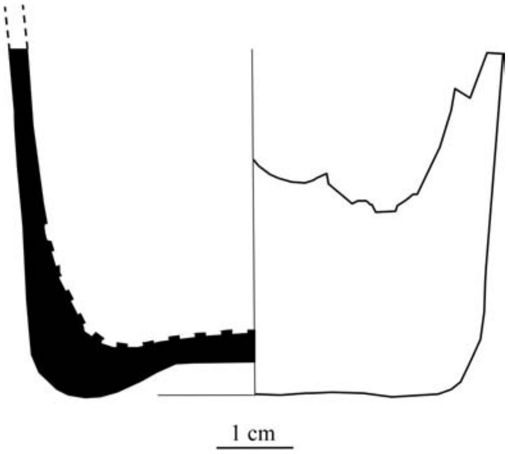

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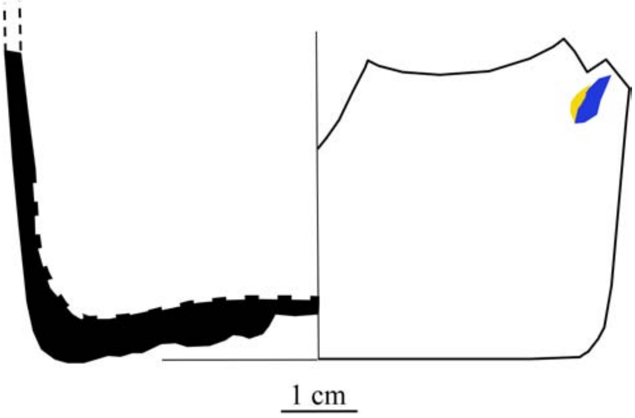

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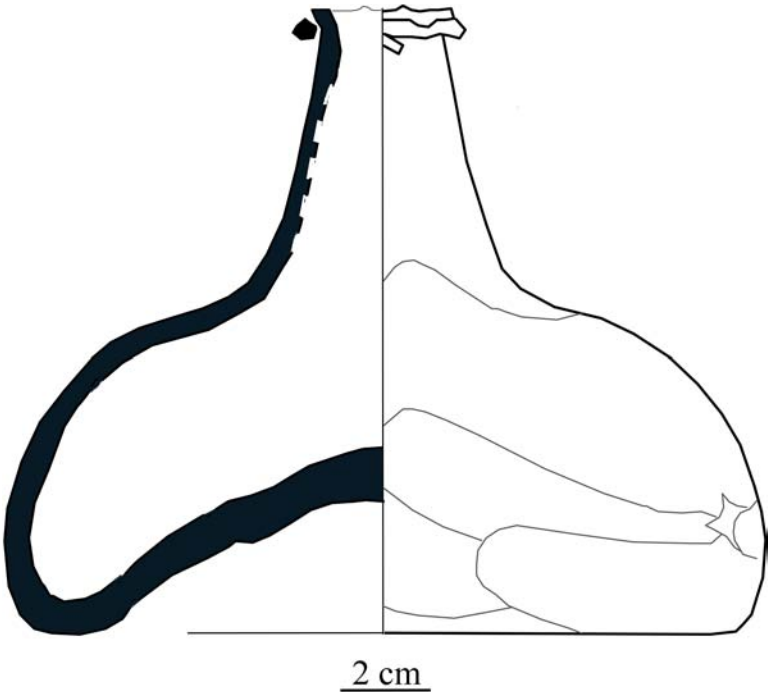

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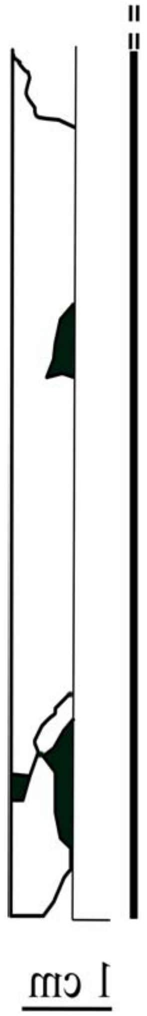

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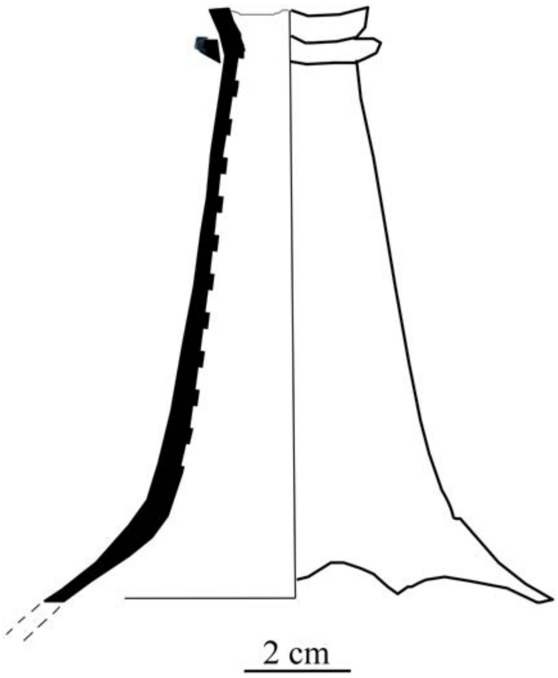

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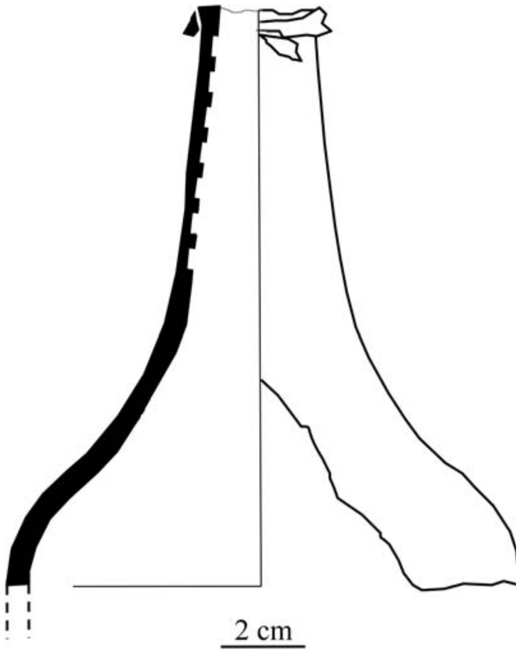

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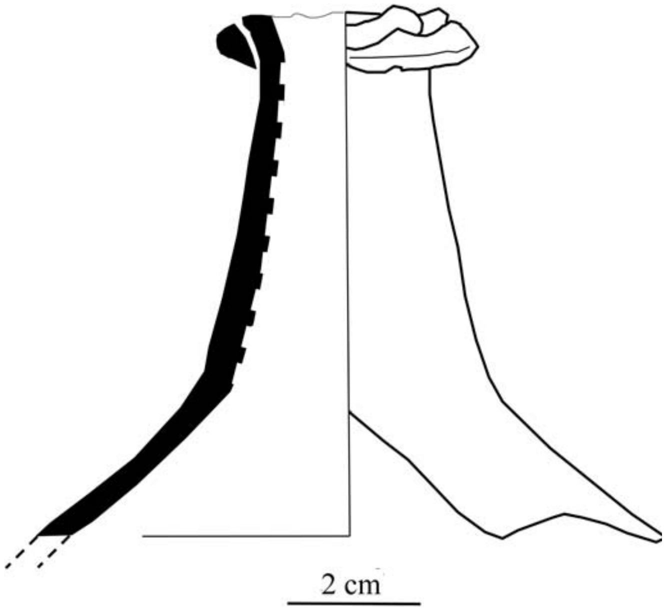

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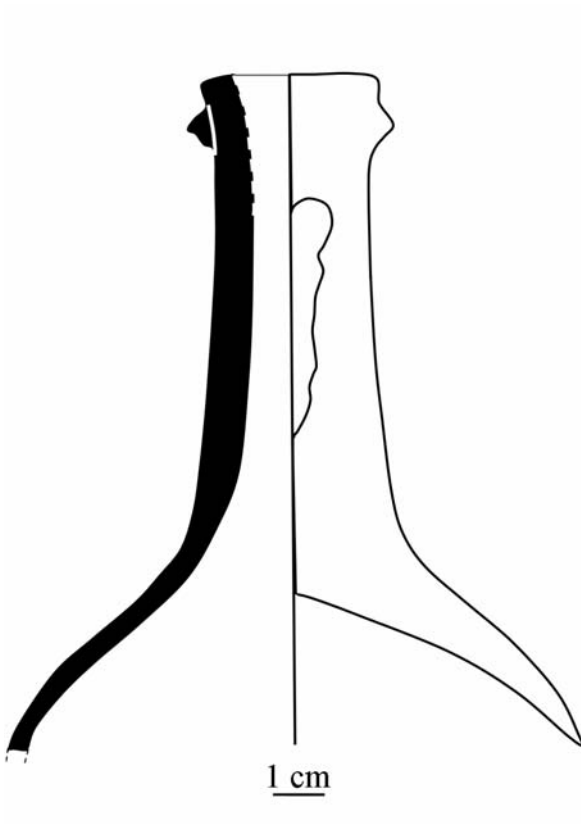

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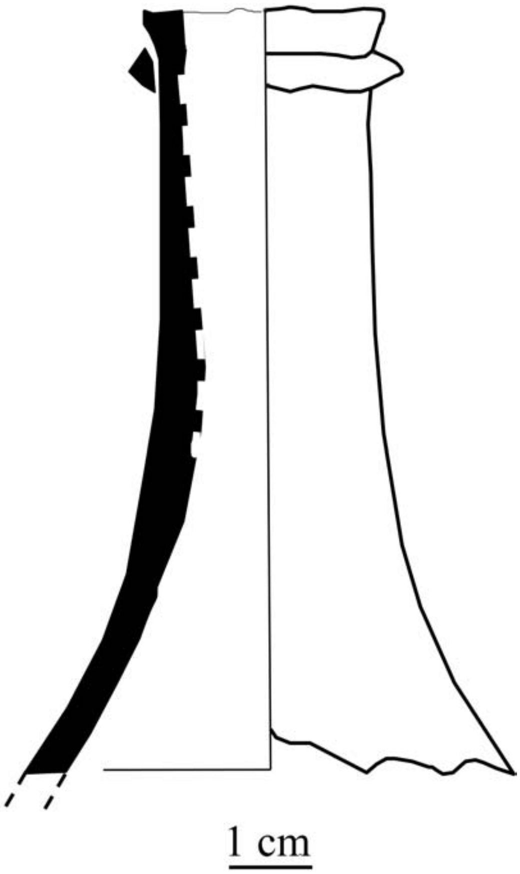

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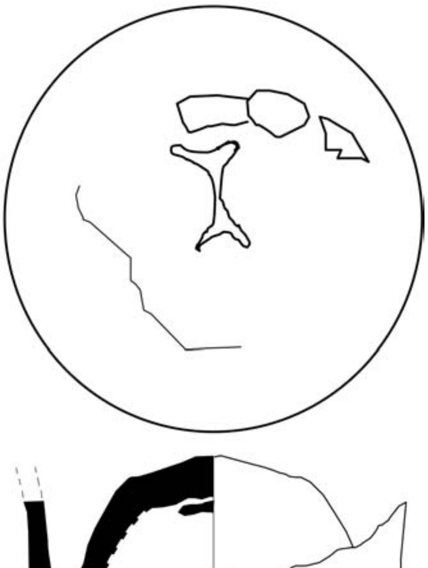

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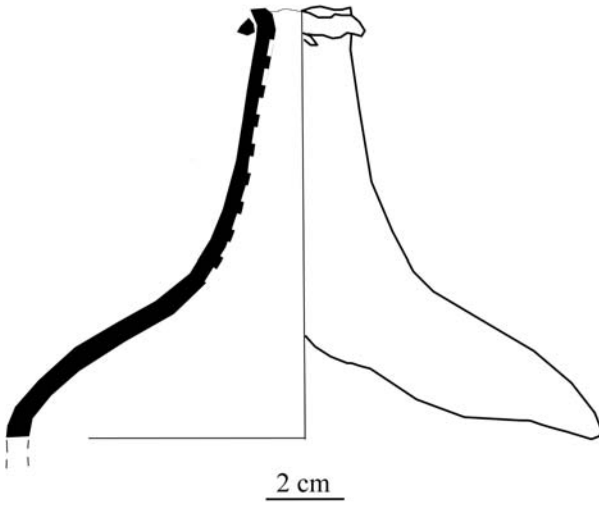

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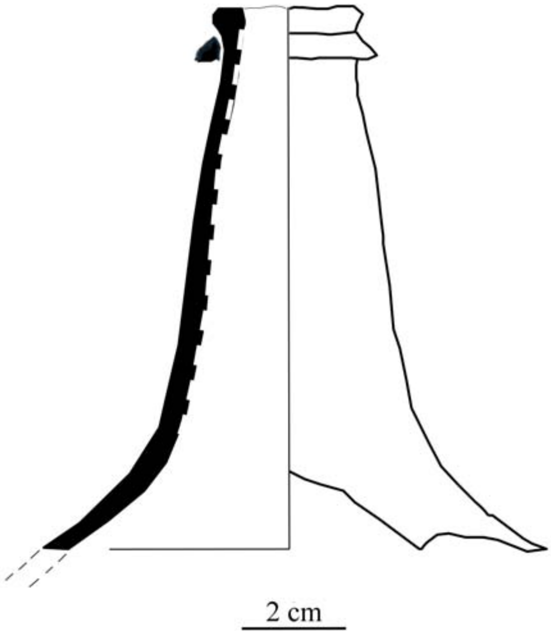

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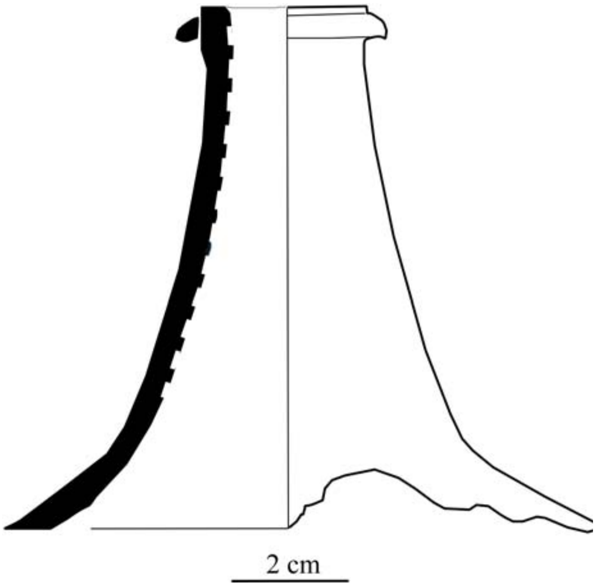

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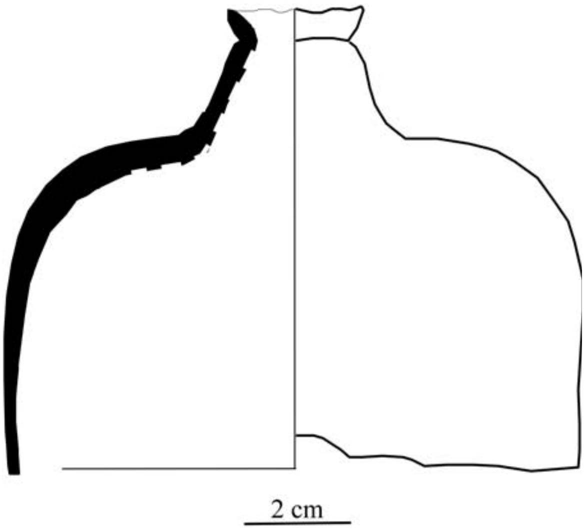

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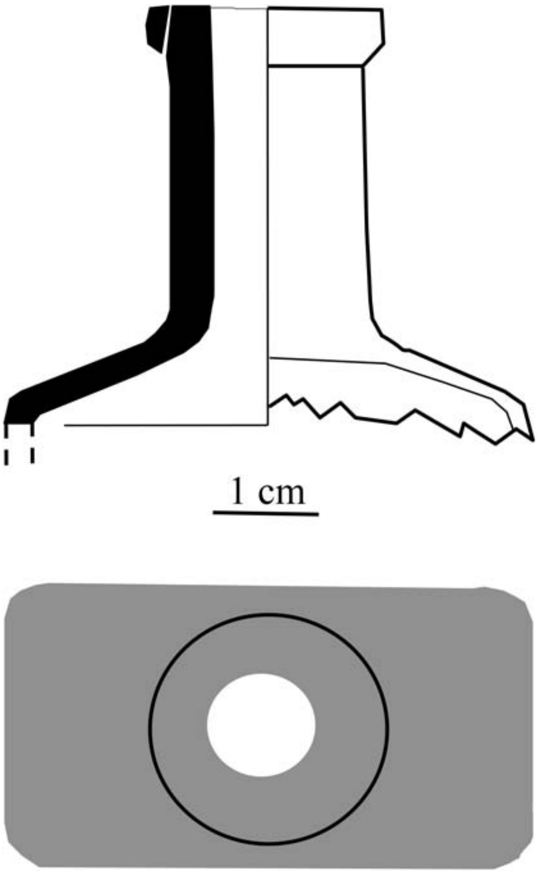

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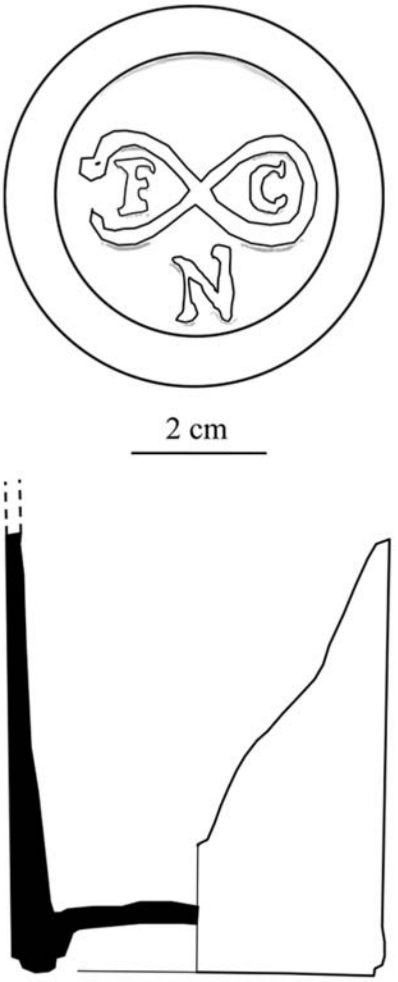

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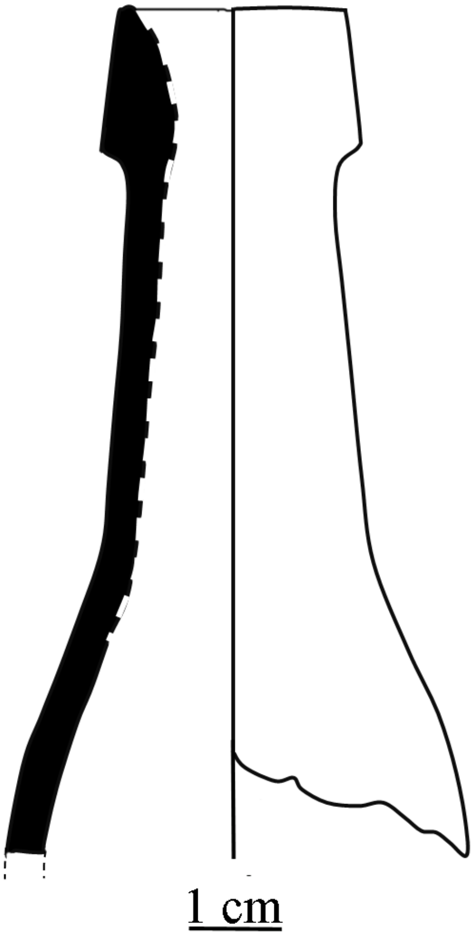

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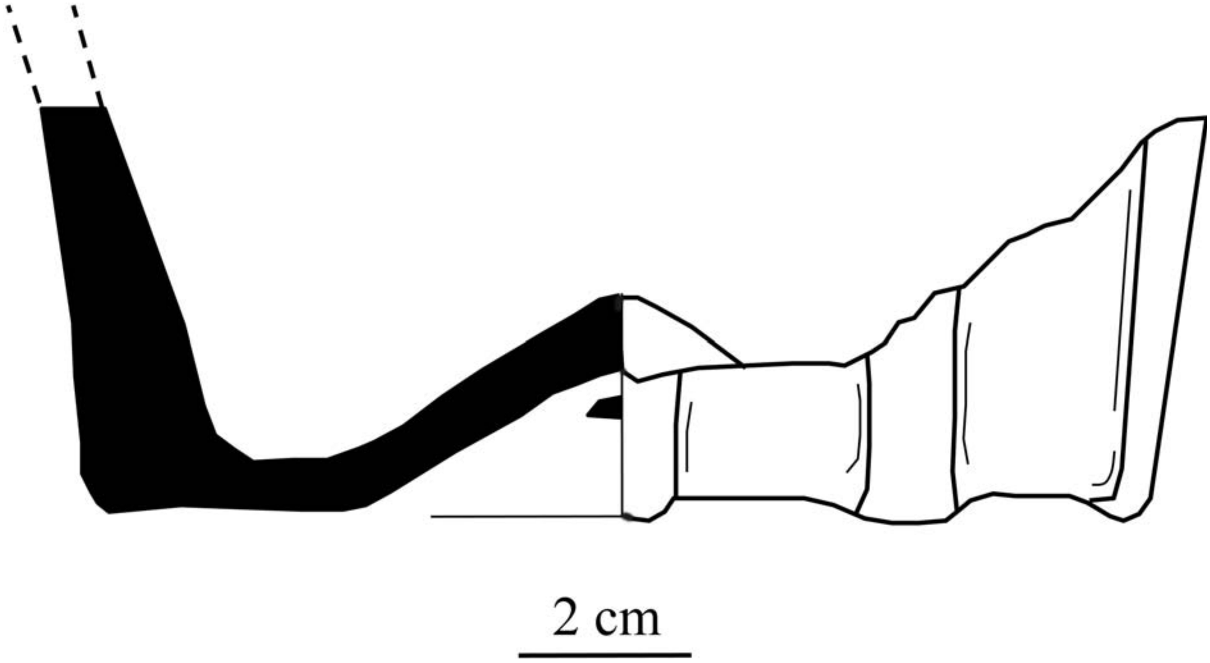


LRA0126

Appendix IV: Santa Clara-a-Velha Monastery (Coimbra) set (SCV) - Objects information, chemical composition and objects catalogue (Catalogue III).

Table IV.1: Description of analysed samples from Santa Clara-a-Velha Monastery in Coimbra (SCV) with inventory number, object type, glass colouration, part of the object preserved and dating.

Fragment	*Type*	*Colour*	*Part Preserved*	*Age (century AD)*
SCV-V14	Drinking glass with mould blown decoration. The decoration has a lozenge motif with 4-petalled flowers in the middle.	Blue	Fragment of rim wall	17th
SCV-V51	Vessel with mould blown decoration. The decoration has a lozenge motif.	Green	Fragments of base and walls with folded rim	17th
SCV-V60	Bowl with ribbed decoration	Yellow	Fragments of base, walls and walls with folded rim	17th
SCV-V79	Gourd	Green	Neck and rim mouth	17th
SCV-V82	Gourd	Purple (reddish)	Neck and rim mouth	17th
SCV-V94	Jar with mould blown ribbed decoration	Green	Base and fragments of wall	17th
SCV-V95	Bottle with ribbed decoration on the body	Green	Neck and part of the attached body	17th
SCV-V102	Drinking glass	Green	Base followed by one knops	17th
SCV-V115	Gourd	Light blue	Neck and rim mouth	17th
SCV-V154	Flask with funnel mouth and ribbed globular body	Dark purple	Mouth and part of the body	17th
SCV-V170	Vessel	Purple (reddish)	Neck and rim mouth	17th
SCV-V171	Vessel with funnel mouth	Purple (reddish)	Mouth and a small part of the attached body	17th
SCV-V177	Gourd	Yellow	Neck and rim mouth and part of the attached globular body	17th

SCV-V182	Vessel with mould blown decoration. The decoration has a lozenge motif.	Purple (reddish)	Base, fragments of walls and rim walls	17th
SCV-V191	Vessel with filigree decoration	Uncoloured with white filigree threads	Probably the top of a lid	17th
SCV-V193	Vessel with engraved decoration and an applied prunt (resembling a berry)	Uncoloured	Fragment with the prunt	17th
SCV-V194	Goblet with lion head on stem and covered with gilded decoration	Dark grey	Several fragments of rim walls, stem and foot	17th
SCV-V195	Vessel with engraved decoration	Uncoloured (slightly grey)	Wall and knops	17th
SCV-V210	Gourd	Turquoise blue	Neck and rim mouth	17th
SCV-V247	Vessel with filigree decoration	Blue with white filigree threads	Base and rim walls	17th
SCV-V298	Bowl with mould blown decoration. The decoration has a lozenge motif.	Yellow	Walls and folded rim walls	17th
SCV-V319	Cuppingglass	Green	Walls and rim wall	17th
SCV-V329	Vessel with mould blown twisted ribbed decoration	Green	Walls and rim wall	17th
SCV-V335	Ink pot with mould blown decoration. The decoration has a lozenge motif.	Blue	Fragments of base, walls and rim walls	17th
SCV-V336	Two-handled jar with mould blown decoration. The decoration has a lozenge motif.	Green	Fragments of base, walls and folded rim walls. 1 handle	17th
SCV-V342	Drinking vessel with knops on the stem	Green	Foot and part of walls	17th
SCV-V352	Gourd	Green	Neck and rim mouth and part of the attached globular body	17th
SCV-V355	Bottle with funnel mouth and body with ribbed mould blown decoration	Green	Mouth and part of the attached body	17th
SCV-V365	Gourd with mould blown decoration on the body	Green	Fragment of mouth and part of the attached body	17th
SCV-V380	Vessel with vertical ribbed decoration	Green	Fragment of neck	17th
SCV-V390	Gourd	Green (brownish)	Fragment of mouth	17th
SCV-V396	Jar or pitcher	Green	Fragment of beak	17th

SCV-V404	Vessel	Uncoloured	Foot and part of the attached body	17th
SCV-V408	Vessel with funnel mouth	Uncoloured	Mouth and part of the attached body	17th
SCV-V420	Vessel	Uncoloured (greyish)	Foot	17th
SCV-V422	Vessel with funnel mouth	Uncoloured (greenish)	Mouth	17th
SCV-V423	Gourd	Light blue	Mouth	17th

Table IV.2: Composition of samples from Santa Clara-a-Velha Monastery in Coimbra (SCV) determined by μ-PIXE, in weight percent of oxides.

Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_5	SrO	BaO	PbO
SCV-V14	19.8	3.1	4.2	62.4	0.23	0.02	0.97	2.17	5.60	0.13	0.29	0.62	0.08	0.03	50 μg/g	50 μg/g	0.15	0.02	0.02	< 30 μg/g
SCV-V51	18.6	5.7	8.3	59.0	0.45	0.02	0.80	1.30	3.45	0.25	0.45	1.45	60 μg/g	20 μg/g	30 μg/g	0.01	50 μg/g	0.02	0.02	< 30 μg/g
SCV-V60	16.3	3.3	5.5	61.4	0.24	0.04	0.70	3.76	6.83	0.19	0.78	0.89	< 20 μg/g	< 10 μg/g	0.01	0.01	< 10 μg/g	0.04	< 0.01	0.03
SCV-V79	19.9	5.6	6.8	55.5	0.45	0.03	0.86	2.08	6.67	0.28	0.35	1.26	< 60 μg/g	30 μg/g	50 μg/g	0.01	< 10 μg/g	0.03	< 0.01	< 20 μg/g
SCV-V82	15.0	4.8	4.8	64.0	0.43	0.02	0.74	2.36	5.09	0.23	1.22	0.94	< 40 μg/g	20 μg/g	0.01	0.01	< 10 μg/g	0.02	0.04	< 10 μg/g
SCV-V94	13.8	4.7	2.0	63.6	0.37	0.03	0.90	2.07	10.54	0.25	0.53	0.75	< 40 μg/g	< 10 μg/g	0.05	50 μg/g	< 70 μg/g	0.03	< 0.01	0.05
SCV-V95	21.0	5.4	7.9	55.0	0.42	0.02	0.92	1.56	5.37	0.31	0.59	1.35	50 μg/g	30 μg/g	40 μg/g	0.01	< 20 μg/g	0.02	< 0.01	< 20 μg/g
SCV-V102	17.3	4.2	4.5	57.5	0.09	0.98	0.91	2.89	9.46	0.23	0.52	0.95	< 0.01	< 10 μg/g	20 μg/g	70 μg/g	< 20 μg/g	0.04	< 0.01	< 50 μg/g
SCV-V115	17.6	3.1	2.3	66.5	0.09	0.07	0.76	2.53	6.07	0.09	0.02	0.64	< 30 μg/g	< 10 μg/g	< 10 μg/g	50 μg/g	< 10 μg/g	0.06	< 0.01	0.01
SCV-V154	16.3	5.4	5.5	62.4	0.50	0.04	0.97	1.51	3.38	0.29	2.19	1.32	60 μg/g	30 μg/g	0.02	0.01	< 50 μg/g	0.02	0.04	< 20 μg/g
SCV-V170	14.2	3.8	6.6	58.5	0.37	0.04	0.84	4.35	8.39	0.22	1.72	0.82	60 μg/g	30 μg/g	0.01	30 μg/g	60 μg/g	0.03	0.05	< 30 μg/g
SCV-V171	16.6	5.0	5.1	62.9	0.32	0.03	0.75	2.26	4.54	0.22	1.09	0.98	40 μg/g	30 μg/g	70 μg/g	0.01	< 10 μg/g	0.03	0.03	< 10 μg/g
SCV-V177	18.9	4.2	7.7	55.3	0.18	0.04	0.56	4.32	7.40	0.17	0.58	0.59	< 30 μg/g	< 10 μg/g	30 μg/g	60 μg/g	< 10 μg/g	0.04	0.04	< 30 μg/g
SCV-V182	18.2	6.8	6.2	59.4	0.56	< 0.01	0.83	1.37	3.57	0.23	1.17	1.46	0.01	50 μg/g	70 μg/g	0.01	0.02	0.02	0.03	< 30 μg/g
SCV-V191	16.3	2.5	1.2	67.7	< 0.12	0.08	0.69	3.79	6.62	0.06	0.31	0.38	< 20 μg/g	< 10 μg/g	40 μg/g	40 μg/g	< 20 μg/g	0.03	0.04	0.03
SCV-V193	18.1	2.8	0.8	68.0	0.13	0.12	0.61	2.47	5.91	0.03	0.38	0.33	< 20 μg/g	30 μg/g	40 μg/g	60 μg/g	0.01	0.03	0.01	0.03
SCV-V194	19.2	3.2	6.1	57.8	0.28	0.05	0.75	4.69	6.06	0.25	0.55	0.77	150 μg/g	50 μg/g	140 μg/g	90 μg/g	200 μg/g	0.05	0.04	0.25
SCV-V195	18.0	2.7	0.8	68.3	0.11	0.11	0.65	2.39	5.68	0.04	0.45	0.39	< 25 μg/g	40 μg/g	30 μg/g	50 μg/g	< 20 μg/g	0.05	0.01	0.03
SCV-V210	18.3	2.9	1.4	62.9	< 0.05	0.24	0.69	2.12	5.58	0.04	0.46	0.39	70 μg/g	50 μg/g	0.94	60 μg/g	< 20 μg/g	0.02	0.01	1.89
SCV-V247 – blue body	20.1	3.0	5.1	59.7	0.20	0.04	0.86	3.98	5.78	0.15	0.31	0.56	0.04	0.01	20 μg/g	70 μg/g	0.07	0.03	0.03	0.06
SCV-V298	11.5	5.2	6.2	61.4	0.42	0.02	0.87	3.37	9.04	0.23	0.73	0.72	< 40 μg/g	30 μg/g	60 μg/g	60 μg/g	< 20 μg/g	0.03	< 0.03	< 40 μg/g
SCV-V319	20.4	5.6	7.1	57.4	0.40	0.02	0.82	2.03	3.74	0.27	0.49	1.47	50 μg/g	30 μg/g	70 μg/g	0.01	< 10 μg/g	0.02	< 0.01	< 20 μg/g
SCV-V329	15.6	6.0	6.0	64.9	0.42	0.01	0.75	1.61	2.98	0.26	0.20	1.12	< 20 μg/g	20 μg/g	20 μg/g	60 μg/g	< 10 μg/g	0.02	< 0.01	< 10 μg/g
SCV-V335	17.1	3.9	6.1	57.8	0.09	0.05	0.68	5.69	7.43	0.18	0.36	0.55	50 μg/g	30 μg/g	< 10 μg/g	50 μg/g	0.03	0.03	0.03	< 0.01
SCV-V336	21.0	4.8	9.2	54.1	0.40	0.03	0.81	2.63	4.15	0.30	0.60	1.77	0.01	30 μg/g	60 μg/g	0.01	< 30 μg/g	0.02	0.03	60 μg/g
SCV-V342	16.9	8.0	8.6	57.0	0.53	0.01	0.80	1.14	3.71	0.28	1.26	1.73	< 0.01	30 μg/g	0.01	0.01	< 20 μg/g	0.03	< 0.04	< 60 μg/g
SCV-V352	20.6	5.5	7.7	56.7	0.33	0.02	0.91	1.77	3.26	0.31	1.13	1.66	< 0.01	20 μg/g	60 μg/g	0.01	< 10 μg/g	0.03	< 0.01	< 30 μg/g
SCV-V355	17.3	4.8	5.1	60.4	0.31	0.03	0.78	3.59	6.18	0.19	0.46	0.70	< 20 μg/g	< 10 μg/g	20 μg/g	0.01	< 10 μg/g	0.04	0.03	< 20 μg/g
SCV-V365	18.7	6.1	6.1	60.8	0.35	0.06	1.00	1.43	3.22	0.31	0.43	1.26	< 20 μg/g	30 μg/g.	30 μg/g	0.01	< 10 μg/g	0.03	< 0.01	< 10 μg/g
SCV-V380	18.0	6.9	6.3	59.7	0.56	0.01	0.80	1.45	3.66	0.26	0.98	1.23	50 μg/g	20 μg/g	60 μg/g	70 μg/g	< 10 μg/g	0.03	< 0.01	< 30 μg/g
SCV-V390	16.4	6.6	9.2	54.2	0.73	0.03	0.78	1.89	5.03	0.36	2.08	2.37	< 20 μg/g	40 μg/g	0.02	0.01	0.01	0.03	0.04	< 0.01
SCV-V396	18.5	5.7	8.7	57.8	0.44	0.05	0.96	1.57	3.75	0.28	0.50	1.52	0.01	60 μg/g	20 μg/g	0.01	0.01	0.02	0.03	< 30 μg/g
SCV-V404	13.7	4.1	1.3	65.5	< 0.06	0.05	0.60	6.53	6.76	0.22	0.57	0.53	< 20 μg/g	< 10 μg/g	30 μg/g	70 μg/g	< 10 μg/g	0.06	< 0.01	< 20 μg/g
SCV-V408 *	11.5	3.5	1.5	64.0	0.19	n.m.	0.84	5.46	11.89	0.07	0.34	0.61	< 10 μg/g	< 10 μg/g	20 μg/g	50 μg/g	< 10 μg/g	0.07	0.04	10 μg/g
SCV-V420	21.1	3.4	4.4	61.2	0.16	0.04	1.00	2.51	4.66	0.14	0.38	0.69	0.01	40 μg/g	0.01	40 μg/g	0.01	0.02	0.02	0.04
SCV-V422	17.8	4.3	4.8	58.1	0.27	0.02	0.85	2.72	8.91	0.10	0.81	0.92	< 40 μg/g	< 10 μg/g	< 10 μg/g	0.01	< 10 μg/g	0.06	0.03	< 50 μg/g
SCV-V423	16.9	6.6	9.2	54.3	0.73	0.02	0.82	1.85	4.85	0.34	1.93	2.25	0.01	30 μg/g	0.02	0.01	< 50 μg/g	0.03	0.04	< 30 μg/g

* Sample analysed by LA-ICP-MS.

n.m. stands for “not measured”.

