NOVA SCHOOL OF SCIENCE & TECHNOLOGY

DEPARTMENT OF CONSERVATION AND RESTORATION

PRESERVING THE CRAFT:

DECODING PORTUGUESE GLASS ARCANA AND THEIR RECIPES

ANA CATARINA REIS SANTOS

Master in Conservation and Restoration

DOCTORATE IN CONSERVATION AND RESTORATION OF CULTURAL HERITAGE

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Preserving the craft:
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To the one who had the patience
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Abstract

The term *arcanum* derives from Latin and means "secret". It is the most accurate term to describe personal batch books where glassmakers documented their compositions and experiments, without particular concern for presentation or legibility. These documents accompanied their authors throughout their professional careers, containing empirical knowledge, trade secrets, and competitive advantages.

Glass production in Portugal from the eighteenth to the twentieth century remains a field with many unexplored questions. Studying primary sources from this period—the *arcana*—offers significant advantages. These records not only confirm what was produced in Portugal during this time but also provide insight into the raw materials used, their origins, and the commercial exchanges involved in the glass industry.

The aim of this thesis is to reproduce glass recipes in three colours—amber, blue, and green—found in the four known Portuguese *arcana*: from Marinha Grande Factory, the glassmakers Castro and Oliveira Guerra, the Gaivotas Factory, and the Northern Portuguese Glass Centre Factory. Beyond the reproduction and validation of the *arcana* as cultural heritage, the glass samples were chemically, thermally, and mechanically characterised to create a database of compositions produced in Portugal between the eighteenth and twentieth centuries. Until now, knowledge of this chronology has been scarce, as the few existing studies focus on specific case studies, with no comprehensive research covering national glass production as a whole.

One of the main conclusions of this thesis is that glass production in Portugal might have been aligned with developments in the rest of Europe. New materials emerging in the industry were incorporated, and objects and compositions were produced with the same technical complexity as those from major European glassmaking centres. The database of reproduced and characterised recipes developed in this study will enable future comparisons with historical objects in national museums, allowing for their accurate provenance and dating. This contributes to the previously proposed hypothesis that Portugal produced high-quality glass.

Keywords: Arcanum, Glass batch book, Recipes reproduction, 18th-20th centuries, Materials characterisation

Resumo

Arcano deriva do latim e significa "segredo". É o termo mais correto para nos referirmos aos cadernos de receitas de uso pessoal, onde eram normalmente registadas as composições e experiências de um vidreiro, sem que houvesse uma preocupação com a apresentação ou a legibilidade do documento. Este objeto acompanhava o autor ao longo da sua carreira profissional, contendo todo o conhecimento empírico, segredos e vantagens de mercado de um determinado vidreiro.

Tendo em conta que a produção vidreira do século XVIII ao XX permanece repleta de questões e assuntos por explorar até aos dias de hoje, o estudo das fontes primárias da época — os arcanos — oferece uma grande vantagem. Este estudo permite não só confirmar o que era produzido em Portugal durante este período, como também compreender que matérias-primas terão sido utilizadas, de onde provinham e que trocas comerciais estavam envolvidas nesta indústria.

O objetivo desta tese é, assim, reproduzir receitas de vidro de três cores — ambar, azul e verde — existentes nos quatro arcanos portugueses que se conhecem em Portugal: a Fábrica da Marinha Grande, vidreiros Castro e Oliveira Guerra, a Fábrica de Vidro Gaivotas e a Fábrica do Centro Vidreiro Norte de Portugal. A par da reprodução e validação do arcano enquanto património, os vidros foram caracterizados quimicamente, termicamente e mecanicamente, de modo a criar uma base de dados de composições produzidas em Portugal entre os séculos XVIII e XX. Até agora, o conhecimento existente sobre esta cronologia era escasso, uma vez que os poucos estudos existentes são mais referentes a casos de estudo específicos, não havendo nenhum estudo geral que abrangesse toda a produção nacional.

Uma das principais conclusões desta tese é que a produção de vidro em Portugal não estava de todo atrasada em relação ao resto da Europa, uma vez que eram utilizados os novos materiais que estavam a surgir na indústria e se conseguiam produzir objetos e composições com a mesma complexidade técnica que outros grandes centros de produção de vidro europeus. A base de dados de receitas reproduzidas e caracterizadas construída a partir deste estudo vem assim possibilitar a comparação futura com os objetos históricos presentes nos museus nacionais e a correta atribuição da sua proveniência e datação, contribuindo para a hipótese anteriormente avançada de que Portugal produzia vidro de elevada qualidade.

Palavras-chave: Arcano, Livros de receitas de vidro, Reprodução de receitas,

Século XVIII-XX, Caracterização material

Publications

Journal

- Reis Santos, C., Ruivo, A., Carneiro, A., Veiga, J. P., Palomar, T., & Coutinho, I. (2024). Amber "Alchemy": Recreating and Investigating Yellow Glass Formulations. *Materials, 17(23).* https://www.mdpi.com/1996-1944/17/23/5699

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Exhibition

- "Aqui há Vidro" – Temporary exhibition with Gaivotas Factory collection, Lisbon. *EMS — Vale de Milhaços Gunpowder Factory, 2024.*

Conference proceedings

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Oral presentations and Posters

- Reis Santos, C., Carneiro, A., Veiga, J. P., Palomar, T., & Coutinho, I. (2025). From craft to heritage: Decoding glass *arcana* for technological preservation. *Interim Meeting of the ICOM-CC working group Art Technological Source Research, Caparica, Portugal.*

- Reis Santos, C. (2024). Arte, ciência e indústria do vidro: o caso do arcano da Fábrica de Vidros Gaivotas, de Lisboa. *História & Património do Vidro: Encontro de Cultura Científica e Industrial, Seixal, Portugal.* **[INVITED]**

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- Reis Santos, C., Coutinho, I., & Vilarigues, M. (2022). The Value of Reproduction in the Preservation of Glass Cultural Heritage. *Recent Advances in Glass and Ceramics Conservation 2022.* **[POSTER]**

- Reis Santos, C., & Coutinho, I. (2022). A ciência e os segredos da produção de vidro em Portugal, entre os séculos XVIII e XX. *IV Congresso Ibero Americano de Investigações em Conservaçãoo e Restauro, Lisbon, Portugal.*

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Acronyms

COAI	Comissão Organizadora das Exposições de Arqueologia Industrial (Organising Committee for Industrial Archaeology Exhibitions)
COG	Castro and Oliveira Guerra glassmakers
DSC	Differential Scanning Calorimetry
EDP	Electricidade de Portugal (Electricity of Portugal)
EDXRF	Energy Dispersive X-ray Fluorescence
EMS	Ecomuseu Municipal do Seixal (Seixal Municipal Ecomuseum)
GF	Gaivotas Factory
HLLA	High Lime Low Alkali
IPPC	Instituto Português do Património Cultural – Secretaria de Estado da Cultura (Portuguese Institute of Cultural Heritage - Secretary of State for Culture)
MGF	Marinha Grande Factory
NPGC	Northern Portuguese Glass Centre Factory
RPM	Rede Portuguesa de Museus (Portuguese Museum Network)
RTP	Rádio e Televisão de Portugal (Radio and Television of Portugal)
STIV	Sindicato dos Trabalhadores da Indústria Vidreira (Glass Industry Workers' Union)
TAP	Transportes Aéreos Portugueses (Portuguese Air Transports)
UV-Vis	Ultraviolet-Visible Spectroscopy

VP-SEM-EDS Variable-Pressure Scanning Electron Microscopy—Energy-Dispersive X-ray Spectroscopy

WDXRF Wavelength Dispersive X-ray Fluorescence

INTRODUCTION

> *"Aristocratic and popular, satisfying at the same time the requirements of luxury and the most trivial domestic needs, the inseparable companion of rich and poor alike, the crystalline cup on the lips of royalty, the simple glass in the mouth of the labourer, glass dominates triumphantly in all social strata and in all circumstances of life. Being one of the most utilitarian and universally spread industries, and also one of the oldest and most indispensable, it is nevertheless one of those that has remained more stationary in its fundamental manufacturing processes."*[1]
>
> Sousa Viterbo, *Artes Industriaes e Industrias portuguezas - O vidro e o papel* [2]

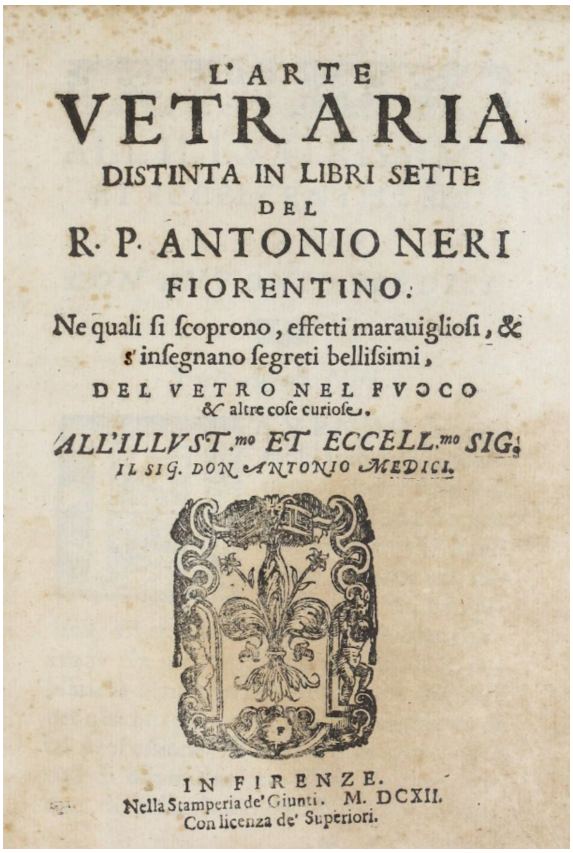
The decision to begin this thesis with the above quotation was made for two reasons: first, it encapsulates the significance of the chosen chronology and the nature of the object under study; secondly, it is contended that glass and more specifically the recipes and processes used to make everyday glass objects did not change much over time, constituting a significant historical legacy worth exploring. Old glass objects are part of the collective memory and in this case evoke memories of Portuguese homes, industries and everyday life. To many individuals they are associated with memories of childhood, family traditions and shared experiences of a society undergoing transformation from manual, small-scale to industrial large-scale glassmaking. The present study focusses on the recipes for glass production contained in *arcana* or batch books from the eighteenth to the twentieth centuries, which still pose questions so far unanswered, and aims to preserve the knowledge and wisdom of the master glassmakers who created these objects currently kept in museums, private collections or simply in use in many homes as they were passed from one generation to the next within the same family.

The making of three specific colours in glass—amber, blue and green—was given particular emphasis, this choice being based on their prevalence in the recipes and their association with the utilitarian glass objects that characterised the mass production of the period.

[1] Free translation to English by the author. Original text in Portuguese: "Aristocrata e popular, satisfazendo ao mesmo tempo os requisitos do luxo e as mais triviaes exigencias domesticas, companheiro inseparavel do rico e do pobre, taça cristalina nos labios da realeza, copo singelo na bocca do operario, o vidro domina triumphante em todas as camadas sociaes e em todas as circumstancias da vida. Sendo umas das industrias mais utilitarias e universalmente derramadas, sendo por egual uma das mais antigas e indispensaveis, é todavia uma d'aquellas que se teem conservado mais estacionarias nos seus processos fundamentaes de fabricação."

The aim is to complement previous research on luxury glass types, such as the lead or potassium-based colourless crystal studied during the research I carried out in the context of my MSc thesis, and offers a broader and more representative view of the history of glass industry in Portugal. By reconstructing these recipes, my research not only recovers a fragment of the past but also validates the *arcana* as historical artefacts. This work also aims to stimulate interest in the systematic study of *arcana* worldwide, opening a largely unexplored field of research and inspiring future efforts to preserve and study similar records elsewhere.

In this context, it is worth clarifying the difference between a historical treatise on glass-making and an *arcanum*. Most written sources on research of historical glass have focused on the study, understanding, and reproduction of recipes found in such historical treatises on glass such as those of Antonio Neri's *L'Arte Vetraria* (**Figure 0.1**) or Robert Dossie's *The Handmaid to the Arts* [3–9].


L'ARTE
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Nella Stamperia de' Giunti. M. DCXII.
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Figure 0.1: Cover of Antonio Neri, *L'art Vetraria*. Source: Internet Archive

These treatises aimed to make public all the information available on glassmaking, including its artistic, scientific, historical and technological aspects. They are educational documents about the art of glass production and related materials, tools to decorate, mould production and furnaces construction. Their content goes beyond simple recipes, and some treatises even attempt to explain phenomena so that the reader can control and adapt the knowledge transmitted therein [9]. The ability to contain diverse types of information makes treatises

objects valued by a wide range of audiences, including researchers, historians, artisans, artists, and merely curious people. Lately, however, another historical source is beginning to be explored—the batch book— and its value for learning about glassmaking in the past has been recognised as priceless. Batch books are often called *arcana* [10, 11]. The word derives from Latin and means "secret", denoting the confidential nature of the information they contain.

The *arcana*, as they will be referred to from now on, are not books in the traditional sense; rather, they are notebooks in which glassmakers, more specifically the batch maker,[2] recorded their recipes and personal experiences with glass production and compositions (**Figure 0.2**).



Figure 0.2: Compilation of example pages of the four *arcana* under study: Marinha Grande, Northern Portuguese Glass Centre, Castro and Oliveira Guerra (first line, left to right) and Gaivotas Factory (yellow page).

These *arcana* served as a practical reference for ensuring consistency in glass production, containing detailed information about the proportions of raw materials needed to create specific types of glass. They might also include instructions on whether the recipe worked, how long a glass had been in the furnace, and under what redox conditions, and sometimes,

[2]There has not yet been a study covering all roles within the operational chain of glass factory labour; however, the term "batch maker" (*compositor* in Portuguese) appears in the labour records of various glass factories and is used to describe the person responsible for the chemical composition of batches.

they even included the origin of the raw materials they were using. These notebooks were for personal use and often lacked concern for legibility by others. Instead, they accompanied the batch maker from factory to factory, serving as a summary or evidence of how good and indispensable that glassmaker was.

This thesis presents a systematic study of a unique collection of four Portuguese *arcana*, dating from the eighteenth to the twentieth century. This collection, which represents the only known examples of its kind in Portugal, is being analysed together for the first time. This investigation provides invaluable insight into the materials, techniques, and processes employed in Portuguese glassmaking over three centuries, therefore contributing to address challenging questions, notably those related to the attribution and dating of historical glass objects in Portuguese museums, which has often remained unclear. A systematic approach is taken, whereby the recipes recorded in the batch books are analysed and reproduced under controlled laboratory conditions (**Figure 0.3**). By examining these records, it is possible to gain a comprehensive understanding of the raw materials, manufacturing techniques and production trends. In this context, a database of historical glass compositions is being established to start connecting the recipes to objects in museum collections. This approach will clarify uncertainties regarding Portugal's glassmaking heritage and provide a foundation for future studies.

An interdisciplinary methodology is employed, combining scientific and historical methods. In order to provide a more visual representation of the methodology and its interconnections with other approaches and studies, a schematic diagram has been created to summarise the methodology (**Figure 0.3**). Historical recipes are decoded by interpreting archaic terminology and identifying modern equivalents for historical references. Selected recipes are reproduced, and the resulting glass is analysed through chemical, thermal, optical, and mechanical techniques, such as Wavelength Dispersive X-ray Fluorescence (WDXRF), Ultraviolet-Visible Spectroscopy (UV-Vis), Differential Scanning Calorimetry (DSC), Dilatometry, and Vickers Hardness Testing. Through this dual approach, a unique perspective on Portuguese glass production is offered, contributing to a relatively unexplored field at the global level.

This investigation poses various relevant questions:

- Which recipes were most frequently used in Portuguese glass production?
- How did these recipes evolve over time?
- Were specific recipes associated with particular objects?
- To what extent were new chemical elements, isolated in the nineteenth and twentieth centuries, incorporated into Portuguese glassmaking?

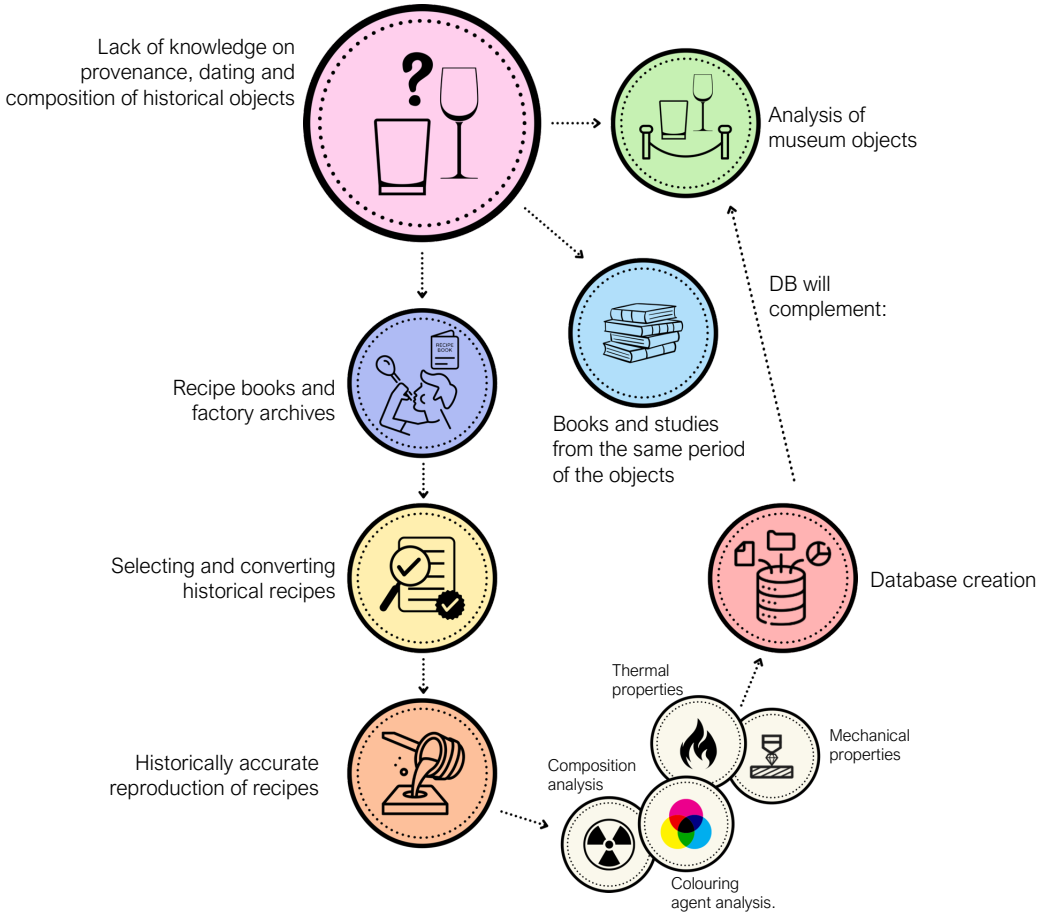

Figure 0.3: The underlying research question is shown in pink. There are three methods for studying a particular glass object or collection (green, blue, purple). After choosing the most appropriate approach (purple), the methodology was outlined and the type of characterisation selected. The data resulting from this (red) will complement the information and the study from the others (green and blue).

By addressing these questions, ambiguities in historical records can be clarified, and insights into the development of the glass industry in Portugal are expected, notably on the materials and techniques used in glassmaking. Although deemed important, social and economic factors are excluded from this investigation, which focuses on understanding the compositions used in Portuguese glassmaking to support future studies, particularly in the context of glass conservation. The findings will help conservators and museum professionals to preserve and identify historical glass objects.

This research, however, is not restricted to the technical aspects of glass production, as the study of Portuguese glass batch books contribute to the preservation of the country's glass heritage by unveiling how glass was made in the past. This knowledge can be used in conservation, research and art, in particular, by inspiring glass artists to reinterpret historical recipes, while helping to preserve museum objects.

This thesis is structured so that each chapter can be analysed independently, while contributing to a broader understanding of the different themes explored throughout the work.

Each chapter addresses specific research questions that guide the study of historical *arcana* and their relevance to the history of glass production in Portugal.

Chapter 1 contextualises glass production in Portugal from the eighteenth to the twentieth centuries, reviewing the existing literature and identifying the gaps that remain to be studied. It considers what is currently known about the industry and whether this level of knowledge is consistent with the historical scale of production. Although sources on glassmaking are scarce, Portugal had a significant glass industry during this period, raising questions about the extent of historical documentation and the possible reasons for these gaps.

Chapter 2 presents a general examination of each *arcanum*, including an overview of its recipes and ingredients, offering insights into the evolution of the glass industry in Portugal over three centuries. By comparing *arcana* from different periods, this study explores the possibility that changes in recipes may reflect shifts in taste and technology, considering a potential transition in preferred techniques, materials, and aesthetic choices over time.

Chapter 3 focuses on glass production, explaining the nature of glass and the different approaches taken over time in studies of the reproduction of historical glass recipes. It details the methodology used in this thesis and provides a framework for replication in similar research. Particular attention is given to the key issues that need to be considered when attempting historically accurate reproduction, from the interpretation of historical documents to the challenges of translating them into laboratory experiments.

Chapter 4 discusses the practical results of the recipes reproduced, organised by colour—amber, blue and green. It examines not only the visual results and whether they were as expected, but also the full characterisation of the glasses produced, including chemical, mechanical and thermal analyses of different colours. The chapter also examines which compositions and colourants were most valued in different periods and whether certain colourants affected the physical properties of the glass. TThe presence of some colours in a greater number of historical objects may indicate a preference among glassmakers, but it could also reflect other factors such as the availability of raw materials, technological constraints, or market demand, which are also considered in this discussion.

Finally, **Chapter 5** summarises the findings of the previous chapters, drawing connections between them and highlighting the importance of future research in the various areas covered. It reflects on aspects of the *arcana* that remain unexplored and considers how the study of these historical documents can contribute to various fields, particularly to the conservation and restoration of cultural heritage.

1

Industrial Context of Portuguese Glassmaking

1.1 Glass in Portugal: key contributions

It is important to clarify that the aim of this chapter is not to rewrite or revise the history of glass in Portugal. Instead, it seeks to synthesise the perspectives shared by main authors over the years and briefly contextualise the history of glass in Portugal within a chronological framework. This approach allows the reader a better understanding of how and where the *arcana* fit into the Portuguese glass industry.

To contextualise properly the Portuguese batch books under consideration, it would be necessary to undertake a comprehensive and systematic study of the manufacturers that had a significant impact on the development of the Portuguese glass industry. Such a study requires the inclusion of a detailed survey of the periods during which these manufacturers operated, the workers involved, their respective roles and training, as well as an extensive commercial analysis. It would also involve identifying each factory's suppliers and tracing the origins of the raw materials used in glass production. To date, no such study has been conducted. Therefore, this survey aims to present what is currently known while acknowledging the uncertainties and discrepancies among various authors.

As observed by Amado Mendes, the historical development of glass in Portugal did not capture the attention of researchers in the nineteenth and twentieth centuries [12]. The few authors who addressed the topic, such as Brito Aranha and Pinho Leal, mentioned it without delving into its origins or evolution [12–14]. In the early twentieth century, Sousa Viterbo[1] published the book *O Vidro e o Papel* (Glass and Paper), as part of the series *Artes Industriaes e Industrias Portuguezas* (Industrial Arts and Portuguese Industries). In this work, he presents a brief prosopography of the glassmakers and glass painters who worked in Portugal from the fifteenth to the seventeenth century [2]. It was not until the mid-twentieth century that the first book dedicated exclusively to the history of glass in Portugal was published: *O Vidro em Portugal* (Glass in Portugal) from Vasco Valente, which remains a milestone reference in this field [15]. However, this book provides little information about glass production in Portugal beyond the twentieth century. While it

[1] Sousa Viterbo (1845-1910) was a Portuguese historian, archaeologist and writer interested in the history of industrial techniques and the arts in Portugal. He stood out for his studies of the glass, ceramics and metallurgy industries, publishing fundamental works for understanding the country's technological and artisanal development.

mentions some factories that were still operational at the time of publication, it does not delve deeper into their activities or context. According to Amado Mendes, this represents a significant gap, as the twentieth century could arguably be considered the most dynamic period in the history of Portugal's glass industry [12]. In the twenty-first century, other works dedicated to glass in Portugal or to specific factories have appeared [12, 16, 17], providing a more in-depth contextualisation of the history of glass in Portugal in more recent periods, but they are far from being complete and still lack important information to be then compared with other countries [18–21].

This situation is not very different from that in the rest of Europe, since, with the exception of a few countries, most do not have a complete contemporary context of their glass production, and the studies that do appear are always in the context of a particular factory or archaeological context. Given that the *arcana* under consideration date from the eighteenth to the twentieth centuries, this thesis will now focus specifically on the manufactures of this period.

In the eighteenth century, there was a transition from a time when glassworks and furnaces were predominantly scattered around the country, to one in which large-scale factories were established, featuring more extensive infrastructures and higher levels of production (**Figure 1.1**). This led to the creation of new glassmaking centres, such as Coina and Marinha Grande [12]. During the same century, under the rule of King João V—a great glass enthusiast—the glass industry experienced significant development [22]. In 1719, the king ordered the establishment of the *Real Fábrica de Vidros de Coina* (Royal Glass Factory of Coina)[2] [12, 16]. It should be emphasised that, at the European level, similar developments were occurring in other countries to intensify domestic production and reduce imports. The rulers of each country actively sponsored the creation of various factories to directly benefit from these industries [12]. However, although this movement occurred across Europe, the founding of the *Real Fábrica de Vidros de Coina* was relatively early. For instance, the *La Real Fábrica de Cristales de La Granja* (Royal Glass Factory of La Granja, Spain) only appeared in 1736 [12]. The Coina region was strategically chosen to host this industry due to its abundance of sand suitable for glass production, access to wood used to fuel the furnaces, and its river port, which facilitated commercial transitions. This may explain why Sousa Viterbo published a document mentioning Afonso Pires, a glassmaker active in Coina in 1470, suggesting that the area had been used for glassmaking in earlier times [2, 12]. The Coina Factory passed through three administrations during its life: the Royal Administration (1719-1735), the British Company (1735-1741) and finally the administration of the Irishman John Beare (1741-1747). This factory is known to have produced at least four different types of glass: k-rich (drinking vessels), soda-lime (bottles and window glass), High Lime Low Alkali (HLLA) (green bottles) and lead glass (colourless tableware) [23]. In the meantime, due to the increased consumption of wood

[2] For ease of reading by non-Portuguese speakers, the names of the glassworks have been freely translated by the author.

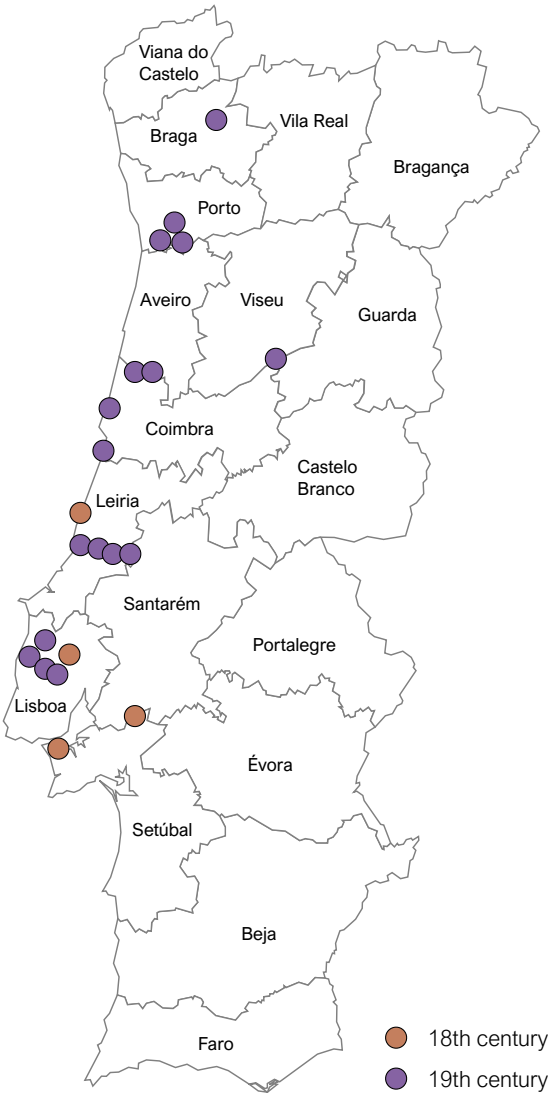

Figure 1.1: Map showing the location of glass factories operating in mainland Portugal (18th and 19th centuries), adapted from Amado Mendes, in *História do Vidro e do Cristal em Portugal*.[12]

and firewood in Lisbon, legal restrictions were introduced on tree felling. Given the special needs of the glass industry, the Coina Factory was forced to find alternative solutions and began using coal in its production from 1735 onwards [16]. However, this was not an ideal solution, as the use of this fuel increased costs of glass production. Portuguese coal had low calorific value[3] and importing coal from England further increased expenses [16]. The factory subsequently began relocating to the Marinha Grande region, under John Beare's management. He brought with him masters, furnace officers, locksmiths, apprentices, and potters [16, 24]. Given this context, it is natural that even today it remains difficult to distinguish between the production of Coina and Marinha Grande factories by relying

[3]Meaning it produces less heat when burned. This makes it less efficient as a fuel for glass production, where high and consistent temperatures are essential for melting and working the material.

solely on visual and stylistic aspects [23]. By 1767, the factory under the management of John Beare had ceased trading, and William Stephens[4] took charge of its operations a few years later. Various factors contributed to this premature closure, but the most cited reason is Beare's own management. However, it is said that John Beare lacked only one key element to make his factory as successful as William Stephens did: a patron or a minister comparable to the Marquis of Pombal [12].

The *Real Fábrica de Vidros da Marinha Grande* (Royal Glass Factory of Marinha Grande) began operations under the administration of William Stephens on 7 July 1769 (**Figure 1.2**). For 223 years, it became a landmark institution in the history of glass in Portugal. The Royal Factory was renamed the National Glass Factory in 1890 and later became the Stephens Brothers School-Factory in 1954 [12].



Figure 1.2: Portrait of William Stephens. Source: *O Vidro em Portugal* from Vasco Valente [15]

The importance of the factory is demonstrated by a document cited in Barros' book, which states that in 1770 the factory began producing "all kinds of crystal glass" [24]. When compared with studies on the invention and dissemination of the method for producing lead crystal, this suggests that Portugal may have been one of the first European countries to access this composition [25]. It is not surprising that Portugal had access to this composition, given that its glass industry was closely linked to the British one, largely due to the nationality of the directors of the Royal Glass Factory of Marinha Grande.

[4]Baptism name. In Portuguese documentation and even when referring to himself, William ended up being translated as Guilherme [24].

Under William Stephens' management, factory production quadrupled within a decade and grew tenfold over 20 years, benefiting from strong state support during this period [12].

William Stephens demonstrated an exemplary commitment to his work, evidenced by a notable story. Following a visit to an inn whose owner praised the quality of glass produced in Marinha Grande, Stephens unsuccessfully attempted to break a glass. He subsequently arrived at the factory and demanded the production of high-quality glass, that is brokable to maintain the need for further acquisition.

> William Stephens: — "That's how it should be. But from now on, no more cups or glasses will be made that won't break"[5]
>
> P. W. de Brito Aranha, *A Marinha Grande em 1870 nas memórias historico-estatisticas de algumas villas e povoações de Portugal* [13]

The Stephens brothers managed the factory for approximately six decades, ending in 1826. William Stephens died in 1803 and was succeeded by his brother, John James Stephens,[6] who passed away in 1826 [12]. By 1789, the factory was already exporting glass to England and its colonies. At the turn of the nineteenth century, the factory improved its production quality by importing sand from England, clay from Spain, k-rich raw material from America, and fine tartar from Oporto [12]. However, some critics maintained that the quality remained poor, which comes to contradict the story by William Stephens. After John James' death, the factory and its assets were passed to the Portuguese State. This began a period of leases, various administrations and company changes, culminating in its closure in 1992. It should also be emphasised that, like many other industries, the Marinha Grande Factory suffered greatly during the French invasions (1807–1811) [26]. Naturally, other glassworks existed during the eighteenth century, such as the *Fábrica da praia do Calvário* (Calvário Beach Factory) in Barroca d'Alva, about which there is not much information, possibly because it only worked for a short time [12, 15].

In the early nineteenth century, in 1807, the *Real Fábrica de Vidros de Vilarinho das Furnas* (Royal Glass Factory of Vilarinho das Furnas) was established in Gerês mountains, a region rich in raw materials and fuel. However, due to the French invasions and riots in the neighbouring population, it was looted and set on fire in July 1808 [12, 15]. In Europe, the industrial revolution in glass was somewhat delayed, beginning in the mid-nineteenth century—around half a century later than the textile sector—and its history only developed later [12]. Until the nineteenth century, glass production remained small-scale and was used in modest quantities. Glass had not yet become widely adopted, and wooden, ceramic, or leather containers were more commonly used for packaging. From the mid-nineteenth century onwards, scientific advances and progress in various engineering disciplines, namely

[5] Free translation to English by the author. Original text: "— Assim deve ser. Mas de hoje por diante não se hão de fazer mais copos, nem vidros, que não se quebrem."

[6] Baptism name. Like his brother, John also had a Portuguese name: João Diogo [24].

in the field of glass furnaces, enabled and stimulated the mass production of glass and expanded its applications [12].

Another significant nineteenth century factory was the *Fábrica de Vidros Gaivotas* (Gaivotas Glass Factory) in Lisbon, founded in 1811/12 by Silvério Taibner, a merchant of of German descent (owner from 1811 to 1820). This factory benefited greatly from the French invasions, as most of the workers from the temporarily closed Marinha Grande Factory were recruited by the Lisbon factory. The Gaivotas Factory produced various types of glass, including plain, cut, engraved and moulded glass for domestic use, bottles of all kinds (except black glass), flasks, bottles for perfumes and pharmaceutical uses and glass for lighting purposes (**Figure 1.3**). Despite no known market issues affecting the sales of its products, the factory closed down in 1985 [12, 15, 27].



Figure 1.3: Catalogue page of the Gaivotas Glass Factory lighting items. Source: EMS-CDI

It is impossible to discuss modern Portuguese glass production without mentioning the emblematic Vista Alegre Factory. Although it is now primarily associated with porcelain, it was dedicated to glass production from 1824 to 1880. The factory's founder, José Ferreira Pinto Basto, involved his fifteen children in business, and ownership remained with the Pinto Basto family for several generations. Like Marinha Grande, the factory's success was bolstered by royal support. King João VI allowed it to use the title of Royal Factory and the royal insignia [12, 15]. Like the Gaivotas Factory, the Vista Alegre Factory likely benefited from the period of crisis in Marinha Grande. It produced a wide variety of glassware, including flasks, bottles, jugs, glasses, laboratory glass, inkwells, kitchen glass, mugs, and goblets. The quality of these objects has been compared favourably to those produced abroad, with no significant differences noted in labour or raw materials. Between 1837 and 1840, there was reportedly a significant production of crystal glass. However,

with improvements in porcelain production, interest in glass and crystal production waned. By 1880, Vista Alegre ceased glass production entirely, demolishing its furnace and selling all the moulds [12, 15].

In the nineteenth century, glass was produced on a small scale throughout the world and its use was therefore modest. However, from the mid-1800s, advances in science and various engineering disciplines enabled and encouraged the mass production of glass in large quantities, while at the same time expanding its applications [12]. In Portugal, the industrial revolution took longer to be implemented. Considering that historical information on the twentieth century is particularly scarce and that it was a century marked by various changes specific to each factory and region, I will approach the twentieth century in a purely descriptive manner, listing the factories and technological changes related to the glass sector during this period.

From the late nineteenth century, in 1889 to be precise, Portugal went from having half a dozen glass factories to more than thirty by the early 1920s. By 1957, certain preferred locations had been identified, leading to a reduction in the number of factories (possibly due to the merging of some of them) [12]. Nevertheless, some 23 glass factories remained in operation throughout Portugal—a significant number given the size of the country.

In the nineteenth century, the following factories were active: the *Santos Barosa* Factory, founded in 1889 in Marinha Grande, which specialised in making bottles; the *Central* Factory, founded in 1894 in the same region by José Ferreira Custódio Junior, which produced flat glass; the *Nova Fábrica de Vidros da Marinha Grande* (Marinha Grande's New Glass Factory) (1895-1999), founded in Marinha Grande by António Augusto Dias de Freitas and Jorge Croft. During its years of operation, the Marinha Grande's New Glass Factory had several owners, like the National Glass Factory of Marinha Grande and Vista Alegre [12]. Perhaps because of its association with these emblematic national factories, the Marinha Grande's New Glass Factory gained international recognition within a few years and became a European benchmark [12].

The Guia Glass Factory, located in Guia (Pombal), was founded in 1904 as a partnership between João Leal, João Gomes Leal, José Tiago Duarte and José de Oliveira, producing flat glass and bottles. The Almeida, Morais & C$^{\underline{a}}$ Ld$^{\underline{a}}$ Factory, founded in 1905, specialised in the manufacture of flat glass and was one of the best equipped factories in Marinha Grande for this purpose. The glass pane factory owned by Guilherme Pereira Roldão was founded in the same region in 1906. Similarly, the glass pane factory of Mariano Pereira Henriques (1912-1920), located in Marinha Grande, produced both flat glass and bottle glass.

In the Lisbon region, *Empresa Vidreira Lisbonense* was founded in 1888 and produced flat glass, mirrors, glass chimneys and bottles. It was technologically, advanced for its time, but when it went bankrupt, its machinery was acquired by the company of *Marinha Grande's New Glass Factory*. The *Amora Glass Factory*, inaugurated in Seixal in 1888, operated until

1926. This factory tried to fill in a gap in the Portuguese glass industry by concentrating on the production of bottles (**Figure 1.4**). It employed workers from Germany, imported raw materials and moulds, and successfully produced bottles of a quality comparable to the imported ones. However, the high costs involved led to its closure. Notably, this factory was a pioneer in container glass production in Portugal, building the first tank furnace in the country and being an early adopter of semi-automatic bottle production. Finally, the *Boémia Factory*, established in 1902 in Oliveira de Azeméis, later became the central nucleus of the company Northern Portuguese Glass Centre company, founded in 1926 [12].

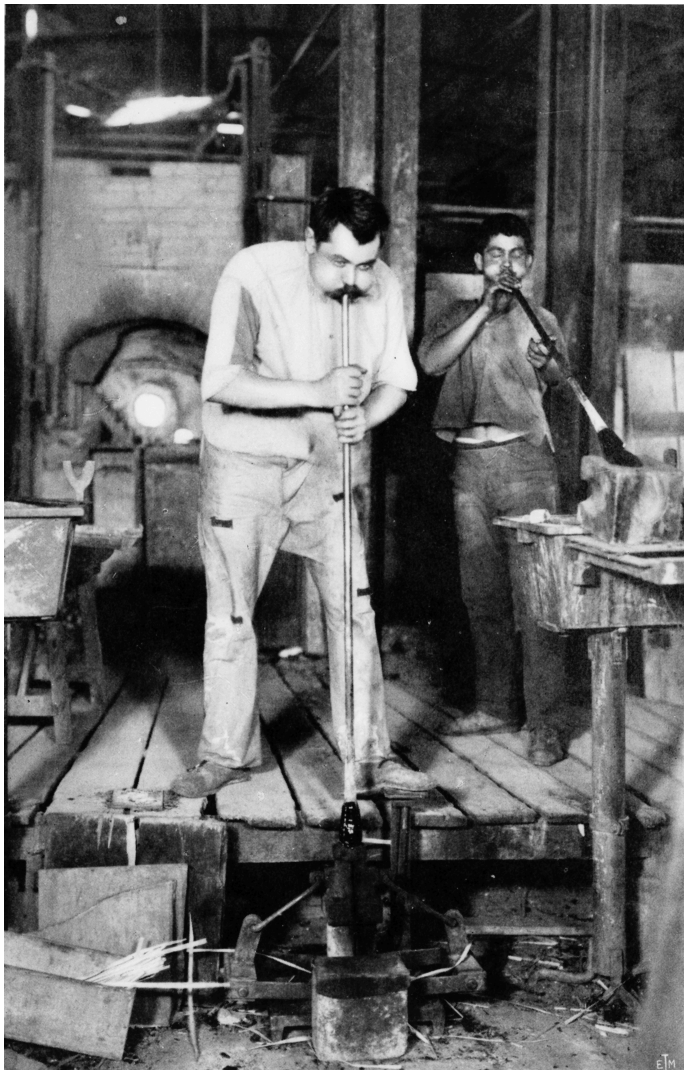

Figure 1.4: Worker blowing a bottle. Source: Catalogue of the Glass Factory Company in Lobatas, Amora, 1908 - EMS-CDI

In addition to this extensive list of factories, many others are known to have existed, as outlined by Amado Mendes [12]. Although little is known about most of them or their operations, they were short-lived. It can therefore be assumed that, with a few exceptions, Portugal showed some resistance to the mechanisation of glass production. This reluctance meant that manufacturing processes remained heavily dependent on manual

labour, increasing the need for skilled glassmakers. However, the number of Portuguese glassmakers was insufficient to meet demand, so it was necessary to recruit foreign craftsmen, which in turn further increased production costs [12].

On a technological level, the nineteenth and twentieth centuries saw significant changes in glass production methods. These changes were mainly driven by the increased demand for certain types of glass—mirrors and windows, due to the expansion of iron architecture, and bottles, due to wine exports. Glass production in Portugal remained manual until 1941. This delayed transition was the result of a lengthy and controversial process that caused dissatisfaction among manufacturers, as I will explain below [12].

In the first two decades of the twentieth century, although most factories produced flat glass, supply fell far short of demand. The modernisation of the building industry and the growth of the automotive sector necessitated large imports. In the 1930s, however, overproduction became a problem, leading to the creation of a cartel of authorised glass manufacturers under special legislation. Despite this measure, imports remained high due to Portugal's entirely manual production methods, highlighting the need for modernisation and mechanisation [12]. But recognising the financial burden of this transition, the authorities decided that a single production unit should suffice for the domestic market and potential exports. However, the centralisation of glass pane production caused discontent among the workers, especially the flat glass glassblowers (cylinder handlers, stretchers and glass cutters), who feared both unemployment and the loss of their centuries-old craft. Glass had been handmade in Marinha Grande since at least 1769. Union leaders, like others in the glass industry, fought for workers' rights. This led to the creation of a special subsidy for displaced workers—the "disabled flat glassblower's" subsidy (*inválidos da vidraça*). Even factory managers and academics opposed the move. While acknowledging its inevitability—Portugal was the last country still producing handmade glass—they argued that quality should take precedence over quantity [12].

Despite opposition, the *Companhia Vidreira Nacional*, Ld^{a} (Covina) was founded in 1936 and established its factory in Santa Iria de Azóia (Loures). It began full-scale production in 1941 and held a national monopoly in the manufacture of flat glass. Its location in the Lisbon metropolitan area marked one of the first major industrial investments outside Marinha Grande, further increasing local discontent [12]. Technologically, Covina initially used the Fourcault process. In 1962, Saint-Gobain acquired a stake in the company, which led to the construction of a new Pittsburgh glass furnace, which was commissioned in 1969. In 1986, a flat furnace was introduced [12].[7]

Bottle glass production also evolved to meet European standards. From the mid-nineteenth to the mid-twentieth century, Portuguese bottle making gradually moved from entirely manual methods to semi-automatic and then fully automatic machines. The breakthrough came in 1905 with a US-patented machine capable of producing 25,000 bottles per hour [12].

[7] Covina was not closed until 2021.

However, full automation did not arrive in Portugal until 1950, although the Amora factory had been using semi-automatic machines since 1903. As the consumption of bottle glass grew, so did the professional group specialising in its production—the bottlemakers—who even formed their own association in 1919. However, like the traditional glassmakers, their profession quickly became obsolete. This led to protests, union meetings and public demands, which explains the long transition to semi-automatic and then automatic production. Little information is available on developments after 1950 [12].

Glassware includes all other glass objects not mentioned above, including lead crystal (24-32% lead content), household and artistic items, flasks, laboratory and pharmaceutical glassware, and lighting products. Like other types of glass, glassware production had to be modernised [12]. Mechanisation initially focused on secondary tasks such as crushing and mixing raw materials, and later on cutting and edging items with semi-automatic machines[12]. Contrary to some accounts, production did not triple between 1943 and 1951 [12, 28]. From 1951 to 1962, production grew at an annual rate of 17.4%. Unlike flat glass and bottle making, glassware production remained labour intensive [12]. This is evidenced by the fact that in 1964 most of the pot furnaces in Portugal were still in use and only semi-automatic machines were in use. However, the sector faced challenges that hindered progress, in particular a lack of research and innovation. The period after the 25 April Revolution[8] was particularly turbulent, with economic, social, labour and wage conflicts, as in other industries [12].

[8]The 25 Abril (Carnation Revolution) was a military-led coup on April 25, 1974, that overthrew Portugal's authoritarian New State regime, restoring democracy and ending colonial wars.

1.2 Overview of Portuguese Glassmaking *Arcana*

1.2.1 Marinha Grande Glass Factory (MGF)

Despite comprehensive analysis and prolonged observation, the attribution of the authors of the five notebooks remains uncertain. The question of whether there is more than one author or if these notebooks are copies of others, remains unresolved. Given this uncertainty, these notebooks will be collectively referred to as the Marinha Grande Glass Factory arcanum in this study, associating them with the factory itself rather than a specific author, as is appropriate given the circumstances. This discussion will be further elaborated in **Chapter 2**.

From the *Fábrica de Vidros da Marinha Grande* (Marinha Grande Glass Factory—MGF), five small notebooks[9] (MG1-MG5) from the period between 1793 and 1798 were digitised and handed over to the VICARTE Research Unit for study by the Marinha Grande Municipal Council (**Figure 1.5**). The research group that initiated the study suggested that two of the five notebooks (MG4 and MG5) were authored by William Stephens. This assumption was based on the initials "G.S." (from Guilherme Stephens) found in MG5, written in handwriting similar to that of William Stephens. MG4, although unsigned, was attributed to the same author due to the similarity in handwriting. The signed notebook—MG5—has been the most extensively explored, studied, and reproduced by previous researchers [29–32].

Little is known about William Stephens. He was of English nationality and came to Portugal as a merchant in 1752. His three brothers, including John James, arrived later [27]. After losing all his possessions in the earthquake of the 1st of November of 1755, he viewed the situation as an opportunity and sought permission to establish a lime factory to produce these material needed for the reconstruction of Lisbon [27]. Given the scarcity of wood fuel at the time, he agreed not to use it and instead relied on coal imported from England, for which he also demanded certain import privileges. Although the factory flourished, its production had to be reduced once the rebuilding of Lisbon was completed [27]. Later, William Stephens went bankrupt, and all his assets were seized, mainly because the State failed to pay him for some of his supplies. He eventually petitioned the King for compensation for the lime he had already provided, but this aid did not arrive until 1764 [27].

In 1767, William Stephens travelled to Marinha Grande to rebuild the Royal Glass Factory, though it remains unclear whether this was at his own request or by royal decree. Either way, it was there that he reached the light of his career, transforming Marinha Grande into the largest industrial centre in the district. He is fondly remembered as a model entrepreneur and a promoter of prosperity who cared not only for the factory but also for

[9] Although they are considered a set—Marinha Grande Factory (MGF)—the notebooks have distinct IDs.

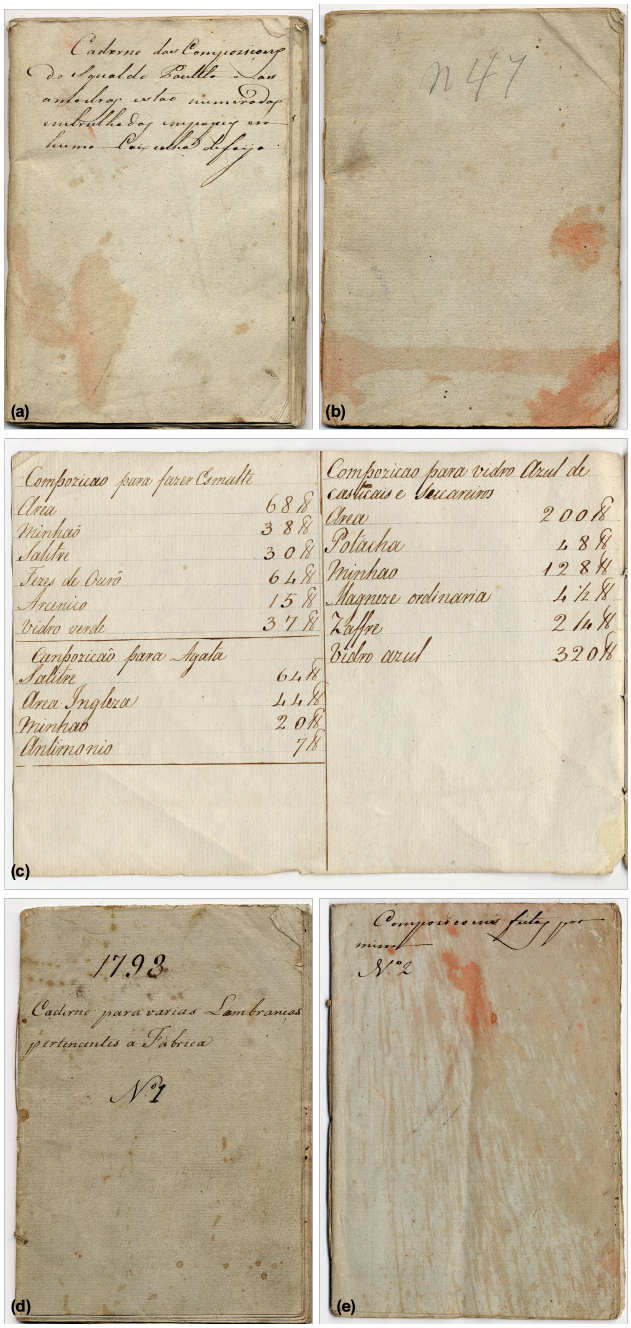

Figure 1.5: First page of each of the notebooks that are part of this *arcanum*. (a): MG1; (b): MG2; (c): MG3; (d): MG4; (e): MG5

his workers. The details of his death remain uncertain, but it is believed that he died in London around 1803 [27].

The research developed in this thesis has led to the proposal that the remaining three notebooks were probably written by two different authors. Two of these (MG1 and MG2) include introductory texts that could help identify their authors. The first, MG1, is

titled "Notebook of compositions by Igualdo Pauletta (...),"[10] with entries dated 1798. The second reads "Composition made by Pauletta (...),"[11] with dates of glass production mentioned throughout the recipes. Interestingly, although not noted in prior studies, this research revealed that MG1 is an expanded copy of MG2, suggesting a process of revision or refinement.

1.2.2 João Augusto de Castro and Augusto de Oliveira Guerra glassmakers (COG)

The *arcanum* of João Augusto de Castro and Augusto de Oliveira Guerra (COG) is the first glass *arcanum* made public in Portugal. It covers the period from 1875 to 1925, and it is the batch book of the glassmaker João Augusto de Castro (from 1875 to 1900), later taken over and continued by Augusto de Oliveira Guerra (from 1900 to 1925). The original document is currently kept at the Torre do Tombo National Archive–Leiria District Archive, with access restricted to a microfilm version for conservation reasons. José Pedro Barosa was responsible for a publication about the document, presenting the entire *arcanum* in an issue of *Estudos e Documentos do Museu Santos Barosa* (Studies and Documents of the Santos Barosa Museum) (**Figure 1.6**). He also included a detailed preface to contextualise and advocated for the preservation and accessibility of similar materials to researchers [10].

João Augusto de Castro was the first owner of the *arcanum*. According to José Pedro Barosa, Castro's connections to the glass industry and whether he had formal training in the field remain uncertain. However, it is believed that in 1862, at the age of 20, he began working as an apprentice glassmaker at Gaivotas Factory under the direction of João da Cruz e Costa. From then on, he held key positions in various factories, such as technical director and compositor [10, 33].

As for Augusto de Oliveira Guerra, the second author of the *arcanum*, it is known that he was born in Marinha Grande, the son of a worker at the National Glass Factory of Marinha Grande. He began working as an apprentice glassblower at the age of 11 [10]. Showing exceptional talent early on, he was invited in 1902 by Francisco de Abreu e Sousa—a prominent figure in the glass industry, who began his career at the Côvo Factory (active since the sixteenth century) and went on to manage and establish several factories—to take over as director of work and production at the Boémia Factory in Oliveira de Azeméis. At the time, Guerra was only 23 years old and already possessed the *arcanum* of João Augusto de Castro. His expertise, combined with the knowledge contained in the *arcanum*, proved invaluable, securing him significant roles within the glass industry, particularly in the North Portuguese Glass Centre. This contribution helped establish the region as the second most important glass production centre in Portugal, after Marinha Grande, at the

[10] Free translation to English by the author. Original text in Portuguese: Caderno das Composições de Igualdo Pauletta.

[11] Free translation to english by the author. Original text in Portuguese: Composições feita por Pauletta.

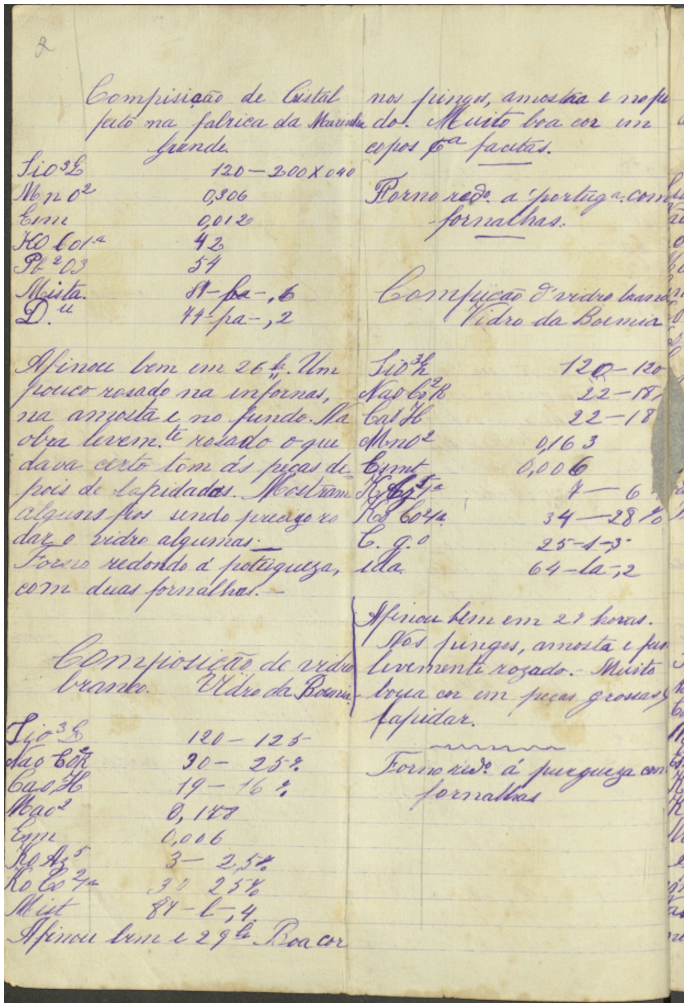

Figure 1.6: First page with recipes from Castro and Oliveira Guerra *arcanum*

beginning of the twentieth century. From then on, Guerra occupied influential positions in various factories, further cementing his legacy in the Portuguese glass industry.

1.2.3 Gaivotas Glass Factory (GF)

Regarding the Gaivotas Factory (GF), the available information is limited. The author of the *arcanum* is believed to be Francisco António Rodrigues, since it was his heirs who provided the VICARTE Research Unit with the digitalisation of the *arcanum*. It is believed to have been written between 1935 and 1975, based on the dates found on the *arcanum*, which are the oldest and most recent entries. In order to reinforce this attribution, the date was compared with the historical context of the factory (**Figure 1.7**).

The factory was founded in 1811[12] by Silvério Taibner, a German master glassmaker who lived in Marinha Grande [10]. It was located in the parish of Misericórdia (Lisbon) at nr.

[12]Some authors say that it began the following year, in 1812. [34] Taking into account the documents and catalogues consulted on the factory, the only date mentioned is 1811, so this is the date that will be taken as the start of production.

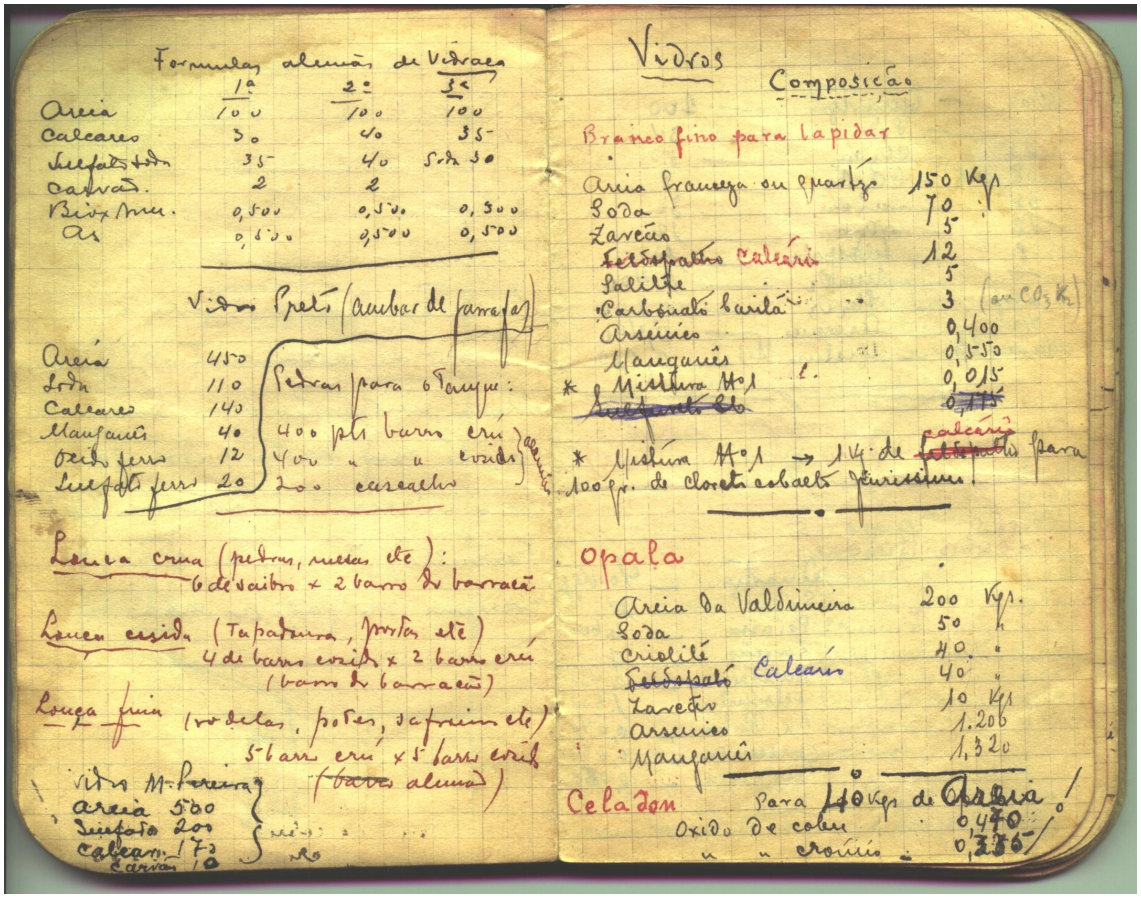

Figure 1.7: First page from Gaivotas Factory *arcanum*

12 Gaivotas Street. Very little is known about its history until 1934. During this period, the factory had several owners, including Manuel Joaquim Afonso, Francisco Alberto dos Santos, João Miguel Pereira, Jacinto José de Oliveira, and Tomás José de Oliveira, who played a significant role in revitalising the factory in 1870 [27]. In 1934, it came under the ownership of a rental group consisting of Dr. Júlio May de Oliveira, José Antunes de Oliveira, António dos Santos Guia Gameiro e Santos, and the company Tavares, Pinto & Abreu Lda [27].