Table IV.3: REE and trace elements concentration in µg/g for the SCV samples, measured by LA-ICP-MS.

Samples	B	Ti	V	Cr	Co	Ni	Cu	Zn	As	Rb	Sr	Y	Zr	Nb	Mo	Sn	Sb	Ba	La
SCV-V14	85.2	883	11.4	8.3	752	190	39.7	44.0	1073	16.0	403	5.6	56.0	2.8	4.2	160	0.4	181	9.8
SCV-V51	230	1600	16.0	19.0	12.6	15.0	21.4	93.2	24.1	13.9	275	9.7	82.0	4.9	0.3	9.6	0.3	189	15.9
SCV-V60	100	1284	14.8	8.6	18.7	13.5	85.2	80.1	17.6	44.3	595	8.5	102	4.1	1.9	192	1.0	449	13.0
SCV-V79	173	1783	17.6	17.2	3.9	11.1	24.6	71.9	4.6	12.2	441	11.2	138	4.7	0.2	8.9	0.3	189	23.3
SCV-V82	175	1592	14.1	10.6	6.5	11.4	52.6	68.1	11.3	29.5	372	9.6	128	4.3	0.6	16.6	0.6	325	14.5
SCV-V94	119	1571	14.3	10.6	3.3	7.6	462	43.9	14.3	36.8	409	8.9	141	4.3	0.3	24.3	3.3	260	13.2
SCV-V95	182	1982	15.4	17.2	4.6	11.9	24.1	75.8	6.1	11.4	370	13.9	184	5.9	0.1	9.6	0.2	228	29.4
SCV-V102	115	1524	15.6	10.4	9.9	10.7	17.7	50.1	4.5	25.3	595	9.4	135	4.4	1.3	13.3	0.2	348	13.6
SCV-V115	56.2	558	11.0	8.6	1.6	4.4	9.2	25.2	1.7	27.6	825	3.3	30.5	1.7	0.2	6.8	0.2	69.9	4.8
SCV-V154	242	1779	13.6	18.2	6.7	14.0	131.7	75.7	30.8	16.2	315	10.1	119	4.7	0.5	8.6	0.4	349	13.9
SCV-V170	65.2	540	12.1	8.1	5.5	10.1	81.3	52.5	10.4	18.8	481	4.8	34.7	1.5	0.5	342	1.3	125	5.8
SCV-V171	193	1557	15.0	12.3	5.9	12.3	51.8	76.1	12.0	27.6	342	9.2	116	4.2	0.4	18.4	0.3	284	13.7
SCV-V177	107	1082	19.4	12.2	3.9	5.9	21.7	38.3	12.1	63.2	599	6.6	60.0	3.2	0.6	9.0	0.3	325	11.2
SCV-V182	163	1502	21.5	20.4	65.2	28.2	50.8	81.1	156.3	18.5	428	8.9	79.5	4.0	1.1	8.5	0.4	278	14.9
SCV-V191	57.1	324	8.4	7.4	14.9	6.6	27.2	22.7	9.5	18.4	417	2.5	21.8	0.9	0.8	273	0.3	295	3.3
SCV-V193	68.5	196	7.5	6.9	18.9	20.2	35.1	33.3	34.3	13.4	427	1.6	9.3	0.6	1.1	270	0.4	136	1.8
SCV-V194	80.4	1822	15.6	9.1	105	35.1	105	51.8	151.3	42.6	568	15.1	231	7.0	1.7	1504	2.0	360	34.9
SCV-V195	68.8	210	7.3	6.8	18.5	19.4	35.3	34.2	34.1	13.4	437	1.7	9.9	0.6	1.0	277	0.4	138	1.86
SCV-V210	99.8	307	8.1	6.4	52.5	40.0	8793	37.0	133	14.3		2.8	21.0	1.0	1.4	18503	18.3	92.9	3.39
SCV-V247 - Blue body	76.1	1182	12.9	9.6	321	112	20.9	49.3	501	41.0		8.3	97.3	3.5	2.6	305		237	15.9
SCV-V298	166	1654	16.5	9.0	3.7	11.8	55.2	59.3	12.6	24.5	593	13.7	187	4.8	0.5	6.7		277	27.5
SCV-V319	200	1995	17.1	22.3	12.8	20.2	44.1	82.4	24.3	20.6	337	10.9	118	5.4	0.3	8.7	0.5	226	15.9
SCV-V329	185	1960	16.0	16.9	3.5	9.4	19.5	53.3	4.2	25.3	303	10.5	131	4.9	0.2	8.3	0.2	193	14.8
SCV-V335	69.7	1415	15.5	10.5	56.5	19.1	12.1	41.2	202	48.7	524	10.6	153	4.2	1.6	44.2	0.0	289	26.5
SCV-V336	179	2183	20.5	22.1	16.1	20.2	42.5	96.4	9.7	24.6	412	14.4	145	6.5	1.3	68.2	0.5	332	25.7
SCV-V342	280	1791	23.2	21.3	7.5	18.5	69.6	88.6	18.7	10.3	322	11.0	103	4.9	0.5	6.7	0.5	208	18.5
SCV-V352	224	2174	18.7	24.5	8.1	16.4	44.0	66.7	13.9	18.5	324	11.4	124	5.7	0.3	8.2		238	16.3
SCV-V355	136	1154	13.3	9.8	3.4	6.9	17.5	42.8	5.9	28.2	556	7.5	100	3.2	0.3	8.2	0.1	200	16.4
SCV-V365	216	1939	17.5	17.1	4.3	11.6	20.0	62.5	4.9	14.1	436	13.7	193	5.7	0.1	18.7	0.4	217	28.3
SCV-V380	228	1888	15.0	19.4	6.1	13.3	57.5	68.5	16.6	17.4	327	10.9	133	4.7	0.4	7.8		236	15.4
SCV-V390	243	2299	27.0	26.7	9.0	17.0	160	81.9	25.8	19.3	405	15.1	165	5.9	0.6	19.1	3.3	387	26.9
SCV-V396	180	1941	16.5	17.0	76.7	38.3	15.6	85.3	77.0	16.6	347	13.2	140	6.0	1.2	10.3	0.4	278	26.0
SCV-V404	52.8	903	8.2	7.1	3.6	4.8	12.3	20.4	3.4	37.4	556	6.1	225	2.8	2.0	7.8	0.7	128	9.4
SCV-V408	51.5	407	10.1	6.9	3.9	5.3	13.1	39.9	4.2	21.0	587	2.8	25.3	1.2	1.0	7.5	0.7	169	4.2
SCV-V420	84.2	1141	12.6	10.6	67.4	29.7	64.8	40.8	111	21.5	338	5.8	67.5	6.6	3.2	216	0.6	181	11.3
SCV-V422	98.9	493	12.0	7.1	14.1	11.9	11.8	66.6	14.2	7.7	826	3.9	29.1	1.7	1.6	16.7	0.8	235	5.4
SCV-V423	237	2317	26.8	27.3	8.9	16.8	162	81.9	24.9	19.3	408	15.2	165	5.9	0.5	17.5	2.0	389	27.5

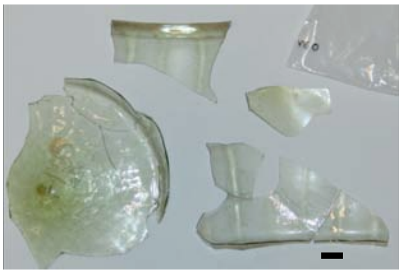
Table IV.3 (cont.): REE and trace elements concentration in µg/g for the SCV samples, measured by LA-ICP-MS.

Samples	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Hf	Pb	Th	U
SCV-V14	16.6	1.9	7.9	1.5	0.2	1.1	0.1	1.0	0.2	0.5	0.1	0.5	0.1	1.5	77.2	2.8	1.4
SCV-V51	31.2	3.4	13.6	2.6	0.5	2.1	0.3	1.8	0.3	0.9	0.1	1.0	0.1	2.2	14.1	5.9	1.7
SCV-V60	25.0	2.7	11.4	2.2	0.3	1.8	0.2	1.5	0.3	0.8	0.1	0.8	0.1	2.7	349	4.8	1.7
SCV-V79	48.4	5.2	21.4	3.9	0.6	2.8	0.4	2.2	0.4	1.1	0.1	1.2	0.1	3.8	15.3	8.9	1.8
SCV-V82	27.4	3.0	12.3	2.4	0.3	1.8	0.2	1.7	0.3	0.9	0.1	1.0	0.1	3.3	24.4	5.3	1.3
SCV-V94	26.6	2.9	11.8	2.2	0.3	1.7	0.2	1.7	0.3	0.9	0.1	1.0	0.1	3.7	521	5.2	1.3
SCV-V95	58.7	6.5	25.9	4.7	0.6	3.3	0.4	2.8	0.5	1.4	0.2	1.4	0.2	4.7	12.8	11.7	2.4
SCV-V102	25.5	2.9	11.8	2.3	0.3	1.9	0.2	1.6	0.3	0.9	0.1	1.0	0.1	3.4	41.4	4.9	1.4
SCV-V115	9.0	1.0	4.0	0.8		0.4	0.1	0.6	0.1	0.3	0.1	0.3	0.1	0.8		1.4	0.5
SCV-V154	27.2	2.9	12.0	2.3	0.4	1.8	0.3	1.8	0.3	1.0	0.1	1.1	0.1	3.1	12.9	5.3	1.7
SCV-V170	11.1	1.2	4.8	0.9	0.2	0.9	0.1	0.8	0.1	0.4	0.1	0.4	0.1	0.9	483	1.7	0.5
SCV-V171	27.0	2.9	11.9	2.3	0.3	1.8	0.2	1.7	0.3	0.8	0.1	0.9	0.1	3.1	23.3	4.9	1.4
SCV-V177	21.2	2.3	9.4	1.8	0.3	1.5	0.2	1.2	0.2	0.6	0.1	0.7	0.1	1.5	10.6	3.7	1.4
SCV-V182	28.7	3.1	12.5	2.6	0.4	1.8	0.3	1.7	0.3	0.9	0.1	0.9	0.1	2.1	18.1	5.1	1.5
SCV-V191	6.1	0.6	2.7	0.5		0.3	0.1	0.4	0.1	0.2		0.2	0.1	0.5	252	0.9	0.3
SCV-V193	3.4	0.3	1.4	0.3		0.0	0.1	0.2	0.1	0.1		0.1		0.2	272	0.4	0.4
SCV-V194	69.7	7.8	32.3	5.8	0.6	4.4	0.5	3.0	0.5	1.5	0.2	1.5	0.2	5.9	20835	14.5	2.7
SCV-V195	3.4	0.3	1.5	0.3		0.1	0.1	0.3	0.1	0.1		0.1		0.2	388	0.5	0.4
SCV-V210	6.2	0.7	2.7	0.5	0.1	0.5	0.1	0.5	0.1	0.2		0.3		0.5	19498	0.9	0.6
SCV-V247 - Blue body	33.4	3.6	15.1	2.9	0.4	2.0	0.3	1.5	0.3	0.8	0.1	0.8	0.1	2.4	667	5.3	1.4
SCV-V298	53.1	5.9	23.5	4.2	0.4	3.1	0.4	2.4	0.4	1.3	0.1	1.4	0.2	4.8	7.8	11.2	2.2
SCV-V319	32.8	3.4	13.6	2.5	0.5	2.1	0.3	2.0	0.4	1.1	0.1	1.1	0.1	3.1	29.3	5.7	1.7
SCV-V329	28.6	3.1	12.5	2.4	0.4	1.8	0.3	1.9	0.3	1.0	0.1	1.1	0.1	3.5	14.5	5.4	1.5
SCV-V335	59.8	6.1	23.7	4.2	0.5	2.7	0.4	2.1	0.4	1.0	0.1	1.0	0.1	3.9	97.5	9.8	2.9
SCV-V336	51.5	5.5	22.2	4.4	0.6	3.3	0.4	2.8	0.5	1.4	0.2	1.4	0.2	3.8	86.5	10.1	2.8
SCV-V342	36.1	4.0	16.3	3.0	0.5	2.5	0.3	2.0	0.4	1.1	0.1	1.2	0.1	2.8	9.5	7.1	1.9
SCV-V352	33.1	3.4	14.0	2.7	0.4	2.1	0.3	2.1	0.4	1.1	0.1	1.2	0.1	3.2	13.8	5.9	1.9
SCV-V355	35.2	3.7	14.8	2.7	0.3	1.8	0.2	1.4	0.2	0.7	0.1	0.7	0.1	2.5	10.4	6.1	1.4
SCV-V365	56.3	6.2	24.4	4.5	0.5	3.2	0.4	2.6	0.5	1.3	0.2	1.5	0.2	5.0	25.7	11.8	2.4
SCV-V380	30.4	3.3	13.2	2.6	0.4	2.0	0.3	2.0	0.4	1.1	0.1	1.2	0.1	3.4	9.0	5.6	1.8
SCV-V390	53.7	5.9	23.3	4.5	0.6	3.4	0.5	2.8	0.5	1.5	0.2	1.5	0.2	4.3	21.5	10.4	2.6
SCV-V396	52.2	5.6	22.0	4.1	0.5	3.1	0.4	2.5	0.5	1.3	0.1	1.3	0.2	3.7	16.0	10.9	2.6
SCV-V404	17.5	1.7	7.1	1.2	0.1	1.0	0.1	0.9	0.2	0.6	0.1	0.6	0.1	5.8	3.9	2.5	0.9
SCV-V408	8.5	0.8	3.4	0.6	0.1	0.4	0.1	0.4	0.1	0.2		0.2		0.6	22.8	1.2	0.7
SCV-V420	19.7	2.1	8.6	1.7	0.2	1.3	0.2	1.1	0.2	0.5	0.1	0.5	0.1	1.6	356	3.0	1.1
SCV-V422	10.4	1.1	4.4	0.9	0.1	0.7	0.1	0.7	0.1	0.3	0.1	0.3	0.1	0.7	26.5	1.6	2.6
SCV-V423	55.5	6.0	23.6	4.5	0.6	3.4	0.5	2.9	0.5	1.6	0.2	1.6	0.3	4.3	19.6	10.5	2.6

Catalogue III


SCV-V14


SCV-V51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SCV-V79


SCV-V82


SCV-V90


SCV-V94


SCV-V95


SCV-V102

SCV-V106

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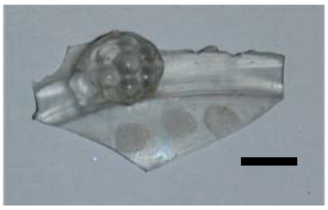
SCV-V177

SCV-V182

SCV-V191



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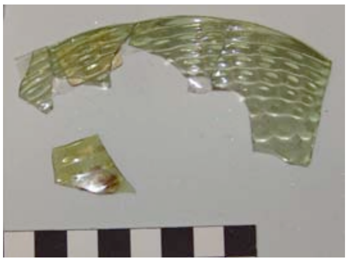
SCV-V195

SCV-V210

SCV-V247

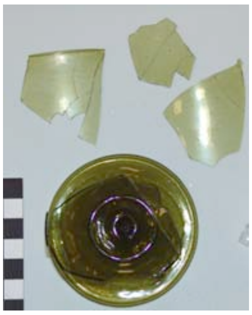
SCV-V298

SCV-V319



SCV-V329

SCV-V336



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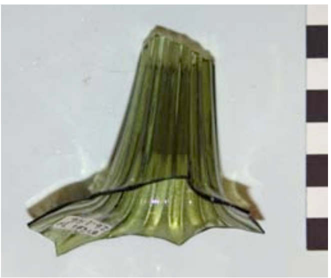
SCV-V352


SCV-V355


SCV-V365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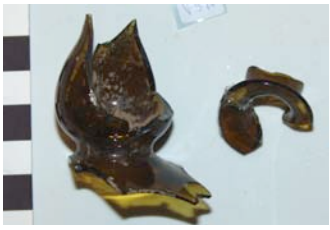
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SCV-V396


SCV-V404


SCV-V408

SCV-V420


SCV-V422


SCV-V423

Appendix V: Courtyard of the Universidade de Coimbra set (CPU) - Objects information, chemical composition and objects catalogue (Catalogue IV).

Table V.1: Description of analysed samples from the courtyard of the Universidade de Coimbra (CPU) with inventory number, object type, glass colouration, part of the object preserved and dating

Samples	***Type***	***Colour***	***Part preserved***	***Age (century AD)***
CPU0001	Vessel (probably flask)	Uncoloured glass with greenish hue	Long neck with rim	17th c.
CPU0002	Vessel (probably a small pocket bottle)	Uncoloured glass with brownish hue	Part of neck and body	17th c.
CPU0003	Vessel (beaker or oil lamp)	Uncoloured glass with greenish hue	Base and part of walls	17th c.
CPU0004	Flask with mould blown spiraled ribbed decoration	Uncoloured glass with greenish hue	Neck and rim and part of body	17th c.
CPU0005	Vessel	Uncoloured glass with greenish/ brownish hue	Folded rim or base	17th c.
CPU0006	Vessel with filigree decoration	Uncoloured base glass with white filigree strings	Part of wall	17th c.
CPU0008	Mould-blown decorated bossed beaker	Yellow	Base and part of part of wall and rim	17th c.
CPU0009	Mould-blown decorated bossed vessel	Yellow	Small part of wall	17th c.
CPU0010	Vessel	Dark green/ brownish with purple stains	Part of base and wall	17th c.
CPU0011	Vessel	Uncoloured	Fragment of folded base or rim	17th c.
CPU0012	Vessel	Uncoloured glass with yellowish hue	Part of wall and folded rim	17th c.
CPU0013	Vessel	Uncoloured	Part of wall and folded rim	17th c.
CPU0014	Vessel (probably a flask)	Uncoloured glass with yellowish hue	Part of neck	17th c.

CPU0015	Vessel (probably a flask)	Uncoloured glass with yellowish hue	Part of neck and rim	17th c.
CPU0016	Vessel (probably a flask)	Uncoloured	Part of neck	17th c.
CPU0017	Vessel (probably a drinking glass)	Uncoloured glass with greenish/ yellowish hue	Fragment of folded base	17th c.
CPU0018	Vessel	Uncoloured glass with greenish hue	Part of base	17th c.
CPU0019	Vessel	Uncoloured glasswith yellowish hue	Part of base	17th c.
CPU0020	Vessel	Uncoloured glass with greenish hue	Part of wall	17th c.
CPU0021	Vessel (beaker or oil lamp)	Uncoloured glass with greenish hue	Base	17th c.
CPU0022	Vessel (beaker or oil lamp)	Uncoloured glass with greenish hue	Base and part of wall	17th c.
CPU0023	Vessel	Uncoloured with yellowish hue	Part of base and wall	17th c.
CPU0024	Wing	Uncoloured with yellowish hue	Wing	17th c.
CPU0025	Wing	Uncoloured with yellowish hue	Wing	17th c.
CPU0026	Vessel	Dark blue	Small part of wall	17th c.
CPU0027	Vessel	Uncoloured with yellowish hue	Part of base	17th c.
CPU0028	Vessel with strings (probably mould-blown)	Uncoloured with yellowish hue	Wall fragment	17th c.
CPU0029	Vessel	Uncoloured	Small wall fragment	17th c.
CPU0030	Vessel	Uncoloured	Fragments of folded rims	17th c.
CPU0031	Vessel	Uncoloured	Small part of folded rim	17th c.
CPU0032	Globular flask with mould-blown ribbed decoration and gilded decoration with floral and zoomorphic motifs	Uncoloured base glass	Several fragments of base, wall and truncated cone mouth	17th c.
CPU0033	Window glass	Uncoloured glass with greenish hue	Fragments of window glass	17th c.

Table V.2: Composition of samples courtyard of the Universidade de Coimbra (CPU) determined by μ-PIXE in weight percent of oxides.

Samples	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**As_2O_3**	**SrO**	**BaO**	**PbO**
CPU0001	14.3	3.0	5.6	61.6	0.22	0.03	0.78	4.67	8.36	0.19	0.44	0.71	0.04	< 20 μg/g	20 μg/g	20 μg/g	40 μg/g	0.04	0.03	< 50 μg/g
CPU0002	18.1	2.2	2.0	65.3	0.30	0.05	1.16	3.44	6.37	0.05	0.26	0.52	40 μg/g	< 10 μg/g	20 μg/g	30 μg/g	0.01	0.04	0.02	0.01
CPU0003	9.5	2.2	3.6	67.4	0.13	0.05	0.59	6.66	8.91	0.05	0.41	0.27	< 30 μg/g	< 10 μg/g	< 10 μg/g	10 μg/g	< 10 μg/g	0.03	0.03	< 20 μg/g
CPU0004	12.1	2.2	3.6	66.6	0.20	0.04	0.73	5.44	7.95	0.11	0.25	0.46	< 70 μg/g	< 10 μg/g	30 μg/g	20 μg/g	< 10 μg/g	0.02	0.03	< 40 μg/g
CPU0005	16.9	2.6	2.5	65.5	0.31	0.09	0.77	6.05	4.26	0.06	0.37	0.57	40 μg/g	20 μg/g	< 10 μg/g	40 μg/g	0.01	0.02	< 0.03	< 90 μg/g
CPU0006	18.4	2.2	1.9	65.8	0.26	0.06	1.14	2.96	6.30	0.05	0.25	0.48	50 μg/g	20 μg/g	20 μg/g	30 μg/g	< 40 μg/g	0.03	0.01	0.03
CPU0008	17.2	3.5	5.0	59.0	0.14	0.07	0.69	4.41	8.76	0.14	0.36	0.49	< 70 μg/g	< 10 μg/g	30 μg/g	30 μg/g	50 μg/g	0.03	< 0.04	0.01
CPU0009	16.8	3.6	1.8	63.6	0.30	0.08	0.74	3.83	7.36	0.10	0.59	1.12	60 μg/g	< 20 μg/g	30 μg/g	40 μg/g	80 μg/g	0.05	0.04	70 μg/g
CPU0010	19.1	1.7	3.0	65.5	0.31	0.04	1.18	3.57	3.79	0.18	0.54	1.06	80 μg/g	30 μg/g	60 μg/g	40 μg/g	< 30 μg/g	0.03	0.02	0.02
CPU0011	13.1	2.2	5.8	63.7	0.51	0.03	0.87	4.21	8.61	0.22	0.25	0.42	< 40 μg/g	< 10 μg/g	< 10 μg/g	20 μg/g	< 20 μg/g	0.04	0.03	40 μg/g
CPU0012	15.0	2.8	3.6	63.8	0.21	0.06	0.86	3.83	8.77	0.09	0.36	0.42	< 90 μg/g	< 40 μg/g	30 μg/g	30 μg/g	< 20 μg/g	0.04	0.03	70 μg/g
CPU0013	9.4	2.3	3.6	67.3	0.13	0.05	0.58	6.70	9.04	0.07	0.44	0.29	< 30 μg/g	< 20 μg/g	< 20 μg/g	20 μg/g	< 10 μg/g	0.03	0.03	< 20 μg/g
CPU0014	14.2	2.8	5.6	61.6	0.25	0.03	0.80	4.87	8.53	0.20	0.41	0.69	< 90 μg/g	< 20 μg/g	< 20 μg/g	30 μg/g	60 μg/g	0.03	< 0.06	< 0.01
CPU0015	13.8	3.0	2.9	64.6	0.16	0.07	0.65	5.21	8.63	0.14	0.36	0.44	< 50 μg/g	< 10 μg/g	< 10 μg/g	30 μg/g	< 10 μg/g	0.03	< 0.03	50 μg/g
CPU0016	13.8	3.1	2.9	64.8	0.10	0.07	0.65	5.20	8.48	0.13	0.33	0.42	< 90 μg/g	< 20 μg/g	< 20 μg/g	30 μg/g	< 20 μg/g	0.03	0.03	< 30 μg/g
CPU0017	13.7	3.1	2.8	64.8	0.17	0.06	0.66	5.17	8.56	0.14	0.34	0.43	< 50 μg/g	30 μg/g	< 20 μg/g	20 μg/g	< 10 μg/g	0.03	< 0.03	< 20 μg/g
CPU0018	18.1	2.2	2.0	67.2	0.22	0.04	1.23	2.30	5.41	0.09	0.44	0.57	40 μg/g	20 μg/g	< 10 μg/g	30 μg/g	< 30 μg/g	0.03	0.02	0.04
CPU0019	12.8	2.0	5.8	63.7	0.41	0.04	0.89	4.35	8.93	0.25	0.30	0.45	< 50 μg/g	< 20 μg/g	< 20 μg/g	30 μg/g	< 10 μg/g	0.03	< 0.05	< 40 μg/g
CPU0021	15.2	2.7	3.5	64.1	0.23	0.06	0.84	3.78	8.43	0.09	0.45	0.46	< 50 μg/g	30 μg/g	0.01	30 μg/g	< 10 μg/g	0.04	0.03	< 30 μg/g
CPU0022	16.9	2.2	4.7	64.9	0.26	0.04	0.94	3.53	4.64	0.22	0.50	1.11	0.01	20 μg/g	20 μg/g	40 μg/g	0.01	0.02	< 0.04	60 μg/g
CPU0023	15.6	2.7	2.1	65.9	0.19	0.06	0.81	4.84	6.81	0.10	0.25	0.61	< 60 μg/g	< 30 μg/g	0.02	20 μg/g	< 40 μg/g	0.04	< 0.03	0.02
CPU0024	13.2	2.2	3.6	67.2	0.20	0.05	0.69	4.98	6.64	0.18	0.38	0.58	< 60 μg/g	< 10 μg/g	10 μg/g	30 μg/g	< 30 μg/g	0.03	0.03	60 μg/g
CPU0025	18.5	2.1	1.9	66.2	0.23	0.05	1.18	2.64	6.02	0.08	0.28	0.50	40 μg/g	20 μg/g	20 μg/g	30 μg/g	40 μg/g	0.04	0.01	0.02
CPU0026	17.3	4.1	2.1	60.7	0.34	0.08	0.55	3.75	8.14	0.10	0.65	1.12	0.15	0.05	0.01	70 μg/g	0.23	0.04	0.05	< 0.05
CPU0027	15.6	2.6	3.6	62.9	0.28	0.04	0.87	4.28	8.62	0.17	0.57	0.46	< 50 μg/g	< 20 μg/g	< 10 μg/g	20 μg/g	< 10 μg/g	0.03	0.03	< 20 μg/g
CPU0028	13.5	2.7	1.3	67.1	0.25	0.03	0.81	5.60	7.62	0.04	0.49	0.28	< 70 μg/g	< 70 μg/g	20 μg/g	20 μg/g	< 20 μg/g	0.02	0.01	0.05
CPU0030	15.3	2.7	3.6	64.2	0.23	0.05	0.88	3.76	8.30	0.10	0.40	0.44	< 50 μg/g	< 30 μg/g	70 μg/g	20 μg/g	< 20 μg/g	0.03	0.03	< 20 μg/g
CPU0032	17.3	3.2	3.7	61.2	0.28	0.07	0.81	4.85	6.93	0.13	0.70	0.72	0.01	30 μg/g	30 μg/g	50 μg/g	0.01	0.04	0.04	0.04
CPU0033	2.6	3.4	3.5	61.7	1.90	0.04	0.37	5.25	19.47	0.18	0.61	0.85	< 0.1	0.01	0.01	80 μg/g	0.01	0.04	0.20	80 μg/g

Catalogue IV

CPU0001

CPU0002

CPU0003

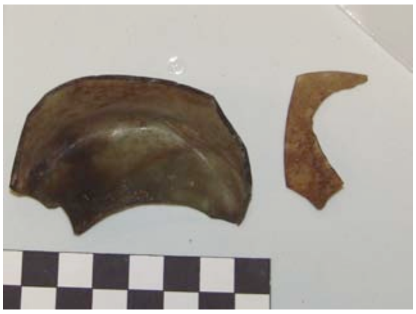
CPU0004

CPU0005

CPU0006

CPU0008

CPU0009



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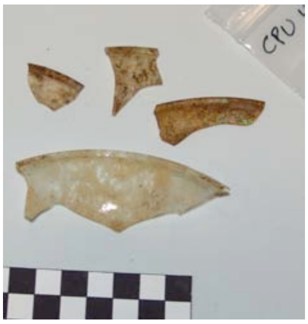
CPU0011



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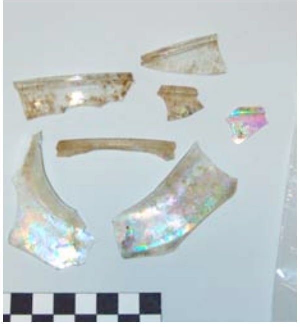

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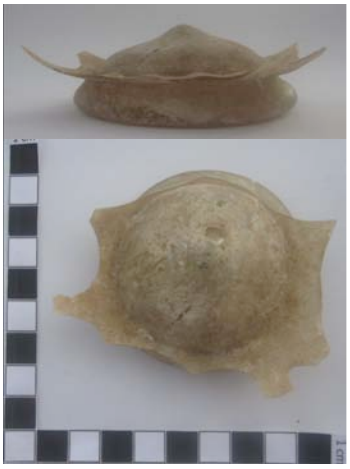
CPU0014

CPU0015

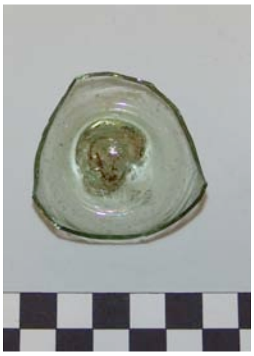
CPU0016



CPU0017

CPU0018

CPU0019



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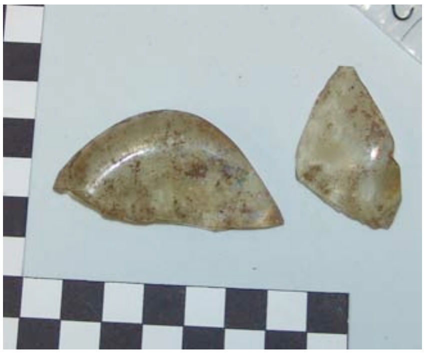
CPU0022



CPU0023

CPU0024

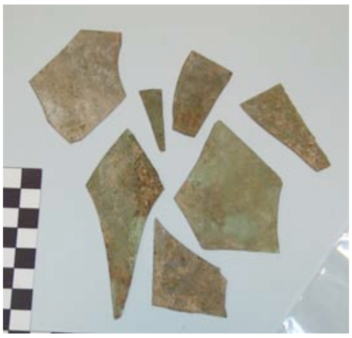
CPU0025

CPU0026

CPU0027

CPU0028

CPU0030



CPU0033

CPU0032

Appendix VI: Praça Miguel Fernandes (Beja) set (PMF) – Objects information, chemical composition and objects catalogue (Catalogue V).

Table VI.1: Description of analysed samples from Praça Miguel Fernandes in Beja (PMF) with inventory number, object type, glass colouration, part of the object preserved and dating.

Fragments	***Type***	***Colouration***	***Part preserved***	***Age (century A.D.)***
PMF0401	Vessel with cord applied and worked with pincers	Uncoloured	Part of wall	14th / 15th c.
PMF0438	Vessel with coloured rim	Uncoloured base glass with turquoise rim	Part of wall with rim	14th / 15th c.
PMF0444	Drinking glass with foot	Green	Part of folded base	14th / 15th c.
PMF0458	Vessel decorated with prunts	Turquoise	Prunt	14th / 15th c.
PMF0470	Drinking glass with foot	Green	Part of base and stem	14th / 15th c.
PMF0517	Vessel with coloured rim and mould blown spiralled strings	Uncoloured base glass with blue rim	Part of wall with rim	14th / 15th c.
PMF0600	Drinking glass with foot	Yellow	Base of foot with fold	14th / 15th c.
PMF0605	Molten fragment	Green	Fragment	14th / 15th c.
PMF0610	Vessel with a large folded rim	Green	Fragment of rim	14th / 15th c.
PMF0617	Beaker mould blown decorated with vertical applied strings	Green	Base and part of body	14th / 15th c.
PMF0691	Vessel	Uncoloured with light green hue	Part of wall	14th / 15th c.
PMF0387	Mould blown bossed beaker	Uncoloured with bluish/ greyish hue	Base and part of body	16th / 17th c.
PMF0510	Vessel (probably beaker) mould blown decorated with lozenge motif enclosing four-petalled flowers	Yellow	Part of wall and rim	16th / 17th c.
PMF0527	Drink glass with foot and mould blown decorated with strings	Uncoloured with gray hue	Foot (base and stem)	16th / 17th c.
PMF0530	Vessel with strings forming a large lozenge motif	Uncoloured glass with light blue hue	Part of wall	16th / 17th c.
PMF0540	Vessel	Uncoloured	Fragment of wall and rim	16th / 17th c.

PMF0546	Drinking glass	Green	Fragment of stem	16th / 17th c.
PMF0550	Vessel with mould blown strings	Uncoloured glass with light blue hue	Fragment of wall and rim	16th / 17th c.
PMF0556	Vessel (probably drinking glass)	Uncoloured glass with light gray hue	Part of wall with rim	16th / 17th c.
PMF0568	Vessel (probably drinking glass) with mould blown decoration of vertical strings	Uncoloured glass with light gray hue	Part of wall with rim	16th / 17th c.
PMF0569	Vessel (probably drinking glass)	Uncoloured glass with light gray hue	Fragment of folded base	16th / 17th c.
PMF0570	Vessel with string (probably mould blown) applied vertically in S – shape	Uncoloured glass with light blue hue	Part of wall with rim	16th / 17th c.
PMF0996	Drinking glass	Uncoloured glass with light gray hue	Part of body with rim	16th / 17th c.
PMF1010	Vessel	Uncoloured glass with light gray hue	Part of wall with rim	16th / 17th c.
PMF1023	Vessel with wing	Dark blue	Wing and small wall part	16th / 17th c.
PMF1025	Vessel (probably drinking glass)	Uncoloured glass with light gray hue	Part of wall with rim	16th / 17th c.
PMF0863	Drinking glass	Uncoloured	Stem and part of body	18th c.

Table VI.2: Composition of samples from Praça Miguel Fernaneds in Beja (PMF) determined by μ-PIXE in weight percent of oxides.

Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SrO	BaO	PbO
PMF0401	20.5	3.9	3.7	61.8	0.50	0.06	1.10	2.41	4.32	0.24	0.49	1.01	< 80 μg/g	30 μg/g	40 μg/g	50 μg/g	< 30 μg/g	0.01	< 0.05	< 20 μg/g
PMF0438 body glass	18.4	2.2	3.4	65.0	0.56	0.02	1.25	3.35	4.12	0.47	0.17	0.92	< 0.01	< 10 μg/g	40 μg/g	0.01	< 40 μg/g	0.01	< 0.1	< 30 μg/g
PMF0438 turquoise rim	18.2	2.2	3.4	64.0	0.55	0.03	1.14	3.33	4.19	0.44	0.16	0.89	< 0.01	< 20 μg/g	1.32	0.01	< 30 μg/g	0.01	< 0.08	< 70 μg/g
PMF0444	19.4	3.6	4.7	61.9	0.53	0.04	0.99	2.72	3.98	0.46	0.25	1.43	< 0.01	20 μg/g	70 μg/g	70 μg/g	< 40 μg/g	0.01	< 0.1	< 60 μg/g
PMF0458	13.1	3.3	1.6	69.3	0.15	0.06	0.86	2.12	8.81	0.05	0.03	0.49	< 40 μg/g	< 10 μg/g	30 μg/g	40 μg/g	< 20 μg/g	0.03	0.01	< 20 μg/g
PMF0470	9.1	3.3	7.3	67.9	1.13	0.07	0.94	2.58	5.04	0.33	0.46	1.85	< 70 μg/g	30 μg/g	70 μg/g	0.01	< 10 μg/g	n.d.	0.04	< 30 μg/g
PMF517 body glass	16.4	3.3	2.9	67.2	0.58	0.03	0.96	2.33	4.37	0.13	0.50	1.07	0.03	< 10 μg/g	< 10 μg/g	70 μg/g	< 50 μg/g	0.01	< 0.04	< 50 μg/g
PMF517 blue rim	15.9	3.3	2.9	66.4	0.58	0.04	0.92	2.52	4.39	0.13	0.53	1.83	0.21	< 30 μg/g	0.21	0.06	< 0.02	n.d.	< 0.04	< 0.01
PMF600	20.3	3.8	4.6	60.8	0.53	0.04	1.13	2.67	4.29	0.25	0.29	1.27	< 0.01	< 10 μg/g	30 μg/g	70 μg/g	< 30 μg/g	0.01	< 0.06	< 40 μg/g
PMF605	18.9	4.4	5.1	59.0	0.62	0.05	1.03	3.90	4.91	0.29	0.11	1.59	< 0.01	< 10 μg/g	40 μg/g	70 μg/g	< 30 μg/g	0.01	< 0.04	< 30 μg/g
PMF610	20.1	4.2	5.1	58.8	0.74	0.06	0.90	2.37	5.03	0.28	0.45	1.60	< 0.01	< 10 μg/g	< 10 μg/g	60 μg/g	< 10 μg/g	0.02	< 0.07	0.08
PMF0617	19.7	5.2	4.9	60.4	0.50	0.04	1.02	2.33	3.81	0.28	0.35	1.44	< 0.01	20 μg/g	30 μg/g	60 μg/g	< 20 μg/g	0.02	< 0.06	< 30 μg/g
PMF0691	18.3	3.3	4.0	65.2	0.47	0.04	1.06	2.45	3.55	0.28	0.33	0.99	0.01	< 10 μg/g	< 10 μg/g	60 μg/g	< 30 μg/g	0.02	< 0.06	< 50 μg/g
PMF0387	12.9	3.6	1.5	64.8	0.37	0.06	0.78	6.89	6.56	0.44	1.16	0.67	0.01	< 10 μg/g	0.02	70 μg/g	< 40 μg/g	0.06	< 0.03	0.03
PMF0510	17.2	2.3	4.9	63.5	0.29	0.04	1.15	3.70	5.35	0.20	0.35	0.95	< 60 μg/g	< 10 μg/g	20 μg/g	40 μg/g	< 50 μg/g	0.02	< 0.03	0.01
PMF0527	16.9	3.2	2.1	60.8	0.27	0.05	0.87	5.26	9.53	0.07	0.51	0.46	50 μg/g	40 μg/g	20 μg/g	30 μg/g	50 μg/g	0.05	0.03	< 10 μg/g
PMF0530	15.9	3.0	3.9	66.4	0.33	0.05	0.93	2.01	6.00	0.13	0.49	0.78	0.01	< 10 μg/g	< 10 μg/g	40 μg/g	0.01	0.03	0.03	< 0.01
PMF0540	18.6	1.9	6.0	62.9	0.42	0.02	1.30	3.76	3.22	0.16	0.92	0.82	0.01	40 μg/g	0.02	70 μg/g	0.02	0.02	0.05	< 0.02
PMF0546	18.2	3.0	4.6	59.5	0.31	0.05	0.97	4.40	7.53	0.15	0.48	0.61	0.01	30 μg/g	40 μg/g	30 μg/g	0.02	0.04	0.04	0.03
PMF0550	16.8	2.2	3.2	66.9	0.30	0.04	1.14	2.47	6.19	0.08	0.28	0.30	50 μg/g	20 μg/g	< 10 μg/g	20 μg/g	< 20 μg/g	0.03	0.02	< 40 μg/g
PMF0556	15.1	3.2	2.6	62.5	0.18	0.06	0.83	5.99	8.79	0.06	0.30	0.27	< 30 μg/g	< 10 μg/g	< 10 μg/g	20 μg/g	< 20 μg/g	0.04	0.03	< 10 μg/g
PMF0568	15.7	2.5	3.6	66.8	0.21	0.05	0.91	3.36	5.48	0.12	0.50	0.62	60 μg/g	30 μg/g	20 μg/g	30 μg/g	50 μg/g	0.03	0.03	0.01
PMF0569	15.6	2.4	3.6	67.3	0.18	0.06	0.93	3.06	5.48	0.11	0.63	0.58	60 μg/g	30 μg/g	40 μg/g	50 μg/g	< 20 μg/g	0.03	0.03	< 40 μg/g
PMF0570	16.2	3.0	4.0	66.6	0.34	0.05	0.94	1.95	5.79	0.12	0.42	0.67	0.01	40 μg/g	20 μg/g	20 μg/g	0.01	0.02	0.02	< 0.01
PMF0996	15.7	2.4	3.6	67.0	0.23	0.06	0.94	3.06	5.56	0.11	0.66	0.61	0.01	30 μg/g	30 μg/g	40 μg/g	70 μg/g	0.03	0.03	< 0.01
PMF1010	16.1	2.2	2.3	66.4	0.22	0.06	1.00	4.08	6.63	0.07	0.37	0.53	60 μg/g	30 μg/g	< 10 μg/g	30 μg/g	60 μg/g	0.03	0.02	0.06
PMF1023	16.9	2.6	3.5	62.8	0.31	0.05	1.22	4.25	7.52	0.12	0.13	0.62	0.08	0.03	40 μg/g	40 μg/g	0.11	0.04	< 0.02	< 0.03
PMF1025	15.0	2.4	3.5	66.9	0.26	0.05	0.92	3.30	5.93	0.14	0.76	0.72	60 μg/g	30 μg/g	40 μg/g	40 μg/g	0.01	0.04	0.03	< 0.01
PMF0863	0.5	0.1	1.4	55.0	< 0.20	< 0.17	0.22	11.35	2.99	0.11	0.19	0.16	< 20 μg/g	< 20 μg/g	0.02	< 10 μg/g	< 0.40	n.d.	< 0.02	27.94

Catalogue V

14th-15th c. PMF0401

14th-15th c. PMF0438

14th-15th c. PMF0444

14th-15th c. PMF0458

14th-15th c. PMF0470

14th-15th c. PMF0517

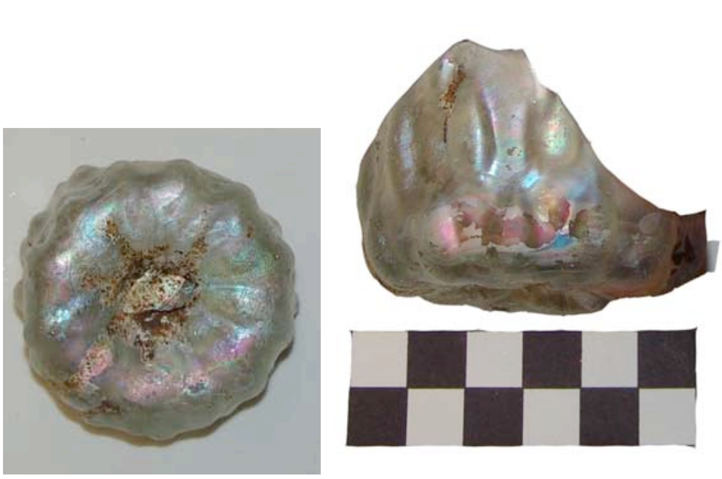
14th-15th c. PMF0600

14th-15th c. PMF0605

14th-15th c. PMF0610

14th-15th c. PMF0617

14th-15th c. PMF0691



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16th-17th c. PMF0546

16th-17th c. PMF0550

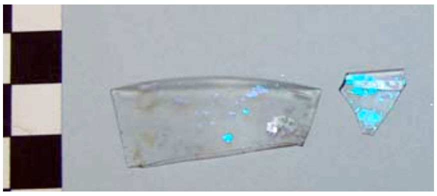
16th-17th c. PMF0556

16th-17th c. PMF0568

16th-17th c. PMF0569

16th-17th c. PMF0570

16th-17th c. PMF0996



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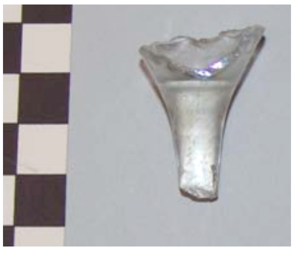
16th-17th c. PMF1025



18th c. PMF0863

Appendix VII: São João de Tarouca Monastery set (SJT) - Objects information, chemical composition and objects catalogue (Catalogue VI).

Table VII.1: Description of analyzed samples from São João de Tarouca Monastery assemblage (SJT) with inventory number, object type, glass colouration, part of the object preserved and dating.

Fragment	***Type***	***Colour***	***Part preserved***	***Age (century AD)***
SJT0001	Vessel	Uncoloured with yellowish hue	Base fragment	17th c.
SJT0003	Vessel with mould-blown decoration of lozenge motifs	Uncoloured with greenish hue	Base with applied cord	17th c.
SJT0005	Vessel with bossed mould-blown decoration	Uncoloured with yellow hue	Base and part of wall	17th c.
SJT0006	Beaker mould-blown decorated with lozenge motif enclosing a four-petalled flower inside.	Light olive green	Part of wall with rim	17th c.
SJT0007	Vessel with mould-blown decoration with lozenge motifs enclosing smaller lozenges	Light green hue	Fragments of base, wall and rim	17th c.
SJT0011	Bottle or flask decorated with filigree	Uncoloured base glass with white filigree strings	Neck and rim	17th c.
SJT0012	Drinking glass with filigree applied	Uncoloured base glass with white filigree strings	Foot base and part of wall and rim	17th c.
SJT0014	Vessel with applied filigree	Uncoloured base glass with white filigree strings	Part of wall and rim	17th c.
SJT0021	Wing with applied cord worked with pincers	Uncoloured with yellowish hue	Wing	17th c.
SJT0038	Vessel in truncated cone shape with white strings applied in spiral	Uncoloured with white strings	Part of wall and rim	17th c.
SJT0097	Vessel	Uncoloured, severely corroded surface	Part of wall and rim	17th c.

SJT0098	Vessel (probably beaker)	Green with filigree applied (stained with reddish on with strings)	Base and part of wall	17th c.
SJT0100	Vessel (probably jar or pitcher)	Green	Base, part of rimed wall and beak	17th c.
SJT0105	Vessel with engraved and gilded decoration	Uncoloured	Part of wall	17th c.
SJT0107	Oil lamp	Uncoloured with bluish hue	Base and part of wall	17th c.
SJT0109	Oil lamp	Turquoise	Base and part of wall	17th c.
SJT0110	Vessel (flask or bottle)	Uncoloured with a green/ bluish hue	Neck and mouth, truncated cone shape	17th c.
SJT0112	Vessel in ice glass (“ghiaccio”)	Uncoloured with a bluish hue	Part of base with applied cord	17th c.
SJT0113	Flask with mould-blown spiraled string decoration	Uncoloured	Neck, rim and part of wall	17th c.
SJT0114	Vessel (probably drinking glass)	Uncoloured with light grey hue	Part of wall	17th c.
SJT0115	Vessel with decoration worked with pincers	Uncoloured with bluish/ grayish hue	Part of wall and rim	17th c.
SJT0116	Vessel	Turquoise	Part of rim	17th c.
SJT0120	Drinking glass	Uncoloured	Four fragments of foot base	17th c.
SJT0122	Vessel with filigree or stings applied	Uncoloured base glass with white strings appied	Part of wall and rim	17th c.
SJT0123	Vessel with applied filigree	Uncoloured base glass with bluish hue and with white filigree strings	Part of wall	17th c.
SJT0126	Small flask	Natural yellowish/ brownish hue	Mouth and rim	17th c.
SJT0127	Vessel with decoration worked with pincers and a cord applied	Uncoloured with light blue hue	Part of wall	17th c.
SJT0128	Gourd	Green	Neck and rim	17th c.
SJT0131	Vessel with mould-blown decoration of vertical strings	Uncoloured glass with green hue	Part of wall and rim	17th c.
SJT0132	Vessel (bottle or gourd)	Yellow/light brownish	Part of neck	17th c.
SJT0133	Vessel (probably drinking glass) with folded foot	Uncoloured with yellowish hue	Base and part of wall	17th c.

SJT0134	Vessel (probably drinking glass)	Turquoise	Folded base	17th c.
SJT0135	Vessel with stings applied near the rim	Uncoloured with white stings	Part of wall and rim	17th c.
SJT0138	Drinking glass with folded foot and mould-blown decoration	Uncoloured	Base and part of wall.	17th c.

Table VII.2: Composition of fragments from São João de Tarouca Monastery (SJT) determined by μ-PIXE in weight percent of oxides.

Samples	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**As_2O_3**	**SnO2**	**SrO**	**BaO**	**PbO**
SJT0001	17.2	4.0	4.3	57.6	0.13	0.08	0.60	5.58	9.10	0.09	0.49	0.45	< 70 μg/g	< 30 μg/g	< 10 μg/g	20 μg/g	< 10 μg/g	n.m.	0.10	0.04	< 40 μg/g
SJT0003	16.5	4.1	2.9	59.0	0.16	0.07	0.71	7.00	8.06	0.11	0.29	0.68	< 50 μg/g	30 μg/g	30 μg/g	20 μg/g	0.01	n.m.	0.05	0.02	50 μg/g
SJT0005	15.2	4.1	3.2	58.7	0.20	0.06	0.69	7.25	9.58	0.12	0.35	0.48	< 50 μg/g	< 20 μg/g	20 μg/g	20 μg/g	< 30 μg/g	n.m.	0.07	0.04	< 40 μg/g
SJT0006	16.1	3.7	5.2	60.7	0.21	0.06	0.75	3.62	7.66	0.22	0.72	0.94	< 60 μg/g	< 20 μg/g	20 μg/g	50 μg/g	< 30 μg/g	n.m.	0.05	0.05	0.02
SJT0007	18.3	2.4	5.0	62.0	0.24	0.03	0.95	3.66	5.56	0.22	0.51	0.95	< 60 μg/g	< 20 μg/g	< 10 μg/g	30 μg/g	70 μg/g	n.m.	0.03	0.03	< 60 μg/g
SJT0011	18.7	2.4	1.8	67.9	0.22	0.07	0.99	2.96	4.05	0.08	0.27	0.52	40 μg/g	20 μg/g	20 μg/g	20 μg/g	40 μg/g	n.m.	0.02	0.01	0.02
SJT0012	18.6	3.8	2.7	62.3	0.16	0.05	0.91	3.21	7.06	0.08	0.35	0.62	0.01	30 μg/g	20 μg/g	20 μg/g	0.01	n.m.	0.04	0.02	0.05
SJT0014	14.0	3.2	2.6	61.2	0.21	0.08	0.67	6.91	9.66	0.09	0.47	0.62	50 μg/g	50 μg/g	30 μg/g	30 μg/g	0.01	n.m.	0.05	0.21	0.05
SJT0021	16.9	3.4	3.8	61.6	0.17	0.07	0.69	5.14	7.39	0.09	0.36	0.37	< 50 μg/g	< 20 μg/g	20 μg/g	30 μg/g	< 30 μg/g	n.m.	0.04	0.04	0.01
SJT0038	19.5	2.6	2.1	63.7	0.20	0.08	0.96	4.59	5.31	0.06	0.36	0.48	30 μg/g	20 μg/g	10 μg/g	30 μg/g	< 20 μg/g	n.m.	0.04	0.02	0.01
SJT0097	18.0	3.5	2.7	61.8	0.14	0.07	0.77	4.94	7.30	0.05	0.21	0.35	< 40 μg/g	< 10 μg/g	30 μg/g	< 10 μg/g	< 70 μg/g	n.m.	0.04	0.02	0.05
SJT0098	11.5	2.8	3.6	63.8	0.38	0.06	0.64	6.28	9.64	0.10	0.15	0.95	< 50 μg/g	< 10 μg/g	20 μg/g	40 μg/g	< 20 μg/g	n.m.	0.03	0.02	0.01
SJT0100	15.6	4.3	4.8	62.8	0.40	0.03	0.87	2.72	6.33	0.22	0.78	0.92	50 μg/g	< 10 μg/g	70 μg/g	40 μg/g	< 20 μg/g	n.m.	0.02	0.03	< 60 μg/g
SJT0105	18.0	2.5	1.8	66.5	0.16	0.08	0.85	4.17	4.63	0.10	0.43	0.71	50 μg/g	30 μg/g	70 μg/g	30 μg/g	50 μg/g	n.m.	0.02	0.03	0.01
SJT0107	17.5	2.7	2.2	65.7	0.22	0.07	0.95	3.64	5.78	0.09	0.27	0.55	60 μg/g	20 μg/g	80 μg/g	20 μg/g	60 μg/g	n.m.	0.03	0.02	0.03
SJT0109	16.6	3.3	4.4	61.5	0.59	0.06	0.65	4.49	6.12	0.16	0.84	1.10	0.01	0.01	60 μg/g	60 μg/g	0.03	n.m.	0.03	0.06	0.06
SJT0110	16.2	2.1	2.7	68.0	0.20	0.04	0.89	3.02	5.40	0.10	0.58	0.61	< 60 μg/g	30 μg/g	20 μg/g	30 μg/g	0.01	n.m.	0.04	< 0.02	0.03
SJT0112	14.7	3.5	2.3	62.1	0.14	0.06	0.69	8.22	7.31	0.07	0.36	0.50	0.01	< 10 μg/g	30 μg/g	20 μg/g	70 μg/g	n.m.	0.04	0.03	0.02
SJT0113	18.2	2.9	2.3	63.5	0.23	0.07	0.83	4.27	6.12	0.09	0.40	0.63	0.01	30 μg/g	0.01	40 μg/g	< 0.01	n.m.	0.04	0.02	0.09
SJT0114	17.9	2.3	2.0	65.6	0.22	0.05	0.99	3.93	6.24	0.07	0.19	0.47	40 μg/g	10 μg/g	10 μg/g	30 μg/g	< 40 μg/g	n.m.	0.04	0.02	0.03
SJT0115	16.4	4.6	3.7	59.3	0.13	0.10	0.56	6.59	7.27	0.11	0.58	0.43	< 30 μg/g	40 μg/g	< 10 μg/g	30 μg/g	60 μg/g	n.m.	0.06	0.05	0.01
SJT0116	16.4	3.3	4.4	61.6	0.51	0.07	0.64	4.44	6.18	0.18	0.87	1.17	0.01	0.01	60 μg/g	70 μg/g	0.02	n.m.	0.04	0.06	0.07
SJT0120	19.7	2.1	2.1	63.4	0.23	0.04	1.06	3.70	6.40	0.10	0.42	0.59	40 μg/g	30 μg/g	40 μg/g	40 μg/g	0.01	n.m.	0.03	0.04	0.03
SJT0122	18.0	2.5	2.6	65.9	0.29	0.05	0.98	2.93	5.27	0.10	0.49	0.80	0.01	30 μg/g	20 μg/g	40 μg/g	0.01	n.m.	0.03	0.03	0.03
SJT0123	19.7	2.1	2.9	62.9	0.23	0.07	1.01	3.54	6.12	0.10	0.41	0.70	0.01	40 μg/g	0.02	50 μg/g	0.01	n.m.	0.03	0.02	0.01
SJT0126	13.6	2.1	3.4	62.0	0.51	0.05	0.60	4.88	8.46	0.14	2.41	1.16	0.01	< 10 μg/g	0.02	70 μg/g	0.03	n.m.	0.11	0.02	0.14
SJT0127	17.0	3.4	2.3	61.7	0.19	0.05	0.86	6.55	7.19	0.05	0.24	0.37	< 50 μg/g	< 20 μg/g	< 10 μg/g	20 μg/g	40 μg/g	n.m.	0.07	0.02	0.02
SJT0128	17.2	6.9	6.5	58.0	0.54	0.02	0.88	1.51	6.10	0.24	0.06	1.87	0.01	20 μg/g	< 10 μg/g	60 μg/g	< 70 μg/g	n.m.	0.03	< 0.04	< 40 μg/g
SJT0131	18.8	2.6	2.9	63.1	0.25	0.06	1.01	3.48	6.34	0.12	0.32	0.83	0.01	30 μg/g	20 μg/g	40 μg/g	70 μg/g	n.m.	0.04	0.03	0.19
SJT0132	16.2	3.9	7.8	58.1	0.30	0.03	0.80	3.03	7.67	0.22	0.82	0.86	40 μg/g	< 10 μg/g	30 μg/g	30 μg/g	30 μg/g	n.m.	0.03	0.04	< 50 μg/g
SJT0133	16.3	3.4	2.5	64.7	0.28	0.07	0.74	4.95	5.98	0.10	0.26	0.66	< 60 μg/g	< 20 μg/g	< 10 μg/g	30 μg/g	0.01	n.m.	0.02	0.03	0.02
SJT0134	15.6	3.0	3.8	64.1	0.43	0.06	0.65	4.45	5.90	0.15	0.74	0.99	0.01	0.01	50 μg/g	60 μg/g	0.03	n.m.	0.04	0.05	0.04
SJT0135 body glass	12.7	3.0	2.3	61.3	0.28	0.05	0.64	9.74	8.04	0.11	0.49	0.82	0.01	50 μg/g	20 μg/g	30 μg/g	0.01	n.m.	0.03	< 0.02	0.01
SJT0135 white filigree	11.9	2.8	2.2	52.5	0.14	0.05	0.47	7.50	6.58	< 0.09	0.29	0.75	< 30 μg/g	< 10 μg/g	< 10 μg/g	< 0.1	< 10 μg/g	7.50	n.m.	0.38	6.84
SJT0138	19.6	2.1	2.0	65.5	0.22	0.05	1.18	2.54	5.90	0.08	0.26	0.52	50 μg/g	30 μg/g	30 μg/g	20 μg/g	40 μg/g	n.m.	0.03	0.02	0.03

n.m. stands for “not measured”

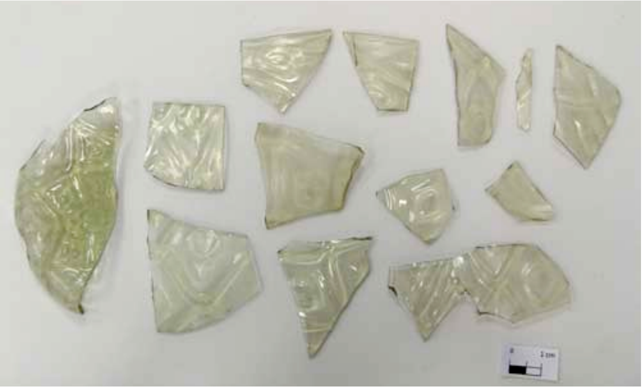
Catalogue VI

SJT0001

SJT0003

SJT0005

SJT0004 and SJT0006



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SJT0011

SJT0012

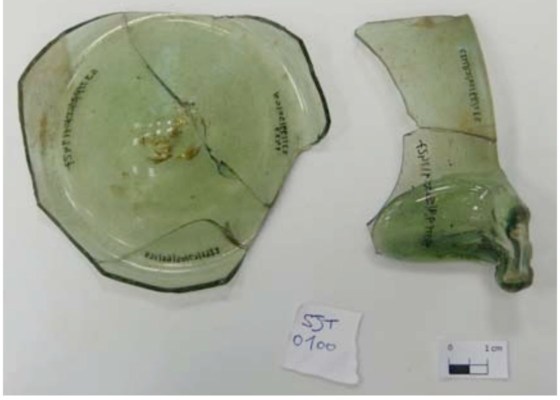
SJT0014

SJT0021

SJT0038

SJT0097

SJT0098



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SJT0107

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SJT0114

SJT0115

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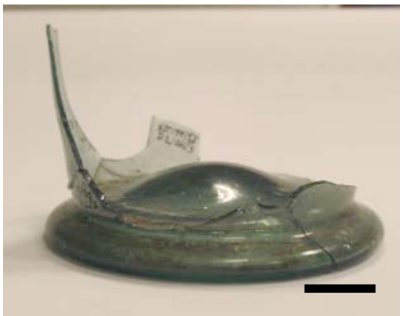
SJT0132

SJT0133



SJT0134

SJT0135

SJT0138

Appendix VIII: μ-PIXE and LA-ICP-MS values obtained for glass reference standards Corning A, Corning B, Corning C and N612.

Table VIII.1: μ-PIXE values obtained for the glass standards (average of 7 measurements). Certified (Brill, 1999, p. 544) average of measured composition, standard deviation, and relative standard deviation in percentage.

Standards	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**PbO**	**SnO_2**	**Sb_2O_3**	**BaO**	**SrO**
CMoG B																			
Avg. (n = 7)	16.7	0.9	4.5	60.8	0.66	1.33	8.85	0.10	0.21	0.32	0.06	0.09	2.41	0.17	0.52	-	-	0.15	-
StDev	1.1	0.1	0.7	4.5	0.12	0.43	2.26	0.05	0.10	0.05	0.04	0.03	0.62	0.09	0.14	-	-	0.04	-
Relative StDev (%)	6.8	7.1	16.1	7.4	17.62	32.16	25.54	50.11	49.15	14.76	65.54	29.47	25.71	51.22	26.23	-	-	29.48	-
Certified	17.0	1.03	4.36	62.27	0.82	1.00	8.56	0.089	0.25	0.34	0.046	0.099	2.66	0.19	0.61	0.04	0.46	0.12	0.019
CMoG C																			
Avg. (n = 7)	1.07	2.34	0.81	34.68	0.11	2.53	4.56	0.80	-	0.29	0.19	-	1.14	0.04	38.09	-	-	11.41	-
StDev	0.13	0.25	0.15	1.36	0.02	0.09	0.25	0.06	-	0.04	0.02	-	0.11	0.01	2.33	-	-	0.34	-
Relative StDev (%)	12.5	10.6	18.6	3.9	18.78	3.76	5.58	7.81	-	13.68	11.44	-	9.59	26.35	6.11	-	-	2.94	-
Certified	1.07	2.76	0.87	36.20	0.14	2.84	5.07	0.79	-	0.34	0.18	-	1.13	0.052	36.7	0.19	0.03	11.40	0.29

Table VIII.2: LA-ICP-MS values obtained for the glass standards. CMoG A certified (Wagner *et al.*, 2012) and measured composition, and Nist 612 certified for the elements (United States Of America, Department Of Commerce, 2012).