At the beginning of 1938, a new company was formed, and the engineer Francisco António Rodrigues was appointed as its technical director. Rodrigues, a highly skilled glass technician, had previously modernised the New Factory of Marinha Grande, transforming it into Portugal's leading producer of opal glass and lighting objects [27]. He was renowned for introducing new glass colours and regarded as one of the best glass technicians to have worked in Marinha Grande. He also served as the director of the William Stephens Industrial School [27]. Given that the timeline of Rodrigues' work at the factory coincides with the period attributed to the *arcanum*, it is believed that Francisco António Rodrigues is the author of the *arcanum*, even though it is unsigned. The factory ceased operations in 1985 [34].

Technically, the Gaivotas Glass Factory operated a circular furnace with five pots and was equipped with a four-horsepower steam engine [15]. The factory produced items, primarily intended for everyday use that were distributed throughout Portugal. However, only one study, conducted by the author, has analysed a set of glass objects attributed to this factory from a later period, after 1975 [35]. It remains unknown which objects were most produced, which glass types were preferred, or what technologies were used during the *arcanum*'s timeline (1935–1975). Despite its significance in the national context, the Gaivotas Glass Factory appears to have been largely forgotten in collective memory.

Until a few years ago, it was thought that the factory's entire collection had been destroyed, leaving only three known documents: a 1955 factory catalogue available at the *Corning Museum of Glass Rakow Library* (and referenced on the website of a national auction house), which provides information on glass container shapes and prices; a catalogue of lighting items mentioned only on the auction house's website; and the *arcanum* covering the period between 1935 and 1975. In 2023, however, VICARTE's team was informed of the existence of part of the factory's documentary and material collection, which had been stored just a few kilometers away from the research unit.

Before contextualising what happened to the Gaivotas Factory collection from 1985 to the present day, it is important to highlight that this factory operated for approximately 170 years in the heart of Lisbon. It was the third longest-running glass factory in Portugal—after Marinha Grande and Côvo—making it almost inconceivable how much information and historical context exists about its operations.

From 1960 onwards, the factory transitioned from using coal and wood as fuel to town gas. However, this change led to a significant increase in costs, which became unsustainable and negatively impacted on the the factory's profits [36]. By 1977, the price of gas supplied by Electricidade de Portugal (Electricity of Portugal) (EDP) to Gaivotas was nearly as high as the price of domestic gas prices. Combined with rising costs of raw materials—80% of which were imported—and the loss of key markets, such as Portuguese-speaking African countries, the company faced severe financial difficulties [36]. In 1983, the company even issued a letter appealing to the Director General of EDP for support, citing the challenges they were experiencing. With the factory on the verge of closure and facing bankruptcy, the glassworkers union, Sindicato dos Trabalhadores da Indústria Vidreira (Glass Industry Workers' Union) (STIV), petitioned the Secretaria de Estado da Cultura (Secretary of State for Culture) to transform the company into a school for manual glassmaking and a living glass museum [36]. This initiative was naturally supported by the workers, who hoped to retain their jobs and maintain activity at the site. As far as the author knowns, this type of petition was unprecedent.

In 1984, the Comissão Organizadora das Exposições de Arqueologia Industrial (Organising Committee for Industrial Archaeology Exhibitions) (COAI) (Organising Committee for Industrial Archaeology Exhibitions) was established and received a selection of items from

the Gaivotas Factory. In April of that year, Jorge Custódio, as part of COAI, compiled a report on the factory and submitted it to the Ministry of Culture, outlining plans to transform the site into a school and museum. The classification process for the building at Rua das Gaivotas 10-20B/24 in Lisbon was then initiated, encompassing not only the factory structure but also its manufacturing equipment, tools, moulds, catalogues, and other glassmaking and decorating utensils. The Instituto Português do Património Cultural – Secretaria de Estado da Cultura (Portuguese Institute of Cultural Heritage - Secretary of State for Culture) (IPPC) was tasked with inventorying these assets. The proposal was approved in January 1985. However, despite this classification, the concerned authorities failed to implement measures for its conservation and safeguarding [36].

That same year, the company's bankruptcy was judicially declared, yet the Gaivotas Factory remained far from being a protected cultural site. In February, the building was classified as a Property of Public Interest. In 1989, due to continued inaction on the matter, the vice-president of the IPPC requested that the bankruptcy administrator postpone an auction related to the factory. In December of that year, an external team hired by the IPPC sorted through the remaining movable assets at the site. They also packed documentation intended for transfer to the National Archives Institute for selection, study, and conservation—a step that never materialised [36].

In 1992, the Secretary of State for Culture revoked the classification order for the Gaivotas Factory for unknow reasons. The objects were kept in the factory for as long as possible (**Figure 1.8**). After the Ecomuseu Municipal do Seixal (Seixal Municipal Ecomuseum) (EMS) (Municipal Ecomuseum of Seixal) was integrated into the Rede Portuguesa de Museus (Portuguese Museum Network) (RPM) in 2000, the issue resurfaced due to the urgent need to remove the collection from the deteriorating building. That year, the EMS team conducted a technical visit to assess the site and once again noted the lack of historical and heritage knowledge regarding the factory (**Figure 1.9**). AS a museum of territory, the EMS had the intention of developing a collection dedicated to industrial activies (since Seixal was a strong industrial region). Lacking material records from the Amora Glass Factory that operated in Seixal, the EMS began considering receiving the GF collection [36].

After several years, the factory's assets were transferred to other facilities under the custody of the Instituto dos Museus e da Conservação, I.P. (Institute of Museums and Conservation). It was not until 2009 that a phased solution was found for the priority transfer of the documentary collection to the EMS – Vale de Milhaços Gunpowder Factory. The documents were cleaned, packaged, and transported by an external company. The EMS considered the collection a "resource for the study and contextualisation of industrial glassmaking, particularly in the Lisbon region and the south bank of the Tagus, as well as for research into the processes industrialisation in the nineteenth century and de-industrialisation in the twentieth century". Some glass objects were also kept, following prior selection. In 2012, the EMS received the remaining moulds and tools, which had been stored elsewhere.



Figure 1.8: Interior of the Gaivotas Factory, already abandoned. Photograph by Graça Filipe, 1994. EMS-CDI

The formal process of permanently transferring the collection to the municipality of Seixal was completed in 2013.



Figure 1.9: Detail of the Gaivotas Factory retail shop. Photograph by José Carlos Henrique, 2000. EMS-CDI

In 2023, a partnership was established between the Department of Conservation and Restoration at NOVA FCT, the VICARTE Research Unit, and the EMS to create curricular and extracurricular internships for Bachelor's degree and MSc students in Conservation and Restoration. The main tasks of these internships include identifying the contents of the boxes (**Figure 1.10 (a)**), carrying out preventive conservation (**Figure 1.10 (c) and (d)**), cataloguing the items in a database with identification photographs, assigning

registration numbers, and ensuring proper packaging (**Figure 1.10 (b)**).



Figure 1.10: Project to preserve and study the Gaivotas Factory collection in progress. (a) - Condition of the collection that has not yet been handled in deposit at Vale de Milhaços Gunpowder Factory - Ecomuseu Seixal; (b) - New packaging; (c) - Student dry cleaning documents. Source: Daniel Rocha - PÚBLICO Journal [37]; (d) - Some of the students from the last internship.

By 2024, 13 students had already completed internships with the collection, resulting in the registration of more than 1,450 documents and glass objects from the Gaivotas collection. The necessity to raise awareness for this collection and its study is imperative; consequently, several initiatives were organised to publicise the ongoing work. These included an interview with given to a major nationwide newspaper *O Público*, available both in print and online [37], an interview given to a local radio station, and an exhibition of approximately 60 objects from the factory's collection (**Figure 1.11**).

In summary, the following key findings have been identified from the Gaivotas Factory collection to date, highlighting its potential for research across various fields (**Figure 1.12**).

Although some of the open boxes are rather disorganised, with documents crumpled and piled up inside, they provide an insight into the factory's business archive and how it was structured. There was a clear concern to preserve the documents and, more importantly, to ensure that they could be accessed and consulted when needed. The collection includes carefully labelled files and folders containing Christmas cards sent to the factory, justifications for workers' absences, medical examination records and more. There are also various samples of materials sent by other companies (such as caps and rubber seals for containers) and numerous sales catalogues for automatic and semi-automatic glass-making machines. Although less than 50 boxes have been opened so far—from the circa 600 boxes—it is clear that this collection has immense research potential, particularly because it was originally



Figure 1.11: Inauguration of the "*Aqui há vidro*" exhibition at Vale de Milhaços Gunpowder Factory on 29 November 2024.

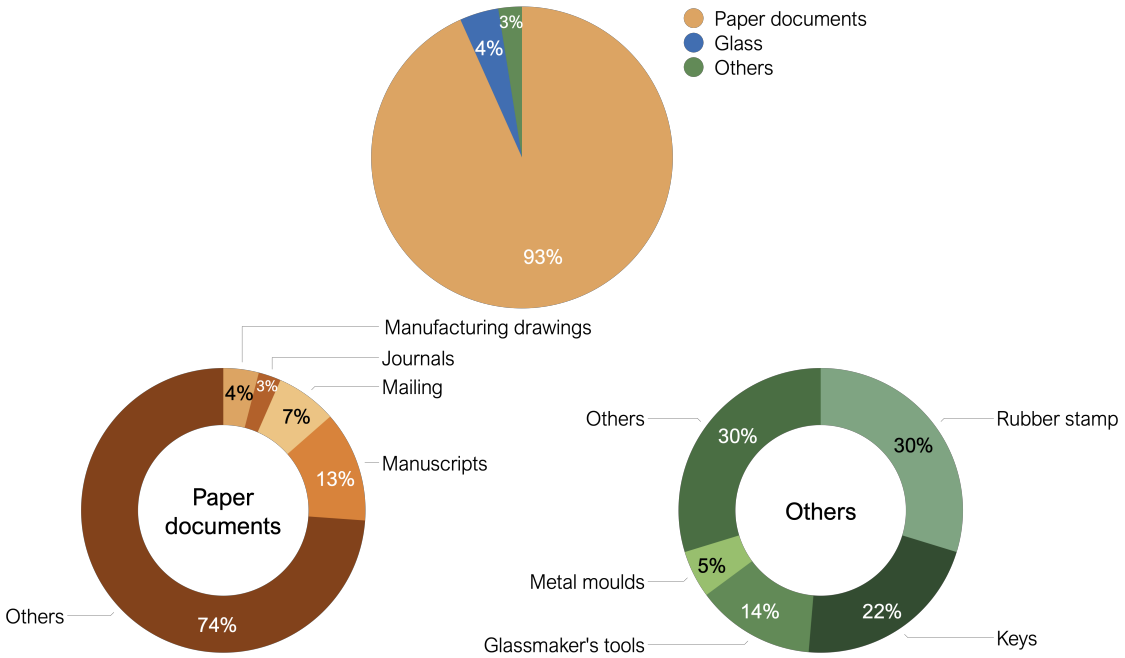

Figure 1.12: Distribution of document and object types found in the Gaivotas Factory collection. The three pie charts represent the percentage of different categories identified within the collection.

well organised - something that is no longer the case today.

However, some specific contents deserve particular attention. Of the material catalogued so far, 3% consists of scientific journals, mainly the Glass Technology. This indicates a strong interest on the part of the factory to keep abreast of new glass technologies and compositions, possibly with the intention of implementing them in production. In relation to this research focus, we have also found a thesis and an internship report, both evaluated by Francisco Rodrigues (the possible author of the *arcanum*), one of the factory partners.

The collection also contains a significant amount of correspondence (7%), particularly letters received and sent by the factory, and more specifically by Francisco Rodrigues. These documents not only show the promotion of different models and technologies, but also include exchanges with Chamber of Commerce in various countries, trade unions and industrial associations. This suggests that the factory was well known both nationally and internationally, which is remarkable given that today it seems to have fallen into collective oblivion, with little or no recognition of its importance.

Approximately 4% of the recorded documentation consists of technical drawings of glass objects (**Figure 1.13**). However, it is unclear whether these were actually used by the factory's glassmakers or whether they were simply project designs that were never executed. Interestingly, about 100 of the 600 boxes stored at Vale de Milhaços Gunpowder Factory contain glass objects, so there is a possibility that some of the drawn designs may correspond to existing glass objects. This underlines the importance of cataloguing the entire collection.

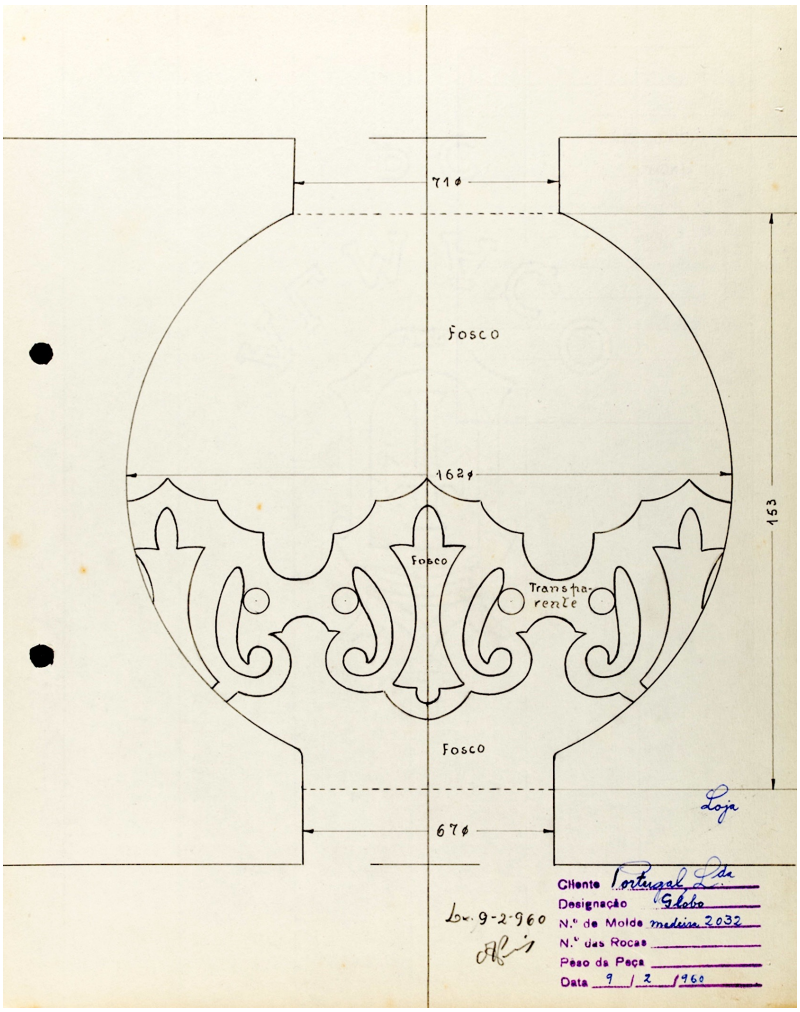

Figure 1.13: Light globe decoration drawing. Photography by António Silva, 2024. EMS-CDI.

Handwritten documentation makes up about 13% of the collection.[13] This category includes records of orders placed with the factory, with details of quantities and customers; purchase logs for consumables; records of glassmakers' working hours and hourly wages; delivery notes; and invoices for each sale, including transactions with notable Portuguese companies such as Rádio e Televisão de Portugal (Radio and Television of Portugal) (RTP) and Transportes Aéreos Portugueses (Portuguese Air Transports) (TAP), as well as international perfume brands such as Lacoste and Nina Ricci.

Other items such as keys and stamps were also found in the document boxes. However, the glassmakers' moulds (**Figure 1.14**) and tools were not packed in these boxes, as they were recovered separately at a later stage, as mentioned above.

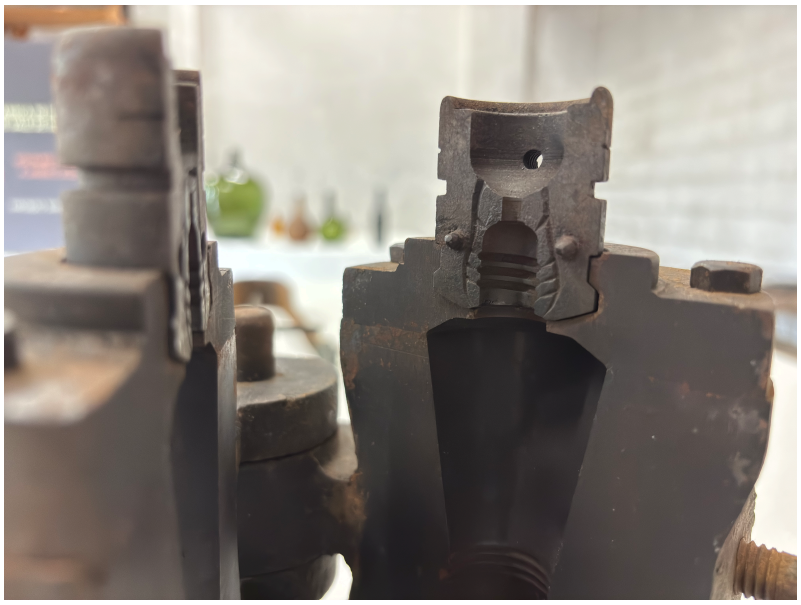

Figure 1.14: Metal mould for producing a glass flask with a threaded neck. Photography taken by the author, 2024.

These findings underline the immense historical, technological and industrial value of the Gaivotas Factory collection. The diversity of the material, ranging from business records and technical documents to physical objects, reveals not only the internal workings of the factory, but also its links to wider industrial networks. Properly cataloguing and studying this collection will help preserve its heritage, and also provide valuable insights into glass production in Portugal and beyond.

[13]The names of the documents conform to the rules in force at the EMS and every effort has been made to retain the terms already defined so that the data can be included in the database used by the museum.

1.2.4 Northern Portuguese Glass Centre Factory (NPGC)

The Northern Portuguese Glass Centre Factory has an *arcanum* (NPGC), a digital copy of which was provided by the Municipal Archive of Oliveira de Azeméis to the VICARTE research unit for study [38]. It is dated 1 September 1955, but no additional information is currently known (**Figure 1.15**).

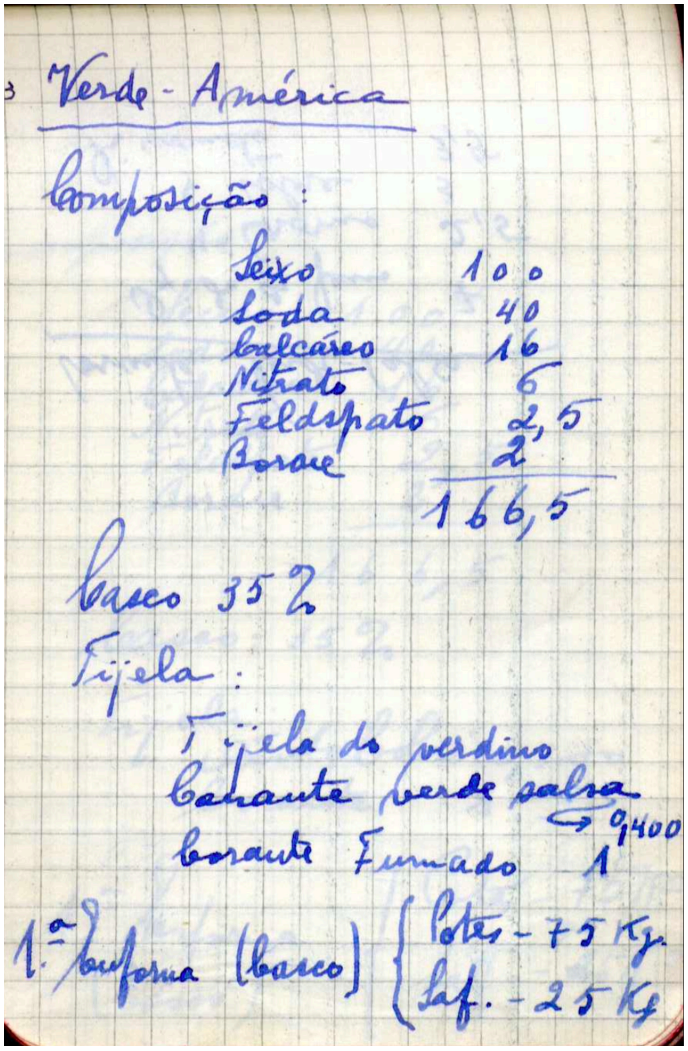

Figure 1.15: Example of a page from Northern Portuguese Glass Centre *arcanum*

The Oliveira de Azeméis region is considered the birthplace of glass in Portugal, with glass production beginning in the sixteenth century at the Côvo Glass Factory. Over time, the region hosted several commercial enterprises linked to the glass industry. However, following multiple financial crises, a decision was made in 1926 to establish a single factory with greater production and administrative capacity: the Northern Portuguese Glass Center (NPGC). The factory was managed by Augusto Guerra, Ramiro Gomes Mateiro, and António Antunes. By 1947, the NPGC was able to meet domestic demand while also exporting its products [12].

In the 1950s and 1970s, the company underwent significant expansion, building new facilities and acquiring modern machinery, which increased production capacity. At its peak, the NPGC could produce five tons of glass every 24 hours. The factory remained operational until 2000, when it declared bankruptcy and ceased production. During its most successful period, the NPGC introduced several transformative innovations in glass production in Portugal [12].

The *arcanum* of the NPGC is being studied for the first time in the scope of this thesis. Dated to 1955, it is part of a documentary collection recovered from the former factory site in Oliveira de Azeméis. Although little is known about its original context, this study is expected to offer valuable insights into mid-twentieth-century glass production techniques and practices in Portugal.

During the period of the COVID-19 lockdown in 2021, the remaining structures of the factory were demolished (**Figure 1.16**).



Figure 1.16: State of the factory after a visit by a group of researchers who were in the process of submitting a research project to study the factory archival material. Photograph by Inês Coutinho, 2020

2

Characterising the *arcana*

2.1 Analysis of the *arcana*

This chapter will examine and analyse each *arcanum* in more detail, focusing on the number of recipes, glass colours present and other relevant elements. It is important to clarify some aspects of the methodology used to enumerate the recipes. Each *arcanum* contains not only recipes for glass compositions, but also recipes for dyes, enamels and even glass decoration techniques (such as acid etching). Although all these recipes have been given identification numbers, they are not included in the total number of glass recipes. Note that in many cases there are two or three columns mentioning the quantities of raw material used, following the recipe title. Where the only difference between the columns was the quantity of raw materials, the recipe was considered as a single entry. In cases in which ingredients have been added or removed, a new identification number has been assigned.

2.1.1 Marinha Grande Factory *arcanum* (MGF)

The MGF is the oldest *arcanum* (1793-1798), so it naturally raises many questions (**Tables A.2, A.3, A.4, A.5 and A.6**). It contains 145 entries in the database, 94% of which are glass recipes (**Figure 2.1**). Most of the remaining entries are recipes for smalt[1] or enamel, which may refer to the same compound but are described using both terms.

A significant proportion of the recipes (26%) do not specify the type of glass produce, as this information is absent from recipes names, notes, or accompanying comments. The second most common type is colourless glass, accounting for 18% of all the *arcanum* glass recipes. Most of these recipes use potassium-lead glass, referred to as crystal glass. Manganese is used as a bleaching agent, while saltpeter serves as a fining agent.

Blue glass recipes make up 15% of the *arcanum*. The majority use a mixture of sodium and lead as the base glass, with cobalt oxide as the colouring agent. However, there are references to a wide range of base compositions, including sodic, potassium-lead, purely lead-based, and purely potassic glass. Some recipes even suggest using all the available glass at the factory, regardless of its colour—likely because cobalt oxide's strong colouring power overrides other metal oxides. Notably, most blue glass recipes do not mention arsenic or other fining agents.

[1] Smalt is a deep blue pigment consisting of a powdered glass that contains oxide of cobalt. It was used for painting, glass production, enamels and even food. In this case, I assume that they used the word to refer to an enamel, as the name smalt is sometimes preceded by colours other than blue.

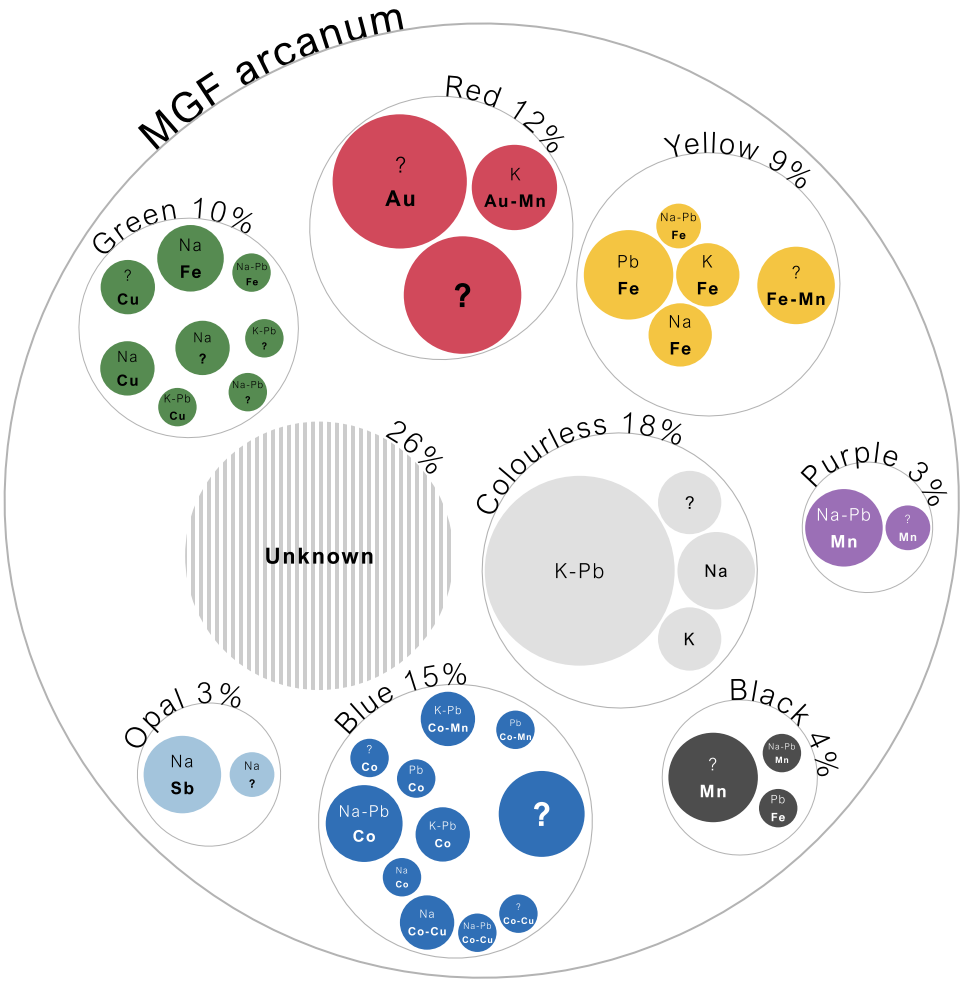

Figure 2.1: Circle packing chart with recipes from the MGF *arcanum*. Each circle shows the fluxes (top) and the colourant (in bold). Question marks mean that either the base/colouring composition could not be deciphered or there is no visible correlation. The size of each circle is proportional to the number of composition and colour recipes. The percentage value is rounded to one decimal place.

Red glass recipes represent around 12%, reflecting the preference of the eighteenth century for this colour. Most are potassium-based glass with colloidal gold particles as the colourant. Some include gold and manganese, along with lead as a network former. However, since manganese was a commonly used ingredient—often described as the "soap of glassmakers"—it is unclear whether it influenced the colour or was added out of habit.

Green glass accounts for around 10% of the recipes, with most having a sodic composition, although some use lead-based glass, occasionally combined with sodium or potassium. Considering the *arcanum* dates from the 18th century, most green recipes use copper or iron oxide as the colouring agents, likely alternating based on the desired shade. For darker green, iron oxide was likely used, while copper oxide was preferred for lighter shades. Arsenic, a common fining agent, is rarely mentioned in the green recipes, possibly because

many are intended for bottle production, as indicated in the notes.

Yellow or amber glass recipes make up about 9%. Most specify lead-based glass, but as with blue, there are examples using various base glass compositions, including references to "glass of all qualities". This highlights that some colourants require specific base compositions while others do not. Iron oxide is the primary colouring agent in most recipes, although some also include manganese oxide. Despite amber glass production typically requiring ingredients such as sulphates and reducing agents like charcoal or flour, none of these recipes explicitly mention such components [39].

The least common recipes are for black (4%), opal (3%), and purple glass (3%). Black glass recipes largely disregard the base composition, often listing "glass of all compositions" as an ingredient. They rely on large quantities of manganese oxide to achieve the colour. Rather than using a specific black colourant, these recipes saturate the glass with metal oxides, resulting in extremely dark glass that appears deep purple or brown. Purple glass also uses manganese oxide as the colourant and a soda-lead glass base. Opalescent glass recipes consistently use soda-lime glass with antimony as the opacifying agent, one of the earliest known materials used for this effect [40].

2.1.2 Castro and Oliveira Guerra glassmakers *arcanum* (COG)

The *arcanum* COG dates from the period 1875 to 1925 and contains 186 entries: 161 are glass recipes, one describes an acid treatment for decoration, and the rest concern crucible production (**Tables A.7, A.8, A.9, A.10, A.11 and A.12**). It is a highly diverse *arcanum*, with recipes for colourless, blue, green, yellow, opalescent, purple, black, pink, and red glass (**Figure 2.2**). Only 4% of the recipes do not specify the glass colour due to missing details in the titles or notes.

As with the former *arcanum*, colourless glass recipes are the most common, accounting for 32%. Most of these are for soda-lime (ordinary glass). Recipes for sodium-lead glass, with or without potassium, are labelled as "half crystal," possibly referring to compositions containing lead but not enough to qualify as crystal glass by British standards [25]. Recipes for crystal glass are potassium-lead compositions, while those for potassium-soda glass are named "Bohemian glass." Manganese oxide is the most common bleaching agent, and some recipes mention cobalt oxide, alone or mixed with nickel, to mask greenish tints from iron impurities [11, 41]. Most recipes also include arsenic oxide and antimony as fining agents.

Blue glass recipes are the second most frequent, representing 19% of the total. While most have a soda-lime base, recipes exist for various compositions, including K-Pb, Na-Pb, Na-K, K, and Na-K-Pb glass. As seen in the previous *arcanum*, in the COG *arcanum* the blue recipes often use cullet of all compositions. Colourants include cobalt oxide for darker tones and copper oxide for lighter shades. Soda-lime recipes typically use cobalt oxide, while copper oxide is more common in lead-containing glass. Some recipes mix colourants, such as cobalt with cryolite (for blue opalescent glass), cobalt with copper, or

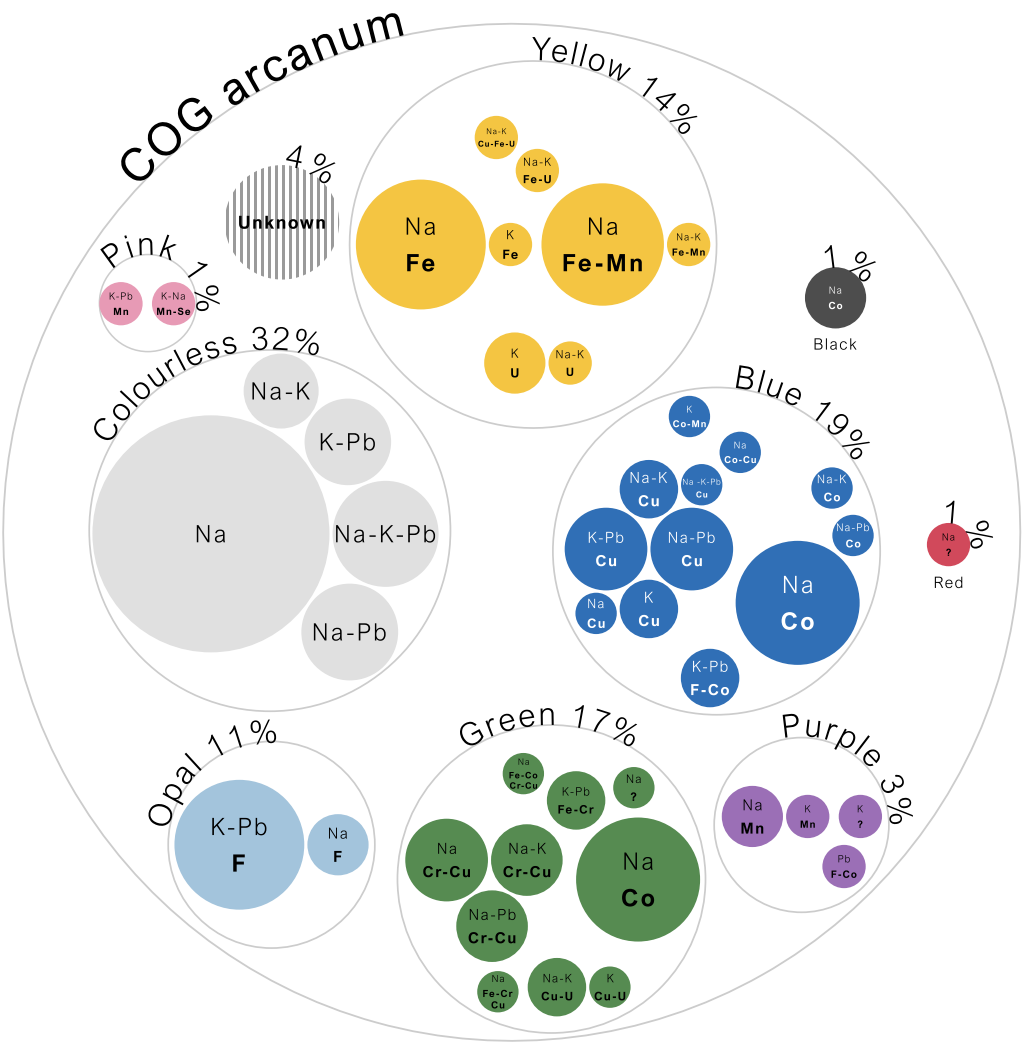

Figure 2.2: Circle packing chart with recipes from COG glassmakers *arcanum*. Each circle shows the fluxes (top) and the colourant (in bold). Question marks mean that either the base/colouring composition could not be deciphered or there is no visible correlation. The size of each circle is proportional to the number of composition and colour recipes. The percentage value is rounded to one decimal place.

cobalt with manganese. Names indicate potential uses, with cobalt glass referred to as "navy blue" (*azul marinho*) or "branding iron" (*azul ferrete*) and copper glass as "sky blue" (*azul celeste*) or "dichroid" (*azul dicroide*). Recipes also suggest that cobalt glass was used for flash glass.

Green glass recipes make up 27% and show changes reflecting the introduction of new elements in the glass industry. Most are soda-lime glass with chromium oxide and copper as colourants, though these combinations also appear in soda-potassium and soda-lead compositions. Recipes with iron oxide and chromium are specific to potassium-lead glass. Uranium appears for the first time, used alongside copper in potassium-containing recipes (Na-K or potassium glass). Notable entries include "olive green glass for French-style bottles" (*verde azeitona para garrafas à francesa*), which mention zaffer (a cobalt oxide

source) but no other colourants. Although cobalt is typically associated with blue glass, it can produce green hues under specific conditions, such as low-temperature melting and a particular composition [40, 42]. The presence of these recipes highlights the high level of expertise and material knowledge possessed by historical glassmakers. Other green glass names include "parsley green" (*verde salsa*) for chalices, "green for flash glass" (*verde para dobrar*), and "dichroic green" (*verde dicroide*) for uranium-copper recipes.

Yellow glass recipes account for 14% and include both amber and yellow glass. Most are soda-lime glass with iron oxide, or a mix of iron and manganese, as colourants, producing amber glass. Recipe names include "olive oil-coloured glass"(*cor de azeite*), "gold-coloured glass" (*cor de ouro*) and "topaz yellow glass". Yellow glass recipes with a soda-potassium or potassium-only base often use uranium, alone or mixed with iron or copper, and have names like "canary-coloured glass" (*amarelo cor de canário*), "sulphur-coloured glass" (*amarelo cor de enxofre*), and "dichroid yellow" (*amarelo dicroide*).

Opalescent glass recipes make up 7% of the *arcanum*. Most are potassium-lead glass with cryolite, a fluoride source, to create the opalescent effect. Some also include cobalt, chromium, or manganese oxides to produce opalescent colours like blue, green, or purple.

Purple glass recipes represent 3%. Most are soda-lime glass coloured with manganese oxide, named "violet." A recipe for "dark lavender" uses lead-based glass and achieves the colour by combining cryolite with cobalt. Black glass recipes account for only 1% and are produced by adding cobalt oxide to soda-lime glass or a mix of cullet from all colours. Pink glass recipes match black in quantity and use potassium-sodium or lead-based compositions with manganese oxide (with or without selenium) as the colourant. The *arcanum* contains only one recipe for red glass, but the entry is illegible, leaving the colouring agent unknown.

2.1.3 Gaivotas Factory *arcanum* (GF)

The GF (1935-1925) contains the largest number of recipes, 213 in total, 94% of which are for glass production (**Tables A.13, A.14, A.15, A.16, A.17, A.18 and A.19**), while the rest are for related materials and processes (e.g., crucible production, mixtures for decolouring glass, acid treatments for decoration, among others) (**Figure 2.3**).

Colourless glass recipes account for 32%. Most describe ordinary soda-lime glass, also referred to as glass for cutting. Some recipes are for "singing crystal" (*cristal de som*) or "singing glass" (*vidro de som*) which includes sodium, potassium, and lead. The term "singing" likely refers to the presence of lead which gives glass certain characteristics.[2] Lead glass with potassium or sodium appears less often and is named Venetian crystal or fine

[2]The act of touching the rim of a glass cup and producing sound, often by running a wet finger along its edge, is known as glass singing or making a glass sing. This phenomenon occurs due to vibrations caused by friction between the finger and the glass. As the vibrations travel through the material, they create sound waves, and the pitch of the sound depends on the glass's size, shape, and thickness, as well as the amount of liquid inside. This principle is also used in musical instruments like the glass harp, where multiple glasses are tuned to create melodies [43].

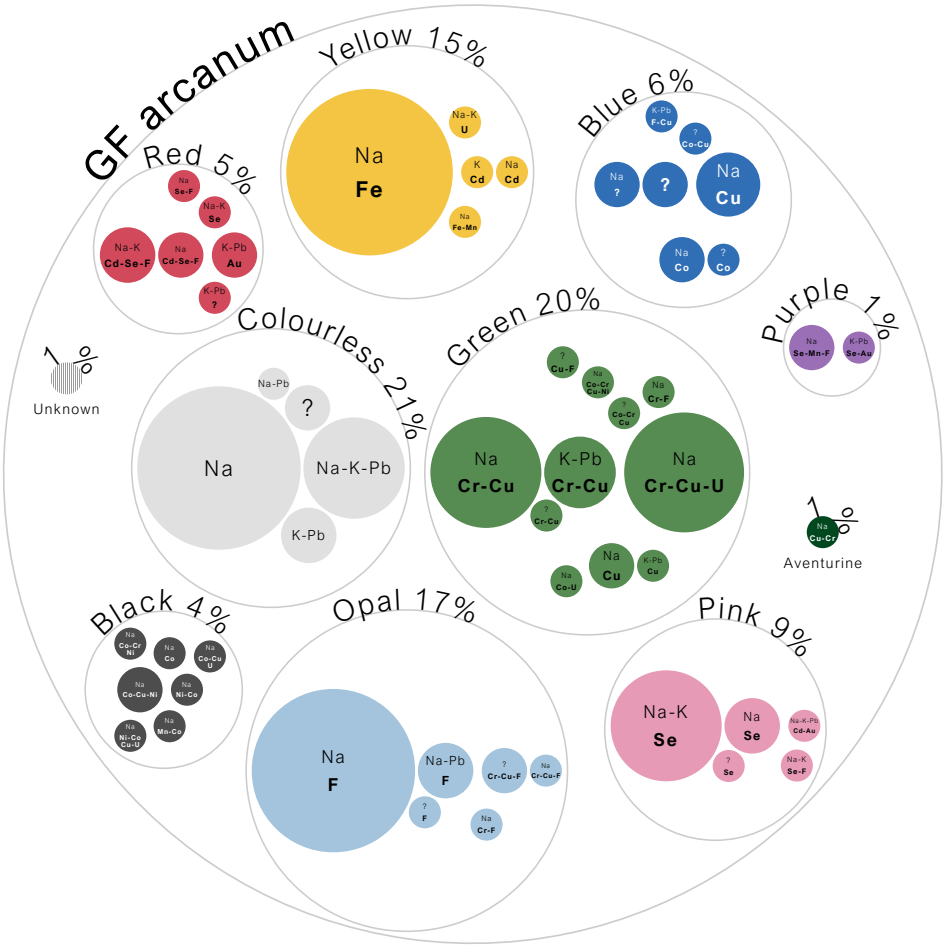

Figure 2.3: Circle packing chart with recipes from GF *arcanum*. Each circle shows the fluxes (top) and the colourant (in bold). Question marks mean that either the base/colouring composition could not be deciphered or there is no visible correlation. The size of each circle is proportional to the number of composition and colour recipes. The percentage value is rounded to one decimal place.

cutting glass, respectively. Nearly all recipes mention nickel and cobalt oxides, like the previous *arcana* COG, with some also including charcoal as an ingredient.

Green glass recipes are the second most common, comprising 20% of the total. Most use soda-lime glass, but some use potassium-lead glass. During this period, chromium oxide became a widely used colourant, giving glass its distinctive green colour. In many recipes, it appears alongside copper oxide, creating shades named "parsley green" (*verde salsa*) or "China green" (*verde da china*). In some cases, these are combined with uranium to produce opalescent glass. Other variations include combinations of Co-Cu-Cr, Co-Cr-Cu-Ni, Co-U, Cu, F-Cr, and F-Cu. Notably, some recipes also mention cobalt as a green colourant, like in the previous *arcanum*, indicating an advanced understanding of its behaviour under specific conditions [40, 42].

Given the types of glass and objects associated with this factory (Chapter 1), it is not surprising that many recipes focus on opalescent and amber glass. Opalescent glass recipes make up 17% of the total, and are most often referred to as opal, although some are called celadon, referring to greenish opalescent glass. Most are soda-lime based, with a few using soda-lead compositions. Copper oxide and chromium are the main colouring agents used in celadon glass.

Amber glass, grouped as yellow glass, accounts for 15% of the recipes. Despite their titles, most describe the production of amber glass. These recipes are mainly soda-lime based, with two using potassium or soda-potassium glass. The most common colouring agent is iron sulphate, with the sulphate likely introduced as elemental sulphur, and the reducing agent is often flour. These recipes are named as champagne yellow or bottle yellow. One recipe mentions iron and manganese sulphates to make "black bottle glass". There are also recipes for cadmium yellow and, for the first time, uranium yellow.

Recipes for pink glass are more prominent in this *arcanum*, accounting for 9% of the total. Most compositions are soda-potassium, although some include soda-lime or sodium-potassium-lead glass. Selenium is the main colouring agent, with a few recipes using cryolite with selenium or cadmium with gold.

Blue glass recipes are less used, accounting for 6%. Most use soda-lime glass with copper oxide as the colouring agent (e.g. "navy blue" (*azul marinho*) or "champagne blue"). Other recipes include cobalt oxide ("blue for flasks"), cobalt and copper oxide (*azulino*) or copper oxide with cryolite ("blue singing glass", in portuguese *azul de som*).

Red glass recipes account for 5% of the total, showing a change in consumer preferences compared to the MGF *arcanum*. Most are soda-lime based, with some soda-potassium-lead compositions. The most common colourants are cadmium oxide, selenium and cryolite. A smaller number use gold, selenium with gold, or gold mixed with cryolite.



Figure 2.4: Example of a smoked glass from Gaivotas Factory. Photograph taken by the author (2024).

Black glass recipes, which make up 8% of the total, are divided into two categories: black glass and smoked glass (Figure 2.4). Black glass recipes are soda-lime based and include various oxide mixtures such as Ni-Co, Mn-Co, Co-Cr-Ni and Co, given the strong colouring power of cobalt. "Smoked glass" (*vidro fumado*) recipes also use cobalt and uranium in smaller amounts to achieve a greyish tone.

Finally, purple and aventurine recipes are the least common in this *arcanum*, making up 1% and less than 1% respectively. Purple glass recipes are soda-lime based and use selenium mixtures as the colouring agent. Aventurine recipes mention copper and chromium oxides, probably to achieve a green hue with metallic particles.

2.1.4 Northern Portuguese Glass Centre *arcanum* (NPGC)

The NPGC arcanum (1955) is the most recently discovered and has never been studied before (**Table A.1**). It contains 25 recipes, 21 of which are for glass, with the remaining focused on glass colourants (**Figure 2.5**). These colourants are mixtures of metal oxides, carefully separated and weighed in specific proportions without being melted. Although this is the smallest *arcanum*, it contains a wide variety of recipes, including at least one for each of the most used colours. However, it also contains a recipe which will not be examined here, as it was not possible to determine what colour it might be. As expected, there is a higher proportion of colourless glass recipes, as this type of glass seems to be the base for most productions. Nevertheless, understanding the other recipes and colours is also crucial.

Twenty-four percent of the recipes are for colourless glass, most of which are made from soda-lime glass, commonly called ordinary glass, with arsenic used as the fining agent. Most of the recipes use pebbles as a source of silica (known to be the purest source of silica [44], but they also use a combination of nickel and cobalt oxides to mask the greenish colour usually caused by iron impurities (the use of these two oxides also appears in the former two *arcana*). Notably, unlike the recipes for coloured glass, the composition of colourless glass does not include cullet. One of the colourless glass recipes is entitled as crystal glass but its composition differs from the well-known English crystal and consists of a mixture of potassium and lead glass [25].

The recipes for blue glass, which make up 19% of the total, are of soda-lime glass. One of the recipes is for blue with copper and the others are for cobalt on its own and for cobalt with copper. All the recipes mention the use of 35% cullet, and the vast majority do not mention the use of arsenic. This absence of arsenic may be due to the fact that cobalt is one of the most appreciated colourants by glassmakers due to its ease of use and homogenisation. Additionally, most of the recipes mention the use of pebbles, but one recipe divides the source of silica between pebbles and sand. Recipes with cobalt as the colouring agent are named as flash glass or dark blue glass. Copper recipes are named "marine" or "sky blue" (*azul celeste ou marinho*).

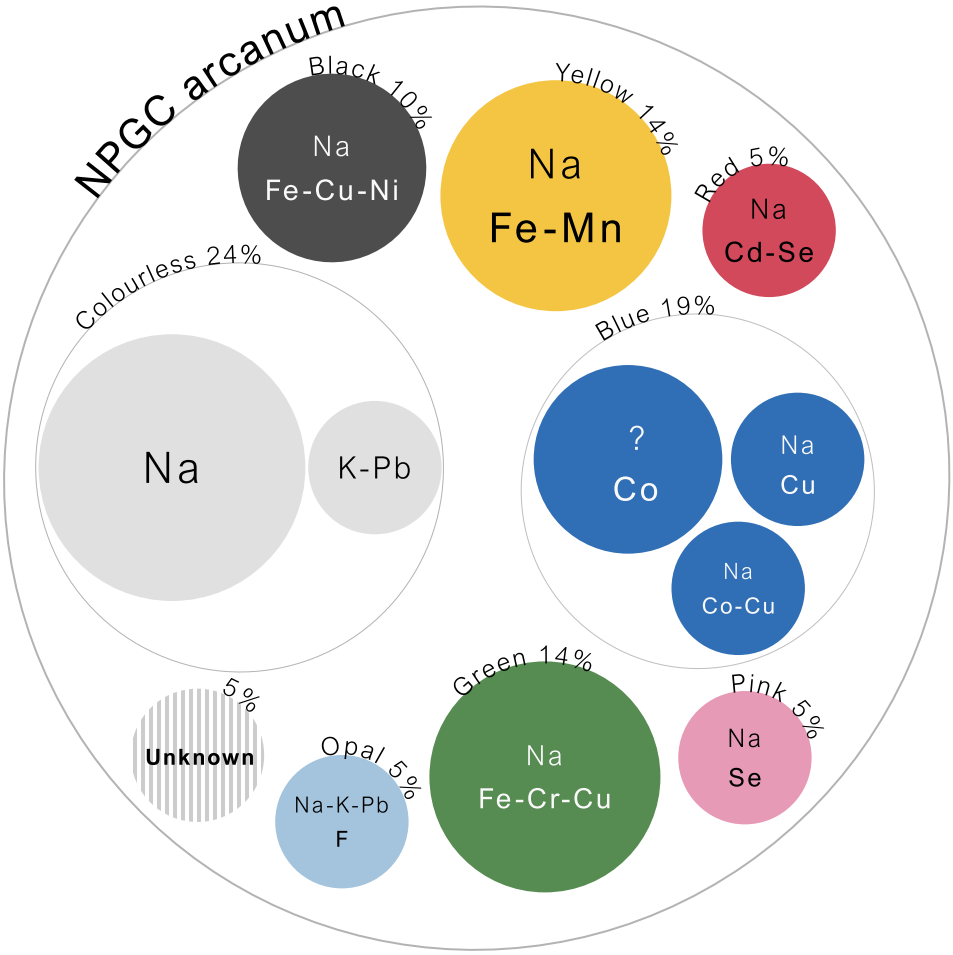

Figure 2.5: Circle packing chart with recipes from NPGC *arcanum*. Each circle shows the fluxes (top) and the colourant (in bold). Question marks mean that either the base/colouring composition could not be deciphered or there is no visible correlation. The size of each circle is proportional to the number of composition and colour recipes. The percentage value is rounded to one decimal place.

The green glass recipes account for 14% of the total and are all made from soda-lime glass. While they all contain the same combination of colourants—iron, chromium, and copper oxides—the proportions differ, probably resulting in subtle differences in colour. The recipes using pebbles do not mention arsenic, but the one that mixes sand and pebbles does. All the recipes contain 35% cullet, yet the names offer little indication of the types of objects this glass was intended to create, leaving its specific uses unclear.

Like other types of glass, yellow glass recipes use a soda-lime base and either pebbles or a 1:1 mixture of pebbles and sand as the source of silica. Yellow glass recipes account for 14% of all glass recipes and consist of iron and manganese amber glass. This combination of colouring agents is known for producing amber glass (the colour of a beer bottle) [39, 40], yet it is consistently referred to as yellow glass. Most of the recipes also mention the use

of 35% cullet and arsenic as a fining agent. However, one of the recipes includes corn flour, which may function as a reducing agent and help remove bubbles from the composition. It is important to highlight a significant difference between the yellow recipes from the NPGC and those in other *arcana*: in most cases, the source of iron is the sand itself. This reliance means that the recipe is almost ineffective without knowledge or control of the sand's origin. However, in this *arcanum*, sand is not used as the source of silica; instead, quartz pebbles are utilised. This allowed the glassmakers to have complete control over the amount of iron in the composition, likely making it easier to achieve the desired colour successfully.

The black glass recipes are very similar to each other, all being soda-lime glass with iron, copper, and nickel oxides as colouring agents. These recipes make up 10% of the total and all use the same proportion of cullet as the other coloured glasses. As with the others, pebbles are mentioned as the source of silica, and one of the recipes specifies that it is intended for buttons, which could indicate that it was for making clothing buttons or small decorations.

The last three colours in the *arcana*, each representing 5% of the total, are red, pink, and opal. The red and pink recipes are very similar, both using soda-lime glass with selenium as the primary colouring agent. The red glass recipe also includes cadmium and, for the first time, specifies the amount of cullet in kilos rather than percentage. The pink glass recipe, on the other hand, mentions the use of tin and 100% cullet. The opal recipe is a sodium-based glass with added potassium and lead. It includes 35% cullet and uses cryolite to create the opalescent effect. Cryolite contains fluoride, which causes a phase separation process, leading to the formation of fluoride crystals [40].

2.2 In-depth review and comparison

The MGF *arcanum* consists of a set of scans of notebooks numbered from one to five. The numbering associated with each digitisation was done in advance by the group that initiated the research on this set of notebooks [31]. Despite this numbering, the set is considered as a single object, a single *arcanum*, as it has always been preserved and interpreted as a cohesive set. All citations from this *arcanum* provided hereafter are free translations from the original Portuguese. The first notebook (MG1) is dated 1798 and contains the following sentence on its first page "Notebook of the compositions of Igualdo Pauletta and the samples are numbered, wrapped in papers in an old bean box". To date, no references have been found to a glassmaker or batch maker of this name, so it is impossible to confirm whether Igualdo was a worker in Marinha Grande, a visiting foreign glassmaker, or someone else entirely. However, similar information is repeated on the following page. It is written differently and the year 1798 is added (**Figure 2.6 (a)**). From this point on, the recipes are numbered consecutively from 1 to 55, and almost always include a reference to the sample of glass produced. For example: "This composition produced straw yellow glass, as shown in the sample". Following this note on the result, some recipes also include notes on variations that can be made with the remaining glass from that composition. For example: "Pouring a portion of tartar into it (...) made a glass that looks like silk". This notebook is written with a fountain pen. The pages are extremely clean and organised, with graphite lines ensuring that all the information is aligned and clean. Very few words have been scratched out, and there are no notes that appear to have been added later in pencil. Given its preservation, the lack of rush or hesitation in writing, and the orderly nature of the entries, this notebook raises many questions as to whether it is an original or a copy. On the other hand, it is clear from the recipes that have been tested and perhaps used, suggesting that it is likely that all the recipes will work.

The second notebook (MG2) begins on its second page with a sentence very similar to the one in MG1, which raised some curiosity (**Figure 2.6 (b)**). The recipes in this notebook are numbered from 1 to 32, with the date of the recipe next to each number, for example: "Composition made on 13 April 1798". Only a few recipes mention the existence of a glass sample of the result, but most include notes on additions and variations to the original recipes. The handwriting in this notebook is very similar to that of MG1, making it almost certain that they were both written by the same person. However, this notebook is a little more difficult to interpret, with erased words, ink smudges and a more uneven presentation. There are no corrections to the quantities given in the recipes, which again raises the question of whether this document is original. After extensive research and cross-referencing, it was discovered that notebook number 1 (MG1) is an extended copy of notebook number 2 (MG2). Most recipes are identical, but new ones have been added in between. Comments in the original recipes have also been clarified or revised in the MG1 version. Despite these small differences, and in accordance with the methodology of the various authors who have studied this *arcanum*, these have been considered as two separate

notebooks. Consequently, even the recipes that repeat quantities have been numbered individually and included in the total number for this *arcanum*.

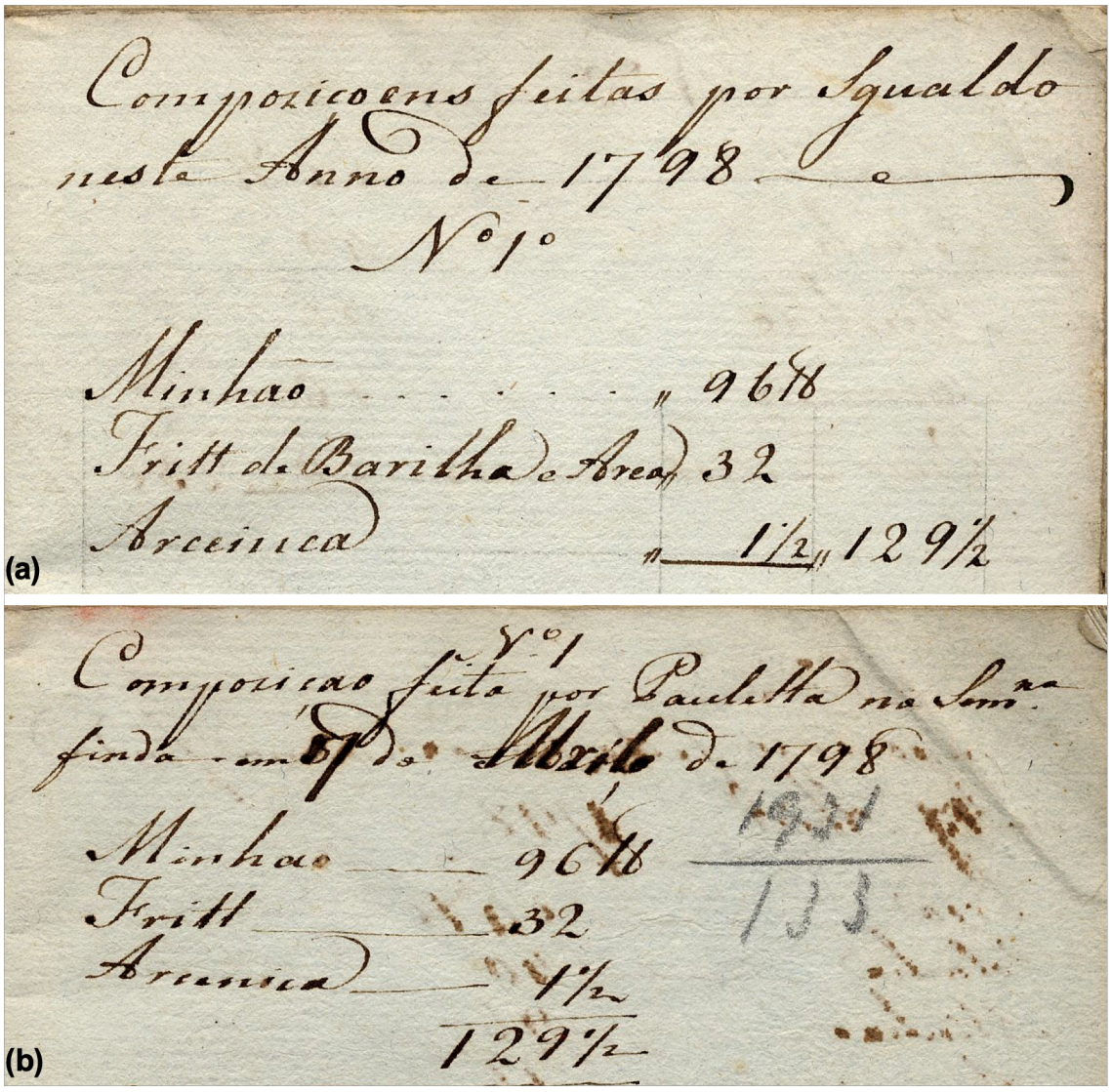

Figure 2.6: First pages with recipes, from notebooks MG1 (a) and MG2 (b). Both refer to Igualdo Pauletta. Igualdo (a), Pauletta (b)

Notebook number 3 (MG3) is the most distinctive of the set (**Figure 2.7 (a)**). It is laid horizontally, has no obvious information on its cover (as it has not been digitised), and the handwriting is different from the first two notebooks. There are no signatures, names or dates in MG3. It is relatively small, containing only 13 recipes, all presented in list form with titles, ingredients and quantities at the front. There are no comments about the results, and unlike the previous notebooks, there are no notes suggesting the addition of new ingredients to the leftover glass to create variations. As with the MG1 (**Figure 2.7 (b)**), graphite lines are visible to demarcate the writing area, and there are no erased words or corrections to quantities. The pages are clean and show no evidence of frequent handling, raising the question of whether this notebook was ever used in a working context,

or whether it originated from a meeting with another batch maker.