	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	Sb_2O_3
Average CMoG A (wt%)	13.7	2.45	0.93	67.1	0.10	0.15	2.86	5.77	0.78	0.99	1.09	1.67
Std CMoG A (±)	0.4	0.10	0.04	0.5	0.00	0.01	0.02	0.12	0.01	0.02	0.03	0.04
CMoG A reference	13.4	2.50	0.820	67.82	0.085		3.46	4.94	0.739	1.13	0.979	1.86
Average N612 (wt%)	13.2	0.014	2.06	73.0	0.013	0.081	nd	11.5	0.0078	0.0047	0.0065	0.0045
Std N612 (±)	0.4	0.0003	0.08	0.7	0.004	0.013	0.0012	0.2	0.0002	0.0001	0.0012	0.00004
N612 reference	14		2	72			0.0064	12	0.0050	0.0037	0.0051	0.0034
oxide µg/g	Li_2O	B_2O_3	V_2O_5	Cr_2O_3	CoO	NiO	CuO	ZnO	GaO	As_2O_3	Rb_2O	SrO
Average CMoG A	114	2009	58.1	15.5	1639	225	11323	514	0.78	26.6	88.0	1008
Std CMoG A (±)	8	111	0.6	4.7	58	7	266	5	0.03	7.1	1.7	20
CMoG A reference	110	2740	70	30	1700	230	11000	480			90	1060
Average N612	91.7	111	63.6	40.5	43.6	50.2	44.5	46.1	44.2	39.5	32.8	86.2
Std N612 (±)	6.4	8	0.2	5.5	1.4	1.8	0.9	0.5	0.3	7.6	0.6	0.5
N612 reference	40			35.0	35.5	38.8	37.7			37.4	31.4	78.4
oxide µg/g	Y_2O_3	ZrO_2	Nb_2O_3	MoO	Ag	Cd	In	SnO_2	Cs_2O	BaO	La_2O_3	CeO_2
Average CMoG A	0.98	54.8	0.67	2.8	14.3	0.50	4.97	1727	0.25	4717	0.57	0.33
Std corning A (±)	0.03	1.4	0.03	0.1	0.3	0.09	0.03	10	0.02	161	0.03	0.03
CMoG A reference		50										
Average N612	47.3	53.8	44.3	40.7	20.1	42.1	37.0	44.8	42.1	40.8	46.2	50.1
N612 reference					22.0	29.9				38.6	36	39
oxide µg/g	PrO_2	Nd_2O_3	Sm_2O_3	Eu_2O_3	Gd_2O_3	Tb_2O_3	Dy_2O_3	Ho_2O_3	Er_2O_3	Tm_2O_3	Yb_2O_3	Lu_2O_3
Average CMoG A	0.04	0.20	0.03	0.88	0.35	0.006	0.048	0.008	0.026	0.004	0.030	0.005
Std CMoG A (±)	0.01	0.02	0.00	0.39	0.03	0.001	0.008	0.001	0.003	0.001	0.008	0.002
Average N612	46.1	45.1	46.5	41.6	39.1	42.6	42.0	43.0	42.8	40.0	45.9	41.1
Std N612 (±)	2.9	2.0	1.5	0.2	4.9	1.0	1.0	1.3	1.3	1.0	0.5	1.3
N612 reference		36	39	36	39		35		39		42	
oxide µg/g	HfO_2	Ta_2O_3	WO	Pt	Au	PbO	Bi	ThO_2	UO_2			
Average CMoG A	1.21	0.12	0.106	3.52	0.11	649	8.7	0.35	0.22			
Std CMoG A (±)	0.06	0.00	0.006	0.04	0.01	8	0.1	0.03	0.02			
Average N612	45.5	36.5	39.8	2.4	4.6	36.9	32.3	44.0	42.3			
Std N612 (±)	1.8	1.5	1.1	0.1	0.2	2.4	0.3	4.0	2.9			
N612 reference		15.7			5	38.57		37.79	37.38			

Appendix IX: Classification tree for the soda-rich glass objects

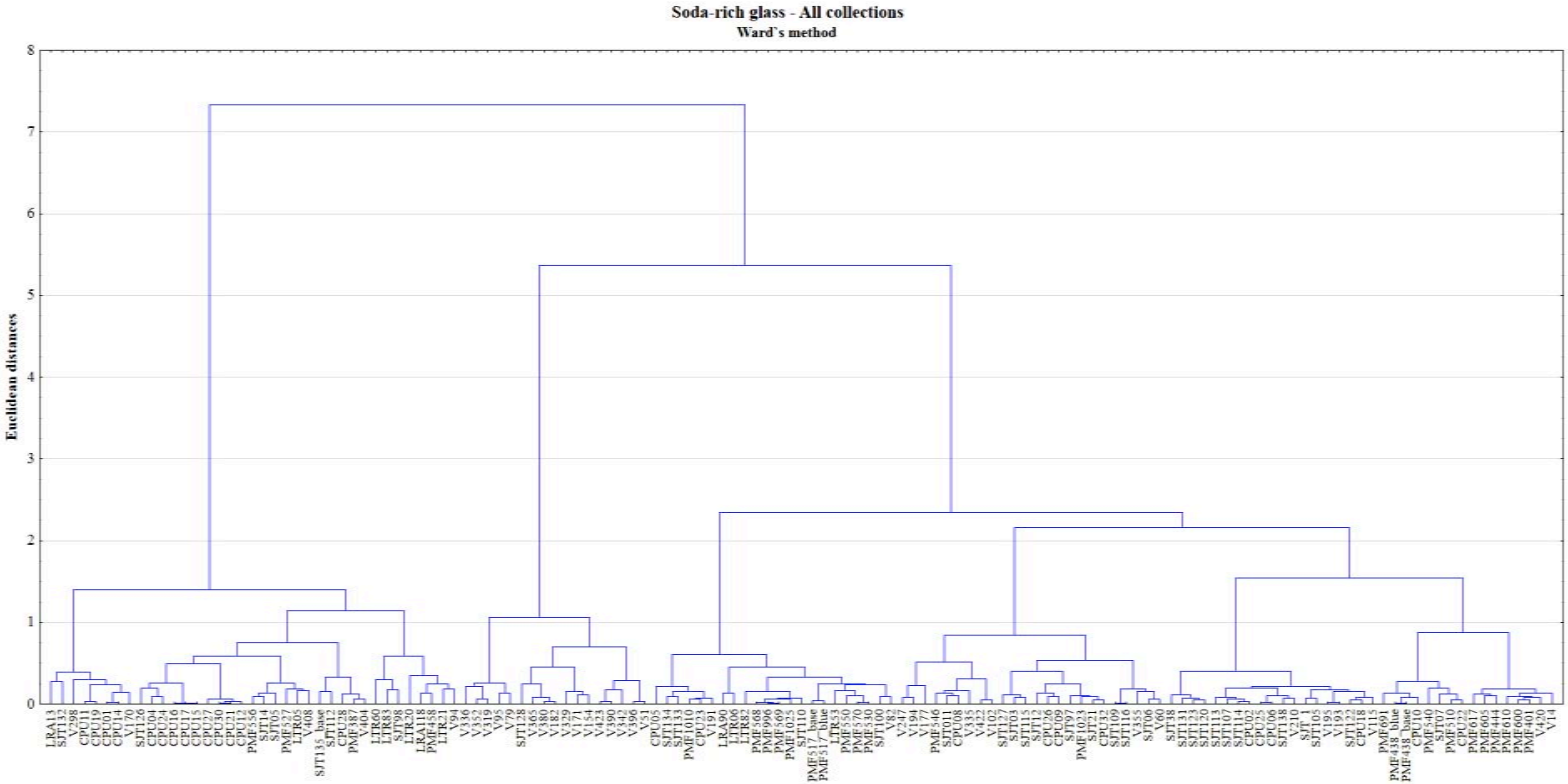


Fig. IX.1: Dendrogram of all the soda-rich glass from all assemblages under study. The dendrogram was achieved by the Ward’s method using Euclidian distances. Data was mean centred and normalised.

Appendix X: Compositions from the literature

Table X.1: Chemical composition (in average) and standard deviations of Venetian and *façon-de-Venise* glasses dated to between the 16th and 17th centuries, in weight percent of oxides (Lima *et al.*, 2012).

Location	***Classification***	***Date***	***Nr. Of samples***	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_3**	**MnO**	**Fe_2O_3**	**PbO**	**SnO_2**
Venice [a,b]	*Cristallo*	16th-18th c.	(n=16)	17.17	1.81	0.68	70.49	0.15	0.30	1.00	2.93	4.88	0.03	0.32	0.24		
			±	1.49	0.38	0.14	1.34	0.04	0.07	0.11	0.41	0.69	<0.03	0.14	0.05		
	Vitrum Blanchum	16th-18th c.	(n=33)	13.64	3.35	1.03	66.90	0.31	0.24	0.86	2.97	9.76	0.05	0.47	0.37		
			±	1.36	0.76	0.37	1.71	0.12	0.08	0.12	1.20	1.18	0.02	0.20	0.08		
	Common	16th-18th c.	(n=8)	13.42	3.11	1.71	64.72	0.33	0.19	0.66	3.30	10.07	0.05	1.27	0.84	0.15	0.10
			±	0.92	0.25	0.15	0.66	0.09	0.04	0.07	0.59	0.57	0.01	0.32	0.08	0.07	0.06
Amsterdam [c]																	
Waterlooplein		17th c.	(n=74)	13.3	2.85	1.79	65.5	0.28	0.13	0.59	5.02	9.13		0.57	0.51		
			±	1.4	0.28	0.46	1.6	0.06	0.04	0.08	1.53	1.32		0.21	0.11		
Keizergracht		17th c.	(n=38)	14.3	3.25	2.12	64.1	0.22	0.12	0.62	4.74	8.83		0.5	0.74		
			±	1.1	0.38	0.35	1.5	0.07	0.04	0.08	0.88	1.24		0.23	0.24		
Antwerp [c]	*Façon-de-Venise*	2nd half 16th c.		14.5	2.85	1.45	63.9	0.32	0.14	0.66	5.56	9.63		0.34	0.42		
			±	1.4	0.45	0.14	2.1	0.07	0.04	0.11	1.24	1.01		0.14	0.07		
	Cristallo	17th c.		15.02	1.68	1.64	69.7	0.35	0.19	0.67	4.51	4.85		0.51	0.32		
			±	0.94	0.24	0.47	1.93	0.77	0.07	0.14	0.83	0.76		0.16	0.07		
	Mixed alkali	17th c.		12.0	1.87	1.59	68.9	0.22	0.15	0.48	8.27	5.40		0.50	0.40		
			±	1.0	0.27	0.10	1.4	0.07	0.06	0.12	0.78	0.53		0.15	0.12		
London [c]																	
Old Broad Street		1st half 17th c.	(n=32)	13.1	3.14	1.76	64.7	0.33	0.20	0.57	5.05	9.62		0.68	0.55		
			±	1.3	0.36	0.21	0.9	0.07	0.04	0.11	1.50	0.56		0.30	0.14		
Aldgate		1st half 17th c.	(n=40)	10.06	2.56	1.46	64.3	0.3	0.13	0.47	9.62	9.40		0.38	0.37		
			±	0.5	0.11	0.16	0.5	0.1	0.03	0.03	0.45	0.47		0.12	0.04		
Spain [d]	Spanish I	end 16th – 17th c.		10.24	1.13	1.09	67.13	1.06	0.23		6.87	9.85		1.38	0.59	0.016	
			±	1.06	0.14	0.31	1.36	0.09	0.09		1.05	1.23		0.42	0.13	0.015	
	Spanish II	end 16th – 17th c.		11.67	3.41	1.72	67.35	0.63	0.31		3.48	9.85		0.62	0.69	0.013	
			±	1.14	0.42	0.54	1.58	0.14	0.08		0.49	1.66		0.25	0.19	0.008	
Tuscany [e]																	
Gambassi	Tuscany Barilla	Mid 16th c.	(n=8)	14.2	3.4	4.6	59.2	0.4	0.1	0.5	5.7	9.5		1.3	0.7		
			±	1.0	0.3	0.3	0.5		0.1	0.1	0.6	0.4		0.4	0.2		
	Tuscany Levantine	Mid 16th c.	(n=1)	14.4	4.1	4.4	60.9	0.5	0.2	0.5	3.9	9.5		1.3	0.7		
San Giovanni Valdarno	Tuscany Barilla	16th c.	(n=11)	14.4	3.1	4.3	59.3	0.4	0.1	0.6	6.0	9.8		1.0	0.6		
			±	1.5	0.4	0.3	1.6	0.1		0.1	0.8	1.2		0.3	0.1		
	Tuscany Levantine	16th c.	(n=3)	15.8	4.5	4.1	60.7	0.5	0.2	0.6	3.6	8.2		1.0	0.6		
			±	0.7	0.3	0.1	1.3	0.1	0.1	0.1	0.1	1.1		0.4	0.1		
	Pebbles Barilla	16th c.	(n=1)	10.3	3.4	1.7	62.7	0.4	0.1	0.5	8.8	10.7		0.7	0.5		
	Pebbles Levantine	16th c.	(n=1)	16	1.4	2.1	67.6	0.6	0.1	0.9	3.0	6.1		1.2	0.6		
Portugal, *Santa Clara-a-Velha* Monastery [f]	*Millefiori* glass (objects' body glass)	17th c.	Inventory numbers														
			SCV171	15.2	2.41	1.35	62.8	0.23	0.26	0.82	2.67	6.43		0.61	0.66	3.01	2.30
			SCV173	14.3	3.06	1.27	65.1	0.25			3.30	8.45		0.33	1.01	0.23	
			SCV176	13.6	3.32	1.11	63.6	0.20	0.32	0.74	1.49	7.97		0.24	0.73	3.90	
			SCV-V66	16.9	2.76	7.61	58.2	0.36	0.15	0.88	4.12	5.92	0.20	1.13	1.15		
			SCV-V67	19.2	6.61	7.84	54.3	0.82	0.07	0.88	1.85	4.71	0.66	0.95	2.15		
			SCV-V68	13.2	2.97	3.81	58.4	0.36	0.09	0.46	5.72	11.14	0.29	1.34	1.66	0.13	
			SCV-V74	15.6	2.94	2.49	59.8	0.32	0.22	0.74	3.13	7.24		0.33	0.94	2.83	2.35
			SCV-V108	15.4	2.98	4.57	60.8	0.29	0.19	0.78	5.50	6.54	0.14	0.46	0.81	0.11	0.06

[a] Verità & Zecchin, 2009a

[b] Verità & Zecchin, 2009b

[c] de Raedt *et al.*, 2002.

[d] Ulitzka, 1994.

[e] Cagno *et al.*, 2010.

[f] Lima *et al.*, 2012.

Table X.2: Chemical composition (in average) and standard deviations of HLLA glasses with known provenance and bottles dated between the 16th and 19th centuries, in weight percent of oxides.

Location	*Classification*	*Date*	*No of samples*	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	SrO	BaO	PbO
England - Silkstone, Yorkshire [a] Production center / glass factory	Glassworking waste																	
	phase 1	?	(n = 6)	1.5	5.4	4.0	54.1	3.2	0.3	0.3	8.0	20.5	0.2	0.8	2.1	0.06		<0.3
				1.1	0.7	0.5	3.0	1.0	0.1	0.2	1.6	2.2	0	0.5	0.3	0.02		
	phase 2	1670 - 1700	(n = 32)	1.1	4.9	4.3	53.5	2.9	0.3	0.3	8.4	21.2	0.3	0.8	2.1	0.06		<0.3
				0.3	0.7	0.6	3.1	0.6	0.1	0.1	1.0	1.9	0.1	0.4	0.4	0.02		
	phase 4	1680 - 1700	(n = 39)	1.6	4.8	3.6	57.2	2.0	0.3	0.3	3.9	23.8	0.2	0.5	1.9	0.09		<0.3
				0.4	1.0	0.3	2.3	0.3	0.2	0.1	1.1	1.9	0.1	0.2	0.5	0.02		
England - Bolsterstone, Yorkshire [b] Production center / glass factory	Bottle	17th - 18th c.	(n = 1)	1.4	6.4	3.0	57.6				1.2	26.7						
England - Vauxhall, London [d] Production center / glass factory	?	Late 17th c.	(n = 10)	1.1	2.4	2.4	60.7	2.4	0.2	<0.2	7.4	21.5	0.2	0.2	1.5	0.07		<0.1
				0.9	0.4	0.2	1.6	0.3	0.2		1.2	2.2	<0.1	<0.1	0.3	0.02		
England - Cheese Lane, Bristol [e] Production center / glass factory	Fragments	18th c.	(n = 3)	2.5	4.2	5.9	58.7	1.1	0.3	0.3	3.2	21.3	0.3	0.3	2.7	0.13		
				0.5	0.6	0.7	1.8	0.1	0.1	0.1	0.4	0.8	0.1	0.1	0.2	0.01		
England - Gawber glasshouse, Yorkshire [f] Production center / glass factory	Bottle	?	(n = 1)	1.0	4.2	7.9	52.9				2.4	27.2		1.4	2.4			
England - Bedminster, Bristol [g] Production center / glass factory	Glassworking waste																	
	Group A	18th c. and later	(n = 7)	1.3	4.2	5.4	58.4	<0.2	0.5	0.3	2.2	24.9	0.3	0.3	1.7		0.6	
				0.3	0.2	0.6	1.1		0.1	0.1	0.1	1.0	<0.1	<0.1	0.2		0.1	
	Group B		(n = 11)	2.0	4.4	5.2	56.9	0.6	0.5	0.3	2.2	25.3	0.3	0.2	2.2		<0.3	
				0.3	0.6	0.6	1.1	0.2	0.1	0.1	0.1	1.2	0.1	<0.1	0.2			
England - Limekiln Lane, Bristol [i] Production center / glass factory	Glassworking waste and bottle fragments	Latter 17th c. to early 19th c.	(n = 28)	1.8	3.6	4.6	57.3	1.7	0.41	0.33	3.1	24.4	0.25	0.24	2.1	0.10	0.1	
				0.5	0.9	0.8	1.4	0.5	0.14	0.11	1.7	2.7	0.03	0.07	0.3	0.02	0.2	
England - St. Thomas Street, Bristol [j] Production center / glass factory	Glassworking waste																	
	phase 4A	Early to mid 18th c.	(n = 10)	2.2	4.7	5.4	56.7	0.9	0.3	0.4	2.6	23.9	0.25	0.25	2.5			
				0.4	0.2	0.3	1.0	0.2	0.1	0.1	0.2	0.1	0.02	0.07	0.1			
	phase 4B	Late 18th c. to early 20th c.	(n = 6)	1.8	2.8	3.6	57.7	1.6	0.6	0.4	2.2	26.9	0.21	0.21	2.0			
				0.2	0.1	0.1	0.5	0.1	0.1	0.1	0.3	0.3	0.02	0.03	0.2			
England - Newent, Gloucestershire [l] Production center / glass factory	Glassworking waste	Early 17th c.	(n = 21)	2.0	3.7	4.4	56.8	2.5	0.18	0.51	8.1	19.7	0.23	0.31	1.36	0.06		
				0.6	0.3	0.3	1.4	0.2	0.06	0.19	1.3	1.5	0.03	0.09	0.17	0.02		
England - Hightown, Yorkshire [m] Production center / glass factory	Glassworking waste																	
	phase I	c. 1844 - 1872	(n = 5)	6.5	3.18	5.56	58.06	<0.01	0.50	<0.01	1.02	22.02	0.20	1.22	3.08	<0.01		<0.05
				1.2	0.25	0.44	0.71		0.09		0.12	1.39	0.03	0.46	0.20			
England – Hightown, Castleford, West Yorkshire [k] Production centre / glass factory	Bottle fragments Phase 1	c. 1852 - 1874	(n = 2)	7.2	3.2	6.2	57.7		0.56		1.21	20.32	0.25	0.04	2.80	0.02	<0.20	<0.01
				0.2	0.005	0.04	0.2		0.1		0	0.66	0.04	0.03	0.15	0		
Ireland - Shinrone, Co. Offaly [n] Production center / glass factory	Glassworking waste (lumps and dribbles)	Early to Mid. 17th c.	(n = 24)	1.67	2.46	1.88	61.76	1.52	0.63		3.95	24.81	0.15	0.24	0.86			
				0.51	0.24	0.32	1.62	0.10	0.14		0.38	1.13	0.04	0.05	0.18			
	Glassworking waste (overblows, etc.)	Early to Mid. 17th c.	(n = 12)	1.56	2.55	2.07	62.23	1.54	0.73		3.96	24.01	0.15	0.24	0.88			
				0.22	0.17	0.16	0.69	0.10	0.11		0.22	0.38	0.04	0.04	0.12			
Belgium - Clairefontaine [o] Cistercian nunnery	Vessels																	
	Group 4.1	Mid 18th c.	(n = 10)	3.4	4.2	3.1	59	1.1		0.6	4	22		1.1	1.4			
				0.8	0.6	0.5	1	0.1		0.1	1	2		0.2	0.2			
	Group 4.2		(n = 11)	0.5	3.6	3	56	1.5		0.1	6	26		1.0	1.3			
				0.1	0.9	1	2	0.2		0.1	2	3		0.3	0.3			
France - Bouches-du-Rhône [p]	Carro3 (ship) Shipwreck	< 1851	(n = ?)	2.87	1.94	8.94	56.1	0.10		0.14	1.58	24.8	0.22	0.05	1.81		1.05	
				0.5	0.2	1.2	2.7	0.02		0.1	0.3	2.2	0.1	0.01	0.6		0.5	
	Arles - Production centre / glass factory	19th c.	(n = ?)	2.16	1.88	8.70	56.3	0.75		0.5	1.80	25.1	0.28	0.11	2.10		0.04	
				0.3	0.3	0.6	1.3	0.1		0.2	0.6	1.2	0.02	0.03	0.1		0	
Portugal – *Coina* Royal Glass Factory [q]		1st half 18th c.	(n = 5)			3.20	61.49	0.68		0.25	1.71	21.44	0.24	0.35	1.60	0.10	0.24	0.04
						0.63	4.04	0.15		0.20	0.63	0.66	0.08	0.26	0.57	0.07	0.24	0

[a] Dungworth *et al.*, 2006
[b] Cable, 1987
[c] Dungworth, 2006
[d] Dungworth & Mortimer, 2005
[e] Ashurst, 1970
[f] Blakelock, 2007
[g] Dungworth, 2005
[h] Dungworth, 2007
[i] Dungworth, 2010
[j] Gardner, 2009
[k] Lucas, 2010
[l] Farrelly *et al.*, 2014
[m] Herremans *et al.*, 2012
[n] Gratuze & Serra, 2010
[o] Lopes *et al.*, 2009

Table X.3: Chemical composition (in average) and standard deviations of potassium rich glasses dated between the 14th and 18th centuries, in weight percent of oxides.

Location		*Description*	*Dating*	*No of samples*	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	BaO	As_2O_3	SnO_2	PbO	CaO/K_2O
Bohemia [a]		Group A	14th to 15th c.	(n = 22)	0.72	2.89	1.99	60.08	1.02	0.32		13.90	17.18	0.10	0.75	0.45	0.32		0.023	0.022	1.24
				±	0.75	0.38	0.50	0.46	0.30	0.03		2.55	1.51		0.07	0.18	0.05		0.012	0.036	
		Group B	15th c.	(n = 5)	0.50	2.65	2.62	56.42	1.05		0.12	20.92	14.61	0.34	0.51	0.62					0.70
				±	0.24	0.26	1.26	1.49	0.09		0.04	0.92	0.89	0.09	0.15	0.14					
		Group C	1st half 16th c.	(n = 7)	0.32	2.39	2.81	58.09	1.11		0.16	18.08	14.50	0.37	0.65	0.90					0.80
				±	0.28	0.79	1.28	5.55	0.28		0.07	2.55	1.55	0.08	0.15	0.26					
		Group D	2nd half 16th c.	(n = 28)	1.16	2.56	1.89	62.71	1.03	0.37	0.31	12.12	16.40	0.16	1.07	0.42	0.29		0.034	0.22	1.35
				±	1.12	0.60	0.65	2.37	0.36	0.18	0.30	1.71	1.56	0.13	0.31	0.16	0.14		0.065	0.19	
		Group E	1st half 17th c.	(n = 9)	0.86	2.37	2.51	60.64	1.18		0.30	13.91	15.19	0.29	0.88	0.72	1.69			0.08	1.09
				±	0.87	0.60	0.82	3.07	0.16		0.17	1.60	1.40	0.15	0.29	0.26					
		Group F	1st half 19th c.	(n = 6)	1.72	0.11	0.15		0.74			15.28	4.77		0.02	0.15				0.34	0.31
				±	1.70	0.07	0.05		0.54			2.60	2.21		0.02	0.15				0.26	
Germany [b]	Altmünden	Goblet	c. 1710	(n = 1)	0.18		0.15	72.88				16.43	0.39		0.05	0.07		1.26		9.48	0.02
	Dresden	Goblet	c. 1740	(n = 1)	0.53			66.38			0.4	15.42	5.10		0.03	0.08		2.41		8.91	0.33
	Germany	Plaque	1700 - 1750	(n = 1)			0.11	69.50				20.17	3.42		0.07	0.04		2.57		5.73	0.17
	Zechlin	Goblet	c. 1740	(n = 1)	0.43			76.77				14.66	2.10		0.06			2.27		2.70	0.14
		Goblet	c. 1740	(n = 1)	0.44		0.20	75.22				16.11	3.05		0.05	0.04		1.99		2.63	0.19
		Goblet	1738 - 1747	(n = 1)	0.5			76.78				15.10	2.21		0.05	0.03		1.67		2.27	0.15
	Potsdam [a1]		15th - 17th c.	(n = 20)	1.0	2.7	2.1	60 - 65	2.2			7.0	18.3		0.46	0.48					2.61
Poland [b]	Nalikobi	Goblet	c. 1740	(n = 1)			0.92	70.04				19.69	4.78		0.12	0.19		1.84		2.09	0.24
		Flute		(n = 1)			0.73	68.85				20.50	5.32		0.12	0.13		1.81		2.01	0.26
		Goblet		(n = 1)			0.73	69.31				20.79	5.24		0.14	0.12		1.67		1.85	0.25
Belgium [c]	Antwerp		17th century	(n = 8)	7.1	2.2	1.6	63.3	0.4			15.5	7.9		0.5	0.4					0.51
				±	1.0	0.2	0.2	0.6	0.1			2.5	1.7		0.2	0.1					
Belgium [d]	Mechelen		17th century	(n = 14)	6.6	1.5	0.4	72.0	n.d.			13.2	4.2		0.06	0.08					0.32
				±	2.1	0.5	0.2	2.5				1.1	1.6		0.01	0.02					
The Netherlands [e]	Groningen	Group 2	1687 - 1698	(n = 14)	7.7	< 2.5	1.4	65.9	< 1.0		0.6	14.4	5.8	0.08	0.55	0.33	0.05			4.0	2.5
				±	1.8		0.4	1.9			0.2	2.6	1.3	0.02	0.54	0.10	0.05			2.4	
		Group 3a		(n = 6)	7.4	< 2.5	1.6	53.6	< 1.0		0.4	14.8	7.3	0.08	0.11	0.34	0.03			14.1	2.0
				±	1.9		0.4	3.3			0.4	2.4	2.2	0.02	0.07	0.13	0.01			2.9	
Portugal [f]	*Coina* glass factory	Vessels	1st half 18th c.	(n = 4)			3.82	67.05	1.30		0.15	14.56	9.22	0.02	0.17	0.11	0.03	0.65		2.87	0.63
				±			0.42	4.26	0.13		0.04	1.17	0.58	0.00	0.09	0.05	0.01	0.42		2.41	
		Rod *a retortoli*		(n = 1)			3.80	69.33	1.27		0.29	11.47	9.86	0.03	0.09	0.10	0.03	0.10		3.60	0.86
		Window glass		(n = 1)			4.20	59.70	1.53		0.19	18.27	9.65	0.02	0.66	0.17	0.05	0.84		4.61	0.53

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[a] Smrcek, 1999.

[a1] Bronk, H. 1998. Chemisch-analytische Untersuchungen frühneuzeitlicher Gläser Mittel- und Südeuropas unter Anwendung einer quasi-zerströrungsfreien Mikroprobenahmetechnik. Mensch & Buch Verlag, Berlin, 1998. Consulted in Smrcek, 1999.

[b] Kunicki-Goldfinger *et al.*, 2005.

[c] De Raedt *et al.*, 2002.

[d] Van der Linden *et al.*, 2005

[e] Müller & Stege, 2006

[f] Lopes *et al.*, unpublished data.

Table X.4: Chemical composition (in average) and standard deviations of mixed alkali glasses dated between the 14th and 18th centuries, in weight percent of oxides.

Location		***No of samples***	***Date***	***Na_2O***	***MgO***	***Al_2O_3***	***SiO_2***	***P_2O_5***	***SO_3***	***Cl***	***K_2O***	***CaO***	***TiO_2***	***MnO***	***Fe_2O_3***	***SrO***	***PbO***
England - Silkstone [a]	Phase 1	(n = 6)	?	8.3	5.5	3.1	62.7	1.3	0.2	0.9	5.9	9.3	0.2	0.4	1.1	0.27	1.40
		±		0.4	0.3	0.1	0.2	0.1	0.0	0.1	0.1	0.2	0.0	0.0	0.0	0.01	0.10
	Phase 2.1	(n = 7)	c. 1670	6.9	2.9	1.4	68.3	0.3	0.1	0.5	6.6	10.5	< 0.1	1.0	1.4	0.05	< 0.3
		±		0.4	0.1	0.3	1.9	0.3	0.1	0.1	0.2	1.6		0.1	0.2	0.01	
	Phase 2.2	(n = 5)		3.5	3.7	4.7	60.3	1.7	0.2	0.3	6.8	14.4	0.3	0.8	3.0	0.10	< 0.3
		±		0.4	0.1	0.3	1.9	0.3	0.1	0.1	0.2	1.6	0.1	0.1	1.0	0.02	
England - Cheese Lane, Bristol [b]		(n = 47)	18th c.	7.6	5.3	3.5	67	1.2			4.2	9.7	0.1	< 0.1	1.0	0.40	< 0.3
		±		0.7	0.5	1.1	1.3	0.2			0.3	1.2	0.1		0.3	0.05	
England – Bolsterstone, Yorkshire [c]		(n = 6)	17th-18th c.	6.5	4.9	3.1	63.4	1.6			4.6	11.8			1.1		1.6
		±		0.9	0.5	0.9	1.0	0.3			0.6	2.7			0.2		1.3
England – Gawber, Yorkshire [d]		(n = 3)	18th c. – early 19th c.	6.7	5.2	3.2	65.7		0.4		3.8	13.7			0.89		0.5
		±		1.6	0.6	1.3	0.3		0.4		0.3	3.4			0.37		0
England - Vauxhall, London [e]	Group 1	(n = 28)	Late 17th c.	10.9	2.3	1.6	63.6	0.3	< 0.2	0.5	8.1	9.5	0.1	0.9	0.5	0.06	1.7
		±		1.4	0.6	0.2	2.2	0.1		0.1	1.5	1.4	< 0.1	0.1	0.1	0.02	2.1
	Group 2	(n = 14)		8.2	1.6	2.3	65.2	0.3	< 0.2	0.3	8.1	0.3	0.2	1.0	1.1	0.07	1.3
		±		0.9	0.3	0.5	2.2	0.1		0.2	1.1	1.8	0.1	0.2	0.4	0.02	1.8
England - St. Thomas Street, Bristol [f]		(n = 6)	18th c.	7.4	5.0	3.4	67.4	0.9			4.5	10.4	0.10	0.06	0.71	0.41	
		±		0.7	0.3	0.3	1.3	0.1			0.4	1.1	0.02	0.02	0.14	0.03	
Italy - Gambassi, San Gimignano and San Giovanno Valdarno, Tuscany [g]	A "Barilla"	(n = 38)	14th – 16th	13.6	3	4.4	60.1	0.5	0.2	0.5	6.3	9.3		1.1	0.7		
		±		1.9	0.8	1	2.6	0.2	0.1	0.1	1.2	1.2		0.4	0.3		
Belgium – Antwerp [h]		(n = 17)	17th century	12.0	1.9	1.6	68.9	0.2			8.3	5.4		0.5	0.4		
		±		1.0	0.3	0.1	1.4	0.1			0.8	0.5		0.1	0.1		
Belgium – Mechelen [i]		(n = 3)	17th century	13.5	2.2	0.84	69.6	n.d.			8.2	4.8		0.100	0.07		
		±		0.4	0.3	0.02	0.7				0.8	1.2		0.002	0.01		

[a] Dungworth, 2003 [b] Dungworth & Mortimer, 2005 [c] Cable, 1987 [d] Ashurst, 1970 [e] Dungworth, 2006 [f] Dungworth, 2007

[g] Cagno *et al.*, 2008 [h] De Raedt *et al.*, 2002 [i] Van der Linden *et al.*, 2005

Table X.5: Chemical composition (in average) and standard deviations of lead glasses with known provenance dated between the 17th and 19th centuries, in weight percent of oxides.