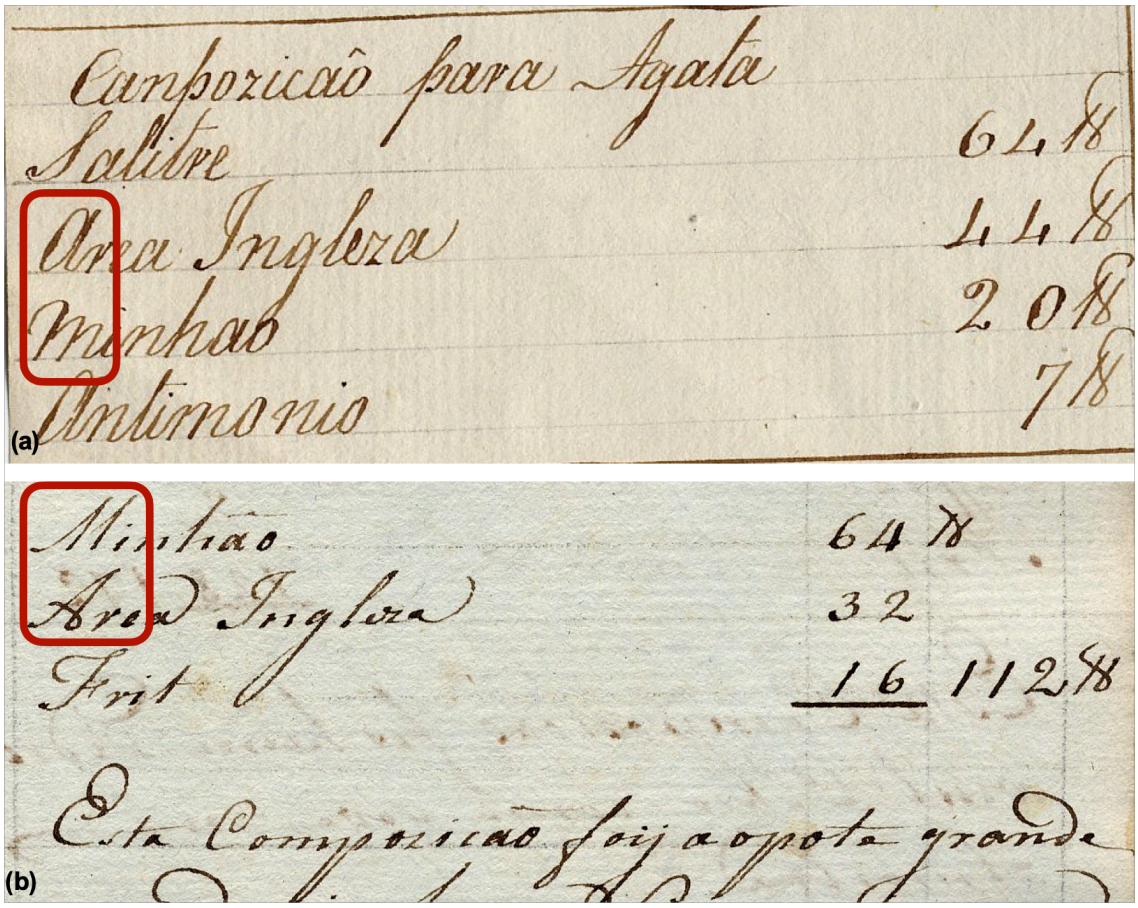

Figure 2.7: Difference in calligraphy between MG3 (a) and MG1 (b)

The remaining two notebooks in this *arcanum*, MG4 and MG5, appear to have the same handwriting. Notebook No. 4 (MG4) has the phrase "Compositions made by me Nr 2" on its cover. The recipes are numbered from 33 to 44, with notes indicating the intended colour of the glass. Most of the recipes are accompanied by brief observations on the results, suggesting that they have been tested. Although MG4 contains few corrections or scratched out words, its pages show signs of handling, including smudges, supporting the idea that it was actively used during the testing phase. The notebook is unsigned and undated, but two recipes refer to a German individual with the surname Dehn [3], suggesting that the recipe was either created or shared by him (**Figure 2.8 (a)**).

The final notebook, MG5, is dated 1793, as indicated on the cover, and entitled "Notebook for various souvenirs belonging to Factory Nr 1". Inside, the recipes are numbered from 1 to 26, suggesting that notebook number 4 is a continuation of this one. The layout follows the same format as the others, with recipe numbers, glass type instructions and comments on results or possible adjustments. However, unlike the previous notebooks, MG5 contains mainly recipes for making crystal or colourless glass (**Figure 2.8 (b)**).

[3]Dubious word. Handwriting is difficult to decipher

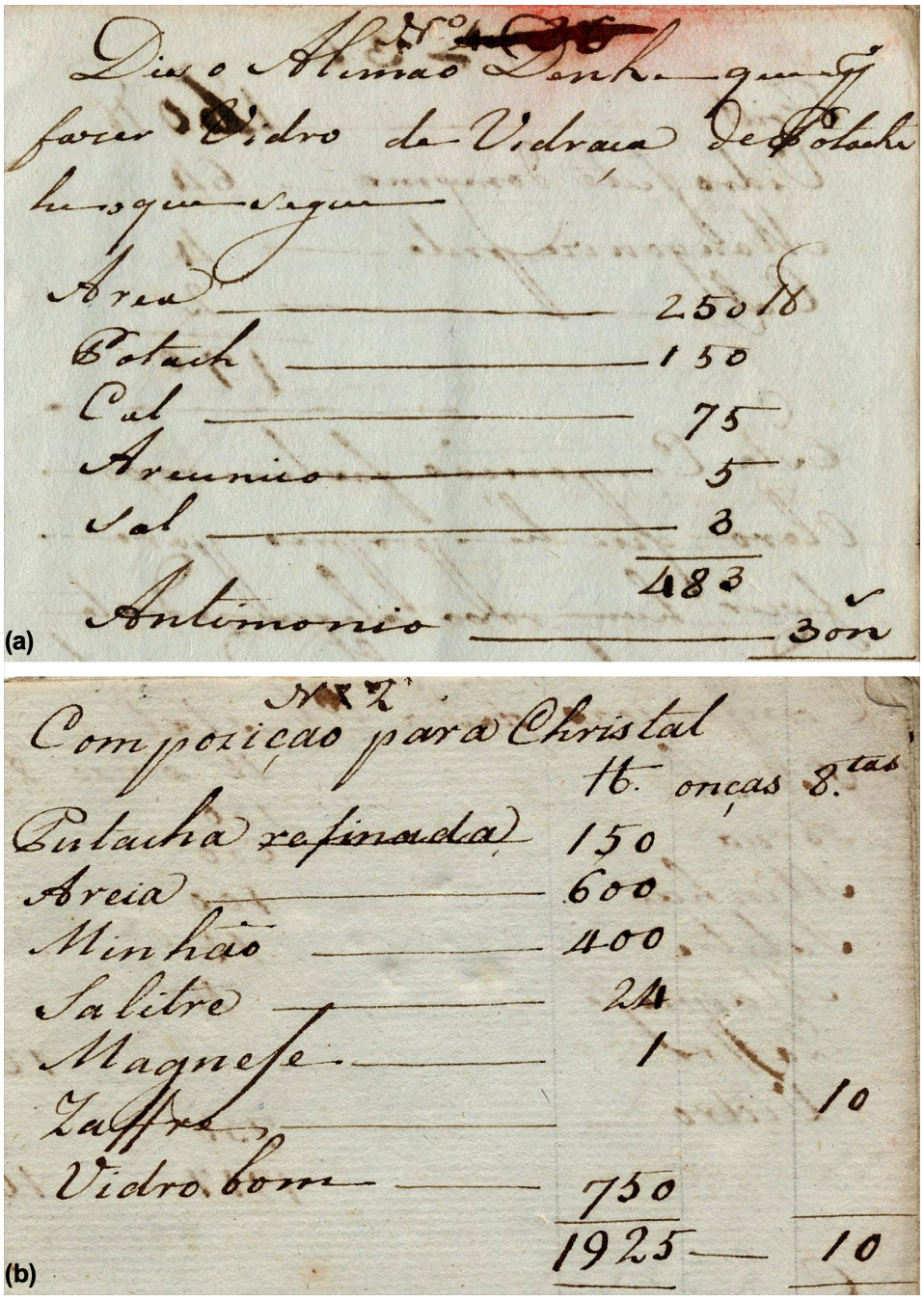

Figure 2.8: Pages from notebooks MG4 (a) and MG5 (b). Reference to German Dehn in MG4 (a)

In addition, MG5 contains four pages of information relating to glass production, such as instructions for identifying false potassium carbonate by taste, flux quantities for specific sands, and even a colour wheel. On one of these pages the initials "G.S." are visible, which, when compared with other factory documents, appear to belong to Guilherme Stephens (**Figure 2.9**). However, the handwriting on these pages differs from the rest of the notebook (**Figure 2.8**), making it impossible to confirm that MG4 and MG5 were written by Stephens.

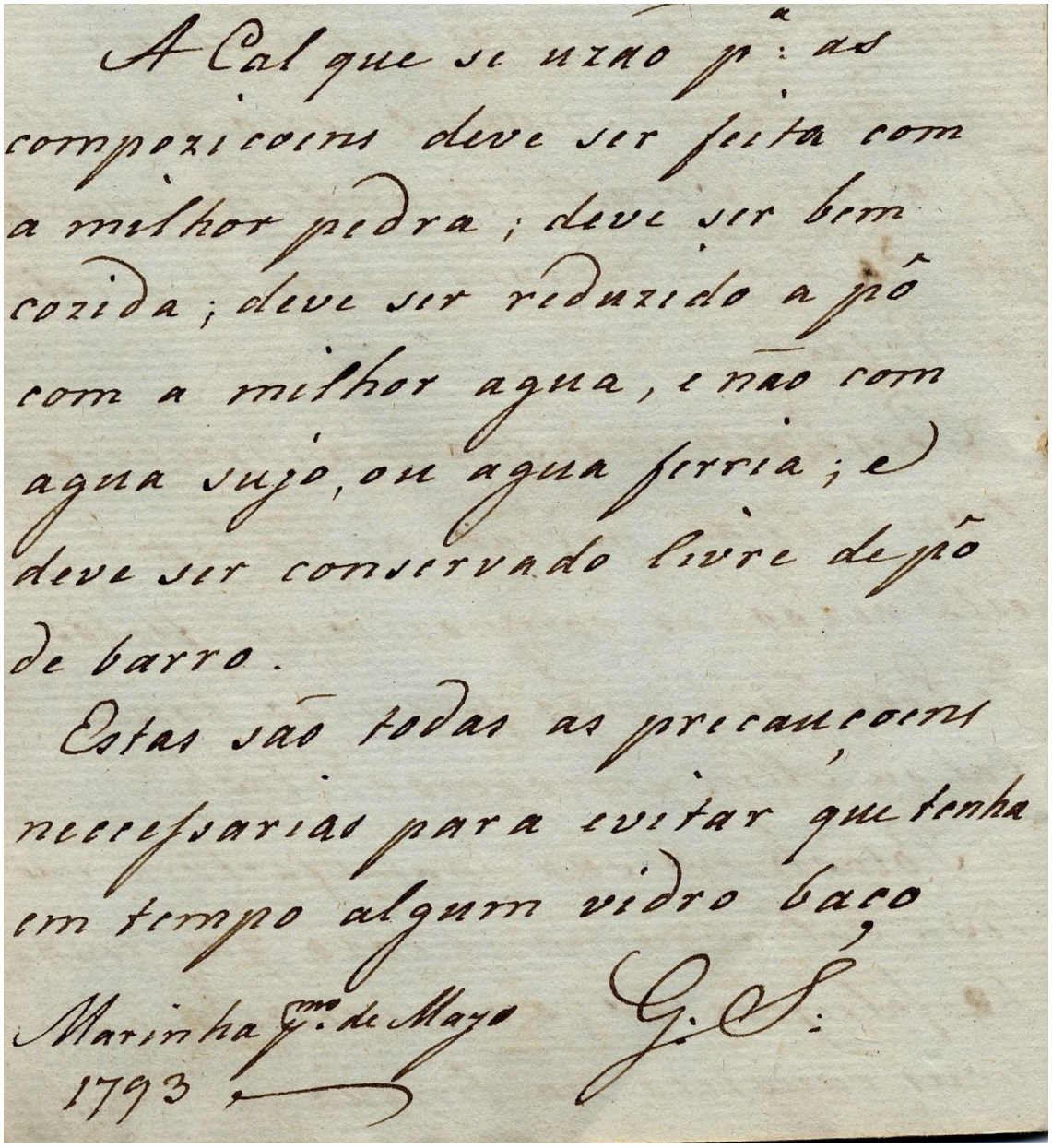

Figure 2.9: MG5 page signs with G.S.

Regarding the COG *arcanum*, the organisation and legibility are completely different. This is undoubtedly the most difficult *arcanum* to read and understand, not only because it has two authors and therefore features two calligraphies and two different methods of organisation, but also because it is an *arcanum* that is not at all like the others in terms of the terminology used.

The recipes belonging to João Augusto de Castro (1875-1900) make up the vast majority of the *arcanum*. Their organisation is almost always the same: the title, the ingredients written mostly in chemical formulae, the respective quantities, and a final comment on how long it took to refine, the final colour, and what type of furnace it was produced in. It also contains many abbreviations and jargon that are difficult to interpret. This is the first notebook of its kind in Portugal in which the raw materials are represented using chemical formulae. This raises questions about the kind of chemical knowledge these professional glassmakers had, where they learnt it, and how they used it in their industrial practice. Did they use chemical formulae because it was the way they had been trained in the practical knowledge of glassmaking, unaware of their scientific significance? Or did they use them to facilitate communication, understanding, and discussion of the recipes among their peers, especially with foreign glassmakers, since it was common for the *arcana* to contain recipes from glassmakers of other countries who visited Portuguese factories?

The chemical notation used is close to that put forward by the Swedish chemist Jöns Jacob Berzelius (1779–1848), who introduced one- and two-letter symbols to represent the chemical elements based on their Latin name and and superscript numbers to represent the proportions of combination in a compound. Berzelius used electrochemistry to determine the electrical character of each element, thus explaining their chemical behaviour. For him, there were two types of matter: imponderable and ponderable bodies, the latter constituting two classes – electropositive and electronegative (later anions and cations, respectively)— depending on whether they were deposited on the positive or negative pole during electrolysis [45, 46]. For Berzelius, oxygen was the most electronegative element, and just as different atoms had different electrical natures, radicals—groups of atoms that remain unchanged during a sequence of reactions—also have electronegativity and electropositivity. Thus, each acid would have a characteristic oxygen-containing radical, with all acid radicals being electronegative, as they all migrated to the positive pole during electrolysis, while metals would be electropositive, as they migrated to the negative pole. All chemical compounds would have an electronegative and an electropositive part that would remain linked by electrochemical affinities, which was the foundation of electrochemical dualism and aligned with the binary nomenclature of Lavoisier and co-authors of the *Méthode de Nomenclature Chimique* (1787). Although Berzelius's theory proved problematic in organic chemistry, it was particularly effective in the study of inorganic compounds, especially salts. These would result from the combination of electropositive basic oxides with electronegative acidic oxides, giving rise to neutral salts, which, however, could still have a residual charge that would allow them to hydrate and give rise to complex salts [45, 46].

Electrolysis, the quantitative and qualitative analysis of substances, as well as Dalton's atomic theory, the formulae and symbols proposed by Berzelius, were integral parts of his widely translated chemistry textbooks, shaping the chemical discourse as they were later incorporated into the writing of chemical equations its use becoming widespread from 1835 onwards. The formulae in the *arcanum* follow closely the logic of Berzelius's electrochemical dualism, with the positive radical written first and the negative second, but in a peculiar way whose logic is important to understand. Taking as an example the page of the *arcanum* referring to a recipe for crystal glass (**Figure 2.10**), the possible interpretation, though always problematic—especially since there is no criteria used consistently by the glassmaker when writing chemical formulae—could be the following, in the order of the compounds presented:

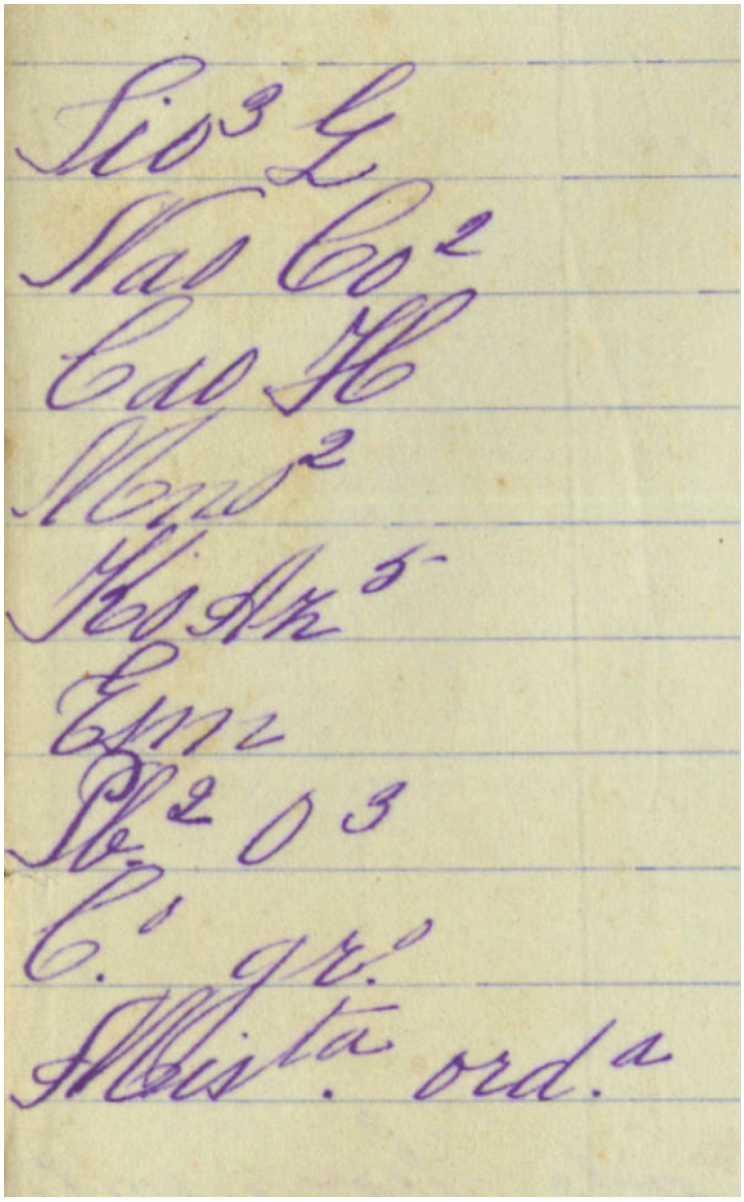

Figure 2.10: Ingredients from the COG *arcanum* recipe for making crystal glass

SiO^3L: This is obtained by the reaction between silica or silicon oxide SiO_2 (obtained from sand) and sodium carbonate (Na_2CO_3 in the current formula), formulated below as $NaOCO^2$, according to Berzelius' notation. However, the glassmaker only writes 'half' of the formula, based on what is relevant to that same manufacture, followed by an L which refers to liquid, as the silica is fused in the manufacturing process.

$NaOCO^2$: In the same vein, the second compound is sodium carbonate, today represented Na_2CO_3, but then considered the combination of a positive oxide, NaO, and a negative oxide, CO^2. It should be noted that in 1875, concepts such as valence, ion, oxidation state, and oxidation number were not yet defined, indicating that the glassmaker only considered metals to be positive, without considering the oxidation number.

CaOH:This was then the representation of calcium hydroxide, today currently formulated $Ca(OH)_2$, related to the calcium oxide used to give the glass stability.

MnO^2: Manganese dioxide, today formulated MnO_2, used in the manufacture of glass to give it a purple colour.

$KOAz^5$: "Az" corresponds to nitrogen, the symbol used in France, and in Portugal (azoto), to represent this element, whose universally accepted symbol is N. It should be noted that, on page 13 of the same *arcanum*, the glassmaker refers to this formula $KOAz^5$ as saltpeter. It is therefore potassium nitrate, KNO_3. The number 5 could be an oversight, or a sign of poor knowledge of chemistry, or even an expedient to deliberately confuse and not completely reveal the recipe.

Next, Esm, seems to be an abbreviation for a possible industrial slang term.

Pb^3O^3: A lead oxide, possibly lead tetroxide, in present day notation Pb_3O_4.

Interpreting glass recipes in the *arcanum* from a scientific point of view is far from trivial for several reasons: the use of chemical notation is not always associated with in-depth knowledge of this science on the part of the glassmakers, and it is difficult to discern the criteria used by each of them for writing formulae, taking into account the scientific context and knowledge of the time in which they lived. Additionally, the secret nature of these recipes may lead us to consider inaccuracies in writing formulae, even in the light of the knowledge of the time, as artifices used by glassmakers to create confusion among their competitors. A few more factors should be emphasised in relation to the first part of this *arcanum*, corresponding to the first author. The difficulty of reading is sometimes increased by the fact that some pages contain up to four recipes at the same time, condensing too much information. Some of the recipes appear in table format, and in these situations, their interpretation is totally impossible due to the excessive abbreviation of terms. Another characteristic of these recipes is that sometimes there are ingredients with three or four variations in the quantities that can be used, which also makes it difficult to interpret them correctly to obtain the result described in the notes. As for the second author, Augusto de Oliveira Guerra, his contribution is minimal (1900-1925), with no indication of a change of

author (this conclusion is reached by comparing the handwriting and the way the recipes are written). He also writes more than one recipe per page, without commenting on the result or the furnace used. He always writes the ingredients in full, using their common names (for example, he refers to cobalt only by the metal, not by its oxide), and in most cases gives only one option for quantities. As far as this *arcanum* is concerned, when the two authors use it, there are hardly any corrections or negative comments about the recipes. There is no mention of a particular recipe not working, or of too much or too little of an ingredient, which is natural in this kind of document, where the notes are the result of experience, not always successful. This may indicate that the recipes were not created by one of the authors, but were passed on to them and they simply wrote them down and reproduced them.

The GF *arcanum* is a true notebook that perfectly fits the definition of an *arcanum* described in the introduction of this thesis. It was handwritten with a pen in a casual, carefree style. The notebook contains comments and corrections, indicating that it was undoubtedly a practical manual in use, although it is not possible to confirm whether it was employed directly in the production of this glass factory. Some corrections suggest that the compositions were initially copied from another source, tested, and only after testing were adjustments made, and the glass recipes optimised. The handwriting remains consistent throughout, suggesting that the author of the *arcanum* did not change. However, the *arcanum* becomes noticeably more disorganised towards the end.

Although there is more than one recipe per page, the recipes are generally legible and easy to decode. This clarity does not extend to the final pages, where some recipes are difficult to interpret, with some written over pencil annotations related to other glass production processes (**Figure 2.11**).

From a certain point onwards, dates are noted for each recipe—a feature not observed in the other *arcana*. Additionally, the *arcanum* includes numerous comments, not only about the quality of the glass or the recipes themselves but also about the function of the glass. These comments address whether the glass composition was suitable for cutting, common use, flash glass, and other purposes. However, there is no mention of melting processes, such as temperatures, times, atmospheres, kiln types, or the final appearance of the glass (e.g., bubbles). This absence of information about melting could suggest two possibilities: either the factory employed a standardised furnace atmosphere and process, making it unnecessary to record such details, or the roles within the factory were highly compartmentalised. In the latter case, the person responsible for recording recipes may not have been involved in the melting process, resulting in no overlap of knowledge between these two functions.

As for the terminologies used, this *arcanum*, being the most recent, employs relatively common and understandable terms. When referring to specific ingredient mixtures, the ratios are listed on separate pages. Chemical formulae are used to identify compounds, and

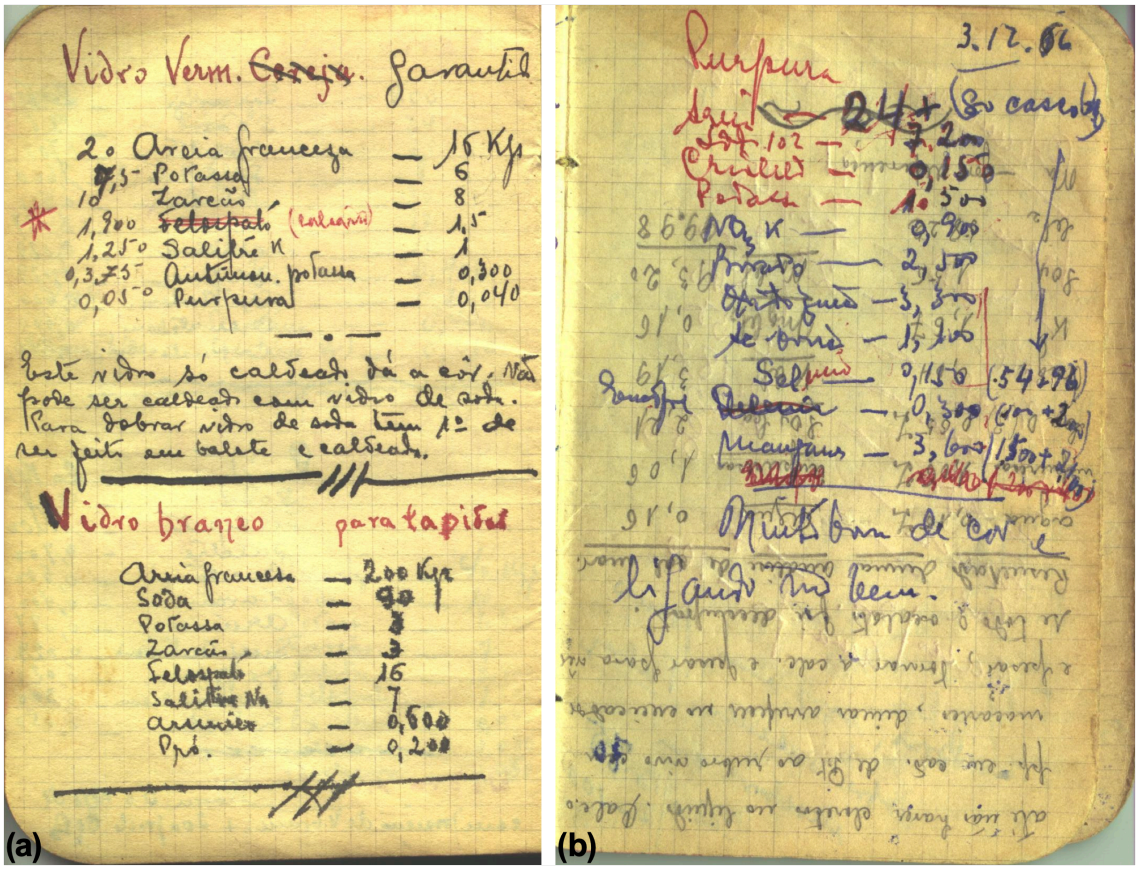

Figure 2.11: Example pages from the beginning and end of the Gaivotas factory *arcanum*

in most cases, the terminology aligns closely with that used today.

The NPGC *arcanum* is highly organised and meticulously clean, with only one recipe per page. It is unsigned but dated on the first page (**Figure 2.12**). This small, pocket-sized notebook, written in pen on squared pages, appears to have been carefully structured. Some recipes include minor corrections in pencil, but none provide information about results, furnace programmes, temperatures, or similar details. It is unlikely an original document; the recipes seem to have been copied and reorganised, as they are systematically grouped by colour.

All coloured glass recipes include 35% cullet. In contrast, among the colourless glass recipes, one for ordinary glass does not include any cullet. This suggests that this ordinary glass may have served as the base composition, acting as cullet and enhancing compatibility between the colourless and coloured glass batches. The organisational structure of the pages is consistent: each begins with the recipe title, followed by the general composition, the percentage of cullet, the list of ingredients for the bowl (smaller quantities, including colouring agents, thinners, and so on), and a final note. This final note almost always says, "1st Potting (cullet): Pots = 75 k and *Safroeiros* [4] = 25 k."

[4]Specific size of a glass melting crucible

The recipes are numbered sequentially, although recipes 9, 12, 17, and 22 are missing. The numbering appears to have been added later using a different pen. Recipes for some colouring mixtures are listed separately. For instance, parsley green and *verdino*[5] colourants are used in distinct ways: Parsley green is a colouring agent for glass of the same name, while America green glass combines parsley green with *verdino* as colourants. It is also worth noting that nearly all the recipes mention pebbles as the source of silica, which is consistent with preliminary studies conducted on raw materials from the factory's region [44].

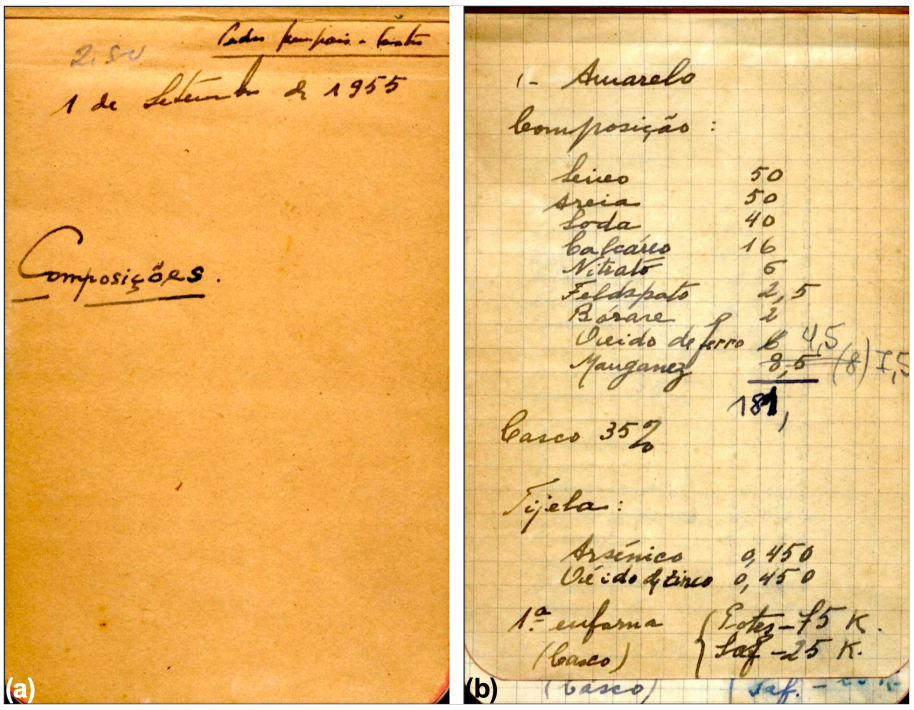

Figure 2.12: First and second pages of the Northern Portuguese Glass Centre *arcanum*

[5]Italian word for green glass.

3

Glass and its recipes

3.1 Glass: Definition and Main Components

The first glass synthesised by man was used to make beads or to model in the form of sharp-edged tools. As time passed, the production method evolved to allow greater for a control over the shape of the objects created. They then began to make bottles by wrapping strips of glass around a compacted sand mould. After the glass cooled, the sand was removed from the interior, leaving a hollow core in the translucent-walled glass (known as core-formed technique) [47]. A few years later, around the 1st century BC, the invention of glass-blowing opened up even more uses for glass. The quality of glass improved dramatically, leading to the production of glass cups and even flat glass, allowing for buildings to have windows. Then came coloured glass, the technique for which was often a family secret passed down from generation to generation. This method of passing on knowledge meant that some recipes were lost over time, only to be rediscovered years later [47].

Why are we so attracted to glass objects? This is probably because of the way they interact with light. Very few materials in nature can transmit visible light in the way that glass can. Metals, for example, are opaque, while many liquids are transparent. Among solids, only a few are transparent, such as diamonds, emeralds, and other precious stones. Our fascination with glass probably comes from its ability to display qualities of different states: it is not quite solid, liquid, or gas; yet it combines elements of all these states in a way that no other material does [47].

A possible definition of glass: "an amorphous solid completely lacking in long-range periodic atomic structure and exhibiting a region of glassy transformation behaviour" [47]. Using a simpler, purely structural definition, glass can be defined as any solid without a crystalline structure [48]. This type of structure was first studied by Zachariasen, who proposed the continuous random network (CRN) model [48]. This model can be summarised by the following four rules [47–50]:

- An oxygen atom (O) should not be bonded to more than two network-forming cations (A). This means that each oxygen atom is linked only to two cations, which prevents excessive bonding with other cations and allows the structure to remain open and flexible.
- The coordination number, n_{AO}, of oxygen around network-forming cations must be

small, typically 3 or 4. This ensures that oxygen atoms are surrounded by a limited number of cations, contributing to an open network structure and avoiding excessive rigidity.

- The oxygen polyhedra should share only corners, not edges or faces. This rule ensures that the polyhedra are connected in a way that maintains the flexibility of the network, preventing rigid connections and allowing for an open structure.

- For a three-dimensional network, at least three corners of each polyhedron must be shared. This ensures sufficient connectivity between the polyhedra, forming a continuous and stable network necessary for glass formation.

On the basis of these rules, it is possible to classify and describe the three main constituents of glass. **Network formers**: These are oxides with well-defined oxygen coordination polyhedra, allowing them to vitrify due to their network structure. Some examples of network formers are SiO_2, GeO_2, B_2O_3, P_2O_5, and As_2O_3. Glass formers generally have strong bonds and low coordination numbers, with tetrahedral coordination (value of 4) being the most common [48].

If a second oxide with weaker, ionic bonding is added, it can cause some depolymerization of the network. For example, adding Na_2O breaks some of the network bonds. The oxygen from Na_2O fits into the network by breaking silicon-oxygen-silicon bridges. A single bridging oxygen (BO), bonded to two silicon atoms, is replaced by two non-bridging oxygens (NBOs), each bonded to one silicon atom. In this process, the NBOs carry a negative charge to balance the positive charge from the Na^+ ions. These second oxides modify the glass structure but do not become part of the network themselves, which is why they are called **network modifiers**. Modifiers, in contrast, have weaker bonds and higher coordination numbers, typically greater than four. These high coordination numbers, combined with a lower cation charge, result in much weaker M-O bonds. This is why modifiers profoundly alter the properties of the glass. For instance, the addition of Na_2O generally reduces viscosity, glass transition temperatures, and melting conditions [48].

In addition to formers and modifiers, there are also conditional glass formers, also known as **stabilisers**. These oxides have an intermediate structural role between formers and modifiers. They do not readily form a glass on their own but can do so in combination with a modifier. Conditional glass formers have geometrically well-defined coordination shells and give rise to structures that can be described as random networks [48].

Two other types of ingredients commonly found in glass are fining agents and colourants. These have complementary functions in glassmaking: although they are not essential for glass formation, they improve the final properties of the material.

The primary function of **fining agents** is to remove bubbles from the batch that form as a result of the decomposition of added compounds (e.g. Na_2CO_3 to Na_2O) [47]. These

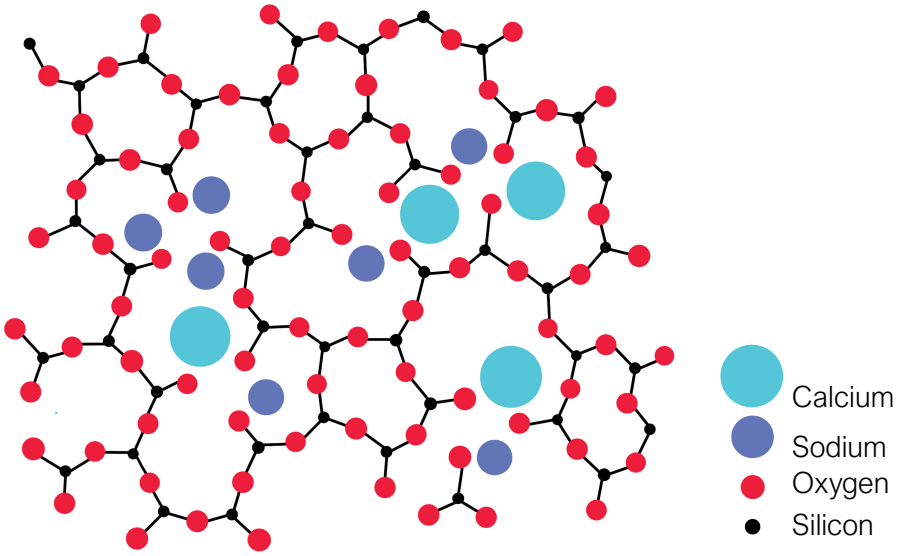

Figure 3.1: Graphical sketch of the glass structure, with network former, modifier and stabiliser represented.

agents can be metal oxides, such as As_2O_3, or organic compounds that facilitate bubble removal during combustion [47].

Colourants, on the other hand, are always metal oxides. The way in which they impart colour to the glass depends on the size of the particles and their specific properties [40, 42]. The most common type of colourant consists of colouring ions, usually d-d transition metals, which produce different colours depending on their valence state [42, 51]. In addition, nanoparticles can act as colourants: in a colloidal state they produce effects such as ruby red or silver yellow glass, while in crystalline dispersions they produce metallic sparkles visible to the naked eye, as seen in aventurine glass [40, 42].

3.2 Methodology: Reproduction of Recipes

3.2.1 Literature review

In response to the lack of systematic research focusing on *arcana* and their significance in the history of glassmaking, a new methodology has been developed by drawing inspiration from similar studies about glass historical reproduction. This approach aims to contribute to glass studies based on *arcana* and highlight their significance in the history of glass production in contemporary research. The bibliographic selection focuses on studies from the last ten years that reproduce historical glass recipes, whether from batch books or treatises, with a particular emphasis on research published in English.

By taking into consideration studies that use raw materials from geographical locations where historical glass objects were found or from locations mentioned in historical documents, as well as studies that gather raw materials—mainly from Europe—to ascertain

whether these or laboratory reagents were used to produce historical glass artifacts. In effect, the use of natural raw materials or of reagents was one of the first questions that arose when this research was initiated. Thus, by focusing on studies directly aligned with the reproduction and analysis of historical glass compositions and materials, this selective approach ensures that both the relevance and cohesiveness of the research framework are maintained.

The use of a practical and interdisciplinary approach to the study of historic glass production, its composition, use, and context has become increasingly common, as evidenced by most of the available studies discussed here, which were published in the last five years. Some studies have focused on this very point: the viability of experimental archaeology to understand the production of glass from a certain period and place [52, 53]. As mentioned above, all studies presented in **Table 3.1** will be discussed as they all include glass reproduction, with different approaches and purposes.

In **Table 3.1**, the columns are organized as follows: reproduction based on historical recipes, in which the authors have used a written source of historical recipes as a starting point and subsequently designed their experiments accordingly; reproduction based on historical compositions, in which the authors began by characterising a particular historical glass composition, and tried to understand its production technology; reproduction using natural raw materials, based on i) the chemical characterisation of a historical glass ii) historical texts that mention a specific material or region iii) glass collected from archaeological sites; finally, reproduction by using laboratory compounds, whenever authors departed from a historical text or chemical composition and tried to simulate the raw material in the laboratory, with all the impurities added on purpose and in a controlled way.

One of the main conclusions drawn from the literature is that there are two basic approaches: the reproduction of glass recipes from manuscripts, treatises, *arcana*, and similar sources and the reproduction of historical glasses based on the chemical characterisation of historical objects. A third subgroup can be added to the former, regarding the reproduction of glass based on where the raw materials are believed to have come from.

In this last group various studies are included, which have focused only on the use of historical raw materials [57–61, 68] Silvestri and co-workers' research was one of the first attempts to use historical raw materials with the intent of confirming or infirming the use of the Campanian littoral sand for Roman glass production [68]. This specific source was mentioned by Pliny in his texts with instructions on how to evaluate the quality of these raw materials for glass production with Roman technology. The sands were collected from five locations on the Campanian nearshore and then melted with a mixture of sodium minerals, simulating natural natron (a naturally occurring mixture of sodium carbonate decahydrate and c.17% sodium bicarbonate with traces of sodium chloride and sodium sulfate). By producing a frit first, this was then melted again to obtain the final glass. They obtained reliable results with successful reproductions and some of the glasses are

Table 3.1: Table listing published studies of historical glass production and the employed methodologies [6, 8, 9, 11, 44, 52–69].

References	Historical recipes	Historical composition	Raw materials	Laboratory compounds
Bandiera, M. et al. 2021 [7]; Bandiera, M. 2021 [45]	X			X
Bianchetti, P. et al. 2000 [46]		X	X	X
Bidegaray, A. I. et al. 2019 [47]		X		X
Brems, D. et al. 2012 [49]; Brems, D. et al. 2012 [48]			X	X
Coutinho, I. et al. 2022 [40]		X	X	X
Dussubieux, L. et al. 2022 [50]			X	
Govantes-Edwards, D. J., Duckworth, C. N., and Córdoba, R. 2016 [43]	X		X	X
Hagendijk, T., Vilarigues, M., and Dupré, S. 2020 [8]	X			X
Jackson, C. M. et al. 2018 [51]			X	X
Jackson, C. M. and Smedley, J. W. 2004 [52]; Jackson, C. M., Booth, C. A., and Smedley, J. W. 2005 [53]			X	X
Ma, Q. et al. 2021 [54]		X		X
Palomar, T., Hidalgo, R. J. D., and Vilarigues, M. 2018 [5]	X			X
Pánová, K., Rohanová, D., and Randáková, S. 2020 [55]; Pánová, K. et al. 2021 [56]	X	X	X	X
Paynter, S. and Dungworth, D. 2011 [57]		X	X	
Paynter, S. and Jackson, C. M. 2018 [58]		X	X	X
Pearson, J. et al. 2021 [44]	X		X	X
Santos, C. R. et al. 2020 [10]	X			X
Silvestri, A. et al. 2006 [59]			X	X
Vilarigues, M. et al. 2023 [60]	X			X

even chemically comparable to some Roman glasses, which reiterates the importance of this type of study.

Brems and co-workers [57, 58] carried out an extensive collection of raw materials, like sand, to demonstrate the possibility of Roman glass production in specific regions of the Western Mediterranean (Spain, France, and Italy) based on historical references from this period and the abundant presence of glass objects. They aimed to test the possibility of obtaining a typical Roman natron glass composition by using the collected sands and adding natron that they had prepared. The choice of the source for collecting raw materials was based on Pliny's text, as he mentioned the existence of glassmaking in those regions, despite the lack of archaeological evidence. The result is that glass could only be obtained from six out of the 178 collected sands, indicating that suitable sand for glass production is scarce and sometimes references in literature are vague and cannot always be taken at face value or followed to the letter.

Jackson and co-workers' research focused first on the ashes used for glassmaking and then on natron, and in both cases, they showed the importance of a specific and appropriate raw material. Regarding the research on the most suitable plant types as sources of alkali ashes, with a particular emphasis on those used in the Middle Ages, the authors showed the importance of plant selection in subsequent operations, including the proportion of other raw materials and the fusion process. The team tested whether it was feasible to detect the specific source of ashes through analysis and concluded that predicting the resulting glass composition through the presence of minerals in raw material is feasible, but the reverse is not. The research on the use of a specific natron source in Roman glass production led them to successfully demonstrate the feasibility of producing glass without any prior treatment and utilizing the technologies available during the Roman period. This production became possible only after unravelling the reactivity of each component and understanding its contributions to the vitreous matrix [60–62].

Dussubieux and co-workers aimed to uncover the organization of the ancient glass industry in India, given the widespread trade of glass beads throughout the country [59]. To this end, the authors gathered reh, a sodic efflorescence, and attempted to make glass from it, as there are references suggesting its use as the sole ingredient in glassmaking. Unfortunately, they were unsuccessful in reproducing any glass, possibly due to the season chosen for collecting raw materials (the authors noted that the season affects the chemical composition of the soil) or the laboratory glass reproduction protocol. Lacking information on the glass melting protocol, including temperature, soaking time, and atmosphere, they experimented with a higher temperature than they believed would be used for a brief period—1200°C for three hours, instead of several days at approximately 1000°C [70]. This resulted in a semi-vitrified material, which was not considered a successful glass production.

Recently, Coutinho and co-workers focused on the collection of silica raw materials from regions in Portugal close to the archaeological sites where large amounts of glass objects

were found [44]. The study had the main objective of identifying possible silica sources used in the seventeenth century to produce glass in Portugal. Glass objects that circulated in Portugal in this chronology are characterized by high alumina levels ($4<Al_2O_3<6$ wt. %), which does not find parallels outside the Portuguese mainland. Lacking the archaeological excavation to find coeval furnaces, exploring possible silica raw materials was pointed out by the authors as a way of studying glass provenance. Sands and pebbles were collected from six distinct Portuguese geographical locations (near the Mondego River in Coimbra). Subsequently melting experiments were conducted by adjusting the amount of sodium oxide, to act as a flux, to align it with the analysed historical glass objects. The efforts resulted in a successful melting of glass in all samples, and it was possible to identify similarities in terms of trace elements between the used sands and those used in historical glass objects.

When analysing research on the reproduction of glasses based on the characterisation of historical glasses, it stands out that most studies have focused on technology and on how to reach a certain result, such as on how to obtain different colours on glasses with a similar composition [55, 56, 64–67]. Such are the cases of the articles published by Bianchetti and team [55], Bidegaray and team [56] and Paynter and co-workers [66, 67], who focused on the study of a specific technique or technology. Bianchetti and co-workers had the objective of reproducing an Egyptian green frit with laboratory prepared and natural raw materials in order to achieve a result compatible with Egyptian technology. The research has shown that it is possible to reproduce an Egyptian green frit that is historically compatible with the originals, by using both the original raw materials and laboratory reagents as they obtained a mineralogical characterisation equivalent to the original technique. By considering the resources of the Egyptian period, the team paid special attention to the tested furnace temperatures, as this factor is fundamental for historically accurate reproduction.

Bidegaray and team, on the other hand, focused on the Roman period and on understanding how purple manganese glass was produced since historical objects from this period and with similar compositions show a purple colour while others are completely colourless. They defined a base-composition by resorting to historical glasses and evaluated various parameters (such as different oxidation states of the colourants, the ratio between them, the addition of organic compounds, and so on) in a systematic and controlled way to understand what imparts the colour and how. It is worth noting that the authors were methodical and clearly explained each of the variables and methods, which helped in understanding the experiment and how to extract information from each parameter. They concluded that the oxidation state of the materials added was extremely important and that in reducing the manganese to the desired colour, it was imperative to add a compound to the mixture, such as charcoal, that would enhance this reduction. Having demonstrated that a combination of factors is necessary to obtain manganese purple, the team also points out that this type of glass could only have been made by the best and most highly trained and knowledgeable glassmakers. This highlights the extensive empirical knowledge of the glassmakers, derived from trial and error, mutual interactions, and years of experience, which enabled them to

recognize that even a minor alteration in composition, often imperceptible in the recipe (such as the oxidation state of a specific element, as they used natural raw materials and not chemical compounds) would yield a different outcome.

Paynter and Dungworth [66] carried out research with the purpose of recreating a HLLA glass composition made with a frit using plant ash and sand to compare it with remains found in an archaeological context dated to the seventeenth century. They used exclusively natural raw materials—plant ash and beach sand—and after melting, the crystalline phases from the obtained glass samples were observed and characterised to then compare results with the archaeological items. They concluded that despite the similarities between the frit they had produced, and glass attributed to the region under consideration, the team believed that the production residue is in fact an intermediate between frit and fully molten glass, and therefore the need to review the methodology for further conclusions was recognized. Paynter and Jackson [67] focused on the study of amber glass from the Roman period to understand the technology involved, and how this glass was marketed and might have been used by the glassmakers. Always working based on the composition of the historical glass, they made reproductions using natural raw materials and chemical reagents, testing different percentages of iron and charcoal, as the balance between the two is one of the key factors in controlling the final amber colour. They concluded that since the iron content in the historical samples is quite low, the presence of this metal in the glass composition had to be a contaminant and not a deliberate addition. However, because it is so low ($<$0.5 wt. %), it is worth noting that the glassmakers certainly had a wide-ranging knowledge about the raw materials specific to produce amber glass. The authors have succeeded in reproducing amber glass and concluded that the iron and carbon contents are extremely important, as is the presence and use of sulfates to form the compound that imparts the colour. Due to the sensitivity of the colour, Paynter and Jackson also argue that, unlike other glasses from the Roman period, the production process for amber glass followed a different approach. In the Roman period, raw materials were typically melted in primary furnaces to produce glass chunks, which were then distributed across the empire. These chunks were later remelted and shaped into objects in secondary glass furnaces. However, in the case of amber glass, the colour was produced and immediately used to make objects, rather than being transported in chunk form. Although amber glass can undergo a second fusion, it is not the most suitable colour for excessive remelting and reuse.

Panová and co-workers [64, 65] focused on the development of Bohemian glass from the fourteenth to the eighteenth century, thus covering three styles—Gothic, Renaissance, and Baroque—and consequently distinct compositions of Bohemian glass, with the aim of dating glass objects in the almost absence of written sources on the subject. To reproduce the glass compositions, they selected raw materials taken from the archaeological contexts of the historical objects and adjusted them with laboratory compounds when necessary. The team concluded that Bohemian historical glasses from this chronology were made according to a simple recipe, which was developed over time with the addition of more compounds and

better control over the purity of the raw materials. The three compositions corresponding to the Gothic, Renaissance, and Baroque model glasses were successfully reproduced and two had a similar composition to the historical glasses.

An approach combining the use of recipes as a starting point for producing and studying a particular glass composition and archaeological data has also developed [6, 8, 9, 41, 52–54, 63, 69]. Govantes-Edwards and co-workers [52] focused on testing the potential of a historical approach through the analysis and reproduction of recipes, by taking into consideration archaeological information. They concentrated on medieval Islamic glass found in the Iberian Peninsula and selected seven texts from this period (from the thirteenth to the seventeenth centuries,[1] although none refer to Islamic glass recipes. The team chose a recipe from the *Epistola Abbreviatoria* to be reproduced with natural raw materials, but after trying to fire all components, only a small fraction near the crucible was vitrified. They pointed out that perhaps the problem was the quantity of chlorides or the soaking time, but since this was just a preliminary attempt, they argued that more studies are needed for more definitive conclusions. Although this research raises more questions than answers, it nevertheless shows the importance and viability of combining different methodologies and approaches when studying glass recipes.

Pearson and team carried out research [53] based on the same manuscript—the *Epistola Abbreviatoria*—but to demonstrate how glassmaking research can benefit from the study of glass recipes. The authors chose a glass recipe and produced 10 variations of the same, using ash as the source of soda, but laboratory compounds as the source of silica. Despite being preliminary research, the authors concluded that it is possible to reproduce these glasses on a small scale at low temperatures (like those used in the Middle Ages) and argued that the quality of the glass is fully dependent on the quality of the raw materials. Essentially this research shows that the reproduction of a simple recipe can generate a wealth of information about the technologies of glass production in a specific period.

The study by Palomar and team [6] aimed to interpret, reproduce, and characterize four recipes from a medieval manuscript dated from the fifteenth century, and written in Castilian—three glasses and one glaze—to understand the glass technology of the period and test the viability of an interdisciplinary methodology, using experimental archaeology, glass chemistry, and glass crafts, in the study of ancient materials. Because most recipes required a base glass, such as a cullet, the author replicated a potash-lime silicate glass with the typical composition of medieval glass, based on previous characterisations by the authors. To minimize the variables, they employed laboratory mixtures to reproduce the four recipes, and when possible, the temperatures supposed to have been used in the Middle Ages based on some studies about pottery firing, despite the absence of information on this aspect in the recipes. After a few attempts, the team was able to successfully reproduce all the

[1] Epistola Abbreviatora from Don Christóforo of Soto Mayor; *Sedacina* from Guillaume Sedacer; *Lapidario* from Alfonso X; *Montpellier manuscript" H490* from Juan Celaya (?); *Itinerarium Hispanicum* from Hieronymous Münzer; *Etymologies* from Isidore of Seville; *Historia natural de Catalunya* from Pedro Gil

selected recipes, and it was found that some of the instructions in the recipes were not useful and did not work the way they were supposed to. This is extremely important for this case-study, as it indicates that recipe instructions or comments cannot always be trusted. We do not know the circumstances under which they were made or what they were compared to, which entails the need for careful reading and interpretation.

Handendijk and team investigated the way recipes are written, more specifically about Kunckel's German version of Neri's *L'Arte Vetraria* from the seventeenth century. Kunckel republished the treatise with comments and corrections, and Handendijk wanted to test whether these comments were relevant to glassmakers [9]. Four different recipes for the same glass were selected, and the base glass was also produced in five different ways, in different types of furnaces—an electric furnace and a wood furnace. They concluded that it is most relevant to investigate more than just the recipe, as different furnaces did produce different results. Regarding Kunckel's version, they point out that although he commented on and corrected several recipes, he does not seem to have tested all of them. They were simply meant to give more information to the reader to fully understand what is happening and how to control it.

Vilarigues and team also focused on the same treatise to further explore the importance of the type of furnace and the temperature for a successful reproduction. In all options they obtained a satisfactory result, mainly at lower temperatures, and this aspect turned out to be much more relevant than the atmosphere of the furnace [69].

Ma and co-workers [63] reproduced a lead-barium glass from 457 - 221 BCE and focused on understanding its technology and how it started to be used in China. Despite being considered a Chinese invention, no specific recipe for this type of glass has yet been found. Therefore, based on some Chinese manuscripts and historical objects, they tried to recreate the recipe with several variations to ascertain whether it was possible to produce it and how. After several attempts, the glass was reproduced correctly, but the conclusion is that the soda-lime base glass was imported and therefore there are no specific recipes for this glass.

The approach used in one of the studies is closer to this thesis was about the reproduction of Roman opaque red glass based on Venetian glass recipes, since there are no written sources from the Roman period, with the purpose of understanding the glassmaking technology in the study of archaeological objects. Bandiera and team [8, 54] focused mainly on the recipes from six Venetian treatises, from which 35 recipes were selected to reproduce and compare the glass obtained with historical objects. Since most of the instructions were vague and did not mention quantities or specific compounds, the authors had to test several options, including different types of furnaces. However, whenever possible the instructions were followed and interpreted with the aim of understanding what kind of knowledge the author was trying to pass on when he wrote the recipe. Following reproduction and characterisation, the samples that did not match the historical objects, in terms of

composition, were excluded from the discussion. They concluded that although the recipes lack some key information, such as the quantities of raw materials or the fusion process, the team considered that despite their scarcity, most annotations and instructions in the recipes were very useful and even helped in interpreting the rest of the recipes.

Concerning studies focusing on glassmakers' *arcana* the research I performed for my Master's thesis, selected thirteenth Portuguese colourless crystal glass recipes from the eighteenth to the twentieth centuries. Santos and co-workers [41] chose colourless crystal recipes—lead crystal and potassium crystal—and these were reproduced systematically, using laboratory reagents, since in most cases the recipes originally used synthetic and purified raw materials. Concerning the raw materials, the known impurities of some ingredients were simulated, such as the addition of some iron oxide content to silicon oxide. For the melting process, an electric furnace was used, and the glass was left to cool inside the furnace. The glass produced was then characterised chemically and thermally, to compare it with historical objects from the same period in national museums. These objects had already been previously characterised to correctly attribute their provenance and context, but due to the lack of information on Portuguese glass industry, this was not possible. The comparison of the reproduced recipes with the historical glass had some positive results, which validated and demonstrated the importance of this type of approach. All these studies have influenced the method created and adopted in this thesis.

Finally, it is important to note that studies associated with glass painting materials have been deliberately excluded. Some of these studies replicate historical recipes found in treatises and ancient texts, but they were omitted since the composition of the painting materials and painting techniques are outside the scope of this thesis [7, 71, 72]. Some studies discuss various historical sources of recipes for the production of a certain type of glass—for example, aventurine glass—and even discuss past attempts by other authors to reproduce it, but since they only focus on written sources without testing or applying the recipes, this kind of study has been excluded [73]. Equally omitted are the studies that do not specifically focus on the composition of a particular glass object but instead develop model compositions to represent specific historical periods, often to conduct degradation analysis or similar research [74–77]. Since in both cases the focus is not the batch books, or their interpretation and practical use they differ fundamentally from the present research as it focuses on decoding, interpreting and reproducing glassmaking recipes and the appreciation of the *arcanum* as an object of historical interest.

3.2.2 Recipe Verification Process

After reviewing the literature and gathering all the information and methodologies employed until today, it is important to outline a well-defined methodology adapted to my case-study—the Portuguese glass *arcana* from the eighteenth to the twentieth centuries. It is worth mentioning that this is a period when chemical knowledge of glass is superior to that of the Roman period. For example, in the twentieth century, the glass industry benefitted from scientific and technical advances from the preceding century, notably the availability of purified raw materials and the isolation and discovery of various chemical elements, which led to their use in glassmaking.

Prior to the laboratory reproduction of glasses, it is essential to establish a replicable method for interpreting and selecting the recipes (Figure 3.2). Initially, all recipes for glass of a specific colour must be identified. Subsequently, a thorough assessment should be conducted to ensure the legibility of these recipes, eliminating those unreadable. Once only legible recipes are considered, the next step is to select those that are reproducible.

For the reproducible recipes, a chemical completeness check should be conducted. Following the composition of any glass, these recipes should have a network former, a flux, and a stabilizer. In the case of coloured glass recipes, they should also include the respective chromophore responsible for the colour. Once recipes that meet these chemical criteria are identified, they should be grouped based on similarities, for example: lead crystal glass, yellow iron glass, chromium green glass, and so on. These groupings allow for the prioritization of recipes to be reproduced that are most representative of the *arcanum* under consideration. For example, if most green glass recipes use chromium as the colourant, it would not be representative or a priority to reproduce the one using iron as colouring agent.

One of the first aspects that caught attention was the establishment of criteria for readability and reproducibility when reading each *arcanum*. For example, an *arcanum* from a certain factory may have 100 recipes, but only 50 are readable. The reason can be the degree of preservation of the *arcanum*'s pages or simply the illegibility of the author's handwriting. Of these 50 recipes, only 20 are reproducible; in other words, the fact that it is possible to read words does not necessarily mean that the exact composition of each ingredient is known. Consequently, in this example, the *arcanum* from this hypothetical factory has 100 recipes, but only 20 are considered reproducible.

Reproducibility is indelibly associated with the secrecy surrounding the *arcana*. Some of these books were written with code words and hidden information. But sometimes it also turns out that this irreproducibility is a consequence of the fact that the authors are so familiar with the subject that writing something that is so obvious leads them to often resort to abbreviations or coeval expressions, which were then current or were part of the factory jargon, but no one knows their meaning nowadays. This task will always be an ongoing one because there is always new information to be unearthed, which can help to

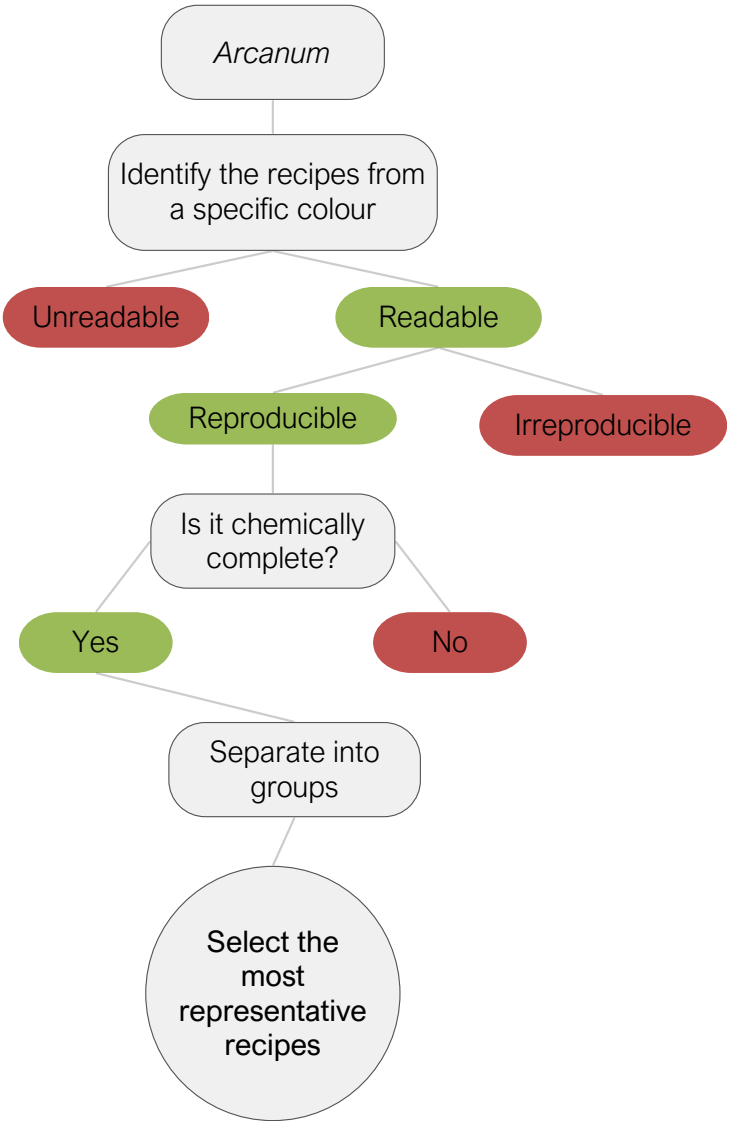

Figure 3.2: Decision tree of the process of interpreting and selecting the recipes to reproduce.

unveil the content of the recipes. Currently, the strategy has been to look for as much information as possible on glassmaking documentation written in a coeval chronology to find possible similarities; for the twentieth century, in addition, the direct contact with surviving Portuguese glassmakers who can shed light on the use and meaning of expressions and abbreviations (**Figure 3.3**).

Before detailing the experimental research that will be carried out, it is important to clarify that the primary objective of recipe reproductions is beyond the characterisation of the glasses, as it entails the understanding of the manufacturing glassmaking practices as well

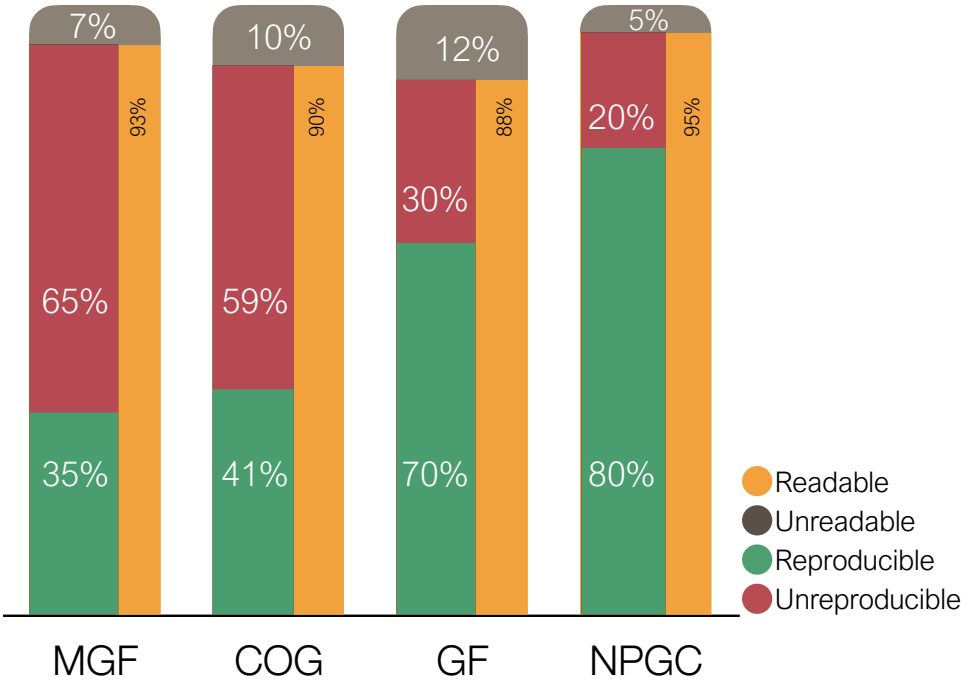

Figure 3.3: Percentage of readable and unreadable recipes for each *arcanum*, with the distribution of readable ones between reproducible and unreproducible.

and the evolution of the industry over time. It also seeks to validate the *arcanum* as an important historical source, by ascertaining that the information contained therein was not only used by glassmakers, but perhaps was at the origin of some of the historical objects that nowadays are in Portuguese museums.

3.3 Experimental Design and Characterisation Methodology

The methodology used in this study focused on the controlled reproduction of historical glass recipes using laboratory-grade reagents. This approach minimized the variables associated with natural raw materials, which can introduce inconsistencies due to variations in collection period, pre-melting preparation, and initial characterisation [6]. Whenever possible, pure reagents were employed, but in cases where historical impurities were known to be significant, they were simulated. For example, since sand as a silica source is always associated with iron oxide contamination, reproducing a recipe from a specific *arcanum* with only pure silica would not yield a historically accurate result. Instead, by analysing glass objects from a particular factory, it was possible to estimate and replicate iron contamination, ensuring a closer match to historical compositions.

For recipes that included cullet, a systematic approach was adopted to ensure historical relevance. When a recipe specified a particular type of cullet, such as parsley green cullet, the corresponding glass was first produced and then incorporated into the mixture. In cases where only colourless cullet was indicated, previous analyses of historical objects were used

to define a base composition, which was then reproduced. However, if the cullet description was too vague, such as light cullet, the recipe was considered non-reproducible. Although this approach introduced challenges in characterising and comparing the reproduced glasses with historical objects, it provided a structured method to assess the feasibility and historical applicability of the recipes.

Since most historical recipes did not specify furnace type or temperature, and the exact conditions used in factories remain unknown, a melting range between 1300 and 1450°C was established. This range was defined based on previous experimental studies [11] and adjusted as necessary. All glass melts were carried out in a Termolab™ type BL electric furnace under ambient atmosphere. Among the different glasses, amber required the highest temperature, as higher temperatures promote a more reducing atmosphere inside the furnace [42, 54, 78]. This choice also optimised the reproduction process, reducing time and increasing efficiency. When necessary, temperature and soaking time adjustments were made, as previous studies indicated that soaking time played a critical role in successful glass production.

After melting, different cooling methods were considered. Some studies left the glass to cool inside the furnace, while others poured it onto a metal plate. Since previous tests showed that furnace cooling often resulted in cracked or fractured samples, the decision was made to pour the molten glass onto a metal plate, followed by annealing in a side-heated electric furnace (BARRACHA model E1) at approximately 470°C for one hour, and then leaving it to cool naturally inside the furnace. This procedure relieved internal stresses and facilitated sample preparation for further characterisation [11]. This methodology has been schematised as shown in **Figure 3.4**. Note that the processing of the sample for the analyses may change depending on the analytical techniques chosen.

The methodology employed in this study combined historical interpretation with controlled experimental reproduction. Recipes were selected based on readability and practical feasibility, distinguishing between those that could be reproduced and those that could not. Laboratory-grade reagents were used to ensure accuracy while incorporating historically relevant impurities where necessary. The melting process was adapted to modern equipment while maintaining a balance between historical fidelity and practical efficiency. This systematic approach not only aimed to verify the technical aspects of historical glassmaking but also to establish a framework for linking compositional and technological features of historical glass to specific production sites and periods, aiding in the identification and attribution of glass objects found in Portuguese museums.

3.3.1 Intermediate procedures

The reproduction of historical recipes, regardless of their chronology, almost always involves a series of intermediate steps, such as the production of frits or certain colouring agents. Below is a detailed explanation of the approach adopted for this work. It should be noted

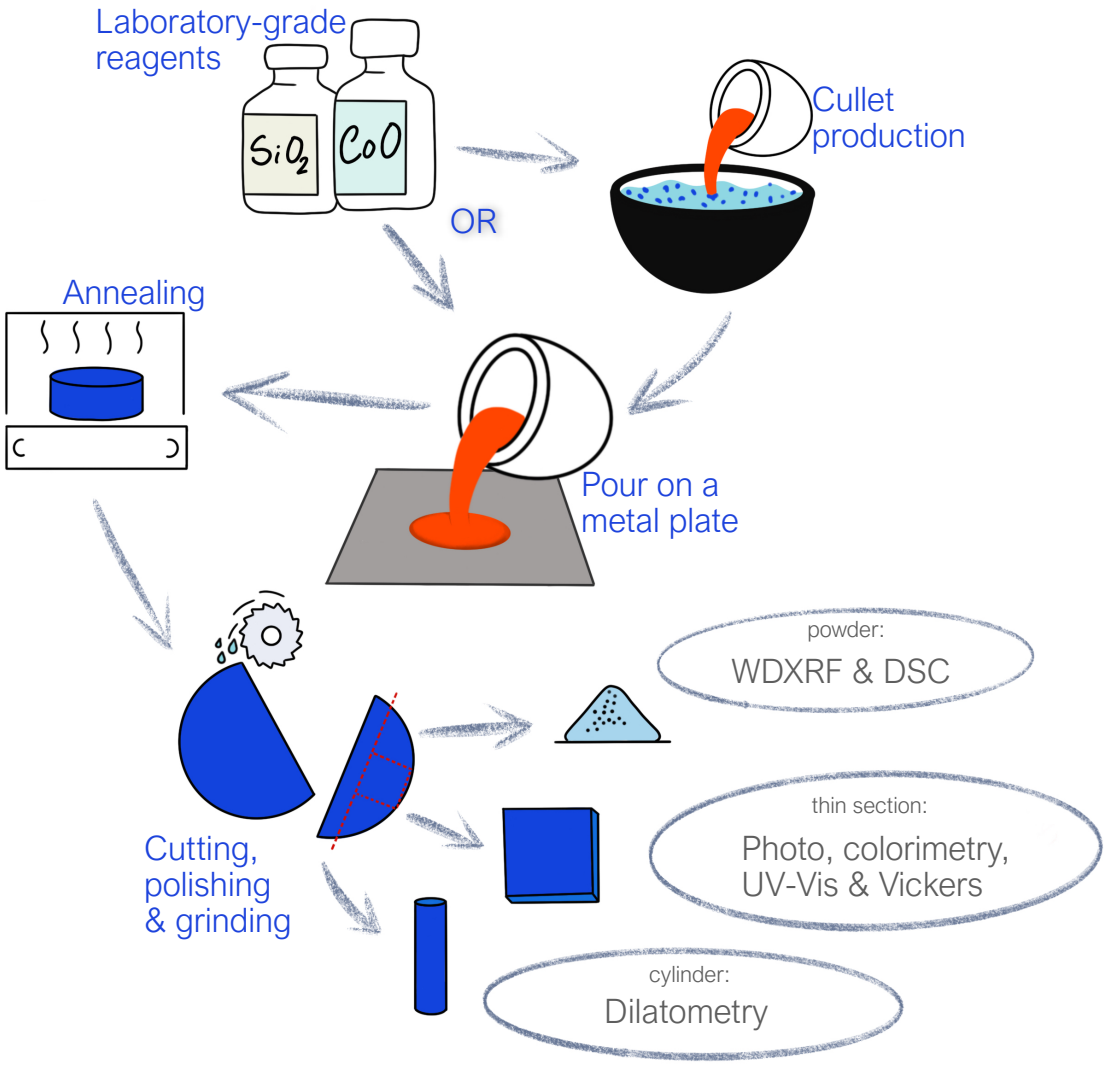

Figure 3.4: Glass sample preparation: Production of final glass or cullet based on historical recipe using laboratory reagents. Heat treatment to enable the sample to be handled and analysed. Cutting, polishing and grinding for characterisation using the above techniques.

that this methodology should be revised whenever necessary and whenever new information on the subject emerges.

Sand: Sand is one of the main ingredients in glass production, so it is essential to know its origin, as its composition varies from place to place. Although other elements may be present, sand is mainly composed of SiO_2 and Fe_2O_3 in varying proportions.

In the recipes of the MGF *arcanum*, the sand used in this factory was analysed and published in a book marking the centenary of the factory [24]. The accuracy of this analysis is unknown, but as it is the only information available. In the COG *arcanum*, the same sand composition was used because, based on the historical context, these recipes date from a period when glassmakers worked at the Marinha Grande factory.

For the GF and NPGC *arcana*, the approach was different as there is little contextual information available about these factories. Colourless glass objects from each factory were analysed by Energy Dispersive X-ray Fluorescence (EDXRF) and the measured iron oxide content was used as a reference to estimate the iron content of the sand used in these arcana.[2]

This information should be updated as new studies become available (**Table 3.2**). Future archival research, in particular the study of order records for sand from each factory, may allow for more accurate reproductions. As there is a soil database in Portugal, it may be possible to locate samples from the relevant sites for further study.

Table 3.2: Proportion of SiO_2 and Fe_2O_3 in the simulated sand in each of the *arcana*.

Arcanum	SiO_2	Fe_2O_3
MGF	99.131%	0.869%
COG	99.131%	0.869%
GF	99.944%	0.057%
NPGC	99.966%	0.034%

Cullet: The approach to reproducing cullet was more complex and not straightforward. However, it was necessary to test an initial methodology in order to explore new approaches in the future and determine what works best for this type of study.

Recipes containing cullet were avoided wherever possible. However, in the NPGC *arcanum*, almost all recipes contain cullet, so a methodology had to be established. In this *arcanum* all the recipes, except for one ordinary colourless glass recipe, contain 35% cullet. The interpretation was that this cullet was colourless.[3] As the production methods of the factory could vary, instead of using the ordinary glass recipe, colourless glass compositions from historical objects attributed to this factory were reproduced and poured into water to produce cullet for all the recipes.

In the MGF *arcanum*, one recipe required cullet and the same procedure was followed. However, the composition of this cullet had already been established in a previous study carried out at the Research Unit, based on analyses of historical MGF objects in national museums [32]. The same composition had also been used in my Master's thesis, when necessary [11, 41].

[2]The glass objects from GF were donated to VICARTE and were collected from the factory after it was closed. The objects from NPGC are essentially fragments of objects found in the factory at the time of the visit mentioned in Figure 1.16.

[3]This conclusion is based on the fact that most of the fragments analysed were made of flash glass. This characteristic makes it logical that there should always be a percentage of colourless glass in the coloured glass. In this way there is greater compatibility between the two glasses when they overlap.

In more specific cases, where a recipe explicitly called for cullet of a particular colour or composition (unless the description was vague, such as "dark cullet"), the required glass was first reproduced and then used as cullet in the final glassmaking process.

Table 3.3: Batch composition of the cullet prepared for the NPGC and MGF arcana recipes

	NPGC	MGF
$MgCO_3$		2.58%
Al_2O_3		1.05%
SiO_2	68.445%	65.80%
P_2O_5		0.44%
K_2CO_3	3.184%	15.45%
$CaCO_3$	9.952%	10.96%
TiO_2	0.029%	
Na_2CO_3	18.348%	3.00%
MnO_2		0.06%
Fe_2O_3	0.034%	0.06%
ZnO	0.009%	
SnO_2		0.04%
Sb_2O_3		0.55%

Frit: The use of frit in glass making was gradually replaced by cullet. However, in the oldest *arcanum*, MGF, frit is present in almost every recipe. A glassmaker who worked at the Marinha Grande factory (not during the period of the *arcanum*, but at a time when many traditional practices were still in use) provided insights into historical frit compositions. He stated that a "soda and sand frit" consisted of sand and sodium carbonate in a 1:1 ratio.[4] For other types of frit, the recipes were classified as irreproducible, either because of a lack of information or because they contained ingredients that could not be reliably identified or sourced.

Zaffre and Smalt: For the production of zaffre and smalt, two blue glass colourants, historical treatises often give different recipes. Rather than using these sources, a study focusing specifically on the materials used in historical glass painting was selected [71]. This study was chosen because its reproduced compositions closely resembled the majority

[4]Personal communication with António Noivo, in November 2022, at the conference "Vidro hoje, uma ponte para o futuro", Marinha Grande.

of blue enamels found in historic stained glass.

Table 3.4: Zaffre and smalt composition and furnace programme

	Zaffre	Smalt	Furnace program
Al_2O_3		1.00%	
SiO_2	66.70%	71.00%	Ramp until 1200°C, 5°C per min. Dwell 10h. Poured into water.
K_2CO_3		21.00%	
CoO	33.30%	7.00%	

3.3.2 Analysis conditions

To briefly explain the techniques used in this thesis, it is important to emphasise once again that this is a groundbreaking study on the subject. Consequently, conducting complex analyses or tests, such as corrosion tests, without first establishing a solid foundation for future studies is of limited value.

The reproduced glasses were first examined under a stereomicroscope, which allowed a preliminary assessment of the final result, identifying the presence of bubbles, inclusions or other manufacturing defects. WDXRF analysis provided information on the final composition of the glass, showing which components had volatilised and which remained in the vitreous matrix. UV-Vis analysis provided insight into the colourants and chromophores responsible for the observed colours. Colorimetry not only confirmed the homogeneity of the colour, but also showed subtle variations in colour could be detected due to the presence of specific chromophores.

Thermal analyses, in particular DSC and dilatometry, were crucial in optimising the reproduction conditions and served as a reference for future studies. They also played an important role in understanding the artistic choices made, in particular the choice of colours. For example, a lower Td allows a longer working time without the need for frequent reheating.

Vickers Hardness analysis was carried out to determine if there were differences in hardness between the different colours, as three different glass colours are being studied in this thesis. Furthermore, if compatibility with historical objects is established, this data can enhance our understanding of specific choices made throughout the history of glass production, helping to explain why certain compositions and colours were associated with particular manufacturing methods or decorative techniques.

Stereomicroscope: The photographs of the reproduced glasses were taken using a Nikon SMZ754T stereomicroscope equipped with a Nikon's DS-Fi3 digital camera and a Leica KL

2500 LCD fibre-optic illumination system. Using a set of 7.5x binoculars and objectives ranging from 0.67x to 5x magnification.

Wavelength Dispersive X-ray Fluorescence: Elemental composition of the glass samples was analysed by Wavelength Dispersive X-ray Fluorescence (WDXRF) using a PANalytical AXIOS spectrometer. The equipment features a Rh X-ray tube and four analyser crystals, operated under helium flow to optimize sensitivity and reduce spectral interferences. The measurements were performed in scanning mode to detect elements with atomic numbers greater than 8, and spectral deconvolution was applied using the iterative least squares method. Elemental quantification was based on the fundamental parameter approach, utilizing certified secondary standards, which provided fast and reliable multi-element analysis.

UV-Vis Absorption Spectroscopy: The UV-Vis absorbance spectra were obtained using an Avantes AvaSpec-2048 fibre optic spectrometer, which operates in the range of 200–1100 nm with a resolution of 2.4 nm. A 200 µm reflection probe was used for measurement, consisting of a central reading fibre surrounded by six lighting fibres, each with a diameter of 200 µm. Spectra were recorded between 350 and 1050 nm in absorbance mode, with an integration time of 13–18 ms and 20 scans per measurement.

Colorimetry: The colour of each sample was quantified using a Lovibond® TR520 handheld spectrophotometer, which was configured with an optical geometry of an 8° viewing angle, diffused illumination, and an 8 mm measurement aperture. The colour coordinates were calculated according to the CIE L*a*b* system, using CIE Illuminant D65 as a reference. Three colorimetric measurements were conducted for each sample to ensure consistency and accuracy of the results.

Differential Scanning Calorimetry: Thermal properties of the glass samples were analysed using a Netzsch Pegasus® DSC 404 F3 differential scanning calorimeter. The furnace can reach temperatures up to 1550°C. The experiments were carried out with a platinum crucible, using a heating rate of 5°C min^{-1} in a nitrogen atmosphere. The glass transition temperature (Tg) was determined from the resulting thermograms, with three analyses conducted per sample to ensure accuracy.

Dilatometry: The glass transition temperature (Tg) was also measured by dilatometry using a Netzsch Gerätebau dilatometer (model 402 PC), with a heating rate of 5°C min^{-1}. The test was performed in collaboration with Cristina Ruiz Santa-Quiteria from the Institute of Ceramic and Glass in Madrid, Spain. Only the most relevant samples were selected for characterization. The dilatometric method allows precise determination of the Tg by monitoring the dimensional changes in the sample as it is heated.

Vickers Hardness Testing: The Vickers hardness of the glass samples was assessed using Zwick-Roell Indentec test equipment. Indentations were made on each sample as many times as necessary to obtain five points with a mean percentage error below 4%, using a load of 0.5 kg and a measurement time of 10 seconds per indentation.

Variable-Pressure Scanning Electron Microscopy—Energy-Dispersive X-ray Spectroscopy: A single cross-section sample was examined using a Hitachi 3700 N scanning electron microscope (Hitachi, Tokyo, Japan) coupled with a Quantax EDS microanalysis system (Bruker AXS GmbH, Karlsruhe, Germany). The system featured a Bruker AXS XFlash Silicon Drift Detector with a Mn Ka spectral resolution of 129 eV at full width at half maximum (FWHM). The analysis was performed under operating conditions of 40 Pa pressure, 20 kV accelerating voltage, a 10 mm working distance, and a 75 µA emission current. Data were acquired and processed using Esprit 1.9, and no surface coating was applied to facilitate subsequent analyses.

3.3.3 Selected recipes

3.3.3.1 Amber

Amber glass recipes show a high degree of variation, particularly in the choice of base glass, which includes soda, potash, lead and mixed compositions (**Figure 3.5**). The main colouring agent is based on iron compounds, often in combination with sulphur or manganese. These elements interact under various redox conditions to produce colours ranging from pale yellow to deep brown. The frequent use of lead in some formulations suggests that, in addition to colour, workability and optical properties have been considered in the formulation.

Some recipes specify minimal addition of fining agents, while others omit them altogether. This omission may indicate that glassmakers relied on the natural refining action of the colourants and reducing agents, or that refining was unnecessary for certain types of glass, particularly those used for utilitarian purposes. The fact that several recipes include sulphur, either in the form of sulphates or as part of the raw materials, reinforces the idea that control of redox reactions was a crucial aspect of amber glass production. Bearing in mind that amber recipes are relatively simple and that the key information is the origin of the raw materials, there are quite a few recipes that have been classified as irreproducible in some of the *arcana* (**Figure 3.6**).

Overall, amber glass recipes demonstrate a balance between empirical knowledge and material adaptability. The variability in composition suggests that glassmakers modified recipes according to furnace conditions, raw material availability and intended applications. The widespread presence of this glass type in several *arcana* reflects its importance in historic glassmaking.

Although the four *arcana* belong to different chronologies and are different in length and number of recipes, the percentage of amber glass recipes is consistent and similar—9–15%. Most amber glass recipes are made from soda–lime glass, with iron or iron and manganese identified as chromophores. As mentioned earlier, iron alone does not produce the desired yellow/amber colour in the glass, but rather the chromophore FeS, which complexes in the glass matrix during the glass melting process. It should also be noted that most recipes

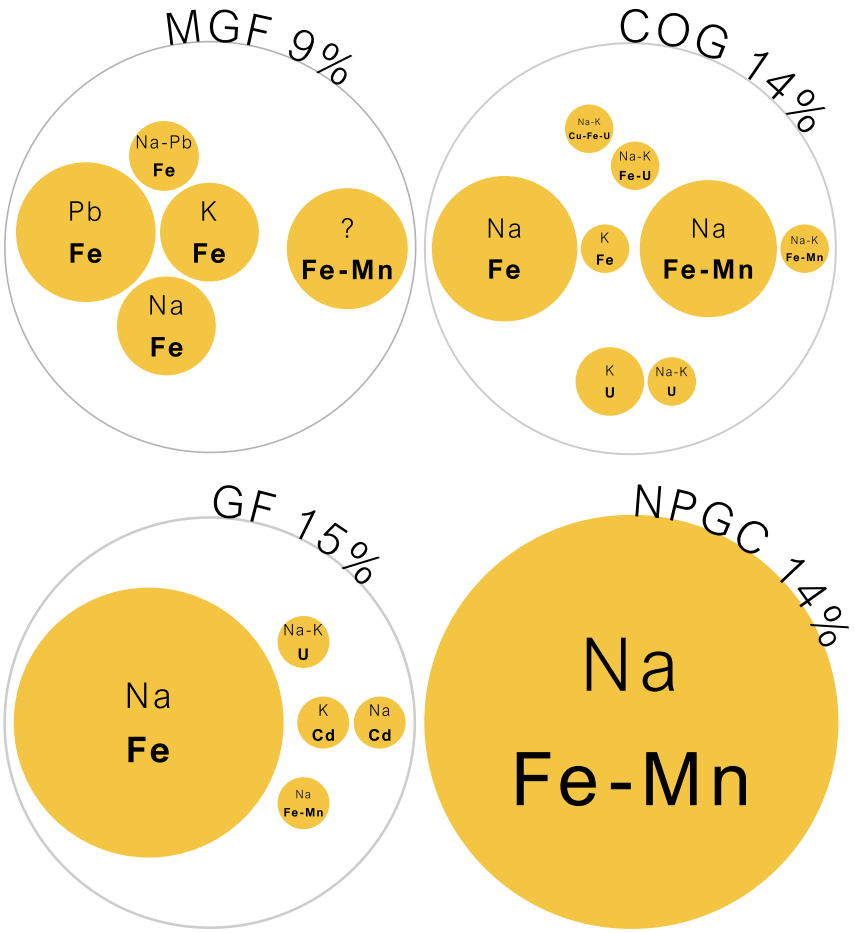

Figure 3.5: Circle packing chart displaying the amber recipes from the four arcana and their percentage in relation to the total recipes in each *arcanum*. Each circle represents the fluxes (top) and the colourant (in bold).

are entitled as "recipe for yellow glass", while just one uses clearly the word "amber" (in a recipe entitled "black glass (bottle amber)"). To better understand the interests of each factory, all recipes for yellow glass were considered, whether producing amber glass or not.

Regarding the specific recipes that were selected. The NP3 recipe was chosen because, among the three available recipes, it is the only one that does not require the addition of cullet, and the amounts of iron and manganese are explicitly stated—something that is not the case when iron is sourced from sand. Regarding the GF *arcanum*, the selected recipes are those that do not include cullet and have the simplest possible composition. G92 uses sulphur as its sulphate source, flour as a reducing agent, and iron derived from sand. G130, in contrast, employs charcoal as a reducing agent instead of flour. G192, like G92, contains sulphur and flour but also includes NaCl, which, according to the literature, enhances the formation of the complex responsible for the amber colour [60]. From the COG *arcanum*, only one recipe, C98, was selected, as it does not mention the use of cullet and has an extremely simple composition, making it suitable for testing various variables.

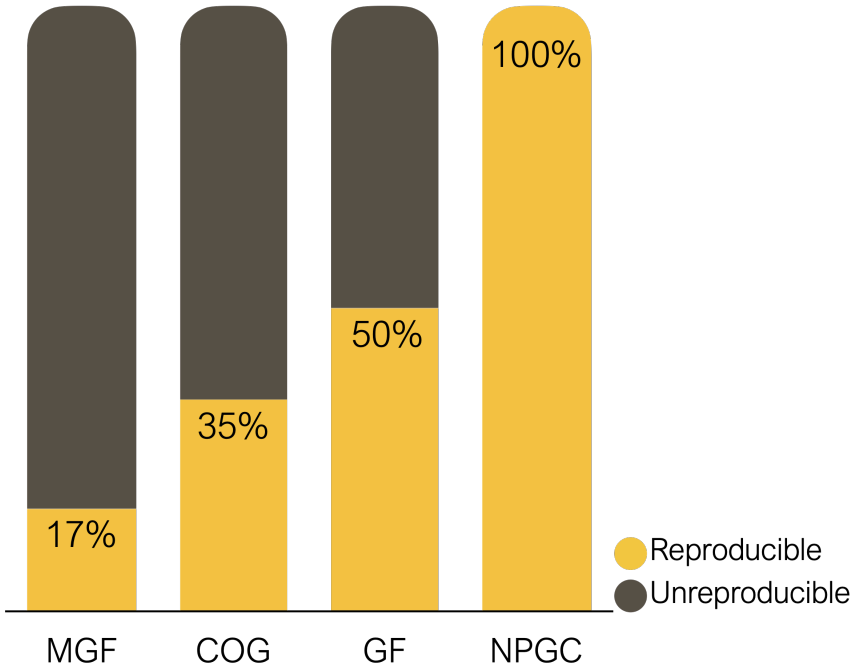

Figure 3.6: Percentage of reproducible and unreproducible yellow/amber recipes for each *arcanum*

3.3.3.2 Blue

Blue glass occurs in 6% to 19% of the *arcana*, with a wide range of base glass compositions including sodium-lead, soda-lime, potassium-lead and mixed alkali glasses (**Figure 3.7**). A feature of most formulations is the extensive use of cullet, often without regard to its original colour. This practice suggests confidence in the high colouring capacity of cobalt oxide, which allows it to override pre-existing colourants in recycled glass. The ability to reuse cullet regardless of its original composition suggests practical and economic considerations in glassmaking.

Cobalt oxide is the predominant colourant, typically producing deep, intense blues. However, copper oxide is also used, particularly in leaded glass, saying that produces lighter blues such as "sky blue" (*azul celeste*). Some recipes experiment with mixed colourants, such as cobalt with manganese, or cobalt with cryolite to create opalescent effects. In a few cases, cobalt is combined with copper to produce unique colour variations.

The names of the blue glass recipes could also provide more information about their intended use. Is it possible find terms such as "navy blue" (*azul marinho*), "branding iron blue" (*azul ferrete*) and "dichroic blue" (*azul dicroide*) suggest a differentiation by tone and perhaps by use. Some recipes indicate cobalt-based glass for flash glass production, a technique involving a thin layer of colored glass over clear glass to create decorative effects.

In particular, blue glass recipes rarely contain fining agents such as arsenic, which are commonly found in other coloured glasses. This omission may be due to the efficiency of cobalt in dispersing evenly throughout the melt, reducing the need for additional fining.

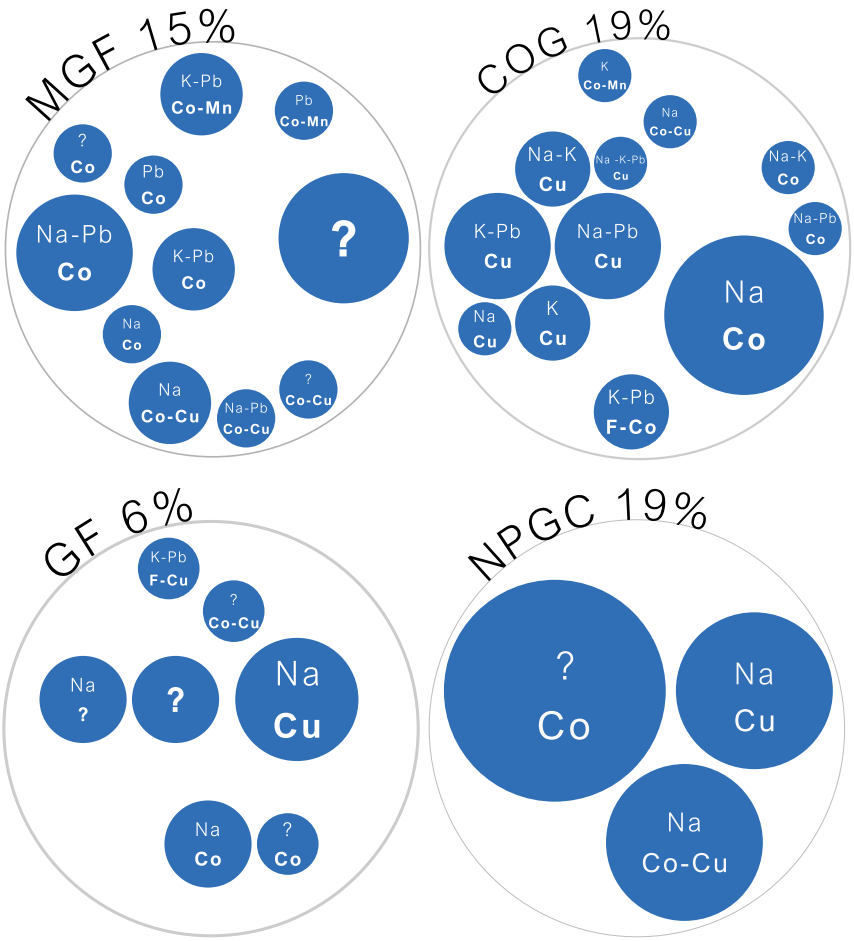

Figure 3.7: Circle packing chart displaying the blue recipes from the four arcana and their percentage in relation to the total recipes in each *arcanum*. Each circle represents the fluxes (top) and the colourant (in bold).

The silica sources mentioned in these formulations vary, with silica being the most common, although some formulations mix sand and silica. This choice is likely to reflect regional differences in raw material availability and processing preferences. Thanks to this ease of producing the colour blue, most recipes for each arcanum, with the exception of MGF, have a high percentage of reproducibility (**Figure 3.8**).

Starting with the MGF *arcanum*, recipe M1_4 was chosen because it was described as producing a very pale blue colour, despite using zaffre as the colourant. Since zaffre is made with cobalt—a colouring agent that typically produces intense colours even in small quantities—this discrepancy suggests a possible issue of interpretation. Three methods of adding cobalt were therefore tested: cobalt oxide, zaffre and smalt. These three options were chosen because, historically, there was little distinction between them and zaffre was often used as a general term for cobalt-based materials, even when referring to cobalt ore [42]. Recipe M3_3 was chosen because of the type of objects it was supposed to produce—candlesticks and ashtrays. As this is an eighteenth century recipe, it is assumed that these items would have been engraved, making their reproduction and characterisation

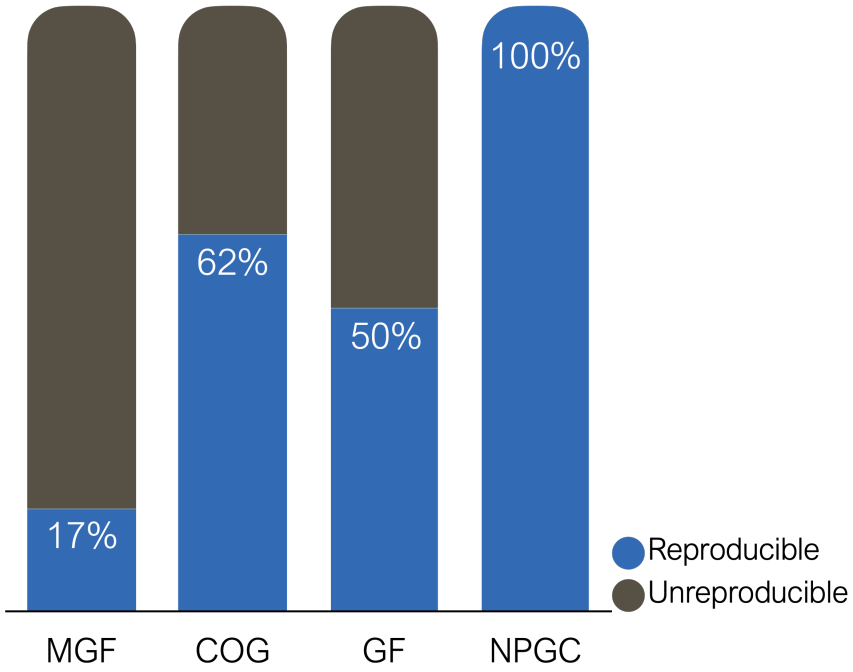

Figure 3.8: Percentage of reproducible and unreproducible blue recipes for each *arcanum*

particularly interesting. Recipe M1_51, although stated to produce green glass, lists copper as the colouring agent and does not contain lead. According to the literature, copper oxide alone cannot produce green glass unless other elements, such as lead, are present. To verify the accuracy of this recipe, we tested whether contamination in the original batch could have affected the final colour [42].

Four recipes were selected from the COG *arcanum*. Recipe C125, described as "dichloride blue", uses copper and lead oxide, raising curiosity as to the type of colour it was intended to produce. Recipes C157 and C158 were chosen because they both involve blue glass - one for flash glass, the other not. Recipe C159, on the other hand, states that it is intended to produce navy blue glass. My interpretation is that this should correspond to dark blue, i.e. a cobalt-based glass. However, the ingredients listed include both copper and cobalt, suggesting a mixture of colourants. Further investigation is required to determine whether cobalt alone was meant to produce the intended shade or if the combination of both elements was intentional.

For the GF *arcanum*, the recipes have very similar names, and none stands out. Thus, it was chosen one with copper and lead for "sound glass" (C46), one with cobalt but no lead for making flasks (G114) and one with copper for making "champagne blue" (G101).

As the NPGC *arcanum* is relatively small, it was possible to reproduce all the existing blue glass recipes. These include one for navy blue with copper (NP4), one for flash glass blue with cobalt (NP5), one for dark blue with cobalt and zinc (NP6) and one for azulino - a mixture of copper, cobalt and zinc (NP7).

3.3.3.3 Green

Green glass accounts for between 10% and 27% of *arcana* and shows considerable diversity in both composition and colouring agents (**Figure 3.9**). The majority of recipes are soda-lime based, but potassium lead and sodium lead variations are also present. Unlike blue glass, which relies primarily on a single dominant colourant, green glass recipes use a variety of metal oxides to achieve different shades. In the earlier *arcana*, particularly in the MGF, most green glass recipes rely on iron and copper as the primary colourants.

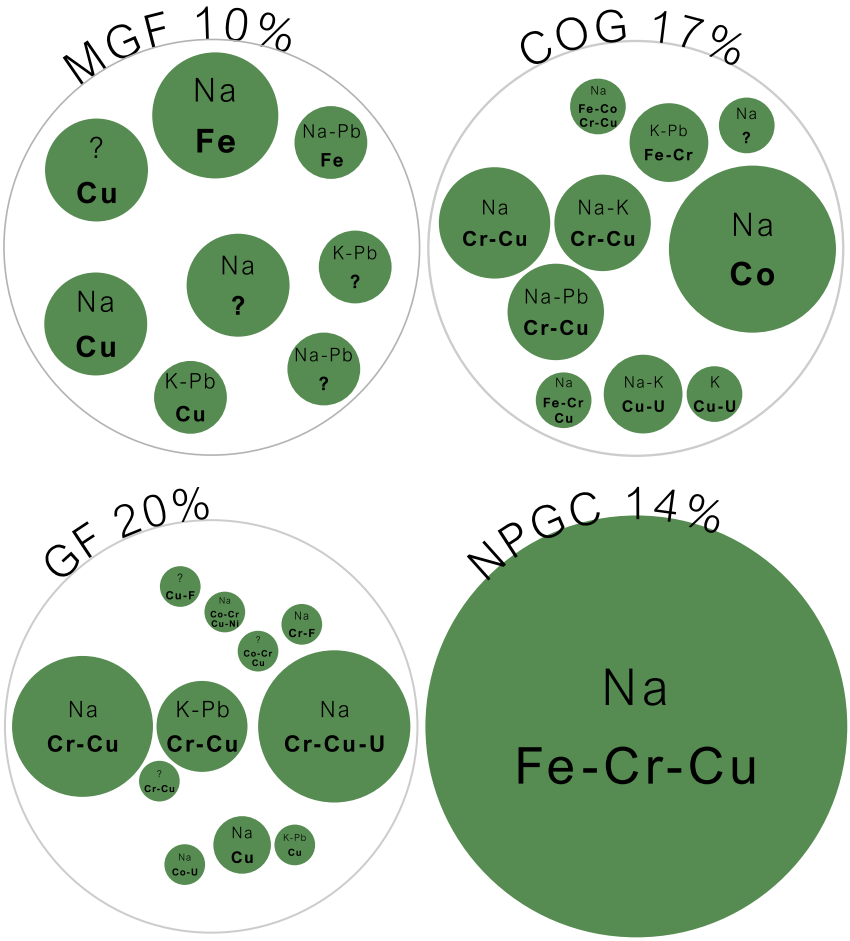

Figure 3.9: Circle packing chart displaying the green recipes from the four arcana and their percentage in relation to the total recipes in each *arcanum*. Each circle represents the fluxes (top) and the colourant (in bold).

However, from the nineteenth century onwards, the recipes show a significant shift towards the use of chromium oxide. This new colourant was often combined with iron or copper—or even both—to produce a variety of greens. In some formulations, chromium and copper are combined to produce shades called "parsley green" (*verde salsa*) and "China green" (*verde da china*). The addition of uranium in some cases indicates the possibility of producing special effect glasses.

An intriguing aspect of some green glass recipes is the inclusion of cobalt oxide, a colourant

typically associated with blue glass. This unexpected use indicates an advanced understanding of colour chemistry, as cobalt can produce green colours under certain conditions, such as low temperature melting or interactions with other metal oxides. Historical sources suggest that glassmakers experimented with these combinations to achieve unique visual effects, further demonstrating their knowledge of the glass.

The importance of fining agents in green glass recipes varies. Some formulations explicitly include arsenic, particularly those using a mixture of sand and silica as the silica source, while others omit it. The presence of cullet in most recipes highlights its importance in glass production, with particular emphasis on the fact that in this case, there are no longer recipes with "cullet of all colours" as there are for blue glass. Some green glass names give a clue to their intended use, such as "olive green for French style bottles" (*verde azeitona para garrafas à francesa*), while others remain ambiguous, leaving questions about their specific applications. Once again, the recipes in this colour show a high percentage of reproducibility, as can be seen in **Figure 3.10**.

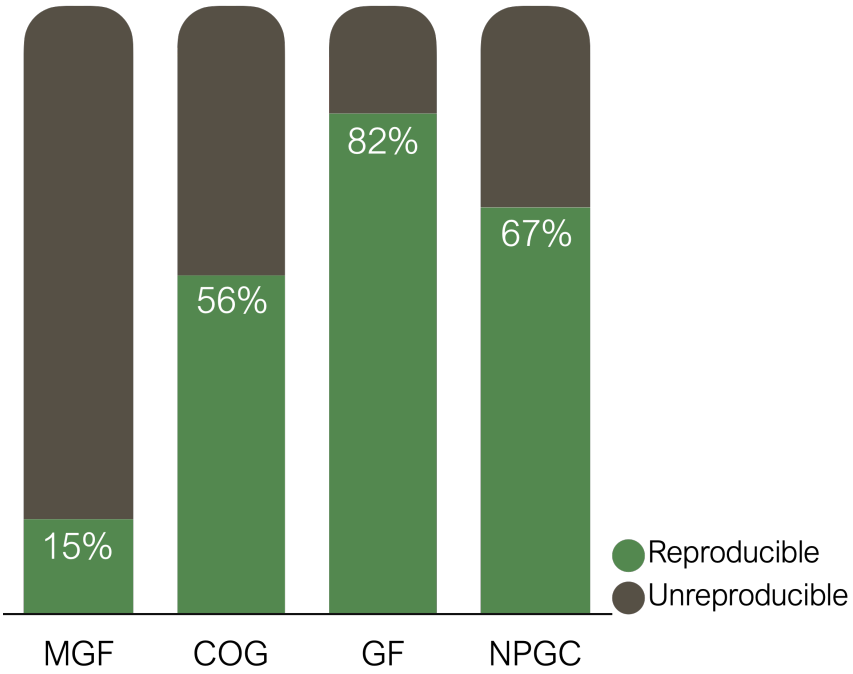

Figure 3.10: Percentage of reproducible and unreproducible green recipes for each *arcanum*

Overall, green glass recipes reflect both continuity and innovation in historical glassmaking. The shift from traditional iron- and copper-based colouration to chromium- and uranium-containing formulations signals the adaptation of new materials as they became available, showcasing the evolving expertise of glassmakers over time.

Unlike the previous colours, in the case of the colour green, it was not possible to select the same group of colourants in all the arcana, because in MGF most of the recipes are with iron or copper and in the others, the recipes are almost always mixtures with chromium.

However, the following recipes were selected: From MGF I chose recipe M1_5 as it is the only reproducible recipe with iron oxide. It is referred to as a recipe that produces a very light shade of iron, because the source of the iron is sand. Recipe M4_3, on the other hand, is the only reproducible recipe with copper oxide as a colouring agent. It claims to produce a "bottle green colour", which raised some questions about its result, since bottle green is normally associated with the production of glass with iron. The fact that both are the only ones capable of being produced today, with the information and context we have from the arcanum of MGF, is due to the fact that most of the recipes were considered incomplete. In other words, many of the recipes mention as ingredients, for example, frit and calcined iron, or lead and copper, which makes it impossible to produce them with the information we currently have from the Marinha Grande Factory.

Most recipes in the *arcanum* COG contain cullet. While I have explained my approach to these cases, I usually avoid selecting such recipes when alternatives exist.Looking then at the recipes without cullet, the vast majority have uranium as an ingredient. Note that these recipes have not been categorised as irreproducible because legislation and laboratory conditions can vary from country to country and the assessment must be made accordingly. At VICARTE it is not possible to use certain compounds such as arsenic and uranium, due to safety and legal restrictions, so these recipes were not selected either. Of the remaining recipes, there is a first recipe for "parsley green" (*verde salsa*), without cullet, and the others of the same name already mention the use of cullets. I then assumed that the initial recipe would be my cullet, C43, and these were used to produce the following ones, C44, C68 and C74. Some say they are for flash glass and others are not, so the aim is to see if there is any visual, thermal or mechanical difference between them.

From the GF arcanum, two recipes were selected, one with exactly the same name as the previous arcanum, G16, in order to understand whether what a particular glassmaker calls "parsley green" is actually a universal name among glassmakers in Portugal or if it's just a personal term, and I selected another with the name "China green" (*verde da china*) (G23), because it has a different name but the colouring mixture is the same, copper and chromium.

Finally, from the arcanum NPGC, there was no selection. The only two reproducible recipes in the arcanum were reproduced. NP23 is curiously called "parsley green" which will allow us to compare the visual results with the others, and NP24 is a recipe for *verdino* which, like the former, contains iron, copper and chromium, but also has the addition of sulphur.

4

Glass production

4.1 The complexities and underlying knowledge on amber yellow glass[1]

Historically, amber glass has been produced and traded by humans since at least the sixth century BC [79]. Its synthesis initially served to create beads that imitated the natural and valuable amber (a fossilized resin). By the Roman era, glassmakers had mastered the production of this colour through meticulous control of their raw materials. Amber glass, a term used to describe hues ranging from golden yellow to dark brown, became popular for crafting vessels around the fourth to third century BCE [40, 67]. Around the nineteenth century, it was realised that this glass had specific properties—nowadays understood as a capacity to filter the wavelength ultraviolet and visible radiations—contributing to preserve its content (e.g., food and medicines) [40]. In fact, by 2006, it was estimated that amber glass constituted 50% of all glass containers in the USA, predominantly for beer packaging [80].

In imparting colour to glass, iron is a versatile colourant, producing colours from yellow (Fe^{3+}) to blue (Fe^{2+}), with green being the most common colour due to the combination of both oxidation states. However, the amber colour discussed here—a brownish yellow—differs from colours typically produced by iron alone. The amber chromophore, now understood to be a ferri–sulphide complex, was long attributed to carbon, a necessary ingredient for its production [40, 80, 81]. In 1959, Weyl provided a comprehensive historical review of "carbon-amber glasses", exploring earlier theories, such as those proposed by Eckert and Zschacke in 1928, who suggested that the colour was associated with iron sulphide formation, although they lacked analytical corroboration [42]. It is notable that this glass colour was probably among the most difficult to attribute to a colouring agent. Only in 1965, through a series of experiments that involved the production of several variations of amber glass recipes, did Brown and Douglas propose that sulphur and iron were probably involved in the amber colouration [81]. Current understanding posits that the amber chromophore is composed of a Fe^{3+} ion with three bridging oxygens (O^{2-}) and one S^{2-} ion, as shown in **Figure 4.1** [80].

Despite various advancements, producing amber glass has proven to be a challenging

[1]This subchapter is published in full in the article: Reis Santos, C.; Ruivo, A.; Carneiro, A.; Veiga, J.P.; Palomar, T.; Coutinho, I. Amber 'Alchemy': Recreating and Investigating Yellow Glass Formulations. Materials 2024, 17, 5699. https://doi.org/10.3390/ma17235699

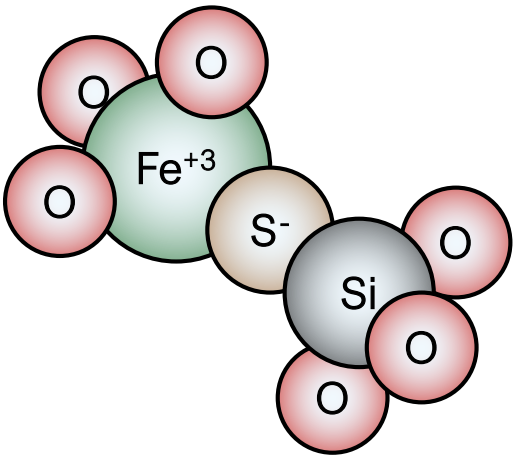

Figure 4.1: Representation of the amber chromophore, adapted from [80].

process. The recipe appears simple—requiring only silica (as a network former), sodium (as a flux), lime (as a stabilizer), iron (typically present in the silica source), sulphur (often from sodium sources like natron), and a reducing agent such as carbon—but it requires careful control of redox reactions. The amber colour is obtained when the co-existence of an oxidized-iron species (Fe^{3+}) and a sulphur-reduced species (S^{2-}) is achieved [40]. The success of Roman glassmakers in producing this colour was probably due to their strict control of raw materials, including a source of silica with sufficient iron oxide, a source of sodium rich in sulphur, such as natron, and a reducing agent such as charcoal [67].

The Industrial Revolution introduced more complex recipes and materials in amber glass production, as evidenced in batch books and patents. For example, the use of pyrite (FeS_2) as an iron and sulphur source became widespread [80, 82]. Although amber glass can be made with inexpensive raw materials, glass factories in the mid-20th century often opted for more expensive components, such as uranium and selenium, to achieve and control the amber colour [42]. By the 1940s, researchers such as Lawton, Holland, and Turner had conducted extensive studies on amber glass production, showing that even with identical batch formulas, factories struggled to replicate colours consistently [42].

An alternative method for producing amber glass involves adding manganese oxide to the mix. In this case, the redox process must still be controlled (Equation 4.1), and the colour results from the balance between iron and manganese oxides and the mix of colour [40]. Achieving consistent amber colour remains to this day difficult, even when employing modern techniques such as the use of real-time sensors and oxygen probes, allowing for precise adjustments to the redox environment during production.

$$Mn^{4+(brown/black)} + 2Fe^{2+(blue)} \leftrightarrow Mn^{2+(yellow)} + 2Fe^{3+(yellow)} \tag{4.1}$$

Since achieving a proper balance between iron and sulphur represents a significant technological challenge, four recipes using this chromophore were selected for further investigation, along with one iron–manganese recipe for comparison. The study will assess the resulting

colour and thermal and mechanical properties, such as glass transition temperature (Tg) and hardness. An additional goal is to determine if the glass produced aligns with the historical recipe descriptions, such as whether a "light amber" recipe indeed results in light amber glass. The objective of this subchapter was not only to reproduce historical recipes from amber glass, but also to ascertain how modern amber glass manufacturing could benefit from a scientific approach to historical recipes found in the *arcana*.

4.1.1 Amber Recipes – Reproduction

The methodology employed for the selection of the recipes has already been described in detail in the preceding Chapter 3. This section, instead is concerned with the process of reproduction and characterisation of the recipes. It is noteworthy that while the selection of recipes was carried out, their similarity emerged as they all share a key trait: the amount of iron, which is crucial for producing amber glass is never specified, as it naturally occurs in the sand. Therefore, when a recipe failed to produce amber glass, variations were developed instead of altering the original formula. Recipe NP3 belongs to the NPGC *arcanum* and is the recipe containing Fe-Mn. Three recipes were selected from the GF *arcanum*—G92, G130, and G192—each with different compositions and reducing agents. Finally, from the COG *arcanum*, only one recipe was selected, C98, featuring a simple composition like most of the recipes found in some of the batch books in Corning's Rakow Library [83].

Because iron oxide is essential to obtaining the amber-yellow colour, different approaches were employed to determine the amount of this oxide that should be added to the initial recipe for each *arcanum*. For the Castro and Oliveira Guerra *arcanum* recipes, the amount of Fe_2O_2 added was based on analyses conducted on the sands used by the Marinha Grande factory, as this *arcanum* is thought to have been used in that factory [24, 41]. For the Gaivotas recipes, since there is no analysis or knowledge of the sands used, several historical colourless glasses produced at the factory were analysed to quantify the minimum amount of iron oxide required. For the NPGC, the approach was the same and the amount of iron oxide was also determined by analysing historical objects. The choice to use colourless objects to determine the percentage of iron in the sand came from the fact that they were the only historical objects we had associated with each of the factories. Considering that the sand would probably be the same for all glass compositions, the minimum iron value was determined.

Table 4.1 shows the amount of iron oxide used in each recipe, along with its variations. The reproduction process always starts with the original recipe, to verify its effectiveness without modifications. Next, several variables were individually modified, such as the amount of iron oxide, the addition of charcoal and the sulphur source.[2] Given the complexity of the glass, recipe C98 was chosen to test all these variables due to its simpler composition, which facilitates the interpretation of results. In the GF *arcanum*, only the original interpretation

[2]Non-laboratory raw materials such as charcoal and flour are characterised in Appendix D.

of each selected recipe was tested.

Table 4.1: Selected recipes and variations [24, 67]

Recipe ID	Version	Main Recipe	Fe/Mn and Reducing Compounds (wt. %)	Reference
G92		Original recipe	0.057% Fe	-
G130		Original recipe	0.057% Fe	-
G192		Original recipe	0.057% Fe	Historical objects
C98	a	Original recipe	0.008% Fe	Historical objects
	b	Original recipe	0.2% Fe	[22]
	c	Original recipe	0.2% Fe + 10% charcoal	[58]
	d1	Natron as sulphur source	0.1% Fe + 20% charcoal	[58]
	d2	"	"	[58]
	d3	"	"	[58]
	e1	Natron as sulphur source	0.2% Fe + 20% charcoal	[58]
	e2	"	"	[58]
	e3	"	"	[58]
	f	"	0.2% Fe + 30% charcoal	[58]
	g	Double amount of e1	0.2% Fe + 20% charcoal	[58]
	h	Natron as sulphur source	0.2% Fe + 10% charcoal	[58]
	i	Natron as sulphur source	0.1% Fe + 10% charcoal	[58]
	j	Natron as sulphur source	0.05% Fe + 20% charcoal	[58]
	k	Original recipe	Fe-Mn from NP3a	-
	l	Natron as sulphur source	0.15% Fe + 20% charcoal	[58]
NP3	a	Original recipe	Original amount Fe-Mn	-
	b	Original recipe	Half amount of Fe-Mn	[58]

Of the five selected recipes, 21 attempts to reproduce amber glass were made and only 10 had a result between light and dark amber, as shown in **Figure 4.2**. Two versions of the NP3 recipe were reproduced, one of each of the GF recipes (G92, G130 and G192). The C98 appeared to be the simplest, with only four ingredients; for this reason, it was chosen to be explored in more depth, with more variables, and 15 versions were reproduced.

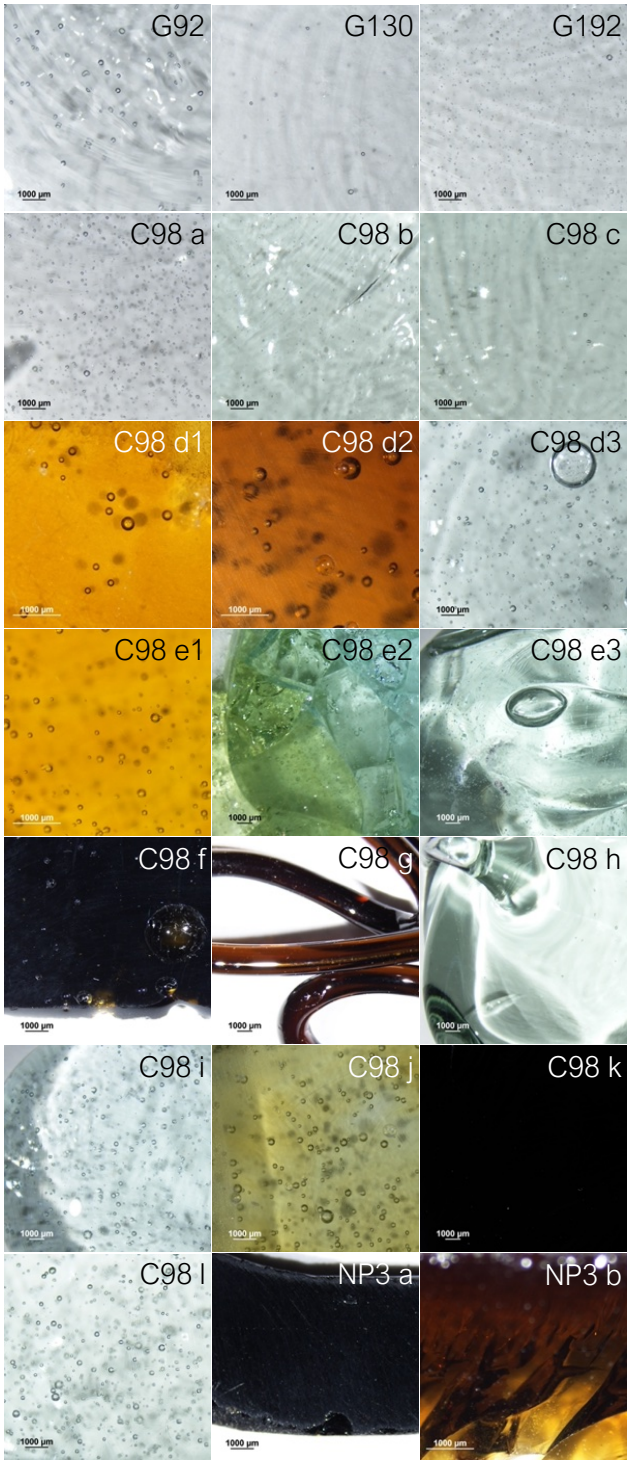

Figure 4.2: Pictures taken with the stereomicroscope of the reproduced amber recipes.

The two reproductions of the NP3 (recipe with Fe-Mn) resulted in dark amber. The sample from the original recipe, NP3 a, produced a very dark, almost black glass. NP3 b had half the amount of Fe-Mn, which slightly altered the colour of the sample, but the difference is only visible in the thinner areas.

Sample G92 had elemental sulphur in its composition and flour as a reducing agent, but the result was a completely colourless glass. G130 had charcoal as a reducing agent, but the same result was obtained. G192, despite having a more complex composition and more ingredients, resulted in the same as before, a colourless glass. In all three recipes, the problem is believed to be the amount of iron oxide added (0.057 wt.%), so for future work on amber glass from this factory, more information on its context is needed to ascertain the raw materials that were used.

Regarding recipe C98, it was chosen to be explored in more depth and with more variables. Sample C98 a used the amount of iron oxide from the analyses of the sand used by the Marinha Grande Factory [24]. As expected, due to the lack of a reducing agent, this recipe resulted in colourless glass. In sample C98 b, more iron oxide was added, according to existing studies about the reproduction of amber glass [67]. Since there was still no reducing agent, the result was again colourless glass. Therefore, in sample C98 c, charcoal was added to the composition. The result was a bluish to colourless glass, as can be seen in **Figure 4.2**. According to other studies about natron composition, the problem seems to be the way sulphur is added [60]. The following results will therefore be presented together with the chemical characterisation of the glasses using WDXRF, to understand what may or may not be affecting the formation of the ferric sulphide complex.

4.1.2 Chemical Characterisation

Although the initial interpretation of the recipe did not yield the anticipated outcome, it offered a chance to investigate and refine numerous variables. By making successive adjustments to a few variables, it was the intention to gain valuable insights into the role of each ingredient and to enhance our understanding of the characteristics of the recipe. **Table 4.2** presents a quantitative analysis of all the samples discussed in this section.[3]

The data indicates that some samples—C98 d2, C98 g and C98 j—present a higher content of alumina than expected. This is due to the alumina crucible contamination. Since the focus of the study is on colour control and variation, it seems reasonable to conclude that alumina does not play a significant role in this context. However, it will have an impact on the mechanical properties of the glasses, which will be reflected in the Tg and Vickers Hardness values. When compared to historical samples, these will not have this influence from the crucible, as the extent of the contamination area of the crucibles used in the past

[3]Although the chemical composition of materials in conservation science is usually expressed in wt. %, the conversion to mol % is given in Appendix D – Table D.2.