Location	Classification	No of samples	Date	Al_2O_3	SiO_2	K_2O	CaO	MnO	Fe_2O_3	PbO	K_2O/CaO
England - Silkstone, Yorkshire [a] **Production centre / glass factory**	Group I	(n = 30)	1674-1685	0.4	65.3	16.7	0.5	0.1	0.08	16.44	33.4
			±	0.2	2.4	0.8	0.4	0.19	0.06	2.39	
	Group II	(n = 10)	1674-1692	0.5	58.8	12.43	0.1	0.02	0.07	27.16	124
			±	0.2	1.2	0.29	0	0	0.01	1.21	
	Group III / IV	(n = 7)	1680-1720	0.5	53.7	9.33	0.1	0.02	0.06	36.07	93.3
			±	0.2	2.9	0.68	0	0.01	0.02	2.70	
England - Silkstone, Yorkshire [b] **Production centre / glass factory**	Group IIa	(n = 2)	1685-1710	0.6	56.0	12.05	0.1	0.05	0.12	31.05	120.5
			±	0.06	0.2	0.07	0.06	0.02	0.01	0.07	
The Netherlands – Groningen [c]	Group 4	(n = 9)	1687-1698	2.2	52.9	13.1	1.8	0.08	0.18	29.4	7.3
			±	0.4	3.0	2.1	1.0	0.13	0.10	2.2	
Portugal – Coina Royal Glass Factory [d]		(n = 4)	1st half 18th c.	0.4	49.0	8.27	2.21	0.12	0.15	35.94	3.74
			±	0.1	2.9	1.56	2.36	0.08	0.09	6.61	

[a] Dungworth & Brain, 2009 [b] Dungworth & Brain, 2013 [c] Müller & Stege, 2006 [d] Lopes *et al.*, unpublished results

Appendix XI: Bottle anatomy scheme

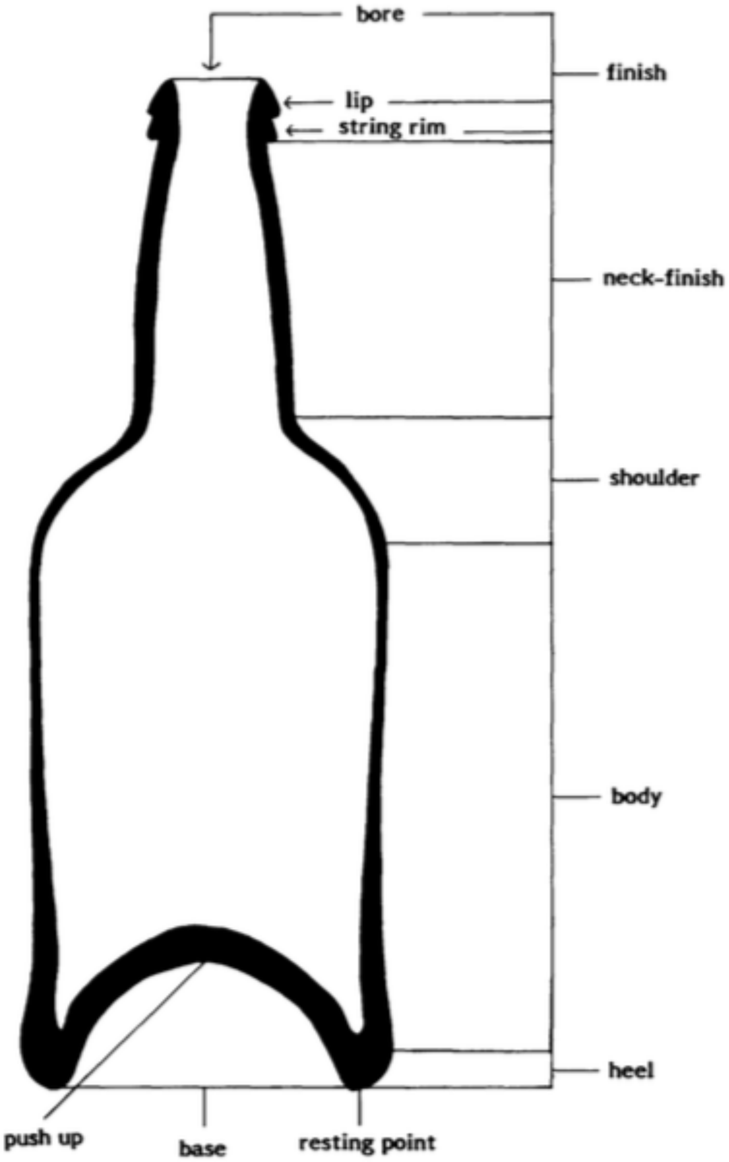
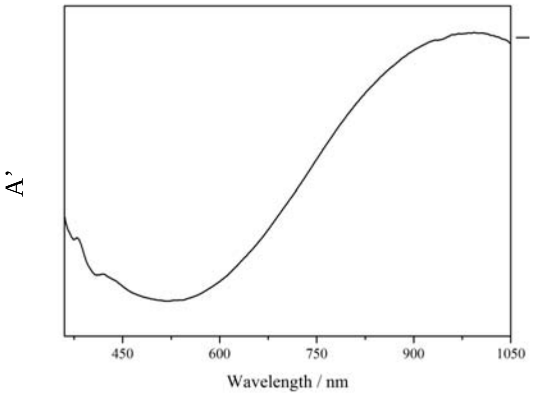


Fig. XI.1: The bottle anatomy. Image withdrawn from (Jones, 1986).

Appendix XII: UV-Vis spectroscopy spectra of the glass fragments from the studied assemblages

Absorbance spectra from Museu do Teatro Romano in Lisbon (LTR) objects



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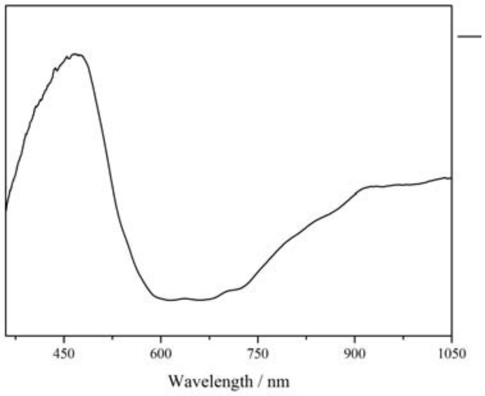

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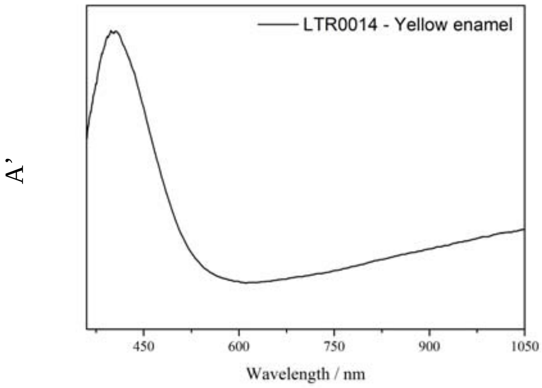
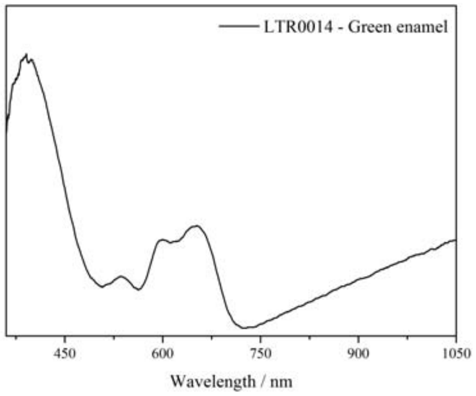
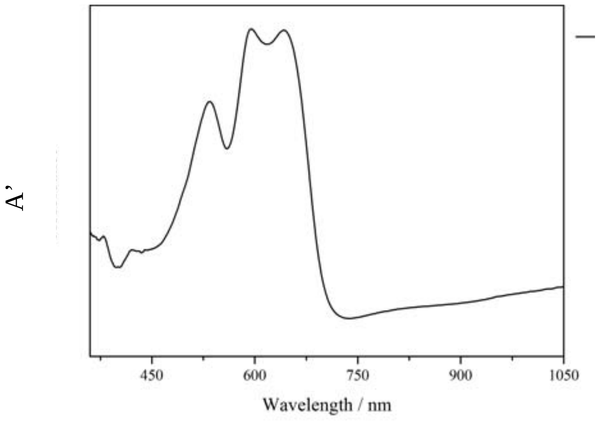


LTR0014 – yellow enamel



LTR0014 – green enamel



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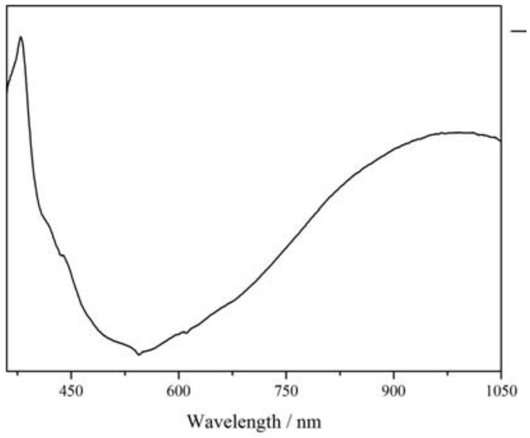

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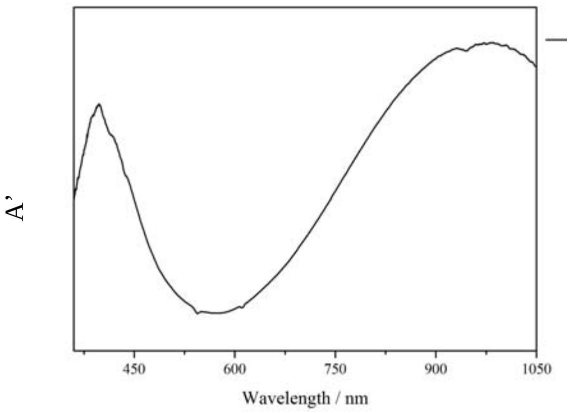

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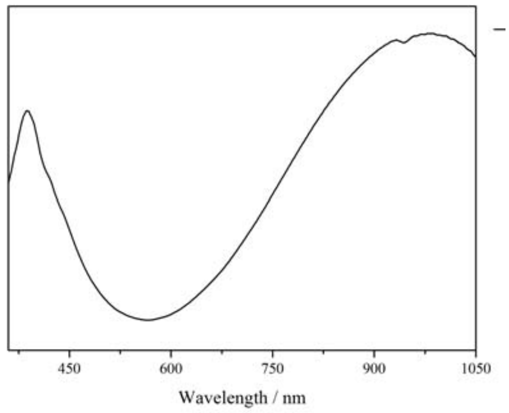

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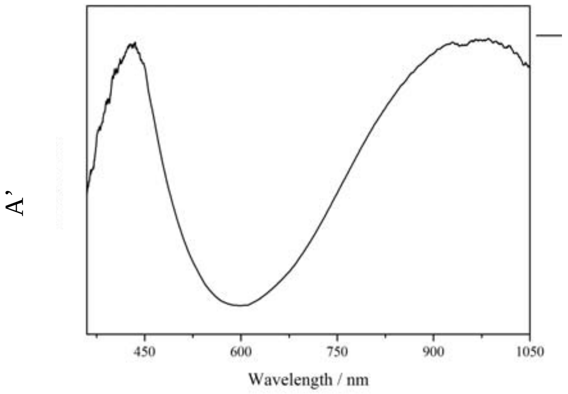

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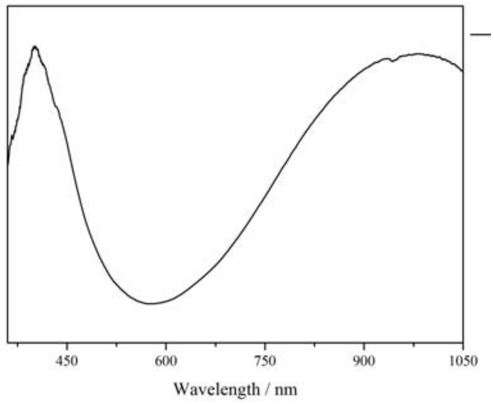

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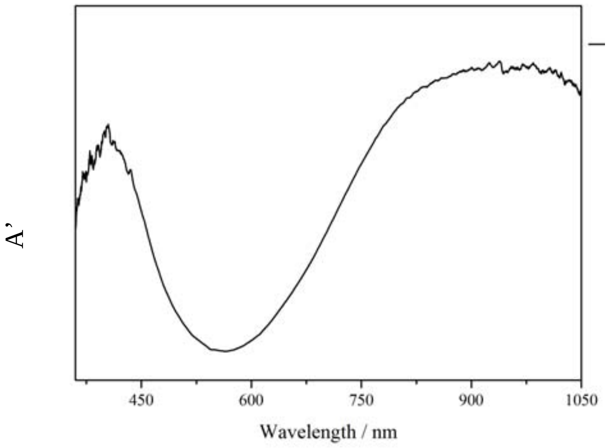

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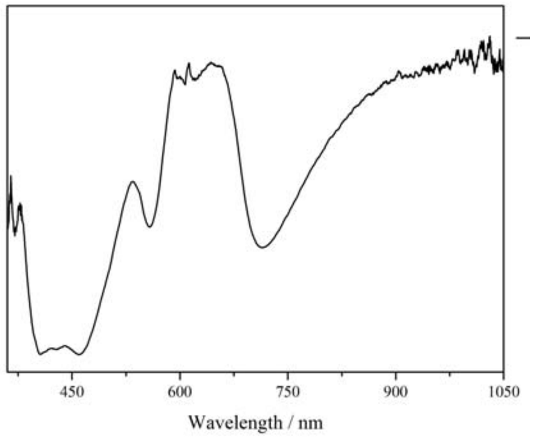

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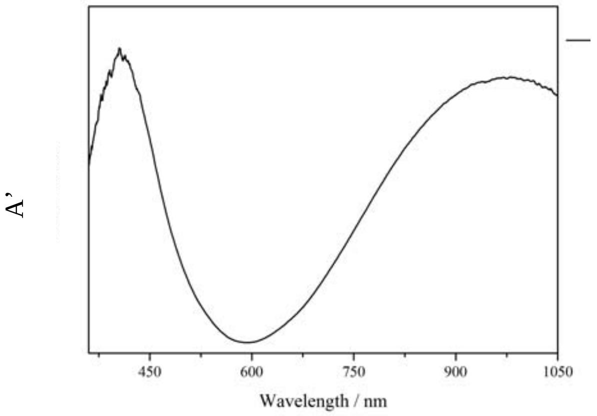

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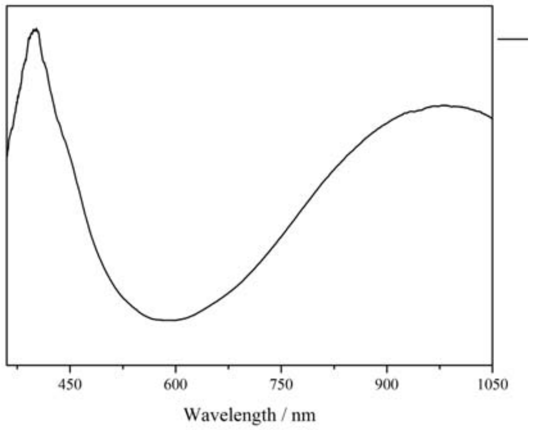

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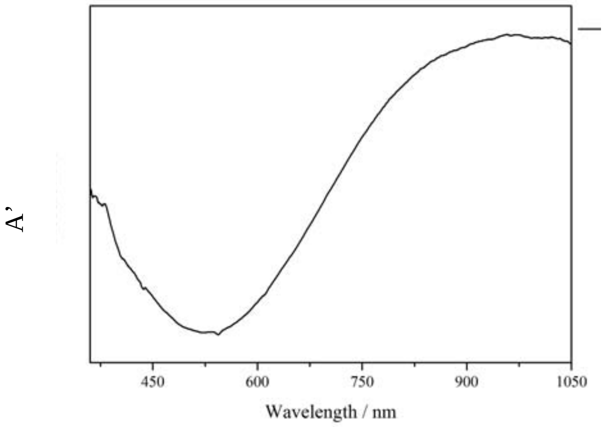

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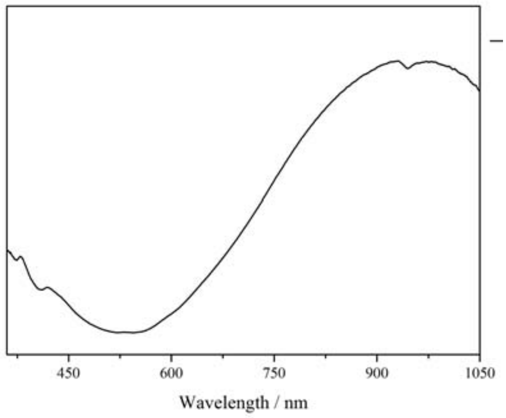

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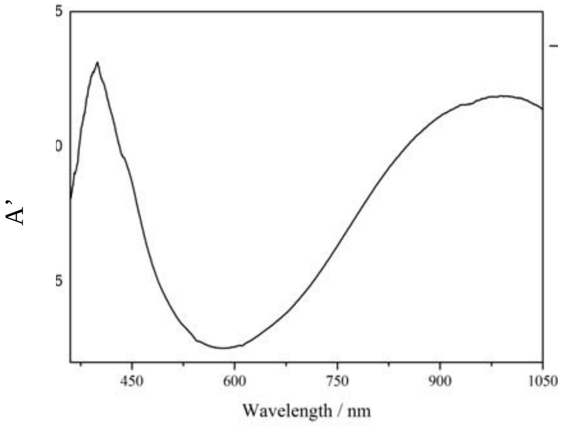

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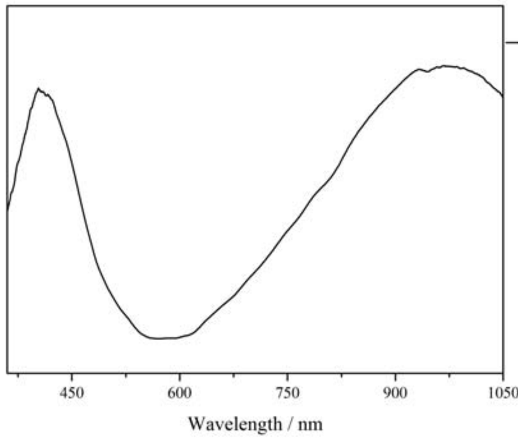

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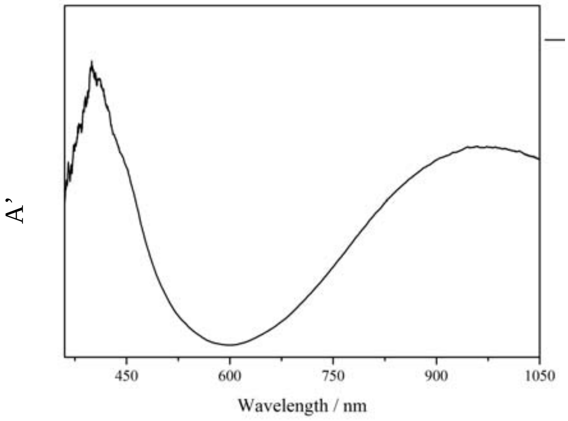

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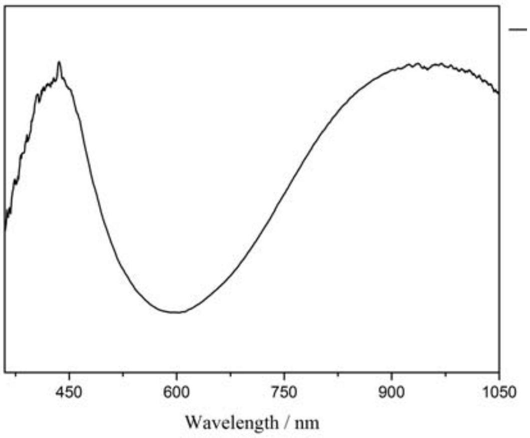

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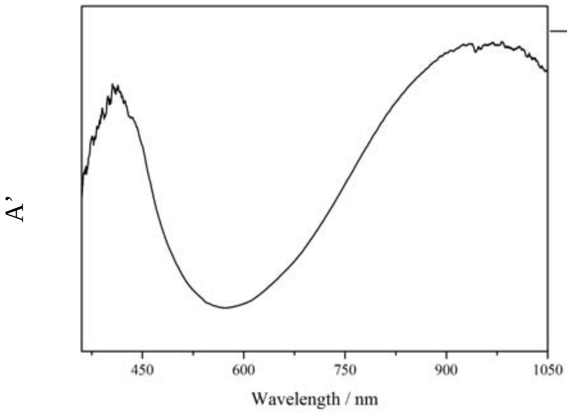

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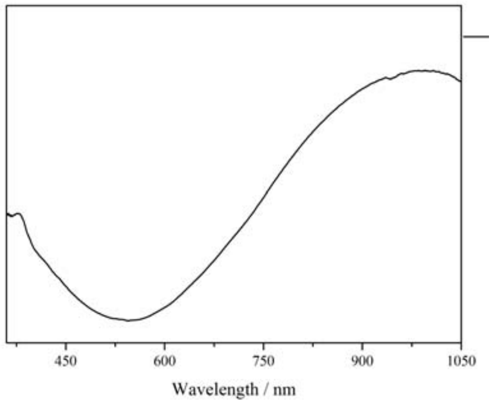

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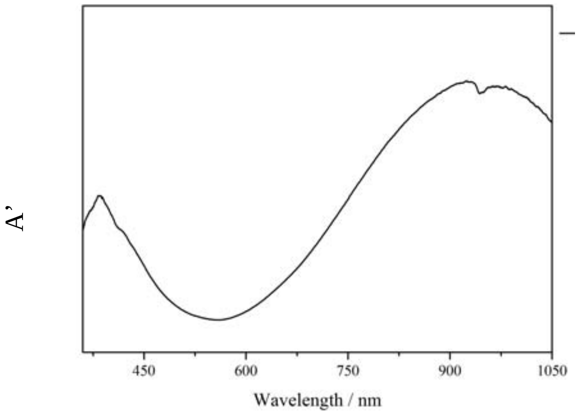

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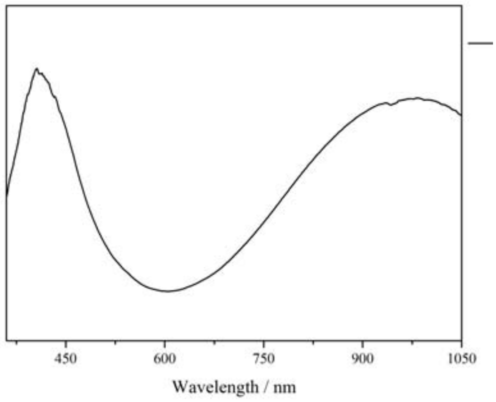
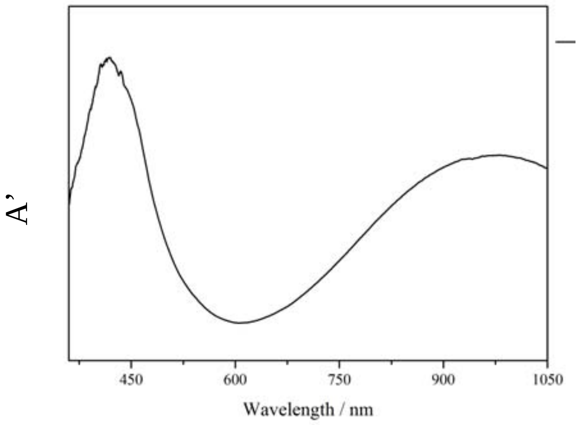


LTR0096

Absorbance spectra from Rua do Arsenal in Lisbon (LRA) objects



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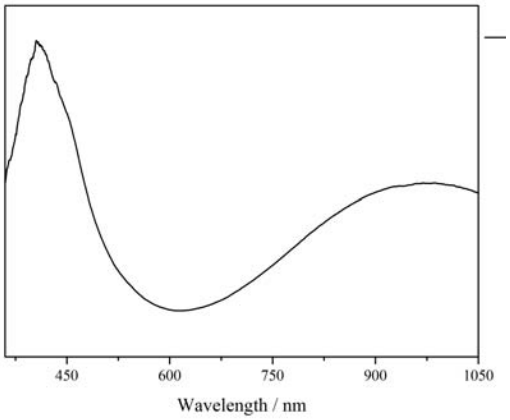

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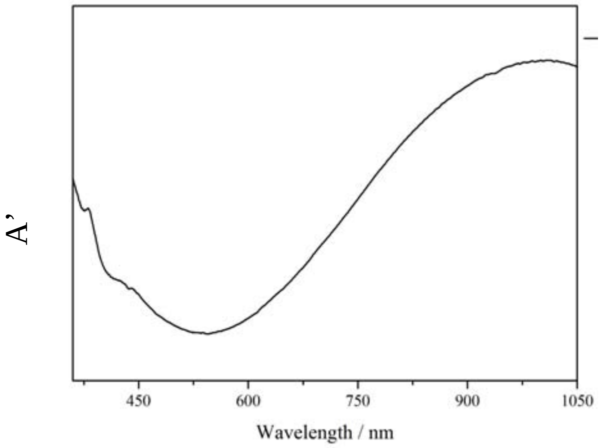

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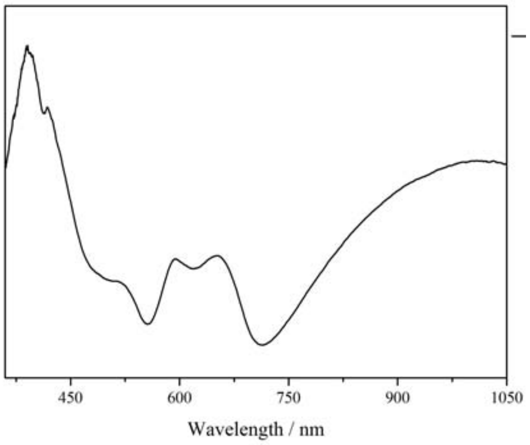

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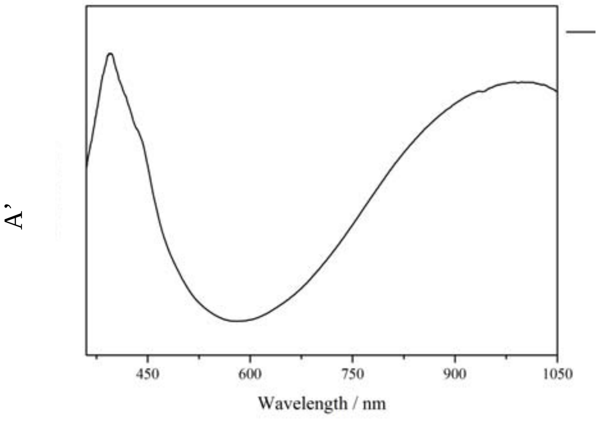

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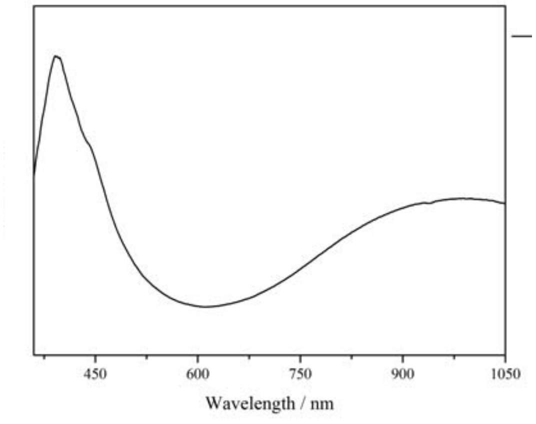

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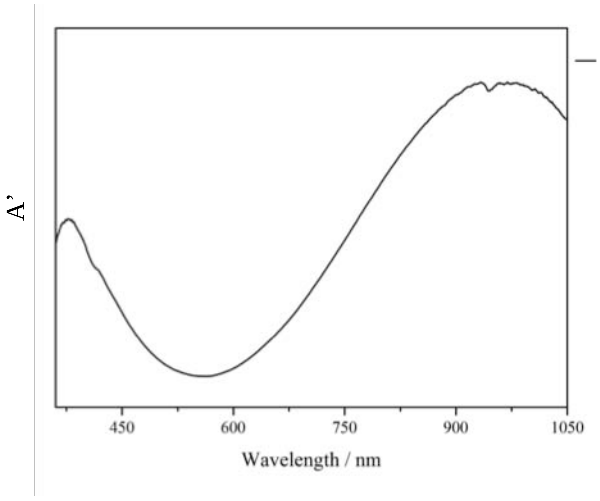
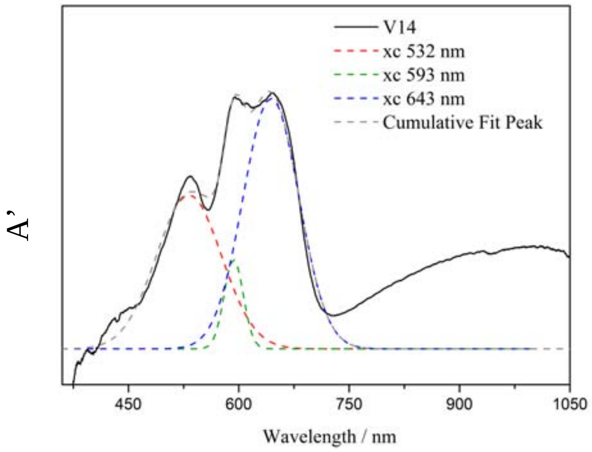


LRA0105

Absorbance spectra from Santa Clara-a-Velha Monastery (SCV) objects



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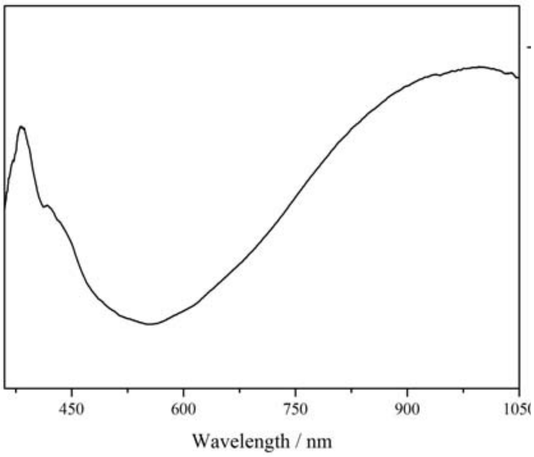

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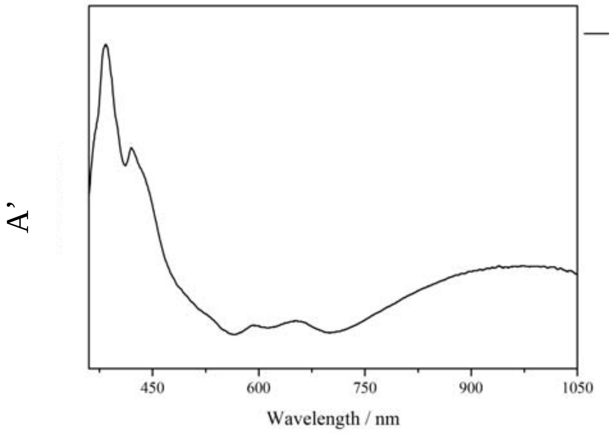

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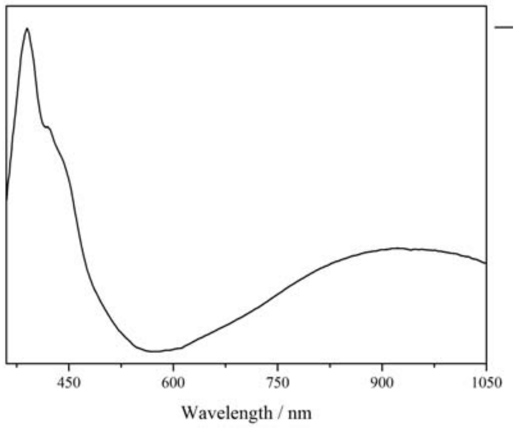