Table 4.2: Wavelength-Dispersive X-ray Fluorescence Spectroscopy results of amber samples in weight percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	MnO	Fe_2O_3	ZnO
G92	18.4		0.8	73.9	0.91		0.05	5.83		0.07	0.01
G130	16.5		0.2	76.5	0.18		0.06	6.44		0.06	0.01
G192	16.3		0.9	76.1	0.1	0.48	0.05	6.05		0.06	
C98 a	16.8		0.6	66.4	0.85		0.03	15.2		-	
C98 b	16.9	0.3	1.3	65.3	0.5		0.02	15.4		0.32	
C98 c	15.3		1.4	66.1	0.76		0.13	16		0.27	
C98 d1	11.1	0.2	2.2	66.6	0.08	0.29	0.12	19.1		0.18	0.01
C98 d2	10	0.1	6.4	66.4	0.08	0.18	0.09	16.5		0.18	0.01
C98 d3	8.5	0.2	0.8	70	0.23	0.51	0.11	19.3		0.19	
C98 e1	9.9	0.2	1.9	66.3	0.05	0.32	0.13	20.8		0.41	0.01
C98 e2	11.4	0.2	2.2	68.2		0.22	0.13	17.3		0.36	0.01
C98 e3	10		0.6	69.9	0.24	0.56	0.12	18.1		0.37	
C98 f	10.1	0.2	2.7	64.6	1.07	0.63	0.19	20.1		0.37	0.01
C98 g	8.6	0.2	5.2	67.5	0.37	0.94	0.44	16		0.64	0.01
C98 h	11.8		1.3	69.9	0.31	0.57	0.05	15.7		0.34	
C98 i	9.8		3.2	67.6	0.17	0.4	0.09	18.5		0.19	0.01
C98 j	10.4	0.2	4.5	67.8		0.18	0.12	16.6		0.11	0.01
C98 k	13.1		3.6	54.4			0.08	13.5	5.8	9.47	0.02
C98 l	10		1.7	69.1	0.3	0.36	0.12	18.1		0.22	0.01
NP3 a	8.1	0.9	11	64.5			0.2	2.11	4.27	6.85	1.89
NP3 b	8.2	0.9	13	67			0.21	2.34	2.25	3.92	2

(which were much bigger than the ones used in the current work) has already been studied [84].

Glass production in the nineteenth century already used chemical reagents produced in factories and laboratories, but their purity was not as rigorous and controlled as it is nowadays. Consequently, despite the original recipe indicating the use of sodium carbonate, the current evidence does not allow for the identification of associated impurities, or the determination of the specific sodium sources employed in amber production. Therefore, based on these facts and the literature, the basic recipe was modified by changing the sodium source to a mixture of sodium bicarbonate, sodium sulphate and sodium chloride, in a ratio of 40:30:30 wt.% [67].

Sample C98 d1 was the first successfully reproduced amber glass, with the following differences from the original: an increase in the amount of iron, the addition of sulphur with

sodium and the addition of charcoal. From this recipe, two more samples were reproduced, C98 d2 and C98 d3, based on the exact same recipe, with the aim of testing the reproducibility. In the last one, the result was a colourless glass, despite the attempt to reproduce it under the same conditions. This difference in result may have been caused by variations in the percentage of water in the raw materials or batch moisture [80]. An electrical fault during the melting process is another possibility, though it is uncertain whether it played a role. In the characterization of the amber (C98 d1 and C98 d2) and colourless (C98 d3) samples, the main difference is the SO_3 amount, which in the case of C98 d3 is much higher than in the other samples. Samples G92, G130 and G192 also have a higher SO_3 content than samples C98 d1 and C98 d2. According to the literature, the lower the amount of SO_3, the more reduced the composition of the glass [42, 80]. This shows that for the samples G92, G130 and G192, the proportion, melting conditions or atmosphere in the glass matrix were not the most suitable for reducing the batch [80]. The differences in the percentage of SO_3 in recipes of the same composition (for example, C98 d1 and C98 d3) may indicate a greater volatilisation of SO_3, which influences the redox conditions of the batch. Again, this may be due to batch moisture conditions.

As, according to the literature, the ideal proportion of iron oxide in amber glass is between 0 and 0.5 wt.%, the subsequent samples were made increasing this oxide from 0.05 wt.% to 0.2%. Again, three attempts were made with the same composition, and only C98 e1 produced the amber colour. The C98 e2 sample, although not completely colourless, has a much more subtle and heterogeneous colour. It is possible to see some areas which are more yellowish and others more bluish, possibly due to the higher concentration of Fe^{3+} and Fe^{2+} ions. The significant difference in characterization is again the SO_3 amount, which in the case of sample C98 e2 is below the detection limit, indicating that it has perhaps volatilised more than in the other samples. The difference in colour may have been due to a lack of homogenisation of the composition. Sample C98 f (30% charcoal) has the same amount of iron as C98 e1 (20% charcoal) and different charcoal amounts, so a slight difference in colour was to be expected, but not too pronounced, as the amount of colourant is the same. However, the result for C98 f was almost black glass, with the amber colour only visible in very thin areas, clearly due to the increased amount of reducing agent. This could mean that the reducing agent is playing an even more important role than expected by directly altering the colour. Given this drastic difference in results with just the addition of more charcoal, further analysis is being carried out to understand how it interacts with the glass matrix and whether it might remain in the composition (rather than volatilising completely as would be expected). In order to define the methodology for investigating the influence of charcoal, elemental mapping was carried out on sample C98 f (**Figure 4.3**). As can be seen, there is a large presence of carbon (in red), which may indicate that some of the percentage of charcoal remains in the glass, However, further analyses will be needed to confirm this hypothesis, which will be considered in future research.

The amount of reducing agent plays a fundamental role, sometimes even more important

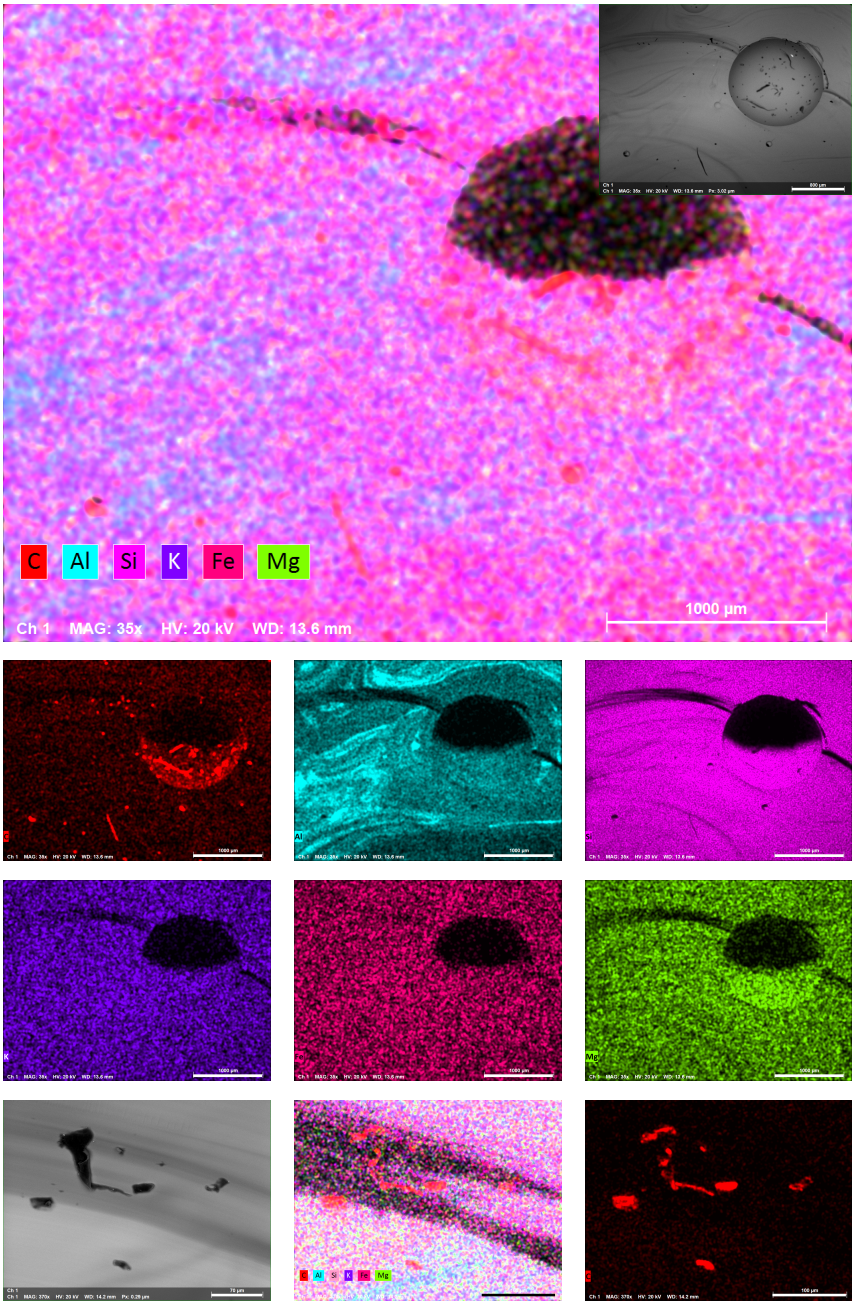

Figure 4.3: VP-SEM-EDS elemental mapping of C98 f glass.

than the different amounts of iron. Samples C98 d1 and C98 e1, with 0.1 and 0.2 wt.% iron oxide, respectively, and both with 20 wt.% charcoal, have a very similar visual result. However, samples C98 e1 and C98 f, with the same amount of iron oxide (0.2 wt.%) and 20 and 30 wt.% charcoal, respectively, produced two completely different glass colours (amber, and a very dark amber resembling black, respectively).

Sample C98 g was made using the exact same recipe as sample C98 e1, but testing with the double of the total amount of raw materials. Instead of 60 g in total, 120 g was produced, and the result obtained was quite different for the two samples, with sample C98 g being

noticeably darker. This shows that the result depends on several variables, including the batch quantity.

According to the literature, the ideal percentage of charcoal is between 10 and 20% [67]. Samples C98 h and C98 i contain 10% of charcoal and 10% and 20% of iron respectively. Both resulted in colourless glass, suggesting that although 10% of charcoal is sufficient to make amber glass according to the literature, it may not be enough to work with the proportions in this recipe. Returning to 20% of charcoal, two more variations were tested. Sample C98 j has 0.05% iron oxide, an amount very similar to the G samples. The result was a very light, greenish amber, but it proved possible the production of amber with extremely low iron content. Sample C98 l has 0.15% iron and although this is theoretically an amount that should produce an amber colour, since the samples with 0.10% and 0.20% (C98 d1 and C98 e1) worked perfectly, the result was not satisfactory. **Table 4.2** shows a higher SO_3 value compared to the amber samples.

Finally, sample C98 k was an attempt to understand the influence of the base composition on Fe-Mn amber, starting from the C98 recipe, but with the same Fe-Si and Fe-Mn ratio as the NP3 a recipe. Despite the different base composition, the result was a glass that is nearly black, and indistinguishable from the NP3 a sample.

4.1.3 Thermal Properties

Thermal characterisation was carried out using DSC and dilatometry techniques **Table 4.3**, which allowed for the measurement of the glass transition temperature (Tg), the dilatometric softening point (Td) and the thermal expansion coefficient (αL) of seven of the samples.

Table 4.3: Results from thermal analyses to reproduced amber glasses.

	C98 d1	C98 d2	C98 e1	C98 f	C98 k	NP3 a	NP3 b
$T_{g\ (onset)}$ DSC (°C)	609	617	607	-	-	583	583
$T_{g\ (onset)}$ DIL (°C)	609	623	612	605	546	581	593
Td (°C)	643	664	649	650	584	644	659
αL (50–500 °C) × 10^{-6}(°C^{-1})	10	10	10	11	12	7	7

The glass transition temperatures of the samples measured by dilatometry range from 546°C to 623°C, in which the samples coloured with FeS have a higher Tg, around 600°C, and the samples coloured with Fe-Mn have a lower Tg, around 550°C. It is worth noting that sample C98 k has the lowest Tg compared to NP3 a and NP3 b. This could be caused by the fact that the first sample has a higher sodium content, which has a direct impact on Tg. The lower Tg of NP3 a and NP3 b glasses have the advantage of requiring lower energy/temperature to melt the glass, making the process faster and less expensive.

As for the softening temperature, it gives us valuable information and can even justify some choices about the uses of amber glass, mainly used for containers rather than for elaborate pieces. The Td of the samples varies between 584°C and 664°C. These temperatures are considered quite high, especially when compared to other compositions known to have been used for blown glass [11]. This characteristic possibly conditioned the type of object that could be produced with these compositions, because it needs a higher temperature for work that requires being constantly reheated to allow it to be blown.

Regarding αL, its values are between 7.0 and 12.2, which indicates that, despite the different compositions, these values remain similar. Samples with a lower αL have a higher percentage of Al_2O_3, since the presence of metal oxides like this means that there are fewer non-bridging oxygens available in the composition, making these glasses more resistant to expansion differences [47].

4.1.4 Vickers Hardness

Hardness tests were carried out to understand the properties of the produced historical glasses. By carrying out hardness analyses on samples produced from historical recipes and creating a database of their characterisation, when a reproduction is attributed to a historical object it is possible to hypothesize the thermal and mechanical properties of that object, without damaging it, in a kind of reverse engineering.

Nine samples were then measured to obtain the Vickers Hardness, as shown in **Table 4.4**.

Table 4.4: Vickers hardness of the reproduced amber samples.

	C98 d1	C98 d2	C98 e1	C98 e2	C98 j	C98 k	NP3 a	NP3 b
HV 0.5	565 ± 20	574 ± 9	590 ± 15	574 ± 4	627 ± 15	605 ± 23	568 ± 15	655 ± 16
GPa	5.5	5.6	5.8	5.6	6.1	5.9	5.6	6.4

The hardness of most of the samples ranges between 565 HV0.5 and 655 HV0.5, values that are significantly high compared to other studies based on historical recipes [11], and even similar to the hardness of borosilicate glass [85].

The samples with the highest hardness are C98 j, C98 k and NP3 b, and the samples with the lowest hardness are C98 d1, C98 e2 and C98 f. As can be seen in **Figure 4.5**, hardness does not seem to be connected to colour or colourants at all. However, by comparing their chemical characterisation in **Table 4.2**, we can see that the samples with the highest percentage of CaO and the lowest percentage of Al_2O_3 are the ones with the lowest hardness, coinciding with what is described in the literature [86]. Although there are no hardness studies on historical compositions (because it is an invasive technique), it can be said that

the glasses have a GPa hardness similar to that of soda-lime glass, as would be expected [87].

4.1.5 Colour Characterisation

Since iron can give several colours to glass, such as blue, green and yellow, colour measurement is essential to understand the small differences in the colours of the various samples and which ones seem similar despite the differences in composition. The scatter plot in **Figure 4.4** represents the L*, a* and b* coordinates of the CIE L*a*b* system. **Figure 4.5** is the simplification of **Figure 4.2**, to help with the interpretation of colour measurements.

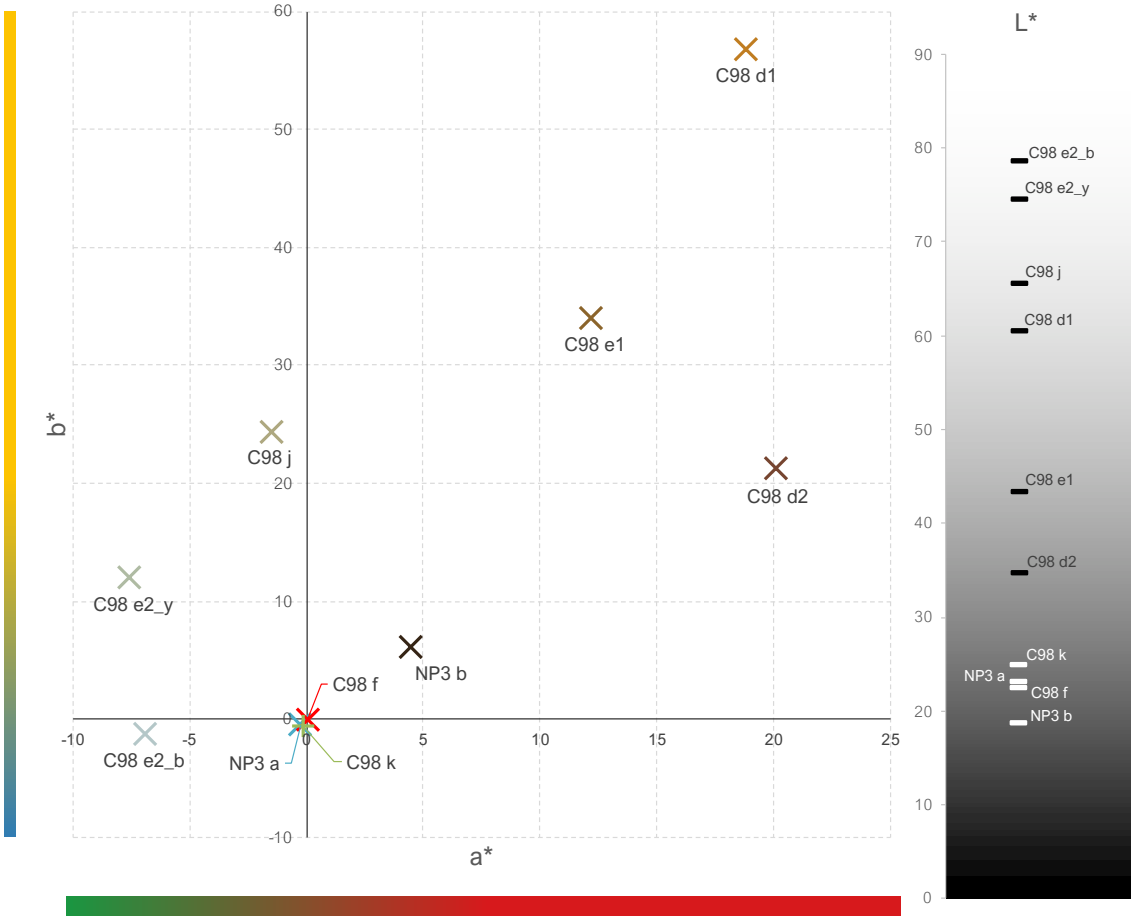

Figure 4.4: Scatter plot of the L*a*b* coordinates of the colorimetry measurements of the reproduced amber glasses.

Figure 4.4 shows that sample C98 d1 is the closest to the yellow and red colours and sample C98 d2 is much closer to the blue, despite their same composition. According to the literature, the most similar sample to the amber colour, in terms of a* and b* values, is sample C98 e1 [88] . In the C98 e2_b and C98 e2_y samples (measurements taken in the bluest and yellowest areas of the sample C98 e2) it is noticeable that, although the colour change is not so significant, the analysis indicated that C98 e2_y has a higher b* value and is more on the yellow side of the plot. Point C98 e3_b, on the other hand, has

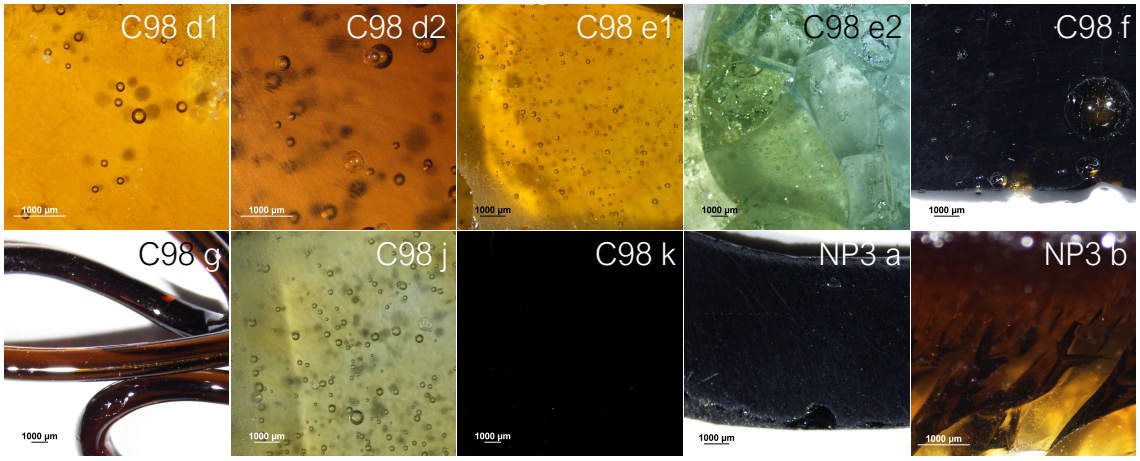

Figure 4.5: Pictures taken with the stereomicroscope of the reproduced amber glasses

negative values, and is closer to the blue area of the plot. In relation to sample NP3 b, it is visually quite dark, but the measurement clearly shows that its colour is much lighter than that of sample NP3 a. Samples NP3 a, C98 f and C98 k, as seen from **Figure 4.5**, are the darkest, almost black, so the b* and a* values are very close to zero. The L* colourimetric measurement confirms this, as samples C98 k, C98 f, NP3 a and NP3 b are the ones with the highest colour intensity.

The chromophores were characterised using UV–Vis absorption spectroscopy in six of the samples shown in **Figure 4.6**. The rest of the amber samples were not characterised by this technique because of their dark colour, which saturates the signal.

Samples C98 d1 and C98 d2, as expected, show an absorption band around 425 nm, characteristic of the FeO_3S sulphide ion. Similarly, samples C98 e1 and C98 j also exhibit a band at 425 nm; however, their spectra appear more absorbent beyond 650 nm, further suggesting the presence of Fe^{2+} ions. Their characteristic bands are found at 1100 and 2100 nm, beyond the detection limit of the equipment used, but the broad absorption band between 650 and 1050 nm supports their presence. On the other hand, samples C98 j, C98 d2, and C98 d1 exhibit lower absorption at the end of the spectrum, which may indicate a lower presence of Fe^{2+} ions—the species responsible for the blue colour in glass. This observation aligns with the colorimetry analysis (**Figure 4.4**), where these three glasses show highest b* values, corresponding to the yellow side of the graph. The coexistence of Fe^{2+} ions (responsible for the blue colour) and Fe^{3+} ions (responsible for the yellow colour) results in the green colour of glass—one of the most common and easiest colours to produce due to the natural presence of both oxidation states in glass [40]. Looking at **Figure 4.4**, it is possible to see that the colorimetry of samples C98 e1 and C98 j is shifted towards the green side of the graph, further supporting the presence of both oxidation states, although they were visually classified as amber glasses. In sample NP3 b, the Fe-Mn amber, the absence of Fe^{2+} ions is noticeable, indicating complete equilibrium between iron and manganese, as expressed by equation 4.1.

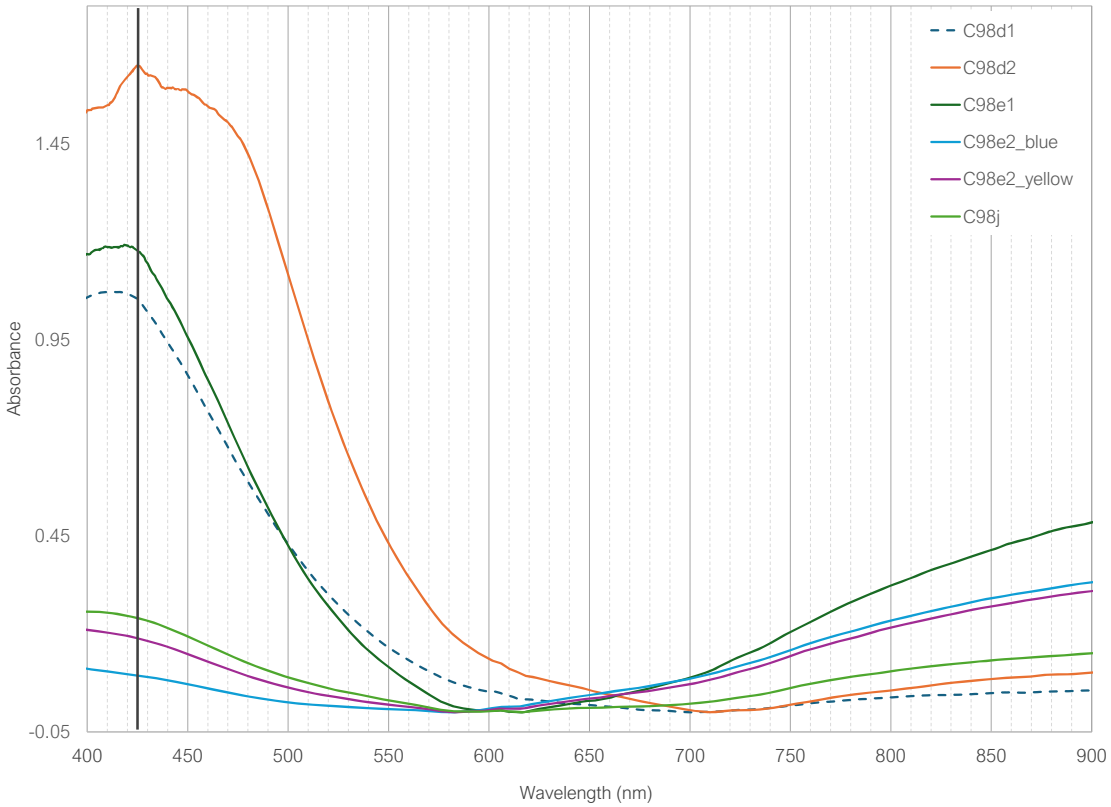

Figure 4.6: Absorbance spectra of the reproduced amber glasses with FeO_3S absorption band marked in black, normalised to the minimum. The reference lines correspond to the soda-lime glass composition described by Navarro [40].

As mentioned above, the C98 e2 sample is not homogeneous, so the analysis was carried out in two different areas, to see if this change was noticeable (**Figure 4.6**). It became apparent that the C98 e2 yellow point has a much more intense band at 425 nm from the Fe^{3+}, while the Fe^{2+} region is slightly less intense. The C98 e2 blue point is exactly the opposite, as it is the bluest sample. It has less absorption in the Fe^{3+} region and slightly more in the Fe^{2+} region.

4.1.6 Concluding remarks

This subchapter has explored the complex amber-glass colour technology from the eighteenth to the twentieth centuries, using historical recipes as primary sources. The research focused on decoding and interpreting amber glass recipes from four Portuguese *arcana*, with particular attention to those employing FeS or Fe-Mn as chromophores. These recipes were reproduced in the laboratory and characterized chemically, thermally, and mechanically, revealing the intricate nature of FeS amber glass production, which requires precise control over a few variables.

One recipe was selected for deeper investigation and underwent significant adjustments during its interpretation. Such modifications were necessary due to the challenges of

converting historical recipes into modern laboratory protocols, where it is often unclear whether a recipe fails due to inherent flaws or misinterpretation. By altering the method of adding certain ingredients—while maintaining the original elemental ratios—the possibility of alternative raw material forms was explored.

This investigation highlights a critical observation: deeper knowledge of glassmaking processes does not inherently entail better results. Despite its widespread historical use, reproducing amber glass with consistent control over raw materials remains a challenge. The findings demonstrated that successful experimental outcomes do not always translate into a comprehensive understanding of the process variables, leading to inconsistencies in reproducing results. This underscores the complexity of interpreting historical recipes and the limitations that persist even with modern scientific advances.

As a result of this study, systematic guidelines for reproducing historical glass are proposed. These guidelines aim to support future research into glass production across different centuries, enabling the continuous refinement of reproduction methodologies. By comparing reproduced glass with historical objects and sources, it becomes possible to assess whether the information is consistent with or contradicts existing interpretations, shedding light on the technological capabilities of the Portuguese glass industry during this period.

Several key findings emerged from the experiments conducted:

- Producing FeS amber glass proved to be significantly more complex than Fe-Mn amber. While Fe-Mn chromophores were easier to manage, they tended to produce very dark colours, making it challenging to achieve softer, lighter amber hues.
- The percentage of SO_3 and its volatility or complexation played a critical role. WDXRF analysis revealed that higher SO_3 content often resulted in colourless glass. Sulphur addition methods also proved crucial, with the desired amber colour only appearing when sulphur was combined with sodium.
- Samples coloured with Fe-Mn chromophores exhibited the lowest glass transition temperature (Tg), though all samples demonstrated high softening points.
- Vickers Hardness Tests indicated that the samples were quite hard, with values comparable to borosilicate glass. However, samples with higher calcium oxide and lower alumina oxide content were slightly less hard.
- Colorimetry results showed that most amber samples skewed toward yellow and red, consistent with the desired amber hues. While FeO_3S was responsible for the amber colouration, some UV–Vis spectra suggested the presence of Fe^{2+}.

By uncovering the techniques and choices behind Portuguese glass production through the study of batch books and recipes, this research bridges the past and present. It provides critical insights into the craftsmanship behind historical objects preserved in museums.

Understanding these recipes enhances not only the conservation and interpretation of these artefacts but also contributes significantly to the broader field of glass conservation. This ensures that the knowledge and techniques of past glassmakers endure, continuing to inform and enrich both the art and science of glassmaking and heritage preservation.

4.2 Chasing the Perfect Blue: Experimental approach to *arcana* recipes

Since its discovery, glass have been produced in a wide variety of colours and with the aim of accurately imitating stones [89]. In the case of blue, it is a colour that has always been highly valued for its vibrancy. In ancient cultures it was seen as a symbol of divinity and power [90].

One of the earliest examples of blue glass is a turquoise sphere from the sixteenth century BCE, which was used to make the eyes of a statue [40]. In those early days glass was a soft, opaque, malleable paste [40]. It is still unclear how the Egyptians first learned to make glass, or how they first made glass out of the raw materials. But there is a theory that foreign artisans captured in military campaigns may have taught the Egyptians how to make glass [91]. However, by the time of Thutmosis IV several core-formed vessels were known to exist, showing that glassmaking in Egypt had become very sophisticated (**Figure 4.7**) [90]. Given that these copper glasses almost always contained a small percentage of tin, it is thought that they were made using bronze as a colouring agent [92].



Figure 4.7: Core-formed glass vase, probably from 1400–1300 BCE, Egypt. This vessel was produced using the core-forming technique with applied trail decoration. Source: CMOG (Accession Number: 66.1.213).

The production of coloured glass required precise control of the conditions in the furnace and the careful addition of specific materials. Of all the colours, blue is the most common in artefacts from the Aegean, Egypt and, to a lesser extent, Mesopotamia regions. Glass coloured with copper seems to be the most common, both in opaque and translucent glass [93, 94]. Copper was used to produce lighter blues, while cobalt was used for more intense blues [95]. These two materials were essential in creating different shades of blue, and copper was also used to make turquoise or light blue glass. This shows that the Egyptians were very skilled at making these bright colours and that they were important in their culture [96].

The colouring of glass is primarily achieved through the incorporation of transition metal oxides, most notably those of copper and cobalt, which modify the absorption and transmission of light [42]. The blue colouration of glass is achieved through the incorporation of these oxides, with the resulting shades of blue depending on the oxidation state and concentration present in the glass melt.

Although this colour is not very challenging to produce in comparison with amber for instance, its behaviour in a silica matrix is somewhat more complex. Under oxidising conditions, Cu^{2+} is formed, while under reducing conditions and at higher temperatures, Cu^{+} and metallic Cu is also produced, the latter is responsible for ruby and aventurine colours, for example. Notably, Cu^{2+} is the ion responsible for both blue and green colours in glass. This blue-to-green transition is due to an increased number of unsaturated oxygen ions relative to saturated ones, which not only influences light absorption by copper compounds but also affects the spatial distribution of oxygen ions around each Cu^{2+} ion [40, 42].

For cobalt, the oxidation states that produce colour in glass are primarily Co^{2+} and to a lesser extent Co^{3+} [42]. While Co^{3+} is less stable and can only form in certain glass compositions and at lower temperatures, it is responsible for green colours in glass. In contrast, Co^{2+} is more abundant and can produce a range of colours, including blue, red and purple, depending on its co-ordination environment [42]. When surrounded by four oxygen ions, it produces a blue glass, while an increase to six or more oxygen ions shifts the colour towards red. In addition, cobalt can contribute to green tones in certain compositions containing iodides at lower temperatures [42].

Although cobalt does not add much difficulty to the glass melting process, it does raise some questions about its workability. It was thought that small amounts of colourants would not affect the melting or even the working properties of the glass, but contrary to this it was found that cobalt, by absorbing infrared radiation, cools faster than a glass of the same composition without cobalt. This property is also found in glasses containing Fe^{2+}, Ni^{2+} and U^{6+} [42].

The study of blue glass recipes from *arcana* of the eighteenth to twentieth centuries provides valuable insights into historical glassmaking practices, revealing how composition,

raw materials, and production methods influenced the final properties of the glass. This research helps to protect knowledge about glassmaking the traditional way, and it helps us understand how the glassmakers could control the colour and transparency by using certain chemicals. Beyond the technical aspects, this study also has important implications for the conservation and authentication of historical glass objects, as it provides reference data that can aid in museum attributions and the interpretation of glass collections. By combining experimental archaeology, material science, and historical research, this work improves our understanding of how blue glass was made and its evolution across different periods and contexts.

4.2.1 Blue Recipes — Reproduction

Based on the visual and practical results of the reproductions, all 14 recipes, corresponding to 17 glasses, produced a blue glass (**Figure 4.8**). With the exception of recipe G46, which had to be reproduced twice, the first attempt (G46a) produced a blue vitreous mass. However, on removal from the furnace, a white liquid flowed out of the crucible first, followed by the melted glass. This liquid later solidified into a brittle white mass completely separate from the glass (**Figure 4.9**). This problem was solved by reproducing the process a second time, melting at a higher temperature. With this adjustment, a homogeneous, fully fused glass was obtained (G46 b). The specific case of this phase separation will be discussed later in this chapter.

Regarding the three reproductions of the M1_4 recipe—one with cobalt oxide (M1_4C1), one with smalt (M1_4S1) and one with zaffre (M1_4Z1)—as shown in **Figure 4.8**, the results of the three reproductions were quite different. M1_4C1 was the darkest, as expected, because the cobalt source consists only of pure cobalt oxide. The other two were less close to black. This may explain the reference to the use of zaffre and smalt as cobalt sources: when mixed with other ingredients that do not produce colour in the glass, their colouring power is easier to control. For M1_51, the result was, as expected, a turquoise-blue colour. This recipe does not contain any ingredient that enables copper to arrange itself in a way that produces the green colour. Recipe M3_3 produced an even darker glass than M1_4Z1. This could be due to the original recipe, which refers not only to zaffre but also to a blue glass cullet. This means that the colour comes from two sources, resulting in a naturally darker glass. The intensity of the blue may also have been influenced by manganese, which is not mentioned in the M1_4Z1 recipe but is present in M3_3.

As for the reproductions from the COG *arcanum*, the result of C125 was a typical turquoise blue, despite the presence of lead. The name of the recipe, "dichloride blue", might suggest a mixture, perhaps between blue and green, but the glass obtained was extremely homogeneous in colour. The difference between the results for C157 and C158 is clear. C157, which is supposed to be used for flash glass, is much darker - almost black - while C158 is lighter, allowing for the colour to be observed without lapidation. Although C159 is

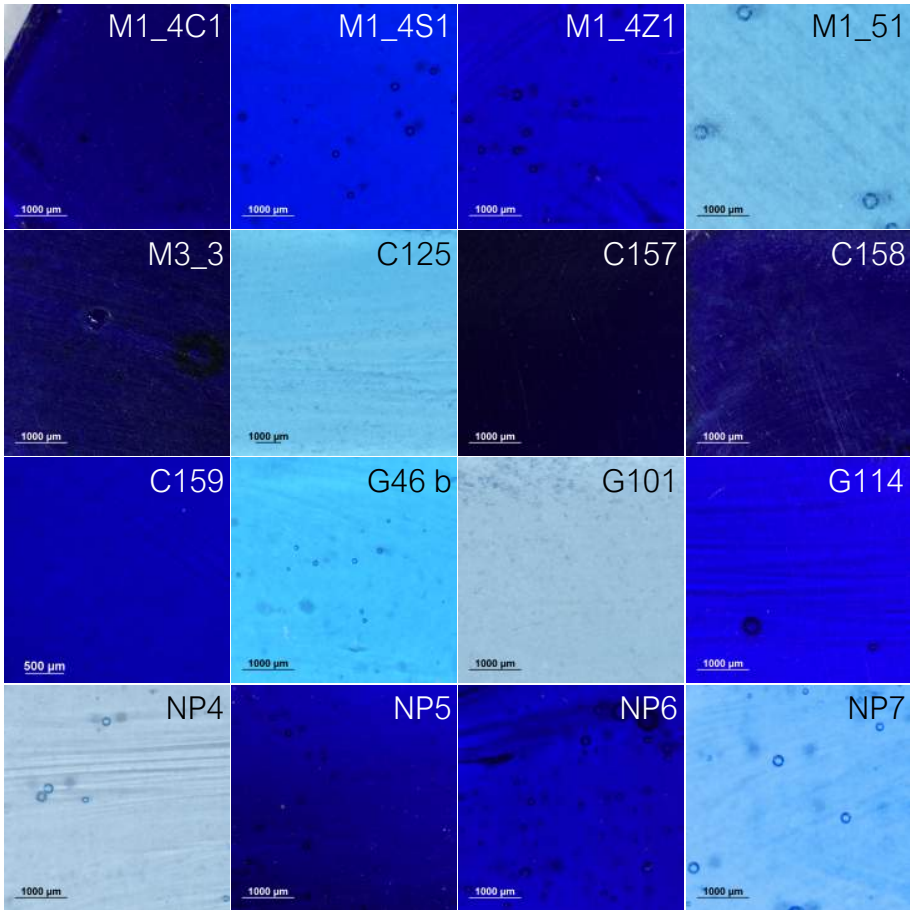

Figure 4.8: Pictures taken with the stereomicroscope of the reproduced blue recipes.

labelled as "navy blue glass," it produced a much darker and more intense shade compared to NP4, which is also referred to as navy blue. This outcome is expected, given that the recipe combines copper and cobalt. However, neither of these results truly matches the navy blue colour, with C157 and C158 appearing to be closer to that colour.



Figure 4.9: Pictures taken with the stereomicroscope of the G46 a glass.

The results for the GF *arcanum* were quite different. G46 b (sound glass), despite the initial problem, produced a very homogeneous and transparent glass with a blue colour very typical of a copper glass, despite the presence of lead. G101, on the other hand, produced extremely clear glass with a shade very similar to the natural tones of colourless glass. G114, as expected, produced a very vivid cobalt blue, like some of the bottles in the

Gaivotas Factory collection.

Finally, presenting the results of the NPGC *arcanum*, the NP4 glass is called navy or sky blue, but it is quite clear and seems more like a sky blue than navy, proving that the names given to the colours were clearly personal choices and did not have the same meaning from one glassmaker to another. NP5 and NP6 are quite similar, the former being slightly darker (as it is a recipe for flash glass) and the latter much more vivid. NP7, on the other hand, is a very unique colour, with a particular ratio of copper to cobalt, resulting in a violet-turquoise blue.

4.2.2 Chemical Characterisation

A deeper analysis of the results first requires examination of the WDXRF data. While the exact composition of the mixture is known before it enters the furnace, the transformations that occur during the heating process are not always linear or fully controlled. Therefore, evaluation of the WDXRF quantification is essential (**Table 4.5**).

Looking at the reproductions of M1_4, the quantification results are in line with expectations. The highest percentage of CoO is found in sample M1_4C1. Glass M1_4Z1 contains 0.57% CoO and is significantly lighter, while M1_4S1 has the lowest cobalt content. Interestingly, although M1_4Z1 and M1_4S1 both contain less than 1% CoO, they exhibit an intense blue colour—quite unexpected given that, according to the result described in the recipe note, these M1_4 recipes were not expected to produce such dark colour, but rather a very faint blue.

This could be due to the presence of 5.55% BaO, which may increase the proportion of Cu^{+} ions. Although Cu^{+} itself does not produce any visible colour, it influences the colouration generated by Cu^{2+}, potentially modifying the final colour of the glass [42, 97].

M3_3 is an extremely dark glass, but its CoO content is relatively low. In fact, it contains exactly the same percentage of CoO (0.31%) as NP6 glass. The striking visual difference could be due to the presence of 1.12% MnO which, although not as strong a colouring agent as cobalt, contributes with brown and purple tones and naturally darkens the glass.

Based on their titles, C157 and C158 were both intended to produce blue glass—one for flash glass and the other not. However, C157 produced a much darker shade with a CoO content of 3.77% compared to 1.02% in C158. Meanwhile, C159, like NP7, contains both copper and cobalt, but the results are very different. While NP7 contains <0.1% CuO and CoO, C159 contains 0.83% CuO and 0.55% CoO. Interestingly, the glass most visually like C159 is M1_4Z1, which contains no copper but has a comparable CoO content. This suggests that the colour of C159 may be predominantly influenced by copper, with little or no effect from cobalt.

Glasses G101 and NP4 appear almost colourless despite the presence of copper. This is probably due to the relatively low CuO content. According to ligand field theory analyses

of soda-lime-silica glass, Cu^{2+} has an absorption coefficient of 3.0 at 780 nm, whereas Co^{2+} exhibits significantly higher absorption coefficients of 31.8, 47.7, and 45.3 at 530, 590, and 645 nm, respectively. This difference explains the stronger colouring effect of cobalt [98]. G101 contains 0.57% CuO and NP4 only 0.24%—both well below the 1.35% CuO in M1_51, which is sufficient to produce a more noticeable colour. Finally, while NP6 is described as "dark blue", NP5 appears darker and has a higher cobalt content (1.57%).

These results highlight how small variations in composition can produce an infinite range of blue hues. This versatility has probably contributed to the enduring popularity of blue glass—not only do different combinations produce different effects, but even small amounts of cobalt can colour large batches of glass efficiently.

Table 4.5: Wavelength-dispersive X-ray fluorescence spectroscopy results of blue samples in weight percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	ZnO	SrO	ZrO_2	SnO_2	Sb_2O_3	BaO	PbO
M1_4C1	16.1		0.9	45.9			0.33				0.89	1.65								34.24
M1_4S1	18.6		0.7	48.4			0.40	0.10			0.79	0.11								30.83
M1_4Z1	18.9		1.1	44.7	1.09		0.25	0.06	0.06		0.73	0.57					0.38			32.15
M1_51	7.6	1.1	1.4	70.0	0.30		10.81	6.66	0.03	0.05	0.24		1.35			0.01		0.45		
M3_3			0.3	52.4			9.24			1.12	0.13	0.31					0.05			36.48
C125	13.7		0.1	69.0			0.15	4.75	0.05		0.96		0.78	0.01						10.50
C157	13.4		1.1	68.3			1.57	6.65				3.77		0.01	0.01	0.01		2.90	2.23	
C158	16.0		1.1	71.6		0.07	0.33	6.75	0.06		0.04	1.02						1.64	1.26	0.08
C159	16.8	0.2	1.2	69.7			0.44	6.88	0.06		0.03	0.55	0.83		0.01			1.82	1.41	0.03
G46b	1.9		0.9	51.3		0.28	12.31	4.59			0.06		0.92		0.06				5.55	22.11
G101	14.0		0.2	74.4			2.75	7.84	0.04		0.10		0.57	0.01		0.01				0.03
G114	15.4		0.3	73.5			2.16	7.92	0.03		0.11	0.50		0.01	0.01	0.01				0.01
NP4	11.7		0.4	75.5			2.86	8.98	0.05		0.05		0.24	0.01		0.01				0.02
NP5	12.8		0.4	74.4			2.57	8.15	0.07		0.05	1.57		0.01		0.01				0.01
NP6	14.1	0.2	0.7	75.2		0.06	1.42	7.76	0.07		0.06	0.31		0.17						
NP7	13.4		0.5	76.3		0.07	1.37	7.89	0.08		0.04	0.02	0.06	0.20		0.01				

4.2.3 Colour Characterisation

By measuring the colourimetry and L* a* b* values of the glasses, it was possible to clearly distinguish the group of glasses made with copper—G46 b, C125, M1_51, G101, NP4—from those made with cobalt—C157, M3_3, C158, NP5, M1_4C1, M1_4S1, M1_4Z1, M3_3, NP6, G114, and C159 (**Figure 4.10**). This is particularly striking because the colours that copper can produce are blue and green, and the colours that cobalt can produce are blue and red. Bearing in mind that in both cases the colour change is not caused by different ions, but rather by their spatial organisation or the amount of oxygen surrounding them, it will be interesting to explore this further in the future.

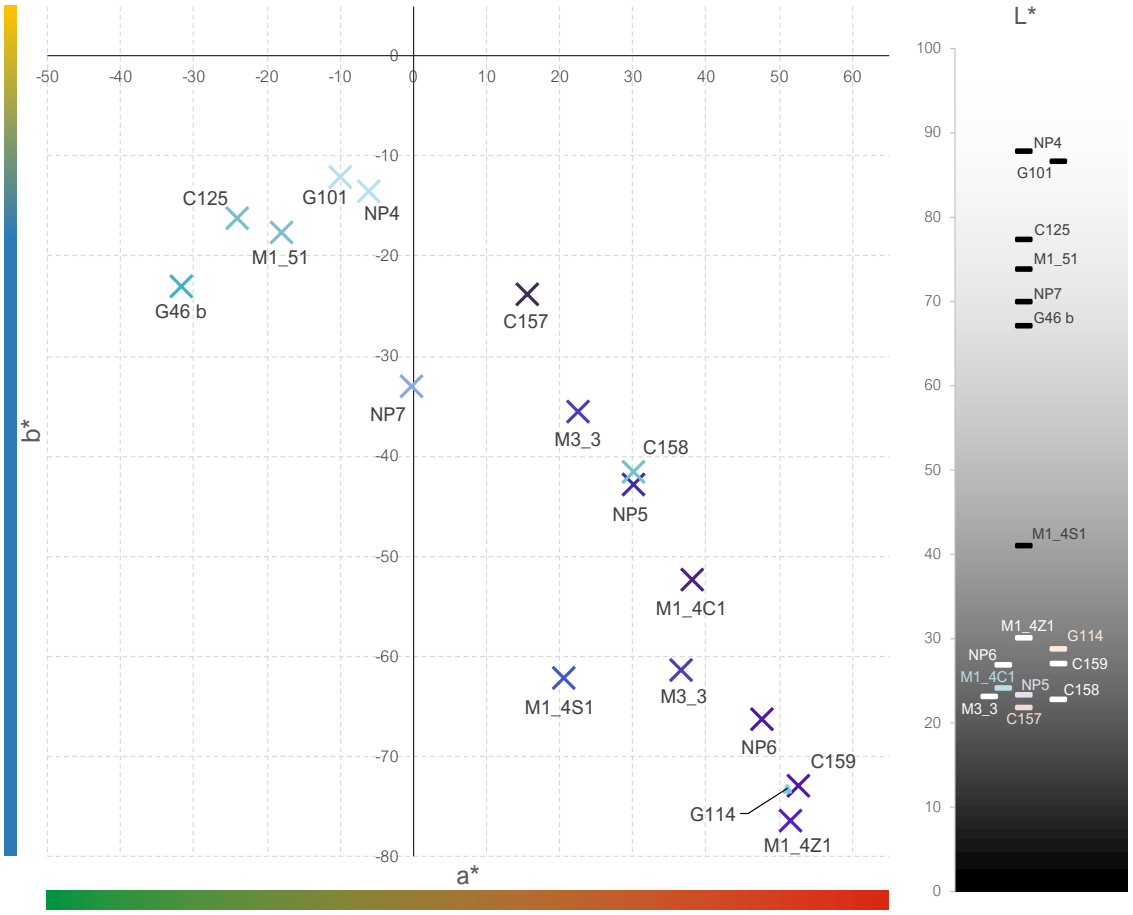

Figure 4.10: Scatter plot of the L*a*b* coordinates of the colorimetry measurements of the reproduced blue glasses.

The colour behaviour of glasses containing both oxides is less straightforward. While NP7 is positioned at the midpoint of the a* axis, C159 falls entirely on the blue/red side of the graph, reinforcing the necessity of chemical characterisation techniques such as XRF and UV-Vis for accurately identifying the colouring agent.

Regarding the glasses where three different cobalt sources were tested (CoO, zaffre, and smalt), although M1_4C1 appears visually darker, the a* and b* values indicate a higher

colour concentration in M1_4Z1. This suggests that the visual difference is primarily due to a variation in luminosity, described by the L* value.

The samples that appear almost colourless—G101 and NP4—also exhibit significant differences in luminosity, with higher L* values. However, in terms of colour measurement, they do not differ substantially from the other samples, despite their near-imperceptible hue.

Examining the L* values alone, it is again evident which glasses were made with cobalt (lower L* values) and which with copper (higher L* values). Comparing this with the composition data (**Table 4.5**) reveals that all glasses containing more than 0.3% CoO have the lowest luminosity, making them the darkest. It is important to note that special attention was given to the thickness of the samples, all of which range between 1 and 2 mm.

Looking at the UV-Vis absorption spectroscopy data, it should be noted that the three glasses with the highest percentage of CoO (M1_4C1, C157 and NP5) could not be measured with the equipment used due to complete signal saturation. The spectra of the remaining glasses are discussed below (**Figures 4.11** and **4.12**).

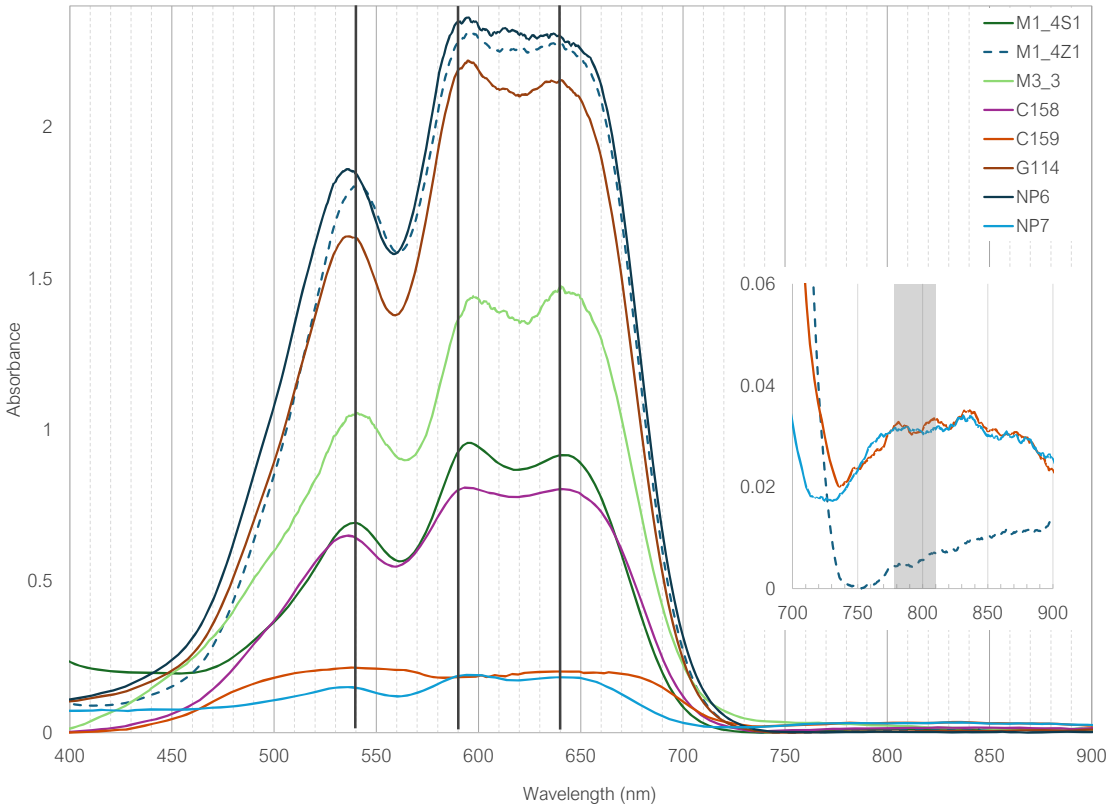

Figure 4.11: Absorbance spectra of reproduced blue glasses with cobalt, with Co^{2+} triple absorption band marked in black and Cu^{2+} absorption in grey, normalised to the minimum. The small spectra is an amplification of the absorption range of glass with copper. The reference lines correspond to the soda-lime glass composition described by Navarro [40].

As shown earlier, cobalt has significant colouring power, particularly the Co^{2+} ions, which

can produce an intense blue colour in the glass at concentrations as low as 0.005%. This ion typically adopts a tetrahedral configuration (CoO_4) resulting in a triple absorption band in the visible region at 540 nm, 590 nm and 640 nm. This band is clearly observed in the spectra of glasses containing cobalt (**Figure 4.11**).

In glasses containing a mixture of cobalt and copper (C159 and NP7), the presence of copper is also visible in the spectra (**Figure 4.11**). The blue colour in these glasses is due to Cu^{2+} ions, which produce a broad absorption band between 780 and 810 nm [40]. However, in the spectra discussed here, the copper band is weak due to the high absorption power of cobalt (**Figure 4.11** in the small spectra).

These results were analysed to investigate possible variations due to compositional differences. Although most of the glasses have complex compositions, making it difficult to draw concrete conclusions, some hypotheses can be suggested. The M3_3, M1_4S1, and M1_4Z1 glasses show a shift to longer wavelengths in the $^4\Gamma_2 \rightarrow {}^4\Gamma_4$ transition, which seems to be related to the high PbO content in these samples [40, 99, 100]. On the other hand, glasses C158, G114, NP6, and NP7 show a shift to shorter wavelengths in the $^4\Gamma_2 \rightarrow {}^4\Gamma_5$ transition, which may be related to the Na_2O content in these glasses [40, 99]. Interestingly, although the literature suggests that the presence of CaO at this concentration induces a shift in the $^4\Gamma_2 \rightarrow {}^4\Gamma_5$ transition, the presence of alumina (Al_2O_3) in glass C159 appears to contribute to a shift in the $^4\Gamma_2 \rightarrow {}^4\Gamma_4$ transition instead [40, 99]. This proves that different oxides can affect the electronic transitions of cobalt in distinct ways.

Although the quantification showed iron oxide in the composition of almost all glasses (from the sand simulation used), its visual presence was hardly noticeable in the glasses containing cobalt, as most of them appear more reddish than green (as noted in the colorimetry section). However, in the spectra of the glasses with the highest iron oxide content—M1_4S1 and M1_4Z1—the faint presence of the Fe^{3+} band around 350 nm can be observed. This small scale of this feature can be attributed to the intensity of the cobalt triple absorption band [40].

Looking at the spectra of the copper coloured glasses (**Figure 4.12**), the difference in the Cu^{2+} band is clear. Without the presence of cobalt, this band is much more pronounced and visible, clearly indicating the chromophore responsible for the colour [40].

Given that copper produces a very different spectrum from cobalt, it is almost impossible to observe variations related to composition. The presence of Cu^{2+} is visible as a broad band around 780 nm and 810 nm (**Figure 4.12**) [40]. The spectra of the G46 b and C125 glasses exhibit the most intense bands, which correspond to their strong colouration, as seen in **Figure 4.8**. Interestingly, the spectra are directly linked to the visual appearance rather than just the composition itself. In other words, although M1_51 has the highest CuO content, it does not exhibit the most intense blue colour—something that is also reflected in the spectra. This outcome in the reproduction process may be a consequence of the high PbO content in the G46 b and C125 glasses [40].

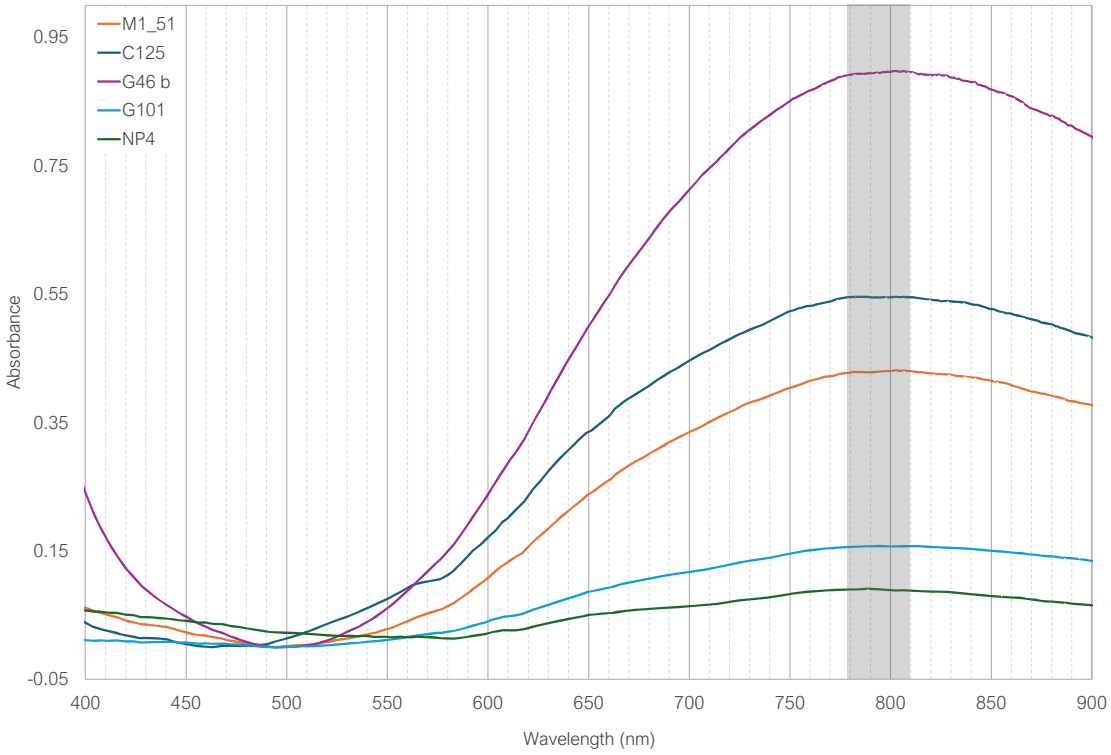

Figure 4.12: Absorbance spectra of the reproduced blue glasses with copper, with Cu^{2+} absorption band in grey, normalised to the minimum. The reference bar correspond to the soda-lime glass composition described by Navarro [40]

4.2.4 Vickers Hardness

When analysing the Vickers hardness data (**Table 4.6**), the first conclusion that can be drawn is that there is no direct relationship between the colouring agent and the hardness. In other words, glasses coloured with cobalt are neither harder nor softer than those coloured with copper and vice versa. There is, however, a group of glasses with significantly lower hardness. The glasses M1_4C1, M1_4S1, M1_4Z1, M3_3 and C125 have values ranging from 436 to 497 HV0.5, with the glass M3_4 having the lowest hardness - interestingly, this is the glass whose recipe specifies it as "glass for candlesticks and ashtrays", i.e. a glass intended for cutting. This measurement helps to confirm the truthfulness and expertise of the glassmaker in terms of mechanical properties.

Since this hardness is not related to colour, it is important to study the composition and identify commonalities between these five glasses. As expected, the main difference is the lead content. The glasses in recipe M1_4 contain more than 30% PbO, M3_3 more than 35% and C125 more than 10% PbO. However, glass G46b also has a high lead content (over 20%) but does not have the same hardness as the other glasses. This difference can be explained by the presence of potassium and barium oxides in the composition of G46 b, metals known to increase the hardness of glass.

The other glasses have relatively similar and higher hardness values, ranging from 510

Table 4.6: Vickers hardness of the reproduced blue samples.

	M1_4C1	M1_4S1	M1_4Z1	M1_51	M3_3	C125	C157	C158
HV 0.5	479 ± 11	426 ± 13	461 ± 10	537 ± 8	436 ± 15	497 ± 8	552 ± 14	571 ± 22
GPa	4.7	4.2	4.5	5.3	4.3	4.9	5.4	5.6
	C159	G46b	G101	G114	NP4	NP5	NP6	NP7
HV 0.5	544 ± 9	534 ± 11	570 ± 18	578 ± 15	510 ± 9	546 ± 7	571 ± 15	516 ± 8
GPa	5.3	5.2	5.6	5.7	5.0	5.4	5.6	5.1

to 578 HV0.5. Despite this increase, all the glasses still show values that are perfectly acceptable for glass that can be decorated by lapidary or engraving [11]. The M1_4 glasses, due to their higher PbO content, have a significantly lower GPa hardness, similar to that of soda-lime-borate glass. In the future it would be important to test more samples with lead to understand the effect of colourants [86].

Finally, I would like to highlight the G114 glass, which was specified in the recipe as a composition to produce blue bottles. In fact, this glass has the highest hardness value. Given the practical use of the bottles, which must withstand frequent handling, it is advisable to make them from more resistant glass. This further underlines the high level of knowledge and control the glassmakers had over their recipes.

4.2.5 Thermal Properties

The following presentation and discussion will address the results of dilatometric analyses, which are concerned with the observation of changes in glass when subjected to heating or cooling (**Table 4.7**). It can tell us about the glass transition temperature (Tg), the dilatometric softening point (Td) and the coefficient of thermal expansion (αL). The ability to accurately reproduce the thermal properties of ancient glass is a key element in deciphering the technical processes used by glassmakers in historical contexts. This is particularly relevant to our study of glass arcana in Portugal, where knowledge of the precise thermal behaviour of historic glass materials can contribute to the identification, conservation and accurate reproduction of historic recipes.

The Tg and Td values do not vary greatly between most of the glasses analysed, with the exception of glass M1_4Z1, which has a Tg of 420°C and a Td of 457°C, much lower than the others. This can be explained by its high Na_2O content (18.9%), which weakens the glass network.

In terms of PbO, there is a significant difference between the glasses. M1_4Z1 has the highest PbO content (32.10 wt. %), which will be one of the factors contributing to its

Table 4.7: Results from thermal analyses of the reproduced blue glasses.

	MG1_4Z1	C157	C158	C159	G46 b	G101	G114
$T_{g\ (onset)}$ DIL (°C)	420	520	528	521	528	510	512
Td (°C)	457	567	570	567	584	557	558
αL (50–500 °C) × 10^{-6}(°C^{-1})	15	9	10	10	8	10	9

lower thermal resistance. PbO is known to reduce glass viscosity and facilitate melting, but it can also weaken the glass structure, reducing hardness and increasing thermal expansion. This may explain the high αL of 14.8 for M1_4Z1, which is directly related to its low Tg and Td [40, 42].

On the other hand, G46 glass, which also contains PbO (22.10 wt. %), has good thermal resistance with a Tg of 528°C and a Td of 584°C. This suggests that despite the significant amount of PbO, other factors in the glass composition, such as the low levels of Na_2O, CaO and the presence of other oxides such as BaO, may compensate for the effects of PbO to make the glass more heat resistant [40, 42].

Glasses such as C158, C159, G101 and G114 have very low levels of PbO and their thermal properties are not significantly affected. Despite the higher Tg and Td (compared to M1_4Z1), the thermal stability of these glasses is more influenced by the balanced composition of Na_2O, CaO and other network modifiers that provide stiffness and thermal resistance [40, 42].

In addition to the oxides of PbO, Na_2O and CaO, which are the main factors responsible for the variation in (αL), glasses with lower amounts of these modifiers, such as G46, C158 and C159, have good thermal resistance, with higher transition temperatures and lower (αL), resulting in greater thermal stability [40, 42].

4.2.6 Concluding remarks

The conclusions of this chapter suggest that the production of blue glass was relatively straightforward and accessible, especially compared to the challenges associated with reproducing amber glass recipes discussed in the previous chapter. A key observation in this study was the clear preference for cobalt blue over copper blue. Cobalt was predominantly used to create darker tones in glass made using the flash glass technique, while lighter tones were used in non-overlapping glass. This chromatic differentiation suggests a high level of technical skill on the part of the glassmakers, who adjusted the intensity of the colour to achieve the desired final effect.

The accurate interpretation of recipes proved to be a crucial factor in the reproduction of historic glass, as has been noted in other chapters of this thesis. In the case of recipe M1_4, uncertainty about the source of the cobalt led to three different tests, each of which

produced visually different glasses. This problem is particularly evident in older *arcana*, where standardised chemical nomenclature and purified reagents were not yet established. The lack of precise information on the form of the colouring agent (e.g. oxides or mixed compounds) is a major challenge for both interpretation and reproduction of these recipes.

Elemental analysis using WDXRF showed that even small amounts of additional colourants can directly influence the final colour of the glass. The results also confirmed that cobalt has a significantly higher colouring power than copper, which may explain its widespread historical use, particularly in contexts where intense and stable colours are required. This distinction was further supported by the colorimetric analysis: samples containing copper showed a relatively homogeneous distribution and those containing cobalt also grouped together cohesively. These results suggest that the colours produced by each of these agents are distinct and characteristic, allowing for relatively reliable identification even in historic glass samples.

UV-Vis absorption spectroscopy also showed that the composition of the glass affected the spectra obtained, suggesting that this technique could provide an initial assessment of the chemical composition of historic glasses. Although it does not allow for the precise identification of all constituents, it can serve as a useful preliminary screening tool before more specific analytical techniques are applied.

In terms of Vickers Hardness, the results indicate that colourants do not have a significant effect on the mechanical properties of the glass. As expected, glasses with higher lead content had lower hardness. However, no significant differences in hardness were observed between glasses containing cobalt and those containing copper, suggesting that the introduction of these colourants does not affect the mechanical strength of the material.

Dilatometric analyses showed no direct correlation between the glass transition temperature and the type of colourant used. However, the coefficients of thermal expansion obtained were consistent with the intended function of the objects produced, reinforcing the idea that the composition of the glass was adjusted to meet the functional requirements of the final products. This observation suggests that glassmakers not only mastered glass colouring, but also had an empirical understanding of the physical properties of the material, adapting formulations according to the intended use of each piece.

Overall, these results show that the production of blue glass, particularly using cobalt, was a well-understood and widely practiced process between the eighteenth and twentieth centuries. They also highlight the importance of rigorous interpretation of historical sources, as small variations in the reading of arcana can lead to significantly different results. These findings reinforce the need for an interdisciplinary approach combining documentary analysis, experimental reproduction and scientific characterisation to accurately decipher historical glass recipes.

4.3 Beyond the Green Bottle: Reproduction and Analysis of Green Glass Recipes

It is not yet known exactly when and where glass was first made, but it is certain that man-made glass has been found in contexts dating from the third millennium BCE and the beginning of the second millennium BCE. Among these early remains is a pale yellow-green bead from Tell Judeideh (Syria) dating from the same period. Given the political and social context in which glass was used at the time, it was considered a precious material and was even used as currency [101].

Concerning green glass, although it is often said that iron is an impurity associated with the use of sand and that iron is capable of producing the green colour in glass, the first glasses produced on a large scale contained copper, lead and antimony [42, 101]. This may indicate the use of yellow and blue glass to produce green, or the use of similar technologies to achieve the green colour.

The use of chromium as a colouring agent in glass dates back to the early nineteenth century. It was discovered in a mineral in the form of lead chromate in 1795 [42]. Until this discovery, iron oxide was used whenever it was necessary to produce dark green glass.



Figure 4.13: Olive Green Venetian and Chrome Yellow Venetian (1988), blown and hot-worked glass, by Dale Chihuly with assistant Lino Tagliapietra, Seattle, Washington, United States. Source: CMOG (Accession Number: 89.4.9).

This use of chromium was done using its trivalent form, which Cr^2O^3 is its most stable oxide [42]. Cr^{3+}, the most stable oxidation state, is formed in neutral or slightly reducing atmospheres and gives the green colour [40]. The Cr^{6+} oxidation state is responsible for the yellow colour [40, 42] (**Figure 4.13**).

However, this new colourant, capable of producing a colour significantly different from those previously available, had its challenges. Chromium does not form stable compounds with silica, making them almost immiscible [40, 42]. The solubility of chromium must therefore be increased by adding a high alkali content. Low temperatures also exacerbate this problem [42].

Another peculiarity is that chromium alone has almost no absorption in the red region of the spectrum, meaning that it could not be used for some applications such as light signalling. For this reason it always had to be mixed with copper [42].

Returning to copper as a colourant, but in this case in the production of green, the ion responsible for the green colour in glass, Cu^{2+}, is exactly the same as that responsible for blue [40, 42]. The same amount of CuO will produce a light blue colour in a soda-lime glass. However, if the same amount is added to a borosilicate or a glass with a high magnesium or lead contents, the resulting colour will be green. This transition from blue to green is due to an increase in the number of unsaturated ions relative to the number of saturated ions. The absorption of light by copper compounds is influenced not only by the number of oxygen ions surrounding each Cu^{2+} ion, but also by their spatial distribution [42].



Figure 4.14: Prunted Beaker (Nuppenbecher) (1400–1599), free-blown. Source: CMOG (Accession Number: 50.3.38).

4.3.1 Green Recipes — Reproduction

In this study, 10 recipes for green glass were selected for study, resulting in the reproduction of 12 glasses in shades ranging from very light to dark green (**Figure 4.15**). The recipes were mainly taken from different *arcana* with similar titles, with a special focus on the recipes for "parsley green". The reproduction showed that in most cases recipes with the same title produced glasses with comparable shades (C44b, C68, C74, G16). However, in some cases, recipes with the same title produced significantly different results (NP23). This finding reinforces the idea that terminology and expressions related to glass colouring can vary significantly between factories and between glassmakers.

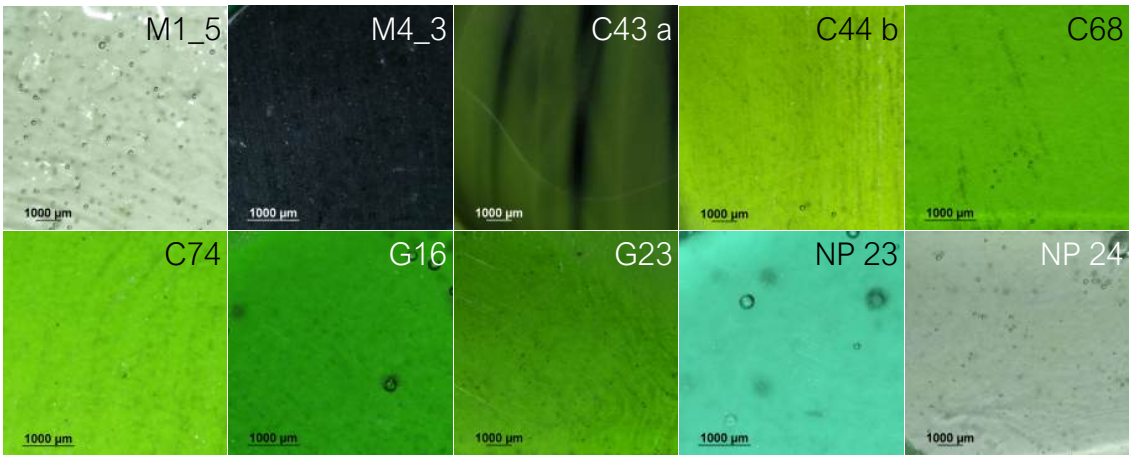

Figure 4.15: Pictures taken with the stereomicroscope of the reproduced green recipes.

The M1_5 and NP24 glasses had the palest green colour, accompanied by a subtle green colour. In contrast, M4_3 glass, as its title suggests (bottle green), produced a much darker shade, making it particularly suitable for bottle production. Glasses C43 and C44, like G46, exhibited phase separation. However, in this case, it was somewhat expected due to the immiscibility of chromium and silica (**Figure 4.16 (a)** and **(b)**) [42]. Both glasses came out of the furnace fully melted but with significant heterogeneity. C43a showed intense phase separation, with a yellow liquid forming on the surface of the molten glass (**Figure 4.16 (c)** and **(d)**). C44a, on the other hand, was extremely difficult to pour.

Recipe C43 was produced twice, with the temperature increased by 50 degrees in the second attempt (C43b). This second melt resulted in a more homogeneous glass that could be poured, as it did not exhibit the pronounced phase separation and yellow liquid observed in the first attempt. However, C43b still presented some heterogeneity and an unusual texture. On the other hand, C44 showed perfect homogeneity on the second attempt (C44 b), with the same increasing of temperature. Glasses C44b and C74 were found to be the most visually similar, exhibiting a warmer, more yellowish tone, while C68 and G23 were found to be similar, both exhibiting a more brownish tone. The NP23 glass was found to be the most visually different, with a bluish-green colour that was quite different from the others.

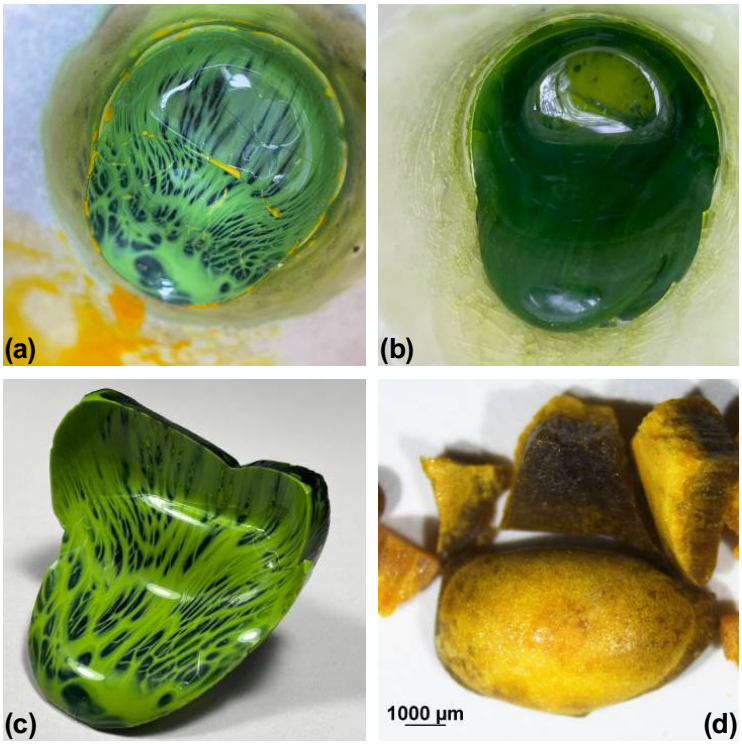

Figure 4.16: Result of the first attempt to reproduce recipes C43 a (a) and C44 a (b). Detail photographs of the phase separation of glass C43 a (c) and (d).

An examination of the composition of the glasses was then carried out to understand these visual differences.

4.3.2 Chemical Characterisation

As far as colouring agents are concerned, taking into account the selection of recipes, the colour is given by using only three oxides, alone or in a mixture: Cr_2O_3, Fe_2O_3 and CuO (**Table 4.8**). This is because there are not many other ways to produce the green colour in glass [40].

To begin with the M1_5 and NP24 glasses, which are the most visually similar, both have a small percentage of colouring oxides. M1_5 has a greenish tint due solely to the presence of iron in the silica (the percentage of iron in the sand used by the factory has been reproduced) in a quantity of approximately 0.8 wt.%. Although NP24 glass has more colouring oxides in its composition, its colour is even more muted because, although it contains chromium, iron and copper, all three are present at levels inferior to 0.1%. The most abundant colouring agent is iron, but the presence of sulphur may favour the oxidation state of Fe^{3+} (responsible for the yellow colour).

M4_3 glass is the darkest in colour, almost opaque (**Figure D.1**). This appearance may be due to the high percentage of CuO in the composition as it does not contain any other oxide in the function or quantity of an opacifier, such as P_2O_5. The use of copper in the

manufacture of bottle glass is curious, given that the most common oxide used is iron [102].

Glasses C43 and C44 have relatively similar compositions, although one could be poured from the furnace as a fairly homogeneous molten glass (C44b) and the other could not. This small difference may be due to the fact that the C44b glass has a higher percentage of PbO, which affects the Tg of the glasses, lowering it.

On the other hand, glasses C68, C74, G16 and G23 look very similar. The Cr_2O_3 value of the first three is very similar, although the value of the other colourants (Fe_2O_3 and CuO) varies slightly. This shows the high colouring power of chromium compared to the others. As for the G23 glass, although it is clear that it is based on the same oxides, it's colour differs slightly towards a more brownish tone. This may be due to the fact that it has a slightly lower percentage of Cr_2O_3 than the others and a higher percentage of PbO. Although lead oxide is not a colouring oxide, it has a direct effect on the colour, especially when present in higher quantities [40].

Finally, looking at the NP23 glass, this is the glass that is most visually different from all the others. The same difference is easily seen in the WDXRF quantification values. This glass is therefore one of those with the lowest percentage of Cr_2O_3 and one of those with the highest percentage of CuO, which corresponds to the turquoise green appearance seen in **Figure 4.15**.

Table 4.8: Wavelength-dispersive X-ray fluorescence spectroscopy results of green samples in weight percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	CuO	ZnO	ZrO_2	Sb_2O_3	PbO
M1_5	17.8		1.9	50.9			0.39	0.07	0.08		0.86					28.00
M4_3			0.4	47.2			12.00	3.55			0.49	6.76				29.60
C43 b			0.1	51.9		0.05	36.60	8.99		1.53	0.16			0.01		0.68
C44 b			0.3	53.0		0.06	33.30	8.78	0.03	1.54	0.05					2.82
C68	11.2	0.1	0.5	57.8			18.30	10.10	0.04	1.22	0.06	0.19				0.46
C74	4.8		0.4	56.7		0.02	25.90	10.40	0.03	1.19	0.05	0.33		0.00		0.26
G16	17.5		1.2	75.2			2.12	0.10	0.06	1.15	0.03	0.44	0.23		0.22	1.77
G23	1.1		0.9	52.5			16.00	0.03	0.06	0.79	0.04	0.15				28.40
NP23	13.8		1.0	74.7	0.93	0.06	1.31	7.42	0.06	0.15	0.29	0.28	0.01	0.01		0.01
NP24	15.0	0.3	1.0	73.2		0.08	1.36	7.61	0.07	0.02	0.09	0.02	0.18	0.01		0.01

4.3.3 Vickers Hardness

In relation to hardness, as evidenced by the colours presented and discussed, the colouring agents appear to exert minimal influence on the mechanical properties of the glasses (**Table 4.9**).

Table 4.9: Vickers Hardness of the reproduced green samples.

	M1_5	M4_3	C44 b	C68	C74	G16	G23	NP23	NP24
HV 0.5	448 ± 13	434 ± 13	451 ± 7	557 ± 13	523 ± 20	461 ± 11	428 ± 16	498 ± 12	527 ± 21
Gpa	4.4	4.3	4.4	5.5	5.1	4.5	4.2	4.9	5.2

The hardnesses of the glasses range from 557 to 428 HV0.5, with the glass designated as "crystal" (C68) being the hardest. The high percentage of calcium oxide (CaO) in the composition of both C68 and C74 glasses (10.1 wt.% and 10.4 wt. % respectively) appears to be a primary contributing factor to their high hardness, which is among the highest observed in green glass reproductions. Conversely, NP24 glass exhibits a hardness of 529 HV0.5, attributable not only to its 7.61 wt.% CaO content but also its high SiO_2 percentage of 73.2 wt.%, among the highest in the study.

On the other hand, although G16 has a similar percentage of SiO_2 to the previous glass (75.2 wt.%), it lacks the same amount of CaO in its composition, resulting in a much lower hardness. It is obvious that glasses with increased PbO content have inherently lower hardness values. These glasses are M1_5 (449 HV0.5), M4_3 (434 HV0.5) and G23 (428 HV0.5). While all three have high levels of PbO, the combination with the other oxides is quite different. While M1_5 contains 28 wt. % PbO, although it also has 17.8 wt.% Na_2O, it is harder than M4_3, which has no Na_2O but K_2O (12 wt.%) and 29.6 wt.% PbO. Conversely, the softer green glass is characterised by a high percentage of PbO, significant amounts of K_2O and a minimal presence of CaO [40, 42]. Similar to the blue glass, the same trend is observed when comparing the glasses with higher lead content with the literature [86]. The glasses M1_5, M4_3, C44 b, G16 and G23 have a significantly lower GPa hardness (< 5 GPa), with values similar to the GPa hardness of soda-lime-borate glass [86]. Notably, glasses C44 b and G16 also show reduced hardness despite containing only 2.82 wt% and 1.77 wt% PbO respectively.

4.3.4 Colour Characterisation

The colorimetry analysis of the samples enables the understanding of the variations in tone and luminosity of the glasses, with the data being correlated with their chemical composition (**Figure 4.17**). The chromatic properties of the glasses are predominantly influenced by Cr_2O_3, which is responsible for the intense green colour, while Fe_2O_3 can

result in yellowish green or brown tones, depending on its oxidation state and CuO that contributes to a bluish-green colour.

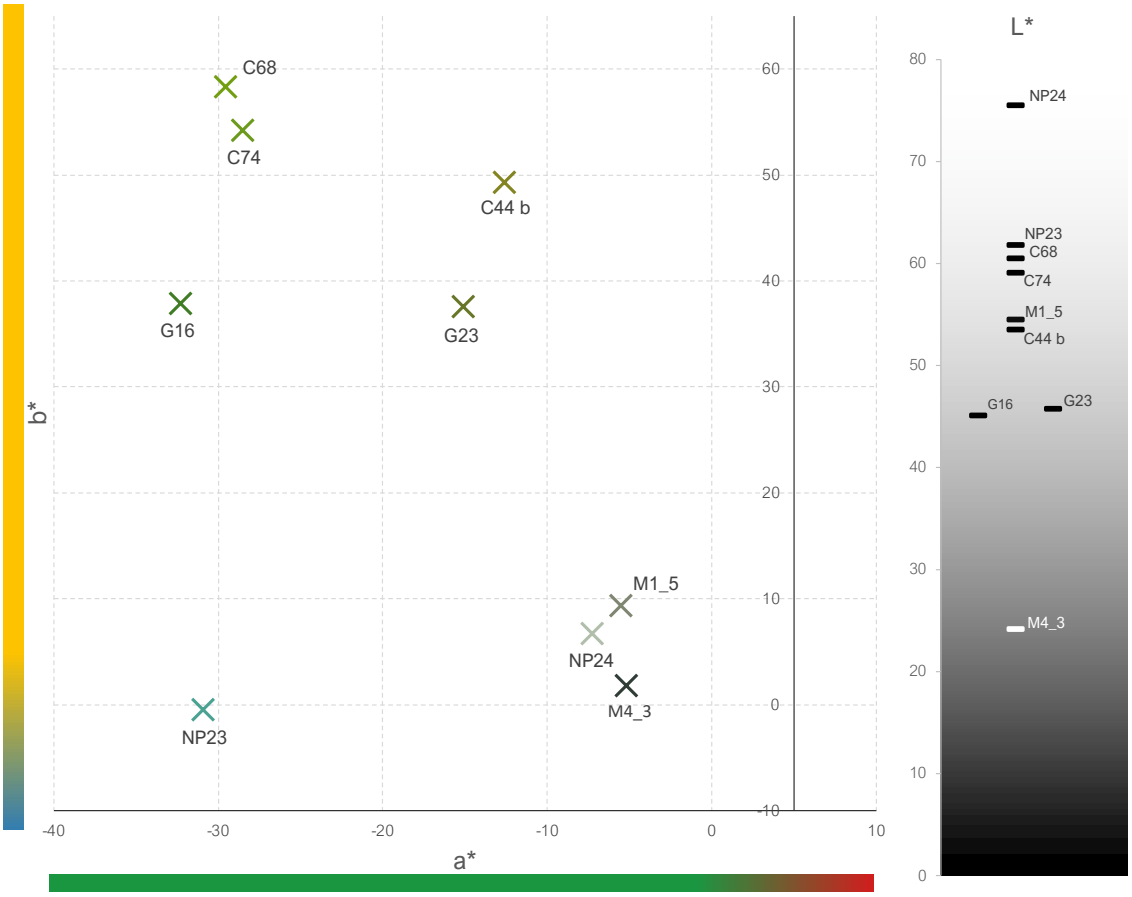

Figure 4.17: Scatter plot of the L*a*b* coordinates of the colorimetry measurements of the reproduced green glasses.

The M4_3, NP24 and M1_5 glasses exhibit very similar a* and b* values, yet the results in **Figure 4.15** demonstrate significant disparities. M1_5 and NP24 are characterised by an extremely light, almost colourless appearance, while M4_3 displays a notably darker colour. This variation is evident in the L* value, with M4_3 naturally occupying the least luminous position among the green glasses. In other words, although the shade of green is similar, a more purplish colour (due to the deviation to blue and red sides), the drastic difference in luminosity reflects that visually the colours of the M1_5 and NP24 do not resemble the M4_3 in the slightest.

Regarding to undertones in the green glass, the blue visible in NP23 is quite explicit in the colorimetry measurements, as this glass is the only one with negative b* values—on the blue side of the graph.

The other glasses, G16, G23, C44b, C74 and C68, are visually quite similar and naturally, the L* a* and b* measurements are closer. However, C44b, C74 and C68 exhibit a yellow

hue (with a higher b* value), while G23 displays a red hue (due to its more positive a* value).

Analysis of the oxidation states of the metals that give glass its colour is therefore fundamental to understanding and substantiating these subtle variations in tone. A thorough analysis of the results obtained from UV-Vis spectroscopy clearly demonstrates subtle alterations in the composition of the glass samples, which are evident in the resulting changes in colour (**Figure 4.18**). Some of the glasses were not characterised using this technique. As M1_5 is an extremely clear glass, its spectrum was highly "noisy", preventing the extraction of relevant information. Glasses M4_3 and C43 a could also not be analysed as the former is almost opaque and the latter has a non-homogeneous colour, making transmittance and UV-Vis reflectance measurements impossible.

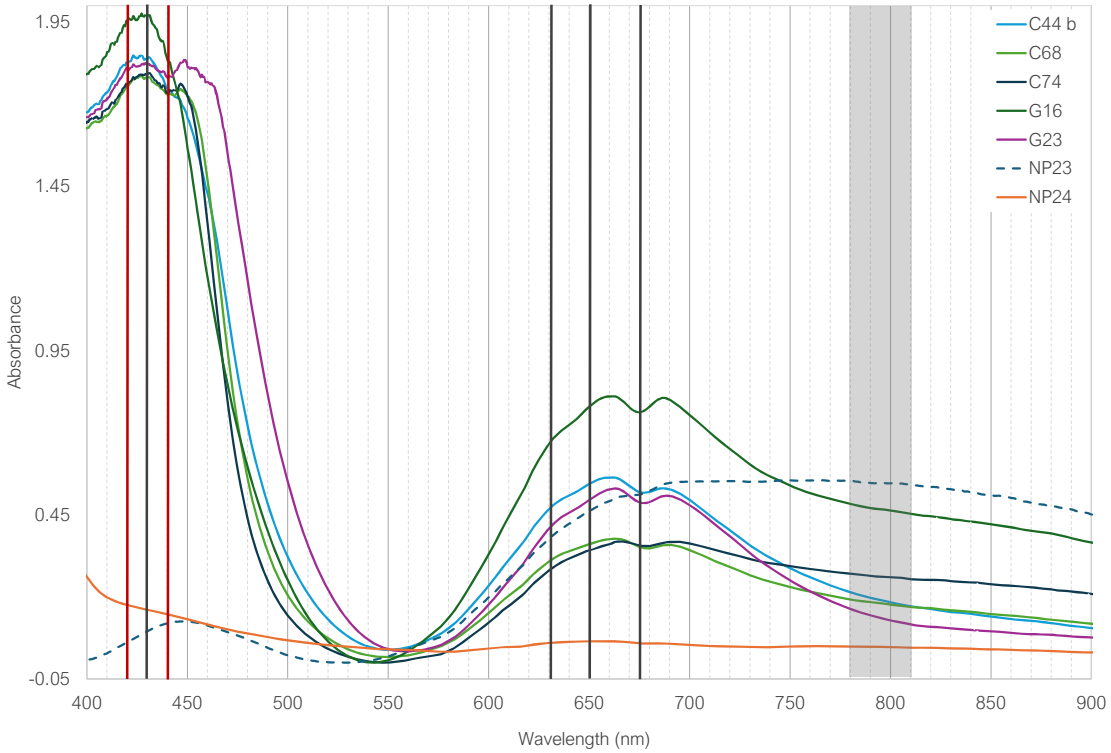

Figure 4.18: Absorbance spectra of the reproduced green glasses, with Cr^{3+} four absorption bands marked in black, Fe^{3+} in red, and Cu^{2+} absorption in grey, normalised to the minimum. The reference lines correspond to the soda-lime glass composition described by Navarro [40].

The NP24 glass, despite its nearly colourless appearance, shows a very low level of absorption in the regions corresponding to the Fe^{3+}, Cr^{3+} and Cu^{2+}. However, the intensity of these bands, particularly Cr^{3+} and Cu^{2+}, is rather weak, as would be anticipated given the glass's colour [40]. This corresponds to its very light colouring, due to the low content of colouring agents (Cr_2O_3, Fe_2O_3 and CuO $< 0.1\%$ wt. %).

The glasses with the highest Cr^{3+} peak intensity were G16 and C44 b, which correspond

exactly to the glasses with the highest Cr_2O_3 content. These appear to be shifted, which could be due to the influence of lead [40]. Given the detection limits of the equipment used, it is not possible to verify the presence of bands corresponding to Cr^{6+}. However, taking into account the high K_2O content in glasses C44 b, C68 and C74 and comparing them with the colorimetric results—where these three are the glasses with the most positive b* values, i.e. the most yellow—it is possible to assume that there is some presence of this ion, which is why they are the glasses with the most vivid colours [40, 103].

In the Cu^{2+} region, as expected, the spectra with the highest intensity correspond to the glasses with the highest CuO content—NP23, G16 and C74. CuO is only able to produce green in glass when combined with other oxides such as PbO, and the presence of this compound in these three glasses is almost non-existent [40, 42]. This coincides with the colorimetric measurement of sample NP23, which is the bluest, indicating that Cu^{2+} can be organised to produce the blue colour, but given the strong colouring power of Cr_2O_3, its blue colour is less noticeable [40, 42].

4.3.5 Thermal Properties

The results of the thermal characterisation will now be presented and discussed (**Table 4.10**).

Table 4.10: Results from thermal analyses of the reproduced green glasses.

	M4_3	C44 b	C68	G23	NP23	NP24
$T_{g\ (onset)}$ DIL (°C)	484	580	499	497	534	536
Td (°C)	533	627	546	558	580	577
αL (50–500 °C) × 10^{-6}(°C^{-1})	8	12	13	8	8	8

As mentioned above, not all glasses could be characterised, so only the most relevant ones were selected for this case study, with the remaining samples to be analysed in the future. Of the glasses that presented melting problems, C44 b had the highest Tg at 580°C. This is probably due to the limited miscibility of Cr_2O_3 with SiO_2, which requires either a higher melting temperature or a significant addition of alkali compounds [40, 42]. In this case, the glass already contained a significant amount of K_2O, so the problem of poor homogenisation and pouring difficulties was solved simply by increasing the temperature.

The glass with the lowest Tg at 484ºC was M4_3, as expected given its high PbO content, which lowers Tg [47]. As this recipe is identified as a bottle glass formulation, a lower Tg could indicate that this composition facilitated glassblowing, allowing the bottle to be formed without frequent reheating. This in turn would increase the number of objects produced in the same time. G23 had the next lowest Tg at 497°C, again due to the presence

of PbO which weakens the glass matrix and reduces the Tg [47].

The NP23 and NP24 glasses had very similar Tg values, with NP23 being slightly higher, possibly due to its higher Cr_2O_3 content [40, 42]. The green glasses generally had slightly higher Tg and Td values than the blue glass (**Table 4.7**), which may be related to the properties of chromium as a colouring agent, as noted earlier [40, 42].

It is also worth noting that the thermal expansion of the green glass, despite some melting difficulties, was relatively lower than that of the other coloured glasses analysed in this work. In the case of cobalt blue and iron-based amber glass, this is probably due to the fact that these colourants induce rapid cooling, which affects their thermal expansion properties [42].

4.3.6 Concluding remarks

Green glass is technically more challenging to produce than, for example, blue glass. With the exception of pure iron green glass, which is not discussed here, chromium green glass has batch solubility limitations, while copper green glass requires a specific composition. These limitations have not been fully recognised, even for amber glass, which in theory can be produced in any composition.

To ensure comparability and reduce variability, the selected recipes were chosen on the basis of their names and basic compositions. Most of them focused on reproducing the so-called "parsley green" recipes. However, the results varied considerably between different arcana, particularly between COG and NPGC, showing that these names are more personal than standardised within the glass industry.

Due to the particular challenges of reproducing chrome glass and the lack of temperature information in the recipes, C43 and C44 had to be produced twice. The first attempt resulted in a phase-separated glass that could not be cast or manipulated.

The remaining glasses produced a range from very dark green, almost black, to light green, almost colourless. Most of the potash glass recipes were well suited to the production of chromium glass, suggesting that the historic glassmakers were highly skilled.

In terms of hardness, all samples except the lead rich ones showed values comparable to previous glasses, reinforcing the idea that colour does not significantly affect hardness. However, the same cannot be said for thermal properties. There was a clear correlation between the colourant and the coefficient of thermal expansion. Compared to amber and blue glass, green glass had a lower coefficient of expansion and was less susceptible to deformation.

Finally, in terms of colour, colorimetry revealed slight variations even between visually similar samples. These variations were consistent with the results of the UV-Vis absorption spectroscopy characterisation. As most of these glasses contain three colourants—iron, chromium and copper—combined with different compositions, it is difficult to pinpoint the exact causes of the spectral variations.

5

Final Remarks

The aim of this thesis was not only to study Portuguese glass production from the eighteenth to the twentieth centuries through the analysis of glass *arcana*, but also to evaluate and contextualise these historical documents as heritage collections in their own right. Such records have increasingly been used to gain a better understanding of historical glass production, to date objects, and to carry out degradation tests. Recognising that *arcana* have only recently begun to be considered valuable heritage objects, this study used them to reflect the evolution of both technical knowledge and artistic practices in Portugal over several centuries. The methodology adopted involved interpreting, reproducing, and characterising the glass recipes they contain—thus opening the door to future studies comparing these experimental reproductions with historical objects.

The *arcana* reveal that, despite the relatively under-explored nature of this chronology in Europe—with most studies focusing on specific archaeological contexts—Portuguese glassmakers possessed remarkable technical expertise. The wide range of recipes, from challenging colours such as amber yellow to more straightforward formulations, demonstrates the ability to produce a wide variety of objects, including bottles, jars, flat glass, flash glass and lapidary glass. This diversity reflects a rich glassmaking tradition in Portugal, and also highlights a significant gap between the industry's longstanding heritage and the limited studies devoted to it.

The study of these historical sources presents considerable challenges. The disorganised handwriting and archaic language require careful interpretation to avoid modernising the recipes. To overcome these challenges, a systematic and controlled experimental approach was adopted—using laboratory-prepared substitutes for natural raw materials (for example, replacing sand with a mixture of SiO_2 and Fe_2O_3) to reduce variability. Such measures were essential as even small misinterpretations can lead to significant differences in the final glass product.

A notable example of this approach was the reproduction of an amber glass recipe. Recognising that success depended heavily on the correct interpretation of sometimes incomplete information, only one amber recipe was selected for adaptation. Various studies indicate that while sulphate complexes with iron play a crucial role in the production of amber glass, the presence of carbonates and chlorides further facilitates this complexation. Consequently, the adaptation involved mixing three compounds as sodium sources—while maintaining the original proportions—which ultimately allowed for the reproduction of the desired amber

colour. However, to confirm the historical accuracy of this reproduction, further analysis and comparison with historical objects will be required.

After analysing and summarising the four *arcana*, it is clear that tastes and preferences in glassmaking changed over time, reflecting broader shifts in society (**Figure 5.1**), it is important to keep in mind that the MGF refers to the eighteenth century, the COG to the nineteenth century, and the GF and NPGC to the twentieth century. In the eighteenth century, glass production catered to the tastes of royalty and the courts, with a preference for red and colourless (crystal) glass. Blue was also highly prized for similar reasons.

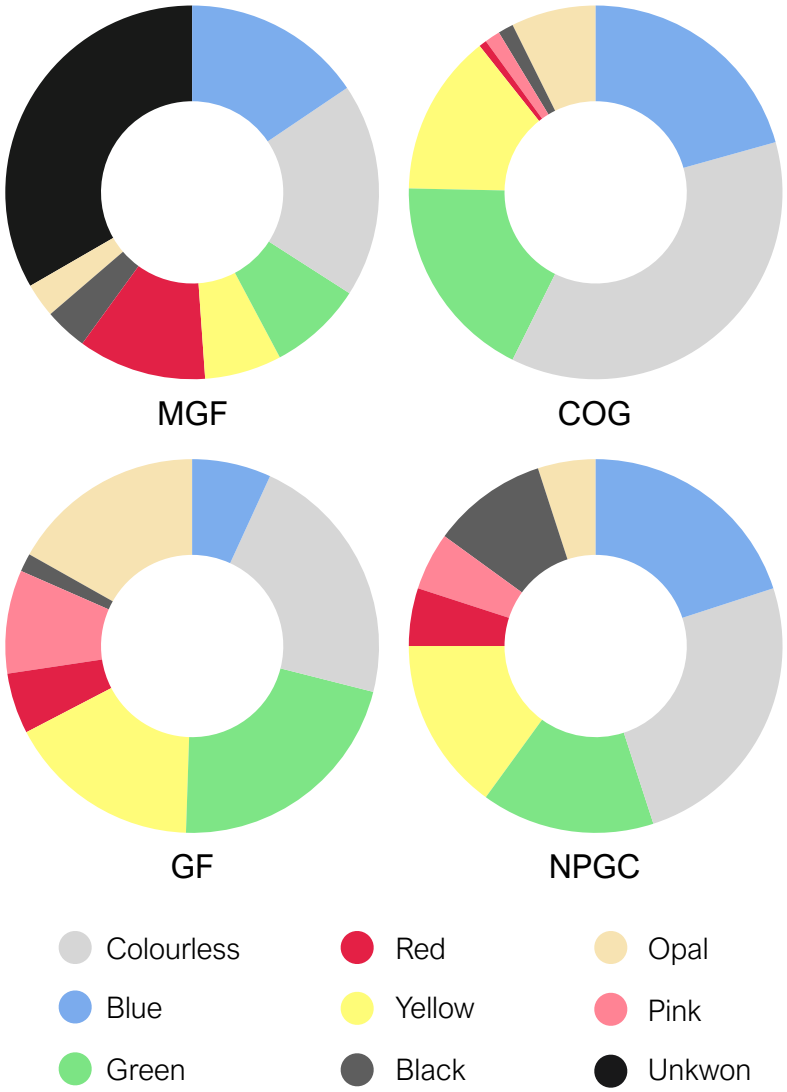

Figure 5.1: Representation of the number of recipes of each colour in each *arcanum*.

In the nineteenth century, the popularity of flash glass objects increased, and blue and green colours became more important due to their intense colours and the potential for cutting decoration in flash glass. In the twentieth century, glass production became more driven by market needs. GF, located in central Lisbon—where innovation and progress were

concentrated—focused on more utilitarian glass, such as yellow/amber for flasks production (for pharmaceutical use) or opal for lighting. In the twentieth century, the NPGC produced a wide variety of glass and colours, demonstrating that by this time, glassmaking techniques had been refined to a high level of expertise

In terms of colourants, there have been both shifts in preferences and technical advances as new colourants have come onto the market. This can be seen by looking at the four most popular colours over the three centuries and four arcana. Starting with the most prominent colour in MGF—red. In the eighteenth century, red glass (**Figure 5.2**) was produced using a single method that was both highly technical and extremely expensive: the use of gold to create ruby red glass. In the twentieth century, however, with the introduction of new compounds in the glass industry, red glass was instead produced exclusively with cadmium or a combination of cadmium and selenium in GF and NPGC.

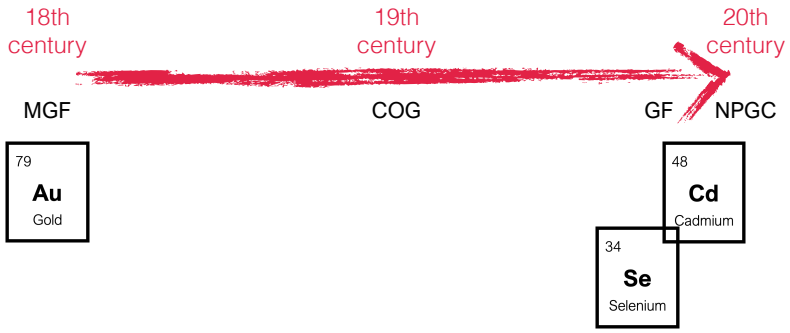

Figure 5.2: Scheme of the main colourants used in the production of red glass over the centuries and the various *arcana* under study.

A similar evolution can be observed for yellow glass (**Figure 5.3**). In the eighteenth century, only yellow/amber glass coloured with iron was produced. In the nineteenth and twentieth centuries, however, uranium-based yellow glass became increasingly popular. It was used alone or in combination with iron at both COG and GF. Meanwhile, at NPGC, amber glass production shifted to a mixture of iron and manganese.

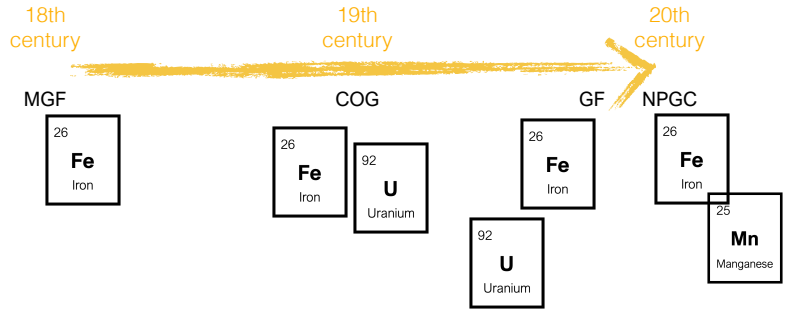

Figure 5.3: Scheme of the main colourants used in the production of yellow glass over the centuries and the various *arcana* under study.

Green glass followed a similar pattern (**Figure 5.4**). In the eighteenth century the only

available colourants were iron and copper. By the nineteenth century, however, iron had become irrelevant to COG, and green glass was instead coloured with chromium and copper, and in some cases cobalt. In the twentieth century, cobalt seems to have fallen out of use, possibly because it is difficult to handle. At GF, green glass was now produced with a mixture of chromium, copper and occasionally uranium. At NPGC, however, there is no record of uranium being used, with chromium, copper and iron being the primary colourants.

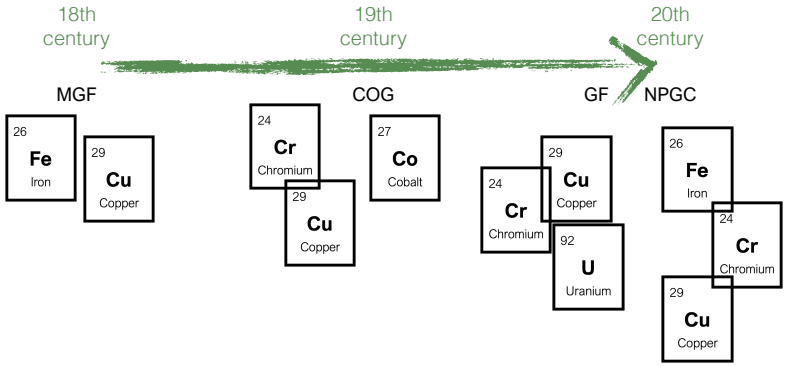

Figure 5.4: Scheme of the main colourants used in the production of green glass over the centuries and the various arcana under study.

Finally, in the eighteenth century, blue glass was produced at MG using cobalt (**Figure 5.5**). In the following century, COG also used copper, but in smaller quantities. In the twentieth century, both GF and NPGC continued to use both cobalt and copper for blue glass, although cobalt became less important in GF.

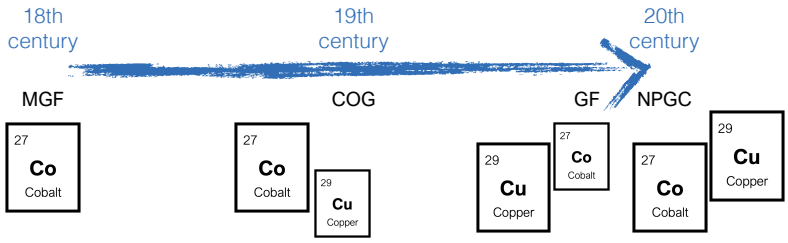

Figure 5.5: Scheme of the main colourants used in the production of blue glass over the centuries and the various arcana under study.

Regarding the specific conclusions from the reproductions in this thesis, it should be noted that making glass is not simply a matter of following a recipe. It is not enough to have a recipe book and a furnace; relying solely on the information contained in the recipes is insufficient. This highlights the extensive empirical knowledge of the glassmakers, who, even if they did not fully understand the underlying chemistry, knew that by repeating certain steps with specific raw materials, they could consistently achieve the desired result.

Thus, the outcomes of this study were based not only on the interpretation of recipes but also on the scientific knowledge acquired about glass production. Amber glass, despite

its long history, proved to be extremely challenging to reproduce, with repeated trials yielding varying results. However, the successful reproductions aligned with the recipes: amber recipes are intended mainly for the production of flasks (possibly laboratory flasks), and the hardness and thermal properties of the reproduced amber glass are consistent with that purpose. In the blue recipes, those designated as sound, crystal, or for cutting glass demonstrated coherent thermal and mechanical properties—specifically, lower Tg and hardness. Green glass, on the other hand, is the only colour in this study where the colouring agent had a positive influence on the thermal properties, particularly the coefficient of expansion.

Given how little information is available about this period in Portuguese glass production—and considering that many factories, such as the Gaivotas factory, have been little studied—the use of *arcana* as primary sources is of paramount importance. By going back to the source of knowledge, rather than relying solely on historical objects that may be flawed in their contextualisation, this study provides new insights. For example, the MGF *arcanum* reveals a strong focus on recipes for red glass—a colour historically associated with wealth and indicative of glassmakers' expertise—which later gave way to recipes for pharmacy or perfumery glass as tastes evolved. In addition, this research has begun to clarify when certain compositions began to be used in Portugal, although some questions remain unanswered at the European level. Many possibilities for future research remain open. In addition to exploring additional recipes—such as those for red and purple glass with gold nanoparticles—there is a need for more in-depth investigation of the compositions already studied. Future work should also address the experimental challenges encountered, such as the detailed role of soda composition, the involvement of sulphur, the influence of charcoal on the vitreous matrix, and the causes of phase separation in some samples. Collaboration with museums and conservation institutions, coupled with advanced analytical techniques such as mass spectrometry and high-resolution tomography, could further refine these findings and enhance our understanding of historical glass production. Overall, this thesis advances our knowledge of Portuguese glassmaking traditions and lays the groundwork for future studies that bridge scientific analysis with heritage conservation.

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A

List of recipes for each *arcanum*

Table A.1: Transcription of the title of each recipe from the Northern Portuguese Glass Centre *arcanum* and other relevant information

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Amarelo	Yellow	NPGC	Na	Fe-Mn	Yes	Yes	Yes
Amarelino	Yellow	NPGC	Na	Fe-Mn	Yes	Yes	Yes
Amarelo Neutro	Yellow	NPGC	Na	Fe-Mn	No	Yes	Yes
Azul Celeste ou Marinho	Blue	NPGC	Na	Cu	Yes	Yes	Yes
Azul ≪ Doublé ≫	Blue	NPGC	Na	Co	Yes	Yes	Yes
Azul escuro	Blue	NPGC	Na	Co	Yes	Yes	Yes
Azulino	Blue	NPGC	Na	Co-Cu	Yes	Yes	Yes
Branco (F. Potes)	Colourless	NPGC	Na	-	Yes	No	No
Branco corrente (F.E.)	Colourless	NPGC	Na	-	No	Yes	No
Branco vidreira	Colourless	NPGC	Na	-	No	Yes	Yes
Branco neutro (F. E.)	Colourless	NPGC	Na	-	No	Yes	Yes
Levere	Unknown	NPGC	Na	Fe-Mn	Yes	Yes	Yes
Cristal	Colourless	NPGC	K-Pb	-	No	Yes	No
Encarnado	Red	NPGC	Na	Cd-Se	Yes	Yes	Yes
Opala	Opal	NPGC	Na-K-Pb	F	Yes	Yes	No
Preto	Black	NPGC	Na	Fe-Cu-Ni	Yes	Yes	Yes
Preto (de botões)	Black	NPGC	Na	Fe-Cu-Ni	Yes	Yes	Yes
Rosalino	Pink	NPGC	Na	Se	Yes	Yes	Yes
Verde américa	Green	NPGC	Na	Fe-Cr-Cu	Yes	Yes	No
Verde Salsa	Green	NPGC	Na	Fe-Cr-Cu	Yes	Yes	Yes
Verdino	Green	NPGC	Na	Fe-Cr-Cu	Yes	Yes	Yes

Table A.2: Transcription of the title of each recipe from the Marinha Grande Factory *arcanum* and other relevant information (Part 1).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Nº1	Yellow	MG1	Na-Pb	Fe	No	Yes	Yes
Nº2	Colourless	MG1	K-Pb	-	No	Yes	Yes
Nº3	Blue	MG1	Na-Pb	Co	Yes	No	No
Nº4	Blue	MG1	Na-Pb	Co	No	Yes	Yes
Nº5	Green	MG1	Na-Pb	Fe	No	Yes	Yes
Nº6	Purple	MG1	Na-Pb	Mn	No	Yes	Yes
Nº7	Yellow	MG1	Pb	Fe	No	Yes	No
Nº9	Green	MG1	Na	Fe	No	Yes	No
Nº10	Purple	MG1	Na-Pb	Mn	No	Yes	Yes
Nº11	Colourless	MG1	Na	-	No	Yes	No
Nº12 - Composição para Vidro incarnado ou Rubim de Veneza	Red	MG1	K	Au	No	Yes	No
Sem nome (Receita final da Nº12)	Red	MG1	K	Au	No	Yes	No
Nº 14	Red	MG1	K-Pb	Au	Yes	Yes	No
Nº17	Red	MG1	K	Au-Mn	No	Yes	No
Nº18	Blue	MG1	Na	?	No	Yes	No
Nº19	Unknown	MG1	Na-Pb	Mn	No	Yes	Yes
Nº20	Unknown	MG1	Na-Pb	Fe-Mn	No	Yes	Yes
Nº21	Unknown	MG1	Na-Pb	Co-Cu	No	Yes	Yes
Nº22	Colourless	MG1	Na	Mn	No	Yes	No
Nº23	Blue	MG1	?	?	Yes	Yes	No
Nº24	Agata	MG1	K	Au	No	Yes	No
Nº25	Yellow	MG1	Na	Fe	No	Yes	No
Nº26	Red	MG1	K	Au-Mn	Yes	Yes	No
Nº27	Green	MG1	Na	Fe	No	Yes	No
Nº28	Red	MG1	K	Au	Yes	Yes	No
Nº29	Red	MG1	Na	?	Yes	Yes	No
Nº30	Unknown	MG1	?	Mn	Yes	Yes	No
Nº31	Unknown	MG1	Na	Cu	Yes	No	No

Table A.3: Transcription of the title of each recipe from the Marinha Grande Factory *arcanum* and other relevant information (Part 2).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Nº32	Yellow	MG1	Pb	Fe	No	Yes	Yes
Nº33	Unknown	MG1	Na-Pb	?	No	Yes	Yes
Nº34	Yellow	MG1	Pb	Fe	No	Yes	No
Nº35	Blue	MG1	Pb	Co	No	Yes	No
Nº36	Green	MG1	?	Cu	Yes	Yes	No
Nº37	Black	MG1	?	Mn	Yes	Yes	No
Nº38	Blue	MG1	?	Co-Cu	Yes	Yes	No
Nº39	Opal	MG1	Na	?	No	Yes	No
Nº40	Blue	MG1	Na	Co-Cu	Yes	Yes	No
Nº41	Blue	MG1	Na	Co-Cu	Yes	No	No
Nº42	Green	MG1	Na	Cu	No	Yes	No
Nº43	Unknown	MG1	Na	?	No	Yes	No
Nº44	Agata	MG1	K-Pb	Sb	No	Yes	No
Nº45	Blue	MG1	?	Co	Yes	Yes	No
Nº46	Opal	MG1	Na	Sb	No	No	No
Nº47	Opal	MG1	Na	Sb	No	Yes	No
Nº48	Green	MG1	Na	?	Yes	Yes	No
Nº49	Yellow	MG1	?	Fe-Mn	Yes	Yes	No
Nº50	Yellow	MG1	?	Fe-Mn	Yes	Yes	No
Nº51	Green	MG1	Na	Cu	Yes	Yes	No
Nº52	Blue	MG1	Na	Co	Yes	Yes	No
Nº53	Black	MG1	?	Mn	Yes	Yes	No
Nº54	Black	MG1	?	Mn	Yes	Yes	No
Nº55	Opal	MG1	Na	Sb	No	No	No
Nº1 Compoziçao feita por Pauletta na Sem.^{na} finda em 17 de Abril de 1798	Yellow	MG2	Pb	Fe	No	Yes	No
Nº3 Compoziçao feita em 13 de Abril 1798	Blue	MG2	Na-Pb	Co	Yes	Yes	No
Nº4 compoziçao feita em 16 de Abril 1798	Blue	MG2	Na-Pb	Co	No	Yes	No
Nº5 Compoziçao 18 de abril de 1798	Green	MG2	Na-Pb	?	No	Yes	No

Table A.4: Transcription of the title of each recipe from the Marinha Grande Factory *arcanum* and other relevant information (Part 3).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Nº6 Compoziçao feita em 21 de Abril 1798	Purple	MG2	Na-Pb	Mn	No	Yes	No
Nº7 Compoziçao em 30 de abril 1798	Black	MG2	Pb	Fe	No	Yes	No
Nº8 Compozicao 6 de Maio de 1798	Blue	MG2	Na-Pb	Co-Cu	No	No	No
Nº9 Em 4 de Maio de 1798	Green	MG2	Na	?	No	Yes	No
Nº10 Compoziçao feita em 8 de Maio de 1798	Black	MG2	Na-Pb	Mn	No	Yes	No
Nº11	Colourless	MG2	?	-	No	No	No
Nº12	Red	MG2	K	Au	No	Yes	Yes
Nº14 Compoziçao feita na Semana 26 de 1798	Red	MG2	K-Pb	?	Yes	Yes	No
Nº15	Unknown	MG2	K-Pb	Sb	No	Yes	Yes
Nº16 Compozição feita em 26 de Mayo 1798	Blue	MG2	K-Pb	Co	Yes	Yes	Yes
Nº17 compoziçao feita em 26 de Mayo 1798	Red	MG2	K	Au-Mn	No	Yes	No
Nº18	Blue	MG2	?	?	No	Yes	No
Nº19	Unknown	MG2	Pb	Mn	No	Yes	No
Nº20	Unknown	MG2	Na-Pb	Fe-Mn	No	Yes	Yes
Nº21	Unknown	MG2	Na-Pb	Co-Cu	No	Yes	Yes
Nº 22	Colourless	MG2	Na	-	No	Yes	No
Nº23	Blue	MG2	?	?	Yes	Yes	No
Nº24	Agata	MG2	K	Au	No	Yes	Yes
Nº25	Yellow	MG2	Na	Fe	No	Yes	No
Nº26	Red	MG2	K	Au-Mn	Yes	Yes	No
Nº27	Green	MG2	Na	Fe	No	Yes	No
Nº28 Compoziçao pª incarnado	Red	MG2	K	Au	Yes	Yes	No
Nº29	Red	MG2	Na	?	Yes	Yes	No
Nº 30	Unknown	MG2	?	Mn	Yes	Yes	No
Nº 31	Unknown	MG2	Na	Cu	Yes	No	No
Nº 32	Unknown	MG2	Pb	Sb	No	Yes	No
Nº 33	Unknown	MG2	Pb	-	No	Yes	No
Nº 34	Unknown	MG2	Pb	-	No	Yes	No

Table A.5: Transcription of the title of each recipe from the Marinha Grande Factory *arcanum* and other relevant information (Part 4).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Compozicão para Agata	Agata	MG3	K-Pb	Sb	No	Yes	No
Compozicao para vidro Azul de Casticais e acucareiros	Blue	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao para fazer Vidro Azul Claro ou Lopes Laze	Blue	MG3	K-Pb	Co	Yes	Yes	No
Compozicao para o Potte (Nº1) do Thomas	Unknown	MG3	K-Pb	Mn	No	Yes	Yes
Compozicao para o Potte Nº2	Unknown	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao para os Cavallos Nº 3	Unknown	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao para Nº4	Unknown	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao para Nº 5	Unknown	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao para o Vidro das Caixas vindas do Porto ou Lisboa	Unknown	MG3	K-Pb	Co-Mn	Yes	Yes	No
Compozicao Nº6	Unknown	MG3	?	?	No	No	No
Compozicao Nº 7 para Rubim	Red	MG3	K	Au-Mn	Yes	Yes	No
Nº + 33 compozição de Vidro amarello cor de Topazio pª fazer contas de Ouro introduzindo lhe dentro a compozição do Alio Estanho e Azou que estava feita por Fr.^{co} Dante	Yellow	MG4	K	Fe	No	Yes	No
Nº~~2~~ 34 Compoziçao feita por mim pª fazer Vidro Robim que sere pª fazer o Coral	Red	MG4	K	Au	Yes	Yes	No
Nº35 compozição de vidro verde aq^{u} chamo verde Garrafa	Green	MG4	K-Pb	Cu	No	Yes	Yes
~~Nº4 36~~ Dias o Alemao Dentro que pª fazer Vidro de Vidraça de Potacha he o que segue	Colourless	MG4	K	-	No	Yes	Yes
Nº~~5~~ 36	Purple	MG4	?	Mn	Yes	Yes	No
Nº~~6~~ 37	Blue	MG4	Pb	Co-Mn	No	Yes	No
Nº7 38	Green	MG4	?	Cu	No	Yes	No
39	Yellow	MG4	?	Fe-Mn	No	Yes	No
Nº8	Unknown	MG4	K	Mn	No	Yes	Yes
41	Red	MG4	K-Pb	?	No	Yes	No
Compoziçao que tenho munto experimentado pª fazer o vidro cor de ouro e que he milhor pª	Yellow	MG4	K	Fe	No	Yes	No
Compozição de Vidraça	Colourless	MG5	?	-	Yes	Yes	No
Nº1 Compozição para Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº2 Compozição para Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº3 compozição para Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº4 Compozição para Christal com vidro de Escumas	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº5 Compozição para Christal com Vidro de ferro	Colourless	MG5	K-Pb	-	Yes	Yes	No