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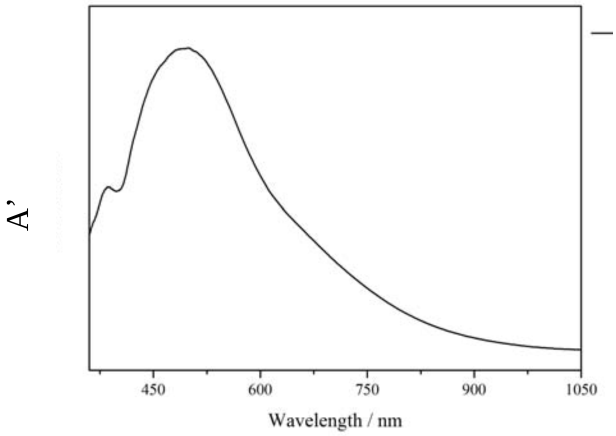

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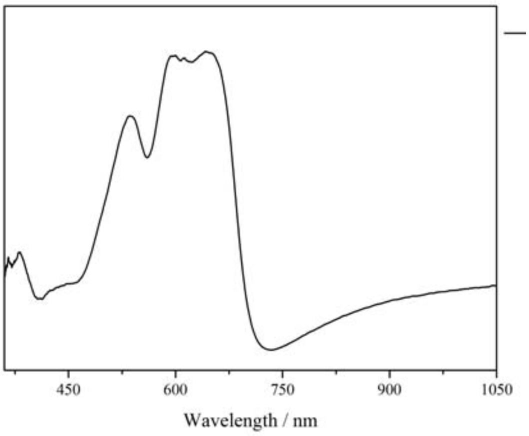

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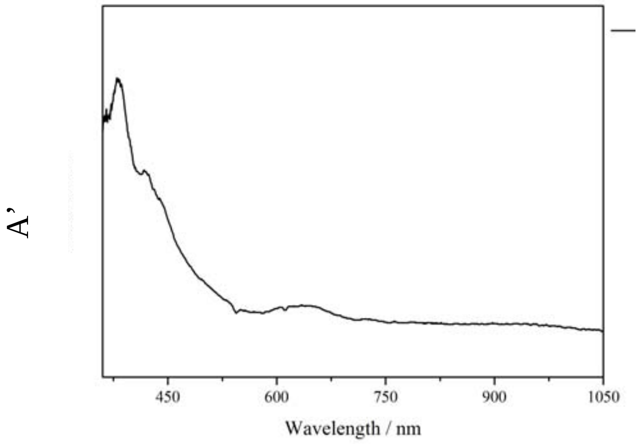

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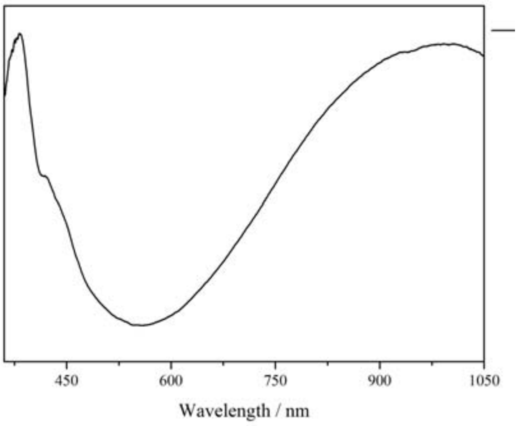

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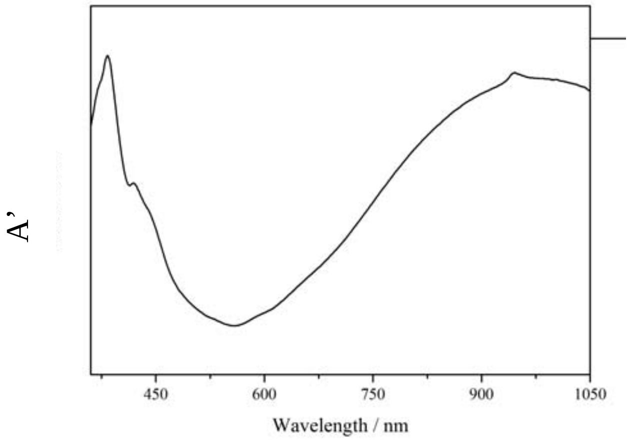

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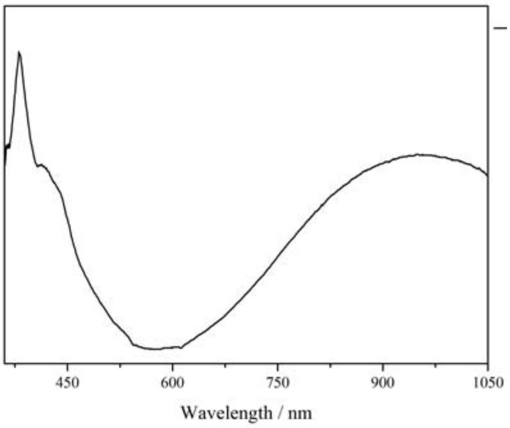

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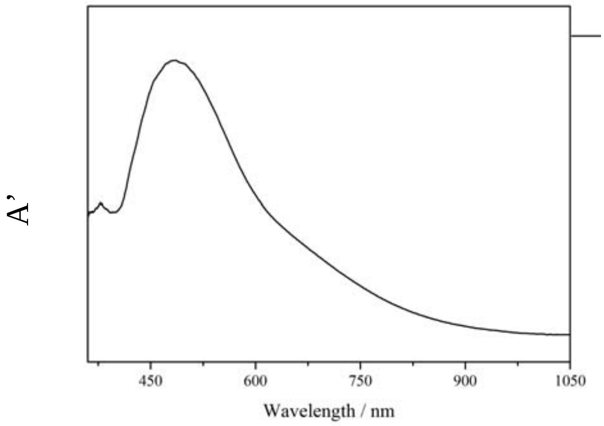

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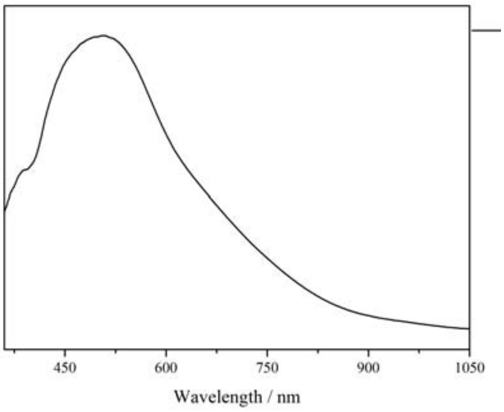

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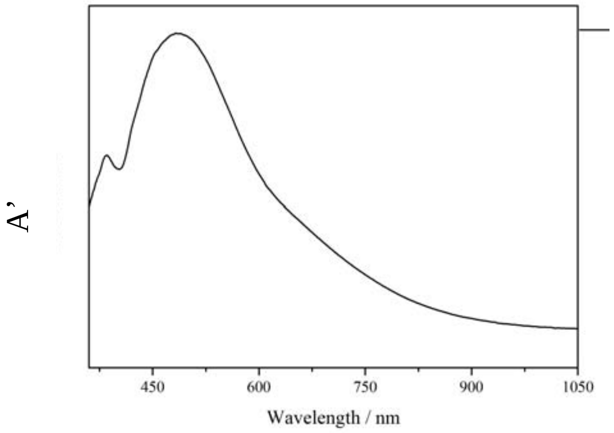

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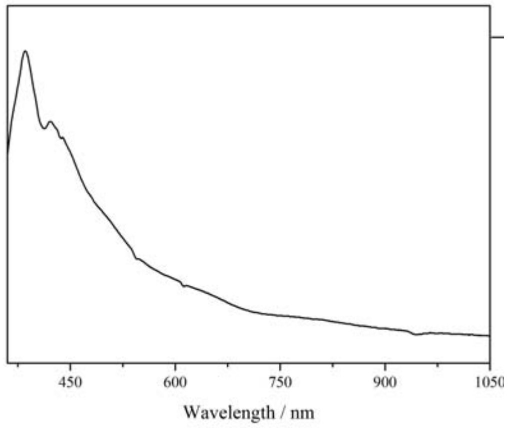

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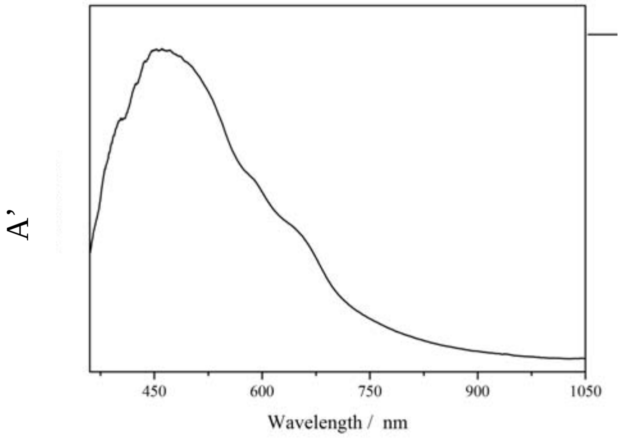

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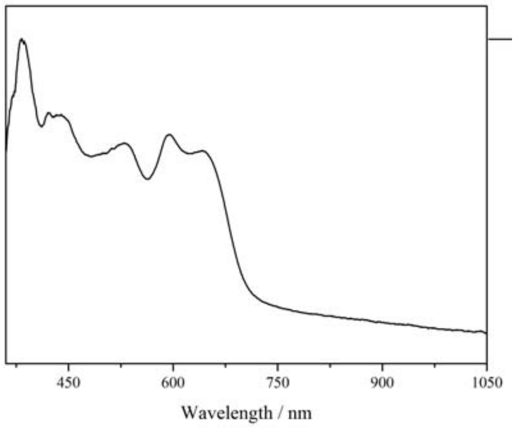

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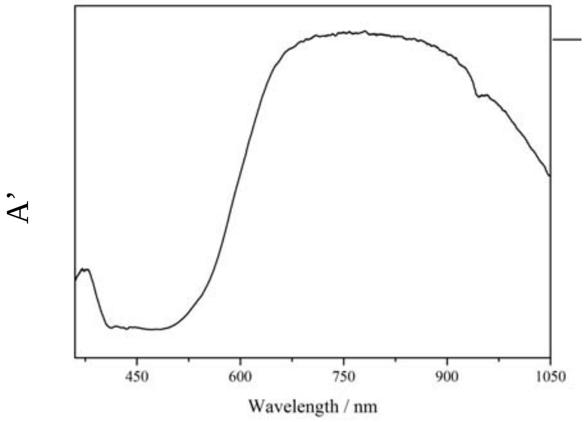

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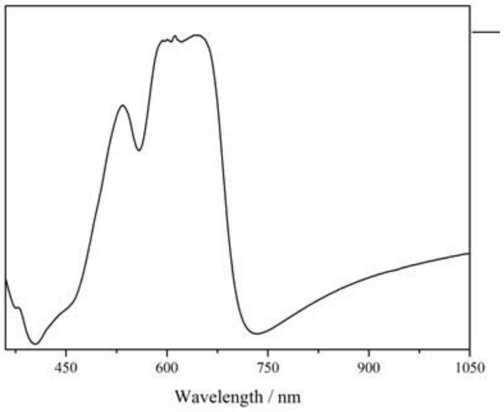

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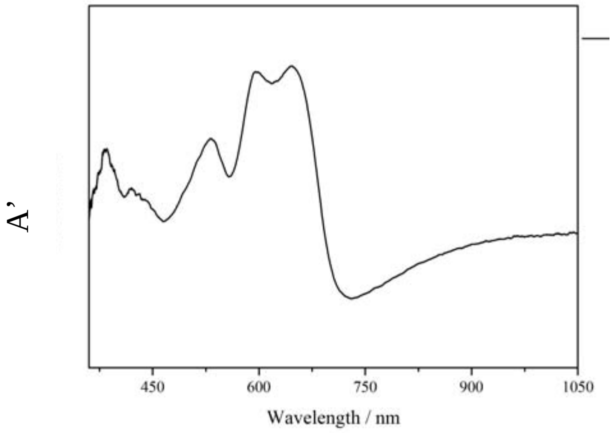

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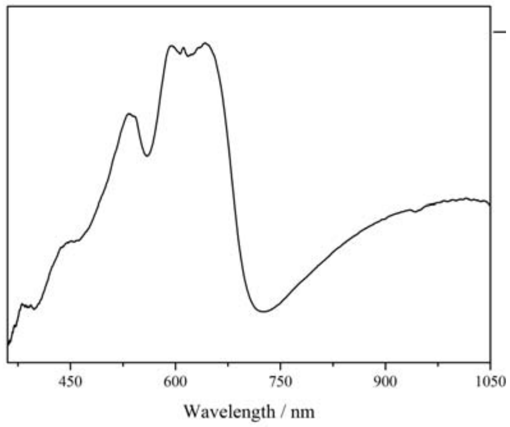

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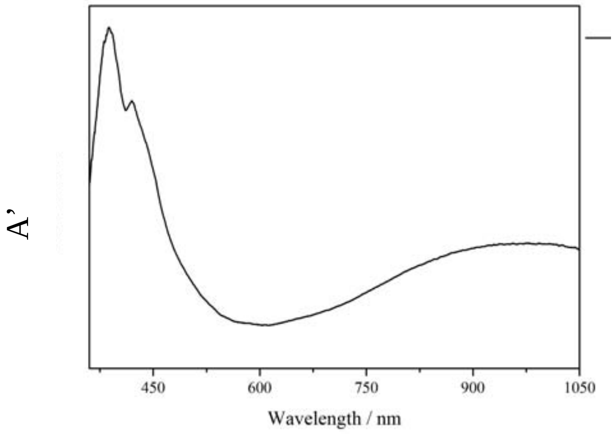

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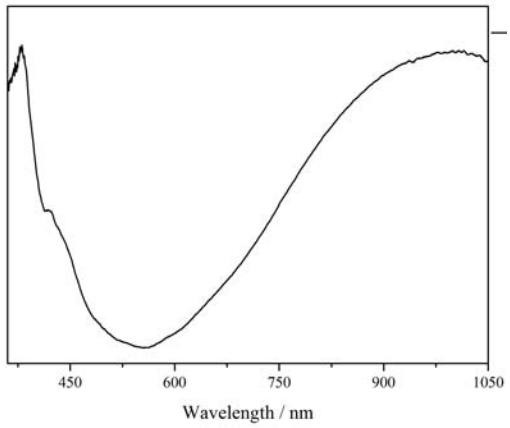

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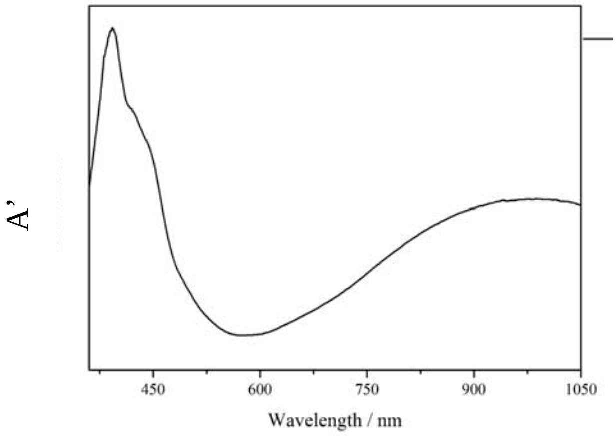

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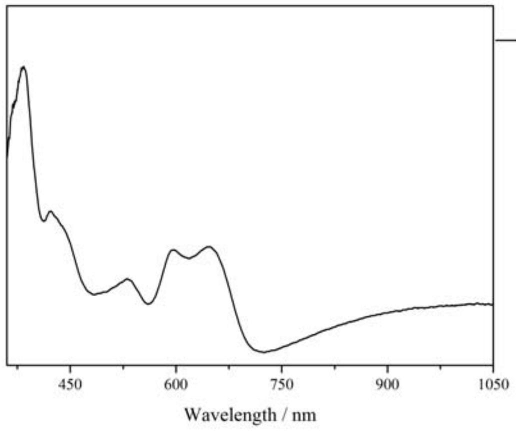

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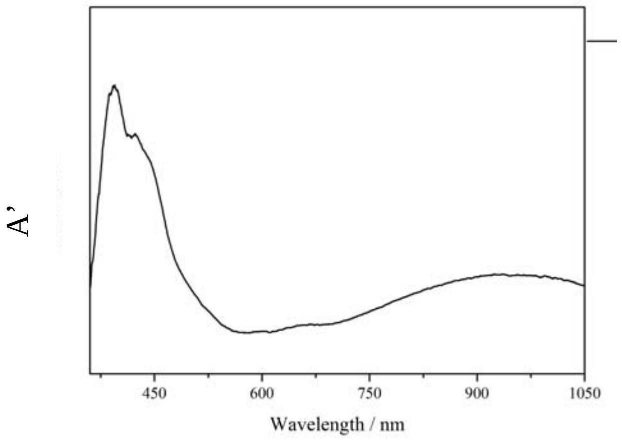

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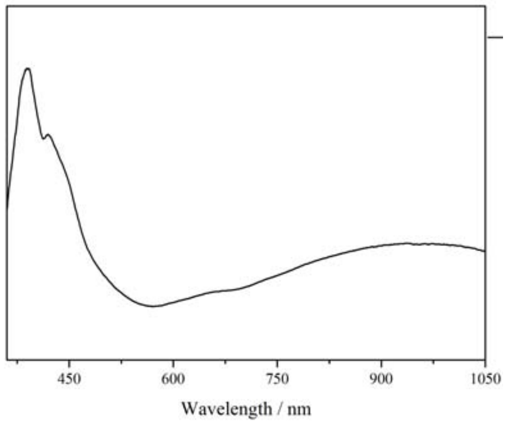

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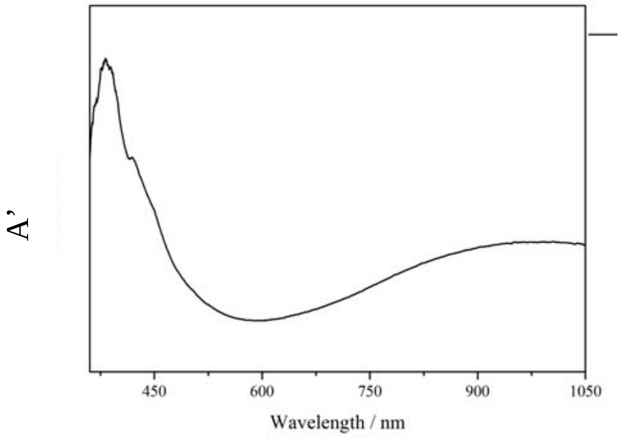

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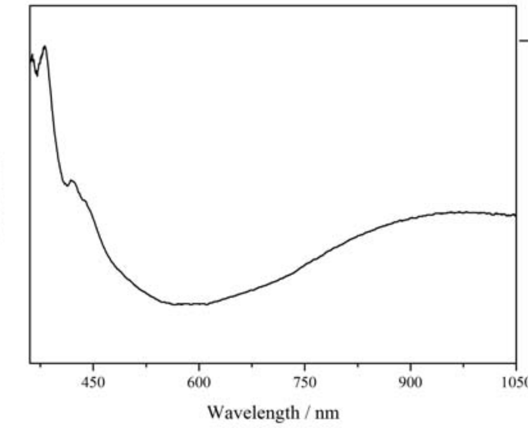

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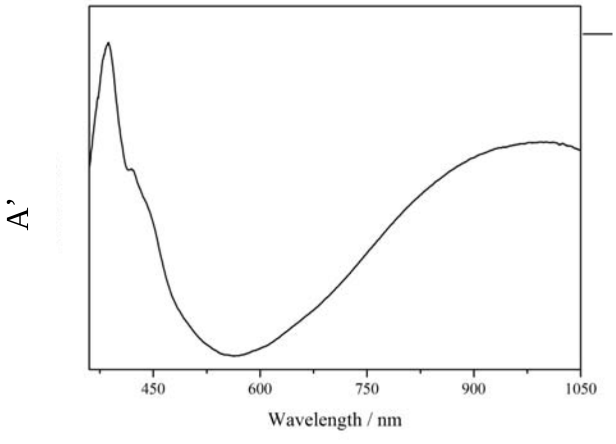

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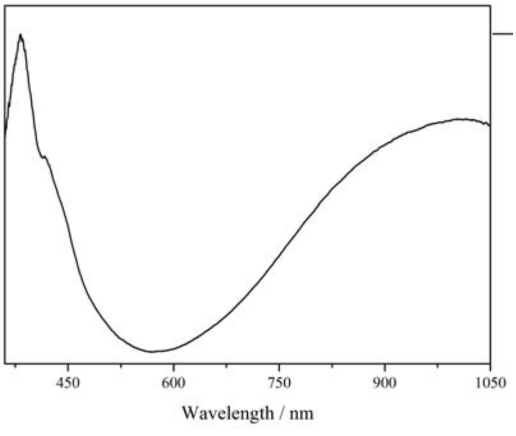
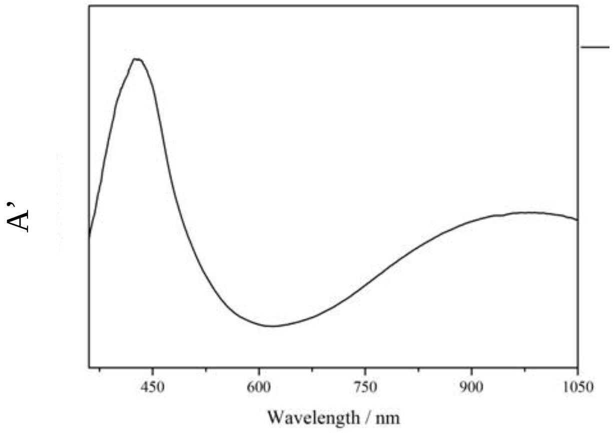


SCV-V380



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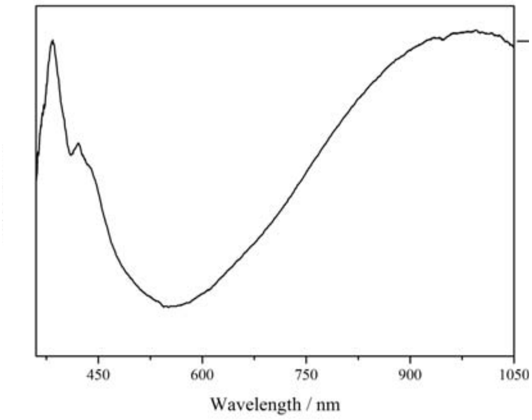

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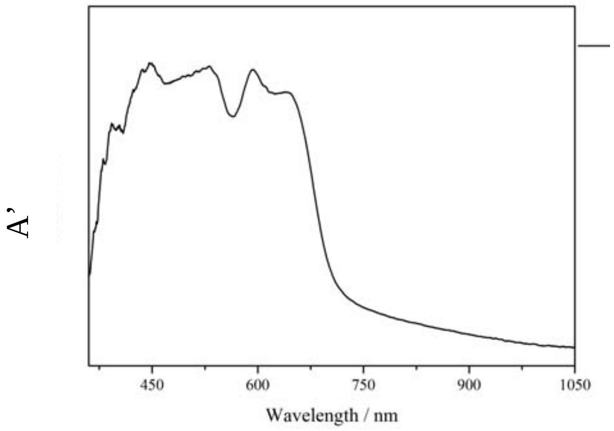

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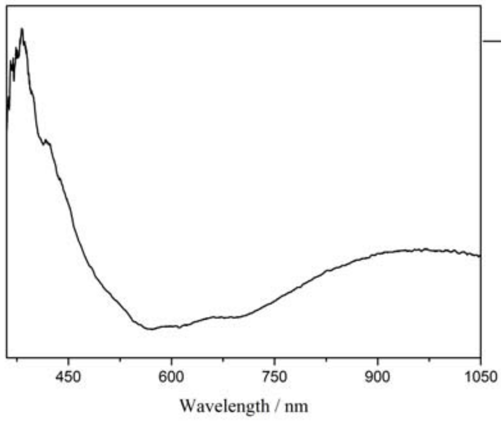

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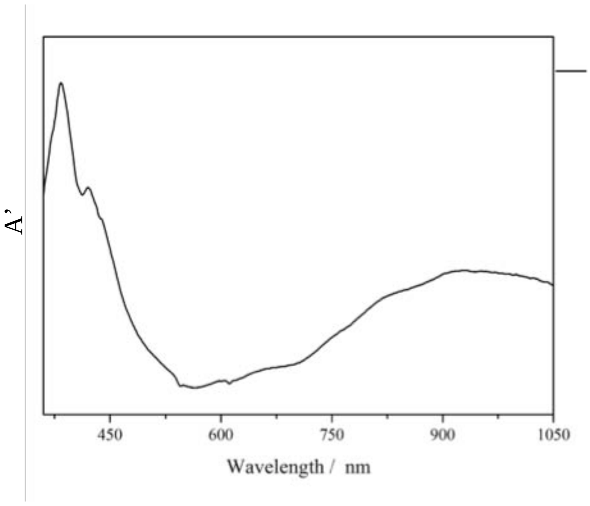
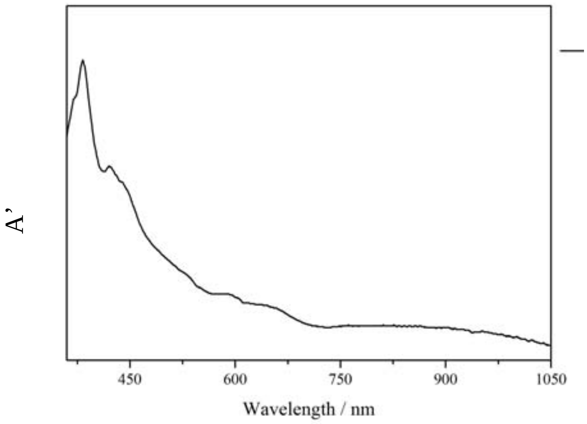
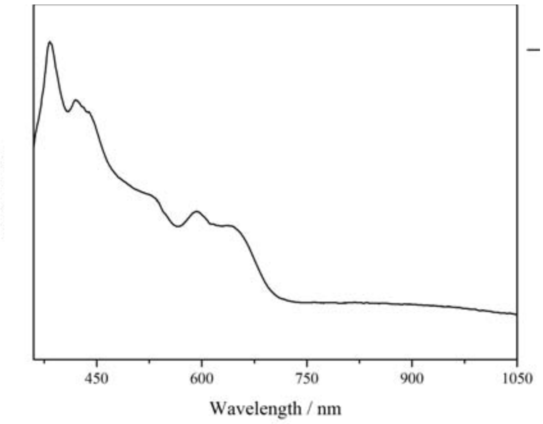


SCV-V423

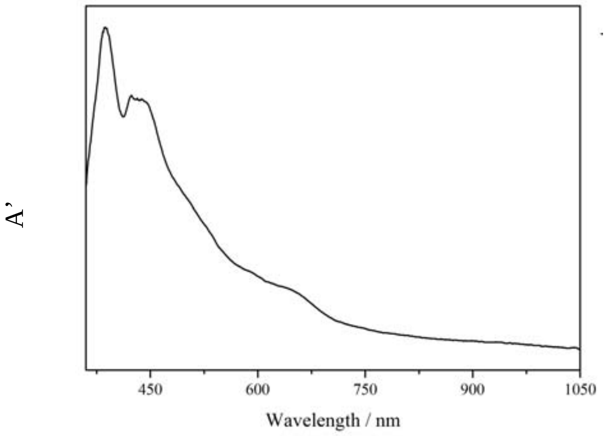
Absorbance spectra from Pátio da Universidade in *Coimbra* (CPU) objects



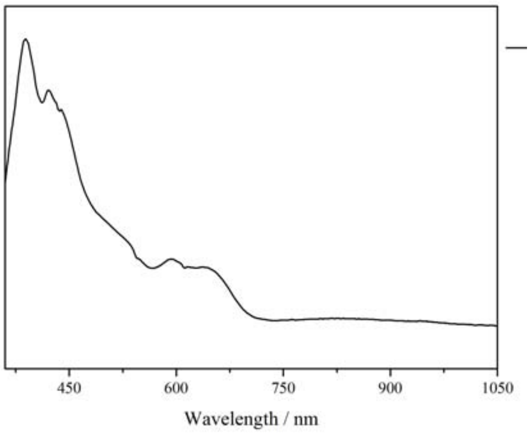
CPU0001



CPU0002



CPU0008



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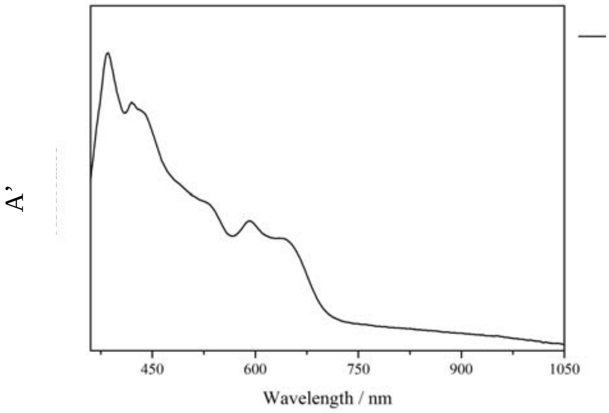

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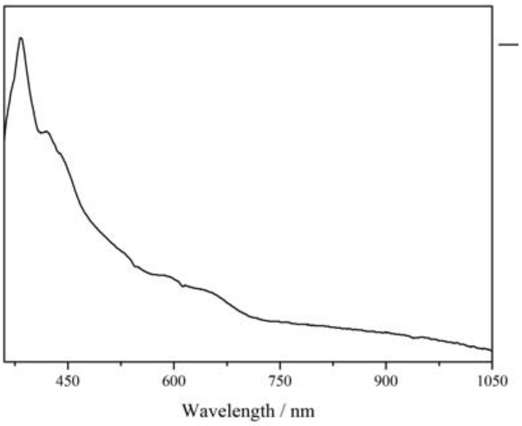

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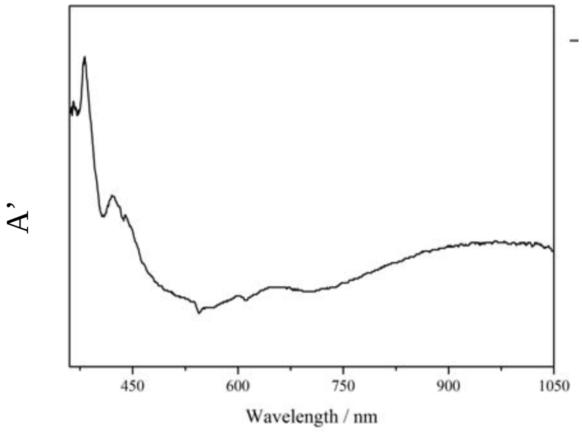

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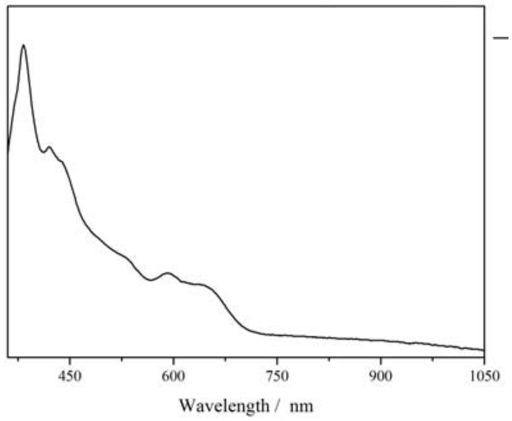

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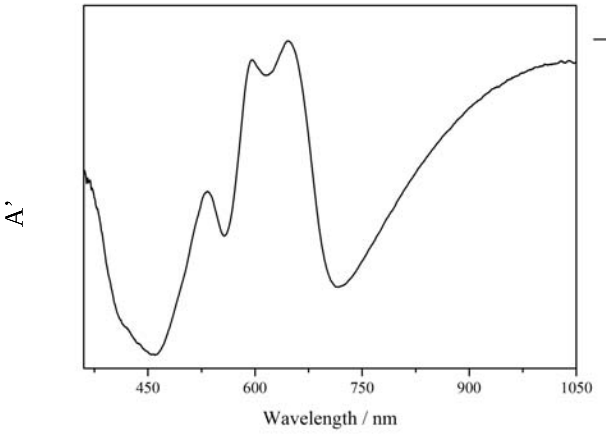
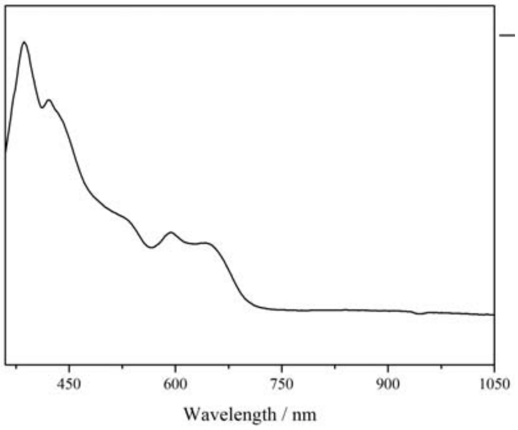
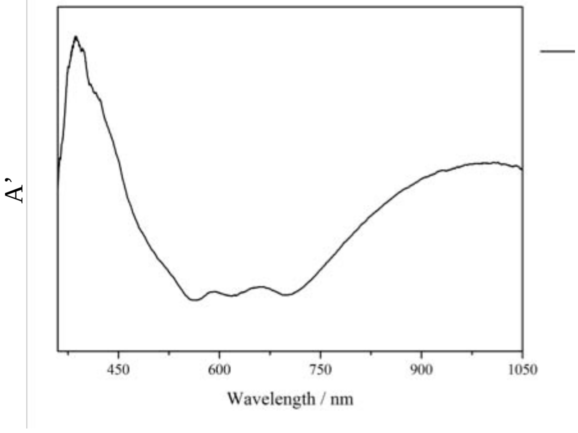


CPU0026

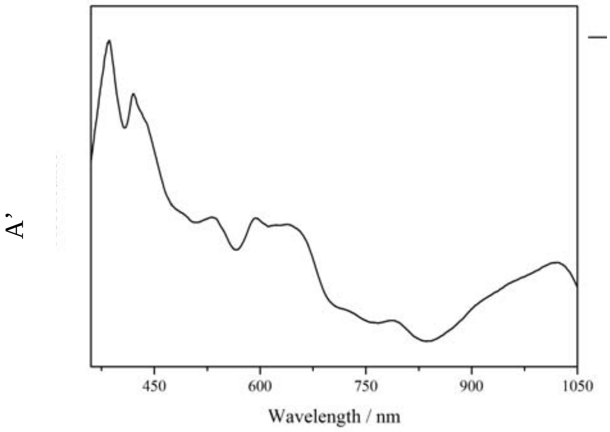


CPU0032

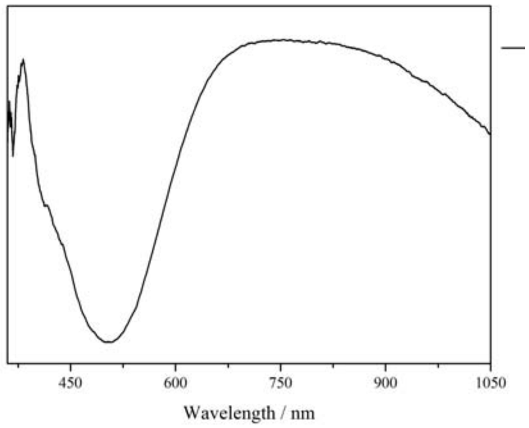


CPU0033

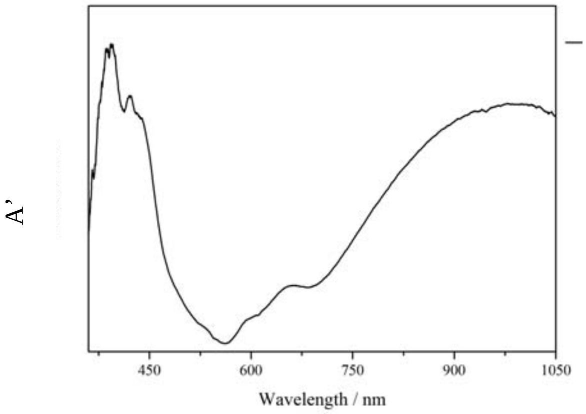
Absorbance spectra from Praça Miguel Fernandes in Beja (PMF) objects



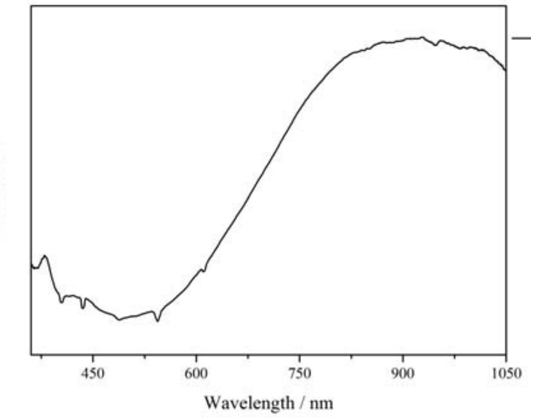
PMF0387



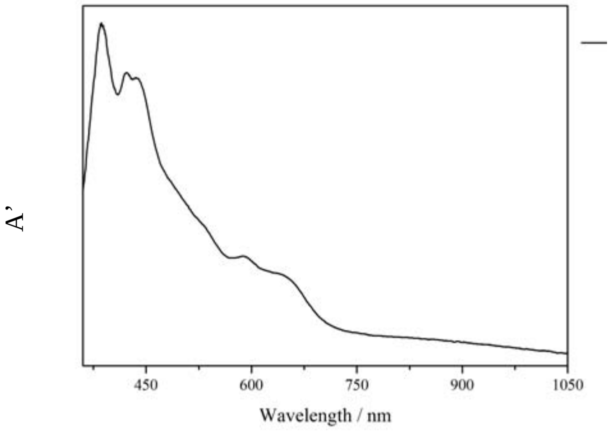
PMF0438 – blue rim



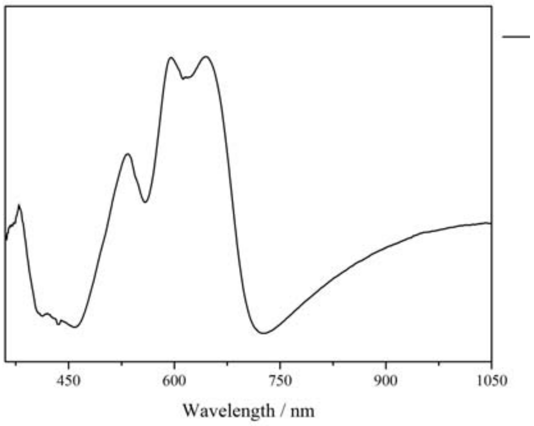
PMF0444



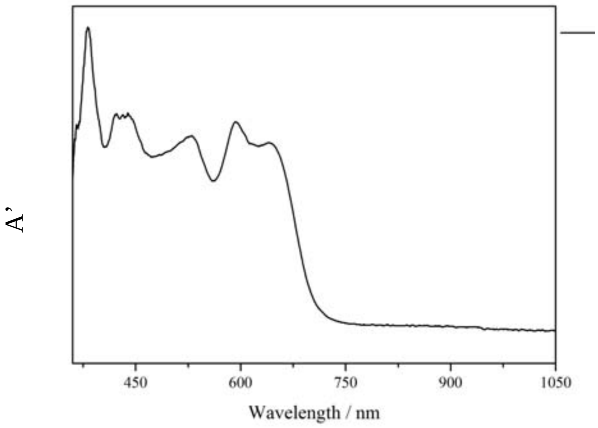
PMF0458



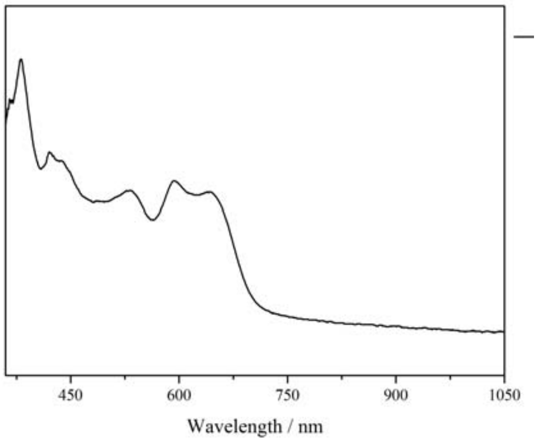
PMF0510



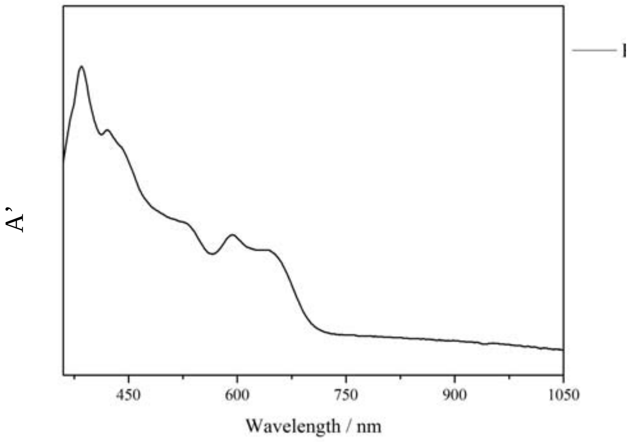
PMF0517



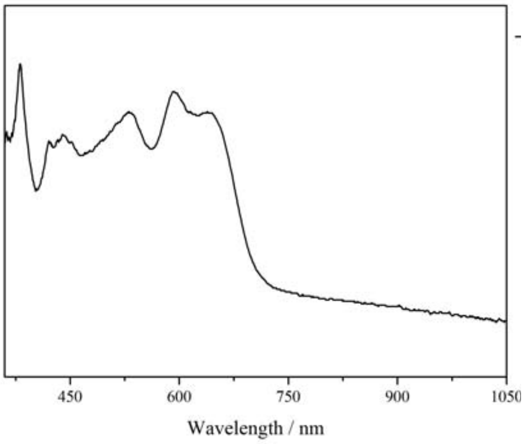
PMF0530



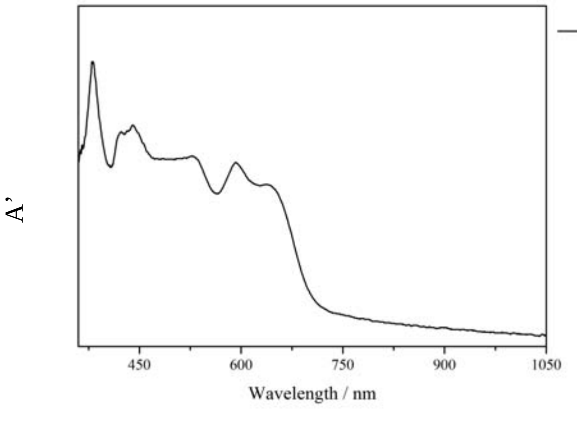
PMF0540



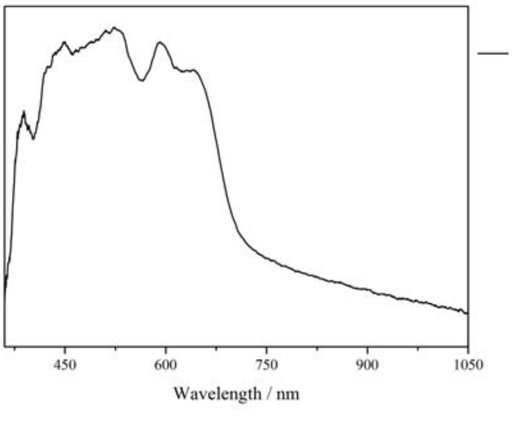
PMF0546



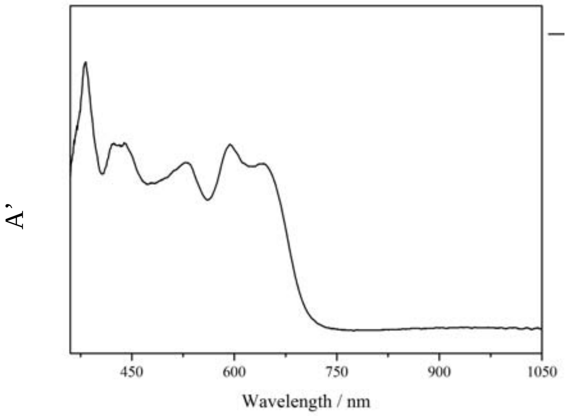
PMF0550



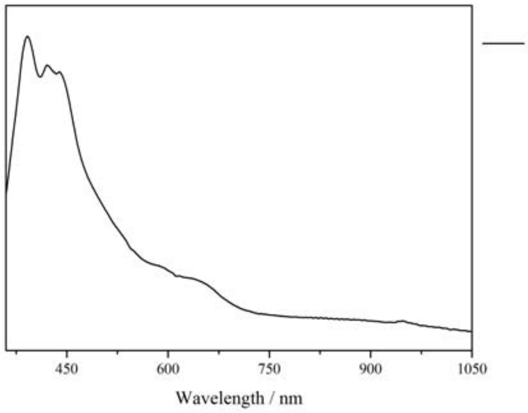
PMF0568



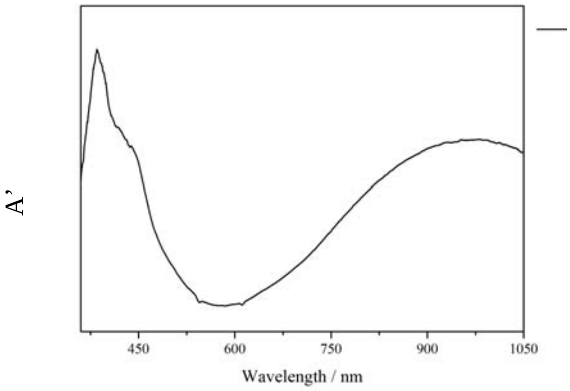
PMF0569



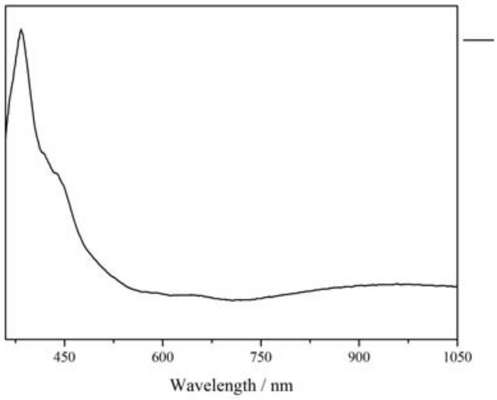
PMF0570



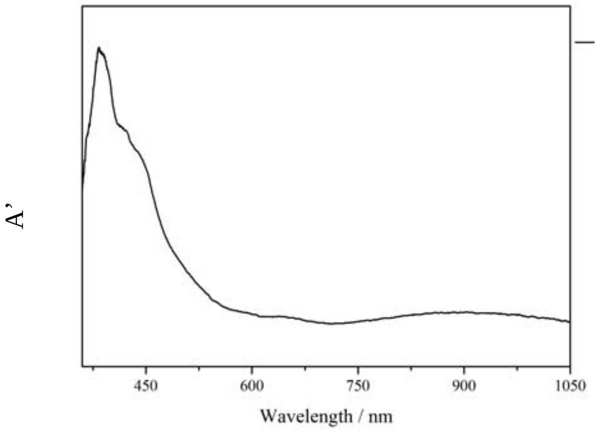
PMF0600



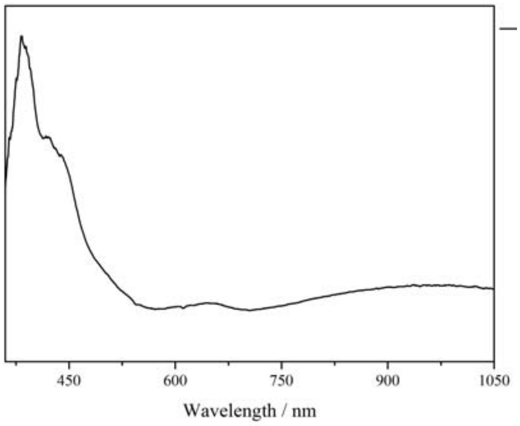
PMF0605



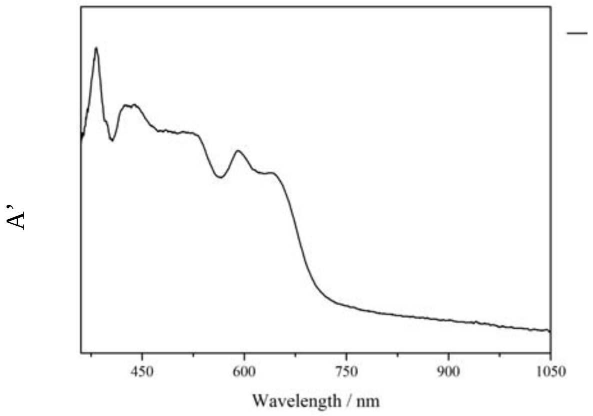
PMF0609



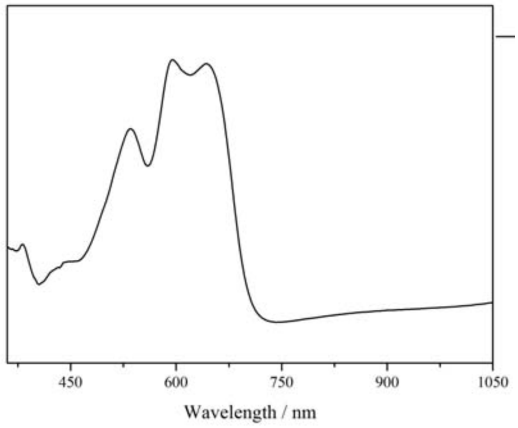
PMF0614



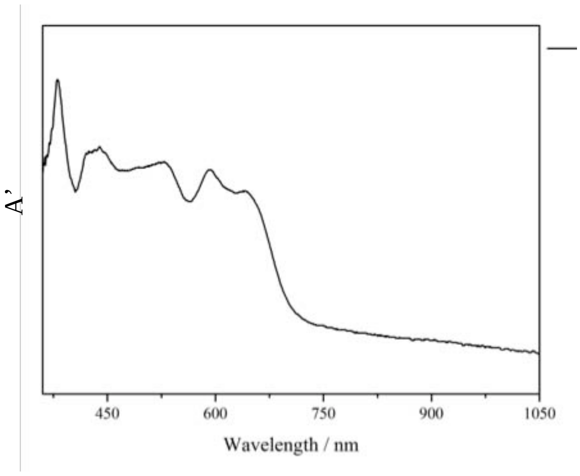
PMF0617



PMF0996

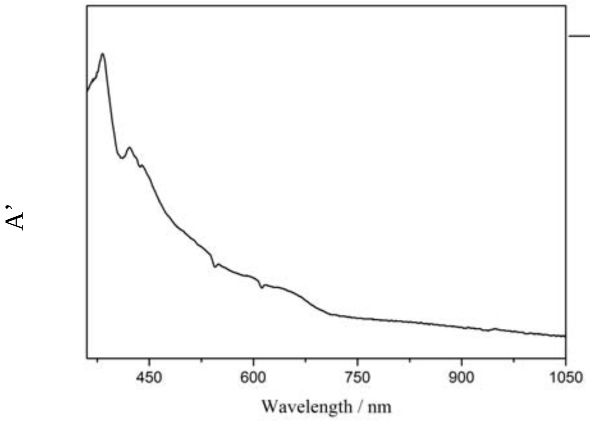


PMF1023

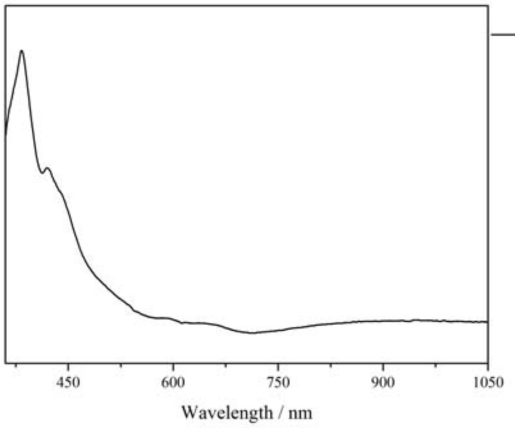


PMF1025

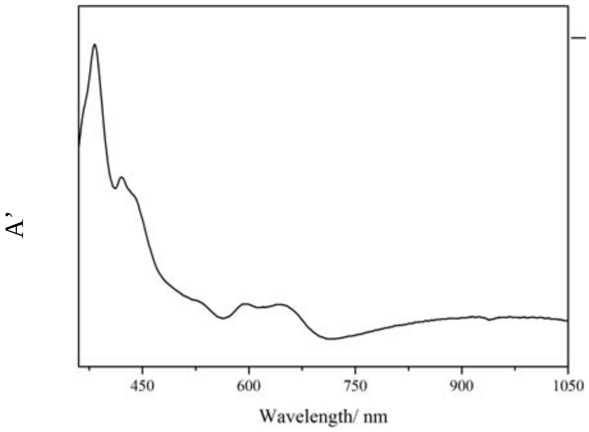
Absorbance spectra from São João de Tarouca Monastery (SJT) objects



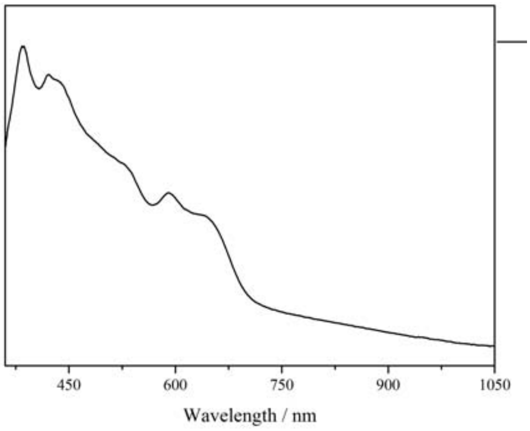
SJT0005



SJT0006



SJT0007



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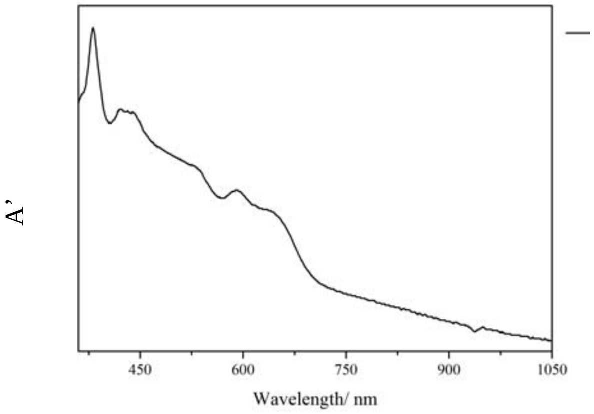
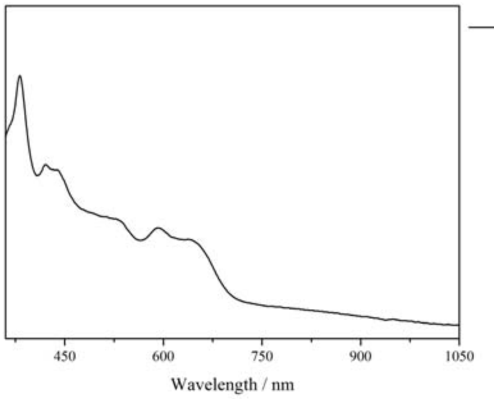
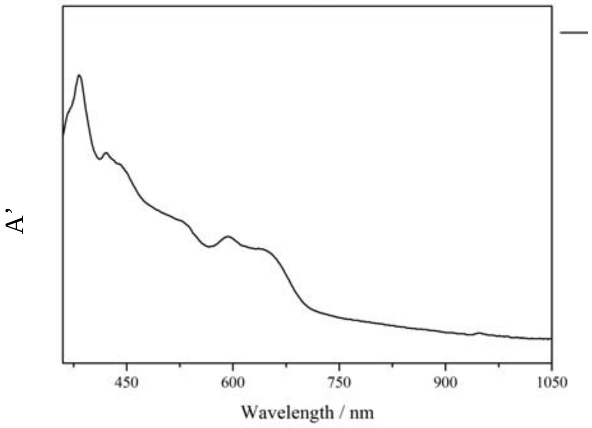


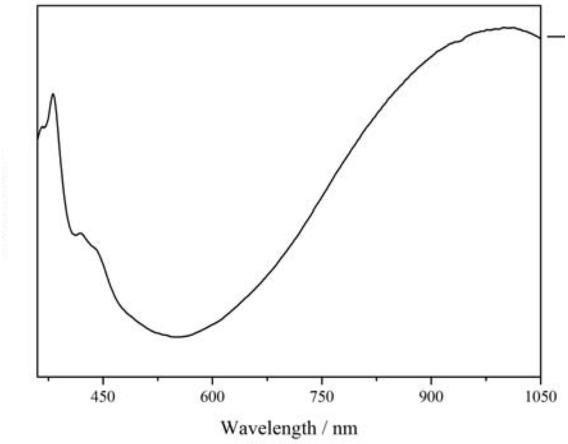
SJT0011



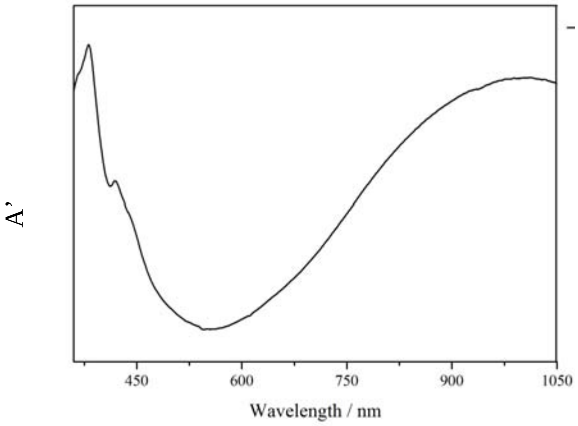
SJT0012



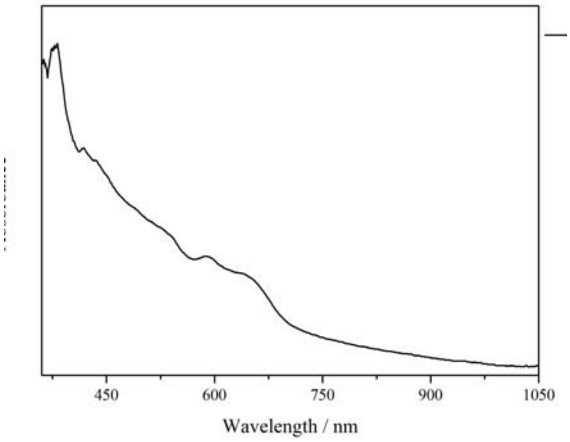
SJT0014



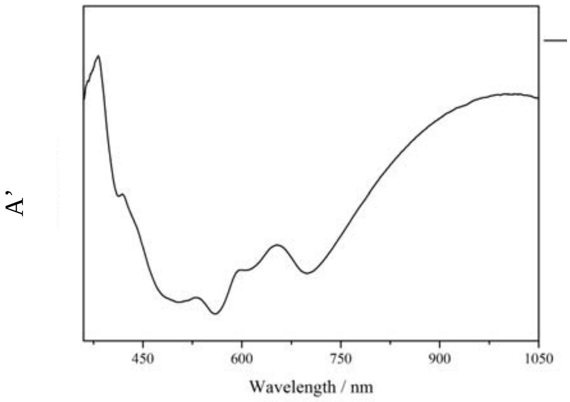
SJT0098



SJT0100



SJT0105



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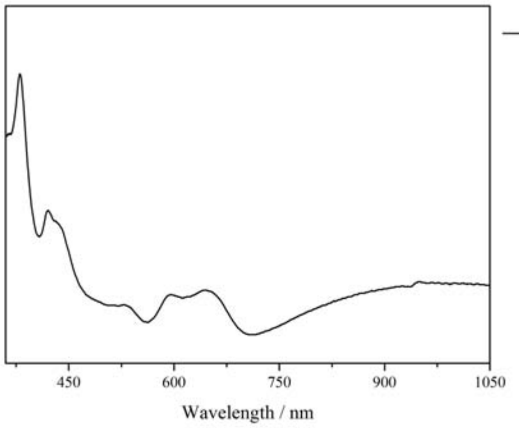
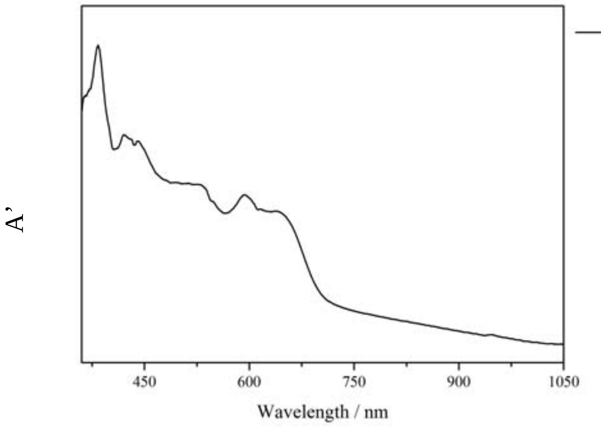
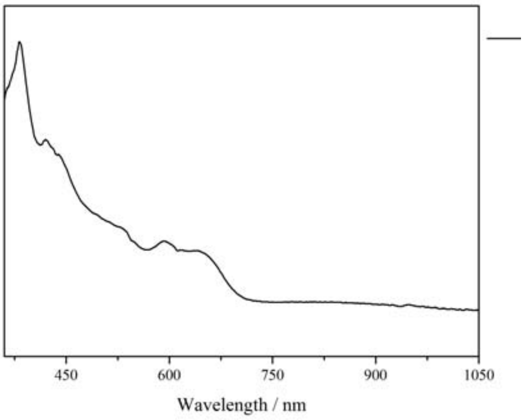