Table A.6: Transcription of the title of each recipe from the Marinha Grande Factory *arcanum* and other relevant information (Part 5).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Nº6 Compozição para Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº7 Compozição de Cristal	Colourless	MG5	K	-	Yes	Yes	Yes
Nº8 Compoziçao para Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº9 Compoziçao de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº10 compozição para vidro azul	Blue	MG5	K-Pb	Co-Mn	Yes	Yes	Yes
Nº11 Compozição de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
12 Compozição de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº13 compozição de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº14 Compoziçao de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº15 Compozição de Christal	Colourless	MG5	K-Pb	-	Yes	Yes	Yes
Nº16 Compozição que fes o S^{r} G^{me}	Unknown	MG5	K-Pb	Mn	No	Yes	Yes
Nº17 Compozição de Cristal	Colourless	MG5	K-Pb	Mn	No	Yes	Yes
Nº18 Compozição de Cristal 6 Marco 1793	Colourless	MG5	K-Pb	Co-Mn	Yes	Yes	Yes
Nº19 Compozição de Cristal do ~~S^{r} G^{me} 6 Marco 1793~~	Colourless	MG5	K-Pb	Mn	No	Yes	yes
Nº20 Compozição experiencia	Blue	MG5	K	?	No	Yes	No
Compoziçao que ?	Unknown	MG5	?	?	Yes	Yes	No
Nº21 Compoziçao de Vidro de Ferro	Green	MG5	K-Pb	?	Yes	Yes	No
Nº22	Unknown	MG5	K-Pb	?	Yes	Yes	Yes
Nº23 20 de Abril de 1793	Unknown	MG5	K-Pb	Co-Mn	Yes	Yes	Yes
(Correção receita anterior)	Unknown	MG5	K-Pb	Co-Mn	Yes	Yes	Yes
Maijo 8 de 1793 Nº24	Unknown	MG5	K-Pb	Co-Mn	Yes	Yes	Yes
Em 8 de Maijo de 1793	Unknown	MG5	K	Mn	No	Yes	No
Para Potes Cobertos	Unknown	MG5	K-Pb	Mn	Yes	Yes	Yes
Nº26 Compozicao de Cristal	Colourless	MG5	K-Pb	Mn	Yes	Yes	Yes

Table A.7: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 1).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Composição de Cristal feito na Fábrica da Marinha Grande	Colourless	COG	K-Pb	-	Yes	Yes	No
Composição de vidro branco. Vidro da Boemia	Colourless	COG	Na	-	Yes	Yes	No
Composição d'vidro branco. Vidro da Boemia	Colourless	COG	Na-K	-	Yes	Yes	No
Composição de vidro branco vidro da Boemia	Colourless	COG	?	?	No	No	No
Composição de meio cristal servindo pª obra lapidada	Colourless	COG	Na-K-Pb	-	Yes	No	No
Composição de vidro branco. Vidro da Boemia	Colourless	COG	Na-K	-	Yes	Yes	No
Composição de meio Cristal servindo pª lapidar e pª moldar	Colourless	COG	Na-K-Pb	-	Yes	Yes	No
Composição de meio Cristal servindo pª lapidar e para moldar	Colourless	COG	Na-K-Pb	-	Yes	Yes	No
Composição de meio Cristal servindo para moldar e lapidar	Colourless	COG	Na-Pb	-	Yes	Yes	No
Composição de meio cristal para moldar e pª fdo grosso	Colourless	COG	Na-Pb	-	Yes	Yes	No
Composição de Cristal feito na fabrica da Marinha Grande Nº1	Colourless	COG	K-Pb	-	Yes	Yes	No
Composição de Vidro Branco de Boemia Nº2	Colourless	COG	?	-	Yes	No	No
Composição de vidro branco vidro da Boemia Nº3	Colourless	COG	Na-?	-	Yes	No	No
Composição de vidro branco vidro da Boemia Nº4	Colourless	COG	Na-?	-	Yes	No	No
Composição de vidro branco Vidro da Boemia Nº5	Colourless	COG	Na-K	-	Yes	Yes	No
Composição de meio cristal servindo pª obra ? Lapidar Nº6	Colourless	COG	Na-K-Pb	-	Yes	Yes	No
Composição de meio cristal servindo pª lapidar e pª moldar Nº7	Colourless	COG	Na-K-Pb	-	Yes	No	No
Composição de meio cristal servindo para lapidar e para moldar Nº8	Colourless	COG	Na-K-Pb	-	Yes	No	No
Composição de meio cristal servindo pª moldar e pª fundo grosso Nº9	Colourless	COG	Na-Pb	-	Yes	Yes	No
Composição de meio Cristal servindo pª moldar pª f^{do} grosso Nº10	Colourless	COG	Na-Pb	-	Yes	Yes	No
Composição de cristal para moldar obra que seja de facetas Nº11	Colourless	COG	Na-Pb	-	Yes	Yes	No
Composição pª vidro ordinario de areia Nº12	Colourless	COG	Na	-	Yes	Yes	No
Composição pª vidro ordinario de seixo Nº13	Colourless	COG	Na	-	Yes	Yes	No
Composição pª vidro ordinario de seixo Nº14	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça Nº15	Colourless	COG	Na	-	Yes	No	No
Composição p/ vidraça Nº16	Colourless	COG	Na	-	Yes	Yes	No
Composição p/ vidraça Nº17	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça Nº18	Colourless	COG	Na	-	Yes	Yes	No

Table A.8: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 2).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Composição p/ vidraça Nº19	Colourless	COG	Na	-	Yes	Yes	No
Composição p/ vidraça Nº20	Colourless	COG	Na	-	Yes	Yes	No
Composição p/ vidraça Nº21	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça Nº22	Colourless	COG	Na	-	Yes	Yes	No
Composição p/ vidraça Nº23	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça Nº24	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça Nº25	Colourless	COG	Na	-	Yes	Yes	No
Composição pª vidraça amarellada, a franceza servindo pª chamines e garrafas a franceza Nº26	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Composição para vidraça Nº27	Colourless	COG	Na	-	Yes	Yes	No
Composição para vidraça servindo para o mesmo efeito da composição nº26 Nº28	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Vidro cor de ouro para cristal Nº29	Yellow	COG	Na	Fe	Yes	Yes	No
Vidro côr de azeite claro para garrafas Nº30	Yellow	COG	Na	Fe	No	Yes	Yes
Vidro côr de azeite mtº carregada pª garrafas a ingleza Nº31	Yellow	COG	Na	Fe-Mn	No	Yes	No
Vidro amalelo topasio pª cristal Nº32	Yellow	COG	Na	Fe-Mn	No	Yes	No
Vidro verde salsa pª dobrar cristal Nº33	Green	COG	K-Pb	Fe-Cr	No	Yes	Yes
Vidro verde salsa para cristal Nº34	Green	COG	K-Pb	Fe-Cr	Yes	Yes	Yes
Vidro azul marinho pª cristal Nº35	Blue	COG	K	Co-Mn	No	Yes	Yes
Vidr azul ferrete pª cristal Nº36	Blue	COG	Na	Co	Yes	Yes	Yes
Vidro ~~ferrete~~ preto opaco Nº37	Black	COG	Na	Co	Yes	Yes	No
Vidro preto, opaco Nº38	Black	COG	Na	Co	Yes	Yes	Yes
Vidro opala Nº39	Opal	COG	K-Pb	P	Yes	Yes	No
Vidro azul celetre Nº40	Blue	COG	K	Cu	Yes	Yes	No
Vidro azul celetre	Blue	COG	K-Pb	Cu	Yes	Yes	Yes
Vidro azul celestre	Blue	COG	K-Pb	Cu	Yes	Yes	Yes
Vidro azul celestre	Blue	COG	Na-K	Cu	Yes	Yes	Yes
Vidro azul celestre	Blue	COG	K	Cu	Yes	Yes	No
Vidro azul celestre	Blue	COG	Na-K	Cu	Yes	Yes	Yes
Vidro côr alaibastro	Unknown	COG	K-Pb	Sn	Yes	Yes	No

Table A.9: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 3).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Vidro cor alabastro	Unknown	COG	K-Pb	Sn	Yes	Yes	No
Vidro opaco côr de rosa ?	Pink	COG	K-Pb	Mn	No	Yes	Yes
Vidro amarelo topasio pª Cristal	Yellow	COG	Na	Fe	Yes	Yes	No
Vidro amarelo topasio para cristal	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Vidro amarelo topasio para cristal	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Vidro amarelo topasio para cristal	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Vidro amarelo topasio pª cristal	Yellow	COG	Na	Fe	Yes	Yes	No
Vidro azul ferrete pª cristal	Blue	COG	Na	Co	Yes	Yes	Yes
Vidro azul ferrete pª cristal	Blue	COG	Na	Co	Yes	Yes	No
Vidro opala	Opal	COG	K-Pb	P	Yes	Yes	No
Vidro opala	Opal	COG	K-Pb	P	No	Yes	No
Vidro verde salsa pª cristal	Green	COG	Na	Cr-Cu	Yes	Yes	Yes
Vidro verde azeitona escura pª garrafa á ingleza	Green	COG	Na	Co	Yes	Yes	No
Vidro verde azeitona para garrafas a francesa mas ainda um pouco escuro	Green	COG	Na	Co	Yes	Yes	No
Vidro verde azeitona pª garrafas á francesa	Green	COG	Na	Co	Yes	Yes	No
Vidro verde azeitona pª garrafas á francesa	Green	COG	Na	Co	Yes	Yes	Yes
Vidro verde azeitona pª garrafas á francesa	Green	COG	Na	Co	Yes	Yes	No
Vidro verde salsa pª cristal	Green	COG	Na-K	Cr-Cu	Yes	Yes	Yes
Vidro verde esmeralda pª cristal	Green	COG	Na-K	Cr-Cu	Yes	Yes	No
Vidro azul dicroide pª cristal	Blue	COG	Na-K-Pb	Cu	Yes	Yes	No
Vidro opaco amarelo côr de enxofre	Yellow	COG	K	U	No	Yes	Yes
Vidro verde opaco = chrisoprase =	Green	COG	K	Cu-U	No	Yes	Yes
Vidro côr de canario pª liso ou moldado (Amarelo dicroide)	Yellow	COG	K	U	Yes	Yes	No
Vidro verde dicroide para cristal	Green	COG	Na-K	Cu-U	No	Yes	Yes
Vidro opaco côr de alfazema escura	Purple	COG	Pb	F-Co	No	Yes	Yes
Vidro opaco azul antigo	Blue	COG	K-Pb	P-Co	No	Yes	Yes
Vidro opaco côr azul (?)	Blue	COG	K-Pb	P-Co	No	Yes	Yes
Vidro de côr violeta para cristal	Purple	COG	Na	Mn	Yes	Yes	Yes

Table A.10: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 4).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Vidro côr de canario mto mais diclurido do que o da composição nomero 69	Yellow	COG	Na-K	Fe-U	Yes	Yes	Yes
Vidro verde opaco mais verde do que o da composição nº68	Green	COG	Na-K	Cu-U	No	Yes	Yes
Vidro verde azeitona pª garrafas á franceza	Green	COG	Na	Co	Yes	Yes	Yes
Vidro cor de canario fluorescente	Yellow	COG	Na-K	Cu-Fe-U	No	Yes	Yes
Vidro azul ferrete pª vidraça	Blue	COG	Na	Co	Yes	Yes	Yes
Vidro azul ferrete pª vidraça	Blue	COG	Na	Co	Yes	Yes	Yes
Vidro azul ferrete para vidraça	Blue	COG	Na	Co	Yes	Yes	No
Vidro cor amor perfeito pª vidraça	Unknown	COG	Na-K	Co	Yes	Yes	No
Vidro verde salsa para vidraça	Green	COG	Na-K	Cr-Cu	Yes	Yes	Yes
Vidro amarelo topasio para vidraça	Yellow	COG	Na	Fe	No	Yes	Yes
Vidro côr de violeta para vidraça	Purple	COG	Na	Mn	Yes	Yes	No
Vidro verde salsa para vidraça	Green	COG	Na-Pb	Cr-Cu	Yes	Yes	No
Vidro azul ferrete pª vidraça	Blue	COG	Na	Co	Yes	Yes	No
Vidro amarelo topasio para vidraça	Yellow	COG	Na	Fe	No	Yes	Yes
Vidro azul celestre claro	Blue	COG	Na-Pb	Cu	Yes	Yes	No
Vidro azul ordinário	Blue	COG	Na	?	Yes	Yes	No
Vidro amarelo topasio	Yellow	COG	Na-K	Fe-Mn	Yes	Yes	No
Verre bleu celestre	Blue	COG	Na-Pb	Cu	Yes	Yes	No
Verre bleu celestre	Blue	COG	Na-Pb	Cu	Yes	Yes	No
Verre bleu ? opague	Blue	COG	Na-Pb	Co	Yes	Yes	Yes
Verre opale	Opal	COG	K-Pb	P-Co-Mn	No	Yes	No
Verre opale	Opal	COG	K-Pb	Mn	No	Yes	No
Verre jaune soufre	Yellow	COG	Na-K	U	No	Yes	No
Verre Jaune topaze	Yellow	COG	Na	Fe	Yes	Yes	Yes
Verre opale	Opal	COG	K-Pb	P-Mn	Yes	Yes	No
Verre opale	Opal	COG	K-Pb	P-Mn	Yes	Yes	No
Verre bleu celeste	Blue	COG	K-Pb	Cu	Yes	No	No
Azul ferrete	Blue	COG	Na	?	No	No	No

Table A.11: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 5).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Amarelo	Yellow	COG	Na	Fe-Mn	Yes	Yes	No
Rocho	Purple	COG	Na	?	No	No	No
Verde esmeralda	Green	COG	Na-Pb	Cr-Cu	No	Yes	Yes
Opala	Opal	COG	K-Pb	?	No	Yes	No
Verde amarello	Green	COG	Na	Cr-Cu	No	Yes	Yes
Verde salça	Green	COG	Na-Pb	Cr-Cu	No	Yes	No
Verde bronze	Green	COG	Na	?	Yes	Yes	No
Verre bleu celestre	Blue	COG	K-Pb	Cu	Yes	Yes	no
Verre blue celestre	Blue	COG	Na	Cu	Yes	Yes	Yes
Verre opale	Opal	COG	K-Pb	P-Mn	Yes	Yes	No
Verre opala	Opal	COG	Na	Mn	No	No	No
(sem título)	Unknown	COG	K-Pb	?	No	Yes	No
Vidro azul diclorido	Blue	COG	Na-Pb	Cu	No	Yes	Yes
(sem título)	Unknown	COG	Na	?	No	No	No
Verde typo pª garrafas	Green	COG	Na	Fe-Cr-Cu	No	Yes	Yes
---	Unknown	COG	Na	Co-Mn	No	Yes	Yes
Formula de fazer vidro Amarelo	Yellow	COG	K	Fe	No	Yes	No
Formula de fazer vidro Amarelo violeta	Purple	COG	K	Mn	No	Yes	Yes
Vidro branco	Colourless	COG	Na	-	No	Yes	Yes
Vidro branco isto é não sabendo que côr é	Colourless	COG	Na	-	No	Yes	Yes
Vidro Verde para doês	Green	COG	Na	Co	No	Yes	No
Vidro branco	Colourless	COG	Na	-	No	Yes	No
Vidro Verde	Green	COG	Na	Co	No	Yes	No
Vidro Verde	Green	COG	Na	Co	No	Yes	No
Vidro Branco	Colourless	COG	Na	-	No	Yes	No
Vidro Vranco	Colourless	COG	Na	-	No	Yes	No
Vidro Branco	Colourless	COG	Na	-	No	Yes	No
Vidro Branco ordinário servindo para chamines ? Ordinário nº3	Colourless	COG	Na	-	No	Yes	Yes

Table A.12: Transcription of the title of each recipe from the Castro and Oliveira Guerra *arcanum* and other relevant information (Part 6).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Readable	Reproducible
Composição ordinária nº6	Colourless	COG	Na	-	No	Yes	Yes
Composição nº11	Colourless	COG	Na	-	No	No	No
Composição ?	Unknown	COG	Na-Pb	Mn	No	No	No
Composição Rosalino	Pink	COG	Na-K	Mn-Se	No	Yes	Yes
? ? Vermelho Quimado	Red	COG	Na	?	No	No	No
Blue Celeste	Blue	COG	Na-K	Co	No	Yes	Yes
Cristal	Colourless	COG	K-Pb	-	No	Yes	Yes
Opale vert	Opal	COG	Na	P-Cr-Cu	No	Yes	Yes
Cristal feito por mim e composto em 3 de Novembro de 1922	Colourless	COG	K-Pb	-	No	Yes	Yes
Vidro amarelo muito bom com pouca espessura e boa cor para frascaria	Yellow	COG	Na	Fe	No	Yes	Yes
Vidro para lapidar	Colourless	COG	Na	-	No	Yes	Yes
Vidro mais ordenario mas tambem da para lapidar	Colourless	COG	Na	-	No	Yes	Yes
Composição de vidro branco ordinário para ser aplicado na fabrica Progresso	Colourless	COG	Na	-	No	Yes	Yes
Para os potes do lado é	Colourless	COG	Na	-	No	Yes	Yes
Composição de mais de meio cristal feita e composta por Augusto d'Oliveira Guerra 17/8/25	Colourless	COG	Na	-	No	Yes	Yes
Composição de Vidro Verde para esbater e dublé	Green	COG	Na	Fe-Co-Cr-Cu	No	Yes	Yes
Composição de Vidro azul para dublé	Blue	COG	Na	Co	No	Yes	Yes
Composição de Vidro azul sem ser para dublé	Blue	COG	Na	Co	No	Yes	Yes
Composição de vidro azul marino	Blue	COG	Na	Co-Cu	No	Yes	Yes
Vidro Verde p esbater	Green	COG	Na	Cr-Cu	No	Yes	No
Vidro verde para calices	Green	COG	Na	Cr-Cu	No	Yes	Yes

Table A.13: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 1).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Formulas alemãs de vidraça	Colourless	GF	Na	-	No		No	No
Vidro Preto (ambar de garrafas)	Yellow	GF	Na	Fe-Mn	No		Yes	Yes
Vidro M. Pereira	Colourless	GF	Na	-	No		Yes	Yes
Branco fino para lapidar	Colourless	GF	Na-Pb	-	No		No	No
Opala	Opal	GF	Na-Pb	F	No		Yes	No
Celadon	Celadon	GF	?	Cr-Cu	No		Yes	No
Cristal de Som	Colourless	GF	Na-K-Pb	-	No		Yes	No
Cristal de Som (Mesma que anterior)	Colourless	GF	Na-K-Pb	-	No		Yes	Yes
Vidro Rosa	Pink	GF	Na-K-Pb	Cd-Au	No		Yes	Yes
Verde salsa	Green	GF	Na	Cu	No		Yes	Yes
Verde Japão	Green	GF	Na	Cr-Cu	No		Yes	Yes
Vidro Azul	Blue	GF	?	?	Yes		Yes	No
Vidro Verm. ~~Cereja~~ garantido	Red	GF	K-Pb	Au	No		Yes	Yes
Vidro branco para lapidar	Colourless	GF	Na	-	No		Yes	No
Cristal de Som (garantido)	Colourless	GF	Na-K-Pb	-	No		Yes	No
Verde Salsa	Green	GF	Na	Cr-Cu	No		Yes	Yes
Vidro Preto	Black	GF	K-Pb	Ni-Co	No		Yes	Yes
Cristal de Veneza	Colourless	GF	K-Pb	-	No		Yes	Yes
Cristal Nº1 (garantido)	Colourless	GF	Na-K-Pb	-	No		Yes	Yes
Vermelho Cereja	Red	GF	K-Pb	Au	No		Yes	Yes
Roxo (Ametista)	Purple	GF	K-Pb	Au-Se	No		No	No
Vidro branco para lapidar	Colourless	GF	Na	-	No		Yes	No
Verde da China	Green	GF	K-Pb	Cr-Cu	No		Yes	Yes
Vidro branco (para lapidar)	Colourless	GF	Na	-	No		No	No
Vidro branco para o Tanque	Colourless	GF	Na	-	No		Yes	No
Vidro verde escuro	Green	GF	Na	Cr-Cu	No		Yes	No
Vidro branco para lapidar	Colourless	GF	Na-K-Pb	-	No		Yes	No

Table A.14: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 2).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Vidro de Som	Colourless	GF	Na-K-Pb	-	No		Yes	Yes
Verde Salsa (Para cálices e esbatidos)	Green	GF	Na	Cu	No		Yes	No
Amarelo da China	Yellow	GF	Na-K	U	No		Yes	Yes
Verde Japão	Green	GF	K-Pb	Cr-Cu	No		Yes	Yes
Vidro de Som	Colourless	GF	Na-K-Pb	-	No		No	No
Vidro branco (pª lapidar)	Colourless	GF	Na	-	No		Yes	No
Vidro de Som	Colourless	GF	K-Pb	-	No		Yes	Yes
Vidro de Som	Colourless	GF	Na-K-Pb	-	No		Yes	Yes
Vidro branco para o tanque	Colourless	GF	Na	-	No		Yes	No
Verde da china	Green	GF	K-Pb	Cr-Cu	No		Yes	Yes
Vidro de som - Residencia	Colourless	GF	K-Pb	-	No		Yes	Yes
Vidro Preto	Black	GF	Na	Mn-Co	No		Yes	Yes
Vidro branco (Potes)	Colourless	GF	Na	-	No		Yes	No
Verde Salsa	Green	GF	Na	Cr-Cu	No		Yes	Yes
Celadon	Celadon	GF	?	F-Cr-Cu	Yes		Yes	No
Verde da China	Green	GF	K-Pb	Cr-Cu	No		Yes	Yes
Verde da China (Igual à anterior)	Green	GF	K-Pb	Cr-Cu	No		Yes	Yes
Vidro Fumado	Black (smoked)	GF	Na	Co-Cu-U	No		Yes	Yes
Azul (de som)	Blue	GF	K-Pb	F-Cu	No		Yes	Yes
Amarelo (para ligar com todo o vidro)	Yellow	GF	K	Cd	No		Yes	Yes
Verde escuro (para ligar com o opala)	Green	GF	?	F-Cu	Yes		Yes	No
Vidro Branco (optimo)	Colourless	GF	Na	-	No		No	No
Aventurina	Aventurine	GF	Na	Cr-Cu	No		Yes	Yes
Vidro amarelo	Yellow	GF	Na	Cd	No		Yes	Yes
Verde da China (Hastes ??)	Green	GF	Na	Cr-Cu	Yes	White	Yes	Yes
Azul marinho (Hastes ??)	Blue	GF	Na	?	Yes		Yes	No
Opala (em potes)	Opal	GF	Na-Pb	F	Yes		Yes	Yes

Table A.15: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 3).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Vidro Opalescente	Opal	GF	Na-Pb	F	No		Yes	No
Verde da China (Som)	Green	GF	K-Pb	Cu	No		Yes	Yes
Verde para pés	Green	GF	?	Cr-Cu	Yes		Yes	No
Encarnado - Optimo	Red	GF	K-Pb	?	No		No	No
Verde escuro bom para ligar com o opala	Green	GF	Na	F-Cr	No		No	No
Celadon	Celadon	GF	Na	F-Cr-Cu	Yes	Celadon	Yes	Yes
Opala (com criol. ??)	Opal	GF	Na	F	Yes		Yes	Yes
Opala (com criol. ??)	Opal	GF	Na	F	No		Yes	Yes
Opala pª safroeiros	Opal	GF	Na	F	No		Yes	Yes
Compos. de Vidraça da ?	Colourless	GF	Na	-	No		Yes	Yes
Opala (em potes)	Opal	GF	Na	F	No		Yes	Yes
Branco	Colourless	GF	Na	-	Yes		Yes	Yes
1º ensaio de composição	Colourless	GF	Na	-	No		Yes	No
Opala (Potes)	Opal	GF	Na	F	No		Yes	Yes
Branco	Colourless	GF	Na	-	No		Yes	Yes
Vidraça	Colourless	GF	Na	-	No		Yes	Yes
Vidraça	Colourless	GF	?	-	No		No	No
Azulino	Blue	GF	?	Co-Cu	Yes		Yes	No
Verdino	Green	GF	?	Co-Cr-Cu	Yes		Yes	No
Azul claro para ??	Blue	GF	?	?	Yes		No	No
Branco (GF)	Colourless	GF	Na	-	No		No	No
Branco (GF) (igual à anterior)	Colourless	GF	Na	-	No		Yes	No
Opala (GF)	Opal	GF	Na	F	No		Yes	No
Opala (GF)	Opal	GF	Na	F	No		Yes	Yes
Amarelo para Champagne	Yellow	GF	Na	Fe	Yes	Light Yellow	Yes	No
Amarelo para Champagne (Igual à anterior)	Yellow	GF	Na	Fe	No		Yes	Yes
Azul para doublé/opala	Blue	GF	?	Co	No		Yes	No

Table A.16: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 4).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Rosa para doublé rosa	Pink	GF	Na	Se	No		Yes	Yes
Verde para doublé verde/opala	Green	GF	Na	Cr-Cu	Yes	Green	Yes	Yes
Verde para doublé verde/opala (igual à anterior)	Green	GF	Na	Cr-Cu	No		Yes	Yes
Azul marinho para doublé - opala	Blue	GF	Na	Cu	No		Yes	No
Rosa (para ligar c/ opala)	Pink	GF	Na-K	Se	No		Yes	Yes
Amarelo para champagne	Yellow	GF	Na	Fe	Yes	Light Yellow	Yes	No
Amarelo carregado pª frascos	Yellow	GF	Na	Fe	No		Yes	Yes
Verde para pés (Belé?)	Green	GF	Na	Cr-Cu-U	No		Yes	Yes
Vidro rosa	Pink	GF	Na	Se	Yes	Pink	No	No
Verde Champ	Green	GF	Na	Cr-Cu-U	No		Yes	Yes
Amarelo (frascos ?)	Yellow	GF	Na	Fe	Yes		Yes	No
Verde (pª opaleiro)	Green	GF	Na	Cr-Cu-U	Yes		Yes	Yes
Verde salsa (frascos)	Green	GF	Na	Cr-Cu	No		Yes	Yes
Amarelo (champagne)	Yellow	GF	Na	Fe	Yes		Yes	No
Verdine	Green	GF	Na	Cr-Cu-U	No		Yes	Yes
Azul (champagne)	Blue	GF	Na	Cu	Yes		Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes
Rosa	Pink	GF	Na	Se	No		Yes	Yes
Amarelo Champagne	Yellow	GF	Na	Fe	Yes	Champagne	Yes	No
Rosa	Pink	GF	Na-K	Se	Yes	Pink	Yes	Yes
Amarelo champagne	Yellow	GF	Na	Fe	Yes	Dark	Yes	No
Rosa	Pink	GF	Na-K	Se	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	Yes	Light, Dark, Opal.	Yes	No
Vidro fumado	Black (smoked)	GF	Na	Ni-Co-Cu-U	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	Yes	Light, Dark	Yes	No
Champagne	Yellow	GF	Na	Fe	Yes	Light, Dark	Yes	No
Verde (opal)	Green	GF	Na	Cr-Cu-U	No		Yes	Yes

Table A.17: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 5).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Opala	Opal	GF	Na	F	No		Yes	Yes
Azul frascos	Blue	GF	Na	Co	No		Yes	Yes
Amarelo para frascos Universal	Yellow	GF	Na	Fe	No		Yes	Yes
Amarelo frascos claro	Yellow	GF	Na	Fe	No		Yes	Yes
Amarelo champagne	Yellow	GF	Na	Fe	Yes	Light, Dark	Yes	No
Verde opalino	Green	GF	Na	Cr-Cu-U	Yes		Yes	Yes
Champagne	Yellow	GF	Na	Fe	Yes	Light, Dark	Yes	No
Verde opalino	Green	GF	Na	Cr-Cu-U	Yes		Yes	Yes
Verde doublé opalino	Green	GF	Na	Cr-Cu-U	Yes		Yes	No
Champagne	Yellow	GF	Na	Fe	Yes		Yes	Yes
Celadon	Celadon	GF	Na	F-Cr	No		No	No
Rosa pálido (opaco)	Pink	GF	Na-K	F-Se	No		Yes	Yes
Verde opaleio	Green	GF	Na	Cr-Cu-U	No		Yes	Yes
Amarelo - Champagne	Yellow	GF	Na	Fe	Yes		Yes	No
Verde opalieiro	Green	GF	Na	Cr-Cu-U	No		Yes	Yes
Branco	Colourless	GF	?	-	Yes		Yes	No
Opala	Opal	GF	Na	F	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	No		Yes	Yes
Verde opalino (antigo)	Green	GF	Na	Co-U	No		Yes	Yes
Moderno	Colourless	GF	Na	-	No		Yes	Yes
Rosa	Pink	GF	Na-K	Se	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	No		Yes	Yes
Verde (moderno) mais claro	Green	GF	Na	Cr-Cu-U	Yes		Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	No		Yes	Yes
Rosa	Pink	GF	Na-K	Se	Yes		No	No
Champagne	Yellow	GF	Na	Fe	No		Yes	No

Table A.18: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 6).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Branco	Colourless	GF	Na	-	Yes		Yes	Yes
Amarelo (frasco)	Yellow	GF	Na	Fe	Yes		Yes	No
Opala	Opal	GF	Na	F	Yes		Yes	Yes
Champagne	Yellow	GF	Na	Fe	No		No	No
Azul	Blue	GF	Na	?	No		Yes	No
Rosa	Pink	GF	Na-K	Se	No		Yes	Yes
Verde	Green	GF	Na	Cr-Cu	No		Yes	Yes
Opala	Opal	GF	Na	F	No		No	No
Opala (frasco ?)	Opal	GF	Na	F	No		Yes	Yes
Opala - forno novo	Opal	GF	Na	F	No		Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes
Vidraça	Colourless	GF	Na	-	No		No	No
Vidro fumado	Black (smoked)	GF	Na	Co-Cu-Ni	Yes	White	Yes	Yes
Branco	Colourless	GF	Na	-	No		No	No
Branco	Colourless	GF	Na	-	No		Yes	Yes
Amarelo	Yellow	GF	Na	Fe	No		Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes
Champagne	Yellow	GF	Na	Fe	No		Yes	Yes
Azul (double)	Blue	GF	Na	Cu	No		Yes	Yes
Rosa	Pink	GF	Na-K	Se	No		Yes	Yes
Verde	Green	GF	Na	Cr-Cu	No		Yes	Yes
Azul (frascos)	Blue	GF	Na	Co	No		Yes	Yes
Opalas ??	Opal	GF	?	?	No		No	No
Fumado	Black (smoked)	GF	Na	Co-Cu-Ni	Yes	White	Yes	Yes
Verde (fantasia)	Green	GF	Na	Cr-Cu	Yes	White, Green	Yes	Yes
Opala	Opal	GF	Na	F	No		Yes	Yes

Table A.19: Transcription of the title of each recipe from the Gaivotas Factory *arcanum* and other relevant information (Part 7).

Name	Colour	Arcana	Base glass	Cromophor	Cullet	Type of cullet	Readable	Reproducible
Encarnado	Red	GF	Na	Se-F	No		Yes	Yes
??	Unknown	GF	?	?	No		No	No
Vidro base pª cores (??)	Colourless	GF	Na	-	Yes	Colour, Opal	Yes	No
Encarnado	Red	GF	Na	Cd-Se-F	No		Yes	Yes
Purpura	Purple	GF	Na	Mn-Se-F	No		Yes	Yes
Opala	Opal	GF	Na	F	No		No	No
Purpura	Purple	GF	Na	Mn-Se-F	Yes	White	Yes	Yes
Champagne	Yellow	GF	Na	Fe	Yes	White, Yellow	Yes	No
Encarnado	Red	GF	Na-K	Cd-Se-F	No		Yes	No
Encarnado ??	Red	GF	Na	Cd-Se-F	No		Yes	No
Encarnado ??	Red	GF	Na-K	Cd-Se-F	No		Yes	No
Encarnado	Red	GF	Na-K	Cd-Se-F	No		Yes	No

B

Digitalisation of recipes

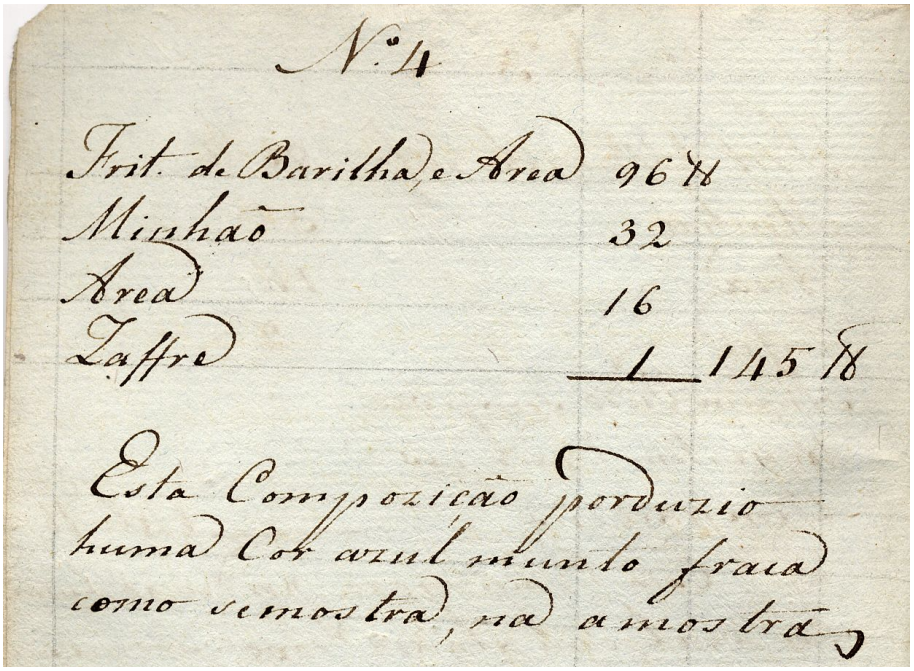


Figure B.1: Blue recipe M1_4

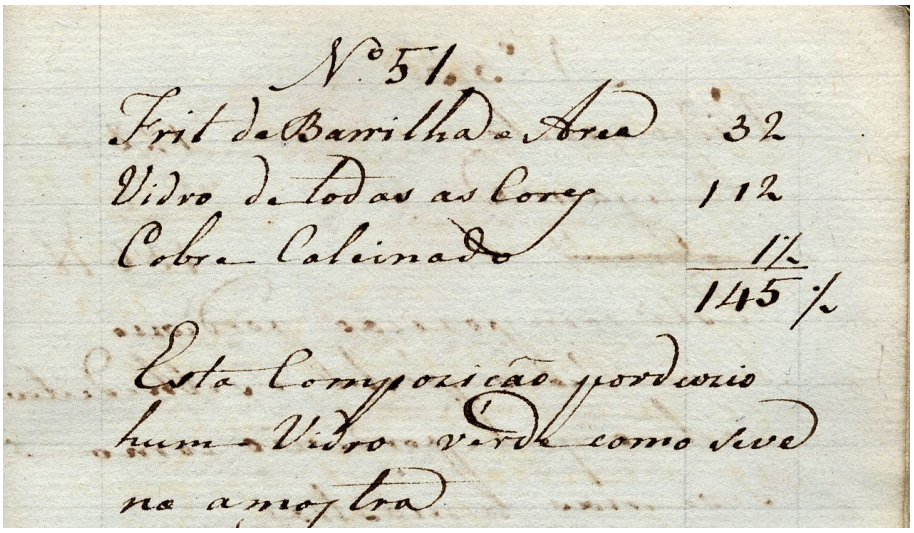
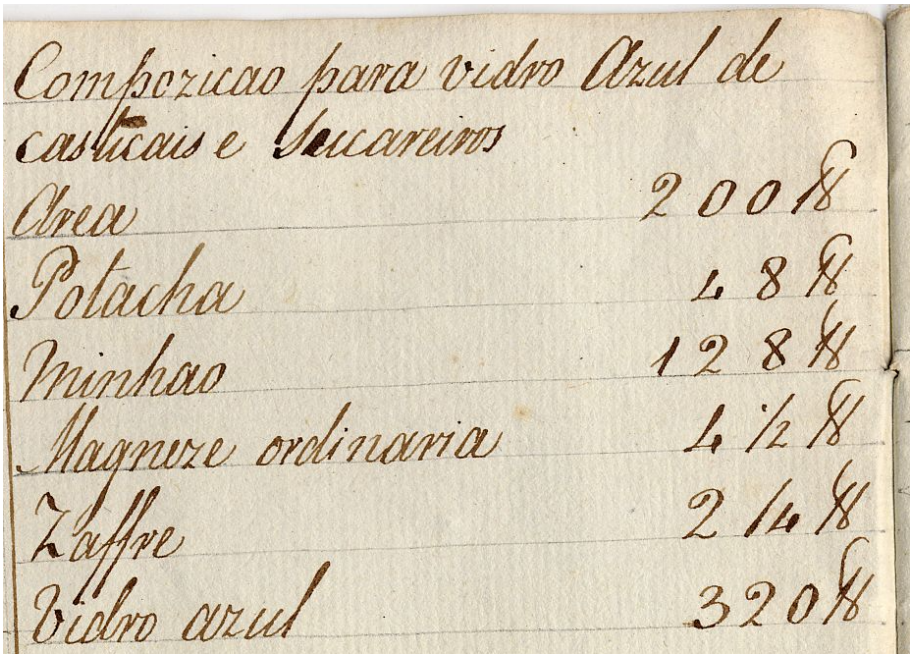


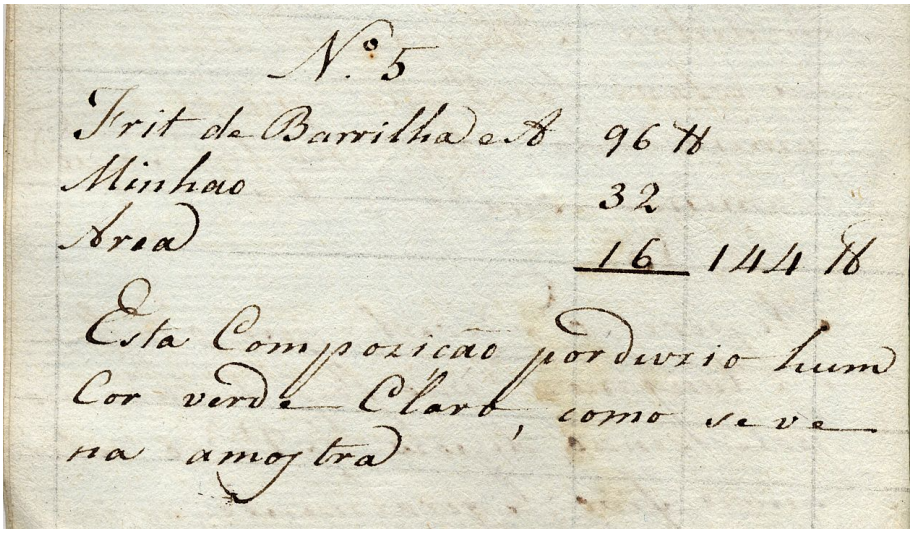
Figure B.2: Blue recipe M1_51



Compozicao para vidro Azul de
casticais e Sucareiros

Area	200 ℔
Potacha	48 ℔
Minhao	128 ℔
Magneze ordinaria	4 ½ ℔
Zaffre	2 ¼ ℔
Vidro azul	320 ℔

Figure B.3: Blue recipe M3_3



N.º 5

Frit de Barrilha e A	96 ℔	
Minhao	32	
Area	16	144 ℔

Esta Compozicão porduzio hum
Cor verde Claro, como se ve
na amostra

Figure B.4: Green recipe M1_5

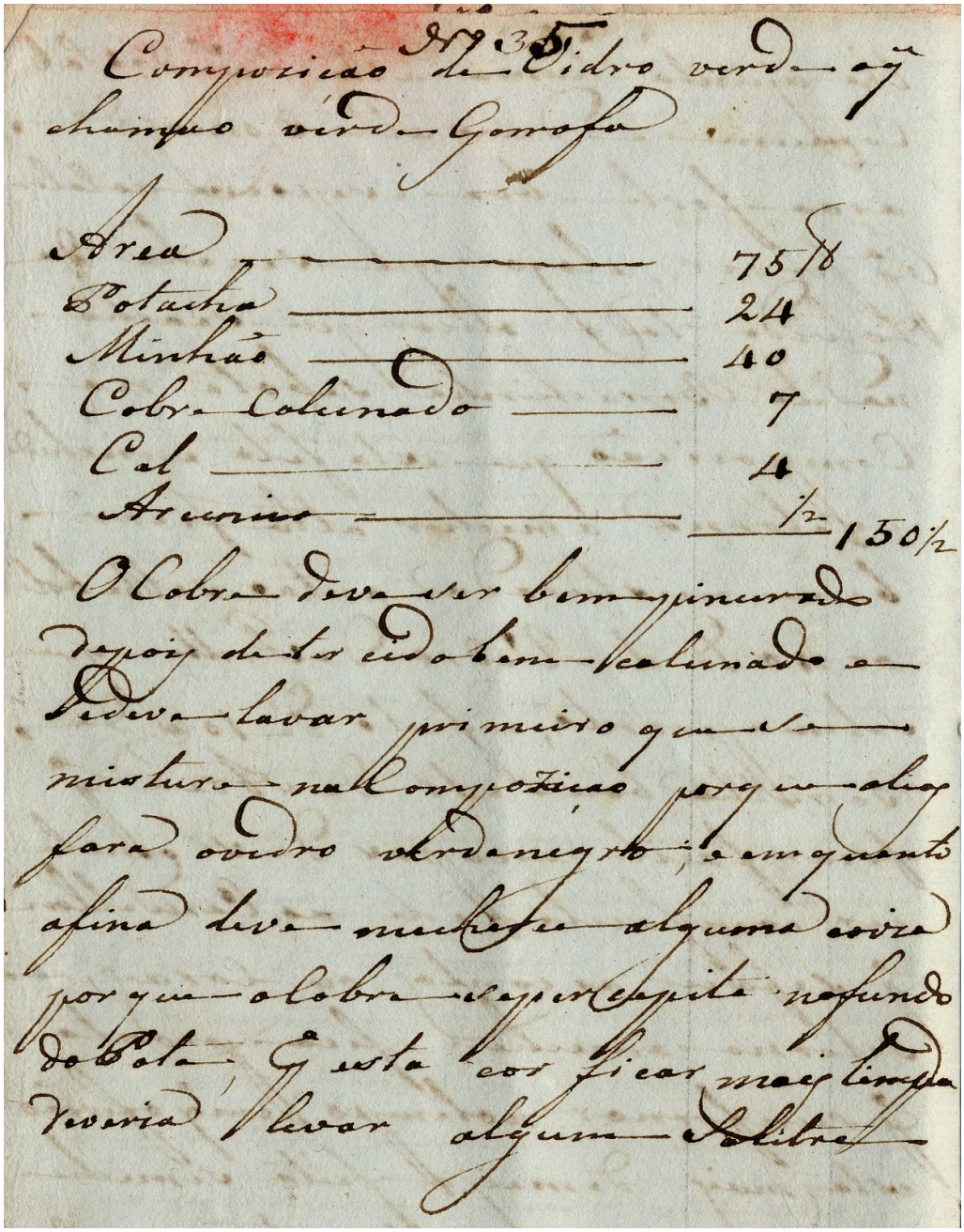


Figure B.5: Green recipe M4_3

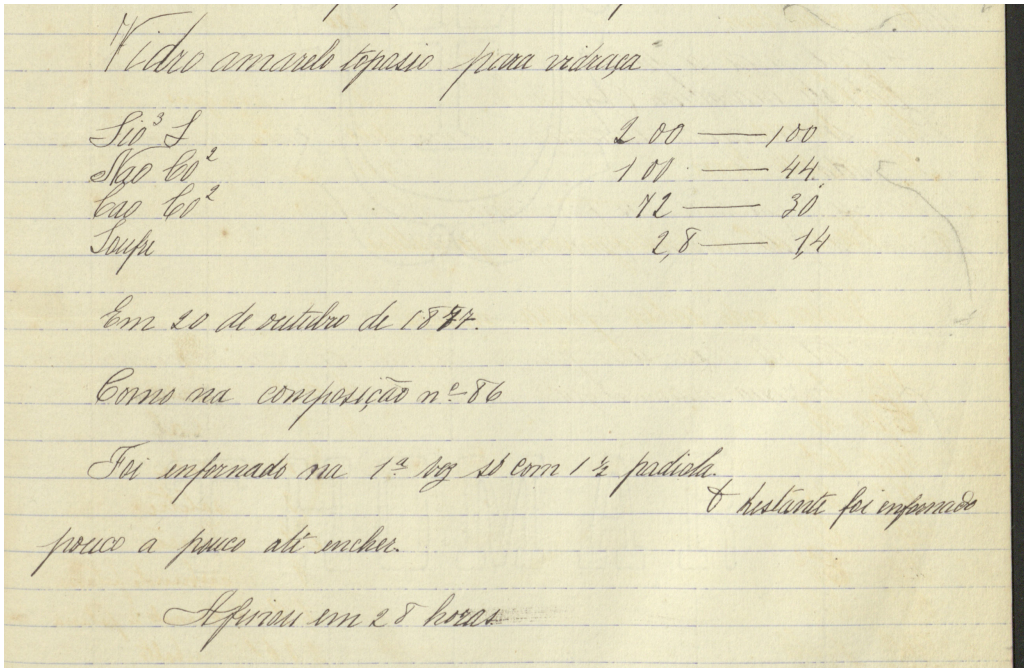


Figure B.6: Yellow recipe C98

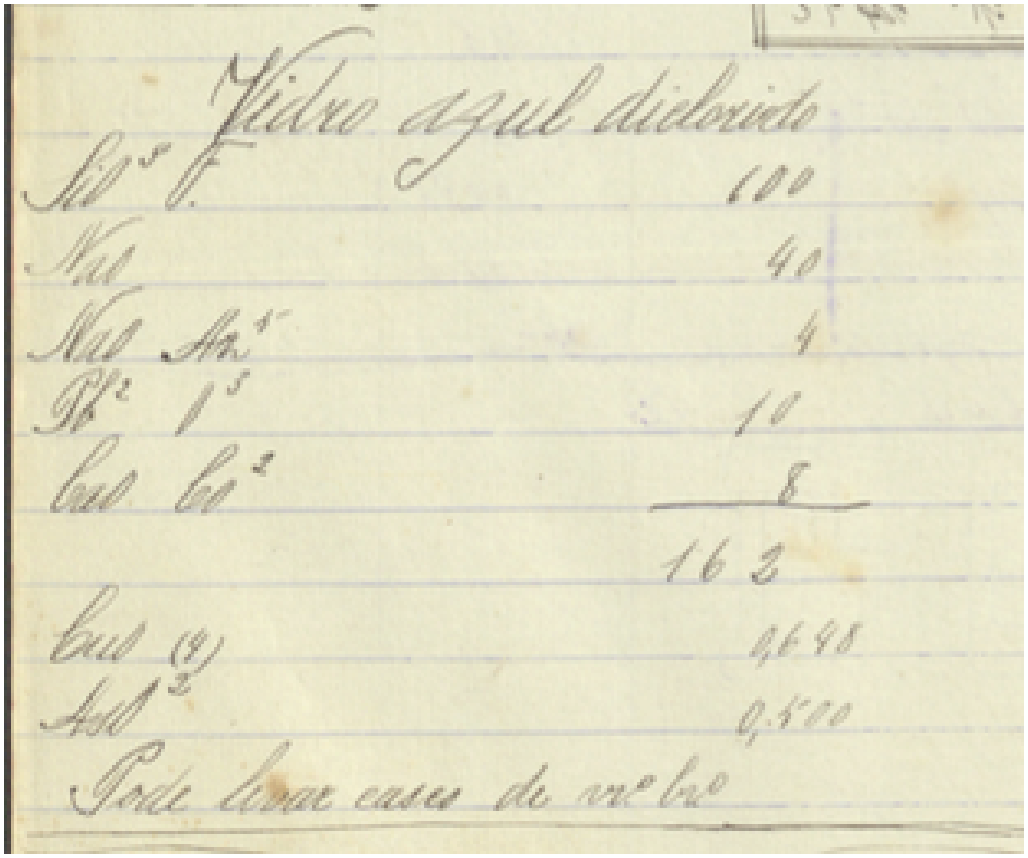


Figure B.7: Blue recipe C125

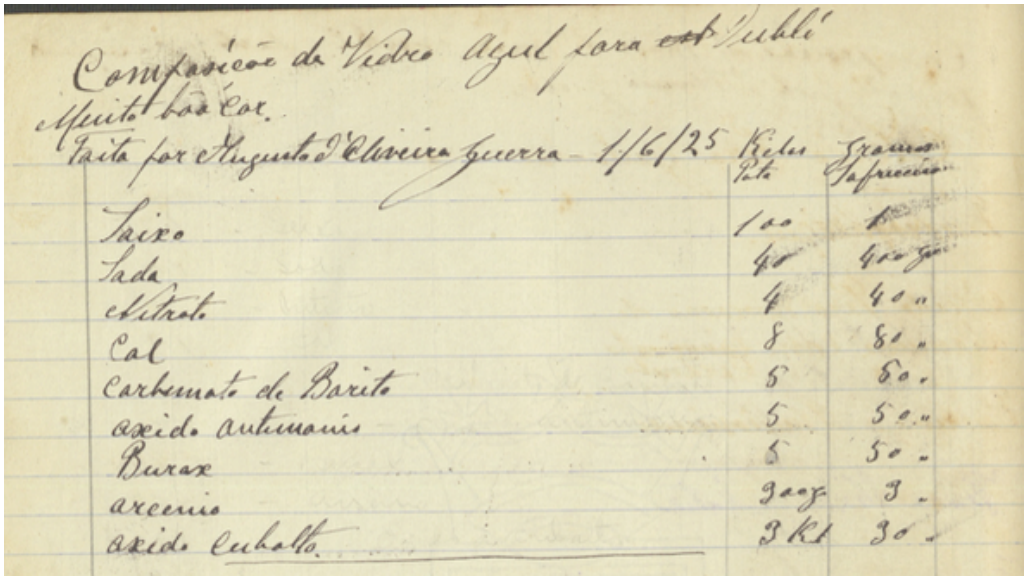


Figure B.8: Blue recipe C157

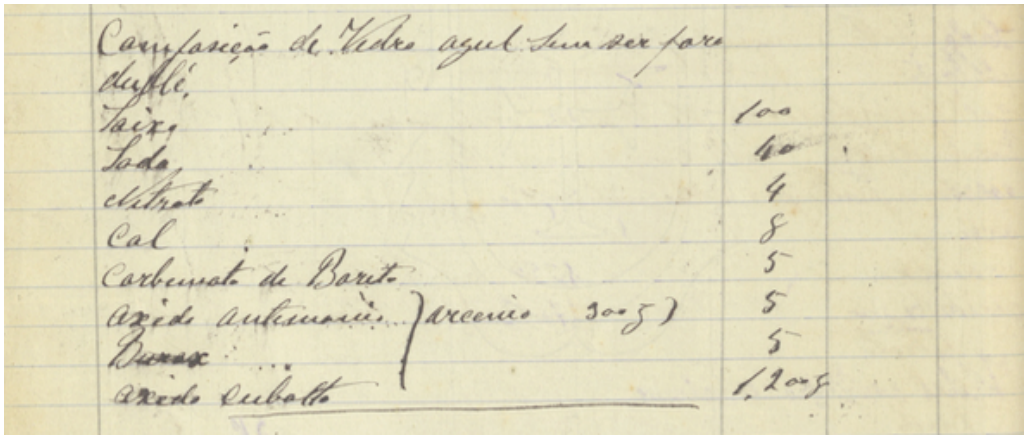


Figure B.9: Blue recipe C158

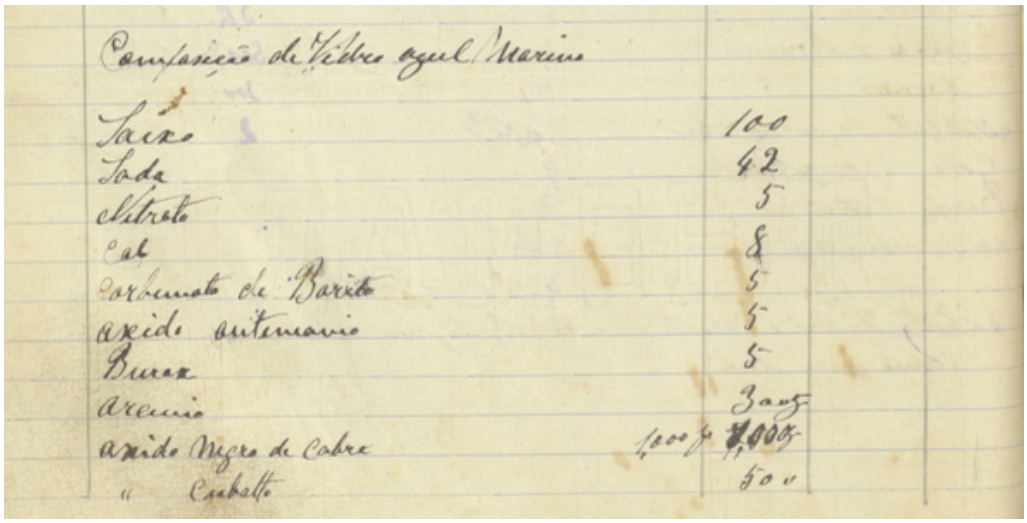


Figure B.10: Blue recipe C159

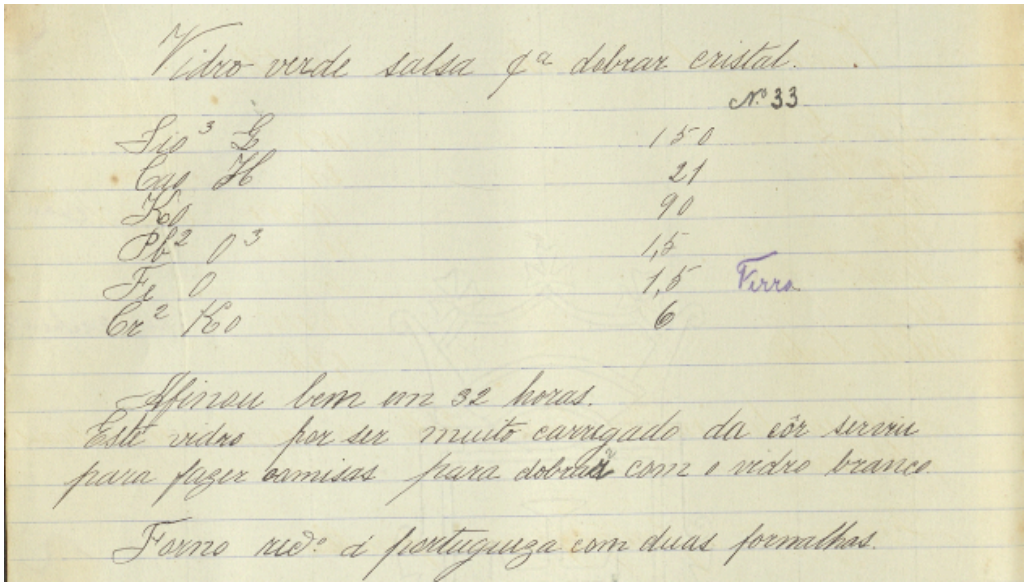


Figure B.11: Green recipes C43

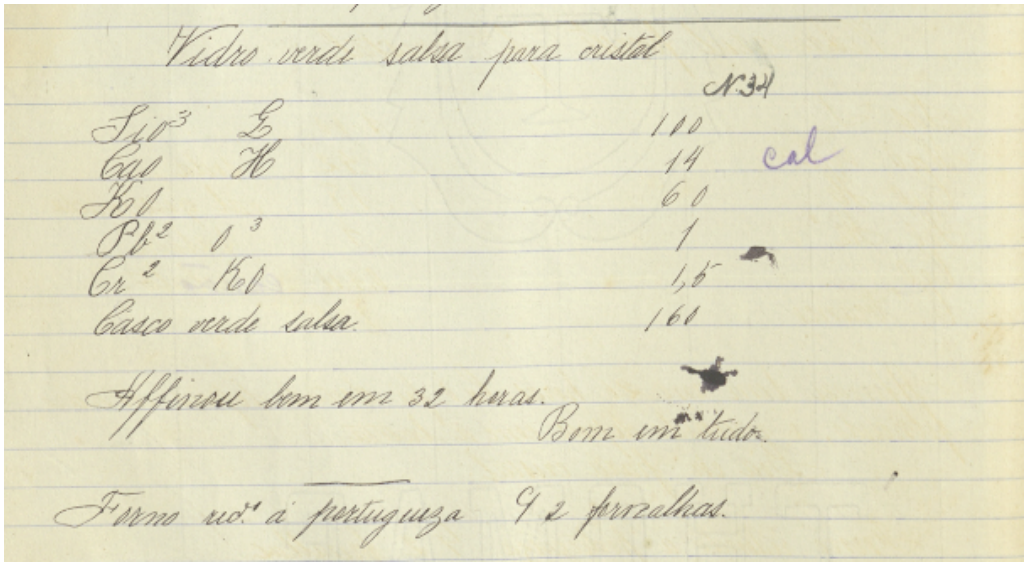
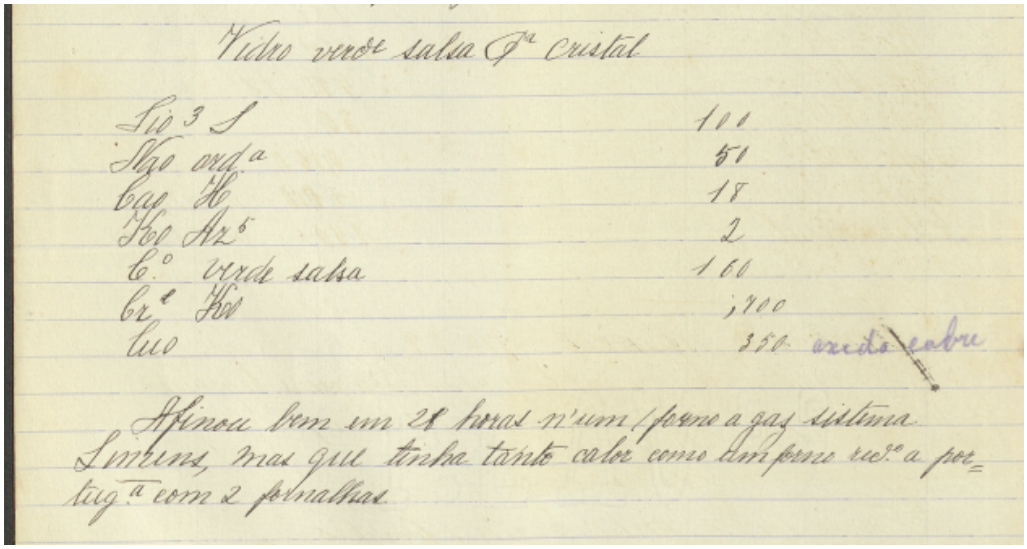


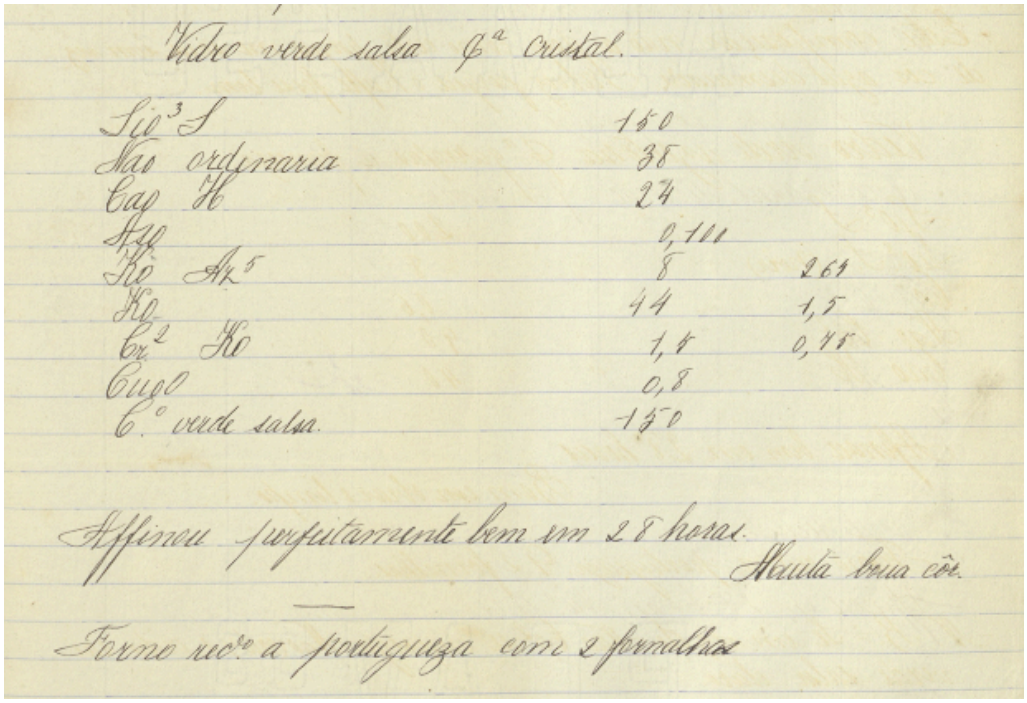
Figure B.12: Green recipe C44


Vidro verde salsa Qª cristal

$Si O^3 S$	100
Na2O ordª	51
Ca O H	18
K2O Az5	2
Cº verde salsa	160
Cr2 K6	1,700
Cu O	350 oxido cobre

Affinou bem em 28 horas n'um forno a gaz sistema Siemens, mas que tinha tanto calor como um forno recº a portuguª com 2 fornalhas.