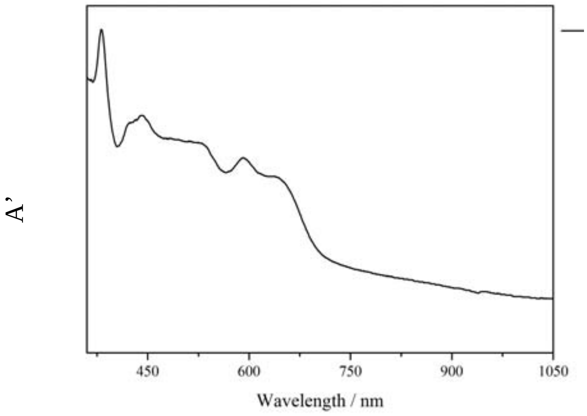
SJT0110



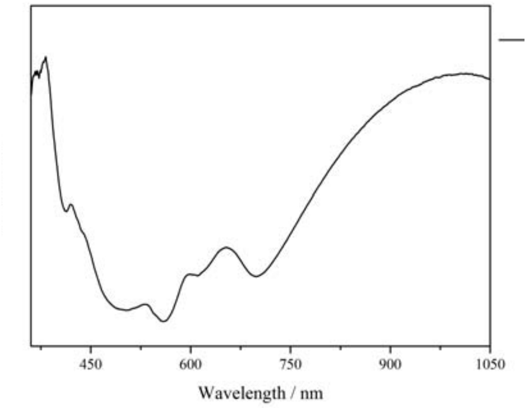
SJT0112



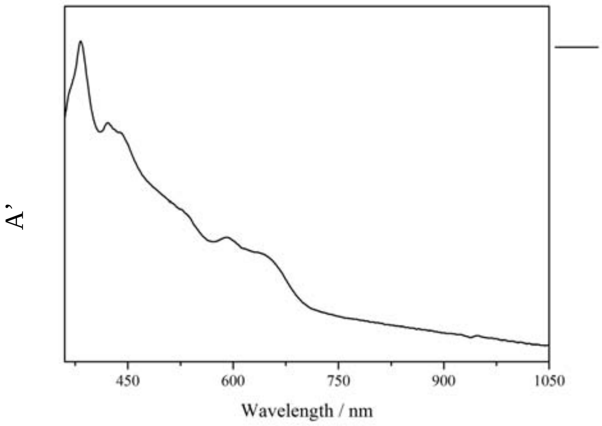
SJT0113



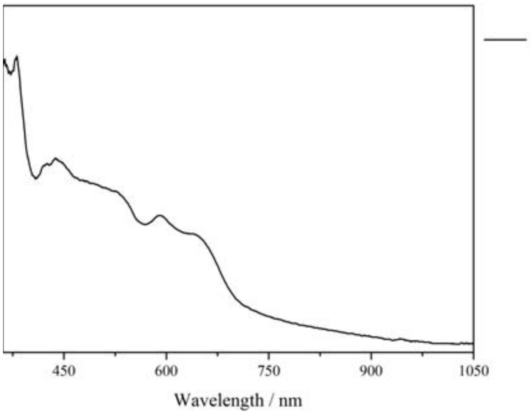
SJT0114



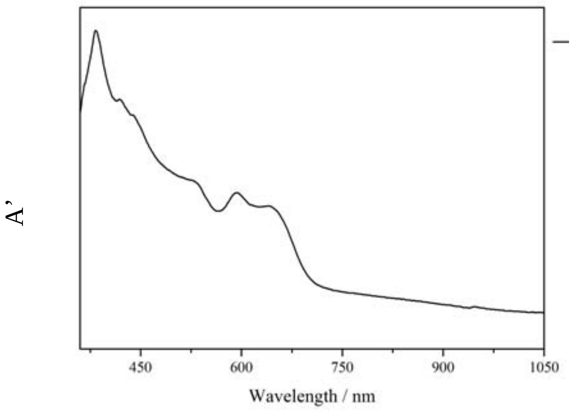
SJT0116



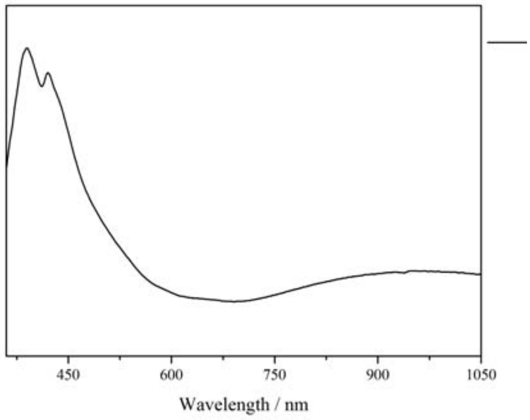
SJT0120



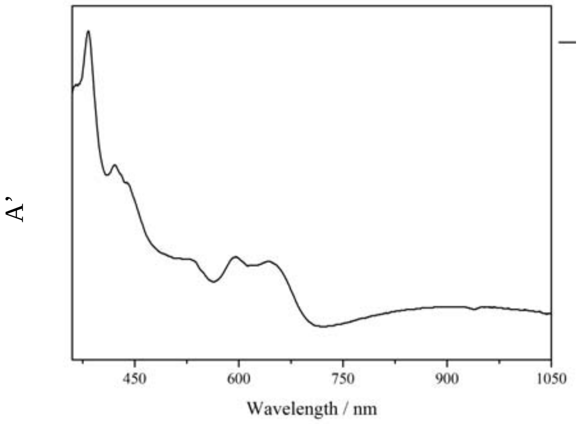
SJT0122



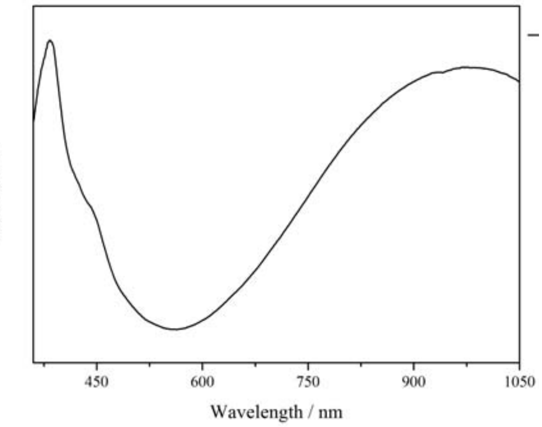
SJT0123



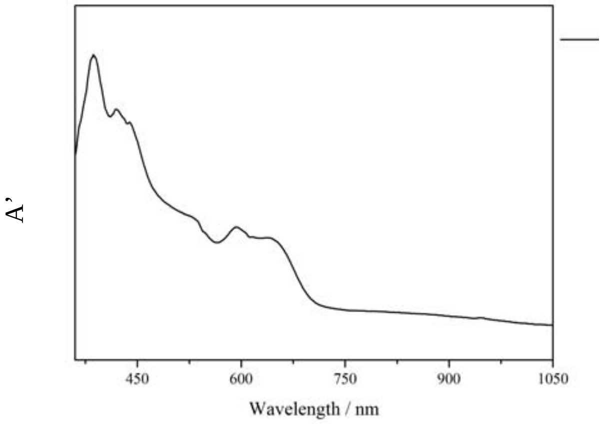
SJT0126



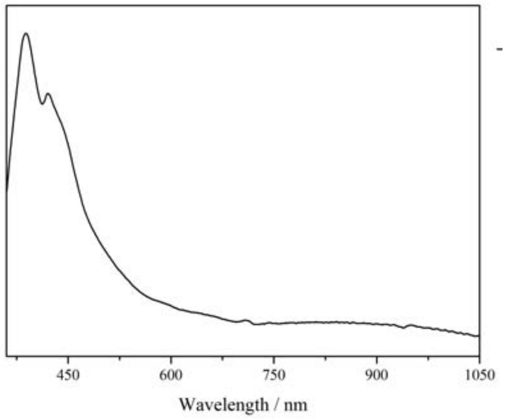
SJT0127



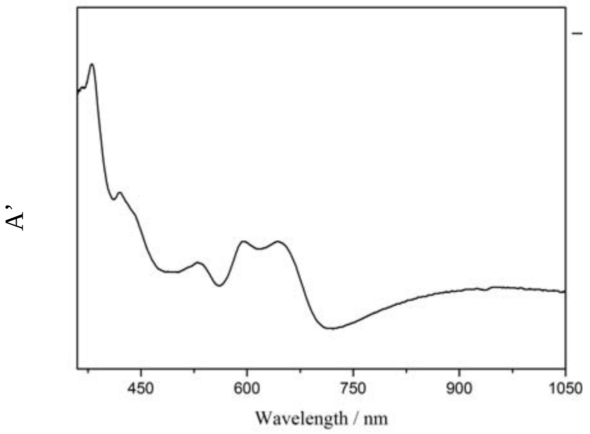
SJT0128



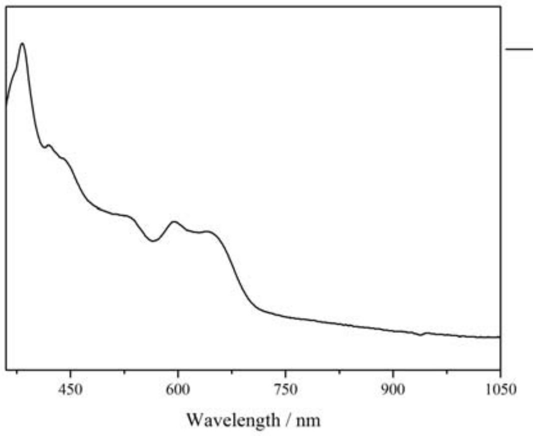
SJT0131



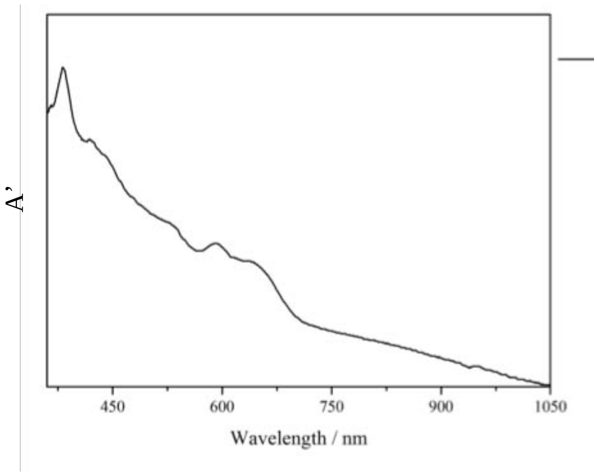
SJT0132



SJT0134



SJT0135



SJT0138

Appendix XIII: Tables with samples organised by the groups defined within each glass studied set.

Table XIII.1: Average of the composition of each *façon-de-Venise* group defined in the PCA analysis.

Groups	Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	NiO	CuO	ZnO	As_2O_3	SrO	PbO
G. I $_{fdV}$	**SCV-V191**	16.3	2.5	1.2	67.7	< 0.12	0.08	0.69	3.79	6.62	0.06	0.31	0.38	< 20 µg/g	< 10 µg/g	40 µg/g	40 µg/g	< 20 µg/g	0.03	0.03
	SCV-V193	18.1	2.8	0.8	68	0.13	0.12	0.61	2.47	5.91	0.03	0.38	0.33	< 20 µg/g	30 µg/g	30 µg/g	60 µg/g	0.01	0.03	0.03
	SCV-V195	18.0	2.7	0.8	68.3	0.11	0.11	0.65	2.39	5.68	0.04	0.45	0.39	< 25 µg/g	40 µg/g	30 µg/g	50 µg/g	< 20 µg/g	0.05	0.03
	SCV-V408 *	11.5	3.5	1.5	64	0.19	n.m.	0.84	5.46	11.89	0.07	0.34	0.61	< 10 µg/g	< 10 µg/g	20 µg/g	50 µg/g	< 10 µg/g	0.07	10 µg/g
	Avg.	16.0	2.9	1.1	67.0	0.14	0.10	0.70	3.53	7.53	0.05	0.37	0.43	-	23 µg/g	30 µg/g	50 µg/g	-	0.05	0.02
	StDev.	3.1	0.4	0.3	2.0	0.04	0.02	0.10	1.44	2.94	0.02	0.06	0.12	-	15	8	8	-	0.02	0.01
G. II $_{fdV}$	**PMF0530**	15.9	3.0	3.9	66.4	0.33	0.05	0.93	2.01	6.00	0.13	0.49	0.78	0.01	< 10 µg/g	< 10 µg/g	40 µg/g	0.01	0.03	< 0.01
	PMF0550	16.8	2.2	3.2	66.9	0.3	0.04	1.14	2.47	6.19	0.08	0.28	0.30	50 µg/g	20 µg/g	< 10 µg/g	20 µg/g	< 20 µg/g	0.03	< 40 µg/g
	PMF0568	15.7	2.5	3.6	66.8	0.21	0.05	0.91	3.36	5.48	0.12	0.5	0.62	60 µg/g	30 µg/g	20 µg/g	30 µg/g	50 µg/g	0.03	0.01
	PMF0569	15.6	2.4	3.6	67.3	0.18	0.06	0.93	3.06	5.48	0.11	0.63	0.58	60 µg/g	30 µg/g	40 µg/g	50 µg/g	< 20 µg/g	0.03	< 40 µg/g
	PMF0570	16.2	3.0	4.0	66.6	0.34	0.05	0.94	1.95	5.79	0.12	0.42	0.67	0.01	40 µg/g	20 µg/g	20 µg/g	0.01	0.02	< 0.01
	PMF0996	15.7	2.4	3.6	67.0	0.23	0.06	0.94	3.06	5.56	0.11	0.66	0.61	0.01	30 µg/g	30 µg/g	40 µg/g	70 µg/g	0.03	< 0.01
	PMF1010	16.1	2.2	2.3	66.4	0.22	0.06	1.00	4.08	6.63	0.07	0.37	0.53	60 µg/g	30 µg/g	< 10 µg/g	30 µg/g	60 µg/g	0.03	0.06
	PMF1023	16.9	2.6	3.5	62.8	0.31	0.05	1.22	4.25	7.52	0.12	0.13	0.62	0.08	0.03	40 µg/g	40 µg/g	0.11	0.04	< 0.03
	PMF1025	15.0	2.4	3.5	66.9	0.26	0.05	0.92	3.3	5.93	0.14	0.76	0.72	60 µg/g	30 µg/g	40 µg/g	40 µg/g	0.01	0.04	< 0.01
	SJT0011	18.7	2.4	1.8	67.9	0.22	0.07	0.99	2.96	4.05	0.08	0.27	0.52	40 µg/g	20 µg/g	20 µg/g	20 µg/g	40 µg/g	0.02	0.02
	SJT0038	19.5	2.6	2.1	63.7	0.20	0.08	0.96	4.59	5.31	0.06	0.36	0.48	30 µg/g	20 µg/g	10 µg/g	30 µg/g	< 20 µg/g	0.04	0.01
	SJT0105	18.0	2.5	1.8	66.5	0.16	0.08	0.85	4.17	4.63	0.10	0.43	0.71	50 µg/g	30 µg/g	70 µg/g	30 µg/g	50 µg/g	0.02	0.01
	SJT0122	18.0	2.5	2.6	65.9	0.29	0.05	0.98	2.93	5.27	0.10	0.49	0.80	0.01	30 µg/g	20 µg/g	40 µg/g	0.01	0.03	0.03
	SJT0123	19.7	2.1	2.9	62.9	0.23	0.07	1.01	3.54	6.12	0.10	0.41	0.70	0.01	40 µg/g	0.02	50 µg/g	0.01	0.03	0.01
	Avg.	17.0	2.5	3.0	66.0	0.25	0.06	0.98	3.27	5.71	0.10	0.44	0.62	0.02	50 µg/g	50 µg/g	50 µg/g	0.02	0.03	0.02
	StDev.	1.5	0.3	0.8	1.6	0.06	0.01	0.10	0.81	0.83	0.02	0.17	0.13						0.01	

Table XIII.2: Composition of the gourd shaped vessels.

Samples	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**CoO**	**NiO**	**CuO**	**ZnO**	**As_2O_3**	**SrO**	**BaO**	**PbO**
SCV-V079	19.9	5.6	6.8	55.5	0.45	0.03	0.86	2.08	6.67	0.28	0.35	1.26	< 60 µg/g	30 µg/g	50 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 20 µg/g
SCV-V082	15.0	4.8	4.8	64.0	0.43	0.02	0.74	2.36	5.09	0.23	1.22	0.94	< 40 µg/g	20µg/g	0.01	0.01	< 10 µg/g	0.02	0.04	< 10 µg/g
SCV-V115	17.6	3.1	2.3	66.5	0.09	0.07	0.76	2.53	6.07	0.09	0.02	0.64	< 30 µg/g	< 10 µg/g	< 10 µg/g	50 µg/g	< 10 µg/g	0.06	< 0.01	0.01
SCV-V177	18.9	4.2	7.7	55.3	0.18	0.04	0.56	4.32	7.40	0.17	0.58	0.59	< 30 µg/g	< 10 µg/g	30 µg/g	60 µg/g	< 10 µg/g	0.04	0.04	< 30 µg/g
SCV-V210	18.3	2.9	1.4	62.9	< 0.05	0.24	0.69	2.12	5.58	0.04	0.46	0.39	70 µg/g	50 µg/g	0.94	60 µg/g	< 20 µg/g	0.02	0.01	1.89
SCV-V352	20.6	5.5	7.7	56.7	0.33	0.02	0.91	1.77	3.26	0.31	1.13	1.66	< 0.01	20 µg/g	60 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 30 µg/g
SCV-V365	18.7	6.1	6.1	60.8	0.35	0.06	1.00	1.43	3.22	0.31	0.43	1.26	< 20 µg/g	30 µg/g	30 µg/g	0.01	< 10 µg/g	0.03	< 0.01	< 10 µg/g
SCV-V390	16.4	6.6	9.2	54.2	0.73	0.03	0.78	1.89	5.03	0.36	2.08	2.37	< 20 µg/g	40 µg/g	0.02	0.01	0.01	0.03	0.04	< 0.01
SCV-V423	16.9	6.6	9.2	54.3	0.73	0.02	0.82	1.85	4.85	0.34	1.93	2.25	0.01	30 µg/g	0.02	0.01	< 50 µg/g	0.03	0.04	< 30 µg/g
SJT0128	17.2	6.9	6.5	58.0	0.54	0.02	0.88	1.51	6.10	0.24	0.06	1.87	0.01	20 µg/g	< 10 µg/g	60 µg/g	< 70 µg/g	0.03	< 0.04	< 40 µg/g

Table XIII.3: Average of the composition of each mould blown decorated group defined in the PCA analysis.

Groups	**Samples**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**SrO**	**PbO**
G. I $_{MB}$	**SCV-V51**	18.6	5.7	8.3	59.0	0.45	0.02	0.80	1.30	3.45	0.25	0.45	1.45	0.02	< 30 µg/g
	SCV-V79	19.9	5.6	6.8	55.5	0.45	0.03	0.86	2.08	6.67	0.28	0.35	1.26	0.03	< 20 µg/g
	SCV-V95	20.9	5.4	7.9	55.0	0.42	0.02	0.92	1.56	5.37	0.31	0.59	1.35	0.02	< 20 µg/g
	SCV-V154	16.3	5.4	5.5	62.4	0.50	0.04	0.97	1.51	3.38	0.29	2.19	1.32	0.02	< 20 µg/g
	SCV-V182	18.2	6.8	6.1	59.3	0.56	0.00	0.83	1.37	3.57	0.23	1.17	1.46	0.02	< 30 µg/g
	SCV- V336	21.0	4.8	9.2	54.1	0.40	0.03	0.81	2.63	4.15	0.30	0.60	1.77	0.02	0.01
	SCV- V380	18.0	6.9	6.3	59.7	0.56	0.01	0.80	1.45	3.66	0.26	0.98	1.23	0.03	< 30 µg/g
	SCV-V396	18.5	5.7	8.7	57.8	0.44	0.05	0.96	1.57	3.75	0.28	0.50	1.52	0.02	< 30 µg/g
	Avg.	18.9	5.8	7.4	57.9	0.47	0.02	0.87	1.68	4.25	0.28	0.85	1.42	0.023	-
	StDev.	1.6	0.7	1.3	2.8	0.06	0.01	0.07	0.45	1.17	0.03	0.61	0.18	0.003	-
G. II $_{MB}$	**SCV-V14**	19.8	3.1	4.2	62.4	0.23	0.02	0.97	2.17	5.60	0.13	0.29	0.62	0.02	< 30 µg/g
	SCV-V115	17.6	3.1	2.3	66.5	0.09	0.07	0.76	2.53	6.07	0.09	0.02	0.64	0.06	0.01
	SJT0007	18.3	2.4	5.0	62.0	0.24	0.03	0.95	3.66	5.56	0.22	0.51	0.95	0.03	< 60 µg/g
	SJT0113	18.2	2.9	2.3	63.5	0.23	0.07	0.83	4.27	6.12	0.09	0.40	0.63	0.04	0.09
	SJT0122	18.0	2.5	2.6	65.9	0.29	0.05	0.98	2.93	5.27	0.10	0.49	0.80	0.03	0.03
	SJT0131	18.8	2.6	2.9	63.1	0.25	0.06	1.01	3.48	6.34	0.12	0.32	0.83	0.04	0.19
	SJT0138	19.6	2.1	2.0	65.5	0.22	0.05	1.18	2.54	5.90	0.08	0.26	0.52	0.03	0.03
	PMF0517 body	16.4	3.3	2.9	67.2	0.58	0.03	0.96	2.33	4.37	0.13	0.50	1.07	0.01	< 50 µg/g
	PMF0510	17.2	2.3	4.9	63.5	0.29	0.04	1.15	3.70	5.35	0.20	0.35	0.95	0.02	0.01
	PMF0530	15.9	3.0	3.9	66.4	0.33	0.05	0.93	2.01	6.00	0.13	0.49	0.78	0.03	< 0.01
	PMF0550	16.8	2.2	3.2	66.9	0.30	0.04	1.14	2.47	6.19	0.08	0.28	0.30	0.03	< 40 µg/g
	PMF0568	15.7	2.5	3.6	66.8	0.21	0.05	0.91	3.36	5.48	0.12	0.50	0.62	0.03	0.01
	PMF0570	16.2	3.0	4.0	66.6	0.34	0.05	0.94	1.95	5.79	0.12	0.42	0.67	0.02	< 0.01
	Avg.	17.6	2.7	3.4	65.1	0.28	0.05	0.98	2.88	5.70	0.12	0.37	0.72	0.03	-
	StDev.	1.3	0.4	1.0	1.9	0.11	0.01	0.12	0.74	0.52	0.04	0.14	0.21	0.01	-

Table XIII.4: Average of the composition of each HLLA (wine glass bottles) group defined in the PCA analysis.

Groups	Samples	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	Cl	K_2O	CaO	TiO_2	MnO	Fe_2O_3
G. I $_{HLLA}$	**LTR0001**	2.5	2.8	3.4	57.3	1.52	0.29	2.34	25.97	0.29	0.16	2.98
	LTR0002	2.8	2.7	3.3	57.8	1.60	0.34	2.34	25.12	0.30	0.16	3.04
	LRA0009	2.0	2.5	2.5	59.7	1.76	0.33	2.56	26.35	0.16	0.13	1.69
	LRA0012	1.6	2.5	3.8	60.1	1.45	0.33	2.07	24.75	0.20	0.17	2.67
	LRA0015	1.8	2.6	3.3	60.4	1.89	0.32	3.45	23.42	0.21	0.30	2.02
	LRA0016	1.7	3.2	3.8	57.9	1.82	0.28	2.06	25.94	0.21	0.28	2.34
	LRA0018	1.6	3.1	3.6	58.5	1.93	0.25	2.13	25.52	0.20	0.30	2.31
	LRA0020	1.9	3.5	3.2	58.7	1.45	0.21	2.04	26.00	0.17	0.12	2.32
	LRA0033	2.1	3.1	3.5	60.4	1.81	0.34	2.14	23.46	0.20	0.24	2.29
	LRA0034	1.7	3.2	3.7	58.0	1.88	0.26	2.12	25.83	0.20	0.31	2.34
	LTR0039	2.1	2.9	3.9	59.0	1.86	0.36	2.59	23.61	0.25	0.14	2.81
	LRA0044	2.1	3.1	3.6	60.5	1.80	0.33	2.14	23.38	0.20	0.24	2.30
	LRA0049	2.0	3.4	3.9	58.6	1.82	0.31	2.24	24.27	0.21	0.24	2.61
	LRA0056	1.4	3.0	3.7	59.2	1.80	0.24	2.15	25.02	0.20	0.32	2.36
	LRA0060	1.7	2.7	3.3	60.6	1.77	0.27	3.64	23.20	0.20	0.26	1.96
	LRA0064	1.7	3.2	3.7	57.9	1.88	0.26	2.14	25.84	0.20	0.31	2.35
	LRA0068	2.1	3.1	3.6	60.0	1.76	0.35	2.12	23.74	0.20	0.24	2.30
	LTR0090	2.7	3.8	3.3	59.8	1.84	0.39	2.27	22.72	0.19	0.11	2.56
	LTR0091	2.8	2.9	2.5	61.0	1.94	0.38	2.32	23.65	0.16	0.12	1.81
	LRA0161	2.7	3.2	4.0	58.8	1.81	0.36	2.45	23.40	0.22	0.19	2.53
	Avg.	2.0	3.0	3.5	59.2	1.77	0.31	2.37	24.56	0.21	0.22	2.38
	StDev	0.4	0.3	0.4	1.1	0.15	0.05	0.43	1.19	0.03	0.07	0.35
G. II $_{HLLA}$	**LTR0030**	3.2	2.6	3.6	61.5	1.12	0.60	1.29	21.08	0.27	0.68	1.40
	LTR0033	4.1	2.9	4.9	62.4	1.33	0.43	2.38	19.02	0.25	0.29	1.72
	LTR0040	3.3	3.2	3.6	61.0	1.50	0.53	2.11	22.14	0.24	0.71	1.37
	LTR0049	3.5	3.0	3.8	60.4	2.48	0.60	3.08	20.80	0.20	0.56	1.20
	LTR0051	3.3	3.2	5.5	57.8	2.10	0.55	3.58	20.25	0.41	0.87	1.83
	LTR0056	4.1	2.9	4.3	61.9	1.19	0.61	1.67	18.68	0.27	0.85	1.38
	LTR0065	3.5	3.6	4.1	57.8	1.53	0.65	2.38	23.31	0.29	0.90	1.57
	LTR0079	2.7	3.0	3.5	60.0	1.43	0.44	4.21	22.07	0.24	0.56	1.32
	LTR0080	3.8	2.3	3.2	62.7	1.03	0.65	1.55	22.77	0.13	0.38	1.29
	LTR0085	3.9	3.8	3.6	59.8	1.27	0.47	3.54	20.86	0.28	0.61	1.30
	LTR0087	3.6	3.3	3.4	58.8	1.23	0.59	3.01	22.68	0.29	0.81	1.87
	LTR0089	3.4	2.8	3.3	61.0	2.35	0.61	2.32	21.40	0.20	1.30	0.96
	LTR0093	2.7	3.0	3.6	59.9	2.36	0.62	2.34	22.87	0.21	0.65	1.30
	LTR0096	3.2	3.1	4.7	59.6	2.16	0.57	2.28	20.51	0.31	0.61	2.66
	LRA0105	2.6	3.4	4.2	58.8	2.34	0.63	2.69	22.58	0.27	0.89	1.30
	Avg.	3.4	3.1	3.9	60.2	1.70	0.57	2.56	21.40	0.26	0.71	1.50
	StDev	0.5	0.4	0.7	1.5	0.53	0.07	0.81	1.41	0.06	0.24	0.40
G. III $_{HLLA}$	**LRA0058**	0.4	2.6	2.8	62.1	2.30	0.10	5.53	21.57	0.16	1.13	0.80
	LRA0072	0.5	3.5	2.8	57.7	2.55	0.11	6.71	23.00	0.16	1.41	0.87
	LRA0074	0.5	2.7	2.8	61.5	2.34	0.09	5.56	21.96	0.16	1.16	0.82
	LTR0095	0.3	2.5	2.0	59.0	2.62	0.09	3.45	27.84	0.20	0.43	1.26
	Avg.	0.4	2.8	2.6	60.1	2.45	0.10	5.31	23.59	0.17	1.03	0.94
	StDev	0.1	0.5	0.4	2.1	0.16	0.01	1.35	2.90	0.02	0.42	0.22
G. IV $_{HLLA}$	**LRA0091**	6.6	0.4	3.0	70.0	0.03	0.09	0.95	15.23	0.44	0.31	2.88
	LRA0092	5.0	0.8	9.3	63.0	0.08	0.10	2.56	15.85	0.38	0.15	2.49
	Avg.	5.8	0.6	6.2	66.5	0.06	0.10	1.75	15.54	0.41	0.23	2.68
	StDev	1.1	0.3	4.5	5.0	0.04	0.01	1.14	0.44	0.04	0.11	0.27

Table XIII.5: Average of the composition of the potassium rich group defined in the PCA analysis.

Groups	**Samples**	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**Cl**	**K_2O**	**CaO**	**TiO_2**	**MnO**	**Fe_2O_3**	**As_2O_3**	**CaO/K_2O**	**As_2O_3/K_2O**
G. I_K	**LTR0007**	0.9	0.4	< 5µg/g	78.4	< 5µg/g	0.14	12.30	7.47	0.01	0.01	0.07	0.28	0.61	0.04
	LTR0014	0.8	0.6	< 5µg/g	75.2	0.08	0.11	13.35	8.70	0.03	0.16	0.12	0.75	0.65	0.09
	LTR0042	0.4	0.1	0.1	75.3	0.05	0.20	13.31	9.52	0.01	0.15	0.05	0.68	0.72	0.07
	LTR0043	0.6	0.5	0.0	73.9	0.07	0.23	13.24	10.05	0.01	0.16	0.06	0.90	0.76	0.09
	LTR0044	0.6	0.2	0.2	73.4	0.07	0.21	14.30	10.06	0.01	0.21	0.08	0.61	0.70	0.06
	LRA0001	0.2	0.3	0.1	73.7	0.08	0.20	14.43	9.43	0.01	0.06	0.04	1.40	0.65	0.15
	LRA0002	0.3	0.3	0.2	73.4	0.08	0.20	14.45	9.71	0.01	0.07	0.05	1.34	0.67	0.14
	LRA0003	0.3	0.6	0.3	72.8	0.05	0.17	15.46	8.23	0.01	0.04	0.03	2.05	0.53	0.25
	LRA0004	0.3	0.6	0.5	72.9	0.08	0.27	15.04	8.34	0.02	0.08	0.20	1.53	0.55	0.18
	LRA0005	0.3	0.3	0.1	73.3	0.08	0.21	14.51	9.73	0.01	0.06	0.04	1.37	0.67	0.14
	LRA0006	0.4	0.2	0.4	71.1	0.05	0.22	14.72	10.98	0.01	0.09	0.10	1.62	0.75	0.15
	LRA0007	0.6	0.4	0.2	70.9	0.06	0.22	17.04	9.05	0.01	0.04	0.05	1.42	0.53	0.16
	LRA0076	0.4	0.2	0.4	70.9	0.04	0.20	14.77	11.04	0.01	0.09	0.07	1.68	0.75	0.15
	LRA0126	0.6	0.2	0.3	76.0	0.08	0.17	13.18	9.09	0.01	0.01	0.07	0.38	0.69	0.04
	Avg.	0.5	0.3	0.2	73.6	0.07	0.20	14.29	9.39	0.01	0.09	0.07	1.14	0.66	0.12
	StDev.	0.2	0.2	0.2	2.1	0.01	0.04	1.18	1.01	0.01	0.06	0.04	0.54	0.08	0.06

Appendix XIV: µ-Raman wavenumbers' assignments

Table XIV.1: Wavenumbers (cm^{-1}) and assignments of the compounds found in the analysed enamels from fragment LTR0014 (Coentro *et al.*, 2012; Legodi & Waal, 2007).

	Wavenumber (cm^{-1})	***Assignment***
Naples Yellow (bindheimite mineral)	120 - 139	Pb – O lattice vibration
	330	Pb – O lattice vibration
	504 - 504	SbO_6 octahedra symmetrical elongation
Magnetite	330	Fe – O symmetrical bending
	638	Fe – O symmetrical stretching
Hematite	223 - 225	Fe – O symmetrical stretching
	292 - 295	Fe – O symmetrical bending
	408 - 410	Fe – O symmetrical bending
	495	Fe – O symmetrical stretching
	608 - 610	Fe – O symmetrical bending
	650	Fe – OH asymmetrical stretching
	1308 - 1310	Fe – OH asymmetrical stretching
Mixture of Magnetite + Hematite	223 - 225	Fe – O symmetrical stretching
	292 - 295	Fe – O symmetrical bending
	408 - 410	Fe – O symmetrical bending
	526	Fe – O asymmetrical bending
	665	Fe – O symmetrical stretching

Appendices Part II

Appendix I: Glass degradation mechanisms and its detailed description.

The first reaction to occur is the ionic exchange, where alkaline ions negatively charged are extracted from the glass matrix forming a sodium or potassium hydroxide solution. In order to maintain the matrix neutrality, these leached ions are replaced by H_3O^+ ions (Davinson, 2003; Robinet *et al.,* 2009).

1) Ionic exchange:
$\Xi\mathrm{Si} — \mathrm{O^-Na^+} + \mathrm{H^+} \rightarrow \Xi\mathrm{Si} — \mathrm{OH} + \mathrm{Na^+}$
$\Xi\mathrm{Si} — \mathrm{O^-Na^+} + \mathrm{H_3O^+} \rightarrow \Xi\mathrm{Si} — \mathrm{OH} + \mathrm{H_2O} + \mathrm{Na^+}$

2) Hydration: when water enters glass like a solvent
$\Xi\mathrm{Si} — \mathrm{O^-Na^+} + \mathrm{H_2O} \rightarrow \Xi\mathrm{Si} — \mathrm{OH} + \mathrm{Na^+} + \mathrm{OH^-}$

3) Hydrolysis: when water is able to break Si-O-Si bounds in order to form silanes (reversible)
$\Xi\mathrm{Si} — \mathrm{O} — \mathrm{Si}\Xi + \mathrm{H_2O} \rightarrow \Xi\mathrm{Si} — \mathrm{OH} + \mathrm{OH} — \mathrm{Si}\Xi \rightarrow \Xi\mathrm{Si} — \mathrm{O} — \mathrm{Si}\Xi + \mathrm{H_2O}$

If the glass being attacked is a soda glass, a more unstable composition, cracks will be formed on glass surface, allowing water to penetrate deeper on glass bulk and continuing the alkali leaching corrosion process (Robinet *et al.*, 2009).

This process of ionic exchange between water and glass will result in a superficial layer of glass very rich in silica and also hydrated. Water, due to ionic exchange will be overloaded in H+ ions increasing this way its alkalinity and its potential to attack glass (Davinson, 2003; Robinet *et al.,* 2009).
The silica network dissolution corresponds to the breakdown of siloxane bonds existent on the glass/ solution interface (Robinet *et al.*, 2009).

1) Dissolution:
$\Xi\mathrm{Si} — \mathrm{O} — \mathrm{Si}\Xi + \mathrm{OH^-} \rightarrow \Xi\mathrm{Si} — \mathrm{O^-} + \mathrm{HO} — \mathrm{Si}\Xi$
$\Xi\mathrm{Si} — \mathrm{O^-} + \mathrm{H_2O} \rightarrow \Xi\mathrm{Si} — \mathrm{OH} + \mathrm{OH^-}$

2) Network rearrangement:
$\Xi\mathrm{Si} — \mathrm{OH} + \mathrm{HO} — \mathrm{Si}\Xi \rightarrow \Xi\mathrm{Si} — \mathrm{O} — \mathrm{Si}\Xi + \mathrm{H_2O}$

This dissolution process is followed by the formation of a gel layer composed by hydrated silica species, which will condensate forming a new amorphous, hydrated and porous material. Corroded glass will be composed by a leached layer between a gel layer and bulk glass (Robinet *et al.*, 2009).