Figure B.13: Green recipe C68


Vidro verde salsa Qª cristal.

$Si O^3 S$	150	
Na2O ordinaria	38	
Ca O H	27	
Al2O3	0,100	
K2O Az5	8	2,64
K2O	44	1,5
Cr2 K6	1,4	0,46
Cu O	0,8	
Cº verde salsa	150	

Affinou perfeitamente bem em 28 horas. Mistura boa côr.

Forno recº a portuguesa com 2 fornalhas

Figure B.14: Green recipe C74

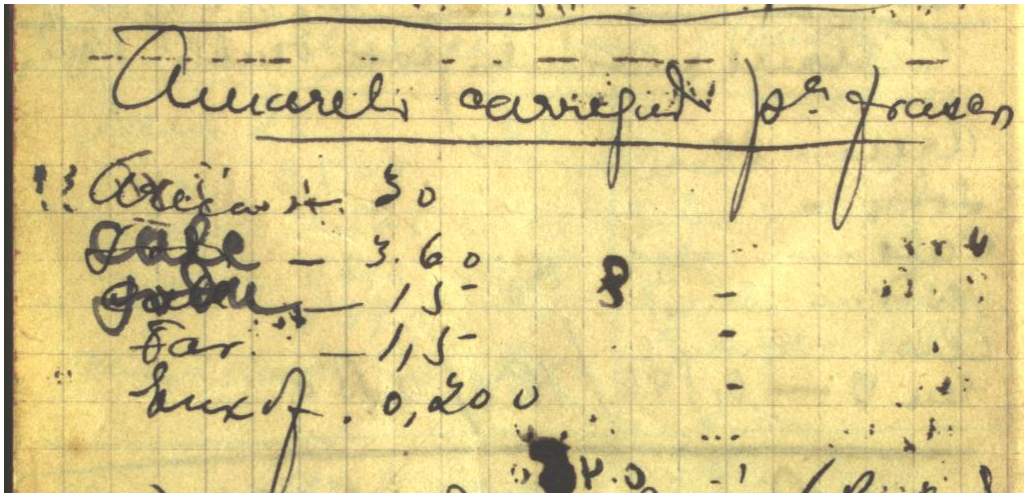


Figure B.15: Yellow recipe G92

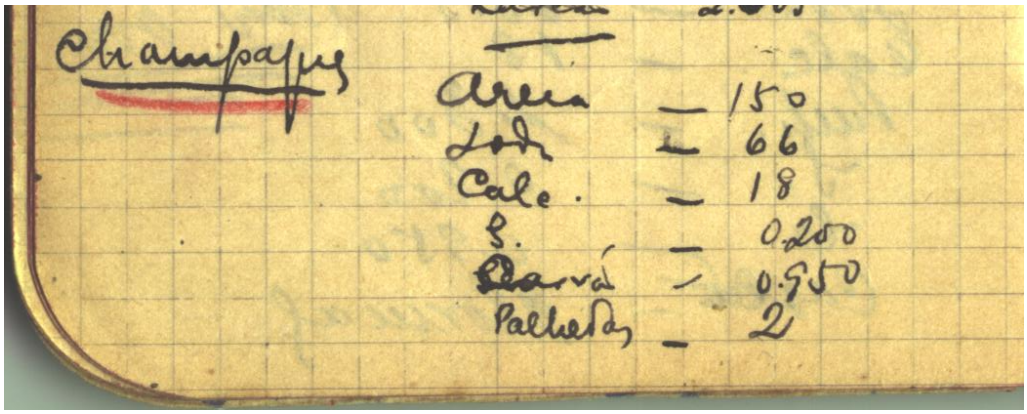


Figure B.16: Yellow recipe G130

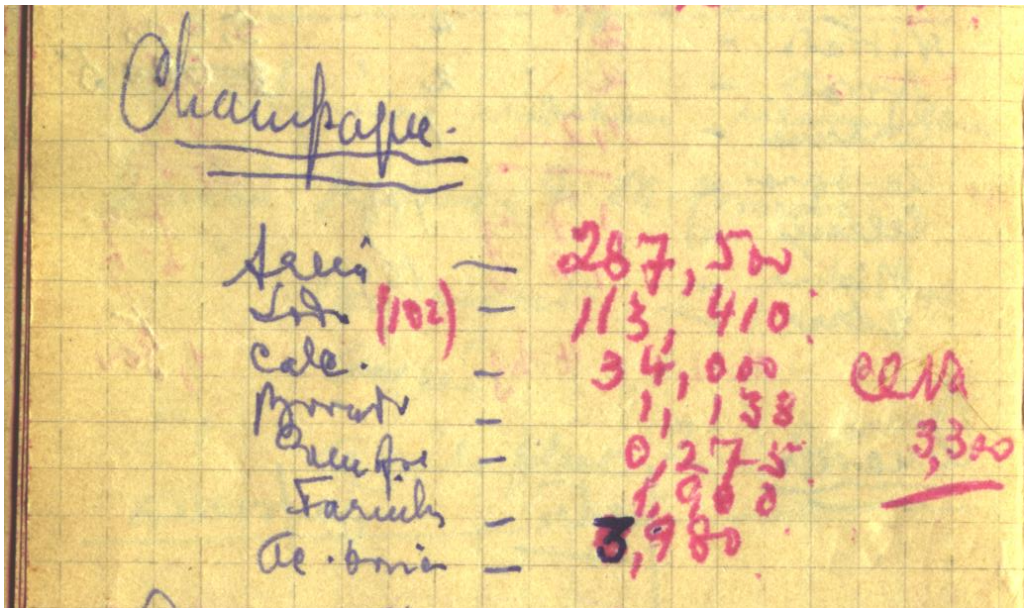


Figure B.17: Yellow recipe G192

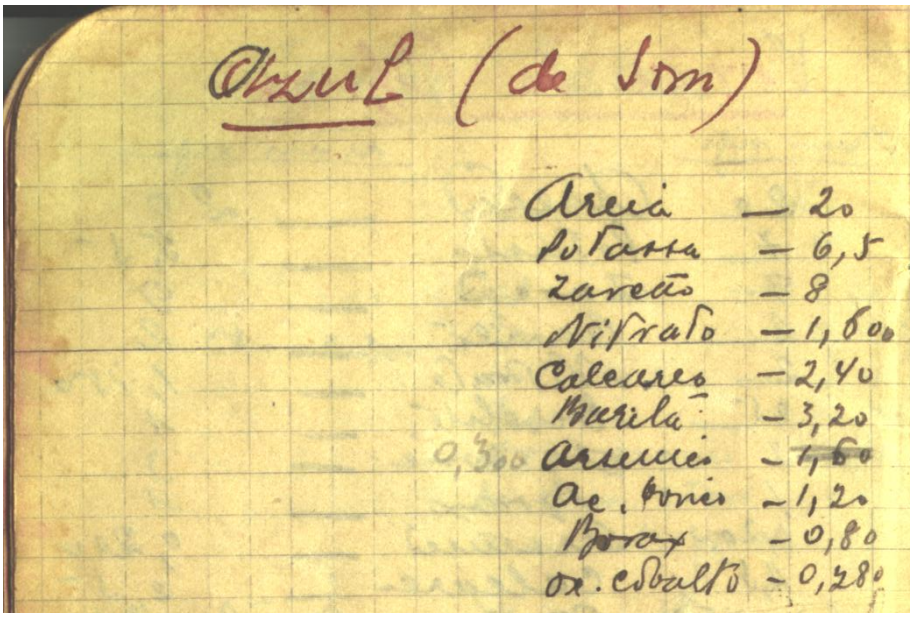


Figure B.18: Blue recipe G46

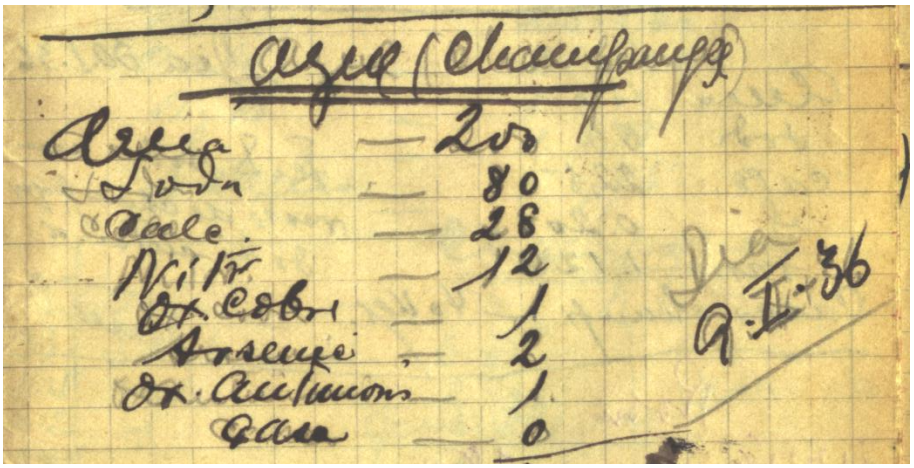


Figure B.19: Blue recipe G101

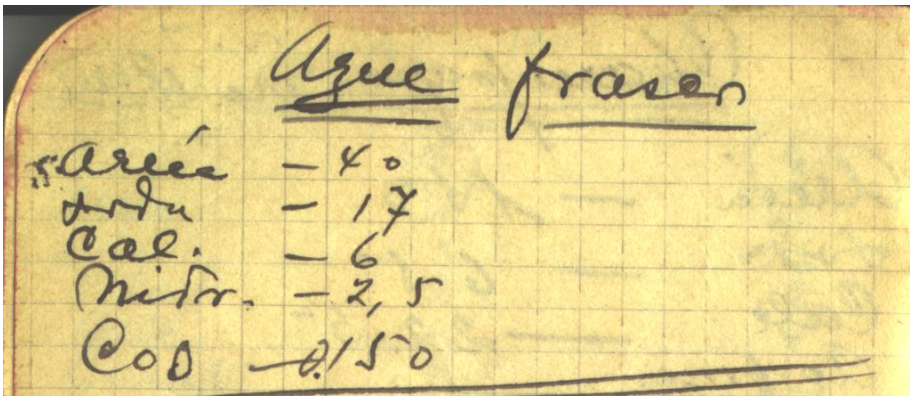


Figure B.20: Blue recipe G114

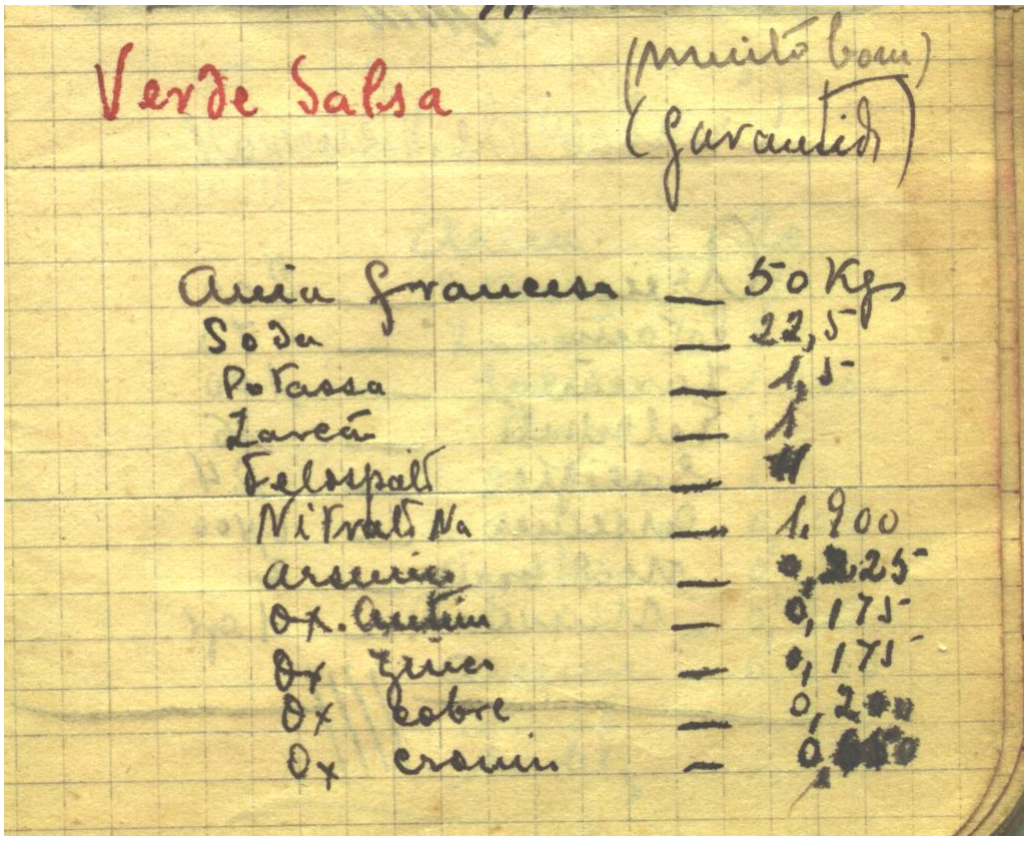


Figure B.21: Green recipe G16

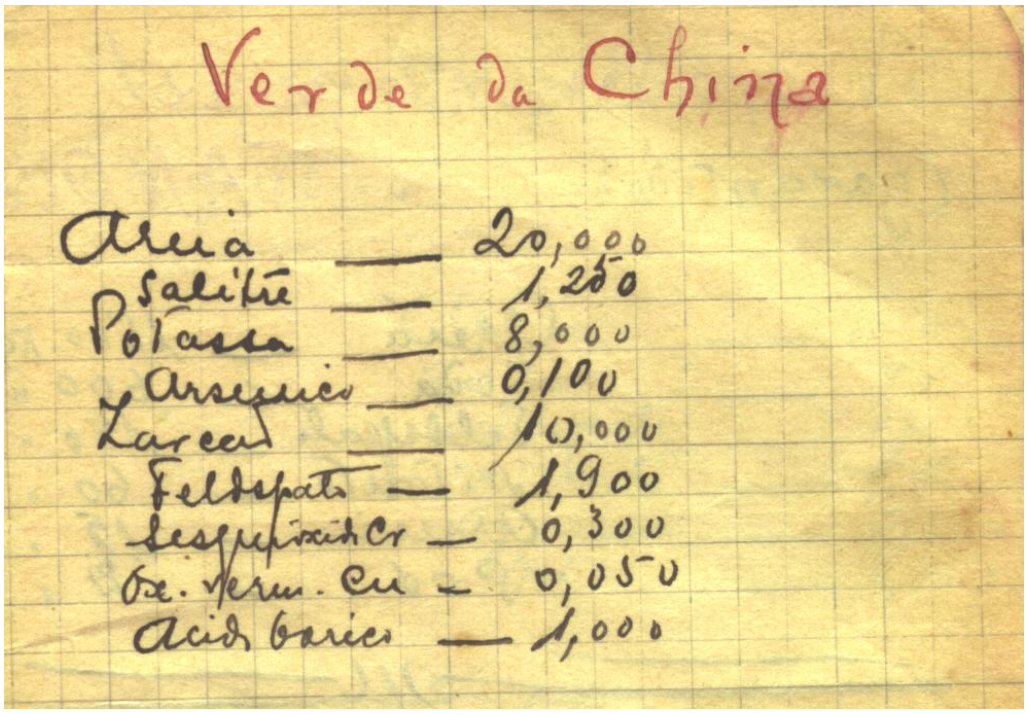


Figure B.22: Green recipe G23

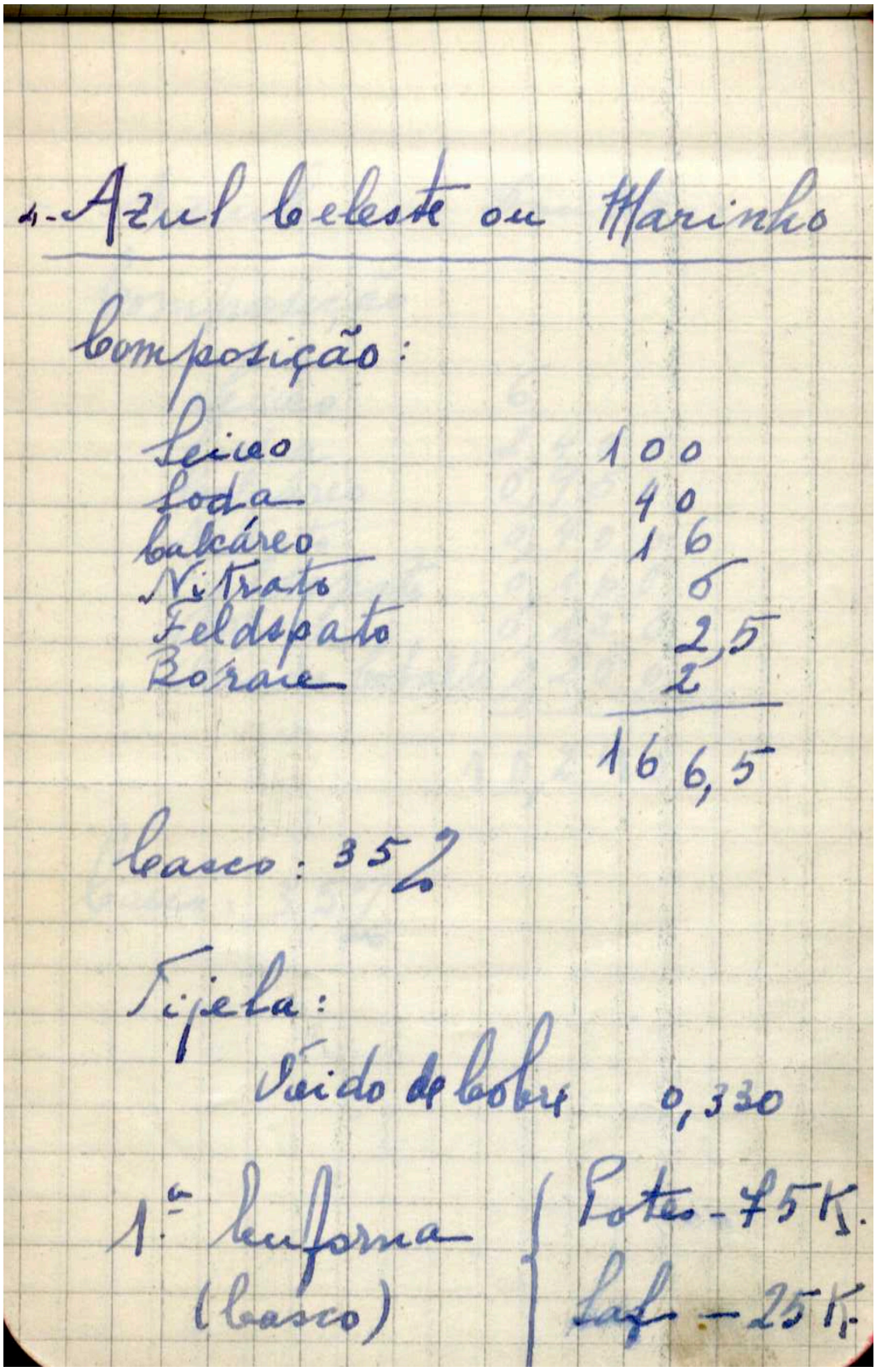


Figure B.23: Blue recipe NP4

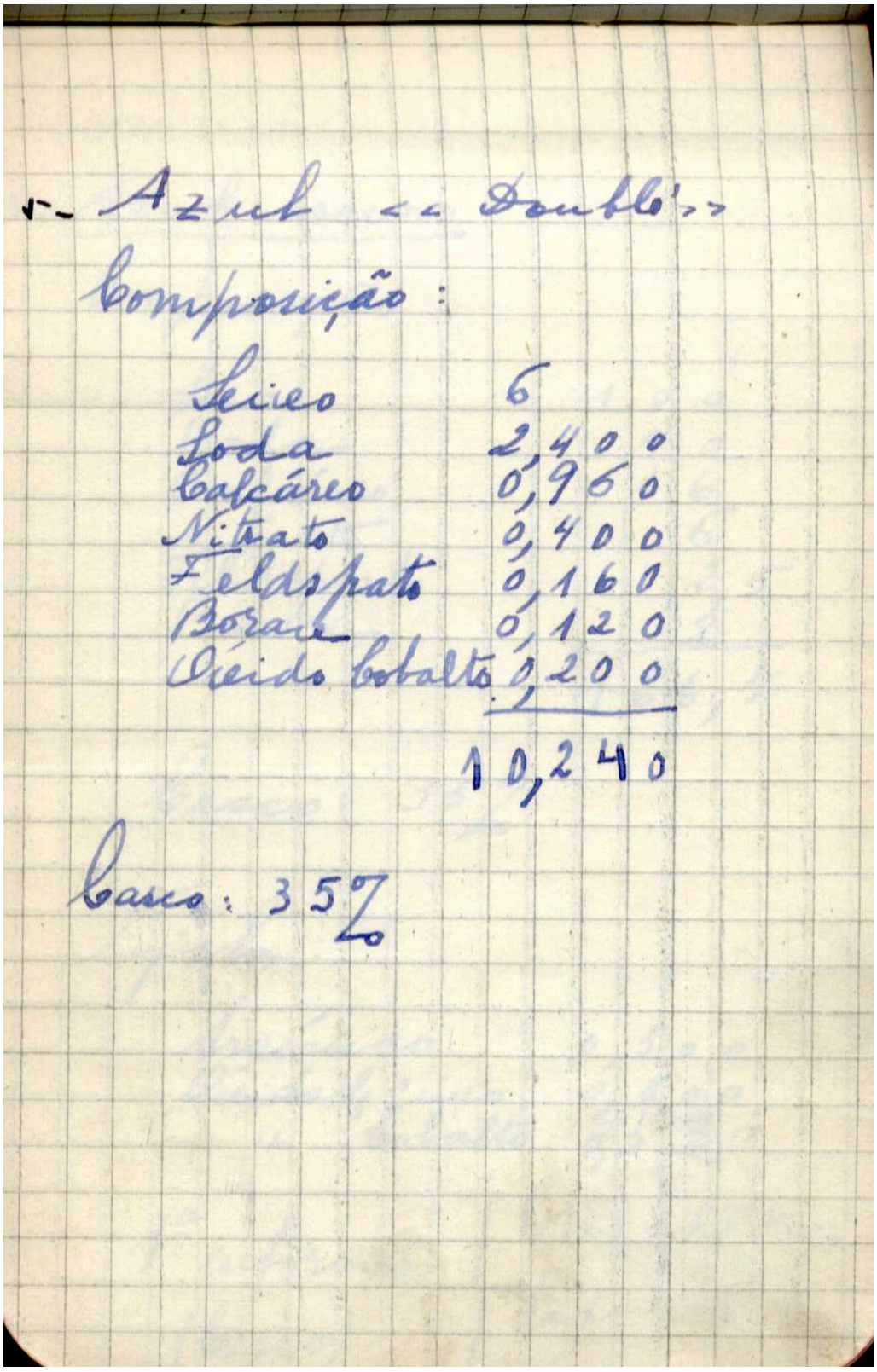


Figure B.24: Blue recipe NP5

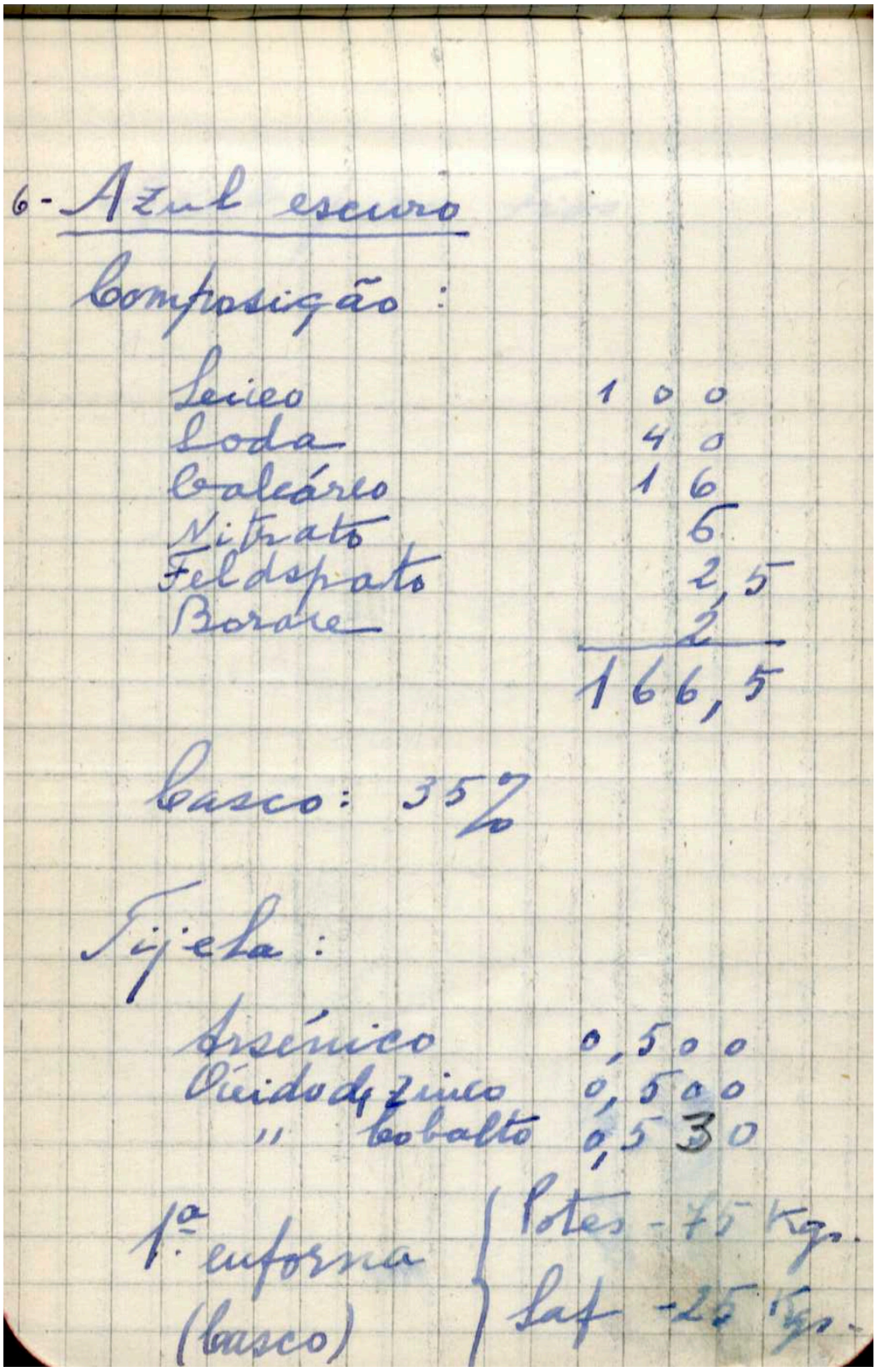


Figure B.25: Blue recipe NP6

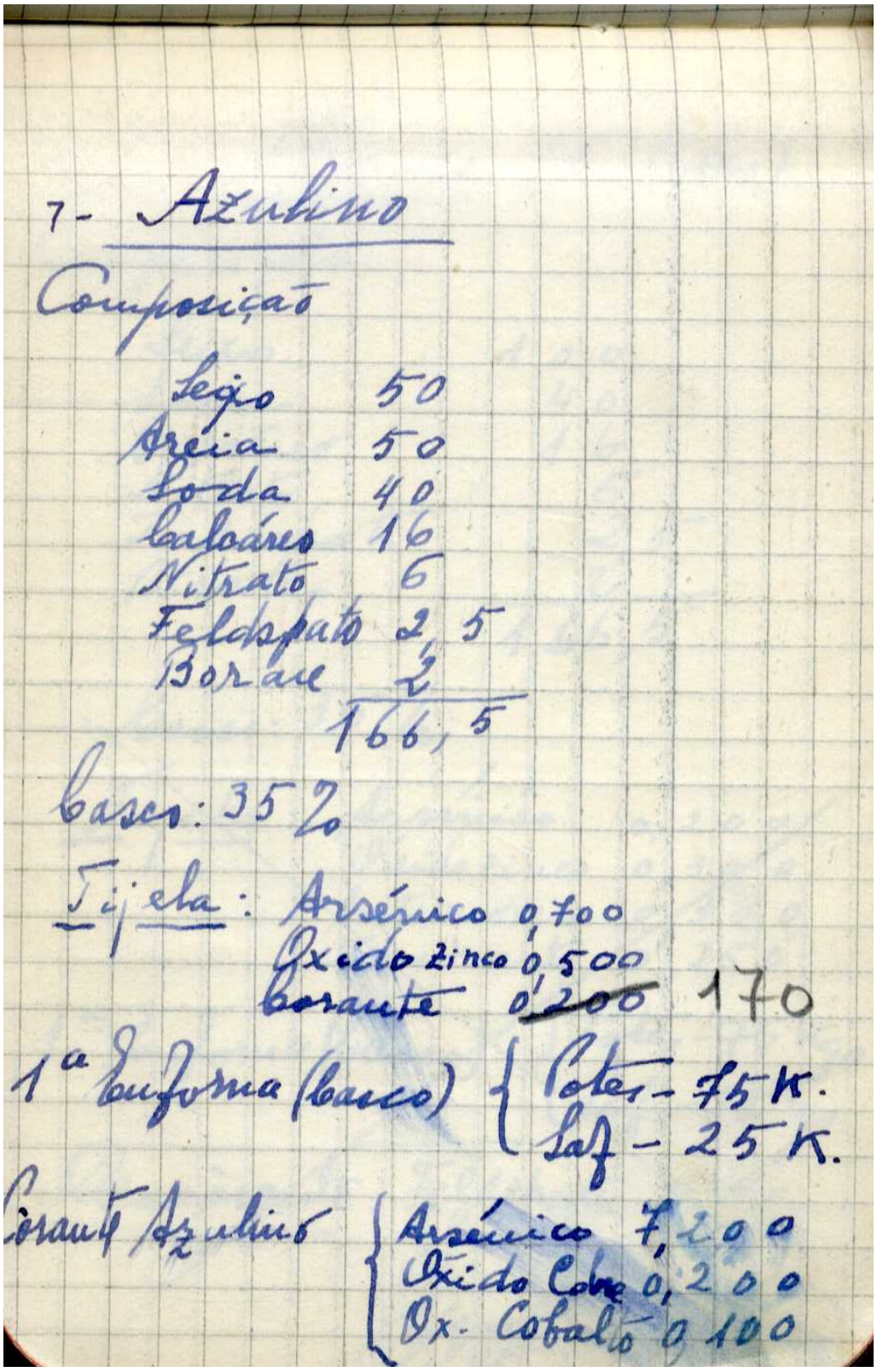


Figure B.26: Blue recipe NP7

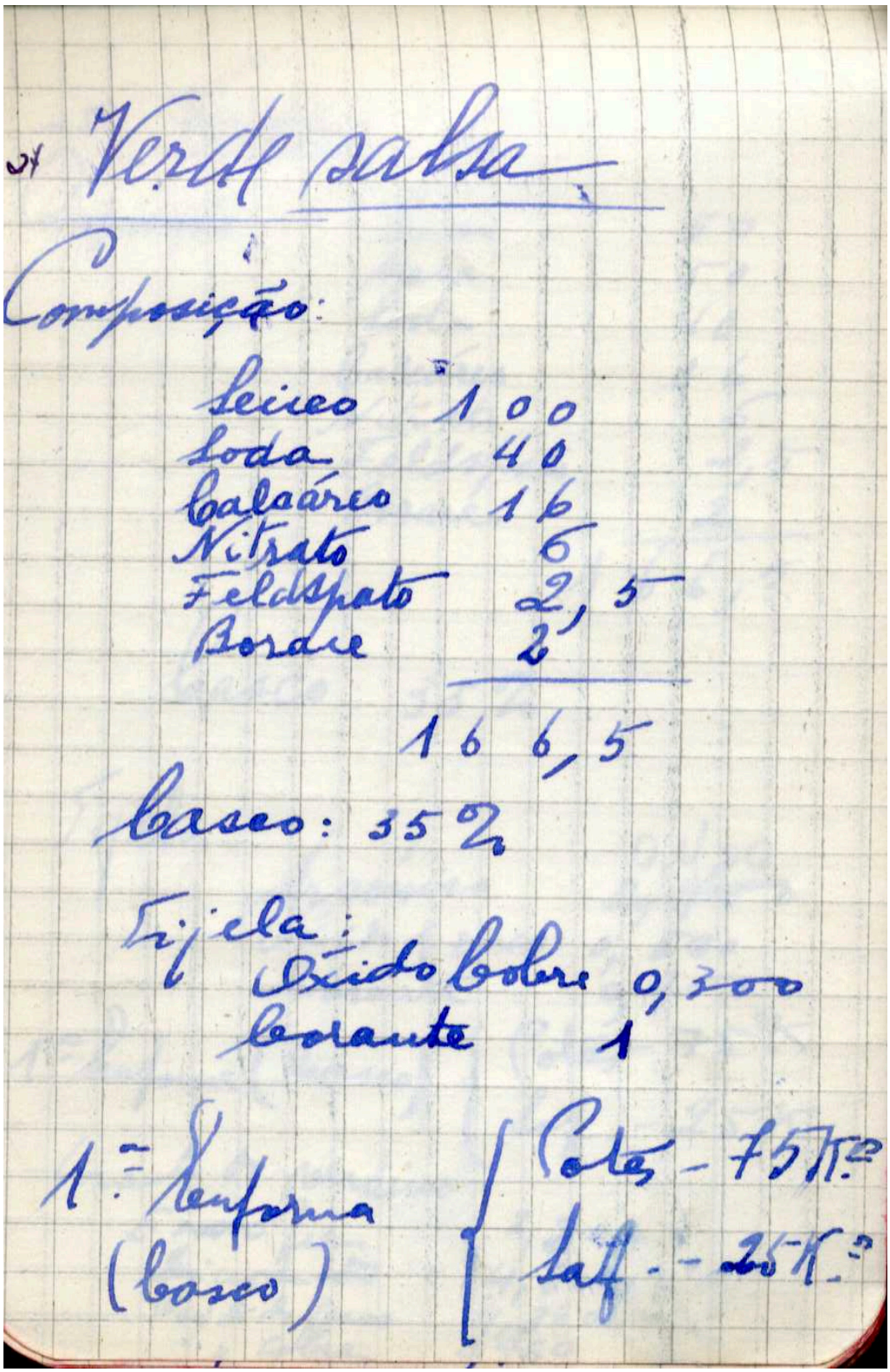


Figure B.27: Green recipe NP23

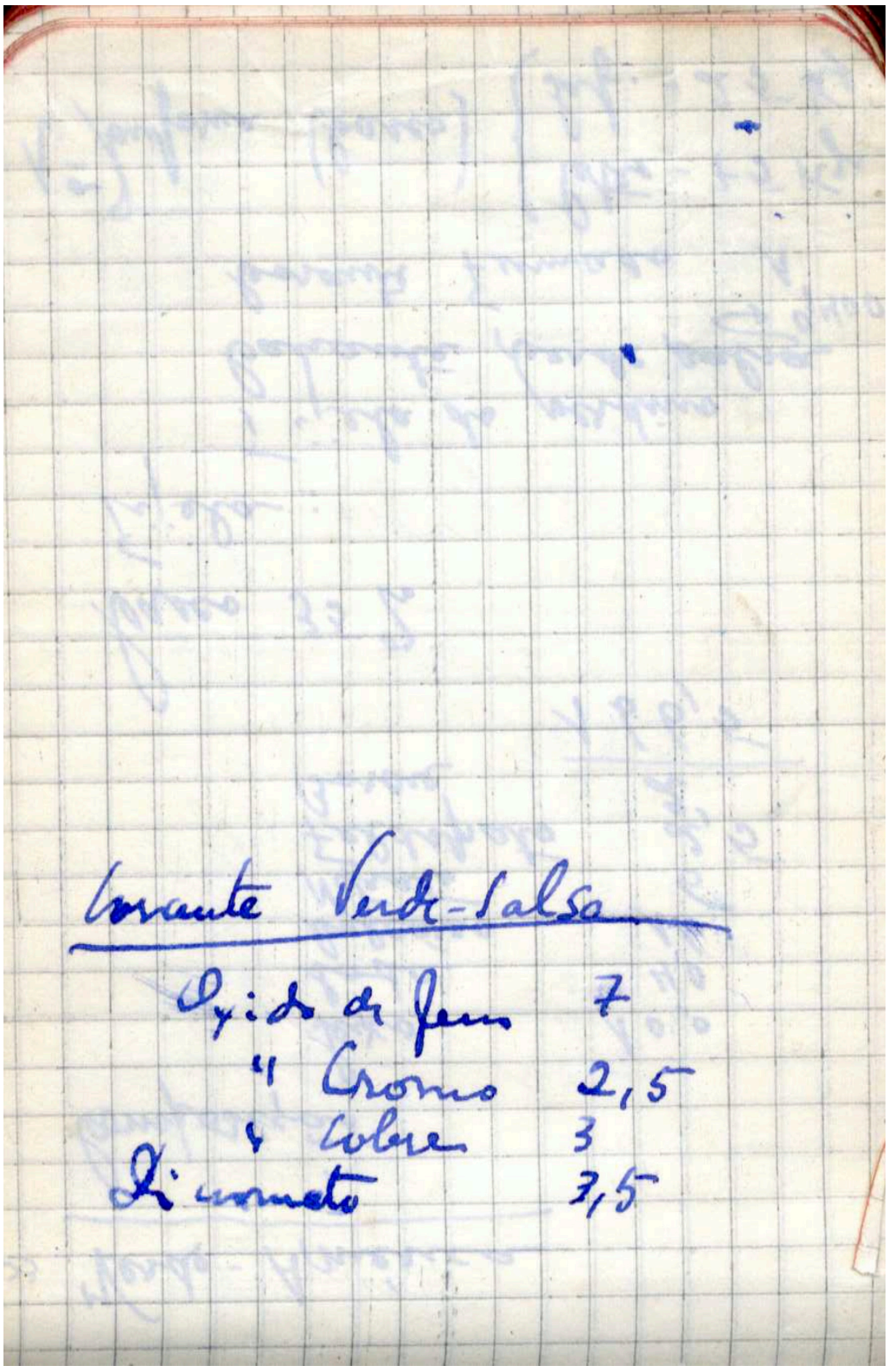


Figure B.28: Colourant from recipe NP23

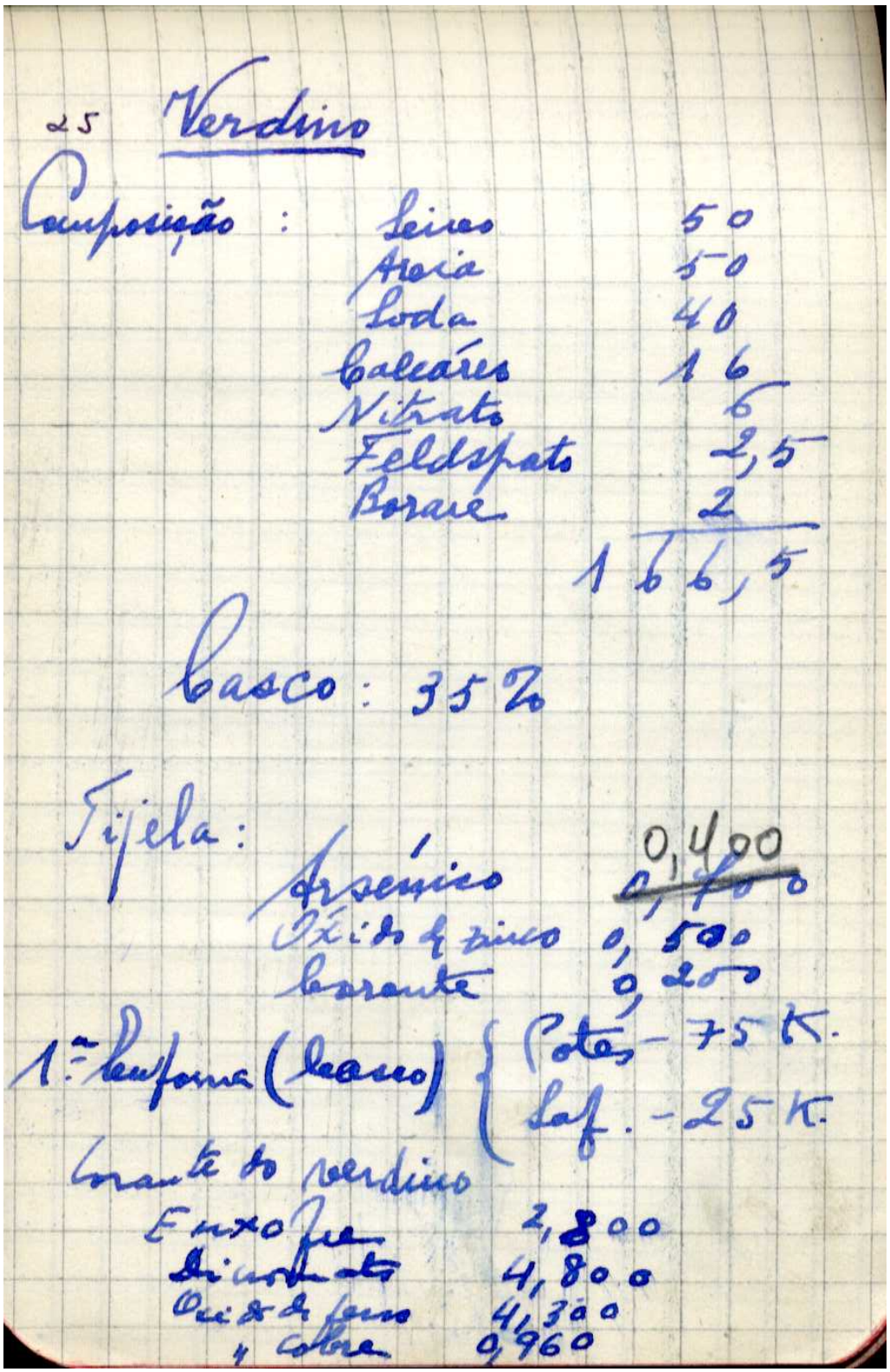


Figure B.29: Green recipe NP24

C

Reproduced recipes

Table C.1: Furnace programmes for the reproduction of different glass colours

	Melting program	Annealing
Amber glasses	Ramp until 600ºC, 2ºC per min. Dwell 2h Ramp until 900ºC, 2ºC per min. Dwell 2h Ramp until 1450ºC, 2ºC per min. Dwell 2h	
Blue glasses	Ramp until 600ºC, 2ºC per min. Dwell 2h Ramp until 900ºC, 2ºC per min. Dwell 2h Ramp until 1350ºC, 2ºC per min. Dwell 2h	470ºC Dwell 1 hour
Green glasses	Ramp until 600ºC, 2ºC per min. Dwell 2h Ramp until 900ºC, 2ºC per min. Dwell 2h Ramp until 1400ºC, 2ºC per min. Dwell 2h	

Note: For the blue glass recipes, recipe G46 b was melted at a final temperature of 1450°C. The green glass recipes C43 a and C44 a were initially melted at 1350°C.

Table C.2: Weights in grams for the reproduction of amber glass recipes.

	$CaCO_3$	$CaMg(CO_3)_2$	Charcoal	Fe_2O_3	Flour	H_3BO_3	MnO_2	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	Na_2CO_3	Na_2SO_4	$NaAlSi_3O_8$	NaCl	$NaHCO_3$	$NaNO_3$	SiO_2	S	ZnO	
G92	3.578			0.022	1.495				14.909						29.834	0.199		
G130	3.794		0.202	0.017		0.421			13.935						31.604	0.043		
G192	3.815			0.023	0.213	0.449		0.132	12.726			0.374			32.252	0.033		
C98 a	9.615			0.002					13.348						26.678	0.374		
C98 b	9.603			0.101					13.343						26.679	0.374		
C98 c	9.605		5.014	0.100					13.344						26.684	0.376		
C98 d1	10.348		10.000	0.050						4.765		4.765	6.354		23.767			
C98 d2	8.874		10.002	0.052						4.943		4.942	6.590		24.654			
C98d3	8.878		10.026	0.051						4.938		4.939	6.587		24.650			
C98 e1	10.348		10.000	0.100						4.765		4.765	6.354		23.767			
C98 e2	8.875		10.005	0.102						4.941		4.941	6.592		24.651			
C98 e3	8.876		10.008	0.100						4.943		4.941	6.590		24.663			
C98 f	10.348		15.000	0.100						4.765		4.765	6.354		23.767			
C98 g	20.696		20.000	0.200						9.530		9.530	12.708		47.534			
C98 h	8.875		5.003	0.105						4.943		4.945	6.593		24.657			
C98 i	8.874		5.001	0.049						4.941		4.943	6.592		24.653			
C98 j	8.873		10.006	0.027						4.945		4.945	6.593		24.656			
C98 k	9.605			3.468			2.934		13.339						26.673			
C98 l	8.877		10.004	0.076						4.944		4.943	6.591		24.653			
NP3 a	0.403	1.623		2.641		1.218	2.237	5.284	2.436		12.197			0.816	20.327		0.811	
NP3 b	0.410	1.625		1.133		1.225	1.112	5.287	2.443		12.193			0.816	20.329		0.815	

Table C.3: Weights in grams for the reproduction of blue glass recipes.

	SiO_2	Soda and sand frit[1]	H_3BO_3	CoO	Zaffre[1]	Smalt[1]	CuO	ZnO	$NaNO_3$	MnO_2	$CaCO_3$	KNO_3	Na_2CO_3	K_2CO_3	Fe_2O_3	$BaCO_3$	$BaSO_4$	$NaAlSi_3O_8$	Sb_2O_3	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	Pb_3O_4	Cullet[1]	
M1_4C1	8.759	52.968		0.552											0.070						17.651		
M1_4S1	8.756	52.965				0.551									0.071						17.653		
M1_4Z1	8.757	53.030			0.552										0.073						17.656		
M1_51		17.604					0.797															61.606	
M3_3	22.765				0.258					0.516				5.463	0.005						13.575	36.428	
C125	48.770						0.321		1.972		3.934		19.671		0.426						4.913		
C157	45.395			1.354							6.434	1.807	18.127			2.290			2.294	2.263			
C158	47.560			0.575					1.907		6.790		19.027			2.376			2.378	2.376			
C159	46.648			0.234			0.464		2.333		6.665		19.593			2.331			2.334	2.337			
G46 a	22.725		1.363				0.317		1.818		2.728			7.392	0.014		3.639			0.910	9.095		
G46 b	36.363		2.185				0.510		2.916		4.367			11.829	0.024		5.823			1.451	14.547		
G101	49.653						0.248				6.953	2.98	19.876		0.038				0.245				
G114	48.705			0.181							7.313	3.045	20.713		0.038								
NP4	31.166						0.103				4.99	1.868	12.468					0.78		0.624		28.001	
NP5	18.737			0.624							2.998	1.247	7.495					0.501		0.374		48.024	
NP6	31.041			0.162				0.155			4.965	1.866	12.418					0.775		0.623		28.024	
NP7	31.102			0.018			0.035	0.156			4.978	1.887	12.440		0.006			0.776		0.626		28.017	

[1]See Chapter 3 for the composition and method of manufacture of these ingredients.

Table C.4: Weights in grams for the reproduction of green glass recipes.

	S	SiO_2	Soda and sand frit[1]	H_3BO_3	ZnO	CuO	Cu_2O	$NaNO_3$	Na_2CO_3	KNO_3	$CaCO_3$	K_2CO_3	Fe_2O_3	Cr_2O_3	Sb_2O_3	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	Pb_3O_4	$NaAlSi_3O_8$	$K_2Cr_2O_7$	Cullet[1]	
M1_5		6.606	40.005										0.060				13.332				
M4_3		29.139				2.857					2.858	9.407	0.254				15.674				
C43 a		33.329									6.447	21.534	0.335	1.333			0.332				
C43 b		33.331									6.447	21.532	0.333	1.332			0.336				
C44 a		17.832									4.442	12.235		0.264			1.192			28.524	
C44 b		17.830									4.440	12.232		0.267			1.190			28.521	
C68		18.124				0.063			11.780	0.362	5.042			0.124						28.999	
C74		21.624				0.115			8.196	1.153	5.239	7.875		0.201						21.624	
G16		36.439			0.128	0.146		1.384	16.395			1.094		0.472	0.127		0.729	2.911			
G23		28.160		1.405			0.072			1.768		11.269	0.017	0.421			14.085	2.676			
NP23		30.986				0.153		1.854	12.395		4.959		0.136	0.048		0.621		0.780	0.069	28.135	
NP24	0.017	23.315			0.118	0.005		1.398	9.334		3.732		0.021			0.47		0.582	0.018	21.002	

[1] See Chapter 3 for the composition and method of manufacture of these ingredients.

D

Supplementary material (WDXRF tables and transmited light pictures)

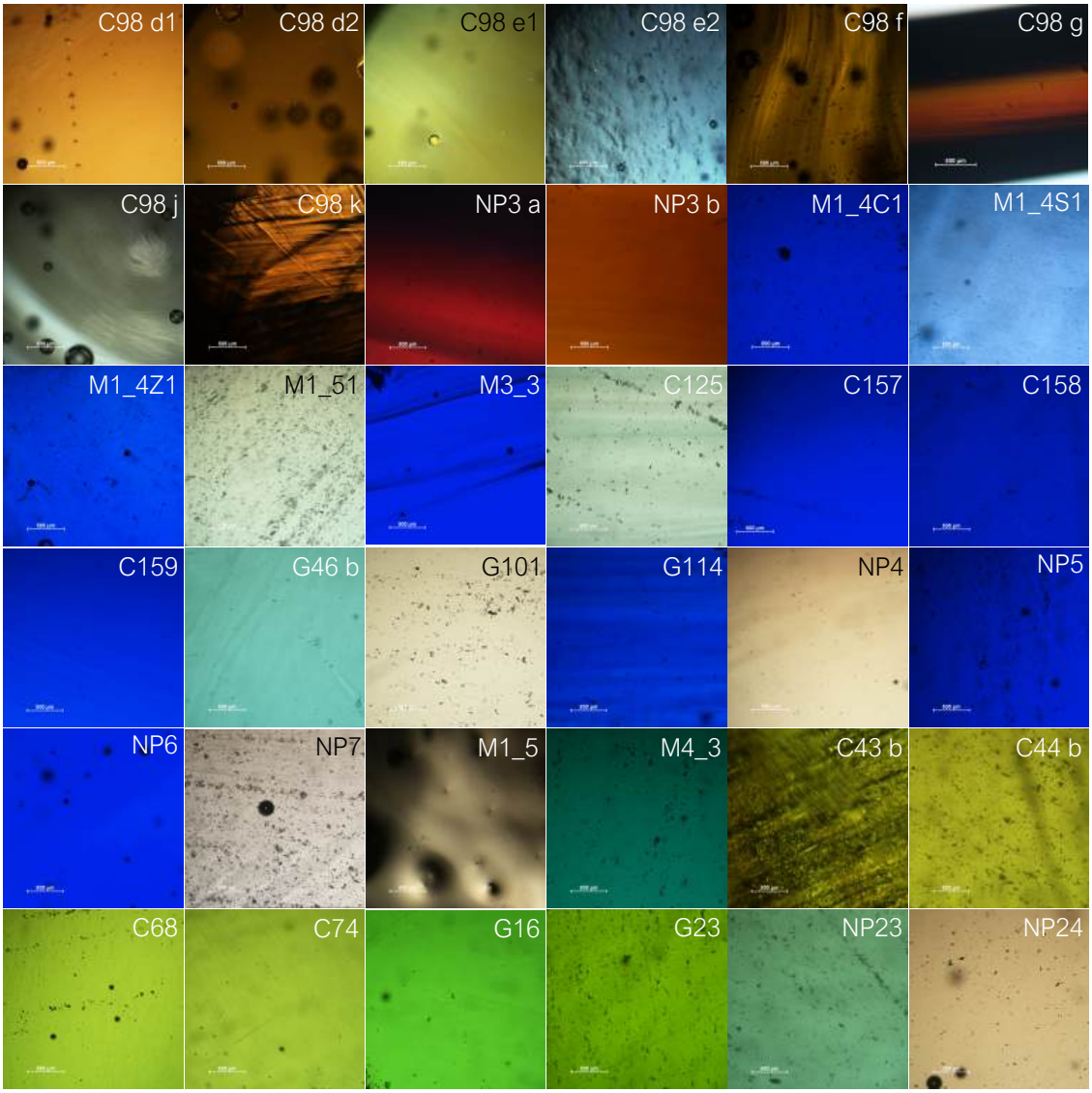


Figure D.1: Microscopic image of reproduced glasses under transmitted light

Table D.1: Wavelength dispersive X-ray fluorescence spectroscopy results of the non-laboratory compounds used to reproduce the glasses.

Sample	Sum before normalisation	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	Cl	K_2O	CaO	TiO_2
Charcoal 1	13.00		2.54	0.77	3.21	1.36	2.41		17.50	72.20	
Charcoal 2	4.10				1.82	6.03	2.07		38.90	51.20	
Charcoal 3	27.80		1.46		0.23	0.76	0.33		9.13	88.10	
Dolomite	62.60		30.80	0.14	0.28					68.80	
Flour	4.90		3.03	0.98	2.12	30.50	13.00	3.95	17.10	29.30	
$NaAlSi_3O_8$	86.40	8.32	0.27	19.10	70.80	0.21			0.25	0.76	0.27

Table D.2: Wavelength-Dispersive X-ray Fluorescence Spectroscopy results of the reproduced amber glasses in molar percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	SO_3	Cl	K_2O	CaO	MnO	Fe_2O_3	ZnO
G92	18.00		0.80	74.50	0.69		0.03	6.30		0.03	0.01
G130	16.01		0.29	76.60	0.14		0.04	6.91		0.02	0.01
G192	15.82		0.53	76.21	0.08	0.81	0.03	6.49		0.02	
C98 a	16.37		0.35	66.35	0.64		0.02	16.27			
C98 b	16.40	0.50	0.77	65.36	0.38		0.01	16.52		0.12	
C98 c	14.88		0.83	66.33		0.57	0.08	17.20		0.10	
C98 d1	10.75	0.30	1.29	66.52	0.06	0.49	0.08	20.44		0.07	0.01
C98 d2	9.87	0.10	3.84	67.62	0.06	0.31	0.06	18.00		0.07	0.01
C98 d3	8.17	0.30	0.47	69.40	0.17	0.86	0.07	20.50		0.07	
C98 e1	9.56	0.30	1.11	66.02	0.04	0.54	0.08	22.19		0.15	0.01
C98 e2	11.05	0.30	1.30	68.21		0.37	0.08	18.54		0.14	0.01
C98 e3	9.63		0.35	69.42	0.18	0.94	0.08	19.26		0.14	
C98 f	9.80	0.30	1.59	64.63	0.80	1.07	0.12	21.55		0.14	0.01
C98 g	8.44	0.30	3.10	68.36	0.28	1.61	0.28	17.36		0.24	0.01
C98 h	11.41		0.76	69.70	0.23	0.96	0.03	16.77		0.13	
C98 i	9.52		1.89	67.77	0.13	0.68	0.06	19.87		0.07	0.01
C98 j	11.23	0.30	2.95	65.19		0.34	0.09	19.81		0.05	0.01
C98 k	13.77		2.30	58.98			0.06	15.68	5.33	3.86	0.02
C98 l	9.68		1.00	68.97	0.22	0.61	0.08	19.36		0.08	0.01
NP3 a	8.71	1.50	7.19	71.54			0.14	2.51	4.01	2.86	1.55
NP3 b	8.69	1.50	8.38	73.26			0.15	2.74	2.08	1.61	1.61

Table D.3: Wavelength-Dispersive X-ray Fluorescence Spectroscopy results of the reproduced blue glasses in molar percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	MnO	Fe_2O_3	CoO	CuO	ZnO	SrO	ZrO_2	SnO_2	Sb_2O_3	BaO	PbO
M1_4C1	21.34		0.73	62.77			0.29				0.46	1.81								12.61
M1_4S1	23.76		0.54	63.78			0.34	0.14			0.39	0.12								10.94
M1_4Z1	24.78		0.88	60.46	0.62		0.22	0.09	0.06		0.37	0.62					0.20			11.71
M1_51	7.73	1.72	0.87	73.48	0.13		7.24	7.49	0.02	0.04	0.09		1.07			0.01		0.10		
M3_3			0.24	71.80			8.08			1.30	4.76	0.34					0.03			13.46
C125	14.54		0.06	75.54			0.10	5.57	0.04		0.40		0.64	0.01						3.09
C157	13.74		0.69	72.22			1.06	7.53				3.20		0.01	0.01	0.01		0.63	0.92	
C158	15.99		0.67	73.83		0.05	0.22	7.46	0.05		0.02	0.84						0.35	0.51	0.02
C159	16.84	0.31	0.73	72.07			0.29	7.62	0.05		0.01	0.46	0.65		0.01			0.39	0.57	0.01
G46b	2.44		0.70	67.92		0.28	10.40	6.51			0.03		0.92		0.05				2.88	7.88
G101	13.74		0.12	75.33			1.78	8.51	0.03		0.04		0.44	0.01						0.01
G114	15.09		0.18	74.28			1.39	8.58	0.02		0.04	0.41		0.01	0.01					
NP4	11.48		0.24	76.43			1.85	9.74	0.04		0.02		0.18	0.01						0.01
NP5	12.56		0.24	75.33			1.66	8.84	0.05		0.02	1.27		0.01						
NP6	13.77	0.30	0.42	75.73			0.05	8.37	0.05		0.02	0.25		0.13						
NP7	13.09		0.30	76.87		0.05	0.88	8.52	0.06		0.02	0.02	0.05	0.15						

Table D.4: Wavelength-Dispersive X-ray Fluorescence Spectroscopy results of the reproduced green glasses in molar percentage of oxides.

Sample	Na_2O	MgO	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	TiO_2	Cr_2O_3	Fe_2O_3	CuO	ZnO	ZrO_2	Sb_2O_3	PbO
M1_5	22.26		1.44	65.66			0.32	0.10	0.08		0.42					9.72
M4_3			0.33	65.42			10.61	5.27			0.26	7.08				11.04
C43 b			0.07	60.47		0.04	27.20	11.22		0.70	0.07			0.01		0.21
C44 b			0.21	62.15		0.05	24.91	11.03	0.03	0.71	0.02					0.89
C68	11.75	0.16	0.32	62.56			12.63	11.71	0.03	0.52	0.02	0.16				0.13
C74	5.16		0.26	62.93		0.02	18.34	12.37	0.03	0.52	0.02	0.28				0.08
G16	17.70		0.74	78.44			1.41	0.11	0.05	0.47	0.01	0.35	0.18		0.05	0.50
G23	1.47		0.73	72.45			14.08	0.04	0.06	0.43	0.02	0.16				10.55
NP23	13.61		0.60	75.97	0.40	0.05	0.85	8.09	0.06		0.11	0.22	0.01			
NP24	14.82	0.46	0.60	74.61		0.06	0.88	8.31	0.05	0.01	0.03	0.02	0.14			